

Stabilization of Nickel(0) by Hemilabile P,N-Ferrocene Ligands and Their Ethylene Oligomerization Activities

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Ligand displacement reactions of Ni(COD)₂ with a ferrocenediyl iminophosphine, viz., [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂] (**1**) or [C₅H₄CH=NC(H)(CH₃)(C₆H₅)]Fe[η-C₅H₄PCy₂] (**2**), in the presence of *t*-BuNC, CO, or PhC≡CPh give the appropriate mixed-ligand Ni(0) complexes, viz., [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂]Ni⁰(CN*t*-Bu)₃ (**3**), [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂]Ni⁰(CO)₂ (**4a**), {[C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂]}₂Ni⁰(CO)₂ (**4b**), and [C₅H₄CH=NC(H)(CH₃)(C₆H₅)]Fe[η-C₅H₄PCy₂]Ni⁰(η²-PhC≡CPh) (**5**). The X-ray crystal and molecular structures of **4b** and **5** are described. The hemilability of iminophosphine is illustrated by the formation of both P,N-chelating and imine-pendant functions. All the complexes examined are catalytically active toward ethylene oligomerization at 30 °C, with **5** showing the best activity, followed by **3** and **4**.

Introduction

Ethylene oligomerization developed at Shell, BP Amoco, and Chevron Phillips has provided the industry with highly desirable linear α-olefins in the C₆–C₂₀ range. These oligomers are important precursors for detergents, plasticizer alcohols, synthetic lubricants, and fine chemicals and as comonomers in the production of linear low-density polyethylene.^{1,2} They also provided good incentives for catalytic research in nickel coordination complexes, especially those of Ni(II). For example, the SHOP-type [P,O] system developed by Keim³ and Ostoja⁴ affords highly linear α-olefins (C₆–C₂₀). Brookhart used Ni(II) diimine [N,N] complexes with a large excess of methylaluminoxane (MAO) to produce highly active α-olefin catalysts for ethylene oligomerization with high selectivity.⁵ [N,O] chelating neutral nickel catalysts have been reported by DuPont,⁶ Grubbs,⁷ Brookhart,⁸ etc.,⁹ whereas [P,N] chelating nickel ethylene oligomerization catalysts have been studied by Braunstein¹⁰ and others.¹¹

Our interest in the coordination¹² and catalytic¹³ chemistry of dppe [1,1'-bis(diphenylphosphino)ferrocene] stems from its coordinative variance.¹⁴ Such ligand adaptability tends to complement and support the metal geometric and coordinative changes along the catalytic path. To maximize this advantage, we need to design hemilabile ligands with suitable heterodifunctional donors that could match the need of the metal and

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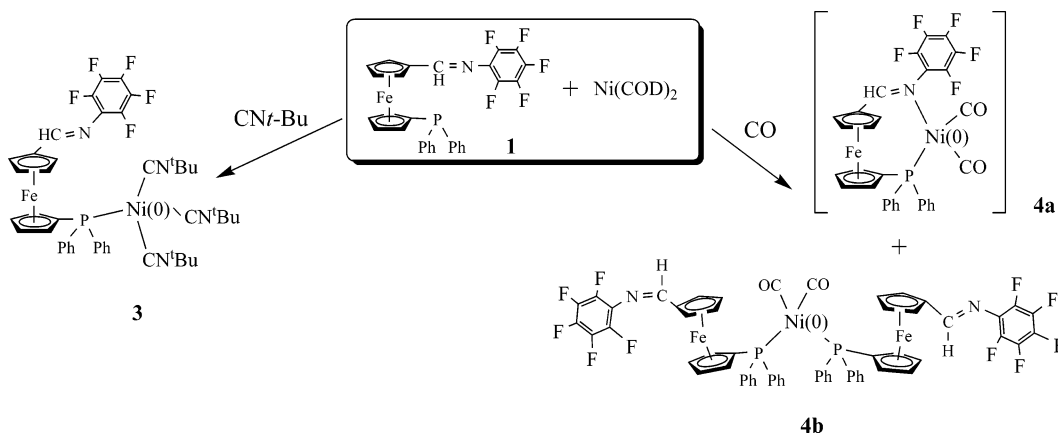
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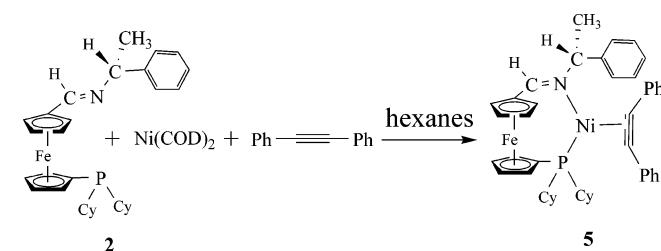
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Scheme 1



