

Article

On-Purpose Oligomerization by 2-*t*-Butyl-4-arylimino-2,3-dihydroacridylnickel(II) Bromides

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Abstract: In this study, 2-*t*-butyl-4-arylimino-2,3-dihydroacridylnickel dibromides were synthesized by nickel-template one-pot condensation, and well characterized along with the single-crystal X-ray diffraction to one representative complex, revealing a distorted tetrahedral geometry around nickel. When activated with modified methylaluminoxane (MMAO), all nickel complexes exhibited high activities (up to $1.91 \times 10^6 \text{ g mol}^{-1} (\text{Ni h}^{-1})$) toward major trimerization of ethylene. When activated with ethylaluminum dichloride (EtAlCl_2), however, the title complexes performed good activities (up to $1.05 \times 10^6 \text{ g mol}^{-1} (\text{Ni h}^{-1})$) for selective dimerization of ethylene. In comparison to analogous nickel complexes, higher activities were achieved with the substituent of *t*-butyl group, especially in the rare case of nickel complexes performing trimerization of ethylene.

Keywords: nickel complex; ethylene dimerization; ethylene trimerization; selectivity



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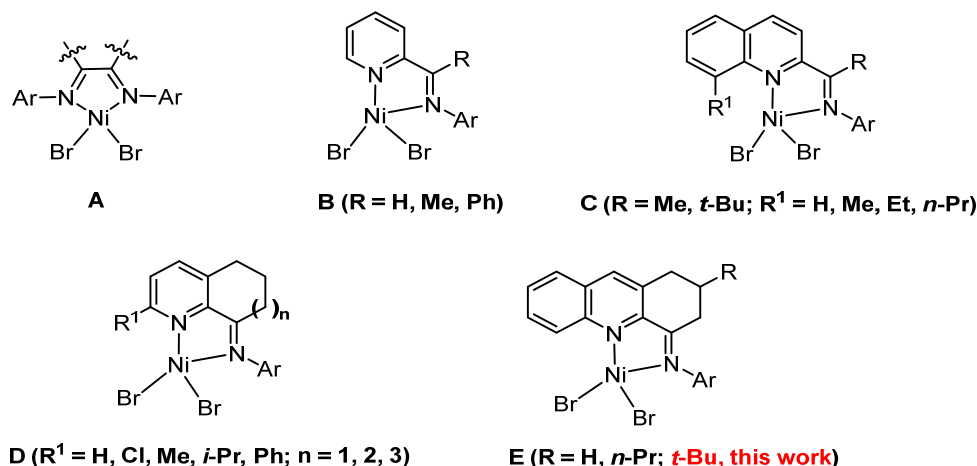


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1. Introduction

In 1995, Brookhart's group first reported ethylene polymerization using α -diimino-Ni(II) (**A**, Scheme 1) and Pd(II) complexes [1–3]. Subsequently, modifications of α -diimine derivatives for their nickel catalysts were developed [4–10]. Moreover, other N'N bidentate nickel complexes, including 2-iminopyridines [11–13] (**B**, Scheme 1), 2-imidazol pyridines [14,15], 2-iminoquinolines [16–19] (**C**, Scheme 1), and cycloalkyl-fused iminopyridines [20–32] (**D**, Scheme 1), were developed in parallel toward ethylene oligomerization and/or polymerization. Regarding the model catalysts [33–35], characteristic differences have been observed for their products, indicating major polyethylenes for model **A** [4–10] and both polyethylenes and oligomers for models **B** [11–13], **C** [16–19], and **D** [20–32]; however, only oligomers were indicated for model **E** [36,37]. Torches are commonly used by refinery companies due to the carbohydrates in refinery gases, in which ethylene accounts for more than one-fifth of the contents. Driven to selectively transfer ethylene into higher-order carbohydrate compounds, it is worthwhile to further investigate model **E** and its derivative catalysts in order to explore its scope and find the practicing catalyst.

The 4-arylimino-1,2,3-trihydroacridylnickel complexes (**E**, R = H, Scheme 1), activated by trimethylaluminum, oligomerized ethylene to form oligomers in the range of C₄ to C₁₆ [36], being less active than model **D** [22]. Following that, the 2-propyl-4-arylimino-1,3-dihydroacridylnickel complexes (**E**, R = *n*-Pr, Scheme 1) were developed, but they resulted in a negative effect on the oligomerization activity [37]. With the aim of extensively studying the influence of the substituent, expecting better solubility using tert-butyl, here, the 2-*t*-butyl-4-arylimino-1,3-dihydroacridylnickel bromides (**E**, R = *t*-Bu, Scheme 1) are synthesized and investigated toward ethylene oligomerization.

