Bis(carbene)pyridine Complexes of the Early to Middle Transition Metals: Survey of Ethylene Oligomerization and Polymerization Capability

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Bis(carbene)pyridines of the type 2,6-bis(1-(alkyl/aryl)imidazol-2-ylidene)pyridine have been complexed to Ti, V, Cr, Fe, and Co and single-crystal X-ray structures obtained for two of the complexes (M = Cr, Fe). The structures confirm the tight chelate bite angles (ca. 76−79°) enforced by this ligand. All complexes have been evaluated as catalysts for ethylene oligomerization and polymerization in combination with a variety of cocatalysts. While Ti and V complexes of this ligand give rise to highly active ethylene polymerization catalysts, Cr complexes produce exceptionally active Schulz−Flory oligomerization catalysts in combination with MAO. In contrast, complexes of Fe and Co are inactive, and possible reasons for this are suggested.

Introduction

N-heterocyclic carbenes have become established as efficient ancillary ligands for homogeneous catalysis, and over the past decade, an increasing number of catalytic transformations have been carried out using these transition-metal carbene complexes. Such reactions include Heck-type coupling, hydroformylation and hydrogenation, and olefin metathesis.[1] It is interesting to note that, with few exceptions, most examples of these ligands being employed in catalysis have exploited late-transition-metal complexes; early-transition-metal carbene complexes have been sparsely examined in this respect. However, early-transition-metal complexes are likewise efficient catalysts for a diverse range of reactions, an example being the ubiquity of these metals in olefin oligomerization and polymerization chemistry.

Research activity into the design of new organometallic catalysts for olefin polymerization continues to increase. While metallocene catalysts have provided great advances in α-olefin polymerization technology over the past 15 years, attention is nowadays increasingly being focused toward nonmetallocene alternatives.[2] With the notable exception of metathesis-based polymerization (Ru−carbene),[3] heterocyclic carbenes have not found widespread application in olefin polymerization. This is possibly due in part to the propensity of alkylmetal carbene complexes to decompose via alkyl−imidazolium eliminations.[4] Alkylmetal intermediates are expected to be involved in each step of the polymerization cycle. This reaction has been found to occur for late-transition-metal complexes,[5] and we reasoned that its effect may be attenuated by employing early-transition-metal carbene complexes.

Of the limited examples of ethylene polymerization using heterocyclic carbene complexes,[6] most have involved the use of early transition metals, although reported activities have in general been rather low. We recently communicated initial results in which pyridyl−bis(carbene) ligands of the types **L^1**−**L^3** on Cr were employed as highly effective catalysts for ethylene oligomerization.[7] Late-transition-metal complexes of this class of ligand have recently been reported.[8,9] These ligands are structurally related to the bis(imino)pyridines, which have found significant applications in olefin polymerization when attached to V, Cr, Co, and Fe.[10] Prompted by the recent disclosure of a highly active Ti−carbene-based polymerization system,[11] herein we report full results of our work with this ligand. The ability of early- and middle-transition-metal carbene

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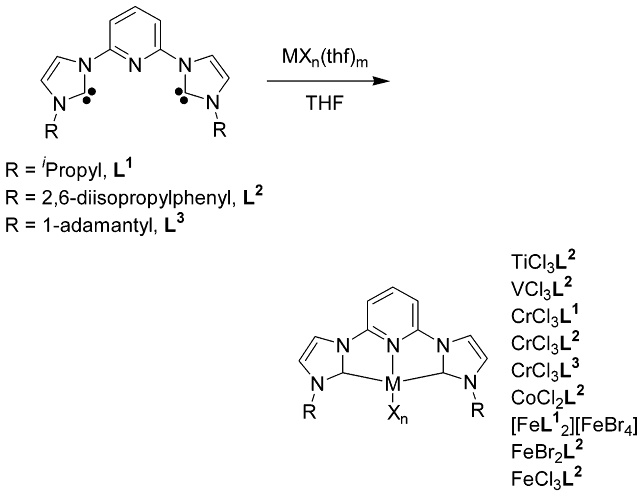
Scheme 1. Preparation of Bis(carbene)pyridine Complexes



complexes to catalyze olefin polymerization has been surveyed by preparing complexes of $\mathbf{L^1}$−$\mathbf{L^3}$ with the first-row transition metals Ti, V, Cr, Fe, and Co.