Scheme 2



system of interest. A notable example is the recent use of an iminophosphine, $[\eta\text{-C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{H}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{P}(t\text{-Bu})_2]$, to promote Suzuki coupling¹⁵ and ethylene oligomerization,¹⁶ the latter of which is catalyzed by Ni(I). These results, coupled with the landmark findings of Wilke et al. that Ni(0) complexes, such as $\text{Ni}(\text{COD})_2$, could catalyze olefin oligomerization,¹⁷ encouraged us to explore the complementary use of new Ni(0) with hemilabile P,N-ferrocene ligands to promote ethylene oligomerization. The catalytic chemistry of zerovalent organonickel complexes¹⁸ is poorly understood compared to that of Ni(II).

Results and Discussion

We focus on the design of hemilabile ligands on Ni(0) that are stabilized by π -acids such as carbonyl (CO) and isocyanide (RNC). Although RNC is known to be a better σ -donor but weaker π -acceptor than CO,^{19,20} their relative effects on the efficacy of Ni(0) in promoting ethylene oligomerization are less clear. Our first target, therefore, was to synthesize a range of related Ni(0) complexes for direct comparison. Ferrocenyli iminophosphines are our choice ligands, as they are coordinatively and electronically adaptive. Their inherent hemilability would give extra structural flexibility to the associated catalytic metal center. Two representative iminophosphines of different coordinative abilities are chosen as models, viz., $[\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{F}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PPh}_2]$ (**1**) and $\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{H})(\text{CH}_3)(\text{C}_6\text{H}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PCy}_2]$ (**2**). $\text{Ni}(\text{COD})_2$ reacts with **1** and a 3-fold excess of *t*-BuNC under argon to give a Ni(0) tris(isocyanide) complex, $[\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{F}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PPh}_2]\text{Ni}^0(\text{CN}t\text{-Bu})_3$ (**3**). Its structure, with a pendant imine, has been described.¹⁶ Under atmospheric CO, a mixture of $\text{Ni}(\text{COD})_2$ and a molar equivalence of **1** gives two Ni(0) dicarbonyl complexes, $[\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{F}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PPh}_2]\text{Ni}^0(\text{CO})_2$ (**4a**) and $\{[\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{F}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PPh}_2]\}_2\text{Ni}^0(\text{CO})_2$ (**4b**) (Scheme 1). The IR and mass spectral data of **4a** suggest that it is mononuclear with bidentate iminophosphine and terminal carbonyls. The

C–N stretching frequency does not conclusively support π -imine complexation. There is also no spectroscopic evidence to propose imine coordination in **4b**. Complex **4a** is related to the established $\text{Ni}(\text{CO})_2(\eta^2\text{-R}_2\text{PAPR})_2$ ²¹ except that the former carries a heterofunctionality of iminophosphine.

Surprisingly, a similar reaction of **1** with $\text{Ni}(\text{COD})_2$ and diphenylacetylene does not give the expected $(\text{PN})\text{Ni}^0(\eta^2\text{-PhC}\equiv\text{CPh})$. Instead, the known dinuclear $[(\text{COD})\text{Ni}^0]_2(\mu_2, \eta^2\text{-PhC}\equiv\text{CPh})$ ²² was detected after product crystallization from the reaction mixture. This may be attributed to the weak binding ability and steric hindrance of **1**. This problem can be solved by changing to **2** as a supporting ligand. Under argon and excess diphenylacetylene, a new Ni(0) alkyne complex, $[\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{H})(\text{CH}_3)(\text{C}_6\text{H}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PCy}_2]\text{Ni}^0(\eta^2\text{-PhC}\equiv\text{CPh})$ (**5**), can be isolated. Spectroscopic evidence points to a chelating iminophosphine (Scheme 2).