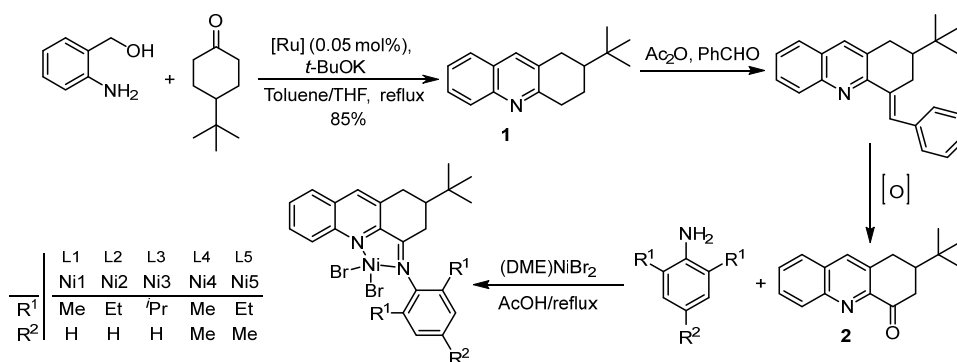


Scheme 1. Representative N^N bidentate nickel complexes A–E toward ethylene oligomerization and/or polymerization.

2. Results and Discussion

2.1. Synthesis and Characterization of 2-Tert-butyl-4-arylimino-2,3-dihydroacridylnickel(II) Bromides

The 2-*t*-butyl-1,3,4-trihydroacridine was synthesized through the coupling reaction of 2-aminobenzaldehyde and 4-*tert*-butylcyclohexanone using a ruthenium catalyst [38], according to the reported process [39]. Then, 4-benzylidene-2-(*tert*-butyl)-1,2,3,4-tetrahydroacridine, formed by the condensation reaction of 2-*t*-butyl-1,3,4-trihydroacridine with benzaldehyde, was oxidized with ozone in a solution of dichloromethane and MeOH at $-40\text{ }^{\circ}\text{C}$ to produce 2-*t*-butyl-2,3-dihydroacridine-4-one in good yield [40,41] (Scheme 2; the synthesis and characterization are available in the Supplementary Materials).



Scheme 2. Synthetic route of the 2-*t*-butyl-2,3-dihydroacridine-4-one, and the one-pot method for the 2-*t*-butyl-4-arylimino-1,3-dihydroacridylnickel bromides complexes.

The condensation reaction of 2-*t*-butyl-2,3-dihydroacridine-4-one and anilines did not result in the formation of the desired products; therefore, the template reaction of 2-*t*-butyl-2,3-dihydroacridine-4-one and the corresponding anilines with (DME)NiBr₂ was conducted in acetic acid to prepare the title nickel complexes, as in previous studies (Scheme 2) [36,37]. All nickel complexes showed their FT-IR spectra in the range of $1616\text{--}1621\text{ cm}^{-1}$, indicating the C=N stretching vibration [36,37] and consistent with the elemental analysis.

Single crystals of NiL1 suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into the NiL1 dichloromethane solution at ambient temperature. The molecular structure is shown in Figure 1 and the selected bond lengths and angles are listed in Table 1.

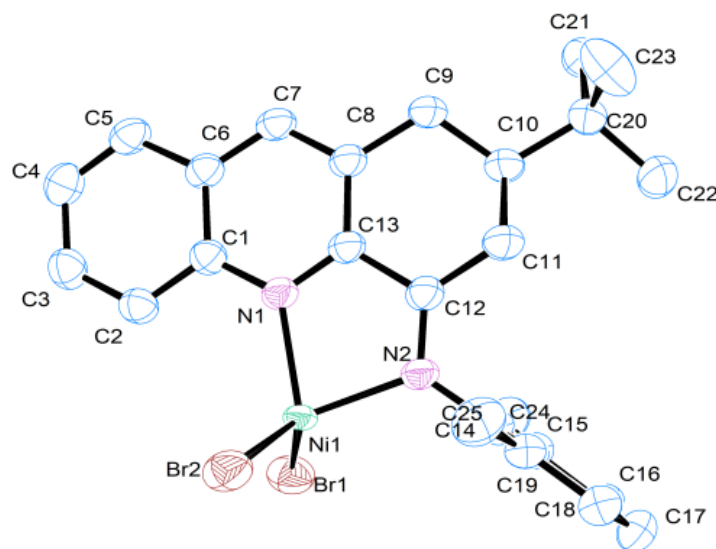


Figure 1. ORTEP diagram of **NiL1**, with the thermal ellipsoids shown at the 30% probability level. All hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for **NiL1**.