Results and Discussion

Synthesis. The bis(carbene)pyridines $\mathbf{L^1}$−$\mathbf{L^3}$ (Scheme 1) were prepared by deprotonation of the corresponding imidazolium bromides using $KN(SiMe_3)_2$. The preparation of $\mathbf{L^2}$ has been reported previously,[12] and an analogous procedure yielded $\mathbf{L^1}$ and $\mathbf{L^3}$ in moderate (50−75%) yields. The ligands were chosen to possess differing degrees of steric hindrance, ranging from the less bulky isopropyl N substituents of $\mathbf{L^1}$ to the larger 2,6-diisopropylphenyl and adamantyl groups of $\mathbf{L^2}$ and $\mathbf{L^3}$. Early- to middle-transition-metal complexes of the ligands were prepared via treatment of the metal halides or metal chloride THF adducts with the pro-ligand in THF solution, as shown in Scheme 1. In all cases a high yield of the isolated complex was obtained (80−100%).

The early-transition-metal complexes were prepared from $MCl_3(thf)_3$, affording purple $TiCl_3\mathbf{L^2}$, orange-brown $VCl_3\mathbf{L^2}$, and green $CrCl_3\mathbf{L^1}$, $CrCl_3\mathbf{L^2}$, and $CrCl_3\mathbf{L^3}$. While the Ti and V complexes are highly air and moisture sensitive, the Cr complexes are air stable, even in solution. Crystals of $CrCl_3\mathbf{L^1}$ grown from DMSO/DCM were analyzed by X-ray crystallography, and the structure has been reported previously.[7] The expected octahedral geometry is displayed (Cr−carbene = 2.087(6), 2.120(6) Å; Cr−N = 2.049 Å), somewhat distorted by the C∧Cr∧N chelate bite angles of 76.3(2) and 75.68(9)°.

When the isopropyl-substituted ligand $\mathbf{L^1}$ is added to a solution of $FeBr_2$, an orange precipitate formed immediately. This product was formulated as the bis(ligand) salt $[Fe\mathbf{L^1}_2][FeBr_4]$, on the basis of its lack of solubility in common solvents and the presence of the diagnostic $[FeL_2]^{2+}$ cluster in the mass spectrum. Crystallization of the complex from hot DMSO yielded orange crystals that were suitable for X-ray analysis and were identified as $[Fe\mathbf{L^1}_2]Br_2\cdot 2DMSO$ (Figure 1).[13] The dication displays an octahedral geometry, distorted by the tight C−Fe−N chelate bite angles of 79.07(8) and 79.29(8)° in the complexed ligand. The Fe−C distances (1.952(2), 1.959(2) Å) are indicative of an Fe−C single bond, as expected for heterocyclic carbenes, and all other bond distances in the complex are unexceptional. The formation of the bis(ligand) complex indicates a lack of steric bulk around the metal. This appears to be due to both the tight chelate bite angles, which pull the N substituents out away from the metal, and the fact that the carbene isopropyl substituent is once removed from the donor atom. The structure of $CrCl_3\mathbf{L^1}$ shows likewise. When the more bulky ligand $\mathbf{L^2}$ was reacted with $FeBr_2$ in THF, a deep red solution formed along with a minor amount of orange precipitate (possibly the bis(chelate) complex on the basis of its color and lack of solubility). A deep red powder was isolated after workup that shows good solubility in THF and DCM and does not show the bis(ligand) ion in the mass spectrum (a $[M - Br]^+$ cluster is observed). This complex is formulated as the mono(ligand) complex, although a structural determination has not been undertaken.[14] The Fe(III) and Co(II) complexes were likewise obtained through reaction of $\mathbf{L^2}$ with $FeCl_3$ and $CoCl_2$, respectively.