All the products were isolated and spectroscopically characterized. All products in solid form are stable in air for a few hours except **5**, which is extremely air- and moisture-sensitive. It decomposes easily in NMR solution in the presence of trace O_2 or H_2O , giving unknown paramagnetic species. Satisfactory elemental analytical and mass spectroscopic data were hence not obtainable. The solutions of **3** and **4** also readily decompose upon extended (>30 min) exposure to air. Under argon, all of them can be kept for a prolonged period (weeks).

Structures. The solution data of **4b** point to a mononuclear Ni(0) dicarbonyl complex with two dangling imine moieties. It thus belongs to the general class of $\text{Ni}^0(\text{CO})_2(\text{PR}_3)_2$,²³ but, to our knowledge, there is no structural precedence of the

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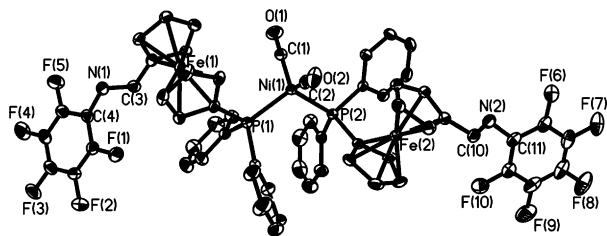


Figure 1. Molecular structure of complex **4b** (H atoms are omitted). Thermal ellipsoids are drawn at the 40% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **4b**

Bond Lengths			
Ni(1)–C(1)	1.777(5)	Ni(1)–C(2)	1.764(5)
Ni(1)–P(1)	2.2096(11)	Ni(1)–P(2)	2.2145(11)
N(1)–C(3)	1.277(5)	N(1)–C(4)	1.410(5)
N(2)–C(10)	1.283(6)	N(2)–C(11)	1.395(6)
C(1)–O(1)	1.133(5)	C(2)–O(2)	1.145(5)
Bond Angles			
C(1)–Ni(1)–C(2)	116.9(2)	C(2)–Ni(1)–P(1)	104.80(15)
C(1)–Ni(1)–P(1)	109.69(14)	C(2)–Ni(1)–P(2)	106.24(14)
C(1)–Ni(1)–P(2)	106.81(14)	P(1)–Ni(1)–P(2)	112.52(4)
C(3)–N(1)–C(4)	119.0(4)	C(10)–N(2)–C(11)	118.3(4)

analogous $\text{Ni}^0(\text{CO})_2(\eta^1\text{-R}_2\text{PAPR}_2)_2$ or other heterodifunctional analogues such as $\text{Ni}^0(\text{CO})_2(\eta^1\text{-R}_2\text{PAXR}_n)$ with dangling donor units. It is rare to have two donor pendants on a single metal since they tend to collapse as a chelate or dimerize as a bridge. We hence had to conduct a single-crystal X-ray crystallographic analysis to confirm if this unusual structure can be sustained in the solid state (Figure 1, Table 1). It indeed shows a tetrahedral Ni(0) with two extended side-arms represented by the imine-phosphine ferrocene ligands monocoordinating through its P site. The variable torsional twist of the C₅ rings allows the dangling imine N atom to move to an *anti* position. The two Ni–P bonds are comparable (2.2096(11) 2.2145(11) Å) and similar to those in **3** (2.2001(10) Å) and $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$ (2.221 Å).^{23a} The two Ni–C bonds (1.777(5) and 1.764(5) Å) are comparable to that of $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$ (1.763 Å)^{23a} but significantly shorter, and presumably stronger, than those found in the isonitrile complex **3** (1.821(4), 1.842(4), and 1.843(4) Å). This is consistent with the expected stronger π -acidity of CO, and hence stronger M–C, compared to RNC.

We have not detected the tricarbonyl derivative of **4**, viz., $[\text{C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{F}_5)]\text{Fe}[\eta\text{-C}_5\text{H}_4\text{PPh}_2]\text{Ni}^0(\text{CO})_3$, which would be the carbonyl analogue of **3**. In this preparation, **4a** is the major product, whereas **4b** is a minor byproduct. The yield of **4b** can be improved by the use of excess **1**, but the formation of **4a** is inevitable. This is understood in terms of the more favorable entropy effect of a chelate, despite a much weaker imino ligating ability. In solution upon addition of excess **1**, complex **4a** can convert (not quantitatively) to **4b**. The co-formation of **4a** and **4b** demonstrates the hemilability of **1** and its ability to stabilize an exposed metal through additional coordination. This would lend support to an active catalyst that is susceptible to decomposition through ligand loss.