NiL1		
Bond lengths (Å)		
Ni(1)-N(1)		2.036(3)
Ni(1)-N(2)		2.057(3)
Ni(1)-Br(1)		2.3396(8)
Ni(1)-Br(2)		2.3441(7)
N(1)-C(13)		1.328(5)
N(1)-C(1)		1.365(5)
N(2)-C(14)		1.448(5)
N(2)-C(12)		1.285(5)
Bond angles (°)		
N(1)-Ni(1)-N(2)		80.57(12)
N(1)-Ni(1)-Br(1)		109.36(10)
N(1)-Ni(1)-Br(2)		108.58(9)
N(2)-Ni(1)-Br(1)		112.21(9)
N(2)-Ni(1)-Br(2)		112.56(9)
Br(1)-Ni(1)-Br(2)		124.62(3)

As shown in Figure 1, there was a distorted tetrahedral geometry around its nickel(II) center coordinated with the N¹N² ligand and two bromides, similar to its nickel analogues [36,37]. The bond lengths of Ni-Br were, individually, 2.3396(8) Å and 2.3441(7) Å. The N1-C13-C12-N2 coordination plane and C2-C3-C4-C5 quinoline plane were almost coplanar, with a dihedral angle of 1.68°; meanwhile, the dihedral angle between the C9-C10-C11 plane and the coordination plane was about 35.11°, reflecting the twisted cyclohexyl ring along with its remote, stretched t-butyl group.

2.2. Ethylene Oligomerization

2.2.1. Exploring the Suitable Co-Catalysts

Inspired by nickel pre-catalysts [2,3,17–19,36,37], potential co-catalysts include diethylaluminum chloride (Et₂AlCl), ethylaluminum sesquichloride (EASC), ethylaluminum dichloride (EtAlCl₂), methylaluminoxane (MAO), and modified methylaluminoxane (MMAO). They were compared with isostructural Ni(II) catalysts using model **E**. Model **E** (E, R = H, Scheme 1) was activated by trimethylaluminum and oligomerized ethylene to form oligomers in the range of C₄ to C₁₆ [36]. Model **E** (E, R = *n*-Pr, Scheme 1) was developed but resulted in a negative effect on the oligomerization activity [37]. In this system

(runs 1–6, Table 2), the advantage is that all nickel complexes bearing a bulky *t*-butyl group showed high activities toward ethylene on-purpose oligomerization compared with previous similar structures, providing more interesting results for researchers who work on nickel-catalyzed ethylene oligomerization. More precisely, when activated with EtAlCl₂, the dimerization was highly selective for all nickel pre-catalysts; however, major trimerization with high activity was rarely achieved with the co-catalyst MMAO, which is a rare case for nickel complexes controlling ethylene on-purpose oligomerization. In short, tiny variations in the nickel complex backbone structure are meaningful for the fine control of ethylene oligomerization product distribution.

Table 2. Ethylene oligomerization results by NiL1 with different co-catalysts ^a.

Run	Co-Catalyst	Al/Ni	T (°C)	t (min)	Activity [10 ⁵ g mol ^{−1} (Ni) h ^{−1}]	Oligomers ^b (%)		
						C4/ΣC	α-C4/C4	C6/ΣC
1	Et ₂ AlCl	300	30	30	3.48	99.9	98.4	–
2	EASC	300	30	30	7.81	99.6	>99.0	0.4
3	EtAlCl ₂	300	30	30	10.50	99.9	99.1	–
4	MAO	2000	30	30	1.29	15.0	66.7	85.0
5	MMAO	2000	30	30	6.10	17.5	>99.0	82.5
6	None ^c	–	30	30	No	–	–	–

^a Conditions: 2.0 μmol of NiL1, 100 mL of toluene, and 10 atm of ethylene. ^b Determined by GC. ΣC denotes the total amount of oligomers. ^c Oligomerization without co-catalyst.

2.2.2. Dimerization by the Catalytic System Ni1–Ni5/EtAlCl₂

To optimize the parameters of NiL1/EtAlCl₂, fixing the Al/Ni ratio at 300 and 30 min under 10 atm of ethylene, dimerization was carried out at different temperatures, such as 20, 30, 40, and 50 °C (Runs 1–4, Table 3), confirming the highest activity of 10.50×10^5 g mol^{−1} (Ni) h^{−1}, observing high selectivity of butene along with α-C4 at >99.0% (Run 2, Table 3). Furthermore, examples of GC under the optimized reaction conditions of NiL1/EtAlCl₂ are presented in the Supplementary Materials (page 4), showing high selectivity of butene. When the temperature was up to 100 °C, the activity decreased to 0.83×10^5 g mol^{−1} (Ni) h^{−1} (Run 5, Table 3). Upon verifying the amounts of co-catalysts (Runs 6–9, Table 3), both fewer and more co-catalysts somewhat deactivated the system, affirming our decision to use an Al/Ni ratio of 300 as the best choice. Regarding the reaction period (Runs 2 and 10–12, Table 3), the shorter the period, the higher the activity observed, which means that the catalytic reaction quickly occurred without an initial period, and the active species were gradually deactivated as its analogues [36,37].

