Paramagnetic (Benzyl)chromium Complexes as Homogeneous Ethylene Polymerization Catalysts

Gautam Bhandari, Youhyuk Kim, Jeffrey M. McFarland,
Arnold L. Rheingold, and Klaus H. Theopold*

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

Received September 16, 1994[®]

The (benzyl)chromium(III) complexes $[Cp^*Cr(Bz)(\mu\text{-}Cl)]_2$ (**1**), $Cp^*Cr(py)(Bz)_2$ (**2**), $Cp^*Cr(THF)(Bz)_2$ (**3**), $[Cp^*Cr(THF)_2Bz]BPh_4$ (**4**), $[Cp^*Cr(bpy)Bz]BPh_4$ (**5**), $Li[Cp^*Cr(Bz)_3]$ (**6**), and $[Li(TMEDA)_2][Cp^*Cr(Bz)_3]$ (**7**) have been prepared. Reaction of **5** with strong bases (^{t}BuLi or $LiN(TMS)_2$) yielded $Cp^*Cr(bpy)Bz$ (**8**), the product of a reduction. The same complex was also produced by treatment of **2** or **3** with 2,2′-bipyridyl (bpy). The crystal structures of **1** (monoclinic, $C2/c$, $a = 14.960(4)$ Å, $b = 16.803(5)$ Å, $c = 13.662(6)$ Å, $\beta = 110.4(3)°$, $Z = 4$), **2** (monoclinic, $P2_1/n$, $a = 9.345(3)$ Å, $b = 16.923(5)$ Å, $c = 16.161(5)$ Å, $\beta = 104.36(2)°$, $Z = 4$), **6** (monoclinic, $P2_1/n$, $a = 11.125(2)$ Å, $b = 15.287(3)$ Å, $c = 15.410(4)$ Å, $\beta = 94.11(2)°$, $Z = 4$), and **8** (triclinic, $P\bar{1}$, $a = 9.056(3)$Å, $b = 11.568(6)$ Å, $c = 11.602(4)$ Å, $\alpha = 73.56(3)°$, $\beta = 88.47(5)°$, $\gamma = 79.35(3)°$, $Z = 4$) have been determined by X-ray diffraction. ^{2}H NMR spectroscopy was used to characterize complexes with perdeuteriated benzyl ligands; signal narrowing factors ($W(^1H)/W(^2H)$) ranged from 12 to 36. Neutral **3**, cationic **4**, and anionic **6** catalyzed the polymerization of ethylene.

Introduction

As part of our wide-ranging investigation of paramagnetic organometallic derivatives containing the Cp*Cr moiety,[1] we have prepared a number of complexes with benzyl ligands. Our studies are motivated—inter alia—by the prominent role of chromium catalysts in the coordination polymerization of ethylene,[2] and it was our hope that the relatively bulky benzyl substituent might stabilize coordinatively unsaturated chromium complexes, which could serve as homogeneous models for the commercially employed heterogeneous catalysts (i.e. Phillips and Union Carbide catalysts).[3] Herein we describe the syntheses and characterization of several new (benzyl)chromium complexes, including cationic, neutral, and anionic examples, as well as their activity as ethylene polymerization catalysts.

Results and Discussion

Syntheses. As described earlier, addition of 1 equiv of Cp*Li to a suspension of $CrCl_3(THF)_3$ in THF resulted in the formation of a blue solution of $[Cp^*Cr(\mu\text{-}Cl)Cl]_2$.[4] Addition of 1 equiv (per Cr) of (benzyl)magnesium chloride (BzMgCl) to this solution induced an immediate color change to purple. Standard workup of the reaction mixture and recrystallization from pentane yielded purple crystals of $[Cp^*Cr(Bz)(\mu\text{-}Cl)]_2$ (**1**) in 72% yield (see Scheme 1). This complex is a representative of a class of dimeric chromium(III) alkyls, which were prepared in this laboratory some time ago and all found to be purple.[4b] The molecular structure of **1** was determined by X-ray diffraction; the result of this determination is shown in Figure 1, and Table 1 lists selected interatomic distances and angles. The molecule exhibits crystallographic inversion symmetry; the pseudooctahedral coordination of the individual Cr^{III} ions in the three-legged piano-stool motif is characteristic of this class of alkyl complexes.[1] At 2.104(6) Å the Cr–C bond lengths are not significantly longer than the 2.09 Å average found in a series of related compounds, and the Cr–Cr distance of 3.343(1) Å rules out significant metal–metal bonding in this edge-sharing bioctahedron.

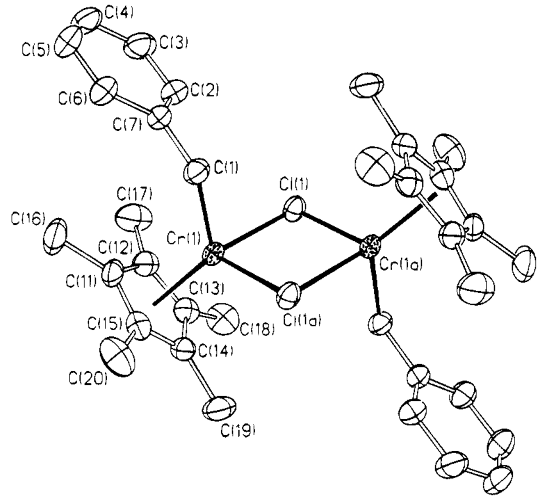


Figure 1. Molecular structure of $[Cp^*Cr(Bz)(\mu\text{-}Cl)]_2$ (**1**). Selected interatomic distances and angles are listed in Table 1.

[®] Abstract published in *Advance ACS Abstracts*, December 15, 1994.

[1] Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263.

[2] (a) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (b) Thomas, B. J.; Noh, S.-K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893. (c) Theopold, K. H.; Heintz, R. A.; Noh, S.-K.; Thomas, B. J. Homogeneous Chromium Catalysts for Olefin Polymerization. In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; American Chemical Society: Washington, DC, 1992; p 591.

[3] (a) Clark, A. *Catal. Rev.* **1969**, *3*, 145. (b) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci., Part A-1* **1972**, *10*, 2621. (c) Karol, F. J.; Brown, G. L.; Davison, J. M. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 413.

[4] (a) Benn, H.; Wilke, G.; Henneberg, D. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1001. (b) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570.

0276-7333/95/2314-0738$09.00/0

Scheme 1

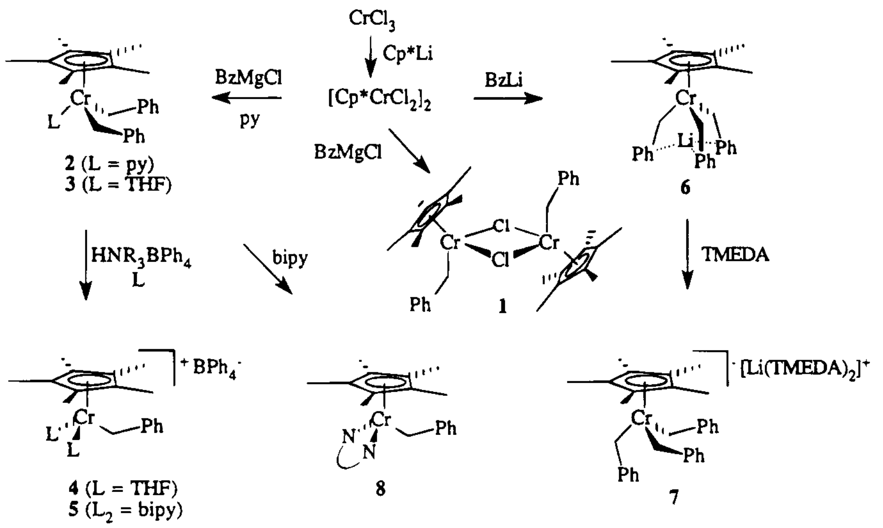


Table 1. Selected Interatomic Distances and Angles for $[Cp^*Cr(Bz)(\mu\text{-}Cl)]_2$ (1)