X-ray single-crystal structural analysis of **5** revealed an unusual combination of a chelating iminophosphine with a side-on alkyne attachment at nickel. The two sterically demanding and contrasting ligands are fused at a distorted planar (mean plane deviation 0.1003 Å) Ni(0) center (Figure 2, Table 2). The Ni–P bond (2.202(2) Å) is comparable to those in **3** and **4b**, but longer than in the Ni(I) complex $[\eta\text{-C}_5\text{H}_4\text{CH}=\text{N}(\text{C}_6\text{H}_5)]\text{-Fe}[\eta\text{-C}_5\text{H}_4\text{P}(t\text{-Bu})_2\text{CN},\text{P}]\text{Ni}^+\text{Cl}^-$ (2.169(2) Å)¹⁶ and Ni(0) complex $[(i\text{-Pr})_2\text{PCH}_2\text{CH}_2\text{NMe}_2]\text{Ni}(\eta^2\text{-PhC}\equiv\text{CPh})$ (2.1565(10) Å).²⁴ The alkyne ligand is symmetrically bound with two identical

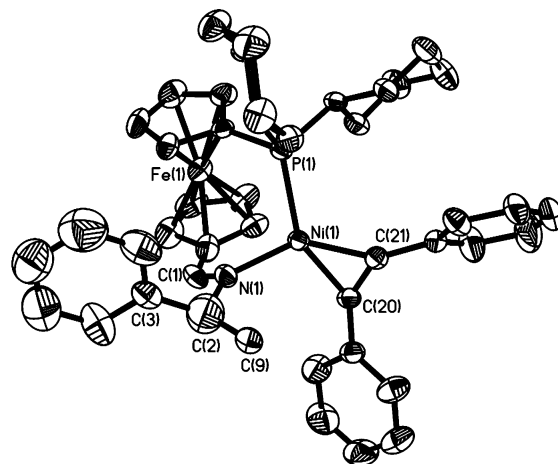


Figure 2. Molecular structure of complex **5** (H atoms are omitted). Thermal ellipsoids are drawn at the 40% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **5**

Bond Lengths			
Ni(1)–C(20)	1.900(7)	Ni(1)–C(21)	1.902(7)
Ni(1)–N(1)	1.945(6)	Ni(1)–P(1)	2.202(2)
N(1)–C(1)	1.287(10)	N(1)–C(2)	1.464(17)
N(1)–C(2A)	1.480(13)	C(20)–C(21)	1.275(9)
Bond Angles			
C(20)–Ni(1)–C(21)	39.2(3)	C(20)–Ni(1)–N(1)	103.7(3)
C(21)–Ni(1)–N(1)	141.3(3)	C(20)–Ni(1)–P(1)	149.4(2)
C(21)–Ni(1)–P(1)	113.1(2)	N(1)–Ni(1)–P(1)	105.51(19)
C(1)–N(1)–C(2)	113.6(9)	C(2)–C(20)–Ni(1)	70.5(5)
C(22)–C(20)–Ni(1)	144.1(6)	C(20)–C(21)–Ni(1)	70.3(5)
C(28)–C(21)–Ni(1)	150.4(6)	C(21)–C(20)–C(22)	145.3(8)
C(20)–C(21)–C(28)	138.9(7)		

Ni–C bonds (1.900(7) and 1.902(7) Å), which are slightly longer, and presumably weaker, than other donor-stabilized diphenylacetylene complexes, e.g., $(\text{dippe})\text{Ni}(\eta^2\text{-PhC}\equiv\text{CPh})$ (av 1.879(2) Å),^{24b} $(t\text{-BuNC})_2\text{Ni}(\eta^2\text{-PhC}\equiv\text{CPh})$ (av 1.884(9) Å),^{25a} and $(2,2\text{-bipyridyl})\text{Ni}(\eta^2\text{-PhC}\equiv\text{CPh})$ (av 1.846(2) Å).^{25b} The weaker C≡C bond (1.275(9) Å) and bent C≡C–C angles (145.3(8)° and 138.9(7)°), compared to free diphenylacetylene (C≡C 1.198(4) Å),²⁶ are in agreement with the expected π^* back-donation²⁷ and consistent with other $\text{L}_2\text{Ni}(\eta^2\text{-PhC}\equiv\text{CPh})$ complexes.^{24,25} Further comparisons in detail would not be justified since the crystallographic data are of marginal quality.

