

Special Issue Reprint

Organometallic Compounds

Design, Synthesis and Application

Edited by
Yanping Ma

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Organometallic Compounds: Design, Synthesis and Application

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Guest Editor

Yanping Ma



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Recent Advancements in the Synthesis of Functional Polyolefins by Non-Bridged
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About the Editor

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Dr. Ma has published over 160 academic papers (33 first/corresponding author papers, H-index 35, nearly 4104 citations) and holds 17 invention patents in polyolefin catalysis. She serves as a Guest Editor for *Molecules* and a reviewer for numerous international journals. She has presided over multiple industrial cooperation projects and possesses extensive experience in polyolefin catalytic technology research and industrial translation.

Article

Controlled Copolymerization of Ethylene and Biosourced Comonomers Using Dibenzobarrelene-Based α -Diimine Nickel Catalyst

Handou Zheng [†], Junsong Wang [†], Zonglin Qiu, Chunyu Feng, Haotian Zhou, Guangshui Tu and Haiyang Gao ^{*}

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Abstract: The development of earth-abundant nickel-based catalysts is currently one of the greatest challenges for the straightforward synthesis of functionalized polyolefins. With environmental protection concerns, controllable copolymerizations of ethylene with biosourced comonomers derived from castor oil, such as methyl 10-undecenoate (U-COOMe), 10-undecen-1-ol (U-OH), or 10-undecenyl bromide (U-Br), were realized using α -diimine nickel catalyst (**Ni-DBB**) with dibenzobarrelene backbone. Catalyst **Ni-DBB** was highly tolerant toward polar comonomers, and functional polyethylenes were successfully prepared. The influences of the polar group, temperature, and comonomer concentration were studied in detail. Catalyst **Ni-DBB** was able to catalyze the copolymerization of ethylene with U-OH to afford high-molecular-weight (~180 kg/mol) functional polyethylene in a controlled fashion. NMR analysis showed that the produced functional polyethylenes were highly branched and had broad melting peaks ranging from 0 to 30 °C. Water contact angle (WCA) measurements showed that the surface of the obtained hydroxyl-functionalized polyethylene changed from hydrophobic to hydrophilic with the introduction of the comonomer U-OH.

Keywords: α -diimine nickel; copolymerization; biosourced monomers; functional polyethylene

1. Introduction

Polyolefins, especially polyethylene (PE), are commercially the most important family of polymeric materials because of their excellent mechanical, physical, and chemical properties [1]. However, the full non-polar nature of the polyolefins also limits their wider applications. Compared to their non-functionalized analogues, functional polyethylenes exhibit beneficial properties such as adhesion, printability, miscibility, and toughness [2,3]. There are three major approaches for the synthesis of functional polyolefins, including free radical copolymerization of ethylene and polar monomers under harsh conditions [4,5], post-functional modification of polyolefins [6], and direct copolymerization of ethylene and polar monomers through coordination polymerization under mild conditions [7]. Undoubtedly, the direct copolymerization with polar monomers is the most promising approach, which allows the preparation of functional polyolefins with controllable microstructure [8].

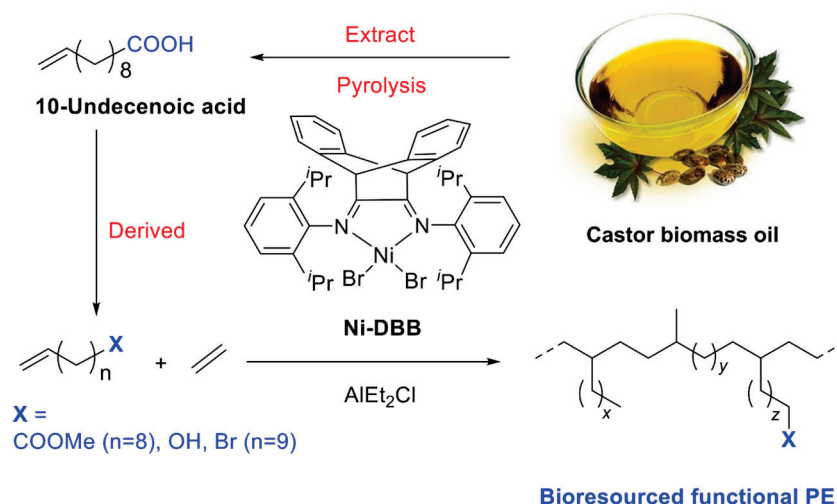
Transition metal catalysts play a crucial role in the coordination copolymerization of ethylene with polar comonomers. However, early transition metals, such as those in groups

4–6, are often inactive for the direct copolymerization of ethylene and polar comonomers due to the high oxophilicity of their metal centers [9,10]. In contrast, late transition metal catalysts are ideal candidates for the copolymerization of ethylene and polar monomers because of their low oxophilicity [11,12]. Several late transition metal Ni/Pd catalysts, such as α -diimine [13–15], phosphine-sulfonate [16–19], salicylaldiminate [20–24], and phosphino-phenolate [25–29], have been developed for effectively copolymerizing ethylene and polar comonomers. A notable example is the α -diimine nickel and palladium catalysts (also known as Brookhart-type catalysts), which often produce branched or highly branched copolymers containing a portion of, or all, terminal polar groups due to chain walking [30,31]. Generally, the α -diimine nickel catalysts are more active for ethylene homopolymerization and have lower chain walking ability than palladium analogues. However, nickel catalysts have lower tolerance toward polar comonomers than palladium catalysts [13,32]. Therefore, the copolymerization of ethylene and polar comonomers using α -diimine nickel catalysts remains a significant challenge due to their relatively high metal oxophilicity. This challenge can be addressed by employing: (a) comonomers bearing sterically hindered functional groups or functional groups positioned far from the polymerizable double bond through long spacers [33,34]; (b) comonomers with protected functional groups [35,36]; or (c) catalytic systems with enhanced tolerance toward polar groups [37,38].

Few α -diimine nickel catalysts have been developed to directly copolymerize ethylene and polar comonomers, although Ni-based catalysts are low-cost and abundant in the Earth's crust [11,39]. Increasing bulky steric hindrance around the metal center is an effective approach to enhance the tolerance of the nickel metal center toward polar groups [40,41]. Introducing bulky anilines such as 2,6-dibenzhydrylanilines and 8-arylnaphthylamine has been widely developed in the design of α -diimine nickel catalysts for copolymerization of ethylene and polar monomers [42–44]. Besides, installing bulky backbones such as camphyl [45,46] and dibenzo-/dinaphthobarrelene backbones [47–50] has also been developed by our group for the copolymerization of ethylene and polar monomers.

With carbon peaking and carbon neutrality goals, as well as environmental protection concerns, the use of biosourced monomers in polymer synthesis is receiving increasing attention [51–53]. Biosourced monomers, such as 10-undecenoic acid (U-COOH), derived from the pyrolysis and extraction of castor biomass oil, have attracted considerable interest in the synthesis of functional polymers because of their biosourced character [54]. It has served as a key precursor in the industrial production of pharmaceuticals, consumer goods, and specialty polymers [55,56]. The flexible long-chain alkyl moiety in its molecular structure contributes to improved flexibility of the resultant polymeric materials. Furthermore, a series of 10-undecenoic acid derivatives can be obtained through chemical transformations such as esterification or other derivatization reactions, which function as critical intermediates in developing biodegradable elastomers, hydrogels, and environmentally benign adhesives [57,58].

In this contribution, a dibenzobarrelene α -diimine nickel catalyst was used in the copolymerization of ethylene and biosourced 10-undecenoic acid derivatives ($\text{CH}_2=\text{CH}-(\text{CH}_2)_n\text{-X}$, $\text{X} = \text{COOMe}$ ($n = 8$), OH , and Br ($n = 9$)) (Scheme 1). Bulky dibenzobarrelene backbone of the ligand effectively enhanced the tolerance of the nickel catalyst towards polar comonomers, and functional polyethylenes were successfully prepared. More importantly, hydroxyl-functionalized polyethylene with high molecular weight ($M_n \sim 180 \text{ kg/mol}$) was synthesized precisely in a controlled fashion.



Scheme 1. Copolymerization of ethylene and biosourced comonomers derived from castor oil using dibenzobarrelene α -diimine nickel catalyst.

2. Results and Discussion

2.1. Copolymerization of Ethylene and Comonomers

Our group has previously developed dibenzobarrelene-based α -diimine nickel and palladium catalysts. Introduction of bulky dibenzobarrelene backbone can enhance thermal stability and controlled fashion in α -diimine nickel-catalyzed ethylene polymerization [47]. Besides, the dibenzobarrelene-based α -diimine palladium catalyst can catalytically prepare functional polyolefins by controlled copolymerization of ethylene and a variety of acrylate comonomers [48,49,51]. Prior to this work, we attempted the copolymerization of ethylene with 10-undecylenic acid (U-COOH). However, only trace amounts of polymer were obtained (entry 13 in Table 1). Herein, the copolymerizations of ethylene with biosourced 10-undecenoic acid derivatives ($\text{CH}_2=\text{CH}-(\text{CH}_2)_n\text{-X}$, $\text{X} = \text{COOMe}$ (U-COOMe, $n = 8$), OH, and Br (U-OH or U-Br, $n = 9$)) using dibenzobarrelene-based α -diimine nickel catalyst **Ni-DBB** were carried out. In these copolymerization systems, a large amount of AlEt_2Cl ($\text{Al}/\text{Ni} = 1600$) as a cocatalyst was used compared to ethylene homopolymerization ($\text{Al}/\text{Ni} = 600$) [47], because a large amount of alkyl aluminum reagents is helpful for protecting the polar groups for successful copolymerization. [59–63]. These functional groups in the olefins preferentially coordinate to Al, forming stable and protected aluminates that serve as true comonomers for successful copolymerization, and deprotection to the free functionality is accomplished by acid wash upon termination of polymerization [64,65].

As shown in Table 1, copolymerizations of ethylene and three biosourced comonomers derived from castor oil with different polar groups were conducted in a temperature range from 20 to 65 °C. Excluding the amount of AlEt_2Cl used as the activator for ethylene polymerization ($\text{Al}/\text{Ni} = 600$, 1.2 mmol), an additional 2.0 mmol of AlEt_2Cl was added in the copolymerization system, resulting in an $[\text{Al}]/[\text{polar monomer}]$ ratio of 1. The polar comonomer incorporation into the copolymer was identified by ^1H NMR spectroscopy, and no homopolymer of polar comonomer was present in the copolymerization products. For the ethylene/U-OH copolymer, the signal corresponding to the hydroxyl protons is difficult to observe. Therefore, the incorporation (mol%) of hydroxyl-containing monomers in the copolymer is typically calculated by integrating the methylene proton signals ($-\text{CH}_2\text{OH}$) relative to the signals of other protons in the ^1H NMR spectrum (see Section 3.3) [39,66,67]. As shown in Figure 1, ^1H NMR spectra of the obtained functional polyethylene clearly show characteristic peaks for U-COOMe (H_a : 3.60 ppm; H_b : 2.30 ppm; H_c : 1.61 ppm), U-OH (H_d : 3.66 ppm; H_e : 1.85 ppm), and U-Br (H_f : 3.40 ppm; H_g : 1.85 ppm), respectively,

which proves the successful copolymerization of ethylene with U-COOMe, U-OH, or U-Br [47,49,68].

Table 1. Copolymerization results of ethylene and comonomers under various temperatures ^a.

Entry	Monomer	T (°C)	Yield (mg)	Act. ^b	Incorporation ^c (mol%)	M _n ^d (kg/mol)	PDI ^d	BD ^e
1	U-COOMe	20	150	150	0.78	104.2	1.15	86
2	U-COOMe	35	122	122	1.01	81.4	1.18	89
3	U-COOMe	50	85	85	1.42	42.3	1.40	91
4	U-COOMe	65	trace	-	-	-	-	-
5	U-OH	20	340	340	0.57	121.7	1.07	88
6	U-OH	35	231	231	0.95	105.6	1.20	87
7	U-OH	50	213	213	1.23	70.2	1.35	82
8	U-OH	65	trace	-	-	-	-	-
9	U-Br	20	360	360	0.33	59.4	1.51	81
10	U-Br	35	303	303	0.36	36.8	1.53	85
11	U-Br	50	260	260	0.41	18.4	1.54	87
12	U-Br	65	218	218	0.47	9.1	1.65	95
13	U-COOH	20	trace	-	-	-	-	-

^a Polymerization conditions: 2 μmol of Ni, Al(AlEt₂Cl)/Ni = 1600, monomers (mol/L) = 0.1, 1.2 atm, 30 min, 20 mL toluene, and 1 mL CH₂Cl₂. ^b Activity in kg copolymer/(mol Ni·h). ^c Determined by ¹H NMR spectroscopy. ^d Determined by GPC in 1,2,4-trichlorobenzene at 150 °C. ^e Branching density (/1000 C), determined by ¹H NMR spectroscopy.

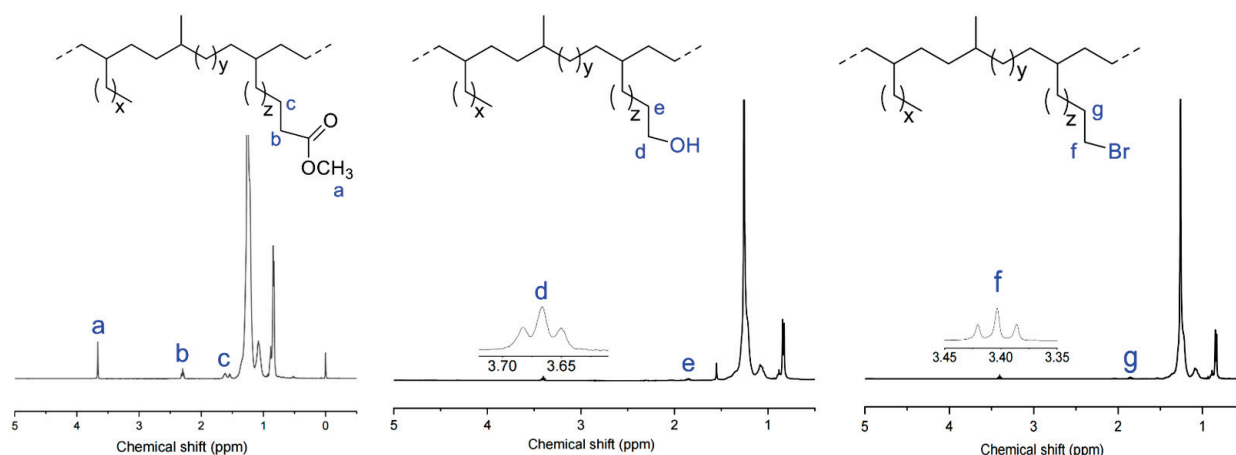


Figure 1. ¹H NMR spectra of the obtained functional polyethylenes in CDCl₃ (entries 3, 7, and 11 in Table 1).

The effects of polar groups on copolymerization were first examined. As shown in Table 1 and Figure 2, copolymerization activity increased but incorporation of polar comonomers decreased in the order of U-COOMe > U-OH > U-Br under identical reaction conditions, strongly indicating that the ester group -COOMe exhibited the strongest poisoning effect on the nickel metal center. This was attributed to the easiest σ -interaction between the ester group and the nickel metal center [32,69,70]. Additionally, copolymer molecular weight followed the order of U-OH > U-COOMe > U-Br. Although copolymerization of ethylene and U-Br showed the highest activity, the resultant copolymer molecular weight was the lowest. This is attributed to the accelerated chain transfer reaction caused by the electron-withdrawing Br group [71,72].

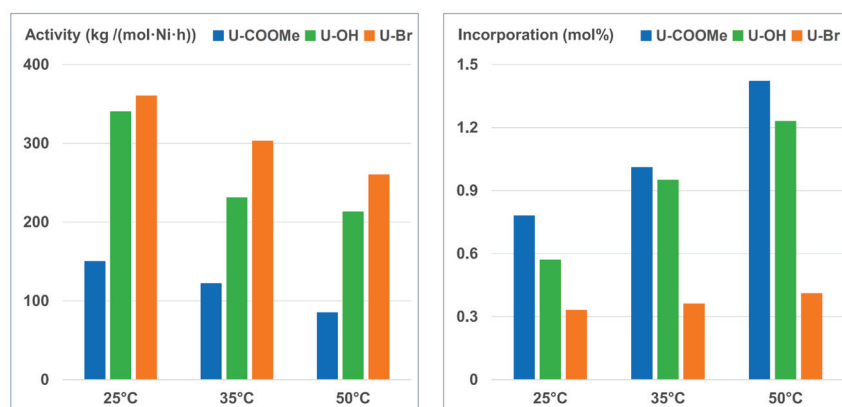


Figure 2. The effects of polar groups on copolymerization activity and comonomer incorporation at different temperatures.

The influences of reaction parameters on the copolymerization of ethylene and polar comonomers using the catalyst **Ni-DBB** were further investigated. As shown in Table 1, the copolymerization activity and the molecular weight of copolymers decreased, but the incorporation of the polar monomer increased with an increase in the temperature from 20 to 65 °C. Besides, the copolymers showed relatively narrow distribution ($PDI < 1.65$), indicating a controlled copolymerization fashion [73]. The molecular weight distribution of the copolymer also became broader with increasing temperatures. These observations suggested that elevated temperature was favorable for the incorporation of polar comonomers and the acceleration of chain transfer. To further illustrate the polar group tolerance of the dibenzobarrelene α -diimine nickel catalyst, copolymerizations were further conducted at various polar monomer concentrations using the catalyst **Ni-DBB** (Table 2). Increasing the comonomer concentration resulted in a lower $[Al]/[polar\ monomer]$ ratio (0.3~0.5), which led to an increase in the incorporation of comonomers, whereas the copolymerization activity and the molecular weight of copolymers decreased (entries 3, 6, 8, and 9 in Table 2). Besides, copolymerization of U-Br was conducted at a higher comonomer concentration. Lowering the relative additional Et_2AlCl /comonomer ratio to 0.3 still allowed the formation of a large amount of copolymer (entry 9 in Table 2), which was a result of reducing the poisoning effect of Br toward the nickel metal center compared to the ester and hydroxyl groups [69,74].

Table 2. Copolymerization results of ethylene and comonomers with various concentrations ^a.

Entry	Monomer	Conc. (mol/L)	Yield (mg)	Act. ^b	Incorporation ^c (mol%)	M_n ^d (kg/mol)	PDI ^d	BD ^e
1	U-COOMe	0.05	170	170	0.42	125.2	1.12	88
2	U-COOMe	0.1	150	150	0.78	104.2	1.15	86
3	U-COOMe	0.2	106	106	1.31	89.1	1.24	83
4	U-OH	0.05	474	474	0.34	145.2	1.05	89
5	U-OH	0.1	340	340	0.57	121.7	1.07	88
6	U-OH	0.2	102	102	1.06	54.1	1.86	78
7	U-Br	0.1	360	360	0.33	59.4	1.51	81
8	U-Br	0.2	280	280	0.62	30.0	1.55	81
9	U-Br	0.3	209	209	0.93	23.7	1.61	80

^a Polymerization conditions: 2 μ mol of Ni, $Al(AlEt_2Cl)/Ni=1600$, 20 °C, 1.2 atm, 30 min, 20 mL toluene and 1 mL CH_2Cl_2 . ^b Activity in kg copolymer/(mol Ni·h). ^c Determined by ^1H NMR spectroscopy. ^d Determined by GPC in 1,2,4-trichlorobenzene at 150 °C. ^e Branching density (/1000 C), determined by ^1H NMR spectroscopy.

The experimental results, as mentioned above, clearly showed that copolymerization of ethylene and U-OH was the most efficient in producing narrowly dispersed copolymers

among the three comonomers. The controlled copolymerization process of ethylene and U-OH using the catalyst **Ni-DBB** was further studied at 20 °C. Figure 3 shows symmetric GPC traces of the copolymers produced at different reaction times without tailing peaks, which shift to the higher molecular weight region with prolonged reaction time. Plots of number-average molecular weights (M_n) as a function of reaction time (Figure 4) also show that M_n grows linearly with the polymerization time, and M_w/M_n (PDI) values are below 1.20. Further, the incorporation of U-OH into copolymers obtained at different time periods remains nearly constant (~ 0.57 mol%), indicating that the comonomer U-OH is uniformly incorporated into polymer chains [48,51]. The hydroxyl functionalized polyethylene with a high molecular weight up to 180 kg/mol can be produced. Therefore, the dibenzobarrelene-based α -diimine nickel catalyst (**Ni-DBB**) is able to catalyze the copolymerization of ethylene and U-OH in a controlled fashion.

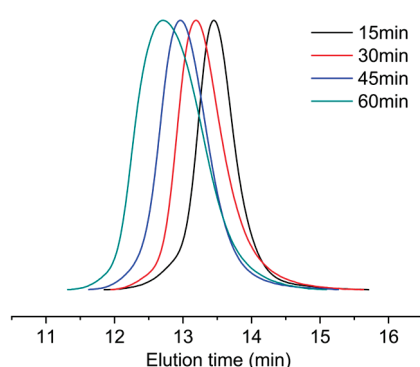


Figure 3. GPC curves of E/U-OH copolymers obtained at different reaction times.

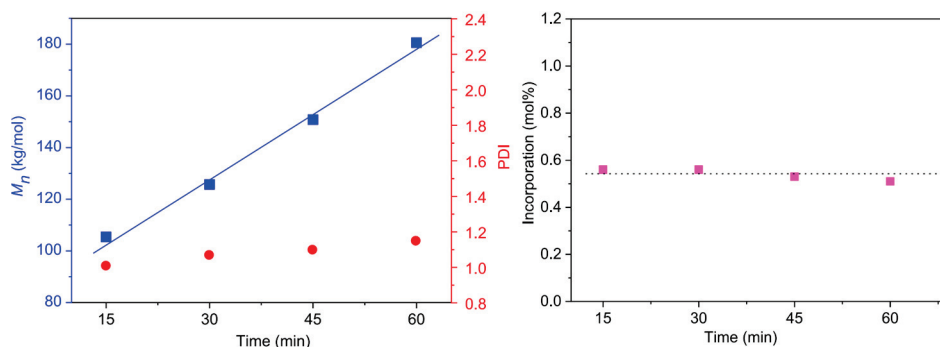


Figure 4. Plots of M_n , PDI, and incorporation of U-OH as a function of reaction time using **Ni-DBB**/ Et_2AlCl at 20 °C.

2.2. Microstructures of Functional Polyethylene

^1H NMR spectroscopy analysis (Figure 1) showed that the obtained functional polyethylene was highly branched (75~101/1000 C), which was different from the semi-crystalline polar polyethylene produced by Coates and co-workers [75]. To gain deep insight into the definitive microstructure of the produced functional polyethylene, the functional polyethylenes were analyzed by ^{13}C NMR spectroscopy (Figure 5). ^{13}C NMR spectra of the obtained functional polyethylene show characteristic peaks for U-COOMe (C_a : 174.35 ppm, C_b : 51.49 ppm), U-OH (C_d : 63.38 ppm), and U-Br (C_f : 33.53 ppm), respectively, which prove the successful copolymerization of ethylene and U-OH or U-Br. The branching distribution is quantitatively calculated on the basis of previous resonance assignments [76,77]. The obtained copolymers mostly contain methyl branches and long-chain branches, and the total content of other short branches, such as ethyl, propyl, butyl,

and amyl, was very low. This is attributed to the chain walking mechanism previously reported in our work [78].

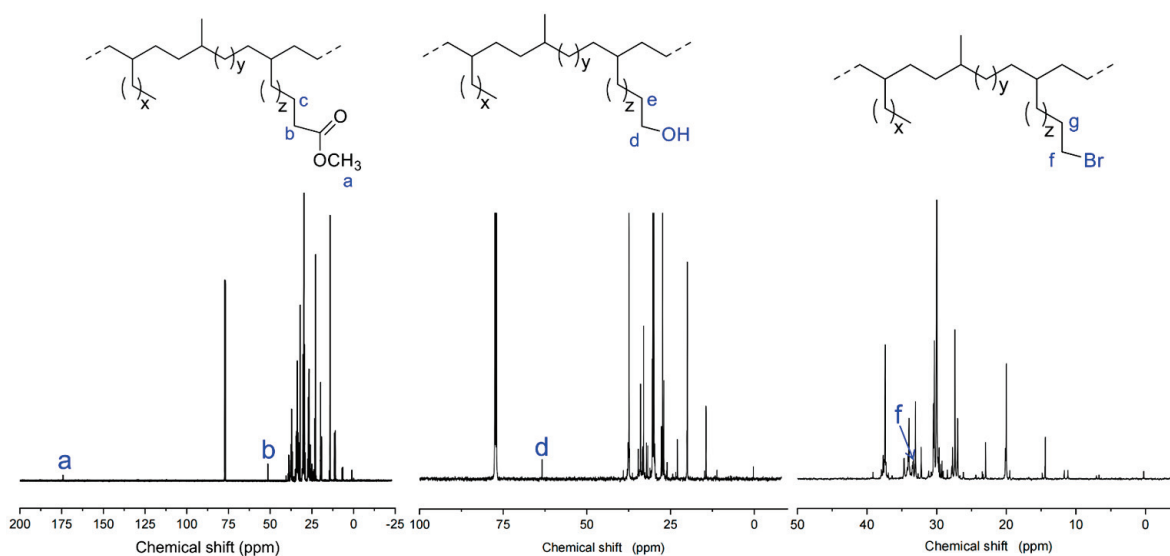


Figure 5. ^{13}C NMR spectra of the obtained functional polyethylenes in CDCl_3 (entries 3, 7, and 11 in Table 1).

Differential scanning calorimetry (DSC) analyses were conducted to examine the thermal behavior of the copolymers. As shown in Figure 6, the DSC curves of these copolymers (up to $150\text{ }^\circ\text{C}$) clearly show that no polyethylene homopolymer is present in the copolymerization products. Moreover, the functional polyethylenes have very broad melting endotherms, which are attributed to inhomogeneous branching distribution and different branching lengths. Generally, three kinds of functional polyethylenes have nearly the same DSC profiles, indicating nearly the same branching structure. This observation also indicates that the polar comonomer does not impact the chain walking process during copolymerization.

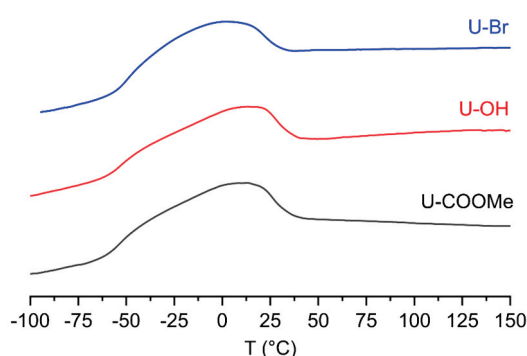


Figure 6. The DSC curves of functional polyethylenes (entries 3, 7, and 11 in Table 1).

2.3. Hydrophilic Property of Functional Polyethylene

The introduction of a small amount of polar groups in polyolefins can dramatically improve material properties such as compatibility, paintability, printability, and adhesion [79,80]. The surface properties of hydroxyl-functionalized polyethylenes (E/U-OH copolymers) with different -OH incorporations were evaluated by measuring the water contact angle (WCA). As shown in Figure 7, the WCA of pure branched polyethylene is 110° [62,68], while the WCA of copolymer decreased dramatically with the increasing

hydroxyl incorporation. The lowest WCA (84°) was obtained when the hydroxyl incorporation was 1.23 mol% [81]. Therefore, the surface of the PE material can be changed from hydrophobic to hydrophilic with the introduction of a small amount of U-OH.

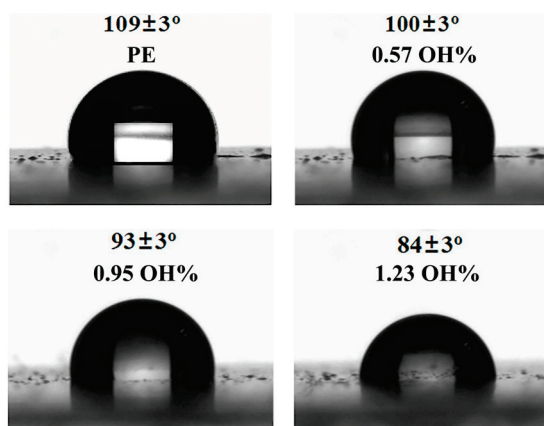


Figure 7. The water contact angle of hydroxyl-functionalized polyethylenes (entries 5–7 in Table 1).

3. Materials and Methods

3.1. General Procedures

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard vacuum-line, Schlenk, or glovebox techniques.

3.2. Materials

Toluene was refluxed over Na/K alloy before use, and dichloromethane was dried over P_2O_5 and was distilled under nitrogen. Et_2AlCl (0.9 M in Toluene) was purchased from Acros. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Methyl 10-undecenoate (U-COOMe), 10-undecen-1-ol (U-OH), and 10-undecenyl bromide (U-Br) were purchased from Aldrich. Other commercially available reagents were purchased and used without purification.

The dibenzobarrelene α -diimine nickel complex, **Ni-DBB**, was prepared according to our previous work [47]. The α -diimine ligand **DBB-L** was first synthesized and fully confirmed by ^1H and ^{13}C NMR. ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.25–7.02 (m, 14H, Ar-H), 4.98 (s, 2H, CH), 2.49 (m, 4H, $CH(CH_3)_2$), 1.15 (d, 12H, CH_3), 1.02 (d, 12H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 158.46, 145.56, 138.54, 136.36, 127.29, 125.38, 124.14, 122.81, 51.12, 23.29, 22.48. Nickel complex **DBB-Ni** was obtained by the addition of the ligand **DBB-L** to a stirring suspension of (dimethoxyethane) $NiBr_2$ in CH_2Cl_2 and confirmed by elemental analysis. Anal. Calcd for $C_{40}H_{44}Br_2N_2Ni$: C, 62.29; H, 5.75; N, 3.63; Found: C, 62.36; H, 5.66; N, 3.51.

3.3. Measurements

The NMR analysis of the copolymers was performed on a Bruker Avance III HD 400 MHz spectrometer. The incorporation (mol%) of U-COOMe in the copolymer was calculated by integrating methyl proton signals ($-OCH_3$) of inserted U-COOMe with respect to signals of other protons in the ^1H NMR spectrum (incorporation mol% = $4I_{OCH_3}/3(I_{CH_3} + I_{CH_2} + I_{CH}) \times 100\%$) [48]. The incorporation (mol%) of U-OH and U-Br in the copolymer was calculated by integrating methylene proton signals ($-CH_2-$) of inserted U-OH/U-Br with respect to signals of other protons in the ^1H NMR spectrum (incorporation mol% = $2I_{CH_2}/(I_{CH_3} + I_{CH_2} + I_{CH}) \times 100\%$) [66,67]. The branching density per 1000 carbon atoms of copolymers was determined by ^1H NMR spectrum. The branching distribution

was quantitatively calculated based on previously reported resonance assignments [76,77]. For each distinguishable type of branch in the ^{13}C NMR spectrum, a representative signal was selected, and the content of each branch type was determined by integrating the area under the corresponding peak. Differential scanning calorimeter (DSC) analyses of PEs were conducted with a PerkinElmer DSC-4000 system. The DSC curves were recorded as second heating curves from $-100\text{ }^{\circ}\text{C}$ to $+150\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and a cooling rate of $10\text{ }^{\circ}\text{C}/\text{min}$. Recorded at second heating curves to examine the thermal behavior of the copolymers. GPC analyses of the molecular weights and molecular weight distributions ($\text{PDI} = M_w/M_n$) of the PE samples at $150\text{ }^{\circ}\text{C}$ were performed on a PL-GPC 220 high-temperature chromatograph equipped with two GPC columns (PLgel 10 μm MIXED-B, Santa Clara, CA, USA), (Agilent Technologies, Palo Alto, CA, USA) and a differential refractive-index detector. 1,2,4-Trichlorobenzene (TCB) (Agilent Technologies, Palo Alto, CA, USA) was used as the eluent at a flow rate of $1.0\text{ mL}/\text{min}$. The molecular weight data were analyzed using narrow polystyrene standards (Polymer Laboratories, Long Beach, CA, USA) and were corrected for polymer samples by universal calibration. The water contact angle (WCA) test was conducted on a goniometer (DSA100S) (KRÜSS Scientific, Hamburg, Germany). Elemental analyses were performed on a Vario EL microanalyzer.

3.4. Procedure for the Copolymerization of Ethylene and Comonomers

A round-bottom Schlenk flask with stirring bar was heated for 2 h at $150\text{ }^{\circ}\text{C}$ under vacuum and then cooled to room temperature. The flask was pressurized to 1.2 atm of ethylene and vented three times. Then the glass reactor was charged with the required amount of freshly distilled toluene, Et_2AlCl , and polar monomer in sequence under 1.2 atm of ethylene. The system was continuously stirred for 5 min at the desired temperature, and then 1 mL of a solution of nickel complex in CH_2Cl_2 was added. The total reaction volume was kept at 21 mL. The ethylene pressure was kept constant at 1.2 atm. Polymerization was terminated by the addition of acidic methanol after releasing ethylene pressure. The resulting precipitated polymers were collected and treated by filtering and washed with methanol several times. The final product was dried under vacuum at $40\text{ }^{\circ}\text{C}$ to a constant weight.

4. Conclusions

In summary, an α -diimine nickel catalyst with a bulky dibenzobarrelene backbone was able to catalyze the copolymerization of ethylene and biosourced comonomers derived from castor oil, such as methyl 10-undecenoate (U-COOMe), 10-undecen-1-ol (U-OH), or 10-undecenyl bromide (U-Br). Copolymerization activity increased, but the incorporation of polar comonomers decreased in the order of $\text{U-COOMe} > \text{U-OH} > \text{U-Br}$. Besides, the copolymer molecular weight followed the order of $\text{U-OH} > \text{U-COOMe} > \text{U-Br}$. The copolymerization activity and the molecular weight of copolymers decreased, but the incorporation of monomer increased with an increase in temperature. Increasing the comonomer concentration led to an increase in the incorporation of comonomers, whereas the copolymerization activity and the molecular weight of copolymers decreased. Controlled copolymerization of ethylene and U-OH was realized at $20\text{ }^{\circ}\text{C}$ to afford a narrowly dispersed copolymer. The produced functional polyethylenes are highly branched, and their hydrophilic properties improve with increasing incorporation of polar groups. This study provides access to synthesize bio-based functional polyolefins by copolymerization of ethylene and biosourced comonomers using earth-abundant nickel catalysts.

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Article

Finely-Tuned Bis(imino)pyridylcobalt Complexes Enhance Ethylene Polymerization: The Role of Bulky and Halogen Substituents

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Abstract: The bis(imino)pyridylcobalt complexes have been finely tuned through using the aniline derivative bearing a *meta*-chloro substituent, besides its *ortho*- and *para*-di(4-fluorophenyl)methyl and *ortho*-methyl substituents for the series of 2-[1-(3-chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methylphenylimino)ethyl)-6-[1-(arylimino)ethyl]pyridylcobalt(II) chlorides (2,6-Me₂Ph, **Co1**; 2,6-Et₂Ph, **Co2**; 2,6-*i*Pr₂Ph, **Co3**; 2,4,6-Me₃Ph, **Co4**; and 2,6-Et₂-4-MePh, **Co5**). The compounds were characterized using elemental analysis, ¹H/¹³C NMR, FT-IR spectroscopy, and the single-crystal X-ray diffraction used in confirming the molecular structures of **Co1**, **Co2**, **Co4**, and **Co5**. The newly synthesized precatalysts, maintaining steric influences with the addition of an electron-withdrawing *meta*-chloro group, achieved higher activities along with better thermal stability, and controlled molecular weights of polyethylenes obtained. Upon activation with either MAO or MMAO, all catalysts exhibited remarkable activity for ethylene polymerization, for example, 9.2×10^6 g mol⁻¹ h⁻¹ by **Co1** at 70 °C with 30 min and 18.0×10^6 g mol⁻¹ h⁻¹ by **Co4** with the first 5 min. **Co4** demonstrated exceptionally thermal stability with the peak activity of 8.9×10^6 g mol⁻¹ h⁻¹ at 70 °C and slightly decreased to 7.2×10^6 g mol⁻¹ h⁻¹ at 80 °C, and even maintained an activity of 1.6×10^6 g mol⁻¹ h⁻¹ at 100 °C. More importantly, all resultant polyethylenes were characterized as having vinyl-terminal and high-linear feature along with narrow dispersity; the molecular weights could be adapted in the ranges from 6.4 to 50.0 kg mol⁻¹. In comparison with previous cobalt analogs, the current system performed better thermal stability and polymerization efficiency. Therefore, such robust complex catalysts are potentially considered for the polyethylene industry.

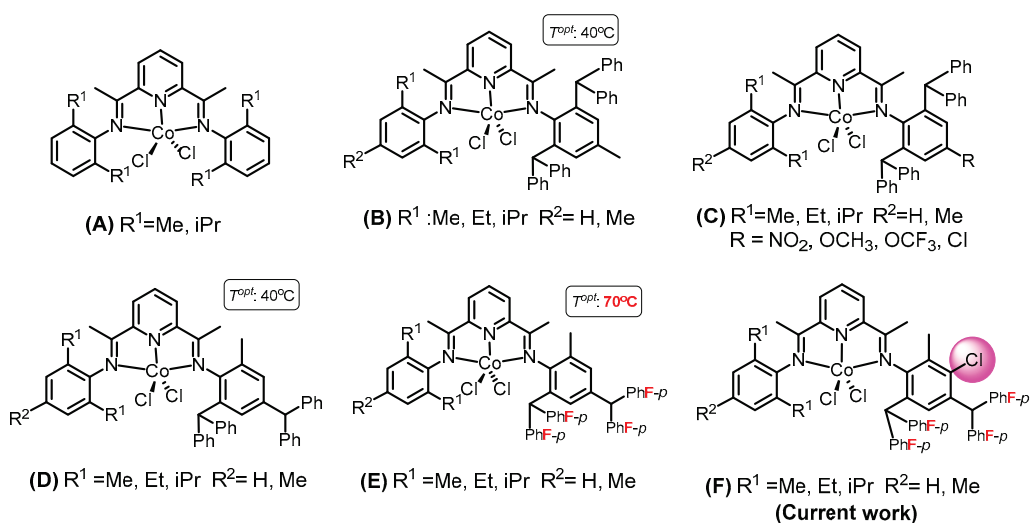
Keywords: unsymmetric bis(imino)pyridylcobalt complex; ethylene polymerization; high activity and thermal stability; highly linear and vinyl-terminal polyethylene

1. Introduction

Polyethylene is one of the most widely used synthetic polymers, valued for its cost-effectiveness, ease of processing, and recyclability [1]. It serves as a key material in a variety of industries, ranging from packaging to automotive, due to its favorable mechanical properties, chemical resistance, and versatility [2]. The sustainability of polyethylene is closely tied to its hydrocarbon structure derived from natural oils, which can also serve as an energy source [3]. The polymerization of ethylene is central to the production of polyethylene [4], and significant advancements have been made in improving the

efficiency and control of this process primarily through the development of highly effective catalysts [5–10].

A promising strategy for enhancing catalytic performance in ethylene polymerization is the incorporation of bulky groups into the ligands of metal catalysts [11–15]. These bulky substituents introduce steric hindrance, which can significantly influence the catalytic activity, polymerization kinetics, and polymer properties [16,17]. Such modification can improve catalyst stability and allow for better control over polymer molecular weights, making them essential in the design of next-generation catalysts. Common bulky groups [7], such as dibenzhydryl [12], anthracenyl, and dibenzosuberyl [18] groups, have been shown to significantly improve the activity and thermal stability of catalysts, particularly those based on late-transition metals. Bis(imino)pyridyl cobalt precatalysts (**A**, Scheme 1) firstly discovered in 1998 [19–21] have demonstrated remarkable performance in producing highly linear polyethylene, with their activity and thermal stability significantly enhanced by the strategic incorporation of bulky substituents. Particularly, the synthesis of cobalt precatalysts featuring unsymmetrical ligands (**B**, Scheme 1) [12] achieved by introducing the bulky group dibenzhydryl into the two *ortho* positions of one of the N-aryl groups, forming the 2-[1-(2,6-dibenzhydrylphenylimino)ethyl]-6-[1-(arylimino)ethyl] pyridylcobalt precatalyst, has been shown to enhance catalytic activity in ethylene polymerization. This resulted in a peak activity of $9.87 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. The steric hindrance from these *ortho*-bulky groups protects the catalytic active sites, leading to improved activity and thermal stability. Meanwhile, electronic effects were explored by varying the substituents at the *para* position of the N-aryl ring in the catalysts (**C**, Scheme 1) [12,22–24]. A high activity was observed when the *para* position is occupied by a methyl group [12], while good thermal stability was achieved with the methoxy group at this site [21]. These findings demonstrate that both bulky substituents and electronic groups play a crucial role in tuning catalyst performance and controlling the polymerization process. In a previous study by our group, we further optimized the catalysts by shifting the dibenzhydryl moieties from one of the *ortho* positions to the *para* position (**D**, Scheme 1) [25], resulting in a significant increase in activity ($18.05 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$). All these catalyst systems produced highly linear polyethylene and narrow polydispersity indices (PDIs), characteristic of single-site active species.



Scheme 1. Structural modifications in bis(imino)pyridylcobalt precatalysts (**A–E**), along with the precatalyst developed in this work (**F**).

Another significant advancement in polyethylene catalyst design is the introduction of halogen groups, such as fluorine and chlorine, which have been shown to further enhance

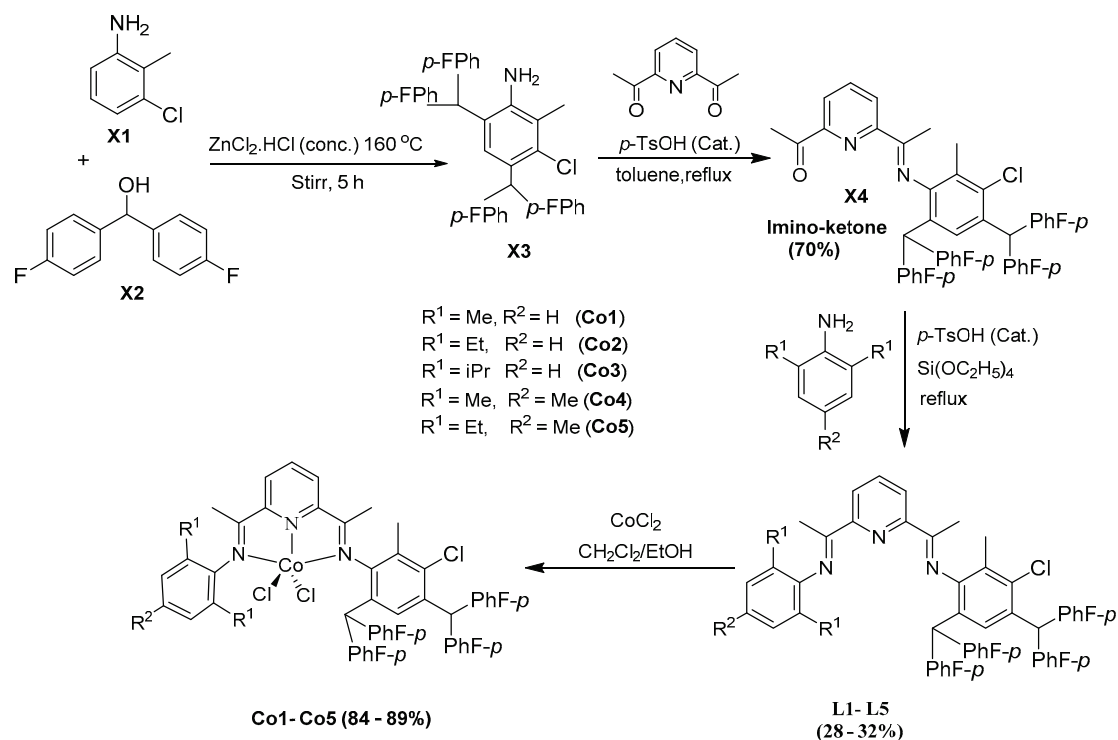
the performance of ethylene polymerization catalysts [26]. These halogen groups were typically introduced into the *ortho* [27,28] and *para* [29] positions of the N-aryl groups or the *para* position of the bulky group [30,31]. The inclusion of halogen substituents not only improves the thermal stability of the catalysts, but also plays a crucial role in controlling the molecular weight distribution of the resulting polymer [31]. For instance, when we introduced the fluoride group into the *para* position of the bulky group in structure **D**, resulting in catalyst **E** in Scheme 1 [30], the optimal polymerization temperature was found to be 70 °C towards ethylene polymerization, a notable improvement over catalysts **B** and **D**, both of which exhibited an optimal temperature of 40 °C. The halogen groups are known to enhance polymerization efficiency by modifying the electronic properties of the metal center. By fine-tuning the steric and electronic properties of the catalyst, these modifications can enable a more controlled polymerization process. As a result, catalysts with halogen substitutions exhibit higher thermal stability, more consistent polymerization behavior, and better control over the molecular weight and polydispersity of the polymer produced.

In this study, we synthesized a series of unsymmetrical bis(arylimino)pyridine-Co (II) complexes by introducing the fluoride group at the *para* positions of the two bulky dibenzhydryl groups attached to the *ortho* and *para* positions of one of the N-aryl groups, as well as a chloride group at the *meta* position of the N-aryl group (**F**, Scheme 1). The rationale for this design was to explore the synergistic effects of bulky and halogen-substituted groups on the catalytic performance of the cobalt complex in ethylene polymerization. Specifically, we aimed to build upon the strong performance of catalyst **E**, particularly its good thermal stability, which was attributed to the *ortho*- and *para*-substituted 4-fluorodibenzyl groups that increase steric hindrance around the metal center. We hypothesized that adding an electron-withdrawing *meta*-chloro group would further modify the Lewis acidity of the cobalt metal center, enhancing its electrophilic character. This modification was expected to promote the polymerization process by improving the catalyst's reactivity. By combining these steric and electronic effects, we anticipated an overall enhancement in catalytic activity and thermal stability, and control over polymer properties like molecular weights. To evaluate the catalytic properties of these newly designed complexes, we activated these cobalt complexes with methyl aluminoxane (MAO) or modified-methyl aluminoxane (MMAO) as co-catalyst. A detailed study was conducted under various conditions, including the Al/Co ratio, temperature, ethylene pressure, and reaction time, to thoroughly investigate the influence of these factors on the catalyst's performance. Our study systematically explored how electronic and steric variations influenced the catalyst's structure and polymerization capabilities. Additionally, we compared the catalytic performance of these newly cobalt catalysts with earlier versions of similar catalysts, highlighting the impact of halogen and bulky group modifications on the overall polymerization behavior. The results underscore the potential of this strategy for designing highly active, thermally stable catalysts with precise control over polymer molecular weight distribution, an important characteristic for industrial-scale polyethylene production.

2. Results and Discussion

2.1. Synthesis and Characterizations of Ligands and Cobalt Complexes

A series of 2,6-bis(arylimino)pyridine derivatives with an asymmetric framework were synthesized through a multi-step procedure with good overall yields. The synthesized compounds include 2-[1-(3-chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methyl-phenylimino)-ethyl]-6-(arylimino)ethyl] pyridine, with varying aryl groups: 2,6-Me₂Ph (**L1**), 2,6-Et₂Ph (**L2**), 2,6-iPr₂Ph (**L3**), 2,4,6-Me₃Ph (**L4**), and 2,6-Et₂-4-MePh (**L5**), as shown in (Scheme 2).



Scheme 2. The synthesis route of ligands and their corresponding cobalt complexes.

The synthesis began with the preparation of the bulky 4,6-bis(bis(4-fluorophenyl)-methyl)-3-chloro-2-methylaniline (**X3**) using methods described in the previous literature [30–32]. The synthesis commenced with the reaction of 3-chloro-2-methylaniline (**X1**) with bis(4-fluorophenyl)methanol (**X2**) to afford the target bulky aniline **X3**. Next, the condensation of 2,6-diacetylpyridine with one equivalent of **X3** resulted in the primary formation of the imine-ketone 2-acetyl-6-[1-(3-chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methylphenylimino)ethyl)pyridine (**X4**). The imine-ketone intermediate **X4** was treated with different anilines, under acidic conditions, leading to the formation of ligands **L1** to **L5**. Subsequently, **L1** to **L5** were reacted with anhydrous cobalt (II) chloride in a solvent mixture of ethanol and dichloromethane, producing 2-[1-(3-chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methylphenylimino)-ethyl]-6-[1(arylimino)ethyl]pyridylcobalt(II) chlorides: (aryl = 2,6-Me₂Ph **Co1**, 2,6-Et₂Ph **Co2**, 2,6-iPr₂Ph **Co3**, 2,4,6-Me₃Ph **Co4**, and 2,6-Et₂-4-MePh **Co5** in yields of 84–89% (as shown in Scheme 2).

The obtained compounds **X3**, **X4**, and ligands **L1–L5** were structurally characterized using ¹H, ¹³C NMR, and/or elemental analysis (Section 3 and Figures S1 and S2). ¹⁹F NMR spectroscopy was performed on **L1–L5** to investigate the fluorine environments. As illustrated in Figure S3, the free ligand spectra displayed signals with chemical shifts around δ –116 ppm. There were no significant differences in the chemical shift positions of these fluoride substituents, as they are attached to the *para* position of the bulky dibenzhydryl group, and are not influenced much by changes in the other N-aryl moiety. The cobalt complexes (**Co1** to **Co5**) were characterized using elemental analysis techniques and FT-IR spectroscopy (Figure S4). **Co1**, **Co2**, **Co4**, and **Co5** were further subjected to single-crystal X-ray diffraction for structural elucidation. Single crystals of **Co1**, **Co2**, **Co4**, and **Co5** used for X-ray investigations were grown by gradually diffusing n-heptane into a solution of dichloromethane containing the respective complex. The perspectives of crystal structures are shown in Figures 1–4, with selected bond lengths and angles summarized in Table 1, while full crystallographic details are available in Table S1. These crystal structures of **Co1**, **Co2**, **Co4**, and **Co5** exhibited similar conformations and will be collectively described. Each

complex structure features a solitary cobalt center coordinated by an N[∞]N[∞]N-chelating bis(arylimino)pyridine and two chloride ions, forming a distorted square pyramid geometry. To quantify this distortion, the geometric tau value (τ_5) was calculated using the equation $\tau_5 = (\beta - \alpha)/60$, where β represents the largest angle and α represents the second largest angle in the coordination sphere. The value of τ_5 for **Co5** is 0.14 which indicates a nearly perfect square pyramid, while a value of one suggests a perfect trigonal bipyramid. For **Co4**, **Co2**, and **Co1**, τ_5 values were 0.41, 0.45, and 0.41, respectively, indicating some deviation from a perfect square pyramid. The bond lengths between cobalt and nitrogen were analyzed and it was found that the Co(1)-N(2) bond lengths were consistently shorter than those Co(1)-N(1) and Co(1)-N(3), indicating a stronger coordination between cobalt and the central nitrogen atom. Specifically, the Co(1)-N(2) bond lengths were 2.0321 (15) Å for **Co1**, 2.033 (5) Å for **Co2**, 2.0362 (19) Å for **Co4**, and 2.021 (8) Å for **Co5**. In comparison, the Co(1)-N(1) bond lengths were 2.2918 (15) Å for **Co1**, 2.271 (15) Å for **Co2**, 2.3090 (19) Å for **Co4**, and 2.294 (8) Å for **Co5**, while the Co(1)-N(3) bond lengths were 2.2398 (15) Å for **Co1**, 2.228 (5) Å for **Co2**, 2.204 (2) Å for **Co4**, and 2.233 (9) Å for **Co5**. These consistently shorter Co(1)-N(2) bonds suggest a stronger coordination interaction between cobalt and the nitrogen atom at position N(2). This is consistent with similar findings in the literature [30,31], where shorter Co-N bonds to the central nitrogen are typically indicative of a stronger metal–ligand coordination. Similarly, the bond lengths of Co(1)-Cl(1) [2.2470 (5) Å for **Co1**, 2.2542 (18) Å for **Co2**, 2.2567 (7) Å for **Co4**, and 2.242 (3) Å for **Co5**] and Co(1)-Cl(2) [2.2689 (5) Å for **Co1**, 2.2538 (18) Å for **Co2**, 2.2979 (7) Å for **Co4**, and 2.259 (3) Å for **Co5**] exhibited slight variations while remaining generally consistent across the different cobalt atoms. This consistency in the Co-Cl bond lengths suggests a stable coordination environment, which is advantageous for predicting the behavior of these complexes in various chemical reactions. Additionally, the uniformity in these bond lengths can indicate the reliability of the synthesis method, ensuring the reproducibility and stability of the compounds. The nitrogen–carbon bond lengths N(1)-C(10) [1.432 (2) Å (**Co1**), 1.440 (7) Å (**Co2**), 1.435 (3) Å (**Co4**), and 1.453 (11) Å (**Co5**)] and N(3)-C(43) [1.435 (2) Å (**Co1**), 1.447 (8) Å (**Co2**), 1.445 (3) Å (**Co4**), and 1.410 (14) Å (**Co5**)] exhibit slight variations. These differences can be explained by the subtle variations in the local environment and electronic effects around each cobalt center. Factors such as coordination geometry, ligand field effects, and inter-ligand interactions can affect the bond lengths, resulting in the observed minor variations. Similar tendencies have been observed in other complexes of unsymmetrical bis(arylimino)pyridine [33–35]. The description of X-ray crystallographic studies can be found in the Supporting Information (SI). Finally, the bond lengths between F(1) and C(34) showed some variability [1.361 (2) Å for **Co1**, 1.354 (10) Å for **Co2**, 1.357 (3) Å for **Co4**, and 1.405 (16) Å for **Co5**], suggesting potential differences in the interactions between fluorine and carbon. The bond angles around **Co1**, **Co2**, **Co4**, and **Co5** in Table 2 show how *meta*-chloro, *ortho*- and *para*-di(4-fluorophenyl)methyl, and *ortho*-methyl substituents affect the coordination geometry of cobalt complexes. Comparing **Co1**, **Co2**, and **Co4** with **Co5**, significant differences are observed. For example, the N(1)-Co(1)-N(3) angle in **Co5** (101.8°) is notably smaller than in **Co1**, **Co2**, and **Co4** (approximately 150°), indicating greater steric hindrance around **Co5**. This steric effect is also evident in the N(2)-Co(1)-Cl(2) angle, which is larger in **Co5** (118.2°) compared to **Co1**, **Co2**, and **Co4**, suggesting more space around **Co5** for the chloride ligand. These findings support previous literature that has examined similar substituent effects on transition metal complexes [36]. These results highlight how the combination effect from the substituents on both of the N-aryl rings on the coordination environments around the metal center affect bond angles and overall geometries. The crystal data and structural refinements for **Co1**, **Co2**, **Co4**, and **Co5** can be found in (Table S1).

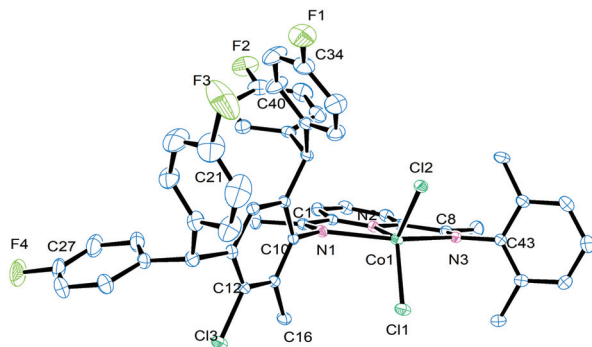


Figure 1. ORTEP representation of Co1 with thermal ellipsoids illustrated at a 30% probability level, and all hydrogen atoms are omitted for clarity.

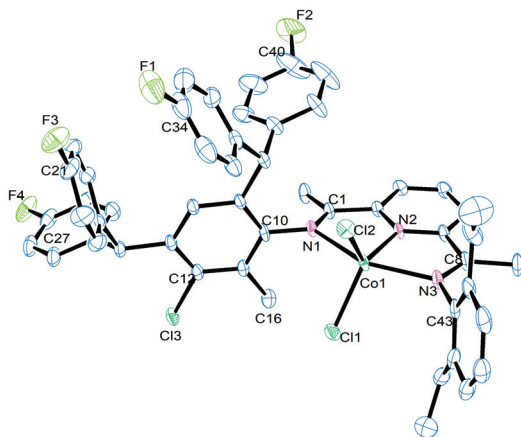


Figure 2. ORTEP representation of Co2 with thermal ellipsoids illustrated at a 30% probability level, and all hydrogen atoms are omitted for clarity.

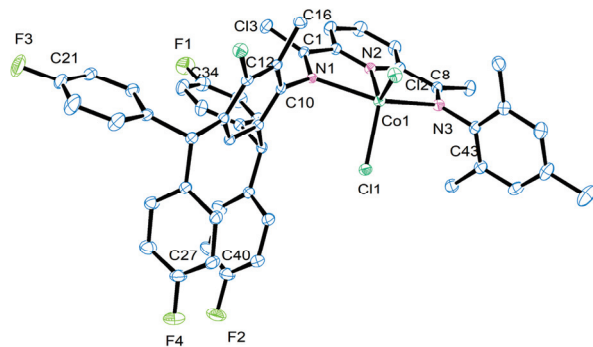


Figure 3. ORTEP representation of Co4 with thermal ellipsoids illustrated at a 30% probability level, and all hydrogen atoms are omitted for clarity.

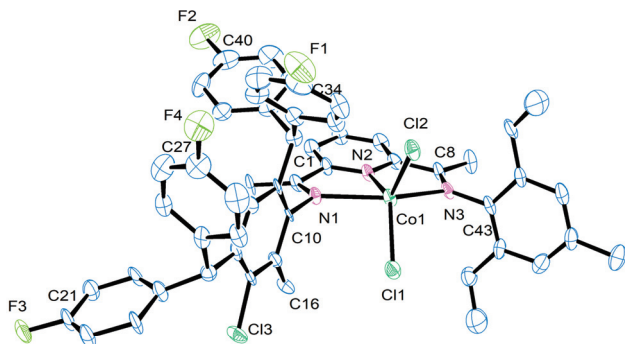


Figure 4. ORTEP representation of Co5 with thermal ellipsoids illustrated at a 30% probability level, and all hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and bond angles (°) for **Co1**, **Co2**, **Co4**, and **Co5**.

Selected Bond Lengths (Å)				
	Co1	Co2	Co4	Co5
Co(1)-N(1)	2.2918 (15)	2.271 (15)	2.3090 (19)	2.294 (8)
Co(1)-N(2)	2.0321 (15)	2.033 (5)	2.0362 (19)	2.021 (8)
Co(1)-N(3)	2.2398 (15)	2.228 (5)	2.204 (2)	2.233 (9)
Co(1)-Cl(1)	2.2470 (5)	2.2542 (18)	2.2567 (7)	2.242 (3)
Co(1)-Cl(2))	2.2689 (5)	2.2538 (18)	2.2979 (7)	2.259 (3)
N(1)-C(10)	1.432 (2)	1.440 (7)	1.435 (3)	1.453 (11)
N(3)-C(43)	1.435 (2)	1.447 (8)	1.445 (3)	1.410 (14)
F(1)-C(34)	1.361 (2)	1.354 (10)	1.357 (3)	1.405 (16)
Selected Bond Angles (°)				
N(1)-Co(1)-N(2)	74.57 (6)	74.40 (18)	73.65 (7)	75.5 (3)
N(1)-Co(1)-N(3)	149.96 (6)	150.44 (18)	150.53 (7)	101.8 (2)
N(2)-Co(1)-N(3)	75.46 (6)	76.05 (19)	76.90 (8)	75.1 (3)
N(1)-Co(1)-Cl(1)	97.67 (4)	92.86 (14)	96.86 (5)	92.2 (2)
N(2)-Co(1)-Cl(1)	122.45 (4)	123.07 (16)	122.57 (6)	126.4 (3)
N(3)-Co(1)-Cl(1)	99.91 (4)	102.52 (16)	97.92 (5)	101.8 (2)
N(2)-Co(1)-Cl(2)	125.16 (4)	123.49 (16)	126.23 (5)	118.2 (3)
N(3)-Co(1)-Cl(2)	96.50 (4)	96.96 (2)	105.59 (6)	96.2 (2)
Cl(1)-Co(1)-Cl(2)	112.39 (19)	113.26 (7)	110.44 (3)	115.32 (12)
N(1)-Co(1)-Cl(2)	99.05 (4)	99.93 (14)	92.82 (5)	101.3 (2)

2.2. Ethylene Polymerization

Previous research has shown that aluminoxanes, such as MAO (methylaluminumoxane) or MMAO (modified methylaluminumoxane), are effective co-catalysts for activating the bis(imino)pyridine-cobalt catalyst. To evaluate the catalytic properties of **Co1** to **Co5**, both MAO and MMAO were used for comparison. We chose **Co4** as the initial catalyst to establish the optimal reaction conditions for polymerizations under these two co-catalysts. This involved systematically exploring the effects of co-catalyst amount, temperature, reaction duration, and ethylene pressure on the catalytic performance and molecular weight (M_w) of the resulting polyethylene. Toluene was used as the solvent in all experimental procedures and the results of the polymerization experiments were summarized in Tables 2–4 with some of the general descriptions listed in the Supplementary Information.

2.2.1. Optimization of Polymerization Conditions Using **Co4**/MAO

The optimization of reaction conditions for ethylene polymerization using **Co4**/MAO began by varying the co-catalyst amounts, represented by the Al/Co ratio (ranging from 2000:1 to 3250:1) (entries 1–5, Table 2). The highest catalytic activity of $4.0 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ and a peak molecular weight of 20.5 kg mol^{-1} for polyethylene were observed at an Al/Co ratio of 3000:1 (entry 4, Table 2), with the operating temperature maintained at 30 °C, a reaction time of 30 min, and a reaction pressure of 10 atm ethylene. At a lower Al/Co ratio (2000:1), the catalytic activity was relatively lower (entries 1–3), while a further increase in the Al/Co ratio (3250:1) led to a slight reduction in both activity and molecular weight (entry 5). This trend suggests that the co-catalyst concentration has an optimal range, and beyond that, the excess co-catalyst may promote side reactions such as chain transfer and termination, leading to a reduction in the polymer's molecular weight [37–39].

Table 2. Optimization of polymerization conditions using **Co4**/MAO ^a.

Entry	T (°C)	t (min)	Al/Co	PE (g)	Activity ^b	M_w ^c	M_w/M_n ^c	T_m (°C) ^d
1	30	30	2000	2.0	2.0	15.3	2.3	131.6
2	30	30	2500	2.4	2.4	15.7	1.9	130.7
3	30	30	2750	2.7	2.7	18.3	1.7	130.9
4	30	30	3000	4.0	4.0	20.8	2.2	131.6
5	30	30	3250	2.5	2.5	16.1	2.4	131.6
6	40	30	3000	4.1	4.1	20.5	2.6	131.8
7	50	30	3000	4.5	4.5	16.3	2.0	130.7
8	60	30	3000	4.9	4.9	14.6	2.2	130.4
9	70	30	3000	8.9	8.9	10.9	2.0	131.8
10	80	30	3000	7.2	7.2	7.5	2.0	129.1
11	90	30	3000	5.0	5.0	7.1	2.2	128.1
12	100	30	3000	1.6	1.6	6.4	2.9	128.3
13	70	5	3000	3.0	18.0	8.5	2.1	128.0
14	70	15	3000	6.9	13.7	10.0	2.4	129.1
15	70	45	3000	12.9	8.6	11.4	2.1	129.0
16	70	60	3000	13.3	6.6	12.7	2.7	128.8
17 ^e	70	30	3000	4.3	4.3	8.2	2.5	129.0
18 ^f	70	30	3000	0.9	0.9	2.2	2.3	128.0

^a General conditions: 2 μ mol of **Co4**, 100 mL toluene, 10 atm C₂H₄; ^b 10⁶ g mol^{−1} h^{−1}; ^c M_w : kg mol^{−1}, determined by GPC; ^d determined by DSC; ^e 5 atm of C₂H₄; ^f 1 atm of C₂H₄.

Table 3. Optimization of polymerization conditions using **Co4**/MMAO ^a.

Entry	T (°C)	t (min)	Al/Co	PE (g)	Activity ^b	M_w ^c	M_w/M_n ^c	T_m (°C) ^d
1	30	30	2000	2.2	2.2	19.8	1.9	130.8
2	30	30	2500	2.4	2.4	21.6	2.0	130.7
3	30	30	3000	2.9	2.9	23.3	1.9	132.0
4	30	30	3500	4.1	4.1	21.0	2.0	131.5
5	30	30	4000	3.3	3.3	18.4	2.1	132.0
6	40	30	3500	4.5	4.5	20.0	2.1	131.6
7	50	30	3500	4.6	4.6	15.9	2.2	130.7
8	60	30	3500	4.8	4.8	15.0	2.2	130.5
9	70	30	3500	3.2	3.2	10.3	2.3	129.4
10	80	30	3500	0.9	0.9	9.0	2.6	128.9
11	90	30	3500	0.8	0.8	8.1	2.4	128.7
12	60	5	3500	2.1	13.0	11.8	1.1	130.0
13	60	15	3500	2.3	4.7	13.0	1.7	130.9
14	60	45	3500	5.3	3.5	19.3	2.3	131.9
15	60	60	3500	6.1	3.1	22.1	2.9	131.8
16 ^e	60	60	3500	2.0	2.0	19.1	2.0	128.6
17 ^f	60	60	3500	0.5	0.5	6.5	1.9	128.0

^a General conditions: 2 μ mol of **Co4**, 100 mL toluene, 10 atm C₂H₄; ^b 10⁶ g mol^{−1} h^{−1}; ^c M_w : kg mol^{−1}, determined by GPC; ^d determined by DSC; ^e 5 atm of C₂H₄; ^f 1 atm of C₂H₄.

Table 4. Evaluation of **Co1** to **Co5** with either MAO/MMAO under optimized conditions ^a.

Entry	Precat.	Co-Cat.	Activity ^b	M_w ^c	M_w/M_n ^c	T_m (°C) ^d
1	Co1	MAO	9.2	8.3	2.6	129.5
2	Co2	MAO	9.1	14.5	2.4	130.7
3	Co3	MAO	7.1	25.7	2.3	131.8
4	Co4	MAO	8.9	10.9	2.0	131.8
5	Co5	MAO	8.0	17.9	2.1	131.3
6	Co1	MMAO	2.7	14.9	2.2	130.7
7	Co2	MMAO	2.6	29.6	2.1	131.9
8	Co3	MMAO	2.3	50.0	1.9	132.0
9	Co4	MMAO	4.8	15.0	2.2	131.7
10	Co5	MMAO	2.5	32.4	1.8	132.3

^a General conditions: 2 μ mol of cobalt precatalyst, 100 mL toluene, 10 atm C₂H₄, 30 min, Al/Co ratio of 3000:1 and 70 °C for MAO, Al/Co ratio of 3500:1 and 60 °C for MMAO; ^b 10⁶ g mol^{−1} h^{−1}; ^c determined by GPC, M_w : kg mol^{−1}; ^d determined by DSC.

Next, the effect of reaction temperature on the catalytic activity and polymer properties was explored by varying the temperature from 30 to 100 °C (entries 6–12 in Table 2, Figure 5a). As the temperature increased from 30 to 70 °C, the catalytic activity gradually intensified, reaching a peak of $8.9 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 70 °C (entry 9, Table 2). However, higher temperatures above 70 °C resulted in a decrease in catalytic activity, with values dropping to $7.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 80 °C, $5.0 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 90 °C, and a further decrease to $1.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 100 °C. This decrease in catalytic activity at elevated temperatures can be attributed to the thermal instability of the active species, which is a well-documented phenomenon in similar catalytic systems [40]. Despite this, the system exhibited notable thermal stability, with only a 13% decrease in activity at 80 °C compared to the peak activity at 70 °C, and it still demonstrated an excellent catalytic performance even at 100 °C. This suggests that the **Co4**/MAO system retains a significant degree of stability at higher temperatures, with only a moderate decline in activity as the temperature increases. On the other hand, the molecular weight of the resulting polyethylene decreased with increasing temperature, from 20.8 kg mol^{-1} at 30 to 6.4 kg mol^{-1} at 100 °C (entries 4, 6–12 in Table 2 and Figure 5b). This reduction in molecular weight can be attributed to an enhanced rate of chain transfer reactions compared to chain propagation, which is common at higher operating temperatures. Additionally, the reduced solubility of the ethylene monomer at higher temperatures could contribute to the observed decrease in molecular weight, as chain termination could occur via β -hydrogen elimination to the ethylene monomer, resulting in polymers with vinyl end groups, as evidenced by the high-temperature ^1H and ^{13}C NMR spectra presented in the microstructural analysis section. Similar trends of decreasing molecular weight with increasing temperature due to the increased chain transfer rates at elevated temperatures have been reported in the literature [41].

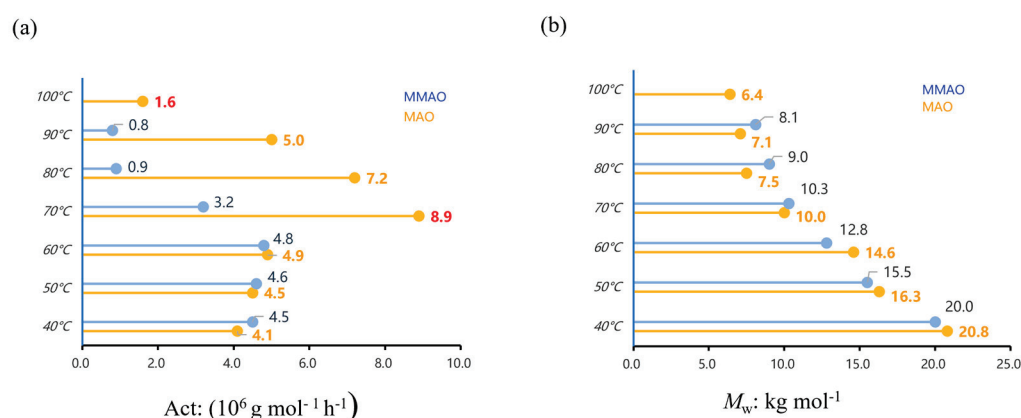


Figure 5. The activity in $10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ (a) and molecular weight in kg mol^{-1} (b) varying with reaction temperatures using **Co4** that is activated by either MAO or MMAO.

The time/activity profile of **Co4**/MAO was assessed at intervals ranging from 5 to 60 min (entries 9, 13–16, Table 2), while maintaining the optimal Al/Co ratio of 3000:1 and reaction temperature of 70 °C. The results showed a gradual decline in catalytic activity over time, with the peak occurring at 5 min ($18.0 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$) and the lowest level observed at 60 min ($6.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$), reflecting the short induction period required to generate the active species. The polymerization system maintained a relatively extended lifespan during prolonged reactions, indicating that the **Co4**/MAO catalyst is stable over the course of the polymerization process.

