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Reactivity of Chromium Complexes of a Bis(imino)pyridine Ligand: Highly Active Ethylene Polymerization Catalysts Carrying the Metal in a Formally Low Oxidation State

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A divalent chromium complex of bis(imino)pyridine, {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCl$_2$ (**1**), was prepared with the aim of studying its reactivity with alkylating agents. Upon treatment with MeLi, the metal center was both reduced and alkylated, forming {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}-CrMe(μ-Me)Li(THF)$_3$ (**2**). Complex **1** is also conveniently reduced with either NaH or metallic sodium to give the new species {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCl (**3**). Despite the appearance of the metal center in a rare monovalent oxidation state, the square-planar geometry of the Cr atom suggests that the metal is most likely divalent, with the electron housed in the ligand π^* orbital. When it is activated with MAO, complex **3** is a very and even more active catalyst for the polymerization of ethylene than either the −CrCl$_2$ or −CrCl$_3$ derivative of this ligand system and yet produces polymers with similar properties. Subsequent reactivity studies of complex **3** have allowed the isolation of several products. Reaction with either LiCH$_2$Si(CH$_3$)$_3$ or MeLi resulted in deprotonation of one of the methyl groups on the ligand backbone, forming {2-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]-6-[2,6-(i-Pr)$_2$PhNC═CH$_2$](C$_5$H$_3$N)}Cr(THF) (**4**) and {2-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]-6-[2,6-(i-Pr)$_2$PhNC═CH$_2$](C$_5$H$_3$N)}Cr(μ-Me)Li(THF)$_3$ (**5**), respectively. On the other hand, alkylation with AlMe$_3$ allowed the successful preparation of another organochromium species, {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCH$_3$ (**7**), along with small amounts of the byproduct {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}Cr(μ-Cl)$_2$Al(CH$_3$)$_2$ (**6**). Interestingly, complex **7**, which also has the deceiving connectivity of a monovalent species, displays an even greater activity for ethylene polymerization than all of the other species reported herein, again producing a polymer with nearly identical characteristics. Activation with IBAO revealed a deactivation pathway similar to that observed with the FeCl$_2$ system. In this case, the stronger reducing power of IBAO resulted in the usual reduction not only of the ligand backbone but also of the metal center. As a result of the metal reduction, partial transmetalation of the ligand system occurred, with formation of [η^4-{2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$-(C$_5$H$_3$N)}Al$_2$(i-Bu)$_3$(μ-Cl)]Cr-(η^6-C$_7$H$_8$) (**8**). By being catalytically inactive, the partly transmetalated **8** suggests that ligand demetalation is a possible catalyst deactivation pathway.

Introduction

Chromium is the key element in the silica-supported Phillips[1] and Union Carbide[2] catalytic systems commercially used for the polymerization of olefins. The importance of these catalysts has provided a compelling rationale for the development of homogeneous Cr(III) catalysts supported by a variety of ligands, including both cyclopentadienyl-based[3] and non-cyclopentadienyl-based systems.[4−10] These catalyst precursors are usually well-defined, and yet the metal oxidation state of the catalytically active species remains debatable, the most commonly accepted being either Cr(III) or Cr(II).

After the initial discovery by Brookhart and Gibson that bis(imino)pyridine ligands enable high activity when coordinated to unconventional Ziegler−Natta metals,[11] extensive investigations were undertaken to unveil the properties of this fascinating ligand system.[12−29] Attempts to isolate possible active species gradually revealed the direct involvement of the ligand in a variety of transformations, including attack at the imino C atom[14,16] or at any position of the pyridine ring,[12,13b,14,16c,17] single[17bc,18] or double deprotonation[13b,14,19,20] of the imino methyl

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(1) Hogan, J. P.; Banks, R. L. (Phillips Petroleum Co.) U.S. Patent 2,825,721, 1958.

(2) (a) Karapinka, G. L. (Union Carbide Corp.) Ger. Offen. D. E. 1,808,388, 1970. (b) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2621. (c) Karapinka, G. L. (Union Carbide Corp.) U.S. Patent 3,709,853, 1973.

(3) (a) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (b) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (c) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284. (d) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473. (e) Theopold, K. H. *CHEMTECH* **1997**, *27*, 26. (f) Emrich, R.; Heinemann, O.; Jolly, P. W.; Krüger, C.; Verhownik, G. P. J. *Organometallics* **1997**, *16*, 1511. (g) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, 15. (h) Döhring, A.; Göhre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhownik, G. P. J. *Organometallics* **2000**, *19*, 388. (i) Jensen, V. R.; Angermund, K.; Jolly, P. W.; Børve, K. J. *Organometallics* **2000**, *19*, 403. (j) Döhring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. *Organometallics* **2001**, *20*, 2234. (k) Enders, M.; Fernández, P.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 5005. (l) Döhring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag: Berlin, 2001; p 127.

(4) (a) Coles, M. P.; Gibson, V. C. *Polym. Bull.* **1994**, *33*, 529. (b) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Little, I. R.; Marshall, E. L.; Ribeiro da Costa, M. H.; Mastroianni, S. *J. Organomet. Chem.* **1999**, *591*, 78.

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protons, and dimerization through either the ring meta C atoms[13b,16c] or the imino methyl groups.[13b,14,15,21] Perhaps most unusual was the possibility of storing up to three electrons in its delocalized π system.[18] This behavior allows the preparation of complexes in which the metal deceivingly appears in unusual low oxidation states but where in reality the frontier orbitals are ligand-centered molecular orbitals.[21] Therefore, the low valency of the metal in these complexes should be regarded as purely formal. Remarkably, however, these species retain the high reactivity expected for a low-valent compound.[21,22−26] The recurrence of dinitrogen fixation among these derivatives[24,25] is the most compelling evidence of this behavior.

The ability of this ligand system to undergo facile electron-transfer processes is perhaps the key to understanding why reduction of the metal center occurs so readily upon alkylation[12−14,26−28] or activation with Al alkyls[13b,28a,b,29] without apparently affecting the catalytic activity of these derivatives. As mentioned above, the metal-to-ligand electron transfer does not necessarily imply quenching of the chemical reactivity. The "low-valent" Fe[26] and Co[28] complexes maintain the same high activity and polymer quality as the divalent precursors, suggesting the formation of an even lower valent electron-rich catalytically active species. An exception to this trend involves vanadium,[12] whose facile reduction upon activation provides a deactivation pathway.

When tested in our laboratory, the Cr(III) bis(imino)pyridine complex displayed, upon activation with MAO at room temperature and under ethylene at atmospheric pressure, disappointingly low catalytic activity.[13b] On the other hand, at higher temperatures and increased pressures of ethylene, Esteruelas[9] and Small[10] observed that the Cr(III) catalyst displays much higher, but varying, degrees of activity. Onthe basis of the results obtained with the Co and Fe analogues, it is possible that activation of the precursor with MAO involves an initial reduction to Cr(II). The Cr(II) derivative was also found to be catalytically active, initially as a polypropylene catalyst by Dow,[30] but also for ethylene polymerization by Small[10] and Esteruelas.[9] The observation by Esteruelas suggested that activation of the Cr(III) precursor does not involve reduction to Cr(II). However, by using UV−vis and analysis of the resulting polymers, Small et al. concluded that the Cr(II) and Cr(III) precursors generate the same active species after reaction with MAO. Attempts in our laboratory to elucidate the organometallic chemistry of the Cr(III) precursor with BzMgCl and AlMe$_3$ did indeed show a facile reduction toward divalent complexes.[13b] While the alkylation with BzMgCl led to a slew of transformations, the reaction with AlMe$_3$ instead resulted in immediate reduction of the metal center. Both products were inactive, possibly suggesting that, similar to the case of vanadium, the reduction toward the divalent state is a catalyst deactivation pathway. However, the reactions were not carried out under polymerization conditions (e.g., alkylaluminum reagents) and it should be noted that the presence of ethylene may hinder reduction or promote different transformations.

Herein, we describe the reduction of the divalent 2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N) CrCl$_2$ catalyst precursor, affording reduced chromium species as might be present in the catalytic cycle and which display very high catalytic activity for ethylene polymerization.

Experimental Section

All operations were performed either under a nitrogen atmosphere using standard Schlenk techniques or in a purified nitrogen-filled

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(5) (a) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651. (b) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541. (c) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895. (d) McAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, A. I.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952.

(6) (a) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 827. (b) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2000**, 1969. (c) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038.

(7) (a) Köhn, R. D.; Haufe, M.; Mihan, S.; Lilge, D. *Chem. Commun.* **2000**, 1927. (b) Köhn, R. D.; Haufe, M.; Kociok-Köhn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4337. (c) Köhn, R. D.; Seifert, G.; Kociok-Köhn, G.; Mihan, S.; Lilge, D.; Mass, H. In *Organometallic Catalysts and Olefin Polymerization*; Blom, R., Follestad, A,, Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag, Berlin, 2001; p 147.

(8) Ikeda, H.; Manoi, T.; Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2002**, *648*, 226.

(9) Esteruelas, M. A.; López, A. M.; Méndez, L.; Oliván, M.; Oñate, E. *Organometallics* **2003**, *22*, 395.

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

(11) (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) 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.

(12) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q. *J. Am. Chem. Soc.* **1999**, *121*, 9318.

(13) (a) Reardon, D.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 786. (b) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2002**, *124*, 12268.

(14) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 13019.

(15) Scott, J.; Gambarotta, S.; Korobkov, I. *Can. J. Chem.* **2005**, *83*, 279.

(16) (a) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (b) Milione, S.; Cavallo, C.; Tedesco, C.; Grassi, A. *Dalton Trans.* **2002**, 1839. (c) Knijnenburg, Q.; Smits, J. M. M.; Budzelaar, P. H. M. *C. R. Chim.* **2004**, *7*, 865.

(17) (a) Clentsmith, G. K. B.; Gibson, V. C.; Hitchcock, P. B.; Kimberley, B. S.; Rees, C. W. *Chem. Commun.* **2002**, 1498. (b) Khorobkov, I.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2002**, *21*, 3088. (c) Blackmore, I. J.; Gibson, V. C.; Hitchcock, P. B.; Rees, C. W.; Williams, D. J.; White, A. J. P. *J. Am. Chem. Soc.* **2005**, *127*, 6012.

(18) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3873.