Distances (Å)			
Cr(1)–Cr(1a)	3.343(1)	Cr(1)–Cl(1)	2.380(5)
Cr(1)–Cl(1a)	2.386(5)	Cr(1)–C(1)	2.104(6)
Cr(1)–C_{Cp^*} (av)	2.237	C(1)–C(7)	1.465(6)
Angles (deg)			
Cl(1)–Cr(1)–C(1)	94.6(2)	Cl(1)–Cr(1)–Cl(1a)	90.9(1)
C(1)–Cr(1)–Cl(1a)	90.2(2)	Cr(1)–Cl(1)–Cr(1a)	89.1(1)
Cr(1)–C(1)–C(7)	121.4(3)		

Table 2. Selected Interatomic Distances and Angles for $Cp^*Cr(py)(Bz)_2$ (2)

Distances (Å)			
Cr–N	2.085(7)	Cr–C(11)	2.125(9)
Cr–C(12)	2.139(9)	Cr–C_{Cp^*} (av)	2.288
C(11)–C(26)	1.483(13)	C(12)–C(36)	1.485(14)
Angles (deg)			
N–Cr–C(11)	100.9(3)	N–Cr–C(12)	99.1(3)
C(11)–Cr–C(12)	93.5(4)	Cr–C(11)–C(26)	119.5(5)
Cr–C(12)–C(36)	124.0(6)		

Gradual addition of 2 equiv (per Cr) of BzMgCl to the $[Cp^*CrCl_2]_2$ solution resulted in a series of color changes, first to purple and finally to brown. Upon addition of an excess of pyridine (py) to the brown solution, its color rapidly changed to green. Normal workup of the reaction mixture and recrystallization from pentane afforded green crystals of $Cp^*Cr(py)(Bz)_2$ (**2**) in 67% yield (see Scheme 1). The molecular structure of **2** was determined by X-ray diffraction; the result of this determination is shown in Figure 2, and Table 2 lists selected interatomic distances and angles. The molecule exhibits no crystallographically imposed symmetry, and the Cr–C bond lengths are slightly longer than the aforementioned 2.09 Å average, probably reflecting a slightly weaker $Cr-C_{Bz}$ bond.

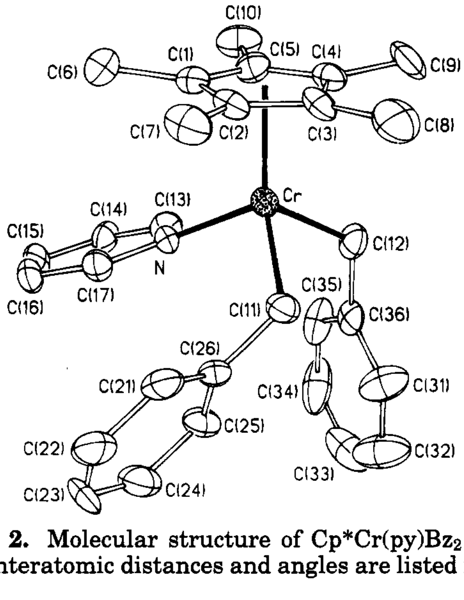


Figure 2. Molecular structure of $Cp^*Cr(py)Bz_2$ (**2**). Selected interatomic distances and angles are listed in Table 2.

Addition of donor molecules other than pyridine yielded analogous adducts. For example, addition of dioxane gave $Cp^*Cr(dioxane)(Bz)_2$, deemed worthy of spectroscopic characterization only. Surprisingly, even THF formed a stable complex, i.e. brown $Cp^*Cr(THF)(Bz)_2$ (**3**), which was isolated and fully characterized. Clean loss of 1 equiv of THF and the formation of $Cp^*Cr(py)(Bz)_2$ were observed by ^1H NMR upon addition of pyridine to a solution of **3** in C_6D_6. The marked stability of neutral **3** is somewhat surprising. For comparison, both $Cp^*Cr(THF)(Me)_2$ and $Cp^*Cr(THF)(CH_2SiMe_3)_2$ are stable only in THF solution. Upon removal of the solvent both lose THF rapidly to form $[Cp^*Cr(\mu\text{-}Me)(Me)]_2$[5] and $Cp^*Cr(CH_2SiMe_3)_2$, respectively. In contrast, **3** loses THF only upon heating (45 °C) under high vacuum, leaving behind a dark viscous oil. The ^1H NMR spectrum of this residue showed resonances consistent with an unligated benzyl complex, tentatively identified as $[Cp^*Cr(Bz)_2]_n$ ($n = 1, 2$). Addition of THF to this material restored the resonances of **3**. As we have not been able to crystallize the presumed $[Cp^*Cr(Bz)_2]_n$, its structure remains uncertain. We note, however, that its effective magnetic moment (determined by the Evans method)[6] measured $\mu_{eff} = 3.0\ \mu_B$ per Cr at room temperature, significantly reduced from the expected value for a mononuclear Cr^{III} complex ($S = {}^3/_2$, 3.87 μ_B). One possible explanation for this lowered moment is antiferromagnetic coupling of the chromium ion atoms in a binuclear structure, e.g.

---

[5] Noh, S.-K.; Sendlinger, S. C.; Janiak, C.; Theopold, K. H. *J. Am. Chem. Soc.* **1989**, *111*, 9127.

[6] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

[7] Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.

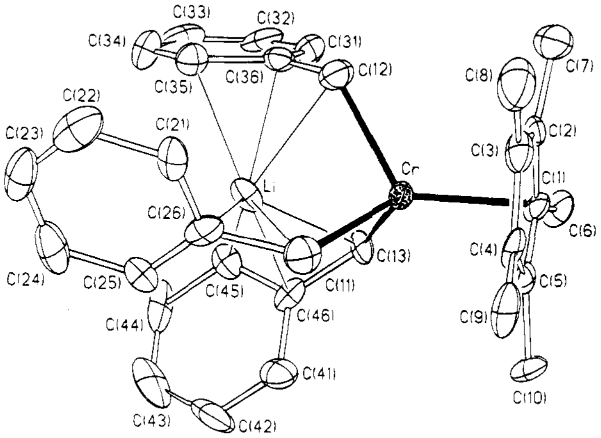


Figure 3. Molecular structure of Li[Cp*CrBz$_3$] (**6**). Selected interatomic distances and angles are listed in Table 3.

Table 3. Selected Interatomic Distances and Angles for Li[Cp*Cr(Bz)$_3$] (6)

Distances (Å)			
Cr–C(11)	2.171(13)	Cr–C(12)	2.178(12)
Cr–C(13)	2.157(13)	Cr–Li	2.540(20)
C(11)–Li	2.402(24)	C(12)–Li	2.419(25)
C(13)–Li	2.363(24)	C(11)–C(26)	1.479(19)
C(12)–C(36)	1.482(13)	C(13)–C(46)	1.481(18)
C(25)–Li	2.411(25)	C(26)–Li	2.252(24)
C(35)–Li	2.432(25)	C(36)–Li	2.348(25)
C(45)–Li	2.492(26)	C(46)–Li	2.311(26)
Cr–C$_{Cp*}$ (av)	2.300		

Angles (deg)			
C(11)–Cr–C(12)	95.2(5)	C(11)–Cr–C(13)	100.4(5)
C(12)–Cr–C(13)	97.9(5)	Cr–C(11)–C(26)	127.9(9)
Cr–C(12)–C(36)	124.3(9)	Cr–C(13)–C(46)	126.8(8)

[Cp*Cr(μ-Bz)(Bz)]$_2$.[7] The reason for the unusually strong coordination of THF to the Cp*Cr(Bz)$_2$ fragment is presently unclear.