Catalytic Oligomerization of Ethylene. Some preliminary results on catalytic oligomerization of ethylene using complexes **3**, **4a**, **4b**, and **5** are summarized in Table 3. Using MAO as the cocatalyst with Al/Ni = 1000, the ethylene oligomerization activity (TOF) decreases in the order **5** (alkyne) > **3** (isonitrile) >> **4b** (carbonyl, excess iminophosphine) > **4a** (carbonyl, limiting iminophosphine). This order follows the decreasing Ni–C bond lengths in these complexes (alkyne > isonitrile > carbonyl). The weaker metal–ligand contacts could lead to

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Table 3. Activities toward Oligomerization of Ethylene^{a,b}

entry	cat.	activator	Al/Ni	time (h)	TOF ^c	oligomer ^d		
						C ₄ /ΣC %	C ₆ /ΣC %	α-olefin % (C ₄)
1 ^e	3	MAO	1000	3	75 000	87.1	12.9	16.5
2 ^e	3	EtAlCl ₂	146	3	91 600	69.9	30.1	45.9
3	4a	MAO	1000	3	476	80.7	19.3	52.5
4	4b	MAO	1000	3	2000	100	0	59.2
5	5	MAO	1000	1	88 000	82.2	17.8	76.6
6	5	EtAlCl ₂	1000	1	64 000	69.7	30.2	53.3

^a Optimized by Endeavor catalyst screening system. ^b Conditions: 0.25 μmol of catalyst, 4 mL of toluene, 30 °C, 300 psi of ethylene. ^c TOF = mol of ethylene consumed/mol of Ni·h⁻¹. ^d mol %. ^e Given in ref 16.

higher ligand lability and make the metal more receptive to the incoming ethylene and hence higher catalytic activity. We are not aware of any prior report on Ni(0) alkyne molecular complexes in ethylene oligomerization. It is intriguing that **5** is generally superior among the complexes that we examined. Its combinative chelating protection and alkyne stabilization could suppress catalyst decomposition or conversion to its inactive dimeric form. The 1-butene selectivity for **5** is much higher than that of **3**. EtAlCl₂ is a better activator than MAO for complex **3** (entry 2) but poorer for **5** (entry 6). Nevertheless, both **3** and **5** perform substantially better than other heterogeneous Ni(0) catalysts,¹⁸ such as Ni⁰(COD)₂ on zeolite [TOF (ethylene) ca. <4000 h⁻¹].^{18b} They (**3** and **5**) are also able to maintain their activities within a reasonable lifetime (a few hours), which is an important consideration in catalyst design.

Conclusions

We have demonstrated herein that appropriately stabilized Ni(0) complexes can be prepared, isolated, structurally characterized, and activated for ethylene oligomerization. The use of Ni(II)²⁸ complexes is much more popular, and they remain probably the catalyst of choice because they are generally much more stable and easier to prepare. However, the results described herein suggested that suitably designed Ni(0) can be prepared and used in one-pot reactions, as it may have an advantage in high activity and oligomeric selectivity. The combinative use of an adaptive hemilabile ligand and a supporting π-accepting ligand would meet these requirements. The use of an alkyne-stabilized catalyst can be viewed as a mimic for olefin entry to Ni-promoted olefin oligomerization. Our next target is to tune the hemilability by adjusting the substituents at the phosphine and imine sites. Such variation would provide a handle to balance the delicate interrelationship between coordinative ability, complex stability, and catalytic activity.