(19) Sugiyama, H.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R.; Thiele, S. K.-H. *Organometallics* **2004**, *23*, 5054.

(20) Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2006**, *45*, 2.

(21) Sugiyama, H.; Korobkov, I.; Gambarotta, S.; Möller, A.; Budzelaar, P. H. M. *Inorg. Chem.* **2004**, *43*, 5771.

(22) (a) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936. (b) Budzelaar, P. H. M.; de Bruin, B.; Gal, A. W.; Wieghardt, K.; van Lenthe, J. H. *Inorg. Chem.* **2001**, *40*, 4649.

(23) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.

(24) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.

(25) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Inorg. Chem.* **2005**, *44*, 1187.

(26) Scott, J.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Organometallics* **2005**, *24*, 6298.

(27) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, 3406.

(28) (a) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. H. M.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4719. (b) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252. (c) Steffen, W.; Blömker, T.; Kleigrewe, N.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2004**, 1188. (d) Kleigrewe, 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.

(29) Scott, J.; Gambarotta, S.; Korobkov, I.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **2005**, *127*, 17204.

(30) Devore, D.; Feng, S. S.; Frazier, K. A.; Patton, J. T. (Dow Chemical) World Pat. WO0069923, 2000.

drybox. The THF complexes of $CrCl_3$ and $CrCl_2$ were prepared according to the standard procedure. The ligand 2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N),[11,31] the complex {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCl$_3$,[13b] LiCH$_2$Si(CH$_3$)$_3$,[32] and {2-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]-6-[2,6-(i-Pr)$_2$PhNC=CH$_2$](C$_5$H$_3$N)}Cr(THF) (**4**)[33] were prepared according to published procedures. Solutions of 1.6 M MeLi in ether, 2 M AlMe$_3$ in toluene, and 10 wt % IBAO in toluene (purchased from Aldrich) and 10 wt % of MAO in toluene (purchased from Chemtura) were used as received. Infrared spectra were recorded on a Mattson 9000 and Nicolet 750-Magna FT-IR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes, and the measurements were carried out at room temperature with a Gouy balance (Johnson Matthey). Magnetic moments were calculated following standard methods, and corrections for underlying diamagnetism were applied to the data. NMR spectra were recorded with a Varian AMX-500 spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Preparation of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCl$_2$·0.75THF (1). A suspension of 2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$-(C$_5$H$_3$N) (0.90 g, 1.87 mmol) and CrCl$_2$(THF)$_2$ (0.50 g, 1.87 mmol) was refluxed in toluene (150 mL) overnight. The resulting purple solid was isolated by decanting the solution and washing with hexane. Excess fresh THF (200 mL) was added and the suspension boiled, followed by a hot filtration to obtain a clear purple solution. The purple solution was slowly cooled to room temperature, upon which time small purple crystals of **1** formed (1.07 g, 1.77 mmol, 95%). Anal. Calcd (found after drying) for $C_{33}H_{43}N_3Cl_2Cr$: C, 65.55 (65.48); H, 7.17 (7.12); N, 6.95 (6.91). IR (Nujol mull, cm^{-1}): ν 3081 (w), 3062 (w), 2910 (s), 2853 (s), 1587 (m), 1553 (s), 1528 (s), 1409 (w), 1318 (s), 1277 (s), 1253 (m), 1242 (w), 1210 (s), 1187 (m), 1148 (w), 1117 (w), 1103 (m), 1069 (s), 1057 (m), 1041 (m), 1025 (m), 984 (w), 937 (m), 909 (m), 839 (w), 817 (s), 809 (s), 800 (s), 780 (s), 762 (m), 741 (m), 725 (s), 694 (m). $\mu_{\text{eff}} = 3.6$ μ_B.

Preparation of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrMe-(μ-Me)Li(THF)$_3$ (2). A suspension of **1** (0.25 g, 0.41 mmol) in diethyl ether (20 mL) was cooled to −35 °C and treated with a cold solution of MeLi (0.54 mL, 0.87 mmol) in ether (1.6 M). The resulting dark greenish brown solution was warmed to room temperature overnight. The solvent was evaporated to dryness and the residue resuspended in hexane (15 mL). Most of the solid dissolved, affording a dark greenish brown solution with a colorless precipitate. The supernatant was separated by centrifugation and stored at −35 °C for 2 days, at which time dark blocklike crystals of **2** were isolated (0.11 g, 0.14 mmol, 35% yield). Anal. Calcd (found) for $C_{47}H_{73}CrLiN_3O_3$: C, 71.73 (71.66); H, 9.35 (9.31); N, 5.34 (5.28). IR (Nujol mull, cm^{-1}): ν 2973−2845 (b, s), 1575 (s), 1493 (w), 1469 (s), 1377 (m), 1355 (w), 1332 (m), 1316 (m), 1280 (w), 1244 (s), 1204 (s), 1176 (w), 1143 (m), 1133 (m), 1100 (w), 1078 (m), 1044 (s), 990 (s), 935 (m), 887 (s), 872 (s), 839 (w), 807 (s), 776 (s), 748 (s), 730 (s), 715 (w), 693 (w), 662 (m), 646 (w). $\mu_{\text{eff}} = 4.24$ μ_B.

Preparation of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCl (3). Method 1. A suspension of **1** (0.25 g, 0.41 mmol) with 2.2 equiv of NaH (0.022 g, 0.91 mmol) in THF (25 mL) was stirred at room temperature for approximately 4 days. During this time, the mixture changed from purple to dark green. After 4 days, the solvent was evaporated in vacuo and the solids were redissolved in toluene (20 mL). The dark green solution was centrifuged to remove a small amount of precipitate and concentrated to approximately 5 mL. Dark green crystals of **3** grew after standing at room temperature for 3 days (0.19 g, 0.34 mmol, 83% yield). Anal. Calcd (found) for $C_{33}H_{43}N_3ClCr$: C, 69.64 (69.59); H, 7.62 (7.61); N, 7.38 (7.40). IR (Nujol mull, cm^{-1}): ν 2854 (s), 1578 (w), 1501 (w), 1462 (s), 1377 (s), 1331 (w), 1315 (m), 1237 (s), 1185 (m), 1177 (m), 1106 (s), 1092 (s), 1024 (m), 948 (s), 827 (s), 756 (s), 727 (s), 693 (s). $\mu_{\text{eff}} = 3.57$ μ_B.

Method 2. A suspension of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$-(C$_5$H$_3$N)}CrCl$_3$ (0.43 g, 0.67 mmol) in THF (15 mL) was reacted with NaH (0.05 g, 2.0 mmol) over a period of 1 week, during which time the mixture became dark green. After evaporation to dryness and addition of toluene, the dark green solution was centrifuged to remove a small amount of insoluble solid and allowed to stand at room temperature. Dark green crystals of **3** precipitated after approximately 3 days (0.076 g, 0.15 mmol, 22%).

Preparation of {2-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]-6-[2,6-(i-Pr)$_2$Ph-NC=CH$_2$](C$_5$H$_3$N)}Cr(μ-Me)Li(THF)$_3$·0.66(toluene) (5). A cold solution of MeLi in diethyl ether (1.6 M, 0.58 mL, 0.92 mmol) was added to a suspension of **3** (0.25 g, 0.44 mmol) in ether (25 mL) at −35 °C. The resulting dark reddish brown solution was stirred and warmed to room temperature for 4 h. After the solvent was evaporated, ether (20 mL) was added to the residue. The dark reddish brown supernatant was separated from the precipitates by centrifugation and dark reddish brown block crystals of **5** were grown after standing for 2 days at −35 °C. The remaining precipitates were dissolved in toluene and centrifuged. Dark reddish brown crystals of **5** were grown from a toluene solution (0.17 g, 0.21 mmol, 48%). Anal. Calcd (found after drying) for $C_{46}H_{69}N_3O_3CrLi$: C, 71.66 (71.61); H, 9.02 (8.97); N, 5.45 (5.44). IR (Nujol mull, cm^{-1}): ν 2975−2838 (b, s), 1602 (w), 1585 (m), 1563 (m), 1508 (w), 1468 (s), 1378 (s), 1302 (m), 1240 (s), 1193 (m), 1171 (m), 1155 (w), 1144 (m), 1110 (w), 1099 (m), 1044 (s), 967 (s), 910 (w), 887 (s), 828 (s), 799 (m), 770 (m), 742 (m), 726 (s), 693 (m), 666 (m). $\mu_{\text{eff}} = 3.81$ μ_B.

Preparation of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N)}Cr-(μ-Cl)$_2$Al(CH$_3$)$_2$ (6). A solution of Me$_3$Al in toluene (2 M, 2.20 mL, 4.39 mmol) was added to a solution of complex **3** (0.25 g, 0.44 mmol) in the same solvent (20 mL) at −35 °C. The mixture immediately changed from dark green to dark brownish green. After the mixture was stirred overnight, the solvent was evaporated and cold hexane (10 mL) added to the residue. The resulting suspension was centrifuged, and the dark green solution, separated from the dark precipitates, afforded dark green crystals of **6** upon standing for 2 days at −35 °C (0.044 g, 0.066 mmol, 15% yield). Anal. Calcd (found) for $C_{35}H_{49}AlCl_2CrN_3$: C, 63.53 (63.47); H, 7.46 (7.41); N, 6.35 (6.33). IR (Nujol mull, cm^{-1}): ν 2963−2855 (s), 1576 (m), 1468 (s), 1377 (s), 1232 (s), 1147 (s), 1104 (s), 1093 (s), 1055 (s), 935 (s), 860 (s), 827 (s), 805 (m), 776 (s), 757 (m), 721 (m), 694 (s), 690 (s). $\mu_{\text{eff}} = 3.86$ μ_B.

Preparation of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$(C$_5$H$_3$N)}-CrCH$_3$·0.5(hexane) (7). The preparation was carried out as for complex **6**, using the same amounts, except that the remaining hexane-insoluble portion was dissolved first in ether, evaporated to dryness, and then dissolved in toluene (15 mL). After centrifugation, the dark greenish brown solution was concentrated to 5 mL, layered with hexane, and allowed to stand at room temperature for 4 days, upon which time dark brown crystals of **7** precipitated (0.18 g, 0.33 mmol, 75% yield). Anal. Calcd (found after drying) for $C_{34}H_{46}N_3Cr$: C, 74.42 (74.39); H, 8.45 (8.41); N, 7.66 (7.60). IR (Nujol mull, cm^{-1}): ν 2900−2849 (s, b), 1633 (m), 1584 (w), 1565 (w), 1464 (s), 1377 (s), 1318 (w), 1303 (w), 1222 (s), 1204 (m), 1150 (m), 1087 (s), 931 (s), 881 (w), 855 (s), 804 (w), 796 (w), 779 (w), 7556 (s), 726 (s), 705 (m), 665 (w). $\mu_{\text{eff}} = 3.54$ μ_B.

