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Ethylene Oligomerization at Coordinatively and Electronically Unsaturated Low-Valent Nickel**

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Research in nickel-catalyzed olefin oligomerization and polymerization continues to progress at an accelerating pace.[1] With the synthesis of new Ni^{II} catalysts that are highly tolerant towards polar substrates and are less oxophilic,[2] we are now able to target specific functional products. This advancement has brought along a host of new ligands, catalysts,[3] and mechanistic data.[4] It has also spilled over into scientific breakthroughs in new nickel chemistry, among which the recent isolation of low-valent coordinatively unsaturated Ni^{I} is particularly noteworthy.[5,6] This immediately gave rise to some pertinent questions, such as how Ni^{I} compares to the classical Ni^{II} and the sensitive Ni^{0} in catalytic performance or whether a coordinatively and electronically unsaturated Ni^{I} center might exhibit enhanced activity.

To address some of these questions, we need to design, prepare, and isolate close counterparts for direct structural and catalytic comparisons. We herein report our preliminary findings in using a ferrocenediyl iminophosphane supporting ligand. The flexibility of the ferrocenyl backbone,[7,8] coupled with the hemilability of the donors,[9] allows the metal to "pick and choose" its donors, and tune its receptivity to the substrates. It also raises our chances of isolating catalytically important intermediates for structural verification. The use of iminophosphanes as ligands for late transition metals for olefin polymerization has been demonstrated.[10]

$NiCl_2(DME)$ (DME = dimethoxyethane) reacts with $[\{\eta\text{-}C_5H_4CH{=}N(C_6H_5)\}Fe\{\eta\text{-}C_5H_4P(t\text{Bu})_2\}]$ to give the Ni^{II} complex $[\{[\eta\text{-}C_5H_4CH{=}N(C_6H_5)]Fe[\eta\text{-}C_5H_4P(t\text{Bu})_2]\}NiCl_2]$ (**1**). Addition of one equivalent of MeLi to **1** in THF at −30 °C resulted in a one-electron reduction to $[\{[\eta\text{-}C_5H_4CH{=}N\text{-}(C_6H_5)]Fe[\eta\text{-}C_5H_4P(t\text{Bu})_2]\}Ni^{I}Cl]$ (**2**; Scheme 1), with no evidence of methylnickel(I/II) products similar to the result from bis(imino)pyridylcobalt(II) with methylaluminoxane (MAO).[11] Ligand replacement of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) with $[\{\eta\text{-}C_5H_4CH{=}N(C_6H_5)\}Fe\{\eta\text{-}$

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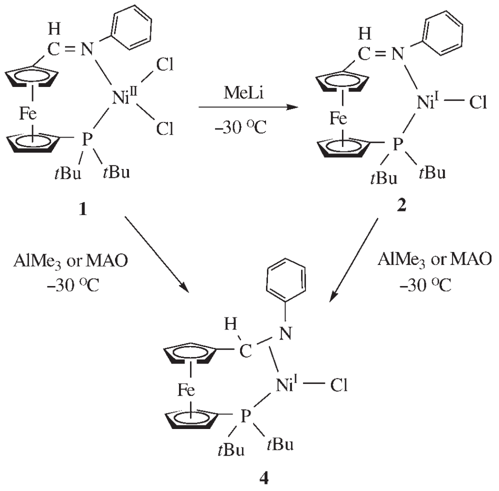
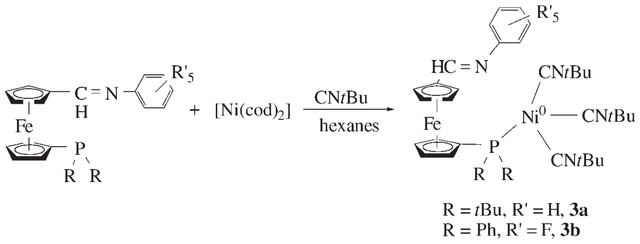


Scheme 1.

$C_5H_4P(tBu)_2\}]$ and $[\{\eta\text{-}C_5H_4CH{=}N(C_6F_5)\}Fe\{\eta\text{-}C_5H_4PPh_2\}]$, in the presence of CN*t*Bu in hexane, yields dark-red solids of $[\{[\eta\text{-}C_5H_4CH{=}N(C_6H_5)]Fe[\eta\text{-}C_5H_4P(tBu)_2]\}Ni^0(CNtBu)_3]$ (**3a**) and $[\{[C_5H_4CH{=}N(C_6F_5)]Fe[\eta\text{-}C_5H_4PPh_2]\}Ni^0(CNtBu)_3]$ (**3b**), respectively (Scheme 2). All the products were isolated and characterized spectroscopically.



Scheme 2.

