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α-Olefin Polymerization with Ether-Coordinated Chromium(III) Alkyls

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Summary: Extremely substitution labile chromium(III) alkyls of the type $[Cp^*Cr(OR_2)_nCH_2SiMe_3]^+[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]^-$ *(R = Me, Et, ⁱPr; n = 1, 2) have been prepared; they are homogeneous catalysts for the polymerization of ethylene and, for the first time, α-olefins (propene, 1-hexene).*

Despite the commercial importance of chromium-based ethylene polymerization catalysts, investigations of their chemistry on a molecular level remain grossly outnumbered by studies of Ziegler−Natta catalysts containing d^0, group 4 elements,[1] due in part to the paramagnetism of relevant chromium compounds. (Pentamethylcyclopentadienyl)chromium(III) alkyls now represent a well-characterized homogeneous model system for heterogeneous ethylene polymerization catalysts containing that metal.[2] As part of our continuing effort to map the reactivity of paramagnetic chromium alkyls, we are aiming to increase their electrophilicity and coordinative unsaturation, in the hopes of—inter alia—facilitating polymerization of α-olefins and assessing the importance of agostic interactions in chromium catalysis. Herein we report a series of cationic chromium alkyls with very weakly bound dialkyl ether ligands, which polymerize propene and 1-hexene.

Addition of 1 equiv of $[H(O^iPr_2)_2]^+[B(C_6H_3(CF_3)_2)_4]^-$ [3] to a cold diethylether solution of $Cp^*Cr(CH_2SiMe_3)_2$, followed by addition of pentane, yielded purple crystals of $[Cp^*Cr(OEt_2)_2CH_2SiMe_3]^+BAr'_4{}^-$ (**1b**) in 94% yield (see Scheme 1). Its recrystallization from dimethyl ether solvent provided $[Cp^*Cr(OMe_2)_2CH_2SiMe_3]^+BAr'_4{}^-$ (**1a**). **1a**,**b** were characterized by standard spectroscopic techniques (see Supporting Information), and the structure of **1b** was determined by X-ray diffraction.[4] While loss of ether and disorder in the CF_3 groups of the counterion, even at a data collection temperature of −69 °C, compromised the structure sufficiently to render individual bond distances and angles unreliable, the chemical nature of the compound is not in doubt; the molecular structure of **1b** is depicted in Figure 1. The fluorinated tetraarylborate lives up to its reputation as a "noncoordinating" anion,[5] being well separated from the chromium complex. The latter adopts the familiar three-legged piano-stool geometry, which has proven characteristic of the Cp^*Cr^{III} fragment. Two coordination sites of the pseudooctahedral chromium complex are occupied by diethyl ether molecules. In keeping with the steric saturation of the metal ion, **1** shows no structural indication of any agostic interactions. Due to the poor ligand properties of acyclic ethers few transition-metal alkyls containing such ligands have proven sufficiently stable for structural characterization.[6] **1b** is a rare example containing two such labile ligands.

