

Article

Controlling Nickel Catalyst Reactivity by Controlling Molecular Catalyst Speciation

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Abstract

Controlling molecular catalyst speciation under reaction conditions can be an effective approach for extending catalyst lifetimes and controlling selectivity. Anchoring molecular catalysts to solid supports, to generate hybrid catalysts, is a means for preventing bimolecular catalyst interactions and preventing the formation of catalyst species such as dimers and multimers. Here we compare a series of different anchoring motifs for molecular nickel catalysts bound to metal oxide supports. The catalysts are anchored to the supports through functional groups on the ligand framework, and carboxylate, ester, and silanol groups are compared in terms of synthetic ease, anchoring stability, catalyst loading on the surface, and catalytic behavior with respect to Suzuki–Miyaura cross-coupling. The results show that covalent bonds between the molecular catalysts and the oxide support lead to increased catalyst surface loadings and higher surface loading, which helps avoid mass transport limitations during catalysis. In addition, the metal–ester-bound catalysts exhibit support-dependent reactivity, which is unique and different from the carboxylate and silanol anchoring groups. Infrared and X-ray photoelectron spectroscopy are used to characterize the molecular nature of the catalysts, and reactivity trends show that the covalent bonding of the catalysts to the surface controls catalyst speciation with respect to geometry and valency, which influences catalytic activity.

Keywords: catalysis; nickel; hybrid; inorganic; organometallic

1. Introduction

Molecular palladium-based transition metal catalysts are prevalent in fine chemical synthesis and widely used in Suzuki–Miyaura, Heck, and Buchwald–Hartwig coupling, to name a few examples [1–3]. The wide use of palladium catalysts is due to their relatively predictable catalyst properties and propensity to undergo Pd(II/0) cycles. However, due to the high cost and rarity of palladium, researchers have pursued the discovery of more sustainable and less expensive catalysts containing first-row transition metals [4–8]. In addition, despite the ubiquity of molecular palladium catalysts, the nuclearity of palladium active sites (i.e., molecular versus nanoparticle) is commonly questioned [9–11]. Nickel can offer a direct alternative to palladium as it is in the same periodic triad. Molecular nickel catalysts are also less susceptible to nucleation due to the distinct differences in thermodynamic properties, such as redox potentials, between nickel and palladium [11,12]. These property differences also allow molecular nickel complexes to access a

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variety of oxidation states and one-electron reactivity, which is rarer for palladium catalysts. Molecular nickel catalysts can thus access different reactivities compared to palladium catalysts, such as the more facile activation of arylchlorides and phenol derivatives [13,14], as well as incorporation into photoredox catalysis cycles [15–17].

With the growing research and utilization of nickel catalysts, Ananikov has warned that “taming” nickel catalysts for controlled and predictable reactivity can be difficult [18]. This focus on nickel catalysts stems from research regarding related palladium catalysts that can show activity in many different molecular and particulate forms [10,19,20]. The range of accessible nickel oxidation states in molecular catalysts includes Ni(0, I, II, III, IV). The most common oxidation states are +1, +2, and +3 [21,22], as the formed Ni(0) species typically require strong reductants and are readily oxidized [23]. Moreover, Ni(IV) can be achieved, but this requires a special consideration of the ligand environment [24]. The range of accessible Ni oxidation states, however, can lead to a variety of Ni species, each differing in valency, arising during catalytic reactions. In addition to multiple valencies, nickel catalysts in homogeneous solution are also prone to dimerization [25]. In some cases, these dimers have been shown to be off-cycle species that are not catalytically active [26]. However, nickel dimers may be active catalysts or lead to side reactivity [27]. In either case, the wide range of nickel species that are accessible during catalytic reactions is an issue that can lead to poor catalytic selectivity and efficiency. This issue is reflected by the common need to use higher nickel catalyst loadings compared to palladium catalysts to achieve comparable activity for the same catalytic reaction [11].

To limit the number of possible catalytic species, molecular nickel catalysts can be anchored onto the surface of solid supports. This hybrid molecular/heterogeneous catalyst motif offers the ability to combine the selectivity of molecular catalysts with the ease of separation and practicality of heterogeneous catalysts [28]. Surface anchoring prevents bimolecular catalyst interactions, thus limiting the number of possible nickel species by preventing the formation of dimers. Furthermore, in cases where the formation of nickel dimers leads to the deactivation of catalysts, these hybrid catalyst motifs can lead to longer catalyst lifetimes and greater catalytic turnover [25]. Overall, limiting the number of possible nickel species during catalytic reactions could lead to more efficient catalytic activity at lower catalyst loadings.