Cationic benzyl complexes were readily prepared. Thus, protonation of **2** in THF with [HNEt$_3$]BPh$_4$ gave [Cp*Cr(THF)$_2$Bz]BPh$_4$ (**4**), directly analogous to the structurally characterized [Cp*Cr(THF)$_2$Me]BPh$_4$.[2b] Purple crystals of **4** were quite soluble in THF and could be crystallized from THF/Et$_2$O. The labile THF ligands in **4** were readily replaced by 2,2′-bipyridine, for example. Thus, addition of 1 equiv of the latter to a THF solution of **4** caused an immediate color change to red-brown. Crystals of [Cp*Cr(bpy)Bz]BPh$_4$ (**5**) were obtained in nearly quantitative yield (93%). On the basis of our earlier work,[2a,b] there can be little doubt that these cationic complexes structurally feature pseudooctahedral coordination (η^5-Cp* and three 2-electron ligands) of chromium in a 15-valence-electron configuration.

Addition of 6 equiv of (benzyl)lithium to a blue solution of [Cp*CrCl$_2$]$_2$ in THF (prepared in situ) resulted in a series of color changes from blue to purple to brown to bright purple again. The use of Grignard reagent in this preparation produced the same sequence of color changes but proved unsuitable for product isolation, due to the formation of intractable, tarry residues. Standard workup and recrystallization from toluene/pentane yielded bright purple crystals of Li[Cp*Cr(Bz)$_3$] (**6**). The result of a crystal structure determination of **6** by X-ray diffraction is shown in Figure 3, and Table 3 contains selected structural parameters. **6** is closely related to **2** in its coordination geometry about Cr. The Cr–C$_{Bz}$ distances (average 2.17 Å) are slightly longer, probably reflecting steric crowding as well as some negative charge on chromium. The most unusual feature of the structure is the position of the lithium atom, which is sequestered by the benzyl groups—much like a baseball caught in a glove—and thereby forced into close proximity to the transition metal (Cr–Li = 2.54 Å). The lithium atom is bonded equally to all three benzyl groups in an allylic fashion. Indeed, the strutural motif bears close resemblance to that found in the triethylenediamine adduct of (benzyl)lithium.[8] All three benzyl groups are tilted such that Li–C(21), Li–C(31), and Li–C(41) are considerably longer than Li–C(25), Li–C(35), and Li–C(45) (0.75 Å on average). Because of this 3-fold asymmetry the molecules found in the crystal are chiral, although both enantiomers are present in equal proportions. The ^{1}H NMR spectrum of **6** is consistent with the molecular structure being the same in solution yet allowing for rapid interconversion of the enantiomers by a rearrangement of the benzyl ligands. In a static structure, the five phenyl protons would be inequivalent; however, only three resonances were observed (see Table 5).

In order to gauge the strength of the interaction of the lithium ion with the organometallic complex ion, an attempt was made to extract the former from its "pocket". Addition of TMEDA to a toluene solution of **6** resulted in immediate precipitation of a purple powder. Crystals of this compound could be grown by slow addition of ether to a saturated solution in CH$_2$Cl$_2$. Its spectroscopic and analytical data were consistent with the formulation [Li(TMEDA)$_2$][Cp*Cr(Bz)$_3$] (**7**). **7** could also be prepared in high yield via the Grignard route (see Experimental Section). The solubility characteristics of **7** are in keeping with its saltlike nature.

Another motivation for the investigation of chromium benzyl derivatives had been our hope to stabilize a Cr^{III}–C double bond, i.e. in a benzylidene complex. Among the proven methods for the formation of alkylidenes are deprotonation of cationic alkyls or sterically induced α-elimination from dialkyl precursors.[9] In this vein, treatment of cationic **5** with strong bases—such as LiN(SiMe$_3$)$_2$ and ^{t}BuLi—afforded a neutral chromium complex. Much to our satisfaction, the reaction of **2** or **3** with 2,2′-bipyridine (an embodiment of the second strategy) also produced the same complex. However, on the basis of the available evidence, we assign the formula Cp*Cr^{II}(bpy)Bz (**8**) to this new complex. Figure 4 shows the molecular structure of **8**, as determined by X-ray diffraction. Interatomic distances and angles are listed in Table 4. Most importantly, the Cr–C$_{Bz}$ bond distance of 2.111(6) Å is not significantly shorter than the corresponding distances in **1**, **2**, and **6**, which contain authentic benzyl ligands. While one might have expected a Cr^{II}–C bond to be slightly longer than the corresponding Cr^{III}–C bond, the observed value does not appear to be consistent with a chromium–carbon double bond. Furthermore, the Cr–C–C$_{ring}$ angle of 114.3(4)°

---

(8) Patterman, S. P.; Karle, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150.

(9) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 131.

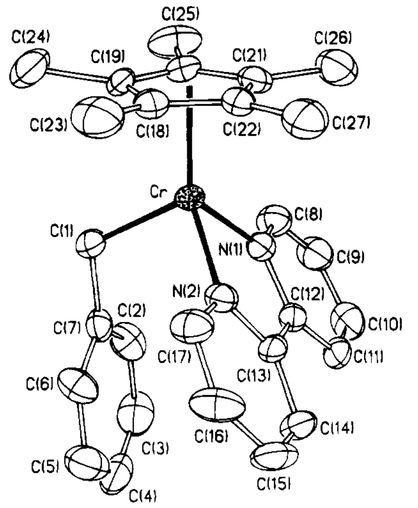


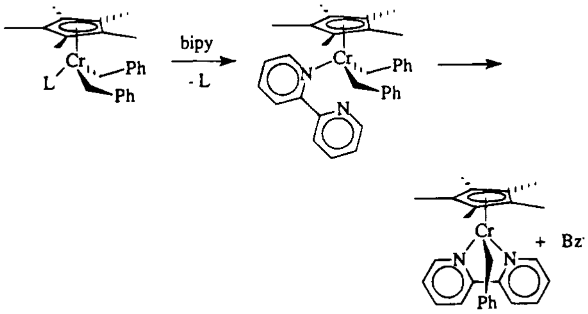
Figure 4. Molecular structure of Cp*Cr(bpy)Bz (**8**). Selected interatomic distances and angles are listed in Table 4.

Table 4. Selected Interatomic Distances and Angles for Cp*Cr(bpy)Bz (8)

	Distances (Å)		
Cr−N(1)	1.986(5)	Cr−N(2)	1.974(6)
Cr−C(1)	2.111(6)	C(1)−C(7)	1.490(10)
$Cr-C_{Cp*}$ (av)	2.250		
	Angles (deg)		
N(1)−Cr−N(2)	79.3(2)	N(1)−Cr−C(1)	93.9(2)
N(2)−Cr−C(1)	95.9(3)	Cr−C(1)−C(7)	114.3(4)

is closer to the expected value for tetrahedral hybridization than those in **1** (121.4°), **2** (119.5, 124.0°), and **6** (124.3, 126.8, 127.9°), arguing against a benzylidene moiety as well. The magnetic behavior of **8** was that expected of a Cr^{II} complex; i.e., its effective magnetic moment at room temperature measured $\mu_{eff} = 3.0(1)\ \mu_B$, consistent with a d^4 (Cr^{II}) configuration with two unpaired electrons, wholly incompatible with a d^3 (Cr^{III}) configuration. Curiously enough, reaction of **8** with the mild acid $[HNEt_3]BPh_4$ cleanly regenerated **5**, but this reaction must be an oxidation (yielding H_2), rather than a simple protonation. Consistent with this interpretation, i.e. the interconversion of **5** and **8** by redox chemistry rather than proton transfer, was their electrochemistry. Independent cyclic voltammetry measurements on THF solutions of **5** and **8** revealed the same reversible redox wave at −1.41 V (vs Fc^+/Fc) for both compounds.

