

# Paramagnetic Alkylchromium Compounds as Homogeneous Catalysts for the Polymerization of Ethylene

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**Abstract:** A class of homogeneous model compounds for chromium-based ethylene polymerization catalysts has been prepared. Abstraction of halide from dimers  $[\text{Cp}^*\text{Cr}^{\text{III}}(\mu\text{-Cl})\text{R}]_2$  in the presence of Lewis bases gave cationic half-sandwich complexes  $[\text{Cp}^*\text{Cr}^{\text{III}}(\text{L})_2\text{R}]^+\text{X}^-$  (R = Me, Et; L = py, 3,5-lut,  $\text{PMe}_3$ , dppe, dmpe, MeCN, THF;  $\text{X}^- = \text{PF}_6^-, \text{BPh}_4^-$ ). The crystal structures of  $[\text{Cp}^*\text{Cr}^{\text{III}}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  (10) and  $[\text{Cp}^*\text{Cr}^{\text{III}}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  (14) were determined by X-ray diffraction. 10 crystallized in the monoclinic space group  $P2_1/c$  with  $a = 8.810$  (2) Å,  $b = 15.425$  (3) Å,  $c = 17.792$  (3) Å, and  $\beta = 89.34$  (9)° with  $Z = 4$ . 14 crystallized in the monoclinic space group  $P2_1/c$  with  $a = 10.718$  (3) Å,  $b = 16.209$  (4) Å,  $c = 21.880$  (6) Å, and  $\beta = 103.63$  (2)° with  $Z = 4$ .  $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  (7) exhibited a reversible reduction wave at  $-1.88$  V (vs  $\text{Fc}^+/\text{Fc}$ ). Chemical reduction of 7 yielded  $\text{Cp}^*\text{Cr}^{\text{II}}(\text{dmpe})\text{Me}$  (16), a paramagnetic ( $\mu_{\text{eff}} = 2.79 \mu_{\text{B}}$ ) alkylchromium(II) complex with a 16-electron configuration. 16 was structurally characterized; it crystallized in the orthorhombic space group  $Pbca$  with  $a = 14.223$  (2),  $b = 16.108$  (3), and  $c = 17.391$  (3) Å with  $Z = 8$ . 14 catalyzed the polymerization of ethylene at ambient temperature and pressure. The mechanism of the catalysis involved dissociation of THF from 14, thus yielding coordinatively unsaturated  $[\text{Cp}^*\text{Cr}^{\text{III}}(\text{THF})\text{Me}]^+$ . The polyethylene was characterized by GPC and  $^{13}\text{C}$  NMR. It exhibited narrow molecular weight distributions ( $M_w/M_n = 1.61\text{--}4.60$ ) and little branching. Reaction of 14 with styrene gave  $\text{Cp}^*\text{Cr}^{\text{II}}(\eta^6\text{-Ph-BPh}_3)$  (17), a model for the catalyst deactivation process. The X-ray crystal structure of 17 showed it to crystallize in the monoclinic space group  $P2_1/c$  with  $a = 11.486$  (4) Å,  $b = 11.732$  (4) Å,  $c = 20.716$  (6) Å, and  $\beta = 100.25$  (3)° with  $Z = 4$ . One of the phenyl groups of the tetraphenylborate anion was coordinated to chromium. A direct comparison of the reactivity of divalent and trivalent chromium with ethylene was made. While  $[\text{Cp}^*\text{Cr}^{\text{III}}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  (7) polymerized ethylene at 90 °C,  $\text{Cp}^*\text{Cr}^{\text{II}}(\text{dmpe})\text{Me}$  (16) reacted with ethylene at room temperature; however, facile hydrogen  $\beta$ -elimination prevented the formation of polymer.

## Introduction

The coordination polymerization of small olefins (ethylene, propene) is arguably the most important industrial process involving organometallic intermediates.<sup>1</sup> Despite a large research effort and much practical progress since the original discoveries by Ziegler and Natta, a detailed understanding of the reaction mechanisms and the factors that determine activity and selectivity of the polymerization catalysts remains elusive.

Among the transition metals that catalyze the polymerization of olefins, chromium occupies a prominent position. Broadly speaking, two classes of chromium-based heterogeneous catalysts are used commercially. The so-called Phillips catalyst<sup>2</sup> is prepared by deposition of  $\text{CrO}_3$  on silica followed by activation with hydrogen. On the other hand, Union Carbide has developed catalysts formed by treatment of silica with low-valent organometallic compounds, most notably chromocene ( $\text{Cp}_2\text{Cr}$ ).<sup>3</sup> Questions about the chemical nature of the active site(s), the oxidation state of the active chromium, and the mechanism of initiation have been the subject of a longstanding debate, which continues to this day.<sup>4</sup>

It is our belief that the study of organometallic compounds of chromium in solution can make a valuable contribution to the understanding and rational modification of these heterogeneous catalysts. However, much of the known organometallic chemistry of said metal concerns low-valent carbonyl derivatives and/or diamagnetic complexes with 18-electron configurations.<sup>5</sup> Such molecules are unlikely candidates for modeling highly reactive (coordinatively unsaturated) and oxide-supported alkylchromium compounds. On the basis of the general notion that open-shell molecules (paramagnetic organometallics or "metallaradicals") may be more reactive,<sup>6</sup> and thus more appropriate, models for catalytic intermediates, we are exploring the reactivity of a class of paramagnetic alkylchromium(III) compounds.<sup>7</sup> Herein we report the synthesis and characterization of several paramagnetic

alkylchromium compounds and their reactions with olefins. Some of these results have been the subject of a prior communication.<sup>8</sup>

## Results and Discussion

**Preparation of Alkylchromium(III) Compounds.** The starting point for our studies of alkylchromium(III) compounds has been a series of complexes of the type  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})\text{R}]_2$  and their Lewis base adducts of the general formula  $\text{Cp}^*\text{Cr}(\text{L})(\text{Cl})\text{R}$ ,<sup>9</sup> which may

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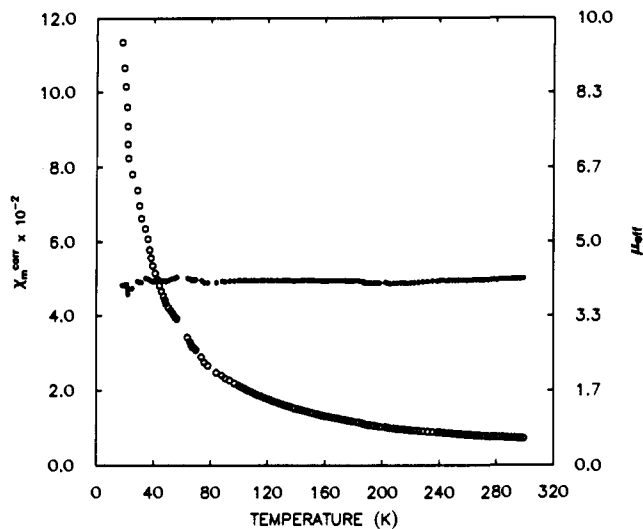
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**Figure 1.** Molar magnetic susceptibility ( $\chi_m$ , open circles) and effective magnetic moment ( $\mu_{\text{eff}}$ , filled circles) of  $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  (**7**).

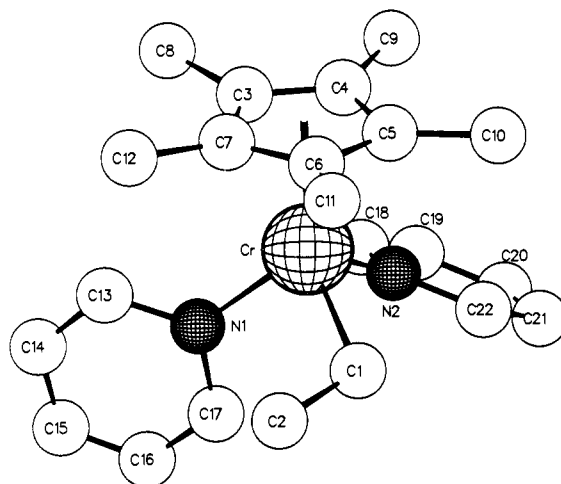
be prepared by addition of 2 equiv of the ligand of choice to the dimers (Scheme 1). None of these compounds reacted with olefins at an appreciable rate. We reasoned that halide abstraction from the complexes might open a coordination site for olefins and thus facilitate reaction. Addition of 1.0 equiv of  $\text{TlPF}_6$  to a THF solution of  $\text{Cp}^*\text{Cr}(\text{py})(\text{Cl})\text{Et}$  (**3**) resulted in a color change from purple to dark brown and the formation of a gray precipitate ( $\text{TlCl}$ ). From the solution was isolated the cationic half-sandwich complex  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  (**10**) as well as a small amount of the dimer  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})\text{Et}]_2$ . Apparently the coordinatively unsaturated fragment  $[\text{Cp}^*\text{Cr}(\text{py})\text{Et}]^+$  had abstracted pyridine from the starting material, effecting the observed ligand redistribution. As the starting material for this reaction may be generated in situ by addition of pyridine to  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})\text{Et}]_2$ , reaction of the latter with  $\text{TlPF}_6$  in the presence of 4.0 equiv of pyridine yielded **10** in near-quantitative yield. This reaction works for a variety of added ligands, and in this manner we have prepared a series of cationic alkylchromium(III) compounds (see Scheme 1). These complexes were purple or brown solids, which could be recrystallized from THF/ether mixtures. They were stable at ambient temperature but decomposed upon exposure to air. Their  $^1\text{H}$  NMR spectra (see Experimental Section) featured broad isotropically shifted resonances expected of pseudooctahedral chromium(III) complexes ( $d^3$ ).<sup>10</sup> The temperature dependencies of the molar magnetic susceptibility ( $\chi_m$ ) and the effective magnetic moment ( $\mu_{\text{eff}}$ , measured in the solid state with a Faraday balance) of the representative  $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  are shown in Figure 1. The data were characteristic of a simple paramagnet, and the room temperature moment of  $4.14 \mu_B$  was consistent with three unpaired electrons.<sup>11</sup> Similarly, the magnetic susceptibility of  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  was measured at room temperature only and gave  $\mu_{\text{eff}} = 3.89 \mu_B$ .

