$[(\eta^5\text{-}C_5R_5)CrR]_n$: A New Class of Paramagnetic Alkyls and Hydrides of Divalent Chromium

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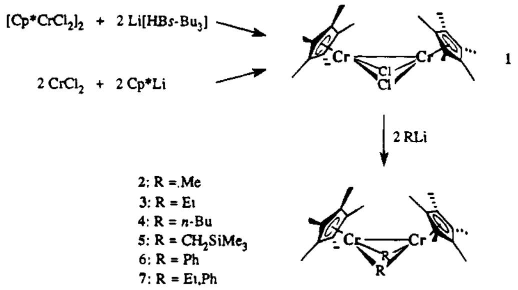
Abstract: $[Cp^*Cr^{II}(\mu\text{-}Cl)]_2$ (**1**), prepared by reduction of $[Cp^*Cr^{III}(\mu\text{-}Cl)Cl]_2$ with $Li[HBEt_3]$ or by reaction of $Cr^{II}Cl_2$ with Cp*Li, served as the precursor for the synthesis of a series of dinuclear chromium(II) alkyls of the type $[Cp^*Cr^{II}(\mu\text{-}R)]_2$ (R = Me (**2**), Et (**3**), ⁿBu (**4**), Ph (**5**), CH_2SiMe_3 (**6**)). They feature short Cr–Cr distances, low magnetic moments, and attenuated reactivity, consistent with strong metal–metal bonding. **3** decomposed in benzene to yield $[(Cp^*Cr^{II})_2(\mu\text{-}Et)(\mu\text{-}Ph)]$ (**7**), and **2** reacted with O_2 to give both $Cp^*Cr^{VI}(O)_2Me$ and $[(Cp^*Cr^{V}(O)Me)_2(\mu\text{-}O)]$ (**8**). Hydrogenolysis of $[Cp''Cr^{II}(\mu\text{-}Me]_2$ (**2a**, Cp″ = $\eta^5\text{-}C_5Me_4Et$) first yielded paramagnetic $[Cp''Cr^{II}(\mu_3\text{-}H)]_4$ (**9**); however, pure **9** must be prepared by reaction of $[Cp''Cr^{II}(\mu\text{-}Cl)]_2$ (**1a**) with $Li[HBEt_3]$. The structure of **9** has been redetermined due to a compositional disorder problem of the original determination. The identification of **9** as a tetrahydride rests on protonation experiments and the ^{13}C NMR observation of five isotopomers $[(Cp''Cr^{II})_4(H_{4-x})(D)_x]$, resulting from H/D exchange. The molecular structures of **1**, **2**, **7**, **8**, and **9** have been determined by X-ray diffraction.

Introduction

Our campaign to explore the organometallic chemistry of paramagnetic metal complexes began, some time ago, with the investigation of chromium(III) alkyls.[1] Much of our fascination with transition metals, and notably chromium, derives from the variety of, and interchange between, accessible oxidation states. The valence state is an important factor in determining the reactivity of metal complexes. Thus, when fortune presented us with an opportunity to broaden the scope of our work to include chromium(II), we gladly accepted. There follows a detailed account of the syntheses, structures, and reactivities of a class of paramagnetic complexes featuring divalent chromium coordinated by substituted cyclopentadienyl ligands (i.e., Cp* = $\eta^5\text{-}C_5Me_5$ and Cp″ = $\eta^5\text{-}C_5Me_4Et$).[2]

Results and Discussion

Scheme 1



$[Cp^*Cr(\mu\text{-}R)]_2$. Syntheses and Structures. We have previously described the preparation of various chromium(III) alkyls via alkylation of $[Cp^*Cr^{III}(\mu\text{-}Cl)Cl]_2$ with organometallic reagents (e.g., RLi; see Scheme 1).[3] Hoping to prepare an analogous chromium hydride, we substituted LiH and Li[HB-ˢBu₃] for the metal alkyls. However, either reaction proceeded with evolution of hydrogen gas (0.47(2) equiv, measured with a Töpler pump) and produced the chloride-bridged dimer $[Cp^*Cr(\mu\text{-}Cl)]_2$ (**1**). It is well possible that the desired $[Cp^*Cr(H)(\mu\text{-}Cl)]_2$ was formed as an unstable intermediate during this reaction. However, we have no evidence for its intervention; we also note that another reported attempt at producing a chromium(III) hydride was also thwarted by reduction.[4] Once the nature of the reaction product had been established, a more direct synthesis from $CrCl_2$ and Cp*Li was attempted and found to produce **1** in reasonable yield (65%), along with small amounts of decamethylchromocene (Cp^*_2Cr). It is noteworthy that the analogous $[CpCr(\mu\text{-}Cl)]_2$ rapidly disproportionates to Cp_2Cr and $CrCl_2$,[5] in effect precluding synthetic elaboration analogous to that described below for the Cp* system.