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[31] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. S. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

[32] Tessier-Youngs, C.; Beachley, O. T., Jr. *Inorg. Synth*. **1986**, *24*, 95.

[33] Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. H. M.; Korobkov, I. Manuscript in preparation.

Preparation of $\{[\eta^4\text{-}\{2,6\text{-}[2,6\text{-(i-Pr)}_2\text{PhN}{=}\text{C(CH}_3)]_2(\text{C}_5\text{H}_3\text{N})\}\text{-Al}_2(\text{i-Bu})_3(\mu\text{-Cl})]\text{Cr}(\eta^6\text{-C}_7\text{H}_8)\}\cdot 0.66$(hexane) (8). A solution of IBAO in toluene (10 w/w %, 6.55 g, 2.20 mmol) was added dropwise to a solution of complex **3** (0.12 g, 0.220 mmol) in toluene (15 mL) at −35 °C. The mixture immediately turned deep brownish red and was slowly warmed to room temperature. The solvent was evaporated in vacuo, and the residue was redissolved in hexane (20 mL), forming a deep brown-red solution which was separated by centrifugation from a substantial amount of insoluble material. Very dark blocklike crystals of **8** were formed after standing for 5 days at room temperature (0.056 g, 0.068 mmol, 31%). A noncharacterizable oily material was also present. The crystals were isolated in pure form by careful washing with small portions of cold hexane to remove the oily contaminant. Anal. Calcd (found upon drying) for $C_{48}H_{69}N_3ClCrAl_2$: C, 69.50 (69.45); H, 8.38 (8.31); N, 5.07 (5.09). IR (Nujol mull, cm^{-1}): ν 2949−2861 (b, s), 1610 (w), 1564 (w), 1462 (s), 1405 (w), 1377 (s), 1318 (m), 1253 (w), 1230 (w), 1179 (s), 1161 (m), 1116 (w), 1066 (m), 1018 (s), 944 (w), 918 (w), 869 (m), 814 (m), 804 (m), 759 (w), 724 (m), 708 (m), 681 (s). $\mu_{eff} = 1.73\ \mu_B$.

Polymerization Results. The catalytic testing was performed under two sets of conditions for the purposes of comparison. The trivalent precursor $LCrCl_3$ was also prepared and tested for comparison under the same conditions. Polymerization under atmospheric ethylene pressure at room temperature proceeded in a Schlenk flask on a vacuum−nitrogen line. Samples were also tested at 40 atm and 50 °C in a 200 mL high-pressure Büchi reactor containing a heating/cooling jacket. In both cases, a preweighed amount of catalyst was dissolved in 100 mL of toluene under N_2 prior to loading the reaction vessel. A solution of 500 equiv of MAO in toluene was added to the catalyst, and the mixture was stirred for 10 min. The Schlenk-line polymerizations were run for 60 min under a continuous flow of ethylene, after first evacuating the nitrogen. High-pressure polymerization mixtures were heated to 50 °C using a thermostatic bath and charged with 40 atm of ethylene, maintaining the pressure throughout the run. In both procedures polymerizations were quenched by addition of MeOH and HCl. The resulting polymer was isolated by filtration, sonicated with a solution of HCl, rinsed, and thoroughly dried prior to measuring the mass. Gel permeation chromatography (GPC) analysis of the polyethylene was carried out by A. Jekel (University of Groningen) on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph using 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C. The samples were prepared by dissolving the polymer in the mobile-phase solvent in an external oven at 0.1% (w/v) and were run using a 4PL-Gel Mixed A column. The molecular weight was referenced to polystyrene ($M_w = 65500$, PDI = 1.02) standards.

X-ray Crystallography. All of the compounds consistently yielded crystals that diffracted weakly, and the results presented are the best of several trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer. Data for the compounds **1**, **2**, and **5**−**8** were collected with a sequence of 650 scans per set at 0.3° ω scans at 0, 120, and 240° in φ. To obtain acceptable redundancy data for compound **3**, the sequence of 650 scans per set with 0.3° ω scans at 0, 90, 180, and 270° in φ was used. Initial unit cell parameters were determined from 60 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[34] Systematic absences in the diffraction data set and unit-cell parameters were consistent with monoclinic $P2_1/c$ for **1**, orthorhombic $Pna2_1$ for **2**, triclinic $P\bar{1}$ for **3**, monoclinic $P2_1/n$ for **5**, monoclinic $P2_1$ for **6**, monoclinic $C2/c$ for **7**, and monoclinic $P2_1/n$ for **8**. Solutions in centrosymmetric space groups for compounds **1**, **3**, **5**, **7**, and **8** and noncentrosymmetric space groups for compounds **2** and **6** yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. The compound molecules were located in common positions in the structures of the complexes **1**−**6** and **8**. In complex **7**, a half-occupancy ether solvent molecule is located on the 2-fold axis of the symmetry element and the Cr molecule is located in the common position ($^1/_4$ ether molecules per chromium center). In complex **5**, the initial solution suggested two cocrystallized, severely disordered toluene solvent molecules. The data set was treated with the Squeeze routine of PLATON[35] with a refined void space per cell of 1246.2 Å^3 and an electron count per cell of 133, consistent with $^8/_3$ toluene molecules per cell. In compound **6**, the asymmetric unit contains 2 molecules of the Cr complex, which brings the Z' number to 2. Complex **8** contains a partially occupied molecule of hexane. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.[36] Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

Complex 1. The structure of complex **1** (Figure 1) is very similar to those of the Fe,[11] Co,[11] and Mn[13] bis(imino)pyridine analogues. The coordination geometry around the Cr center is defined by the three N atoms of the ligand (Cr(1)−N(1) = 2.118(7) Å, Cr(1)−N(2) = 1.993(6) Å, Cr(1)−N(3) = 2.118(6) Å) and two terminal Cl atoms (Cr(1)−Cl(1) = 2.299(2) Å, Cr(1)−Cl(2) = 2.416(3) Å) in an overall distorted-square-pyramidal arrangement. The basal plane is occupied by the nitrogen donor atoms of the tridentate ligand and one chlorine (N(1)−Cr(1)−N(2) = 75.4(3)°, N(2)−Cr(1)−N(3) = 76.2(3)°, N(3)−Cr(1)−Cl(1) = 99.2(2)°, N(1)−Cr(1)−Cl(1) = 101.77(19)°, N(2)−Cr(1)−Cl(1) = 160.95(19)°). The second Cl is located on the apical position (N(1)−Cr(1)−Cl(2) = 98.11(18)°, N(2)−Cr(1)−Cl(2) = 93.16(18)°, N(3)−Cr(1)−Cl(2) = 100.89(18)°, Cl(1)−Cr(1)−Cl(2) = 105.88(10)°). The other bond distances and angles do not show any distinguishing features and compare well with those found in the Fe, Co, and Mn derivatives.[11,13]

Complex 2. The complex consists of a pentacoordinate Cr center surrounded by the ligand's three donor atoms (Cr(1)−N(1) = 2.045(8) Å, Cr(1)−N(2) = 1.921(8) Å, Cr(1)−N(3) = 2.045(8) Å) and two methyl groups in an overall distorted-square-pyramidal geometry ($\tau = 0.31$)[36] (Figure 2). One methyl group, located in the axial position (C(35)−Cr(1)−N(1) = 98.2(3)°, C(35)−Cr(1)−N(2) = 94.3(3)°, C(35)−Cr(1)−N(3) = 101.1(3)°, C(35)−Cr(1)−C(34) = 97.1(4)°), is terminally bound (Cr(1)−C(35) = 2.062(8) Å). The carbon of a second methyl group (Cr(1)−C(34) = 2.134(9) Å) occupies the fourth equatorial position (N(1)−Cr(1)−N(2) = 77.8(4)°, N(2)−Cr(1)−N(3) = 77.2(4)°, N(3)−Cr(1)−C(34) = 101.1(3)°, N(1)−Cr(1)−C(34) = 100.5(4)°, N(1)−Cr(1)−N(3) = 149.3(3)°, N(2)−Cr(1)−C(34) = 168.6(3)°) and is bridging a THF-solvated lithium cation, forming an almost linear Li−C−Cr array (Li(1)−C(34) = 2.362 Å, Cr(1)−C(34)−Li(1) = 166.73°). An examination of the ligand parameters shows a slight shortening in the $C_{Me}-C_{imino}$ bonds (C(1)−C(2) = 1.473(12) Å, C(8)−C(9) = 1.477(12) Å), paralleled by a lengthening in the imino C−N bonds (N(1)−C(2) = 1.376(10) Å, N(3)−C(8) = 1.379(10) Å). Other modifications include a shortening of the $C_{imine}-C_{ortho}$ bond lengths (C(2)−C(3) = 1.417(11) Å, C(7)−C(8) = 1.403(13) Å) and a lengthening of the $C_{ortho}-N_{pyr}$ bond distances (N(2)−C(3) = 1.380(11) Å, N(2)−C(7) = 1.392(11) Å) relative to those of the divalent precursor.

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(34) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(35) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(36) Sheldrick, G. M. Bruker AXS, Madison, WI, 2001.