Heterogeneous supports for hybrid catalysts include polymers, MOFs/COFs, metallic supports, and metal oxides (MOx) [29–32]. While each type of support offers possible advantages, MOx supports exhibit high thermal stability, tunable surface area and surface chemistry, and the choice between insulating or semi-conducting properties [33,34]. The most commonly reported route for synthesizing hybrid catalysts on MOx supports involves anchoring molecular catalysts to the surface through hydrogen bonding between the support and the functional groups on the ligand of the molecular catalysts [35]. This acid/base binding motif, shown in Figure 1, typically uses functional groups such as carboxylates, as well as phosphonates and hydroxymates [36–38]. This class of hybrid catalysts has the advantage of synthetic ease, but the non-covalent bonding between the supports and the molecular catalysts leads to pH-dependent anchoring stability issues [39]. Covalent bonding between molecular catalysts and MOx supports has been achieved with siloxane functional groups (Figure 1) [40]. This hybrid catalyst class has exhibited enhanced anchoring stability in aqueous solvents compared to acid/base binding, but synthetic challenges, such as the oligomerization of the siloxane functional group, have limited the widespread use of this anchoring motif. We have recently reported a new class of hybrid catalysts that anchor molecular catalysts to MOx supports through covalent metal-ester bonds [41]. This synthetically simple procedure can achieve higher catalyst surface loadings compared to previously reported motifs. This class of hybrid catalysts also exhibited measurable electron induction effects between the molecular catalyst and the

metal oxide support, analogous to electrochemically induced inductive effects [42] but without the need for an applied potential. This type of support controllable reactivity had not previously been observed for molecular catalysts anchored to supports through the ligand structure, but support-dependent reactivity has been reported for surface organo-metallic chemistry complexes bound to the support through the catalytically active metal [43,44].

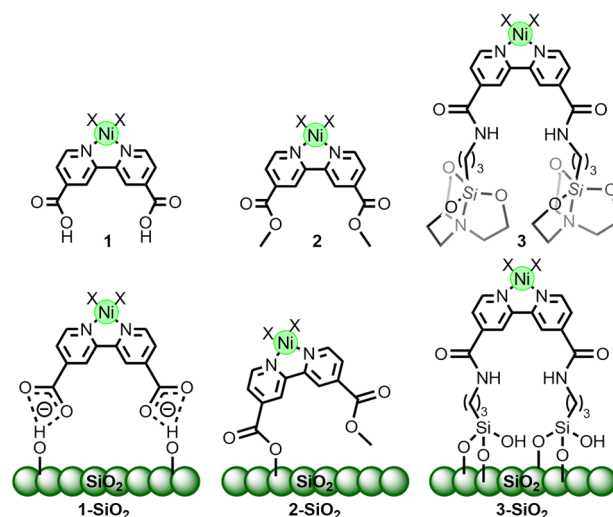


Figure 1. Structures of molecular catalysts 1–3 and hybrid catalysts 1-SiO₂–3-SiO₂. X = Cl[−] or Br[−].

With respect to nickel catalysts, influencing the reactivity of the molecular catalyst through electron induction effects from the MOx support should help control the accessible nickel oxidation states. This control would, in turn, limit the number of possible nickel species during the reaction. Furthermore, the binding of the molecular nickel catalysts to the solid supports isolates the catalysts, thus preventing catalyst dimerization and adding additional control over nickel speciation. Controlling the nickel species should result in more selective reactivity and thus increase the catalytic efficiency of molecular nickel catalysts, which could help in the discovery of nickel catalysts that are capable of directly replacing palladium catalysts [11].

Herein we report the catalytic activity for a molecular nickel catalyst in homogeneous solution and three analogous hybrid nickel catalysts. Reactivity trends and catalyst lifetimes are correlated to the structure and hybrid binding motif where applicable. The advantages and drawbacks of each catalyst are discussed with respect to Suzuki cross-coupling catalysis.