The molecular structure of **1** was determined by X-ray diffraction; the result is shown in Figure 1. The complex crystallized in the orthorhombic space group *Pnma* with unit cell dimensions *a* = 20.860(5) Å, *b* = 14.768(3) Å, and *c* = 7.2274(14) Å. There are four identical molecules per unit cell. Table 1 lists selected interatomic distances and angles. **1** is a dimer with bridging chloride ligands and a Cr–Cr distance of 2.642(2) Å. The Cr_2Cl_2 core adopts a butterfly geometry, and the Cr1–Cl–Cr2 angle measures 69°. The compound is closely related structurally to Chisholm's $[CpCr(\mu\text{-}O^tBu)]_2$.[6] With regard to a possible metal–metal interaction,[7] it is noteworthy that the structure is distorted from an idealized geometry, in which two isolated, planar Cp^*CrCl_2 fragments[8] are joined by sharing of the Cl–Cl edge (see **A**, below). In particular, the

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(1) Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263.

(2) For a preliminary communication, see: Heintz, R. A.; Haggerty, B. S.; Wan, H.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1077.

(3) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570.

(4) Thaler, E.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 374.

(5) (a) Hermans, P. M. J. A.; Scholten, A. B.; Van den Beuken, E. K.; Bussard, H. C.; Roeloffsen, A.; Metz, B.; Reijerse, E. J.; Beurskens, P. T.; Bosman, W. P.; Smits, J. M.; Heck, J. *Chem. Ber.* **1993**, *126*, 553. (b) In our hands, both the reaction of $[CpCrCl_2]_2$ with L-Selectride and the reaction of NaCp with $CrCl_2$ gave chromocene as the only soluble product.

(6) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rideout, D. C. *Inorg. Chem.* **1979**, *18*, 120.

(7) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654.

(8) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

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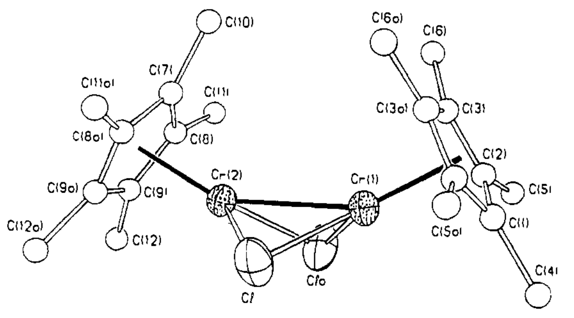


Figure 1. Molecular structure of [Cp*Cr(μ-Cl)]$_2$ (**1**). Selected interatomic distances and angles are listed in Table 1.

Table 1. Selected Interatomic Distances and Angles for [Cp*Cr(μ-Cl)]$_2$ (**1**)

	Distances (Å)		
Cr(1)–Cr(2)	2.642(2)	Cr(1)–Cl	2.331(2)
Cr(1)–C(1)	2.268(10)	Cr(1)–C(2)	2.234(7)
Cr(1)–C(3)	2.260(7)	Cr(1)–Cl(A)	2.331(2)
Cr(1)–C(2A)	2.234(7)	Cr(1)–C(3A)	2.260(7)
Cr(2)–C(8)	2.219(7)	Cr(2)–C(9)	2.272(6)
Cr(2)–Cl(A)	2.335(2)	Cr(2)–C(8A)	2.219(7)
Cr(2)–C(9A)	2.272(6)		
	Angles (deg)		
Cr(2)–Cr(1)–Cl	55.6(1)	Cl–Cr(1)–Cl(A)	93.9(1)
Cr(1)–Cr(2)–Cl	55.4(1)	Cl–Cr(2)–Cl(A)	93.7(1)
Cr(1)–Cl–Cr(2)	69.0(1)		

