

Notes

Aluminum Alkyl-Mediated Route to Novel *N,N,O*-Chelates for Five-Coordinate Iron(II) Chloride Complexes: Synthesis, Structures, and Ethylene Polymerization StudiesVernon C. Gibson,[†] Carl Redshaw,^{*,‡} Gregory A. Solan,^{*,§} Andrew J. P. White,[†] and David J. Williams[†]

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Summary: Two five-coordinate iron(II) chloride complexes bearing 2-imine-6-(methyl alcohol)pyridine chelates have been prepared via an aluminum-mediated methyl migration route from the corresponding 2-acetyl-6-iminopyridine. Both iron complexes display moderate activity for ethylene polymerization on treatment with excess methylaluminoxane, affording highly linear polymers along with some oligomeric products.

Introduction

Since the discovery that sterically bulky 2,6-bis(arylimino)pyridine ligands (**A**, Chart 1) can impart late transition metals, and in particular iron, with extremely high activities for ethylene oligomerization and polymerization,^{1,2} considerable effort has been devoted to catalyst modification with a view to enhancing both activity and control of the microstructure of the resulting polymer.³ In particular, changes to the basic bis(imino)pyridine ligand motif have been targeted, with modifications to the N-imine substituents,^{1–3} the C-imino substituents,^{3a,4} and the central pyridine substituents at the forefront.^{3a,5} More significant variations including substitution of one of the imino groups in **A** for an amino (**B**,

Chart 1. 2,6-Bis(imino)pyridine (**A**), 2-Imino-6-(methylamino)pyridine (**B**), 2-Acetyl-6-iminopyridine (**L1**), and 2-Imino-6-(methyl alcohol)pyridine (**L2**)

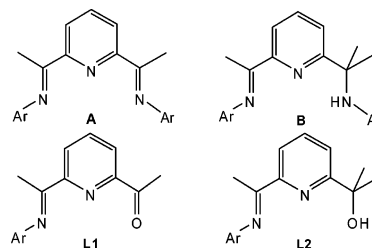


Chart 1),⁶ pyridyl,⁷ thiophenyl,⁸ furanyl,⁸ acetyl (**L1**, Chart 1),⁹ or ethylcarboxylato¹⁰ group have also been reported, with the corresponding iron (and cobalt) catalysts showing low to high activities for both ethylene oligomerization and polymerization.

During the development of these new ligand systems, a number of elegant organometallic synthetic strategies have come to the fore including the use of trimethylaluminum to modify **A** to give, following hydrolysis, the selectively reduced **B**.^{6,11} Indeed, the reactivity of **A** toward a range of alkylaluminums alone has proved most intriguing, with aluminum-based products

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(1) (a) Small, B. L.; Brookhart, M.; Bennet, A. M. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120. (c) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (2) (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849. (b) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.

(3) For reviews see: (a) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (d) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (e) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534. (f) Bianchini, C.; Giambastiani, G.; Rios, G. I.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391.

(4) (a) Kleigrew, N.; Steffen, W.; Blömker, T.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Erker, G.; Wasilke, J.-C.; Wu, G.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 13955. (b) Smit, T.; Tomov, A. K.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2004**, *43*, 6511.

(5) (a) Nüchel, S.; Burger, P. *Organometallics* **2001**, *20*, 4345. (b) Seitz, M.; Milius, W.; Alt, H. G. *J. Mol. Catal. A: Chem.* **2006**, *261*, 246. (c) Kim, I.; Heui Han, B.; Ha, C.-S.; Kim, J.-K.; Suh, H. *Macromolecules* **2003**, *36*, 6689.

(6) (a) Britovsek, G. J. P.; Gibson, V. C.; Mastroianni, S.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 431. (b) Gibson, V. C.; Kimberley, B. S.; Solan, G. A. (BP) WO0020427, 2000.