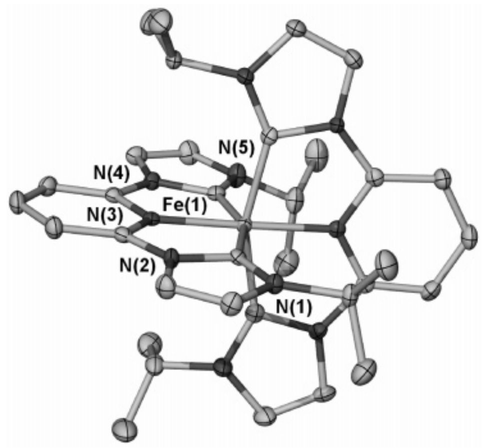


Figure 1. Molecular structure of the cation $Fe\mathbf{L^1}_2$. Selected bond distances (Å) and angles (deg): Fe(1)−N(3), 1.9235(17); Fe(1)−C(4), 1.959(2); Fe(1)−C(12), 1.952(2); N(3)−Fe(1)−C(4), 79.29(8); N(3)−Fe(1)−C(12), 79.07(8); C(4)−Fe(1)−C(12), 158.36(9).

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(14) During the preparation of this paper, an alternative synthesis along with the structure (mono(ligand)) of $FeBr_2\mathbf{L^2}$ was published: Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. *Organometallics* **2004**, *23*, 166.

Table 1. Ethylene Oligomerization with $\mathbf{L}^1$–$\mathbf{L}^3$ Complexes of $\mathrm{CrCl_3}$[a]

entry	catalyst	P_{ethylene} (bar)	T_{max}[b]	productivity[c]	TOF ($\mathrm{h^{-1}}$)	K	α-Ol %
1	$\mathrm{CrCl_3}\mathbf{L}^1$	5	44	727	129 530	0.48	93
2	$\mathrm{CrCl_3}\mathbf{L}^1$	1	33	1 394	49 690	0.46	92
3	$\mathrm{CrCl_3}\mathbf{L}^2$	5	70	2 263	403 290	0.78	93
4	$\mathrm{CrCl_3}\mathbf{L}^2$	2.5	60	2 623	233 760	0.78	90
5	$\mathrm{CrCl_3}\mathbf{L}^2$	1	46	5 490	195 690	0.78	89
6	$\mathrm{CrCl_3}\mathbf{L}^2$	1	25[d]	12 065	430 030	0.75	80
7	$\mathrm{CrCl_3}\mathbf{L}^3$	5	25	15	2 640		
8	$\mathrm{CrCl_3}\mathbf{L}^3$	1	23	73	2 640		
9	$\mathrm{CrCl_3}\mathbf{L}^2$[e]	1	25[d]	27 100	965 990	0.78	80
10	$\mathrm{CrCl_3}\mathbf{L}^2$[f]	1	25[d]	40 440	1 441 500	0.80	86

[a] Conditions: [Cr] = 20 μM, toluene, 500 MAO, 30 min. [b] Temperature reached due to exotherm. [c] In units of g of product (mmol of Cr)$^{-1}$ bar^{-1} h^{-1}. [d] Temperature held constant throughout run. [e] Conditions: 10 μM [Cr], 1000 MAO, 1000 $\mathrm{Al(^iBu)_3}$ scavenger. [f] Conditions: 4.5 μM [Cr], 1000 MAO, 3000 $\mathrm{Al(^iBu)_3}$ scavenger.

tion was conducted in 500 mL Fisher–Porter reactors, with mechanical stirring under a continuous feed of ethylene (1–5 bar). A variety of cocatalysts were employed, as detailed below.

Chromium complexes of ligand $\mathbf{L}^1$ and $\mathbf{L}^2$ were the first to be prepared and tested for ethylene polymerization activity, and these results have been communicated previously.[7] Both complexes are highly active for ethylene oligomerization, giving a Schulz–Flory distribution of α-olefins when activated with MAO (Table 1). The distribution of oligomers, characterized by the K value,[15] is lower for $\mathrm{CrCl_3}\mathbf{L}^1$ (0.46–0.48) than for $\mathrm{CrCl_3}\mathbf{L}^2$ (0.75–0.80), as might be expected on the basis of the increased steric demands of $\mathbf{L}^2$ versus $\mathbf{L}^1$. For both complexes the K value is independent of ethylene pressure. In an attempt to extend the usefulness of these catalysts to ethylene polymerization, an analogue with very bulky adamantyl N substitution was prepared, $\mathrm{CrCl_3}\mathbf{L}^3$. While this complex did produce polyethylene, along with trace amounts of oligomers, the large substituents have a marked detrimental effect on activity (entries 7 and 8).