Reduction of a cationic Cr^{III} complex by electron-rich reagents is not surprising; however, the formation of **8** by the reaction with bipyridine is unusual. Ligand substitution of pyridine (or THF) with the bidentate bipyridine would form a seven-coordinate complex, namely $Cp^*Cr(bpy)(Bz)_2$. As indicated by the lack of precedent for any such molecules in our previous work, this may well be an unstable coordination environment for Cr^{III}, which strongly prefers octahedral coordination. One possible pathway toward regaining the latter would be homolytic scission of a Cr−benzyl bond of the seven-coordinate intermediate, thereby leaving **8** (eq 1). On



(1)

the basis of this working hypothesis, we have searched the reaction mixtures for products derived from benzyl radicals (toluene, 1,2-diphenylethane). None were found. However, monitoring the reaction by ^1H NMR revealed the presence of several small resonances attributable to paramagnetic reaction products other than **8**. Unfortunately, we have been unable—despite many attempts—to isolate or identify these species. It is possible that benzyl radicals formed in the way described above might attack the starting material or product, to form other organometallic compounds. Indeed, the early literature on organochromium chemistry provides evidence for such reactions.[10] However, under the present circumstances, our mechanistic proposal is but one possible explanation for the formation of **8**.

^2H NMR. ^1H NMR spectra of Cr^{III} complexes suffer from severe line broadening, leading—inter alia—to overlapping signals, uncertain integrals, and failure to detect some resonances altogether.[11] ^2H NMR spectroscopy of suitably labeled compounds has been advanced as a solution to these problems.[12] Owing to the ready availability of deuteriated benzyl groups from toluene-d_8, we decided to test the benefits of this technique. Using C_7D_7K and C_7D_7Li as reagents,[13] we have prepared $Cp^*Cr(THF)(Bz\text{-}d_7)_2$ (**3**-d_{14}), $[Cp^*Cr(THF)_2(Bz\text{-}d_7)]BPh4$ (**4**-d_7), $Li[Cp^*Cr(Bz\text{-}d_7)_3]$ (**6**-d_{21}), and $[Li(TMEDA)_2][Cp^*Cr(Bz\text{-}d_7)_3]$ (**7**-d_{21}) and recorded their ^1H and ^2H NMR spectra. The results are listed in Table 5. Several observations are worth commenting on. There occurred indeed a significant sharpening of the benzyl resonances, leading to better resolution of signals and more reliable integrals. The individual effects did not quite approach the theoretical value (i.e. $W(^2H)/W(^1H) = 42.4$),[12d] but in at least one case the effect was sufficient to resolve an asymmetrically shaped ^1H NMR peak of **6** into two separate ^2H resonances in the spectrum of **6**-d_{21}. Comparison of the ^2H and ^1H spectra also showed that one set of phenyl protons (presumably ortho H) had consistently been missed in the ^1H NMR (see question marks in Table 5), due to extreme broadening and/or overlap. In contrast to Köhler's findings,[12c] and despite searching the shift range ±3500 ppm, we have been unable to detect a ^2H NMR resonance for the benzylic position of, for example, **6**-d_{21}. While we have never detected a ^1H NMR resonance for protons in a position α to chromium in a

---

(10) Zeiss, H. H.; Sneeden, R. P. A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 435.

(11) (a) La Mar, G. N.; Horrocks, W. D.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973. (b) Bertini, I.; Luchinat, C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin/Cummings: Menlo Park, CA, 1986.

(12) (a) Wheeler, W. D.; Kaizaki, S.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 3248. (b) Wheeler, W. D.; Legg, J. I. *Inorg. Chem.* **1984**, *23*, 3798. (c) Grohmann, A.; Köhler, F. H.; Müller, G.; Zeh, H. *Chem. Ber.* **1989**, *122*, 897. (d) Hebendanz, N.; Köhler, F. H.; Scherbaum, F.; Schlesinger, B. *Magn. Reson. Chem.* **1989**, *27*, 798. (e) Blümel, J.; Hofmann, P.; Köhler, F. H. *Magn. Reson. Chem.* **1993**, *31*, 2.

(13) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

Table 5. ^1H and ^2H Chemical Shifts of Selected Benzyl Complexes and Signal Narrowing Factors

compd	$\delta(^1H)$	$\delta(^2H)$	$\delta(^1H, d_n)^a$	$W(^1H)/W(^2H)$
3 (benzene)	−2.08 (19H)		−1.58 (15H)	
	?	−0.64 (4H)		
	5.90 (4H)		6.50 (4H)	
	ca. 23 (4H)		ca. 24 (4H)	
	28.71 (2H)	30.74 (2H)		21.3
	?	43.68 (4H)		
4 (THF)	−41.79 (15H)		−41.93 (15H)	
	−0.12 (2H)	−0.48 (2H)		13.8
	6.9−7.3 (20H)		6.8−7.3 (20H)	
	32.96 (1H)	32.97 (1H)		11.7
	?	34.43 (2H)		
6 (benzene)	−0.64 (6H)	−0.51 (6H)		13.0
	2.73 (15H)		3.57 (15H)	
	36.34 (9H)	36.12 (3H)		17.8
	?	37.72 (6H)		
7 (THF)	−0.69 (6H)	−1.98 (6H)		22.1
	2.15, 2.3 (32H)		2.15, 2.3 (32H)	
	20.31 (15H)		20.75 (15H)	35.5
	32.26 (3H)	33.81 (3H)		
	?	36.16 (6H)		

[a] ^1H NMR shifts of deuteriated complexes.

Table 6. Ethylene Polymerization Activity of (Benzyl)chromium Complexes and Polymer Characterization

compd[a]	solvent	time (min)	yield (mg)	M_w	M_n	M_w/M_n
1	benzene	480				
2	pentane	120				
3	pentane	45	224	7 044	4 996	1.41
3	THF	45				
4	CH_2Cl_2	45	556	29 940	14 896	2.01
6	toluene	120	515	12 520	5 140	2.44
6[b]	toluene	200	335	27 320	12 320	2.22
6 + 1 BzLi[b]	toluene	200	207	26 480	12 140	2.18
6 + 2 BzLi[b]	toluene	200	143	20 640	9 039	2.22
7	CH_2Cl_2	120				
8	pentane	120				

[a] Conditions: 50 mL of solution, [cat] = 2.2 mM, $P_i(C_2H_4)$ = 1.2 atm, room temperature. [b] Conditions: 51 mL of solution, [cat] = 0.84 mM, $P_i(C_2H_4)$ = 1.3 atm, room temperature.

mononuclear Cr^{III} complex, the failure of ^2H NMR spectroscopy in this particular instance was unexpected and somewhat disappointing. The routine identification of all hydrogen atoms (except hydrides) in paramagnetic complexes was one of the attractive features of the technique, and it is cast into doubt by our results. Finally, Table 5 reveals several examples of PIECS (i.e. *P*aramagnetic *I*sotope *E*ffects on *C*hemical *S*hifts).[14] For example, the ^1H chemical shifts associated with the Cp* ligands of the unlabeled compounds differ significantly from those of their deuteriated analogs. This kind of unusually large and long-range isotope effect is common in NMR spectra of paramagnetic compounds.[15]