(37) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

Table 1. Crystal Data and Structure Analysis Results for Complexes 1−3 and 5−8

	1	**2**	**3**	**5**	**6**	**7**	**8**
formula	$C_{36}H_{49}Cl_2CrN_3O_{0.75}$	$C_{47}H_{73}CrLiN_3O_3$	$C_{33}H_{43}ClCrN_3$	$C_{50.62}H_{74.28}CrLiN_3O_3$[b]	$C_{70}H_{98}Al_2Cl_4Cr_2N_6$	$C_{35}H_{48.50}CrN_3O_{0.25}$	$C_{52}H_{78}Al_2ClCrN_3$
mol wt	658.68	787.02	569.15	831.79	1323.30	567.27	886.58
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$Pna2_1$	$P\bar{1}$	$P2_1/n$	$P2_1$	$C2$/c	$P2_1/n$
a (Å)	13.644(4)	28.334(12)	8.528(19)	13.217(14)	14.337(17)	27.8(3)	10.895(6)
b (Å)	15.007(4)	12.367(5)	8.731(19)	17.70(2)	14.879(17)	14.95(14)	19.206(11)
c (Å)	18.454(5)	13.407(6)	23.05(5)	22.278(12)	17.38(2)	21.6(2)	23.981(14)
α (deg)	90	90	95.08(4)	90	90	90	90
β (deg)	100.880(5)	90	95.40(4)	95.46(8)	98.86(2)	126.86(15)	101.029(11)
γ (deg)	90	90	109.66(3)	90	90	90	90
V (Å^3)	3710.7(18)	4698(3)	1595(6)	5187(9)	3663(7)	7190(117)	4925(5)
Z	4	4	2	4	2	8	4
radiation (Kα, Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	213(2)	208(2)	210(2)	203(2)	207(2)	208(2)	203(2)
D_{calcd} (g cm^{-3})	1.179	1.113	1.185	1.065	1.200	1.048	1.196
μ_{calcd} (mm^{-1})	0.481	0.283	0.467	0.260	0.509	0.343	0.359
F_{000}	1400	1708	606	1800	1404	2444	1912
R, R_w[a]	0.0800, 0.1237	0.0762, 0.1130	0.0606, 0.1557	0.0588, 0.1426	0.0736, 0.1469	0.0650, 0.1507	0.0741, 0.1626
GOF	1.009	1.012	1.031	1.005	1.031	1.038	1.050

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$; $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$. [b] The initial solution suggested two cocrystallized, severely disordered toluene solvent molecules. The data set was therefore treated with the Squeeze routine of PLATON[35] with a refined void space of 1246.2 Å^3 per cell and an electron count of 133 per cell, consistent with $^8/_3$ toluene molecules per cell. The suggested formula for the measured crystal is given.

Complex 3. Complex **3** (Figure 3) consists of a Cr center bound to the three N atoms of the ligand (Cr(1)−N(1) = 2.092(5) Å, Cr(1)−N(2) = 1.934(4) Å, Cr(1)−N(3) = 2.062(5) Å) and a terminal Cl atom (Cr(1)−Cl(1) = 2.287(4) Å) in an overall distorted-square planar geometry (N(1)−Cr(1)−N(2) = 76.66(16)°, N(2)−Cr(1)−N(3) = 77.95(13)°, N(1)−Cr(1)−N(3) = 154.46(14)°, N(1)−Cr(1)−Cl(1) = 103.24(13)°, N(3)−Cr(1)−Cl(1) = 102.29(11)°, N(2)−Cr(1)−Cl(1) = 175.61(10)°). Some of the bond distances and angles of the ligand backbone are different from those of complex **2**. The C═N and the N_{pyr}−C_{ortho} bonds have been lengthened, by an average of approximately 0.025 Å and 0.035 Å, respectively, and the C_{imine}−C_{ortho} bond length has been lengthened correspondingly, by approximately 0.035 Å.

Complex 5. Complex **5** (Figure 4) consists of a tetracoordinate Cr center bound to the three nitrogen atoms of the ligand system (Cr(1)−N(1) = 2.034(4) Å, Cr(1)−N(2) = 1.993(3) Å, Cr(1)−N(3) = 2.028(4) Å) and a methyl group (Cr(1)−C(34) = 2.129(4) Å). In turn, the methyl group bridges a THF-solvated Li cation (Li(1)−C(34) = 2.391 Å, Cr(1)−C(34)−Li(1) = 172.28°). The geometry about the Cr center is distorted square planar, with the methyl group raised slightly from the plane defined by the ligand (N(1)−Cr(1)−N(2) = 77.72(16)°, N(1)−Cr(1)−N(3) = 155.13(14)°, N(1)−Cr(1)−C(34) = 103.32(17)°, N(2)−Cr(1)−N(3) = 77.55(16)°, N(2)−Cr(1)−C(34) = 172.97(16)°, N(3)−Cr(1)−C(34) = 101.54(16)°). Similar to the case for complex **4**, the C_{methyl}−C_{imine} bond lengths have been shortened to an average of 1.426 Å (C(13)−C(14) = 1.465(6) Å, C(20)−C(21) = 1.387(6) Å). Consequently, the C═N bond distances have also been lengthened (N(1)−C(14) = 1.383(5) Å, N(3)−C(20) = 1.381(5) Å). Other modifications to the ligand backbone include a degree of elongation and contraction slightly larger than that seen for complex **4** in the N_{pyr}−C_{ortho} and C_{imine}−C_{ortho} distances.

Complex 6. The structure of complex **6** (Figure 5) consists of a pentacoordinate Cr center bound to the tridentate ligand (Cr(1)−N(1) = 2.105(8) Å, Cr(1)−N(2) = 1.923(8) Å, Cr(1)−N(3) = 2.131(8) Å) and two Cl atoms (Cr(1)−Cl(1) = 2.468(4) Å, Cr(1)−Cl(2) = 2.526(4) Å) in a severely distorted square pyramidal geometry (τ = 0.17).[36] The axial site is occupied by the second Cl atom (N(1)−Cr(1)−Cl(2) = 99.9(2)°, N(2)−Cr(1)−Cl(2) = 133.2(2)°, N(3)−Cr(1)−Cl(2) = 99.9(3)°), even though the angle subtended at the chromium atom by the two Cl atoms is narrow (Cl(1)−Cr(1)−Cl(2) = 82.11(11)°). The other atoms occupy the equatorial positions (N(1)−Cr(1)−N(2) = 77.6(3)°, N(1)−Cr(1)−N(3) = 154.9(3)°, N(1)−Cr(1)−Cl(1) = 98.6(2)°, N(2)−Cr(1)−N(3) = 77.6(3)°, N(2)−Cr(1)−Cl(1) = 144.7(2)°, N(3)−Cr(1)−Cl(1) = 99.2(2)°). In turn, the Cl atoms are bridging one −$AlMe_2$ unit (Cl(1)−Al(1) = 2.248(5) Å, Cl(2)−Al(1) = 2.233(5) Å, Al(1)−C(34) = 1.957(11) Å, Al(1)−C(35) = 1.948(12) Å) in which the Al center is found in a distorted-tetrahedral geometry (Cl(1)−Al(1)−Cl(2) = 94.11(16)°, Cl(1)−Al(1)−C(34) = 106.3(4)°, Cl(1)−Al(1)−C(35) = 109.8(4)°, Cl(2)−Al(1)−C(34) = 109.7(4)°, Cl(2)−Al(1)−C(35) = 110.0(4)°, C(34)−Al(1)−C(35) = 123.0(5)°). The bond distances of the backbone are similar to those of complex **3**.

Complex 7. The Cr center of complex **7** adopts a distorted-square -planar arrangement (Figure 6) very similar to those observed in **3** and **4**. The square plane is formed by the three nitrogen donor atoms of the ligand (Cr(1)−N(1) = 1.947(16) Å, Cr(1)−N(2) = 1.877(12) Å, Cr(1)−N(3) = 1.930(12) Å) and a terminal methyl group (Cr(1)−C(34) = 1.971(13) Å, N(1)−Cr(1)−N(2) = 81.4(7)°, N(2)−Cr(1)−N(3) = 81.7(8)°, N(3)−Cr(1)−C(34) = 98.3(8)°, N(1)−Cr(1)−C(34) = 98.6(7)°, N(1)−Cr(1)−N(3) = 163.11(15)°, N(2)−Cr(1)−C(34) = 178.96(18)°). The ligand system appears to deviate slightly from that of complex **3**, showing a curious lengthening of all bonds of the backbone. The largest stretch is in the C═N bond distance, from an average of 1.321 Å to 1.356 Å. However, the most extreme modification is a parallel elongation of approximately 0.03 Å in the C_{imine}−C_{ortho} bond length, as opposed to an equivalent contraction of the distance.

Complex 8. The crystal structure of **8** shows the ligand system connected to a toluene-solvated chromium atom and a $^{i}Bu_2Al(\mu$-Cl)Al^{i}Bu unit bound to the nitrogen atoms of the folded ligand (Figure 7). One Al is found coordinated to all three nitrogens of the ligand (Al(1)−N(1) = 2.140(5) Å, Al(1)−N(2) = 2.002(5) Å, Al(1)−N(3) = 1.924(5) Å), an ^{i}Bu moiety (Al(1)−C(41) = 1.967(6) Å), and a chlorine atom (Al(1)−Cl = 2.393(3) Å) in a geometry which can described as either distorted trigonal bipyramidal or square pyramidal (τ = 0.493)[36] (N(1)−Al(1)−N(2) = 77.5(2)°, N(1)−Al(1)−N(3) = 142.7(2)°, N(1)−Al(1)−Cl(1) = 104.55(16)°, N(1)−Al(1)−C(41) = 94.9(2)°, N(2)−Al(1)−N(3) = 82.4(2)°, N(2)−Al(1)−Cl(1) = 85.09(16)°, N(2)−Al(1)−C(41) = 172.3(3)°, N(3)−Al(1)−Cl(1) = 104.56(17)°, N(3)−Al(1)−C(41) = 103.4(3)°, Cl(1)−Al(1)−C(41) = 98.2(2)°). The Cl atom and the N of the pyridine ring in turn bridge the second Al atom (Al(2)−Cl = 2.291(3) Å, Al(2)−N(2) = 1.963(5) Å), whose coordination is completed by two ^{i}Bu groups (Al(2)−C(45) = 1.968(7) Å, Al(2)−C(49) = 1.952(7) Å) in a distorted-tetrahedral arrangement (N(2)−Al(2)−Cl = 88.80(16)°, N(2)−Al(2)−C(45) = 111.9(3)°, N(2)−Al(2)−C(49) = 116.3(3)°, Cl−Al(2)−C(45) = 108.5(2)°, Cl−Al(2)−C(49) = 104.0(2)°, C(45)−Al(2)−C(49) = 121.4(3)°). The