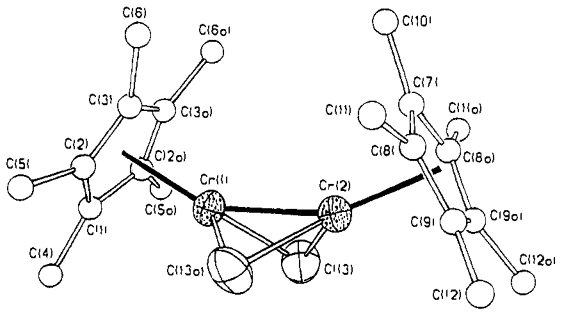


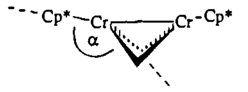
Figure 2. Molecular structure of [Cp*Cr(μ-CH$_3$)]$_2$ (**2**). Selected interatomic distances and angles are listed in Table 2.

Table 2. Selected Interatomic Distances and Angles for [Cp*Cr(μ-CH$_3$)]$_2$ (**2**)

	Distances (Å)		
Cr(1)–Cr(2)	2.263(3)	Cr(1)–C(1)	2.277(19)
Cr(1)–C(2)	2.255(13)	Cr(1)–C(3)	2.245(13)
Cr(1)–C(13)	2.182(11)	Cr(1)–C(2A)	2.255(13)
Cr(1)–C(3A)	2.245(13)	Cr(1)–C(13A)	2.182(11)
Cr(2)–C(9)	2.272(9)	Cr(2)–C(8)	2.240(15)
Cr(2)–C(8A)	2.240(15)	Cr(2)–C(13)	2.190(11)
Cr(2)–C(13A)	2.190(11)		
	Angles (deg)		
Cr(2)–Cr(1)–C(13)	59.0(3)	Cr(1)–Cr(2)–C(13)	58.7(3)
Cr(1)–C(13)–Cr(2)	62.3(3)	C(13)–Cr(1)–C(13A)	94.8(6)

Cp* rings are bent back slightly (**B**), so that the angle α between

A



B

the line connecting the Cp* centroid with the chromium and the plane defined by the chromium and both chlorides is less than 180° (174.6° for Cr1 and 175.6° for Cr2). This displacement of the metals toward each other indicates an—albeit weak—attractive force between the chromium atoms.

Alkylation of **1** with lithium alkyls or Grignard reagents yielded a series of novel chromium(II) alkyls (see Scheme 1).[9] They were dark brown paramagnetic solids, freely soluble in pentane, and very sensitive to moisture and air. The molecular structure of the representative [Cp*Cr(μ-CH$_3$)]$_2$ (**2**) was determined by X-ray diffraction, and the molecule is depicted in Figure 2. Like the chloride precursor, **2** crystallized in the orthorhombic space group *Pnma*. Its unit cell dimensions were a = 20.172(12) Å, b = 14.714(18) Å, and c = 5.537(4) Å. Table 2 lists the interatomic distances and interatomic angles. The molecule is a puckered dimer, like the bridging chloride complex **1**, and the Cr–Cr distance has decreased to 2.263(3) Å. In this respect **1** and **2** provide yet another example of the shortening of metal–metal distances upon substitution of a three-center/four-electron bridging ligand (e.g., μ-Cl$^-$) with a three-center/two-electron bridge (e.g., μ-CH$_3^-$). We have recently analyzed this phenomenon in detail for Cr^{III} complexes,[10] but the effect is general and has been described earlier.[11] The Cr–CH$_3$–Cr angle is 62°, and the angles α (see **B**) between the Cr–Cp* centroid lines and the planes defined by one chromium atom and both methyl carbons (C13, C13A) are smaller than the comparable values for **1** (i.e., 167.9° for Cr1 and 165.4° for Cr2). The attractive force signaled by this distortion, as well as the very short Cr–Cr distance, provides structural evidence for significant metal–metal bonding in **2**.