Polymerization. In order to further our understanding of the structural requirements of chromium catalysts for ethylene polymerization, a selection of the complexes described above (i.e. **1**, **2**, **3**, **4**, **6**, **7**, and **8**) was tested for catalytic activity. In a typical experiment 0.111 mmol of catalyst was dissolved in 50 mL of solvent and exposed to 1.2 atm of ethylene at room temperature for up to 2 h. Precipitation of a white powder and a pressure decrease signaled formation of polyethylene. The polymer was isolated by filtration, washed with acetone, and dried in vacuo prior to molecular weight determination. Under these mild reaction conditions, only $[Cp^*Cr(THF)_2Bz]BPh_4$, $Cp^*Cr(THF)(Bz)_2$, and $Li[Cp^*Cr(Bz)_3]$ afforded significant amounts of polyethylene (see Table 6 for details). It is remarkable that the charge of the chromium complexes does not appear to be an important variable, as the catalysts include a cation, a neutral complex, and an anion. We have previously shown that the ethylene polymerization catalyst $[Cp^*Cr(THF)_2Me]BPh_4$ loses THF in solution and that the polymerization is inhibited by added THF.[2b] Presumably, the six-coordinate chromium must lose a ligand and open a coordination site for binding of ethylene, for polymerization to commence. By analogy, we suggest that polymerizations with the benzyl derivative $[Cp^*Cr(THF)_2Bz]BPh_4$ as well as $Cp^*Cr(THF)(Bz)_2$ proceed by a similar mechanism, involving substitution of the relatively weakly bound THF by ethylene. The observation that $Cp^*Cr(THF)(Bz)_2$ does not exhibit catalytic activity in THF solution is consistent with this proposal. The catalytic activity of $Li[Cp^*Cr(Bz)_3]$ was therefore a surprise, as dissociation of a benzyl ligand in toluene seemed unlikely to us. However, as the presence of small concentrations of (benzyl)lithium in toluene solutions of **6** could not be rigorously confirmed by ^1H NMR, we have probed the effect of added (benzyl)lithium on the catalytic activity. The results of these experiments are shown in Table 6 and Figure 5. While **6** is stable in the presence of the lithium reagent, there emerges a clear inhibitory effect of (benzyl)lithium on the rate of polymerization. We are thus forced to suggest that in toluene solution **6** exists in equilibrium with (benzyl)lithium and a coordinatively unsaturated chromium complex, probably $Cp^*Cr(Bz)_2$. The last species, or a dimer thereof, may also be formed by dissociation of THF from **3**, as outlined above. This formulation is also supported by the observation of the corresponding mass as the largest fragment in the mass spectra of both **2** and **3**.

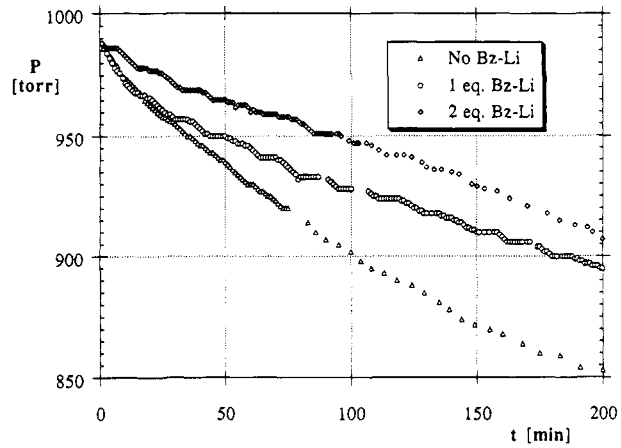


Figure 5. Ethylene uptake (pressure drop) due to polymerization by $Li[Cp^*CrBz_3]$ and various amounts of BzLi.

Conclusions

A variety of new (benzyl)chromium complexes has been prepared and structurally characterized. These

---

[14] Heintz, R. A.; Neiss, T. G.; Theopold, K. H. *Angew. Chem.* **1994**, *106*, 2389; *Angew. Chem., Int. Ed. Engl.*, in press.

[15] (a) Horn, R. R.; Everett, G. W., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 7173. (b) Evans, B.; Smith, K. M.; La Mar, G. N.; Viscio, D. B. *J. Am. Chem. Soc.* **1977**, *99*, 7070. (c) Theopold, K. H.; Silvestre, J.; Byrne, E. K.; Richeson, D. S. *Organometallics*, **1989**, *8*, 2001. (d) Hebendanz, N.; Köhler, F. H.; Scherbaum, F.; Schlesinger, B. *Magn. Reson. Chem.* **1989**, *27*, 798. (e) Medforth, C. J.; Shiau, F.-Y.; La Mar, G. N.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1991**, 590.

compounds reinforce our notion of the preference of Cr(III) for the pseudooctahedral coordination geometry of the Cp*CrX$_3$ fragment with a 15-valence-electron configuration. Expansion of the coordination sphere to Cp*CrX$_4$ is avoided strongly—i.e. even at the cost of loss of a benzyl ligand and reduction to Cr(II). On the other hand, dissociation of weakly bound ligands, to form Cp*CrX$_2$, seems energetically feasible. Such coordinatively unsaturated 13-electron complexes appear to be intermediates in the catalysis of ethylene polymerization by Cr(III) alkyls.

Experimental Section

General Techniques. All manipulations of compounds were carried out by standard Schlenk, vacuum, and glovebox techniques. Pentane, diethyl ether, tetrahydrofuran, and toluene were distilled from purple sodium benzophenone/ketyl solutions. C_6H_6, C_6D_6 and THF-d_8 were all predried with Na and stored under vacuum over Na/K alloy. Pyridine was dried with CaH_2 and vacuum-distilled onto 4 Å molecular sieves. CD_2Cl_2 was dried with CaH_2 and stored under vacuum over 4 Å molecular sieves. $CrCl_3$ (anhydrous) was purchased from Strem Chemical Co. $C_6H_5CH_2MgCl$ was purchased from Aldrich Chemical Co. as a 2 M solution in ether or THF. $C_6H_5CH_2K$ and $C_6H_5CH_2Li$ were prepared by literature procedures;[13] substitution of toluene-d_8, and use of pentane as reaction solvent (instead of toluene), yielded their deuteriated analogs $C_6D_5CD_2K$ and $C_6D_5CD_2Li$. Organometallic reagents were titrated with diphenylacetic acid prior to use. CP grade ethylene was purified with a column of MnO and 4 Å molecular sieves. $CrCl_3(THF)_3$ and LiCp* were synthesized by literature procedures. ^1H NMR spectra were taken on Bruker AM-250 or WM-250 spectrometers. ^2H NMR spectra were recorded on the Bruker WM 250 spectrometer, using a 10 mm broad-band probe tuned to the ^2H resonance frequency. FTIR spectra were recorded on a Mattson Alpha Centauri spectrometer with a resolution of 4 cm^{-1}. Mass spectra were obtained by the University of Delaware Mass Spectrometry Facility. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY 13492. Characterization of polyethylene samples was conducted at Chevron Chemical Company, Kingwood, TX. Room-temperature magnetic susceptibilities were determined using a Johnson Matthey magnetic susceptibility balance which utilizes a modification of the Gouy method. Molar magnetic susceptibilities were corrected for diamagnetism using Pascal's constants.

Bis((η^5-pentamethylcyclopentadienyl)(benzyl)(μ-chloro)chromium(III)), [Cp*(Bz)Cr(μ-Cl)]$_2$, (1). A THF solution (50 mL) of [Cp*CrCl$_2$]$_2$ was formed by stirring $CrCl_3(THF)_3$ (0.791 g, 2.11 mmol) and Cp*Li (0.300 g, 2.11 mmol) together overnight. A 2.11 mL (1.00 equiv) amount of BzMgCl (1.0 M in Et_2O, 2.11 mmol) was added dropwise to this blue solution. The color of the solution rapidly changed to purple. The solution was stirred for 1.5 h, after which time 4–5 drops of 1,4-dioxane were added to aid the precipitation of $MgCl_2$. The volatiles were removed in vacuo, and the solid was extracted with toluene and crystallized from a mixture of toluene and pentane at −40 °C. Yield: 0.475 g (72%). ^1H NMR (C_6D_6): −21.45 (br, 15H), 1.78 (br, 2H), 22.05 and 23.19 (sh) (br, 3H) ppm. IR (KBr): 3055 (w), 3018 (w), 2953 (m), 2912 (s), 2854 (m), 1592 (m), 1484 (s), 1447 (m), 1377 (m), 1206 (m), 1027 (m), 746 (s), 698 (s), 531 (w), 442 (w) cm^{-1}. UV/vis (Et_2O): 543 (ϵ = 1470 M^{-1} cm^{-1}), 654 (sh, ϵ = 460 M^{-1} cm^{-1}) nm. Mp: 166 °C. μ_{eff} = 3.0(1) μ_B/Cr (295 K). Anal. Calcd for $C_{34}H_{44}Cl_2Cr_2$: C, 65.07; H, 7.07; N, 0.0. Found: C, 64.01; H, 6.48; N, <0.02. Mass spectrum (m/e): 536 (Cp*$_2$Cr$_2$Cl$_2$Bz$^+$).