For both $\mathrm{CrCl_3}\mathbf{L}^1$ and $\mathrm{CrCl_3}\mathbf{L}^2$, MAO was found to be the cocatalyst of choice. Other activators investigated were $\mathrm{Et_2AlCl}$ and $\mathrm{Al^iBu_3/B(C_6F_5)_3}$, which gave inferior results. An immediate exotherm resulted upon addition of activator, with no induction period. The catalytic activity decreases over a 30 min run, as noted by a decrease in ethylene consumption. This deactivation is dependent on the temperature, and above 50 °C a very rapid deactivation is observed. The catalyst benefits from a longer lifetime at lower temperatures, although the rate of ethylene conversion also decreases at lower temperature. For $\mathrm{CrCl_3}\mathbf{L}^2$ this results in the productivity over a 30 min run being greatest at 25 °C, as shown in Figure 2.

The activity of $\mathrm{CrCl_3}\mathbf{L}^2$ is increased as the catalyst concentration is decreased and $\mathrm{Al^iBu_3}$ is added as a scavenger (entries 9 and 10). Under optimal conditions an average TOF of well over 10^6 h^{-1} can be achieved.

As $\mathbf{L}^2$ provided the most stable and active catalyst for Cr, this ligand was employed in evaluating Ti and V carbene complexes, $\mathrm{TiCl_3}\mathbf{L}^2$ and $\mathrm{VCl_3}\mathbf{L}^2$. A variety of cocatalysts were employed, as shown in Table 2.

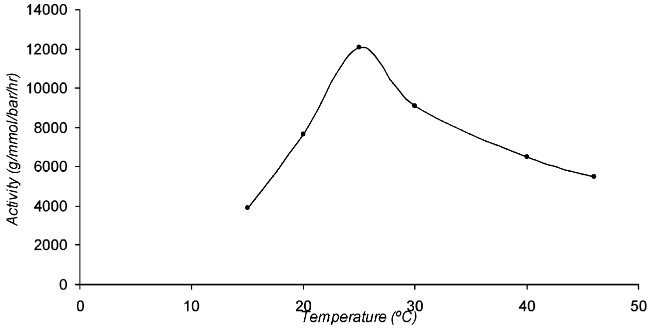

Figure 2. Activity of $\mathrm{CrCl_3}\mathbf{L}^2$ as a function of temperature ([Cr] = 20 μM, toluene, 500 MAO, 30 min).

Table 2. Ethylene Polymerization with Complexes $\mathrm{TiCl_3}\mathbf{L}^2$ and $\mathrm{VCl_3}\mathbf{L}^2$ [a]

entry	catalyst	cocatalyst (amt, equiv)	productivity[b]	TOF ($\mathrm{h^{-1}}$)
1	$\mathrm{TiCl_3}\mathbf{L}^2$	MAO (500)	791	28 195
2	$\mathrm{TiCl_3}\mathbf{L}^2$	MAO (1000)	652	23 240
3	$\mathrm{TiCl_3}\mathbf{L}^2$	MAO (100)	82	2 925
4	$\mathrm{TiCl_3}\mathbf{L}^2$	DMAO (500)	286	10 195
5	$\mathrm{TiCl_3}\mathbf{L}^2$	DMAO (500), TIBAL (30)	358	12 760
6	$\mathrm{TiCl_3}\mathbf{L}^2$	co-MAO (500)	694	24 740
7	$\mathrm{TiCl_3}\mathbf{L}^2$	$\mathrm{Et_2AlCl}$ (500)	29	1 035
8	$\mathrm{VCl_3}\mathbf{L}^2$	MAO (500)	1280	45 625
9	$\mathrm{VCl_3}\mathbf{L}^2$	MAO (1000)	907	32 330
10	$\mathrm{VCl_3}\mathbf{L}^2$	DMAO (500), TIBAL (30)	586	20 890
11	$\mathrm{VCl_3}\mathbf{L}^2$	co-MAO (500)	1446	51 545
12	$\mathrm{VCl_3}\mathbf{L}^2$	$\mathrm{Et_2AlCl}$ (500)	278	9 910

[a] Conditions: [M] = 20 μM, 1 bar of ethylene, toluene, ambient temperature, 30 min. [b] In units of g of product (mmol of M)$^{-1}$ bar^{-1} h^{-1}.