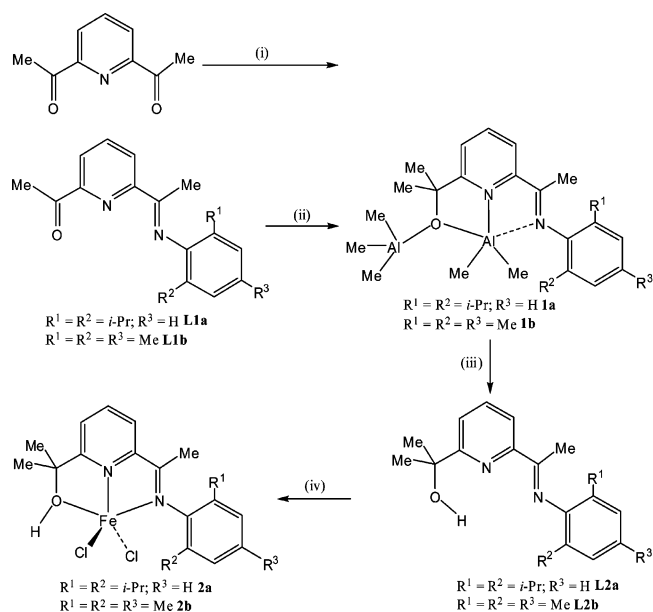
(7) Britovsek, G. J. P.; Baugh, S. P. D.; Hoarau, O.; Gibson, V. C.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Inorg. Chim. Acta* **2003**, *345*, 279.

(8) (a) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Laschi, F. *Organometallics* **2003**, *22*, 2545. (b) Bianchini, C.; Giambastiani, G.; Mantovani, G.; Meli, A.; Mimeo, D. J. *Organomet. Chem.* **2004**, *689*, 1356. (c) Bianchini, C.; Gatteschi, D.; Giambastiani, G.; Rios, I. G.; Ienco, A.; Laschi, F.; Mealli, C.; Meli, A.; Sorace, L.; Toti, A.; Vizza, F. *Organometallics* **2007**, *26*, 726.

(9) (a) Kaul, F. A. R.; Puchta, G. T.; Frey, G. D.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2007**, *26*, 988. (b) Fernandes, S.; Bellabarba, R. M.; Ribeiro, A. F. G.; Gomes, P. T.; Ascenso, J. R.; Mano, J. F.; Dias, A. R.; Marques, M. M. *Polym. Int.* **2002**, *51*, 1301. (c) Bennett, A. M. A. (DuPont) U.S. Patent 5955555, 1999. (d) Sommazzi, A.; Milani, B.; Proto, A.; Corso, G.; Mestroni, G.; Masi, F. (Enichem) WO0110875, 2001. (e) de Boer, E. J. M.; Deuling, H. H.; van der Heijden, H.; Meijboom, N.; van Oort, A. B. (Shell) W00158874, 2001.

(10) (a) Sun, W. -H.; Tang, X.; Gao, T.; Wu, B.; Zhang, W.; Ma, H. *Organometallics* **2004**, *23*, 5037. (b) Su, B.-Y.; Zhao, J.-S. *Polyhedron* **2006**, *25*, 3289.

(11) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523.

Scheme 1^a

^a Reagents and conditions: (i) ArNH_2 , EtOH, H^+ ; (ii) 2AlMe_3 , 100 °C, 12 h, toluene; (iii) H_2O , room temperature; (iv) FeCl_2 , 90 °C, 15 min, *n*-BuOH.

being isolated from alkyl migration to not only the imine carbon but also the pyridine C2 and C4 positions.^{12–14}

In this note we are concerned with employing trimethylaluminum to mediate the formation of 2-imine-6-(methyl alcohol)-pyridine (**L2**, Chart 1) from **L1**. In addition, full characterization of the resultant iron(II) halide complexes is reported and their application as precatalysts for ethylene oligomerization/polymerization probed.

Our entry point into this work is the 2-acetyl-6-iminopyridines, 2-($\text{O}=\text{CMe}$)-6-($\text{ArN}=\text{CMe}$) $\text{C}_5\text{H}_3\text{N}$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, **L1a**; $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, **L1b**), which are readily accessible by the condensation reaction of equimolar amounts of the corresponding aniline.^{1b,6b,9,15} On treatment with Me_3Al (2 equiv), both **L1a** and **L1b** undergo alkylation of the ketone moiety of the ligand backbone and concomitant adduct formation to afford the air-sensitive bimetallic 2-imino-6-methoxydepyridine complexes [2-($\text{ArN}=\text{CMe}$)-6- $\{(\text{Me}_3\text{Al})\text{OCMe}_2\}\text{C}_5\text{H}_3\text{N}\}]\text{AlMe}_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, **1a**; $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, **1b**) in good yield (>70%) (Scheme 1). Complexes **1a** and **1b** have been both characterized by ^1H NMR spectroscopy and give satisfactory microanalytical data (see Experimental Section). In addition, a single-crystal X-ray diffraction study was performed on **1a**.

