

of the cyclic product **11**, alongside lesser amounts of the directly reduced product **10**. A sequence of propagation steps analogous to that outlined in eq 2 (halogen abstraction, 1,5-H atom transfer, cyclization, chain transfer) accounts for the formation of **11**, which now contains a simple benzyl group. The (*o*-bromophenyl)dimethylsilyl group<sup>12</sup> is readily introduced by standard silylation conditions, and, in the example studied, it provided a better ratio of cyclic to reduced products than did the *o*-bromobenzyl group. The reduction of **12** under the Stork conditions provided a 61% isolated yield of **14**.

The option to place a radical precursor at a site other than that where the radical is ultimately required can simplify the preparation of substrates for complex synthetic applications. Variations of the translocation strategy outlined herein should provide access to a variety of stabilized radicals for use in cyclization or addition reactions.

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**Supplementary Material Available:** Spectroscopic characterization of all cyclic products in eq 3 and 4 and Table I (6 pages). Ordering information is given on any current masthead page.

(12) (*o*-Bromophenyl)dimethylsilyl chloride was prepared by silylation of *o*-bromophenyllithium. See: Chen, L. S.; Chen, G. J.; Tamborski, C. J. *Organomet. Chem.* **1980**, 193, 283. This procedure was modified as follows: dimethyldichlorosilane was added before *n*-butyllithium, and the product was isolated by nonaqueous workup (evaporation of the THF, dilution with hexane, filtration, and concentration). We thank Drs. Richard Elliott and Thomas Fevig for the preparation of this silyl chloride.

## Cationic Chromium(III) Alkyls as Olefin Polymerization Catalysts

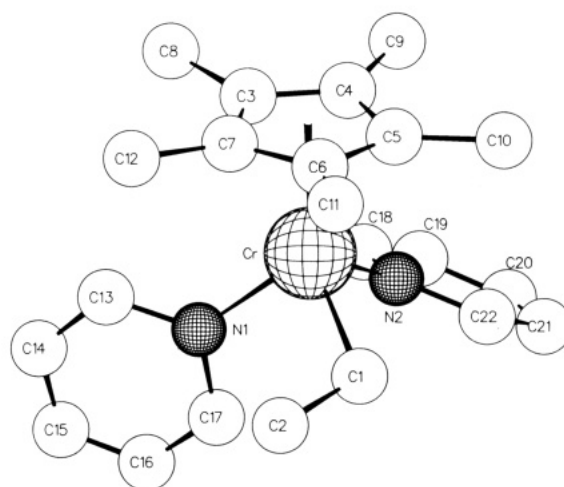
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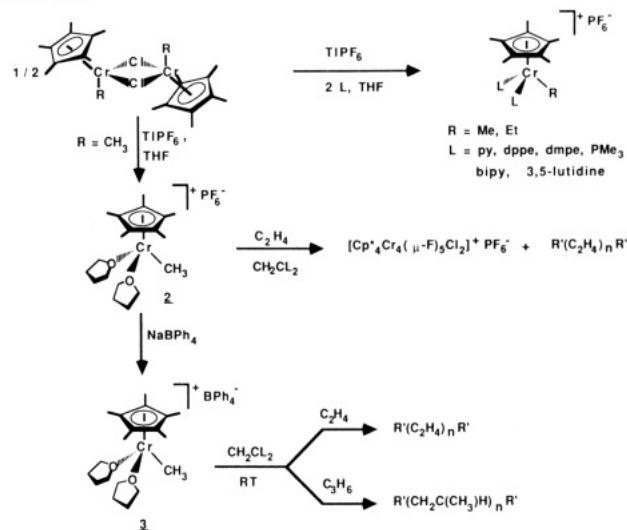
Chromium-based catalysts are used in the commercial coordination polymerization of small olefins.<sup>1</sup> A particular catalyst of this type is prepared by deposition of chromocene ( $\text{Cp}_2\text{Cr}$ ) on silica.<sup>2</sup> The species thus generated is thought to retain one cyclopentadienyl ligand, which is not incorporated into the growing polymer chain. We are exploring the reactivity of a class of paramagnetic chromium alkyls containing cyclopentadienyl ligands ( $\text{C}_5\text{H}_5$  or  $\text{C}_5\text{Me}_5$ ).<sup>3</sup> These compounds appear to be close structural models of the active site proposed for the heterogeneous catalyst. Herein we describe a number of cationic chromium(III) alkyls, some of which are catalysts for the polymerization of ethylene and propene.