$[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  catalyzed the polymerization of ethylene as monitored by  $^1\text{H}$  NMR spectroscopy, albeit very slowly. In the hope that weakening of the metal-ligand bonds might enhance this reactivity, we have also prepared the THF-containing derivative  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{PF}_6^-$  (**9**). This compound indeed reacted rapidly with ethylene. However, it also suffered from rapid decomposition via fluoride abstraction from the hexafluorophosphate anion by the extremely Lewis acidic chromium. This reaction led inter alia to the unusual fluoride-bridged complex  $[\text{Cp}^*\text{Cr}_4(\mu\text{-F})_5\text{Cl}_2]^+\text{PF}_6^-$ , which we have described previously.<sup>12</sup>

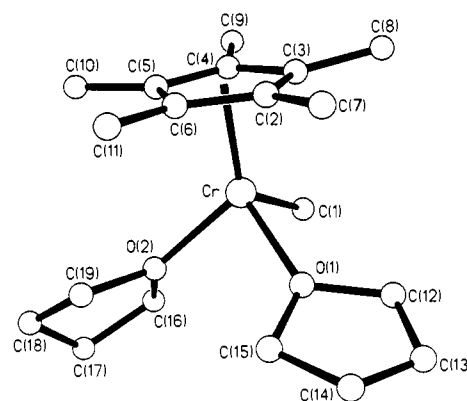
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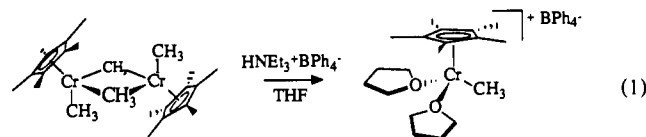


**Figure 2.** Molecular structure of  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  (**10**) (hexafluorophosphate counterion omitted). See Table I for interatomic distances and angles.



**Figure 3.** Molecular structure of  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  (**14**) (tetraphenylborate counterion omitted). See Table II for interatomic distances and angles.

To avoid this deactivation we sought to replace the  $\text{PF}_6^-$  counterion with a less reactive anion. Accordingly, reaction of **9** with  $\text{NaBPh}_4$  yielded  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  (**14**). More recently, we have found a more direct preparative route to this compound involving the protonation of  $[\text{Cp}^*(\text{Me})\text{Cr}(\mu\text{-Me})_2]$  (see eq 1).<sup>13</sup>



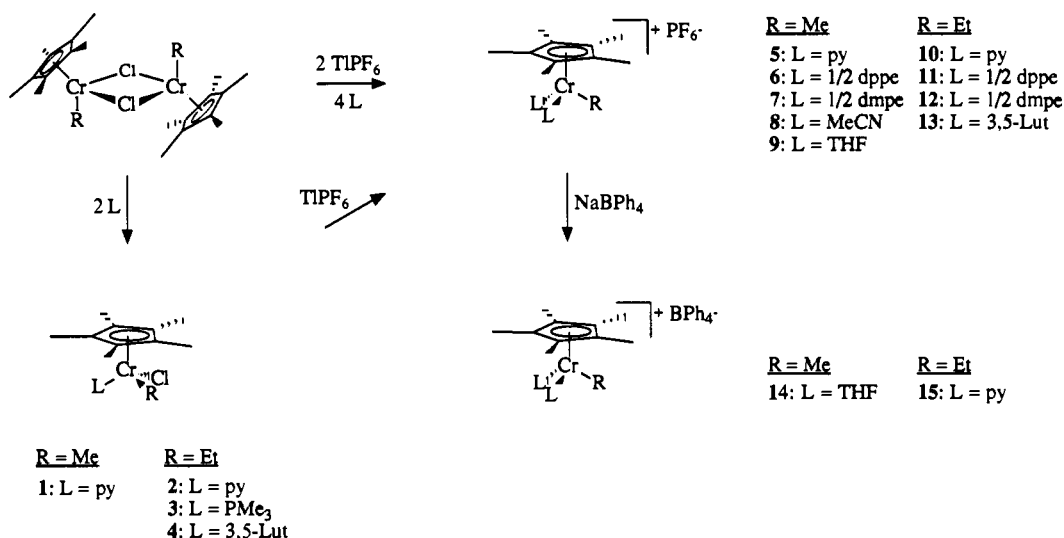
**Crystal Structures of  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  and  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$ .** Complexes **5–15** are rare examples of cationic alkylchromium(III) compounds.<sup>14</sup> Thus, we felt that structural characterization of some representative examples was appropriate.  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]^+\text{PF}_6^-$  (**10**) and  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  (**14**) were chosen for this purpose, and the results of the X-ray diffraction studies are depicted in Figures 2 and 3.

**10** crystallizes in the monoclinic space group  $P2_1/c$ , and the cationic chromium complex possesses no crystallographically required symmetry. Selected interatomic distances and angles are listed in Table I. The crystal consists of well-separated cations and anions. The chromium atom of the complex cation is bound to an  $\eta^5$ -pentamethylcyclopentadienyl ring, two pyridine molecules,

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## Scheme I

Table I. Selected Interatomic Distances and Angles for [Cp\*Cr(py)<sub>2</sub>Et]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (10)

Distances (Å)			
Cr-C1	2.094 (12)	Cr-C3	2.312 (11)
Cr-C4	2.295 (11)	Cr-C5	2.218 (12)
Cr-C6	2.250 (12)	Cr-C7	2.279 (11)
Cr-N1	2.083 (9)	Cr-N2	2.085 (9)
C1-C2	1.521 (17)	C3-C4	1.381 (15)
C3-C7	1.425 (16)	C3-C8	1.511 (16)
C4-C5	1.447 (16)	C4-C9	1.492 (16)
C5-C6	1.421 (15)	C5-C10	1.514 (17)
C6-C7	1.407 (16)	C6-C11	1.506 (17)
C7-C12	1.517 (17)	N <sub>py</sub> -C <sub>py</sub> (av)	1.360
C <sub>py</sub> -C <sub>py</sub> (av)	1.341		
Angles (deg)			
C1-Cr-N1	92.8 (4)	C1-Cr-N2	94.2 (4)
N1-Cr-N2	88.1 (3)	Cr-C1-C2	113.2 (8)
C4-C3-C7	109.2 (10)	C4-C3-C8	125.6 (10)
C7-C3-C8	124.9 (10)	C3-C4-C5	107.3 (9)
C3-C4-C9	126.1 (11)	C5-C4-C9	126.5 (10)
C4-C5-C6	107.8 (10)	C4-C5-C10	124.1 (10)
C6-C5-C10	127.8 (10)	C5-C6-C7	107.6 (10)
C5-C6-C11	126.0 (10)	C7-C6-C11	126.0 (10)
C3-C7-C6	108.1 (10)	C3-C7-C12	127.2 (11)
C6-C7-C12	124.4 (11)	Cr-N <sub>py</sub> -C <sub>py</sub> (av)	122.3
C <sub>py</sub> -N <sub>py</sub> -C <sub>py</sub> (av)	115.5	C <sub>py</sub> -C <sub>py</sub> -C <sub>py</sub> (av)	120.4

and the methylene carbon of an ethyl group. The angles between the "legs" of this three-legged piano stool closely approximate 90°, attesting to the pseudooctahedral nature of the coordination about chromium in which the Cp\* ring can be thought of as a tridentate ligand occupying one of the trigonal faces of the octahedron. This view is certainly consistent with its magnetic behavior. The chromium-ligand bond distances are normal by comparison with those of similar molecules prepared by us and others. In particular, the Cr-Cl distance of 2.094 (12) Å is characteristic of alkyl groups σ-bound to chromium(III).<sup>7</sup> In light of the electronic unsaturation of the chromium center (15-electron configuration), an agostic Cr-H-C interaction might have been expected.<sup>15</sup> However, the Cr-C1-C2 angle of 113.2 (8)°—if anything—signals a repulsion of the methyl group by the sterically crowded metal.

**14** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* also, and neither cation nor anion contains a crystallographic symmetry element. Interatomic distances and angles are listed in Table II. The cation contains chromium coordinated by an η<sup>5</sup>-pentamethylcyclopentadienyl ligand, two oxygen atoms of the cyclic ether THF, and a methyl group. Once again, the angles between

Table II. Selected Interatomic Distances and Angles for [Cp\*Cr(THF)<sub>2</sub>Me]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> (14)

Distances (Å)			
Cr-C1	2.056 (8)	Cr-C2	2.264 (7)
Cr-C3	2.206 (8)	Cr-C4	2.209 (8)
Cr-C5	2.244 (7)	Cr-C6	2.277 (7)
Cr-O1	2.042 (5)	Cr-O2	2.043 (5)
C2-C3	1.434 (12)	C2-C6	1.410 (10)
C2-C7	1.504 (10)	C3-C4	1.410 (10)
C3-C8	1.510 (11)	C4-C5	1.409 (11)
C4-C9	1.508 (12)	C5-C6	1.442 (10)
C5-C10	1.499 (10)	C6-C11	1.480 (12)
O1-C12	1.4439 (11)	O1-C15	1.403 (12)
C12-C13	1.416 (17)	C13-C14	1.416 (20)
C14-C15	1.498 (14)	O2-C16	1.435 (10)
O2-C19	1.451 (11)	C16-C17	1.507 (13)
C17-C18	1.461 (15)	C18-C19	1.468 (11)
B-C <sub>Ph</sub> (av)	1.640	C <sub>Ph</sub> -C <sub>Ph</sub> (av)	1.388
Angles (deg)			
C1-Cr-C2	127.4 (3)	C1-Cr-C3	93.3 (3)
C1-Cr-C4	90.6 (3)	C1-Cr-C5	121.1 (3)
C1-Cr-C6	151.8 (3)	C1-Cr-O1	94.4 (3)
C1-Cr-O2	93.4 (3)	O1-Cr-O2	91.4 (2)
Cr-O1-C12	121.4 (5)	Cr-O1-C15	128.9 (5)
C12-O1-C15	109.5 (7)	Cr-O2-C16	126.3 (5)
Cr-O2-C19	124.3 (4)	C16-O2-C19	109.5 (6)
C <sub>Ph</sub> -B-C <sub>Ph</sub> (av)	109.5		

the monodentate ligands are close to 90° (i.e., 91.4 (2), 93.4 (3), and 94.4 (3)°). The Cr-C distance (2.056 (8) Å) is the shortest Cr-C<sub>Me</sub> bond length we have yet found, probably a consequence of the cationic nature of **14**. As commonly encountered in structure determinations of THF complexes,<sup>16</sup> some of the heterocycle carbon atoms exhibit large thermal motions. The apparent shortening of the average C-C bond distance (1.46 Å) compared to the value in free THF (1.54 Å)<sup>17</sup> may thus reflect a dynamic disorder. The coordinated oxygen atoms exhibit trigonal-planar geometries (i.e., the sums of the angles about O1 and O2 are 359.8 and 360.0°, respectively), similar to other Cr(III)-THF linkages.<sup>18</sup> However, it has been pointed out that observation of this bonding mode is not sufficient to establish π-donation from THF to the metal.<sup>19</sup> The tetraphenylborate counterion exhibits no close contacts to the chromium complex,

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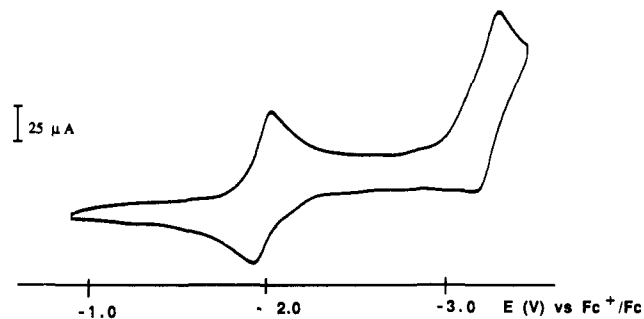
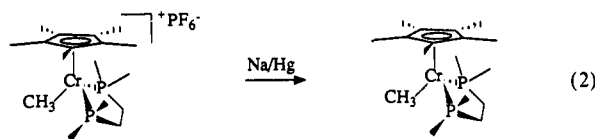


Figure 4. Cyclic voltammogram of  $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  ( $7$ ,  $1.2 \times 10^{-3}$  M) in THF.

and its bond distances and angles are unexceptional.