2. Experimental Section

All reagents were used as received from the manufacturer without any further purification unless noted. Inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific (Waltham, Massachusetts, USA) Finnigan ELEMENT XR double focusing magnetic field) analysis was used to determine the amount of nickel present on the metal oxide supports with rhenium as the internal standard. A quartz torch and injector (Thermo Fisher Scientific, Waltham, USA) and a 0.2 mL/min Micromist U-series nebulizer (GE, Australia) were used for sample introduction. GC-MS (Shimadzu QP-2010S, Canby, Minnesota, USA) product analyses were performed with a 30 m long Rxi-5 ms (Restek, Bellefonte, USA) separation column with a 0.25 mm id, and the oven temperature program consisted of 40 °C for 0.5 min, followed by a 10 °C/min ramp to 280 °C and holding for 2 min. Mass spectrometer electron ionization was conducted at 70 eV, and the spectrometer was scanned from 1000 to 50 *m/z* at low resolution. Infrared (IR) spectra were

obtained using a PerkinElmer Spectrum 100 FT-IT Spectrometer Waltham, USA with a universal ATR (UATR) accessory. X-ray photoelectron spectroscopy data were collected with an AXIS Ultra DLD XPS (Kratos Analytical, United Kingdom) instrument equipped with a non-monochromatic Al K α source (1486.8 eV) operated at 120 W X-ray power, a hemispherical analyzer, and a charge neutralizer. The X-rays were incident at an angle of 45°, with respect to the surface normal. Analysis was performed at a pressure of $\sim 1 \times 10^{-9}$ torr, and high-resolution core-level spectra were acquired in the constant analyzer energy mode using a pass energy of 40 eV and a 0.05 eV step size. XPS experiments were performed by using a low-energy electron beam, directed at the sample, for charge neutralization. A curve fitting procedure was carried out using Casa XPS software version 2.327, and peak approximation was carried out by using a combination of Gaussian–Lorentzian functions, with the subtraction of Shirley-type background. The binding energy (BE) scale of the scans was corrected with reference to the C 1s peak at 285 eV (adventitious carbon from contamination) and given with an accuracy of ± 0.2 eV.

The synthesis of **1**, **2**, **1-SiO₂**, **2-SiO₂**, and **2-ZrO₂** was performed as previously reported [41,43]. The synthesis of **3** was first carried out by synthesizing the [4,4'-bis(3-(triethoxysilyl)propylamide)-2,2'-bipyridine] ligand. A total of 0.2 g (0.82 mmol) of [2,2'-bipyridine]-4,4'-dicarboxylic acid was dissolved in 4 mL (54 mmol) of thionyl chloride and refluxed for 24 h under N₂. The remaining thionyl chloride was distilled off and quenched in a separate flask at 0 °C with 20 mL of toluene followed by the slow addition with stirring of 20 mL cold isopropyl alcohol, 20 mL of MeOH, and 10 mL H₂O. The remaining yellow solid, [2,2'-bipyridine]-4,4'-dicarbonyl dichloride, was then suspended in 10 mL of toluene, and the suspension was cooled to 0 °C, and 0.417 g (1.8 mmol) of 3-(triethoxysilyl)trane propylamine was slowly added over the course of one hour to produce a pink solid. The solid was then filtered, rinsed with dichloromethane, and dried under strong vacuum with no heat. (0.357 g, 59%) ¹H NMR (Figure S3): δ_H (400 MHz; CDCl₃) 8.77–8.73 (4H, m, CH), 7.9 (2H, s, CH), s, 7.68(2H, m, NH), 3.78 (12H, t, CH₂), 3.49 (4H, q, CH₂), 2.80 (12H, t, CH₂), 1.80 (4H, p, CH₂), 0.56 (4H, t, CH₂).

A total of 0.3 g (0.45 mmol) of the [4,4'-bis(3-(triethoxysilyl)propylamide)-2,2'-bipyridine] ligand was then dissolved in 25 mL of acetonitrile at 45 °C under N₂ and stirring, to which 1.1 equivalents of NiBr·DME (DME = ethylene glycol dimethyl ether) was added. The addition of the nickel source resulted in the solution rapidly turning into a deep blue color with a dark red solid crashing out. The solid catalyst **3** was filtered and rinsed with cold THF and dried under vacuum at 45 °C. (0.33 g, 74%) Analytically calculated for C₃₀N₆O₈Si₂H₄₄Br₂Ni with one DME in the coordination sphere adding C₄O₂H₁₀ to the chemical formula resulting in a molecular mass of 981.5186 g/mol: C 41.60; H 5.54; N 8.56. Found: C 41.07; H 5.50; N 8.54.

3-SiO₂ was synthesized by dissolving 0.1 g of [4,4'-bis(3-(triethoxysilyl)propylamide)-2,2'-bipyridine Ni(II)]·2Br[−] in warm THF (50 °C), to which 300 mg of the A300 support was added and stirred under heat and N₂ for 24 h. A300 took on a light red/pink color during the reaction and was vacuum-filtered and rinsed with THF.