Using the optimal conditions established for NiL1/EtAlCl₂ (i.e., Al:Ni molar ratio = 300:1, reaction temperature = 30 °C, and P_{C₂H₄} = 10 atm), all other nickel pre-catalysts, Ni2L–NiL5, were investigated (Runs 13–16, Table 3), and they exhibited higher activities, ranging from 12.14×10^5 g mol^{−1} (Ni) h^{−1} to 16.92×10^5 g mol^{−1} (Ni) h^{−1}. Their activities were in the order: NiL5 > NiL4 > NiL2 > NiL3 > NiL1. The *para*-methyl substituent was helpful in enhancing the catalytic system: NiL4 (R² = Me) > NiL1 and NiL5 (R² = Me) > NiL2, due to its better solubility. The *ortho*-substituents affected the catalytic performance: *Ortho*-ethyl (NiL2) was higher than its analogues, *ortho*-methyl (NiL1) and *ortho*-isopropyl (NiL3), as the electronic influence was reflected in the better activity, with higher electron-withdrawing of ethyl than methyl and isopropyl [31,32]. Isopropyl (NiL3) was still higher than methyl (NiL1) due to the soluble influence, consistent with the observation of *para*-methyl substituents.

Table 3. Ethylene oligomerization results by NiL1–NiL5/EtAlCl₂ ^a.

Run	Pre-Catalyst	Co-Catalyst	Al/Ni	T (°C)	t (min)	Activity [10 ⁵ g mol ^{−1} (Ni) h ^{−1}]	Oligomers ^b (%)		
							C4/ΣC	α-C4/C4	C6/ΣC
1	NiL1	EtAlCl ₂	300	20	30	7.70	99.9	>99.9	-
2	NiL1	EtAlCl ₂	300	30	30	10.50	99.9	99.1	-
3	NiL1	EtAlCl ₂	300	40	30	4.14	99.9	88.1	-
4	NiL1	EtAlCl ₂	300	50	30	1.59	99.9	86.1	-
5	NiL1	EtAlCl ₂	300	100	30	0.83	99.9	79.6	-
6	NiL1	EtAlCl ₂	100	30	30	0.70	99.9	97.6	-
7	NiL1	EtAlCl ₂	200	30	30	2.41	99.9	97.7	-
8	NiL1	EtAlCl ₂	400	30	30	2.73	99.9	98.5	-
9	NiL1	EtAlCl ₂	500	30	30	0.67	99.9	98.2	-
10	NiL1	EtAlCl ₂	300	30	15	15.24	99.9	95.1	-
11	NiL1	EtAlCl ₂	300	30	45	7.80	99.9	99.3	-
12	NiL1	EtAlCl ₂	300	30	60	5.63	99.9	87.5	-
13	NiL2	EtAlCl ₂	300	30	30	15.43	99.9	87.9	-
14	NiL3	EtAlCl ₂	300	30	30	12.14	99.9	94.7	-
15	NiL4	EtAlCl ₂	300	30	30	16.41	99.9	90.9	-
16	NiL5	EtAlCl ₂	300	30	30	16.92	99.9	90.3	-

^a Conditions: 2.0 μmol of pre-catalyst, 100 mL of toluene, and 10 atm of ethylene. ^b Determined by GC. ΣC denotes the total amount of oligomers.

2.2.3. Major Trimerization Using NiL1–NiL5/MMAO

Unlike chromium pre-catalysts, commonly resulting in on-purpose oligomerization [42,43], only a few cases of nickel pre-catalysts achieving major trimerization of ethylene though nickel-promoted dimerization have been reported [25–27]. Therefore, it is worthwhile to investigate the MMAO system in detail using the title complexes. To find the optimal condition on the basis of NiL1/MMAO, the Al/Ni molar ratio was verified from 1000 to 5000 at 30 °C (Runs 1–5, Table 4) under 10 atm of ethylene, and its highest activity was observed at 1.907×10^6 g mol^{−1} (Ni) h^{−1} with the Al/Ni ratio of 4000 (Run 4, Table 4). Examples of GC under the optimized reaction conditions of NiL1/MMAO are presented in the Supplementary Materials (page 4), showing high selectivity of hexenes over 80%. Subsequently, the reaction temperature was set at 20, 30, 40, and 50 °C (Runs 4 and 6–8, Table 4), finding the best at 30 °C (Run 4, Table 4). At 100 °C, the activity was maintained at 5.87×10^5 g mol^{−1} (Ni) h^{−1} (Run 9, Table 4). Again, the activities gradually decreased along with the prolonged reaction time (Runs 4 and 10–12, Table 4), consistent with the EtAlCl₂ system and reported analogues. In all cases, the products remained, with fewer butenes and major hexenes over 80%, confirming that a rare case of characteristic trimerization occurred. There is no better explanation, as there is no direct evidence for the intermediates. The co-catalyst MMAO indeed interacted with nickel species, which could react with two ethylene molecules in forming relatively stable Ni-heterocyclopentane as its intermediates. Such intermediates would further react with another ethylene to break its cyclic intermediates and form new unstable intermediates, quickly cleaving for hexenes [43].