**Preparation of an Alkylchromium(II) Compound.** The ambiguity concerning the active oxidation state of chromium-based polymerization catalysts (Cr(III) versus Cr(II))<sup>4</sup> led us to explore the redox chemistry of the above alkylchromium(III) compounds. Oxidation or reduction of organometallic compounds often effect dramatic changes in their reactivity,<sup>20</sup> and we hoped to ascertain the effect of oxidation state on polymerization activity.

Cyclic voltammetry<sup>21</sup> experiments with most of the cationic complexes were prevented by reactions with the electrolyte  $\text{N}^t\text{Bu}_4^+\text{BF}_4^-$ . However,  $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  ( $7$ ) was sufficiently stable under these conditions to allow recording of a cyclic voltammogram (see Figure 4). In THF solution, the compound exhibited a reversible reduction wave at  $-1.88$  V versus the  $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$  reference. Chemical reduction of  $7$  with sodium amalgam resulted in a color change to brown, and recrystallization of the solid residue from pentane gave brown crystals of analytically pure  $\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}$  ( $16$ ) in 55% yield (eq 2). The



neutral alkylchromium(II) complex was stable at room temperature; however, it decomposed immediately upon exposure to air. The magnetic susceptibility of  $16$  was measured in the temperature interval 3–300 K; it shows the Curie–Weiss behavior expected of a simple paramagnet. At 295 K, the effective magnetic moment was  $\mu_{\text{eff}} = 2.79 \mu_B$ , consistent with two unpaired electrons ( $S = 1$ ) of a low-spin  $d^4$  ion.<sup>11</sup> The analogous  $[\text{Cp}^*\text{Cr}(\text{dmpe})\text{Et}]^+\text{PF}_6^-$  ( $12$ ) also exhibited reversible electrochemistry with a reduction potential of  $-1.77$  V. However, an attempted chemical reduction did not yield the desired  $\text{Cp}^*\text{Cr}(\text{dmpe})\text{Et}$ ; while a color change similar to the reaction of  $7$  was initially observed, workup of the solution met with decomposition to a purple oil. It is possible that hydrogen  $\beta$ -elimination is more facile in the Cr(II) oxidation state and is responsible for the relative instability of  $\text{Cp}^*\text{Cr}(\text{dmpe})\text{Et}$ . Attempts to isolate other  $[\text{Cp}^*\text{Cr}(\text{L})_2\text{R}]^+$  derivatives were unsuccessful.

**Crystal Structure of  $\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}$ .** The molecular structure of  $16$  was determined by X-ray diffraction, and the result is shown in Figure 5 (see Table III for bond distances and angles). The compound crystallizes in the orthorhombic space group  $Pbca$ , and the molecule contains no crystallographic symmetry elements. The coordination sphere of the chromium atom consists of an  $\eta^5$ -pentamethylcyclopentadienyl ring, two phosphorus atoms of the chelating dmpe ligand, and a methyl group arranged in the familiar

Table III. Selected Interatomic Distances and Angles for  $\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}$  ( $16$ )

Distances (Å)			
Cr–P1	2.302 (3)	Cr–P2	2.305 (4)
Cr–C1	2.150 (10)	Cr–C2	2.191 (10)
Cr–C3	2.255 (10)	Cr–C4	2.266 (9)
Cr–C5	2.242 (10)	Cr–C6	2.262 (9)
P1–C13	1.796 (12)	P1–C16	1.819 (13)
P1–C17	1.889 (11)	P2–C12	1.833 (12)
P2–C14	1.845 (11)	P2–C15	1.870 (12)
C2–C3	1.387 (13)	C2–C6	1.466 (13)
C2–C7	1.585 (14)	C3–C4	1.400 (13)
C3–C8	1.537 (14)	C4–C5	1.423 (12)
C4–C9	1.463 (13)	C5–C6	1.491 (13)
C5–C10	1.458 (14)	C6–C11	1.507 (13)
C12–C13	1.484 (16)		

Angles (deg)			
P1–Cr–P2	81.9 (1)	P1–Cr–C1	89.4 (3)
P2–Cr–C1	90.8 (3)	Cr–P1–C13	109.0 (4)
Cr–P1–C16	119.9 (4)	Cr–P1–C17	120.7 (4)
C13–P1–C16	102.4 (5)	C13–P1–C17	98.4 (5)
C16–P1–C17	103.0 (5)	Cr–P2–C12	109.9 (4)
Cr–P2–C14	119.8 (4)	Cr–P2–C15	122.9 (4)
C12–P2–C14	102.7 (5)	C12–P2–C15	100.4 (6)
C14–P2–C15	97.9 (5)		

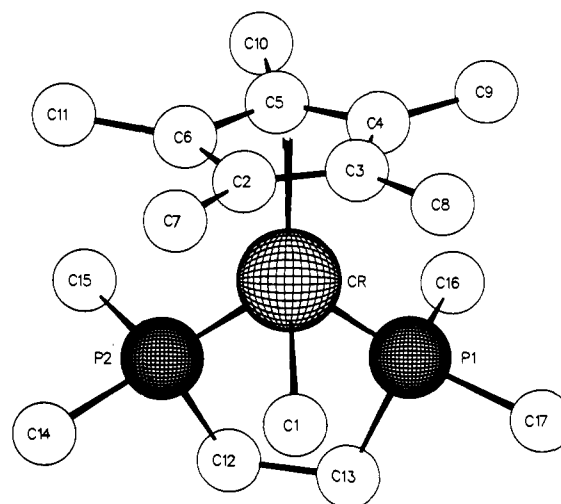


Figure 5. Molecular structure of neutral  $\text{Cp}^*\text{Cr}(\text{dmpe})\text{Me}$  ( $16$ ). See Table III for interatomic distances and angles.

“three-legged piano stool”. The Cr–C1 distance of 2.150 (10) Å is significantly longer than corresponding distances in Cr(III) complexes; however, it falls in the middle of the range reported for other Cr(II)–C  $\sigma$ -bonds.<sup>22</sup> Interestingly, the Cr–C<sub>ring</sub> distances do not follow the same trend; i.e., their average (2.243 Å) is indistinguishable from the corresponding distances in many  $\text{Cp}^*\text{Cr}^{\text{III}}$  derivatives structurally characterized in our laboratory (2.194–2.297 Å).<sup>7</sup> A possible explanation for this invariance may be a strengthening of the metal–ring interaction through increased back-bonding upon reduction from Cr(III) to Cr(II). Additional evidence for this effect may be seen in a modest lengthening of the C–C bonds of the Cp\* ligand. The average C<sub>ring</sub>–C<sub>ring</sub> distance in  $16$  of 1.433 Å is longer than any observed in our Cr(III) complexes (1.389–1.426 Å).<sup>7</sup> Finally, the Cr–P distances are of equal length (2.30 Å) and are rather short by comparison with other Cr(II)–phosphine complexes.<sup>23</sup>

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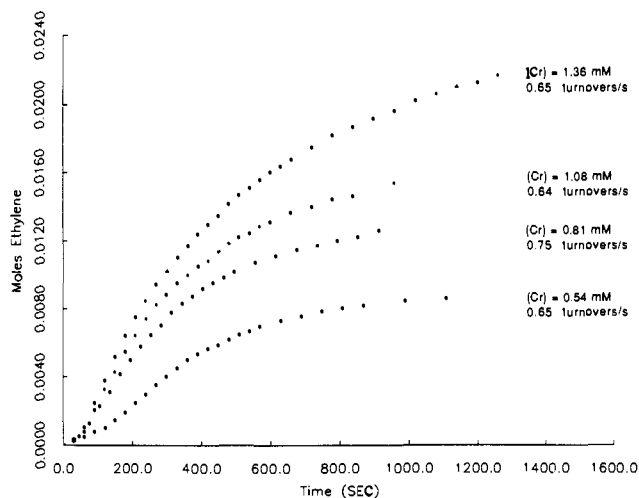


Figure 6. Ethylene uptake versus time by solutions of  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  (**14**) in  $\text{CH}_2\text{Cl}_2$ .

Table IV. Effects of Catalyst Concentration, Temperature, and THF Concentration on Ethylene Polymerization Rate at  $P(\text{C}_2\text{H}_4) = 1.6$  atm

[cat.] (mM)	<i>T</i> (K)	[THF] <sup>a</sup> (mM)	rate (mol/s)	turnovers/s
0.54	292	0	$1.75 \times 10^{-5}$	0.58
0.81	292	0	$3.03 \times 10^{-5}$	0.67
1.08	292	0	$3.46 \times 10^{-5}$	0.58
1.35	292	0	$4.39 \times 10^{-5}$	0.58
0.81	292	0	$3.03 \times 10^{-5}$	0.67
0.81	283	0	$2.07 \times 10^{-5}$	0.46
0.81	273	0	$1.06 \times 10^{-5}$	0.24
0.81	266	0	$0.91 \times 10^{-5}$	0.20
0.81	292	0	$3.03 \times 10^{-5}$	0.67
0.81	292	0.89	$1.78 \times 10^{-5}$	0.39
0.81	292	4.43	$0.57 \times 10^{-5}$	0.13
0.81	292	8.87	$0.34 \times 10^{-5}$	0.07

<sup>a</sup> Added THF.

**Polymerization of Ethylene.** Solutions of  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  in  $\text{CH}_2\text{Cl}_2$  were reasonably stable. Upon exposure to ethylene (typical conditions:  $P(\text{C}_2\text{H}_4) = 1.0\text{--}1.5$  atm;  $T = 0\text{--}20$  °C), they catalyzed the polymerization of the olefin. We have probed this reaction in some detail, and the experiments described below were all carried out with  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+\text{BPh}_4^-$  as the catalyst.

