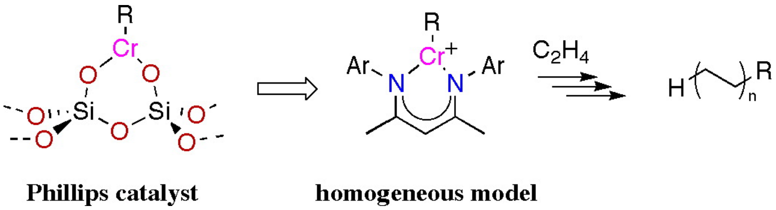
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

A Chromium Catalyst for the Polymerization of Ethylene as a Homogeneous Model for the Phillips Catalyst

Leonard A. MacAdams, Gerald P. Buffone, Christopher
D. Incarvito, Arnold L. Rheingold, and Klaus H. Theopold

J. Am. Chem. Soc., **2005**, 127 (4), 1082-1083• DOI: 10.1021/ja043877x • Publication Date (Web): 07 January 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Chromium Catalyst for the Polymerization of Ethylene as a Homogeneous Model for the Phillips Catalyst

Leonard A. MacAdams, Gerald P. Buffone, Christopher D. Incarvito, Arnold L. Rheingold, and Klaus H. Theopold*

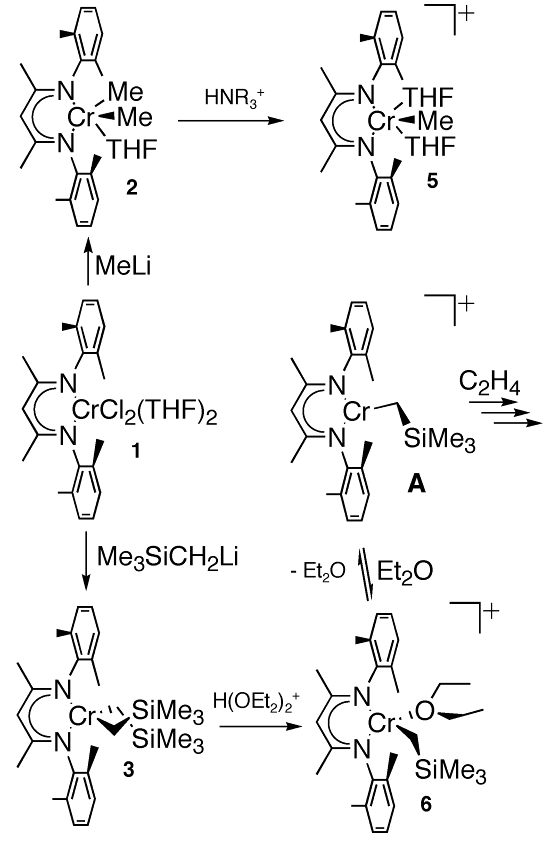
Center for Catalytic Science and Technology, Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received October 7, 2004; E-mail: theopold@udel.edu

In pursuit of a homogeneous model system for the heterogeneous Phillips catalyst for olefin polymerization,[1] we have turned to chromium coordinated by "nacnac" ligands ($(Ar)_2$nacnac = 2,4-pentane-*N,N′*-bis(aryl)ketiminato).[2] The bidentate coordination with hard N-donors approximates the proposed binding of chromium to the silica surface via two oxygen linkages, while the N-substituents allow for steric protection of the active site.[3] While our initial experiments using the $(Ph)_2$nacnacCr(III) fragment demonstrated catalytic activity,[2a] subsequent attempts to isolate a well-defined single-site catalyst were thwarted by disproportionation and ortho-metalation reactions.[2b] Herein we describe the structural characterization and reactivity of a cationic chromium alkyl catalyst that is active in the absence of any cocatalyst.

Addition of $(2,6\text{-}Me_2Ph)_2$nacnacLi to a slurry of $CrCl_3(THF)_3$ in THF yielded the dichloride $(2,6\text{-}Me_2Ph)_2nacnacCrCl_2(THF)_2$ (**1**). Reaction of **1** with lithium alkyls in ether produced the neutral dialkys $(2,6\text{-}Me_2Ph)_2nacnacCr(THF)Me_2$ (**2**), $(2,6\text{-}Me_2Ph)_2nacnacCr(CH_2SiMe_3)_2$ (**3**, see Scheme 1), and $(2,6\text{-}Me_2Ph)_2nacnacCr(Bn)_2$ (**4**), all of which have been structurally characterized. **2** adopts a square pyramidal geometry, while **3** and **4** are rare examples of pseudotetrahedral Cr(III) complexes.