All catalytic reaction flasks were thoroughly cleaned by soaking in a concentrated nitric acid solution followed by a soak in a base bath. The flasks were then rinsed with deionized water and dried overnight in a furnace. All stir bars used in this study were new out of the package to avoid any possible Pd contamination. In a round-bottom flask, 0.5 mmol of aryl halide, 1.5 mmol of boronic acid, and 1.7 mmol of K₃PO₄ were added to 20 mL of dioxane. Solid hybrid catalysts were then weighed out to an amount that equated to 0.015 mmols of nickel catalyst (3 mol% with respect to the aryl halide). The total weight of each hybrid catalyst varied depending on the degree of nickel catalyst loading on the support. The reaction solutions were then heated to 105 °C for the entirety of the reaction. Post-reaction solutions were centrifuged to separate the solid catalyst from the reaction

solution. The decanted solutions were then passed through a syringe filter and injected neat into a liquid injection GC-MS for product analysis. Catalyst reusability experiments were performed by filtering the solid catalyst from the reaction solution, rinsing the catalyst with hexanes and diethylether, drying under vacuum, and placing the reactions in a fresh reaction solution.

3. Results and Discussion

The catalysts compared in this study are shown in Figure 1. The molecular [(2,2'-bipyridine-4,4'-R)nickel(II)]·2Cl[−], where R is carboxylate (**1**) or methyl ester (**2**), complexes were synthesized and isolated according to a previously reported procedure [45]. Details for the synthesis of previously unreported catalyst **3** can be found in the Experimental Section, and the ligand synthesis procedure was adapted from a previous report [46]. The anchoring of **1** onto an Aerosil 300 SiO₂ support to generate hybrid catalyst **1-SiO₂** followed a published procedure for a related hybrid nickel catalyst [25]. The SiO₂ support was chosen for its high thermal stability, inert reactivity, and high (300 m²·g^{−1}) surface area [25]. The synthesis of catalyst **2-SiO₂** has been previously reported [41], and the synthesis procedure of **3-SiO₂** was adapted from a previous report [46].

The initial characterization of the catalysts was carried out with FTIR, and the spectra are shown in Figure 2. The carbon–oxygen bond stretching frequencies for **1** appear near 1720 cm^{−1} and 1610 cm^{−1}, indicating that as-synthesized **1** exists in a mixture of protonation states [47]. The carbon–oxygen stretching frequencies for methyl ester catalyst **2** appear at 1739 cm^{−1} and 1720 cm^{−1} as expected for C=O stretching frequencies for ester groups. For catalyst **3**, the C=O stretching frequencies for amine groups are observed at 1645 cm^{−1} and 1555 cm^{−1} [48]. Upon the anchoring of **1** onto a SiO₂ support to form **1-SiO₂**, the carbon–oxygen frequencies appear near 1620 cm^{−1} for the bridging binding mode, with a weak signal at 1725 cm^{−1} for the end-on binding mode [47]. The anchoring of **2** onto a SiO₂ support through covalent binding to generate **2-SiO₂** leads to a new C=O stretching frequency at 1747 cm^{−1} along with a parent peak at 1739 cm^{−1}. This splitting pattern for **2-SiO₂** has previously been observed and is assigned to the singly bonded structure shown in Figure 1 [41]. Lastly, the anchoring of **3** to a SiO₂ support to generate **3-SiO₂** leads to minimal shifts in the IR spectra. The minimal shifts in the C=O IR frequencies are due to the amine groups being separated from the metal oxide support by a saturated carbon chain which is expected to dampen any electronic effects the support could have on the molecular catalyst [46]. With ligand binding to the surface confirmed by FTIR, inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the extent of catalyst loading by measuring the weight percent of nickel in each hybrid catalyst. Table 1 summarizes the ICP-MS results along with the calculated loadings in units of catalyst molecules per nm² surface area. As can be seen from Table 1, the covalent bonding of the molecular catalyst to the oxide support (catalysts **2-SiO₂** and **3-SiO₂**) increases catalyst loading compared to the non-covalent bonding of hybrid catalyst **1-SiO₂**. In addition, smaller ester bonding moieties, which are also not prone to oligomerization during hybrid catalyst synthesis, lead to higher catalyst loading compared to siloxane binding.