Both catalysts were active in ethylene polymerization, and in no case was an induction period observed. Along with MAO cocatalyst (500 equiv), the titanium complex was highly active for polymerization (entry 1). Increasing the amount of MAO did not lead to an increase in activity (entry 2), although with a low cocatalyst loading (100 equiv) the activity decreased significantly (entry 3).

The cocatalyst formed by removing trimethylaluminum from MAO, by washing with pentane and drying under vacuum ("dried-MAO", DMAO) was also tested, both neat and with 30 equiv of triisobutylaluminum (TIBAL) added (entries 4 and 5). With this cocatalyst, $\mathrm{TiCl_3}\mathbf{L}^2$ proved less active than with unmodified MAO. Also tested were co-MAO (10% ^{i}Bu), which gave an activity similar to MAO, and $\mathrm{Et_2AlCl}$, which was a poor activator.

The vanadium complex was somewhat more active than Ti, and very high activities (>1000 g mmol^{-1} bar^{-1} h^{-1}) could be achieved by utilizing MAO and co-MAO (entries 8 and 11). In common with the Ti system, a greater loading of MAO did not improve activity, and in fact the activity of $\mathrm{VCl_3}\mathbf{L}^2$ along with 1000 equiv of MAO was somewhat reduced (entry 9). Again $\mathrm{Et_2AlCl}$ led to a lower activity, while DMAO/TIBAL gave an intermediate activity. The use of ethyl trichloroacetate, which has been used to reoxidize vanadium polymerization catalysts that suffer from reduction,[16] led to a decrease in activity with $\mathrm{VCl_3}\mathbf{L}^2$ and all cocatalysts. As was found for the Cr systems, the Ti and V catalysts are at their most active at the start of a run and slowly deactivate over a 30 min period.

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(15) $K = k_{\mathrm{prop}}/(k_{\mathrm{prop}} + k_{\mathrm{ch\ transfer}})$ = (mol of C_{n+2})/(mol of C_n).

(16) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229.

The polyethylene produced by both systems was of very high molecular weight (>2 M) and, as such, could not be dissolved for GPC analysis. The melting temperature of the polymers (Ti, 141 °C, entry 1; V, 144 °C, entry 8) is consistent with high-density polyethylene with no significant branching.

Both $[\mathrm{Fe}\mathbf{L^1}_2][\mathrm{FeBr}_4]$ and $\mathrm{FeBr}_2\mathbf{L^2}$, when treated with MAO, were totally inactive for ethylene polymerization. For the bis(ligand) Fe complex this is not unexpected, given the coordinatively saturated nature of the Fe center in the cationic species. The solution that resulted from testing of $\mathrm{FeBr}_2\mathbf{L^2}$ was analyzed by positive ion FAB MS, in an attempt to elucidate the fate of the Fe complex. No peaks corresponding to an Fe complex were observed. However, a peak corresponding to the methylated ligand was observed. As carbene complexes of late transition metals are known to decompose via reductive elimination of an alkylimidazolium cation, we postulate that this species originates from carbene−methyl elimination following methylation of the Fe complex by MAO. In the hope that an $\mathrm{Fe^{III}}$ precatalyst might be active, the complex $\mathrm{FeCl}_3\mathbf{L^2}$ was also prepared and tested. Once again, this complex was inactive for ethylene oligomerization or polymerization. Finally, the one example of a Co carbene complex prepared, $\mathrm{CoCl}_2\mathbf{L^2}$, was inactive when treated with MAO. Although this was not studied further, it is worth noting in this respect that the reductive elimination of an imidazolium cation from Co has recently been reported for the first time ($\mathrm{Co^I} \rightarrow \mathrm{Co^{-I}}$).[17] It therefore seems that this ligand motif is less suited to Fe and Co olefin polymerization catalysts than to earlier transition-metal counterparts.