Scheme 1. Synthesis of $(2,6\text{-}Me_2Ph)_2$nacnacCr(III) Alkyls



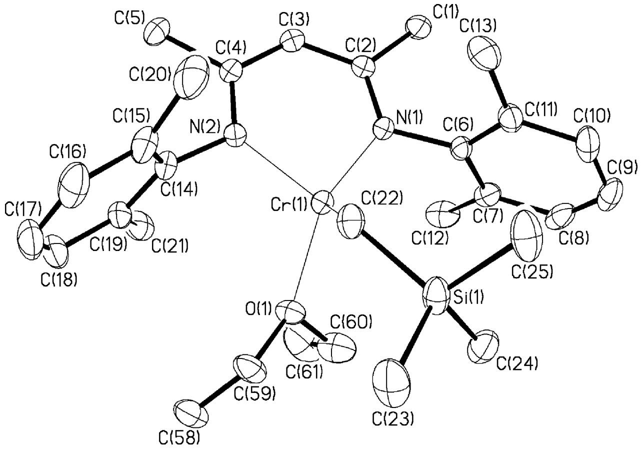


Figure 1. Molecular structure of **6** (the BARF anion has been omitted for clarity). Selected bond distances [Å] and angles [°]: Cr(1)−C(22), 1.930(3); Cr(1)−O(1), 2.056(2); Cr(1)−N(1), 1.934(3); Cr(1)−N(2), 1.930(3); N(1)−Cr(1)−N(2), 89.77(11); O(1)−Cr(1)−C(22), 95.55(13).

Despite their coordinative and electronic unsaturation-four-coordinate **3** has an 11-electron configuration-none of the neutral dialkyls reacted with ethylene. This is in notable contrast to $Cp^*Cr(CH_2SiMe_3)_2$, an analogue of **3** that polymerizes ethylene at low temperatures and pressures.[4] Even formation of a cationic nacnac chromium alkyl does not guarantee catalytic activity. Thus, square pyramidal $[(2,6\text{-}Me_2Ph)_2nacnacCr(THF)_2Me]BPh_4$ (**5**), which was prepared by protonolysis of **2** with 1 equiv of $HNEt_3BPh_4$, did not exhibit any polymerization activity. Once again, we note the contrast to related $[Cp^*Cr(THF)_2Me]BPh_4$, a functional homogeneous model for the Union Carbide catalyst.[5]

However, treatment of **3** with $H(OEt_2)_2^+BARF^-$ ($BARF^- = B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$) in dichloromethane resulted in loss of 1 equiv of $SiMe_4$ and concomitant formation of the brown ether adduct $[(2,6\text{-}Me_2Ph)_2nacnacCr(OEt_2)CH_2SiMe_3]BARF$ (**6**), which could be recrystallized from CH_2Cl_2/pentane. The molecular structure of **6** has been determined by X-ray diffraction, and the result is depicted in Figure 1.[6]

6 adopted distorted tetrahedral coordination of chromium, with the N(1)−Cr(1)−O(1) angle of 136° representing the largest deviation from the ideal tetrahedral angle. The metal−ligand bond distances are rather short, befitting the cationic nature and low coordination number of **6**. The ^1H NMR spectrum of **6** exhibited isotropically shifted and broadened resonances, as expected for a paramagnetic chromium(III) species, and the effective magnetic moment of μ_{eff} (295 K) = 4.1(1) μ_B is consistent with three unpaired electrons of a Cr(III) (d^3) ion in the inevitable high-spin configu-

10.1021/ja043877x CCC: $30.25 © 2005 American Chemical Society

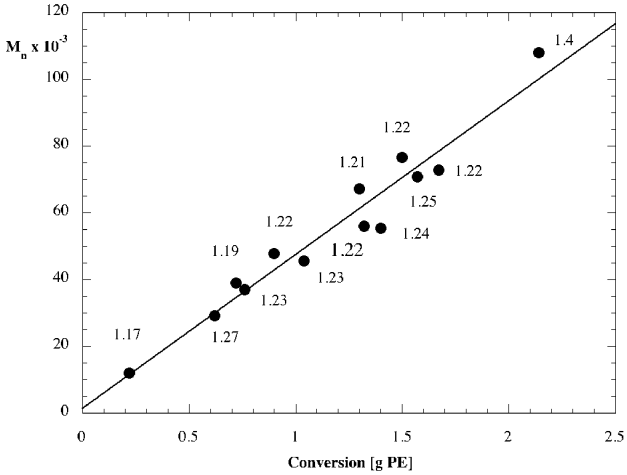


Figure 2. Plot of M_n of various polyethylene samples vs ethylene conversion (0.036 mmol **6**, $p_{\text{ethylene}} = 10-40$ psig). Numbers denote M_w/M_n for each sample.

ration. **6** did not lose the coordinated ether upon prolonged exposure to high vacuum.