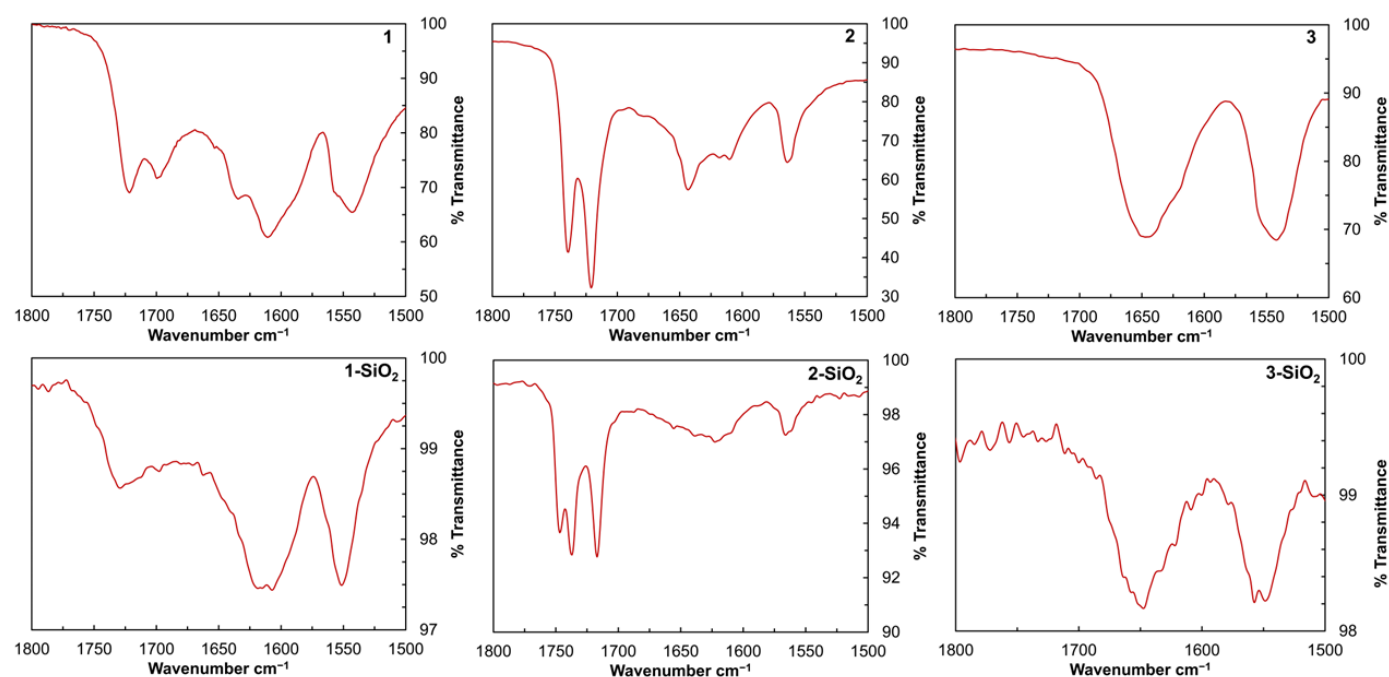


Figure 2. FTIR spectra of molecular catalysts **1–3** and hybrid catalysts **1-SiO₂**, **2-SiO₂**, and **3-SiO₂**.

Table 1. Summary of FTIR and ICP-MS characterization data.

Catalyst	Carbonyl cm ⁻¹	Ni wt% Loading	Molecules·nm ⁻²
1	1721(s) 1698(m) 1634(w) 1610(s)	n/a	n/a
2	1739(s) 1720(s)	n/a	n/a
3	1646(s) 1542(s)	n/a	n/a
1-SiO₂	1729(w) 1619(s)	0.1	0.03
2-SiO₂	1747(s) 1737(s) 1717(s)	5.9	2.0
3-SiO₂	1647(s) 1548(s)	2.0	0.7

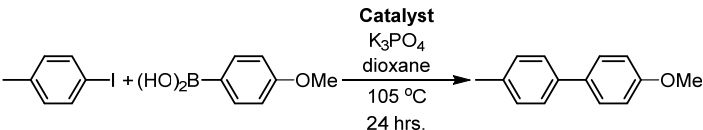
FTIR data described as s (strong), m (medium), and w (weak) based on relative intensities within each spectrum. Molecules of catalyst per nm² calculated using 300 nm²·g⁻¹ for A300 SiO₂ support.

Suzuki cross-coupling was chosen as the test reaction to compare the reactivity and catalytic lifetimes of the catalysts. The multiple redox steps that occur during the Suzuki coupling cycle allow for access to multiple different nickel valencies, and thus control over different nickel species can be observed. Beyond nickel species differing in valency, sterically unencumbered nickel catalysts have shown the propensity to dimerize under the reaction conditions needed to perform thermally activated cross-coupling [25,26]. These persistent, inactive nickel dimer species appear unique to thermally driven reactions, as nickel is widely used in photoredox cross-coupling, and it has been shown that nickel dimers can be reduced by photocatalysts, which regenerates catalytically active, monomeric species [15,49]. Hybrid catalysts, which immobilize the molecular species on supports, could prevent dimerization without the need for a strong in situ reductant and exhibit ever greater control over speciation.