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 1−3 and 5−8

Complex **1**							
Cr(1)−N(1)	2.118(7)	Cr(1)−Cl(1)	2.299(2)	C(1)−C(2)	1.470(10)	N(1)−C(2)	1.294(9)
Cr(1)−N(2)	1.993(6)	Cr(1)−Cl(2)	2.416(3)	C(8)−C(9)	1.495(10)	N(3)−C(8)	1.298(9)
Cr(1)−N(3)	2.118(6)						
N(1)−Cr(1)−N(2)	75.4(3)	N(1)−Cr(1)−Cl(1)	101.77(19)	N(1)−Cr(1)−Cl(2)	98.11(18)	N(3)−Cr(1)−Cl(2)	100.89(18)
N(2)−Cr(1)−N(3)	76.2(3)	N(2)−Cr(1)−Cl(1)	160.95(19)	N(2)−Cr(1)−Cl(2)	93.16(18)	Cl(1)−Cr(1)−Cl(2)	105.88(10)
N(3)−Cr(1)−Cl(1)	99.2(2)	N(1)−Cr(1)−N(3)	146.5(3)				
Complex **2**							
Cr(1)−N(1)	2.045(8)	Cr(1)−C(35)	2.062(8)	C(1)−C(2)	1.473(12)	N(1)−C(2)	1.376(10)
Cr(1)−N(2)	1.921(8)	Cr(1)−C(34)	2.134(9)	C(8)−C(9)	1.477(12)	N(3)−C(8)	1.379(10)
Cr(1)−N(3)	2.045(8)	Li(1)−C(34)	2.362				
N(1)−Cr(1)−N(2)	77.8(4)	N(1)−Cr(1)−C(34)	100.5(4)	C(35)−Cr(1)−N(1)	98.2(3)	C(35)−Cr(1)−C(34)	97.1(4)
N(2)−Cr(1)−N(3)	77.2(4)	N(1)−Cr(1)−N(3)	149.3(3)	C(35)−Cr(1)−N(2)	94.3(3)	Cr(1)−C(34)−Li(1)	166.73
N(3)−Cr(1)−C(34)	101.1(3)	N(2)−Cr(1)−C(34)	168.6(3)	C(35)−Cr(1)−N(3)	101.1(3)		
Compound **3**							
Cr(1)−N(1)	2.092(5)	Cr(1)−N(3)	2.062(5)	C(1)−C(2)	1.504(6)	N(1)−C(2)	1.311(5)
Cr(1)−N(2)	1.934(4)	Cr(1)−Cl	2.287(4)	C(8)−C(9)	1.497(6)	N(3)−C(8)	1.331(5)
N(1)−Cr(1)−N(2)	76.66(16)	N(3)−Cr(1)−Cl(1)	102.29(11)	N(1)−Cr(1)−N(3)	154.46(14)	N(2)−Cr(1)−Cl(1)	175.61(10)
N(2)−Cr(1)−N(3)	77.95(13)	N(1)−Cr(1)−Cl(1)	103.24(13)				
Compound **5**							
Cr(1)−N(1)	2.034(4)	Cr(1)−C(34)	2.129(4)	N(1)−C(14)	1.383(5)	C(19)−C(20)	1.461(6)
Cr(1)−N(2)	1.993(3)	C(13)−C(14)	1.465(6)	N(3)−C(20)	1.381(5)	N(2)−C(15)	1.372(5)
Cr(1)−N(3)	2.028(4)	C(20)−C(21)	1.387(6)	C(14)−C(15)	1.409(6)	N(2)−C(19)	1.359(5)
N(1)−Cr(1)−N(2)	77.72(16)	N(3)−Cr(1)−C(34)	101.54(16)	N(1)−Cr(1)−N(3)	155.13(14)	N(2)−Cr(1)−C(34)	172.97(16)
N(2)−Cr(1)−N(3)	77.55(16)	N(1)−Cr(1)−C(34)	103.32(17)				
Compound **6**							
Cr(1)−N(1)	2.105(8)	Cr(1)−Cl(2)	2.526(4)	Al(1)−C(34)	1.957(11)	C(8)−C(9)	1.509(13)
Cr(1)−N(2)	1.923(8)	Cl(1)−Al(1)	2.248(5)	Al(1)−C(35)	1.948(12)	N(1)−C(2)	1.327(12)
Cr(1)−N(3)	2.131(8)	Cl(2)−Al(1)	2.233(5)	C(1)−C(2)	1.497(14)	N(3)−C(8)	1.334(11)
Cr(1)−Cl(1)	2.468(4)						
N(2)−Cr(1)−Cl(1)	144.7(2)	N(1)−Cr(1)−N(2)	77.6(3)	N(3)−Cr(1)−Cl(1)	99.2(2)	Cl(1)−Al(1)−C(35)	109.8(4)
N(2)−Cr(1)−Cl(2)	133.2(2)	N(1)−Cr(1)−Cl(1)	98.6(2)	N(3)−Cr(1)−Cl(2)	99.9(3)	Cl(2)−Al(1)−C(34)	109.7(4)
Cl(1)−Cr(1)−Cl(2)	82.11(11)	N(1)−Cr(1)−Cl(2)	99.9(2)	Cl(1)−Al(1)−Cl(2)	94.11(16)	Cl(2)−Al(1)−C(35)	110.0(4)
N(1)−Cr(1)−N(3)	154.9(3)	N(2)−Cr(1)−N(3)	77.6(3)	Cl(1)−Al(1)−C(34)	106.3(4)	C(34)−Al(1)−C(35)	123.0(5)
Compound **7**							
Cr(1)−N(1)	1.947(16)	Cr(1)−N(3)	1.930(12)	C(1)−C(2)	1.532(16)	N(1)−C(2)	1.356(12)
Cr(1)−N(2)	1.877(12)	Cr(1)−C(34)	1.971(13)	C(8)−C(9)	1.500(10)	N(3)−C(8)	1.356(10)
N(1)−Cr(1)−N(2)	81.4(7)	N(3)−Cr(1)−C(34)	98.3(8)	N(1)−Cr(1)−N(3)	163.11(15)	N(2)−Cr(1)−C(34)	178.96(18)
N(2)−Cr(1)−N(3)	81.7(8)	N(1)−Cr(1)−C(34)	98.6(7)				
Compound **8**							
Al(1)−N(1)	2.140(5)	Al(2)−C(49)	1.952(7)	Cr(1)−C(37)	2.060(7)	C(4)−C(5)	1.395(9)
Al(1)−N(2)	2.002(5)	Cr(1)−C(3)	2.119(6)	Cr(1)−C(38)	2.073(7)	C(5)−C(6)	1.438(10)
Al(1)−N(3)	1.924(5)	Cr(1)−C(4)	1.952(7)	Cr(1)−C(39)	2.088(7)	C(6)−C(7)	1.440(9)
Al(1)−C(41)	1.967(6)	Cr(1)−C(5)	2.000(7)	C(1)−C(2)	1.512(9)	N(2)−C(7)	1.457(7)
Al(1)−Cl	2.393(3)	Cr(1)−C(6)	2.158(7)	N(1)−C(2)	1.300(7)	C(7)−C(8)	1.343(8)
Al(2)−Cl	2.291(3)	Cr(1)−C(34)	2.094(7)	C(2)−C(3)	1.435(9)	C(8)−C(9)	1.508(9)
Al(2)−N(2)	1.963(5)	Cr(1)−C(35)	2.064(7)	N(2)−C(3)	1.459(8)	N(3)−C(8)	1.378(8)
Al(2)−C(45)	1.968(7)	Cr(1)−C(36)	2.083(7)	C(3)−C(4)	1.428(8)		
N(2)−Al(1)−C(41)	172.3(3)	N(2)−Al(1)−N(3)	82.4(2)	N(2)−Al(2)−C(45)	111.9(3)	C(3)−N(2)−Al(1)	116.1(4)
N(1)−Al(1)−N(3)	142.7(2)	C(41)−Al(1)−Cl	98.2(2)	N(2)−Al(2)−C(49)	116.3(3)	C(3)−N(2)−Al(2)	113.7(4)
N(3)−Al(1)−Cl	104.56(17)	C(41)−Al(1)−N(1)	94.9(2)	Cl-Al(2)−C(45)	108.5(2)	C(7)−N(2)−Al(1)	109.7(4)
N(1)−Al(1)−Cl	104.55(16)	C(41)−Al(1)−N(3)	103.4(3)	Cl-Al(2)−C(49)	104.0(2)	C(7)−N(2)−Al(2)	105.1(4)
N(2)−Al(1)−Cl	85.09(16)	Al(1)−Cl-Al(2)	82.97(8)	C(45)−Al(2)−C(49)	121.4(3)	Al(1)−N(2)−Al(2)	103.0(2)
N(2)−Al(1)−N(1)	77.5(2)	N(2)−Al(2)−Cl	88.80(16)	C(3)−N(2)−C(7)	108.6(5)		

ligand appears folded, and the major distortion is observable around the pyridine ring, which adopts an η^4 coordination with a Cr atom (Cr(1)−C(3) = 2.119(6) Å, Cr(1)−C(4) = 1.952(7) Å, Cr(1)−C(5) = 2.000(7) Å, Cr(1)−C(6) = 2.158(7) Å). In turn, the Cr atom is η^6 bound to a molecule of toluene with a distance to the centroid of 1.541(7) Å. The pyridine ring is no longer planar (N(2)−C(3)−C(4) = 117.4(5)°, C(3)−C(4)−C(5) = 112.8(6)°, C(4)−C(5)−C(6) = 117.7(6)°, C(5)−C(6)−C(7) = 121.1(6)°, C(6)−C(7)−N(2) = 113.9(5)°, C(3)−N(2)−C(7) = 108.6(5)°), with the largest deviation occurring at the N of the ring. Bound to the ring and two Al atoms, the N is now clearly sp^3 (C(3)−N(2)−C(7) = 108.6(5)°, C(3)−N(2)−Al(1) = 116.1(4)°, C(3)−N(2)−Al(2) = 113.7(4)°, C(7)−N(2)−Al(1) = 109.7(4)°, C(7)−N(2)−Al(2) = 105.1(4)°, Al(1)−N(2)−Al(2) = 103.0(2)°). In comparison to the bond distances observed in all other complexes, drastic modifications are apparent in the ligand backbone. First of all, the disruption of aromaticity in the pyridine ring, due to the sp^3 nature of the N atom and the η^4 coordination of the Cr atom, has resulted in lengthening of all bonds in the pyridine ring (N(2)−C(3) = 1.459(8) Å, C(3)−C(4) = 1.428(8) Å, C(4)−C(5) = 1.395(9) Å, C(5)−C(6) = 1.438(10) Å, C(6)−C(7) = 1.440(9) Å, N(2)−C(7) = 1.457(7) Å). The fact that the Cr atom is only bound to two-thirds of the ring creates an

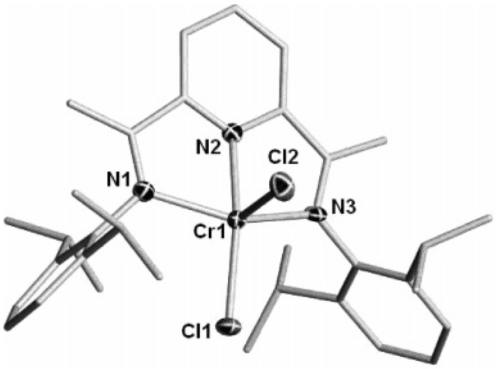

Figure 1. Thermal ellipsoid plot of **1**, drawn at the 30% probability level.