Figure 6 depicts uptake measurements of ethylene consumed by various amounts of catalyst. These curves show a short induction phase, a period of high activity, and finally a decline in activity, indicating catalyst decay. During the course of a typical polymerization run, the color of the solution gradually turned from red-brown to bright purple, the final color of spent catalyst. Removal of the polyethylene by filtration and evaporation of solvent yielded a purple oil. We have been unable to isolate any organometallic decomposition products from these residues. However, extraction with ether yielded a small amount of triphenylboron, indicating that even the tetraphenylborate counterion may not be impervious to attack by the electrophilic metal center. Typical polymerization experiments (with 60 mg (0.090 mmol) of catalyst in 20 mL of  $\text{CH}_2\text{Cl}_2$ ) exhibited some activity for ca. 1–2 h and produced ca. 0.5–2.0 g of polyethylene, depending on the reaction conditions (lower temperatures produced more

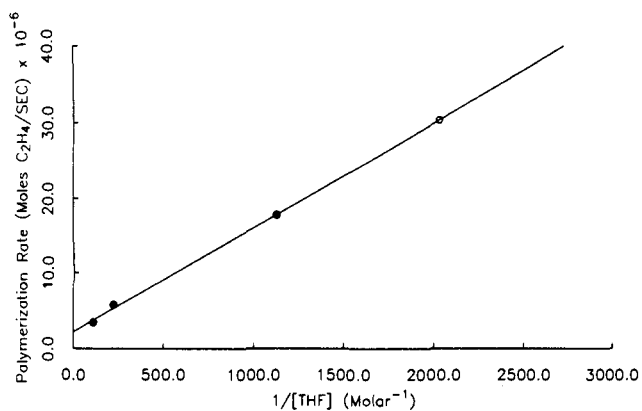
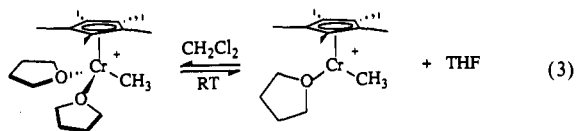


Figure 7. Ethylene polymerization rate versus inverse concentration of added THF. Open circle marks polymerization rate in the absence of added THF.

polymer). Assuming all chromium to be active, these yields correspond to 200–800 turnovers. Fitting the steepest part of the uptake curves with straight lines allowed the determination of polymerization rates (see Table IV). While the resulting rate constants are certainly associated with considerable errors—due to the gradual decomposition of the catalyst and the crude manometric measurements—they proved internally consistent and exhibited reasonable trends. For example, Figure 6 shows four different experiments at various catalyst concentrations; the turnover frequencies (determined for the period of highest activity) are roughly the same. The activity of the catalyst is comparable to that of  $\text{Cp}_2\text{Cr}/\text{SiO}_2$ ,<sup>3</sup> although the homogeneous catalyst decomposes more readily. Variation of the reaction temperature (266–292 K; see Table IV) yielded an estimate of the activation energy of  $E_a = 8$  (1) kcal/mol; the corresponding value for chromocene on silica was reported to be 10.1 kcal/mol.

The polymerization reaction was strongly inhibited by added THF, consistent with the hypothesis that a ligand must be lost from the alkylchromium complex to facilitate binding of ethylene. We have found two lines of evidence in support of a dissociation equilibrium between the sterically saturated 15-electron complex  $[\text{Cp}^*\text{Cr}(\text{THF})_2\text{Me}]^+$  and the pseudo-five-coordinate 13-electron species  $[\text{Cp}^*\text{Cr}(\text{THF})\text{Me}]^+$  (eq 3). First, the <sup>1</sup>H NMR spectrum



of a 0.05 M  $\text{CD}_2\text{Cl}_2$  solution of **14** exhibited resonances of uncoordinated THF besides the broad and isotropically shifted resonances for bound THF. Comparison of the integrated intensity of the former resonances with that of an internal standard ( $\text{Cp}_2\text{Fe}$ ) allowed the determination of the concentration of free THF and in turn the equilibrium constant for the dissociation (eq 3); at 19 °C in  $\text{CD}_2\text{Cl}_2$ ,  $K_{\text{diss}} = 1.2 \times 10^{-3}$  M. Second, the inhibition of the polymerization by THF provided an independent means of determining the same equilibrium constant. If only the coordinatively unsaturated  $[\text{Cp}^*\text{Cr}(\text{THF})\text{Me}]^+$  is an active catalyst, the polymerization rate at a constant "chromium" concentration should be inversely proportional to the THF concentration. A plot of the relevant data from Table IV is shown in Figure 7 and shows the expected linear relationship. Extrapolation of the line so obtained to the polymerization rate measured in an experiment with no added THF provides a rough measure of the concentration of free THF generated by dissociation of **14**. This value may then be used to calculate the dissociation constant ( $K_{\text{diss}}$ ). By this procedure and in  $\text{CH}_2\text{Cl}_2$  at 19 °C,  $K_{\text{diss}} = 8.3 \times 10^{-4}$  M. We note that the two independently determined values of  $K_{\text{diss}}$  at very different catalyst concentrations are essentially equal. Under the polymerization conditions, ca. 60% of the chromium exists in the form of the highly unsaturated 13-electron complex  $[\text{Cp}^*\text{Cr}(\text{THF})\text{Me}]^+$ .

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**Table V.** Molecular Weights, Polydispersity, and Branching of Polyethylenes<sup>a</sup>

<i>T</i> (K)	[THF] (mM)	<i>M<sub>w</sub></i>	<i>M<sub>n</sub></i>	<i>M<sub>w</sub>/M<sub>n</sub></i>	branching <sup>b</sup>
293	0	33 760	17 520	1.93	?
283	0	47 240	20 160	2.34	4.0
273	0	77 070	16 740	4.60	0
293	4.5	23 020	14 310	1.61	?
293	13.5	24 370	14 970	1.63	2.6

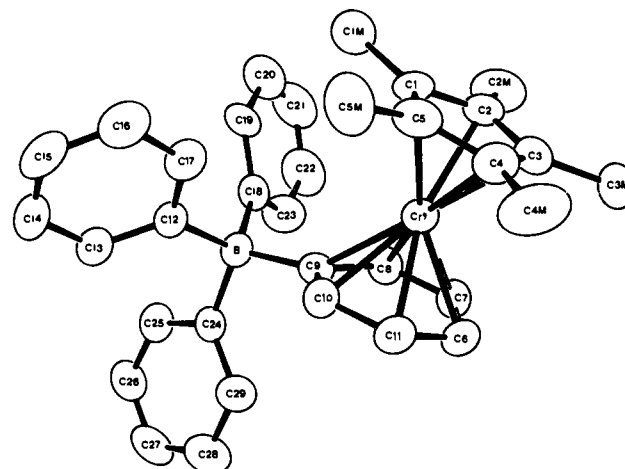
<sup>a</sup>[Cat.] =  $4.5 \times 10^{-3}$  M,  $P(\text{C}_2\text{H}_4) = 1.5$  atm. <sup>b</sup>Expressed as side chains per 1000  $\text{CH}_2$  units.

**14** did not catalyze the polymerization of propene. Prolonged exposure (4 days) of a chlorobenzene solution of **14** to an excess (10 equiv) of propene resulted in the uptake of 2.5 equiv of propene (measured by a Töpler pump). Addition of HCl followed by GC/MS analysis of the volatiles revealed the presence of propane, butane, and butene.

**Polymer Characterization.** The polyethylene was initially characterized by IR (the spectra were indistinguishable from that of authentic high-density polyethylene) and melting point (135–140 °C). The molecular weight distributions of various polyethylene samples were determined by gel permeation chromatography (GPC), and the results are listed in Table V. The molecular weights are relatively low, and their distributions are fairly narrow.<sup>24</sup> The low polydispersities ( $M_w/M_n$ ) are in accord with the homogeneous nature of the catalyst; i.e., reactivity differences caused by different surface sites are not a factor. <sup>13</sup>C NMR spectroscopy provided some information on the microstructure of the polymers. The data in Table V show very few branches in the polymer chain. Curiously, all the branches appear to consist of alkyl chains containing six or more carbon atoms; we plan to address the origin of this phenomenon in future experiments.

**Catalyst Deactivation. Crystal Structure of  $\text{Cp}^*\text{Cr}(\eta^6\text{-Ph-BPh}_3)$ .** Although we have not been able so far to isolate a characterizable chromium complex from spent catalyst residues, the formation of triphenylboron during polymerization hinted at attack on the tetraphenylborate counterion as a possible decomposition pathway. In this context, the product of a reaction of catalyst **14** with styrene is of interest. Dissolution of **14** in a 1:1 mixture of styrene and  $\text{CH}_2\text{Cl}_2$  eventually yielded a brown solution from which orange crystals of a new compound were isolated. Spectroscopic data, elemental analysis, and finally structural characterization by X-ray diffraction showed this complex to be  $\text{Cp}^*\text{Cr}(\eta^6\text{-Ph-BPh}_3)$  (**17**), a chromium(II) sandwich complex in which one of the phenyl rings of the “noninteracting”  $\text{BPh}_4^-$  counterion is coordinated to the chromium. A possible mechanism for the formation of **17** consists of the insertion of styrene into the chromium–methyl bond, homolysis of the thus formed alkyl (i.e., reduction to Cr(II)), and finally trapping of the unsaturated cationic chromium fragment by the tetraphenylborate anion. While **17** did not appear to be formed during ethylene polymerization, it may serve as a model for intermediates in the degradation of **14**.

**17** crystallizes in the monoclinic space group  $P2_1/c$ , and the individual molecules exhibit no crystallographic symmetry. The molecular structure is shown in Figure 8, and interatomic distances and angles are listed in Table VI. Several other compounds containing tetraphenylborate moieties with coordinated phenyl groups have been described.<sup>25</sup> The Cr–C distances to the six-membered ring average 2.185 Å, close to the value of the Cr–C distances in chromocene ( $\text{Cp}_2\text{Cr}$ ; 2.17 Å)<sup>26</sup> and indistinguishable

**Figure 8.** Molecular structure of  $\text{Cp}^*\text{Cr}(\eta^6\text{-Ph-BPh}_3)$  (**17**). See Table VI for interatomic distances and angles.**Table VI.** Interatomic Distances and Angles for  $\text{Cp}^*\text{Cr}(\eta^6\text{-Ph-BPh}_3)$  (**17**)

Distances (Å)			
Cr–C1	2.214 (4)	Cr–C2	2.189 (5)
Cr–C3	2.158 (5)	Cr–C4	2.163 (5)
Cr–C5	2.190 (5)	Cr–C6	2.199 (5)
Cr–C7	2.138 (4)	Cr–C8	2.156 (5)
Cr–C9	2.301 (4)	Cr–C10	2.169 (5)
Cr–C11	2.144 (5)	C1–C5	1.416 (6)
C2–C2	1.430 (6)	C1–C1M	1.480 (6)
C2–C3	1.435 (6)	C2–C2M	1.493 (7)
C3–C4	1.419 (7)	C3–C3M	1.489 (6)
C4–C5	1.419 (6)	C4–C4M	1.509 (6)
C5–C5M	1.503 (6)	C6–C7	1.383 (6)
C6–C11	1.404 (6)	C7–C8	1.423 (6)
C8–C9	1.421 (5)	C9–C10	1.413 (6)
C9–B	1.666 (6)	C12–B	1.634 (6)
C18–B	1.650 (7)	C24–B	1.630 (6)
$\text{C}_{\text{Ph}}\text{-C}_{\text{Ph}}$ (av)	1.389		
Angles (deg)			
B–C9–Cr	143.8 (3)	C6–C7–C8	120.6 (4)
C7–C6–C11	119.3 (4)	C6–C11–C10	119.3 (4)
C7–C8–C9	122.0 (4)	C8–C9–C10	115.4 (4)
C9–C10–C11	122.2 (4)	$\text{C}_{\text{Ph}}\text{-B-C}_{\text{Ph}}$ (av)	109.4

from the corresponding measure involving the  $\text{Cp}^*$  ligand of **17** itself (2.183 Å). The C–C bonds of the coordinated arene (1.414 Å average) are slightly elongated over the same distances in the remaining phenyl groups (1.389 Å average); this is presumably due to  $\pi$ -back-bonding from the metal. While the tetraphenylborate fragment does not deviate appreciably from the ideal tetrahedral geometry about boron, some relief of steric strain is provided by a modest distortion of the  $\eta^6$ -phenyl ligand such that the ipso carbon (C9) is displaced by 0.107 Å out of the least-squares plane defined by C7, C8, C10, C11 and away from the metal. In addition, the C9–B distance (1.666 (6) Å) is the largest among the four carbon–boron bonds, although not by a big margin. Finally, the planes of the  $\text{Cp}^*$  ligand and the coordinated arene are not parallel; the dihedral angle between the planes defined by C1–C5 and C7, C8, C10, and C11 measures 10.7°.