Magnetism. Metal–metal interactions may—inter alia—be gauged by the extent to which the unpaired electrons of isolated complex fragments are paired up in polynuclear assemblies. All the complexes described above are paramagnetic. However, depending on the nature of the compound, their magnetic moments are more or less reduced from the values expected of isolated Cr^{II} ions. While the d^4 electronic configuration could in principle give rise to four unpaired electrons per chromium, a "low-spin" situation with two unpaired electrons ($S = 1$, $\mu_{eff} = 2.83\ \mu_B$/Cr) is more likely. For example, Cp*Cr^{II}(dmpe)CH$_3$ (dmpe = 1,2-bis(dimethylphospino)ethane), a chromium(II) alkyl featuring chromium in a three-legged piano stool arrangement akin to that of individual Cr atoms in **1** and **2**, has an effective magnetic moment of 2.79 μ_B.[12] A dinuclear assembly of two of the above fragments, without any metal–metal interaction, should have $\mu_{eff} = 4.0\ \mu_B$/dimer. Antiferromagnetic coupling[13] or metal–metal bonding—i.e., M–M interactions of different magnitudes[14]—would reduce this number.

Figures 3 and 4 depict the results of variable temperature magnetic susceptibility measurements on **1** and **2**. The effective magnetic moments are seen to be temperature dependent, and

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[9] For other chromium(II) alkyls, see: (a) Krausse J.; Marx, G.; Schödl G. *J. Organomet. Chem.* **1970**, *21*, 159. (b) Krausse, J.; Schödl, G. *J. Organomet. Chem.* **1971**, *27*, 59. (c) Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1314. (d) Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713. (e) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339. (f) Hermes, A. R.; Morris, R. J.; Girolami, G. S. *Organometallics* **1988**, *7*, 2372. (g) Koschmieder, S. U.; McGilligan, B. S.; McDermott, G.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 3427. (h) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L. *Organometallics* **1992**, *11*, 2452. (i) Hao, S.; Gambarotta, S.; Bensimon, C. *J. Am. Chem. Soc.* **1992**, *114*, 3556. (j) Hao, S.; Song, J.-I.; Berno, P.; Gambarotta,S. *Organometallics* **1994**, *13*, 1326. (k) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

[10] Janiak, C.; Silvestre, J.; Theopold, K. H. *Chem. Ber.* **1993**, *126*, 631.

[11] (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *1*, 4. (b) Mason, R.; Mingos, D. M. P. *J. Organomet. Chem.* **1973**, *50*, 53.

[12] Thomas, B. J.; Noh, S. -K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893.

[13] Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.

[14] Hay, P. J.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

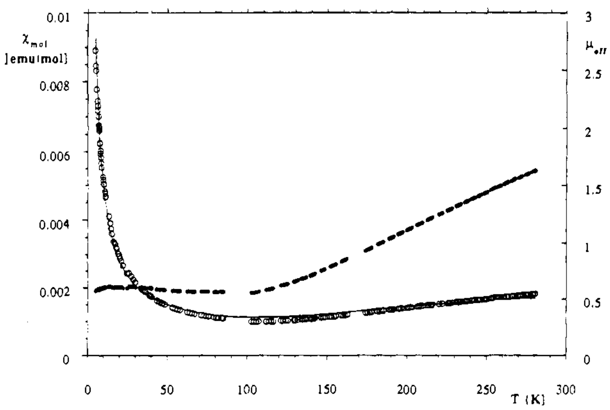


Figure 3. Temperature dependencies of the molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, solid circles) of $[Cp^*Cr(\mu\text{-}Cl)]_2$ (**1**). The line represents the fit with eq 1. $J(\mathbf{1}) = -212(3)\ cm^{-1}$, $P = 0.96(1)$, and TIP $= 6.3(2) \times 10^{-4}$ emu mol^{-1}.

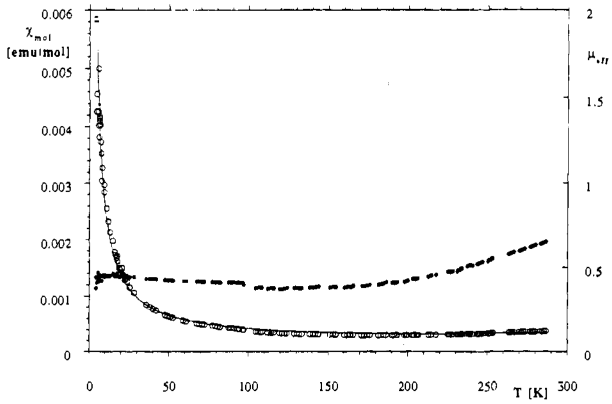


Figure 4. Temperature dependencies of the molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, solid circles) of $[Cp^*Cr(\mu\text{-}CH_3)]_2$ (**2**). The line represents the fit with eq 1. $J(\mathbf{2}) = -471(50)\ cm^{-1}$, $P = 0.97(1)$, and TIP $= 1.8(2) \times 10^{-4}$ emu mol^{-1}.