Single-crystal X-ray diffraction[12] revealed that **2** crystallizes with two independent molecules (A and B) per unit cell (molecule A is shown in Figure 1). It shows a trigonal planar (mean plane deviation 0.0045 Å) Ni^I center with three heteroatom donors, namely N, P, and Cl. There is no evidence of significant intermolecular contacts. This 15-electron, three-coordinate Ni^I is thus an unusual coordinatively exposed and electronically unsaturated paramagnetic complex. Despite the apparent electronic deficiency and coordinative exposure, there is no evidence of any electron donation by obvious means, such as dimerization, hydride formation, agostic Ni···H (Fc or Bu) interactions, π–imine coordination, or Fe→Ni dative bonding. This type of low-coordinate, low-valent Ni^I complex is rare but not unprecedented (e.g. β-diketiminatonickel(I)[5] and diphosphane-supported alkylnickel(I) complexes[6]). The Ni–N bond length (1.995(2) Å) is between that to Ni^I (1.876(1) Å)[5a] and the iminophosphanenickel(II) (2.043(6) Å),[10c] whereas the Ni–P bond (2.2251(8) Å) is also intermediate between the P,N-bound Ni^0 complex $[(iPr)_2PCH_2CH_2NMe_2)Ni(PhC{\equiv}CPh)]$ (2.1565(10) Å)[13] and a Ni^{II} complex (2.338(2) Å).[10c] The Ni–Cl bond (2.1929(9) Å) is similar to those in a P,N-chelating tetrahedral Ni^{II} complex (2.191(1) and 2.217(1) Å).[14a] To stabilize the low coordination, the chelating ligand needs to expand its spatial protection by stretching the bite angle to 112.34(6)° (compared to 98.4(1)° and 110.94(8)° in related Pd^{II} and Pd^0 complexes)[9] in order to be more compatible with a trigonal planar geometry.

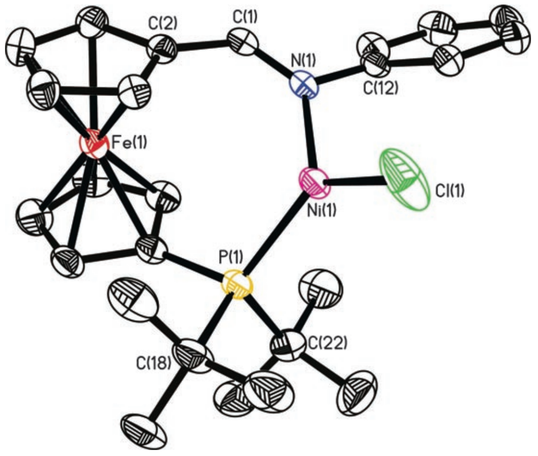


Figure 1. ORTEP representation of the X-ray structure of molecule A in **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability. Selected bond lengths [Å] and angles [°]: Ni(1)–N(1) 1.995(2), Ni(1)–P(1) 2.2251(8), Ni(1)–Cl(1) 2.1929(9), C(1)–N(1) 1.288(3); N(1)-Ni(1)-Cl(1) 119.23(7), N(1)-Ni(1)-P(1) 112.34(6), Cl(1)-Ni(1)-P(1) 128.43(4).

The solid-state structure of **3b** reveals a tetrahedral Ni^0 complex supported by three isocyanide ligands, with the iminophosphane in an unexpected unidentate mode (Figure 2). This demonstrates that an electron-rich metal

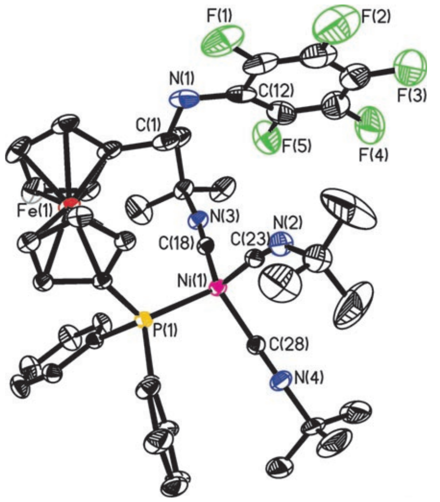


Figure 2. ORTEP representation of the X-ray structures of **3b**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability. Selected bond lengths [Å] and angles [°]: Ni(1)–P(1) 2.2001(10), Ni(1)–C(18) 1.843(4), Ni(1)–C(23) 1.821(4), Ni(1)–C(28) 1.842(4), C(1)–N(1) 1.282(6), C(18)–N(3) 1.161(4), C(23)–N(2) 1.168(5), C(28)–N(4) 1.159(5); C(23)-Ni(1)-C(28) 103.74(17), C(23)-Ni(1)-C(18) 116.59(17), C(18)-Ni(1)-P(1) 112.17(11), C(28)-Ni(1)-P(1) 104.52(12), C(23)-N(2)-C(24) 148.7(4), C(18)-N(3)-C(19) 173.7(4), C(28)-N(4)-C(29) 171.6(4).