**Effect of Oxidation State.** The availability of two isostructural alkylchromium compounds differing only in their formal oxidation state—namely,  $[\text{Cp}^*\text{Cr}^{\text{III}}(\text{dmpe})\text{Me}]^+\text{PF}_6^-$  (**7**) and  $\text{Cp}^*\text{Cr}^{\text{II}}(\text{dmpe})\text{Me}$  (**16**)—allowed us to make a direct comparison of their reactions with ethylene. Thus, the reaction of **7** with an excess of ethylene in  $\text{CD}_2\text{Cl}_2$  was monitored by <sup>1</sup>H NMR. The reaction was very slow and required heating to 90 °C for 1 week. However, after that time all but a trace of the ethylene had been consumed and the appearance of two new broad resonances at 1.52 and 1.23 ppm as well as the formation of a white precipitate indicated the

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formation of long-chain hydrocarbons (i.e., polyethylene). The forcing conditions required for this conversion are not surprising, as the chelating phosphine ligand is bound very strongly to Cr(III). It could have been argued that the demonstration of the catalytic activity of **7** was not crucial, because the catalytic proficiency of Cr(III) had been proven by the THF complex **14**. However, to ensure the validity of the comparison the polymerization activity of **7** under some conditions was deemed important.

The reaction of the alkylchromium(II) compound **16** with ethylene took an altogether different course. Exposure of a C<sub>6</sub>D<sub>6</sub> solution of **16** to an excess of ethylene at room temperature over 1 week resulted in the uptake of 2.6 equiv of ethylene and the formation of small amounts of propene and butene as volatile products. Treatment of the organometallic residue with HCl and subsequent analysis of the volatile products by <sup>1</sup>H NMR and GC/MS yielded methane, propane, butane, and hexene. Significantly, no indication for the formation of polyethylene was found. Heating solutions of **16** and ethylene in an NMR tube resulted in rapid consumption of ethylene and the appearance of <sup>1</sup>H NMR resonances attributable to higher olefins.

These observations establish that the alkylchromium(II) compound also reacts with ethylene by insertion into the metal-carbon bond. However, in contrast to that of chromium(III) hydrogen β-elimination of the newly formed alkyl is apparently more facile in the lower oxidation state. Greater stabilization of the intermediate olefin complex by the comparatively electron-rich Cr(II) center is a likely rationale for this difference in reactivity. As far as olefin polymerization is concerned, it is clear that chromium(III) is the more suitable oxidation state for catalysis, at least in our system.

## Conclusions

A class of cationic alkyl complexes of chromium(III) has been prepared and characterized spectroscopically and structurally. The complexes catalyze the polymerization of ethylene and thus serve as homogeneous model compounds for commercial catalysts based on chromium. The mechanism of the polymerization by the highly active catalyst [Cp\*Cr(THF)<sub>2</sub>Me]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> has been probed in some detail. It involves dissociation of a THF ligand to generate a 13-electron complex, which rapidly undergoes multiple insertions of ethylene. The polymer has a narrow molecular weight distribution and exhibits little branching. Reduction to the +II oxidation state alters the reactivity pattern of the alkylchromium compounds such that hydrogen β-elimination becomes preferred. Bearing in mind the relative stability of chromium compounds in the +II and +III oxidation states in general,<sup>27</sup> we suggest that trivalent chromium is probably responsible for the activity of commercial catalysts.

It is becoming clear that paramagnetic organometallic derivatives of chromium—and by extrapolation, other transition metals—exhibit a rich reaction chemistry of their own. The potential for new findings and relevance to major applications in catalysis is well worth the extra effort required in the investigation of these less accessible oxidation states. Thus, we are continuing our exploration of organochromium chemistry related to catalytic transformations of organic molecules.

## Experimental Section

**General Techniques.** NMR spectra were recorded on Varian XL 200 or Bruker WM 300 spectrometers. IR spectra were obtained on a Mattson Instruments Alpha Centauri spectrometer. All manipulations involving air-sensitive organometallic compounds were carried out in a Vacuum Atmospheres inert atmosphere glovebox under N<sub>2</sub> or on a Schlenk line with Ar or N<sub>2</sub>. Solvents (with the exception of CH<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>Cl) were distilled under N<sub>2</sub> from purple benzophenone ketyl. CH<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>Cl were distilled under N<sub>2</sub> from CaH<sub>2</sub>. [Cp\*Cr(R)Cl]<sub>2</sub> (R = Me, Et) and Cp\*Cr(R)(py)Cl (R = Me, **1**; R = Et, **2**) were prepared as previously described.<sup>9</sup> TlPF<sub>6</sub> was purchased from Strem Chemicals and used as received. NaBPh<sub>4</sub> was recrystallized from THF. Styrene was purchased from Aldrich Chemical Co. and distilled prior to use. Ethylene and propylene were purchased from Matheson and passed

through a column of activated 4A molecular sieves. Melting points were measured with a Mel-Temp apparatus and are uncorrected. GC experiments were performed on a Hewlett-Packard 5890 A gas chromatograph with either a Pora Pak Q column (for gaseous samples) or a capillary column (cross-linked 5% phenylmethylsilicone, HP No. 190935 No. 100, 5 m, 0.20/0.32-mm i.d.) and a flame ionization detector. Mass spectral measurements (CI or FABMS) were performed by the Cornell Mass Spectrometry Facility. Elemental analyses were carried out by Chemical Analytical Services, Berkeley, CA. Magnetic susceptibility measurements were performed on a Faraday balance.

**Electrochemical Measurements.** Electrochemical measurements were performed in a drybox with a Soltec Model VP-6423S X-Y recorder and a BAS Model CV-27 potentiostat. Reference electrodes consisting of cracked glass bead outer shells (Fisher Scientific) containing a silver wire immersed in either a saturated solution of AgCl/Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> in THF or a saturated solution of AgCl/Me<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> in acetonitrile. The potential of the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> couple versus the THF reference electrode was +0.82 V (ΔE<sub>p</sub> = 0.36 V). The potential of the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> couple versus the acetonitrile electrode was +0.71 V (ΔE<sub>p</sub> = 0.09 V). Cyclic voltammograms were recorded in a single-compartment cell with either a 0.02-in. or 0.03-in. Pt disk working electrode; a 0.03-in. Pt wire served as the auxiliary electrode. In all cases, the supporting electrolyte was 0.2 M [tBu<sub>4</sub>N]BF<sub>4</sub>.

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)(chloro)(trimethylphosphine)chromium(III), Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(PMe<sub>3</sub>) (**3**). Trimethylphosphine (0.794 mmol) was vacuum transferred into a flask containing 0.192 g of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl]<sub>2</sub> (0.381 mmol) in 30 mL of diethyl ether. The mixture was warmed to room temperature and stirred for 15 h. The solvent was evaporated under vacuum, and the solid was recrystallized from pentane to yield purple-black cubes of Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(PMe<sub>3</sub>) (205 mg, 82%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.25 (br, 15 H), -25.13 (br, 9 H) ppm. IR (KBr): 2907 (s), 2830 (vs), 1418 (m), 1416 (s), 1282 (s), 1121 (s), 1024 (s), 954 (vs), 837 (w), 735 (s), 583 (w), 461 (s) cm<sup>-1</sup>. Mp: 99–105 °C dec. Anal. Calcd for C<sub>15</sub>H<sub>29</sub>ClCrP: C, 54.96; H, 8.92. Found: C, 54.74; H, 8.88.

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)(chloro)(3,5-lutidine)chromium(III), Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(3,5-lut) (**4**). 3,5-Lutidine (0.50 g, 4.67 mmol) was added all at once to a stirred solution of 1.155 g of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl]<sub>2</sub> (2.29 mmol) in 35 mL of THF. The solution became red-purple. After 2 h, the solvent was evaporated under vacuum. The resulting solid was recrystallized from diethyl ether to yield black needles of Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(3,5-lut) (1.514 g, 92%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): -0.45 (br, 2 H), -5.58 (vbr, 15 H), -9.00 (br, 2 H), -12.17 (br, 1 H), -17.09 (br, 6 H), -45.52 (vbr, 3 H) ppm. IR (KBr): 2907 (s), 2836 (s), 1595 (s), 1277 (m), 1248 (m), 1153 (s), 1150 (s), 928 (w), 865 (vs), 769 (vs), 703 (vs), 565 (m), 472 (s), 402 (vs) cm<sup>-1</sup>. Mp: 135–145 °C dec. Anal. Calcd for C<sub>19</sub>H<sub>29</sub>ClCrN: C, 63.59; H, 8.14; N, 3.90. Found: C, 63.66; H, 8.20; N, 3.90.

**Reaction of Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(py) (**2**) with TlPF<sub>6</sub>.** TlPF<sub>6</sub> (0.165 g, 1.76 mmol) was added all at once to a stirred solution of 0.580 g of Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(py) (1.75 mmol) in 20 mL of THF. The solution became darker brown, and a gray precipitate formed. After 12 h, the solution was filtered and the solvent was evaporated under vacuum. The resulting solid was extracted with diethyl ether, forming a purple solution. The remaining solid was recrystallized in THF/diethyl ether to yield **10** (394 mg, 87%). The diethyl ether solution was concentrated to yield purple-black crystals of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl]<sub>2</sub> (60 mg, 27%).