Abstraction of chloride from dimeric alkyl complexes of the type  $[\text{Cp}^*\text{Cr}(\text{R})\text{Cl}]_2$  in the presence of Lewis bases yielded a series of mononuclear chromium complexes (see Scheme I).<sup>4</sup> Like their precursors, these compounds feature 15 valence electrons only. However, in contrast to the dimeric starting materials, and due to their monomeric nature, they exhibit the full effective magnetic



**Figure 1.** The molecular structure of the  $\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}$  cation. The  $\text{PF}_6^-$  counterion is omitted for clarity. Selected bond distances:  $\text{Cr}-\text{C}1$ , 2.094 (12) Å;  $\text{Cr}-\text{N}1$ , 2.083 (9) Å;  $\text{Cr}-\text{N}2$ , 2.085 (9) Å;  $\text{C}1-\text{C}2$ , 1.521 (17) Å. Interatomic angles:  $\text{C}1-\text{Cr}-\text{N}1$ , 92.8 (4)°;  $\text{C}1-\text{Cr}-\text{N}2$ , 94.2 (4)°;  $\text{N}1-\text{Cr}-\text{N}2$ , 88.1 (3)°;  $\text{Cr}-\text{C}1-\text{C}2$ , 113.2 (8)°.

### Scheme I



moment of three unpaired electrons per chromium atom. For example, when 2.0 equiv of  $\text{TIPF}_6$  were added to a THF solution of  $\text{Cp}^*\text{Cr}(\text{Et})\text{Cl}]_2$  containing 4.0 equiv of pyridine, the color of the solution changed from purple to brown and a grey precipitate ( $\text{TiCl}$ ) formed. Filtration, removal of solvent, and recrystallization of the solid residue from THF/pentane yielded analytically pure  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  (**1**) in 74% yield.<sup>5</sup> The crystal structure of **1** was determined by X-ray diffraction (see Figure 1).<sup>6</sup> The compound consisted of well-separated cations and  $\text{PF}_6^-$  anions. The chromium atom exhibited the pseudooctahedral coordination environment of a three-legged piano stool. The chromium-carbon distance ( $\text{Cr}-\text{C}1$ , 2.09 Å) was essentially the same as that in the structurally characterized dimer  $[\text{Cp}^*\text{Cr}(\text{Me})\text{Cl}]_2$ . The  $\text{Cr}-\text{C}1-\text{C}2$  angle (113°) was slightly larger than the perfect tetrahedral angle, presumably reflecting the steric demand of the metal fragment. Despite the electron-deficient nature of the complex, no indication of an agostic  $\text{M}-\text{H}-\text{C}$  interaction<sup>7</sup> between the chromium atom

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(4) Satisfactory elemental analyses have been obtained for all compounds reported herein. Details of the syntheses and full characterizations will be reported in a full paper.

(5) **1**:  $^1\text{H}$  NMR ( $\text{THF}-d_6$ ) 22.4, 18.9, -13.0 ppm; IR (KBr) 3587 (w), 3080 (m), 2919 (s), 2856 (s), 2728 (w), 1604 (s), 1487 (s), 1445 (s), 1382 (s), 1217 (m), 1130 (m), 1065 (s), 1012 (s), 846 (vs), 765 (s), 708 (s), 640 (s), 556 (vs), 443 (m), 401 (m)  $\text{cm}^{-1}$ ; mp 165-170 °C;  $\mu_{\text{eff}}$  = 3.87  $\mu_B$  at 298 K. Anal. Calcd for  $\text{C}_{22}\text{H}_{30}\text{CrF}_6\text{N}_2\text{P}$ : C, 50.87; H, 5.82; N, 5.39. Found: C, 50.83; H, 5.97; N, 5.27.