(η^5-Pentamethylcyclopentadienyl)bis(benzyl)(pyridine)chromium(III), Cp*Cr(py)(Bz)$_2$ (2). A THF solution (50 mL) of [Cp*CrCl$_2$]$_2$ was formed by stirring $CrCl_3(THF)_3$ (1.003 g, 2.67 mmol) and Cp*Li (0.382 g, 2.69 mmol) together for 1 h. A 2.67 mL (2.00 equiv) amount of BzMgCl (2.0 M in THF, 5.3 mmol) was added dropwise to this blue solution. Pyridine (2 mL) was added after another 1 h, and the solution was stirred for an additional 20 min. 1,4-Dioxane (3 mL) was then added to aid the precipitation of $MgCl_2$. After all volatiles were removed, the solid was extracted with Et_2O and crystallized from the same solvent at -40 °C. Total yield: 0.801 g (67%). Higher yields (80%) may be obtained by starting with isolated [Cp*CrCl$_2$]$_2$. ^1H NMR (C_6D_6): −53.51 (br, 1H), 0.52 (br, 4H), 4.08 (br, 15H), 20.37 (br, 2H), 31.86 (br, 2H), 35.38 (br, 4H) ppm. IR (KBr): 3063 (s), 3013 (s), 2904 (s), 2866 (s), 1591 (s), 1483 (s), 1442 (s), 1377 (m), 1209 (s), 1026 (s), 976 (m), 800 (w), 748 (s), 698 (s), 530 (m) cm^{-1}. UV/vis (pentane): 428 (ϵ = 2340 M^{-1} cm^{-1}), 565 (sh, ϵ = 1100 M^{-1} cm^{-1}) nm. Mp: 135 °C. μ_{eff} = 4.2(1) μ_B (294 K). Anal. Calcd for $C_{29}H_{34}NCr$: C, 77.65; H, 7.64; N, 3.12. Found; C, 77.78; H, 7.85; N, 3.17. Mass spectrum (m/e): 369 (Cp*Cr(Bz)$_2$$^+$).

(η^5-Pentamethylcyclopentadienyl)bis(benzyl)(tetrahydrofuran)chromium(III), Cp*Cr(THF)(Bz)$_2$ (3). A THF solution (50 mL) of [Cp*CrCl$_2$]$_2$ was formed by stirring $CrCl_3(THF)_3$ (1.009 g, 2.69 mmol) and Cp*Li (0.384 g, 2.70 mmol) together for 1 h. A 2.65 mL (2.00 equiv) amount of BzMgCl (2.0 M in THF, 5.3 mmol) was added dropwise to this blue solution. 1,4-Dioxane (3 mL) was added after 1 h, and the solution was stirred for an additional 1 h. After all volatiles were removed, the residue was extracted with pentane and dried. Crystallization from pentane gave 0.456 g (48%) of **3**. ^1H NMR (C_6D_6): −2.02 (br, 15H), −1.75 (sh), 5.90 (br, 4H), 23 (v br, 4H), 28.71 (br, 2H) ppm. IR (KBr): 3057 (s), 3005 (s), 2903 (s), 2869 (s), 1589 (s), 1483 (s), 1448 (s), 1377 (m), 1209 (s), 1020 (s), 977 (s), 860 (s), 800 (w), 748 (s), 698 (s), 530 (m), 416 (w) cm^{-1}. UV/vis (pentane): 456 (sh, ϵ = 1330 M^{-1} cm^{-1}), 721 (ϵ = 380 M^{-1} cm^{-1}) nm. Mp: 78 °C. μ_{eff} = 4.2(1) μ_B (295 K). Anal. Calcd for $C_{28}H_{37}OCr$: C, 76.16; H, 8.45. Found: C, 76.04: H, 8.23. MS (*m/e*): 369 (Cp*Cr(Bz)$_2$$^+$).

(η^5-Pentamethylcyclopentadienyl)bis(benzyl)chromium(III), [Cp*Cr(Bz)$_2$]$_n$. A small sample of **3** was heated to 45 °C under high vacuum for ca. 1 h. After this time the solid had been transformed into a brown viscous oil. ^1H NMR (C_6D_6): −6.25 (br, 4H), −1.19 (br, 15H), 22.76 (br, 2H) ppm. IR (Nujol): 3051 (m), 3012 (m), 1592 (s), 1482 (s), 1426 (m), 1383 (m), 1259 (w), 1211 (m), 1175 (m), 1087 (m), 1026 (s), 978 (m), 882 (w), 824 (w), 800 (m), 745 (s), 698 (s), 645 (w) cm^{-1}. UV/vis (pentane): 453, 726 nm. μ_{eff} = 3.0 μ_B (296 K), determined by the Evans method.

(η^5-Pentamethylcyclopentadienyl)bis(perdeuteriobenzyl)(tetrahydrofuran) chromium(III), Cp*Cr(THF)(Bz-d_7)$_2$ (3-d_{14}). (Bz-d_7)K was used instead of BzMgCl in the procedure described above. Recrystallized yield: 38%. NMR: see Table 5. IR (KBr): 2961 (m), 2905 (s), 2855 (m), 2267 (m), 2114 (w), 1555 (s), 1446 (m), 1369 (s), 1170 (m), 1031 (m), 1019 (m), 858 (m), 832 (w), 795 (w), 743 (w), 550 (s), 455 (m) cm^{-1}. MS (*m/e*): 383 (Cp*Cr(Bz-d_7)$_2$$^+$).

(η^5-Pentamethylcyclopentadienyl)(benzyl)bis(tetrahydrofuran)chromium(III) Tetraphenylborate, [Cp*Cr(THF)$_2$(Bz)]BPh$_4$ (4). A 0.650 g (1.47 mmol) amount of Cp*Cr(Bz)$_2$THF was dissolved in 40 mL of THF. A 0.620 g (1.00 equiv, 1.47 mmol) amount of HNEt$_3$BPh$_4$ was slowly added to this solution while stirring. The color of the solution changed to purple over 30 min. The solution was stirred for an additional 1 h. All volatiles were then removed by evaporation. The purple residue was redissolved in THF and crystallized from THF/Et_2O at −40 °C. Yield: 0.970 g (89%). ^1H NMR (CD_2Cl_2): −43.85 (br, 15H), 7.38 and 7.06 (br, 36H), 32.98 (br, 2H), 45.15 (v br, 3H) ppm. IR (Nujol): 3053 (s), 2924 (s), 2854 (s), 1942 (w), 1878 (w), 1818 (w), 1579 (m), 1481 (s), 1458 (s), 1425 (m), 1377 (m), 1253 (w), 1205 (w), 1178 (w), 1130 (w), 1016 (m), 862 (s), 750 (s), 736 (s), 705 (s), 613 (m) cm^{-1}. UV/vis (THF): 356 (ϵ = 33 720 M^{-1} cm^{-1}), 526 (ϵ = 1450 M^{-1} cm^{-1}) nm. Mp: 119 °C. μ_{eff} = 4.1(1) μ_B (294 K). Anal. Calcd for $C_{49}H_{58}O_2BCr$: C, 79.34; H, 7.88. Found: C, 79.11; H, 7.73.