Other NiL2–NiL5/MMAO systems were extensively conducted under the optimal conditions (i.e., Al/Ni = 4000, 30 °C, 30 min, and 10 atm C₂H₄) (Runs 13–16, Table 4), achieving high activities. Their activities were in the order: NiL2 > NiL1 > NiL5 > NiL4 > NiL3 (Figure 2). Strangely, a negative influence of the complexes with an additional *para*-methyl group was observed [36,37]. The influences of their substituents were generally considered as both electronic and steric, in addition to the solubility of the complexes, but all factors weakly accumulated for the final performance. Importantly, the selectivity of the C6 fraction was significantly affected by the steric influence of the substituents, which are generally considered steric. The NiL3 with substituent ⁱPr achieved selectivity of C6 up to 95.4% (Run 14, Table 4). In general, high selectivity for ethylene trimerization to hexenes

was observed by all five nickel complexes activated by MMAO, indicating a rare model of nickel pre-catalysts for ethylene trimerization.

Table 4. Ethylene oligomerization results by NiL1–NiL5/MMAO ^a.

Run	Pre-Catalyst	Co-Catalyst	Al/Ni	T (°C)	t (min)	Activity [10 ⁵ g mol ^{−1} (Ni) h ^{−1}]	Oligomers ^b (%)		
							C4/ΣC	α-C4/C4	C6/ΣC
1	NiL1	MMAO	1000	30	30	3.60	7.5	81.3	92.5
2	NiL1	MMAO	2000	30	30	6.10	17.5	>99.0	82.5
3	NiL1	MMAO	3000	30	30	14.18	15.0	66.7	85.0
4	NiL1	MMAO	4000	30	30	19.07	13.1	78.6	86.9
5	NiL1	MMAO	5000	30	30	14.41	11.6	73.5	88.4
6	NiL1	MMAO	4000	20	30	6.93	12.9	72.6	87.1
7	NiL1	MMAO	4000	40	30	14.82	12.1	88.8	87.9
8	NiL1	MMAO	4000	50	30	13.50	18.0	66.6	82.0
9	NiL1	MMAO	4000	100	30	5.87	23.1	56.3	76.9
10	NiL1	MMAO	4000	30	15	35.91	13.2	88.9	86.8
11	NiL1	MMAO	4000	30	45	11.64	14.1	75.9	85.9
12	NiL1	MMAO	4000	30	60	10.21	16.9	86.9	83.1
13	NiL2	MMAO	4000	30	30	21.23	23.0	58.3	77.0
14	NiL3	MMAO	4000	30	30	15.71	9.5	95.4	90.5
15	NiL4	MMAO	4000	30	30	15.80	17.5	61.2	82.5
16	NiL5	MMAO	4000	30	30	18.92	16.3	68.6	83.7

^a Conditions: 2.0 μmol of pre-catalyst, 100 mL of toluene, and 10 atm of ethylene. ^b Determined by GC. ΣC denotes the total amount of oligomers.

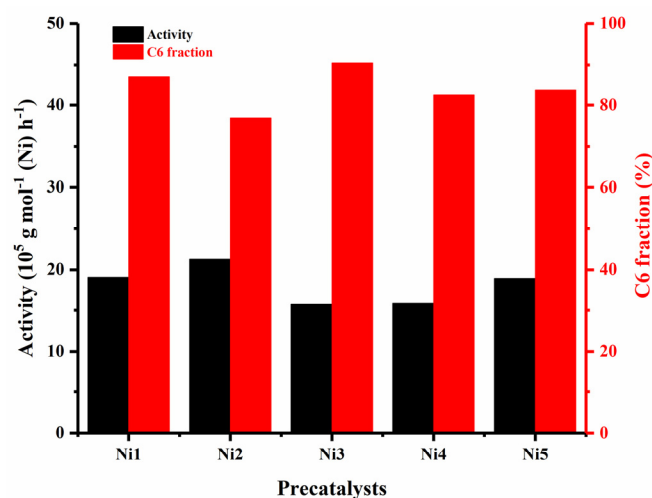


Figure 2. A bar chart exhibiting the catalytic activities and C6 fraction in total oligomers for five nickel complexes activated with MMAO (Table 4, Runs 4 and 13–16).