Polymerization experiments at varying ethylene pressures (5 and 1 atm) were conducted to investigate the influence of pressure on the catalytic activity of **Co4**/MAO and polymer molecular weight (entries 9, 17, and 18, Table 2). The results clearly revealed

that higher pressures enhanced both catalytic performance and polymer molecular weight. Specifically, at 5 atm of ethylene, the catalytic activity was nearly halved compared to 10 atm, with the molecular weight of polyethylene decreasing to 8.2 kg mol^{-1} (entry 17, Table 2). Conversely, at 1 atm, the catalytic activity dropped significantly to $0.9 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, and the polymer molecular weight decreased to 2.2 kg mol^{-1} . These findings suggest that the higher ethylene pressure improves the solubility of the ethylene monomer and facilitates better coordination and insertion, thereby enhancing both catalytic activity and molecular weight.

In the above optimization of polymerization conditions of **Co4**/MAO, the produced polyethylenes consistently exhibited a narrow dispersity (M_w/M_n range from 1.7 to 2.9; entries 1–18, Table 2). The well-defined molecular weight distribution is indicative of a controlled chain growth process, with minimal variations in the chain lengths of the resulting polyethylene. This is a significant advantage for producing polymers with consistent and predictable properties, which is essential for many industrial applications. Furthermore, the melting temperatures of the produced polyethylenes ranged from 128.0°C to 131.6°C , which is optimal for high-density polyethylene (HDPE) with a narrow molecular weight distribution. The combination of narrow molecular weight distribution and high melting point indicates that **Co4**/MAO is a promising catalyst system for the synthesis of high-quality polyethylene materials.

2.2.2. Optimization of Polymerization Conditions Using **Co4**/MMAO

In order to enhance the performance of **Co4**/MMAO, a similar optimization strategy was employed by substituting MMAO for MAO. The full set of results is detailed in Table 3. The impact of varying the Al/Co ratio on **Co4**/MMAO was studied by adjusting the ratio from 2000:1 to 4000:1 (entries 1–5, Table 3), with the temperature kept constant at 30°C . The results showed a steady increase in catalytic activity, reaching a peak at a ratio of 3500:1 (entry 4, Table 3) with a value of $4.1 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. Beyond this point, increasing the co-catalyst amounts led to a decline in activity, with the decreased value of $3.3 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at a ratio of 4000:1 (entry 5, Table 3). As for the molecular weight of the polyethylene, the highest value of 23.3 kg mol^{-1} was achieved at 3000:1 and decreased progressively as the ratio was increased at 4000:1. This trend is consistent with increased rates of chain transfer and termination reactions at higher co-catalyst concentrations [42].

Polymerizations conducted at temperatures ranging from 30 to 90°C (entries 4, 6–11, Table 3) revealed a peak activity of $4.8 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 60°C (entry 4 in Table 3, Figure 6a). Although this peak activity was lower than that achieved with **Co4**/MAO, the optimal temperature of 60°C further underscored the exceptional thermal stability of **Co4** catalyst. When temperatures exceeded 60°C , the catalytic activity dropped to $3.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 70°C , $0.9 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 80°C , and further to $0.8 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 90°C (entries 9, 10 and 11, Table 3). Molecular weights of the polyethylene displayed a pattern akin to those observed with MAO (Figure 6b), decreasing from 21.0 to 8.1 kg mol^{-1} as the temperature increased from 30 to 90°C . The polyethylenes also exhibited a relatively narrow dispersity throughout this temperature range (entries 4, 6–11, Table 3). The impact of run time on **Co4**/MMAO was examined at different intervals, ranging from 5 to 60 min (entries 8, 12–15, Table 3), while maintaining a constant temperature of 60°C and an Al/Co ratio of 3500:1. The highest activity, measuring $13.0 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, was observed at the 5-min mark (entry 12, Table 3). As the reaction time increased, the catalytic activity gradually decreased, reaching $3.1 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ after 60 min (entry 15, Table 3). Despite this decline, the activity levels remained significant, indicating the prolonged effectiveness of the active species. Furthermore, the molecular weight of the polyethylenes increased progressively over time.

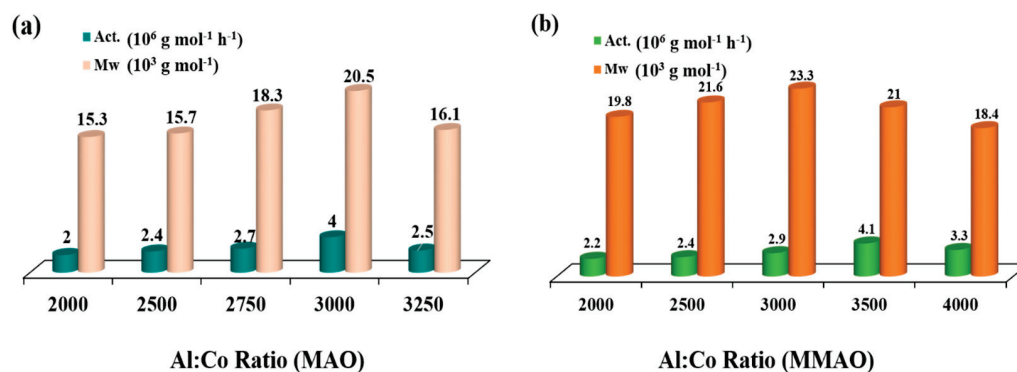


Figure 6. Catalytic activity and polymer M_w at different Al/Co ratios. (a) MAO, (b) MMAO.

The impact of ethylene pressure on **Co4**/MMAO was investigated under optimal conditions for run temperature and Al/Co ratio (entries 8, 16, and 17, Table 3). The highest catalytic activity was observed at the highest ethylene pressure, which is consistent with the findings from the MAO study. The catalytic activity decreased to $2.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at a pressure of 5 atm, and further reduced to $0.5 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 1 atm. Correspondingly, the molecular weight of the polyethylene dropped to 19.1 kg mol^{-1} at 5 atm, and further declined to 6.5 kg mol^{-1} at 1 atm. These observations can be attributed to a common kinetic phenomenon, where the polymerization rate is directly proportional to the monomer concentration induced by pressure.

Similar to the case of **Co4**/MAO, the dispersity of the polyethylenes (M_w/M_n) is narrow, ranging from 1.1 to 2.9 across all polymerization conditions using **Co4**/MMAO, indicating that both co-catalysts are effective for producing high-quality polyethylene.

2.2.3. Evaluation of **Co1** to **Co5** with Either Methyl Aluminoxane (MAO) or Modified-Methyl Aluminoxane (MMAO) Under Optimized Conditions

The catalytic performance of cobalt complexes **Co1**, **Co2**, **Co3**, and **Co5** were tested under the optimal conditions specified for either **Co4**/MAO (70 °C, Al/Co ratio of 3000:1, 30 min run time, 10 atm ethylene pressure) or **Co4**/MMAO (60 °C, Al/Co ratio of 3500:1, 30 min run time, 10 atm ethylene pressure) towards ethylene polymerization.

The experiment results are presented in Table 4. When MAO was used as a co-catalyst, all the cobalt precatalysts showed significant catalytic efficiency in ethylene polymerization. The efficiency ranged from 7.1 to $9.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, with the **Co1** achieving the highest activity of $9.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, closely followed by **Co2** and **Co4**. **Co5** showed a moderate activity of $8.0 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, while **Co3**, with bulkier *ortho*-isopropyl substituents, displayed the lowest catalytic activity of $7.1 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. In contrast, **Co3** produced polyethylene with the highest molecular weight of 25.7 kg mol^{-1} , and then **Co5** with 17.9 kg mol^{-1} , suggesting that steric hindrance from bulky *ortho*-isopropyl substituents may reduce chain transfer, thereby leading to longer polymer chains. This effect is indicative of how structural variations in the precatalysts can influence both catalytic efficiency and polymer properties, with larger substituents potentially shielding the active site and hindering chain transfer reactions, resulting in higher molecular weight polyethylenes.

Similarly, the catalytic performance of **Co1**–**Co5** under MMAO (entries 6–10, Table 4) followed a similar trend but exhibited lower activities to those observed with MAO. Under MMAO, the **Co4** has the highest activity ($4.8 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$) instead of **Co1** in the case of MAO. This can likely be explained by the different activation processes associated with each co-catalyst. The steric effects from the N-aryl substituents continued to significantly impact performance, with the least hindered 2,4,6-trimethyl **Co4** and 2,6-dimethyl **Co1** achieving higher catalytic ranges (entries 6 and 9, Table 4). Similarly, the bulkiest precatalysts, **Co3** ($M_w = 50.0 \text{ kg mol}^{-1}$) and **Co5** ($M_w = 32.4 \text{ kg mol}^{-1}$), have lower activities but produced

the highest molecular weight polyethylene, further supporting the hypothesis that larger substituents shield the active site and suppress chain transfer, leading to higher molecular weight polyethylenes. Figure 7 illustrates the variation in the activities of catalysts and molecular weight of polyethylene produced using precatalysts **Co1–Co5** under (a) MAO and (b) MMAO. As seen, **Co1** and **Co4** consistently show higher activities and relatively moderate molecular weights, while **Co3** and **Co5**, despite their lower activities, produce polyethylenes with the highest molecular weights. These results highlight the critical role of catalyst structure in determining both catalytic efficiency and polymer characteristics, with steric effects playing a pivotal role in controlling polymerization outcomes. The comparison of activity and molecular weight at different temperatures (a) and reaction time (b) using the MAO/MMAO catalytic system can be found in Figures S5 and S6, while the GPC curves at different Al/Co ratios, temperatures, and reaction time using the MMAO catalytic system are provided in Figure S7. Most of the DSC curves of polyethylene samples are provided in Figure S8.

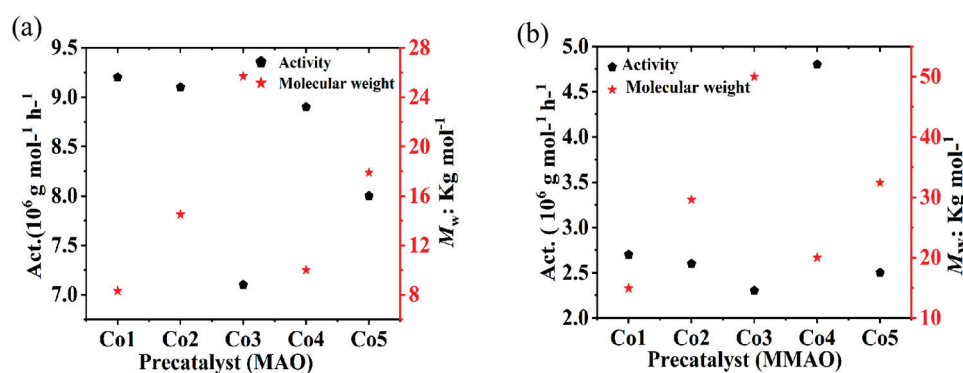


Figure 7. Comparison of polymerization activity and M_w for different precatalysts from **Co1** to **Co5** using MAO (a) and (b) MMAO (data in Table 4).

2.3. Microstructural Attributes of the Produced Polyethylenes

Tables 2–4 indicate that all polyethylene samples produced in this study have melting points (T_m) ranging from 128.0 to 132.0 °C, which is typical for linear polyethylenes. The bis(imino)pyridine-cobalt catalysts employed in this research are well-known for their ability to produce polymers with minimal branching [43]. These catalysts demonstrate a high level of control over the polymer structure, enabling the synthesis of highly linear polyethylenes. To gain a deeper understanding of the microstructure and chain termination mechanism, high-temperature ¹H/¹³C NMR spectroscopy were performed on selected polyethylene samples (entries 4 and 9, Table 4). For acquiring high-quality NMR spectra, the dissolution of these samples was carried out in deuterated tetrachloroethylene (C₂D₂Cl₄) at a temperature of 100 °C ensuring sufficient solubility for effective spectral measurement.

Using the **Co4**/MAO system (entry 4, Table 4) as a representative example, the ¹H NMR spectra of the polyethylene sample in Figure 8 displayed a pronounced peak at 1.35 ppm, characteristic of the –CH₂– repeating units, which further confirms the highly linear structure of the resulting polyethylene. Additionally, two downfield multiplet signals at 5.0 ppm and 5.8 ppm were attributed to the protons of the vinyl group (–CH=CH₂). The peak at 5.0 ppm is attributed to two protons, while the peak at 5.8 ppm corresponds to a single proton. These vinyl protons are indicative of the termination mechanism, particularly β-hydride elimination [42], a well-known pathway for chain termination in catalyzed olefin polymerization. Meanwhile, the ¹H NMR spectrum also revealed a prominent signal at δ 0.91 ppm, attributed to the saturated terminal methyl group (–CH₃), with a relative integration value of 4.01. This integration suggests the coexistence of both saturated (–CH₃) and unsaturated end groups (–CH=CH₂) in the polyethylene by **Co4**/MAO, further

supporting the notion that the chain termination process involves chain transfer reactions to alkyl aluminum species. This chain transfer reaction results in the formation of both saturated and unsaturated terminal groups, confirming the dual nature of chain termination mechanisms occurring during polymerization. The ^{13}C NMR spectra in Figure 9 of the polyethylene prepared by **Co4**/MAO further supports these findings, confirming the highly linear nature of the polymer. The spectrum also clearly shows signals corresponding to both vinyl and saturated methyl end groups, further validating the presence of both types of terminal groups and the expected polymer microstructure. These results suggest that the **Co4**/MAO system not only promotes the formation of linear polyethylene but also favors β -hydride elimination for chain termination, resulting in vinyl-terminated polymer chains.

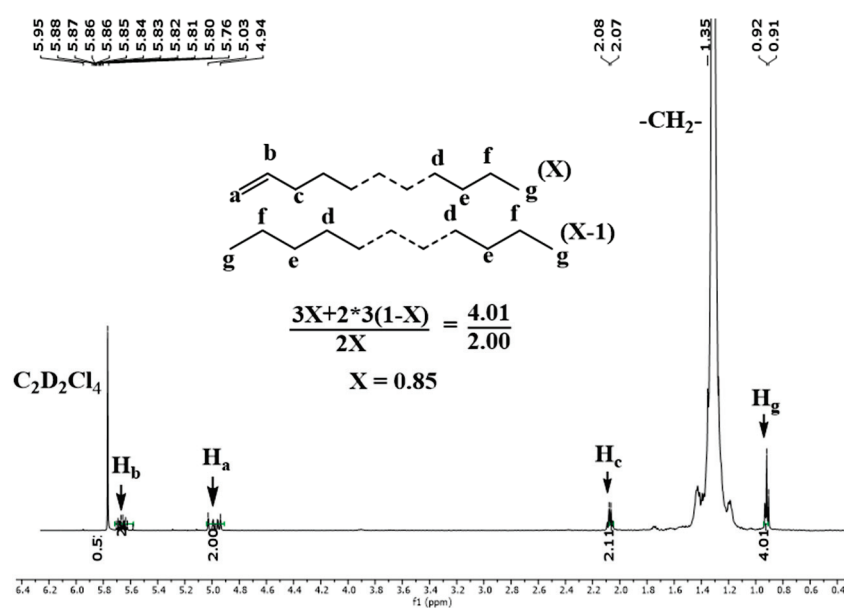


Figure 8. ^1H NMR spectrum of polyethylene produced using **Co4**/MAO (entry 4 in Table 4) recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 $^\circ\text{C}$.

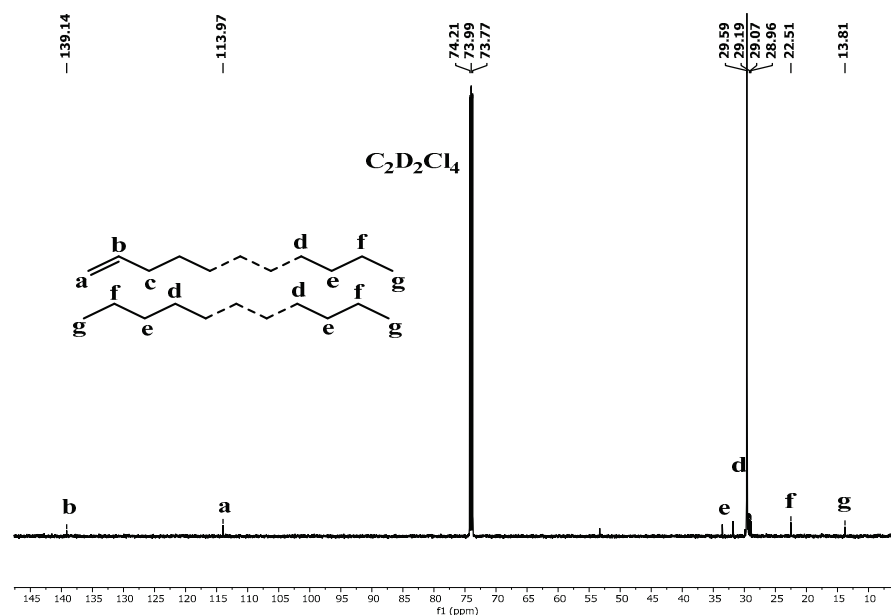


Figure 9. ^{13}C NMR spectrum of polyethylene produced using **Co4**/MAO (entry 4 in Table 4) recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 $^\circ\text{C}$.

Similarly, the $^1\text{H}/^{13}\text{C}$ NMR spectra of polyethylene prepared by **Co4**/MMAO in Figures S9 and S10 revealed a comparable linear microstructure. Both saturated ($-\text{CH}_3$) and unsaturated end groups ($-\text{CH}=\text{CH}_2$) were identified in this sample as well, indicating that while the **Co4**/MMAO system also produces linear polyethylenes, the chain termination process occurs in a similar manner to that of **Co4**/MAO, involving a combination of chain transfer to alkyl aluminum species and β -hydride elimination.

To better understand the dominant microstructure and elucidate the chain termination mechanism in more detail, the relative proportion of vinyl-terminated polyethylene ($-\text{CH}=\text{CH}_2$) and fully saturated polyethylene ($-\text{CH}_3$) was evaluated. The molar fraction X representing the portion of vinyl-terminated polyethylene was calculated using the integration of the H_a and H_g signals in the ^1H NMR spectrum ($3X + 2 \times 3(1 - X)/2X = \text{H}_g/\text{H}_a$). When X equals 1, it indicates 100% vinyl-terminated polyethylene. Once the value of X is determined, $(1 - X)$ can be used to represent the proportion of fully saturated polyethylene ($-\text{CH}_3$). From this analysis, a vinyl-terminated fraction of 0.85 (85%) was determined for the polyethylene prepared with **Co4**/MAO at 70 °C. This high vinyl-terminated fraction suggests that the chain termination process is predominantly governed by β -hydride elimination. In contrast, for the polyethylene produced using **Co4**/MMAO at 60 °C, the vinyl-terminated fraction was calculated to be 0.59 (59%). The lower fraction of vinyl-terminated end groups indicates a greater tendency for chain transfer to alkyl aluminum species in this system compared to **Co4**/MAO at 70 °C.

These results indicate that while both **Co4**/MAO and **Co4**/MMAO systems promote β -hydride elimination as the primary chain termination mechanism, the reaction conditions particularly the type of co-catalysts and temperature play significant roles in determining the proportion of vinyl-terminated polyethylenes. In summary, the polymerization systems studied here produce highly linear polyethylenes with both saturated and unsaturated end groups, with the dominant chain termination mechanism being β -hydride elimination. The ratio of vinyl-terminated to fully saturated polyethylene is influenced by reaction conditions, highlighting the importance of careful control of polymerization conditions in tailoring the structure and properties of the resulting polymers.

2.4. Comparative Analysis of the Present Catalyst System with Previously Documented Examples

The development of cobalt precatalysts for ethylene polymerization has been a central focus of research, highlighting several critical challenges associated with these catalysts. These challenges include limited catalytic activity, inadequate molecular weights of the resulting polymers, and broad molecular weight distributions. Moreover, persistent issues such as low thermal stability and the high demands for co-catalysts have impeded practical applications. Consequently, ongoing research initiatives are dedicated to improving catalytic performance and enabling the synthesis of novel polyethylene products to address these challenges [9].

As discussed in the introduction, steric hindrance introduced by *ortho*-substituted bulky groups, as seen in complex **B** (Scheme 1), plays a key role in protecting catalytic active sites, thereby enhancing both catalytic activity and thermal stability. A significant improvement in catalytic performance was achieved when one *ortho*-substituted bulky dibenzhydryl group was retained, while the other was shifted to the *para* position, resulting in complex **D**. This structural modification led to an improvement in both activity and stability. Further enhancement in thermal stability was observed when a fluoride group was incorporated at the *para* position of the bulky dibenzhydryl groups, leading to the development of complex **E**. Complex **E** exhibited a higher optimal polymerization temperature of 70 °C, significantly higher than the 40 °C optimal temperature of complexes **B**

and **D**. Moreover, complex **E** demonstrated a maximum operating temperature of 80 °C, compared to the 50 °C limitation for complexes **B** and **D**.

Building on the structure of complex **E**, the newly developed complex **F** in this work was further optimized by adding an electron-withdrawing *meta*-chloro group. This modification enhanced the thermal stability of the catalyst, making complex **F** more resilient at higher temperatures. Complex **F** displayed exceptional thermal stability, maintaining an activity of $1.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 100 °C—much higher than the maximum operating temperatures of complexes **B**, **D**, and **E**. When evaluating optimal temperature performance, complex **F** achieved the highest catalytic activity of $9.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 70 °C. Although this value is slightly lower than that of complex **B** ($9.87 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$) and complex **D** ($18.1 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$), both of which exhibit a higher activity at lower temperatures (40 °C), complex **F** stands out because it can maintain a high activity at elevated temperatures. In contrast, complexes **B** and **D**, optimized for lower temperatures, would likely degrade if exposed to higher thermal conditions. Complex **E** also reaches its peak activity at 70 °C, showing a value of $10.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ when using **Co4**/MAO after a shorter reaction time of 15 min. In comparison, complex **F** achieved a higher activity of $13.7 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, demonstrating superior performance.

To further assess the performance of complex **F**, we compared its catalytic behavior with complex **E** under identical reaction conditions at varying time intervals. As shown in Figure 10, complex **F** consistently outperformed complex **E** at all measured time points—5 min, 15 min, 30 min, and 60 min—when tested at the same optimal temperature of 70 °C. At 5 min, complex **E** showed an activity of $10.9 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, while complex **F** exhibited a significantly higher activity of $18.0 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. This early advantage indicates that complex **F** is more reactive or efficient than complex **E** in the initial stages of the reaction. As the reaction progressed, the activity of complex **E** decreased to $10.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 15 min, while complex **F** maintained a higher activity of $13.7 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. This trend continued with the activity of complex **E** dropping to $5.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 30 min, while the activity of complex **F** remained higher at $8.9 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. By 60 min, the activity of complex **E** had further decreased to $2.9 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$, while the activity of complex **F** remained at $6.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$. Over time, complex **F** consistently exhibited nearly double the activity of complex **E**, underscoring its greater stability and efficiency over extended periods.

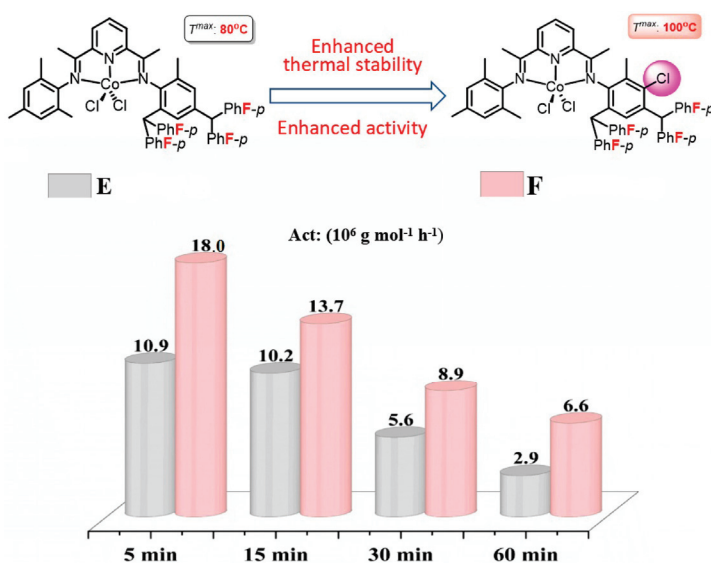


Figure 10. Comparative analysis of activity levels of compounds **E** (Scheme 1) and **F** (this work) over time at 70 °C. All experiments were conducted under optimized conditions at 10 atm of C_2H_4 using MAO as the co-catalyst.

Compared to complexes **B**, **D**, and **E**, which show higher activity at lower temperatures but fail to sustain performance under elevated thermal conditions, complex **F** stands out as the most efficient and effective compound. Its ability to maintain a high activity at 70 °C and demonstrate exceptional thermal stability at 100 °C makes it the most promising catalyst for high-performance applications that demand both efficiency and thermal stability.

In conclusion, complex **F** in this work outperforms previous catalysts in both catalytic activity and thermal stability, particularly at higher temperatures. With its superior performance at 70 °C and exceptional thermal stability at 100 °C, complex **F** is the most promising catalyst for advanced ethylene polymerization. Its combination of high activity, resilience, and thermal stability positions it as the ideal candidate for high-performance applications in industrial settings.

3. Experimental Section

3.1. Synthesis of 4,6-Bis(bis(4-fluorophenyl)methyl)-3-chloro-2-methylaniline (**X3**)

A 500-mL round-bottom flask containing a magnetic stir bar was charged with 10.6 g (75 mmol) of 3-chloro-2-methylaniline (**X1**), and 16.5 g (75 mmol) of bis(4-fluorophenyl)-methanol (**X2**). The mixture was stirred at 160 °C for 30 min to form a homogeneous solution. A catalytic amount of ZnCl₂ (2.0 g) in 5 mL of HCl was then added dropwise to the solution, and the reaction was allowed to continue stirring at 160 °C for 5 h. After cooling, the solid product was dissolved in 250 mL of dichloromethane and washed sequentially with saturated aqueous NH₄Cl, followed by NaCl. The organic phase was separated, dried over anhydrous MgSO₄, and concentrated using a rotary evaporator. Since precipitation was not observed with various solvents, alumina column chromatography was employed using petroleum ether/ethyl acetate (*v/v* = 500/1) as the eluent, yielding the product as a yellow powder **X3** (14.5 g, 53%). ¹H NMR (400 Hz, CDCl₃, TMS) showed peaks at δ 6.95–6.82 (m, 17H, Ar), 5.83 (s, 1H, –CH–), 5.77 (s, 1H, –CH–), 3.58 (bs, 2H, –NH₂), 2.26 (s, 3H, –CH₃). The ¹³C NMR spectrum (101 MHz, CDCl₃, TMS) showed peaks at δ 162.99, 162.61, 160.55, 160.18, 141.97, 138.96, 138.93, 137.50, 137.46, 133.41, 130.66, 130.58, 130.28, 126.08, 120.78, 115.68, 115.46, 115.16, 114.95, 77.48, 77.16, 76.84, 52.30, 50.75, 14.70, 1.16.

3.2. Synthesis of 2-Acetyl-6-[1-(3-chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methylphenylimino)-ethyl]pyridine (**X4**)

A total of 2.4 g (15 mmol) of 2,6-diacetylpyridine and 0.057 g (0.3 mmol) of *p*-toluene sulfonic acid were added to a 250-mL two-neck round-bottom flask containing 100 mL of toluene. The mixture was stirred and heated to reflux at 115 °C. After 45 min, a solution of 9.4 g (15 mmol) of 4,6-bis(bis(4-fluorophenyl)methyl)-3-chloro-2-methylaniline **X3** in toluene was added dropwise to the reaction mixture. The mixture was refluxed for an additional 10 h, with the completion of the reaction confirmed by TLC analysis. Then, the mixture was cooled to room temperature. All volatile components were removed under reduced pressure using a vacuum rotary. The residual solid was purified using basic alumina column chromatography, with petroleum ether/ethyl acetate (*v/v* = 500/1) as the eluent, resulting in the formation of the title compound **X4** as a yellow solid yielding 8.0 g (72%). The ¹H NMR spectrum (400 MHz, CDCl₃, TMS) showed peaks at δ 8.38 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.93 (t, *J* = 7.8 Hz, 1H), 6.99–6.66 (m, 17H), 6.16 (s, 1H), 5.85 (s, 1H), 5.26 (s, 1H), 3.72 (q, *J* = 7.0 Hz, 3H), 2.72 (s, 3H), 2.05 (s, 3H), 1.67 (s, 3H). The ¹³C NMR spectrum (101 MHz, CDCl₃, TMS) showed peaks at δ 199.98, 169.34, 162.75, 160.38, 154.83, 152.70, 147.25, 138.52, 138.31, 137.76, 137.54, 136.20, 133.67, 131.38, 130.90, 130.83, 130.76, 130.67, 130.60, 130.54, 130.47, 129.93, 124.56, 124.40, 123.08, 115.48, 115.40, 115.33, 115.27, 115.19, 115.14, 115.11, 114.93, 77.48, 77.16, 76.84, 52.39, 50.85, 25.74, 17.02, 15.66. FT-IR (cm^{−1}): 3060 (w), 3012 (w), 2926 (w), 2836 (w), 2829 (w), 1804 (w), 1649

(ν (C=N), s), 1584 (w), 1528 (w), 1491 (m), 1463 (w), 1429 (w), 1364 (s), 1309 (m), 1234 (m), 1150 (w), 1120 (w), 1078 (w), 1042 (w), 1014 (w), 990 (w), 940 (w), 892 (w), 828 (w), 816 (m), 790 (w), 760 (s), 734 (m), 701 (m), 668 (w).

3.3. Synthesis of 2-[1-(3-Chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methylphenylimino)-ethyl]-6-(arylimino)ethyl] (L1 to L5)

L1 (Ar = 2,6-Me₂C₆H₃)

A mixture of imino-ketone (1.378 g, 2.00 mmol) and 2,6-dimethyl aniline (0.290 g, 2.40 mmol), along with *p*-toluenesulfonic acid (0.152 g) were mixed with 20 mL of tetraethyl silicate in a 250-mL flask. The mixture was refluxed and heated at 150 °C under nitrogen atmosphere for 5 h. Upon completion of the reaction (checked by TLC), the reaction mixture was allowed to cool to ambient temperature and tetraethyl silicate was evaporated under reduced pressure, and the resulting solid was eluted with petroleum ether/ethyl acetate (4:1, *v/v*) on an alumina column. The second fraction obtained during elution was concentrated to produce a yellow powder (0.53 g, 31% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, *J* = 7.8 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.91 (t, *J* = 7.9 Hz, 1H), 6.99–6.71 (m, 19H), 6.17 (s, 1H), 5.86 (s, 1H), 2.18 (s, 3H), 2.11–2.03 (m, 9H), 1.69 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.63, 167.19, 162.82, 162.79, 162.75, 162.71, 160.39, 160.36, 160.31, 160.27, 155.41, 154.60, 148.79, 147.71, 138.70, 138.67, 138.61, 138.57, 138.46, 138.43, 137.89, 137.86, 137.00, 135.86, 133.60, 131.30, 130.94, 130.85, 130.76, 130.67, 130.60, 130.57, 130.49, 129.88, 128.06, 125.51, 125.48, 124.37, 123.24, 122.64, 122.21, 115.42, 115.36, 115.30, 115.21, 115.15, 115.11, 115.09, 114.90, 77.48, 77.16, 76.84, 52.38, 50.82, 18.10, 18.06, 17.12, 16.53, 15.66. ¹⁹F NMR (565 MHz, CDCl₃) δ −116.22, −116.35, −116.51, −116.65. FT-IR (cm^{−1}): 3045 (w), 2965 (w), 2921 (w), 1645 (ν (C=N), s), 1595 (m), 1566 (w), 1504 (s), 1460 (m), 1427 (w), 1359 (m), 1321 (w), 1298 (m), 1224 (s), 1153 (m), 1121 (w), 1094 (w), 1035 (w), 1015 (m), 968 (w), 870 (w), 820 (s), 764 (m), 744 (w), 711 (w), 691 (w). The calculated elemental analysis for C₅₀H₄₀ClF₄N₃ (794.33) with [EtOH] is as follows: C, 74.32; H, 5.52; N, 5.00. The found values were C, 73.98; H, 5.00; N, 4.88.

L2 (Ar = 2,6-Et₂C₆H₃)

Using a method akin to the one outlined for the production of L1, L2 was prepared as a yellow powder (0.57 g, 32% yield). The ¹H NMR spectrum (400 MHz, CDCl₃, TMS) shows the following chemical shifts: δ 8.47 (d, *J* = 7.8 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.91 (t, *J* = 7.8 Hz, 1H), 7.16–6.70 (m, 19H), 6.17 (s, 1H), 5.86 (s, 1H), 2.39 (ddt, *J* = 18.5, 14.9, 7.5 Hz, 3H), 2.18 (s, 3H), 2.07 (s, 3H), 1.56 (s, 4H), 1.26–1.08 (m, 6H). The ¹³C NMR spectrum (100 MHz, CDCl₃, TMS) shows the following chemical shifts: δ 169.66, 166.98, 162.83, 162.80, 162.75, 162.71, 160.39, 160.36, 160.31, 160.27, 155.39, 154.61, 147.79, 147.73, 138.71, 138.67, 138.61, 138.58, 138.46, 138.43, 137.90, 137.87, 137.03, 135.87, 133.60, 131.30, 131.27, 130.95, 130.87, 130.85, 130.77, 130.68, 130.60, 130.57, 130.50, 129.89, 126.12, 124.37, 123.57, 122.63, 122.20, 115.42, 115.37, 115.30, 115.21, 115.15, 115.12, 115.09, 114.90, 77.48, 77.16, 76.84, 52.39, 50.82, 24.75, 24.72, 17.12, 16.89, 15.67, 13.88, 13.86, 1.17. ¹⁹F NMR (565 MHz, CDCl₃) δ −116.20, −116.32, −116.48, −116.62. The FT-IR spectrum (cm^{−1}) shows the following peaks: 3030 (w), 2962 (w), 2865 (w), 1642 (ν (C=N), s), 1598 (m), 1574 (w), 1504 (s), 1457 (m), 1415 (w), 1365 (m), 1327 (w), 1300 (w), 1265 (w), 1224 (s), 1156 (m), 1124 (w), 1094 (w), 1074 (w), 1018 (w), 968 (w), 932 (w), 882 (w), 853 (w), 841 (w), 817 (s), 767 (m), 744 (w), 714 (w). The calculated elemental analysis for C₅₂H₄₄ClF₄N₃ (822.39) with [2EtOH] is as follows: C, 72.76; H, 5.64; N, 4.90. The found values were C, 73.07; H, 5.49; N, 4.53.

L3 (Ar = 2,6-*i*Pr₂C₆H₃)

Using a method akin to the one outlined for the production of **L1**, **L3** was prepared and obtained as a brown powder with a yield of 0.49 g (28%). The ^1H NMR spectrum (400 MHz, CDCl_3 , TMS) showed peaks at δ 8.45 (dd, $J = 7.7, 4.9$ Hz, 1H), 8.26 (d, $J = 7.7$ Hz, 1H), 7.90 (t, $J = 7.8$ Hz, 1H), 7.22–6.71 (m, 19H), 6.17 (s, 1H), 5.86 (s, 1H), 2.87–2.69 (m, 2H), 2.33–2.16 (m, 3H), 2.07 (s, 3H), 1.70 (s, 3H), 1.29–1.11 (m, 12H). The ^{13}C NMR spectrum (100 MHz, CDCl_3 , TMS) exhibited peaks at δ 169.68, 162.85, 162.73, 160.33, 160.29, 154.66, 147.69, 138.68, 138.61, 138.43, 137.92, 137.07, 136.04, 135.92, 133.62, 131.30, 130.96, 130.88, 130.85, 130.77, 130.68, 130.61, 130.58, 130.50, 129.91, 124.39, 123.97, 123.22, 122.80, 122.29, 115.42, 115.38, 115.32, 115.21, 115.17, 115.13, 115.11, 114.92, 77.48, 77.16, 76.84, 52.39, 50.82, 28.53, 28.46, 23.41, 23.05, 23.03, 17.28, 17.14, 15.69. ^{19}F NMR (565 MHz, CDCl_3) δ –116.28, –116.42, –116.58, –116.71. The FT-IR spectrum (cm^{-1}) displayed peaks at 3050 (w), 2959 (w), 2865 (w), 1645 (v (C=N), s), 1598 (m), 1566 (w), 1507 (s), 1457 (m), 1439 (w), 1349 (m), 1324 (w), 1298 (w), 1227 (s), 1189 (m), 1156 (m), 1124 (w), 1094 (w), 1077 (w), 1047 (w), 1003 (m), 985 (w), 932 (w), 867 (w), 817 (w), 770 (w), 738 (w), and 688 (w). The calculated elemental analysis for $\text{C}_{54}\text{H}_{48}\text{ClF}_4\text{N}_3$ (850.44) with [MeOH] is as follows: C, 74.86; H, 5.94; N, 4.76. The found values were C, 75.19; H, 5.70; N, 4.58.

L4 (Ar = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$)

Using a method akin to the one outlined for the production of **L1**, **L4** was obtained as a yellow powder with a yield of 0.56 g (32%). The ^1H NMR spectrum (400 MHz, CDCl_3 , TMS) showed signals at δ 8.50 (d, $J = 7.8$ Hz, 1H), 8.27 (d, $J = 7.8$ Hz, 1H), 7.90 (t, $J = 7.8$ Hz, 1H), 6.98–6.70 (m, 19H), 6.17 (s, 1H), 5.86 (s, 1H), 2.30 (s, 3H), 2.18 (s, 3H), 2.07–1.95 (m, 9H), 1.69 (s, 4H). The ^{13}C NMR spectrum (100 MHz, CDCl_3 , TMS) displayed peaks at δ 169.65, 167.51, 162.80, 162.75, 162.71, 160.39, 160.36, 160.31, 160.27, 155.48, 154.57, 147.72, 146.16, 138.71, 138.68, 138.61, 138.58, 138.47, 138.44, 137.89, 137.86, 136.98, 135.86, 133.60, 132.50, 131.31, 130.94, 130.85, 130.77, 130.67, 130.60, 130.57, 130.49, 129.88, 128.99, 128.75, 125.42, 125.39, 124.38, 122.69, 122.18, 115.42, 115.37, 115.30, 115.21, 115.16, 115.11, 115.09, 114.90, 77.48, 77.16, 76.84, 52.38, 50.82, 29.85, 27.06, 20.88, 18.03, 18.00, 17.73, 17.12, 16.98, 16.50, 15.66, 1.17. ^{19}F NMR (565 MHz, CDCl_3) δ –116.25, –116.38, –116.54, –116.69. The FT-IR spectrum (cm^{-1}) displayed peaks at 3078 (w), 3062 (w), 2962 (w), 2918 (w), 2847 (w), 1648 (v (C=N), s), 1589 (w), 1577 (w), 1507 (s), 1454 (w), 1427 (w), 1368 (m), 1309 (w), 1256 (w), 1218 (s), 1177 (w), 1156 (m), 1112 (w), 1094 (m), 1012 (m), 968 (w), 882 (w), 820 (s), 797 (w), 758 (w), 747 (w), 708 (w), and 673 (w). The calculated elemental analysis for $\text{C}_{51}\text{H}_{42}\text{ClF}_4\text{N}_3$ (808.36) with [H_2O] is as follows: C, 74.13; H, 5.37; N, 5.08. The found values were C, 74.52; H, 5.42; N, 4.65.

L5 (Ar = 2,6-Et₂-4-MeC₆H₂)

Using a method akin to the one outlined for the production of **L1**, **L5** was synthesized as a yellow powder with a yield of 0.57 g (32%). The ^1H NMR spectrum (400 MHz, CDCl_3 , TMS) showed peaks at δ 8.47 (d, $J = 7.8$ Hz, 1H), 8.27 (d, $J = 7.8$ Hz, 1H), 7.91 (t, $J = 7.8$ Hz, 1H), 7.16–6.70 (m, 19H), 6.17 (s, 1H), 5.86 (s, 1H), 2.39 (ddt, $J = 18.5, 14.9, 7.5$ Hz, 3H), 2.18 (s, 3H), 2.07 (s, 3H), 1.56 (s, 4H), 1.26–1.08 (m, 6H). The ^{13}C NMR spectrum (100 MHz, CDCl_3 , TMS) showed peaks at δ 169.67, 162.85, 162.82, 162.77, 162.72, 160.38, 160.32, 155.42, 154.60, 147.73, 138.69, 138.62, 138.58, 138.46, 137.91, 137.88, 137.01, 135.87, 133.61, 132.81, 131.30, 130.95, 130.87, 130.85, 130.77, 130.68, 130.60, 130.58, 130.50, 129.89, 126.88, 124.38, 122.72, 122.18, 115.42, 115.37, 115.31, 115.21, 115.16, 115.12, 115.10, 114.91, 77.48, 77.16, 76.84, 52.39, 50.82, 24.74, 24.72, 21.15, 17.13, 16.87, 15.68, 14.00, 1.17. ^{19}F NMR (565 MHz, CDCl_3) δ –116.27, –116.40, –116.56, –116.70. The FT-IR spectrum (cm^{-1}) showed peaks at 3068 (w), 2965 (w), 2921 (w), 1645 (v (C=N), s), 1572 (w), 1501 (s), 1460 (m), 1415 (w), 1398 (w), 1365 (m), 1315 (w), 1256 (w), 1218 (s), 1177 (w), 1156 (m), 1118 (w), 1080 (w), 1012 (w), 994 (w), 882 (w), 823 (s), 791 (w), 764 (w), 723 (w), and 670 (w). The calculated

elemental analysis for $C_{53}H_{46}ClF_4N_3$ (836.42) with [2MeOH] is as follows: C, 73.36; H, 6.04; N, 4.67. The found values were C, 73.40; H, 5.66; N, 4.44.

3.4. Synthesis of 2-[1-(3-Chloro-4,6-bis((di(4-fluorophenyl)methyl)-2-methylphenylimino)-ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) Chlorides (**Co1** to **Co5**)

Co1 (Ar = 2,6-Me₂C₆H₃)

L1 (0.127 g, 0.16 mmol) and $CoCl_2 \cdot 6H_2O$ (0.038 g, 0.16 mmol) were combined in a mixture of dichloromethane (5 mL) and ethanol (4 mL) in a Schlenk tube. The resulting reaction mixture was stirred at room temperature for 12 h, and the volatile components were evaporated under reduced pressure. The resulting product was precipitated with diethyl ether (30 mL). The precipitate was filtered, washed with diethyl ether, and dried under reduced pressure. **Co1** was obtained as a brown powder with a yield of 0.14 g (84%). The FT-IR spectrum (cm^{-1}) of **Co1** showed the following peaks: 3045 (w), 2947 (w), 2918 (w), 1628 (v, C=N), 1589 (s), 1507 (s), 1465 (m), 1436 (w), 1368 (m), 1315 (w), 1253 (w), 1230 (s), 1156 (s), 1094 (m), 1012 (m), 979 (w), 935 (w), 882 (w), 826 (s), 788 (w), 767 (w), 720 (w), and 688 (w). The calculated elemental analysis for $C_{51}H_{43}Cl_3CoF_4N_3$ (939.20) with [3H₂O] is as follows: C, 61.67; H, 4.97; N, 4.23. The found values were C, 61.55; H, 4.49; N, 4.24.

Co2 (Ar = 2,6-Et₂C₆H₃)

Using the same method and molar ratios as described for **Co1**, **Co2** was obtained as a brown powder (0.15 g, 89% yield). The FT-IR spectrum (cm^{-1}) showed peaks at 3068 (w), 2962 (w), 2874 (w), 1630 (v (C=N), w), 1504 (s), 1451 (m), 1368 (m), 1318 (w), 1259 (w), 1224 (s), 1156 (s), 1094 (m), 1015 (m), 976 (w), 935 (w), 876 (w), 829 (s), 811 (s), 773 (w), 744 (w), and 711 (w). The calculated elemental analysis for $C_{53}H_{47}Cl_3CoF_4N_3$ (967.26 g) with [CH₂Cl₂] is as follows: C, 61.64; H, 4.69; N, 3.99. The found values were C, 62.09; H, 4.59; N, 4.12.

Co3 (Ar = 2,6-*i*Pr₂C₆H₃)

Using the same method and molar ratios as described for **Co1**, **Co3** was obtained as a brown powder with a yield of 0.15 g (86%). The FT-IR spectrum (cm^{-1}) showed peaks at 3053 (w), 2956 (w), 2918 (w), 1628 (v (C=N) (s), 1580 (s), 1507 (s), 1463 (m), 1439 (w), 1374 (m), 1318 (w), 1268 (w), 1227 (s), 1153 (m), 1097 (w), 1009 (w), 938 (w), 909 (w), 832 (s), 791 (w), 773 (w), 741 (w), and 717 (w). The calculated elemental analysis for $C_{55}H_{51}Cl_3CoF_4N_3$ (995.31) with [MeOH] is as follows: C, 65.47; H, 5.40; N, 4.09. The found values were C, 65.22; H, 4.90; N, 4.05.

Co4 (Ar = 2,4,6-Me₃C₆H₂)

Using the same method and molar ratios as described for **Co1**, **Co4** was obtained as a green powder (0.15 g, 89% yield). The FT-IR spectrum (cm^{-1}) showed peaks at 3030 (w), 2909 (w), 2862 (w), 1625 (C=N) w, 1592 (m), 1504 (s), 1465 (m), 1427 (w), 1368 (m), 1315 (w), 1253 (w), 1218 (s), 1156 (m), 1103 (w), 1015 (m), 973 (w), 873 (w), 832 (s), 811 (s), 791 (w), 767 (w), and 741 (w). The calculated elemental analysis for $C_{52}H_{45}Cl_3CoF_4N_3$ (953.23) with [MeOH] is as follows: C, 64.61; H, 5.01; N, 4.26. The found values were C, 64.60; H, 4.49; N, 4.22.

Co5 (Ar = 2,6-Et₂-4-MeC₆H₂)

Using the same method and molar ratios as described for **Co1**, **Co5** was obtained as a brown powder (0.15 g, 87% yield). The FT-IR spectrum of **Co5** (cm^{-1}) showed peaks at 3053 (w), 2962 (w), 2874 (w), 1622 (v (C=N) (s), 1598 (s), 1507 (s), 1463 (m), 1436 (w), 1368 (m), 1318 (w), 1265 (w), 1221 (s), 1156 (m), 1133 (w), 1095 (m), 1009 (m), 935 (w) 876 (w),

823 (s), 782 (w), and 735 (w). The calculated elemental analysis for (C₅₄H₄₉Cl₃CoF₄N₃, (981.28) with [2H₂O] is as follows: C, 63.76; H, 5.25; N, 4.13. The found values were C, 63.18; H, 4.79; N, 3.97.

4. Conclusions

This study presents the synthesis and evaluation of a series of unsymmetrical 2,6-bis(arylimino)pyridine cobalt(II) complexes (**Co1** to **Co5**), which were designed with sterically and electronically modified N-aryl substituents to enhance their catalytic performance in ethylene polymerization. Upon activation with aluminoxanes (MAOs) or modified-methyl aluminoxanes (MMAOs), the catalysts exhibited impressive catalytic activity, with **Co1** achieving the highest activity of $9.2 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 70 °C. Notably, the catalysts demonstrated exceptional thermal stability, with complex **Co4** maintaining high activity even at elevated temperatures ($1.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ at 100 °C), making them suitable for industrial applications where robust performance under high-temperature conditions is essential. The key to the catalysts' success lies in the strategic incorporation of bulky *para*-fluorodibenzyl groups and electron-withdrawing *meta*-chloro substituents. The steric hindrance provided by the *para*-fluorodibenzyl groups enhanced the stability of the catalysts, while the *meta*-chloro group increased the Lewis acidity of the cobalt center, thereby improving catalytic efficiency and polymerization activity. These design features allowed for the production of high linearity polyethylene with narrow molecular weight distributions and molecular weights ranging from 6.4 to 50.0 kg mol^{−1}, further confirming the catalysts' effectiveness in controlling polymerization. The study underscores the importance of fine-tuning the steric and electronic properties of the N-aryl substituents to optimize catalyst performance. Certain configurations of these substituents led to the higher activity and stability during the polymerization process. These findings not only advance the understanding of cobalt-based catalysts, but also provide valuable insights for the development of next-generation catalysts for polyethylene production.

In conclusion, the strategic modification of cobalt(II) chloride N[^]N[^]N[^]-pincer complexes through tailored steric and electronic adjustments has resulted in catalysts with high activity, excellent thermal stability, and precise control over the polymer molecular weight. These results contribute to the ongoing efforts to develop more efficient, thermally robust cobalt-based catalysts for industrial-scale polyethylene production. Further research is needed to explore additional structural modifications and to extend these findings to other polymerization processes, paving the way for the design of more advanced catalysts for a range of industrial applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules30040859/s1>, Figure S1: ¹H NMR and ¹³C NMR spectra of Sterically Hindered Aniline **X3** and **X4**; Figure S2: ¹H NMR and ¹³C NMR spectra of imino-ketone and ligands **L1–L5**; Figure S3: ¹⁹F NMR spectra of ligands **L1–L5**; Figure S4: FT-IR spectra of ligands **L1–L5** and Complexes **Co1–Co5**; Figures S5 and S6: Comparison of activity and molecular weight at different temperatures (a) and reaction time (b) using MAO/MMAO catalytic system; Figure S7: GPC curves at different Al/Co ratio, temperatures and reaction time using MMAO catalytic system; Figure S8: DSC curves of polyethylene samples obtained at different conditions; Figures S9 and S10: ¹H NMR and ¹³C NMR spectra of polymer produced by **Co4**/MMAO under optical conditions. Table S1: Crystal data and structural refinements for **Co1**, **Co2**, **Co4** and **Co5**. Refs [44,45] are cited in the Supplementary Materials.

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Article

The Effect of Alkyl Substituents on the Formation and Structure of Homochiral (R^*,R^*) - $[R_2Ga(\mu-OCH(Me)CO_2R')_2]$ Species—Towards the Factors Controlling the Stereoselectivity of Dialkylgallium Alkoxides in the Ring-Opening Polymerization of *rac*-Lactide

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Abstract: Building on our previous studies, which have demonstrated that homochiral propagating species— (R^*,R^*) - $[Me_2Ga(\mu-OCH(Me)CO_2R)_2]$ —were crucial for the heteroselectivity of $[Me_2Ga(\mu-OCH(Me)CO_2Me)_2]$ in the ring-opening polymerization (ROP) of racemic lactide (*rac*-LA), we have investigated the effect of alkyl groups on the structure and catalytic properties of dialkylgallium alkoxides in the ROP of *rac*-LA. Therefore, we have isolated and characterized the *rac*- $[R_2Ga(\mu-OCH(Me)CO_2Me)_2]$ ($R = Et$ (**1**), *i*Pr (**2**) and *rac*- $[R_2Ga(\mu-OCH(Me)C_5H_4N)_2]$ ($R = Et$ (**3**), *i*Pr (**4**)) complexes, to demonstrate the effect of alkyl groups on the chiral recognition induced the formation of the respective homochiral species— (R^*,R^*) - $[R_2Ga(\mu-OCH(Me)CO_2Me)_2]$ and (R^*,R^*) - $[R_2Ga(\mu-OCH(Me)C_5H_4N)_2]$. Moreover, we have investigated the structure of (S,S) - $[R_2Ga(\mu-OCH(Me)CO_2Me)_2]$ ($R = Et$ ((*S,S*)-**1**, $R = iPr$ ((*S,S*)-**2**)) and their catalytic activity in the ROP of *rac*-LA. With an increase in the bulkiness of alkyl substituents on gallium the following can be observed: (a) the tendency for the formation of homochiral complexes decreased, (b) the symmetry of homochiral (S,S) - $[R_2Ga(\mu-OCH(Me)CO_2Me)_2]$ ($M = Me, Et$ (*S,S*)-**1**), *i*Pr (*S,S*)-**2**) changed, and both have resulted in (c) lower or no heteroselectivity across these complexes in the ROP of *rac*-LA. Importantly, the results have confirmed the crucial role of the chiral-induced formation of homochiral asymmetric dimers on the heteroselectivity of dialkylgallium alkoxides in the ROP of *rac*-LA.

Keywords: biodegradable polyesters; polylactide; tacticity; heterotactic; dimers; diastereomers

1. Introduction

Over the last two decades, there has been great interest in stereoselective catalysts/catalytic systems for the ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) [1–4], in order to synthesize PLA of different stereostructures and properties [5,6]. Many efforts have been made in order to determine the effect of the various elements of the structure of metal alkoxide propagating species in the ROP of *rac*-LA on their stereoselectivity, resulting in the development of numerous metal alkoxides capable of the isoselective or heteroselective ROP of *rac*-LA [2,7–9]. Notably, there have been considerably fewer reports

concerning dimeric metal alkoxides, which can polymerize *rac*-LA in a stereoselective fashion [10–12], leading to isotactically [13–16] and heterotactically [17–23] enriched PLA in comparison with monomeric species [2,7–9]. Irrespective of the dimeric/monomeric structure of the stereoselective propagating species, there are two widely accepted mechanisms of stereoselectivity control in the coordination-insertion polymerization of *rac*-lactide, as well as other chiral and prochiral monomers, i.e., enantiomorphic site control (ESM) and chain end control (CEM) mechanisms [24,25]. They define two main structural elements responsible for the stereoselectivity of both monomeric and dimeric propagating species—the presence of asymmetry on the metal center and the presence of chiral carbon on the last inserted monomeric unit in the growing PLA chain. However, the cooperativity between metal centers, which can be observed only in the case of dimeric catalysts (or higher aggregates), and which has been recently reported for the dimeric metal alkoxides in the ROP of *rac*-LA [12,26–28], should be considered an important factor affecting their stereoselectivity. We have demonstrated that the cooperative effects between two metal centers of dimeric gallium and indium alkoxides manifested in the change in the stereoselectivity of the investigated complexes in the ROP of *rac*-LA [1]. In this case, the formation of excess homochiral dimeric species was responsible for the heteroselectivity of dimethylgallium and dimethylindium alkoxides in the ROP of *rac*-lactide, with a positive non-linear effect. With regard to the latter, Nozaki and coworkers have shown that excess homochiral zinc dimeric complexes were responsible for the stereoselective copolymerization of olefines with CO₂ [29]. Therefore, one should consider the formation of the excess of homochiral dimeric species over heterochiral ones in the ROP, a strategy for stereoselectivity control that is comparable to enantioselective organic transformations, where excess *R,R* or *S,S* dimeric catalytic species are decisive for the enantiomeric excess (*ee*) of the product [30]. Interestingly, the difference in the stereoselectivity between homochiral and heterochiral dimeric metal alkoxide was reported in the case of Y [31], Cu [32], and In [33,34] complexes. Moreover, the formation of homochiral dimeric Zr and Hf [35], Sc [36], and In [37] complexes could have been responsible for their stereoselectivity, although it was not clearly indicated. Notably, the different activities of homochiral and heterochiral dimeric aluminum alkoxides have been recently observed in the ROP of cyclic esters [38]. Therefore, the factors influencing the formation of homochiral/heterochiral dimeric metal alkoxides should be considered an interesting area of research.

With regard to our previous studies, we have considered dialkylgallium alkoxides, which tend to form dimers both in the solid state and solution [1,39], a good starting point for further research on factors controlling the formation of homochiral/heterochiral dimers, and subsequently, their catalytic activity in the ROP of *rac*-LA. Although the selected class of complexes has been thoroughly investigated with regard to their synthesis and structure [39], the issue concerned with the formation of homochiral/heterochiral species has been barely discussed, not only for dialkylgallium derivatives, but also for group 13 metal dialkylalkoxides. Except for our studies on [Me₂M(μ-CH(Me)CO₂Me)₂] (M = Ga, In) with chiral centers on an alkoxide ligand [1], the chiral recognition leading to exclusively homochiral dimers was reported in the case of the analogous dimethylaluminum derivatives of *rac*-ethyl lactate [40]. However, although *rac*-[Me₂Al(μ-CH(Me)CO₂Et)₂] mimicked propagating species in the ROP of *rac*-LA with dialkylaluminum alkoxides, they did not allow for the stereoselective polymerization of *rac*-LA due to an essential lack of activity at mild conditions and extensive transesterification observed at higher temperatures [41]. Therefore, with regard to our studies on the structure and catalytic activity of dialkylgallium and dialkylindium alkoxides in the ROP of *rac*-LA [1,42], we have focused on the effect of the alkyl groups of [R₂Ga(μ-CH(Me)CO₂Me)₂], on the formation and structure of homochiral species, and their impact on their stereoselectivity in the ROP

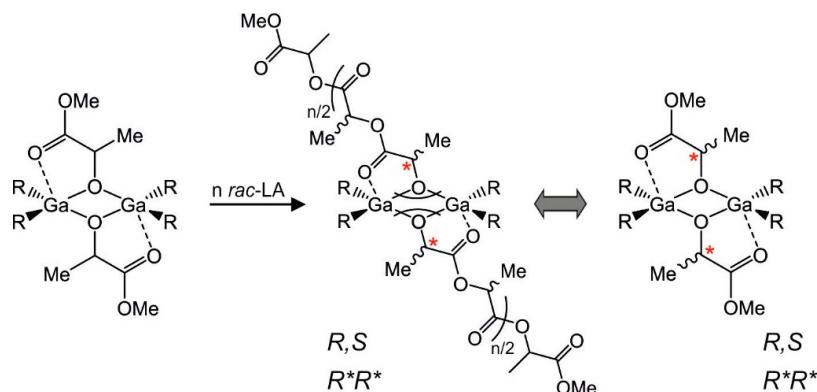
of *rac*-LA. Studies on the dialkylgallium alkoxides should be particularly interesting, given the high stereoselectivity in the ROP of *rac*-LA and the low tendency for transesterification side reactions in comparison with aluminum [41] and indium [1] analogues.

Hereby, we report the synthesis, structure, and catalytic activity of *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ and (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, *i*Pr) in the ROP of *rac*-LA, as well as the synthesis and structure of *rac*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Et, *i*Pr). We discuss how the effect of alkyl substituents affects their structure, most importantly with regard to the tendency for the formation of homochiral complexes. Based on structure-activity studies, we demonstrate that the decrease in the tendency for the formation of homochiral (*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂PLA)]₂ (PLA—growing polylactide chain) considerably influences the stereoselectivity of dialkylgallium alkoxide species in the ROP of *rac*-LA. This constitutes further evidence for the crucial role of homochiral dimeric dialkylgallium alkoxide species in the stereoselective ROP of *rac*-lactide.

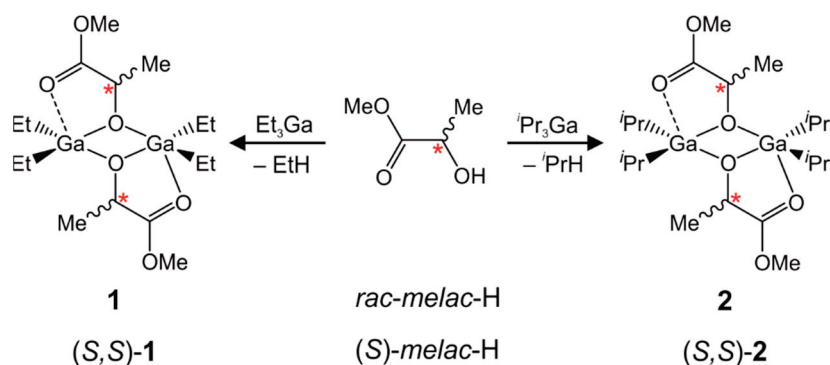
2. Results and Discussion

In order to demonstrate how gallium-bonded alkyl groups affect the structure and catalytic properties of dialkylgallium alkoxide propagating species in the ROP of *rac*-lactide (*rac*-LA), we initially focused on the synthesis and structure of (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ and *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, *i*Pr), as well as *rac*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Et, *i*Pr), with regard to their dimethylgallium analogues, previously reported by us [1]. Due to the presence of a methyl lactate ligand (*melac*), which is expected to mimic the growing PLA chain [41,43–45], both *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et (**1**), *i*Pr (**2**)) and (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et ((*S,S*)-**1**), R = *i*Pr ((*S,S*)-**2**)) are expected to represent model complexes for the dialkylgallium propagating species in the ROP of *rac*-LA (Scheme 1). Therefore, the studies of (*S,S*)-**1** and (*S,S*)-**2** were expected to show the effect of alkyl groups on the structure of homochiral—(*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂PLA)]₂—species, which were decisive for the stereoselective ROP of *rac*-LA with analogous dimethylgallium alkoxides [1]. On the other hand, the structures of *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et (**1**), *i*Pr (**2**)) were expected to demonstrate the effect of alkyl groups on the ratio of homochiral—(*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂PLA)]₂—to heterochiral—(*R,S*)-[R₂Ga(μ-OCH(Me)CO₂PLA)]₂ (R = Et, *i*Pr)—propagating species in the ROP of *rac*-LA, both in the absence and presence of pyridine derivatives [1]. The latter was previously used to enhance the formation of the homochiral (*R*,R**)-[Me₂Ga(μ-OCH(Me)CO₂PLA)]₂ species. Finally, *rac*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Et (**3**), *i*Pr (**4**)), where OCH(Me)C₅H₄N represents an alkoxide ligand with pyridine functionality, further served as model complexes in order to demonstrate the effect of alkyl groups on the formation of homochiral/heterochiral dialkylgallium alkoxides in the presence of pyridine derivatives. In addition to the main scope of our research presented above, it should be noted that there is a paucity of data on diethylgallium alkoxides [46,47] or aryloxides [48–54], and, as far as we are aware, there are no fully characterized di-*iso*-propylgallium alkoxides/aryloxides, in contrast to dimethylgallium or even bulky di-*tert*-butylgallium analogues [39].

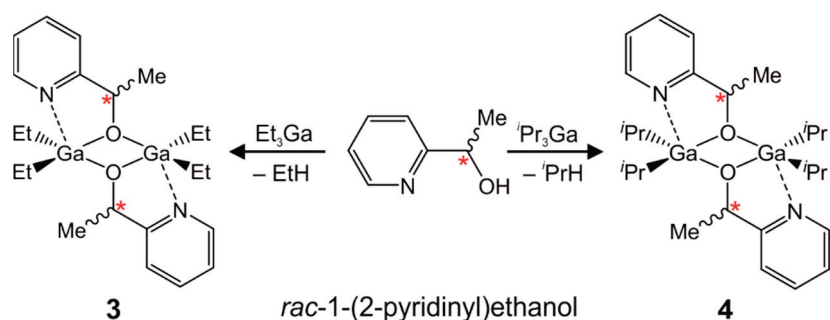
rac-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et (**1**) and *i*Pr (**2**)) and (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et ((*S,S*)-**1**), *i*Pr ((*S,S*)-**2**)) complexes were synthesized in the equimolar reaction between R₃Ga (R = Et, *i*Pr) and *rac*-methyl lactate or *S*-methyl lactate, respectively (Scheme 2). *rac*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Et (**3**) and *i*Pr (**4**)) were synthesized analogously, in the reaction of trialkylgallium compounds with *rac*-HOCH(Me)C₅H₄N (Scheme 3). All complexes were purified by crystallization and isolated as colorless crystals in moderate to high yields. Single crystals suitable for X-ray analysis were obtained for complexes **2**, **3**, **4**, as well as (*S,S*)-**1** and (*S,S*)-**2**.



Scheme 1. The structure of propagating species— $[R_2Ga(\mu-OCH(Me)CO_2PLA)]_2$ —in the ROP of *rac*-LA with dialkylgallium alkoxides, modeled by the dialkylgallium methyl lactate derivatives. Red stars indicate chiral centers which lead to the formation of either homochiral or heterochiral species. In our study, the homochiral (R^*,R^*) species are modeled by (S,S) - $[R_2Ga(\mu-OCH(Me)CO_2Me)]_2$; the heterochiral (R,S) species by (R,S) - $[R_2Ga(\mu-OCH(Me)CO_2Me)]_2$.



Scheme 2. Synthesis of *rac*- $[R_2Ga(\mu-OCH(Me)CO_2Me)]_2$ ($R = Et$ (**1**) and iPr (**2**)) and (S,S) - $[R_2Ga(\mu-OCH(Me)CO_2Me)]_2$ ($R = Et$ ((S,S) -**1**) and iPr ((S,S) -**2**)). Red stars indicate chiral centers.



Scheme 3. Synthesis of *rac*- $[R_2Ga(\mu-OCH(Me)C_5H_4N)]_2$ ($R = Et$ (**3**), iPr (**4**)). Red stars indicate chiral centers.

2.1. Structure of *rac*- $[R_2Ga(\mu-OCH(Me)CO_2Me)]_2$ ($R = Et$ (**1**), iPr (**2**))

rac- $[iPr_2Ga(\mu-OCH(Me)CO_2Me)]_2$ (**2**) crystallized as centrosymmetric dimer (R,S)-**2** (Figure 1), similarly to the previously reported (R,S) - $[Me_2Ga(\mu-OCH(Me)CO_2Me)]$ complex [1]. The coordination sphere of gallium atoms adopted a distorted trigonal-bipyramidal geometry, with the methine carbons of iPr groups and alkoxide oxygen of the *melac* ligand defining the equatorial plane. The carbonyl oxygen of *melac* ester functionality and the bridging alkoxide oxygen of the second monomeric unit were located in the axial positions, which is typical for five-coordinate group 13 dialkylalkoxides [39], analogous to dialkylaluminum complexes [55]. The presence of iPr resulted in the significantly longer Ga–C bonds (1.9837(15) Å and 1.9899(15) Å), in comparison to Ga–C bonds (1.9584(18) Å and

1.9611(17) Å) of the analogous dimethyl derivative—(*R,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)] [1]. While this observation is in line with the structure of dialkylgallium alkoxides bearing ethyl and *tert*-butyl alkyl groups [39], it should not be surprising as it can be associated with both larger steric hindrances of *i*Pr groups, and especially with the lower basicity of monoanionic (CH₃)₂HC[−] ligands in comparison with H₃C[−]. Notably, the increase in the steric hindrances of a gallium-bonded alkyl groups did not result in the longer Ga...O(2) chelate interaction (2.449(5) Å) between the gallium and carbonyl group of *melac* ligand in comparison with the analogous dimethyl derivative 2.5220(13) Å. Moreover, the stronger chelate bond in the case of the di-*iso*-propyl derivative **2** could be indicated by the distance of bridging Ga–O bonds in the *trans* position to chelate Ga–O=C ones [55]. In the latter case, the longer bridging Ga–O bond (2.0547(10) Å) in the *trans* position to the chelate Ga–O(2) bond (2.449(5) Å) was observed in comparison with the analogous distances of 2.0231(11) Å within the Ga₂O₂ central ring of (*R,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)] [1]. Notably, with regard to the discussion on the structure of (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)] (R = Me, Et ((*S,S*)-**1**), *i*Pr ((*S,S*)-**2**)) (see below), the presence of *isopropyl* groups in (*R,S*)-**2** had a considerable effect on the Ga(1)–O(1)–Ga(1¹)–C(2)/Ga(1¹)–O(1¹)–Ga(1)–C(2¹) torsion angles (164.94(14)° / −164.94(14)° in comparison with the analogous angles of (*R,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)] (146.08(15)° / −146.69(15)°).

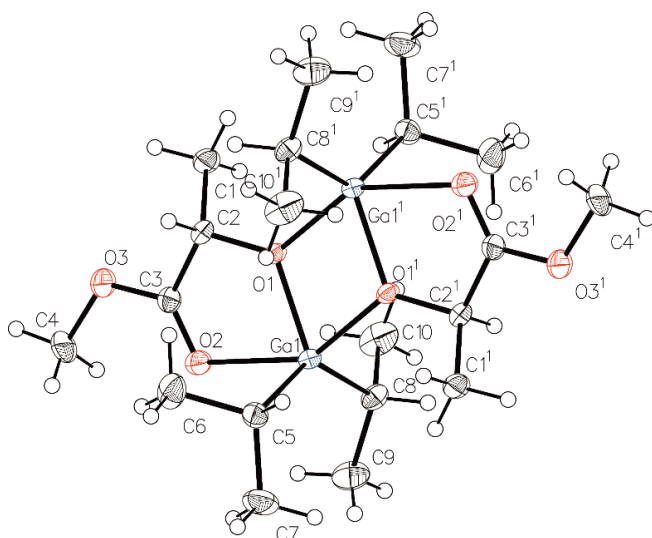


Figure 1. Molecular structure of (*R,S*)-**2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (deg) are as follows: Ga(1)–C(5) 1.9899(15), Ga(1)–C(8) 1.9837(15), Ga(1)–O(1) 1.9421(10), Ga(1)–O(1)¹ 2.0547(10), Ga(1)–O(2) 2.449(5), and O(2)¹–Ga(1)–O(1) 147.69(7). The selected torsion angles (deg) are as follows: Ga(1)–O(1)–Ga(1)¹–C(2) −164.94(14) and Ga(1)¹–O(1)¹–Ga(1)–C(2)¹ 164.94(14).

With regard to our studies on the structure of [Me₂Ga(μ-OCH(Me)CO₂Me)]₂ in solution [1], ¹H NMR spectra of **1** and **2** were expected to demonstrate the effect of alkyl groups on the distribution of homochiral—(*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, *i*Pr)—and heterochiral—(*R,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, *i*Pr)—species, as they have been crucial for the heteroselectivity of dialkylgallium alkoxide species in the ROP of *rac*-LA. On the other hand, the FTIR studies should be considered as indicative of the strength of the Ga...O=C chelate interaction between gallium and the *melac* ligand. Notably, in the latter case, the FTIR spectra of (*S,S*)-**2** and (*S,S*)-**1**, which are discussed below, showed essentially no effect across gallium-bonded ethyl or *iso*-propyl groups in comparison with (*S,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂ [42]. The dissolution of (*R,S*)-**2** led to the equimolar mixture of (*R*,R**)-**2** and (*R,S*)-**2** dimers, which was revealed by ¹H NMR and the presence of two sets of signals that are characteristic of homochiral and heterochiral species. The

presence of three septets at 1.01, 1.08, and 1.17 ppm, in a 1:2:1 ratio, corresponding to methine protons of Ga-CH(CH₃)₂ groups, was especially indicative of their ratio. Analogously, the equimolar mixture of (*R*,R**)-**1** and (*R,S*)-**1**, in the solution of **1** was evidenced by two quartets at 0.61 and 0.77 ppm, and a multiplet at 0.69 ppm, in a 1:1:2 ratio, corresponding to methylene protons of the Ga-CH₂CH₃ groups of the respective (*R,S*)-**1** and (*R*,R**)-**1** species. In the case of both **1** and **2**, it confirmed the presence of dimeric species, while the observed equimolar mixture of homochiral and heterochiral species was analogous to *rac*-[Me₂Ga(μ-OCH(Me)CO₂Me)₂] [1]. Similarly to the latter, the fast exchange between (*R,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)₂] and (*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂Me)₂] species was expected. Notable, in the case of **2**, the minor septet, overlapping with the septet at 0.77 ppm and corresponding to (*R,S*)-**2** (Figure 2), could suggest the presence of monomeric ⁱPr₂Ga(μ-OCH(Me)CO₂Me) (<4% based on the integration). In this case, the increased tendency of **2** to dissociate in solution was in line with the significantly longer bridging Ga-O' bond in the Ga₂O₂ ring in comparison with the analogous Ga-O bridging bond of *rac*-[Me₂Ga(μ-OCH(Me)CO₂Me)₂] [1]. However, even in the case of **2**, with the bulkiest alkyl groups among the discussed [R₂Ga(μ-OCH(Me)CO₂Me)] (R = Me, Et, ⁱPr), dimeric species were dominant, which also the case in the presence of different pyridine derivatives (Figure 2).