Table 2 lists the product yields achieved for catalyzed Suzuki cross-coupling reactions and summarizes the results of the control reactions. Every reaction was performed at a common nickel mol% loading; thus product yields directly correlate to the turnover numbers of the catalysts. The first entry in Table 2 shows that molecular catalyst **1** in homogeneous solution is only able to perform cross-coupling catalysis at 10% product yield, which is comparable to previously reported molecular nickel catalysts for thermally driven Suzuki cross-coupling reactivity [25,26]. While the yields are low, it is indicated

that catalysis occurred from **1**, as no cross-coupling reactivity is observed in the absence of nickel or in the presence of ligandless nickel salts. Monitoring the product yields obtained using **1** with GC-MS analysis showed that product formation ceased after roughly one hour and that extending the reaction to 24 h did not result in additional product formation. This indicates that catalyst deactivation, attributed to catalyst dimerization, is the main determinant of the low product yields. The literature has also shown that changes in catalyst speciation can lead to active species such as nanoparticles; however, the deactivation observed in our catalyst rules out the “cocktail of catalysts” possibility [19]. Altering the electron density of the carbon nucleophile boronic acid did not have an appreciable effect on product yields. Changing the identity of the carbon electrophile from iodotoluene to bromotoluene led to a decrease in yield (10% to 4%). The oxidative addition of C-Br bonds is more thermodynamically demanding than the oxidative addition of C-I bonds [50]. In addition, while I[−] abstraction is a known possible route for the activation of iodo-substrates, Br[−] abstraction is rarer due to the higher bond dissociation energy of C-Br bonds [51]. Thus, the lower yields are attributed to less favorable carbon electrophile activation, and these results indicate that catalyst deactivation is not associated with carbon electrophile activation. Molecular catalyst **2** in homogeneous solution also led to low product yields and product formation ceasing near one hour. Lastly, **3** in homogeneous solution did not exhibit catalytic activity. This is likely due to multiple deactivation routes which include Ni-Ni dimer formation and the oligomerization of the silatrane moiety on the ligand structure.

Table 2. Cross-coupled product yield comparison.

	
Catalyst ^a	% Yield ^b
1	10
2	2
3	0
1-SiO₂	<1
2-SiO₂	25 ^d
3-SiO₂	30
None	0
NiCl ₂	0
NiBr ₂	0
SiO ₂	0
ZrO ₂	<1
NiCl ₂ /SiO ₂ ^c	0
NiCl ₂ /ZrO ₂ ^c	<1
2-ZrO₂	61

^a Standard conditions: 3 mol% Ni catalyst loading with respect to iodotoluene substrate, 0.5 mmol iodotoluene, 1.5 mmol 4-methoxyphenyl boronic acid, 1.7 mmol K₃PO₄, 20 mL dioxane. ^b Yields of cross-coupled product determined by GC-MS. ^c Total of 0.015 mmols of Ni halide salt and 100 mg of oxide support added to reaction flask. ^d Homocoupled products of carbon nucleophile and electrophile also observed in GC chromatograph.

Anchoring catalysts **1–3** onto solid SiO₂ supports to generate hybrid catalysts leads to a change in observed product yields. The hybrid catalyst **1-SiO₂** at the standard 3 mol% Ni loading led to minimal cross-coupled product formation. This is in contrast to the

molecular analog **1** leading to a 10% product yield. This drop in product yield can be attributed to mass transport limitations with **1-SiO₂**. As reported in Table 1, the loading of molecular catalyst **1** onto SiO₂ leads to a catalyst surface loading of only 0.03 molecules per nm² [52]. The low loading of **1** onto SiO₂ supports is caused by the non-covalent nature of the surface binding site. While it might be hypothesized that two binding sites are better than one, the rigidity of the 4,4'-dicarboxylate-2,2'-bipyridine ligand requires specifically spaced surface hydroxyl sites to achieve catalyst anchoring. The results here show that this requirement for two binding sites leads to less loading, as the analogous [(2,2':6',2''-terpyridine-4'-benzoate)Ni(II)]·2Cl catalyst, which binds to oxide surfaces via one anchoring site, was able to achieve 10x greater surface loading on the same SiO₂ support [25]. The low catalyst loading of **1-SiO₂** leads to the inadequate mixing of the active Ni catalyst and the substrates as the majority of solid added to the reaction mixture is inactive SiO₂ support. Increasing the Ni mol% loading to 5% or decreasing it to 1% by adding more or less solid hybrid catalyst led to no discernable changes in observed product yield, indicating that the surface loading of the molecular catalyst on the support is the main driving factor of mass transport limitations.