Summary and Conclusion

We have investigated the potential of heterocylic carbene ligands to act as ancillary ligands for ethylene oligomerization and polymerization by surveying first-row early- to middle-transition-metal complexes of the bis(carbene)pyridine motif. Although we have examined only one ligand structure, such that this work is not intended to be representative of all heterocyclic carbene ligands, the results collected here, together with other studies on related late-transition-metal carbene systems, provide valuable insights into the potential for exploiting heterocyclic carbene ligands in olefin chain-growth processes. While late-transition-metal (Pd) complexes of this ligand undergo alkyl−carbene coupling reactions,[9,18] and there is evidence for this in the Fe complexes reported here, the early transition metals Ti, V, and Cr appear less prone to this chemistry. This is revealed by the extremely high activities obtained for ethylene polymerization and oligomerization and the clearly observable ligand infuence on the Cr system. These results show that heterocyclic carbene complexes have extremely good potential for olefin chain growth reactions, and high-performance systems based on these ligands can be expected to result from further studies in this field. Finally, while the discovery of highly active olefin polymerization catalysts based on late-transition-metal carbene complexes cannot be ruled out, we postulate that the development of new olefin oligomerization and polymerization systems based on heterocyclic carbene complexes will be especially fruitful for the early transition metals.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox, using solvents purified and dried by standard procedures. The preparation of $\mathbf{L^2}$ [12] and $\mathrm{CrCl}_3(\mathbf{L^1}-\mathbf{L^3})$ complexes[7] has been reported previously.

2,6-Bis(1-isopropylimidazolium)pyridine Dibromide ($\mathbf{L^1\cdot 2HBr}$). *N*-Isopropylimidazole (10.1 g, 92 mmol) and 2,6-dibromopyridine (7.27 g, 30.7 mmol) were mixed and heated to 150 °C for 2 days. The cooled mixture was triturated with 50 mL of THF, the washings were filtered off, and the product was washed twice more with THF. Drying in vacuo yielded a sandy powder. Yield: 7.37 g (53%). ^{1}H NMR (250 MHz, $\mathrm{CD_3OD}$): δ 10.38 (s, 2H, NC(*H*)N); 8.69 (d, J = 2 Hz, 2H, NC(*H*)C(H)N); 8.50 (m, J = 8 Hz, 1H, py *H*-4); 8.24 (d, J = 8 Hz, 2H, py *H*-3,5); 8.10 (d, J = 2 Hz, 2H, NC(H)C(*H*)N), 4.97 (m, J = 7 Hz, 2H, C*H*($\mathrm{CH_3}$)$_2$), 1.72 (d, J = 7 Hz, 12H, CH(CH_3)$_2$). ^{13}C NMR (63 MHz, $\mathrm{CD_3OD}$) δ: 147.3 (N*C*N); 146.0, 135.9 (pyridyl *C*); 123.1, 121.2 (N*CC*N); 115.9 (pyridyl *C*); 55.8 (*C*($\mathrm{CH_3}$)$_2$); 23.0 (C(*C*H_3)$_2$).

2,6-Bis(1-adamantylimidazolium)pyridine Dibromide ($\mathbf{L^3\cdot 2HBr}$). This precursor was prepared in the same manner as above in a yield of 47%. ^{1}H NMR (250 MHz, DMSO-d_6): δ 10.23 (s, 2H, NC(*H*)N); 9.0 (s, br, 2H, NC(*H*)C(H)N); 8.61 (m, br, 1H, py *H*-4); 8.45 (m, br, 4H, py *H*-3,5 + NC(H)C(*H*)N); 2.27 (s, br, 18H, adamantyl); 1.75 (s, br, 12H, adamantyl). ^{13}C NMR (63 MHz, DMSO-d_6): δ 145.3 (N*C*N); 144.2, 133.6 (pyridyl *C*); 120.6, 119.9 (N*CC*N); 114.8 (pyridyl *C*); 60.6 (N*C* adamantyl); 41.3, 34.8, 28.9 (adamantyl *C*).