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)bis(pyridine)chromium(III) Hexafluorophosphate, [Cp\*Cr(CH<sub>3</sub>)(py)<sub>2</sub>]PF<sub>6</sub> (**5**). Pyridine (0.150 g, 1.90 mmol) was added all at once to a stirred solution of 0.220 g of [Cp\*Cr(CH<sub>3</sub>)Cl]<sub>2</sub> (0.46 mmol) in 25 mL of THF. The solution became red-brown. After 5 min, 0.360 g of TlPF<sub>6</sub> (1.03 mmol) was added all at once with stirring. Over the course of several hours, a gray precipitate formed and the solution turned brown. After 4 h, the solution was filtered and the solvent evaporated under vacuum. The solid was recrystallized from THF/diethyl ether to yield black cubes of **5** (150 mg, 32%). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>): 18.71 (br, 4 H), -4.11 (br, 1 H), -12.0 (br, 15 H), -14.93 (br, 4 H), -24.93 (br, 1 H), -42.42 (br, 3 H) ppm. IR (KBr): 3587 (w), 3119 (w), 3070 (w), 2921 (s), 2874 (s), 2801 (m), 1604 (vs), 1487 (s), 1445 (vs), 1384 (s), 1238 (m), 1218 (s), 1161 (m), 1125 (m), 1069 (s), 1046 (s), 1013 (s), 838 (vs), 760 (vs), 703 (vs), 640 (s), 557 (vs), 521 (s), 498 (s), 436 (m) cm<sup>-1</sup>. Mp: 153–163 °C dec. Anal. Calcd for C<sub>21</sub>H<sub>28</sub>CrF<sub>6</sub>N<sub>2</sub>P: C, 49.90; H, 5.58; N, 5.54; P, 6.13. Found: C, 49.45; H, 5.61; N, 5.23; P, 5.60.

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)[1,2-bis(diphenylphosphino)ethane]chromium(III) Hexafluorophosphate Tetrahydrofuran, [Cp\*Cr(CH<sub>3</sub>)(dppe)]PF<sub>6</sub>·THF (**6**). TlPF<sub>6</sub> (0.360 g, 1.031 mmol) was added all at once to a stirred solution containing 0.220 g of [Cp\*Cr(CH<sub>3</sub>)Cl]<sub>2</sub> (0.463 mmol) and 0.378 g of 1,2-bis(diphenylphosphino)ethane (0.949 mmol) in 20 mL of THF. The solution slowly turned

(27) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 679–697.



red-brown, and a gray precipitate formed. After 3 h, the solution was filtered and the solvent was evaporated under vacuum. The resulting solid was recrystallized from THF/diethyl ether to yield red-brown needles of **6** (469 mg, 66%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 13.68 (br, 4 H), 11.85 (br, 6 H), 8.60 (br, 4 H), 6.16 (br, 6 H), -16.48 (br, 15 H) ppm. IR (KBr): 3055 (w), 2934 (m), 2911 (w), 1485 (m), 1437 (s), 1099 (m), 1000 (w), 840 (vs), 746 (s), 695 (s), 557 (s), 524 (s), 419 (w) cm<sup>-1</sup>. Mp: 193–196 °C dec. Anal. Calcd for C<sub>41</sub>H<sub>50</sub>CrF<sub>6</sub>OP<sub>3</sub>: C, 60.22; H, 6.16; P, 11.36. Found: C, 60.52; H, 6.25; P, 11.66.

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)[1,2-bis(dimethylphosphino)ethane]chromium(III) Hexafluorophosphate, [Cp\*Cr(CH<sub>3</sub>)(dmpe)]PF<sub>6</sub> (**7**). 1,2-Bis(dimethylphosphino)ethane (0.200 g, 1.33 mmol) and 0.468 g of TlPF<sub>6</sub> (1.34 mmol) were added all at once to a stirred solution of 0.320 g of [Cp\*Cr(CH<sub>3</sub>)Cl]<sub>2</sub> (0.673 mmol) in 20 mL of THF. The solution turned red, and a gray precipitate slowly formed. After 2 h, the solution was filtered and the solvent was evaporated under vacuum. The red-brown solid was recrystallized from THF/diethyl ether to yield red plates of **7** (457 mg, 69%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 14.39 (br, 15 H), -4.05 (vbr, 2 H), -17.18 (br, 6 H), -20.44 (vbr, 2 H), -25.42 (vbr, 3 H), -50.26 (br, 6 H) ppm. IR (KBr): 3675 (m), 2920 (vs), 2962 (s), 2876 (s), 2836 (m), 1430 (vs), 1379 (s), 1304 (s), 1289 (s), 1148 (s), 1095 (s), 955 (vs), 939 (vs), 903 (s), 847 (vvs), 742 (vs), 712 (vs), 647 (m), 630 (m), 558 (vs), 486 (vs), 429 (s) cm<sup>-1</sup>. Mp: 250–260 °C dec.  $\mu_{\text{eff}} = 4.22 \mu_{\text{B}}$  (298 K). Anal. Calcd for C<sub>17</sub>H<sub>34</sub>CrF<sub>6</sub>P<sub>3</sub>: C, 41.05; H, 6.89; P, 18.68. Found: C, 41.31; H, 6.95; P, 18.44.

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)bis(acetonitrile)chromium(III) Hexafluorophosphate, [Cp\*Cr(CH<sub>3</sub>)(NCMe)<sub>2</sub>]PF<sub>6</sub> (**8**). **9** (see below; 0.250 g, 0.508 mmol) was dissolved in ca. 15 mL of acetonitrile. The solution immediately became dark brown and was stirred for 5 min. The solvent was evaporated under vacuum, and the residue was dissolved in a mixture of 40% acetonitrile/60% diethyl ether. Crystals formed upon slow diffusion of diethyl ether into this solution at -35 °C. Filtration yielded black cubes of **8** (195 mg, 89%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -4.17 ppm. IR (KBr): 3587 (w), 3221 (w), 3005 (m), 2940 (s), 2878 (m), 2795 (w), 2319 (s), 2287 (s), 1546 (m), 1449 (m), 1427 (m), 1386 (m), 1121 (m), 1040 (m), 1034 (m), 906 (m), 844 (vs), 782 (m), 627 (w), 559 (s), 514 (s), 420 (m) cm<sup>-1</sup>. Mp: 104–106 °C dec. Anal. Calcd for C<sub>15</sub>H<sub>24</sub>CrF<sub>6</sub>N<sub>2</sub>P: C, 41.96; H, 5.63; N, 6.52. Found: C, 41.71; H, 5.59; N, 6.80.

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)bis(tetrahydrofuran)chromium(III) Hexafluorophosphate, [Cp\*Cr(CH<sub>3</sub>)(THF)<sub>2</sub>]PF<sub>6</sub> (**9**). TlPF<sub>6</sub> (1.084 g, 3.10 mmol) was added all at once to a stirred solution of 0.700 g of [Cp\*Cr(CH<sub>3</sub>)Cl]<sub>2</sub> (1.47 mmol) in 20 mL of THF. After several hours, the purple solution turned red-purple and a gray precipitate formed. The solution was stirred for 10 h and then filtered. The solvent was evaporated, and the residue was washed with diethyl ether. The material was then recrystallized from THF/diethyl ether at -35 °C to yield 778 mg of **3** as dark purple needles (54%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -25.6 (br 15 H), 8.98 (br 4 H), 8.00 (br 4 H) ppm. IR (nujol): 1250 (w), 1172 (w), 1120 (m), 1040 (w), 1012 (s), 891 (w), 838 (vs), 726 (w), 642 (w), 555 (s), cm<sup>-1</sup>. Mp: 115–120 °C dec. Anal. Calcd for C<sub>19</sub>H<sub>34</sub>CrF<sub>6</sub>O<sub>2</sub>P: C, 46.44; H, 6.97. Found: C, 46.54; H, 7.05.

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)bis(pyridine)chromium(III) Hexafluorophosphate, [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)(py)<sub>2</sub>]PF<sub>6</sub> (**10**). Pyridine (0.440 g, 5.56 mmol) was added all at once to a stirred solution of 0.645 g of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl]<sub>2</sub> (1.28 mmol) in 25 mL of THF. The solution became red-brown. After 5 min, 0.902 g of TlPF<sub>6</sub> was added all at once with stirring. Over the course of several hours, a gray precipitate formed and the solution turned brown. After 4 h, the solution was filtered and the solvent evaporated under vacuum. The solid was recrystallized from THF/diethyl ether to yield black cubes of **10** (986 mg, 74%). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>): 22.4 (br, 1 H), 18.9 (br, 7 H), -13.0 (br, 15 H) 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) cm<sup>-1</sup>. Mp: 165–170 °C dec.  $\mu_{\text{eff}} = 3.87 \mu_{\text{B}}$  (298 K). Anal. Calcd for C<sub>22</sub>H<sub>30</sub>CrF<sub>6</sub>N<sub>2</sub>P: C, 50.87; H, 5.82; N, 5.39. Found: C, 50.83; H, 5.97; N, 5.27.

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)[1,2-bis(diphenylphosphino)ethane]chromium(III) Hexafluorophosphate, [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)(dippe)]PF<sub>6</sub> (**11**). TlPF<sub>6</sub> (0.605 g, 1.86 mmol) was added all at once to a stirred solution containing 0.465 g of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl]<sub>2</sub> (0.924 mmol) and 0.741 g of 1,2-bis(diphenylphosphino)ethane (1.86 mmol) in 40 mL of THF. A gray precipitate slowly formed. After 12 h, the solution was filtered and the solvent was evaporated under vacuum. The solid was recrystallized from THF/diethyl ether to yield black crystals of **11** (737 mg, 53%). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>): 14.42 (br, 4 H), 11.95 (br, 8 H), 7.78 (br, 4 H), 5.51 (br, 8 H), -23.8 (vbr, 15 H) ppm. IR (KBr): 3059 (w), 2951 (s), 2912 (s), 2859 (m), 1976 (w), 1890 (w), 1825 (w), 1573 (w), 1485 (m), 1435 (s), 1416 (m), 1310 (w), 1161 (w), 1102 (m), 1098 (m), 1060 (m), 1000 (m), 834 (vs), 745 (s), 696 (s), 671 (s), 649 (m), 557

(vs), 524 (s), 485 (m), 419 (m) cm<sup>-1</sup>. Mp: 103–112 °C dec. Anal. Calcd for C<sub>38</sub>H<sub>44</sub>CrF<sub>6</sub>P<sub>3</sub>: C, 60.08; H, 5.84; P, 12.23. Found: C, 60.26; H, 6.04; P, 12.06.

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)[1,2-bis(dimethylphosphino)ethane]chromium(III) Hexafluorophosphate, [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)(dmpe)]PF<sub>6</sub> (**12**). TlPF<sub>6</sub> (0.285 g, 0.816 mmol) was added all at once to a stirred solution containing 0.200 g of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl]<sub>2</sub> (0.397 mmol) and 0.120 g of 1,2-bis(dimethylphosphino)ethane (0.799 mmol) in 20 mL of THF. The solution slowly turned red-brown, and a gray precipitate formed. The solution was filtered, and the solvent was evaporated under vacuum. The resulting solid was recrystallized from THF/diethyl ether to yield red-brown crystals of **12** (345 mg, 85%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.75 (br, 15 H), -17.80 (br, 6 H), -48.32 (br, 6 H) ppm. IR (KBr): 2972 (m), 2917 (m), 2870 (s), 1457 (w), 1431 (s), 1381 (m), 1308 (m), 1292 (m), 1148 (w), 1130 (w), 1025 (w), 950 (s), 935 (s), 903 (m), 876 (s), 836 (vs), 740 (m), 712 (m), 650 (w), 557 (s), 465 (m) cm<sup>-1</sup>. Mp: 132–135 °C dec. Anal. Calcd for C<sub>18</sub>H<sub>36</sub>CrF<sub>6</sub>P<sub>3</sub>: C, 42.28; H, 7.10. Found: C, 42.57; H, 7.16. Mass spectrum, *m/e* (relative intensity): 201 (27.3), 202 (20.9), 334 (26.1), 335 (43.9), 336 (62.5), 337 (53.3), 338 (25.2), 363 (20.1), 364 (22.8), 365 (100).