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon with an M. Braun Labmaster 130 inert gas system. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (¹H at 300.14 MHz, ¹³C at 75.43 MHz, and ³¹P at 121.49 MHz). Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in-house. Ni(COD)₂ and pentafluoroaniline were used as supplied by Fluka Chemical Co. and Lancaster, respectively. MAO (methylaluminoxane) (10 wt % in toluene solution), EtAlCl₂ (25 wt % in toluene solution), diphenylacetylene, and *tert*-butyl isocyanide were purchased from Aldrich

and used as received. [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂] and [C₅H₄CH=NC(H)(CH₃)(C₆H₅)]Fe[η-C₅H₄PCy₂] were synthesized by a literature procedure.²⁹

Synthesis of [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂]⁰[Ni⁰(CN*t*-Bu)₃](3)**.** To a red solution of [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂] (41 mg, 0.073 mmol) in *n*-hexane (5 mL) was added Ni(COD)₂ (20 mg, 0.073 mmol), and the mixture was stirred at rt for 20 min to give an orange solution. CN*t*-Bu (18 mg, 0.217 mmol) in hexane (1 mL) was added and the reaction mixture further stirred at rt for 2 h. The resultant red-orange solution was filtered through a layer of Celite. The solvent was removed to afford a red-orange solid of **3** (52 mg, 0.060 mmol, 82% yield). IR [KBr, cm⁻¹]: ν_{C≡N} 2105 (w), 2027 (w). ν_{CN} 1623 (m), 1516 (m, sh), 1504 (s). ¹H NMR (C₆D₆): δ 7.77 (s, 1 H, CH=N), 7.89 (t, *J* = 7.2 Hz, 4 H, phenyls), 7.18–7.03 (m, 6 H, phenyls), 4.95 (t, *J* = 1.6 Hz, 2 H, Cp), 4.78 (q, *J* = 1.6 Hz, 2 H, Cp), 4.65 (t, *J* = 1.62 Hz, 2 H, Cp), 4.44 (t, *J* = 1.6 Hz, 2 H, Cp), 1.07 (s, 27 H, CN*t*-Bu). ¹³C NMR (C₆D₆): δ 171.44 (NC(CH₃)₃), 168.48 (CH=N), 144.45 (Ph), 144.15 (Ph), 134.45 (Ph), 134.28 (Ph), 128.10 (Ph), 128.00 (Ph), 80.43 (Cp), 76.90 (Cp), 76.73 (Cp), 75.15 (Cp), 73.20 (d, Cp), 71.90 (Cp), 31.54 (NC(CH₃)₃). ³¹P NMR (C₆D₆): δ 20.56. Anal. Calcd for C₄₄H₄₆F₅N₄PFeNi: C 60.65, H 5.32, N 6.43. Found: C 60.85, H 5.07, N 6.55.