Green-yellow crystals of **1a** suitable for a structure determination were grown by the slow cooling of a saturated hot acetonitrile solution. The complex crystallizes with two independent molecules (A and B) in the asymmetric unit with only minor variations apparent between molecules. A perspective view of molecule A in **1a** is depicted in Figure 1, along with selected bond distances and angles. The following discussion refers to one of the independent molecules (A), the values in square brackets being for the second independent molecule (B); for a

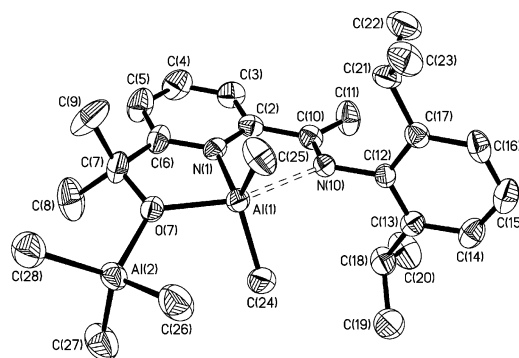


Figure 1. Molecular structure of one (A) of the two independent molecules present in the crystals of **1a** (50% probability ellipsoids); hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)–O(7) 1.907(3), Al(1)–N(1) 1.994(4), Al(1)–C(24) 1.952(5), Al(1)–C(25) 1.959(5), Al(1)···N(10) 2.427(4), Al(2)–O(7) 1.917(3), Al(2)–C(26) 1.984(5), Al(2)–C(27) 1.983(5), Al(2)–C(28) 1.986(5), C(7)–O(7) 1.436(5), C(10)–N(10) 1.288(5), C(24)–Al(1)–C(25) 125.2(3), O(7)–Al(1)···N(10) 152.82(13), O(7)–C(7)–C(8) 110.2(4), O(7)–C(7)–C(9) 109.4(4), O(7)–Al(2)–C(26) 106.2(2), C(26)–Al(2)–C(27) 112.2(3), C(27)–Al(2)–C(28) 111.4(2).

full structural description see the Supporting Information. The geometry at Al(1) is best described as trigonal pyramidal, the metal lying ca. 0.19 Å [0.20 Å] out of the basal {N(1),C(24),C(25)} plane in the direction of the apical atom O(7). The imino nitrogen N(10) approaches the opposite face of the basal plane at a distance of 2.427(4) Å [2.472(4) Å], a value significantly shorter than that of 2.575(4) Å seen in the closely related imino-amide-pyridine species [2-($\text{ArN}=\text{CH}$)-6-(ArNCHMe) $\text{C}_5\text{H}_3\text{N}$]- AlMe_2 ($\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$).¹¹ The Al–N(1)_{pyridine} distance of 1.994(4) Å [1.978(3) Å] is significantly shorter than that seen in the imino-amide-pyridine complex¹¹ [2.029(4) Å], probably reflecting the difference between the 6-(OCMe_2) unit here in **1a** and the corresponding 6-(ArNCHMe) moiety in the literature species. The Al–O(7) separations do not differ significantly, being 1.907(3) Å [1.915(3) Å] to Al(1) and 1.917(3) Å [1.911(3) Å] to Al(2); the geometry at O(7) is trigonal planar. The geometry at Al(2) is only slightly distorted tetrahedral, with angles in the range 106.2(2)–112.2(3)° [105.3(2)–114.9(3)°].

In the ^1H NMR spectra of **1a** and **1b**, the $\text{Me}_2\text{C}=\text{O}$ protons are seen as singlets at ca. δ 1.82, while the aluminum-methyl resonances are observed more upfield as two distinct singlets (**1a** δ –0.67, –0.83; **1b** δ –0.70, –0.83). The presence of inequivalent aluminum-methyl environments is further supported in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1b** with two resonances at δ –3.2 and –4.5 for the Al–Me carbon atoms. While the FAB mass spectrum of **1b** gave little information, the spectrum for **1a** displayed a peak corresponding to the molecular ion; as expected, this peak is short-lived and decays over a period of minutes.