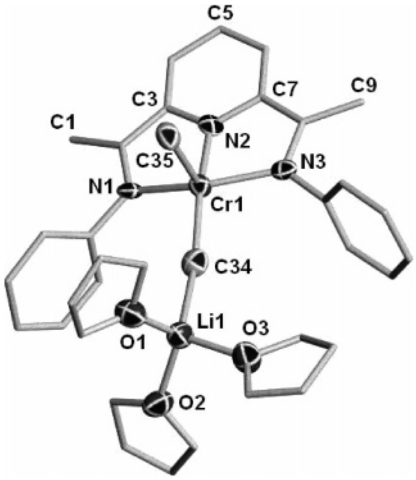

Figure 2. Thermal ellipsoid plot of **2**, drawn at the 30% probability level. The isopropyl groups of the ligand have been removed for clarity.

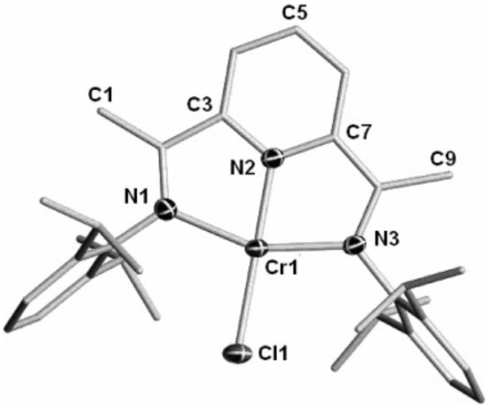

Figure 3. Thermal ellipsoid plot of **3**, drawn at the 30% probability level.

asymmetric localization of the electron density throughout the rest of the ligand backbone. On the half of the ligand in which the pyridine ortho C is bound to the Cr, the C=N and $C_{imine}-C_{ortho}$ bonds assume semi-normal distances (N(1)−C(2) = 1.300(7) Å, C(2)−C(3) = 1.435(9) Å), as expected for localization of the double bond on the imine function. However, the other half of the ligand backbone, that further away from the Cr coordination, assumes the opposite arrangement (N(3)−C(8) = 1.378(8) Å, C(8)−C(7) = 1.343(8) Å).

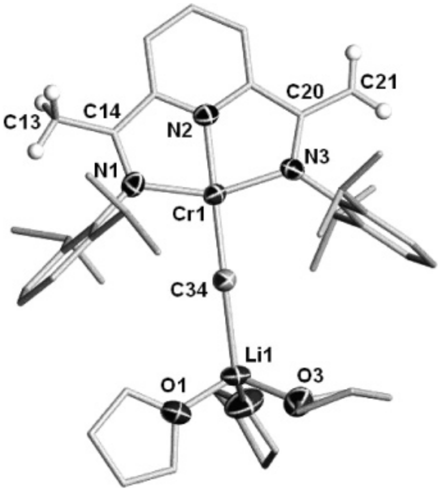

Figure 4. Thermal ellipsoid plot of **5**, drawn at the 30% probability level.

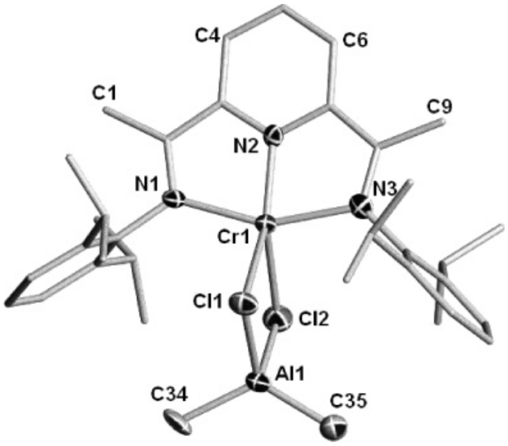

Figure 5. Thermal ellipsoid plot of **6**, drawn at the 30% probability level.

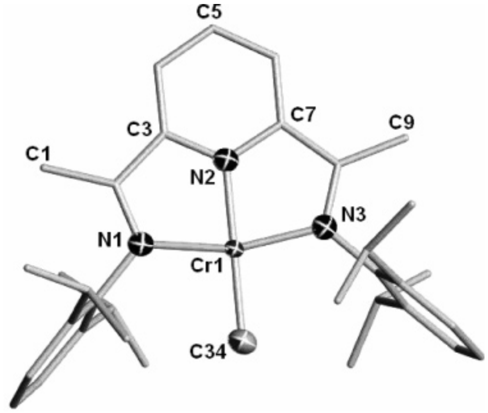

Figure 6. Thermal ellipsoid plot of **7**, drawn at the 30% probability level.

Results and Discussion

Alkylation of trivalent chromium compounds often affords reduction toward the divalent state.[38] The trivalent (bis(imino)pyridinato)chromium(III) complexes seem to follow the same trend in spite of the unique electronic flexibility of this particular ligand system. We have previously described that treatment with a mild reducing agent such as Me_3Al yields a divalent complex in crystalline form.[13b] Therefore, the starting point of this work, aimed at investigating the oxidation state of the catalytically

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[38] (a) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (b) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2003**, 1164.

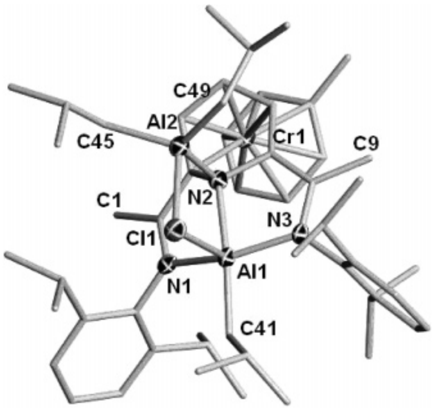

Figure 7. Thermal ellipsoid plot of **8**, drawn at the 30% probability level.

active species, was to use a complex already containing the metal in its divalent state. The synthesis of the divalent {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrCl$_2$ (**1**) was carried out in a straightforward manner by refluxing CrCl$_2$(THF)$_2$ in toluene and in the presence of the 2,6-diisopropylphenylbis(imino)-pyridine ligand. Purple microcrystals of **1** were isolated in 95% yield from THF, while slow crystallization afforded X-ray-quality crystals. The crystal structure (Figure 1) confirmed that the complex possesses the same structure as the previously reported FeCl$_2$ and CoCl$_2$ adducts with an overall square-pyramidal arrangement of the metal center.[11] The magnetic moment at room temperature ($\mu_{\text{eff}} = 3.6\ \mu_{\text{B}}$) was substantially lower than that expected for the d^4 configuration of high-spin divalent chromium, diagnosing the same phenomenon of charge transfer and consequent internal coupling, previously observed with other metal complexes of this ligand.[21,29,39]

As mentioned above, the reaction of the trivalent chromium derivative with Me$_3$Al affords reduction to a divalent complex where two Me$_3$Al residues are bridged to the metal center via bridging chlorines.[13b] Different from the case of vanadium, we find no evidence for straightforward alkylation at the divalent center[13b] and, therefore, we have now attempted to form Cr−C bonds by reacting **1** with MeLi. It is worth remembering that, in the case of the Fe analogue, the reaction of MeLi afforded a range of derivatives, including a formally zerovalent species which has the same catalytic ethylene polymerization activity and produced the same polymer as the starting divalent precursor.[26]

The reaction with 2 equiv of MeLi was carried out at −35 °C in ether (Scheme 1), affording {2,6-[2,6-(i-Pr)$_2$PhN═C(CH$_3$)]$_2$(C$_5$H$_3$N)}CrMe(μ-Me)Li(THF)$_3$ (**2**) in crystalline form (Figure 2). The presence of two Me groups and one lithium cation assigns the *formal* monovalent state to the chromium atom. Similar to the case of Fe, however, the appearance of this complex as a rare case of monovalent organochromium is probably deceiving, as complex **2** can more realistically be described as a divalent chromium center coupled to a ligand radical anion. Accordingly, the ligand backbone shows the same small and yet reproducible modifications of bond distances (Table 3) normally observed in the case of a one-electron reduction of the ligand.[40] The room-temperature magnetic moment ($\mu_{\text{eff}} = 4.2\ \mu_{\text{BM}}$) again suggests the presence of a high-spin d^4 electronic configuration of a Cr(II) center antiferromagnetically coupled to a ligand radical anion.