Exposure of CH_2Cl_2 solutions of **6** at room temperature to ethylene (10−40 psig, 5−25 min) resulted in an immediate color change from brown to green, and seconds thereafter solid polyethylene precipitated. Polymer yields indicated a “moderate” average activity of 22(8) g PE/mmol·h·atm,[7] decreasing slightly with reaction time. ^{13}C NMR revealed only trace levels of methyl branches (<0.2 Me/1000 C). The low polydispersities of the polymers thus obtained ($M_w/M_n \cong 1.2$) and the dependence of the polymer molecular weight (M_n) on conversion (see Figure 2) suggest that the process has at least some of the features characteristic of a living polymerization.[8] There are few homogeneous catalysts for the polymerization of ethylene thought to be living;[9] to our knowledge none involve chromium.[10] Polymer produced at higher ethylene pressure (300 psig) exhibited a somewhat broader molecular weight distribution ($M_w/M_n = 1.73$); however, this may be attributable to the effects of the pronounced exotherm observed in this experiment (20 °C to 75 °C within the first minute).

Our model system reproduces the Phillips catalyst’s ability to produce “linear low-density polyethylene” (LLDPE) by copolymerization of ethylene with α-olefins. Thus, **6** catalyzed the copolymerization of ethylene with 1-hexene.[1] ^{13}C NMR analysis of a polymer produced in the presence of 1-hexene (20 g of 1-hexene in 30 mL of CH_2Cl_2, 200 psig C_2H_4) showed the presence of 103 butyl side chains per 1000 backbone carbons. Remarkably, its polydispersity ($M_w/M_n = 1.78$) is similar to that of the homopolymer, and the molecular weight ($M_n = 108\ 000$) is even larger.

We suggest that the active species in these polymerizations is the three-coordinate nine-electron species $[(2,6\text{-}Me_2Ph)_2\text{nacnac}CrCH_2SiMe_3]^+$ (**A** in Scheme 1) rather than the four-coordinate ether adduct **6**. Several lines of evidence support this notion. First, addition of 1 equiv of THF to **6** yields catalytically inactive $[(2,6\text{-}Me_2Ph)_2\text{nacnac Cr(THF)}CH_2SiMe_3]$BARF. Furthermore, addition of small amounts of Et_2O to catalyst solutions significantly decreases their activity. Finally, dilution of the catalyst increased its specific activity; i.e., the effect expected due to a concentration-dependent shift of a dissociation equilibrium.

Three-coordinate cationic Cr(III) alkyls supported by bidentate nitrogen ligands catalyze the polymerization of ethylene and the copolymerization of ethylene with α-olefins. Therefore, we suggest that a species akin to **A** represents a reasonable candidate for the active surface species of the heterogeneous Phillips catalyst. Further studies concerning the effect of charge, formal oxidation state, and ligand structure on the reactivity of chromium alkyls with olefins will be the subject of future publications.

Acknowledgment. This research was supported by grants from the NSF (CHE-0132017) and Chevron Phillips Chemical Co.

Supporting Information Available: Experimental and characterization details for **1**−**6** (PDF); X-ray structural data for **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Hogan, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2637−2652. (b) McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47−98.

(2) (a) Kim, W. K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543. (b) MacAdams, L. A.; Kim, W. K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952−960. (c) Theopold, K. H.; MacAdams, L. A.; Puttnual, C.; Buffone, G. P.; Rheingold, A. L. *Polym. Mater. Sci. Eng.* **2002**, *86*, 310.

(3) For related chromium chemistry see: (a) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1651−1652. (b) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895−1903.

(4) Heintz, R. A.; Leelasubcharoen, S.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 5477−5485.

(5) Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893−902.

(6) Crystal data for **5**: $C_{61}H_{58}BCrF_{24}N_{2O}Si$, $M_w = 1381.99$, space group $P2(1)/c$, $a = 13.628(2)$ Å, $b = 25.586(4)$ Å, $c = 18.371(3)$ Å, $V = 6405.4(16)$ Å^3, $Z = 4$, $D = 1.433$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 3.09$ cm^{-1}, $F(000) = 2820$, $T = 203$ K, 15 198 independent reflections, $R1 = 0.0747$, $wR2 = 0.2154$.

(7) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429−447.

(8) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257.

(9) (a) Brookhart, M.; Volpe, A. F., Jr.; De Simone, J. M. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1991**, *32*, 461−462. (b) Brookhart, M.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378−5380. (c) Mashima, K.; Fujikawa, S.; Urata, H.; Tanaka, E.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1623−1624. (d) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2001**, *34*, 1140−1142. (e) Matsugi, T.; Matsui, S.; Kojoh, S.; Takagi, Y.; Inoue, Y.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 566−567. (f) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477−493. (g) Matsugi, T.; Matsui, S.; Kojoh, S.; Takagi, Y.; Inoue, Y.; Nakano, T.; Fujita, T.; Kashiwa, N. *Macromolecules* **2002**, *35*, 4880−4887. (h) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327−3336. (i) Mitani, M.; Nakano, T.; Fujita, T. *Chem. Eur. J.* **2003**, *9*, 2397−2403. (j) Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542−2544.

(10) For a living ethylene oligomerization system containing Cr, see: (a) Mani, G.; Gabbai, F. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2263−2266. (b) Ganesan, M.; Gabbai, F. P. *Organometallics* **2004**, *23*, 4608−4613.

JA043877X