Table 7. Crystallographic Data for [Cp*Cr(Bz)(μ-Cl)]$_2$ (1), Cp*Cr(py)Bz$_2$ (2), Li[Cp*CrBz$_3$] (6), and Cp*Cr(bpy)Bz (8)

	1	2	6	8
		(a) Crystal Parameters		
formula	$C_{34}H_{44}Cl_2Cr_2$	$C_{29}H_{34}CrN$	$C_{31}H_{36}CrLi$	$C_{27}H_{29}CrN_2$
fw	503.50	448.59	467.56	433.54
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*n*	$P\bar{1}$
a, Å	14.960(4)	9.345(3)	11.125(2)	9.056(3)
b, Å	16.803(5)	16.923(5)	15.287(3)	11.568(6)
c, Å	13.662(6)	16.161(5)	15.410(4)	11,602(4)
α, deg	73.56(3)			
β, deg	110.4(3)	104.36(2)	94.11(2)	88.47(5)
γ, deg	79.35(3)			
Z	4	4	4	4
cryst dimens, mm	0.30 × 0.40 × 0.90	0.36 × 0.36 × 0.40	0.28 × 0.30 × 0.36	0.20 × 0.20 × 0.36
cryst color	red	dark red	black	black
D(calc), g cm^{-3}	1.296	1.203	1.188	1.257
μ(Mo K$_\alpha$), cm^{-1}	8.60	4.64	4.30	5.01
T, K	293	293	293	293
		(b) Data Collection		
diffractometer	Siemens R3	Siemens R3	Siemens P4	Siemens R3
monochromator	graphite	graphite	graphite	graphite
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
2θ scan range, deg	4–48	4–47	4–45	4–45
data collected (*hkl*)	±17,+19,+15	±11,+19,+19	±12,+17,+17	±10,±13,+13
no. of rflns collected	2646	3962	3562	2604
no. of indep rflns	2527	3663	3417	2500
no. of obsd rflns ($F_o > n\sigma(F_o)$)	1843 ($n = 5$)	1393 ($n = 5$)	1422 ($n = 3$)	1820 ($n = 4$)
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
var in stds, %	<1	<1	4	<1
		(c) Refinement		
R(F), %	4.04	6.56	8.97	5.87
R(w*F*), %	5.56	7.07	7.73	6.01
Δ/σ(max)	0.07	0.01	0.07	0.02
$\Delta(\varrho)$, e Å^{-3}	0.28	0.37	0.54	0.37
N_o/N_v	10.7	5.4	5.0	7.0
GOF	1.12	1.24	1.16	1.37

(η^5-Pentamethylcyclopentadienyl)(perdeuteriobenzyl)bis(tetrahydrofuran)chromium(III) Tetraphenylborate, [Cp*Cr(THF)$_2$(Bz-d_7)]BPh$_4$, (4-d_7). The same procedure as above was followed, using **3**-d_{14} as starting material. Yield: 67%. NMR: see Table 5. IR (KBr): 3054 (m), 3037 (m), 2998 (m), 2982 (m), 2917 (m), 2879 (m), 2270 (w), 1579 (w), 1558 (w), 1479 (m), 1458 (w), 1428 (m), 1377 (w), 1261 (w), 1183 (w), 1153 (w), 1067 (w), 1042 (m), 1032 (m), 846 (m), 743 (s), 707 (s), 612 (m), 602 (m), 549 (m) cm^{-1}.

(η^5-Pentamethylcyclopentadienyl)(benzyl)(2,2′-bipyridine)chromium(III) Tetraphenylborate, [Cp*Cr(bpy)(Bz)]BPh$_4$ (5). 0.80 g of [Cp*Cr(Bz)(THF)$_2$]BPh$_4$ (1.08 mmol) was dissolved in 40 mL of THF. A 0.169 g amount of 2,2′-bipyridine was added to this solution while stirring. The color changed from purple to red-brown. After 30 min the volatiles were removed by evaporation. The residue was crystallized from THF/Et$_2$O at −40 °C. Yield: 0.76 g (93%). ^{1}H NMR (CD$_2$Cl$_2$): −79.12 (br, 2H), −59.72 (br, 2H), −14.25 (br, 15H), 0.11 (br, 2H), 7.09 and 7.43 (br, 20H), 22.91 (br, 2H), 28.95 (br, 1H), 37.46 (br, 2H) ppm. IR (KBr): 3049 (s), 2995 (s), 2916 (m), 2877 (m), 1942 (w), 1880 (w), 1815 (w), 1697 (w), 1601 (s), 1477 (s), 1440 (s), 1379 (m), 1311 (w), 1263 (w), 1207 (w), 1176 (w), 1155 (w), 1064 (w), 1026 (m), 842 (w), 734 (s), 704 (s), 609 (m), 447 (w), 428 (w) cm^{-1}. UV/vis (THF): 380 (sh, ϵ = 4520 M^{-1} cm^{-1}), 480 (ϵ = 4110 M^{-1} cm^{-1}), 629 (ϵ = 650 M^{-1} cm^{-1}) nm. Mp: 164 °C dec. μ_{eff} = 4.3(1) μ_B (297 K). Anal. Calcd for $C_{51}H_{50}N_2BCr$: C, 81.27; H, 6.69; N, 3.72. Found: C, 81.23; H, 6.59; N, 3.59.

Lithium (η^5-Pentamethylcyclopentadienyl)tris(benzyl)chromate(III), Li[Cp*Cr(Bz)$_3$] (6). [Cp*CrCl$_2$]$_2$ was formed by reacting CrCl$_3$(THF)$_3$ (1.845 g, 4.92 mmol) with Cp*Li (0.700 g, 4.92 mmol) in THF overnight. The THF was then removed in vacuo and the solid residue redissolved in 40 mL of toluene. To this solution was added dropwise 28.4 mL (3.00 equiv) of BzLi (0.52 M in Et$_2$O). Within minutes the color of the solution changed to bright purple. After the mixture was stirred for 45 min, the solvent was evaporated under vacuum. The residual solid was extracted with toluene. Crystallization from a mixture of pentane and toluene at −40 °C gave purple crystals of Li[Cp*Cr(Bz)$_3$] in 63% yield. ^{1}H NMR (C$_6$D$_6$): −0.64 (br, 6H), 2.73 (br, 15H), 36.34 (br, 9H) ppm. IR (KBr): 3057 (m), 3013 (m), 2903 (s), 2856 (m), 1589 (s), 1477 (s), 1446 (m), 1375 (w), 1205 (s), 1174 (w), 1026 (w), 966 (s), 796 (m), 750 (s), 702 (s), 578 (w), 530 (s) cm^{-1}. UV/vis (Et$_2$O): 536 (ϵ = 1330 M^{-1} cm^{-1}), 603 (sh, ϵ = 890 M^{-1} cm^{-1}) nm. Mp: 175 °C. μ_{eff} = 4.0(1) μ_B (296 K). Anal. Calcd for $C_{31}H_{36}CrLi$: C, 79.63; H, 7.76. Found: C, 79.60; H, 7.65. MS (*m/e*): 459, 369 (Cp*Cr(Bz)$_2^+$).

Lithium (η^5-Pentamethylcyclopentadienyl)tris(perdeuteriobenzyl) chromate(III), Li[Cp*Cr(Bz-d_7)$_3$] (6-d_{21}). The whole preparation (see above) was carried out in THF. Yield: 40%. NMR see table 5. IR (KBr): 2961 (m), 2903 (m), 2854 (m), 2266 (m), 2123 (w), 1555 (s), 1362 (s), 1274 (w), 1165 (m), 1031 (m), 832 (m), 795 (m), 740 (m), 554 (m), 522 (w), 456 (m) cm^{-1}. MS (*m/e*): 479, 383 (Cp*Cr(Bz-d_7)$_2^+$).