3. Experimental Section

3.1. General Procedures

All air- or moisture-sensitive compounds were obtained under an atmosphere of nitrogen using a nitrogen-filled glovebox or standard Schlenk techniques. The solvent (toluene) was dried over sodium and distilled under nitrogen for 8 h prior to use. Methylaluminoxane (1.42 M solution in toluene), modified methylaluminoxane (2.46 M solution in n-heptane), ethylaluminum sesquichloride (EASC 3.30 M in toluene), ethylaluminum dichloride (EtAlCl₂, 1.20 M in hexane), and diethylaluminum chloride (Et₂AlCl, 1.17 M in hexane) were purchased from Anhui Botai Electronic Materials Co. (Chuzhou, China). High-purity ethylene was purchased from Beijing Yanshan Petrochemical Corp. (Beijing, China) and used as received. Other reagents were purchased from Aldrich (St. Louis, MO, USA), Acros (Fukuoka, Japan), or local suppliers. FT-IR spectra were recorded on

a PerkinElmer System 2000 FT-IR spectrometer (PerkinElmer, Waltham, MA, USA), and elemental analyses were determined on a Flash EA 1112 microanalyzer (EA Consumables, Marlton, NJ, USA). Gas chromatography (GC) analysis was performed with a VARIAN CP-3800 (Varian, Palo Alto, CA, USA) gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm internal diameter and 0.25 μ m film thickness) DM-1 silica capillary column.

3.2. Synthesis and Characterization of 2-*t*-Butyl-2,3-dihydroacridine-4-one

Based on previous work [38,39], 2-aminobenzyl alcohol (15.1 g, 123 mmol), 4-*tert*-butylcyclohexanone (20.0 g, 129 mmol, 1.04 eq.), *t*-BuOK (13.44 g, 120 mmol), and [*fac*-PNN]RuH(PPh₃)(CO) [38] (44 mg, 0.06 mmol, 0.05 mol%), in a mixture of THF (50 mL) and toluene (250 mL), were stirred and heated to reflux under an atmosphere of nitrogen. After stirring for 24 h at this temperature, the resultant solution was cooled to room temperature, and water (300 mL) was added. The mixture was stirred for 0.5 h at room temperature and then extracted with ethyl acetate (2 $\times$ 300 mL). The combined organic layers were washed with water (2 $\times$ 100 mL) and dried over anhydrous NaSO₄. Evaporation of the solvent yielded a red oil (30.0 g), which was dissolved in dichloromethane (20 mL), and hexane (100 mL) was introduced. After cooling the mixture to 0 °C, the resulting precipitate was filtered, affording **1** as a yellow solid (24.9 g, 85%). Then, **1** was directly used in the next step.

Under nitrogen atmosphere, 2-*t*-butyl-1,3,4-trihydroacridine (16.0 g, 66 mmol), benzaldehyde (10.6 g, 100 mmol, 1.5 eq.), and acetic anhydride (10.3 g, 100 mmol, 1.5 eq.) were mixed in a bottle and refluxed for 6 h at 160 °C (monitored by TLC). When the reaction was completed, the acetic anhydride was removed by rotary evaporation. Then, distilled water (100 mL) was added for rotary evaporation to remove excess benzaldehyde. More distilled water was added to wash the residue solid and then it was filtered to obtain the yellow crude product. The crude product was recrystallized in methanol and filtered to obtain the pale-yellow product, 4-benzylidene-2-(*tert*-butyl)-1,2,3,4-tetrahydroacridine (18.8 g, 87% yield). Without further purification, the 4-benzylidene-2-(*tert*-butyl)-1,2,3,4-tetrahydroacridine (15.0 g, 45 mmol) was dissolved with dichloromethane (400 mL) and methanol (400 mL). After cooling to −40 °C, the O₃/O₂ gas was added for the ozone cleavage reaction. After 5 h, the solution gradually became clear and the O₃/O₂ gas was stopped. Then, the reaction solution was gradually raised to room temperature and dimethyl sulfide (6 mL) was added and stirred overnight. The reaction liquid was concentrated under reduced pressure to obtain a pale-yellow oil. Distilled water (60 mL) was added for rotary evaporation to remove benzaldehyde, then it was filtered to obtain a light-yellow solid, and slurried with methanol (100 mL) to yield the white product, 2-*t*-butyl-2,3-dihydroacridine-4-one (4.7 g, 51% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.6 Hz, 1H), 8.08 (s, 1H), 7.75 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.68 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 3.18 (dt, *J* = 15.8, 3.2 Hz, 1H), 3.06 (dt, *J* = 16.6, 3.0 Hz, 1H), 2.94 (ddd, *J* = 15.9, 12.4, 1.4 Hz, 1H), 2.51 (dd, *J* = 16.6, 13.8 Hz, 1H), 2.03 (ddt, *J* = 13.6, 12.4, 3.4 Hz, 1H), 1.00 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 198.2, 148.2, 147.4, 136.6, 136.6, 135.6, 131.2, 129.7, 129.5, 128.8, 126.7, 44.9, 42.5, 32.5, 31.2, 27.0, 27.0. Anal. Calcd. for C₁₇H₁₉NO (253.15): C, 80.60; H, 7.56; N, 5.53. Found: C, 80.75; H, 7.62; N, 5.38%.