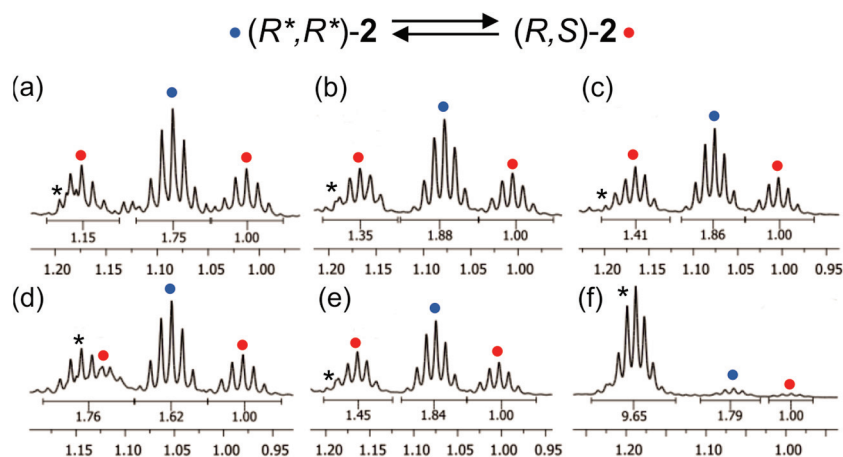


Figure 2. ¹H NMR spectra of **2** (a) and **2**/Py (**2**/pyr (1:2) (b), **2**/pyr (1:6) (c), **2**/pyr (1:60) (d), **2**/pic (1:6) (e), **2**/DMAP (1:6) (f)), in the region corresponding to the methine protons of the Ga-CH(CH₃)₂ groups. (*R*,R**)-**2** (●) and (*R,S*)-**2** (●) are depicted as blue and red dots, respectively. Tentative monomeric ⁱPr₂Ga(OCH(Me)CO₂Me) or ⁱPr₂Ga(OCH(Me)CO₂Me)(Py) species are depicted as stars (*); the integral corresponding to the latter was estimated based on the fact that both septets corresponding to *R,S*-**2** refer to the same number of methine protons. Abbreviations “pyr”, “pic”, and DMAP stand for pyridine, 4-methylpyridine, and 4-(dimethylamino)pyridine, respectively.

In the case of **1**, the ratio of (*R*,R**)-**1**/*(R,S)*-**1** increased with the addition of differently substituted pyridines, i.e., pyridine, 4-methylpyridine, and 4-(dimethylamino)pyridine, and this was strongly dependent on both their donor number [56] and pyridine/**1** ratio (Figure 3). Notably, the formation of only traces of tentatively assumed monomeric Ga species—Et₂Ga(OCH(Me)CO₂Me)(Py)—facilitated by the presence of pyridine derivative, could be suggested by the ¹H NMR spectra (Figure S2.) Importantly, the excess of homochiral (*R*,R**)-[Et₂Ga(μ-OCH(Me)CO₂Me)₂] ((*R*,R**)-**1**) species was much lower in comparison with analogous (*R*,R**)-[Me₂Ga(μ-OCH(Me)CO₂Me)₂] [1], as previously reported for *rac*-[Me₂Ga(μ-OCH(Me)CO₂Me)₂]/Py (Py—pyridine derivative), (Figure 3). On the other hand, no excess homochiral (*R*,R**)-**2**, was observed under the same conditions, irrespective of the donor number and excess of pyridine derivative added to **2** (Figure 2). On the contrary, the slight excess of heterochiral ((*R,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)₂]) was observed either without or with, e.g., the pyridine derivative added (Figure 2), which

resulted in the (R^*,R^*) -2/ (R,S) -2 ratio of 0.45–0.48, essentially, irrespective of the donor number of the pyridine derivative or Py :2 ratio. Interestingly, the percentage of tentatively assumed monomeric Ga species increased with both the donor number of pyridine or 4-methylpyridine and the Lewis base/2 ratio, reaching up to 17% in the case of the 4-methylpyridine/2 ratio of 60:1. In the case of DMAP/2, a ratio of 6:1 was observed, where DMAP represents a 4-(dimethylamino)pyridine of the highest donor number among all pyridine derivatives used, and the percentage of monomeric gallium species reached over 75%. The formation of such tentatively proposed monomeric species could be facilitated by the formation of $iPr_2Ga(OCH(Me)CO_2Me)(Py)$, where Py represents the pyridine derivative. Although no monomeric dialkylgallium alkoxides could be isolated in our studies, several X-ray structures of $tBu_2GaOPh(Py)$ have been reported and well characterized so far [57]. With regard to the latter, further studies on the synthesis and structure of monomeric $iPr_2Ga(OCH(Me)CO_2Me)(Py)$ should be conducted. However, the dimeric species decisive for the stereoselectivity of dialkylgallium alkoxides are the primary focus of this article. While in the case of rac -[$R_2Ga(\mu-OCH(Me)CO_2Me)$] ($R = Me$ [1], Et (1), iPr (2)) the essentially equimolar ratio of homochiral ((R^*,R^*) -[$R_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$) to heterochiral ((R,S) -[$R_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$) species was observed irrespective of the alkyl group, the alkyl groups considerably affected the distribution of homo- and heterochiral species in the presence of pyridine derivatives. Therefore, gallium-bonded alkyl groups can be considered responsible for the distribution of homo- and heterochiral species, as well as for the pyridine derivatives of different coordination efficiencies to gallium.

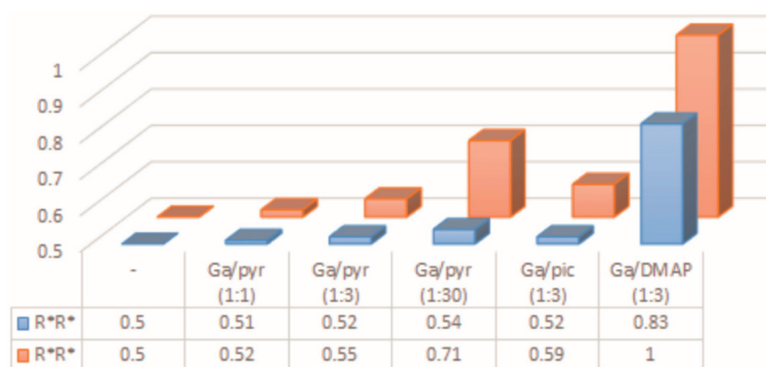


Figure 3. Molar fraction of homochiral species (R^*,R^*) for 1/ Py (Py —pyridine derivative) (blue) and rac -[$Me_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ / Py (orange) [1], calculated on the basis of the ratio of methylene protons and methyl protons of the Ga-Me and Ga-Et groups, respectively. Abbreviations “pyr”, “pic”, and DMAP stand for pyridine, 4-methylpyridine, and 4-(dimethylamino)pyridine, respectively.

2.2. Structure of (S,S) -[$R_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ ($R = Et((S,S)$ -1), $iPr((S,S)$ -2))

(S,S) -[$Et_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ ((S,S) -1) (Figure 4) and (S,S) -[$iPr_2Ga(\mu-OCH(Me)CO_2(PLA))$] $_2$ ((S,S) -2) (Figure 5) crystallized as dimers, with the coordination sphere of both gallium atoms adopting a distorted trigonal-bipyramidal geometry, similarly to the previously reported (S,S) -[$Me_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ complex [42]. For a whole series of compounds— (S,S) -[$R_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ ($R = Me, Et, iPr$)—the carbons of alkyl groups and alkoxide oxygen of the *melac* ligand defined the equatorial plane, and the carbonyl oxygen of the *melac* ester’s functionality and the bridging alkoxide oxygen of the second monomeric unit were located in the axial positions. Notably, the Ga–C bond distances of (S,S) -[$R_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ decreased in series iPr ((S,S) -2; 1.985–1.996 Å) > Et ((S,S) -1; 1.962–1.978 Å) > Me (1.952–1.962 Å). Similarly, the Ga–O bridging bonds within the Ga_2O_2 central ring were significantly longer in the case of (S,S) -2 (2.055(3) and 2.053(3)) and (S,S) -1 (2.021(4) and 2.058(3)), in comparison with (S,S) -[$Me_2Ga(\mu-OCH(Me)CO_2Me)$] $_2$ (2.0269(18) and 2.0349(17) Å). Both findings were in line

with the differences between the structures of **2** and (R,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)] [1] discussed above. Importantly, for both (S,S) -**1** and (S,S) -**2**, the X-ray diffraction analyses revealed the presence of asymmetric dimers, which is in line with the structure of the previously characterized (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂ complex [1,42]. Similarly to the latter, the observed asymmetry was the effect of the differently distorted methine carbon of *melac* ligands from the GaOCCO planes (Figure 6), which could be quantified by measuring the Ga–O–Ga–CH(Me) torsion angles [1]. However, the difference between the two different torsion angles Ga–O–Ga–CH(Me) in dimeric (S,S) -**1** (Figure 6b) and (S,S) -**2** (Figure 6c) were much smaller in comparison with (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂ (Figure 6a). Therefore, the presence of more sterically hindered Et and ⁱPr, in comparison with Me groups, resulted in significantly smaller distortion from the symmetric species, for which no or an equal level of distortion of both methine carbon *S-melac* ligands from the GaOCCO planes was expected. It is impossible to indicate unequivocally all the factors responsible for the above observation at this point in our research. However, one should note the presence of the center of symmetry in (S,S) -**1** and (S,S) -**2** resulting from the arrangement of ethyl and *iso*-propyl groups, respectively, in cases where the *S-melac* ligands are not taken under consideration (Figure 5). Such an effect was not evidenced for small gallium-bonded Me groups in (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂. Therefore, in the case of (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et, ⁱPr) complexes, the alkyl groups resulted in the formation of species of different symmetry, although the C₂ point group was initially expected due to the presence of *S-melac* ligands of the same absolute configuration. Notably, the presence of two different structural elements, i.e., the alkyl groups on the gallium and *S-melac* ligands, which favored the formation of (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Et, ⁱPr) complexes of different symmetry, could be responsible for the higher tension within their central Ga₂O₂ ring in comparison with the analogous dimethyl derivative. This was reflected by the Ga(O1)–O(1)–Ga(1B)–O(1B) torsion angles of 3.3° ((*S,S*)-**2**) and 2.4° ((*S,S*)-**1**), larger in comparison with 2.0° in the case of (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂. The increased preference for the formation of centrosymmetric species for more bulky alkyl groups, should also be expected for the heterochiral (R,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et, ⁱPr) complexes discussed above, for which the presence of *melac* ligands of the opposite absolute configuration does not prevent the formation of centrosymmetric complexes. Such reasoning is in line, e.g., with the lower tendency for the formation of homochiral (*R*,R**)-[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et, ⁱPr) in solution, presented and discussed above in the case of *rac*-[R₂Ga(μ -OCH(Me)CO₂Me)]₂, **1** and **2**.

In solution, the ¹H NMR spectrum of (S,S) -**1** revealed one set of signals, which was in line with the presence of (S,S) -[Et₂Ga(μ -OCH(Me)CO₂Me)]₂. Additionally the dimeric structure of **1**, both in the solid state and solution, supported the proposed structure of (S,S) -**1**, which was additionally in agreement with the tendency of dialkylgallium alkoxides to form dimeric species [39]. Similarly, the major set of signals evidenced by the ¹H NMR spectrum of (S,S) -**2**, was assigned to (S,S) -[ⁱPr₂Ga(μ -OCH(Me)CO₂Me)]₂. In this case, the additional minor septet corresponding to methine protons of the GaCH(CH₃)₂ groups (Figure S5) could be assigned to monomeric species, tentatively proposed for **2**. It can also indicate the presence of an equilibrium between dimeric (S,S) -[ⁱPr₂Ga(μ -OCH(Me)CO₂Me)]₂ and monomeric [ⁱPr₂Ga(*S*-OCH(Me)CO₂Me)] species, shifted considerably towards the former species. While the structure of (S,S) -**1** and (S,S) -**2** in solution, revealed by NMR spectra, was in line with the structure of *rac*-**1** and *rac*-**2**, discussed above, infrared spectroscopy was especially indicative of the effect of alkyl groups on the chelate Ga...O=C interaction of (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et, ⁱPr). The FTIR of both (S,S) -**1** and (S,S) -**2** in CH₂Cl₂ revealed the presence of absorption bands of C=O groups at 1724 cm^{−1}, essentially the same, accounting for experimental error, in comparison with (S,S) -[Me₂Ga(μ -

$\text{OCH(Me)CO}_2\text{Me})_2$ ($\nu_{\text{C=O}} = 1725 \text{ cm}^{-1}$) [42]. Moreover, the deconvolution of the C=O band, leading to bands at 1724 and 1740 cm^{-1} , corresponding to the coordinated and uncoordinated C=O groups of the *melac* ligand, was indicative of the percentage of the latter. In the case of (*S,S*)-**1**, it was revealed that 88% of C=O groups remained coordinated to gallium, which was exactly the same value as in the case of (*S,S*)- $[\text{Me}_2\text{Ga}(\mu\text{-OCH(Me)CO}_2\text{Me})_2]$ [42]. A slightly higher percentage of coordinated C=O groups was observed for (*S,S*)-**2** (90%), which could explain the slightly stronger chelate Ga–O bonds in the case of **2** in comparison with both **1** and $[\text{Me}_2\text{Ga}(\mu\text{-OCH(Me)CO}_2\text{Me})_2]$, as revealed by X-ray analysis.

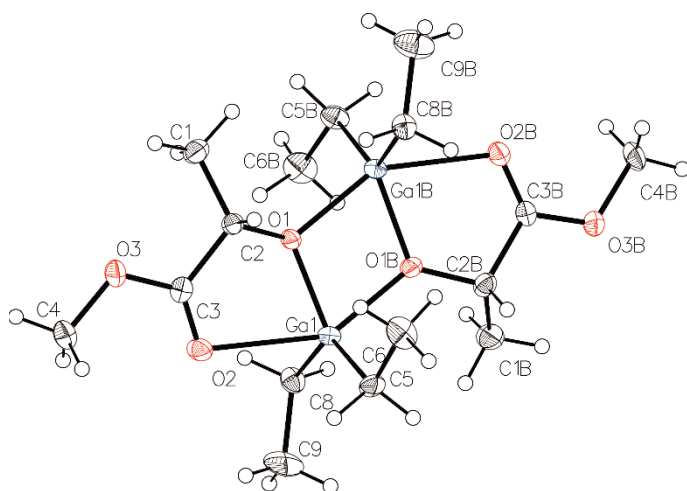


Figure 4. Molecular structure of (*S,S*)-**1** with ellipsoids at the 50% probability level. The selected bond lengths (Å) and angles are as follows: Ga(1)–C(5) 1.974(5), Ga(1)–C(8) 1.962(5), Ga(1)–O(1) 1.927(4), Ga(1)–O(1B) 2.021(4), Ga(1)–O(2) 2.518(4), Ga(1B)–C(5B) 1.973(5), Ga(1B)–C(8B) 1.978(5), Ga(1B)–O(1B) 1.953(4), Ga(1B)–O(1) 2.058(3), Ga(1B)–O(2B) 2.405(4), O(2)–Ga(1)–O(1B) 147.70(12), and O(2B)–Ga(1B)–O(1) 148.14(12). The selected torsion angles (deg) are as follows: Ga(1)–O(1)–Ga(1B)–C(2)–157.3(5) and Ga(1B)–O(1B)–Ga(1)–C(2B)–163.7(5).

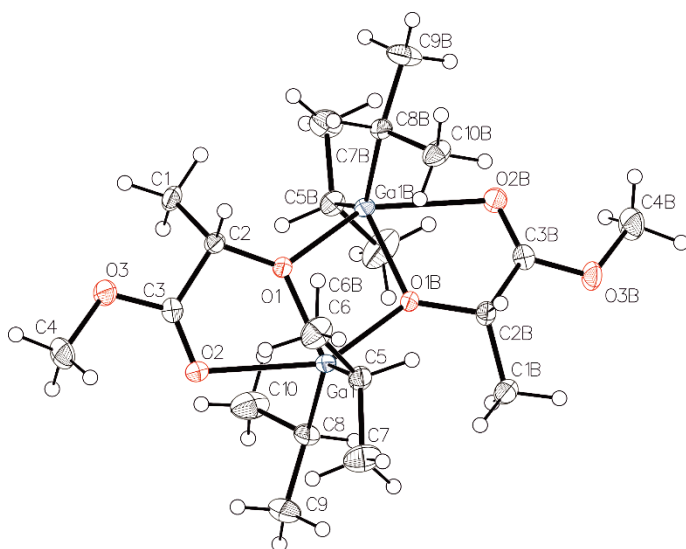


Figure 5. Molecular structure of (*S,S*)-**2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (deg) are as follows: Ga(1)–C(5) 1.985(4), Ga(1)–C(8) 1.988(5), Ga(1)–O(1) 1.944(3), Ga(1)–O(1B) 2.055(3), Ga(1)–O(2) 2.435(3), Ga(1B)–C(5B) 1.996(4), Ga(1B)–C(8B) 1.984(4), Ga(1B)–O(1B) 1.940(3), Ga(1B)–O(1) 2.053(3), Ga(1B)–O(2B) 2.467(3), O(2)–Ga(1)–O(1B) 148.28(11), and O(2B)–Ga(1B)–O(1) 147.93(11). The selected torsion angles (deg) are as follows: Ga(1)–O(1)–Ga(1B)–C(2)–168.3(4) and Ga(1B)–O(1B)–Ga(1)–C(2B)–161.7(4).

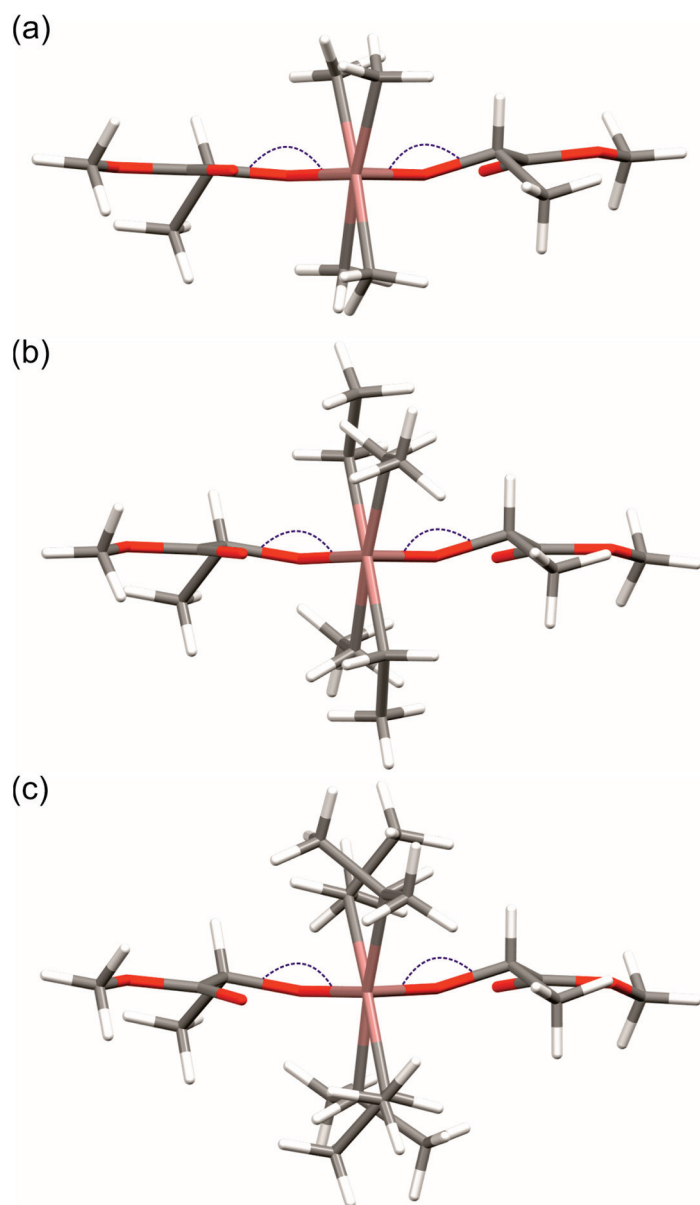


Figure 6. The view of the molecular structures of (S,S) - $[R_2Ga(\mu-OCH(Me)CO_2Me)_2]$ ($R = Me$ (a), Et (b), and iPr (c)) along the Ga-Ga axis. Different Ga-O-Ga-CH(Me) torsion angles (deg) are indicated by the dashed blue arches for the following: (S,S) - $[Me_2Ga(\mu-OCH(Me)CO_2Me)_2]$ (-156.7 and -171.7), (S,S) -1 (-157.3 and -163.7), and (S,S) -2 (-168.3 and -161.8). Gallium and oxygen atoms are depicted as brown and red, respectively.

2.3. Structure of rac - $[R_2Ga(\mu-OCH(Me)C_5H_4N)_2]$ ($R = Et$ (3), iPr (4))

Complexes **3** and **4** were characterized in the solid state by X-ray diffraction analysis, which revealed, in both cases, the presence of centrosymmetric heterochiral dimers (R,S) - $[R_2Ga(\mu-OCH(Me)C_5H_4N)_2]$ (Figures 7 and 8). This was in sharp contrast to the analogous dimethyl derivatives, which led upon crystallization solely to the (R^*,R^*) - $[Me_2Ga(\mu-OCH(Me)C_5H_4N)_2]$ of the C_2 symmetry [1]. However, the observed structure of **3** and **4** was in line with the effect of the ethyl and *iso*-propyl groups on the tendency for the formation of centrosymmetric dialkylgallium alkoxide species, as shown above for the $[R_2Ga(\mu-OCH(Me)CO_2Me)_2]$ complexes. In the case of **3** and **4**, five-coordinate gallium atoms adopted a distorted trigonal-bipyramidal geometry. Carbon atoms of gallium-bonded alkyl groups and the alkoxide oxygen of the $OCH(Me)C_5H_4N$ ligand defined the equatorial plane. The nitrogen of the pyridine functionality of the $OCH(Me)C_5H_4N$ ligand

and a bridging alkoxide oxygen atom of the second monomeric unit were located in the axial positions. Notably, the presence of ethyl, and especially *iso*-propyl groups, did not essentially restrain the formation of Ga–N bonds to the fifth coordinate site of gallium in comparison to the analogous dimethyl derivative. This was demonstrated by the Ga–N distances for the following $[\text{R}_2\text{Ga}(\mu\text{-OCH}_2\text{C}_5\text{H}_4\text{N})]_2$ complexes: 2.2789(18) Å (R = Me), 2.2908(11) Å (R = Et; **3**), and 2.2759(18) Å (R = *i*Pr; **4**). On the other hand, the presence of a *i*Pr group resulted in the elongation of the bridging Ga–O' bond (2.1632(13) Å) within central Ga_2O_2 ring in comparison to the analogous bond in (*R**,*R**)-[Me₂Ga(μ -OCH(Me)C₅H₄N)]₂ (2.0931 Å), as well as in **3** (2.0906(8) Å).

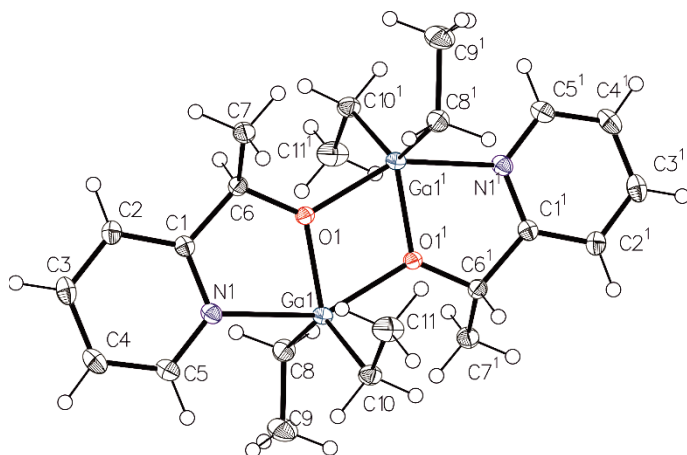


Figure 7. Molecular structure of (*R,S*)-**3** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (deg) are as follows: Ga(1)–C(8) 1.9854(10), Ga(1)–C(10) 1.9808(10), Ga(1)–O(1) 1.9340(8), Ga(1)–O(1)¹ 2.0906(8), Ga(1)–N(1) 2.2908(11), N(1)–Ga(1)–O(1)¹ 148.49(3).

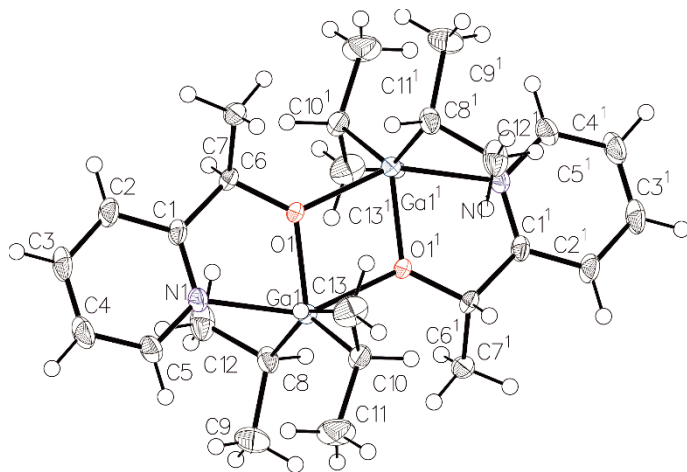


Figure 8. Molecular structure of (*R,S*)-**4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Ga(1)–C(8) 1.992(3), Ga(1)–C(10) 1.996(4), Ga(1)–O(1) 1.9100(13), Ga(1)–O(1)¹ 2.1632(13), Ga(1)–N(1) 2.2759(18), N(1)–Ga(1)–O(1)¹ 150.22(6).

In solution, the ¹H NMR spectrum of **3** revealed one set of signals, which was not in agreement with either the molecular structure of (*R,S*)-**3** in the solid state or the mixture of (*R,S*)-**3** and (*R**,*R**)-**3** diastereomers, which was expected given the structures of **1** and **2** (see above). This could either suggest the presence of tentative monomeric—[Et₂Ga(μ -OCH(Me)C₅H₄N)]₂—or dimeric homochiral species—(*R**,*R**)-[Et₂Ga(μ -OCH(Me)C₅H₄N)]₂—in solution. The presence of the latter was further indicated by the ¹H NMR spectrum of **4**, which revealed two sets of signals that, analogously to

2 and (*S,S*)-**2**, should be ascribed to the dimeric homochiral species—(*R*,R**)-[ⁱPr₂Ga(μ-OCH(Me)C₅H₄N)]₂—and the tentative monomeric [ⁱPr₂Ga(μ-OCH(Me)C₅H₄N)]₂ species in a ratio of about 3:1. Although the ratio could not be determined precisely due to the overlapping signals (Figure S7), the presence of a higher percentage of monomeric species, in comparison with the structure of **2** and (*S,S*)-**2**, was in line with the structure of **2** in the presence of pyridine derivatives (see above), as well as with the interaction of pyridine functionality with Ga. Although the presence of only homochiral dimers—(*R*,R**)-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Et, ⁱPr)—for **3** and **4** was initially surprising given the structure of **1** and **2**, this is in line with the suggested structure of *rac*-[Me₂Ga(μ-OCH(Me)C₅H₄N)]₂, as well as with the tendency of *rac*-[Me₂Ga(μ-OCH(Me)CO₂Me)] for the formation of homochiral species in the presence of pyridines [1]. Despite the remaining questions and uncertainties concerning the structure of these complexes in solution, the minor effect of alkyl groups on the distribution of homo (*R*,R**) and heterochiral (*R,S*) dimers for *rac*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Me, Et, ⁱPr) was observed in contrast to their solid state structures. Notably, in the solid state, the tendency for the formation of centrosymmetric heterochiral dimers in the case of **3** and **4** was facilitated for diethyl- and especially di-*iso*-propylgallium *melac* derivatives in comparison to methyl derivatives [1]. This was in line with a reduced tendency for the formation of homochiral species with growing alkyl groups in the case of *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Me, Et (**1**) and ⁱPr (**2**)) in the presence of pyridine derivatives. The latter should be of special interest with regard to the ROP of *rac*-lactide using [R₂Ga(μ-OCH(Me)CO₂Me)]₂, as well as the structure of the [R₂Ga(μ-OCH(Me)CO₂PLA)]₂ propagating species.

2.4. Ring-Opening Polymerization of *rac*-LA with [R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Me, Et, ⁱPr)

In order to investigate the effect of the alkyl groups of [R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, ⁱPr) on their activity, and especially their stereoselectivity in the ROP of *rac*-LA, we examined the catalytic properties of (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et ((*S,S*)-**1**), ⁱPr ((*S,S*)-**2**)), chosen analogously to (*S,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂, and previously used by us in polymerization studies [1,42]. Additionally, (*S,S*)-**1**/pyridine (1:6) and (*S,S*)-**2**/pyridine (1:6) were used in order to generate propagating species with the excess of homochiral—(*R*,R**)—dimers and served as a representative examples of the catalytic systems—(*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂/Py (Py—pyridine derivative)—described above. One should note that after the insertion of *rac*-LA into the Ga–O bond of (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, ⁱPr), the formation of both heterochiral (*R,S*)-[R₂Ga(μ-OCH(Me)CO₂PLA)]₂ and homochiral (*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂PLA)]₂ propagating species should be expected, analogous to the previously described dimethylgallium derivatives (Scheme 1) [1].

The ROP of *rac*-LA, with (*S,S*)-**1**, (*S,S*)-**1**/pyridine, (*S,S*)-**2**, (*S,S*)-**2**/pyridine, as well as (*S,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂ and (*S,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂/pyridine, was conducted at 40 °C and 70 °C. (Table 1) At 40 °C (Table 1, Entries 1–6), the insertion of *rac*-LA occurred solely into the Ga–O_{alkoxide} bond and led to the PLA with OH and *S-melac* end groups (Scheme 4), which was in each case verified by ¹H NMR and MALDI-TOF analysis (see the Supplementary Materials). The latter indicated that there were essentially no transesterification reactions for the (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂/pyridine catalytic systems, which confirmed the lack of activity of amines towards *rac*-LA at the polymerization conditions and the coordination insertion mechanism of the ROP of *rac*-LA with dialkylgallium alkoxide species. This was in line with previously reported results on the ROP of *rac*-LA with (*S,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂ and (*S,S*)-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂/pyridine [1]. Although, at 70 °C (Table 1, Entries 7–12), the insertion of *rac*-LA into Ga–O_{alkoxide} bond was evidenced both by the ¹H NMR and MALDI

TOF analysis, the higher tendency for side reactions, both the intermolecular transesterification and formation of cyclic PLA, were evidenced by the MALDI-TOF analyses. For a series of catalysts— (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et ((S,S)-1) and ^{*i*}Pr ((S,S)-2)—the side reactions were essentially eliminated in the case of (S,S)-2, most probably due to the presence of ^{*i*}Pr groups—the bulkiest among all investigated [R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et, ^{*i*}Pr) complexes. For a series of catalytic systems— (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂/pyridine (1:6), (S,S)-1/pyridine (1:6) and (S,S)-2/pyridine (1:6)—the side reactions were more pronounced; however, the lowest extent was observed in the case of di-*iso*-propyl species. Although the reader must note that the MALDI-TOF analysis is not a quantitative method, the effect of ^{*i*}Pr groups on the decreased tendency for side reactions, especially transesterification, should be considered. The differences in the activities of both (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ catalysts, at 70 °C, and (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂/pyridine (1:6) catalytic systems, both at 40 °C and 70 °C, were too small to substantially demonstrate the effect of the alkyl groups. However, in the case of the (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ catalysts, at 40 °C, and in the absence of pyridine (Table 1, Entries 1–3), for which the lowest activity of propagating species was observed, the *rac*-LA conversions decreased in the following series: (S,S)-2 > (S,S)-1 > (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂. Such an observation could be the result of the decreasing distances of bridging Ga–O bonds with the decreasing bulkiness of the alkyl groups in series ^{*i*}Pr > Et > Me. While the highest activity was observed for (S,S)-2, we cannot exclude the effect of the presence of minor fractions of other species, tentatively ascribed as monomeric species, in this case.

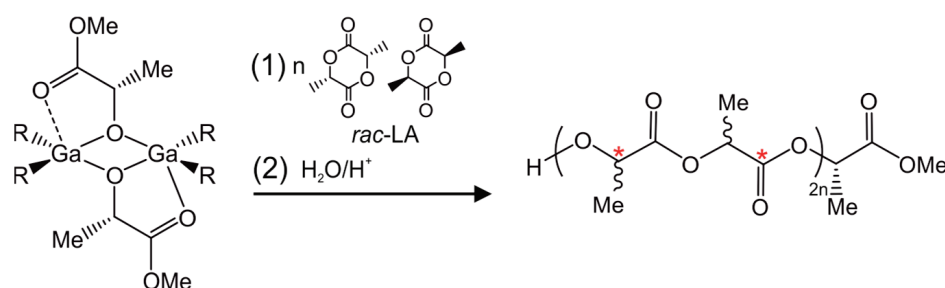
Table 1. Polymerization of *rac*-LA with (S,S) -[R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et ((S,S)-1) and ^{*i*}Pr ((S,S)-2)); *rac*-LA/Ga = 25, time = 96 h.

No.	Cat.	Pyridine (Equiv.)	Temp. [°C]	Solvent	Conv. [%]	10 ^{−3} M _n ^b	10 ^{−3} M _n ^c	P _m ^d
1 ^a	(S,S) -[Me ₂ Ga(<i>melac</i>)] ₂	-	40	DCM	82	2.0	3.0	0.50
2	(S,S)-1	-	40	DCM	87	2.6	3.2	0.50
3	(S,S)-2	-	40	DCM	93	3.9	3.4	0.50
4 ^a	(S,S) -[Me ₂ Ga(<i>melac</i>)] ₂	6	40	Tol.	90	2.0	3.3	0.66
5	(S,S)-1	6	40	Tol.	83	3.0	3.1	0.58
6	(S,S)-2	6	40	Tol.	89	3.9	3.3	0.50
7	(S,S) -[Me ₂ Ga(<i>melac</i>)] ₂	-	70	Tol.	97	2.5	3.6	0.50
8	(S,S)-1	-	70	Tol.	97	3.8	3.6	0.50
9	(S,S)-2	-	70	Tol.	92	3.8	3.4	0.50
10	(S,S) -[Me ₂ Ga(<i>melac</i>)] ₂	6	70	Tol.	97	2.7	3.6	0.50
11	(S,S)-1	6	70	Tol.	97	3.5	3.6	0.50
12	(S,S)-2	6	70	Tol.	96	3.9	3.6	0.50

^a Although indicted entries concern the previously reported ROP of *rac*-LA with (S,S) -[Me₂Ga(μ -OCH(Me)CO₂Me)]₂ [1], they refer to the new samples obtained in the current studies, at exactly the same conditions as the ROP of *rac*-LA with (S,S)-1 and (S,S)-2; ^b determined by ¹H NMR; ^c expected according to LA/Ga ratio and conversion; ^d calculated on the basis of homonuclear decoupled ¹H NMR spectra according to Chamberlain et al. [43].

For the ROP of *rac*-LA with [R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et ((S,S)-1) and ^{*i*}Pr ((S,S)-2) (Table 1, Entries 1–3 and 7–12), only atactic PLA was formed, even at mild conditions at which no side reactions could be detected. However, in the case of catalytic systems [R₂Ga(μ -OCH(Me)CO₂Me)]₂ (R = Me, Et)/pyridine (1:6) (Table 1, Entries 4–6), the formation of heterotactically enriched PLA was observed. The essential lack of heteroselectivity at 70 °C (Table 1, Entries 10–12) should be considered a result of both high temperature as well as the effect of side reactions at polymerization conditions. Most importantly, the heteroselectivity, expressed as a probability of *racemo*-linkages (*P_r*) in the formed PLA, strongly

correlated with the excess of homochiral dimeric propagating species, which should be expected based on the structure studies of $[\text{R}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Me})_2]$ ($\text{R} = \text{Me}$ [1], Et ((*S,S*)-1) and *i*Pr ((*S,S*)-2) in the presence of pyridine (see the discussion above). Notably, essentially no stereoselectivity was observed in the case of (*S,S*)-2 and (*S,S*)-2/pyridine, which indicates that there is essentially no effect of minor species, tentatively assigned to monomeric species, on the stereoselectivity. Most importantly, despite the limited number of examples, the obtained results clearly demonstrate that the chiral recognition induced the formation of homochiral dimeric (*R*,R**)- $[\text{R}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{PLA})_2]$ propagating species and should be considered responsible for their stereoselectivity in the ROP of *rac*-LA. While the presence of bulky alkyl groups in $[\text{R}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{PLA})_2]$ has no adverse effect on their activity and can be somehow helpful in order to limit side reactions, it considerably decreases or even eliminates the excess of homochiral (*R*,R**)- $[\text{R}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Me})_2]$ species and therefore the stereoselectivity.



Scheme 4. ROP of *rac*-LA with (*S,S*)- $[\text{R}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Me})_2]$ ($\text{R} = \text{Me}$, Et and *i*Pr). Red stars indicate chiral centers in the PLA.

3. Materials and Methods

3.1. General Procedures

All operations were carried out under dry argon using standard Schlenk techniques. Solvents and reagents were purified and dried prior to use. Solvents were purified using MBRAUN Solvent Purification Systems (MB-SPS-800) and stored over molecular sieves. *rac*-Lactide was purchased from Sigma-Aldrich (Merck, Warsaw, Poland) and further purified by crystallization from anhydrous toluene and then sublimated. (*S*)-methyl lactate and (*rac*)-methyl lactate were purchased from Sigma-Aldrich. *rac*-HOCH(Me) $\text{C}_5\text{H}_4\text{N}$ (*rac*-1-(2-pyridinyl)ethanol) was synthesized according to the literature [58]. All alcohols were stored under argon, over 4 Å molecular sieves, at least 48h before they were used for the reaction with trialkylgallium compounds. Me_3Ga was purchased from STREM Chemicals, Inc. and used as received. Et_3Ga and *i* Pr_3Ga , which we received as a gift, were synthesized in the research group of Prof. Kazimierz B. Starowieyski at Warsaw University of Technology. *i* Pr_3Ga was freshly distilled under vacuum prior to use. (*S,S*)- $[\text{Me}_2\text{Ga}(\mu\text{-OCH}(\text{Me})\text{CO}_2\text{Me})_2]$ was synthesized according to our article [42]. The ^1H and ^{13}C NMR spectra were recorded on Varian 700 MHz (Varian, Palo Alto, CA, USA) and Agilent 400 MHz spectrometers (Agilent Technologies, Santa Clara, CA, USA), with shifts given in ppm according to the deuterated solvent shift. FTIR spectra were recorded on a FTIR Perkin Elmer System 2000 instrument (Perkin Elmer, Waltham, MA, USA). MALDI-TOF spectra were recorded on a Bruker Model ultrafleXtreme instrument (Bruker, Billerica, MA, USA). Elemental analysis was performed on a Vario EL III instrument (Heraeus, Hanau, Germany) for (*S,S*)-1 and (*S,S*)-2. Although, for (*S,S*)-1, the obtained values were low for carbon with 0.6%, they represent the best values we could obtain experimentally. EA for (*S,S*)-2 was significantly low in carbon and hydrogen. This could result from the EA measurement or sample handling without an inert atmosphere.

3.2. Synthesis of Gallium Complexes

The representative method for the synthesis of **1**, (*S,S*)-**1**, **2**, (*S,S*)-**2**, **3**, and **4** was as follows. The stirred solution of trialkylgallium— R_3Ga ($R = Et, ^iPr$; 3.0 mmol)—in CH_2Cl_2 (1 mL) was added dropwise to the solution of *S*-methyl lactate/*rac*-methyl lactate/*rac*-1-(2-pyridinyl)ethanol (3.0 mmol) in CH_2Cl_2 (9 mL), at $-40\text{ }^\circ C$. Subsequently, the cooling bath was removed, and the reaction mixture was warmed slowly to room temperature. Upon increasing the solution temperature, the evolution of gas was observed. The reaction mixture was stirred at room temperature for 5 h. Then, the solvent and volatiles were removed under a vacuum to give, in each case, a white crystalline solid. (*S,S*)-**1** and (*S,S*)-**2** were recrystallized from *n*-hexane, and **1**, **2**, **3**, **4** from the methylene chloride/*n*-hexane solution, at $-20\text{ }^\circ C$, to give colorless crystals in moderate to high yields, the latter depending on the concentration of the solution and CH_2Cl_2 /*n*-hexane ratio.

(*S,S*)-**1**: ^1H NMR (CD_2Cl_2 , 700 MHz): 0.35, (q, $^3J(H,H) = 8.0\text{ Hz}$, 4H, $GaCH_2CH_3$), 1.04 (t, $^3J(H,H) = 8.0\text{ Hz}$, 6H, $GaCH_2CH_3$), 1.39 (d, $^3J(H,H) = 6.9\text{ Hz}$, 3H, $CHCH_3$), 3.77 (s, 6H, OCH_3), 4.44 (q, $^3J(H,H) = 6.9\text{ Hz}$, 1H, $CHCH_3$). ^{13}C $\{^1H\}$ NMR (CD_2Cl_2 , 175 MHz): 5.9, 10.2, 22.1, 53.3, 68.3, 179.1. FTIR: 1724 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{34}Ga_2O_6$: C, 41.61, H, 7.42. Found: C, 40.96, H, 7.32.

(*S,S*)-**2**: 0.83 (sept, $^3J(H,H) = 7.6\text{ Hz}$, 2H, $GaCH(CH_3)_2$), 1.12 (d, $^3J(H,H) = 7.6\text{ Hz}$, 12H, $GaCH(CH_3)_2$), 1.42 (d, $^3J(H,H) = 6.9\text{ Hz}$, 3H, $CHCH_3$), 3.78 (s, 3H, OCH_3), 4.52 (q, $^3J(H,H) = 6.9\text{ Hz}$, 1H, $CHCH_3$). ^{13}C $\{^1H\}$ NMR (CD_2Cl_2 , 175 MHz): 17.4, 21.7, 22.3, 53.5, 68.85, 179.69. FTIR: 1724 cm^{-1} (C=O).

1: ^1H NMR (toluene- d_8 , 700 MHz): 0.61 (q, $^3J(H,H) = 8.1\text{ Hz}$, 1H, $GaCH_2CH_3$), 0.74–0.65 (m, 2H, $GaCH_2CH_3$), 0.77 (q, $^3J(H,H) = 8.1\text{ Hz}$, 1H, $GaCH_2CH_3$), 1.46–1.25 (m, 9H, $CHCH_3$, $GaCH_2CH_3$), 3.21, 3.22 (s, 3H, OCH_3), 4.44–4.39 (m, 1H, $CHCH_3$).

2: ^1H NMR (toluene- d_8 , 700 MHz): 1.05–0.98 (sept, $^3J(H,H) = 7.6\text{ Hz}$, 1H, $GaCH(CH_3)_2$), 1.12–1.05 (sept, $^3J(H,H) = 7.6\text{ Hz}$, 2H, $GaCH(CH_3)_2$), 1.21–1.14 (m, 1H, $GaCH(CH_3)_2$), 1.50–1.33 (m, 30H, $CHCH_3$, $GaCH(CH_3)_2$), 3.22, 3.23 (s, 6H, OCH_3), 4.52–4.47 (m, 2H, $CHCH_3$).

3: ^1H NMR (CD_2Cl_2 , 400 MHz): 0.36 (q, $^3J(H,H) = 8.0\text{ Hz}$, 4H, $GaCH_2CH_3$), 0.96 (t, $^3J(H,H) = 8.0\text{ Hz}$, 6H, $GaCH_2CH_3$), 1.52 (d, $^3J(H,H) = 6.6\text{ Hz}$, 3H, $CHCH_3$), 5.23 (q, $^3J(H,H) = 6.6\text{ Hz}$, 1H, $CHCH_3$), 7.37–7.29 (m, 2H, $CH_{(C_5H_4N)}$), 7.84–7.77 (m, 1H, $CH_{(C_5H_4N)}$), 8.43–8.37 (m, 1H, $CH_{(C_5H_4N)}$).

4: ^1H NMR (CD_2Cl_2 , 400 MHz): 0.78–0.92 (m, 2H, $GaCH(CH_3)_2$), 1.06 (m, 12H, $GaCH(CH_3)_2$), 1.49 (d, $^3J(H,H) = 6.6\text{ Hz}$, 3H, $CHCH_3$), 5.33 (q, $^3J(H,H) = 6.6\text{ Hz}$, 1H, $CHCH_3$), 7.33–7.49 (m, 2H, $CH_{(C_5H_4N)}$), 7.88–7.95 (m, 1H, $CH_{(C_5H_4N)}$), 8.27–8.33 (m, 1H, $CH_{(C_5H_4N)}$).

3.3. General Procedure for the ROP of *rac*-LA with (*S,S*)-**1** and (*S,S*)-**2**

To a *rac*-LA (334.8 mg, 2.32 mmol, 25 eq) solution in CH_2Cl_2 , or a suspension in toluene, (10 mL) the solution of the catalyst (0.09 mmol, 1 eq Ga) in the same solvent was added. The reaction was stirred at the indicated temperature for 96 h in order to support high conversions. For the polymerizations in toluene, the dissolution of *rac*-LA was observed with its conversion, while after 96 h, the whole *rac*-LA was dissolved. Each polymerization was quenched by the addition of a HCl solution (5%, 50 mL). The organic phase was separated, washed twice with water (50 mL), dried over anhydrous $MgSO_4$, and dried under vacuum to give PLA as a white solid. ^1H NMR ($CDCl_3$, 400 MHz): (a) PLA signals, 1.52–1.60 (m, 3H, $CHCH_3$), 5.11–5.26 (m, 1H, $CHCH_3$); (b) end groups: 1.47–1.50 (m, $CHCH_3$), 3.73, 3.74 (s, OCH_3), 4.31–4.38 (m, $CHCH_3$).

3.4. Crystal Structure Determination

Select crystals of **1–3** were measured on the Bruker D8 Venture single crystal diffractometer equipped with a CMOS II detector and LT device using a Mo sealed tube as a radiation source ($\lambda = 0.71073 \text{ \AA}$). The samples were measured at lowered temperatures as follows: 100 K for (*R,S*)-**3** and 130 K for (*S,S*)-**1**, (*R,S*)-**2**, and (*S,S*)-**2**. The data were collected using Bruker APEX3 software [59], followed by the integration in the Bruker SAINT program [60] and scaled in Bruker SADABS [61], [samples: (*R,S*)-**3**, (*S,S*)-**1**, (*R,S*)-**2**] or TWINABS [62], [sample: (*S,S*)-**2**]. A single crystal of (*R,S*)-**4** was measured on an Oxford Diffraction κ -CCD Gemini A Ultra diffractometer. Cell refinement and data collection, as well as data reduction and analysis, were performed with Rigaku Oxford CRYSLIS^{PRO} software (Rigaku Oxford Diffraction CrysAlisPro Software System, 2024, v. 1.171.43.136a). Using Olex2 [63], the structure was solved with ShelXT [64], structure solution program using Intrinsic Phasing, and refined with ShelXL [65], a refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. Flack parameters were calculated from selected quotients (Parsons' method) [66]. CCDC2406865-2406869 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/> (accessed on 1 January 2025) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Crystal Data for (*R,S*)-**2** $\text{C}_{20}\text{H}_{42}\text{Ga}_2\text{O}_6$ ($M = 517.97 \text{ g/mol}$): monoclinic, space group $P2_1/c$ (no. 14), $a = 10.5816(5) \text{ \AA}$, $b = 15.3600(5) \text{ \AA}$, $c = 7.9356(3) \text{ \AA}$, $\beta = 100.808(2)^\circ$, $V = 1266.92(9) \text{ \AA}^3$, $Z = 2$, $T = 130.00 \text{ K}$, $\mu(\text{MoK}\alpha) = 2.155 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.358 \text{ g/cm}^3$, 37,190 reflections measured ($5.86^\circ \leq 2\theta \leq 56.5^\circ$), 3118 unique ($R_{\text{int}} = 0.0291$, $R_{\text{sigma}} = 0.0133$), used in all calculations. The final R_1 was 0.0208 ($I > 2\sigma(I)$) and wR_2 was 0.0485 (all data).

Crystal Data for (*S,S*)-**2** $\text{C}_{20}\text{H}_{42}\text{Ga}_2\text{O}_6$ ($M = 517.97 \text{ g/mol}$): monoclinic, space group $P2_1$ (no. 4), $a = 7.8664(2) \text{ \AA}$, $b = 15.5512(4) \text{ \AA}$, $c = 10.4906(3) \text{ \AA}$, $\beta = 100.1397(9)^\circ$, $V = 1263.29(6) \text{ \AA}^3$, $Z = 2$, $T = 130.0(5) \text{ K}$, $\mu(\text{MoK}\alpha) = 2.161 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.362 \text{ g/cm}^3$, 33,428 reflections measured ($5.88^\circ \leq 2\theta \leq 50.76^\circ$), 4573 unique ($R_{\text{int}} = 0.0203$, $R_{\text{sigma}} = 0.0065$), used in all calculations. The final R_1 was 0.0209 ($I > 2\sigma(I)$) and wR_2 was 0.0668 (all data).

Crystal Data for (*S,S*)-**1** $\text{C}_{16}\text{H}_{34}\text{Ga}_2\text{O}_6$ ($M = 461.87 \text{ g/mol}$): triclinic, space group $P1$ (no. 1), $a = 8.1834(7) \text{ \AA}$, $b = 8.2430(7) \text{ \AA}$, $c = 8.7070(8) \text{ \AA}$, $\alpha = 113.352(3)^\circ$, $\beta = 90.424(3)^\circ$, $\gamma = 94.829(3)^\circ$, $V = 536.78(8) \text{ \AA}^3$, $Z = 1$, $T = 130.0(5) \text{ K}$, $\mu(\text{MoK}\alpha) = 2.534 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.429 \text{ g/cm}^3$, 15,512 reflections measured ($5.76^\circ \leq 2\theta \leq 52.98^\circ$), 4348 unique ($R_{\text{int}} = 0.0313$, $R_{\text{sigma}} = 0.0330$), used in all calculations. The final R_1 was 0.0186 ($I > 2\sigma(I)$) and wR_2 was 0.0466 (all data).

Crystal Data for (*R,S*)-**3** $\text{C}_{22}\text{H}_{36}\text{Ga}_2\text{N}_2\text{O}_2$ ($M = 499.97 \text{ g/mol}$): triclinic, space group $P\bar{1}$ (no. 2), $a = 8.7984(5) \text{ \AA}$, $b = 8.8724(5) \text{ \AA}$, $c = 8.9171(5) \text{ \AA}$, $\alpha = 82.408(2)^\circ$, $\beta = 66.358(2)^\circ$, $\gamma = 67.060(2)^\circ$, $V = 587.00(6) \text{ \AA}^3$, $Z = 1$, $T = 100.00 \text{ K}$, $\mu(\text{MoK}\alpha) = 2.313 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.414 \text{ g/cm}^3$, 32,854 reflections measured ($4.988^\circ \leq 2\theta \leq 59.996^\circ$), 3435 unique ($R_{\text{int}} = 0.0215$, $R_{\text{sigma}} = 0.0108$), used in all calculations. The final R_1 was 0.0155 ($I > 2\sigma(I)$) and wR_2 was 0.0421 (all data).

Crystal Data for (*R,S*)-**4** $\text{C}_{26}\text{H}_{44}\text{Ga}_2\text{N}_2\text{O}_2$ ($M = 556.07 \text{ g/mol}$): monoclinic, space group $P2_1/n$ (no. 14), $a = 10.0033(3) \text{ \AA}$, $b = 12.2497(4) \text{ \AA}$, $c = 11.8020(4) \text{ \AA}$, $\beta = 94.142(3)^\circ$, $V = 1442.41(8) \text{ \AA}^3$, $Z = 2$, $T = 293.15 \text{ K}$, $\mu(\text{Mo K}\alpha) = 1.890 \text{ mm}^{-1}$, $D_{\text{calc}} = 1.280 \text{ g/cm}^3$, 20,992 reflections measured ($6.652^\circ \leq 2\theta \leq 55.752^\circ$), 3440 unique ($R_{\text{int}} = 0.0283$, $R_{\text{sigma}} = 0.0175$), used in all calculations. The final R_1 was 0.0295 ($I > 2\sigma(I)$) and wR_2 was 0.0827 (all data).

4. Conclusions

In summary, we have focused on the effect of alkyl substituents on the structure of *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂, (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂, and *rac*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂ (R = Me, Et, ^{*i*}Pr), as well as the catalytic properties of (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ and (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂/pyridine in the ROP of *rac*-LA. We expected these studies to be especially indicative for the effect of alkyl substituents of [R₂Ga(μ-OCH(Me)CO₂PLA)]₂ (PLA—growing polylactide chain) propagating species on their tendency to form homochiral species and the influence of the latter on their stereoselectivity in the ROP of *rac*-LA.

In solution, *rac*-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Et, ^{*i*}Pr) have shown a much lower tendency for the formation of homochiral (*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ species in the presence of pyridine in comparison with the previously reported *rac*-[Me₂Ga(μ-OCH(Me)CO₂Me)]₂ complexes [1]. The analogue's effect has been demonstrated by the formation of heterochiral *R,S*-[R₂Ga(μ-OCH(Me)C₅H₄N)]₂, (R = Et, ^{*i*}Pr), in contrast to homochiral (*R*,R**)-[Me₂Ga(μ-OCH(Me)C₅H₄N)]₂ [1], upon crystallization. Notably, the X-ray analysis of the homochiral (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Me, Et, ^{*i*}Pr) complexes has further proven the greater tendency of diethyl and di-*iso*-propyl derivatives for the formation of centrosymmetric species, which affects their structures considerably. Importantly, the decreasing tendency to form homochiral species (*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ with larger alkyl substituents on gallium was in line with the heteroselectivity of the (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ and (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Me, Et, ^{*i*}Pr)/pyridine catalytic systems in the ROP of *rac*-LA, which decreased in series R = Me > Et > ^{*i*}Pr. The observed correlation supports the crucial role of homochiral (*R*,R**)-[R₂Ga(μ-OCH(Me)CO₂R)]₂ species on the heteroselectivity of dialkylgallium alkoxides, as previously reported by us [1]. Notably, the findings described in this article constitute a new example indicating that chiral recognition induced the formation of homochiral dimeric metal alkoxides, which can be used in order to tune the stereoselectivity in the coordination polymerization of lactide and other chiral heterocyclic monomers that interest us.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/molecules30010190/s1>: Figures S1–S7: ¹H NMR spectra for complexes **1**, **2**, (*S,S*)-**1**, (*S,S*)-**2**, **3**, and **4**; Figure S8: Exemplary ¹H NMR spectrum of PLA obtained with gallium complexes; Figures S9–S11: Decoupled ¹H NMR spectra (methine region) of PLA obtained with (*S,S*)-[R₂Ga(μ-OCH(Me)CO₂Me)]₂ (R = Me, Et, ^{*i*}Pr)/pyridine (1:6) at 40°C; Figures S12 and S13: FTIR data for complexes (*S,S*)-**1**, (*S,S*)-**2**; Figures S14–S16: MALDI-TOF of PLA obtained with (*S,S*)-**1** and (*S,S*)-**2**; Table S1. Crystal data and structure refinement details for (*R,S*)-**2**, (*S,S*)-**1**, (*S,S*)-**2**, (*R,S*)-**3**, and (*R,S*)-**4**.

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Article

Synthesis of Branched Cyclo-Olefin Copolymers Using Neutral α -Sulfonate- β -Diimine Nickel Catalyst

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Abstract: The homopolymerization of norbornene and the copolymerization of norbornene and ethylene were carried out using the neutral α -sulfonate- β -diimine nickel catalyst **SD-Ni**. The neutral α -sulfonate- β -diimine catalyst is highly active in the homopolymerization of norbornene, producing vinyl-addition polynorbornene (PNB) with a high molecular weight. The copolymerization of norbornene (NB) and ethylene (E) using the catalyst **SD-Ni** was also investigated. The α -sulfonate- β -diimine catalyst **SD-Ni** shows distinctive catalytic copolymerization properties to produce high-molecular-weight E-NB copolymers with low norbornene incorporation. Importantly, microstructure analyses confirm that the resultant E-NB copolymers are branched cyclo-olefin copolymers (COCs) with branched polyethylene units.

Keywords: cyclo-olefin copolymer; norbornene; ethylene; nickel catalyst; copolymerization

1. Introduction

Polymers of cyclic olefins such as norbornene (NB) with rigid and saturated cyclic units on polymer chains have garnered widespread attention due to their attractive properties such as excellent chemical resistance, good UV resistance, low dielectric constant, excellent transparency, and a large refractive index [1,2]. However, polynorbornene (PNB) produced by vinylic addition polymerization is a very brittle material at room temperature, which largely limits its application. Furthermore, the PNB material also exhibits very poor melt processability because its glass transition temperature (T_g) is very high and near to its decomposition temperature [3].

The incorporation of flexible units into the rigid PNB chain to produce cyclo-olefin copolymers (COCs) by the copolymerization of norbornene with ethylene, α -olefins, and styrene comonomers is an effective strategy to improve toughness and decrease glass transition temperature (T_g) [4–6]. Because ethylene is a cheap and abundant monomer, the copolymerization of norbornene and ethylene has received considerable attention and has been successfully commercialized [7,8]. Since the first copolymerization of norbornene and ethylene using zirconocene catalysts [9], various catalysts including early transition metal group IV catalysts and late transition metal group VIII catalysts have been mainly developed for the synthesis of COCs by the copolymerization of norbornene with ethylene [10–12].

Compared to early transition metal group IV catalysts including metallocene [8], half-sandwich catalysts, [13,14] constrained-geometry group catalysts (CGCs) [1], and

non-metallocene [15–20], late transition metal, nickel, and palladium catalysts are more challenging for the copolymerization of norbornene and ethylene [21–24]. Although late transition metal, nickel, and palladium catalysts are highly active for the homopolymerization of norbornene and ethylene, they often produce low-molecular-weight PNB with a vinyl chain end for norbornene polymerization in the presence of ethylene because ethylene is a very efficient chain transfer agent [25,26]. Only a few catalytic systems can afford high-molecular-weight alternating or block copolymers [26–31]. For example, our group reports the synthesis of polyethylene-*block*-polynorbornene (PE-*b*-PNB) copolymers using an amine–imine nickel catalyst (**A** in Figure 1) by sequential monomer addition in a living fashion [26]. Neutral phosphorylate nickel complexes (**B** in Figure 1) are efficient catalysts for the copolymerization of norbornene with ethylene to produce an essentially alternating copolymer [27,28]. Anilinoanthraquinone nickel catalysts (**C** in Figure 1) can catalyze the copolymerization of norbornene and ethylene with high activity to generate random copolymers with high norbornene content of 63.7–92.2 mol% [29]. Phosphine sulfonate nickel catalysts (**D** in Figure 1) also show good activity for the copolymerization of norbornene and ethylene to produce copolymers with norbornene incorporation of up to 10.1 mol% [30,31].

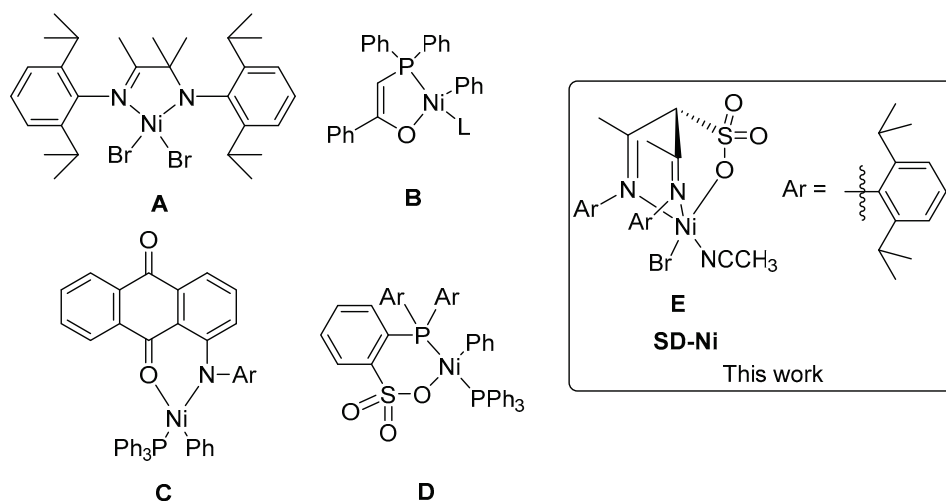


Figure 1. Nickel complexes for the copolymerization of norbornene with ethylene.

From the perspective of the microstructure of the chain, COCs with different sequences such as alternating, random, and block copolymers have been synthesized but the incorporated ethylene units are completely linear [20,26,32,33]. The branched ethylene units have never been reported to the best of our knowledge although a branched structure can further improve toughness and decrease the glass transition temperatures of the materials. In theory, branched COCs are not prepared by early transition metal group IV catalysts but are probably synthesized by late transition metal catalysts based on the chain-walking mechanism of ethylene polymerization [34–36].

In this paper, we initially report the synthesis of branched cyclo-olefin copolymers by the copolymerization of norbornene and ethylene using a neutral α -sulfonate- β -diimine nickel catalyst. In this catalytic system, ethylene can be successively inserted into the main chain and does not play the role of a chain transfer agent. The chain-walking process leads to the formation of branched ethylene units incorporated into the PNB chain.

2. Results and Discussion

The neutral α -sulfonate- β -diimine nickel complex has a tridentate molecular structure (**E** in Figure 1), and has been previously synthesized by our group [37]. We have also

reported the ethylene polymerization properties of the neutral α -sulfonate- β -diimine nickel complex [37]. Herein, we further studied norbornene homopolymerization before the investigation of the copolymerization of norbornene and ethylene.

When the neutral α -sulfonate- β -diimine nickel complex **SD-Ni** was employed in norbornene polymerization in the absence of any cocatalysts (entry 1 in Table 1), no catalytic activity was observed. Therefore, the cocatalyst is essential to activate the nickel complex for norbornene polymerization. Methylaluminoxane (MAO) was herein chosen as a cocatalyst for activating the nickel complex **SD-Ni**, and the Al/Ni ratio effects on norbornene polymerization were first studied.

Table 1. Norbornene homopolymerization results using **SD-Ni** ^a.

Entry	Al/Ni	T (°C)	Yield (g)	Act. ^b	M_n ^c (kg/mol)	M_w ^c (kg/mol)	M_w/M_n ^c
1	0	50	-	-	-	-	-
2	1000	50	0.782	0.78	632.9	1025.4	1.62
3	2000	50	1.123	1.12	549.6	961.9	1.75
4	3000	50	1.402	1.40	489.6	788.3	1.61
5	4000	50	2.672	2.67	446.2	736.2	1.65
6	5000	50	2.396	2.40	388.8	734.9	1.89
7	4000	0	1.356	1.36	613.9	1141.9	1.86
8	4000	25	1.868	1.87	774.4	1339.7	1.73
9	4000	80	3.413	3.41	256.5	451.4	1.76
10	4000	100	3.083	3.08	194.7	375.7	1.93

^a Polymerization conditions: 2 μ mol Ni, NB = 0.0638 mol, 20 mL toluene, reaction time 0.5 h. ^b Activity, in unit of 10^6 g PNB/(mol Ni h). ^c M_w and M_w/M_n were determined by high-temperature gel permeation chromatography (GPC).

As shown in Table 1, the catalytic activity of **SD-Ni** for norbornene polymerization increases, and then decreases as the Al/Ni ratio increases from 1000 to 5000. An optimum Al/Ni ratio is 4000 for norbornene polymerization, which is higher than that for ethylene polymerization (Al/Ni = 1000). This may be because norbornene monomer is bulkier than ethylene monomer. Moreover, the Al/Ni ratio has an influence on the molecular weight of the produced polynorbornene (PNB). With an increase in the Al/Ni ratio, the molecular weights of PNBs decreased consistently, strongly indicating that chain transfer to aluminum cocatalyst takes place [38,39].

The reaction temperature also affected the catalytic activities and PNB molecular weight; therefore, the effects of temperature are further studied at the fixed Al/Ni ratio of 4000. As shown in Table 1, the catalytic activity of **SD-Ni** increases for norbornene polymerization, and then decreases as the polymerization temperature increases from 0 to 100 °C. At 80 °C, **SD-Ni** exhibits the highest activity of 3.41×10^6 g PNB/(mol Ni h). Furthermore, polymerization temperature has an important influence on the molecular weight of the produced polynorbornene. As temperature increases from 0 to 25 °C, the PNB molecular weight increases. This is because increased temperature can promote the coordination and insertion of bulky norbornene at low temperatures. As temperature increases from 25 to 100 °C, the PNB molecular weight decreases due to the acceleration of the chain transfer to the aluminum cocatalyst at high temperatures [40,41].

All of the produced PNBs catalyzed by the catalyst **SD-Ni** are soluble in organic solvents such as chlorobenzene and *o*-dichlorobenzene. High-temperature gel permeation chromatography (GPC) was used to determine the molecular weight and distribution of the produced PNBs using 1,2,4-trichlorobenzene as an eluent at 150 °C (Figure 2). The produced PNBs are high-molecular-weight polymers, and the highest M_w is up to 1339.7 kg/mol. The molecular weight distributions are normal (M_w/M_n = 1.5~2.0).

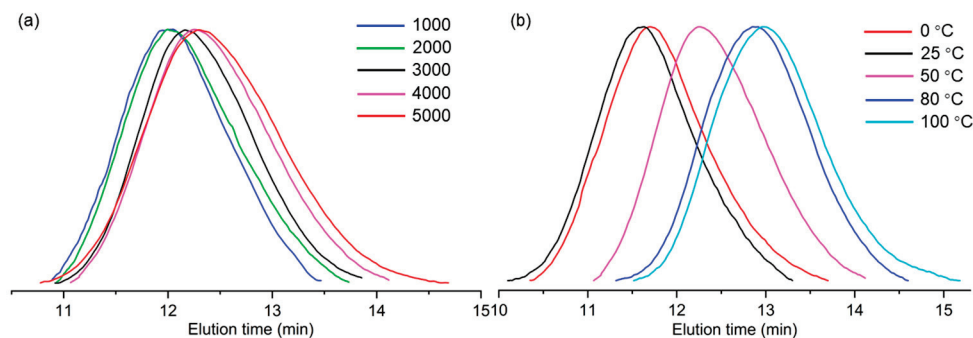


Figure 2. GPC curves of PNB samples prepared by **SD-Ni** under different Al/Ni ratios (a) and different temperatures (b).

The microstructure of the produced PNBs was further characterized. The FT-IR spectrum (Figure 3a) reveals no traces corresponding to double bonds observed at 1680–1620, 966, and 735 cm^{-1} , and the appearance of vibration bands of the bicyclic structure of norbornene at 941 cm^{-1} . The ^1H NMR spectrum (Figure 3b) also shows no double bond at 5.0–6.0 ppm, indicating that the produced PNBs are vinyl-addition polymers [42–44]. The ^{13}C NMR spectrum further confirms vinyl-addition PNB, showing that several resonances are present at 28–55 ppm (Figure 4). The resonances at 29.4–33.0, 35.5–38.5, 38.8–42.8, and 46.1–54.0 ppm are assigned to C_5 and C_6 , C_7 , C_1 and C_4 , C_2 and C_3 , respectively [30,45–48].

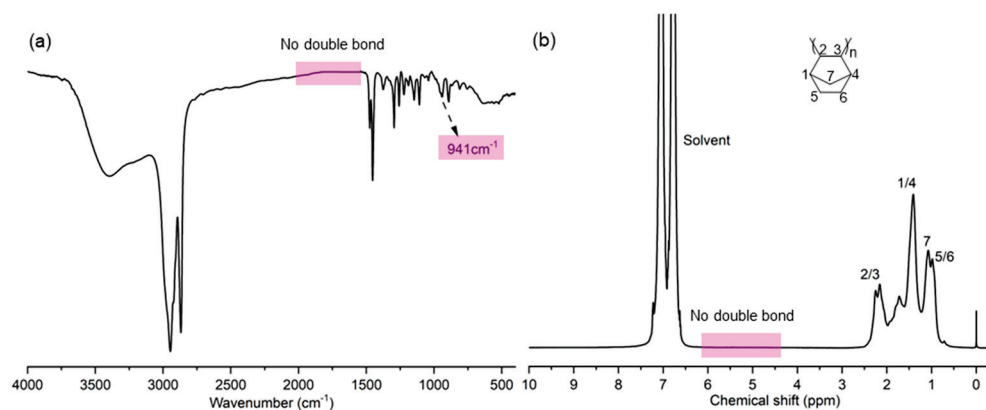


Figure 3. FT-IR (a) and ^1H NMR (b) spectra of PNB (entry 5 in Table 1).

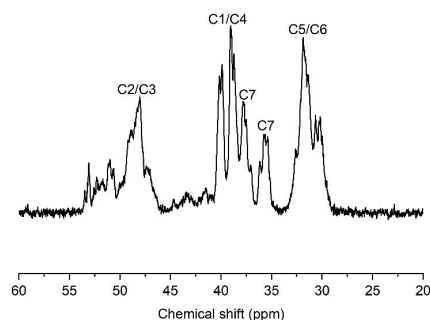


Figure 4. ^{13}C NMR spectrum of PNB (entry 5 in Table 1).

The wide-angle X-ray diffraction (WAXD) pattern of PNB (Figure 5) shows that there are two broad and diffuse diffraction peaks at near 2θ values of 9.64° and 18.28° , indicating that the PNB is an amorphous polymer with long-range disorder [49,50]. The glass transition temperature (T_g) of the PNB was determined by DSC testing. No well-defined endothermic signal is determined in the temperature range from -20 to 300°C because the glass transition temperature of PNB is close to its decomposition temperature.