(6) Black cubes from  $\text{THF}/\text{Et}_2\text{O}$ ; monoclinic  $P2_1/c$ ;  $a$  = 8.810 (2) Å,  $b$  = 15.425 (3) Å,  $c$  = 17.792 (3) Å,  $\beta$  = 89.34 (9)°;  $Z$  = 4;  $R$  = 0.083,  $R_w$  = 0.099.

(7) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, 250, 395.

and the alkyl group was found.

**1** catalyzed the polymerization of ethylene, albeit very slowly. We reasoned that binding of the olefin by substitution of a pyridine might be the rate-limiting step of this reaction and thus sought an analogue of **1** with more labile ligands. Addition of 2.0 equiv of  $\text{TiPF}_6$  to a THF solution of  $[\text{Cp}^*\text{Cr}(\text{Me})\text{Cl}]_2$  followed by standard workup yielded dark purple crystals of  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{PF}_6^-$  (**2**).<sup>3b</sup> To our surprise this compound proved stable enough for isolation and full characterization. However, when a solution of **2** in  $\text{CD}_2\text{Cl}_2$  was exposed to 6 equiv of ethylene in a sealed NMR tube, no residual ethylene could be detected in the tube by the time the  $^1\text{H}$  NMR was recorded. Instead two broad resonances at 1.52 and 1.23 ppm were observed, indicating the formation of long-chain saturated hydrocarbons, and a white solid (polyethylene) precipitated from the solution. Substitution of  $\text{THF}-d_8$  for  $\text{CD}_2\text{Cl}_2$  as a reaction medium substantially slowed the polymerization reaction, consistent with our notion that the olefin molecule must replace one of the ligands bound to chromium before insertion can take place. Unfortunately **2** also proved reactive enough to eventually self destruct. Solutions of it changed color from purple to a brilliant blue during the course of several hours. This decomposition involved attack on the hexafluorophosphate anion by the highly Lewis acidic chromium, leading to polynuclear chromium complexes held together by fluoride bridges (see Scheme I).<sup>3c</sup> In order to avoid this catalyst deactivation, the tetraphenylborate salt  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  (**3**) was prepared by anion metathesis of **2** with  $\text{NaBPh}_4$ .<sup>8</sup> Solutions of **3** proved stable over several days, facilitating a more detailed study of the polymerization reaction.

Exposure of a solution of **3** (100 mg in 50 mL of  $\text{CH}_2\text{Cl}_2$ ) to 1 atm of ethylene at room temperature initially resulted in a rapid uptake of the olefin, which eventually slowed down and came to a halt after approximately 3 h. At this point the color of the solution had changed to a blue shade of purple and 560 mg of a white solid had precipitated from the solution. The IR spectrum of this solid was indistinguishable from that of authentic high-density polyethylene, and its melting range was 123–124 °C. Gel permeation chromatography (GPC) analysis showed the sample to have a relatively narrow molecular weight distribution ( $M_w = 6530$ ,  $M_n = 3025$ ,  $d = 2.16$ ). A similar experiment at higher ethylene pressure (3 atm) yielded 660 mg of polyethylene (mp 129–137 °C) with higher molecular weight and dispersity ( $M_w = 23200$ ,  $M_n = 5690$ ,  $d = 4.08$ ). The activity of the catalyst was determined by monitoring the pressure drop in a large reaction volume charged initially with 1.5 atm of ethylene. At ambient temperature (22 °C) the initial rate of insertion was 0.24 turn-overs/s. We believe that the eventual deactivation of the catalyst was caused by impurities in the ethylene (i.e.,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ), because passing the ethylene through a bed of activated 4A molecular sieves led to a doubling in the yield of polyethylene.

The reaction of **3** with propene was much slower.  $^1\text{H}$  NMR spectra of a sample containing ca. 10 equiv of propene in a sealed tube showed a gradual decrease in intensity of the olefinic signals accompanied by the appearance of signals for new hydrocarbons. However, the reaction stopped before the propene was consumed completely and the nature of the products (molecular weight, tacticity) remains to be established.