The chemistry of **1a**,**b** reflects the weakness of their $Cr-OR_2$ bonds. Addition of donor solvents (e.g. THF, DME) led to immediate replacement of both dialkyl ethers and produced the comparatively robust, purple alkyls $[Cp^*Cr(THF)_2CH_2SiMe_3]^+BAr'_4{}^-$ (**1d**) and $[Cp^*Cr(DME)CH_2SiMe_3]^+BAr'_4{}^-$ (**1e**). However, while solid **1a** could be kept under vacuum without ligand loss and maintained its purple color when dissolved in noncoordinating solvents, **1b** displayed a greater tendency to extrude one of its ligands. When exposed to vacuum, purple crystals of **1b** (UV/vis/near-IR: solid, 536, 700 nm; Et_2O, 531 ($\epsilon = 1100$), 703 ($\epsilon = 360$) nm) were rapidly transformed into an orange powder (UV/vis/near-IR: solid, 506, 746 nm), concomitant with a weight loss of 5.5% (theoretical 6% for loss of 1 equiv of Et_2O). Exposure of the orange solid to Et_2O vapors restored the purple color and original mass of **1b**. Dissolution of **1b** in noncoordinating solvents gave orange solutions (UV/vis/near-IR: CH_2Cl_2, 507 ($\epsilon = 825$), 739 ($\epsilon = 475$) nm; o-$C_6H_4F_2$, 503 ($\epsilon = 760$), 742 ($\epsilon = 470$) nm). On the basis of these observations, we assign the formula $[Cp^*Cr(OEt_2)CH_2SiMe_3]^+BAr'_4{}^-$ (**2b**) to the orange compound. The thermal stability of solutions of **2b** (and hence **1b**) in noncoordinating solvents (CH_2Cl_2, o-$C_6H_4F_2$) is limited (see below), and to date, it has resisted all of our attempts to determine its crystal structure. **2b** showed no spectroscopic evidence of any agostic interactions, though, and we suggest that it is a coordinatively unsaturated pseudo-5-coordinate chromium alkyl with a 13-electron configuration.

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(2) (a) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (b) Noh, S.-K.; Heintz, R. A.; Janiak, C.; Sendlinger, S. C.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 775. (c) Thomas, B. J.; Noh, S.-K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (d) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (e) Bhandari, G.; Rheingold, A. L.; Theopold, K. H. *Chem. Eur. J.* **1995**, *1*, 199.

(3) $[H(OEt_2)_2]^+[B(C_6H_3(CF_3)_2)_4]^-$ was prepared according to: Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. The isopropyl etherate was obtained by recrystallization from $^iPr_2O$.

(4) **1b**: purple cubes from Et_2O/pentane; monoclinic, $P2_1/n$; $a = 12.573(1)$ Å, $b = 12.829(1)$ Å, $c = 37.210(1)$ Å, $\beta = 95.991(2)°$, $T = -69$ °C, $V = 5969.2$ Å^3, $Z = 4$, $R = 0.146$, $R_w = 0.140$.

(5) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

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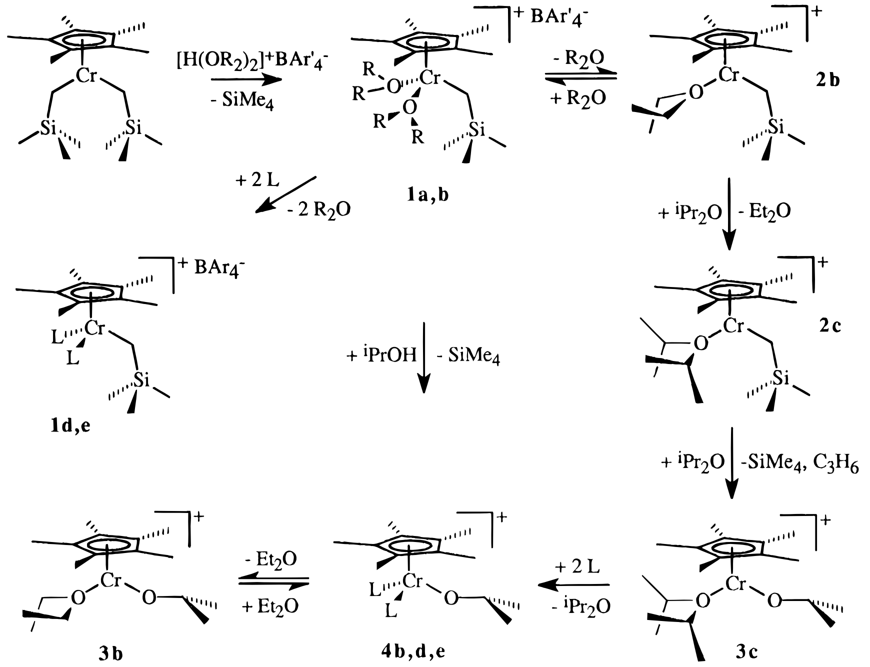
Scheme 1[a]



[a] Identity of L and/or R_2O: **a**, Me_2O; **b**, Et_2O; **c**, ${}^iPr_2O$; **d**, THF; **e**, DME.