Bis(tetramethylethylenediamine)lithium (η^5-Pentamethylcyclopentadienyl)tris(benzyl)chromate(III), Li(TMEDA)$_2$[Cp*Cr(Bz)$_3$] (7). A THF solution (50 mL) of [Cp*CrCl$_2$]$_2$ was formed by stirring CrCl$_3$(THF)$_3$ (1.501 g, 3.98 mmol) and Cp*Li (0.568 g, 4.00 mmol) together for 1 h. A 6.0 mL (3.00 equiv) amount of BzMgCl (2.05 M in THF, 12.30 mmol) was added dropwise to this blue solution. 1,4-Dioxane (3 mL) was added after 1 h, and the solution was stirred for an additional 1 h. The purple solution was filtered and 3 mL of TMEDA added to it. This solution was stirred for an additional 1 h. After all volatiles were removed, the residue was extracted with ether and dried. Crude yield: 2.39 g (85%). By NMR this crude solid was found to be pure. ^{1}H NMR (CD$_2$Cl$_2$): −28.84 (br, 15H), −0.80 (br, 2H), 2.11, 2.34 (br, 32H), 7.2 (br, 10H), 34.2 (br, 1H), 38.23 (v br, 2H) ppm. IR (KBr): 3058 (m), 3048 (m), 3000 (sh), 2979 (sh), 2952 (s), 2905 (sh), 2885 (vs), 2848 (s), 2795 (m), 1587 (vs), 1478 (vs), 1456 (s), 1288 (m), 1211 (s), 1028 (s), 945 (s), 798 (m), 789 (m), 745 (s), 687 (s) cm^{-1}. UV/vis (THF): 554 (ϵ = 680 M^{-1} cm^{-1}), 633 (sh, ϵ = 360 M^{-1} cm^{-1}). Mp: 141 °C dec. $\mu_{\mathrm{eff}} = 4.2(1)\ \mu_B$ (295 K). Anal. Calcd for $C_{43}H_{68}N_4CrLi$: C, 73.78; H, 9.79; N, 8.00. Found: C, 73.83; H, 9.59; N, 7.68. MS (*m/e*): 459, 369 ($Cp^*Cr(Bz)_2^+$).

Bis(tetramethylethylenediamine)lithium (η^5-Pentamethylcyclopentadienyl)tris(perdeuteriobenzyl)chromate(III), Li(TMEDA)$_2$[Cp*Cr(Bz-d_7)$_3$] (7-d_{21}). An excess of TMEDA (0.5 mL) was added to a solution of **6**-d_{21} (100 mg, 0.2 mmol) in toluene/pentane (1:4). The mixture was stirred for 30 min at room temperature and then cooled to −40 °C to induce crystallization; yield 72%. NMR: see Table 5. IR (KBr): 2969 (m), 2954 (s), 2889 (s), 2845 (s), 2795 (m), 2263 (m), 2197 (w), 2109 (w), 1550 (s), 1469 (s), 1457 (s), 1366 (s), 1287 (m), 1245 (w), 1177 (m), 1159 (m), 1127 (w), 1069 (w), 1031 (m), 1014 (w), 947 (m), 821 (m), 782 (m), 741 (m), 550 (m), 519 (w), 497 (w) cm^{-1}. MS (*m/e*): 479, 383 ($Cp^*Cr(Bz_{(d)})_2^+$).

(η^5-Pentamethylcyclopentadienyl)(benzyl)(2,2′-bipyridine)chromium(II), Cp*Cr(bpy)(Bz) (8). Method A. A 0.200 g (0.453 mmol) amount of Cp*Cr(Bz)$_2$(THF) was dissolved in 30 mL of THF. To this solution was added 0.071 g (0.46 mmol) of 2,2′-bipyridine. After 3 h the solvent was removed by evaporation. The remaining residue was dissolved in Et_2O and crystallized at −40 °C. Yield: 0.062 g (32%). ^{1}H NMR (C_6D_6): 2.87 (br, 2H), 10.59 (br, 15H), 20.96 (br, 2H), 21.68 (br, 1H), 24.78 (br, 1H), 87.95 (br, 2H), 91.74 (br, 2H) ppm. IR (KBr): 3005 (m), 2956 (m), 2904 (s), 1574 (s), 1492 (s), 1446 (s), 1373 (m), 960 (s), 731 (s), 694 (m) cm^{-1}. UV/vis (pentane): 486 (sh, ϵ = 1200 M^{-1} cm^{-1}), 506 (ϵ = 1300 M^{-1} cm^{-1}), 663 (ϵ = 790 M^{-1} cm^{-1}), 1004 (ϵ = 380 M^{-1} cm^{-1}), 1079 (ϵ = 390 M^{-1} cm^{-1}). Mp: 150 °C. $\mu_{\mathrm{eff}} = 3.0(1)\ \mu_B$ (295 K). Anal. Calcd for $C_{27}H_{30}N_2Cr$: C, 74.63; H, 6.96; N, 6.45. Found: C, 74.76; H, 7.04; N, 6.09. Mass spectrum (*m/e*): 434 (M$^+$), 343 ($Cp^*Cr(bpy)^+$).

Method B. A 0.222 g (0.29 mmol) amount of **5** was dissolved in 40 mL of THF. This solution was then cooled to −78 °C. A 0.17 mL (1.7 M in hexanes) amount of ^{t}BuLi was syringed into the purple solution. The color of the solution immediately changed to brown. The reaction mixture was stirred at −78 °C for 15 min and then warmed to room temperature. The THF was evaporated under vacuum and the residue extracted with pentane and dried. This solid was found to be pure by ^{1}H NMR. Yield: 90 mg (70%).

X-ray Crystallographic Structure Determinations for 1, 2, 6, and 8. Crystallographic data are collected in Table 7. The specimens were all mounted in Lindemann capillary tubes and photographically characterized. Crystals of **1**, **2**, and **7** were found to possess 2/*m* Laue symmetry. **1** possessed systematic absences in the data indicating either *C*2/*c* or *Cc*, with *Z* = 4; the presence of inversional molecular symmetry strongly indicated the former centrosymmetric alternative, which was verified by the results of refinement. Both **2** and **7** were found to belong to the $P2_1/n$ space group, while **8** showed $\bar{1}$ Laue symmetry and the preferred space group, based on the results of the refinement, was $P\bar{1}$. Ψ-Scan data showed negligible variation for all samples, and no corrections for absorption were needed. For **1** a correction for a portion of the crystal out of the beam was applied. The Cr atoms in each structure were located from Patterson maps. All non-hydrogen atoms were anisotropically refined, except for C(11) in **6**, which persistently produced non-positive-definite thermal parameters. For **2** and **6**, phenyl rings were constrained to be rigid, planar hexagons. Hydrogen atoms were treated as idealized contributions. All computations used SHELXTL software (various versions) (G. Sheldrick, Siemens XRD, Madison, WI).

Electrochemical Measurements. CV measurements were carried out using a Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat. All measurements were made under a nitrogen atmosphere in a drybox. The working electrode was a platinum-disk electrode (1.66 mm diameter, scan rate 0.1−0.2 V s^{-1}) and a platinum wire served as an auxiliary electrode. The reference electrode was composed of a silver wire in contact with 0.01 M $AgNO_3$ and 0.1 M $[NBu_4]PF_6$ in MeCN. The reference electrode was separated from the cell by a compartment having a porous Vycor tip. This was filled with the supporting electrolyte and solvent. All measurements were carried out in THF (distilled from Na/K), with 0.5 M $[NBu_4]ClO_4$ as electrolyte. Concentrations of **4** and **7** were in the range 1−3 mM. Potentials were referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple at the end of each run. *iR* compensation was applied.

Acknowledgment. We thank Drs. M. Carney and D. L. Beach of Chevron Chemical Co. for helpful discussions and polymer characterization data. This research was supported by grants from Chevron Chemical Co. and the National Science Foundation (Grant No. CHE-91225580). K.H.T. was the recipient of an Alfred P. Sloan Research fellowship (1992−1994).

Supplementary Material Available: Tables of positional and thermal parameters from the X-ray structure determinations of **1**, **2**, **6**, and **8** (13 pages). Ordering information is given on any current masthead page.

OM940724H