opts for the stronger π-accepting environment provided by isonitrile, especially in its angular mode [C(23)–N(2)–C(24) = 148.7(4)°]. This is facilitated by the lability of the imine donor and the ability of the ferrocenyl ligand to sustain a unidentate mode with a dangling functional entity. The Ni–P bond (2.2001(10) Å) is slightly shorter than that of **2** (2.2251(8) Å). The Ni–C bond of bent isocyanide (1.821(4) Å) is slightly stronger than that of the other two Ni–C bonds (1.843(4) and 1.842(4) Å), with the latter being similar to that of the ethylene polymerization active Ni^{II}–isocyanide complex $[NiBr_2(CNAr)_2]$ (1.846(2) Å)[15] and the Ni^0–isocyanide complex $[Ni(C_6H_5N{=}NC_6H_5)(CNtBu)_2]$ (1.841(5) Å).[16]

Isolation of **1**–**3** pointed to some valuable features of iminophosphane as a ligand. It supports a metal (Ni) in its normal, intermediate, and low valency, it is sensitive to the coordinative change of the metal, and it uses its hemilability to adjust the electronic donation. These are essential qualities that could raise the catalytic performance and enable us to isolate catalytically important intermediates. It also enables us to directly compare the activity of Ni^{II}, Ni^{I}, and Ni^0 in ethylene oligomerization through the use of **1**, **2**, **3a**, and **3b**. Some preliminary results under ambient conditions are summarized in Table 1. Using MAO as the cocatalyst with an Al/Ni ratio of 1000, the ethylene oligomerization activity (TOF) decreases in the order **2** ≫ **3a** > **1** which reflects the activity order of $Ni^{I} \gg Ni^{0} > Ni^{II}$ (entries 1–3). The 1-butene selectivity for Ni^{II} is, however, higher. All of them give insignificant amounts of high molecular weight polymeric products. We should add, however, that the electronic effect of the iminophosphane ligand could override the metal effect. This is best exemplified in the higher TOF of **3b** (75000), which contains a pentafluorophenyl imine and phenylphosphane, compared to **3a** (10667) (entries 3 and 4, respectively). These residues raise the electrophilicity of the central metal, thus promoting substrate attack.[17]

We have also studied the effect of cocatalyst, temperature, and pressure using **3b** as the catalyst. $EtAlCl_2$ performs better than MAO (entries 5–8), possibly due to facile formation of alkylnickel species in situ, which leads to active nickel hydrides by β-elimination, consistent with the observations of Braunstein and co-workers.[14] A TOF of 119400 (entry 6) is achieved at 30 °C. There is no clear advantage from using a higher temperature (compare entries 5 and 7) or pressure (compare entries 6 and 8). The oligomerization performance depends more on catalyst design and cocatalyst support. With a metal that can attract ethylene efficiently and promote detachment through a β-hydride elimination, one would expect a good yield at ambient conditions with reasonable selectivity. Complex **2** and the reported $(N,N)Ni^{I}$ complex[5c] are both three-coordinate but they present two different assemblies in catalyst design, namely, the use of an anionic chelating ligand (diketiminato) with a terminal neutral ligand (phosphane) and a neutral ferrocenediyl iminophosphane with an anionic halide. The former relies on the lability of the phosphane, whereas the latter relies on anion (e.g. Cl→R, to give alkylnickel(I) species[6a]) or hydride exchange (Cl→H) for activation.

Complex **1** (Ni^{II}) would not survive under the reducing (and basic) conditions generated by excess MeLi. Could it, however, be active and persistent in a catalytic mixture that contains $AlMe_3$ or MAO? Experiments on the reaction of **1** with two equivalents of $AlMe_3$ or MAO at room temperature led to the isolation of the Ni^{I} complex $[\{[\eta\text{-}C_5H_4CH{=}N\text{-}(C_6H_5)]Fe[\eta\text{-}C_5H_4P(tBu)_2]\text{-}\mathit{CN,P}\}Ni^{I}Cl]$ (**4**) (Scheme 1), which can also be independently prepared from **2** and $AlMe_3$ or MAO (1:2). Single-crystal X-ray diffraction analysis[12] revealed that **4** is related to **2** but, significantly, coordination at the N site has slipped to C=N, thus activating the π functionality, while maintaining a planar Ni^{I} (mean plane deviation 0.0147 Å; Figure 3). This lengthens and weakens the C–N bond from 1.288(3) in **2** to 1.435(9) Å in **4**. Accordingly, the Ni–P bond is shorter and presumably stronger (2.169(2) Å) than that in **2** (2.2251(8) Å), while the Ni–Cl bond is correspondingly weaker (2.231(2) Å) than that in **2** (2.1929(9) Å). The fragility of the Ni–Cl bond and the strengthening of the other protective ligands appear to support and "prepare" the metal for its catalytic function. Oligomerization experiments using **4** as the catalyst demonstrate that it is active. Upon activation with excess MAO (1000-fold), it gives a TOF of 14666 in ethylene oligomerization.