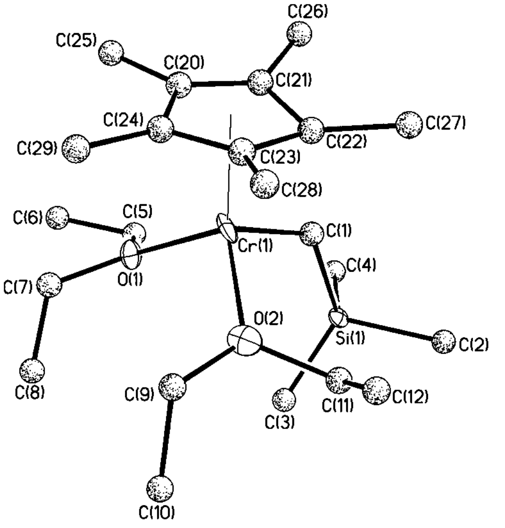


Figure 1. Molecular structure of the chromium cation of $[Cp^*Cr(OEt_2)_2CH_2SiMe_3]^+[B(C_6H_3(CF_3)_2)_4]^-$ (**1b**). Disorder in the ethyl groups of the Et_2O ligands and the CF_3 groups of the anion (not shown) made determination of accurate interatomic distances and angles impossible. Best estimates are as follows: Cr–O1, 2.09(2) Å; Cr–O2, 1.95(2) Å; Cr–C1, 2.09(2) Å.

As expected, **1a**,**b** were extremely active ethylene polymerization catalysts. For example, exposure of a cold solution of **1b** (50 mg in 18 mL of CH_2Cl_2, −78 °C) to ethylene (1.2 atm) quickly resulted in precipitation of polyethylene (30 min, yield 950 mg, $M_w = 73\,620$, $M_w/M_n = 2.74$, mp = 133 °C). Indeed, stirring a suspension of solid **1b** in liquid ethylene for 20 min (ambient pressure, $T < -104$ °C) produced small amounts of polymer. At ambient temperature the polymerization reactions became noticeably hot and rapid deactivation and high polydispersities indicated thermal decomposition of the catalyst. Thus, 50 mg of **1b** dissolved in 0.5 mL of *o*-difluorobenzene, diluted with 29.5 mL of toluene and exposed to ca. 0.8 atm of ethylene beginning at room temperature, yielded 585 mg of polyethylene within 20 min ($M_w = 217\,000$, $M_w/M_n = 9.65$, mp = 133 °C). We also note that Et_2O solutions of **1b** were completely inactive, in accord with the notion of a coordinatively unsaturated 13-electron species as the active catalyst. Exposure of solid **2b** to 1.0 equiv of ethylene (room temperature, 5 min), followed by quenching with D_2O, yielded a mixture of hydrocarbons of the type $Me_3SiCH_2(CH_2CH_2)_nD$ ($n = 0-4$, detected by ^1H NMR and GC–MS), providing direct evidence for ethylene insertion into the chromium–alkyl bond.