Hydrolysis of **1a** and **1b** smoothly generates the protonated ligands 2-($\text{ArN}=\text{CMe}$)-6- $\{(\text{HO})\text{CMe}_2\}\text{C}_5\text{H}_3\text{N}$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, **L2a**; $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, **L2b**) as pale yellow solids in good yield (>70%) (Scheme 1). Characterization by ^1H and ^{13}C NMR and IR spectroscopy and EI mass spectrometry supports the formulations (see Experimental Section). Reaction of **L2** with FeCl_2 in *n*-BuOH at elevated temperature gives the high-spin *N,N,O*-chelate iron complexes [2-($\text{ArN}=\text{CMe}$)-6- $\{(\text{HO})\text{CMe}_2\}\text{C}_5\text{H}_3\text{N}\}]\text{FeCl}_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, **2a**; $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, **2b**), in high (**2a**, ca. 77%) and moderate (**2b**, ca. 32%) isolated yield (Scheme 1). Complexes **2a** and **2b** have been characterized by FAB mass spectrometry and magnetic susceptibility measurements and give satisfactory microanalyti-

(12) Milione, S.; Cavallo, G.; Tedesco, C.; Grassi, A. *J. Chem. Soc., Dalton Trans.* **2002**, 1839.

(13) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *C. R. Chim.* **2004**, 7, 865. (b) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *Organometallics* **2006**, 25, 1036.

(14) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442.

(15) Small, B. L.; Carney, M. J.; Holman, D. M.; O'Rourke, C. E. Halfen, J. A. *Macromolecules* **2004**, 37, 4375.

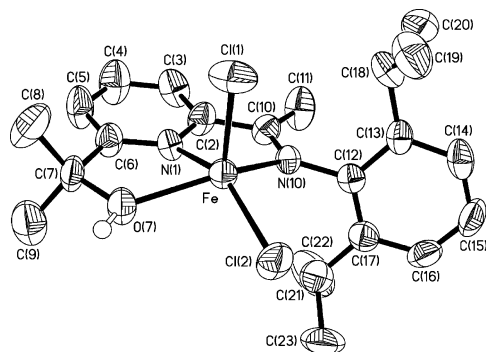


Figure 2. Molecular structure of **2a** (50% probability ellipsoids); hydrogen atoms (apart from H7) omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–O(7) 2.173(6), Fe–N(1) 2.096(7), Fe–N(10) 2.201(7), Fe–Cl(1) 2.266(3), Fe–Cl(2) 2.304(2), C(7)–O(7) 1.458(10), C(10)–N(10) 1.293(10), O(7)–Fe–N(10) 139.4(2), N(1)–Fe–Cl(1) 101.8(2), N(1)–Fe–Cl(2) 148.2(2), Cl(1)–Fe–Cl(2) 109.84(12), C(8)–C(7)–C(9) 110.2(9), N(10)–C(10)–C(11) 125.2(8).

cal data (see Experimental Section). In addition, **2a** has been the subject of a single-crystal X-ray diffraction study.

Dark blue crystals of the iron complex **2a** were grown from a saturated solution of acetonitrile on prolonged standing at ambient temperature. A perspective view of **2a** is shown in Figure 2 along with selected bond distances and angles (see Supporting Information for a full structural discussion). The geometry at the iron center is distorted square pyramidal with Cl(1) occupying the apical site; the basal atoms Cl(2), N(1), O(7), and N(10) are coplanar to within 0.01 Å with the metal lying ca. 0.59 Å out of this plane in the direction of the apical atom. The Fe–imine bond length of 2.201(7) Å is slightly shorter than that typically seen in related species,^{1,2} possibly as a consequence of the relatively long distance to the neutral donor O(7) [2.173(6) Å]; the Fe–pyridine separation is unexceptional.^{1,2,4–7}

For both **2a** and **2b**, molecular ions along with peaks corresponding to the loss of a chloride ligand are evident in their respective FAB mass spectra. In their IR spectra the $\nu(\text{C}=\text{N})$ absorption bands are seen at ca. 1593 cm^{-1} and shifted (by ca. 28 cm^{-1}) to a lower wavenumber in comparison with that seen in the corresponding free ligand (**L2**). The magnetic susceptibility measurements for **2a** and **2b** reveal magnetic moments of ca. 4.62 μ_{B} (Evans balance at ambient temperature), which are consistent with high-spin configurations possessing four unpaired electrons ($S = 2$).