The **3-SiO₂** hybrid catalyst anchors the molecular catalyst to the SiO₂ support through covalent bonding, which aims to overcome the low loading limitations of non-covalent molecule/support interactions [46]. As seen in Table 1, the **3-SiO₂** catalyst does achieve 0.7 molecules per nm² surface loading, which is 20x times greater than that of non-covalent anchored **1-SiO₂**. This higher surface loading eliminates the mass transport limitations observed for **1-SiO₂** and leads to cross-coupling catalytic activity. The **3-SiO₂** hybrid catalyst generates 30x more product yield than **1-SiO₂**. In addition, the anchoring of **3** onto a SiO₂ support to generate hybrid catalyst **3-SiO₂** prevents the two main deactivation routes of **3**, dimerization and oligomerization. Thus, **3-SiO₂** is able to achieve catalytic cross-coupling reactivity, but **3** is not. This is due to the extended catalyst lifetime of **3-SiO₂** compared to **3**. This result highlights how controlling catalyst geometry speciation can lead to enhanced catalytic reactivity.

As shown in Table 1, the **2-SiO₂** hybrid catalyst achieves the highest loading of the three hybrid catalysts compared with a loading of two molecules per nm². This high surface loading is attributed to the single covalent bond between the molecular catalyst and the support [41], in contrast to the multiple bonds required to anchor silatrane to the support in **3-SiO₂**. Table 2 shows that **2-SiO₂** produces the desired cross-coupled product in comparable yields to **3-SiO₂**. However, a deeper analysis of the product distribution from **2-SiO₂** showed that a range of homocoupled and cross-coupled products were obtained. This is indicative of uncontrolled radical reactivity [41]. Thus **2-SiO₂** exhibits the highest activity in the series of catalysts compared here but with low selectivity.

The difference in reactivity observed can be rationalized through the catalytic mechanisms shown in Figure 3. When starting from a Ni(II) oxidation state, the catalyst must first be reduced to enter into the catalytic cycle, as shown in step 1. Boronic acids in the presence of bases have been reported as weak one-electron reductants for Ni(II) catalysts [21]. From the resulting Ni(I) species, three different reactivity routes can take place. The oxidative addition of the carbon electrophile can occur, as shown in the center black cycle of Figure 3. This step is commonly reported for efficient Suzuki cross-coupling catalysts and is followed by transmetalation and subsequent reductive elimination to form the targeted cross-coupled product [11]. This is the predominant route for the catalysts reported here that selectively generated the cross-coupled product, such as **3-SiO₂**. Conversely, going back to the Ni(I) starting point, homogeneous Ni(I) species in solution have been reported to dimerize, as illustrated in the gray route in Figure 3 [26]. This dimerization step deactivates the catalyst, and this deactivation route explains the reactivity observed for catalysts **1**, **2**, and **3**. Lastly, electron-deficient Ni(I) species may not be able to undergo

effective oxidative addition reactions [41]. In these cases, halide abstraction reactions, especially with iodo-aryl substrates, can occur. Computational [53] and experimental studies [50] indicate that halide abstraction reactions can explain the formation of unwanted carbon electrophile dimerization products. This halide abstraction mechanism can explain the observed product distribution for catalyst **2-SiO₂**. The multiple reactivity routes in Figure 3 highlight the importance of controlling molecular nickel catalyst speciation with respect to geometry and valency in order to control reactivity [18].