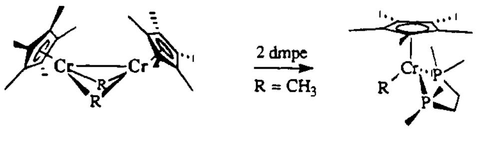
their room temperature values are relatively low ($\mu_{eff}(\mathbf{1}) = 1.63\ \mu_B$, $\mu_{eff}(\mathbf{2}) = 0.65\ \mu_B$). The molar magnetic susceptibilities (χ_m) were fit with an expression describing antiferromagnetic coupling between two $S = 1$ centers within the Heisenberg–Dirac–van Vleck model,[15] and including terms for contamination of the sample with a paramagnetic impurity and temperature independent paramagnetism (TIP) (eq 1). The resulting coupling

$$\chi_m = P\left(\frac{2Ng^2\mu_B^2}{kT}\right)\left[\frac{e^{2J/kT} + 5e^{6J/kT}}{1 + 3e^{2J/kT} + 5e^{6J/kT}}\right] + (P - 1)\left(\frac{Ng^2\mu_B^2S(S + 1)}{3kT}\right) + \text{TIP} \quad (1)$$

constants (J) are a measure of the strength of the metal–metal interaction; their values ($J(\mathbf{1}) = -212(3)\ cm^{-1}$ and $J(\mathbf{2}) = -471(50)\ cm^{-1}$) are comparatively large. Both **1** and **2** are thus reasonably described as exhibiting some metal–metal bonding. This is also reflected in the reactivity of the alkyl complexes (see below).

Table 3 lists the effective magnetic moments of the remaining complexes in this class (**3**–**6** and $[(Cp^*Cr)_2(\mu\text{-}Et)(\mu\text{-}Ph)]$ (**7**); see below). The values (1.0–1.4 μ_B/molecule) appear higher than that of the comparable **2**; however, this is an artifact caused by the absence of temperature dependent data for **3**–**7**. The fit of the temperature dependence of χ_m for **2** revealed a sizable contribution of temperature independent paramagnetism (TIP), which was subtracted from the molar susceptibility before calculation of the magnetic moment. Without this correction, $\mu_{eff}(\mathbf{2})$ would be 1.2 μ_B, i.e., very similar to the values seen in Table 3.

Reactivity. The alkyls introduced above deviate dramatically from the 18-electron rule, that preeminent predictor of stability for low-valent organometallics.[16] In the extreme view of neglecting any contribution from metal–metal bonding, and counting the bridging alkyl groups strictly as 1-electron donors, the chromium atoms in **2**, for example, possess a 12-electron configuration. Such unsaturation might lead one to expect high reactivity/low stability for this complex. In reality, however, **2** is a surprisingly stable molecule. It could be heated to 60 °C in C_6D_6 solution for days without any apparent change, and even temperatures of 100 °C over 24 h caused only minor decomposition, Cp^*_2Cr being the apparent product. This stability must be contrasted with the facile decomposition of chemically related $[Cp^*(CH_3)Cr^{III}(\mu\text{-}CH_3)]_2$, which eliminated methane at room temperature.[17] Furthermore, the latter complex also added ligands rapidly, while **2** did so only very sluggishly. Thus, its reaction with dmpe produced the previously mentioned adduct $Cp^*Cr(dmpe)CH_3$ (eq 2),[12] but the reaction required several hours for completion. Finally, the stability of alkyls containing β-hydrogen (**3**, **4**)—wholly unexpected for a coordinatively unsaturated Cr^{II} derivative—is indeed a testament to a powerful stabilizing factor. We believe this factor to be Cr–Cr bonding. Use of the partially filled frontier orbitals for metal–metal bonding attenuates their availability for alternative interactions (e.g., binding of external ligands, C–H bond breaking, etc.). Having thus added a reactivity criterion to the more common structural and magnetic lines of evidence, we suggest that the case for metal–metal bonding in this particular set of compounds is very strong.[18]