The results of ethylene polymerization tests at 1 bar with precatalysts **2a** and **2b** with methylaluminoxane (MAO) as activator are collected in Table 1 (runs 1 and 2). The tests were carried out in a Schlenk flask with toluene as the solvent. The results show that both the new 2-imino-6-(methylalcohol)pyridine iron complexes on treatment with MAO are active ethylene polymerization catalysts. The highest activity of 276 $\text{g mmol}^{-1} \text{h}^{-1} \text{bar}^{-1}$ is obtained with **2b**, which under similar conditions is significantly less than that observed for the closest related bis(imino)pyridine catalyst [2,6-((2,4,6-Me₃C₆H₂)N=CMe)₂C₅H₃N]FeCl₂/MAO,^{1,2} while in a similar range to the imino-amine-pyridine catalyst [2-((2,6-*i*-Pr₂C₆H₃)N=CMe)-6-((2,6-*i*-Pr₂C₆H₃)NHCMe₂)C₅H₃N]FeCl₂/MAO.⁶ The difference in activity between **2a** and **2b** mirrors the trend seen for 2,6-diisopropylphenyl versus mesityl bis(imino)pyridine catalysts.^{1–3}

Inspection of the molecular weight data reveals very broad molecular weight distributions for the polyethylene obtained using **2a** and **2b** with M_w values comparable to those obtained with [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N]FeCl₂/MAO and [2,6-((2,4,6-Me₃C₆H₂)N=CMe)₂C₅H₃N]FeCl₂/MAO, respec-

tively.^{1,2} Indeed a pronounced bimodal distribution is seen with **2a**/MAO, a feature that is common for bis(imino)pyridine iron precatalysts in the presence of large excesses of MAO.^{1–3} It is probable that as with precedents in this area,^{1,2} the lower molecular weight peak corresponds ($M_{\text{pk}} = 1340$) to an almost fully saturated material. This is supported by the ¹H NMR spectra of the oligomeric fractions obtained during both runs, which show significantly enhanced levels of methyl chain ends (with regard to the vinylic ends). Furthermore, analysis of the vinylic region of the spectra reveals the presence of greater than 99% α -olefins. It is apparent that these systems, as with bis(imino)pyridine iron catalysts,^{2b} can facilitate chain-transfer reactions by both β -H elimination and chain transfer to aluminum.

In conclusion, we have successfully employed trimethylaluminum to promote the formation of a new family of tridentate 2-arylimino-6-(methylalcohol)pyridine *N,N,O*-ligands (**L2**), which can be readily complexed with iron(II) chloride. Moderate activities in ethylene polymerization are displayed for the resultant catalysts with values significantly lower than in related bis(arylimino)pyridine iron systems.

Experimental Section

General Techniques and Materials. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent¹⁶ and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College, London Metropolitan University, and Medac Ltd. GPC data were recorded at Rapra Technology using a Polymer Labs/Varian GPC220 instrument [with PLgel guard + 2 $\times$ mixed bed-B columns (30 cm, 10 μm)] at 160 °C in 1,2,4-trichlorobenzene with a refractive index detector. NMR spectra were recorded on a Bruker spectrometer at 250 MHz (¹H) and 62.9 MHz (¹³C) at 293 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent; coupling constants are quoted in Hz. IR spectra (Nujol mulls) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. The EI (electron impact) and FAB (fast atom bombardment) mass spectra were recorded using a Kratos Concept spectrometer with NBA as the matrix. Magnetic susceptibility studies were performed using an Evans balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods,¹⁷ and corrections for underlying diamagnetism were applied to data.¹⁸

Iron dichloride, trimethylaluminum (2.0 M in toluene), and methylaluminoxane (10% solution in toluene) were purchased from Aldrich Chemical Co. 2-Acetyl-6-[1-((2,6-diisopropylphenyl)imino)ethyl]pyridine (**L1a**) and 2-acetyl-6-[1-((2,4,6-trimethylphenyl)imino)ethyl]pyridine (**L1b**) were prepared using previously reported procedures.⁹ CP grade ethylene (99.9%) was purchased from BOC and used without further purification. All other chemicals were obtained commercially and used as received unless stated otherwise.