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)bis(3,5-lutidine)chromium(III) Hexafluorophosphate, [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)(3,5-lut)<sub>2</sub>]PF<sub>6</sub> (**13**). TlPF<sub>6</sub> (0.300 g, 0.850 mmol) was added all at once to stirred solution of 0.304 g of Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)Cl(3,5-lut) (**4**; 0.847 mmol) dissolved in a mixture of 1 mL of 3,5-lutidine and 20 mL of THF. The solution slowly turned brown, and a gray precipitate formed. After 5 h, the solution was filtered and the solvent was evaporated under vacuum. The solid was recrystallized from THF/diethyl ether to yield black needles of **13** (345 mg, 71%). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>): -5.35 (br, 4 H), -11.17 (br, 2 H), -14.38 (br, 15 H), -17.10 (br, 12 H) ppm. IR (KBr): 3588 (w), 2921 (s), 2846 (s), 2713 (s), 1793 (w), 1601 (vs), 1459 (s), 1380 (s), 1278 (m), 1247 (m), 1145 (s), 1052 (m), 1023 (m), 844 (vs), 769 (s), 558 (vs), 470 (m), 403 (s) cm<sup>-1</sup>. Mp: 175–180 °C dec. Anal. Calcd for C<sub>26</sub>H<sub>38</sub>CrF<sub>6</sub>N<sub>2</sub>P: C, 54.26; H, 6.65; N, 4.87. Found: C, 54.39; H, 6.69; N, 4.78.

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)bis(tetrahydrofuran)chromium(III) Tetraphenylborate, [Cp\*Cr(CH<sub>3</sub>)(THF)<sub>2</sub>]BPh<sub>4</sub> (**14**). Method A. NaBPh<sub>4</sub> (0.176 g, 0.514 mmol) was added all at once to a stirred solution of 0.253 g of [Cp\*Cr(CH<sub>3</sub>)(THF)<sub>2</sub>]PF<sub>6</sub> (**9**) (0.515 mmol) in 20 mL of THF. After 1 h, the solution was filtered and the solvent was evaporated under vacuum. The solid residue was recrystallized from THF/diethyl ether to yield black needles of **14** (0.260 g, 76%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.0 (br, 8 H), 8.0 (br, 8 H), 7.36 (8 H), 7.05 (8 H), 6.93 (4 H), -26.5 (br, 15 H) 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), cm<sup>-1</sup>. Mp: 135–138 °C dec. Anal. Calcd for C<sub>43</sub>H<sub>54</sub>BCrO<sub>2</sub>: C, 77.58; H, 8.18. Found: C, 77.62; H, 8.21.

Method B. [Cp\*(CH<sub>3</sub>)Cr( $\mu$ -CH<sub>3</sub>)<sub>2</sub>] (0.122 g, 0.281 mmol) was dissolved in 15 mL of THF and 0.237 g of HNEt<sub>3</sub><sup>+</sup>BPh<sub>4</sub><sup>-</sup> (0.562 mmol) added to the stirred solution. The solution immediately changed color from green to red, and gas (CH<sub>4</sub>) evolved. Removal of the solvent and recrystallization of the residue from THF/Et<sub>2</sub>O yielded **15** (0.292 g, 78%), indistinguishable in all respects from the material prepared by method A.

( $\eta^5$ -Pentamethylcyclopentadienyl)(ethyl)bis(pyridine)chromium(III) Tetraphenylborate, [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)(py)<sub>2</sub>]BPh<sub>4</sub> (**15**). NaBPh<sub>4</sub> (0.106 g, 0.310 mmol) was added all at once to a stirred solution of 0.153 g of [Cp\*Cr(C<sub>2</sub>H<sub>5</sub>)(py)<sub>2</sub>]PF<sub>6</sub> (**10**; 0.295 mmol) in 10 mL of THF. After 2.5 h, the solution was filtered and the solvent was evaporated under vacuum. The solid was recrystallized from THF/diethyl ether to yield black needles of **15** (110 mg, 58%). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>): 19.1 (br), 6.86 (br), -13.3 (br, 15 H) ppm. IR (KBr): 3053 (s), 2987 (s), 2938 (s), 1942 (w), 1880 (w), 1817 (w), 1578 (m), 1478 (s), 1423 (s), 1377 (m), 1345 (m), 1185 (m), 1126 (m), 1035 (s), 1013 (s), 914 (s), 848 (s), 735 (vs), 705 (vs), 611 (s), 503 (m), 400 (m) cm<sup>-1</sup>. Mp: 166–169 °C dec. Anal. Calcd for C<sub>46</sub>H<sub>50</sub>BCrN<sub>2</sub>: C, 79.64; H, 7.26; N, 4.04. Found: C, 79.57; H, 7.24; N, 3.98.

( $\eta^5$ -Pentamethylcyclopentadienyl)(methyl)[1,2-bis(dimethylphosphino)ethane]chromium(II), Cp\*Cr(CH<sub>3</sub>)(dmpe) (**16**). At -35 °C, 1.386 g of 0.5% Na/Hg amalgam (0.301 mmol of Na) was added all at once to a stirred solution of 0.150 g of [Cp\*Cr(CH<sub>3</sub>)dmpe]PF<sub>6</sub> (**7**) (0.302 mmol) in 20 mL of THF. The solution was warmed to room temperature and slowly became dark orange. After 45 min, the solution was filtered and the solvent was evaporated under vacuum. The solid was recrystallized from pentane to yield brown cubes of **16** (59 mg, 55%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 5.84 (br, 15 H), -15.88 (br, 12 H) ppm. IR (KBr): 2956 (vs), 2884 (vs), 2777 (vs), 2713 (s), 1476 (m), 1414 (vs), 1377 (vs), 1270 (vs), 1284 (s), 1157 (s), 1116 (m), 1021 (s), 920 (vs), 896 (vs), 848 (m),



Table VII. Crystal Data and Data Collection Parameters for 10, 14, 16, and 17

	10	14	16	17
formula	C <sub>22</sub> H <sub>30</sub> CrF <sub>6</sub> N <sub>2</sub> P	C <sub>43</sub> H <sub>54</sub> BCrO <sub>2</sub>	C <sub>17</sub> H <sub>34</sub> CrP <sub>2</sub>	C <sub>34</sub> H <sub>35</sub> BCr
formula weight	519.45	665.7	352.40	506.46
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	Pbca	P2 <sub>1</sub> /c
Z	4	4	8	4
a, Å	8.810 (2)	10.718 (3)	14.223 (2)	11.486 (4)
b, Å	15.425 (3)	16.209 (4)	16.108 (3)	11.732 (4)
c, Å	17.792 (3)	21.880 (6)	17.391 (3)	20.716 (6)
β, deg	89.34 (9)	103.63 (2)		100.25 (3)
V, Å <sup>3</sup>	2417.7	3694 (2)	3984.5 (12)	2747 (3)
d <sub>calc</sub> , g/cm <sup>3</sup>	1.43	1.197	1.175	1.22
crystal dimensions, mm	0.4 × 0.4 × 0.4	0.7 × 0.4 × 0.1	0.4 × 0.4 × 0.4	0.55 × 0.37 × 0.14
diffractometer	Syntex P2 <sub>1</sub>	Syntex P2 <sub>1</sub>	Syntex P2 <sub>1</sub>	CAD4
radiation <sup>a</sup>	Cu Kα	Mo Kα	Cu Kα	Cu Kα
temperature, °C	25	-50	25	25
scan method	θ-2θ	θ-2θ	θ-2θ	θ-2θ
2θ range, deg	0-114	4.0-45.0	0-100	0-50
scan rate, deg/min	variable (1° ω scans)	3.00-29.50°/min in ω	variable (1° ω scans)	variable (1° ω scans)
no. of data collected	3237	5378	2500	7575
no. of unique data >3σ	2059	2961	1129	2507
no. of parameters refined	353	424	182	325
absorption coefficient	55.2 cm <sup>-1</sup>	0.334 mm <sup>-1</sup>	62.62 cm <sup>-1</sup>	4.25 cm <sup>-1</sup>
R	0.083	0.079	0.076	0.045
R <sub>w</sub>	0.099	0.098	0.097	0.048

<sup>a</sup> Cu, λ = 1.5418 Å; Mo, λ = 0.71072 Å.

822 (s), 796 (m), 761 (m), 709 (s), 681 (vs), 627 (vs), 618 (m), 585 (m), 469 (s), 452 (m), 425 (m) cm<sup>-1</sup>. Mp: 127-135 °C dec. Anal. Calcd for C<sub>17</sub>H<sub>34</sub>CrP<sub>2</sub>: C, 57.94; H, 9.72; P, 17.58. Found: C, 57.61; H, 9.51; P, 17.30. Mass spectrum, *m/e* (relative intensity): 135 (90.71), 150 (38.16), 151 (94.62), 152 (50.73), 211 (100), 337 (90.78), 338 (63.37), 352 (92.13), 353 (60.27).

(η<sup>5</sup>-Pentamethylcyclopentadienyl)chromium(II) η<sup>6</sup>-Tetraphenylborate. Cp\*Cr(η<sup>6</sup>-Ph-BPh<sub>3</sub>) (17). [Cp\*Cr(CH<sub>3</sub>(THF)<sub>2</sub>]BPh<sub>4</sub> (14) (0.80 g, 0.120 mmol) was dissolved in a mixture of 4 mL of styrene and 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution slowly turned brown. After 12 h, the solvent was evaporated under vacuum. The solid was recrystallized in toluene (or THF) to yield orange needles of 7 (20 mg, 33%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): -15.5 (br 15 H), 8.25, 7.63, 7.47, 7.31, 7.03, 6.88, 6.58 (20 H total) ppm. IR (KBr): 3056 (s), 2985 (m), 2909 (m), 1947 (w), 1884 (w), 1818 (w), 1750 (w), 1581 (m), 1481 (s), 1427 (s), 1387 (m), 1261 (m), 1185 (m), 1140 (m), 1067 (m), 1031 (m), 980 (m), 846 (s), 799 (m), 732 (s), 705 (vs), 613 (s), 513 (w), 472 (m), 432 (s) cm<sup>-1</sup>. Mp: 246-248 °C dec. Anal. Calcd for C<sub>34</sub>H<sub>35</sub>BCr: C, 80.63; H, 6.97. Found: C, 80.90; H, 6.98.