Not surprisingly, however, ethyl complex **3** did decompose more easily than **2**. Monitoring a C_6D_6 solution of **3**, which was intermittently heated to 50 °C, by NMR, eventually revealed the formation of ethane and a new organometallic complex. The infrared spectrum of the latter exhibited a weak band at 2241 cm^{-1}, consistent with a C–D stretching vibration, and thus indicating incorporation of the deuteriated solvent. Repetition of the reaction in C_6H_6 yielded a similar complex, however missing the aforesaid IR band. Ultimately the nature of this new compound was determined by X-ray crystallography as $[(Cp^*Cr)_2(\mu\text{-}Et)(\mu\text{-}Ph)]$ (**7**), a mixed ligand example of the class of compounds described herein. During the reaction, one of the bridging ethyl groups of **3** has apparently been replaced with a μ-phenyl moiety, which must be derived from the solvent. **7** crystallized in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions of $a = 13.551(5)$ Å, $b = 8.925(5)$ Å, and $c = 21.916(11)$ Å. The molecular structure is shown in Figure 5, and selected interatomic distances and angles are listed in Table 4. The gross features of the structure are very similar to those

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(15) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: New York, 1986; p 90.

(16) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

(17) (a) Noh, S.-K.; Sendlinger, S. C.; Janiak, C.; Theopold, K. H. *J. Am. Chem. Soc.* **1989**, *111*, 9127. (b) Noh, S.-K.; Heintz, R. A.; Janiak, C.; Sendlinger, S. C.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 775.

(18) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; p 178. (b) Edema, J. J. H.; Gambarotta, S. *Comments Inorg. Chem.* **1991**, *11*, 195.

Table 3. Effective Magnetic Moments of Cr^{II} Complexes at Room Temperature[a]

compound	μ_{eff} (per molecule) (μ_B)	μ_{eff} (per Cr) (μ_B)	compound	μ_{eff} (per molecule) (μ_B)	μ_{eff} (per Cr) (μ_B)
$[Cp^*Cr(\mu\text{-}Cl)]_2$ (**1**)	2.0(1)	1.4(1)	$[Cp^*Cr(\mu\text{-}CH_2SiMe_3)]_2$ (**5**)	1.4(1)	1.0(1)
$[Cp^*(Cr(\mu\text{-}Me)]_2$ (**2**)	1.2(1)	0.9(1)	$[Cp^*Cr(\mu\text{-}Ph)]_2$ (**6**)	1.2(1)	0.9(1)
$[Cp^*Cr(\mu\text{-}Et)]_2$ (**3**)	1.2(1)	0.9(1)	$[(Cp^*Cr)_2(\mu\text{-}Et)(\mu\text{-}Ph)]$ (**7**)	1.4(1)	1.0(1)
$[Cp^*Cr(\mu\text{-}{}^nBu)]_2$ (**4**)	1.0(1)	0.7(1)	$[Cp''Cr(\mu_3\text{-}H)]_4$ (**9**)	3.5(1)	1.8(1)

[a] Moments listed here are not corrected for temperature independent magnesium (TIP).

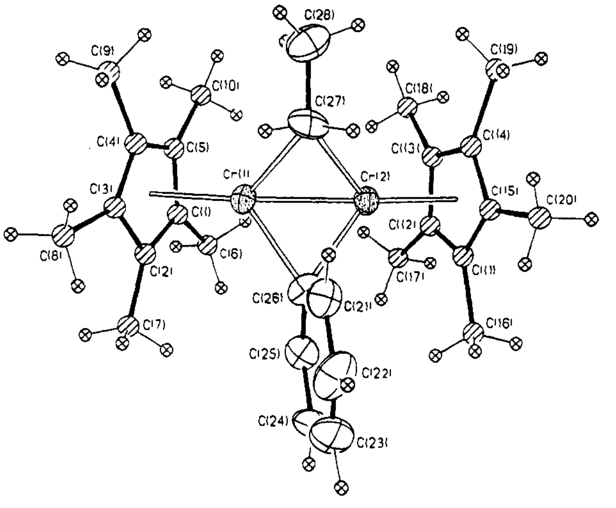


Figure 5. Molecular structure of $[(Cp^*Cr)_2(\mu\text{-}Et)(\mu\text{-}Ph)]$ (**7**). Selected interatomic distances and angles are listed in Table 4.