Scheme 1

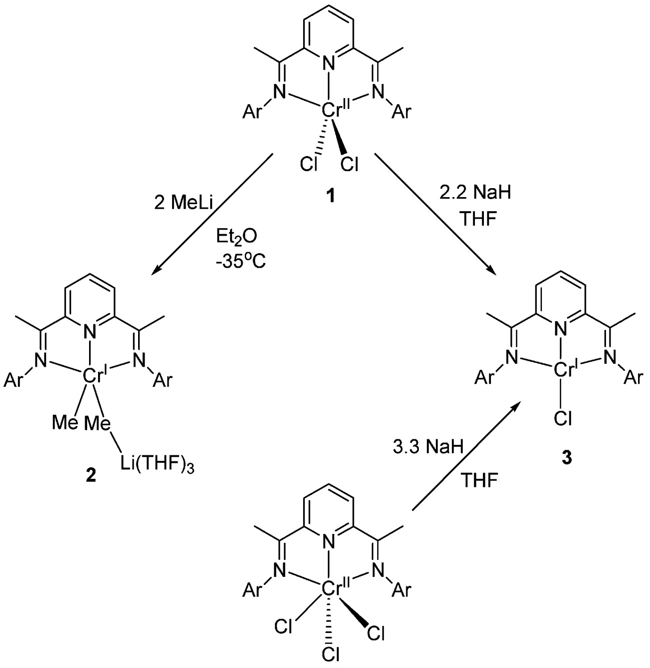

Table 3. Comparative Bond Distances (Å)

Cr−N	N$_{\text{imine}}$−C$_{\text{imine}}$	C$_{\text{imine}}$−C$_{\text{ortho}}$	C$_{\text{ortho}}$−N$_{\text{pyr}}$	C$_{\text{methyl}}$−C$_{\text{imine}}$
Complex **1**−LCrCl$_2$				
1.993(6)	1.294(9)	1.484(10)	1.329(9)	1.470(10)
2.118(7)	1.298(9)	1.463(10)	1.359(9)	1.495(10)
2.118(6)				
Complex **2**				
1.921(8)	1.376(10)	1.417(11)	1.380(11)	1.473(12)
2.045(8)	1.379(10)	1.403(13)	1.392(11)	1.477(12)
2.045(8)				
Complex **3**−LCrCl				
1.934(4)	1.311(5)	1.447(6)	1.374(5)	1.504(6)
2.062(5)	1.331(5)	1.429(6)	1.384(5)	1.497(6)
2.092(5)				
Complex **4**[40]				
1.953(4)	1.374(6)	1.459(6)	1.360(6)	1.416(7)
2.020(4)	1.372(6)	1.436(6)	1.366(6)	1.443(7)
2.022(4)				
Complex **5**				
1.993(3)	1.383(5)	1.409(6)	1.359(5)	1.465(6)
2.028(4)	1.381(5)	1.461(6)	1.372(5)	1.387(6)
2.034(4)				
Complex **6**				
1.923(8)	1.327(12)	1.422(13)	1.377(11)	1.497(14)
2.105(8)	1.334(11)	1.417(13)	1.404(11)	1.509(13)
2.131(8)				
Complex **7**				
1.877(12)	1.356(12)	1.469(12)	1.384(10)	1.532(16)
1.930(12)	1.356(10)	1.468(17)	1.393(15)	1.500(10)
1.947(16)				
Complex **8**				
	1.300(7)	1.435(9)	1.459(8)	1.512(9)
	1.378(8)	1.343(8)	1.457(7)	1.508(9)

Regardless of how we consider the oxidation state of the chromium center, the result of the alkylation reaction is the formation of a "reduced" species containing one additional electron with respect to the initial divalent complex. Previous work has demonstrated that deliberate reduction of the FeCl$_2$[24] and VCl$_3$[25] precursors may lead to the formation of species with

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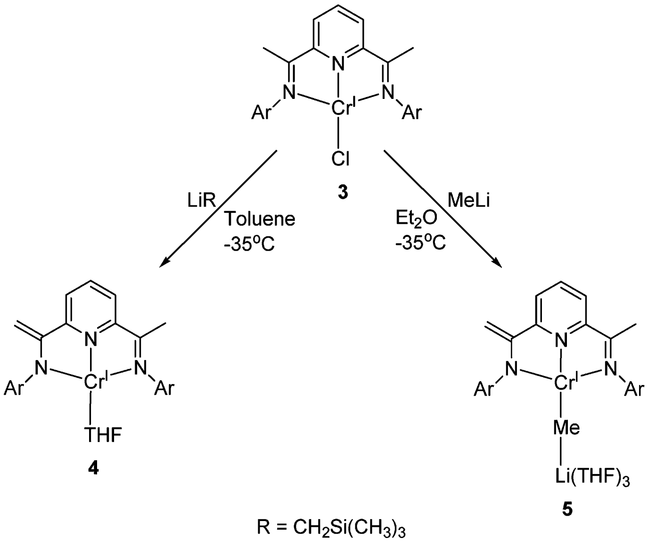
[39] Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.

[40] Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442.

Scheme 2



an overall zerovalent appearance. The remarkable feature of these species is that, although the low-valent appearance is purely formal, given the very substantial metal to ligand electron transfer, the chemical reactivity remained that expected of a low-valent metal species. The recurrence of dinitrogen fixation in the case of Fe,[24] V,[25] Co,[15,28b] and even Cr[33] speaks for the genuine low-valent type of behavior of these reduced complexes. Even more remarkably, the reduction does not appear to affect the catalytic behavior in ethylene polymerization, since the two-electron-reduced Fe species can produce not only dinitrogen complexes but can also be activated to perform very fast polymerizations and form the same type of polymer as its divalent precursor.[26]

Reduction of complex **1** was further attempted with 2.2 equiv of NaH as a reductant. The slow reaction was carried out in THF over a period of 1 week, affording dark green X-ray-quality crystals of $\{2,6\text{-}[2,6\text{-(i-Pr)}_2PhN{=}C(CH_3)]_2(C_5H_3N)\}CrCl$ (**3**) (Scheme 1) in good yield. Complex **3**, whose appearance is also that of a monovalent chromium complex (Figure 3), could also be prepared, albeit in lower yield, by reducing the $CrCl_3$ derivative with 3.3 equiv of NaH. The square-planar geometry strongly suggests the presence of a divalent metal center. Even in this case, the room-temperature magnetic susceptibility ($\mu_{eff} = 3.57\ \mu_B$) can be explained in terms of a high-spin d^4 Cr(II) center in a square-planar ligand field that is magnetically coupled to a radical anion.

In line with the behavior of the reduced Fe analogue,[26] **3** is an extremely active polymerization catalyst (vide infra). Thus, we have attempted further alkylation in order to probe the stability of the "monovalent" oxidation state while in the presence of alkylating agents (as for example during the polymerization reaction). The reaction of **3** with 1 equiv of $LiCH_2Si(CH_3)_3$ or MeLi afforded $\{2\text{-}[2,6\text{-(i-Pr)}_2PhN{=}C(CH_3)]\text{-}6\text{-}[2,6\text{-(i-Pr)}_2PhNC{=}CH_2](C_5H_3N)\}Cr(THF)$ (**4**) and $[\{2,6\text{-}[2,6\text{-(i-Pr)}_2PhN{=}C(CH_3)]_2(C_5H_3N)\}CrCH_3][Li(THF)_4]$ (**5**), respectively (Scheme 2). Complex **4** was previously obtained in crystalline form via reduction of **3** with NaH under Ar.[33] In both of these species (Figure 4)[33] one of the two methyl groups has undergone deprotonation, thus making the ligand monoanionic in the process. This is clearly indicated by a decrease in the ketimine bond length corresponding to an increase in the C═N bond distance (Table 3). The fourth coordination site of **4** contains a molecule of THF, while complex **5** is bound by a bridging Me−Li unit. Therefore, it appears that the extent of reduction has remained unmodified as the result of the alkylation reaction.

Accordingly, the magnetic moments ($\mu_{eff} = 3.51$ and $3.81\ \mu_B$) are similar to that of **3** and fall in the range expected for a d^4 high-spin square-planar divalent chromium coupled to the ligand radical anion. A small contraction in the $C_{imine}-C_{ortho}$ bond distances, paralleled by an elongation of the $N_{pyr}-C_{ortho}$ bond lengths, is also in agreement with partial reduction of the ligand.[39,40]

The involvement of the imino methyl groups in acid−base type reactions with alkylating agents, forming singly and doubly deprotonated forms of the ligand, is well-documented in the chemical reactivity of this particular ligand system.[13b,14,17b,c,18−20] In most cases, the single deprotonation preludes a dimerization via formation of a C−C bond between the $CH_2{=}$ moieties of two different molecules. This process engages the redox chemistry of the metal center. Therefore, the isolation of a complex in which the ligand has undergone only single deprotonation is a rare event, having only been witnessed for Li[17b,c,18] and Ga.[41]

As briefly mentioned above, complex **3** is a potent polymerization catalyst while in combination with MAO. Since the reaction with MAO did not lead to isolable products, the reaction of **3** with $AlMe_3$ may be regarded as a viable alternative in the pursuit of a potential active species for the polymerization reaction. When complex **3** was reacted with excess $AlMe_3$ in hexane, two products, $\{2,6\text{-}[2,6\text{-(i-Pr)}_2PhN{=}C(CH_3)]_2(C_5H_3N)\}Cr(\mu\text{-}Cl)_2Al(CH_3)_2$ (**6**) and $\{2,6\text{-}[2,6\text{-(i-Pr)}_2PhN{=}C(CH_3)]_2(C_5H_3N)\}CrCH_3$ (**7**), were isolated and separated by fractional crystallization from hexane and toluene, respectively (Scheme 3). Both complexes have been characterized by X-ray crystallography (Figures 5 and 6).

Complex **6**, featuring the Cr center surrounded by the ligand and bound to an $-AlMe_2$ unit by two bridging Cl atoms, again suggests a formal monovalent state for the Cr center. Therefore, the formation of **6** is simply the result of coordination of an $AlClMe_2$ unit to **3**. This is substantiated by the value of the magnetic moment ($\mu_{eff} = 3.86\ \mu_B$), which is very similar to that of **3**. The presence of an aluminum-bound chlorine atom may be a consequence of the formation of complex **7**, which is a direct replacement of the Cl atom on the metal center with a CH_3 unit. Again, the ligand backbone deformations of both compounds suggest reduction of the ligand by one electron (Table 3)[39,40] and can therefore be described as Cr(II) centers bound to ligand radical anions.

It is interesting to note that addition of Me_3Al to the highly active catalyst precursor **3** does not result in further reduction of the metal center, in contrast to the case of Co[28ab] or Fe.[29] However, addition of a different activator, namely IBAO, indeed led to reduction of the metal center and partial transmetalation (Scheme 3), forming $[\eta^4\text{-}\{2,6\text{-}[2,6\text{-(i-Pr)}_2PhN{=}C(CH_3)]_2(C_5H_3N)\}Al_2(i\text{-}Bu)_3(\mu\text{-}Cl)]Cr\text{-}(\eta^6\text{-}C_7H_8)$ (**8**) (Figure 7).