The high activity in the polymerization of ethylene encouraged us to try α-olefins. Monitoring a solution of **1a** and 10 equiv of propene in CD_2Cl_2 at −8 °C by ^1H NMR showed the gradual disappearance of the resonances of the olefin over the course of 2 h and the rise of several new resonances in the 0.8–2.0 ppm region, consistent with the formation of polypropene.[7] A small pair of resonances (δ 4.72, 4.65 ppm), characteristic of a *gem*-dialkyl olefin such as might be formed by β-hydrogen elimination from a growing polypropene chain, was also observed. In a larger scale polymerization, exposure of a solution of **1a** (100 mg in 30 mL of CH_2Cl_2, 2.7 mM, −6 °C) to 0.8 atm of propene produced 180 mg of an oily residue (>50 turnovers). GC–MS analysis of this oil showed it to be a mixture of propene oligomers (i.e. $CH_2{=}C(Me)(CH_2C(H)Me)_{n-1}H$) ranging from C_9 to C_{51} in size ($n = 3-17$), with a maximum at C_{18}/C_{21}. Curiously, raising the propene pressure to 5.8 atm did not significantly increase the yield or the molecular weight of the polymer. Similarily, monitoring a reaction of **1a** with 15 equiv of 1-hexene (7 °C) by NMR showed complete conversion of the olefin to polymer after 1 h, and GC–MS analysis revealed a distribution of molecular weights ranging from C_{12} to C_{66} ($n = 2-11$), with a maximum at C_{24}. We note that the mass spectra did not show any evidence for (trimethylsilyl)methyl end

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(7) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: San Diego, CA, 1988; pp 365–370.

groups; thus, we assume that chain transfer by β-hydrogen elimination rapidly generates a chromium hydride (i.e. $Cp^*Cr(OMe_2)_nH]^+BAr'_4$) as the majority catalyst. Attempts to prepare this hydride by hydrogenolysis of **1a** have been unsuccessful to date, yielding a complicated mixture of decomposition products.

On the basis of the apparent stabilization of the coordinatively unsaturated 13-electron alkyl by sterically more demanding ligands, we hoped to prepare, and isolate, such a complex using diisopropyl ether. However, when **1b** was dissolved in $^iPr_2O$, the orange color of the initially formed $[Cp^*Cr(^iPr_2O)CH_2SiMe_3]^+$ ion (**2c**) rapidly (<30 s) changed to green. Adding pentane and cooling the solution at this point yielded green crystals of the isopropoxide complex $[Cp^*Cr(O^iPr_2)O^iPr]^+BAr'_4{}^-$ (**3c**). NMR experiments showed that $SiMe_4$ and propene were also formed during this reaction. **3c** itself was not stable in the presence of excess $^iPr_2O$; its green solution eventually turned purple, and we have not identified any of the ultimate decomposition products. Addition of better ligands to the green solution of **3c** yielded blue $[Cp^*Cr(OEt_2)_2O^iPr]^+BAr'_4{}^-$ (**4b**), $[Cp^*Cr(THF)_2O^iPr]^+$-$BAr'_4{}^-$ (**4d**), and $[Cp^*Cr(DME)O^iPr]^+BAr'_4{}^-$ (**4e**), respectively. Like **1b**, **4b** reversibly lost 1 equiv of diethyl ether under vacuum to form green $[Cp^*Cr(OEt_2)O^iPr]^+$-$BAr'_4{}^-$ (**3b**). Cleavage of ethers by strong bases (here the CH_2SiMe_3 group) is precedented,[8] and the extreme electrophilicity of the cationic, 13-electron chromium center probably enhances the leaving-group tendency of the alkoxide moiety. We attribute the limited thermal stability of **1b** to a similar elimination reaction (yielding ethylene and a chromium ethoxide). This decomposition pathway may limit the general utility of ethers as ancillary ligands for highly electron deficient metal alkyls.

While we have long held pseudo-5-coordinate intermediates with 13-electron configurations responsible for the polymerization activity of Cp^*Cr^{III} alkyls, the present results show that such molecules can be prepared (i.e. **2b**,**c**). Their reactivity is high and for the first time includes the polymerization of α-olefins. Nevertheless, the comparatively high selectivity of this chromium system for ethylene is remarkable, and the current strategy for overcoming the reticence of α-olefins has pushed the system to the limits of stability. Our search for other chromium-based homogeneous α-olefin polymerization catalysts is continuing.

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Supporting Information Available: Text giving a summary of the crystal structure determination and tables giving the positional and thermal parameters of **1b** and tables of spectroscopic data for all complexes (7 pages). Ordering information is given on any current masthead page.

OM960697Q

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[8] (a) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 382. (b) March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1977; pp 925−926.