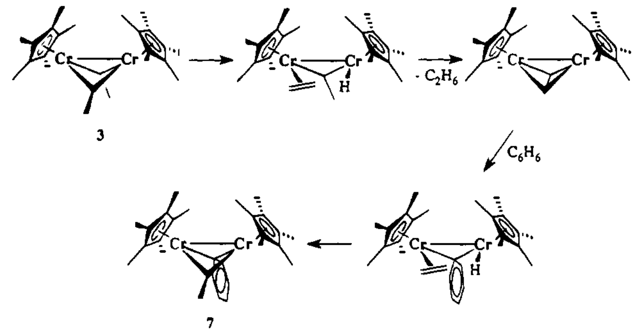
Table 4. Selected Interatomic Distances and Angles for $[(Cp^*Cr)_2(\mu\text{-}Et)(\mu\text{-}Ph)]$ (**7**)

	Distances (Å)		
Cr(1)−Cr(2)	2.289(4)	Cr(1)−C(1)	2.288(18)
Cr(1)−C(2)	2.297(17)	Cr(1)−C(3)	2.360(19)
Cr(1)−C(4)	2.292(19)	Cr(1)−C(5)	2.272(19)
Cr(1)−C(26)	2.158(16)	Cr(1)−C(27)	2.204(16)
Cr(2)−C(11)	2.265(20)	Cr(2)−C(12)	2.258(18)
Cr(2)−C(13)	2.193(21)	Cr(2)−C(14)	2.245(23)
Cr(2)−C(15)	2.297(21)	Cr(2)−C(26)	2.175(19)
Cr(2)−C(27)	2.252(20)	C(27)−C(28)	1.519(26)
	Angles (deg)		
Cr(2)−Cr(1)−C(26)	58.5(5)	Cr(2)−Cr(1)−C(27)	60.1(5)
C(26)−Cr(1)−C(27)	90.7(7)	Cr(1)−Cr(2)−C(26)	57.8(4)
Cr(1)−Cr(2)−C(27)	58.1(4)	C(26)−Cr(2)−C(27)	89.0(6)
Cr(1)−C(26)−C(21)	119.9(13)	Cr(2)−C(26)−C(21)	107.2(13)
Cr(1)−C(26)−C(25)	118.8(12)	Cr(2)−C(26)−C(25)	118.5(13)
C(21)−C(26)−C(25)	116.6(15)	Cr(1)−C(26)−Cr(2)	63.8(5)
Cr(1)−C(27)−C(28)	117.7(13)	Cr(2)−C(27)−C(28)	117.7(13)
Cr(1)−C(27)−Cr(2)	61.8(5)		

of **2**. The Cr−Cr distance (2.289(4) Å) is almost as short, and the distances and angles defining the Cr_2C_2 core of the molecule reveal only small, predictable differences. The phenyl group bridges the Cr−Cr bond in the familiar perpendicular orientation, and the extrapolation to the molecular structure of **5** is straightforward.

Possible mechanistic alternatives for the formation of **7** include a direct phenyl-for-ethyl exchange by σ-bond metathesis[19] or a sequence of β-hydrogen elimination, reductive elimination of ethane, oxidative addition of benzene, and finally ethylene insertion into a Cr−H bond. The former pathway does not offer a ready explanation for the failure of **2** to undergo a similar exchange. In addition, in C_6D_6 solution it would be expected to yield ethane-d_1 and **7**-d_5. However, the mass spectral fragmentation pattern of the compound produced in C_6D_6 was consistent with the incorporation of all six deuterium atoms, i.e., **7**-d_6. Therefore, the second pathway seems to be operative. A related question concerns the possibility of dissociation of the binuclear metal unit during the reaction. In particular, **7** might be the thermodynamically favored product of a redistribution reaction between **3** and **5**, with the latter being the primary product of the decomposition of **3**. To test this hypothesis, an equimolar mixture of **3** and **5** was heated to 50 °C in C_6D_6. Consecutive NMR spectra showed that the concentration of **5** remained constant, while the resonances of **3** disappeared and were replaced by those of **7**-d_6 and ethane. The failure to observe the equilibration of **3** and **5** with **7**, in either direction, rules out dissociation of the binuclear metal complexes under the condition of this reaction. On the basis of these observations, we propose the reaction mechanism outlined in Scheme 2 for the formation of **7**. The exact structures of the intermediates are of course speculative, but serve to rationalize the integrity of the binuclear unit throughout.