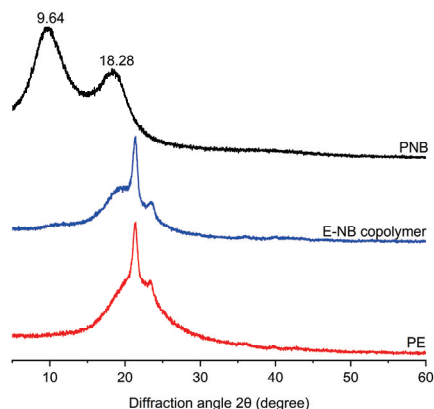


Figure 5. WAXD curves of PNB (entry 5 in Table 1); E-NB copolymer (entry 4 in Table 2); and PE (entry 1 in Table 2).

Table 2. Copolymerization results of norbornene and ethylene using **SD-Ni**^a.

Entry	T (°C)	[NB] (mol/L)	Yield (g)	Act. ^b	I _{NB} ^c (mol %)	M _w ^d	M _w /M _n ^d	T _m /T _g ^e
1	50	-	0.916	45.8	-	207.1	1.43	82.3, 103.5/-
2	25	0.4	0.353	17.6	2.3	32.2	1.53	70.3, 100.5/-
3	50	0.4	0.485	24.2	4.8	44.1	1.41	61.6, 90.1/-
4	80	0.4	0.213	10.7	7.2	39.8	1.61	40.5, 79.5/-
5	50	0.8	0.352	17.6	10.6	62.8	1.64	53.3, 84.3/-
6	50	1.2	0.285	14.3	22.1	74.1	1.52	-/77.1

^a Polymerization conditions: 5 μmol Ni, 5 atm ethylene, Al (MAO)/Ni = 1000, 40 mL toluene, reaction time 4 h. ^b Activity, in unit of 10³ g COC/(mol Ni h). ^c Determined by ¹³C NMR spectroscopy. ^d M_w (kg/mol) and M_w/M_n were determined by high-temperature gel permeation chromatography (GPC). ^e Determined by differential scanning calorimetry (DSC).

We have previously studied the ethylene polymerization properties of the neutral α -sulfonate- β -diimine nickel complex **SD-Ni** [37]. Inspired by its high activity for the homopolymerization of norbornene and ethylene, we further carried out the copolymerization of norbornene and ethylene using the catalyst **SD-Ni** and the copolymerization results are summarized in Table 2. GPC analyses (Figure 6) of the copolymerization products show that their distributions remain below 2.0 and exhibit a unimodal distribution, indicating that copolymerizations truly occur and the products are copolymers rather than a blend of homopolymers.

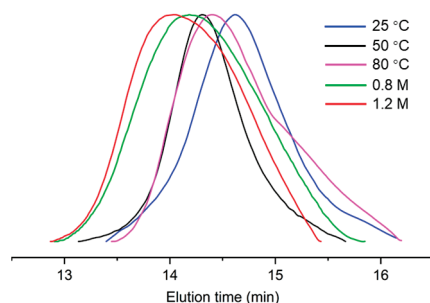


Figure 6. GPC curves of E-NB copolymers prepared by **SD-Ni**.

The effects of polymerization temperature on the copolymerization of norbornene and ethylene were studied at the fixed norbornene concentration (0.4 M). By increasing temperature from 25 to 80 °C, the copolymerization activity increases and then decreases. At 50 °C, copolymerization activity reaches a maximum value of 24.2×10^3 g COC/(mol

Ni h). Compared to the homopolymerization activity of ethylene (entry 1 in Table 2), the copolymerization activity decreases because the insertion of bulky norbornene is more difficult than ethylene monomer [31]. Additionally, the α -sulfonate- β -diimine nickel showed comparable copolymerization activity compared to previously reported late transition metal catalysts [27–30]. The influence of polymerization temperature on copolymer molecular weight also shows the same tendency. The copolymer produced at 50 °C has the highest molecular weight. Moreover, increasing temperature leads to an increase in the incorporation of norbornene; the produced E-NB copolymers contain low norbornene incorporation (<10 mol%), which supports the conclusion that the insertion of bulky norbornene is slower than ethylene monomer. Because of low norbornene incorporation, the produced E-NB copolymers display broad melting temperatures due to long ethylene sequences and branched structures. A clear trend is that melting temperatures decrease as polymerization temperatures increase due to greater norbornene incorporation and higher branch density (Figure 7).

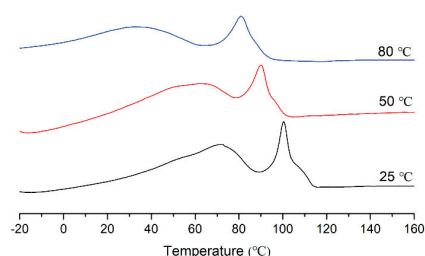


Figure 7. DSC curves of E-NB copolymers produced at different temperatures (entries 2–4 in Table 2).

The effects of norbornene feed on the copolymerization of norbornene and ethylene were studied at 50 °C. By increasing norbornene concentration from 0.4 to 1.2 M, the copolymerization activity decreases gradually. This observation also supports the idea that ethylene is inserted more favorably than bulky norbornene by the nickel catalyst **SD-Ni**. It is noteworthy that the copolymer molecular weight increases with increasing norbornene concentration, strongly indicating that the chain transfer reaction to the ethylene monomer is favorable during copolymerization. This result is consistent with the homopolymerization result of norbornene mentioned above. Furthermore, increasing norbornene concentration leads to the increasing incorporation of norbornene. At a norbornene concentration of 1.2 M, the incorporation of norbornene reaches 22.1 mol%. As a result, the obtained E-NB copolymer has a T_g of 77.1 °C but not a T_m (Figure 8).

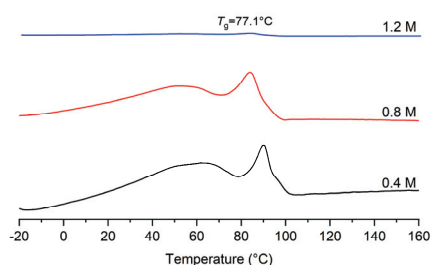


Figure 8. DSC curves of E-NB copolymers produced at different norbornene concentrations (entries 3, 5, 6 in Table 2).

Additionally, we note that the melting temperatures of the copolymers are lower than those of previously reported E-NB copolymers produced by other catalysts. In phosphine-sulfonate nickel catalysts, the obtained E-NB copolymers with 7 mol% and 4 mol% incorporations of NB show melting temperatures of 90 °C and 108 °C [30]. However, the E-NB copolymers with the same NB incorporations produced by our nickel catalyst

SD-Ni display lower and broader melting temperatures (79.5 °C and 90.1 °C), which are ascribed to branched polyethylene units. Furthermore, the E-NB copolymer produced at 0.8 M (entry 5 in Table 2) has a lower melting temperature than the E-NB copolymer produced at 80 °C although the former has higher NB incorporation (10.6 mol%) than the latter (7.2 mol%). This is a result of the high branching density of polyethylene, as high temperatures favor chain walking.

Microstructures of the E-NB copolymers were further investigated by ^1H , ^{13}C NMR spectroscopies. As shown in Figure 9a, the ^1H NMR spectrum of E-NB copolymers is more complex than previously reported spectra because of the presence of various branchings. The calculation of the branching density of the PE blocks is difficult because the signals of CH and CH_2 of norbornene units and PE units overlap. Therefore, the branching density of the PE blocks can be speculated according to the PE produced by the homopolymerization of ethylene (30~50/1000C) [37]. As shown in Figure 9b, the ^{13}C NMR spectrum of the copolymer containing a norbornene incorporation of 7.2% obtained at a norbornene concentration of 0.4 M primarily displays signals of branched polyethylene, and several weak peaks are observed and assigned to norbornene units. Based on the previous assignment of polyethylene [36], the peak at 19.98 ppm is assigned to the methyl group, and the peak at 14.60 ppm is assigned to the long-chain branching. Therefore, the obtained E-NB copolymers are branched COCs. To the best of our knowledge, this is the first report on branched COCs with branched ethylene units. The formation of branched COCs can be ascribed to two reasons. On one hand, the neutral α -sulfonate- β -diimine nickel catalyst displays distinctive copolymerization properties. In this catalytic system, the ethylene monomer is favorably inserted rather than a norbornene monomer and does not act as a chain transfer agent, which is different from previously reported nickel catalysts [25,26]. On the other hand, the neutral α -sulfonate- β -diimine nickel catalyst has good chain-walking ability, which assures the formation of branched ethylene units [37].

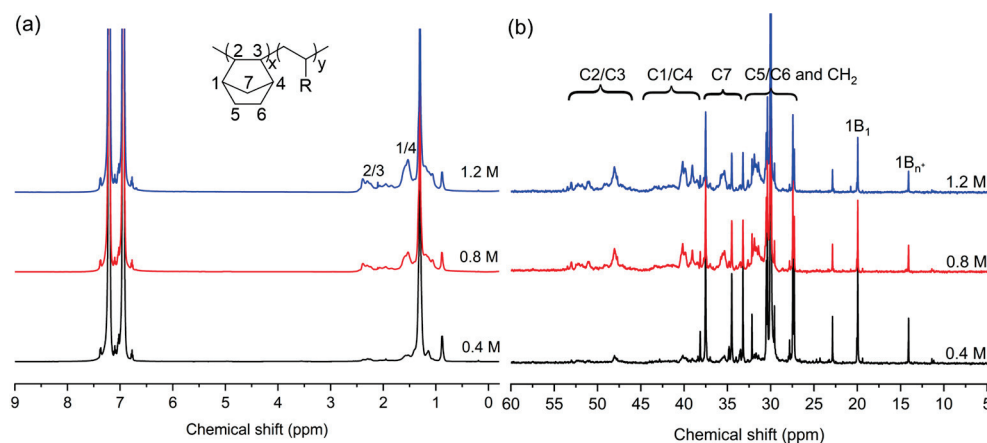


Figure 9. ^1H NMR (a) and ^{13}C NMR (b) spectra of E-NB copolymers produced at different concentrations (entries 3, 5, 6 in Table 2).

In the ^{13}C NMR spectra of E-NB copolymers with high NB incorporation prepared at high norbornene concentrations (Figure 9b), signals of polynorbornene obviously heighten but resonances of branching polyethylene weaken. According to previous reports and assignments [51–54], the copolymers have random structures. The ^{13}C NMR analysis is in strong agreement with the DSC analysis. Wide-angle X-ray diffraction analysis (WAXD) (Figure 5) shows that the obtained E-NB copolymer is amorphous and has low stereoregularity. Compared to the WAXD patterns of homopolymers (PE and PNB), the obtained E-NB copolymer exhibits broad halos.

Clearly, branched polyethylene units originate from chain walking, which is a common phenomenon during nickel- and palladium-catalyzed ethylene polymerization. Our experimental results also show that ethylene is more favorably inserted into the α -sulfonate- β -diimine nickel catalyst than bulky norbornene monomer because of the low electrophilicity of the neutral nickel center and bulky steric hindrance of the catalyst. Resultantly, the continuous insertion of ethylene monomer is more conducive to the formation of branched PE units through the chain-walking mechanism during the copolymerization of ethylene and norbornene.

3. Materials and Methods

3.1. General Procedures

All operations with air- and moisture-sensitive compounds were conducted under a dried and purified nitrogen atmosphere, utilizing standard vacuum-line and Schlenk techniques, or a glovebox.

3.2. Materials

Toluene was distilled from Na/K alloy under nitrogen before use. Norbornene was purchased from HWRK Chem Co. Ltd. (Beijing, China) and purified by distillation over CaH_2 at a reduced pressure. Methylaluminoxane (MAO, 30 wt% in toluene) was purchased from Akzo-Nobel (Amsterdam, The Netherlands). Other commercially available reagents were purchased and used without purification. The α -sulfonate- β -diimine nickel was prepared according to the our previously reported literature [37]. The 2.672 g PNB sample (entry 5 in Table 1) was further purified by extraction by 10% HCl/ethanol solution and then dried to a constant weight before FT-IR and ^1H NMR analysis.

3.3. Measurements

^1H , ^{13}C NMR spectra of polymers were carried out on a Bruker 500 MHz at 120 °C with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. Polymer solutions were prepared in $o\text{-C}_6\text{H}_4\text{Cl}_2/o\text{-C}_6\text{D}_4\text{Cl}_2$ (50% *v/v*) in a 10 mm sample tube. DSC analyses were conducted with a PerkinElmer DSC-4000 system. During testing, mechanical refrigeration was used with nitrogen protection, and the mass of solid samples ranged from 3.0 to 6.0 mg. The DSC curves were recorded as second heating curves from −20 to 300 °C at a heating/cooling rate of 10 °C/min. FT-IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer (Thermo Nicolet, Waltham, MA, USA). The KBr pellet method was employed, with a measurement range of 4000–400 cm^{-1} and a resolution of 2 cm^{-1} . GPC analysis of the molecular weights and molecular weight distributions (M_w/M_n) of the polymers at 150 °C was performed on a PL-GPC 220 high-temperature chromatograph equipped with two GPC columns (USA PLgel 10 μm MIXED-B) and a differential refractive-index detector. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL/min. An appropriate amount of polymer was weighed and dissolved in TCB to prepare a 1 g/mL solution. The solution was heated on a preheating stage at 150 °C for 4 h until the polymer fully dissolved. The dissolved solution was filtered through a polyimide membrane using a specialized filter and then tested using an automatic sampling system. The molecular weight data were analyzed using narrow polystyrene standards (Polymer Laboratories, Long Beach, CA, USA) and were corrected for polymer samples by universal calibration. The wide-angle X-ray diffraction (WAXD) curve of the polymer powder was obtained using a D-Max-2200 VPC powder X-ray diffractometer (RIGAKU Corporation, Tokyo, Japan). The polymer was loaded into the sample holder groove, ensuring that the polymer powder was evenly distributed without significant accumulation or voids. Clean weighing paper was used to evenly press the powder, gradually compacting it to fit tightly

within the groove. CuK α radiation ($\lambda = 0.154$ nm, 40 kV) was used as the X-ray source. The diffraction angle was scanned over a range of 5–60° at a scanning rate of 10°/min.

3.4. Norbornene Homopolymerization

In a typical polymerization procedure, a 50 mL Schlenk round-bottom flask was preheated at 150 °C for 2 h. The required amounts of MAO, toluene, and a solution of norbornene were added to the flask under a nitrogen atmosphere with continuous stirring. Once the reaction temperature was stabilized, the system was stirred for an additional 5 min before injecting the desired amount of nickel complex into the toluene. After the norbornene polymerization had proceeded for the specified time, the reaction was carefully quenched with a 10% HCl/ethanol solution. The resulting precipitated polymers were collected by filtration, washed several times with ethanol, and dried at 50 °C to a constant weight.

3.5. Copolymerization of Norbornene with Ethylene

A mechanically stirred 100 mL Parr reactor was dried at 150 °C and vacuumed for 2 h. The autoclave was pressurized to 2 atm pressure of ethylene and vented three times. The required amounts of MAO solution, norbornene, and toluene were added into the autoclave at the desired polymerization temperature. The system was maintained by continuously stirring for 5 min, and then 4 mL solution of nickel complex in toluene was charged into the autoclave. The ethylene pressure was raised to the specified value, and the reaction was carried out for a certain time. The reaction temperature was controlled by means of a heater or cooler and was monitored by an internal thermocouple. Polymerization was terminated by a mixture of 10% HCl/ethanol solution after releasing the ethylene pressure. The resulting precipitated polymers were collected by filtration, washed several times with ethanol, and dried at 50 °C to a constant weight.

4. Conclusions

The neutral α -sulfonate- β -diimine catalyst is highly active in the homopolymerization of norbornene, producing ultra-high-molecular-weight PNB ($M_w = 1339.7$ kg/mol). Under optimum conditions of Al/Ni of 4000 and 80 °C, the highest activity of 3.41×10^6 g PNB/(mol Ni h) is realized. For the copolymerizations of norbornene and ethylene, the α -sulfonate- β -diimine catalyst **SD-Ni** shows distinctive catalytic properties to produce E-NB copolymers containing low levels of norbornene incorporation. The incorporation of norbornene can be adjusted by the polymerization temperature and the norbornene feed. The microstructure analyses confirm that the resultant E-NB copolymers are branched COCs with branched polyethylene units. Branched COCs have not been prepared previously by other catalysts, and their properties will be further studied in the future.

Author Contributions: Conceptualization and writing—original draft preparation, D.L.; conceptualization and writing—review and editing, L.P.; data curation, W.D.; methodology, X.X.; data curation, H.G. (Heng Gao); formal analysis, H.Z.; funding acquisition and supervision, H.G. (Haiyang Gao). All authors have read and agreed to the published version of the manuscript.

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Article

Reactions of an Anionic Gallylene with Azobenzene or Azide Compounds Through C(sp²)-H and C(sp³)-H Activation

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Abstract: The activation of inert C–H bonds remains a challenge in current chemistry. Here, we report the excellent reactivity of the anionic gallylene species [LGa:][Na(THF)₃] (L = [(2,6-*i*Pr₂C₆H₃)NC(CH₃)₂]^{2−}, **1**) that allows the selective activation one *ortho* sp² C–H bond of several azobenzene and azide derivatives at ambient temperature, with the transfer of the hydrogen atom to one of the nitrogen atoms. The process leads to the formation of the aryl amido products [LGa-κ²N,C-PhNN(H)(*p*-R-C₆H₃)] [Na(solvent)₃] (**2**, R = H solvent = DME (1,2-Dimethoxyethane); **3**, R = −OMe, solvent = DME; **4**, R = −NMe₂ solvent = THF), [LGa-κ²N,C-(*m*-CH₃-C₆H₄)NN(H)(*m*-CH₃-C₆H₃)] [Na(15-C-5)₂] (**5**) with new Ga–C and Ga–N bonds. Moreover, **1** is also effective for the C–H activation of two azides RN₃ (R = 2,4,6-Me₃C₆H₂ or 2,6-*i*Pr₂C₆H₃), resulting in the formation of gallium amides [LGa(NH-2-(CH₂)-4,6-Me₂C₆H₂)] [Na(15-C-5)₂] (**6**) and [LGa(NH-2,6-*i*Pr₂C₆H₃)₂] [Na(THF)₅] (**7**) through intra- or intermolecular sp³ C–H amination. Significantly, these reactions occur for the highly challenging activation of inert C(sp²)-H and C(sp³)-H bonds, thus demonstrating the excellent reactivity of the Ga(I) species **1**. The products **2–7** were characterized by X-ray crystallography, ¹H and ¹³C NMR, UV–vis spectroscopy, and density functional theory (DFT) calculations.

Keywords: C–H activation; gallylene; azobenzene; organic azides; α-diimine ligands

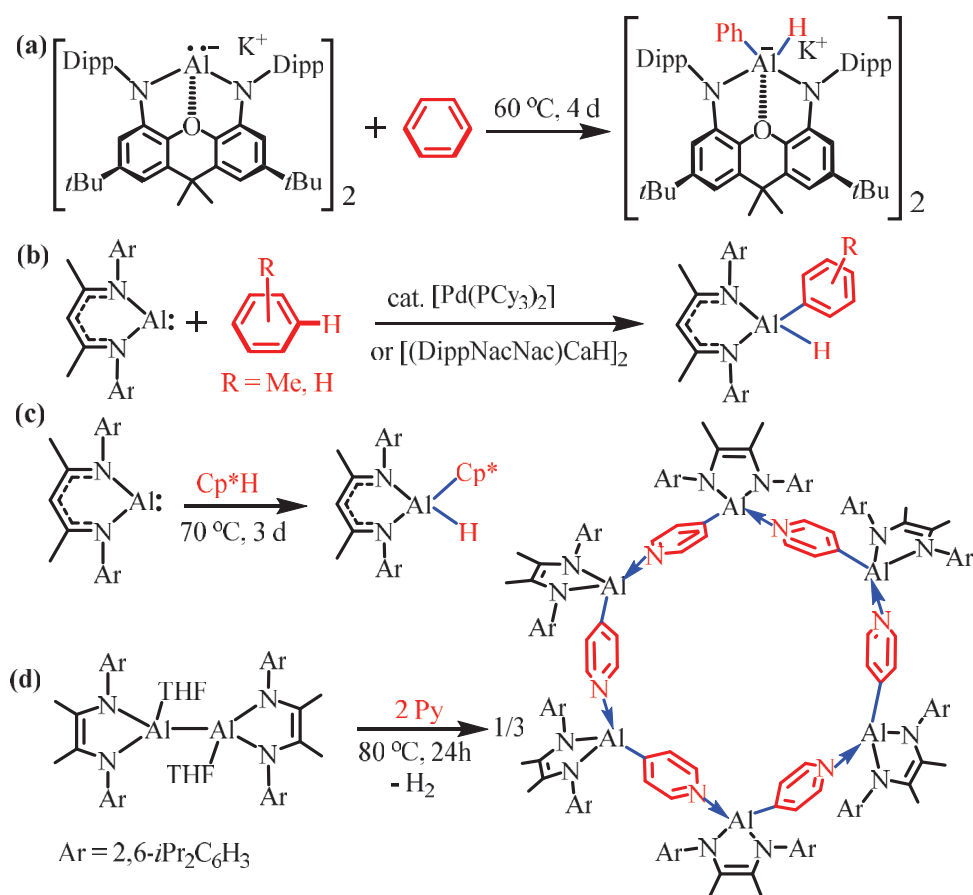
1. Introduction

The activation of C–H bonds has evolved into a well-established synthetic methodology for the construction of new C–C and C–Heteroatom bonds [1,2]. Traditionally, the field of C–H activation has predominantly focused on transition metals due to their characteristic partially occupied valence *d* orbitals [3–6]. Over the past decade, it has become increasingly apparent that low-valent main group metal complexes, owing to the imposed variable oxidation states of the metal, can exhibit transition-metal-like behavior in bond activation despite their lack of valence *d* orbitals [7]. This property, together with their ability to overcome the high cost and toxicity associated with common transition metal catalysts, makes them a promising alternative for small molecule activation [8]. However, compared to transition metals, examples of direct reactions involving stable main group elements in C–H bond activation still remain limited.

Low-valent group 13 element species have shown excellent reactivities towards various molecules, including activation of C–H bonds. In particular, the highly reactive, nucleophilic anionic Al(I) species can activate C–H bonds efficiently, although frequently in conjunction with elevated temperature, prolonged reaction duration, or catalysts.

The Aldridge and Goicoechea group reported the oxidative addition of a benzene C–H bond using the first anionic Al(I) complex [Al(NON)][−] (NON = 4,5-bis(2,6-di-*i*Pr-

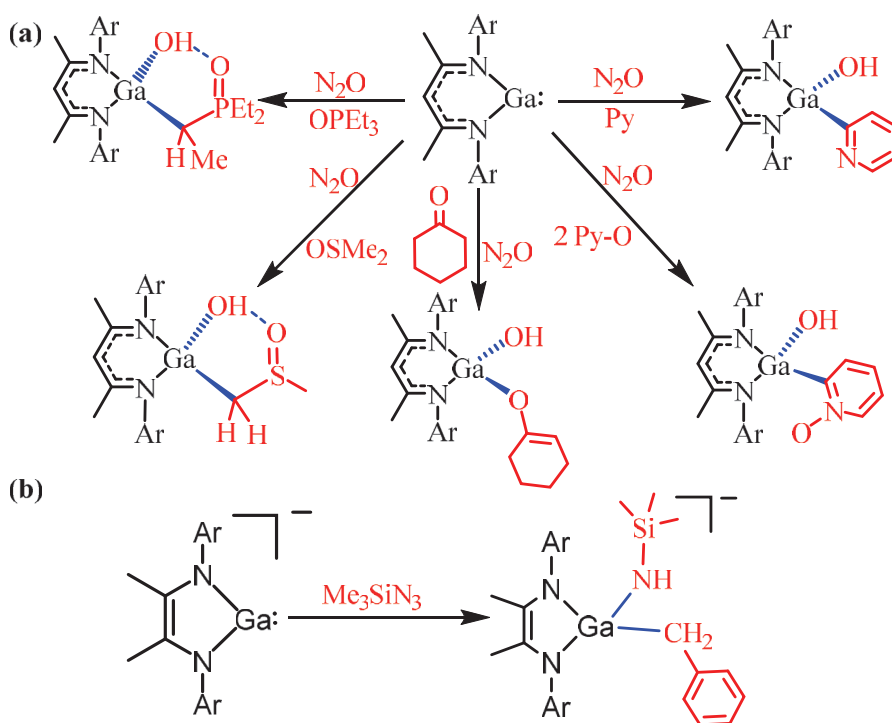
anilido)-2,7-di-*t*Bu-9,9-di-Me-xanthene) (Scheme 1a) [9]. Crimmin and colleagues reported the oxidative addition of low-valent β -diketiminate Al(I) complex $^{\text{Dipp}}\text{NacNacAl}$ ($^{\text{Dipp}}\text{NacNac} = [\text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{-NAr}]^-$, ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$)) with C–H bonds of toluene, benzene, and xylenes but only in the presence of a palladium catalyst (Scheme 1b) [10]. In a similar reaction, Harder et al. successfully achieved the oxidative addition of sp^2 C–H bond on non-activated arenes (toluene, benzene, and xylene) to $[(^{\text{Dipp}}\text{NacNac})\text{Al}(\text{I})]$ at ambient temperature through the catalytic presence of $[(^{\text{Dipp}}\text{NacNac})\text{CaH}]_2$ (Scheme 1b) [11]. The Nikonov group reported the oxidative addition of a C–H bond in sterically hindered pentamethylcyclopentadiene under controlled conditions at 70 °C for 3 days, leading to the formation of the alkyl hydride derivative of the four-coordinate aluminum $[(^{\text{Dipp}}\text{NacNac})\text{AlH}(\text{C}_5\text{Me}_5)]$ (Scheme 1c) [12]. In 2021, our group reported a case of dialumane-mediated C–H activation of pyridines to form a unique metallo-macrocycle compound (Scheme 1d) [13].



Scheme 1. Examples of C–H bond activation at low-valent Al(II/I) centers. The blue bonds represent newly formed chemical bonds. (a) C–H activation of benzene by aluminylium anion $[\text{K}\{\text{Al}(\text{NON})\}]_2$. (b,c) C–H activation of unactivated arenes (benzene, toluene, xylenes) and Cp^*H by $[(^{\text{Dipp}}\text{NacNac})\text{Al}(\text{I})]$. (d) C–H activation of pyridine by $[\text{LAl}(\text{THF})]_2$.

In contrast to Al(I) species, investigations on C–H bond activation by low-valent Ga compounds under ambient conditions are relatively rare. The Nikonov group reported that the oxidation of a Ga(I) compound, $^{\text{Dipp}}\text{NacNacGa}(\text{I})$, to transient gallium oxide or imide $^{\text{Dipp}}\text{NacNacGa} = \text{X}$ ($\text{X} = \text{O}$ or NR) can facilitate the addition to non-activated C–H bonds in both aromatic and aliphatic substrates, resulting in the formation of alkyl(aryl) hydroxides of gallium (Scheme 2a) [14–16]. Schulz et al. reported that the reactions of gallium phosphinidene with acetone or acetophenone proceeded via $\text{C}(\text{sp}^3)\text{-H}$ bond activation, leading to the enolization of ketones [17]. Recently, we set out to investigate the reactions of the anionic gallylene species $[\text{LGa}]^-$ (**1**) with organic azides. It was found that

in the reaction with TMSN_3 , compound **1** activated a C–H bond of the methyl group on toluene through a transient anionic $\text{Ga}=\text{N}$ species to produce a benzylic amido complex (Scheme 2b) [18]. To further explore the C–H bond activation ability of this gallylene, likely through the $\text{Ga}=\text{N}$ imido intermediate, we carried out the reactions of **1** with azobenzene derivatives and bulky azides. Remarkably, both $\text{C}(\text{sp}^2)\text{--H}$ and $\text{C}(\text{sp}^3)\text{--H}$ bond activation processes were observed at ambient temperature, affording the products **2–7**. Herein, the reaction processes and characterization of the products are presented.

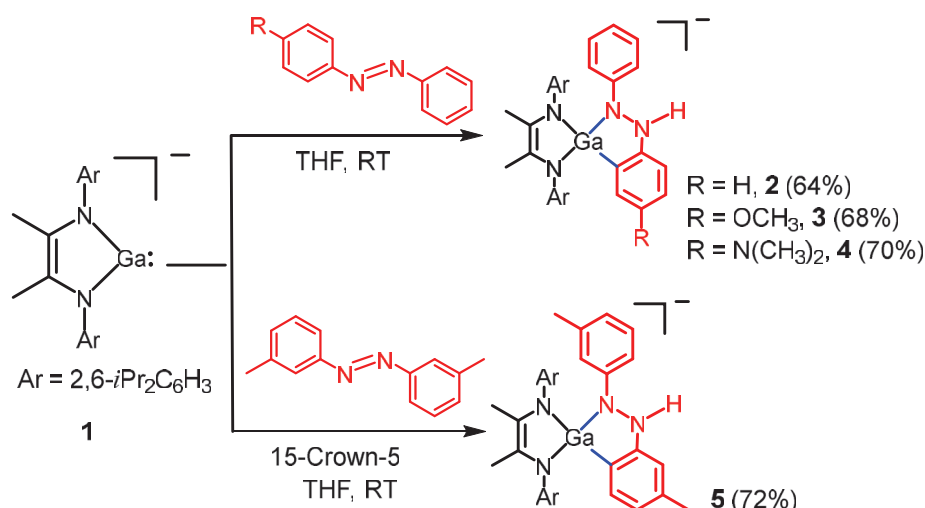


Scheme 2. Examples of C–H bond activation at low-valent Ga(I) centers. The blue bonds represent newly formed chemical bonds. (a) Sequential oxidation/C–H activation on DippNacNacGa(I) . (b) C–H activation of methyl in toluene by gallylene species $[\text{LGa:}][\text{Na(THF)}_3]$ (**1**).

2. Results and Discussion

2.1. Synthesis of Complexes **2–5**

The reaction of the gallylene species **1** with azobenzene $\text{PhN}=\text{NPh}$ resulted in the formation of an anionic complex $[\text{LGa-}\kappa^2\text{N,C-PhNN(H)(C}_6\text{H}_4)][\text{Na(DME)}_3]$ (**2**, 64% yield), through activation of one *ortho*-position C–H bond in a phenyl group of azobenzene and subsequent transfer of this hydrogen to the nitrogen atom to which this phenyl ring is attached. Similarly, the reactions of **1** with azo compounds containing electron-donating groups, 4-methoxyazobenzene, 4-dimethylaminoazobenzene, and 3,3'-dimethylazobenzene also led to selective *o*-C–H activation of the phenyl ring bearing the electron-donating group, resulting in the formation of analogous complexes $[\text{LGa-}\kappa^2\text{N,C-PhNN(H)(p-OCH}_3\text{-C}_6\text{H}_3)][\text{Na(DME)}_3]$ (**3**, 68%), $[\text{LGa-}\kappa^2\text{N,C-PhNN(H)(p-N(CH}_3)_2\text{-C}_6\text{H}_3)][\text{Na(THF)}_3]$ (**4**, 70%) and $[\text{LGa-}\kappa^2\text{N,C-(m-CH}_3\text{-C}_6\text{H}_4)\text{NN(H)(m-CH}_3\text{-C}_6\text{H}_3)][\text{Na(15-C-5)}_2]$ (**5**, 72%, Scheme 3). It is noticeable that in the above complexes **2–5**, the azobenzene substrate, either without substituents or with electron-donating groups, underwent *o*-C–H bond cleavage and H transfer to the N atom on the same side. For further validation of this selective C–H activation, mono-acetyl and trifluoromethyl-substituted azobenzene substrates were tested. However, conducting the reaction at an elevated temperature of 80 °C did not yield the desired product, possibly due to the diminished reactivity resulting from strong electron-withdrawing effects.



Scheme 3. Reaction of **1** with azobenzene derivatives to yield complexes **2–5**. The blue bonds represent newly formed chemical bonds.

Complexes **2–5** were crystallized by slow evaporation of a THF/DME solution at ambient temperature. The crystal data and structure determination details can be found in Tables S1 and S2, while the selected bond lengths and angles are provided in Table 1. These complexes contain a monoanionic gallium moiety [LGa- κ^2 N,C-ArNN(H)Ar][−] and one Na⁺ counter-cation in different bonding modes. In the structures of **2–5**, upon C–H activation and hydrogen transfer, the azo compound changed to an amido-amino aryl moiety, which bonds to the gallium atom through the amido and *ortho*-carbanion groups to constitute a five-membered metallocycle (Figures 1–3 and Supplementary Materials, Figure S19). Thus, together with a chelating α -diimine ligand, the Ga center resides in a distorted tetrahedral geometry containing two five-membered coordination cycles.

Table 1. Selected bond lengths (Å) and angles (°) for complexes **2–5**.

Compounds	2	3	4	5
Bond length [Å]				
Ga–N1	1.911(2)	1.887(8)	1.888(2)	1.901(9)
Ga–N2	1.897(2)	1.872(8)	1.894(2)	1.883(9)
C1–N1	1.418(4)	1.415(1)	1.428(3)	1.395(14)
C2–N2	1.418(4)	1.453(1)	1.421(3)	1.435(14)
C1–C2	1.355(4)	1.339(2)	1.354(4)	1.334(10)
Ga–N3	1.965(3)	2.026(1)	2.017(2)	1.963(6)
Ga–C36	1.967(3)	1.916(1)	1.959(2)	1.952(7)
N3–N4	1.426(4)	1.374(1)	1.354(3)	1.417(8)
N3–C29	1.366(4)	1.363(2)	1.388(3)	1.368(9)
N4–C35	1.404(4)	1.355(1)	1.387(3)	1.408(9)
C35–C36	1.404(4)	1.442(2)	1.416(4)	1.388(9)
N4–H	0.8800	0.8800	0.8800	0.8700
Bond angles [°]				
N1–Ga–N2	87.1(1)	88.7(4)	88.2(9)	87.4(2)
N2–Ga–N3	114.5(1)	114.5(4)	116.50(9)	114.4(5)
N2–Ga–C36	129.1(1)	126.5(4)	125.2(1)	128.2(5)
N1–Ga–N3	113.6(1)	115.4(4)	112.6(9)	114.1(5)
N3–Ga–C36	85.7(1)	83.5(5)	83.9(10)	85.4(2)
N1–Ga–C36	128.9(1)	130.3(5)	132.6(10)	129.4(5)

Azobenzene is known to be a promising building block for photo-switches owing to its facile reversible *cis*–*trans* isomerization upon irradiation/heating. Thus, the efficient and direct synthesis of intricate polysubstituted azobenzenes has garnered significant attention [19,20]. In this respect, the regio- and chemoselective activation of

C–H bonds by transition metals has been an attractive and challenging strategy for synthesizing sterically constrained azo compounds [21,22]. Azo ligands, known for their redox non-innocent character, have found extensive applications in coordination and organometallic chemistry [22]. The metal complexes containing azo ligands, like azobenzene, 2,2'-azobispyridine, and phenylazopyridine, have been extensively studied [19,23,24]. In most cases, azo ligands exhibit a significant double-bond character between the nitrogen atoms, as well as a dative $M \leftarrow :N$ bond with weak intramolecular interaction between the metal center and N atoms [22]. Conversely, the reduction of the N=N double bond to a single bond is seldom observed. Jones and Murphy reported a reaction of the gallylene $[\text{Ga}\{\text{N}(\text{Ar})\text{C}(\text{H})_2\}][\text{K}(\text{tmeda})]$ with $\text{PhN}=\text{NPh}$ to produce a doubly reduced product $[\{\kappa^2\text{N},\text{C}-\text{PhNN}(\text{H})(\text{C}_6\text{H}_4)\}\text{Ga}\{\text{N}(\text{Ar})\text{C}(\text{H})_2\}]$ through C–H bond activation in azobenzene [25]. Roesky and Stalke reported that the activation of the *o*-C–H moiety in azobenzene occurred through the reaction with silylene L^1SiNPh_2 ($\text{L}^1 = \text{PhC}(\text{N}^t\text{Bu}_2)$) [26].

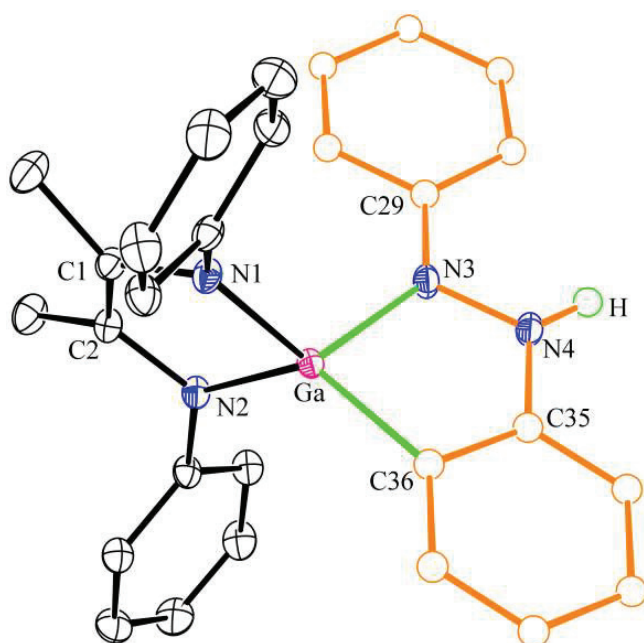


Figure 1. Molecular structure of **2**. Thermal ellipsoid plot (30%). H atoms except N4–H, $\text{Na}(\text{DME})_3$ counterion, and *i*Pr groups on the ligands are omitted for clarity. The green bonds represent newly formed chemical bonds.

In complexes **2–5**, both of the GaC_2N_2 chelating rings exhibit a high degree of planarity, with minimal deviations ($\Delta = 0.142\text{--}0.152 \text{ \AA}$) from the least-squares plane. The Ga–amide bond lengths (Ga–N3, $1.959(5)\text{--}2.026(1) \text{ \AA}$) within the coordinated azo moiety are slightly longer compared to other related gallium amides [15,25] and are significantly longer than those to the α -diimine ligands ($1.872(8)\text{--}1.911(2) \text{ \AA}$). The lengths of the new Ga–C bonds formed through *o*-C–H bond activation of the phenyl group of azobenzene ($1.916(1)\text{--}1.967(3) \text{ \AA}$) closely resemble the Ga–C bonds found in alkyl or aryl derivatives of NacNacGa ($1.9903(17)\text{--}2.0117(15) \text{ \AA}$) [15]. The amido–amino N3–N4 bond lengths ($1.426(4)$, $1.374(12)$, $1.354(4)$, and $1.417(8) \text{ \AA}$ in compounds **2–5**, respectively) in the transformed azo moiety exhibit significant elongation compared to the typical free azo N=N double bond (ca. $1.24 \text{ \AA}$) [23]. Instead, they are closer to N–N single bond distances (ca. $1.45 \text{ \AA}$) [27]. The C(Ph)–N bond distances ($1.355(1)\text{--}1.410(7) \text{ \AA}$) in the compounds are notably shorter compared to those observed in diazobenzene ($1.43 \text{ \AA}$).

The hydrogen transfer to the nitrogen atom was evidenced by the X-ray diffraction data and ^1H NMR and IR spectra. The difference map reveals a significant residual electron density in the vicinity of N4 in the azobenzene fragment, indicating the presence of a hydrogen atom bonded to nitrogen. This was also confirmed by the appearance of

a distinct N–H proton resonance at $\delta = 5.52, 5.18, 5.12,$ and 5.51 ppm in the ^1H NMR spectra. Meanwhile, IR spectra exhibit absorption bands at $3338, 3252, 3380,$ and 3235 cm^{-1} , corresponding to the N–H stretch for compounds 2–5, respectively. The ^1H NMR spectra of crystals from 2–5 show an asymmetry in the α -diimine ligands. The methyl protons within the *i*Pr groups exhibit four doublets, while the methine protons of the *i*Pr moiety display two septets. It is worth noting that compound 2 exhibits an additional set of similar ^1H NMR signals with the product (Figure S1). These signals have slightly different chemical shifts and coupling constants compared to the product, but their integrals and peak shapes are similar to the product.

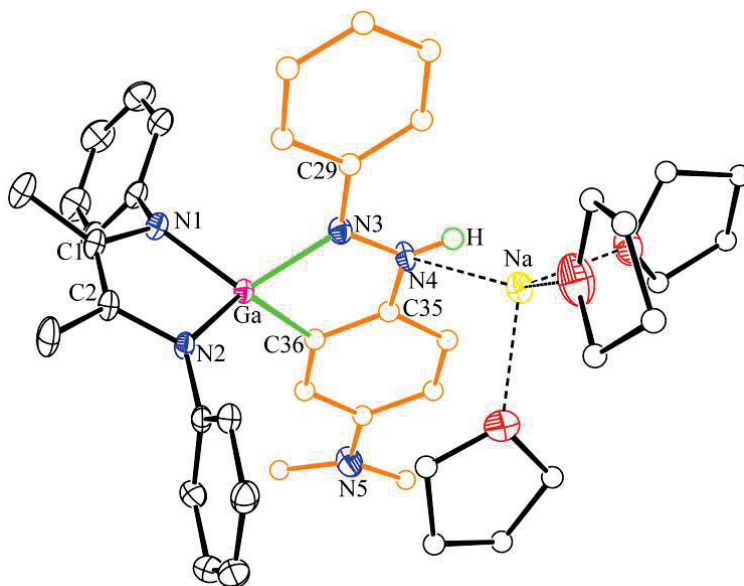


Figure 2. Molecular structure of 4. Thermal ellipsoid plot (30%). H atoms except N4–H and *i*Pr groups on the ligands are omitted for clarity. The green bonds represent newly formed chemical bonds.

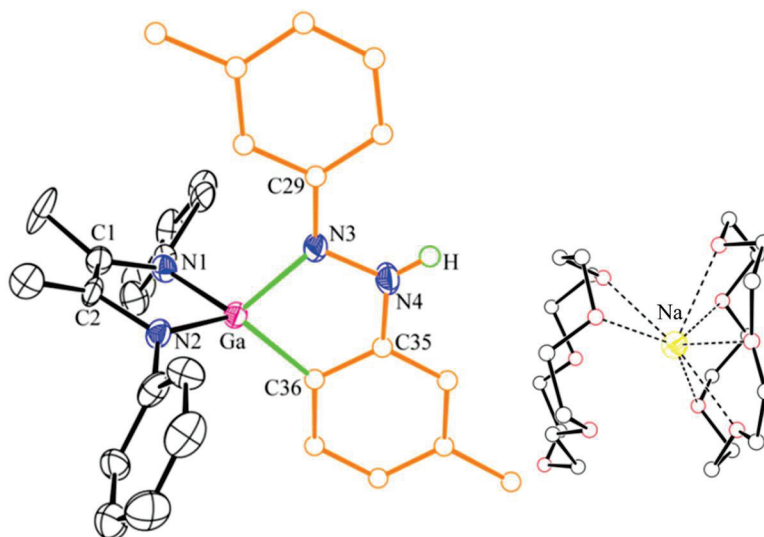
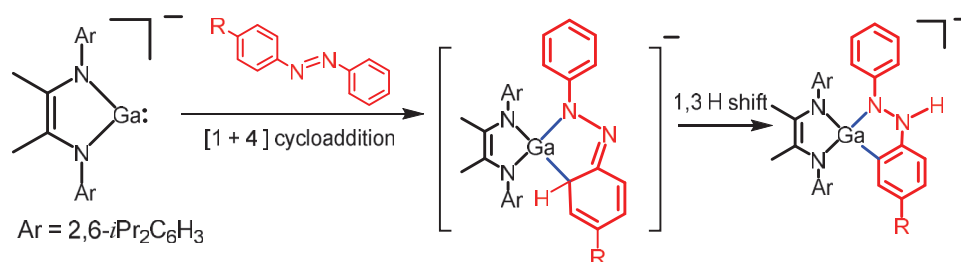


Figure 3. Molecular structure of 5. Thermal ellipsoid plot (30%). H atoms except N4–H and *i*Pr groups on the ligands are omitted for clarity. The green bonds represent newly formed chemical bonds.

We speculated that this could potentially serve as an intermediate in the reaction process. A plausible mechanism may involve a $[1 + 4]$ cycloaddition of the Ga(I) center of compound 1 with azobenzene to afford the $[\text{LGa-}\kappa^2\text{N,C-PhNN(C}_6\text{H}_5)]$ intermediate, followed by a 1,3-migration of the ortho-aryl proton to the nitrogen center (Scheme 4). Additionally, distinct signals at 2.72 and 5.67 are observed, corresponding to the hydrogen

chemical shift in Ga–CH and Ga–CH–CH-moieties within the isomer. Notably, these specific signals were absent in compounds **3–5**; however, attempts to isolate the intermediate have thus far been unsuccessful. A precedent for this mechanism is established by the reaction of $[\text{Ga}\{\text{N}(\text{Ar})\text{C}(\text{H})_2\}][\text{K}(\text{tmeda})]$ with azobenzene, leading to the formation of the doubly reduced product $[\{\kappa^2\text{N},\text{C}-\text{PhNN}(\text{H})(\text{C}_6\text{H}_4)\}\text{Ga}\{\text{N}(\text{Ar})\text{C}(\text{H})_2\}][\text{K}][25]$. The isomer ratio, as determined from the NMR spectrum (Figure S1), is approximately 3:1 (product **2**/intermediate). In the ^1H NMR spectrum, no isomers with electron-donating groups were observed in compound **3** (or in compounds **4** and **5**). On the basis of these results, we propose that small molecules containing electron-donating groups are more prone to undergo reactions analogous to electrophilic substitution, directly converting unstable intermediates into products. Conversely, in the presence of electron-withdrawing groups on the azobenzene, such as mono-acetyl and trifluoromethyl-substituted azobenzene, the formation of corresponding products was not observed. The IR spectrum of the absorption at $1575\text{--}1630\text{ cm}^{-1}$ [28], corresponding to the N=N stretching mode, disappeared. The UV-vis spectrum of complex **2–5** was recorded in THF. The absorption bands at wavelengths of $268\text{--}358\text{ nm}$ are ascribed to the $\pi\text{--}\pi^*$ transition from the dianionic α -diimine ligand (Figures S13–S18 in Supplementary Materials). Moreover, the location and coordination mode of the Na^+ counter-cation are different in these complexes. In **2** and **3**, the Na^+ ion is not bonded to the main structural motif but is solvated by three DME molecules. In contrast, in compound **4**, the sodium ion is coordinated with the N4 atom of the azo ligand and with three THF molecules. In the case of complex **5**, the Na^+ ion is trapped by two 15-Crown-5 molecules to form a sandwich structure.



Scheme 4. Possible mechanism for the reaction of gallieses with azobenzene. The blue bonds represent newly formed chemical bonds.

To gain a more comprehensive understanding of the electronic structures of complexes **2–5**, DFT studies at the B3LYP level with the 6–31G* basis were conducted employing model compounds **2H–5H**, wherein the 2,6-diisopropyl groups on the phenyls in ligand **L** were substituted with hydrogen atoms (for details, see Supplementary Materials, Figure S20, and Tables S3 and S4). The originally N=N double bond now exhibits a bond order of approximately 1.00, which is consistent with a reduction resulting in an N–N single bond. The Ga–N3(amide) bond exhibits an average bond order of 0.52, indicating the formation of a covalent Ga–N bond. This value is somewhat higher than the calculated average bond order of 0.44 for the Ga–N bonds to the α -diimine ligand, consistent with the presence of covalency in the latter case. According to natural population analysis (NPA), the negative partial charges observed on ligand **L** in **2H–5H** (average -1.39 e) are almost identical to those in the precursor **1** (-1.40 e), while the charges on gallium (average 1.66 e) in **2H–5H** are significantly higher than those observed in **1** (0.49 e). These results demonstrate that the original Ga(I) center participated in the 2e-reduction of azobenzene, while the α -diimine ligand remained unchanged. Accordingly, the entire azobenzene fragment exhibits negative partial charges of approximately -1.26 e , corresponding to the dianion character of the amido aryl moiety.

2.2. Synthesis of Complexes **6** and **7** from the Reactions of **1** with AZIDES

In recent decades, a wide range of main group complexes with distinctive bonding and structural characteristics have been synthesized and extensively investigated for their

reactivity [29–33]. The reactions of organic azides with main group species provide a direct synthetic approach for N-containing main group organometallic compounds, encompassing multiple bonds and heterocycles [34]. The carbene analogs [LE:] (E = main group 13 and 14 elements) have been found to react with azides to form E=N imido species, some of which then combine with a second azide via [2 + 3] cycloaddition to produce tetrazole heterocycles [35–41]. Alternatively, the highly polarized E=N double bond in the imido can also break non-activated C–H bonds in aromatic and aliphatic substrates [15,35,39,42,43]. Regioselective intramolecular C(sp³)–H amination has been facilitated by the development of various metal-based catalytic systems, enabling the synthesis of N-heterocycles with diverse ring sizes and functional groups through a radical-type pathway [44–46].

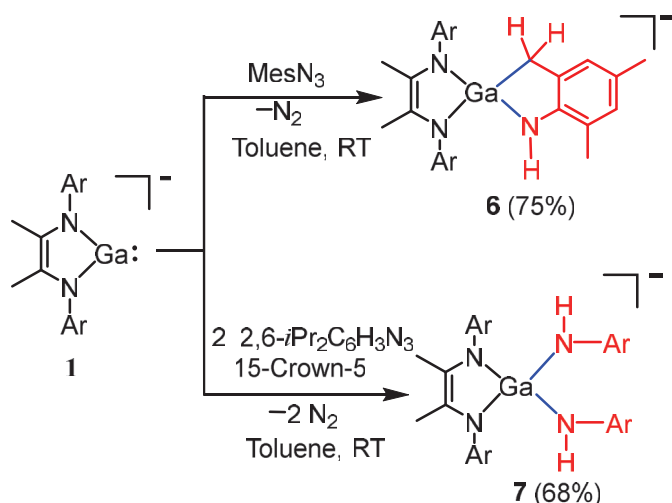
We previously reported the use of gallylene species [LGa][Na(THF)₃] (**1**) in a reaction with organic azides as a promising approach to synthesizing gallium imides. However, treatment of **1** with benzylazide (benzyl-N₃) or trimethylsilyl azide (Me₃SiN₃) in toluene led to the formation of anionic, dimeric tetrazole [LGa(benzyl-N₄-benzyl)]₂[Na(THF)]₂ or benzylic amido complex [LGa(NHSiMe₃)(benzyl)][Na(THF)₄], respectively [18]. Building upon the existing literature, our study aims to investigate the reactivity of transient gallium imide [LGa=NR][−] towards inert C–H bonds. In this study, we report the reaction of **1** with 2,4,6-Me₃C₆H₂N₃ or 2,6-*i*Pr₂C₆H₃N₃ and demonstrate in situ intramolecular or intermolecular C–H amination at the emerging Ga=N moiety.

The reaction between gallylene **1** and 1.0 equivalent 2,4,6-Me₃C₆H₂N₃ resulted in intramolecular C–H activation on one methyl group of the azide 2,4,6-Me₃C₆H₂N₃ at ambient temperature, forming the complex [LGa(NH-2-(CH₂)-4,6-Me₂C₆H₂)]₂[Na(15-C-5)]₂ (**6**, 75% yield, Scheme 5). The reaction is postulated to proceed through a gallium imide LGa=NMe₃ intermediate that undergoes C–H activation and addition of the hydrogen to the nitrene, similar with the previously documented C–H activation on a transient gallium imide [18,35]. The reaction of gallylene **1** with 2.0 equivalent Me₃N₃ was also investigated, exhibiting similar reaction phenomena. The solution gradually transitions from an orange-red to a brownish-red color, accompanied by the release of nitrogen; however, isolation of the corresponding product has not been achieved. The reaction product, [LGa(NH-2-(CH₂)-4,6-Me₂C₆H₂)]₂[Na(15-C-5)]₂ (**6**), was characterized using ¹H and ¹³C NMR spectroscopy, while its structure was confirmed through single-crystal X-ray diffraction analysis. The ¹H NMR spectrum of yellow crystals of **6** shows an asymmetry in the α-diimine ligands. The methyl protons within the *i*Pr groups exhibit three doublets, while the methine protons of the *i*Pr moiety display two septets (δ_H 3.87 and 4.19, 4H, CH(CH₃)₂). The protons of the (CH₃)₂C₂ backbone in **6** exhibit a singlet signal (δ_H 1.51, 6H, (CH₃)₂C₂). A new peak at 3.21 ppm is attributed to the presence of an NH moiety, while the IR spectrum indicates the occurrence of the N–H stretching vibration (ν_{NH} = 3499 cm^{−1}).

The polarized M=N bond (M = Al, In) in the transient imide has been reported to undergo further C–H activation across the M=N bond, either through interaction with the supporting ligand [35,42,43] or via hydrogen atom abstraction from a methyl in one molecule of toluene solvent [39]. Reaction of NaCnacGa and organic azide N₃SiMe₃ leads to the formation of an imide NaCnacGa=NSiMe₃ intermediate, which exhibits the ability to cleave unreactive sp³ and sp² C–H bonds in various substrates (pyridine, cyclohexanone, ethyl acetate, DMSO, and OPET₃), resulting in the generation of gallium aryl/alkyl amides [(Nacnac)GaR(NHSiMe₃)] [15]. However, the intramolecular C–H activation has not been observed for Ga species.

X-ray diffraction analysis of **6** revealed a κ²-C,N-[NH-2-(CH₂)-4,6-Me₂C₆H₂] ligand chelating to a four-coordinate gallium (III) center (Figure 4). The sodium counter cation is trapped within two 15-Crown-5 molecules through five and two oxygen atoms, respectively. The Ga center connects two fused rings (GaC₂N₂ and GaC₃N) arranged in an almost orthogonal configuration, with a dihedral angle of 85.3°. The GaC₂N₂ and GaC₃N rings exhibit perfect planarity, as evidenced by their minimal deviations from the least-squares plane (Δ = 0.021 and 0.129 Å). The Ga–N bond lengths (1.913(4) and 1.912(4) Å) to the α-diimine nitrogens are similar to the distance of Ga–N3 (1.929(4) Å) to the amido nitrogen

atoms, which closely resembles observations of other related gallium amides [15]. A peak from difference maps that can be attributed to a N-bound proton, was refined to the N–H bond distance of 0.88 Å. Intramolecular C–H activation has been observed in Al and In amido derivatives [35,42], leading to the formation of a dianionic alkyl-amide ligand through C–H activation across a transient M–N_{imide} bond. The newly formed Ga–C bond length (1.995(5) Å) is comparable to the Ga–C bond lengths observed in aryl or alkyl derivatives of [NacNacGa] (range 1.9903(17)–2.0117(15) Å), which contain a single amide ligand [15].



Scheme 5. Reaction of **1** with 2,4,6-trimethylphenylN₃ and 2,6-*i*Pr₂C₆H₃N₃ to yield **6** and **7**. The blue bonds represent newly formed chemical bonds.

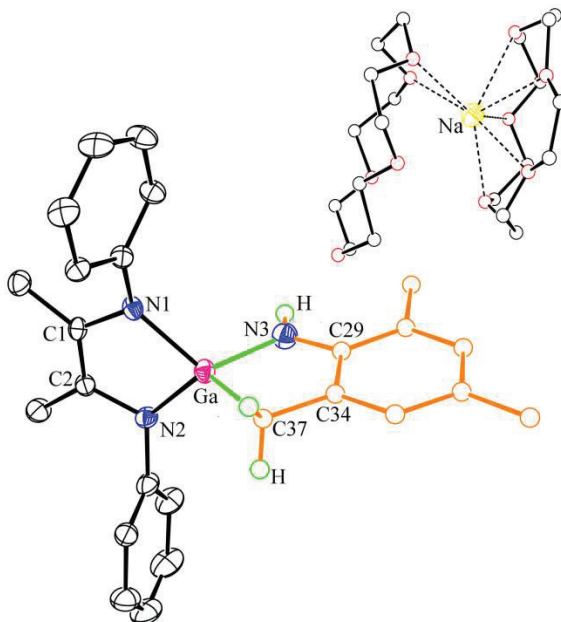


Figure 4. Molecular structure of **6**. Hydrogen atoms and *i*Pr groups have been omitted. The green bonds represent newly formed chemical bonds. Selected bond lengths [Å] and angles [°]: Ga–N1 1.913(4), Ga–N2 1.912(4), N–C1 1.419(5), N2–C2 1.428(6), C1–C2 1.356(6), Ga–N3 1.929(4), Ga–C37 1.995(5), N3–C29 1.372(6), C29–C34 1.407(7), C34–C37 1.506(7), N3–H 0.880, N1–Ga–N3 116.06(17), N1–Ga–C37 128.6(2), N2–Ga–N1 86.86(16), N2–Ga–N3 118.46(17), N2–Ga–C37 122.73(19), N3–Ga–C37 87.6(2).

DFT calculations on complex **6** (Figure S20) demonstrate a planar NC₃ core, exhibiting bond orders of 1.21 for N3–C29, 1.68 for C29–C34, and 1.03 for C34–C37, thereby confirming the charge delocalization across the N–C=C–C unit. The WBIs of the Ga–N3 and Ga–C37

bonds (0.47 and 0.63) are slightly higher, compared to those observed for the Ga–N1 (0.43) and Ga–N2 (0.42) bonds. The Ga atom exhibits NPA charges of 1.65 e, while the ligand L displays negative charges of −1.41 e. The entire NC₃ fragment shows negative charges of −1.23 e (Table S4, Supplementary Materials), primarily localized on the N3 (−1.02 e) and C37 (−0.98 e) atoms.

In addition, the reaction of **1** with 1.0 equivalent 2,6-diisopropylC₆H₃N₃ led to the formation of the bis-amide complex [LGa(NH-2,6-*i*Pr₂C₆H₃)₂][Na(THF)₅] (**7**, with low yield, 29% yield). Subsequently, altering the ratio of compound **1**: 2,6-diisopropylC₆H₃N₃ to 1: 2 still led to the generation of compound **7** in the moderate yield (68% yield). We speculate that **6** and **7** are formed by essentially similar C–H activation processes, where the first is the result of intramolecular activation and the other is attributed to intermolecular hydrogen atom abstraction from the solvent (toluene) due to steric repulsion [18]. The structure of compound **7** is asymmetric due to the steric hindrance, as evidenced from the ¹H NMR spectra. In particular, the *i*Pr methine protons exhibit two septets. The broad peak observed at 2.79 ppm is attributed to the presence of an NH functionality, while IR spectroscopy indicates the occurrence of a N–H stretch ($\nu_{\text{NH}} = 3364 \text{ cm}^{-1}$).

The structure of diamide complex **7** (Figure 5) reveals a gallium center coordinated to four nitrogen atoms in a distorted tetrahedral manner. The Ga–N bonds to α -diimine ligand (av. 1.911 Å) display similar lengths to the corresponding bonds in **1** (av. 1.918 Å). The α -diimine ring is folded along the N1⋯N2 axis, positioning Ga approximately 0.20 Å away from the averaged N₂C₂ plane, which makes the two bulk NH(Ar) ligands point away from the *i*Pr on the α -diimine ligand. The bond lengths of Ga–N(*i*Pr₂C₆H₃) (1.913(3) and 1.908(4) Å) are similar to those observed for Ga–N(SiMe₃)₂ bonds (1.891(4), 1.884(1) and 1.872(2) Å in monoamide compounds [LGa(NHSiMe₃)(benzyl)][Na(THF)₄] [18], [(HC(MeCDippN)₂)Ga(N₃)N(SiMe₃)₂] [40], and [Cp*{N(SiMe₃)₂}Ga(μ -N₃)]₂ [47], probably due to larger steric hindrance of the amide moiety HN-(*i*Pr₂C₆H₃) around the Ga–N bond. However, the lengths of these bonds exceed the distances reported for imides [Ar'GaNAr[#]] (1.701(3) Å, Ar' = C₆H₃-2,6-(C₆H₃-2,6-*i*Pr₂)₂, Ar[#] = C₆H₃-2,6-(C₆H₂-2,6-Me₂-4-*t*Bu)₂) [48] and [(HC(MeCDippN)₂)GaN-2,6-Trip₂C₆H₃] (1.742(3) Å, Trip = 2,4,6-*i*Pr₃C₆H₂) [49] with a Ga=N double bond.

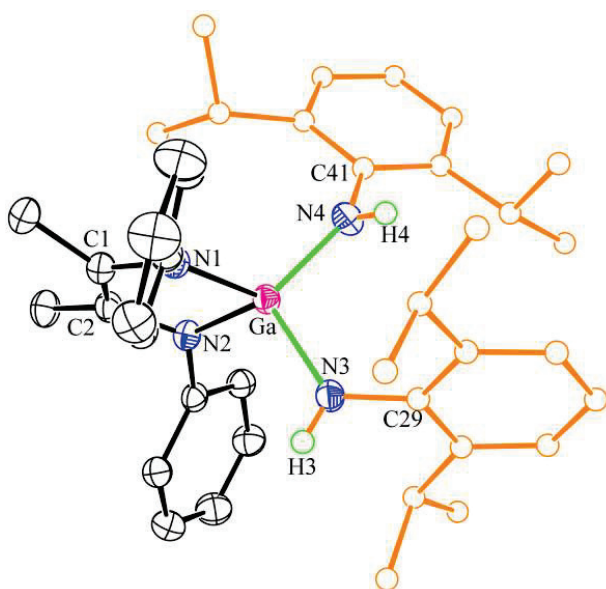


Figure 5. Molecular structure of **7**. Thermal ellipsoid plot (30%). H atoms except N3–H and N4–H, Na(THF)₅ counterion, and the isopropyl groups are omitted for clarity. The green bonds represent newly formed chemical bonds. Selected bond lengths [Å] and angles [°]: Ga–N1 1.910(4), Ga–N2 1.915(4), N1–C1 1.417(4), N2–C2 1.424(5), C1–C2 1.353(5), Ga–N3 1.913(3), Ga–N4 1.908(4), N3–C29 1.397(5), N4–C41 1.401(4), N3–H3 0.8700, N4–H4 0.8700, N1–Ga–N2 88.05(19), N1–Ga–N3 118.07(14), N3–Ga–N2 107.3(2), N4–Ga–N1 116.2(2), N4–Ga–N2 123.07(15), N4–Ga–N3 104.3(2).

The NPA charges on the α -diimine ligand in model compound **7H** (-1.42 e) exhibit a similar range to those observed in **2H–7H** ($-1.39\sim-1.42$ e, Tables S3 and S4). The NPA charges on Ga (1.77 e) are somewhat higher than those observed in **2H–6H** ($1.65\text{--}1.66$ e). Accordingly, both the 2,6-diisopropylphenyl-amido groups exhibit negative partial charges of -0.68 e. The calculated Ga–N3 (1.943 Å) and Ga–N4 (1.935 Å) bond distances closely correspond to the experimental values ($1.913(3)$ and $1.908(4)$ Å), exhibiting an average σ -bond order of 0.47 , as revealed by NBO analysis.

3. Materials and Methods

3.1. General Procedures

All reactions and manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen with standard Schlenk or dry box techniques. The solvents (ether, THF, toluene, and DME) were dried using appropriate methods and were distilled under argon prior to use. Tetrahydrofuran- d_8 is dried over Na/K alloy. The α -diimine ligand **L** and $[\text{LGa}][\text{Na}(\text{THF})_3]$ **1** $\text{L}=[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2]$ were prepared according to procedures outlined in the literature [50]. Sodium metal, Gallium chloride (GaCl_3), Azobenzene, 4-Methoxyazobenzene, 4-Dimethylaminoazobenzene, and 15-Crown-5 were purchased from Alfa Aesar (Heysham, Britain). 3,3'-Dimethylazobenzene was purchased from Macklin (Shanghai, China). Azides were prepared from the corresponding amines via their diazonium salts [51]. The ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE III-400 MHz spectrometers (Rheinstetten, Germany). The IR spectra were recorded using a Thermo scientific Nicolet AVATAR 360 FT-IR (Thermo Scientific, Waltham, MA, USA). UV–visible spectra were recorded by an Agilent Technologies Cary 100 UV–vis spectrophotometer (Santa Clara, CA, USA). Elemental analyses were carried out on Elementar VarioEL III instrument (Hanau, Germany). The X-ray diffraction data were collected with a Bruker METAJET D8 VENTURE (diffractometer with graphite-monochromated Ga $K\alpha$ radiation) and Bruker APEX-II CCD (diffractometer with graphite-monochromated Mo $K\alpha$ radiation) (Berlin, Germany). An empirical absorption correction using SADABS was applied for all data [52]. The structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using the SHELXL–2014 programs [53]. Some solvents, such as DME and THF, are disordered and display unusual thermal parameters, which were removed using the SQUEEZE routine implemented within the software program PLATON [54], and the resulting .fab file was processed with OLEX2 1.2 [55] using the ABIN instruction (see Supplementary Materials for X-ray crystal structure determination details). The structure optimization and NBO bonding analysis for the model compounds **2H–7H** were carried out at the DFT (B3LYP) level with the 6-31G* basis [56,57] sets using the Gaussian 09 program [58]. Bonding analyses were performed by means of natural bond orbital (NBO) analysis and natural population analysis (NPA). Wiberg bond indices (WBI) were evaluated with Weinhold's natural bond orbital method [59–61] (see Supplementary Materials for DFT computations details).

3.2. Synthesis of $[\text{LGa-}\kappa^2\text{N,C-PhNN(H)(C}_6\text{H}_4)][\text{Na(DME)}_3]$ (**2**)

Azobenzene (0.183 g, 1 mmol) was added to the THF solution of compound **1** (1 mmol). The resultant black-green solution was stirred at room temperature for 1 day. All volatiles were removed in vacuum. The residue was dissolved in 5 mL of DME. After 5 days, the black-green crystals were grown by slow evaporation of the solution at room temperature (yield: 0.608 g, 0.64 mmol, 64%). ^1H NMR (400 MHz, $\text{THF-}d_8$, 298 K): δ/ppm : 0.54 (d, $J = 6.8$ Hz, 6H , $\text{CH}(\text{CH}_3)_2$), 0.79 (d, $J = 6.8$ Hz, 6H , $\text{CH}(\text{CH}_3)_2$), 1.26 (m, 12H , $\text{CH}(\text{CH}_3)_2$) overlap with 6H , NCCH_3), 3.26 , 3.42 (DME), 3.98 (sept, $J = 6.8$ Hz, 2H , $\text{CH}(\text{CH}_3)_2$), 4.11 (sept, $J = 6.9$ Hz, 2H , $\text{CH}(\text{CH}_3)_2$), 5.52 (s, 1H , NH), 6.06 (t, $J = 6.9$ Hz, 1H , HNNPh), 6.30 (t, $J = 7.0$ Hz 1H , NNHC_6H_4), 6.54 (m, 1H , Ar-H), $6.65\text{--}6.74$ (m, 4H , Ar-H), $6.76\text{--}6.87$ (m, 4H , Ar-H), $6.88\text{--}6.98$ (m, 3H , Ar-H), 7.36 (d, $J = 6.9$ Hz, 1H , $\text{NNH-C}_6\text{H}_4$). ^{13}C NMR (100.6 MHz, $\text{THF-}d_8$, 298 K): δ/ppm : 15.7 (NCCH_3), 24.6 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{THF-}d_8$), 26.5 , 26.9 , 27.9 ($\text{CH}(\text{CH}_3)_2$), 28.8 ($\text{CH}(\text{CH}_3)_2$), 59.1 , 72.7 (DME), 109.8 (NCCH_3), 113.1 ,

117.5, 122.0, 122.6, 123.2, 123.8, 126.7, 138.0, 146.9, 147.5, 149.1, 152.8, 156.5, 157.2 (Ar-C). IR (Nujol, KBr, ν/cm^{-1}): 3338 w, 3073 m, 2971 s, 2851 s, 1596 m, 1494 s, 1417 s, 1323 m, 1246 s, 1177 w, 1049 m, 793 m. Elemental analysis calcd. for $\text{C}_{52}\text{H}_{80}\text{GaN}_4\text{NaO}_6$ (949.91): C 65.75; H 8.49; N 5.90%; found: C 65.36, H 8.73, N 5.59%.

3.3. Synthesis of $[\text{LGa-}\kappa^2\text{N,C-PhNN(H)(p-OCH}_3\text{-C}_6\text{H}_3)][\text{Na(DME)}_3]$ (3)

Complex 3 was prepared by a similar procedure to that of 2. 4-Methoxyazobenzene (0.213 g, 1 mmol) was added to the THF solution of compound 1 (1 mmol). The resultant black-green solution was stirred at room temperature for 1 day. All volatiles were removed in vacuum. The residue was dissolved in 5 mL of DME. After 4 days, the black-green crystals were grown by slow evaporation of the solution at room temperature (yield: 0.667 g, 0.68 mmol, 68%). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ/ppm : 0.53 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.80 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.27–1.31 (m, 12H, $\text{CH}(\text{CH}_3)_2$ overlap with 6H, NCCH_3), 3.26, 3.42 (DME), 3.53 (s, 3H, OCH_3), 3.99 (sept, $J = 6.7$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 4.10 (sept, $J = 6.6$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 5.18 (s, 1H, NH), 6.07 (t, $J = 6.7$ Hz, 1H, NH-N- C_6H_3), 6.34 (dd, $J = 8.4$ Hz, 1H, Ar-H), 6.46 (b, 1H, Ar-H), 6.50 (d, $J = 8.5$ Hz, 2H, Ar-H), 6.62 (d, $J = 8.4$ Hz, 1H, Ar-H), 6.69 (m, 4H, Ar-H), 6.86 (m, 3H, Ar-H), 6.99 (s, 1H, NH- C_6H_3). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ/ppm : 14.8 (NCCH_3), 25.3 (THF- d_8), 24.6, 26.7, 26.9 ($\text{CH}(\text{CH}_3)_2$), 28.1 ($\text{CH}(\text{CH}_3)_2$), 55.3 (OCH_3), 59.0, 72.5 (DME), 67.4 (THF- d_8), 106.9 (NCCH_3), 109.9, 114.2, 115.4, 116.6, 117.5, 120.4, 122.1, 122.8, 126.6, 127.5, 128.6, 148.0, 151.7 (Ar-C), 153.1 (Ar-C- OCH_3). IR (Nujol, KBr, ν/cm^{-1}): 3252 w, 3056 vs, 2919 vs, 2715 w, 2569 w, 2407 w, 2347 w, 2228 s, 2065 s, 1886 w, 1766 w, 1596 vs, 1494 vs, 1442 vs, 1067 vs, 1032 vs, 827 vs, 785 vs, 716 vs, 673 s. Elemental analysis $\text{C}_{92}\text{H}_{124}\text{Ga}_2\text{N}_{12}\text{Na}_2\text{O}_2$ (1615.44): calc. C 68.40, H 7.74, N 10.40%; found: C 68.31, H 7.92, N 10.21%. Elemental analysis calcd. for $\text{C}_{53}\text{H}_{82}\text{GaN}_4\text{NaO}_7$ (979.93): C 64.96; H 8.43; N 5.72%; found: C 64.49, H 8.65, N 5.34%.