**X-ray Crystallography. General Comments.** With the exception of 17, the X-ray structure determinations were carried out at Cornell University. The structure of 17 was determined at Yale University. At Cornell, the crystallographic calculations were performed on a Prime 9950 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were the following: RANTAN 80 and MULTAN 78 (locally modified to perform all Fourier calculations) by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York England, 1980; BDLs 78A by K. Hirotsu and E. Arnold, Cornell University, 1980; CRYSTALS by D. J. Watkin and J. R. Caruthers, Oxford University, 1981; REDUCE and UNIQUE, data reduction programs, by M. E. Lenowonowicz, Cornell University, 1978; PLOT by G. VanDuyne, Cornell University, 1987; and TABLES by G. VanDuyne, Cornell University, 1986.

**Crystal Structure Determination of 10.** A single crystal of 10 was sealed in a glass capillary under N<sub>2</sub>. The capillary was mounted on a Syntex P2<sub>1</sub> diffractometer. Crystal data and a summary of parameters pertinent to the data collection are given in Table VII. Lattice constants were determined by a least-squares fit of 15 diffractometer-measured 2θ values. The chromium atom was located via a Patterson synthesis. All other non-hydrogen atoms were located by subsequent difference Fourier maps. Hydrogen atom parameters were generated from assumed geometries and were not refined. A disorder in the fluorine atoms of the PF<sub>6</sub><sup>-</sup> anion was modeled by placing one-third of the sites on the face of the octahedron occupied by the remaining two-thirds of the sites, and the program CRYSTALS was used to refine the structure. Block-diagonal least-squares refinement was carried out by the program BDLs. Fractional coordinates and thermal parameters are included in the supplementary material.

**Crystal Structure Determination of 14.** A single crystal of 14 was sealed in a glass capillary under N<sub>2</sub>. Crystal data and a summary of parameters pertinent to the data collection are given in Table VII.

Lattice constants were determined by a least-squares fit of 15 diffractometer-measured 2θ values. The structure was solved by direct methods. Hydrogen atom parameters were generated from assumed geometries and were not refined. No absorption correction was applied. Full-matrix least-squares refinement was carried out with SHELXTL PLUS on a Micro VAX II. Fractional coordinates and thermal parameters are included in the supplementary material.

**Crystal Structure Determination of 16.** A single crystal of 16 was sealed in a glass capillary under N<sub>2</sub>. The capillary was mounted on a Syntex P2<sub>1</sub> diffractometer. Crystal data and a summary of parameters pertinent to the data collection are given in Table VII. Lattice constants were determined by a least-squares fit of 15 diffractometer-measured 2θ values. The chromium atom was located via the Patterson synthesis. All other non-hydrogen atoms were located by subsequent difference Fourier maps. Hydrogen atom parameters were generated from assumed geometries and were not refined. At the end of the final isotropic refinement, an empirical absorption correction was applied. The minimal, maximal, and average absorption corrections were 0.730, 1.289, and 0.974. Block-diagonal least-squares refinement was carried out with the program BDLs. Fractional coordinates and thermal parameters are included in the supplementary material.

**Crystal Structure Determination of 17.** A single crystal of 17 was sealed in a glass capillary under N<sub>2</sub>. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated diffractometer with graphite-monochromated Mo Kα radiation. Crystal data and a summary of parameters pertinent to the data collection are given in Table VII. Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry. The data were corrected for absorption with the ψ-scan method and the empirical absorption correction program in TEXSAN. The structure was solved with the VERY HARD option in MITHRIL. Iterations of the wFOUR synthesis in DIRDIF resulted in the solution of the entire non-hydrogen structure. All of the hydrogens, with the exception of H5, were located in a difference Fourier synthesis. The full-matrix refinement of the non-hydrogen atoms and inclusion of the hydrogen scattering factors resulted in convergence to an unweighted residual of 0.045 and a weighted residual of 0.048. All intramolecular bond distances are within normal ranges. Fractional coordinates and thermal parameters are included in the supplementary material. Principal programs employed were the following: MITHRIL by C. J. Gilmore, University of Glasgow, Scotland, 1984; DIRDIF by P. T. Beurskens, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984; TEXSAN-TEXRAY by Molecular Structure Corporation, 1985; URANUS by S. K. Kearsley, Yale University, 1985.

**Ethylene Polymerizations.** An apparatus consisting of a 250-mL reaction flask, a 1000-mL gas reservoir, a mercury manometer, and a gas purification column (containing MnO on vermiculite and 4A sieves), all connected by copper tubing and a small piece of vacuum tubing, was used. The desired amount of catalyst was placed in a 250-mL Schlenk flask and dissolved in the appropriate solvent. The flask was then attached to the manometer assembly, and the entire system was evacuated. The system was then filled with ethylene (~1.5 atm). Ethylene was

periodically admitted to the system. After ethylene uptake had ceased, the solution was filtered and the polymer was washed with  $\text{CH}_2\text{Cl}_2$  and then dried under vacuum. See Table V for the results of the GPC analysis. Ethylene-uptake rate measurements were carried out in the same apparatus.  $\text{CH}_2\text{Cl}_2$  (49 mL) was placed in a 100-mL Schlenk flask in the glovebox. The flask was attached to the polymerization apparatus. The system was evacuated and then back-filled with ethylene and allowed to equilibrate to the desired initial pressure to insure saturation of the solvent with ethylene. The solvent was stirred vigorously with a magnetic stirrer. For temperature control, the flask was immersed in a water bath (19 °C), an ice water bath (0 °C), or an ethanol bath cooled by a Neslab cryocool cc-60II immersion cooler (10, -7, and -14 °C). **14** was dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$  and this solution injected into the reaction flask with a gas-tight syringe. The pressure was periodically recorded, and the moles of ethylene taken up by the solution were calculated and plotted as a function of time. The rates of polymerization were determined from the initial slopes of these curves.

**Reaction of 16 with Ethylene. Uptake Measurements and Analysis of the Products.** **16** (97 mg, 0.275 mmol) was placed in a 25-mL round-bottom flask. The flask was evacuated, and 3 mL of  $\text{C}_6\text{D}_6$  was vacuum transferred into the flask; 8.6 equiv of ethylene (2.363 mmol; 651 Torr in 67 mL at 23 °C) was condensed in. The solution was warmed to room temperature and stirred for 1 week. The flask was then attached to a Toepler pump, and the gas remaining in the flask was collected and analyzed by GC: 1.661 mmol of ethylene remained; 0.051 mmol of methane, 0.0068 mmol of ethane, 0.0050 mmol of propene, and 0.061 mmol of butene were formed. The solution was then treated with 0.98 equiv of gaseous HCl (0.270 mmol; 74 Torr in 67 mL at 23 °C). The gases were once again collected in the Toepler pump and analyzed by GC: 0.040 mol of ethylene remained; 0.135 mmol of methane and 0.022 mmol of ethane were produced. Thus, 0.135 mmol of **16** reacted with

0.666 mmol of ethylene. The volatiles remaining in the solution were vacuum transferred and analyzed by GC/MS and  $^1\text{H}$  NMR. Two GC fractions were analyzed: The first was butene. Mass spectrum,  $m/e$  (relative intensity): 37 (4.0), 38 (7.2), 39 (46.2), 40 (12.7), 41 (100), 42 (3.6), 43 (8.5), 50 (5.4), 53 (6.7), 55 (21.2), 56 (39.5), 57 (1.8), 58 (1.8). The second was hexene. Mass spectrum,  $m/e$  (relative intensity): 38 (4.4), 39 (45.6), 40 (13.8), 41 (100), 42 (69.4), 43 (50.2), 53 (7.7), 54 (5.8), 55 (58), 56 (90.7), 57 (4.9), 69 (24.1), 70 (1.5), 84 (29.6), 85 (2.3).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.81 (m, 20 H), 1.23 (m, 20 H), 1.58 (m, 2 H), 1.97 (t, 5 H), 3.99 (s, 30 H), 4.95 (m, 2 H), 5.05 (m, 1 H), 5.42 (m, 1 H), 5.75 (m, 1 H) ppm.

**Magnetic Measurements.** The magnetic susceptibility of polycrystalline samples of **10** at room temperature and of **7** and **16** over the temperature range 3–300 K was measured with a Faraday balance. Variable temperature control was obtained with a Janis helium flow cryostat. The samples were loaded into high-purity quartz ampules in a drybox, which were evacuated and then sealed. The diamagnetic force due to the sample holder was subtracted over the entire temperature range. The susceptibility was measured at 10 field strengths to check for ferromagnetic impurities (Honda-Owens method). Calibration was performed with  $\text{HgCo}(\text{SCN})_4$  ( $16.44 \times 10^{-6}$  emu/g at 298 K). The data were corrected for diamagnetism with use of Pascal constants.

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**Supplementary Material Available:** Tables of atomic positional and thermal parameters for **10**, **14**, **16**, and **17** (10 pages). Ordering information is given on any current masthead page.

## Reaction Classification and Retrieval. A Linkage between Synthesis Generation and Reaction Databases

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**Abstract:** A program is described that translates widely used reaction databases such as REACCS and SYNLIB into the same terms as are used for synthesis design by the SYNGEN program. This therefore makes it possible to look up in these databases all reactions that are of the same family as any reaction generated by SYNGEN. Of the computer-accessible reactions in REACCS, about three-fourths of the constructions may be classified and retrieved by SYNGEN, constituting a precedent library of ~19 000 reactions. A further 9000 are retrievable from SYNLIB.

For a number of reasons, we elected to develop our program, SYNGEN, for synthesis design from a basis of chemical logic and not from a database library of reactions contained in the program.<sup>1</sup> As a result, the output from SYNGEN is presented as "theoretically reasonable" construction reactions but without literature precedent. Now, however, several extensive collections of reactions are available as computer-searchable databases.<sup>2</sup> The extent of overlap among these databases is reported to be small,<sup>3</sup> and so we have developed a linkage program to locate in these databases the literature precedents for our generated reactions. This means

that the synthetic routes that SYNGEN creates for any target were previously just "paper chemistry", i.e., not tied to specific literature examples. Hence, the laboratory chemist could not assess realistically their practical efficacy in his particular case. Now, with an interface to commercial databases of reactions, however, it is possible for the SYNGEN user to access the literature for concrete examples of closely matching molecules to locate the details required.

In order to create such an interface, we specifically focus first on the *reaction* rather than the *compounds* in order to find all parallel cases. Subsequently, we narrow the definition to get closer matching of the detailed substitution around the reaction center. We examine first the *net structural change* in the reaction rather than structures or substructures of reactants and products. To this end we use a layered, or taxonomic, set of reaction classifications, from the general to the particular.<sup>4</sup>

In effect, we classify successive layers of definition for sorting and retrieving reactions, logically analogous to the system of Beilstein for classifying molecular structures. This classification

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(2) The databases examined were REACCS from Molecular Design Ltd., San Leandro, CA, and SYNLIB from Distributed Chemical Graphics, Inc., Meadowbrook, PA.

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