The structure involves three metal centers: two aluminum atoms and one chromium. The chromium atom has been partially dislodged from the ligand system and appears to be exclusively η^5 bound to part of the pyridine ring but not to the N donor atom. The three ligand N donor atoms are instead used to hold an $Al_2(i\text{-}Bu)_3Cl$ unit. The fact that the Al-containing unit is dicationic suggests that the ligand system is dianionic. The Cr center, on the other hand, could reasonably be regarded as

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[41] Scott, J.; Phull, H.; Gambarotta, S.; Korobkov, I. Manuscript in preparation.

[42] Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31,* 1181.

Scheme 3

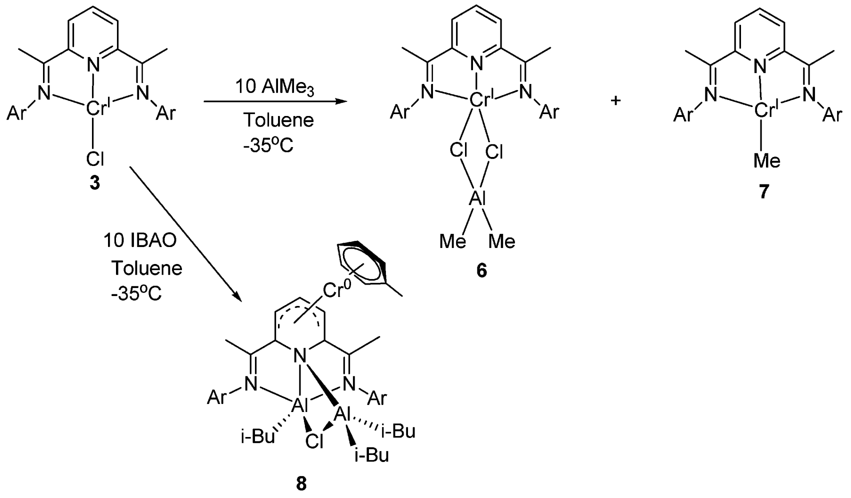

Table 4. Ethylene Polymerization Results

run no.	complex	amt of cat. (μmol)	amt of MAO (equivs)	$P(C_2H_4)$ (atm)	temp (°C)	time (min)	yield of PE (g)	activity (g of PE/((mmol of cat.)/h/atm))	M_w	M_n	PDI
1	$LCrCl_3$	15.6	500	1	23	60	1.39	89	28 500	1 640	17.4
2	$LCrCl_3$	20.3	500	40	50	60	7.24	357	57 400	2 060	27.9
3	**1**	19.7	500	1	23	60	3.05	155	8 250	1 100	7.5
4	**1**	22.8	500	40	50	30	28.24	2 477	9 280	2 650	3.5
5	**2**	15.2	500	1	23	60	1.74	114	26 600	1 580	16.8
6	**2**	10.2	500	40	50	60	9.82	966	34 200	1 970	17.4
7	**3**	13.2	500	1	23	60	10.04	759	8 010	3 090	2.6
8	**3**	22.8	500	40	50	60	68.71	3 014	41 000	1 710	24.0
9	**4**	16.5	500	1	23	60	2.72	165			
10	**4**	23.1	500	40	50	60	61.23	2 645	202 100	1, 810	111.7
11	**4**	31.4	1000	40	50	60	67.8	2 160			
12	**7**	17.1	500	1	23	60	19.2	1200			
13	**7**	18.8	500	40	50	60	79	4 202	27 600	1 650	16.7

present in the zerovalent state. The η^6 coordination of one molecule of toluene is also another indicating factor, given the well-established ability of zerovalent chromium to form arene complexes. Taken together, the formation of **8** is the result of a three-electron reduction, with two electrons located on the ligand and the other one on the Cr center, and a partial transmetalation of the ligand system from Cr to Al. Similar to the case for the closely related Fe analogue,[29] complex **8** is paramagnetic, with a room-temperature value of the magnetic susceptibility of 1.73 μ_B. Calculations performed on the Fe analogue indicated that the electrons stored on the ligand can be found in either the singlet or the triplet state,[29] and the paramagnetism in this case also suggests the presence of a mixing of the two states at room temperature. Although the NMR spectrum of **8** is contained within the range expected for a diamagnetic system, the peaks are very broad and overlapping, making their convincing assignment on the basis of position and integration impossible.

Having observed the partial transmetalation of the transition metal for the second time, and with a metal of a very different nature, it is tempting to speculate that this might be a general behavior for complexes of this ligand system. The reaction pathway leading to the final metal extrusion and formation of (bis(imino)pyridinato)Al derivatives certainly may be, rather than metal reduction, responsible for catalyst deactivation and decomposition in these highly active systems.

Polymerization Results. Table 4 outlines the results of the catalytic testing. It can be observed that, in all cases, raising the pressure (1 → 40 bar) and temperature (23 → 50 °C) of the reaction increased the activity of the catalyst significantly, normally by at least 1 order of magnitude or greater. The most intriguing trend, however, is the increase in activity with a decrease of the *formal* oxidation state (runs 1/2, 3/4, and 7/8). The activity of the Cr(III) precursor under 40 atm of ethylene (357 g of PE/mmol), is only half that of the "monovalent" **3** at atmospheric pressure (759 g of PE/mmol). The difference in activity between **3** and **2**, both of which contain Cr in the *formal* monovalent oxidation state, could be ascribed either to the different geometry and coordination number of the metal centers, with square planar being more active than square pyramidal, or perhaps to the presence of a weakly bound MeLi unit able to afford additional transformations (i.e., reduction). The highest activity was observed with complex **7**. It remains very active even at atmospheric ethylene pressure (1200 g of PE/mmol), *being even more active than the corresponding (bis(imino)-pyridine)$FeCl_2$ precursor* (~650 g of PE/mmol) under identical conditions. Runs 10 and 11 compare the results of varying the amount of cocatalyst, showing a slight decrease in the catalytic activity upon doubling the MAO concentration. The increased amount of MAO may lead to an increase in the rate of deactivation or possibly coordination of excess TMA to a dormant species of the type [Cr](μ-Me)$_2$AlMe$_2$.[43]

Most of the polymer samples were analyzed by GPC (Figure 8). All samples display the same broad distribution of molecular weights common among complexes of this ligand system,[12,29] sometimes even exhibiting bi- or polymodal behavior. The main trend to be observed is an increase in the molecular weight of the polymer with an increase in pressure for the Cr(III) and Cr(II) adducts, both displaying very similar GPC traces. The

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(43) Kissin, Y. V.; Qian, C.; Xie, G.; Chen, Y. *J. Polym. Sci. A: Polym. Chem.* **2006**, *44*, 6159.

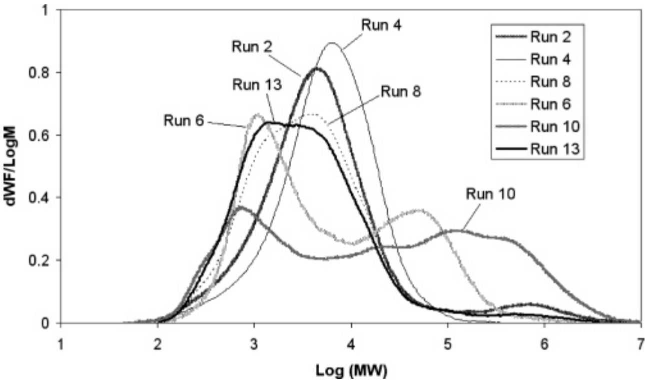

Figure 8. Gel permeation chromatograms of selected polymer samples.

GPC of the polymer produced by **3** is also very similar to those produced by the Cr(III) and Cr(II) species but undergoes a decrease in molecular weight upon an increase in ethylene pressure. The similarities in the GPC and the increase in activity from Cr(III) to Cr(I) suggest potentially the same active species in all three cases. Complex **7**, the main product of activation of **3** with $AlMe_3$, interestingly produced a polymer sample almost identical with that produced by **3**, suggesting the formation of the same active species. In turn, this suggests that complex **3** is a precursor to complex **7**, which is a precursor to the active species for the Cr(I) catalyst. Complexes **2** and **4**, on the other hand, have a similar bimodal distribution, indicative of competing active species, or a change in the active species with time.[43] According to previous results, the formation of the $=CH_2$ function, as resulting from single deprotonation, makes the complex susceptible to reductive dimerization. This transformation may be possible even during the catalytic cycle. The similarities between the polymers produced by **2** and **4** suggest that the presence of a weakly bound MeLi unit in **2** could result in deprotonation of one of the methyl groups, as witnessed in the formation of complex **5**. Therefore, complexes **2** and **4** may undergo the same type of catalyst activation. Complex **8** is catalytically inactive.

All attempts to copolymerize ethylene with a range of terminal olefins failed, in spite of the very promising high activity. High-temperature NMR of the polymer samples in 1,3,5-trichlorobenzene revealed that all of the polymers are highly linear with no assignable presence of branching. In those cases when bimodality was observed (Figure 8), diffusion order spectroscopy (DOSY) NMR experiments revealed the presence of highly linear oligomers containing terminal olefinic groups. The presence and the absence of long chain branching are direct consequences of the lack of copolymerization of α-olefins.

From the results presented above, it appears that reduction of these chromium complexes, implying electron transfer to the ligand at the expense of the metal center, leads to a more active catalyst precursor. In other words, formation of the active species appears to involve reduction of the ligand system as well as alkylation, in line with previous observations with the Fe and Co systems.[26,28,29] Therefore, it is tempting to speculate that the high catalytic activity of complexes of this ligand system is dominated by the ability of the ligand to accept negative charge and that formation of the active species requires the presence of electron density on the ligand backbone.

In conclusion, Cr species supported by the bis(imino)pyridine ligand system with low-valent appearance have been isolated and characterized. These complexes are highly active ethylene polymerization catalyst precursors. The activities of the monovalent Cr complexes were found to be much higher than those of the Cr(III) or Cr(II) precursors, indicating that overall reduction of the system (with electron density mainly located on the ligand) enhances the catalytic activity. The presence of the electron on the ligand backbone seems to be an important factor for increased activity by bis(imino)pyridine catalysts. Similar to the case for Fe, the deactivation pathway has been established, involving reduction and transmetalation of the ligand system to the Al cocatalyst.

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Supporting Information Available: Tables and CIF files giving complete crystallographic data for the complexes reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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