3.3. Synthesis and Characterization of Complexes NiL1–NiL5

[4-(2,6-Dimethylphenylimino)-2-*tert*-butyl-1,3-dihydroacridine nickel dibromides] NiL1

NiBr₂(DME) (0.1 g, 0.4 mmol) and 2-(*tert*-butyl)-2,3-dihydroacridin-4(1H)-one (0.1 g, 0.4 mmol) were suspended in glacial acetic acid (5 mL). Then, 2,6-dimethylaniline (0.05 g, 0.4 mmol) was added, and the reaction mixture was refluxed under stirring at 130 °C for 6 h. After that, the solution was allowed to cool to room temperature, and a green solid precipitated. The solid was separated by filtration and washed with diethyl ether to remove the remaining acetic acid and aniline. The solid was dried to obtain a green powder (0.16 g, 91.4% yield). FT-IR (cm^{−1}): 3344(w), 2846(w), 2160(m), 1974(m), 1711(w), 1662(s), 1620(m),

$\nu_{C=N}$), 1570(m, $\nu_{C=N}$), 1489(m), 1458(m), 1357(m), 1335(m), 1275(m), 1192(m), 1154(m), 1027(m), 924(m), 853(w), 805(m), 768(vs), 705(vs). Anal. Calcd. for $C_{25}H_{28}Br_2N_2Ni$ (572.00): C, 52.22; H, 4.91; N, 4.87. Found: C, 52.68; H, 5.38; N, 4.62%.

[4-(2,6-Diethylphenylimino)-2-tert-butyl-1,3-dihydroacridine nickel dibromides] NiL2

Using the same procedure as described above for the synthesis of **NiL1**, **NiL2** was obtained as a green powder (0.21 g, 88.6% yield). FT-IR (cm^{-1}): 3322(m), 2954(m), 2864(m), 1976(w), 1664(s), 1616(s, $\nu_{C=N}$), 1585(w, $\nu_{C=N}$), 1499(w), 1458(m), 1401(w), 1364(w), 1342(m), 1304(w), 1237(w), 1205(m), 1144(m), 1050(w), 1005(w), 919(w), 826(w), 787(s), 756(vs), 670(m). Anal. Calcd. for $C_{27}H_{32}Br_2N_2Ni$ (600.03): C, 53.77; H, 5.35; N, 4.65. Found: C, 53.48; H, 5.15; N, 4.51%.

[4-(2,6-Diisopropylphenylimino)-2-tert-butyl-1,3-dihydroacridine nickel dibromides] NiL3

Using the same procedure as described above for the synthesis of **NiL1**, **NiL3** was obtained as a green powder (0.14 g, 55.4% yield). FT-IR (cm^{-1}): 3015(w), 2963(s), 2656(m), 2549(m), 2524(m), 2161(w), 1972(w), 1666(s), 1616(s, $\nu_{C=N}$), 1586(m, $\nu_{C=N}$), 1549(m), 1500(s), 1460(s), 1390(w), 1366(w), 1344(m), 1289(w), 1238(w), 1207(m), 1152(m), 1035(w), 1009(w), 969(w), 918(w), 850(w), 828(w), 800(m), 756(s), 673(m). Anal. Calcd. for $C_{29}H_{36}Br_2N_2Ni$ (628.06): C, 55.19; H, 5.75; N, 4.44. Found: C, 55.58; H, 5.89; N, 4.79%.

[4-(2,4,6-Trimethylphenylimino)-2-tert-butyl-1,3-dihydroacridine nickel dibromides] NiL4

Using the same procedure as described above for the synthesis of **NiL1**, **NiL4** was obtained as a brown powder (0.13 g, 57.7% yield). FT-IR (cm^{-1}): 3129(w), 2956(m), 2850(w), 2161(w), 1974(w), 1665(s), 1618(s, $\nu_{C=N}$), 1587(w, $\nu_{C=N}$), 1566(w), 1502(w), 1460(s), 1398(w), 1344(m), 1325(m), 1310(w), 1288(w), 1238(w), 1206(m), 1152(s), 1052(w), 1008(w), 973(w), 851(w), 828(w), 790(m), 755(s), 718(w), 672(m). Anal. Calcd. for $C_{26}H_{30}Br_2N_2Ni$ (586.01): C, 53.02; H, 5.13; N, 4.76. Found: C, 53.43; H, 5.35; N, 4.51%.