3.4. Synthesis of $[\text{LGa-}\kappa^2\text{N,C-PhNN(H)(p-N(CH}_3)_2\text{-C}_6\text{H}_3)][\text{Na(THF)}_3]$ (4)

4-Dimethylaminoazobenzene (0.226 g, 1 mmol) was added to the THF solution of compound 1 (1 mmol). The resultant black-green solution was stirred at room temperature for 1 day and concentrated to about 5 mL under reduced pressure. A few drops of DME were added. After 7 days, the black-green crystals were grown by slow evaporation of the solution at room temperature (yield: 0.658 g, 0.70 mmol, 70%). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ/ppm : 0.49 (d, $J = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.75 (d, $J = 6.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.94 (m, 6H, $\text{CH}(\text{CH}_3)_2$), 1.15 (s, 3H, NCCH_3), 1.17 (s, 3H, NCCH_3), 1.24 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 1.58 (s, 6H, NCCH_3), 1.69 (Na-THF), 2.02 (toluene), 3.23, 3.40 (DME), 3.47 (Na-THF), 3.95 (sept, $J = 6.6$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 4.05 (sept, $J = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 5.12 (s, 1H, NH), 6.05 (t, 1H, NHNC_6H_5), 6.32 (m, 1H, Ar-H), 6.47 (d, 2H, Ar-H), 6.67 (m, toluene), 6.79 (m, 5H, Ar-H), 6.93 (m, 3H, Ar-H), 7.11 (m, 3H, Ar-H). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ/ppm : 16.5 (NCCH_3), 22.8, 23.3 ($\text{CH}(\text{CH}_3)_2$), 25.3 (THF- d_8), 26.8, 71.5 (THF), 29.3 ($\text{CH}(\text{CH}_3)_2$), 46.2 ($\text{N}(\text{CH}_3)_2$), 58.9, 72.7 (DME), 67.4 (THF- d_8), 122.1 (NCCH_3), 122.7 (Ga-C), 123.6, 124.5, 135.5, 147.1, 168.9 (Ar-C). IR (Nujol, KBr, ν/cm^{-1}): 3380 w, 3056 m, 2843 vs, 1596 s, 1425 vs, 1357 s, 1237 vs, 1160 m, 1092 vs, 939 m, 785 m. Elemental analysis calcd. for $\text{C}_{54}\text{H}_{79}\text{GaN}_5\text{NaO}_3$ (938.93): C 69.07; H 8.48; N 7.46%; found: C 68.87, H 8.69, N 7.03%.

3.5. Synthesis of $[\text{LGa-}\kappa^2\text{N,C-(m-CH}_3\text{-C}_6\text{H}_4)\text{NN(H)(m-CH}_3\text{-C}_6\text{H}_3)][\text{Na(15-C-5)}_2]$ (5)

In this step, 15-Crown-5 (300 μL , 1 mmol) was added to the THF solution of compound 1 (1 mmol) and stirred at room temperature for 1 day; then, 3,3'-dimethylazobenzene (0.211 g, 1 mmol) was added. The resultant green solution was stirred at room temperature for 1 day and concentrated to about 5 mL under reduced pressure. After 5 days, the green crystals were grown by slow evaporation of the solution at room temperature (yield: 0.827 g, 0.72 mmol, 72%). ^1H NMR (400 MHz, THF- d_8 , 298 K): δ/ppm : 0.54 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.80 (d, $J = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$ overlap with s, 6H, NCCH_3), 2.07 (s, 3H, $\text{C}_6\text{H}_3\text{-CH}_3$), 2.17 (s, 2H, $\text{C}_6\text{H}_3\text{-CH}_3$), 2.22 (s, 1H, $\text{C}_6\text{H}_3\text{-CH}_3$), 3.48 (15-C-5-H), 3.98 (b, 2H, $\text{CH}(\text{CH}_3)_2$), 4.10 (b, 2H, $\text{CH}(\text{CH}_3)_2$), 5.51 (s, 1H,

NH), 5.94 (d, $J = 6.8$ Hz, 1H, $C_6H_3-CH_3$), 6.20 (d, 2H, $C_6H_3-CH_3$), 6.39 (s, 1H, $C_6H_3-CH_3$), 6.70 (m, 6H, Ar-H), 6.82 (m, 2H, $C_6H_3-CH_3$), 7.25 (d, $J = 6.8$ Hz, 1H, $C_6H_3-CH_3$). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ /ppm: 21.9 (NCCH₃), 24.7, 26.5 (Ar-CH₃), 27.1 (CH(CH₃)₂), 28.0 (CH(CH₃)₂), 70.5 (15-C-5-C), 103.8 (NCCH₃), 107.5, 111.1, 113.8, 117.6, 119.1, 122.2, 122.2, 127.4, 128.5, 135.7, 138.0, 152.7, 157.8 (Ar-C). IR (Nujol, KBr, ν/cm^{-1}): 3235 w, 3030 s, 2902 vs, 1971 w, 1613 s, 1425 vs, 1331 s, 1237 s, 1083 vs, 930 s, 768 m. Elemental analysis calcd. for $C_{62}H_{94}GaN_4NaO_{10}$ (1148.12): C 64.86; H 8.25; N 4.88%; found: C 64.74, H 8.30, N 4.65%.

3.6. Synthesis of [LGa(NH-2-(CH₂)-4,6-Me₂C₆H₂)] [Na(15-C-5)₂] (6)

An amount of 300 μ L of 15-Crown-5 was added to the toluene solution of compound **1** (1 mmol) and stirred at room temperature for 1 day; then, 2,4,6-trimethylN₃ (0.223 g, 1 mmol) was added. The solution gradually changes from orange-red to brown-red; this is accompanied by the release of nitrogen. The reaction solution was stirred at room temperature for 1 day and concentrated to about 5 mL under reduced pressure. A few drops of THF were added. The yellow crystal of **6** (yield: 0.800 g, 0.75 mmol, 75%) was obtained in 8 days through the process of slow evaporation at room temperature. ^1H NMR (400 MHz, THF- d_8 , 298 K): δ /ppm: 0.99 (s, 2H, Ga-CH₂ overlap with d, $J = 6.8$ Hz, 6H, CH(CH₃)₂), 1.13 (dd, $J = 6.7$ Hz, 12H, C(CH₃)₂), 1.18 (d, $J = 6.8$ Hz, 6H, C(CH₃)₂), 1.51 (s, 6H, NCCH₃), 1.92 (s, 6H, C₆H₂-(CH₃)₂), 3.21 (s, 1H, NH), 3.47 (15-C-5-H), 3.87 (sept, $J = 6.8$ Hz, 2H, CH(CH₃)₂), 4.19 (sept, $J = 6.9$ Hz, 2H, CH(CH₃)₂), 6.16 (s, 1H, NH-C₆H₂), 6.34 (s, 1H, NH-C₆H₂), 6.74 (t, $J = 7.5$ Hz, 2H, Ar-H) and 6.86 (d,d, $J = 7.4$ Hz, 4H, Ar-H). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ /ppm: 10.3 (Ga-CH₂), 15.4 (NCCH₃), 19.3 (N-phenyl-p-CH₃), 21.2 (N-phenyl-o-CH₃), 21.5, 24.7, 26.1, 26.2, 27.5 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 70.4 (15-C-5-C), 116.0, 116.5 (NCCH₃), 117.6, 121.8, 122.4, 122.6, 126.0, 126.6, 128.9, 128.9, 129.7, 138.4, 148.4, 148.7, 149.6, 155.2 (Ar-C). IR (Nujol, KBr, ν/cm^{-1}): 3499 m, 3176 w, 2962 vs, 2159 w, 1920 m, 1630 vs, 1433 vs, 1229 vs, 1101 vs, 913 vs, 759 vs. Elemental analysis calcd. for $C_{57}H_{91}GaN_3NaO_{10}$ (1071.03): C 63.92, H 8.56 N 3.92%; found: C 63.99, H 8.65, N 3.82%.

3.7. Synthesis of [LGa(NH-2,6-*i*Pr₂C₆H₃)₂] [Na(THF)₅] (7)

2,6-*i*Pr₂C₆H₃N₃ (0.408 g, 2 mmol) was added to the toluene solution of compound **1** (1 mmol). The solution gradually changes from orange-red to brown-red; this process is accompanied by the release of nitrogen. The reaction solution was stirred at room temperature for 1 day and concentrated to about 5 mL under reduced pressure. A few drops of THF were added. The yellow crystal of **7** (yield: 0.823 g, 0.68 mmol, 68%) was obtained in 8 days through the process of slow evaporation at room temperature. ^1H NMR (400 MHz, THF- d_8 , 298 K): δ /ppm: 0.73 (d, $J = 6.4$ Hz, 24H, NH-CH(CH₃)₂), 0.94 (d, $J = 6.6$ Hz, 12H, CH(CH₃)₂), 1.01 (d, $J = 6.6$ Hz, 12H, CH(CH₃)₂), 1.61 (s, 6H, NCCH₃), 1.74 (m, Na-THF overlap with THF- d_8), 2.69 (br, 4H, CH(CH₃)₂), 2.79 (s, 2H, NH), 3.24, 3.40 (DME), 3.58 (m, Na-THF overlap with THF- d_8), 4.14 (sept, $J = 6.7$ Hz, 4H, CH(CH₃)₂), 6.23 (m, 2H, Ar-H), 6.60 (m, 2H, Ar-H), 6.76 (m, 2H, Ar-H), 6.91 (m, 2H, Ar-H). ^{13}C NMR (100.6 MHz, THF- d_8 , 298 K): δ /ppm: 16.2 (NCCH₃), 22.9 (Toulene), 26.4 (THF), 27.5 (CH(CH₃)₂), 27.8 (CH(CH₃)₂), 58.9 (DME), 68.2 (THF), 72.7 (DME), 114.7 (NCCH₃), 121.7, 122.9, 122.3, 123.5, 148.3, 150.6 (Ar-C). IR (Nujol, KBr, ν/cm^{-1}): 3364 m, 2902 vs, 2219 m, 1579 m, 1442 vs, 1348 vs, 1254 vs, 1083 m, 990 s, 742 s. Elemental analysis calcd. for $C_{72}H_{116}GaN_4NaO_5$ (1210.39): C 71.44; H 9.66; N 4.63%; found: C 71.42, H 9.54, N 4.62%.

4. Conclusions

The anionic gallylene species [LGa:]·[Na(THF)₃] (**1**) demonstrates the ability to selectively activate sp^2 C–H bonds of azobenzene derivatives. The presence of electron-donating groups (–OMe, –N(Me)₂, –Me) attached to azobenzene facilitates the formation of anionic complexes **2–5**. This process involves the activation of an ortho-C–H bond within a phenyl group, followed by migration of the hydrogen atom to a nitrogen atom. We further investigated the reactions of azides RN₃ (R = 2,4,6-trimethylphenyl, 2, 6-diisopropylphenyl)

with gallylene **1**, resulting in the formation of a dianionic alkyl-amide (in **6**) or bis-amide (in **7**) ligand through intramolecular or intermolecular hydrogen atom abstraction across a transient Ga=N imide bond.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29215021/s1>, X-ray crystal structure determination details, crystal data, and DFT computations. Figures S1–S12: ^1H NMR and ^{13}C NMR spectrums of **2**–**7**. Figures S13–S18: UV–vis spectra of **2**–**7**. Figure S19: Molecular structure of **3**. Figure S20: Optimized structures of **2H**–**7H** labelled with selected bond orders. Table S1 and S2: Crystallographic data and refinement details for compounds **2**–**7**. Tables S3 and S4: Natural charges (e) of the model compounds **2H**–**7H**. DFT computations.

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Article

Ethylene/Styrene Copolymerization by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-RC}_6\text{H}_2)$ ($\text{R} = \text{H}, \text{SiEt}_3$)-MAO Catalysts: Effect of SiMe_3 Group on Cp for Efficient Styrene Incorporation

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Abstract: The synthesis and structural analysis of $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$ [$\text{OAr} = \text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-RC}_6\text{H}_2$; $\text{R} = \text{H}, \text{SiEt}_3$] revealed that it exhibits higher catalytic activities than $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$, $\text{Cp}^*\text{TiCl}_2(\text{OAr})$, with efficient comonomer incorporation in ethylene/styrene copolymerization in the presence of a methylaluminoxane (MAO) cocatalyst. The catalytic activity in the copolymerization increased upon increasing the charged styrene concentration along with the increase in the styrene content in the copolymers, whereas the activities of other catalysts showed the opposite trend. $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ displayed the most suitable catalyst performance in terms of its activity and styrene incorporation, affording amorphous copolymers with styrene contents higher than 50 mol% (up to 63.6 mol%) and with random styrene incorporation confirmed by ^{13}C -NMR spectra.

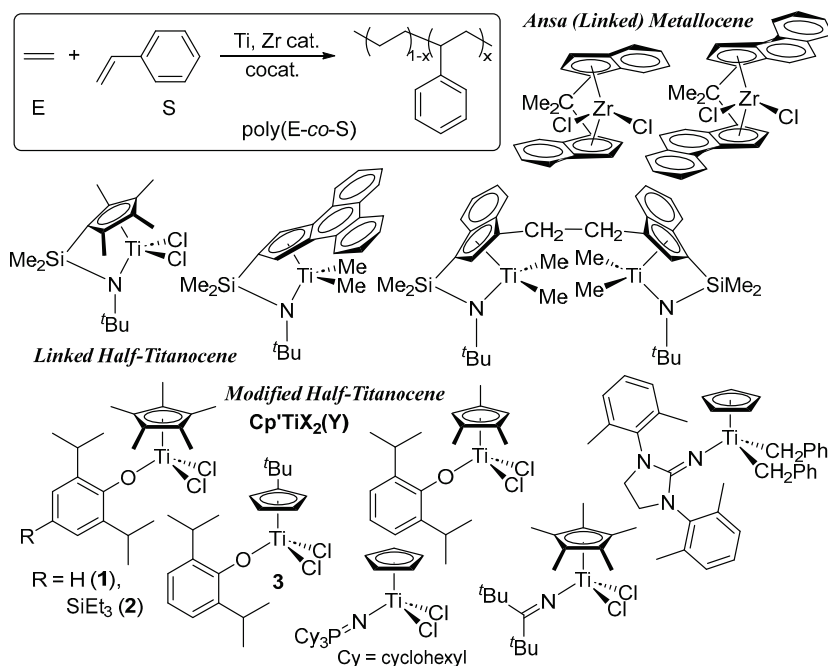
Keywords: titanium; catalyst; homogeneous catalyst; copolymerization; half-titanocene; ethylene; styrene; ligand effect; cyclopentadienyl

1. Introduction

Olefin coordination polymerization using transition metal catalysts is the core technology for the production of polyolefins, and the development of new polymeric materials, especially copolymers consisting of ethylene or propylene with monomers which have never been used by conventional catalysts (Ziegler–Natta, metallocene catalysts, etc.), is a long-term interest in this research field. Catalyst development has been considered to play an important key role in the success of this research area [1–10]. Ethylene copolymers with aromatic vinyl monomers exemplified as ethylene/styrene copolymers are known to be interesting materials whose thermo-mechanical and viscoelastic properties can be modified through the incorporation of a comonomer (styrene) [11]. Half-titanocene complexes [5–9,11–28] have been known as efficient catalysts in terms of having a better capacity for styrene incorporation than ordinary metallocene catalysts [11,29,30].

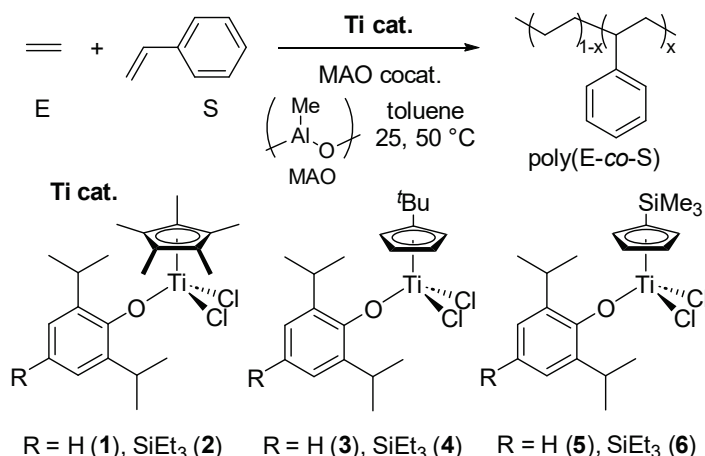
Linked (*ansa*) half-titanocenes (called “constrained geometry type”) [5–7,12–19], certain *ansa*-metallocenes [29,30], and non-bridged modified half-titanocenes (exemplified in Scheme 1) [20–28] are known to be effective transition metal catalysts in ethylene/styrene copolymerization [11]. In particular, the bimetallic linked half-titanocene, $(\text{CH}_2\text{CH}_2)[\text{Me}_2\text{Si}(\text{indenyl})(\text{N}^t\text{Bu})\text{TiMe}_2]_2$ [17,19], and the phenoxide-modified half-titanocene, $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}' = ^t\text{BuC}_5\text{H}_4$ (**3**), 1,2,4- $\text{Me}_3\text{C}_5\text{H}_2$] [20,21], have been recognized as effective catalysts in terms of the synthesis of copolymers with high styrene contents (>50 mol%) [17,19–21]. The resultant copolymers with high styrene contents (ca. >30 mol%) are amorphous, and the glass transition temperature (T_g) increases with the increase in the styrene content (shown below) [21]. However, as described above, catalysts affording

copolymers with high styrene contents (especially >50 mol%) are still limited. Moreover, these phenoxide-modified catalysts (shown above) also exhibited remarkable catalytic activities for syndio-specific styrene polymerization [20,31], whereas the bimetallic linked half-titanocene gave atactic polystyrene [17]. In contrast, the C_5Me_5 (Cp^*) analogues, $Cp^*TiCl_2(O-2,6-iPr_2-4-RC_6H_2)$ [$R = H$ (**1**), $SiEt_3$ (**2**), Scheme 1], exhibited remarkable catalytic activities for ethylene copolymerization with α -olefins [3,8,9]; the $SiEt_3$ analogue (**2**) was effective for ethylene copolymerization with alken-1-ol [32]. These results also suggest that modification of the cyclopentadienyl fragment plays a role in the success of efficient catalysts for the desired ethylene copolymerization [3,8,9]; an introduction of the $SiEt_3$ group would lead to higher activity as a result of better π -donation [32].



Scheme 1. Selected titanium and zirconium catalysts for ethylene/styrene copolymerization.

In this paper, we focus on the phenoxide-modified half-titanocene catalysts for ethylene/styrene copolymerization. We recently realized that the complexes containing the trimethylsilyl-cyclopentadienyl ligand, $(Me_3SiC_5H_4)TiCl_2(O-2,6-iPr_2C_6H_3)$, showed better catalyst performance than the *tert*- BuC_5H_4 analogue (**3**) [20,21] in the copolymerization. We thus herein report our results concerning the synthesis of $(Me_3SiC_5H_4)TiCl_2(O-2,6-iPr_2-4-RC_6H_2)$ [$R = H$ (**5**), $SiEt_3$ (**6**)] and its use as a catalyst for ethylene/styrene copolymerization in the presence of a methylaluminoxane (MAO) cocatalyst (Scheme 2).



Scheme 2. Ethylene/styrene copolymerization by phenoxide-modified half-titanocene catalysts.

2. Results and Discussion

2.1. Synthesis and Structural Analysis of $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ ($\text{R} = \text{H}$, SiEt_3)

The phenoxide-modified half-titanocenes containing the $\text{Me}_3\text{SiC}_5\text{H}_4$ ligand, $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ [$\text{R} = \text{H}$ (**5**), SiEt_3 (**6**)] were prepared according to the previous report by treating $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_3$ [33,34] with $\text{Li}(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ or $2,6\text{-}i\text{Pr}_2\text{-}4\text{-SiEt}_3\text{-C}_6\text{H}_2\text{OH}$ (in the presence of NEt_3) in diethyl ether. $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-SiEt}_3\text{-C}_6\text{H}_2)$ (**4**) was also prepared in the same manner (as described in the Experimental Procedures Section). These complexes were identified by NMR spectra and elemental analysis, and the structures of **5** and **6** were determined by X-ray crystallography (Figure 1, CCDC 2378274, 2378275; the table for the crystal data and the collection parameters are shown in the Supplementary Material). The selected bond distances and angles are summarized in Table 1. The data for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ [$\text{R} = \text{H}$ (**1**) [35], SiEt_3 (**2**) [32]] and $\text{CpTiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**7**) [35] are inserted for comparison.

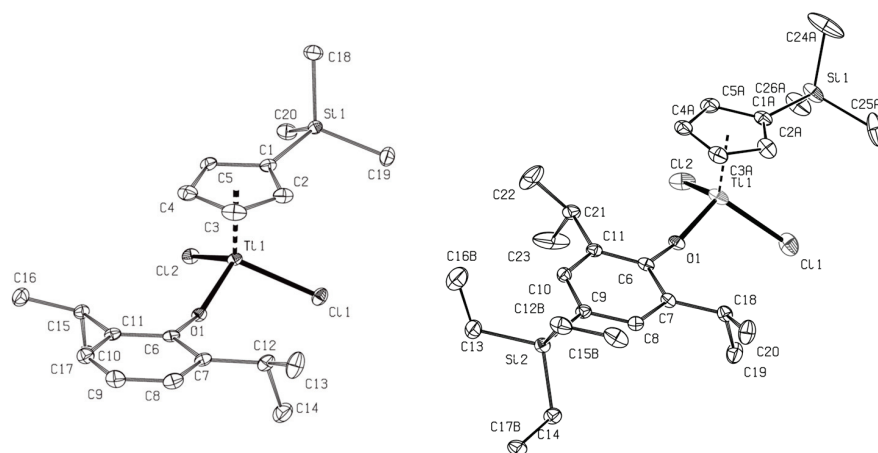


Figure 1. ORTEP drawings for $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ [$\text{R} = \text{H}$ (**5**, left), SiEt_3 (**6**, right)]. Thermal ellipsoids are drawn at 30 % probability level, and hydrogen atoms are omitted for clarity. Additional data including crystal data and collection parameters for structural analysis are shown in Supplementary Material.

Table 1. Selected bond distances (Å) and angles (°) in $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ [$\text{R} = \text{H}$ (**5**), SiEt_3 (**6**)], ^a $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ [$\text{R} = \text{H}$ (**1**) [35], SiEt_3 (**2**) [32]], and $\text{CpTiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**7**) [35] ^a.

	1 ^b	2 ^c	5	6	7 ^b
Bond Distances (Å)					
Ti(1)–Cl(1)	2.305(2)	2.2723(9)	2.2660(5)	2.2721(15)	2.262(1)
Ti(1)–Cl(2)	2.239(2)	2.2677(8)	2.2730(5)	2.2534(14)	2.262(1)
Ti(1)–O(1)	1.772(3)	1.7965(19)	1.7829(13)	1.773(2)	1.760(4)
Si(1)–C(1)	—	1.875(3)	1.876(2)	1.864(7)	—
O(1)–C(6)	1.367(5)	1.363(3)	1.373(2)	1.375(4)	1.368(4)
Ti(1)–C(1)	2.365(7)	2.403(3)	2.3678(17)	2.373(13)	2.282(8)
Ti(1)–C(2)	2.438(7)	2.411(3)	2.3854(19)	2.323(9)	2.299(5)
Ti(1)–C(3)	2.365(7)	2.359(3)	2.348(2)	2.325(8)	2.235(5)
Ti(1)–C(4)	2.311(7)	2.345(3)	2.335(2)	2.390(6)	2.235(5)
Ti(1)–C(5)	2.317(4)	2.357(3)	2.330(2)	2.398(8)	2.299(5)
Bond Angles (°)					
Cl(1)–Ti(1)–Cl(2)	103.45(5)	102.33(3)	105.11(2)	103.74(5)	104.23(7)
Cl(1)–Ti(1)–O(1)	99.1(2)	100.97(7)	102.92(4)	102.31(10)	102.53(9)
Cl(2)–Ti(1)–O(1)	104.1(2)	103.24(7)	102.52(4)	103.04(9)	102.53(9)
Ti(1)–O(1)–C(6)	173.0(3)	174.62(19)	151.41(12)	157.0(2)	163.0(4)

^a CCDC2378274 (complex **5**) and CCDC2378275 (complex **6**) contain the supplementary crystallographic data in detail. ^b Cited from reference 35. ^c Cited from reference 32.

The analyses revealed that these complexes fold a distorted tetrahedral geometry around titanium, and no significant differences are observed in Ti–Cl, Ti–O, and O–C

(phenyl) bond distances among these complexes. It seems that Ti–C(1) and Ti–C(2) in **5** [2.3678(17), 2.3854(19) Å] and Ti–C(4) and Ti–C(5) in **6** [2.390(6), 2.398(8) Å] are rather longer than the others in the cyclopentadienyl ligands, and these results might lead to an assumption that the cyclopentadienyl group would be coordinated as η^3 -fashion. However, these phenomena were also seen in complexes **1** [2.438(7) Å in Ti–C(2)] [35], **2** [2.403(3), 2.411(3) Å in Ti–C(1) and Ti–C(2)] [32], and even **7** [2.299(5) Å in Ti–C(2) and Ti–C(5)] [35]. Therefore, it seems more likely that the observed fact could be probably due to crystal packing in the crystallographic analysis. It was revealed that the Ti(1)–O(1)–C(6 in phenyl) angles in **5** [151.41(12)°] and **6** [157.0(2)°] are apparently smaller than those in **1** and **2** [173.0(3), 174.62(19)°, respectively] [32,35] and **7** [163.0(4)°] [35], suggesting that these complexes (**5,6**) show an inferior π -donation capability from the phenoxide ligand.

2.2. Ethylene/Styrene Copolymerization by $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-4-RC}_6\text{H}_2)$ [$\text{Cp}' = \text{Cp}^*, {}^t\text{BuC}_5\text{H}_4, \text{Me}_3\text{SiC}_5\text{H}_4$, $\text{R} = \text{H}$, SiEt_3]-MAO Catalyst Systems

Table 2 summarizes the results of the ethylene/styrene copolymerization using a series of phenoxide-modified half-titanocene catalysts, $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-4-RC}_6\text{H}_2)$ [$\text{Cp}' = \text{Cp}^*, \text{R} = \text{H}$ (**1**), SiEt_3 (**2**); $\text{Cp}' = {}^t\text{BuC}_5\text{H}_4$, $\text{R} = \text{H}$ (**3**), SiEt_3 (**4**); $\text{Cp}' = \text{Me}_3\text{SiC}_5\text{H}_4$, $\text{R} = \text{H}$ (**5**), SiEt_3 (**6**)] in the presence of an MAO cocatalyst. MAO was used as the white solid (d-MAO) after the removal of AlMe_3 and toluene from the commercially available samples [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co., Shunan, Japan], because the use of MAO is quite effective for obtaining high-molar-mass polymers efficiently, as shown in the previous reports [8,9,20,21,28,32,35]. The resultant polymers usually contained atactic polystyrene generated by MAO itself, and the polymer yields were described after the removal of atactic polystyrene through extraction with acetone (see Experimental Procedures). As shown in Table 2, the contents (atactic polystyrene) were negligible in most cases (>99%), except when the copolymerization runs were conducted by the Cp^* analogues (**1,2**) under high initial styrene concentrations (runs 2–6) due to low catalytic activities (low copolymer yields). These copolymerization runs were terminated after 10 min to control the comonomer (styrene) conversion so it was less than 10% in order to obtain copolymers with uniform compositions. For instance, the styrene conversions in runs 7–15 are 10%, 6.4%, 3.2%, 4.6%, 2.8%, 1.3%, 7.9%, 7.2%, and 6.5%, respectively.

Table 2. Ethylene copolymerization with styrene (St) by $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-4-RC}_6\text{H}_2)$ [$\text{Cp}' = \text{Cp}^*, \text{R} = \text{H}$ (**1**), SiEt_3 (**2**); $\text{Cp}' = {}^t\text{BuC}_5\text{H}_4$, $\text{R} = \text{H}$ (**3**), SiEt_3 (**4**); $\text{Cp}' = \text{Me}_3\text{SiC}_5\text{H}_4$, $\text{R} = \text{H}$ (**5**), SiEt_3 (**6**)]-MAO catalyst systems (ethylene 4 atm, 20 °C, 10 min) ^a.

Run	cat.	St /mL	Yield ^b /mg	Activity ^b	THF Soluble Fraction				
					cont. ^c /wt.%	$M_n^d \times 10^{-4}$	M_w/M_n	T_g^e / ^o C	St ^f /mol%
1	1	3	60.0	720	97	16.7	1.66	−18.5	18.8
2	1	5	50.6	610	90	13.5	1.32	−6.6	27.5
3	1	10	39.5	470	86	6.86	1.26	15.0	42.6
4	2	3	32.4	390	96	9.23	1.65	−15.3	20.6
5	2	5	23.5	280	95	9.91	1.41	−10.8	25.4
6	2	10	19.2	230	93	7.38	1.14	10.7	40.3
7	3	3	429	5150	>99	4.65	1.51	6.6	32.3
8	3	5	406	4870	>99	3.98	1.48	27.6	40.5
9	3	10	371	4450	>99	3.34	1.87	31.0	51.1
10	4	3	197	2360	>99	14.7	1.81	11.4	32.3
11	4	5	180	2160	>99	6.76	1.51	22.2	38.1
12	4	10	154	1850	>99	5.28	2.05	29.5	46.8
13	5	3	323	3880	>99	5.18	1.58	14.2	35.0
14	5	5	450	5400	>99	4.65	1.76	23.2	41.3
15	5	10	723	8680	>99	3.82	1.70	38.9	54.2
16	6	3	361	4330	>99	10.9	1.80	15.3	36.6
17	6	5	411	4930	98	12.8	1.79	30.9	44.9
18	6	10	506	6070	96	8.78	1.71	41.3	55.6

^a Reaction conditions: catalyst 0.50 μmol , toluene and styrene total 30.0 mL, d-MAO 3.0 mmol, 20 °C, ethylene 4 atm, 10min. ^b Activity in kg polymer/mol-Ti·h, polymer yield in acetone insoluble and THF soluble fraction.

^c Percentage (wt%) in acetone insoluble and THF soluble fraction (after removal of atactic polystyrene). ^d GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^e Glass transition temperature (T_g) measured by DSC thermograms. ^f Styrene content in mol% estimated by ^1H NMR spectra in 1,1,2,2-tetrachloroethane- d_2 at 110 °C.

As reported previously [20,21], the *tert*-BuC₅H₄ analogue (3) showed higher catalytic activities than the Cp* analogue (1), and the activity based on the polymer yield decreased with the increase in the initial charged styrene concentration along with the decrease in the *M_n* values (runs 1–3 vs. runs 7–9). The resultant copolymers were amorphous and possessed uniform compositions, confirmed by DSC thermograms [observed as a sole glass transition temperature (*T_g*)]; their uniform compositions were also confirmed previously by GPC–FT-IR and cross-fractionation (CFC) analyses [21]. The *T_g* value increased with the increasing styrene content (estimated by ¹H NMR spectra according to the reported procedure) [20,21]. It was revealed that the introduction of the SiEt₃ group into the *para*-position in the phenoxide led to a decrease in the catalytic activities. The activities of 2 and 4 were lower than those of 1 and 3, respectively, whereas no remarkable differences were observed in the molecular weight and the styrene contents in the copolymers. There was an opposite trend in the ethylene copolymerization with α -olefin, 2-methyl-1-pentene reported previously for 1 and 2 [32], although we are not sure of the reason for this at this moment. As shown in Table S2 (Supplementary Materials), as reported previously for 1 and 3,²¹ the catalytic activities based on the polymer yields decreased upon the addition of styrene.

It should be noted that the Me₃SiC₅H₄ analogue (5) showed higher catalytic activity than the others (1–4), and the styrene contents in the copolymers were close to those produced by the *tert*-BuC₅H₄ analogue (3) under the same conditions (Table 2, Figure 2). Note that the activity by 5 increased upon increasing the charged styrene concentration along with the increase in the styrene content in the resultant copolymers (runs 13–15, Figure 2); the *M_n* value in the resultant copolymer decreased with the increase in the styrene content. Similarly to the observed trend for 2 and 4, the introduction of the SiEt₃ group into the *para*-position in the phenoxide (6) led to a decrease in the catalytic activities (runs 16–18). As observed in the copolymerization by 5, the activity of 6 also increased upon increasing the charged styrene concentration along with the increase in the styrene content in the copolymers. It seems that the *M_n* values in the copolymers prepared with 6 were higher than those prepared with 5.

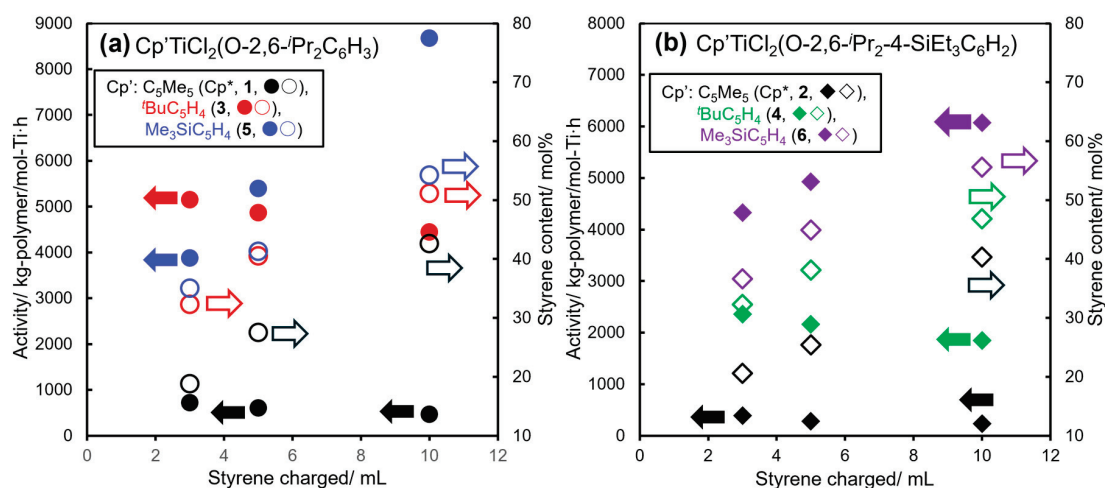


Figure 2. The effect of the cyclopentadienyl fragment on the catalytic activity and the styrene contents of the copolymers in ethylene/styrene copolymerization by Cp*TiCl₂(O-2,6-*i*-Pr₂-4-RC₆H₂) [Cp* = Cp*, R = H (1), SiEt₃ (2); Cp* = ^tBuC₅H₄, R = H (3), SiEt₃ (4); Cp* = Me₃SiC₅H₄, R = H (5), SiEt₃ (6)]–MAO catalyst systems. The detailed data are shown in Table 2. The filled circle or square (arrows) expresses activity and the others express the styrene contents.

Table 3 summarizes the results of the ethylene/styrene copolymerization by 5 and 6 under various conditions (temperature, ethylene pressure). The activity of 5 was affected by the ethylene pressure employed (runs 13, 19, and 28) and increased upon increasing the ethylene pressure along with the decrease in the styrene content in the resultant copolymer. A decrease in the catalyst concentration (0.50 → 0.30 μmol) did not affect the activity, the

M_n values, and the styrene content in the copolymers (runs 13–15, 20–22). The styrene content in the copolymers reached to 63.6 mol% when the copolymerization was conducted under high styrene and low ethylene concentration conditions (run 29). Unfortunately, the activities conducted at 50 °C (runs 23–27) were low compared to those conducted at 20 °C (runs 13–15), and the resultant copolymers possessed low M_n values compared to those conducted at 20 °C. A similar trend was also observed in the copolymerization using the 6-MAO catalyst system (runs 30–33 vs. runs 16–18), whereas the M_n values in the copolymers were higher than those prepared with 5 under the same conditions. As shown in Figure 3, a linear correlation between the T_g values with the styrene contents in the copolymers was observed, as seen in a previous report [11].

Table 3. Ethylene (E) copolymerization with styrene (St) by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2-4\text{-RC}_6\text{H}_2)$ [R = H (5), SiEt_3 (6)]-MAO catalyst systems: effect of ethylene pressure, styrene concentration, and temperature ^a.

Run	cat.	E (μmol)	St (μmol)	temp. (°C)	Yield ^b (mg)	Activity ^b (kg polymer/mol-Ti-h)	THF Soluble Fraction				
							cont. ^c /wt. %	M_n ^d $\times 10^{-4}$	M_w/M_n ^d	T_g ^e /°C	St ^f /mol %
19	5 (0.50)	6	3	20	556	6670	97	9.12	1.88	2.0	29.9
13	5 (0.50)	4	3	20	323	3880	99	5.18	1.58	14.2	35.0
14	5 (0.50)	4	5	20	450	5400	99	4.65	1.76	23.2	46.6
15	5 (0.50)	4	10	20	723	8680	>99	3.82	1.70	38.9	54.2
20	5 (0.30)	4	3	20	192	3840	>99	5.35	1.76	11.4	34.7
19	5 (0.50)	6	3	20	556	6670	97	9.12	1.88	2.0	29.9
21	5 (0.30)	4	5	20	223	4460	99	4.78	1.68	25.7	41.0
22	5 (0.30)	4	10	20	264	5280	>99	4.04	1.80	40.2	54.3
23	5 (0.50)	4	3	50	162	1940	97	2.24	1.61	18.1	38.9
24 ^g	5 (0.50)	4	3	50	110	1320	95	1.96	1.43	14.7	39.4
25 ^h	5 (0.50)	4	3	50	185	2220	97	2.48	1.43	17.4	40.6
26	5 (0.50)	4	5	50	199	2390	90	1.46	1.70	29.3	50.0
27	5 (0.50)	4	10	50	229	2750	86	1.08	1.63	40.6	56.5
28	5 (0.50)	2	3	20	177	2120	>99	4.45	1.47	33.0	52.6
29	5 (0.50)	2	10	20	243	2920	98	1.17	1.90	48.5	63.6
30	6 (0.50)	6	3	20	349	7000	99	20.2	1.99	2.6	27.2
16	6 (0.50)	4	3	20	361	4330	>99	10.9	1.80	15.3	36.6
17	6 (0.50)	4	5	20	411	4930	98	12.8	1.79	30.9	44.9
18	6 (0.50)	4	10	20	506	6070	96	8.78	1.71	41.3	55.6
31	6 (0.50)	4	3	50	217	2610	96	3.84	1.64	18.1	38.8
32	6 (0.50)	4	5	50	291	3490	96	3.18	2.04	32.7	46.6
33	6 (0.50)	4	10	50	359	4310	83	2.95	2.04	44.7	55.1

^a Reaction conditions: toluene and styrene total 30.0 mL, d-MAO 3.0 mmol, 10 min. ^b Activity in kg polymer/mol-Ti-h, polymer yield in acetone insoluble and THF soluble fraction. ^c Percentage (wt%) in acetone insoluble and THF soluble fraction (after removal of atactic polystyrene). ^d GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^e Glass transition temperature (T_g) measured by DSC thermograms. ^f Styrene content in mol% estimated by ^1H NMR spectra in 1,1,2,2-tetrachloroethane- d_2 at 110 °C. ^g MAO 1.0 mmol. ^h MAO 2.0 mmol.

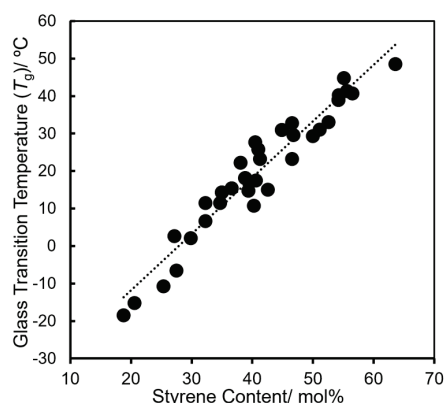


Figure 3. Plots of the glass transition temperature (T_g /°C) versus the styrene content (mol%) in the copolymers estimated by ^1H NMR spectra (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C). The plots were made on the basis of the copolymerization data by catalysts 1–6 in the presence of MAO cocatalyst.

Figure 4 shows a typical ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane- d_2 at 110 °C) in the ethylene/styrene copolymer prepared by the 5-MAO catalyst system (run 13, styrene 35.0 mol%). As reported previously for catalysts 1 and 3 [11,20,21], the resonances corresponding to styrene head-to-tail incorporation and SES or SS ($S_{\beta\beta}$, tail-to tail, called pseudo random) were observed in addition to the resonances ascribed to isolated and alternating styrene incorporation (depicted in Figure 4). These results clearly suggest that styrene incorporation was random in this catalysis. No significant differences in the spectra were observed in the resultant copolymers prepared with 6 (the additional data are shown in the Supplementary Material).

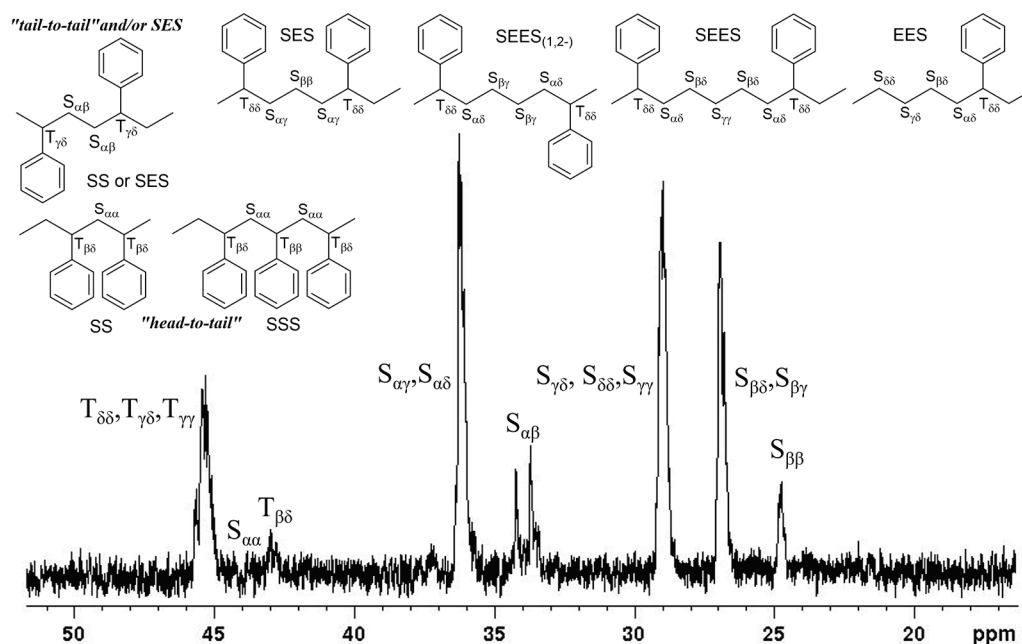


Figure 4. ^{13}C NMR spectrum (in $\text{C}_2\text{D}_2\text{Cl}_4$ at 110 °C, methylene and methine region) of poly(ethylene-co-styrene) prepared by $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (5)-MAO catalyst system; styrene content of 35.0 mol% (run 13).

3. Conclusions

We have demonstrated that newly prepared $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$ [$\text{OAr} = \text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_2$; $\text{R} = \text{H}$ (5), SiEt_3 (6)] exhibited higher catalytic activities than $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$, $\text{Cp}^*\text{TiCl}_2(\text{OAr})$, with efficient comonomer incorporation, in ethylene/styrene copolymerization in the presence of an MAO cocatalyst at 20 °C. The catalytic activity in the copolymerization increased upon increasing the charged styrene concentration along with the increase in the styrene content in the copolymers, whereas the activities of other catalysts showed the opposite trend. Catalyst 5 showed the most suitable catalyst performance in terms of its activity and styrene incorporation, affording amorphous copolymers containing styrene contents higher than 50 mol% (up to 63.6 mol%) with random styrene incorporation. The unique characteristics observed in 5 should be helpful for further designing efficient molecular catalysts for the synthesis of new polyolefins and should provide a new idea for the metal-catalyzed polymerization of various monomers.

4. Materials and Methods

General. All experiments were conducted under a nitrogen atmosphere unless otherwise specified. Anhydrous-grade toluene (Kanto Chemical Co., Inc., Tokyo, Japan) containing a mixture of molecular sieves (3 Å 1/16 and 4 Å 1/8, and $13 \times 1/16$) was stored in a dry box, and styrene (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was stored under nitrogen in a freezer in the dry box and passed through an alumina short column before use. Ethylene (polymerization grade, purity > 99.9%; Sumitomo Seika Co.,

Ltd., Osaka, Japan) was used as received. According to previous reports [20,21,28,32,35], toluene and AlMe_3 in the commercially available MAO solution [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C and completion for 1 h at >100 °C) to afford an AlMe_3 -free MAO white solid (d-MAO) as the cocatalyst employed in this study. $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)$ [$\text{Cp}^*=\text{Cp}^*$ (1), $^t\text{BuC}_5\text{H}_4$ (3)] [35] and $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-SiEt}_3\text{-C}_6\text{H}_2)$ (2) [32] were prepared according to previous reports. TMAO-S generates flammable gases upon exposure to water and/or air, and should be kept under an inert atmosphere.

All ^1H and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer (Bruker 500.13 MHz for ^1H , 125.77 MHz for ^{13}C , Billerica, MA, USA), and chemical shifts are given in ppm and are referenced to SiMe_4 . All spectra for the analysis of the titanium complexes were obtained in the solvent indicated at 25 °C, and the resultant poly(ethylene-co-styrene)s were prepared by dissolving them in 1,1,2,2-tetrachloroethane- d_2 and were measured at 110 °C. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (90° pulse angle) were measured with the conditions of a pulse interval of 5.2 s and an acquisition time of 0.8 s; number of the transients in the analysis was accumulated, ca. 6000. Gel permeation chromatography (GPC) was performed to estimate the molecular weights (M_w , M_n) and their distributions, and the analysis was conducted by using Tosoh HLC-8321GPC/HT (at 140 °C) in *ortho*-dichlorobenzene (containing 0.05 wt% 2,6-di-*tert*-butyl-*p*-cresol) as the eluent. The molecular weight was estimated with a calibration curve by using polystyrene standard samples. Thermal properties in the resultant poly(ethylene-co-styrene)s were analyzed by differential scanning calorimetric (DSC) thermograms (Hitachi DSC-7000X, Hitachi High-Tech Corp. Tokyo, Japan) under nitrogen atmosphere. The analysis of the copolymer samples was conducted upon heating from −100 to 250 °C at 20 °C/min, after preheating from 30 to 250 °C (20 °C/min) and cooling to −100 °C (10 °C/min). In this heating scan, the melting temperature (T_m) and the glass transition temperature (T_g) were chosen from the middle of the phase transition.

Preparation of $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-4-SiEt}_3\text{C}_6\text{H}_2)$ (4). An Et_2O solution (5.0 mL) containing 2,6- $^i\text{Pr}_2\text{-4-SiEt}_3\text{-C}_6\text{H}_2\text{OH}$ (292 mg, 1.0 mmol) and Et_3N (152 mg, 1.5 mmol) was added into an Et_2O (20 mL) solution of $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_3$ (233 mg, 0.85 mmol) in one portion at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et_2O . The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange oil. The resultant oil was then dissolved in a small amount of *n*-hexane. The chilled (−30 °C) solution in the freezer gave orange microcrystals (yield: 76%). ^1H NMR (500 MHz, CDCl_3): δ = 7.20 (s, 2H, Ar-H), δ = 6.82 (t, 2H, J = 2.8 Hz, Cp-H), δ = 6.23 (t, 2H, J = 2.8 Hz, Cp-H), δ = 3.30–3.22 (m, 2H, Ar-CH(CH_3) $_2$), δ = 1.44 (s, 9H, Cp-C(CH_3) $_3$), δ = 1.23 (d, 12H, J = 6.9 Hz, Ar-CH(CH_3) $_2$), δ = 0.99 (t, 9H, J = 7.9 Hz, Ar-SiCH $_2$ CH $_3$), δ = 0.78 (q, 6H, J = 7.9 Hz, Ar-SiCH $_2$ CH $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 165.4, 151.4, 137.2, 133.3, 129.3, 119.3 (Aromatic group), δ = 34.2 (Cp-C(CH_3) $_3$), δ = 31.0 (Cp-C(CH_3) $_3$), δ = 27.0 (Ar-CH(CH_3) $_2$), δ = 23.9 (Ar-CH(CH_3) $_2$), δ = 7.66 (−SiCH $_2$ CH $_3$), δ = 3.73 (−SiCH $_2$ CH $_3$).

Preparation of $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)$ (5). $\text{Li}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (221 mg, 1.2 mmol) was added in one portion to an Et_2O solution (30 mL) containing $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_3$ (350 mg, 1.2 mmol) precooled at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et_2O . The combined filtrate and the wash were taken to dryness under reduced pressure to give orange solids. The resultant solids were then dissolved in a minimum amount of dichloromethane layered by a small amount of *n*-hexane. The chilled (−30 °C) solution in the freezer gave orange microcrystals (yield: 82%). ^1H NMR (500 MHz, CDCl_3): δ = (d, 2H, J = 7.8 Hz, Ar-H), δ = (t, 1H, J = 7.2 Hz, Ar-H), δ = 7.04 (t, 2H, J = 1.9 Hz, Cp-H), δ = 6.40 (t, 2H, J = 2.2 Hz, Cp-H), δ = 3.27–3.19 (m, 2H, Ar-CH(CH_3) $_2$), δ = 1.23 (d, 12H, J = 6.8 Hz, Ar-CH(CH_3) $_2$), δ = 0.40 (s, 9H, Cp-Si(CH_3) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 164.7, 138.3, 136.9, 127.9, 124.5, 123.5, 122.6 (Aromatic group), δ = 27.1

(Ar-CH(CH₃)₂), δ = 23.7 (Ar-CH(CH₃)₂), δ = −0.43 (−Si(CH₃)₃). EA: Found. C 55.52%, H 7.02%; Calcd. for C₂₀H₃₀Cl₂OSiTi: C 55.44%, H 6.98%.

Preparation of (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*Pr₂-4-SiEt₃C₆H₂) (6). An Et₂O solution (5.0 mL) containing 2,6-*i*Pr₂-4-SiEt₃-C₆H₂OH (292 mg, 1.0 mmol) and Et₃N (152 mg, 1.5 mmol) was added in one portion into an Et₂O solution (20 mL) containing (Me₃SiC₅H₄)TiCl₃ (262 mg, 0.9 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et₂O. The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange oil. The oil was then dissolved in a small amount of *n*-hexane, and the chilled (−30 °C) solution in the freezer gave orange microcrystals (yield: 75%). ¹H NMR (500 MHz, CDCl₃): δ = 7.20 (s, 2H, Ar-*H*), δ = 7.04 (t, 2H, *J* = 2.3 Hz, Cp-*H*), δ = 6.43 (t, 2H, *J* = 2.3 Hz, Cp-*H*), δ = 3.27–3.19 (m, 2H, Ar-CH(CH₃)₂), δ = 1.23 (d, 12H, *J* = 6.8 Hz, Ar-CH(CH₃)₂), δ = 0.99 (t, 9H, *J* = 7.9 Hz, Ar-SiCH₂CH₃), δ = 0.78 (q, 6H, *J* = 7.9 Hz, Ar-SiCH₂CH₃), δ = 0.40 (s, 9H, Cp-Si(CH₃)₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 165.5, 137.1, 136.8, 133.4, 129.3, 127.9, 122.5 (Aromatic group), δ = 27.0 (Ar-CH(CH₃)₂), δ = 23.8 (Ar-CH(CH₃)₂), δ = 7.66 (−SiCH₂CH₃), δ = 3.74 (−SiCH₂CH₃), δ = −0.43 (−Si(CH₃)₃). EA: Found. C 57.18%, H 8.005%; Calcd. for C₂₆H₄₄C₁₂OSi₂Ti: C 57.03%, H 8.100%.

Typical Reaction Procedure for Ethylene Copolymerization with Styrene. A typical reaction procedure for the copolymerization of ethylene with styrene by a (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*Pr₂C₆H₃) (5)-MAO catalyst (Table 2, run 13) is as follows: Toluene (26.0 mL) and d-MAO (white solid, 174 mg, 3.0 mmol) were added into the autoclave (100 mL, stainless steel) in the dry box, and the reaction apparatus was then filled with ethylene in the fume hood. A toluene solution (1.0 mL) containing **1** was then added into the autoclave after the addition of styrene (3.0 mL), and the reaction apparatus was then immediately pressurized to the prescribed pressure employed. The mixture was stirred for 10 min, and the polymerization was terminated with the addition of MeOH. The solution was then poured into MeOH (100 mL), and the resultant polymer was adequately washed with MeOH and then dried in vacuo for several hours.

According to previous reports [20,21], the resultant polymer mixture was separated into three fractions. Atactic polystyrene prepared by MAO itself (in a cationic manner) was extracted with acetone. Poly(ethylene-*co*-styrene)s were then extracted with THF from the acetone-insoluble portion, and the polyethylene and syndiotactic polystyrene by-products were separated as the THF-insoluble fraction. The basic experimental procedure is as follows: The resultant polymer solids (after precipitation with MeOH and dried in vacuo) were added to acetone (15.0 mL) in a centrifugal sedimentation tube (50 mL, glass), and the copolymers were separated [with the removal of the atactic polystyrene formed due to MAO] as precipitates by a centrifuge. The procedure was repeated three times. The acetone-insoluble fraction was added into a centrifugal sedimentation tube containing tetrahydrofuran (THF, 15.0 mL), and the THF-soluble and THF-insoluble fractions were separated; the procedure was repeated three times. As reported previously [20,21], the resultant copolymers were soluble in THF and the amount of THF insoluble fractions was negligible in all cases. These fractions were analyzed by ¹H- and ¹³C-NMR spectra, GPC analysis, and DSC thermograms.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29184473/s1>, Crystal data and collection parameters for analysis of (Me₃SiC₅H₄)TiCl₂(O-2,6-*i*Pr₂-4-RC₆H₂) [R = H (**5**), SiEt₃ (**6**)]; ethylene polymerization data for **1–4**; selected NMR spectra of poly(ethylene-*co*-styrene)s and selected DSC thermograms in resultant poly(ethylene-*co*-styrene)s.

Author Contributions: Conceptualization, methodology, writing—original draft preparation, review, and editing, supervision, project administration, and funding acquisition, K.N.; validation, formal analysis, and investigation, T.H. and T.F. (catalyst synthesis and identification); data curation and visualization, T.H. and K.N.; crystallographic analysis, D.S. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data are contained within the article and the Supplementary Material. The crystallographic analysis data for $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-}4\text{-RC}_6\text{H}_2)$ [R = H (5), SiEt_3 (6)] are available as CCDC 2378274 and 2378275, respectively, from The Cambridge Crystallographic Data Centre (CCDC).

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Conflicts of Interest: The authors declare no conflicts of interest.

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Article

Intensive Cycloalkyl-Fused Pyridines for Aminopyridyl–Zinc–Heteroimidazoles Achieving High Efficiency toward the Ring-Opening Polymerization of Lactides

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Abstract: The model precatalyst sp^3 - and sp^2 -N dinitrogen-coordinated zinc–heteroimidazole has been used as an efficient catalyst for the ring-opening polymerization of cyclic esters. Subsequent to our exceptional active 5,6,7-trihydroquinolin-8-amine-zinc catalysts for the ring-opening polymerization (ROP) of ϵ -caprolactone, various pyridine-fused cycloalkanones (ring size from five to eight) are developed for the correspondent fused amine–pyridine derivatives and their zinc–heteroimidazole chloride complexes **Zn1–Zn8** ($LZnCl_2$) bearing *N*-diphenylphosphinoethyl pendants. Activated with two equivalents of $LiN(SiMe_3)_2$, the title zinc complexes efficiently promote the ROP of *L*-lactide (*L*-LA) in situ; among them, **Zn4**/ $2Li(NSiMe_3)_2$ catalyzed 500 equivalent *L*-LA at 80 °C with 92% conversion in 5 min (TOF: 5520 h^{-1}). Under the same conditions, the catalytic efficiency for the ROP of *rac*-LA by **Zn1–Zn8**/ $2Li(NSiMe_3)_2$ was slightly lower than that for *L*-LA (highest TOF: 4440 h^{-1}). In both cases, cyclooctyl-fused pyridyl–zinc complexes exhibited higher activity than others, while the cycloheptyl-fused zinc complexes showed the lowest activity. The microstructure analysis of the polymers showed they possessed a linear structure capped with CH_3O as major and cyclic structure as minor. In this work, all the ligands and zinc complexes were well characterized by $^1H/^{13}C/^{31}P$ NMR, FT-IR spectroscopy as well as elemental analysis.

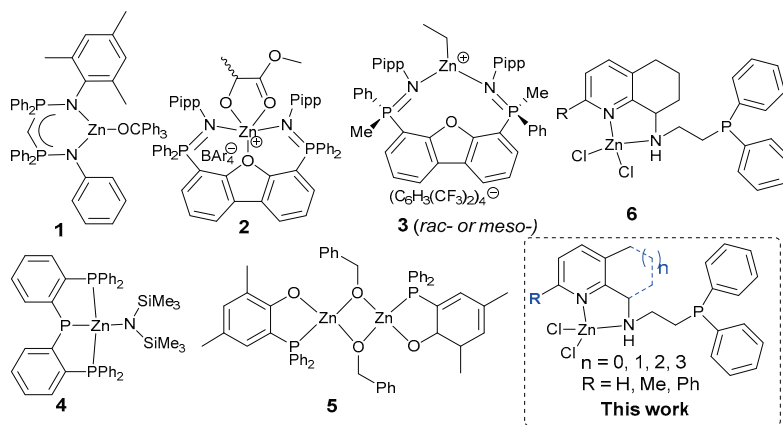
Keywords: zinc complexes; ring-opening polymerization; polylactides

1. Introduction

Aliphatic polyesters, such as polylactide (PLA) and polycaprolactone (PCL), being environment-friendly materials with good biocompatibility and biodegradability, have attracted considerable attention in the past decades [1,2]. The polycondensation of lactic acid and the ROP of lactides are two major processes in the formation of PLAs [3]. The molecular weights of the PLAs obtained through condensation are generally low, so ROP is extensively investigated for PLA production in order to take advantage of their useful properties [4]. Metal-complex precatalysts lead to the ROP of lactides(LA) with not only high efficiency but also the formation of well-defined PLAs [5–7]. Currently, tin(II) 2-ethylhexanoate is the most popular precatalyst for the industrial production of PLAs via ROP [8]; however, due to the potential cytotoxicity of tin, there are concerns about its use for PLA production, which is a limitation [9,10]. Therefore, the development of new metal complex catalysts for the ROP of LA based on non-toxic and environmental-friendly metals is in high demand [11–14]. As an essential element in the human body, as well as having

low toxicity for animals and a low cost [15,16], zinc complexes have become a promising candidate for the ROP of cyclic esters. Targeting efficient zinc catalysts for the ROP of LA, various ligands have been explored such as β -diketiminate [17–20], phenolate [21–26], Schiff bases [27–31], bis(pyrazolyl)amide [32,33], *N*-heterocyclic carbenes [34–36] and guanidines [37–39]. The stereochemical attributes of the ligands are useful factors in controlling the micro-structure and properties of the resultant PLAs [40].

As described above, the ligands of zinc-complex precatalysts commonly contain nitrogen and/or oxygen donors [17–40]. In addition, there have been a few reports on the ROP of LA with zinc complexes containing a phosphorus group. For example, zinc complex **1** (Scheme 1), including a bis(phosphinimino)methyl ligand, catalyzed 100 equivalent *rac*-LA with a > 95% conversion rate within 2 h in toluene at 60 °C [41]. A series of cationic zinc complexes (**2** and **3**, Scheme 1) supported by bis(phosphinimine) ligands performed well in the ROP of *rac*-LA [42–45]. Zinc complex **2** (Scheme 1) achieved the ROP of *rac*-LA with 90% conversion in 50 min at ambient temperature at the molar ratio of [*rac*-LA]/[**2**] = 200:1, characterized by a slightly hetero-enriched microstructure [polymer tacticity (P_r) = 0.63] [42]. Meanwhile, the cationic alkyl zinc complexes *rac*-**3** and *meso*-**3** (Scheme 1), as isolatable stereoisomers, individually catalyzed 1000 equivalent *rac*-LA monomers at 40 °C, resulting in PLAs with 89.6% conversion by *rac*-**3** in 4 h and 95.3% conversion by *meso*-**3** in 3.8 h, more importantly observing a higher molecular weight in PLA of 3.90×10^5 g/mol [45]. Moreover, zinc complex **4** (Scheme 1), bearing a diarylphosphido-diphosphine, also efficiently initiated the ROP of *L*-LA with a 91% yield in the presence of isopropyl alcohol in toluene within 20 min with [*L*-LA]/[**4**] = 200 [46]. The extensive copolymerization of *L*-LA and ϵ -caprolactone (ϵ -CL) proceeded smoothly at 110 °C for random copolymers [47]. Another P⁺O-phosphinophenolate zinc complex **5** (Scheme 1) polymerized 100 equivalents of *rac*-LA with a 97% conversion rate in CH₂Cl₂ after 2 h and showed a good capability of catalyzing the homo(co)-polymerization of *L*-LA or ϵ -CL and trimethylene carbonate (TMC), achieving PCL/PTMC-*co*-PLLA co-polymers and PTMC-*co*-PCL-*co*-PLLA terpolymers [48].



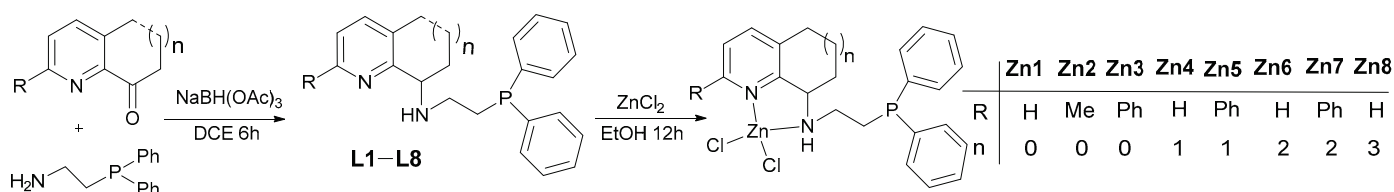
Scheme 1. Zinc complexes containing phosphorus atoms for the ROP of lactides.

Using the soft donor abilities of phosphorus-based ligands [49,50], a series of zinc complexes containing N⁺N⁺P ligands (**6**, Scheme 1) were evaluated for the ROP of ϵ -CL [51], achieving 90% conversion at high molar ratio of [ϵ -CL]/[Zn] = 5000:1 within 2 min, indicating a remarkable TOF of 1.35×10^5 h^{−1}; meanwhile, their iron analogues also performed well for the ROP of ϵ -CL (TOF up to 8.82×10^3 h^{−1}), producing high-molecular-weight PCL (M_n up to 2.43×10^5 g/mol), demonstrating an exceptional model of iron-complex precatalysts [52]. Subsequently, a series of zinc complexes bearing cycloalkyl-fused pyridines with ring sizes tuned from five to eight within their backbones are prepared and achieve good activity for the ROP of lactides (*L*-LA and *rac*-LA) under different parameters (time, temperature, solvent or molar ratio of monomer), indicating the significant influence of the ring size of fused cycloalkyls and of the R group on the ortho-position of pyridine on catalytic performance.

2. Results and Discussion

2.1. Synthesis and Characterization of L1–L8 and Their Zn (II) Complexes Zn1–Zn8

A series of ligands **L1–L8** of monocycloalkyl (ring size from five to eight)-fused pyridine-bearing pendant N-diphenylphosphinoethyl groups, N-(Ph₂PCH₂CH₂)-2-RC₇H₇N-8-NH (R = H **L1**, R = Ph **L2**, R = Me **L3**), N-(Ph₂PCH₂CH₂)-2-RC₉H₉N-8-NH (R = H **L4**, R = Ph **L5**), N-(Ph₂PCH₂CH₂)-2-RC₁₀H₁₁N-8-NH (R = H **L6**, R = Ph **L7**), N-(Ph₂PCH₂CH₂)-2-RC₁₁H₁₃N-8-NH (R = H **L8**), were prepared according to the literature (as shown in Scheme 2) [53–55]. The Zn(II) complexes **Zn1–Zn8** were obtained by treating the ligands **L1–L8** with zinc(II) chloride in ethanol at room temperature for 12 h, respectively. All novel compounds were confirmed by ¹H, ¹³C and ³¹P NMR (shown in Figures S1–S36), FT-IR spectroscopy and elemental analysis. The ³¹P NMR spectrum of ligands showed one signal around −20 ppm, while their corresponding zinc complexes showed a shift around −22 ppm. These little shifts changes in the ³¹P NMR spectra indicated little environmental change around phosphine, and also suggesting the possible dissociation of phosphine to zinc. Subsequently, the structures of **Zn2**, **Zn3**, **Zn7** and **Zn8** were further determined by single-crystal X-ray diffraction, which agreed well with their ³¹P NMR spectra.



Scheme 2. Synthesis of **L1–L8** and Zn (II) complexes **Zn1–Zn8**.

The single crystals of **Zn2**, **Zn3**, **Zn7** and **Zn8** suitable for X-ray determination were obtained by diffusing diethyl ether into a dichloromethane solution. Their crystal structures are depicted in Figures 1–4, respectively, and the selected bond lengths and angles are summarized in Table 1. The molecular structures of **Zn2**, **Zn3**, **Zn7** and **Zn8** are similar, in which the zinc is four-coordinated by two nitrogen atoms and two chlorine atoms to form a distorted tetrahedral geometry. Similar to our previous reports [51], the phosphorus donor did not coordinate to zinc, which agreed well with the little shift in its ³¹P NMR spectra.

Table 1. Selected bond lengths and angles for **Zn2**, **Zn3**, **Zn7** and **Zn8**.

	Zn2	Zn3	Zn7	Zn8
Bond lengths (Å)				
Zn1–Cl1	2.2018(5)	2.2220(6)	2.230(2)	2.2214(4)
Zn1–Cl2	2.2287(5)	2.2053(6)	2.220(2)	2.2081(4)
Zn1–N1	2.0777(15)	2.1162(16)	2.085(7)	2.0442(13)
Zn1–N2	2.1091(15)	2.0846(17)	2.080(7)	2.0920(12)
Bond angles (°)				
Cl2–Zn1–Cl1	115.75(2)	118.29(2)	116.84(10)	117.623(18)
N1–Zn1–Cl1	114.14(5)	106.87(5)	111.9(2)	117.20(4)
N1–Zn1–Cl2	111.37(5)	118.83(5)	118.9(2)	105.86(4)
N1–Zn1–N2	85.08(6)	85.86(7)	82.4(3)	82.74(5)
N2–Zn1–Cl1	113.51(5)	107.26(5)	112.7(2)	109.14(4)
N2–Zn1–Cl2	113.23(5)	114.83(5)	109.0(2)	119.54(4)

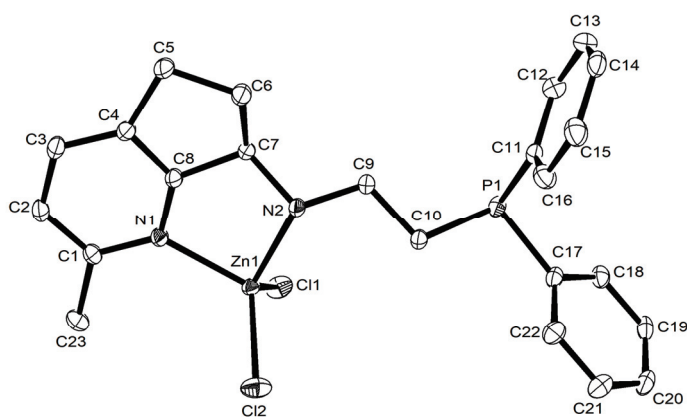


Figure 1. An ORTEP drawing of **Zn2** with thermal ellipsoids of 30% probability. All hydrogen atoms are omitted for clarity.

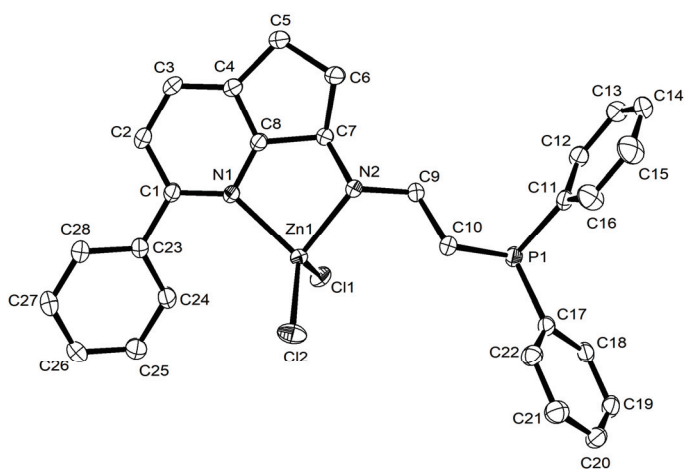


Figure 2. An ORTEP drawing of **Zn3** with thermal ellipsoids of 30% probability. All hydrogen atoms are omitted for clarity.

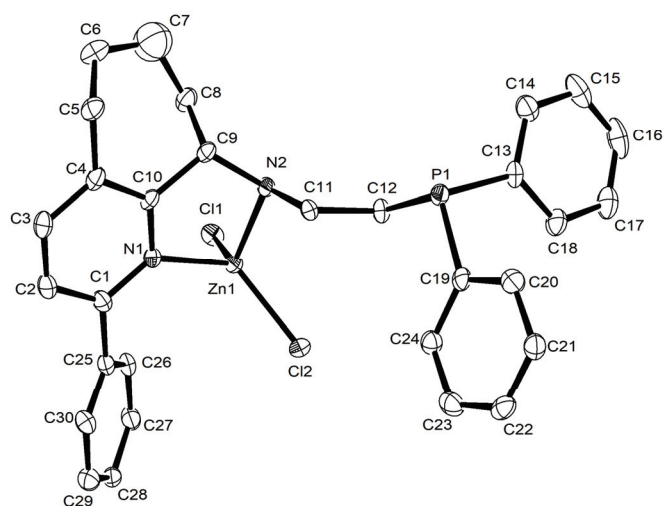


Figure 3. An ORTEP drawing of **Zn7** with thermal ellipsoids of 30% probability. All hydrogen atoms are omitted for clarity.

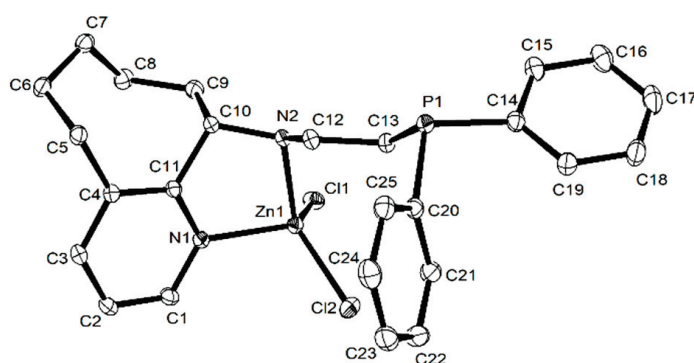


Figure 4. An ORTEP drawing of **Zn8** with thermal ellipsoids of 30% probability. All hydrogen atoms are omitted for clarity.