Synthesis of [2-((2,6-*i*-Pr₂C₆H₃)N=CMe)-6-((Me₃Al)OCMe₂)-C₅H₃N]AlMe₂ (1a**).** Trimethylaluminum (1.24 mL, 2.48 mmol) was added dropwise to a solution of **L1a** (0.40 g, 1.24 mmol) in toluene (40 mL) and the solution heated to reflux overnight. The volatiles were removed under reduced pressure, and the product was extracted into acetonitrile. Filtration followed by concentration and prolonged standing at room temperature afforded green-yellow blocks of **1a**. Yield: 0.46 g, 79%. ¹H NMR (CDCl₃, 293 K): δ 8.30 (t, 1H, ²J_{HH} = 7.9 Hz, py-H), 8.01 (dd, 1H, ²J_{HH} = 7.8 Hz,

(16) Armarego W. L. F.; Perrin, D. D. In *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann, 1996.

(17) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

(18) (a) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, 29, 203. (b) *Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1990; p E134.

Table 1. Results of Ethylene Polymerization Runs Using Precatalysts **2a** and **2b**^a

run	precatalyst	mass of polymer (g)	mass of oligomer (g)	activity (g mmol ⁻¹ h ⁻¹ bar ⁻¹)	<i>M_n</i> ^b	<i>M_w</i> ^b	<i>M_w/M_n</i> ^b	<i>M_p</i> ^b	
								peak 1 (%)	peak 2 (%)
1	2a	1.699	0.037	170	2050	13 4000	66	1340 (59)	81 400 (41)
2	2b	2.755	0.064	276	2820	77 000	27	37 400 (100)	

^a Toluene solvent, 1 bar of ethylene, reaction time 1 h, 25 °C, 500 equiv of MAO as activator. ^bGPC performed in 1,2,4-trichlorobenzene at 160 °C.

³*J*_{HH} = 0.8 Hz, py-H), 7.75 (d, 1H, ²*J*_{HH} = 8.2 Hz, py-H), 7.3 – 7.2 (m, 3H, Ar-H), 2.65 (sept, 2H, ²*J*_{HH} = 7.0 Hz, CHMe₂), 2.31 (s, 3H, MeC=N), 1.83 (s, 6H, Me₂C-O), 1.26 (d, 6H, ²*J*_{HH} = 6.3 Hz, CHMe₂), 1.01 (d, 6H, ²*J*_{HH} = 6.3 Hz, CHMe₂), –0.67 (s, 6H, Me₂Al), –0.83 (s, 9H, Me₃Al). MS (FAB): *m/z* 467 [M + H]⁺. Anal. Calcd for C₂₇H₄₄N₂OAl₂ (sample dried for 12 h in *vacuo*): C, 69.49; H, 9.51; N, 6.01. Found: C, 69.40; H, 9.47; N, 6.13.

Synthesis of [2-{(2,4,6-Me₃C₆H₂)N=CMe}-6-{(Me₃Al)OCMe₂}-C₅H₃N]AlMe₂ (1b**).** By using the same procedure described for **1a**, compound **1b** was obtained as a green-yellow powder. Yield: 0.41 g, 75%. ¹H NMR (CDCl₃, 293 K): δ 8.28 (t, 1H, ²*J*_{HH} = 8.8 Hz, py-H), 7.98 (d, 1H, ²*J*_{HH} = 7.8 Hz, py-H), 7.74 (d, 1H, ²*J*_{HH} = 8.6 Hz, py-H), 6.92 (s, 2H, Ar-H), 2.30 (s, 3H, MeC=N), 2.22 (s, 3H, *p*-Ar-Me), 1.99 (s, 6H, *o*-Ar-Me), 1.82 (s, 6H, Me₂C-O), –0.70 (s, 6H, Me₂Al), –0.83 (s, 9H, Me₃Al). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 171.4 (Me₂C-O), 163.7 (MeC=N), 147.7, 143.5, 142.2, 138.3, 135.4, 129.4, 128.6, 127.6, 125.7, 123.9, 123.2 (Ar/py), 31.1, 21.9, 21.1, 18.9, 16.9 (Me), –3.2, –4.5 (Al–Me). MS (FAB): 296 [M + H – Al₂Me₅]⁺. Anal. Calcd for C₂₄H₃₈N₂OAl₂: C, 67.92; H, 8.96; N, 6.60. Found: C, 67.59; H, 8.71; N, 6.39.