We have shown that a hemilabile iminophosphanylferrocene ligand can stabilize catalytically active low-valent nickel and the resulting complexes can be used directly to catalyze ethylene oligomerization. This highlights the potential use of Ni^0 and Ni^{I} rather than the more popular Ni^{II} in similar catalysis.[18] In Ziegler–Natta-type polymerization, the cata-

Table 1: Oligomerization of ethylene.[a,b]

Entry	Cat.	Activator	*T* [°C]	*P* [psi]	Al/Ni	*t* [h]	TOF[c]	Oligomer $C_4/\Sigma C$ [%]	 $C_6/\Sigma C$ [%]	 α-olefin [%] (C_4)
1	**1**	MAO	30	300	1000	3	8000	87.3	12.7	84.6
2	**2**	MAO	30	300	1000	3	21000	70.3	29.7	72.7
3	**3a**	MAO	30	300	1000	3	10667	76.2	23.8	60.1
4	**3b**	MAO	30	300	1000	3	75000	87.1	12.9	16.5
5	**3b**	$EtAlCl_2$	30	300	146	3	91600	69.9	30.1	45.9
6	**3b**	$EtAlCl_2$	30	300	1000	2	119400	79.2	20.8	41.2
7	**3b**	$EtAlCl_2$	60	300	146	1	96000	59.0	41.0	28.5
8	**3b**	$EtAlCl_2$	30	450	1000	2	120600	70.5	29.5	53.8

[a] Optimized with the Endeavor Catalyst Screening System. [b] Conditions: 0.25 μmol of catalyst, 4 mL of toluene. [c] TOF = mol of ethylene consumed/mol of Ni h^{-1}.

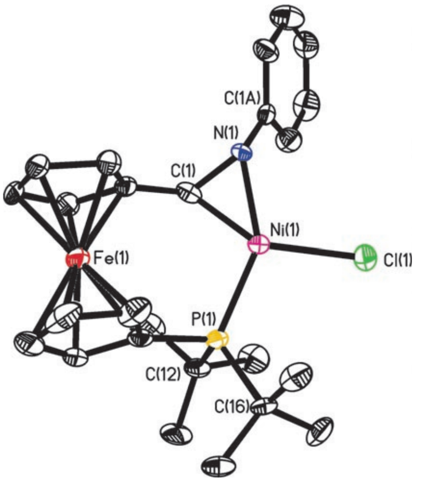


Figure 3. ORTEP representation of the X-ray structure of **4**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 40% probability. Selected bond lengths [Å] and angles [°]: Ni(1)–C(1) 1.887(8), Ni(1)–N(1) 1.963(6), Ni(1)–P(1) 2.169(2), Ni(1)–Cl(1) 2.231(2), C(1)–N(1) 1.435(9); C(1)–Ni(1)–N(1) 43.7(3), C(1)–Ni(1)–P(1) 103.9(2), N(1)–Ni(1)–P(1) 145.91(18), N(1)–Ni(1)–Cl(1) 107.77(7), Cl(1)–Ni(1)–P(1) 106.12(8).

lytically active species is widely believed to be a cationic alkyl–metal complex L_nMR^+.[19] Olefin oligomerization by Ni^{II} is also widely acknowledged to proceed via L_nNiR^+, which readily gives $L_nNi^{II}(H)(alkene)^+$ as a key intermediate.[20] Use of Ni^I complexes, such as **2** and **4**, or Ni^0 complexes, such as **3a** and **3b**, suggests that we can enter the catalytic cycle with non-alkyls and electronically neutral species. The key here is the use of a coordinatively exposed metal in a low oxidation state and a hemilabile ligand. These are features that are usually advantageous to catalytic pathways, such as Suzuki coupling, that hinge on the complementary oxidative addition and reductive elimination, but not olefin oligomerization. They offer new opportunities in catalyst design for polymerization, but they also pose some pertinent questions. For example, does this necessarily require a different mechanistic pathway? Do Ni^I and Ni^0 offer a better prospect in olefin oligomerization? Does the use of mononuclear paramagnetic Ni^I necessarily demand a free radical pathway, such as the one shown in other four-coordinate Ni^I complexes?[21] Our ongoing experiments are driven by these curiosities.

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