The bond distances between the Zn (II) and Cl atoms vary between 2.2018(5) and 2.230(2) Å and the Zn-N bond lengths vary between 2.0442(13) and 2.1162(16) Å. Notably, the bond lengths of the Zn-Cl bond are longer than those of the Zn-N bond, which is in accordance with previous reports [56,57]. As shown in Table 1, the bond length of the Zn-NH bond is longer than that of the Zn-N_{quinoline} bond in both the **Zn2** and **Zn8** structures [2.1091(15) vs. 2.0777(15); 2.0920(12) vs. 2.0442(13) Å], indicating more effective coordination by N_{quinoline} than NH; On the contrary, the bond length of Zn-NH in **Zn3** and **Zn7** is shorter than that of Zn-N_{quinoline}. The different bond lengths between Zn-NH and Zn-N_{quinoline} indicate that the size of substituents and rings influence the molecular structure of the zinc complexes.

The R substituent and fused ring size also greatly affect the structure. For **Zn3**, **Zn5** and **Zn7**, all bearing the same R substituent of phenyl, the dihedral angle between the phenyl ring and pyridine plane is 26.49° in **Zn3** (five-ring), which is much smaller than that (43.07°) in **Zn7** (seven-ring) and that (48.74°) in **Zn5** (six-ring) [51], suggesting the great influence of cycloalkyl ring size. Another interesting observation is that, due to the torsion of different cycloalkyls, the distance from N(H) and P to the pyridine plane varied, as shown by 0.440 Å and 0.537 Å in **Zn3**, 0.703 Å and 1.365 Å in **Zn5** and 0.471 Å and −3.918 Å in **Zn7**, respectively, suggesting the increased distortion of the **Zn7** structure. In addition, regarding the distortion of the rings, the carbon C6 atoms of the cycloalkyl deviate from the pyridyl-based plane with a distance of 0.408 Å for **Zn2**, 0.348 Å for **Zn3**, 1.340 Å for **Zn7** and 1.400 Å for **Zn8**. These different distortions will have an effect on their catalytic activity.

2.2. Ring-Opening Polymerization (ROP) of L-LA by **Zn1-Zn8**/2LiN(SiMe₃)₂

In the beginning, **Zn6** was tested for the ROP of L-LA without any additional initiator, but there was no activity observed, considered the result of the stability of the Zn-Cl bond. According to our previous work [51], a binary system consisting of zinc complexes and two equivalents of LiN(SiMe₃)₂ exhibited extremely high activity toward the ring-opening polymerization of ε-CL in situ; here, a similar system was explored for the ROP of L-LA. Firstly, the effect of LiN(SiMe₃)₂ on the ROP of L-LA was investigated by using **Zn6** in toluene at a molar ratio of [LA]:[Zn] = 250:1 and within 10 min at 30 °C. The results showed that no polymer was obtained when using one equivalent LiN(SiMe₃)₂. However, when increasing the LiN(SiMe₃)₂ from one to two equivalents, the monomer conversion could reach 36% under the same conditions. In addition, the blank experiments showed 10% conversion of monomers was achieved using only two equivalents of LiN(SiMe₃)₂ as catalysts. Therefore, a catalyst system of **Zn6**/2LiN(SiMe₃)₂ was employed for the ROP of L-LA, and the polymerization results are collected in Table 2.

Table 2. Ring-opening polymerization of *L*-LA by **Zn1–Zn8**/2LiN(SiMe₃)₂ ^a.

Run	Cat	<i>L</i> -LA:Zn	Solvent	T/°C	t/min	Conv./% ^b	TOF/h ^{−1}	<i>M</i> _{n(calcd)} ^c	<i>M</i> _n ^d	<i>M</i> _w / <i>M</i> _n ^d
1	Zn6	250:1	toluene	30	10	36	540	1.30	3.99	1.74
2 ^e	Zn6	250:1	toluene	30	10	11	165	0.39	0.59	1.17
3 ^f	Zn6	250:1	toluene	30	10	8	120	0.28	0.51	1.15
4	Zn6	250:1	toluene	30	20	48	360	1.73	4.19	1.62
5	Zn6	250:1	toluene	30	40	65	244	2.34	3.06	1.72
6	Zn6	250:1	toluene	30	60	86	215	3.10	1.65	2.03
7	Zn6	250:1	toluene	50	10	68	1020	2.45	2.72	1.87
8	Zn6	250:1	toluene	60	10	85	1275	3.06	2.83	2.06
9	Zn6	250:1	toluene	70	10	96	1440	3.46	2.77	1.87
10	Zn6	250:1	toluene	80	10	100	1500	3.60	2.66	2.08
11	Zn6	250:1	CH ₂ Cl ₂	30	10	0	0	—	—	—
12	Zn6	250:1	THF	60	10	92	1380	3.31	1.58	2.12
13	Zn6	250:1	hexane	60	10	8	120	0.29	2.52	1.97
14	Zn6	500:1	toluene	80	10	96	2880	6.91	2.49	2.13
15	Zn6	1000:1	toluene	80	10	89	5340	12.81	2.61	2.13
16 ^g	Zn6	1000:1	toluene	80	10	79	4740	11.38	2.38	1.79
17 ^h	Zn6	1000:1	toluene	80	10	65	3900	9.36	2.02	2.33
18	Zn6	500:1	toluene	80	5	63	3780	4.54	1.86	1.97
19	Zn1	500:1	toluene	80	5	75	4500	5.40	1.96	1.90
20	Zn2	500:1	toluene	80	5	70	4200	5.04	1.68	2.04
21	Zn3	500:1	toluene	80	5	44	2640	3.17	2.68	2.01
22	Zn4	500:1	toluene	80	5	92	5520	6.62	3.90	1.75
23	Zn5	500:1	toluene	80	5	53	3180	3.82	1.51	2.17
24	Zn7	500:1	toluene	80	5	36	2160	2.59	1.92	1.99
25	Zn8	500:1	toluene	80	5	92	5520	6.62	1.84	2.27

^a Reaction conditions: 1.0 mL toluene, 10 μmol [Zn] + 20 μmol LiN(SiMe₃)₂; ^b determined by ¹H NMR spectroscopy; ^c 10⁴ g/mol, *M*_{n(calcd)} = molar ratio of [L-LA]/[Zn] × 144 × conv.%; ^d 10⁴ g/mol, GPC data were recorded from THF vs. polystyrene standards using a correcting factor of 0.58 [58]; ^e 1 equiv. BnOH; ^f 3 equiv. BnOH; ^g 3 mL toluene; ^h 5 mL toluene.

In the first instance, the effect of benzyl alcohol (BnOH) on polymerization was investigated with the molar ratio of [L-LA]:[Zn] = 250:1 at a temperature kept at 30 °C (runs 1–3, Table 2). The results indicated that the monomer conversion decreased from 36% to 11% when one equivalent benzyl alcohol was added. Then, the amount of benzyl alcohol was further increased to three equivalents, and the monomer conversion continued to decrease to only 8%. These results revealed that benzyl alcohol could not improve the monomer conversion in this catalytic system. In order to enhance the monomer conversion, the polymerization was screened from 10 min to 60 min under the same conditions (runs 1 and 4–6, Table 2). The results showed that monomer conversion greatly increased from 36% in 10 min to 86% in 60 min with the extension of time, but the molecular weight decreased from 3.99 × 10⁴ to 1.65 × 10⁴ g/mol and the polydispersity became broader, suggesting the increased side reaction of transesterification during longer times. The comparison of the *M*_n values with the calculated values [*M*_{n(calcd)}] shows large differences, which indicates that the polymerizations are not well controlled [59]. The kinetics of polymerization by **Zn6**, shown as a semilogarithmic plot, slightly deviates from the first order with the polymerization rate constant *k*_{app} as 0.03177 min^{−1} (LA/Zn = 250:1) or 0.02294 min^{−1} (LA/Zn = 250:0.5) (Figure S37 in Supplementary Materials).

Secondly, the molar ratio of [L-LA]:[Zn] was fixed at 250:1 and the run time at 10 min, and the influence of temperature on polymerization was also investigated (runs 1 and 7–10, Table 2). As the reaction temperature increased from 30 °C to 80 °C, the monomer conversion rate also increased gradually from 36% to 100%, indicating that higher temperatures favored the increase in the polymerization rate. At the same time, the polymer obtained from 50 °C and 80 °C possessed similar *M*_n values (*M*_n = 2.66–2.83 × 10⁴ g/mol) and molecular weight distributions (*M*_w/*M*_n = 1.87–2.08); within this temperature range, the *M*_n values were all lower than the *M*_{n(calcd)} values. This may be explained by the efficiency

of active species and the effect of transesterification during polymerization [60]. Moreover, the molecular weight distribution of all obtained polymers was broad, suggesting more side reactions of transesterification at higher temperatures [61–63].

Subsequently, in order to explore the role of various solvents for the ROP of *L*-LA, the polymerizations were carried out in dichloromethane at 30 °C with THF and 60 °C with *n*-hexane (runs 11–13, Table 2). When THF was used, high monomer conversion of up to 92% was achieved at $[L\text{-LA}]:[\text{Zn}] = 250:1$ within 10 min. However, when dichloromethane and *n*-hexane were used, the monomer conversion was extremely low, at 0 and 8%, respectively. The reason for this may be related to the coordination competition between the monomer and solvent for the active zinc centers [64,65].

Fixing the temperature at 80 °C and run time at 10 min, increasing the molar ratio of $[L\text{-LA}]:[\text{Zn}]$ from 250:1 to 1000:1 led to a slightly decrease in monomer conversion from 100% to 89% (runs 10, 14, 15, Table 2), but the molecular weights of the polymer were very similar (from 2.46 to 2.66×10^4 g/mol), which were much lower than $M_{n(\text{calcd})}$. Furthermore, the effect of the amount of toluene was also explored at a high molar ratio of $[L\text{-LA}]:[\text{Zn}] = 1000:1$ in 10 min at 80 °C (runs 15–17, Table 2). When increasing the toluene volume from 1 mL to 5 mL, the monomer conversion gradually decreased from 89% to 65% and the molecular weight of the polymer slightly decreased from 2.61×10^4 g/mol to 2.02×10^4 g/mol. This may be attributed to the deactivation of some active species caused by more impurities in toluene [66]. Moreover, the reaction time was reduced from 10 min to 5 min at 80 °C with the molar ratio of $[L\text{-LA}]:[\text{Zn}] = 500:1$, and the monomer conversion also decreased from 96% to 63% (runs 15 vs. 18, Table 2). The average molecular weight of the obtained polymer decreased from 2.61×10^4 g/mol to 1.86×10^4 g/mol.

With the $[L\text{-LA}]:[\text{Zn}]$ ratio kept at 500:1 and temperature and time at 80 °C and 5 min, respectively, all zinc complexes **Zn1–Zn8** were evaluated for the ROP of *L*-LA by using pre-treatment with two equivalents of $\text{LiN}(\text{SiMe}_3)_2$, and the results are shown in runs 18, 19–25 (Table 2). The data revealed that the catalytic system **Zn1–Zn8**/ $2\text{LiN}(\text{SiMe}_3)_2$ can efficiently catalyze the ROP of *L*-LA, in which the catalytic efficiency is related with the size of the substituent group (R) and the size of the pyridyl-fused ring (shown in Figure 5).

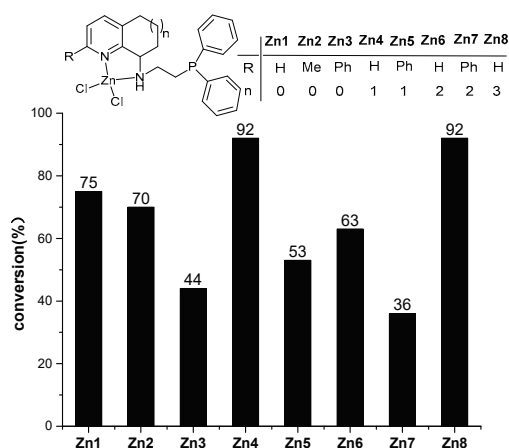


Figure 5. Comparison of the monomer conversion (*L*-LA) achieved using **Zn1–Zn8**/ $2\text{LiN}(\text{SiMe}_3)_2$ (runs 18, 19–25, Table 2).

According to Figure 5, complexes **Zn4** (six-ring) and **Zn8** (eight-ring) show higher monomer conversion rates than the other complexes, both exceeding 90% ($\text{TOF} = 5.52 \times 10^3 \text{ h}^{-1}$), much higher than those of the other zinc complexes. The R also greatly affected the activity, as shown by the following activity order: **Zn1** (75%, H) > **Zn2** (70%, Me) > **Zn3** (44%, Ph); **Zn4** (92%, H) > **Zn5** (53%, Ph); **Zn6** (63%, H) > **Zn7** (36%, Ph). This indicated that the smaller substituents favored the polymerization. The fused ring size also greatly affected the activity, as shown by the following activity order: R = H, **Zn4** (six-ring) = **Zn8** (eight-ring) > **Zn1** (75%, five-ring) > **Zn6** (63%, seven-ring); R = Ph,

Zn5 (53%, six-ring) > **Zn3** (44%, five-ring) > **Zn7** (36%, seven-ring). Thus, **Zn7** and **Zn6** displayed the lowest activity, and the reason is probably due to the more distorted fused seven-ring structures in **Zn7** and **Zn6**. The polymer obtained by using **Zn4** possessed the highest molecular weight ($M_n = 3.9 \times 10^4$ g/mol).

In order to gather more information about the mechanism of the ROP of L-LA, the obtained PLLA (run 18, Table 2) was characterized by a ^1H NMR and MALDI-TOF spectrum. The MALDI-TOF mass spectrum revealed two families of peaks (as shown in Figure 6): both A/A* and B/B* were separated by an m/z of 72, in which the major peaks A/A* can be ascribed to $\text{CH}_3\text{OH} + (\text{C}_3\text{H}_4\text{O}_2)_n + \text{Na}^+/\text{K}^+$ and the minor peaks B/B* are assignable to $(\text{C}_3\text{H}_4\text{O}_2)_n + \text{Na}^+/\text{K}^+$. The ^1H NMR spectrum clearly showed the presence of CH_3O protons around δ 3.75 ppm (shown in Figure 7), which may come from the methanolysis of the polymer chain during the quenching process [60,67,68]. In addition, there was no signal of $-\text{N}(\text{SiMe}_3)_2$ in either the ^1H NMR or MALDI-TOF spectra, which was consistent with a previous report in the literature [51].

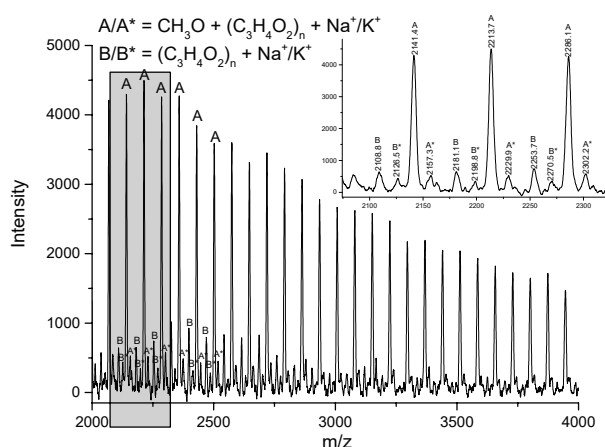


Figure 6. MALDI-TOF mass spectrum of the PLLA obtained using **Zn6**/2LiN(SiMe₃)₂ (run 18, Table 2).

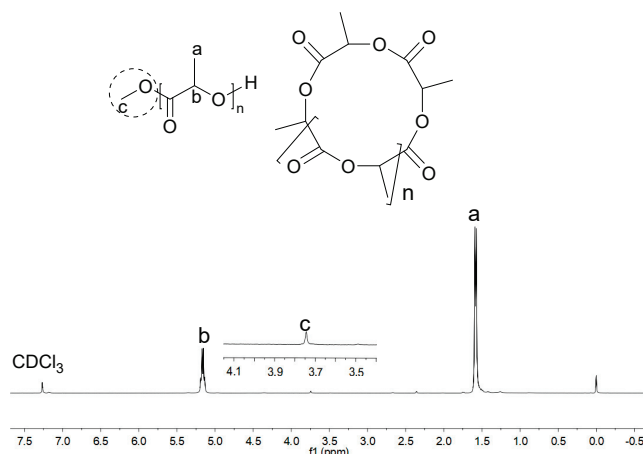
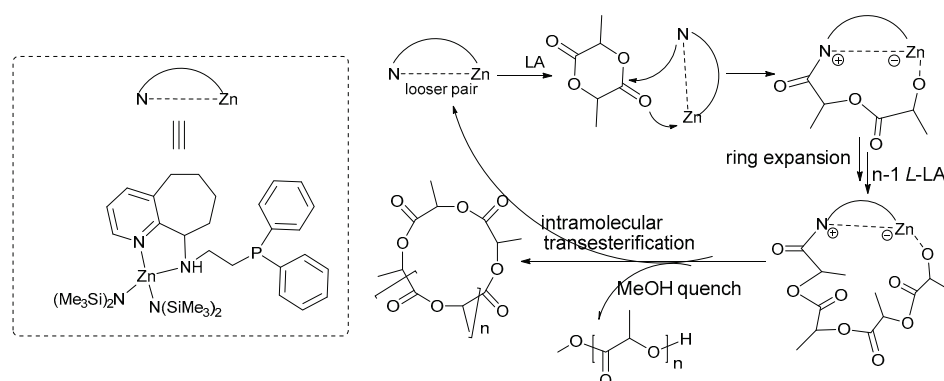


Figure 7. ^1H NMR spectrum of the PLLA obtained using **Zn6**/2LiN(SiMe₃)₂ (run 18, Table 2).

Based on the above results, the mechanism of the ROP of L-LA catalyzed by **Zn1–Zn8**/2LiN(SiMe₃)₂ was proposed, as shown in Scheme 3. It is assumed that a Lewis pair will form during the ROP process and can be ‘loosened up’ at higher temperatures to form a zwitterionic intermediate. Subsequently, this ‘loose’ pair can initiate the polymerization, causing the ring to expand to form the cyclic macrolactone metal ring; this mechanism has also been reported in the literature [51,69,70]. Finally, methanol was added to terminate the polymerization reaction, and a linear polymer capped with a methoxyl group was obtained [71]. Furthermore, its minor cyclic structure may be due to intramolecular transesterification.



Scheme 3. Possible mechanistic pathways for the ROP of *L*-LA using **Zn6**/2LiN(SiMe₃)₂.

2.3. Ring-Opening Polymerization of *rac*-LA by **Zn1–Zn8**/2LiN(SiMe₃)₂

Under the conditions of the molar ratio of the monomer to the catalyst of 500:1, polymerization temperature of 80 °C and reaction time of 5 min, the catalytic performance of **Zn1–Zn8**/2LiN(SiMe₃)₂ for the ROP of *rac*-LA was also investigated. The polymerization results are shown in Table 3.

Table 3. Ring-opening polymerization of *rac*-LA by **Zn1–Zn8**/2LiN(SiMe₃)₂ ^a.

Run	Cat	<i>rac</i> -LA: Zn	T/°C	t/min	Conv./% ^b	TOF/h ^{−1}
1	Zn1	500:1	80	5	59	3540
2	Zn2	500:1	80	5	53	3180
3	Zn3	500:1	80	5	52	3120
4	Zn4	500:1	80	5	71	4260
5	Zn5	500:1	80	5	53	3180
6	Zn6	500:1	80	5	46	2760
7	Zn7	500:1	80	5	18	1080
8	Zn8	500:1	80	5	74	4440

^a Reaction conditions: 1.0 mL toluene, 10 μmol [Zn] + 20 μmol LiN(SiMe₃)₂; ^b determined by ¹H NMR spectroscopy.

The results showed that **Zn1–Zn8**/2LiN(SiMe₃)₂ also displayed good efficiency for the ROP of *rac*-LA but without stereoselectivity and all the resultant polymers were amorphous. Both the substituent and ring size of the ligand greatly influenced the activity, and the order of activity is as follows: **Zn1** (59%, R = H) > **Zn2** (53%, R = Me) > **Zn3** (52%, R = Ph); **Zn4** (71%, R = H) > **Zn5** (53%, R = Ph); **Zn6** (46%, R = H) > **Zn5** (18%, R = Ph). **Zn8**, bearing a small substituent group with an eight-membered ring, exhibited the highest activity (TOF = 4.44 × 10³ h^{−1}), higher than **Zn1–Zn7** (TOF range: 1.08–4.26 × 10³ h^{−1}). Additionally, the catalytic efficiency of the Zn/2LiN(SiMe₃)₂ catalytic system for the ROP of *rac*-LA was generally lower than that for the ROP of *L*-LA (Figure 8).

The microstructure of poly(*rac*-LA) (run 1, Table 3) was also studied by MALDI-TOF and ¹H NMR spectra. The MALDI-TOF mass spectrometry showed two families of A/A* and B/B* (as shown in Figure S38), in which the major family peaks A/A* were attributed to CH₃OH + (C₃H₄O₂)_n + Na⁺/K⁺, as the visible linear structure with a methoxy end group, while the minor family peaks B/B* were assigned as the cyclic structure (C₃H₄O₂)_n + Na⁺/K⁺. According to the ¹H NMR spectrum (as shown in Figure S39), the signal at around 3.75 ppm of the CH₃O protons appeared to further confirm the MALDI-TOF analysis. Therefore, the mechanism is similar to that for the ROP of *L*-LA. All the obtained polymers were sticky. In order to exemplify their stereoselectivity, they were further characterized by using decoupling ¹H NMR (shown in Figure S40) and results showed that their *Pm* values varied approximately between 0.30 and 0.35.

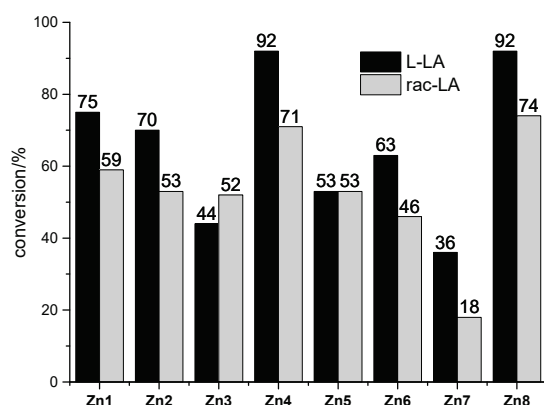


Figure 8. Comparison of the monomer conversions (L-LA and rac-LA) achieved using **Zn1–Zn8**/2LiN(SiMe₃)₂.

3. Materials and Methods

3.1. General Considerations

All operations of moisture- and air-sensitive chemicals were carried out under an atmosphere of high-purity nitrogen using standard Schlenk techniques and a N₂-filled glovebox. LiN(SiMe₃)₂ (1.0 M in THF) was purchased from Aldrich (San Diego, CA, USA) and used as received. Toluene, n-hexane, tetrahydrofuran and diethyl ether were dried by refluxing over sodium benzophenone, distilled under N₂ and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. Dichloromethane was dried over CaH₂ for 48 h, distilled under N₂ and stored over activated molecular sieves (4 Å) in a glovebox prior to use. L-lactide and rac-lactide were purchased from TCI and used as received without further purification. And other reagents were obtained from common commercial suppliers.

All NMR spectra were recorded with Bruker Avance III 400 or Bruker Avance III 400 HD spectrometers (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR) at room temperature. The chemical shifts were related to the position of the NMR signal using tetramethylsilane (TMS) as a reference. And ³¹P NMR spectra were measured on a Bruker Avance II + 400 instrument. Elemental analyses were performed with a Flash EA 1112 microanalyzer, while IR spectra were conducted using a Perkin-Elmer System 2000 FT-IR spectrometer (Thermo Flash Smart, Beijing, China). MALDI-TOF MS analysis was performed with a Bruker Ultraflex mass spectrometer. For MALDI MS analysis, mass spectra were acquired with a SmartBeam laser (355 nm, Bruker, Bremen, Germany) operating at 200 Hz with a laser focus of 50 μm. The device parameters for MALDI MS were chosen as follows: plate offset voltage, 19 kV; deflector detector voltage, 20 kV. Data were processed using DataAnalysis 3.0 (Bruker Daltonics). GPC analysis was performed using a system composed of a 390-LC multidetector (MDS), a 209-LC pump injection module (PIM) and a PL-GPC 50 plus instrument. THF was used as the eluent (flow rate: 1 mL/min, at 40 °C) and the molecular weights and molecular weight distributions were calculated using polystyrene as the standard.

3.2. Synthesis and Characterization of Ligands and Zinc Complexes

3.2.1. 2-(Diphenylphosphino)ethanamine, Ligands (**L1–L8**) and Zinc Complexes (**Zn4, Zn5**) Were Synthesized as Previously Reported [51,53–55]

2-(diphenylphosphino)ethanamine. In a 250 mL double-mouth round-bottom flask filled with nitrogen, ^tBuOK (12.03 g, 105 mmol) and diphenylphosphine (9.63 g, 52.6 mmol) were dissolved in 100 mL dry THF and the solution was stirred for 1 h at ambient temperature. Then, 2-chloroethylamine hydrochloride (6.58 g, 55.6 mmol) was added to the mixture and heated to reflux for 20 h at 80 °C. During the reaction. After cooling to room temperature, THF was removed under reduced pressure. First, 10% HCl was added to make the solution strongly acidic, and then the solution was washed three times with toluene. Secondly, the mixture was extracted three times with toluene after being neutral-

ized with 10% NaOH. Finally, the resulting toluene solution was washed three times with saturated NaCl and dried with MgSO_4 to give a yellow oily liquid (9.4 g, 77% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.47–7.38 (m, 4H), 7.35–7.28 (m, 6H), 2.88–2.80 (m, 2H), 2.24 (t, J = 8.0 Hz), 1.57 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 137.16, 13.64, 132.81, 132.62, 130.78, 130.66, 128.96, 128.84, 128.77, 128.58, 128.51, 38.81, 38.59, 30.91, 30.78. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 22.03.

N-(2-(diphenylphosphaneyl)ethyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-7-amine (L1). 5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (0.5 g, 3.85 mmol), 2-(diphenylphosphino)ethanamine (1.15 g, 5 mmol) and sodium triacetoxyborohydride (1.7 g, 8.05 mmol) were dissolved in 50 mL 1,2-dichloroethane (DCE). The reaction mixture was stirred for 6 h at ambient temperature under a nitrogen atmosphere. After the reaction, the mixture was quenched with saturated NaHCO_3 and the organic layer was extracted three times with ethyl acetate. Then, the mixture was dried with MgSO_4 and the solvent was removed with a rotary evaporator. The crude product was further purified by chromatography on silica gel with petroleum ether/ethyl acetate (5:1, v/v) to yield the product as a green oily liquid (0.7 g, 52% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.37 (d, J = 4.9 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 7.48–7.39 (m, 4H), 7.38–7.28 (m, 6H), 7.09–7.06 (m, 1H), 4.18 (t, J = 7.1 Hz), 3.02–2.74 (m, 4H), 2.43–2.33 (m, 3H), 1.91–1.79 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 163.41, 145.81, 137.49, 137.41, 137.37, 137.29, 135.54, 131.88, 131.70, 131.69, 131.65, 131.52, 127.63, 127.51, 127.47, 127.44, 127.40, 127.38, 121.19, 61.73, 43.97, 30.48, 28.19, 28.07, 27.12. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.74. FT-IR (cm^{-1}): 3049 (m), 2934 (m), 1671 (w), 1583 (m), 1480 (m), 1432 (m), 1423 (m), 1330 (m), 1264 (m), 1182 (w), 1092 (m), 1023 (m), 867 (w), 790 (m), 736 (s), 693.18 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{P}$ (1/2 H_2O): C, 74.35; H, 6.81; N, 7.88. Found: C, 73.91; H, 6.86; N, 7.57.

N-(2-(diphenylphosphaneyl)ethyl)-2-methyl-6,7-dihydro-5H-cyclopenta[b]pyridine-7-amine (L2). The synthesis of L2 followed the same procedure as that of L1, except that 2-methyl-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (1.13 g, 7.7 mmol) was used to yield the product as a green oily liquid (0.94 g, 34% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.45–7.37 (m, 5H), 7.33–7.26 (m, 6H), 6.92 (d, J = 7.7 Hz, 1H), 4.13 (t, J = 6.8 Hz, 1H), 2.98–2.69 (m, 4H), 2.50 (s, 3H), 2.38–2.29 (m, 3H), 2.24 (s, 1H), 1.91–1.76 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 162.88, 155.54, 137.59, 137.46, 137.33, 132.27, 131.91, 131.85, 131.73, 131.65, 131.47, 127.63, 127.46, 127.42, 127.39, 127.36, 120.74, 61.87, 43.98, 43.76, 30.44, 28.27, 28.15, 26.80, 23.05. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 18.57. FT-IR (cm^{-1}): 3049 (m), 2929 (m), 1669 (w), 1584 (m), 1480 (w), 1431 (s), 1327 (m), 1260 (m), 1223 (m), 1181 (m), 1151 (m), 1094 (m), 1023 (m), 833 (w), 798 (m), 737 (s), 691 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{P}$ (2/3 H_2O): C, 74.17; H, 7.13; N, 7.52. Found: C, 74.36; H, 7.06; N, 7.30.

N-(2-(diphenylphosphaneyl)ethyl)-2-phenyl-6,7-dihydro-5H-cyclopenta[b]pyridine-7-amine (L3). The synthesis of L3 followed the same procedure as that for L1, except that 2-phenyl-5,6-dihydro-7H-cyclopenta[b]pyridin-7-one (2.10 g, 10 mmol) yielded the product as a green oily liquid (1.34 g, 32% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.95 (d, J = 7.4 Hz, 2H), 7.57–7.43 (m, 9H), 7.34–7.29 (m, 6H), 4.23 (t, J = 7.2 Hz, 1H), 3.09–2.78 (m, 4H), 2.47–2.38 (m, 3H), 2.20 (s, 1H), 1.95–1.85 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 163.65, 155.08, 138.69, 137.56, 137.50, 137.44, 137.37, 133.95, 132.20, 131.89, 131.70, 131.52, 127.60, 127.50, 127.47, 127.45, 127.41, 127.38, 125.90, 118.29, 61.80, 44.09, 43.87, 30.77, 28.35, 28.23, 26.89. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.35. FT-IR (cm^{-1}): 3053 (m), 2932 (m), 1584 (m), 1480 (w), 1431 (s), 1327 (m), 1260 (m), 1223 (m), 1181 (m), 1151 (m), 1094 (m), 1023 (m), 833 (w), 798 (m), 737 (s), 691 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{27}\text{N}_2\text{P}$ (1/2 H_2O): C, 77.94; H, 6.54; N, 6.49. Found: C, 77.78; H, 6.53; N, 6.50.

N-(2-(diphenylphosphaneyl)ethyl)-5,6,7,8-tetrahydro-quinolin-8-amine (L4). The synthesis of L4 followed the same procedure as that for L1, except that 6,7-dihydroquinolin-8(5H)-one (1.13 g, 7.7 mmol) yielded the product as a yellow oily liquid (1.66 g, 60% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.42 (d, J = 4.2 Hz, 1H), 7.53–7.45 (m, 4H), 7.41–7.29 (m, 7H), 7.11–7.04 (m, 1H), 3.82 (t, J = 5.8 Hz, 1H), 3.03–2.75 (m, 4H), 2.73 (s, 1H), 2.42 (t, J = 7.8 Hz, 2H), 2.15–1.94 (m, 2H), 1.81–1.66 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ

157.26, 146.81, 138.63, 138.53, 138.50, 138.41, 136.85, 132.92, 132.73, 132.66, 132.48, 132.37, 128.59, 128.43, 128.40, 128.37, 128.34, 121.79, 57.79, 44.52, 44.30, 29.24, 29.12, 28.80, 28.52, 19.57. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.38.

N-(2-(diphenylphosphaneyl)ethyl)-2-phenyl-5,6,7,8-tetra-hydroquinolin-8-amine (L5). The synthesis of L5 followed the same procedure as that for L1, except that 2-phenyl-6,7-dihydroquinolin-8(5H)-one (1.71 g, 7.7 mmol) yielded the product as a yellow oily liquid (1.98 g, 60% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.99–7.91 (m, 2H), 7.49–7.21 (m, 15H), 3.78 (t, J = 6.5 Hz, 1H), 2.99–2.64 (m, 5H), 2.42–2.33 (m, 2H), 2.14–1.60 (m, 2H), 1.73–1.60 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 155.97, 153.27, 138.47, 137.73, 137.60, 137.49, 136.58, 131.84, 131.77, 131.65, 131.58, 129.72, 127.57, 127.51, 127.42, 127.35, 125.71, 117.47, 57.07, 43.54, 43.33, 28.51, 28.39, 28.07, 27.58, 19.02. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.44.

N-(2-(diphenylphosphaneyl)ethyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridin-9-amine (L6). The synthesis of L6 followed the same procedure as that for L1, except that 5,6,7,8-tetrahydro-9H-cyclohepta[b]pyridin-9-one (1.23 g, 7.7 mmol) yielded the product as a yellow oily liquid (1.51 g, 52% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.29 (d, J = 4.6 Hz, 1H), 7.44–7.34 (m, 4H), 7.32–7.20 (m, 7H), 6.98 (t, J = 6.0 Hz, 1H), 3.84 (d, J = 9.2 Hz, 1H), 2.89–2.58 (m, 4H), 2.39–2.27 (m, 3H), 1.95–1.88 (m, 2H), 1.74–1.63 (m, 2H), 1.53–1.34 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 161.12, 144.75, 135.79, 131.81, 131.59, 127.45, 127.39, 127.38, 127.32, 127.31, 120.46, 62.27, 44.14, 43.93, 33.20, 33.53, 28.34, 28.23, 27.62, 26.34. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.40. FT-IR (cm^{-1}): 3049 (w), 2921 (m), 1572 (m), 1476 (w), 1430 (m), 1337 (w), 1260 (m), 1090 (m), 1019 (m), 792 (m), 737 (s), 693 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{P}$ (2/3 H_2O): C, 74.59; H, 7.39; N, 7.25. Found: C, 74.43; H, 7.48; N, 7.08.

N-(2-(diphenylphosphaneyl)ethyl)-2-phenyl-6,7,8,9-tetra-hydro-5H-cyclohepta[b]pyridin-9-amine (L7). The synthesis of L7 followed the same procedure as that for L1, except that 2-phenyl-5,6,7,8-tetrahydro-9H-cyclohepta[b]pyridin-9-one (1.74 g, 7.7 mmol) yielded the product as a yellow solid (2.16 g, 62% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.02 (d, J = 7.4 Hz, 2H), 7.53–7.32 (m, 9H), 7.28–7.19 (m, 6H), 3.91 (d, J = 9.3 Hz, 1H), 2.90–2.68 (m, 4H), 2.50–2.31 (m, 2H), 2.09–1.94 (m, 2H), 1.91–1.69 (m, 2H), 1.56–1.32 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 161.54, 153.16, 139.48, 138.75, 138.68, 138.63, 138.55, 137.76, 135.35, 132.80, 132.62, 132.59, 128.60, 128.48, 128.45, 128.35, 126.71, 117.91, 63.07, 45.50, 45.28, 34.29, 33.90, 29.45, 29.35, 29.20, 27.41. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.02. FT-IR (cm^{-1}): 3282 (w), 2928 (m), 1583 (w), 1562 (w), 1455 (w), 1431 (m), 1386 (w), 1332 (w), 1305 (w), 1260 (m), 1090 (m), 1025 (m), 969 (m), 938 (w), 913 (w), 859 (w), 827 (w), 795 (m), 738 (s), 691 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{N}_2\text{P}$ (1/2 H_2O): C, 78.41; H, 7.02; N, 6.10. Found: C, 78.10; H, 6.88; N, 5.95.

N-(2-(diphenylphosphaneyl)ethyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridin-10-amine (L8). The synthesis of L8 followed the same procedure as that for L1, except that 6,7,8,9-tetrahydrocycloocta[b]pyridin-10(5H)-one (1.35 g, 7.7 mmol) yielded the product as a yellow oily liquid (0.93 g, 31% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.42 (d, J = 4.6 Hz, 1H), 7.41–7.30 (m, 5H), 7.28–7.21 (m, 6H), 7.07–7.01 (m, 1H), 4.11–4.05 (m, 1H), 2.81–2.50 (m, 4H), 2.36–2.17 (m, 2H), 2.04–1.97 (m, 2H), 1.68–1.52 (m, 2H), 1.43–1.23 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 159.70, 146.28, 137.78, 137.69, 137.66, 137.56, 135.92, 135.48, 131.88, 131.69, 131.61, 131.43, 127.47, 127.34, 127.27, 120.62, 56.26, 44.07, 43.85, 37.68, 31.67, 31.53, 28.49, 28.37, 26.11, 23.40. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.51. FT-IR (cm^{-1}): 3048 (w), 2923 (m), 1577 (m), 1476 (m), 1430 (s), 1368 (w), 1261 (m), 1184 (w), 1102 (m), 1068 (m), 1023 (m), 965 (w), 924 (w), 844 (w), 800 (m), 737 (s), 693 (s). Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{N}_2\text{P}$ (1/2 H_2O): C, 75.54; H, 7.61; N, 7.05. Found: C, 75.40; H, 7.50; N, 6.94.

N-(2-(diphenylphosphaneyl)ethyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-7-aminozinc dichloride (Zn1). L1 (0.21 g, 0.60 mmol) and ZnCl_2 (0.081 g, 0.60 mmol) were dissolved in 5 mL ethanol, respectively. Then, the ethanol solution of zinc chloride was added dropwise to the ligand solution and stirred for 12 h at room temperature under an atmosphere of nitrogen. The resulting precipitate was collected by direct filtration to yield Zn1 as a green

powder (0.19 g, 68% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.80 (d, J = 5.0 Hz, 1H), 7.78–7.59 (m, 5H), 7.42–7.33 (m, 7H), 4.41–4.36 (m, 1H), 3.21–2.84 (m, 4H), 2.74–2.59 (m, 2H), 2.54–2.38 (m, 2H), 1.91–1.78 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 162.00, 146.91, 137.48, 136.55, 133.32, 133.17, 133.10, 132.94, 130.24, 130.09, 129.07, 129.03, 128.99, 128.95, 124.66, 62.26, 28.11. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 25.86. FT-IR (cm^{-1}): 3200 (m), 3073 (w), 2959 (w), 1606 (m), 1479 (w), 1436 (m), 1346 (w), 1321 (m), 1262 (m), 1204 (m), 1149 (w), 1096 (m), 1073 (w), 1034 (m), 1015 (m), 941 (m), 872 (w), 800 (m), 778 (w), 745 (s), 697 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{Cl}_2\text{N}_2\text{PZn}$ ($1/2\text{H}_2\text{O}$): C, 53.74; H, 4.92; N, 5.70. Found: C, 53.81; H, 4.82; N, 5.45.

N-(2-(diphenylphosphaneyl)ethyl)-2-methyl-6,7-dihydro-5H-cyclopenta[b]pyridine-7-aminozinc dichloride (Zn2). The synthesis of **Zn2** followed the same procedure as that for **Zn1**, except that **L2** (0.28 g, 0.77 mmol) was used to yield **Zn2** as a green powder (0.25 g, 65% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.63 (d, J = 7.8 Hz, 1H), 7.57–7.50 (m, 2H), 7.44–7.37 (m, 5H), 7.35–7.28 (m, 3H), 7.16 (d, J = 7.8 Hz, 1H), 4.37–4.28 (m, 1H), 3.24 (s, 1H), 3.12–2.81 (m, 4H), 2.71 (s, 3H), 2.41–2.28 (m, 1H), 1.86–1.76 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 160.85, 156.68, 136.97, 133.85, 133.42, 133.22, 132.54, 132.36, 129.45, 128.87, 128.80, 128.69, 128.62, 125.14, 63.15, 28.26, 23.09. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 22.19. FT-IR (cm^{-1}): 3196 (m), 2955 (w), 1611 (m), 1587 (w), 1472 (m), 1434 (m), 1382 (w), 1348 (w), 1312 (w), 1265 (w), 1204 (w), 1144 (m), 1096 (m), 1074 (m), 1015 (m), 973 (w), 942 (w), 859 (m), 834 (m), 798 (m), 743 (s), 698 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{25}\text{Cl}_2\text{N}_2\text{PZn}$: C, 55.62; H, 5.07; N, 5.64. Found: C, 55.29; H, 5.08; N, 5.42.

N-(2-(diphenylphosphaneyl)ethyl)-2-phenyl-6,7-dihydro-5H-cyclopenta[b]pyridine-7-aminozinc chloride (Zn3). The synthesis of **Zn3** followed the same procedure as that for **Zn1**, except that **L3** (0.21 g, 0.49 mmol) was used to yield **Zn3** as a green powder (0.20 g, 73% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.91–7.86 (m, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.60–7.49 (m, 6H), 7.44–7.35 (m, 5H), 7.33–7.28 (m, 3H), 4.48–4.37 (m, 1H), 3.24 (s, 1H), 3.12–2.87 (m, 4H), 2.78–2.67 (m, 2H), 2.25–2.14 (m, 1H), 1.89–1.77 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 161.93, 157.37, 137.20, 136.73, 135.32, 133.38, 133.19, 132.62, 132.44, 130.40, 129.38, 128.84, 128.76, 128.66, 128.59, 128.08, 123.99, 63.15, 45.99, 32.64, 28.31, 27.65. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 22.20. FT-IR (cm^{-1}): 3193 (m), 1597 (w), 1576 (w), 1457 (m), 1433 (m), 1339 (w), 1309 (w), 1230 (m), 1206 (w), 1157 (m), 1100 (m), 1072 (m), 1043 (w), 1009 (m), 971 (m), 945 (m), 842 (m), 791 (w), 736 (s), 694 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{27}\text{Cl}_2\text{N}_2\text{PZn}$: C, 60.18; H, 4.87; N, 5.01. Found: C, 59.99; H, 4.84; N, 4.86.

N-(2-(diphenylphosphaneyl)ethyl)-5,6,7,8-tetrahydroquinolin-8-aminozinc dichloride (Zn4) [51]. The synthesis of **Zn4** followed the same procedure as that for **Zn1**, except that **L4** (0.37 g, 1.03 mmol) was used to yield **Zn4** as a white powder (0.38 g, 74% yield).

N-(2-(diphenylphosphaneyl)ethyl)-2-phenyl-5,6,7,8-tetrahydroquinolin-8-aminozinc dichloride (Zn5) [40]. The synthesis of **Zn5** followed the same procedure as that for **Zn1**, except that **L5** (0.28 g, 0.64 mmol) was used to yield **Zn5** as a white powder (0.32 g, 87% yield).

N-(2-(diphenylphosphaneyl)ethyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine-9-aminozinc dichloride (Zn6). The synthesis of **Zn6** followed the same procedure as that for **Zn1**, except that **L6** (0.39 g, 1.0 mmol) was used to yield **Zn6** as a white powder (0.42 g, 78% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.56 (d, J = 4.3 Hz, 1H), 7.68 (d, J = 7.4 Hz, 1H), 7.59–7.47 (m, 4H), 7.40–7.31 (m, 7H), 4.06 (d, J = 8.1 Hz, 1H), 3.13–2.66 (m, 6H), 2.53–2.48 (m, 1H), 2.07–1.73 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 156.82, 144.32, 139.75, 137.35, 132.14, 131.95, 131.90, 131.72, 128.42, 128.35, 127.87, 127.85, 127.80, 127.77, 123.37, 32.33, 28.33, 26.29, 24.67. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 23.01. FT-IR (cm^{-1}): 3201 (m), 3070 (w), 2951 (w), 1591 (m), 1478 (m), 1450 (m), 1431 (s), 1357 (w), 1333 (w), 1261 (m), 1204 (m), 1165 (w), 1094 (m), 1028 (m), 944 (m), 800 (m), 769 (w), 740 (s), 695 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{Cl}_2\text{N}_2\text{PZn}$ ($1/2\text{H}_2\text{O}$): C, 55.46; H, 5.43; N, 5.39. Found: C, 55.22; H, 5.45; N, 5.01.

N-(2-(diphenylphosphaneyl)ethyl)-2-phenyl-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine-9-aminozinc dichloride (Zn7). The synthesis of **Zn7** followed the same procedure as that for **Zn1**, except that **L7** (0.22 g, 0.46 mmol) was used to yield **Zn7** as a white powder

(0.21 g, 78% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.83 (d, J = 6.2 Hz, 2H), 7.73 (d, J = 6.9 Hz, 1H), 7.58–7.45 (m, 8H), 7.39–7.31 (m, 6H), 4.18 (s, 1H), 3.27 (s, 1H), 2.94–2.81 (m, 4H), 2.77–2.64 (m, 2H), 2.56–2.42 (m, 1H), 2.18–1.92 (m, 4H), 1.91–1.79 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 161.54, 153.16, 139.48, 138.75, 138.68, 138.63, 138.55, 137.76, 135.35, 132.80, 132.78, 132.62, 132.59, 128.60, 128.48, 128.45, 128.42, 128.35, 126.71, 117.91, 63.07, 45.50, 45.28, 34.29, 33.90, 29.46, 29.35, 29.20, 27.41. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 20.02. FT-IR (cm^{-1}): 3282 (m), 3057 (w), 2937 (m), 1588 (m), 1566 (m), 1458 (m), 1433 (m), 1388 (m), 1362 (m), 1305 (w), 1234 (m), 1203 (m), 1073 (m), 1045 (m), 987 (m), 931 (m), 910 (m), 848 (m), 749 (s), 700 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{Cl}_2\text{N}_2\text{PZn}$: C, 61.40; H, 5.32; N, 4.77. Found: C, 61.28; H, 5.33; N, 4.58.

N-(2-(diphenylphosphaneyl)ethyl)-5,6,7,8,9,10-hexahydrocycloocta[b]pyridin-10-aminozinc chloride (Zn8). The synthesis of **Zn8** followed the same procedure as that for **Zn1**, except that **L8** (0.19 g, 0.49 mmol) was used to yield **Zn8** as a white powder (0.20 g, 78% yield). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.66 (d, J = 4.4 Hz, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.54–7.39 (m, 6H), 7.37–7.32 (m, 5H), 4.38–4.27 (m, 1H), 3.29 (s, 1H), 3.03–2.88 (m, 1H), 2.85–2.60 (m, 4H), 2.55–2.42 (m, 1H), 2.28–2.17 (m, 1H), 2.08–1.92 (m, 2H), 1.66–1.51 (m, 3H), 1.43–1.33 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 155.60, 146.90, 141.03, 138.84, 135.83, 132.95, 132.77, 129.37, 129.26, 128.88, 128.81, 128.74, 124.79, 60.69, 48.20, 37.26, 32.00, 26.32, 23.92. ^{31}P NMR (162 MHz, CDCl_3 , TMS): δ 22.29. FT-IR (cm^{-1}): 3235. (m), 3059.60 (w), 2925 (m), 1598 (m), 1452 (w), 1436 (m), 1357 (m), 1260 (m), 1197 (m), 1094 (m), 1056 (m), 1015 (s), 948 (m), 868 (w), 801 (m), 745 (w), 736 (s), 696 (s). Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{Cl}_2\text{N}_2\text{PZn}$ (1/2 EtOH): C, 57.01; H, 5.89; N, 5.11 Found: C, 56.70; H, 5.60; N, 5.05.

3.2.2. General Procedure for Ring-Opening Polymerization of L-lactide or rac-LA

A typical polymerization procedure is outlined as follows using **Zn6** as the representative precatalyst. In a Schlenk flask, **Zn6** (0.0051 g, 0.010 mmol) and $\text{LiN}(\text{SiMe}_3)_2$ (0.02 mmol, 2 equiv) were dissolved in 1 mL toluene and the mixture was stirred at room temperature for 30 min under a nitrogen atmosphere. Then, the **Zn6**/ $\text{LiN}(\text{SiMe}_3)_2$ was immediately injected into the monomer (*L*-LA, 0.36 g, 2.5 mmol) to react for the designated time at a specified temperature. After the reaction, the resulting viscous solution was transferred to a flask containing 100 mL cold methanol and stirred. The ring-opening polymerization procedure of the rac-lactide is similar to that of the *L*-lactide above.

3.2.3. X-ray Crystallographic Analyses

Single-crystal X-ray diffraction data for **Zn2**, **Zn3**, **Zn7** and **Zn8** were conducted on an XtaLAB Synergy-R HyPix diffractometer with graphite-monochromated Cu-K α radiation (λ = 1.54184 (Å)) at 169.98(10) K. The cell parameters were obtained through global optimization of the positions of all the reflected signals collected. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed using the SHELXTL-97 package [72–74]. Crystal data and structure refinements for **Zn2**, **Zn3**, **Zn7** and **Zn8** are summarized in Table 4.

Table 4. Crystal data and structure refinements for **Zn2**, **Zn3**, **Zn7** and **Zn8**.

	Zn2	Zn3	Zn7	Zn8
empirical formula	$\text{C}_{23}\text{H}_{25}\text{Cl}_2\text{N}_2\text{PZn}$	$\text{C}_{28}\text{H}_{27}\text{Cl}_2\text{N}_2\text{PZn}$	$\text{C}_{30}\text{H}_{31}\text{Cl}_2\text{N}_2\text{PZn}$	$\text{C}_{25}\text{H}_{29}\text{Cl}_2\text{N}_2\text{PZn}$
formula weight	496.69	558.75	586.81	524.74
temperature/K	170.00(10)	169.98(10)	169.98(10)	169.98(10)
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	P-1	P-1	$\text{P}2_1/\text{c}$	P-1
$a/\text{\AA}$	9.2670(2)	8.8906(3)	12.9499(5)	9.5988(3)
$b/\text{\AA}$	10.2665(3)	10.7637(3)	16.8402(6)	10.9347(4)
$c/\text{\AA}$	12.7846(3)	15.1833(5)	13.0719(5)	13.0072(4)
$\alpha/^\circ$	84.143(2)	108.512(3)	90	84.306(3)
$\beta/^\circ$	75.169(2)	105.259(3)	106.844(4)	75.326(3)
$\gamma/^\circ$	87.433(2)	94.871(2)	90	74.958(3)
volume/ $\text{\AA}^3$	1169.44(5)	1306.49(8)	2728.40(19)	1274.64(8)
Z	2	2	4	2

Table 4. Cont.

	Zn2	Zn3	Zn7	Zn8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.411	1.420	1.429	1.367
μ/mm^{-1}	4.289	3.908	3.770	3.964
F (000)	512.0	576.0	1216.0	544.0
crystal size/ mm^3	$0.25 \times 0.25 \times 0.2$	$0.3 \times 0.3 \times 0.25$	$0.15 \times 0.1 \times 0.02$	$0.33 \times 0.3 \times 0.28$
radiation	CuK α ($\lambda = 1.54184$)	CuK α ($\lambda = 1.54184$)	CuK α ($\lambda = 1.54184$)	CuK α ($\lambda = 1.54184$)
2 θ range for data collection/ $^\circ$	7.184 to 154.478	6.45 to 153.556	7.132 to 154.446	8.378 to 154.348
index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-16 \leq l \leq 14$	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-18 \leq l \leq 19$	$-16 \leq h \leq 16$, $-20 \leq k \leq 21$, $-16 \leq l \leq 16$	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-16 \leq l \leq 14$
reflections collected	13,881	15,346	19,546	15,774
independent reflections	4716 [$R_{\text{int}} = 0.0236$, $R_{\text{sigma}} = 0.0229$]	5274 [$R_{\text{int}} = 0.0245$, $R_{\text{sigma}} = 0.0314$]	5574 [$R_{\text{int}} = 0.0669$, $R_{\text{sigma}} = 0.0560$]	5156 [$R_{\text{int}} = 0.0218$, $R_{\text{sigma}} = 0.0196$]
data/restraints/parameters	4716/0/263	5274/0/307	5574/6/325	5156/0/281
goodness-of-fit on F^2	1.050	1.032	1.100	1.024
final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0319$, $wR_2 = 0.0838$	$R_1 = 0.0367$, $wR_2 = 0.0969$	$R_1 = 0.1142$, $wR_2 = 0.3324$	$R_1 = 0.0272$, $wR_2 = 0.0722$
final R indices [all data]	$R_1 = 0.0333$, $wR_2 = 0.0849$	$R_1 = 0.0388$, $wR_2 = 0.0989$	$R_1 = 0.1221$, $wR_2 = 0.3364$	$R_1 = 0.0281$, $wR_2 = 0.0730$
largest diff. peak/hole/ $\text{e } \text{\AA}^{-3}$	1.13/−0.43	1.53/−0.39	2.67/−0.93	1.04/−0.35

4. Conclusions

In summary, the finely tuned ring sizes of the cycloalkyl-fused pyridine-bearing pendant N-diphenylphosphinoethyl groups are developed as ligands **L1–L8** for their zinc chloride complexes **Zn1–Zn8**. The catalytic systems, **Zn1–Zn8**/2Li(NSiMe₃)₂, display good activities toward the ROP of *L*-LA and *rac*-LA in situ without BnOH. In general, the cyclohexyl- or cyclooctyl-fused pyridyl–zinc catalysts demonstrate competitively higher activities. For *L*-LA, 92% monomer conversion was achieved with the [*L*-LA]: [Zn] molar ratio of 500:1 in only 5 min and at 80 °C. By comparison, the activity for the ROP of *rac*-LA were generally observed to be much lower than that seen for *L*-LA, in which the highest monomer conversion could only reach 74% under the same polymerization conditions and all of the obtained poly(*rac*-LA) product was amorphous. The microstructures of PLAs indicate the linear structures capped with a CH₃O- end group were the major and the zwitterionic species was proposed as the intermediate in the polymerization.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules29174150/s1>. Figures S1–S36: ¹H/¹³C/³¹P NMR spectra of ligand and zinc complexes. Figure S37: Kinetics plot of polymerization of *rac*-LA by **Zn6**/2LiN(SiMe₃)₂. Figures S38 and S39: MALDI-TOF and ¹H NMR spectra of PLAs. Figure S40: Decoupling ¹H NMR spectrum of the poly(*rac*-LA) obtained using **Zn1–Zn8**/2LiN(SiMe₃)₂. CCDC 2330187–2330190 for **Zn2**, **Zn3**, **Zn7** and **Zn8**. For crystallographic data in CIF or another electronic format, see Supplementary Materials.

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Article

Influence of Polytetrafluoroethylene Content, Compaction Pressure, and Annealing Treatment on the Magnetic Properties of Iron-Based Soft Magnetic Composites

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Abstract: To improve the magnetic properties of iron-based soft magnetic composites (SMCs), polytetrafluoroethylene (PTFE) with excellent heat resistance, electrical insulation, and extremely high electrical resistivity was chosen as an insulating coating material for the preparation of iron-based SMCs. The effects of PTFE content, compaction pressure, and annealing treatment on the magnetic properties of Fe/PTFE SMCs were investigated in detail. The results demonstrate that the PTFE insulating layer is successfully coated on the surface of iron powders, which effectively reduces the core loss, increases the resistivity, and improves the frequency stability and the quality factor. Under the combined effect of optimal PTFE content, compaction pressure, and annealing treatment, the iron-based SMCs exhibit a high effective permeability of 56, high saturation magnetization of 192.9 emu/g, and low total core losses of 355 mW/cm³ and 1705 mW/cm³ at 50 kHz for $B_m = 50$ mT and 100 mT. This work provides a novel insulating coating layer that optimizes magnetic properties and is advantageous for the development of iron-based SMCs. In addition, it also provides a comprehensive understanding of the relationship between process parameters and magnetic properties, which is of great guiding significance for scientific research and industrial production.

Keywords: soft magnetic composites; polytetrafluoroethylene; compaction pressure; annealing treatment; magnetic properties

1. Introduction

Soft magnetic composites (SMCs) are obtained by using ferromagnetic powders as raw materials, coating the surface of the powders with an insulating dielectric layer, and then pressing the powders into a desired shape, followed by annealing treatment [1–3]. Because of their unique properties with high magnetic induction, three-dimensional magnetic isotropy, high magnetic permeability, low coercivity, and low core loss, SMCs have attracted considerable attention and are broadly applied in the field of electromagnetic devices such as inductors, filters, motors, and transformers [1–5].

Pure iron powder, as the most cost-effective, widely used, and promising soft magnetic material, has been employed for the preparation of SMCs [6–9]. The performance of iron-based SMCs is greatly affected by insulating layer properties [10–14] and manufacturing parameters such as compaction pressure [15,16] and annealing treatment [17–19]. In general, insulating materials include organics (such as epoxy resin [20], phenolic resin [14, 21], silicone resins [22,23], and polyimide [24]) and inorganics (such as phosphates [25], oxides [26–31], and ferrite [32–34]). Organic-coated iron-based SMCs have the advantages of a simple preparation process, low cost, and excellent magnetic properties, and they are

widely used in industrial production. Regarding traditional organic-coated iron-based SMCs, high pressure is required to compact the iron powders coated with an insulating phase into the designed shape. This process inevitably produces internal stresses and defects, causing an increase in magnetic loss. So, the annealing treatment process should be carried out to choose a high enough temperature that will maximally eliminate internal stresses and defects [35,36]. However, traditional organic insulation materials exhibit low heat-resistant temperatures and poor high-temperature stability. On the one hand, crystallization or decomposition may occur during high-temperature annealing [35,37], resulting in a sharp decrease in electrical resistivity and an increase in eddy current loss for iron-based SMCs. This limits the annealing temperature, which cannot effectively eliminate internal stresses, resulting in high hysteresis loss in iron-based SMCs. On the other hand, high operating temperatures can deteriorate organic insulation materials, thereby reducing the magnetic performance and service life of iron-based SMCs. Therefore, in order to ensure the effective use and long-term stability of iron-based SMCs, the operating temperature range of iron-based SMCs is limited to $-65\sim 125\text{ }^{\circ}\text{C}$. It is difficult to meet the needs of diverse engineering applications and complex service environments as well as high-efficiency, low-energy-consumption, high-frequency, and high-power applications for high-performance, high-reliability iron-based SMCs. Therefore, there is an urgent need to select new insulating coating material and optimize process parameters to prepare high-performance and high-reliability iron-based SMCs.

Polytetrafluoroethylene (PTFE) has been used as an irreplaceable material for various industrial applications. It has been widely used in heat-resistant materials, corrosion-resistant materials, insulation materials, and sealing materials because of its excellent chemical stability, corrosion resistance, heat resistance, sealing performance, electrical insulation, extremely high electrical resistivity, and good aging resistance [38–41]. PTFE shows high thermal stability up to $200\sim 260\text{ }^{\circ}\text{C}$. As an insulation material, it is not only expected to maintain the integrity of the insulation layer while eliminating internal stresses and defects but it is also expected to enable SMCs to operate stably at higher temperatures. In addition, PTFE provides extremely high electrical resistivity, which can significantly reduce eddy current loss and improve the high-frequency magnetic performance of SMCs. Until now, there has been no report on iron-based SMCs prepared by utilizing a PTFE insulating layer.

In this paper, iron-based SMCs were prepared by utilizing PTFE as an insulating layer. The influences of PTFE content, compaction pressure, and annealing temperature on the magnetic properties of Fe/PTFE SMCs were discussed. The optimized process parameters and the performance control method were obtained by the analysis and discussion, which can provide guidance for regulating the properties of soft magnetic composites.

2. Results and Discussion

2.1. Characterization of the Fe/PTFE Composite Powders and Corresponding SMCs

The Fe/PTFE composite powders were fabricated by mixing raw iron powders and different amounts of PTFE powders (0 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt%) through ball milling (see Materials and Methods and Supplementary Materials for experimental details). Figure 1 shows the surface morphology of the raw iron powders and ball-milled Fe/PTFE composite powders containing 3 wt% PTFE at different magnifications. The raw iron particles exhibit relatively good dispersion and a smooth and clean surface (Figure 1a–c). The Fe/PTFE composite powders appear aggregated to some extent. The surface of the composite powders tends to become rougher and exhibits obvious floc aggregates. The floc aggregates are composed of small spherical particles (Figure 1d–f). These results confirm that a relatively thick insulating layer formed on the surface of the iron particles.

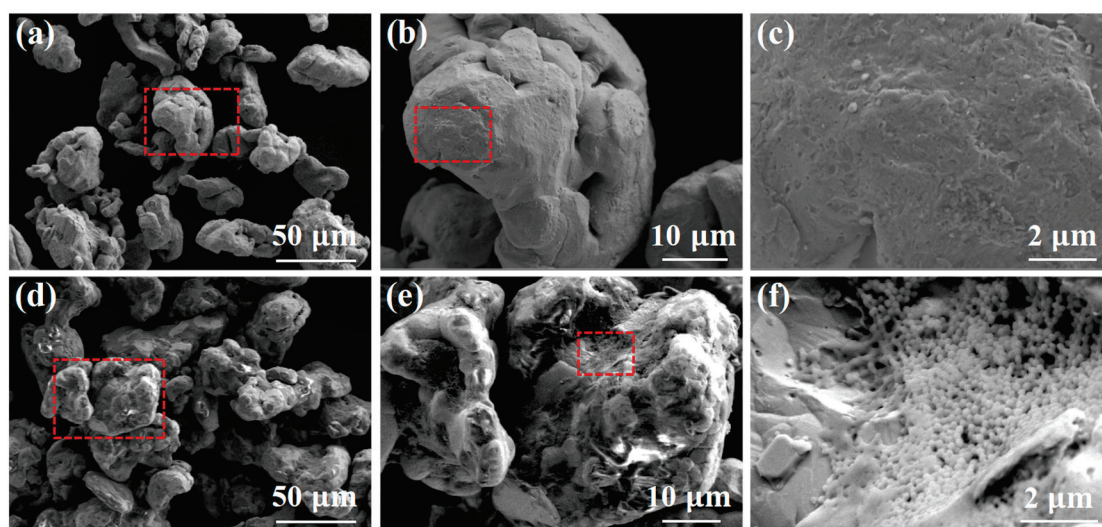


Figure 1. (a) SEM image of the raw iron powders; (b,c) are a partial enlargement corresponding to the red boxes in (a,b); (d) SEM image of the Fe/PTFE composite powders containing 3 wt% PTFE; (e,f) are a partial enlargement corresponding to the red boxes in (d,e).

To further confirm the phase structures of the insulating layer on the surface of the iron particles, an XRD pattern of the Fe/PTFE composite powders containing 3 wt% PTFE (blue line in Figure 2) was carried out. For comparison, XRD patterns of the raw iron powders (red line in Figure 2) and PTFE powders (black line in Figure 2) were also measured. As can be observed, the raw iron powders show three obvious characteristic peaks centered at 44.7° (110), 65.0° (200), and 82.3° (211), respectively, which correspond to the α -Fe phase (JCPDs Card: 99-0064). For the Fe/PTFE composite powders, a new characteristic peak occurs at 18.1° (100), which is consistent with the standard characteristic peak of PTFE (JCPDs Card: 54-1595). The appearance of the characteristic peak proves the presence of PTFE. Combined with SEM images of the Fe/PTFE composite powders containing 3 wt% PTFE (Figure 1d–f), these results confirm that a PTFE insulation layer is successfully coated on the surface of the iron particles.

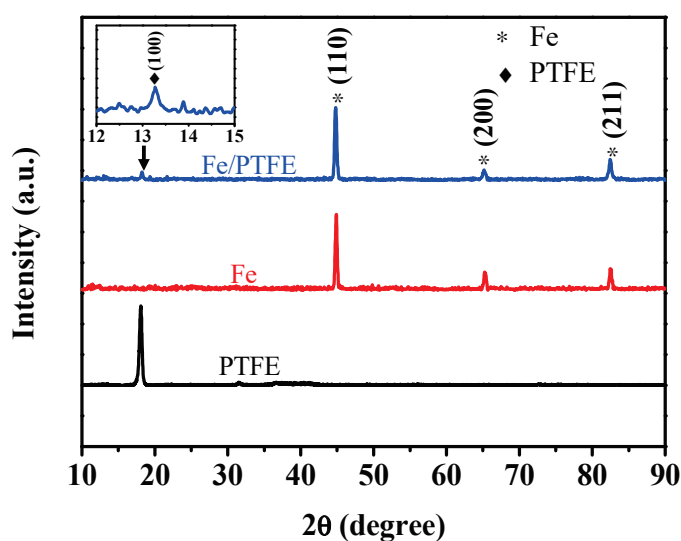


Figure 2. XRD patterns of the PTFE powders (black line), raw iron powders (red line), and Fe/PTFE composite powders containing 3 wt% PTFE (blue line).

The Fe/PTFE composite powders containing 3 wt% PTFE were compacted at 648 MPa, followed by annealing at 150°C for 90 min to obtain Fe/PTFE SMCs (see Materials and

Methods and Supplementary Materials for experimental details). To investigate the microstructure, especially the distribution of the PTFE insulating layer in Fe/PTFE SMCs, back-scattered electron images of the cross-sectional structure of the Fe/PTFE SMCs coated with 3 wt% PTFE were carried out. Figure 3a gives the morphology of the cross-section for the Fe/PTFE SMCs coated with 3 wt% PTFE. Figure 3b is a partial magnification corresponding to the white circle in Figure 3a. It can be seen that the iron particles are separated from each other by a PTFE insulating layer. The corresponding EDS spectra of the PTFE insulating layer and iron particles for the Fe/PTFE SMCs coated with 3 wt% PTFE are shown in Figure 3c,d. It is clear that the iron content decreases while the C content increases and the F content appears at the interface between iron particles, which indicates that the surface of the iron particles is covered by a PTFE insulating layer.

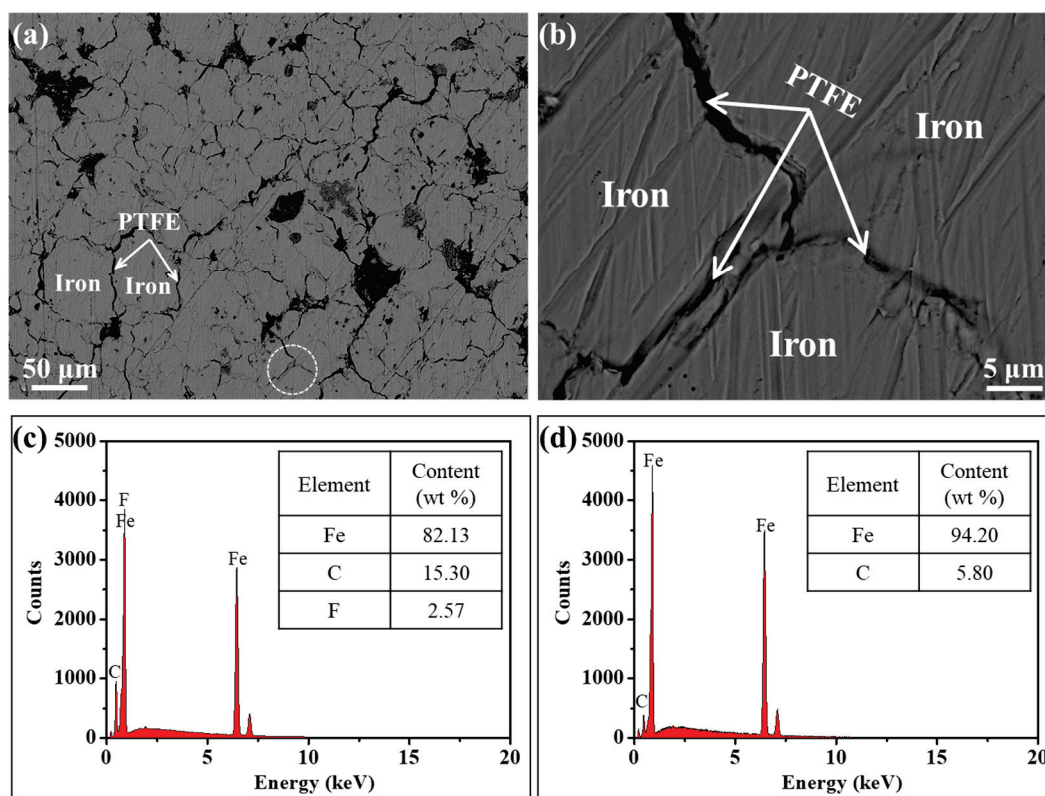


Figure 3. (a) SEM image of the cross-section of Fe/PTFE SMCs coated with 3 wt% PTFE; (b) is a partial enlargement corresponding to the white circle in (a); EDS spectra of (c) PTFE insulating layer and (d) iron particles for the Fe/PTFE SMCs coated with 3 wt% PTFE.

2.2. Effect of PTFE Content on the Magnetic Properties of Fe/PTFE SMCs

The Fe SMCs coated with different PTFE contents (0 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt%) were prepared by compacting at 648 MPa, followed by annealing at 150 °C for 90 min. Figure 4a shows the effective permeability as a function of PTFE contents at three different frequencies. With the increase in PTFE contents from 0 wt% to 5 wt%, the effective permeability decreases gradually from 71.0 to 42.4 (a decrease of 40%) (Table 1). The main reasons are as follows (see Supplementary Materials for Equations (S1) and (S2)): on the one hand, with the increase in PTFE content, the thickness of the insulation layer on the surface of iron particles increases, thereby increasing the air gap between metal particles; on the other hand, the magnetic dilution by nonmagnetic PTFE will increase the internal demagnetization field in Fe SMCs and then weaken the magnetic interaction between the iron particles. However, the Fe SMCs uncoated with PTFE exhibit poor frequency stability subjected to the deteriorating effect of eddy currents. Specifically, as the frequency increases from 1 kHz to 100 kHz, the effective permeability decreases monotonically from 71.0 to 68.5

(a decrease of 4%) (Table 1). Regarding PTFE-coated SMCs, the frequency stability becomes better with the increased PTFE content. This should be because the increase in PTFE coating thickness and resistivity (Table 1) can effectively isolate the adjacent powders and reduce the eddy current. The quality factor is a parameter of the energy storage and consumption performance of SMCs during alternating magnetization. In general, the higher the quality factor on behalf of SMCs, the lower the rate of energy loss. Figure 4b shows the variation in quality factor with tested frequencies for Fe SMCs coated with different PTFE contents. The Fe/PTFE SMCs with 3–5 wt% PTFE exhibit a higher and more stable quality factor at higher frequencies (60–100 kHz), which may be attributed to sufficient PTFE to form a continuous isolating layer. Thus, the 3 wt% PTFE-coated Fe SMCs cause a lower decrease and better frequency stability in effective permeability and a higher and more stable quality factor compared to other Fe/PTFE SMCs.