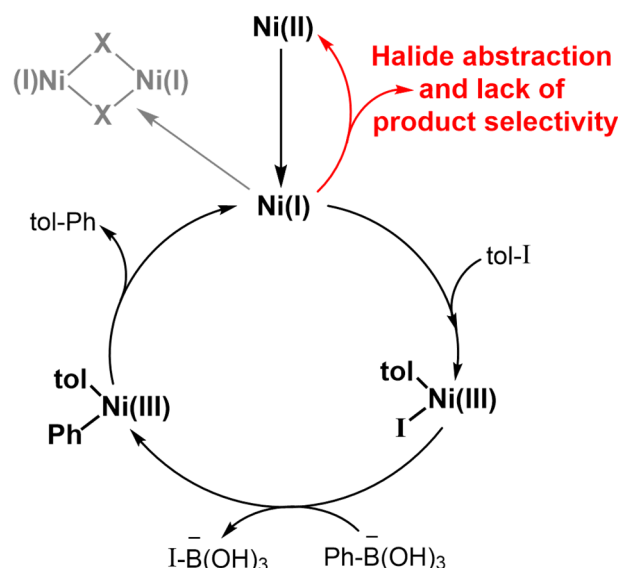


Figure 3. Proposed mechanistic routes for catalyst dimerization (gray), standard Suzuki-Miyaura cross-coupling catalysis (black), and a radical substrate activation pathway (red). $\text{Ni}(\text{II})$ represents a molecular or hybrid nickel catalyst in the as-synthesized Ni^{2+} oxidation state, X represents an anion (e.g., Cl^- , Br^- , or OH^-), and tol = toluene; Ph = phenyl group.

It has been reported that the reactivity of hybrid catalysts anchored to metal oxide supports through covalent ester bonds, like those in **2-SiO₂**, exhibit support-dependent activity [41]. We therefore synthesized **2-ZrO₂** in an attempt to optimize cross-coupling reactivity. **2-ZrO₂** contains the same molecular nickel catalyst as **2-SiO₂** but instead uses a $25 \text{ m}^2\text{-g}^{-1}$ surface area ZrO_2 support. ICP-MS analysis indicated that the molecular catalyst achieved a $1.0 \text{ molecule-nm}^{-2}$ loading on the ZrO_2 support. Performing the standard cross-coupling reaction shown in Table 2, the **2-ZrO₂** catalyst led to the highest yield of the desired cross-coupled product when compared to the other catalysts in this study. Considering this higher activity, we tested **2-ZrO₂** for stability and reusability. For the cross-coupling reaction shown in Table 1, product yields were 61%, 56%, and 54% for three consecutive reactions utilizing **2-ZrO₂** as the catalyst. These obtained yields show that the catalyst exhibits stable reactivity over three reaction cycles, with the slight drop in product yields being attributed to the likely incomplete recovery of the solid catalyst during filtrations between the reactions. Post-reaction characterization of **2-ZrO₂** was also carried out to examine the molecular stability of the catalyst. Due to the paramagnetic nature of the molecular nickel catalyst, XPS analysis was used to characterize the **2-ZrO₂** catalyst and ensure the molecular integrity of the most efficient cross-coupling catalyst of this series. Figure S2 in the supporting information shows the XPS spectrum of **2-ZrO₂** as-synthesized, before the cross-coupling reaction. The spectrum shows the indicative Ni $2\text{p}^{3/2}$ and $2\text{p}^{1/2}$ ionizations near 855 and 875 eV respectively. In addition, the satellite and shake-up peaks observed between 860 and 870 eV and 880 and 890 eV are common spectral characteristics of molecular species. The post-reaction XPS spectrum of **2-ZrO₂**, shown in Figure S1, exhibits all the same ionization energies and characteristics, indicating that the hybrid

catalyst maintained molecular integrity after the catalytic reaction. The increased reactivity is thus attributed to the ability of **2-ZrO₂** to undergo more facile oxidative addition compared to **2-SiO₂** and highlights how controlled valency speciation helps control reactivity. The thermodynamic access to the Ni(III) valency for **2-ZrO₂** led to more selective cross-coupling catalysis, while **2-SiO₂** exhibits Ni(II/I) radical reactivity which could be exploited for different catalytic reactions.

4. Conclusions

Molecular nickel catalysts in homogeneous solution have a propensity to generate a variety of species under thermally driven reactions which can vary in valency and speciation (monomer vs. dimer). The results from this comparative study show that catalyst speciation can have a profound effect on activity and selectivity. Dimerization and oligomerization shut off reactivity and must be prevented by incorporating the molecular catalysts into hybrid catalyst motifs. Hybrid catalysts isolate the molecular catalysts through the covalent bonding of the molecule to a support, which prevents dimerization and leads to longer-lifetime catalysts and greater product yields. In addition, certain hybrid catalyst motifs, such as covalently bonding the catalyst through synthetically simple ester bonds, can offer additional control over catalyst valency, which can increase catalyst selectivity and product yields. Thus, as reviewed by Ananikov [54], controlling speciation along with the traditional tuning of molecular properties represents a two-step method of designing selective and active catalysts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry8080105/s1>, Figure S1: XPS spectrum of the pre-reaction **2-ZrO₂** catalyst.; Figure S2: XPS spectrum of the post-reaction **2-ZrO₂** catalyst.; Figure S3: ¹H NMR spectrum of [4,4'-bis(3-(Triethoxysilyl)propylamide)-2,2'-bipyridine].

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