Synthesis of [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂]⁰(CO)₂(4a)** and [[C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂]₂Ni⁰(CO)₂**(4b)**.** To a red solution of [C₅H₄CH=N(C₆F₅)]Fe[η-C₅H₄PPh₂] (44 mg, 0.078 mmol) in *n*-hexane (5 mL) was added Ni(COD)₂ (21.5 mg, 0.078 mmol), and the mixture was stirred at rt for 10 min to give an orange solution. An atmosphere of carbon monoxide was introduced to the reaction vessel, and the reaction mixture was further stirred at rt for 5 h. The resultant red-orange solution was filtered through a layer of Celite. The filtrate was evaporated under vacuum, leaving a red-orange solid. This solid was redissolved in hexane and cooled at -30 °C for 2 days to precipitate **4b** as a dark red powder (ca. 5 mg, 0.004 mmol, 5% yield). The mother liquid was dried to yield **4a** as a red-orange powder (ca. 32 mg, 0.047 mmol, 61% yield). **4a**: IR [KBr, cm⁻¹]: ν_{CO} 2067 (s), 1989 (s). ν_{CN} 1623 (m), 1515 (m, sh), 1504 (s). ¹H NMR (C₆D₆): δ 7.23 (s, 1 H, CH=N), 7.39–7.32 (m, 4 H, phenyls), 6.62–6.90 (m, 6 H, phenyls), 4.53 (t, *J* = 2 Hz, 2 H, Cp), 4.25 (t, *J* = 1.2 Hz, 2 H, Cp), 4.22 (t, *J* = 2 Hz, 2 H, Cp), 4.19 (t, *J* = 1.6 Hz, 2 H, Cp). ¹³C NMR (C₆D₆): δ 196.3 (CO), 169.1 (CH=N), 132.4, 132.2, 129.2, 128.4, 128.3, 128.2, 128.1, 127.7, 127.4 (Ph), 75.2, 75.1, 73.4, 73.3, 72.8, 70.5 (Cp). ³¹P NMR (C₆D₆): δ 22.92. MS (FAB⁺): *m/z* 650 [M - CO]⁺, 621 [M - 2CO]⁺. Anal. Calcd for C₃₁H₁₉F₅NO₂PFeNi: C 54.92, H 2.82, N 2.07. Found: C 54.67, H 2.81, N 2.65. **4b**: IR [KBr, cm⁻¹]: ν_{CO} 1997 (s), 1939 (s), ν_{CN} 1617 (s), 1516 (s, sh), 1504 (s). ¹H NMR (C₆D₆): δ 7.38–7.31 (m, 5 H, CH=N and phenyls), 6.91–6.88 (m, 6 H, phenyls), 4.57 (t, *J* = 1.6 Hz, 2 H, Cp), 4.22 (t, *J* = 2 Hz, 4 H, Cp), 4.20 (t, *J* = 2 Hz, 2 H, Cp). ¹³C NMR (C₆D₆): δ 200.5 (CO), 169.5 (CH=N), 132.8, 132.7, 132.4, 132.2, 131.3, 131.2, 129.7, 129.3, 128.4, 128.1, 128.2 (Ph), 81.2 (d), 80.8 (d), 79.3, 75.3, 75.1, 73.7, 73.4, 72.7, 72.6, 71.1, 70.6 (Cp). ³¹P NMR (C₆D₆): δ 23.99. MS (FAB⁺): *m/z* 1185 [M - 2CO]⁺, 621 [(C₅H₄CH=N(C₆F₅)]Fe(η-C₅H₄PPh₂)]Ni⁺. Anal. Calcd for C₆₀H₃₈F₁₀N₂O₂P₂Fe₂Ni: C 58.06, H 3.08, N 2.26. Found: C 58.33, H 3.10, N 2.09.

Synthesis of [C₅H₄CH=NC(H)(CH₃)(C₆H₅)]Fe[η-C₅H₄PCy₂]⁰-Ni⁰(η²-PhC≡CPh)(5)**.** To a red solution of [C₅H₄CH=NC(H)(CH₃)(C₆H₅)]Fe[η-C₅H₄PCy₂] (34 mg, 0.06 mmol) in *n*-hexane (5 mL) was added Ni(COD)₂ (17 mg, 0.06 mmol), and the mixture was stirred at rt for 20 min to give an orange solution. Diphenylacetylene in hexane (1 mL) was added, and the reaction mixture was further stirred at rt for 2 h. The resultant red-orange solution was filtered through a layer of Celite. The solvent was removed to afford a red-orange solid of **5** (ca. 18 mg, 0.026 mmol, 43% yield).

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^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$): δ 8.55, 8.15, 7.56–7.00 (m, phenyls), 4.23–4.20 (m, Cp), 4.18 (s, Cp), 4.14 (s, Cp), 4.06 (s, Cp), 3.93–3.90 (m), 3.61, 3.59, 1.53 (d, Cy), 0.91 (t, Cy). ^{13}C NMR (C_6D_6): δ 161.1, 160.1, 139.9 (t, $J = 5.0$ Hz, $\equiv\text{C}-\text{Ph}$), 134.9 (t, $J = 4.4$ Hz, $\equiv\text{C}-\text{Ph}$), 134.4, 133.4, 128.8, 128.5, 128.3, 128.0, 127.7, 127.4, 124.4, 124.3, 124.0 (Ph), 79.4–75.9 (m), 71.4 (d), 71.0 (d), 70.8 (d), 70.4 (d), 70.2 (d), 69.4, 69.1 (d), 67.5 (d) (Cp), 39.5 (d), 38.2 (d), 36.0 (d), 35.8 (d), 31.5, 30.1 (d), 29.7 (d), 29.3, 29.0–22.6 (m) (Cy). ^{31}P NMR ($\text{C}_6\text{D}_5\text{CD}_3$): δ 26.13, 24.87. IR [KBr, cm^{-1}]: ν_{CN} 1633 (s), 1600 (w). Anal. Calcd for $\text{C}_{45}\text{H}_{50}\text{NPF}_e\text{Ni}$: C 72.03, H 6.72, N 1.87. Found: C 69.95, H 7.04, N 1.73. This compound is highly air- and moisture-sensitive, resulting in unsatisfactory elemental analytical data.