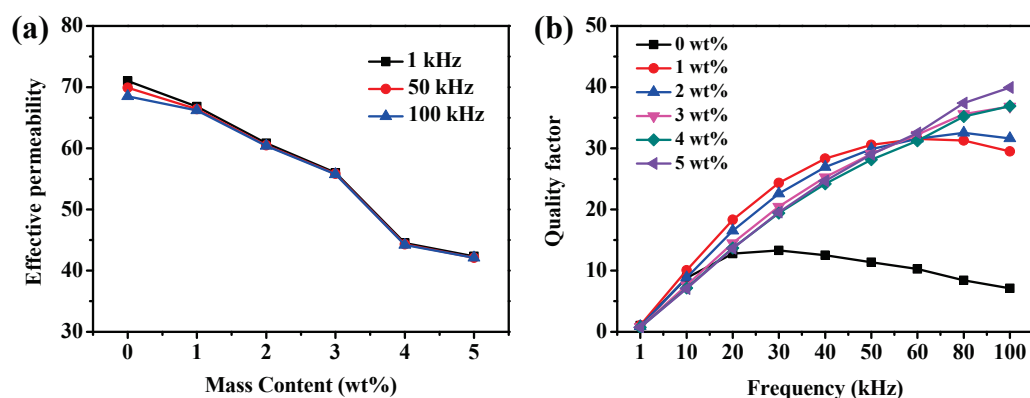


Figure 4. (a) Effective permeability of Fe/PTFE SMCs as a function of PTFE contents at three different frequencies; (b) quality factor of Fe/PTFE SMCs with different PTFE contents versus frequency.

Table 1. Effective permeability, saturation magnetization, coercivity, total core loss, and resistivity of Fe/PTFE SMCs containing different PTFE contents.

PTFE Contents (wt%)	Effective Permeability		Saturation Magnetization (emu/g)	Coercivity (Oe)	Total Core Loss (mW/cm ³)		Resistivity (mΩ·m)
					B _m = 50 mT	B _m = 100 mT	
	1 kHz	100 kHz			50 kHz	50 kHz	
0	71.0	68.5	217.6	15.2	695.1	3001	0.4
1	66.8	66.2	210.5	19.9	398.5	1874	4.3
2	60.8	60.4	197.5	35.5	415.4	1918	4.5
3	56.0	55.8	192.9	54.2	355	1705	19.9
4	44.5	44.2	187.0	62.2	416.5	1901	25.8
5	42.4	42.1	182.7	64	463.1	2057	97.3

The static magnetic properties of the Fe SMCs coated with different PTFE contents were studied. As shown in Figure 5a and Table 1, the value of saturation magnetization in Fe/PTFE SMCs decreases from 217.6 emu/g to 182.7 emu/g with increasing PTFE contents from 0 wt% to 5 wt%; this decreasing saturation magnetization is attributed to the promoted magnetic dilution by the increasing nonmagnetic PTFE contents. However, the coercivity in Fe/PTFE SMCs increases from 15.2 Oe to 64 Oe, indicating an opposite tendency to the variation in saturation magnetization. This should be a consequence of the fact that more pinning sites induced by nonmagnetic PTFE suppress the movement of the magnetic domain walls [31].

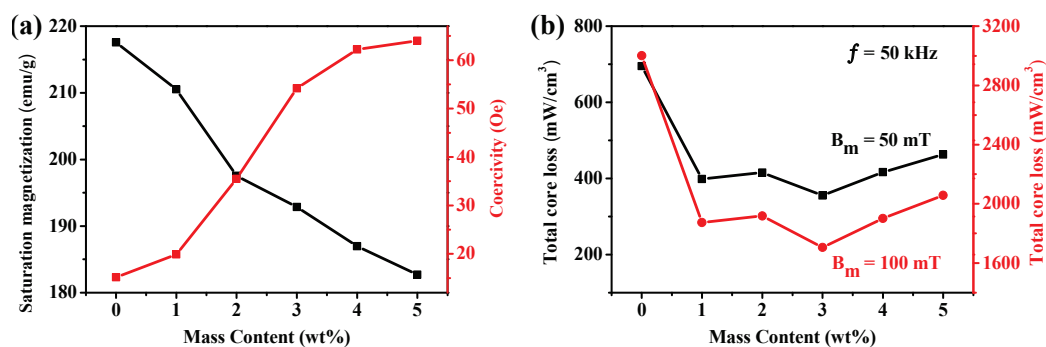


Figure 5. (a) Saturation magnetization (black line) and coercivity (red line) of Fe/PTFE SMCs containing different PTFE contents at a magnetic field of 20,000 Oe; (b) total core loss of Fe/PTFE SMCs with different PTFE contents measured at 50 kHz for $B_m = 50$ mT and 100 mT, respectively.

Low core loss is required for soft magnetic materials for application in the field of electro-magnetic devices. The total core loss (P_t) is calculated using the following equation [3,42–44]:

$$P_t = P_{hy} + P_{ed} + P_{re} \approx K_{hy} A f + K_{ed} B^2 f^2 d^2 / \rho \quad (1)$$

The total core loss (P_t) includes three parts: hysteresis loss (P_{hy}), eddy current loss (P_{ed}), and residual loss (P_{re}). P_{re} is caused by the relaxation process in magnetization and can be ignored because it is much smaller than P_{ed} and P_{hy} [1,45]. P_{hy} is known to be caused by hysteresis behavior and can be obtained from the corresponding hysteresis loop [46]. P_{ed} is caused by an eddy current generated by an alternating current field [47]. Meanwhile, A , B , d , and ρ indicate the area of the DC-hysteresis loop, magnetic flux density, eddy current radius, and electrical resistivity, respectively. K_{hy} and K_{ed} are dimensional constants. According to Equation (1), the hysteresis loss is proportional to the area of the DC-hysteresis loop, and the eddy current loss is inversely proportional to the electrical resistivity of samples. Therefore, improving the soft magnetic DC properties will decrease the area of the DC-hysteresis loop and thus decrease the hysteresis loss. Meanwhile, the increase in resistivity will lead to a decrease in eddy current loss. Figure 5b shows the PTFE content dependence of the total core loss in Fe/PTFE SMCs measured at 50 mT and 100 mT, 50 kHz. As the PTFE content increases, the iron particles are isolated by a PTFE insulation layer, which increases the electrical resistivity in Fe SMCs (Table 1) and reduces their eddy currents. However, the higher level of PTFE content increases the demagnetizing field, which increases the coercivity and area of the DC-hysteresis loop, thereby increasing the hysteresis loss of samples. Therefore, the Fe/PTFE SMCs containing 3 wt% PTFE demonstrate the minimal total core losses of 355 mW/cm³ and 1705 mW/cm³ measured at 50 mT and 100 mT, 50 kHz (Figure 5b and Table 1), which exhibit a 49% and 43% reduction compared to the uncoated Fe SMCs.

Therefore, it is clear that the Fe/PTFE SMCs containing 3 wt% PTFE have a low core loss, high effective permeability, and high saturation magnetization, in comparison with other amounts of PTFE-insulated Fe/PTFE SMCs. As a result, it can be concluded that 3 wt% is a relatively ideal insulating content for the PTFE-coated iron-based soft magnetic composites. To further optimize the magnetic properties of Fe/PTFE SMCs, the effects of compaction pressure and annealing temperature on the magnetic properties of the Fe/PTFE SMCs containing 3 wt% PTFE were investigated.

2.3. Effect of Compaction Pressure on the Magnetic Properties of Fe/PTFE SMCs

The compaction pressure is one of the important factors affecting the magnetic properties of SMCs. To investigate the effect of compaction pressure on the magnetic properties of Fe/PTFE SMCs, the Fe/PTFE SMCs containing 3 wt% PTFE were prepared by pressing at various compaction pressures (540 MPa, 594 MPa, 648 MPa, 702 MPa, and 756 MPa), followed by annealing at 150 °C for 90 min. Figure 6a illustrates the effective permeabil-

ity of Fe/PTFE SMCs at different compaction pressures. It can be found that effective permeability frequency dependence shows a similar tendency. In addition, the effective permeability of all Fe/PTFE SMCs at different compaction pressures decreases only slightly by about 9% with the frequency increases from 1 kHz to 100 kHz, confirming the excellent stability of the effective permeability over the entire frequency range. Meanwhile, the effective permeability of Fe/PTFE SMCs gradually increases from about 53 to 58 for all frequencies with the increasing pressure from 540 MPa to 756 MPa (Figure S1), which can be attributed to an increase in SMCs' density (Table 2 and Equation (S3)), which then leads to a decrease in the internal air gap and an increase in the volume fraction of the magnetic materials. Figure 6b shows the quality factor of Fe/PTFE SMCs prepared at various compaction pressures. It is clear that the quality factor of the Fe/PTFE SMCs compacted at 648 MPa is highest and most stable at higher frequencies (50–100 kHz). As the compaction pressure further increases, cracks appear on the surface of the particles and the damage to the integrity of the insulation layer leads to a deterioration of the quality factor.

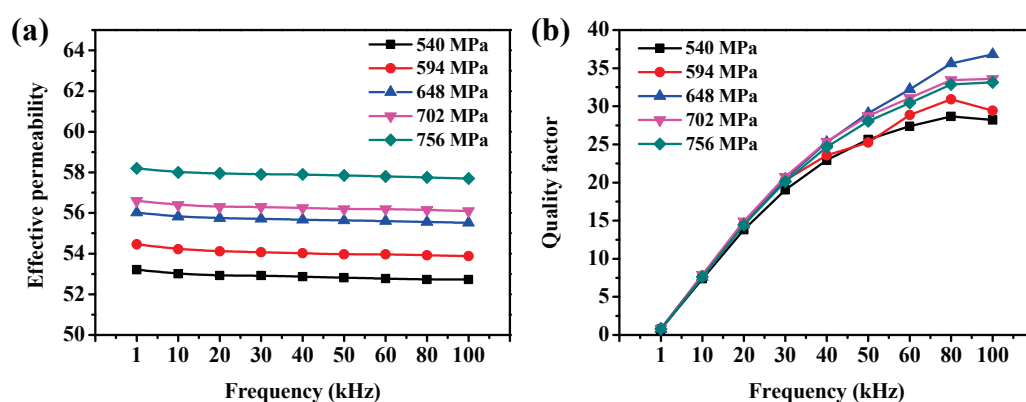


Figure 6. (a) Effective permeability and (b) quality factor of Fe/PTFE SMCs containing 3 wt% PTFE with various compaction pressures versus frequency.

Table 2. Density and resistivity of Fe/PTFE SMCs containing 3 wt% PTFE with various compaction pressures.

Compaction Pressure (MPa)	Density (g/cm ³)	Resistivity (mΩ·m)
540	6.53	9.4
594	6.61	12.9
648	6.74	19.9
702	6.79	10.8
756	6.85	7.4

The effect of compaction pressure on the total core loss of Fe/PTFE SMCs is shown in Figure 7. According to Equation (1), the hysteresis loss is proportional to frequency and the eddy current loss is proportional to the square of frequency. Therefore, the total core loss of all Fe/PTFE SMCs at different compaction pressures significantly increases with increasing frequency, as shown in Figure 7a,b. The hysteresis loss is mainly dependent on the hysteresis behavior. The internal air gap between the magnetic particles can hinder the magnetization process of SMCs, which would decrease with the increase in density of SMCs. Therefore, the hysteresis loss decreases with the increase in compaction pressure from 540 MPa to 648 MPa. The eddy current loss mainly depends on the resistivity of Fe/PTFE SMCs at the same frequency. The higher the resistivity, the lower the eddy current loss. According to Table 2, gradually increased resistivity can be formed to reduce the eddy current loss for Fe/PTFE SMCs compacted from 540 MPa to 648 MPa. But excessive compaction pressure may create cracks in the surface of the particles, thus destroying the

integrity of PTFE insulating layers and decreasing the resistivity between particles, which increases the eddy current loss [16]. Meanwhile, higher compaction pressure increases the residual stress, which increases the hysteresis loss. Therefore, the total core loss of Fe/PTFE SMCs decreases from 430 mW/cm³ to 355 mW/cm³ (50 mT, 50 kHz) and from 2015 mW/cm³ to 1705 mW/cm³ (100 mT, 50 kHz) when the compaction pressure increases from 540 MPa to 648 MPa and then begins to increase with a further increase in the compaction pressure (Figure 7c). Comparing these results, the optimum compaction pressure is 648 MPa.

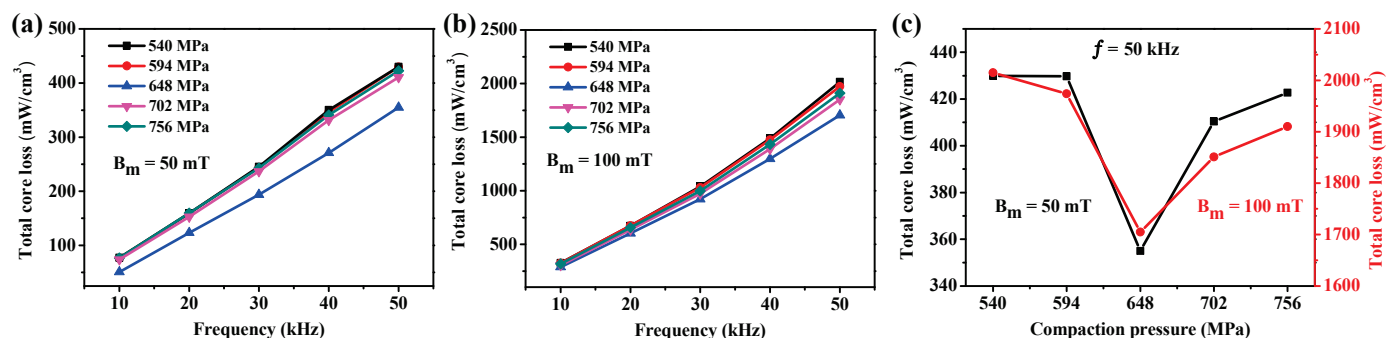


Figure 7. (a,b) Total core loss as a function of frequency for the Fe/PTFE SMCs containing 3 wt% PTFE at different pressures measured at (a) $B_m = 50$ mT and (b) 100 mT; (c) total core loss as a function of compaction pressure for the Fe/PTFE SMCs containing 3 wt% PTFE measured at 50 kHz for $B_m = 50$ mT and 100 mT, respectively.

2.4. Effect of Annealing Treatment on the Magnetic Properties of Fe/PTFE SMCs

Annealing treatment can eliminate the defects and residual stress inside SMCs, which has a significant effect on the magnetic properties of SMCs. The Fe/PTFE SMCs containing 3 wt% PTFE were prepared by pressing at 648 Mpa, followed by annealing at 100–200 °C for 90 min. Figure 8a illustrates the frequency-dependent effective permeability of Fe/PTFE SMCs at different annealed temperatures. The effective permeability of all samples shows excellent stability over the entire frequency range with a slight decrease of about 8‰ as the frequency increases from 1 kHz to 100 kHz at different temperatures. Meanwhile, the effective permeability of Fe/PTFE SMCs increases gradually as the temperature increases from 100 °C to 200 °C and reaches its highest value of about 58 (Figure S2). This result is because the effective permeability of Fe/PTFE SMCs is inversely proportional to the residual stress (Equation (S4)). As the temperature increases from 100 °C to 200 °C, the residual stress gradually decreases. In addition, the enhanced grain growth as well as interparticle bonding also result in a gradual increment in effective permeability.

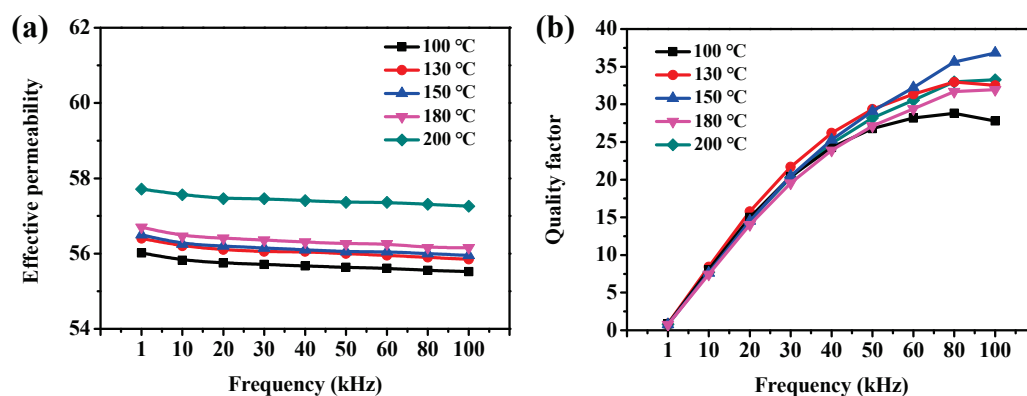


Figure 8. (a) Effective permeability and (b) quality factor as a function of frequency for the Fe/PTFE SMCs containing 3 wt% PTFE annealed at different temperatures.

Figure 9 shows the total core loss of Fe/PTFE SMCs annealed at different temperatures. The total core loss of all samples increases sharply with increasing frequencies. Also, the total core loss gradually decreases from 443 mW/cm³ to 355 mW/cm³ (50 mT, 50 kHz) and from 1970 mW/cm³ to 1705 mW/cm³ (100 mT, 50 kHz) with increasing annealing temperature from 100 °C to 150 °C. As the annealing temperature further increases from 150 °C to 200 °C, the total core loss dramatically increases to 427 mW/cm³ (50 mT, 50 kHz) and 1963 mW/cm³ (100 mT, 50 kHz), respectively. When annealed at lower temperatures (below 150 °C), the increase in annealing temperature releases the internal stress caused by the rapid pressing process, which decreases the total core loss. However, the further increase in annealing temperature above 150 °C results in the insulation layer being broken, which leads to a decrease in resistivity, thus increasing the total core loss. At the same time, the quality factor reaches its highest value at higher frequencies (50–100 kHz) for the Fe/PTFE SMCs annealed at 150 °C. When the annealing temperature exceeds 150 °C, the broken insulation layer leads to a decrease in quality factor (Figure 8b). Therefore, a higher annealing temperature (~150 °C) is considered to be the optimal heat treatment for the Fe/PTFE SMCs.

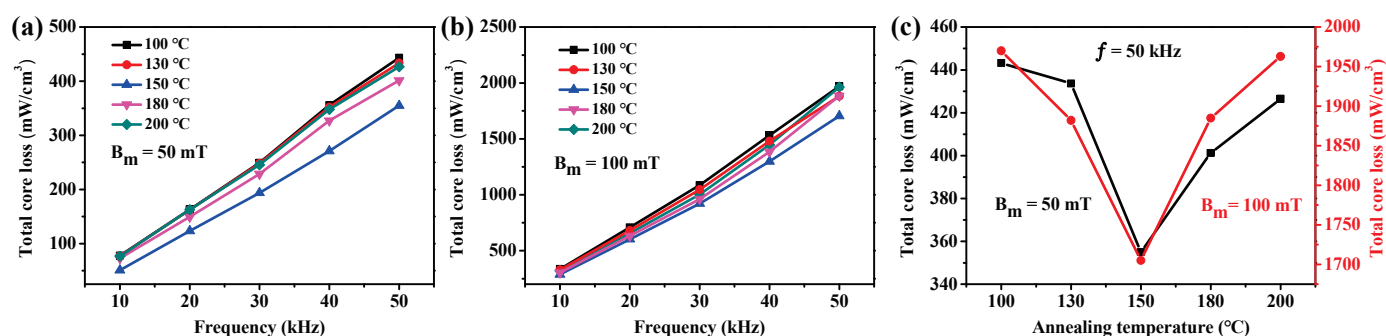


Figure 9. (a,b) Total core loss as a function of frequency for the Fe/PTFE SMCs containing 3 wt% PTFE annealed at different temperatures measured at (a) $B_m = 50$ mT and (b) 100 mT; (c) total core loss as a function of annealing temperature for the Fe/PTFE SMCs containing 3 wt% PTFE measured at 50 kHz for $B_m = 50$ mT and 100 mT, respectively.

Based on all the results shown above, the Fe/PTFE SMCs exhibit a high effective permeability of 56, high saturation magnetization of 192.9 emu/g, and low total core losses of 355 mW/cm³ (50 mT, 50 kHz) and 1705 mW/cm³ (100 mT, 50 kHz) at the optimum PTFE content of 3 wt% for the Fe/PTFE SMCs compacted at 648 Mpa, followed by annealing at 150 °C for 90 min. The effect of coating content and manufacturing parameters on the magnetic properties of iron-based SMCs has been studied previously in a number of works. For example, Sun and colleagues [24] investigated the effect of polyimide content and curing temperature on the magnetic properties for iron-based SMCs and found that a low core loss of 780 W/Kg (measured at 50 mT and 100 kHz) and higher maximum permeability of 305 are achieved at the optimized polyimide content of 1.5 wt% and curing temperature of 400 °C. However, the magnetic flux density of iron-based SMCs coated with a polyimide insulating layer could only reach 1.20 T, which is 26% lower than that in our work. Very recently, by investigating the effect of MnO₂ content on the microstructure and magnetic properties of iron-based SMCs, Zhang et al. [31] disclosed that the total core loss decreases gradually to 327.6 W/kg (50 kHz, 20 mT) when the MnO₂ content increases to 10.0 wt%. However, the saturation magnetization of 180 A·m²/kg and magnetic permeability of 22 are much lower than those in our work. Wu and colleagues [15] investigated the effect of compress pressure on the magnetic properties of iron-based SMCs with a parylene insulating layer. The results indicated that the parylene C-coated iron-based SMCs have a lower value of hysteresis loss coefficient and eddy current coefficient. However, the magnetic induction value increases to 1.01 T at the optimized pressure of 650 MPa, which

is 38% lower than that in our work. Therefore, our work provides progress and guidance for the research and development of high-performance iron-based SMCs.

3. Materials and Methods

3.1. Materials

Raw reduced iron powders (purity > 99.0%) provided by Chaoyang Jinhe Powder Metallurgy Material Co., Ltd. (Chaoyang, China) with a powder size of $\leq 75\ \mu\text{m}$ were used as the matrix material. PTFE powders with an average particle size of $25\ \mu\text{m}$, supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), were used as the insulating coating material.

3.2. Preparation of the Fe/PTFE SMCs

The iron powders and different amounts of PTFE powders (0 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, and 5 wt%, respectively) were mixed by ball milling, with a total of 16 g of the mixture. The obtained Fe/PTFE composite powders were compacted in a toroid die at 648 MPa. Finally, the obtained ring specimens were annealed at $150\ ^\circ\text{C}$ for 90 min. The optimal PTFE content was determined to be 3 wt%. To investigate the effect of compaction pressure, the ball-milled Fe/PTFE composite powders containing 3 wt% PTFE were compacted in a toroid die at 540 MPa, 594 MPa, 648 MPa, 702 MPa, and 756 MPa, respectively. Finally, the obtained ring specimens were annealed at $150\ ^\circ\text{C}$ for 90 min. To explore the effect of annealing temperature, the ball-milled Fe/PTFE composite powders containing 3 wt% PTFE were compacted at 648 MPa into ring specimens. The batch of ring specimens was then annealed at $100\ ^\circ\text{C}$, $130\ ^\circ\text{C}$, $150\ ^\circ\text{C}$, $180\ ^\circ\text{C}$, and $200\ ^\circ\text{C}$ for 90 min, respectively. Finally, the ball-milling time was 60 min and the rotational speed was 150 r/min. All compacted ring specimens had dimensions of an outer diameter of 20 mm, an inner diameter of 10 mm, and a height of 5 mm.

3.3. Characterizations

Surface topography of the raw iron powders, Fe/PTFE composite powders and Fe/PTFE SMCs, and corresponding EDS spectra were investigated by scanning electron microscopy (SEM, Supra 35VP, ZEISS, Jena, Germany) equipped with an energy-dispersive X-ray spectrometer (EDS, IE350PentaFetx-3, Oxford, UK). The phase structures of the raw PTFE powders, raw iron powders, and Fe/PTFE composite powders were characterized by X-ray diffraction (XRD, D500, Siemens, Germany) using $\text{Cu K}\alpha$ radiation with a step size of 0.02° from $2\theta = 10^\circ$ to 90° . Effective permeability and quality factor of Fe/PTFE SMCs were obtained by an impedance analyzer (LCR, IM3570A988-06, HIOKI E.E. CORPORATION, Hioki, Japan) with a frequency range of 1 kHz to 100 kHz at a voltage of 300 mV with ring specimens wound by 20 turns of enameled wire. The static magnetic properties (including the saturation magnetization and coercivity) of Fe/PTFE SMCs were measured with a SQUID-VSM test system (Quantum Design, State of California, USA) with an applied magnetic field of 20,000 Oe at room temperature. The SMCs' density was examined at least 3 times via the principle of Archimedes and the average value was recorded. The electrical resistivity of Fe/PTFE SMCs was tested via a 4-probe method (4-Point Probes Resistivity Measurement System, RTS-8, 4 Probes Technology Ltd., Guangzhou, China). The total core losses of Fe/PTFE SMCs were measured using a B-H curve analyzer (SY-8218, IWATSU, Tokyo, Japan) in a frequency ambit of 10–50 kHz and with a magnetic excitation level of 50 mT and 100 mT.

4. Conclusions

In this work, PTFE with excellent heat resistance, electrical insulation, and extremely high electrical resistivity was chosen to coat the iron powders. After adopting the compaction and annealing treatment processes, Fe/PTFE SMCs with a low core loss, high resistivity, high effective permeability, good frequency stability, high quality factor, and high saturation magnetization were finally prepared. The effects of PTFE content, com-

paction pressure, and annealing treatment on the magnetic properties of Fe/PTFE SMCs were investigated in detail. Results indicate that the low core losses of 355 mW/cm³ (50 mT, 50 kHz) and 1705 mW/cm³ (100 mT, 50 kHz), high effective permeability of 56, and high saturation magnetization of 192.9 emu/g were achieved at the optimum PTFE content of 3 wt% for the iron-based SMCs compacted at 648 Mpa, followed by annealing at 150 °C for 90 min.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29174019/s1>, Figure S1: Effective permeability as a function of compaction pressure for the Fe/PTFE SMCs containing 3 wt% PTFE at different frequencies; Figure S2: Effective permeability as a function of annealing temperature for the Fe/PTFE SMCs containing 3 wt% PTFE at different frequencies. References [48–52] are cited in the Supplementary Materials.

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Review

Metal Complexes of Bispidine Derivatives: Achievements and Prospects for the Future

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Abstract: Multidentate bispidine ligands, including tetra-, penta-, hexa-, hepta-, and octadentate variants, exhibit strong coordination tendencies due to their intrinsic rigidity, significant reorganization potential, and ability to efficiently encapsulate metal ions. These structural attributes profoundly influence the thermodynamic stability, metal ion selectivity, redox behavior, and spin-state configuration of the resulting complexes. Metal ions, in turn, serve as highly suitable candidates for coordination due to their remarkable kinetic inertness, rapid complex formation kinetics, and low redox potential. This review focuses on ligands incorporating the bispidine core (3,7-diazabicyclo[3.3.1]nonane) and provides an overview of advancements in the synthesis of metal complexes involving p-, d-, and f-block elements. Furthermore, the rationale behind the growing interest in bispidine-based complexes for applications in radiopharmaceuticals, medicinal chemistry, and organic synthesis is explored, particularly in the context of their potential for diagnostic and catalytic drug development.

Keywords: bispidine; bispidine framework; metal complexes; synthesis; radiopharmaceuticals; catalyst

1. Introduction

Bispidine 1 (3,7-diazabicyclo[3.3.1]nonane), composed of two condensed piperidine rings, was first synthesized by Mannich and Moss in the 1930s through the condensation of piperidine with paraformaldehyde and primary amines [1]. Its coordination with transition metals was later established by Stetter and Haller in 1957 and 1969, respectively [2]. Since then, the bispidine framework has been extensively studied in coordination chemistry [3–5], organic synthesis [6,7], radiopharmaceuticals [8–11], and medical chemistry [12]. Naturally occurring bispidine derivatives are found in *Genista* and *Lupinus* species in the form of the cyclic alkaloids such as cytisine 2, spartein 3, and lupanin 4 (Figure 1), which exhibit antiarrhythmic, anticonvulsant, and antimicrobial properties [13–15].

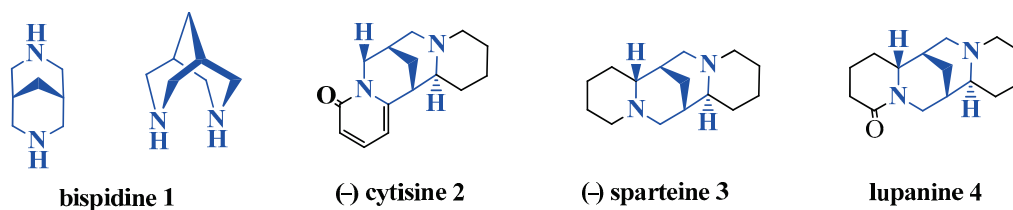
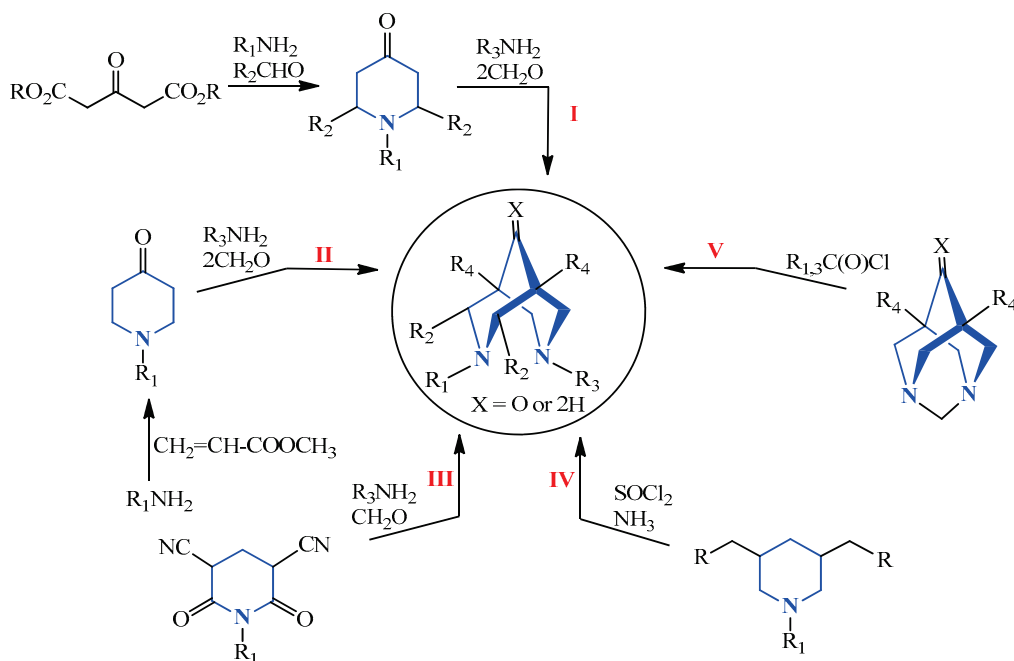


Figure 1. Bispidine framework and natural alkaloids containing it.

Derivatives of 3,7-diazabicyclo[3.3.1]nonane can typically be synthesized through five distinct methods (Scheme 1):



Scheme 1. Synthesis methods of 3,7-diazabicyclo[3.3.1]nonanes. (I) Mannich reaction-based synthesis from carbonyl compounds and aliphatic amines [16]; (II) transformation of 4-piperidones into 3,7-diazabicyclo[3.3.1]nonanes [17]; (III) acid hydrolysis of carboxylic acid nitrile derivatives, reduction and, in some cases, alkylation (or acylation with subsequent reduction) of the obtained 3,7-diazabicyclo[3.3.1]nonanes [18]; (IV) cyclization of 3,5-bifunctional piperidine derivatives [13]; (V) ring-opening of the 1,3-diazaadamantane cycle [19].

2. The Structure of Bispidine Ligands

The bispidine frame can adopt three primary conformations: armchair–armchair, armchair–boat (or boat–chair), and boat–boat. Among these, the armchair–armchair conformation is generally the most energetically favorable and is particularly suitable for capturing one or two protons via intramolecular hydrogen bonding ($\text{N-H}\cdots\text{N}$ and $\text{N-H}\cdots\text{Cl}\cdots\text{H-N}$). This conformation also facilitates efficient metal chelation. The donor centers, specifically N7 and N3, contribute to the rigidity of the ligand framework, while the incorporation of additional donor groups, such as pyridyl moieties at C2 and C4, introduces structural flexibility. Furthermore, bispidine ligands can exhibit configurational isomerism (Figure 2), resulting in different ligand orientations: endo/endo ligands (fully equatorial), exo/endo (axial and equatorial), and exo/exo (fully axial). The endo/endo configuration is particularly advantageous for creating a well-organized coordination environment, ensuring optimal donor positioning for metal complexation [20–22].

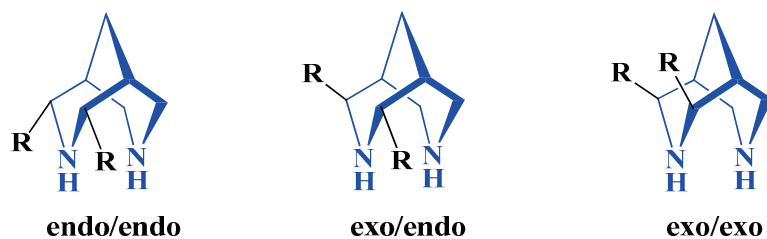


Figure 2. Possible configuration isomers of bispidine.

Studies have demonstrated that NMR spectroscopy can effectively determine the *cis*/*trans* configurations (Figure 3) of substituents at the 2nd and 4th positions [23]. In the armchair–armchair conformation, phenyl substituents at C2 and C4 adopt equatorial positions, resulting in a *cis*-symmetric configuration. However, the introduction of bulky substituents or hydrogen bonds accepting groups at N3 induces a transition to the *trans*-configuration.

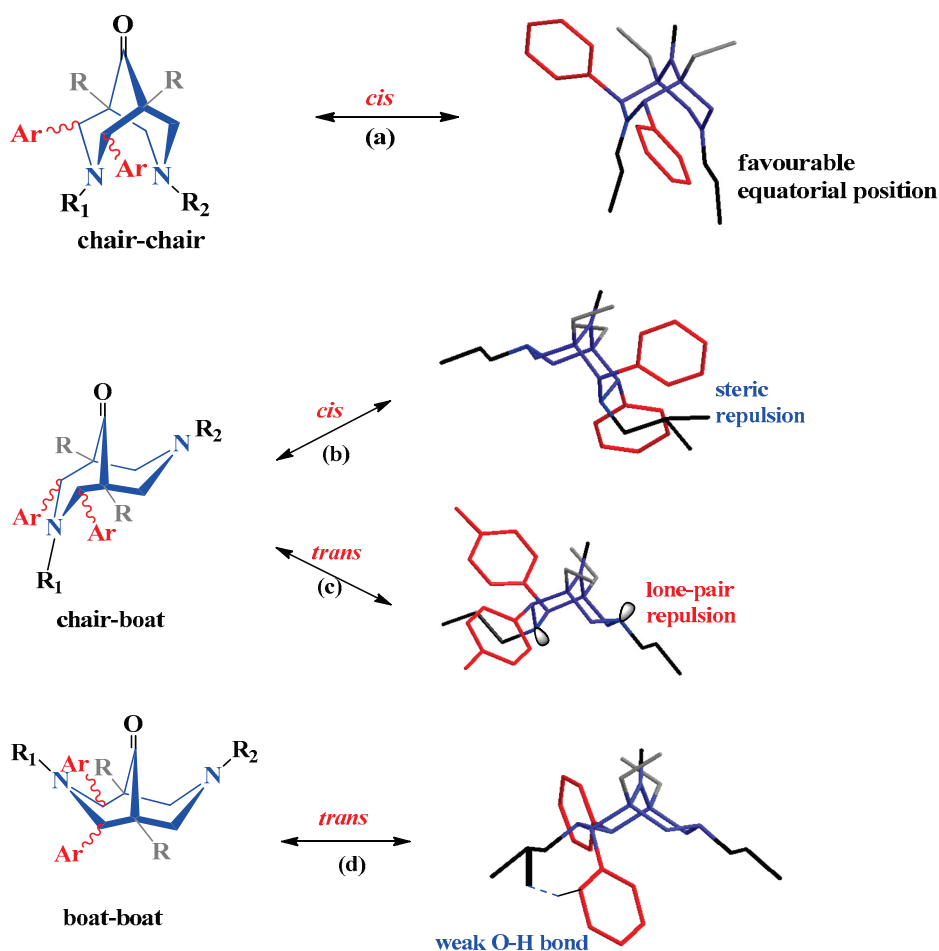


Figure 3. Structural conformations of bispidons. (a) *cis*-chair–chair, (b) *cis*-chair–boat, (c) *trans*-chair–boat, (d) *trans*-boat–chair.

The structures of all ligands and the characteristics of their metal intermediates discussed in the article are shown in Figure 4 and in Table 1.

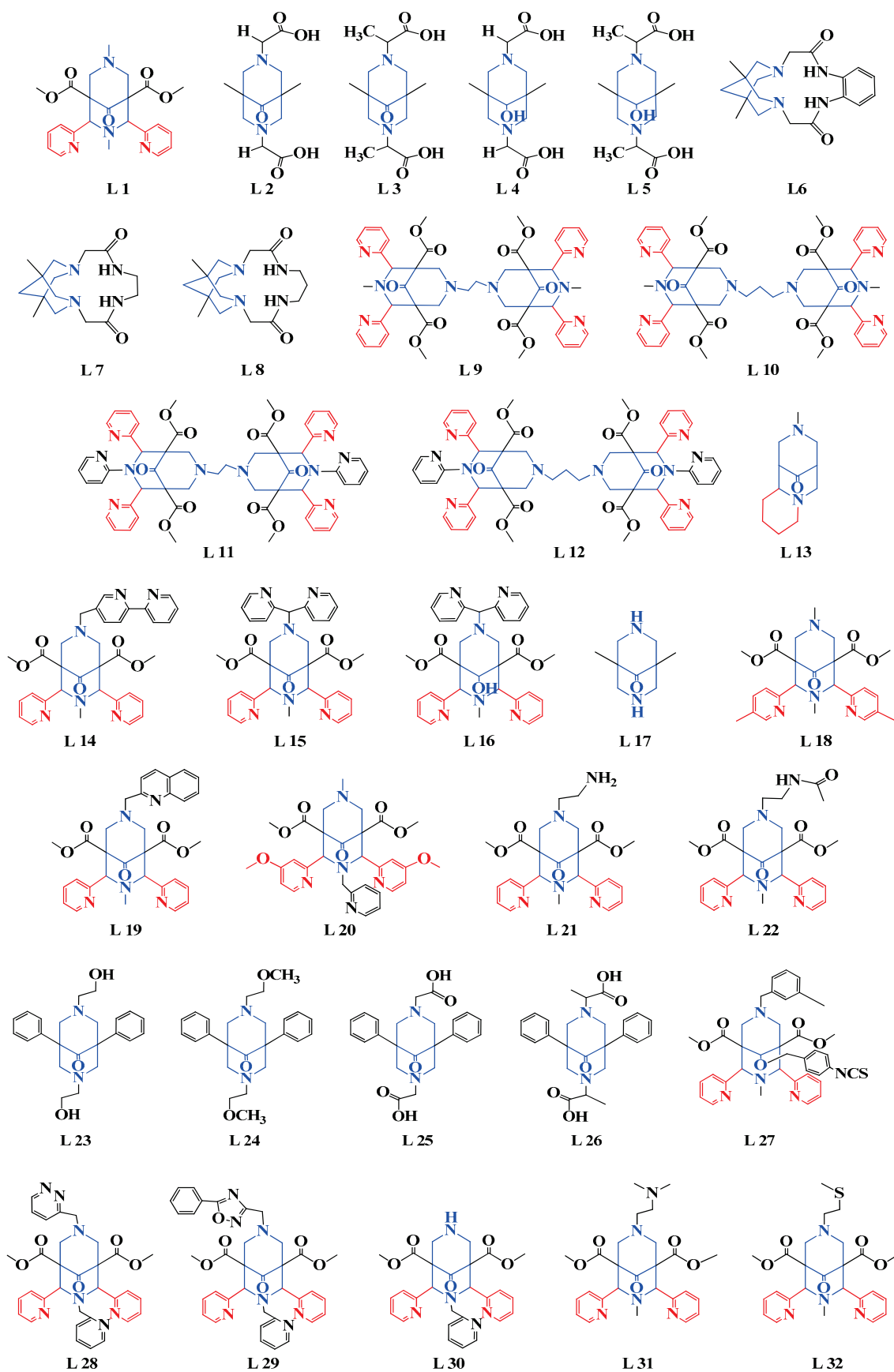


Figure 4. Cont.

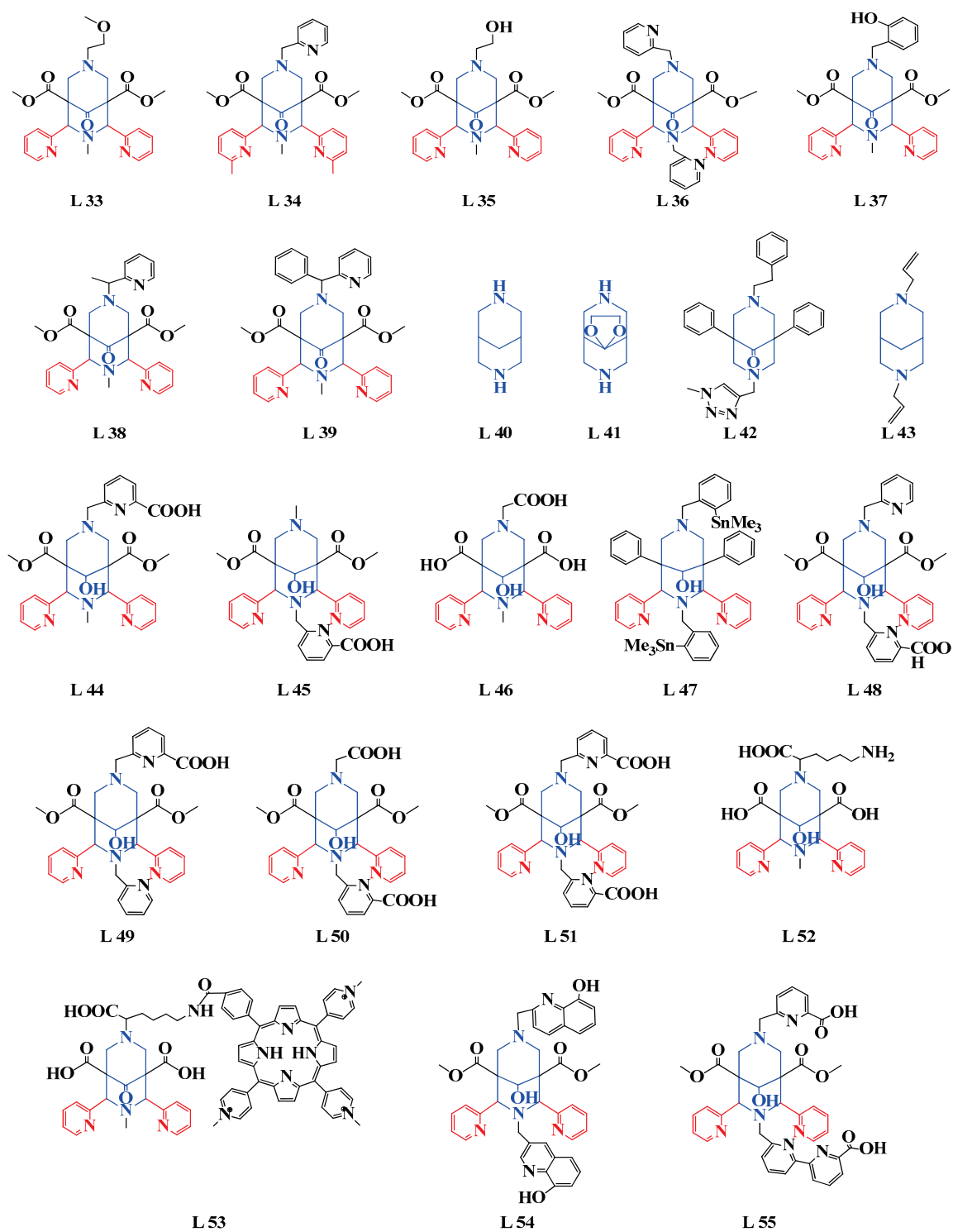


Figure 4. Structures of bispidine ligands.

Table 1. Some characteristics of various metal complexes containing bispidine framework.

No	Salts	Lig. (L)	Complex, Solvent	λ_{max} { ϵ (M ⁻¹ cm ⁻¹)}	Yield, %	The Color of the Solid	Synthesis Method	Application	Ref.
1	CuCl ₂ ·2H ₂ O	L 1	[Cu(L)Cl]Cl·2H ₂ O, MeOH	656 [90]	72	Blue	Diffusion of ether		[24]
2	Cu ₂ (OH) ₂ CO ₃	L 2–5	[L ₂ Cu(OH) ₂] H ₂ O	602–612 [247–252]		Blue	Neutralization with acidic chelate N ₂ O ₂	Radiopharmaceuticals, positron emission tomography (PET)	[25]
3	Cu(OAc) ₂ ·2H ₂ O	L 6 L 7–8	[Cu(L)(O)], MeOH [Cu(L)(OH ₂)], MeOH	483 [149] 476 [117] 524 [189]	56	Red and purple	Recrystallization	⁶⁴ Cu PET visualization	[26]
4	Cu(BF ₄) ₂	L 1, L 9–12	[Cu(L)(NCMe)] ²⁺ , MeCN [Cu ₂ (L)(NCMe)] ⁴⁺ , MeCN, MeOH	450 [510] 453 [577] 456 [685] 468 [651] 532 [1640]	58			Catalytic enzymatic oxidation of catecholamines	[27]
5	CuCl ₂	L 13	[Cu(L)Cl]Cl, MeOH		55	Green	Recrystallization	The catalyst for Henry's enantioselective reaction	[28]
6	Cu(ClO ₄) ₂ ·6H ₂ O	L 14	[Cu(L)](ClO ₄) ₂ , MeOH:H ₂ O	412	70	Green	Heating, concentration at low pressure	The aziridination reaction	[29]
7	Cu(BF ₄) ₂	L 15 L 16	[Cu(L)](BF ₄) ₂ ·3H ₂ O, MeCN [Cu(L)](BF ₄) ₂ ·2H ₂ O, MeCN	626 [119] 630 [112]	74 54	Blue	Evaporation, diffusion of ether heating, diffusion of ether	The aziridination reaction	[30]
8	Cu(ClO ₄) ₂ ·6H ₂ O CuCl ₂ ·2H ₂ O CuBr ₂ ·2H ₂ O Cu(NO ₃) ₂ ·3H ₂ O Cu(CF ₃ COO) ₂ ·4H ₂ O	L 17	[Cu(L) ₂ (ClO ₄) ₂ , EtOH [Cu(L) ₂ Cl]Cl, EtOH [Cu(L) ₂ Br]Br, EtOH [Cu(L) ₂ (NO ₃) ₂ , EtOH [Cu(L) ₂ (CF ₃ COO) ₂ , EtOH	284 [450] 273 [462] 272 [482] 288 [450] 284 [485]	95 – 68 51 –	Pink Blue Purple Yellow	Concentration at low pressure, recrystallization	Development of supramolecular coordination polymers	[31]
9	Cu(CF ₃ SO ₃) ₂ Cu(BF ₄) ₂ ·6H ₂ O	L 1 L 18 L 19	[Cu(L)](CF ₃ SO ₃) ₂ , MeCN [Cu(L)](BF ₄) ₂ ·3H ₂ O, MeCN [Cu(L)](BF ₄) ₂ ·4H ₂ O, MeCN	– 624 [25] 881 [60]	83 88 89		Diffusion of ether	The aziridination reaction	[32]
10	Cu(ClO ₄) ₂ ·6H ₂ O	L 20–21 L 22	[Cu(L)](ClO ₄) ₂ , MeCN [Cu(L)](ClO ₄), MeCN	629 627 564	84 69 92	Blue Blue Purple	Diffusion of ether	⁶⁴ Cu PET visualization	[33]
11	CuCl ₂ Cu(ClO ₄) ₂ Cu(OH) ₂	L 23 L 24 L 25 L 26	[Cu(L)]Cl ₂ , EtOH [Cu(L)](ClO ₄) ₂ , CHCl ₃ [Cu(L)](OH) ₂ , DMF			Blue Purple Dark- blue	Heating, recrystallization	Catalysts for enantioselective reactions	[34]
12	CuX ₂	L 27	[Cu(L)X]X					For the synthesis of radiopharmaceuticals based on Cu(II) ions	[35]
13	Fe(BF ₄) ₂ ·6H ₂ O Fe(ClO ₄) ₂ ·H ₂ O Fe(BF ₄) ₂ ·6H ₂ O	L 36 L 28 L 29 L 30	[Fe(L)] 2BF ₄ , MeCN [Fe(L)]·2ClO ₄ , MeCN [Fe(L)(MeCN)]·2BF ₄ , MeCN	458 [5560] 455 [10,870] 443 [12,570] 444 [7144]	71 36 25 17	Red-black Dark-brown – Dark-brown	Diethyl ether diffusion, heating, recrystallization	For the design of responsive off-on probes	[36]
14	Fe(MeCN) ₂ (OTf) ₂	L 31 L 32 L 33	[Fe(L) MeCN] ²⁺ , MeCN	37 [1061] 380 [1057] 373 [1112]	88 84 88	Yellow Brown Light-yellow	Slow vapor diffusion with diethyl ether	For oxidizing ClO ₂ [–] to ClO ₂	[37]

Table 1. Cont.

No	Salts	Lig. (L)	Complex, Solvent	λ_{max} { ϵ (M ⁻¹ cm ⁻¹)}	Yield, %	The Color of the Solid	Synthesis Method	Application	Ref.
15	Fe(OOCC ₇ H ₁₅) ₂	L 34	[Fe(L)OOCC ₇ H ₁₅](OOCC ₇ H ₁₅)	400	57	Canary	Evaporation, recrystallization	Catalyst for the auto-oxidation process	[38]
16	[Fe(NCCCH ₃) ₂ ·(CF ₃ SO ₃) ₂] Fe(SCN) ₂ FeSO ₄ FeCl ₂ Fe(ClO ₄) ₂ FeCl ₂	L 1	[Fe(L)(CF ₃ SO ₃) ₂ ·CD ₃ CN]	392					
		L 1	[Fe(L)(SCN) ₂], CD ₃ CN	375					
		L 34	[Fe(L)SO ₄], MeOH	404					
		L 35	[Fe(L)Cl]Cl, MeOH	412 [1819]	40–70		Ether diffusion, recrystallization	Catalysts	[39]
		L 36 L 37	[Fe(L)](ClO ₄) ₂ , MeOH [Fe(L)Cl]Cl, MeOH	564 [215] 579 [948]					
17	[Fe(NCCCH ₃) ₂ ·(CF ₃ SO ₃) ₂]	L 38	[Fe(L)(CF ₃ SO ₃) ₂](CF ₃ SO ₃), MeCN		73	Yellow	Recrystallization	A catalyst for bioinspired catalysis	[40]
		L 39	[Fe(L)(CF ₃ SO ₃) ₂](CF ₃ SO ₃)·3H ₂ O, MeCN		33				
18	FeCl ₂ Fe(ClO ₄) ₂ Fe(BF ₄) ₂ ·6H ₂ O	L 16	[Fe(L)Cl]Cl, MeCN	412 [1381]	52				
		L 15	[Fe(L)(OCH ₃) ₂](ClO ₄) ₂ , MeOH	-	49	Yellow	Diffusion of ether	The activation process	[30]
		L 15	[Fe(L)(OCH ₃) ₂](BF ₄) ₂ , MeOH	364 [1245]	54				
19	MnCl ₂ ·4H ₂ O	L 15	[Mn(L)Cl] ₂ [MnCl ₄], MeCN; MeOH		56	Colorless	Evaporation, diffusion of ether	PET visualization	[30]
20	(C ₆ H ₁₀)PtCl ₂	L 40	[Pt(L)Cl]Cl, DMF		87			Cytotoxicity against human cancer cell lines K562 (chronic myeloid leukemia), A2780 (ovarian cancer)	[41]
			[Pt(L)Cl]Cl·C ₃ H ₇ NO, DMF		87	Yellow	Recrystallization, cooling heating, recrystallization		
			[Pt(L)Cl]Cl·3H ₂ O, H ₂ O		60				
21	(C ₆ H ₁₀)PtCl ₂	L 41	[Pt(L)Cl]Cl, DMF		97	Yellow	Heating, recrystallization	Preparation of compounds with cytotoxic activity	[42]
22	PdCl ₂	L 42	[Pd(L)Cl]Cl, MeCN					Might be used as catalysts under microwave irradiation	[43]
23	Ni(acac) ₂	L 43	[Ni(L)](acac) ₂ ·C ₃ H ₁₂		99	Blue	Cooling	Immobilization of metal heterogeneous surfaces	[44]
24	Ni(NO ₃) ₂ ·6H ₂ O	L 1	[Ni(L)(NO ₃) ₂](NO ₃), MeCN; MeOH		98	Pink	Evaporation, recrystallization	A catalyst for bond formation C(sp ²)-C(sp ³)	[45]
25	Zn(OAc) ₂ ·2H ₂ O	L 44 L 45	[Zn(L)](TFA), TFA, MeOH		98 61	Colorless	Evaporation, diffusion of ether	Bifunctional Chelators for ⁶⁴ Cu PET	[46]
26	ZnCl ₂	L 46	[Zn(L)Cl], THF, H ₂ O				Evaporation, centrifugation	Chelator for radiolabeling studies with ⁶⁴ Cu	[47, 48]
27	Co(OAc) ₂ ·2H ₂ O	L 44 L 45	[Co(L)](TFA), TFA, MeOH	470 [123] 475 [117]	32 67	Red Brown	Evaporation, diffusion of ether	Bifunctional Chelators for ⁶⁴ Cu PET	[46]
28	¹⁹⁹ HgCl ₂ Na ²¹⁸ HgCl ₂	L 47	[Hg(L)], EtOH [Hg(L)], THF				Heating, evaporation	Theranostic applications in radiopharmaceuticals	[49]
29	Bi(NO ₃) ₃ ·5H ₂ O	L 48	[Bi(L)](NO ₃) ₂ , MeOH		93		Recrystallization		
		L 49	[Bi(L)(NO ₃) ₂](NO ₃), MeOH		99				
		L 50	[Bi(L)(Br) _{0.5} (NO ₃) _{0.5}], MeOH		60				
		L 51	[Bi(L)(NO ₃) ₂], MeOH [Bi(L)(NO ₃) ₂](NO ₃), MeOH		95 67		Evaporation, recrystallization	Targeted ²¹³ Bi alpha therapy	[50]

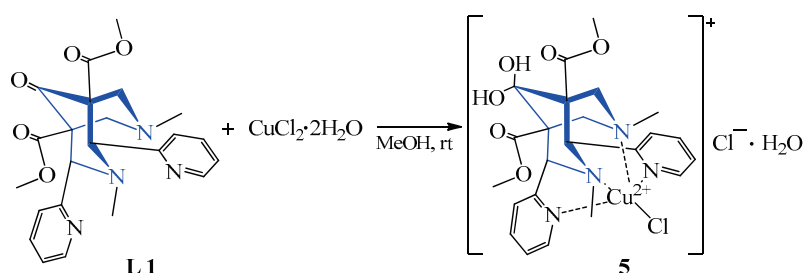
Table 1. Cont.

No	Salts	Lig. (L)	Complex, Solvent	$\lambda_{\max}$ { ϵ ($M^{-1} \text{ cm}^{-1}$)}	Yield, %	The Color of the Solid	Synthesis Method	Application	Ref.
30	GaCl ₃	L 52 L 53	[Ga(L)]Cl, H ₂ O	- 422 (240)	90	White Purple	Heating, recrystallization	PET visualization, creating stable theranostic probes for PET / PDT	[51]
31	Ga(NO ₃) ₃	L 48	[Ga(L)](TFA)(NO ₃), TFA, MeOH:H ₂ O		65	Colorless	Heating, evaporation	Bifunctional Chelators for ⁶⁴ Cu PET	[46]
32	In(ClO ₄) ₃ ·8H ₂ O	L 54	[In(L)](ClO ₄), MeOH		39	Orange	Concentration in a vacuum	Creation of a chelating component in radiopharmaceuticals based on In	[52]
33	In(OAc) ₃ ·5H ₂ O	L 51	[In(L)](TFA), TFA, MeOH, H ₂ O		88	Colorless	Evaporation	Chelators in nuclear medicine used in single-photon emission computed tomography (SPECT)	[53]
	Lu(OAc) ₃ ·4H ₂ O		[Lu(L)](TFA), TFA, MeOH		84		Evaporation, diffusion of ether		
	LaCl ₃ ·7H ₂ O		[La(L)](TFA), TFA, MeOH		81		Evaporation, concentration in vacuum		
34	Nd(OAc) ₃	L 51	[Nd(L)(OH) ₂](TFA)·(MeOH), TFA, MeOH	-		Colorless	Evaporation, diffusion of ether	Acting as an antenna for energy transmission	[54]
	Tb(NO ₃) ₃		[Tb(L)(OH) ₂](TFA)·2H ₂ O·MeCN, TFA, H ₂ O, MeCN	491					
	Dy(OAc) ₃		[Dy(L)(OH) ₂](TFA)·1.5H ₂ O·MeCN, TFA, H ₂ O, MeCN	-					
	Tb(NO ₃) ₃		[Tb(L)](NO ₃) MeOH·H ₂ O, MeOH:H ₂ O	261					
35	Eu(OAc) ₃	L 55	[Eu(L)](OAc), EtOH:MeOH	261	40–70		Heating, evaporation	Biological fluorescent probes with red-shifted absorption	[55]
	Yb(NO ₃) ₃		[Yb(L)](NO ₃) MeOH, H ₂ O, MeOH,	262					

3. Synthesis of Metal Complexes with a Fragment of Bispidine

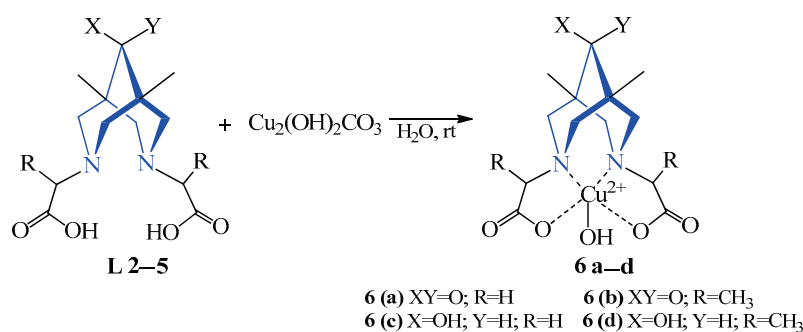
3.1. Bispidine Complexes of d-Block Transition Metals

Bispidine-type ligands (3,7-diazabicyclo[3.3.1]nonane) exhibit significant rigidity; as tetra-, penta-, and hexadentate bispidine derivatives originate from the highly rigid diazaadamantane framework. Transition metal complexes often require structural support from rigid multidentate ligands, making bispidine an ideal candidate for imparting unique coordination geometries. A representative copper-containing complex (**5**) was synthesized by stirring **L 1** in methanol (MeOH) at room temperature for 2 h with a methanolic solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, followed by ether diffusion. The reaction yielded the desired complex with a 72% efficiency (Figure 4, Table 1, Scheme 2) [24].



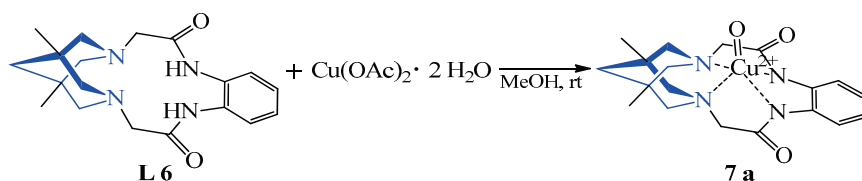
Scheme 2. Synthesis of complex **5**.

Solvent evaporation is commonly used to isolate target complexes following the interaction of a ligand with an inorganic salt, allowing for subsequent crystallization and solvent diffusion. However, this method may be ineffective when complexes exhibit high water solubility, preventing their formation. An alternative approach, demonstrated in [25], involves synthesizing copper complexes with an acidic N_2O_2 -chelate. In this method, aqueous solutions of ligands **L 2–5** and malachite were mixed and stirred overnight, yielding copper complexes **6 a–d** with high efficiency (Scheme 3).



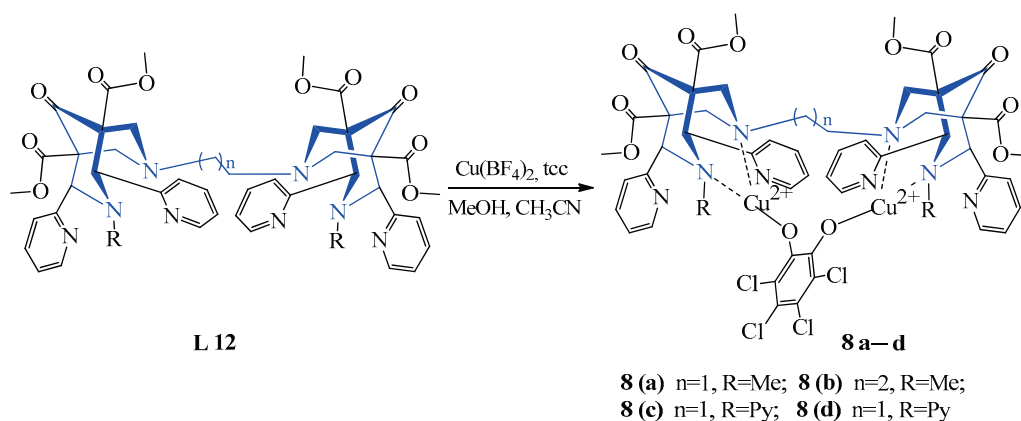
Scheme 3. Synthesis of copper complexes **6 a–d**.

Radioactive tracers play a crucial role in cancer diagnosis, particularly through positron emission tomography (PET). In this technique, a positron-emitting isotope binds to a biological carrier and selectively accumulates in cancerous cells. While ^{62}Cu is primarily limited to perfusion studies due to its short half-life [56,57], ^{64}Cu serves as an optimal positron emitter for both PET and targeted radiotherapy as, in its turn, it is an ideal [58–61]. In a related study, ligands **L 6–8** were combined with a $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution and stirred overnight at room temperature, yielding copper complexes **7 a–c** with an efficiency of 56% (Scheme 4) [26].



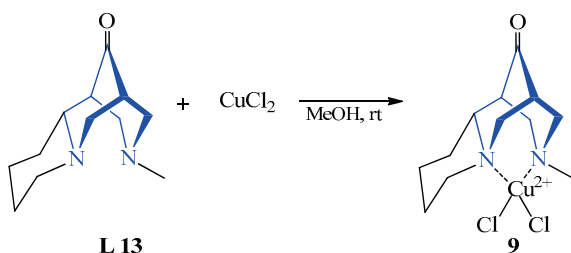
Scheme 4. Reaction of **L 6** with copper salt.

The oxidation of 3,5-di-*tert*-butylcatechin with oxygen was carried out using bispidine–copper complex catalysts **8 a–d** (bispidines with donor groups such as bis-tertiary amine-bispiridyl or bis-tertiary amine-trispiridyl). The catalysts **8 a–d**, featuring bispidine fragments, were synthesized by reacting **L 12**, 3,4,5,6-tetrachlorocatechin (tcc), and $\text{Cu}(\text{BF}_4)_2$ in the presence of acetonitrile and methanol. These reactions yielded the desired complexes with a 58% efficiency (Scheme 5) [27].



Scheme 5. Reaction of bispidine containing ligand **L 12** with copper salt.

When using bispidine ligands with copper as a catalyst in the Henry reaction, the product yield can be enhanced to 96%. To achieve this, complex **9** was synthesized reacting **L 13** with copper chloride (CuCl_2) under continuous stirring for 5 h at 25 °C (Scheme 6) [28]. The yield of reaction products between nitromethane and 4-nitrobenzaldehyde in the presence of a copper complex **9** (20 mol % of each) reaches to 95%, and when using keratin as a catalyst, only 66% [62].

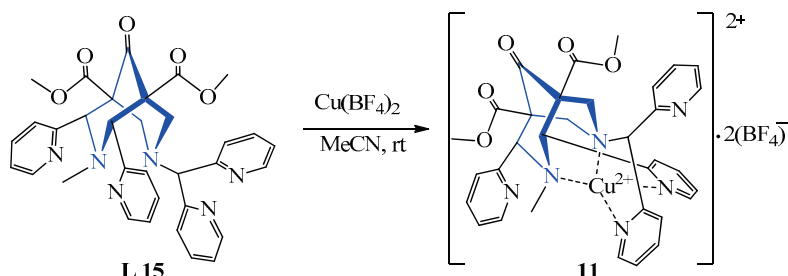


Scheme 6. Synthesis of complex **9**.

Oligonuclear transition metal complexes are of significant interest in photochemistry due to their ability to facilitate photoinduced energy and electron transfer. $\text{Ru}(\text{II})$ polypyridyl complexes serve as effective photoactive components, exhibiting favorable photophysical properties, such as a long excited-state lifetimes and high quantum luminescence yields. However, their application is limited by the high resistance of $\text{Ru}(\text{II})$ complexes to photodegradation. To address this issue, an intermediate copper complex **10**, based on the rigid bispidine ligand **L 14**, has been introduced as a potential alternative [29].

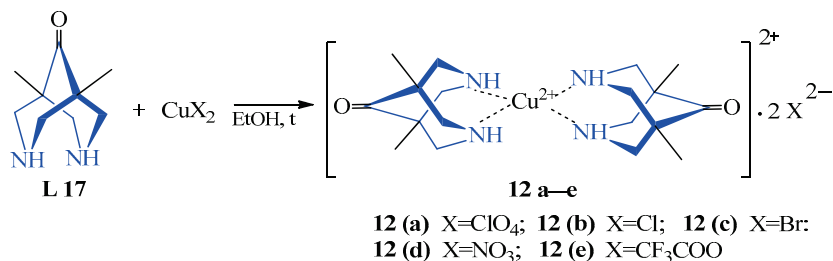
Comba and colleagues (Scheme 7) designed novel ligands **L 15** and **L 16**, 3-(2-methylpyridyl)-7-(bis-2-methylpyridyl)-3,7-diazabicyclo[3.3.1]nonane, featuring two ter-

tiary amine and four pyridine donor groups. These ligands can form both heteronuclear and mononuclear metal complexes and coordinate in different modes acting as pentadentate, hexadentate, or monodentate ligands. This versatility enables the formation of seven-coordinate pentagonal pyramidal and bipyramidal structures. The reaction of **L 15** with $\text{Cu}(\text{BF}_4)_2$ in acetonitrile yields copper complex **11** with an efficiency of 74% [30].



Scheme 7. Synthesis of copper complex **11**.

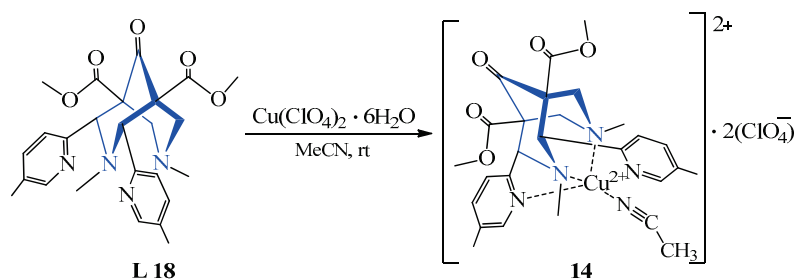
Supramolecular metallogels (SMG) are utilized in film production, nanowire synthesis, and the removal of organic contaminants. To facilitate SMG isolation, research has focused on synthesizing bispindine ligands and their complexes, which can form coordination polymers. In this context, complexes **12 a–e** were synthesized with yields ranging from 51% to 95% by reacting **L 17** and a hydrate copper salt in ethanol, followed by boiling for 2 h (Scheme 8) [31].



Scheme 8. Reaction of **L 17** with copper salts.

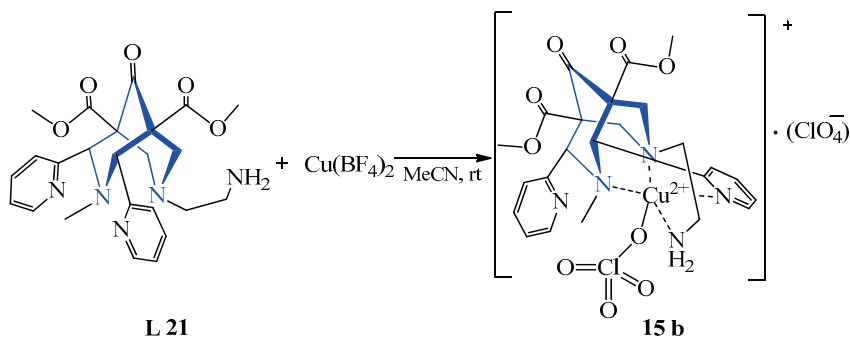
The aziridination reaction catalyzed by transition metals holds significant importance in organic synthesis, particularly in the dihydroxylation and epoxidation of nonfunctionalized alkenes. A highly promising approach involves the transfer of nitrenes to olefins in the presence of transition metal catalysts. In [32], the synthesis of copper complexes **13 a–c**, based on tetra- and pentadentate bispindine ligands **L 1**, **L 18**, **L 19**, is reported for use as catalysts.

The redox potentials and stability constants of $\text{Cu}(\text{II})$ complexes derived from tetradentate bispindine ligands can be changed by substituting pyridine rings. To achieve this, a suspension of **L 18** and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile was stirred for 2 h at room temperature, followed by ether diffusion, resulting in the isolation of complex **14** (Scheme 9) [63].