Synthesis of 2-{(2,6-*i*-Pr₂C₆H₃)N=CMe}-6-{(HO)CMe₂}-C₅H₃N (L2a**).** Degassed water (20 mL) was added to a stirred solution of **1a** (0.45 g, 0.97 mmol) in diethyl ether (30 mL). After stirring for 30 min the aqueous layer was separated and extracted with diethyl ether (2 × 30 mL). The combined organic extracts were dried over MgSO₄ and filtered, and the volatiles were removed under reduced pressure to give **L2a** as a yellow powder. Yield: 0.26 g, 81%. ¹H NMR (CDCl₃, 293 K): δ 8.29 (dd, 1H, ²*J*_{HH} = 7.8 Hz, ³*J*_{HH} = 0.8 Hz, py-H), 7.84 (t, 1H, ²*J*_{HH} = 7.8 Hz, py-H), 7.47 (dd, 1H, ²*J*_{HH} = 7.9 Hz, ³*J*_{HH} = 0.9 Hz, py-H), 7.2–7.1 (m, 3H, Ar-H), 5.24 (s, br, 1H, OH), 2.74 (sept, ²*J*_{HH} = 6.9 Hz, CHMe₂), 2.24 (s, 3H, MeC=N), 1.61 (s, 6H, C(OH)Me₂), 1.15 (d, 12H, ²*J*_{HH} = 6.9 Hz, CHMe₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 166.4 (C=N), 164.9, 154.0, 146.3, 137.7, 135.7, 123.7, 123.0, 119.9, 119.4 (Ar/py), 30.8, 28.3, 23.2, 17.3 (Me). IR (Nujol mull, cm⁻¹): ν(O–H) 3599, ν(C=N) 1622. MS (EI): *m/z* 338 [M]⁺. Anal. Calcd for C₂₂H₃₀N₂O: C, 78.11; H, 8.88; N, 8.28. Found: C, 78.41; H, 9.02; N, 8.11.

Synthesis of 2-{(2,4,6-Me₃C₆H₂)N=CMe}-6-{(HO)CMe₂}-C₅H₃N (L2b**).** By using the same procedure described for **L2a**, compound **L2b** was obtained as a yellow powder. Yield: 0.24 g, 74%. ¹H NMR (CD₂Cl₂, 293 K): δ 8.20 (dd, 1H, ³*J*_{HH} = 7.9 Hz, ⁴*J*_{HH} = 0.5 Hz, py-H), 7.76 (app. t, 1H, ³*J*_{HH} = 7.9 Hz, py-H), 7.38 (dd, 1H, ³*J*_{HH} = 7.9 Hz, ⁴*J*_{HH} = 0.5 Hz, py-H), 6.81 (s, 2H, Ar-H), 6.81 (s, 2H, Ar-H), 5.14 (s, br, 1H, OH), 2.21 (s, 3H, *m*-Ar-Me), 2.12 (s, 3H, MeC=N), 1.92 (s, 3H, *o*-Ar-Me), 1.52 (s, 6H, (OH)CMe₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 166.4 (C=N), 164.5, 154.3, 146.1, 137.8, 135.8, 123.6, 123.1, 120.0, 119.5 (Ar/py), 30.8, 28.3, 18.1, 16.3 (Me). IR (Nujol mull, cm⁻¹): ν(O–H) 3597, ν(C=N) 1620. MS (EI): *m/z* 296 [M]⁺. Anal. Calcd for C₁₉H₂₄N₂O: C, 77.03; H, 8.11; N, 9.46. Found: C, 77.19; H, 8.33; N, 9.34.

Synthesis of [2-{(2,6-*i*-Pr₂C₆H₃)N=CMe}-6-{(HO)CMe₂}-C₅H₃N]FeCl₂ (2a**).** FeCl₂ (0.050 g, 0.39 mmol) was dissolved in *n*-BuOH (10 mL) at 90 °C, and **L2a** was introduced (0.132 g, 0.39 mmol) to yield a blue solution. After being stirred at 90 °C for 15 min, the reaction was allowed to cool to room temperature. Hexane (30 mL) was added to precipitate the product, which was subsequently washed with hexane (3 × 10 mL), filtered, and dried to afford **2a** as a pale blue solid. Yield: 1.06 g, 77%. IR (cm⁻¹): ν(C=N) 1595. MS (EI): *m/z* 465 [M]⁺, 430 [M – Cl]⁺. Anal. Calcd

for C₂₂H₃₀Cl₂N₂OFe: C, 56.77; H, 6.45; N, 6.02. Found: C, 56.91; H, 6.51; N, 5.91. *μ*_{eff}: 4.67 *μ*_B.