2,6-Bis(1-isopropylimidazol-2-ylidene)pyridine ($\mathbf{L^1}$). The diimidazolium salt (3.189 g, 6.97 mmol) was suspended in 10 mL of THF and cooled to −10 °C. To this was added a solution of $\mathrm{KN(SiMe_3)_2}$ (3.00 g, 15.0 mmol) in 20 mL of THF, after which the mixture was stirred for 30 min at −10 °C. After it was warmed to room temperature, the solution was filtered and the solvent removed in vacuo. The residue was washed with 10 mL of pentane at −40 °C and dried in vacuo to give an orange solid. Yield: 1.540 g (75%). ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$): δ 8.50 (d, J = 8 Hz, 2H, py *H*-3,5); 8.00 (d, J = 2 Hz, 2H, NC(*H*)=C(H)N); 7.14 (m, J = 8 Hz, 1H, py *H*-4); 6.50 (d, J = 2 Hz, 2H, NC(H)=C(*H*)N); 4.36 (m, J = 7 Hz, 2H, C(*H*)($\mathrm{CH_3}$)$_2$); 1.25 (d, J = 7 Hz, 12H, CH_3). ^{13}C NMR (63 MHz, $\mathrm{C_6D_6}$): δ 215.2 (N*C*N); 153.0, 140.1, 110.6 (py *C*); 116.8, 116.0 (N*C*=*C*N); 52.5 (*C*($\mathrm{CH_3}$)$_2$); 23.6 (*C*H_3).

2,6-Bis(1-adamantylimidazol-2-ylidene)pyridine ($\mathbf{L^3}$). This ligand was prepared in the same manner as that given above, in a yield of 52%. ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$): δ 8.57 (d, 2H, py *H*-3,5); 8.14 (d, J = 2 Hz, 2H, NC(*H*)=C(H)N); 7.19 (m, J = 8 Hz, 1H, py *H*-4); 6.84 (d, J = 2 Hz, 2H, NC(H)=C(*H*)N); 2.22 (s, br, 12H, adamantyl); 2.00 (s, br, 6H, adamantyl); 1.57 (s, br, 12H, adamantyl). ^{13}C NMR (63 MHz, $\mathrm{C_6D_6}$): δ 215.2 (N*C*N); 152.9, 140.0, 110.6 (py *C*); 115.6, 115.4 (N*C*=*C*N); 56.4 (N*C* adamantyl); 41.3, 34.8, 28.9 (adamantyl *C*).

$\mathbf{TiCl_3L^2}$. $\mathrm{TiCl_3(thf)_3}$ (0.216 g, 0.583 mmol) was suspended/dissolved in 10 mL of THF and $\mathbf{L^2}$·toluene (0.369 g, 0.591 mmol) in 10 mL of THF added. A homogeneous purple solution resulted, which was stirred for 15 min and the solvent removed under vacuum until a slurry formed. Ether (5 mL) was added to complete precipitation, and the product was collected by filtration and washed with 20 mL of ether. Drying under vacuum gave a purple powder. Yield: 0.405 g (100%). ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): δ 8.5 (br, 2H); 7.1 (br, 2H); 3.7 (br, 4H); 1.2 (br, 24H). MS (FAB): m/z 685 $[\mathrm{M}]^+$. Anal. Calcd (found) for $\mathrm{C_{35}H_{41}N_5Cl_3Ti}$: C, 61.28 (60.99); H, 6.02 (6.12); N, 10.21 (10.08).

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VCl_3L^2. $VCl_3(thf)_3$ (0.199 g, 0.533 mmol) was dissolved in 15 mL of THF and L^2·toluene (0.350 g, 0.561 mmol) in 10 mL of THF added. A homogeneous deep red solution resulted, which was stirred for 1 h and the solvent removed under vacuum until ca. 5 mL remained. Ether (5 mL) was added to complete precipitation, and the product was collected by filtration and washed with 10 mL of ether. Drying under vacuum afforeded a light orange-brown powder. Yield: 0.370 g (100%). MS (FAB): *m/z* 652 (20%, $[M - Cl]^+$), 531 (25%, $[L]^+$). Anal. Calcd (found) for $C_{35}H_{41}N_5Cl_3V$: C, 61.01 (60.93); H, 6.00 (5.85); N, 10.16 (9.92).