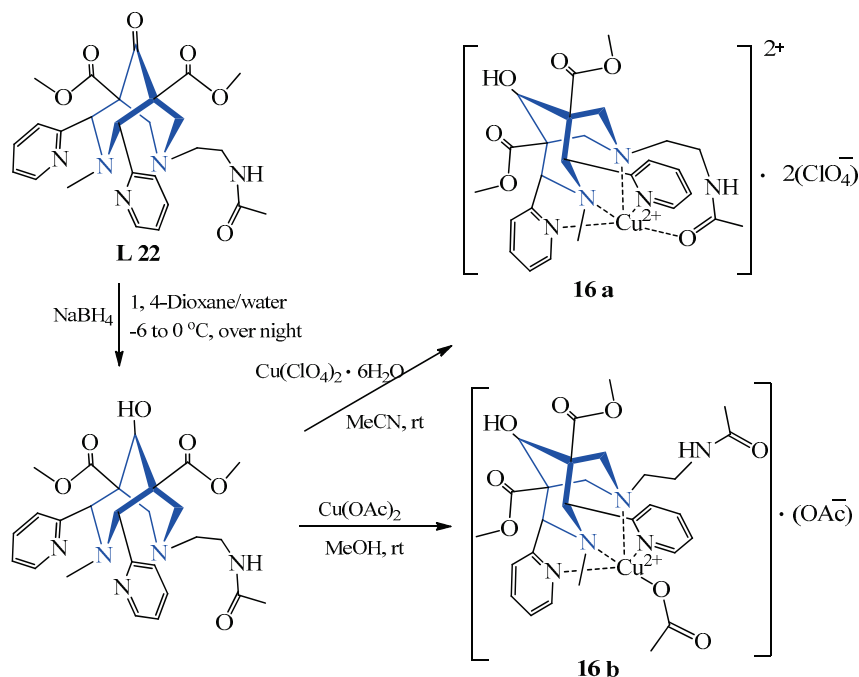
Scheme 9. Synthesis of copper-based complex **14**.

Pentadentate bispidine ligands **L 20–22** (3,7-diazabicyclo[3.3.1]nonanes) have been demonstrated to enhance complex stability and readily interact with biological molecules and fluorescent particles for PET imaging. Additionally, these ligands rapidly form stable complexes with Cu(II). In a representative synthesis, a reaction mixture of **L 21** and copper(II) perchlorate hexahydrate in acetonitrile was stirred overnight at room temperature, followed by ether diffusion, yielding complex **15 b** as blue crystals with a 69.4% yield (Scheme 10) [33].



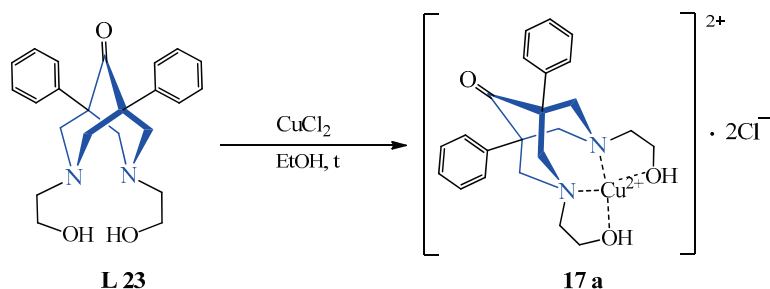
Scheme 10. Synthesis of complex **15 b**.

Bispidine ligands have demonstrated excellent efficiency in forming coordination conjugates with dyes, making them valuable for optical sensor development and imaging systems. Complexes **16 a, b** were synthesized from a ligand **L 22** derivative, reduced with sodium borohydride, and reacted with copper(II) acetate hexahydrate in a mixture of methanol and acetonitrile (Scheme 11) [64].



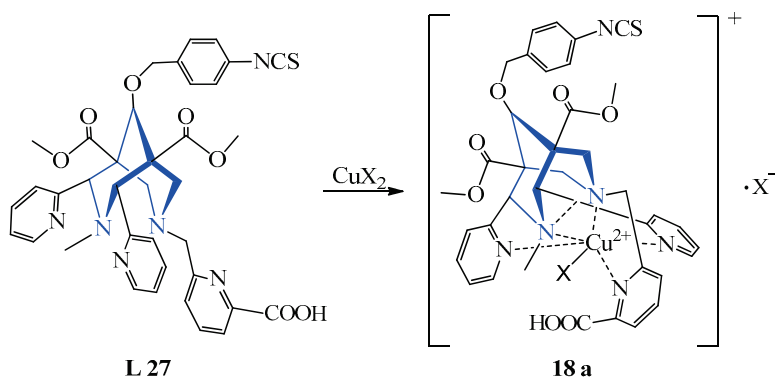
Scheme 11. Synthesis of hexacoordinate Cu complexes **16 a, b**.

Nitrogen atoms within the rigid bicyclic framework contribute to the selectivity and stability of complex formation with metal cations and even neutral atoms [65–67]. Vatsadze et al. [34] synthesized metal complexes **17 a–d** by reacting copper(II) chloride and perchlorate with **L 23–26** in appropriate solvents, followed by heating the mixtures and subsequently crystallizing the products (Scheme 12).



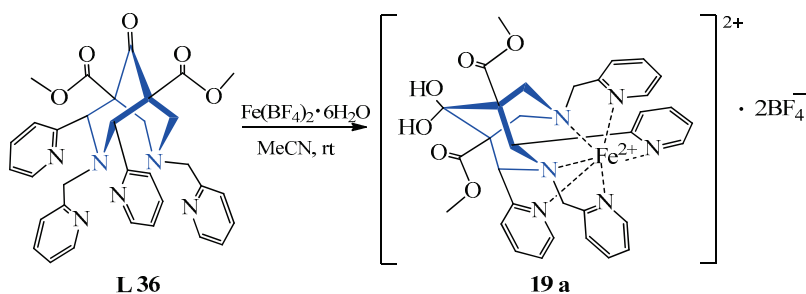
Scheme 12. Reaction tetradentate bispidine ligand **L 23** with copper salt.

The remarkable stability of radioactive copper complexes with bispidine-picolinates offers significant potential not only for PET imaging but also for radionuclide therapy using the therapeutic isotope copper-67 [68–70]. Radiopharmaceuticals based on Cu(II) ions have been synthesized through the formation of copper-containing compounds **18 a, b**, facilitated by the strong complexing properties of hexadentate picolinate-based bispidine ligand **L 27** (Scheme 13) [35].



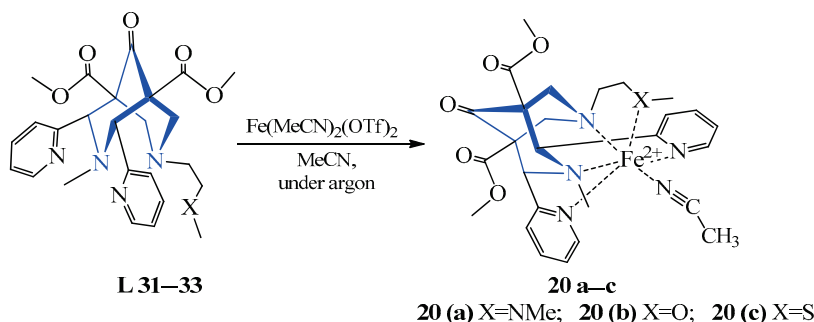
Scheme 13. Synthesis of copper complex **18 a**.

Bispidinone Cu(II) complexes have been extensively studied for PET imaging due to their exceptional stability and ease of bioconjugation [71]. In addition, bispidinone-based metal chelates have been explored as catalysts for various reactions, including aziridination [72], olefin oxidation [73,74], hydroxylation of CH groups [75], halogenation [76], sulfoxidation [77], and their role in non-heme enzyme models [78,79]. Mononuclear Fe(II) coordination complexes, which exhibit low-spin, high-spin, or spin-crossover states, have found applications in biomimetic studies and magnetic resonance imaging (MRI) [80–82]. The reaction of **L 28–30** and **L 36** with iron(II) tetrafluoroborate hexahydrate or iron(II) perchlorate hydrate in degassed anhydrous acetonitrile under an argon atmosphere leads to the formation of metal complexes **19 a–d** with yields ranging from 17% to 71%. These complexes hold the potential to design responsive off-on probes (Scheme 14) [36].



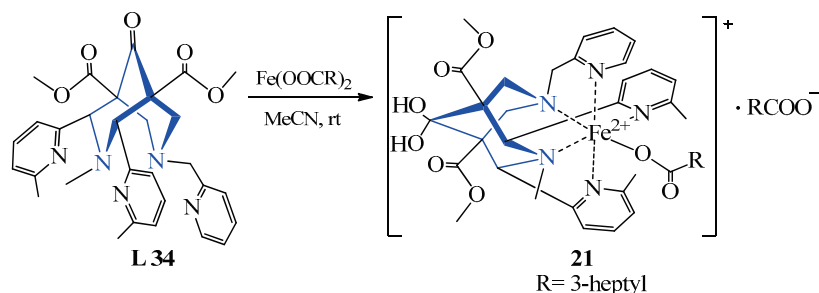
Scheme 14. Synthesis of complex **19 a**.

Iron-containing metalloproteins are well known for their essential role in mediating oxidative transformations within the human body [83–85]. To investigate the influence of equatorial heteroatom substitution on chlorite oxidation, Sahoo et al. [37] synthesized iron-containing complexes **20 a–c** by reacting **L 31–33** with $\text{Fe}(\text{MeCN})_2(\text{OTf})_2$ in acetonitrile (MeCN) at room temperature, followed by slow vapor diffusion of diethyl ether, yielding 84–88%. The complexes demonstrated the ability to oxidize ClO_2^- to ClO_2 under ambient conditions at pH 5.0 in an acetate buffer solution (Scheme 15).



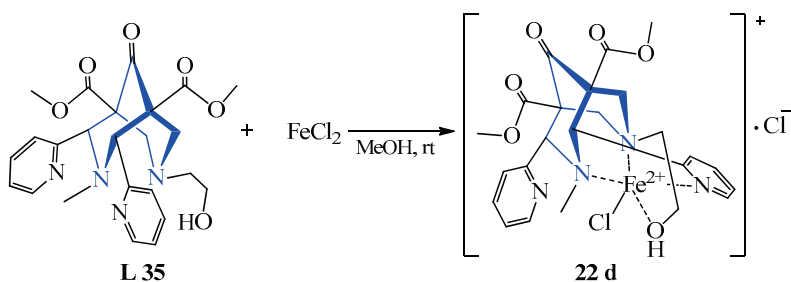
Scheme 15. Reaction of **L 31–33** with an iron salt.

High-valent iron complexes serve as catalysts in oxidation and halogenation reactions, while low-valent complexes are widely utilized in autooxidation processes within the paint industry. In a representative synthesis, iron (II) 2-ethylhexanoate was reacted with **L 34** in acetonitrile at room temperature. Following vacuum evaporation, product **21** was isolated with a 57% yield (Scheme 16) [38].



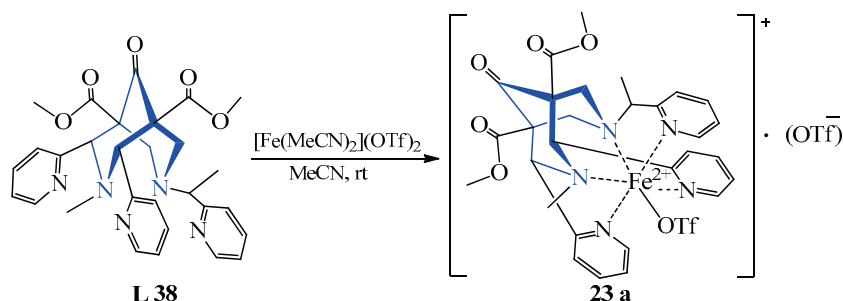
Scheme 16. Synthesis of heptacoordinate Fe complex **21**.

The coordination chemistry of iron is remarkable due to its wide range of oxidation states, which play a crucial role in spin crossover phenomena and the modeling of electron and oxygen transfer enzymes. Iron(II) complexes **22 a–f** were synthesized using bispidine ligands **L1**, **L34–37**, containing two tertiary amines and two, three, or four additional donor groups (pyridine, phenolate, or alcoholate), in reaction with iron(II) salts. The resulting complexes were obtained with yields ranging from 40% to 70% (Scheme 17) [39].



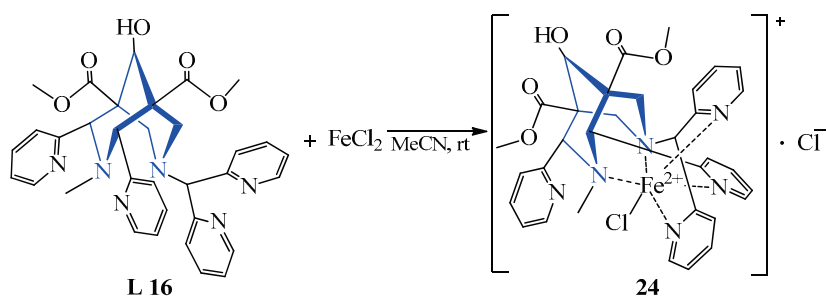
Scheme 17. Reaction tetradentate bispidine ligand **L 35** with an iron salt.

Certain bispidine iron–oxo complexes served as catalysts for the oxidation of non-heme iron [86,87]. Currently, several synthetic methods have been developed for such compounds, including the preparation of iron(II) complexes **23 a, b**. In a representative synthesis, **L 38** was reacted with iron(II) triflate in acetonitrile, yielding iron complex **23a** with a yield of 73% (Scheme 18) [40].



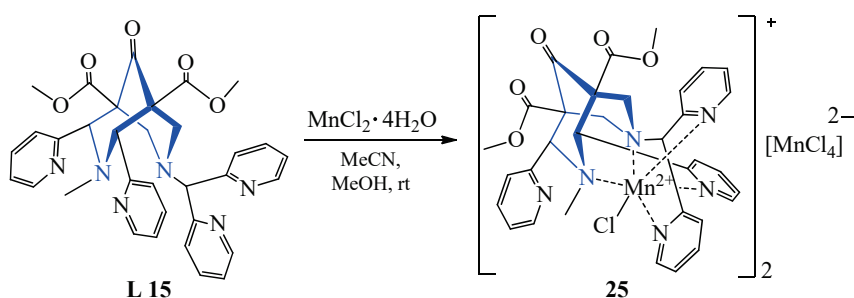
Scheme 18. Synthesis of iron-based complex **23a**.

A reaction mixture of dimethyl 7-(di(pyridine-2-yl)methyl)-9-hydroxy-3-methyl-2,4-di(pyridine-2-yl)-3,7-diazabicyclo[3.3.1]nonan-1,5-dicarboxylate **L 16** and ferric chloride (FeCl_2) in dry acetonitrile was stirred at room temperature overnight. The resulting yellow solution was subjected to diethyl ether diffusion, yielding yellow needle-like crystals of complex **24** with a 52% yield (Scheme 19) [30].



Scheme 19. Synthesis of complex **24**.

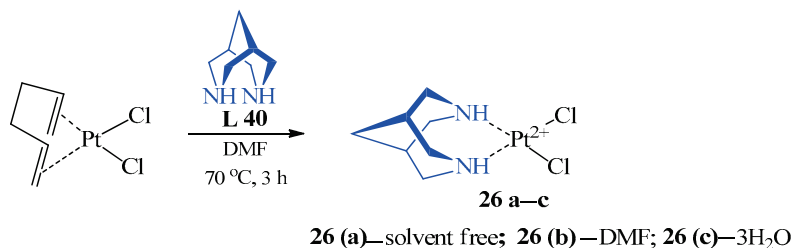
Bispidine Mn(II) complexes with tetradentate ligands typically adopt an octahedral geometry, whereas heptacoordinated Mn(II) complexes can exhibit pentagonal bipyramidal or trigonal prismatic structures. In a representative synthesis, **L 15** and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were suspended in an equimolar acetonitrile–methanol mixture and stirred overnight at room temperature, followed by diethyl ether diffusion. The reaction yielded complex **25** with an efficiency of 56% (Scheme 20) [30].



Scheme 20. Reaction of **L 15** with manganese salt.

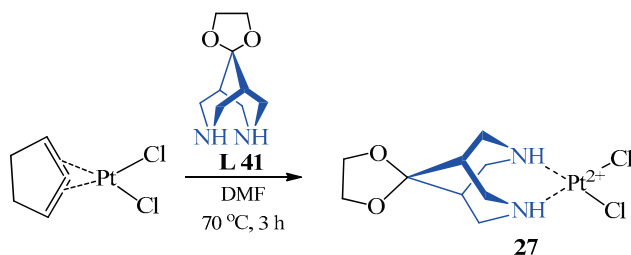
The platinum complex cisplatin ($\text{cis}-(\text{NH}_3)_2\text{PtCl}_2$) exhibits significant pharmacological properties, including alkylating, immunosuppressive, antitumor, and cytostatic effects.

This has driven extensive research into the properties of platinum complexes and the development of efficient synthetic methods. In the pursuit of Pt complexes with cytotoxic activity, Cui et al. [41] synthesized platinum complexes **26 a–c** by reacting (1,5-hexadiene)PtCl₂ with bispidine **L 40** in dimethylformamide (DMF) at 70 °C for 3 h (Scheme 21).



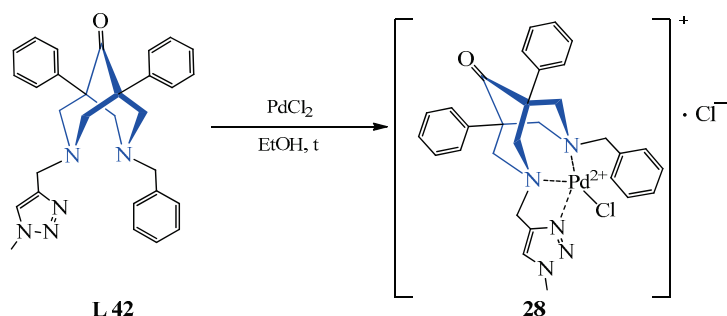
Scheme 21. Reaction of **L 40** with a platinum salt.

Researchers [42] synthesized (spiro[bispidin-9.2'-[1,3]dioxolan])platinum (II) dichloride (**27**) by reacting **L 41** with (C₆H₁₀)PtCl₂ in dimethylformamide (DMF). The reaction was conducted at 100 °C for 2 h, yielding the product with an efficiency of 97% (Scheme 22).



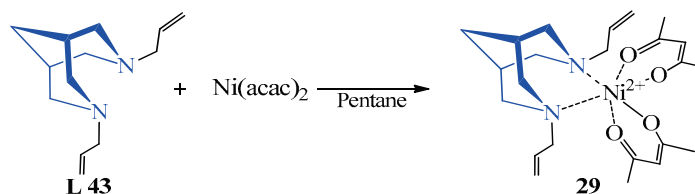
Scheme 22. Synthesis of tetracoordinate Pt complex **27**.

Pyrazole rings, macrocyclic amides, and oxygen-containing substituents (such as alcohols or carboxylate groups) can enhance the number of coordination sites within the bispidine core [88]. To expand its coordination capacity, a, palladium-containing complex (**28**) was synthesized by reacting PdCl₂ with **L 42**, which was obtained via the CuAAC click reaction, in acetonitrile at room temperature for 48 h (Scheme 23) [43].



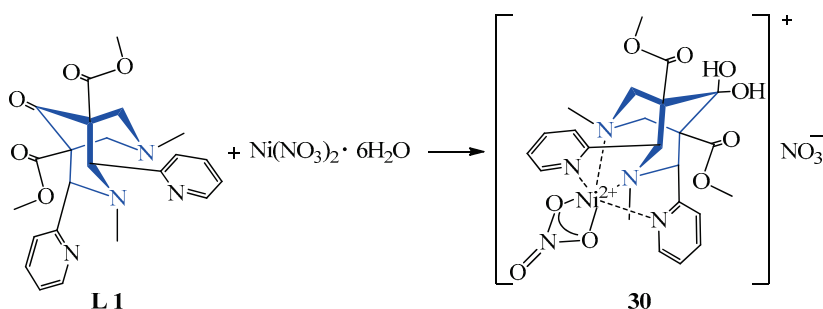
Scheme 23. Reaction of **L 42** with palladium salt.

The ligand **L 43** has been found to be a highly organized bidentate ligand, with its alkyl substituents providing functional groups for further modifications. Nickel acetylacetonate Ni(acac)₂ was reacted with 3,7-Diallyl-3,7-diazabicyclo[3.3.1]nonane **L 43** in the presence of pentane for 1 h at room temperature, yielding (C₇H₁₂N₂allyl₂)Ni(acac)₂ **29** with an efficiency of 99% (Scheme 24) [44].



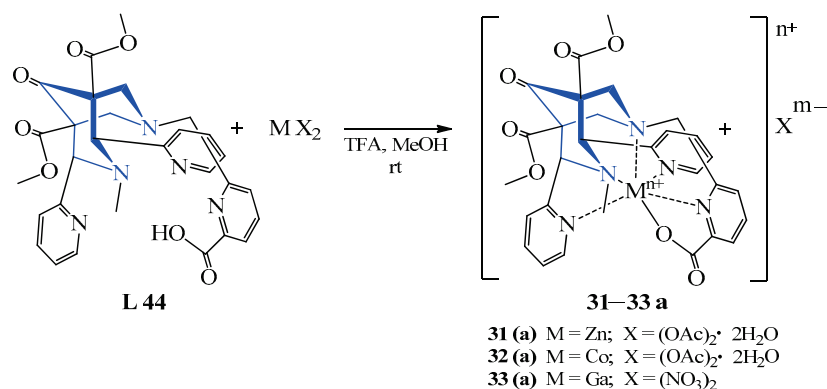
Scheme 24. Synthesis of nickel complex 29.

The formation of $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bonds is a fundamental transformation in organic synthesis. It has been established that sp , sp^2 , and sp^3 carbon atoms can be effectively linked using nickel catalysts. The (bispidine) $\text{Ni}(\text{NO}_3)_2$ complex **30**, which exhibits strong reactivity towards various aryl halides with benzylzine bromides or dialkylzine reagents, was synthesized with a 98% yield by reacting **L 1** with nickel nitrate hydrate (Scheme 25) [45].



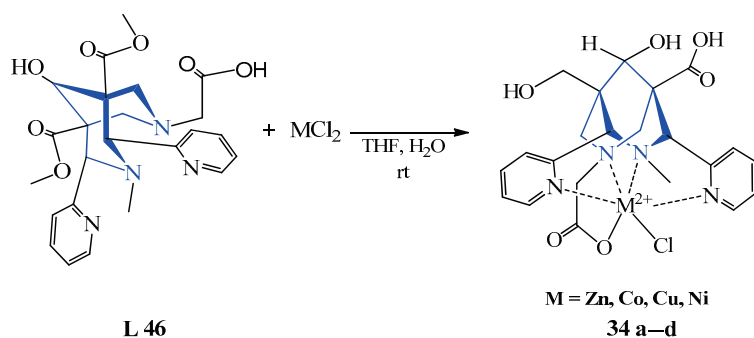
Scheme 25. Synthesis of complex 30.

The stability of metal complexes under physiological conditions is a critical factor in nuclear medicine, which can be achieved using rigid ligands with metal-binding capabilities. The coordination chemistry of hexadentate ligands **L 44–45** with various metal ions ($\text{Zn}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Ga}(\text{III})$) was investigated. The reaction of **L 44** and **L 45** with metal salts resulted in the formation of complexes **31–33** with yields ranging from 32 to 98% (Scheme 26) [46].



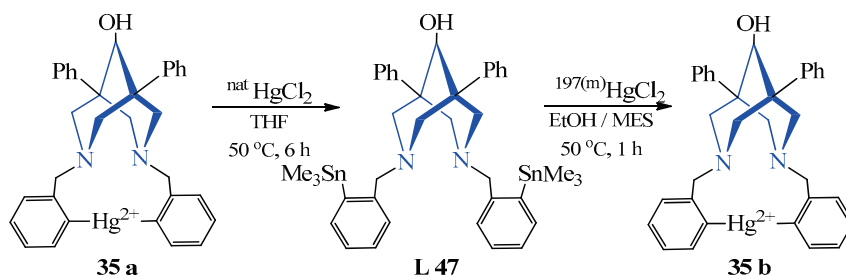
Scheme 26. Reaction of **L 44** with various metal salts.

Positron emission tomography (PET) combined with X-ray computed tomography (CT) provides highly accurate information on tumor progression in various cancers, including lymphoma and epithelial malignancies affecting the lungs, esophagus, cervix, head, and neck [89–91]. However, a key limitation arises from the slow redistribution kinetics of bioconjugates, which may not always align with non-metallic isotopes. To overcome this challenge, the development of metal radioisotopes, specifically metal complexes **34 a–d**, with longer half-lives and simplified radiochemistry, is essential [92]. In pursuit of such compounds, a recent study synthesized coordination complexes of $\text{Zn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Ni}(\text{II})$ with **L 46** (Scheme 27) [47,48].



Scheme 27. Reaction of **L 46** with metal salts.

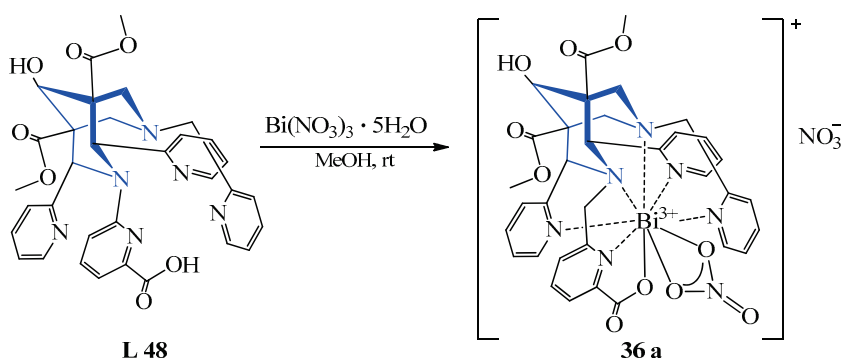
Mercury-197 (^{197}Hg) complexes have been clinically utilized in diagnostics imaging of the kidneys and brain, particularly in the form of chloroperodrine with a radioactive label, due to their stability and the radiochemical properties used. Mercury complexes with a bispidine framework (**35 a, b**) demonstrated high chemical stability in the presence of an excess of sulfur-containing compounds and exhibited strong in vivo stability (Scheme 28) [49].



Scheme 28. Synthesis of mercury complexes **35 a, b**.

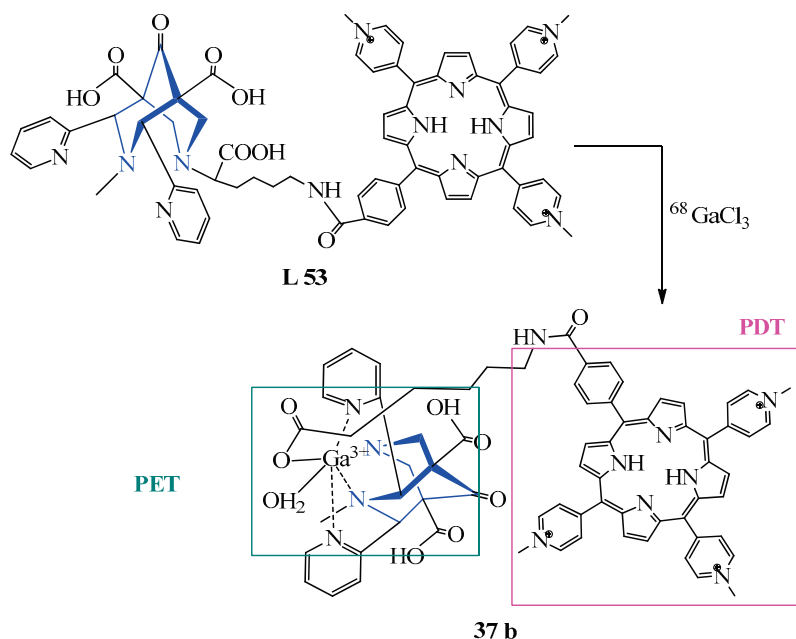
3.2. Complexes of p-Block Elements with Bispidines

There is a significant demand for bismuth-based complexes, driven by the demonstrated effectiveness of targeted cancer radiotherapy using actinium-225, whose daughter isotopes (bismuth-211 and bismuth-213) exhibit high therapeutic potential. The synthesis of complexes **36 a–e** was achieved by reacting bispidine ligands **L48–51** with bismuth nitrate hydrate in the presence of methanol, yielding 60% to 99% (Scheme 29) [50].



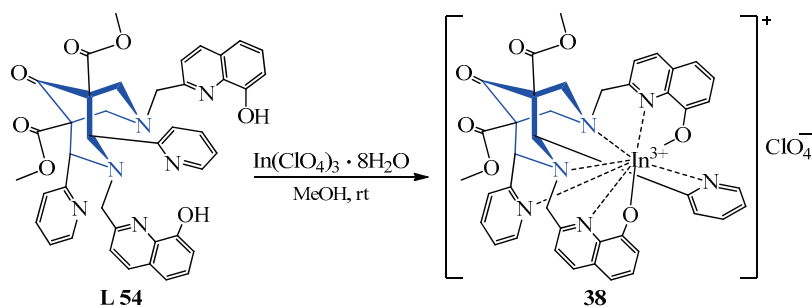
Scheme 29. Synthesis of bismuth-based complex **36 a**.

Gallium-68 (^{68}Ga) complexes are widely utilized in PET/PDT for early disease detection, allowing diagnosis before physical symptoms manifest, as gallium nuclides facilitate efficient targeting of disease sites. Complexes **37 a, b** were synthesized with a 90% yield by reacting ligands **L 52** and **L 53** with GaCl_3 in aqueous suspension overnight at 100 °C (Scheme 30) [51].



Scheme 30. Synthesis of complex **37 b**.

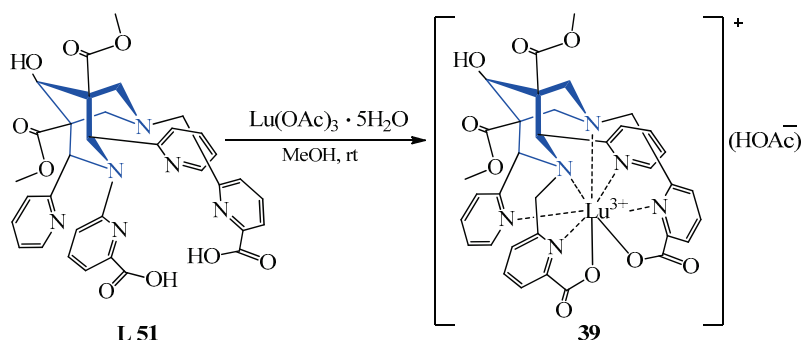
Since the first clinical studies in 1925 demonstrated the effectiveness of bismuth-214 complexes for measuring blood flow between hands, scientific efforts have focused on developing new methods for utilizing other complexes in single-photon emission computed tomography (SPECT), positron emission tomography (PET), and targeted therapies (including alpha, beta, and electron therapy). In a representative synthesis, indium complex **38** was obtained with a 39% yield by reacting bispidine ligand **L 54** with indium perchlorate hydrate $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ at room temperature for 5 h (Scheme 31) [52].



Scheme 31. Reaction heptadentate bispidine ligand **L 54** with an indium salt.

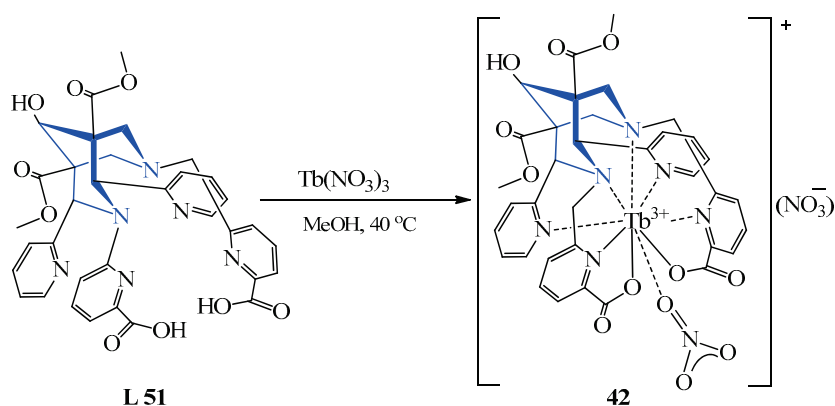
3.3. Bispidine-Containing Lanthanide Complexes

The reaction of **L 51** with indium, lanthanum and lutetium salts resulted in the formation of complexes **39–41**, with yields ranging from 81% to 88% (Scheme 32) [53].



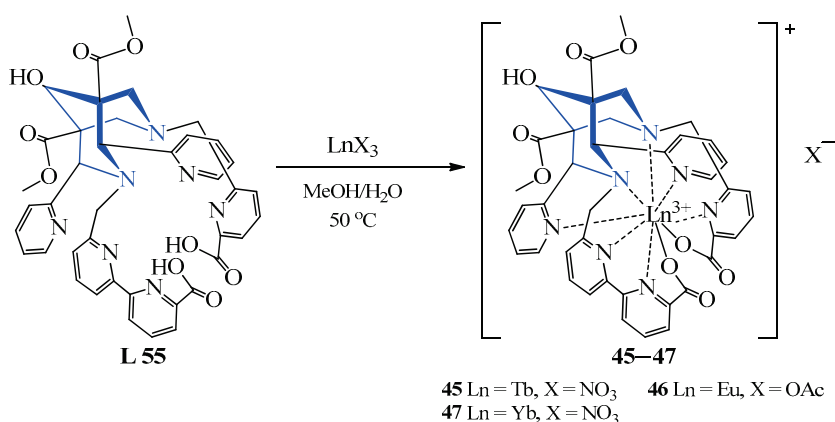
Scheme 32. Reaction hexadentate bispidine ligand **L 51** with a lutetium salt.

The bispidine ligand **L 51**, functioning as an antenna, effectively transferred energy to the lanthanides metal centers, which exhibited high radiation intensity and extended luminescence lifetimes. This highlights the potential of complexes **42–44** for use in fluorescent probe fabrication. A notable example is the terbium complex **42**, synthesized through the reaction of **L 51** with terbium nitrate (Scheme 33) [54].



Scheme 33. Synthesis of terbium complex **42**.

Lanthanide complexes **45–47**, featuring a bispidine framework with photophysical properties, were synthesized using readily available materials, including **L 55** and methanol in an aqueous solutions of lanthanide salts. The resulting products were obtained with yields ranging from 40% to 70% (Scheme 34) [55].



Scheme 34. Synthesis of complexes **45–47**.

The rigid framework and tunable basicity of bispidine ligands significantly influence the stability and selectivity of their metal complexes, enabling the synthesis of tetra-, penta-, hexa- and octadentate metal complexes incorporating a bispidine fragment. These complexes have been applied in various catalytic and biomedical fields. In organic synthesis, bispidine-based copper(II) complexes catalyze aziridination reactions [25,93,94], while nickel (II) pre-catalyst facilitate C-C bond formation [95]. Additionally, copper(II) complexes play a role in the enantioselective Henry reaction [96–98]. Other notable applications include oxygen activation using copper (I) and cobalt (II) [99,100] and oxidation reactions mediated by high-valent iron and manganese complexes with bispidine ligands [101,102]. In medicine, bispidine complexes are explored as potential cytostatic agents in cancer therapy [103]. In radiopharmaceuticals, they are widely used for PET/PDT imaging [104,105].

4. Conclusions

Bispidines constitute a diverse class of ligands well-established in coordination chemistry, exhibiting coordination numbers ranging from 4 to 8. Their adaptability in terms of coordination geometry, donor group variability, and structural rigidity allows for the tailored design of bispidine ligands for specific metal ions and diverse applications.

In radiopharmaceutical development, key factors include efficient radiolabeling, complex stability, and the ease of functionalization for conjugation with biological vectors. This review highlights recent advances in the chemistry of bispidine–metal complexes, demonstrating their high efficiency and broad practical applicability. These developments underscore the significant potential of bispidine complexes in medical and radiopharmaceutical chemistry, particularly for drug development and catalytic systems that mimic natural enzymes. Furthermore, ongoing research in coordination chemistry is expected to yield new discoveries, expanding the scope of bispidine applications.

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Review

Recent Advancements in the Synthesis of Functional Polyolefins by Non-Bridged Half-Titanocenes

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Abstract: Polyolefins are used widely due to their benefits such as being lightweight, chemical inertness, low cost, tunable properties, and easy processability. However, their nonpolar nature significantly limits their high-end applications. The non-bridged half-titanocenes exhibit remarkable catalytic activities with good comonomer incorporations in the olefin polymerization. The synthesis of functional polyolefins has attracted more and more attention recently. The non-bridged half-titanocenes have been used in the preparation of functional polyolefins, in particular the functional olefin copolymers. Herein, the recent advancements in the synthesis of functional polyolefins by non-bridged half-titanocenes were reviewed. The functional polyolefins have been synthesized by direct copolymerization of olefin with functional comonomers using half-titanocenes as precatalysts. In addition, polyolefins containing reactive groups could be synthesized by the olefin (co)polymerization using half-titanocenes as precatalysts. The functional polyolefins were synthesized successfully by the post-functionalization of polyolefin containing reactive groups.

Keywords: functional polyolefins; half-titanocene; copolymerization

1. Introduction

Polyolefins are the most widely used polymer materials and constitute over half of global plastic production [1–5]. Although polyolefins have many benefits, such as being lightweight, chemical inertness, low cost, tunable properties, and easy processability, their nonpolar nature significantly limits their high-end applications. The incorporation of polar groups into polyolefin chains provides an efficient way to improve surface properties, leading to the improvement of adhesion, conductivity, dyeability, printability, and compatibility with other polymers and inorganic fillers in the resultant functionalized polyolefins. Therefore, the efficient introduction of polar groups into hydrophobic polyolefins has attracted much attention from both academic and industrial communities [6–19]. The precise and efficient synthesis of polyolefins containing polar groups has been successfully realized by the direct coordination copolymerization of the olefins with polar monomers using a late transition metal catalyst. However, functional polyolefins with certain branching were usually afforded due to the “chain-walking” mechanism [15–19]. In addition, it is still a challenge to prepare precise copolymers of ethylene with α -olefin or styrene for the late transition metal catalysts. By contrast, the early transition metal catalysts exhibit good catalytic behavior in the preparation of linear polyethylene and precise copolymers of ethylene with α -olefin or styrene [20–22]. However, both the catalytic activity and incorporation ratio were significantly affected due to the strong interaction of the heteroatom with the active species. Alternatively, the precise functional polyolefins have been successfully afforded by

the copolymerization of olefin with protected polar monomer using early transition metal catalysts. Furthermore, the precise functional polyolefins could also be prepared by the post-modification of polyolefins with reactive groups, which were prepared by the copolymerization of olefin with monomers containing reactive groups using early transition metal catalysts [23–25]. Catalysts play important roles in the copolymerization of olefin with protected polar monomer and the copolymerization of olefin with monomers containing reactive groups. The non-bridged half-titanocenes exhibit remarkable catalytic activities with good comonomer incorporations in the olefin copolymerizations [26–30], which have also been used in the preparation of precise functional polyolefins. Herein, the recent advancements in the synthesis of functional polyolefins by non-bridged half-titanocenes were reviewed.

2. Synthesis of Functional Polyolefins by Direct Copolymerization of Olefin with Functional Comonomers

The direct copolymerization of olefin with functional monomers is one of the effective approaches to prepare functional polyolefins. However, the functional groups in the comonomer greatly affect the active center during the polymerization, leading to transfer or termination [13,17,23,24]. Therefore, only special functional comonomers or the protected comonomers could be used in the synthesis of functional polyolefins by the direct copolymerization of olefin with functional comonomers. Different olefin monomers could be used in the direct copolymerization of olefin with functional comonomers, affording different functional polyolefins, such as functional polyethylene and functional polyolefin elastomer.

2.1. Synthesis of Functional Polyethylene

2.1.1. Synthesis of Functional Polyethylene Containing SiR₃ (R = Me, iPr) Groups

The alkenylsilanes could be used as functional comonomers for the preparation of functional polyethylene containing SiH₃ groups. However, the silane group plays a role of chain transfer reagent, leading to functional polyethylenes with long-chain branching and low molecular weight ($M_n = 4.6\text{--}78.6 \text{ kg}\cdot\text{mol}^{-1}$) [31,32]. Compared to SiH₃, the SiMe₃ group should be more easily incorporated into the copolymer during the copolymerization of ethylene with alkenylsilanes. The copolymerization of ethylene with allyltrimethylsilane (ATMS) by Cp₂ZrCl₂ or [(CH₂)₂(indenyl)₂]ZrCl₂/MAO catalysts [33] also led to functional polyethylenes with low molecular weight ($M_w = 1.2\text{--}2.9 \text{ kg mol}^{-1}$), due to the β-hydrogen elimination after the insertion of bulky ATMS. Due to the unique characteristics of half-titanocenes containing anionic ancillary donor ligands for the copolymerization of ethylene with other olefins, these half-titanocenes were used for the efficient synthesis of functional polyethylene containing SiR₃ (R = Me, iPr) groups by the copolymerization of ethylene with vinyltrialkylsilanes (VTMS) [34] or allyltrialkylsilane (ATMS) [35]. The catalytic activity of the half-titanocene is higher in the copolymerization of ethylene with ATMS than that in the copolymerization of ethylene with VTMS due to ATMS being less bulky. Both the catalytic activity of the catalyst and the incorporation ratio of ATMS are obviously influenced by the chemical structure of half-titanocenes. As shown in Figure 1, the half-titanocenes **3** and **4** containing ketimide ligands exhibited higher catalytic activities than that of half-titanocenes **1** and **2** containing phenoxide ligands under similar polymerization conditions. In particular, half-titanocene **4** exhibited the highest catalytic activity of 41,600 kg copolymer·mol^{−1} of Ti·h^{−1}. The half-titanocenes **1** and **2** exhibited better copolymerization ability than their analogs **3** and **4**. The ethylene-ATMS copolymers with a high ATMS incorporation of 24.4 mol% and 25.9 mol% were afforded by using half-titanocenes **1** and **2** as precatalysts, respectively. Interestingly, the molecular weight ($M_n = 116\text{--}370 \text{ kg}\cdot\text{mol}^{-1}$) of the resulting ethylene-ATMS copolymers prepared by half-

titanocenes **3** and **4** was much higher than that ($M_n = 12.7\text{--}28.7 \text{ kg}\cdot\text{mol}^{-1}$) of ethylene-ATMS copolymers prepared by half-titanocenes **1** and **2** [35].

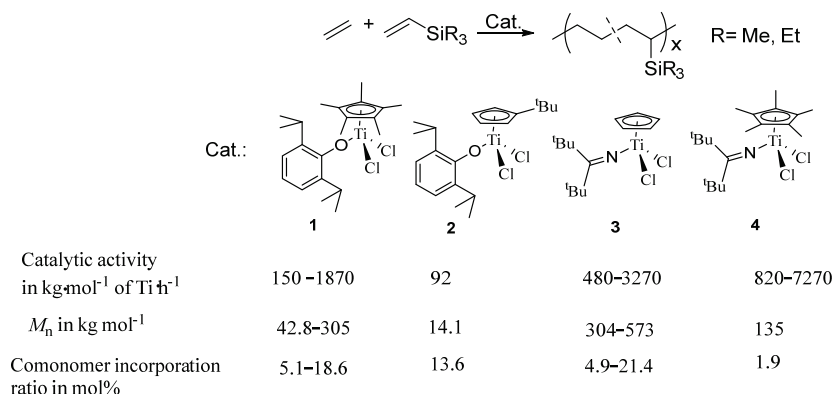


Figure 1. Synthesis of ethylene-ATMS copolymers by using half-titanocenes **1–4**.

2.1.2. Synthesis of Functional Polyethylene Containing OH Groups

Due to the coordination of the lone-pair electrons of heteroatoms in the polar monomer to the metal center of the active site, the low incorporation of the polar monomer was usually observed. In addition, the steric bulkiness also leads to the low incorporation of the polar monomer. The half-titanocenes have been reported as efficient catalysts for ethylene copolymerization with some bulky olefins [26–30]. Therefore, the copolymerization of ethylene with protected 4-penten-1-ol (4P1O) by triisobutylaluminum (TIBA) was investigated by using the half-titanocene catalyst **1**, as shown in Figure 2. The functional polyethylene containing ~10 mol% of OH groups was prepared with relatively low molecular weight ($M_w = 36.6$ kg/mol) [36].

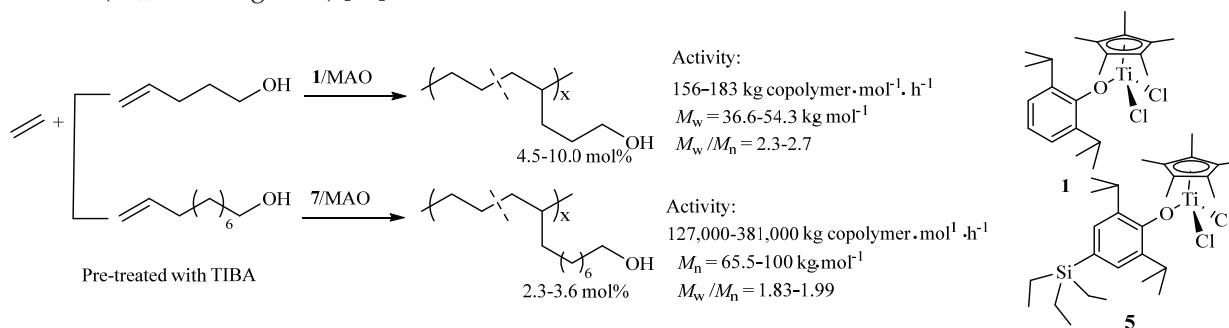


Figure 2. Synthesis of functional polyethylene with OH groups.

The introduction of SiMe₃ and SiEt₃ groups to the para-position of phenoxide ligands in half-titanocenes leads to a remarkable improvement in catalytic activity and copolymerization ability [37]. The copolymerization of ethylene with TIBA protected 9-decen-1-ol (DC-OH) using the half-titanocene containing SiEt₃ group (**5**, as shown in Figure 2) showed high catalytic activity (381,000 kg copolymer·mol⁻¹ of Ti·h⁻¹), affording functional polyethylene containing 2.3–3.6 mol% of OH groups with relatively high molecular weight ($M_n = 65.5\text{--}100$ kg/mol) and unimodal molecular weight distribution ($M_w/M_n = 1.83$) [37]. Interestingly, these catalysts can also be used in the copolymerization of ethylene with 2-allylphenol (AP), a biomimetic fungicide that mimics the compound ginkgol found in ginkgo fruit [38]. Before the copolymerization, the AP comonomer was pretreated with the TIBA to protect the hydroxy group as Al-phenoxide. The half-titanocene **5** exhibited a high catalytic activity of 2430 kg copolymer·mol⁻¹ of Ti·h⁻¹. The copolymerization using **5** gave functional polyethylenes with high molecular weight ($M_n = 13.2\text{--}113$ kg/mol), relatively low M_w/M_n values ($M_w/M_n = 1.70\text{--}2.30$) and uniform compositions at relatively

low AP concentration. A new approach for the protection of the hydroxy group in the AP comonomer by using TIBA and 2,6-*t*Bu₂-C₆H₃OH was proposed, as shown in Figure 3. The catalytic activity of **5** is higher than that of its analogs, as shown in Figure 3. In addition, the catalytic activity increased to 3270 kg copolymer·mol^{−1} of Ti·h^{−1} due to the new protection approach. The functional polyethylenes with higher contents of AP units (1.9–3.8 mol%) and molecular weight (M_n = 44.2–170 kg/mol) were afforded using the **5**/MAO catalytic system [38].

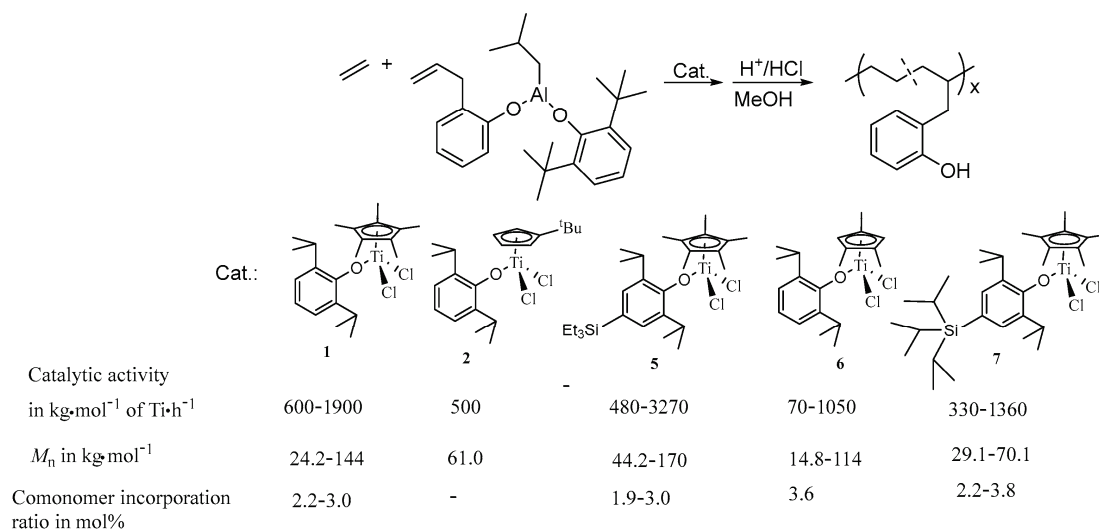


Figure 3. Synthesis of functional polyethylenes by the copolymerization of ethylene with 2-allylphenol.

2.2. Synthesis of Functional Polyolefin Elastomer

Polyolefin elastomer (POE) is a random copolymer of ethylene with α -olefin (with a high content of over 20 wt%) prepared by the coordination copolymerization of ethylene with 1-octene, 1 hexene, or 1-butene [39]. The high-performance POE exhibits excellent mechanical and elastomeric properties, which enables it to attract much attention in the industry. Similarly to the polyethylene, the lack of polar groups in the macromolecular chain limits its wide application. The half-titanocenes have been used as efficient catalysts for the preparation of POE [26–30]. However, the reports for the preparation of functional POE by the direct copolymerization using half-titanocene catalysts is limited. Nomura et al. reported that the half-titanocene/MAO catalytic system can efficiently catalyze the copolymerization of ethylene with long chain 1-dodecene (DD) and polar monomer 9-decen-1-ol (DC-OH), as shown in Figure 4 [37]. Compared to the catalytic activity of the CGC catalyst (14,600 kg copolymer·mol^{−1} of Ti·h^{−1}), the catalytic activity of half-titanocenes **1**, **5**, and **8** is much higher (37,000–638,000 kg copolymer·mol^{−1} of Ti·h^{−1}) in the copolymerization of ethylene with DD and DD-OH. In particular, the incorporation ratio of DD-OH (1.2–1.3 mol%) in the copolymerization catalyzed by **5** and **8** is higher than that (0.9%) catalyzed by the CGC catalyst. Furthermore, the functional POE with OH groups (0.8 mol%) and high molecular weight (M_n = 138 kg·mol^{−1}), narrow molecular distribution (M_w/M_n = 1.83), and a high DD incorporation ratio (15.2%) was afforded by using the advanced half-titanocene catalyst [38].

The half-titanocenes supported by Cp* and the boryloxy ligands have been shown to efficiently catalyze the copolymerization of ethylene with 9-decen-1-ol, affording poly(ethylene-co-9-decen-1-ol) with high catalytic and copolymerization ability, as shown in Figure 5 [40]. In the same polymerization conditions, the catalytic activity of precatalyst **10** (2.99×10^8 g·mol^{−1} of Ti·h^{−1}) and **9** (6.10×10^7 g·mol^{−1} of Ti·h^{−1}) is much higher than that of **7** (4.0×10^5 g·mol^{−1} of Ti·h^{−1}). In addition, both the molecular

weight and the polar comonomer contents (I) of resulting copolymers prepared by using **9** ($M_n = 102$ kg/mol, I = 7.2 mol%) and **10** ($M_n = 90$ kg/mol, I = 10.8 mol%) are higher than those of resulting copolymers prepared by **11** ($M_n = 52$ kg/mol, I = 5.6 mol%). More importantly, the functional polyolefin elastomers with high polar comonomer contents of up to 32.1 mol% were afforded by using **10** as a precatalyst. All the results indicate that the catalytic activity, copolymerization ability, and molecular weight of the resulting copolymer could be obviously improved by introducing boryloxy ligand. Moreover, the resulting hydroxyl-functionalized copolymers exhibit high strength and toughness (high stress at break of up to 33.9 MPa and a high strain value of 670%) due to the hydrogen bonds in the polymer network [40].

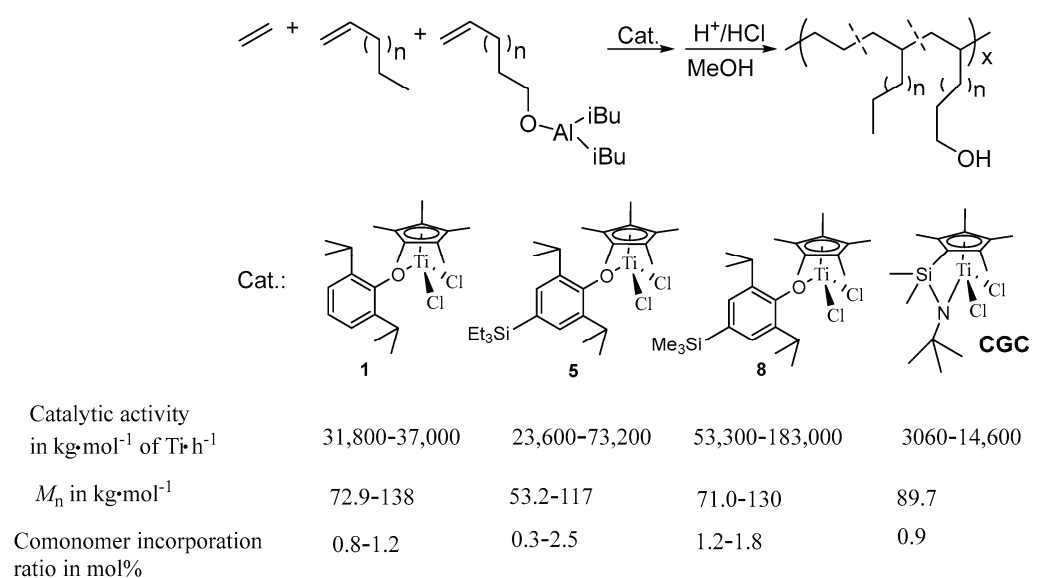


Figure 4. Synthesis of functional polyolefin elastomers by the copolymerization of ethylene with 1-dodecene and 9-decen-1-ol.

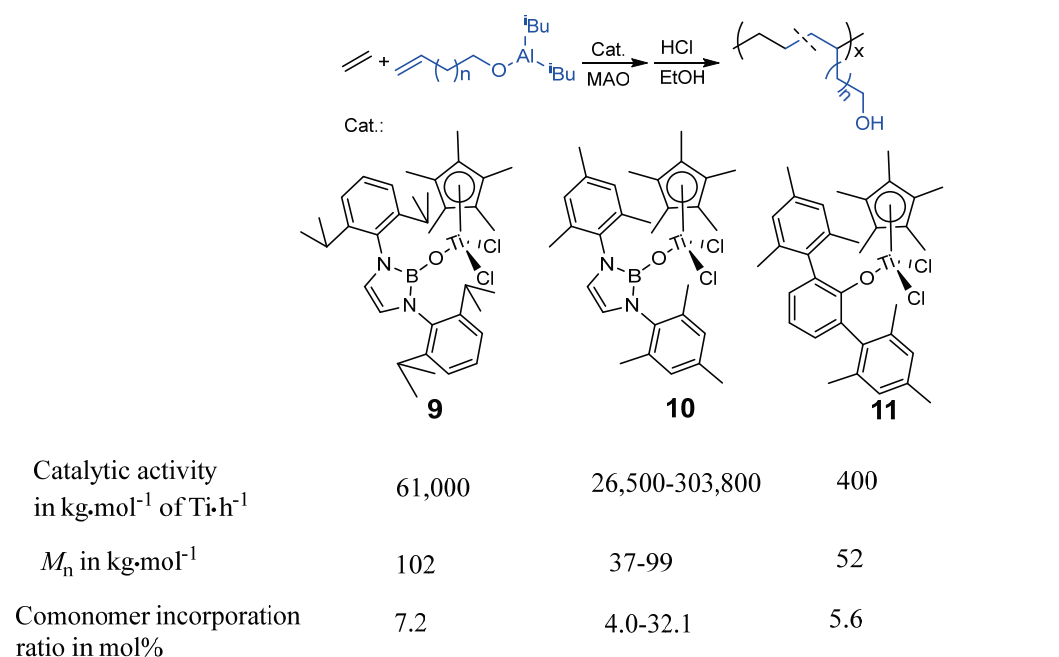


Figure 5. Synthesis of functional polyolefin elastomers by the copolymerization of ethylene with long chain α -olefins containing OH group.

3. Synthesis of Functional Polyolefins by Post-Functionalization of Polyolefin Containing Reactive Groups

Although the direct copolymerization of olefin with functional monomers is effective for the preparation of functional polyolefins, it is still a challenge to prepare functional polyolefins with both high molecular weight and high polar monomer incorporation by the direct copolymerization approach. The post-functionalization of polyolefin containing reactive groups is another approach to prepare functional polyolefins [23,24]. In this approach, the polyolefin containing reactive groups is prepared first by the copolymerization of olefin with another olefin monomer containing reactive groups (for example: C=C double bond). Then, the reactive groups are transferred to functional groups by some reactions such as an oxidation reaction and a thio-ene click reaction. In addition, functional polyolefins containing both a high content of polar groups and a high molecular weight could be afforded. More importantly, various functional groups including hydroxyl, epoxy, and carboxylic groups have been introduced into the polyolefin macromolecular chain [23,24]. The half-titanocenes display high catalytic activity and copolymerization ability for the polymerization and copolymerization of various olefins. In particular, polyolefins with a high content of olefin units containing reactive groups could be successfully prepared using half-titanocene catalysts [41–45]. Herein, the preparation of functional polyolefins by the post-functionalization of polyolefin containing reactive groups, which have been prepared using half-titanocene catalysts, was reviewed.

3.1. Synthesis of Functional Polyethylene by Post-Functionalization Method

The pendent olefin groups of polyolefins can be converted to polar functional groups through chemical modifications under mild conditions. Therefore, the synthesis of polyolefins with olefinic double bonds in the pendent side chains is critical for the preparation of functional polyethylene by the post-functionalization method. Usually, the dienes were used as the comonomer to copolymerize with ethylene to introduce the olefinic double bonds in the pendent side chains without cross-linking. The copolymerization of ethylene with dienes containing two olefins with different reactivities afforded copolymers with pendent olefinic double bonds. The half-titanocenes exhibit excellent catalytic behavior toward the copolymerization of ethylene with various dienes [41–45]. As shown in Figure 6, the half-titanocenes containing anionic oxygen or nitrogen ligands exhibit moderate to high catalytic activity ($97\text{--}45,600\text{ kg polymer}\cdot\text{mol}^{-1}\text{ of Ti}\cdot\text{h}^{-1}$) for the copolymerization of ethylene with vinylcyclohexene (VCH), affording copolymers with low to high molecular weight ($M_w = 59.8\text{--}1151\text{ kg}\cdot\text{mol}^{-1}$), narrow molecular weight distribution ($M_w/M_n = 2.0\text{--}2.6$), and a high VCH incorporation ratio of up to 16.1 mol% [43]. The half-titanocene **4** containing ketimide ligand and Cp ligand showed higher catalytic activity than that of half-titanocene **1** containing phenoxide and Cp* ligands as well as half-titanocene **3** containing ketimide and Cp* ligands [41]. The copolymer with a high VCH incorporation ratio provides starting materials for the preparation of functional ethylene with high polar group content [41].

Limonene, which is an abundant natural product, can be considered a promising monomer. Compared to VCH, limonene contains one 1,1-disubstituted α -olefin structure and a trisubstituted cycloolefin structure. Although limonene can be used to prepare polyolefin containing pendent olefinic double bonds, the coordination polymerization of limonene is still a challenge [42,43]. The half-titanocenes show good catalytic activity toward the copolymerization of ethylene with limonene, affording ethylene copolymers with pendent olefinic double bonds. In particular, the ethylene-limonene copolymers with high molecular weight (M_w up to $128\text{ kg}\cdot\text{mol}^{-1}$), uniform molecular weight distribution ($M_w/M_n = 1.37\text{--}3.19$), and a good limonene incorporation ratio (1.9–3.6 mol%) could be

prepared by using the half-titanocene **6**/MAO catalytic system with catalytic activity in the range of 55–714 kg polymer·mol^{−1} of Ti·h^{−1} [43].

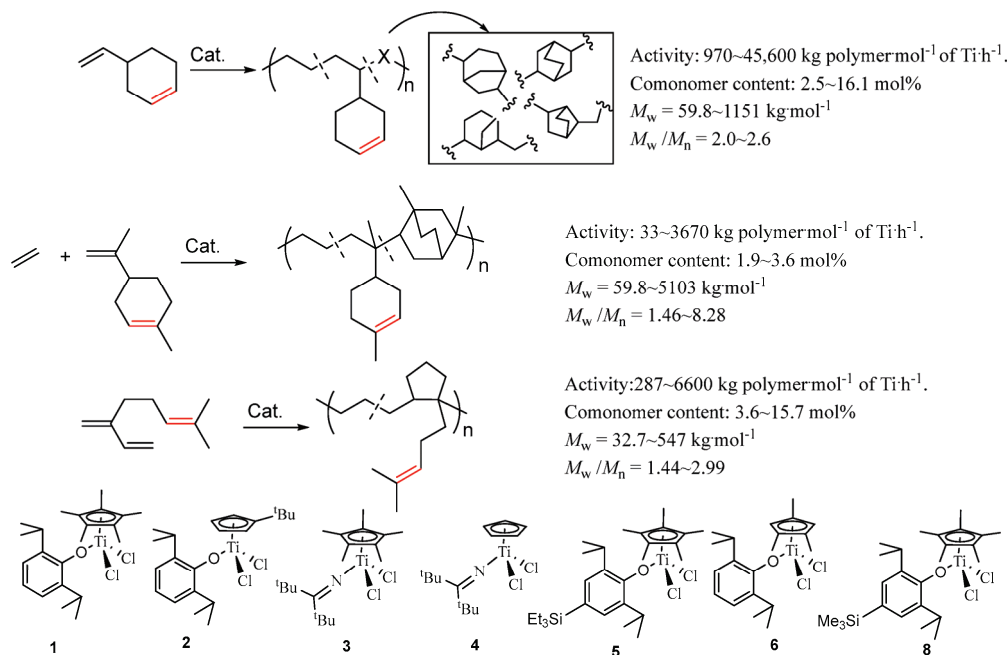


Figure 6. Synthesis of polyethylenes containing pendent olefin groups in the side chain.

β -myrcene (My) containing three double bonds (one conjugated 1,3-diene framework and one trisubstituted double bond) is also a good candidate for the preparation of polyolefin containing pendent olefinic double bonds. However, the coordination copolymerization of ethylene with β -myrcene is still a big challenge. The report of this copolymerization is limited [44,45]. As shown in Figure 6, the half-titanocene catalysts showed rather efficient My incorporation in the copolymerization of ethylene with My. The half-titanocenes containing phenoxide ligand **1**, **2**, and **5** showed higher catalytic activity than their analog **4** containing ketimide ligand. The catalytic activity of half-titanocene **5** for ethylene/My copolymerization could be up to 6600 kg polymer·mol^{−1} of Ti·h^{−1}, which is slightly higher than that (6100 kg polymer·mol^{−1} of Ti·h^{−1}) of half-titanocene **1**. The ethylene/My copolymers with moderate to high molecular weight ($M_w = 32.7\text{--}547\text{ kg}\cdot\text{mol}^{-1}$), unimodal molecular weight distributions, and uniform composition as well as a high My incorporation ratio (up to 15.7 mol%) were afforded [45].

The polyolefin containing pendent olefinic double bonds could be easily functionalized by the reaction of C=C double bonds. As shown in Figure 7, the epoxidation of C=C double bonds in the ethylene/VCH copolymer was successfully realized by using *m*-chloroperbenzoic acid (*m*-CPBA) as oxidation reagent in CHCl₃ at room temperature. The NMR characterization of the resulting functional polyethylene demonstrates a facile functionalization of the olefinic double bond and an introduction of epoxy functional groups have been achieved quantitatively [41].

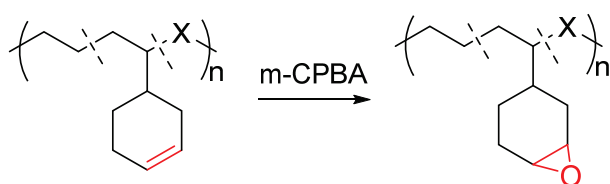


Figure 7. Synthesis of polyethylene containing epoxy functional groups.

3.2. Synthesis of Functional Poly(α -Olefin) by Post-Functionalization Method

The half-titanocenes have also been used as catalysts for the polymerization of α -olefin. In addition, the polymerization of 1,7-octadiene catalyzed by half-titanocene **1** and the **3**/MAO catalytic system afforded polymers with terminal olefinic double bonds in the side chain. Therefore, the copolymerization of 1,7-octadiene and 1-octene was carried to prepare copolymers with double bonds in the side chain. The catalytic activity of the **1**/MAO catalytic system for the copolymerization is as high as 8010 kg polymer·mol⁻¹ of Ti·h⁻¹, leading to copolymers with high molecular weight ($M_w = 660\text{--}991$ kg·mol⁻¹) and uniform molecular weight distribution ($M_w/M_n = 1.52\text{--}1.77$). In addition, the content of the double bonds in the copolymers can be controlled in the range of 1.6–37.3 mol% by the feeding ratio of 1,7-octadiene with 1-octene. As shown in Figure 8, the double bonds in the side chain of the copolymers have been converted to -CH₂-CH₂-OH functional groups by treating the copolymers with 9-BBN and then NaOH/H₂O₂. Furthermore, the OH groups were used as initiating sites to initiate the ring opening polymerization of ϵ -caprolactone (CL), affording graft copolymers of poly(1-octene)-graft-poly(CL) by the “grafting from” method. The molecular weight of the grafting poly(CL) can be controlled by the polymerization time of CL [45].

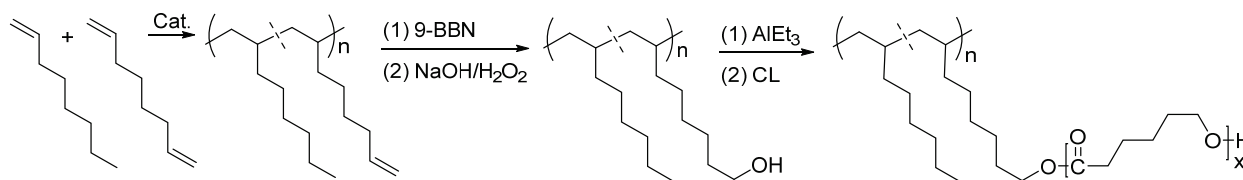


Figure 8. Synthesis of poly(1-octene) with OH functional groups or PCL side chain.

3.3. Synthesis of Functional Ethylene-Propylene Elastomer by Post-Functionalization Method

Ethylene-propylene elastomers, for example, ethylene-propylene-diene rubber (EPDM), have been widely used as sealing materials, wires, and cables. This kind of elastomer exhibits superior elasticity and flexibility at low temperature, excellent heat resistance, and good electrical insulation property. However, the nonpolar nature of the polymer chain significantly limits its high-end applications. The introduction of polar functional groups into the polymer chain could dramatically improve the properties of ethylene-propylene elastomer such as adhesion, dyeability, printability, and compatibility with polar polymers and inorganic fillers [46,47]. The commercial EPDM is a terpolymer of ethylene, propylene, and non-conjugated diene, which contains C=C double bonds in the side chain [48–50]. The double bonds are usually used as cross-linking sites during the vulcanization. From another side, the EPDM could also be considered as “reactive polyolefin intermediate”, in which the C=C double bonds could be modified to obtain functionalized ethylene-propylene elastomer. Nevertheless, the content of ENB in commercial EPDM is usually less than 12 wt%, which limits the amount of polar group content in the resulting functional ethylene-propylene elastomer [51]. The half-titanocenes displayed excellent catalytic behavior toward ethylene/propylene/5-ethylidene-2-norbornene (ENB) or 5-vinyl-2-norbornene (VNB) copolymerization [51–54]. It has been reported that the efficient terpolymerization of ethylene, propylene, and ENB was successfully afforded using half-titanocene containing the imidazolidin-2-iminato ligand. Both a high ENB conversion of 98% and a high content of ENB units up to 6.8 mol% (20.8 wt%) in the resulting EPDM were observed due to the excellent copolymerization ability of the catalytic system. Through the thiol-ene click reaction with mercaptopropionic acid, the C=C double bonds in the ENB units of the EPDM could be successfully reacted and introduced with carboxylic acid groups. The content of carboxylic acid groups in the functional ethylene-propylene elastomers could be adjusted by the content of the ENB units and the amount of click reagent. The enhanced

hydrophilicity was observed in the functional ethylene-propylene elastomers, evidenced by a decreased water contact angle, as shown in Figure 9 [51].

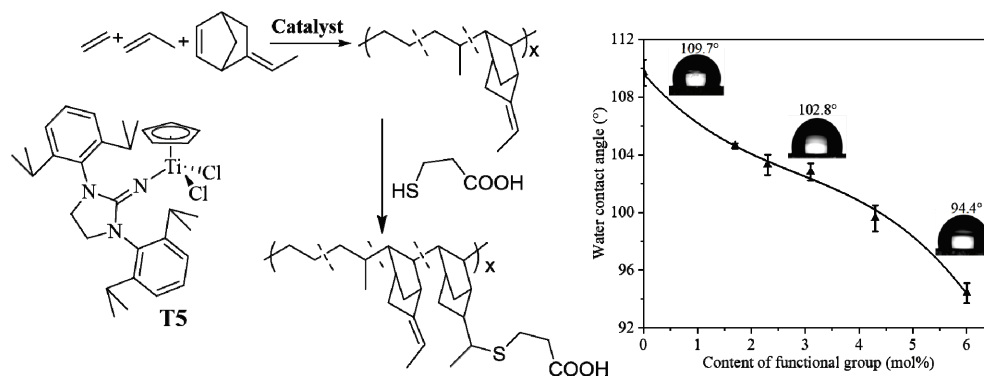


Figure 9. Synthesis and properties of functional EPDM.

4. Conclusions

The synthesis of functional polyolefins using half-titanocenes was reviewed. The half-titanocenes exhibit high catalytic activity and copolymerization ability for the copolymerization of ethylene with other olefin monomers. The functional polyolefins containing SiR3 or OH groups were synthesized by the copolymerization of ethylene with vinyltri-alkylsilanes or olefins containing OH groups. The half-titanocenes showed advantages in catalytic activity and polar monomer incorporation. The functional polyolefins with high molar weight and high polar monomer incorporation were afforded. However, the polar group in the functional polyolefin prepared by the direct copolymerization method was limited. The polyolefins containing reactive groups (especial C=C double bonds) were successfully synthesized. The post-functionalization of the polyolefins containing reactive groups resulted in functional polyolefins with epoxy, COOH, and other polar groups. Various functional polyolefins such as functional polyethylenes, functional polyolefin elastomers, functional poly(α -olefins), and functional ethylene-propylene rubbers could be synthesized by the direct copolymerization method or the post-functionalization method. We personally believe that the half-metallocene will attract more and more attention in the synthesis of advanced polyolefin materials, in particular functional polyolefin materials.

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