Synthesis of [2-{(2,4,6-Me₃C₆H₂)N=CMe}-6-{(HO)CMe₂}-C₅H₃N]FeCl₂ (2b**).** By using the same procedure described for **2a**, compound **2b** was obtained as a blue powder. Yield: 0.37 g, 32%. IR (cm⁻¹): ν(C=N) 1590. MS (FAB): *m/z* 423 [M⁺], 388 [M⁺ – Cl]. Anal. Calcd for C₁₉H₂₄Cl₂N₂OFe: C, 53.90; H, 5.67; N, 6.62. Found: C, 54.11; H, 5.81; N, 6.41. *μ*_{eff} 4.57 *μ*_B.

Ethylene Polymerization/Oligomerization Evaluation. An oven-dried 200 mL Schlenk vessel equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The vessel was charged with the precatalyst (0.01 mmol) and dissolved or suspended in toluene (40 mL). MAO (5.0 mmol, 500 equiv) was introduced, and the reaction mixture left to stir for 5 min. The vessel was purged with ethylene, and the contents were magnetically stirred under 1 bar of ethylene pressure at room temperature for the duration of the test. After 1 h, the test was terminated by the addition of dilute aqueous hydrogen chloride (5 mL) and the polymer collected, washed with MeOH/H⁺ and then water, and dried in a vacuum oven at 40 °C overnight. The yield of the polymer was recorded and the activity calculated (g PE mmol⁻¹ h⁻¹ bar⁻¹) for the 1 h period. The organic soluble phase was separated, dried over magnesium sulfate, and filtered, the solvent was removed under reduced pressure, and the residue was analyzed by ¹H NMR spectroscopy.

X-ray Crystal Structure Determinations. For **1a**. Diffraction data were collected at 183 K using Cu Kα radiation (λ = 1.54178 Å). Solution and refinement of the structure were carried out using the SHELXTL program system.¹⁹ For **1a**: C₂₇H₄₄N₂OAl₂·0.5MeCN, *M* = 487.13 g/mol; monoclinic; space group *P*2(1)/*n*; *a* = 15.5098(9) Å, *b* = 17.722(2) Å, *c* = 22.2233(9) Å, β = 99.838(4)°; *V* = 6018.7(9) Å³; *Z* = 8; *D*(calcd) = 1.075 g/cm³; absorption coefficient = 1.027 mm⁻¹; *F*(000) = 2120. Crystal size 0.80 × 0.23 × 0.06 mm. Reflections collected = 9304 and 8930 independent reflections with *R*(int) = 0.0484. Restraints/parameters = 0/604; goodness-of-fit on *F*² = 1.035; *R*(*I* > 2σ(*I*)) = 0.0652, *wR*₂ = 0.1320; *R*(all data) = 0.1296, *wR*₂ = 0.1637. Figure 1 shows an ORTEP diagram and gives selected bond lengths and angles.

For **2a**. Diffraction data were collected at room temperature using Mo Kα radiation (λ = 0.71073 Å). Solution and refinement of the structure were carried out using the SHELXTL program system.¹⁹ For **2a**: C₂₂H₃₀N₂OCl₂Fe·MeCN, *M* = 506.28 g/mol; monoclinic; space group *P*2(1)/*n*; *a* = 12.481(2) Å, *b* = 12.229(2) Å, *c* = 18.486(3) Å, β = 109.22(2)°; *V* = 2664.2(8) Å³; *Z* = 4; *D*(calcd) = 1.262 g/cm³; absorption coefficient = 0.786 mm⁻¹; *F*(000) = 1064. Crystal size 0.30 × 0.15 × 0.13 mm. Reflections collected = 3662 and 3476 independent reflections with *R*(int) = 0.0582. Restraints/parameters = 1/284; goodness-of-fit on *F*² = 0.990; *R*(*I* > 2σ(*I*)) = 0.0698, *wR*₂ = 0.1278; *R*(all data) = 0.1506, *wR*₂ = 0.1690. Figure 2 shows an ORTEP diagram and gives selected bond lengths and angles.

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(19) SHELXTL PC, version 5.03.; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994. SHELXTL PC, version 5.; Bruker AXS: Madison, WI, 1997.

Supporting Information Available: Tables giving detailed crystallographic data, atomic positional parameters, and complete bond lengths and angles for **1a** and **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>. These data

have also been deposited at the Cambridge Crystallographic Data Centre (reference numbers: 643859 and 643860).

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