$[FeL^1{}_2][FeBr_4]$. $FeBr_2$ (0.153 g, 0.709 mmol) was suspended in 20 mL of THF and a solution of ligand L^1 (0.221 g, 0.748 mmol) in 10 mL of THF added. The mixture was heated to 65 °C for 90 min and stirred overnight at RT. The solvent was filtered off before the product was washed with 20 mL of THF and dried in vacuo to afford an orange powder. Yield: 0.355 g (98%). MS (FAB): *m/z* 646 (60%, $[FeL_2]^+$), 603 (100%, $[FeL_2-C_3H_7]^+$), 430 (30%, $[FeLBr]^+$), 323 (50%, $[FeL_2]^{2+}$). Anal. Calcd (found) for $C_{17}H_{21}N_5FeBr_2$: C, 39.96 (39.87); H, 4.14 (4.20); N, 13.70 (13.97).

$FeBr_2L^2$. $FeBr_2$ (0.085 g, 0.394 mmol) was suspended in 10 mL of THF and a solution of the ligand L^2·toluene (0.250 g, 0.401 mmol) in 10 mL of THF added. The solution turned deep red-violet, followed by a small amount of orange precipitate formation shortly afterward. After 20 min the solution was filtered and the solvent removed under vacuum until ca. 4 mL remained. The product was precipitated by the addition of 6 mL of ether, washed with 10 mL of ether, and dried under vacuum to give a deep red powder. Yield: 0.183 g (62%). MS (FAB): *m/z* 668 (5%, $[M - Br]^+$), 624 (6%, $[M - C_3H_8Br]^+$), 532 (40%, $[LH]^+$). Anal. Calcd for $C_{35}H_{41}N_5Br_2Fe$ (found): C, 56.25 (56.17); H, 5.53 (5.62); N, 9.37 (9.20).

$FeCl_3L^2$. $FeCl_3$ (0.0610 g, 0.376 mmol) was taken up in 10 mL of THF and a solution of the ligand L^2·toluene (0.247 g, 0.396 mmol) in 10 mL of THF added. After the mixture was stirred overnight, the solvent was removed until ca. 5 mL remained and an orange precipitate started to form, after which precipitation was completed by the addition of 10 mL of ether. After washing with further ether the product was dried under vacuum to afford a light orange powder. Yield: 0.254 g (97%). MS (FAB): *m/z* 532 (100%, $[L]^+$). Anal. Calcd (found) for $C_{35}H_{41}N_5Cl_3Fe$: C, 60.58 (60.46); H, 5.95 (5.93); N, 10.09 (9.97).

$CoCl_2L^2$. $CoCl_2$ (0.0520 g, 0.400 mmol) was dissolved in 20 mL of THF and a solution of L^2·toluene (0.260 g, 0.417 mmol) in 10 mL of THF added, resulting in a deep red, homogeneous solution. The solvent was removed until 4 mL remained, and the product was precipitated with ether and washed with further ether (2 × 10 mL). Drying under vacuum gave a red powder. Yield: 0.164 g (62%). MS (FAB): *m/z* 661 (65%, $[MH]^+$), 625 (100%, $[M - Cl]^+$), 590 (10%, $[M - 2Cl]^+$), 532 (10%, $[LH]^+$). Anal. Calcd (found) for $C_{35}H_{41}N_5Cl_2Co$: C, 63.54 (62.94); H, 6.25 (6.15); N, 10.58 (10.39).

Ethylene Polymerization. Catalytic testing was conducted in 500 mL Fisher−Porter reactors under mechanical stirring with a continuous feed of ethylene. The reactor was charged with the precatalyst under nitrogen, before the appropriate volume of toluene was added to attain a concentration of 20 μM. The catalyst solution was then exposed to ethylene before injection of the cocatalyst at ambient temperature. After 30 min the ethylene was vented, GC internal standard added (for oligomer quantification), and the mixture quenched with MeOH followed by 10% HCl. A sample of the organic layer was taken for GC analysis, and the polymer was collected by filtration, washed with MeOH, and dried under vacuum at 60 °C overnight before weighing.

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Supporting Information Available: Crystallographic data, as a CIF file, for $[FeL^1{}_2]Br_2\cdot 2DMSO$. This material is available free of charge via the Internet at http://pubs.acs.org.

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