Several recent observations point toward cationic alkyls as the active species in Ziegler-Natta catalyst preparations based on group 4 elements.<sup>9</sup> Our results indicate that in chromium-based

systems too, cationic metal sites may be responsible for the catalysis. The positive charge of such complexes may indeed be crucial for binding of the electron-rich olefin to a metal center that has little propensity for back-bonding. There remains the intriguing question how the support surface of actual heterogeneous catalysts stabilizes highly Lewis acidic and substitutionally labile metal complexes. We are currently studying this problem as well as the influence of the metal oxidation state on polymerization activity.

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**Supplementary Material Available:** Tables of crystal data and summary of data collection and refinement, fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles for **1** (8 pages); listing of structure factor magnitudes for **1** (10 pages). Ordering information is given on any current masthead page.

### The Relative Ease of Removing a Proton, a Hydrogen Atom, or an Electron from Carboxamides versus Thiocarboxamides

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Measurements of the acidities of acetamide and thioacetamide, their oxidation potentials, and those of their conjugate bases have revealed that the thiocarboxamide group gives up a proton more readily by about 10 kcal/mol, a hydrogen atom by about 16 kcal/mol, and an electron by about 50 kcal/mol (Table I). These differences are associated with the greater inherent ability of sulfur than oxygen to stabilize an anion, a radical, or a radical cation, which is exaggerated in the species derived from the amides by the weaker  $\text{C}=\text{S}$  than  $\text{C}=\text{O}$  bond.

Examination of Table I shows that replacement of the oxygen atom in carboxamides by a sulfur atom causes striking decreases in N–H bond  $pK_{\text{HAS}}$ ,<sup>10</sup> in homolytic N–H bond dissociation energies (BDEs), and in the acidities of the corresponding radical cations ( $pK_{\text{HA}}^{+\bullet}$ ). For  $\text{CH}_3\text{C}(=\text{X})\text{NH}_2$ ,  $\text{PhC}(=\text{X})\text{NH}_2$ , and  $\text{H}_2\text{NC}(=\text{X})\text{NH}_2$  the  $\Delta pK_{\text{HA}}$  values are 9.6, 8.8, and 8.1 kcal/mol, respectively, the  $\Delta\text{BDEs}$  are 16.5, 16.5, and 18, respectively, and the  $\Delta pK_{\text{HA}}^{+\bullet}$  values are 31.5, 23, and 23 kcal/mol, respectively. For the N-phenyl-substituted amides,  $\text{CH}_3\text{C}(=\text{X})\text{NHPh}$ , and

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(5) These BDEs, which are believed to be accurate to about  $\pm 3$  kcal/mol, are based on a thermodynamic cycle. This method has been used previously to estimate BDEs in the gas phase,<sup>6</sup> and a comparable method has been used to estimate the BDE of the O–H bond in hydroquinone and the hydroquinone radical.<sup>7</sup> BDE values for N–H bonds for carboxamides or thiocarboxamides do not appear to have been estimated hitherto; the BDE for the N–H bond in  $\text{NH}_3$  is  $107.4 \pm 1.1$ .<sup>8</sup>

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(10) In the gas phase  $\text{CH}_3\text{C}(=\text{S})\text{NH}_2$  has a higher acidity than  $\text{CH}_3\text{C}(=\text{O})\text{NH}_2$  by 15 kcal/mol, showing that the sulfur effect on acidity is an intrinsic one.<sup>11</sup>

(8) **3**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) 9.0, 8.0, 7.36, 7.05, 6.93, –26.5 ppm; IR (KBr) 3051 (s), 2850 (s), 1940 (w), 1882 (w), 1821 (w), 1762 (w), 1700 (w), 1604 (s), 1578 (s), 1483 (s), 1443 (s), 1424 (s), 1379 (s), 1268 (m), 1214 (m), 1184 (m), 1149 (m), 1130 (s), 1066 (s), 1046 (s), 1032 (m), 1012 (s), 850 (s), 843 (s), 757 (vs), 731 (vs), 703 (vs), 639 (m), 611 (m), 477 (m), 438 (m)  $\text{cm}^{-1}$ ; mp 135–138 °C. Anal. Calcd for  $\text{C}_{43}\text{H}_{54}\text{BCrO}_2$ : C, 77.58; H, 8.18. Found: C, 77.62; H, 8.21.

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