Oligomerization of Ethylene. The catalytic activities of complexes **3**, **4a**, **4b**, and **5** were screened by Endeavor parallel pressure reactor, following recommended procedures. (1) Prepare a stock solution of catalyst (0.001 M, 5 mL). (2) Prepare 8 glass liners with 4 mL of toluene as solvent. (3) Inject the catalyst solution (250 μL , 0.25 μmol) and activator solution. (4) Secure stirrer top with impellers to reactor block. (5) Program reaction temperature, pressure, volume 4 mL, run time, and reaction sequence by using Endeavor Advanced software. (6) Start Endeavor software on PC. (7) Click “Start” on Endeavor software on PC. (8) At the end of each test, the reaction mixture was cooled to 0 $^\circ\text{C}$ and terminated by addition of 1 mL of H_2O . The upper-layer solution was filtered through a layer of Celite and analyzed by GC. The individual products of oligomerization were identified by GC-MS.

Crystal Structure Analyses. Diffraction-quality single crystals were obtained at -30 $^\circ\text{C}$ as follows: **4b** as dark red prisms after 4 days from solution in toluene layered with hexane; **5** as dark red polyhedra after 5 days from solution in hexane. Crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo $\text{K}\alpha$ radiation (λ 0.71073 \AA). The data were corrected for Lorentz and polarization effect with the SMART suite of programs³⁰ and for absorption effects with SADABS.³¹ Structure solution and refinement were carried out with the SHELXTL suite of programs.³² The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The asymmetric unit of **5** contains one titled molecule and one disordered hexane solvent. The hexane is disordered into two positions at 50:50 occupancies. In the titled molecule, the $\text{C}_6\text{H}_5\text{-CHCH}_3$ group is also disordered into two positions at 50:50

Table 4. Selected Crystal Data, Data Collection, and Refinement Parameters of Compounds **4b** and **5**

	4b · C_6H_{14}	5 · C_6H_{14}
formula	$\text{C}_{66}\text{H}_{52}\text{F}_{10}\text{Fe}_2\text{N}_2\text{NiO}_2\text{P}_2$	$\text{C}_{51}\text{H}_{64}\text{FeNNiP}$
fw	1327.45	836.56
cryst size/mm	$0.30 \times 0.20 \times 0.12$	$0.30 \times 0.12 \times 0.08$
temperature/K	223(2)	295(2)
crystal syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	11.0651(8)	9.7577(10)
$b/\text{\AA}$	15.2100(11)	12.6044(14)
$c/\text{\AA}$	17.6504(12)	18.6464(19)
α/deg	86.609(2)	94.371(3)
β/deg	80.427(2)	94.356(3)
γ/deg	83.410(2)	96.860(3)
$V/\text{\AA}^3$	2907.4(4)	2261.9(4)
Z	2	2
$D_c/\text{g cm}^{-3}$	1.516	1.228
radiation used	Mo $\text{K}\alpha$	Mo $\text{K}\alpha$
μ/mm^{-1}	0.948	0.806
θ range/deg	1.75 to 27.50	1.63 to 25.00
no. of unique reflns measd	38 590	13 226
max., min. transmn	0.8947 and 0.7641	0.9383 and 0.7940
final R indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0652$, $wR_2 = 0.1586$	$R_1 = 0.0999$, $wR_2 = 0.1957$
R indices (all data)	$R_1 = 0.0978$, $wR_2 = 0.1741$	$R_1 = 0.1436$, $wR_2 = 0.2125$
goodness-of-fit on F^2 ^c	1.032	1.160
large diff peak and hole, $e \text{\AA}^{-3}$	1.081 and -0.524	0.455 and -0.450

$$^a R = (\sum |F_o| - |F_c|) / \sum |F_o|. \quad ^b wR_2 = [(\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}. \quad ^c \text{GoF} = [(\sum w|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}.$$

occupancies. The data collection and processing parameters are given in Table 4.

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Supporting Information Available: For structures of **4b** and **5**: complete listing of bond lengths and angles, ORTEP diagrams, tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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