[4-(2,6-Diethyl-4-methylphenylimino)-2-tert-butyl-1,3-dihydroacridine nickel dibromides] NiL5

Using the same procedure as described above for the synthesis of **NiL1**, **NiL5** was obtained as a brown powder (0.11 g, 44.6% yield). FT-IR (cm^{-1}): 3129(w), 2954(m), 2850(w), 2162(w), 1975(w), 1665(vs), 1621(s, $\nu_{C=N}$), 1587(w, $\nu_{C=N}$), 1566(w), 1501(w), 1460(s), 1398(w), 1344(m), 1325(m), 1309(w), 1288(w), 1238(w), 1206(s), 1152(s), 1052(w), 1007(w), 971(w), 880(w), 850(w), 828(w), 790(m), 754(s), 672(m). Anal. Calcd. for $C_{28}H_{34}Br_2N_2Ni$ (614.04): C, 54.50; H, 5.55; N, 4.54. Found: C, 54.31; H, 5.23; N, 4.30%.

3.4. X-ray Diffraction Studies

The single crystal of **NiL1** that qualified for XRD studies was obtained by diffusing diethyl ether onto a dichloromethane solution containing the corresponding complex. A suitable crystal of **NiL1** was selected and mounted on an XtaLAB Synergy R (Rigaku Corporation, Tokyo, Japan), HyPix diffractometer, incorporating a graphite-mono-chromated Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) source and a nitrogen cold stream. The crystal was kept at 169.99(10) K during data collection. Using Olex2-1.3, the structures were solved with the ShelXT [44] structure solution program using Intrinsic Phasing and refined with the ShelXL [45] refinement package using Least Squares minimization. The X-ray structure determination and refinement details are presented in Table S1.

3.5. General Ethylene Oligomerization Procedures

For the general procedure of ethylene oligomerization at 10 atm of ethylene pressure, a 0.25 L stainless-steel autoclave equipped with a mechanical stirrer and a temperature controller was prepared. Before the reaction, the reactor was heated in a vacuum at 110 °C and recharged with ethylene three times. The nickel pre-catalyst was dissolved in 50 mL of toluene using standard Schlenk techniques and injected into the reactor under an ethylene atmosphere. When the temperature was reached, the required amounts of co-catalyst and the residual toluene (the total volume of toluene was 100 mL) were injected into the reactor. Ethylene at the desired pressure was introduced to start the reaction, and ethylene was continuously fed at a constant pressure during the reaction. When the reaction was completed, 1 mL of the reaction solution was quenched by the addition of 1 M hydrogen

chloride (HCl). The organic layer was collected to be analyzed by gas chromatography (GC) to determine the distribution of the obtained oligomers.

4. Conclusions

A series of 2-*t*-butyl-4-arylimino-2,3-dihydroacridylnickel(II) bromides were prepared through a nickel-induced template reaction of 2-*t*-butyl-2,3-dihydroacridine-4-one and a corresponding aniline with (DME)NiBr₂. Besides routine and full analysis, the molecular structure of NiL1 was illustrated as a distorted tetrahedral geometry around its nickel(II) center, coordinated with the N[^]N ligand and two bromides. More importantly, all nickel complexes showed high activities toward ethylene on-purpose oligomerization. When activated with EtAlCl₂, the dimerization was highly selective for all nickel pre-catalysts; however, major trimerization with high activity was rarely achieved with the co-catalyst MMAO. The roles of ligands' substituents were illustrated differently: both solubility and electronic influence occurred in the system with EtAlCl₂, but likely mainly electronic influence for the system with MMAO. Though dimerization by nickel commonly occurs, trimerization by nickel is rare but promising when using the title complexes. On that basis, the on-purpose oligomerization by nickel pre-catalysts would be an interesting topic for chemists, both in extending catalytic applications and finding alternative catalysts to replace chromium catalysts. As a promising conceptual procedure, the ethylene within refinery gases could be transformed into butenes and hexenes, such as liquefied petroleum gas (LPG).

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14060342/s1>, Figure S1: ¹H NMR for 2-*t*-butyl-2,3-dihydroacridine-4-one [38,39]. Figure S2: ¹³C NMR for 2-*t*-butyl-2,3-dihydroacridine-4-one. Figure S3: GC of NiL1 (run 2, Table 3). Figure S4: GC of NiL1 (run 4, Table 4). Table S1: Crystallographic data and refinement details for complex NiL1.

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