Scheme 2



Attempts to establish the same mode of reactivity for the n-butyl complex **4** failed. Its thermal decomposition (at 100 °C) yielded Cp^*_2Cr as well as butane and butene. No spectroscopic evidence for a complex analogous to **7** could be found. Finally, the observation of an intermolecular C−H activation of benzene encouraged us to try for the aliphatic equivalent. Heating of a solution of **3** in C_6D_{12} to 50 °C for 42 h yielded ethane and an insoluble black paramagnetic powder. IR analysis of the latter produced no evidence for the incorporation of any deuteriated solvent. The intermolecular activation of aliphatic C−H bonds thus remains beyond the scope of the Cp*Cr fragment.

As the role of chromium in the catalysis of ethylene polymerization provides some motivation for our work,[12,20] we have exposed **2** to ethylene (C_6D_6, 3 atm, 1 week at room temperature). Under these conditions no reaction whatsoever was observed. One might be tempted to count this observation as yet another strike against the activity of chromium(II) for the polymerization of ethylene;[21] however, we suggest that the general inertness of these Cr−Cr-bonded dimers may disqualify

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[19] Thompson, M. E.; Baxter, S. E.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

[20] (a) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (b) Theopold, K. H.; Heintz, R. A.; Noh, S. K.; Thomas, B. J. In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry Series 230; American Chemical Society: Washington, DC, 1992; p 591. (c) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics*, submitted for publication.

[21] 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.

them as realistic model compounds for coordinatively unsaturated site-isolated Cr species stabilized on heterogeneous catalyst supports.

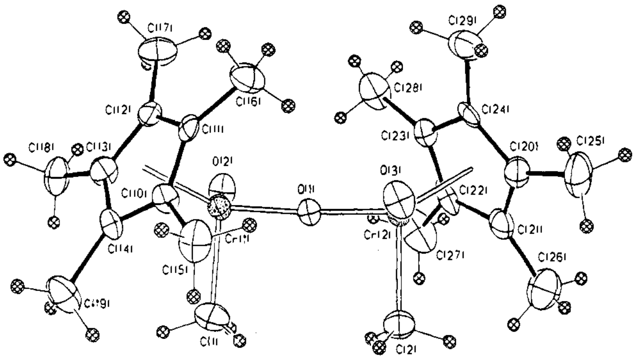
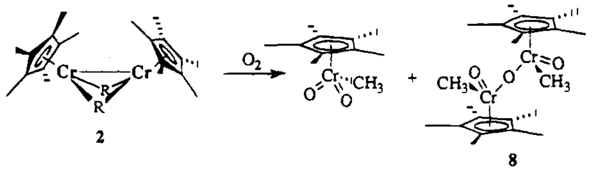


Figure 6. Molecular structure of [(Cp*Cr(O)CH$_3$)$_2$(μ-O)] (**8**). Selected interatomic distances and angles are listed in Table 5.

Table 5. Selected Interatomic Distances and Angles for [(Cp*Cr(O)CH$_3$)$_2$(μ-O)] (**8**)

	Distances (Å)		
Cr(1)−O(1)	1.774(6)	Cr(1)−O(2)	1.603(7)
Cr(1)−C(1)	2.086(11)	Cr(1)−C(10)	2.338(10)
Cr(1)−C(11)	2.297(9)	Cr(1)−C(12)	2.252(10)
Cr(1)−C(13)	2.268(10)	Cr(1)−C(14)	2.313(10)
Cr(2)−O(1)	1.752(6)	Cr(2)−O(3)	1.584(7)
Cr(2)−C(2)	2.055(10)	Cr(2)−C(20)	2.284(10)
Cr(2)−C(21)	2.308(10)	Cr(2)−C(22)	2.318(12)
Cr(2)−C(23)	2.295(10)	Cr(2)−C(24)	2.266(10)
	Angles (deg)		
O(1)−Cr(1)−O(2)	108.8(3)	O(1)−Cr(1)−C(1)	91.1(4)
O(2)−Cr(1)−C(1)	98.0(4)	O(1)−Cr(2)−O(3)	109.3(3)
O(1)−Cr(2)−C(2)	90.2(4)	O(3)−Cr(2)−C(2)	98.7(4)
Cr(1)−O(1)−Cr(2)	173.8(4)		

Some time ago, we discovered that certain chromium(III) alkyls reacted with O$_2$ to produce unusually high valent chromium oxo alkyls.[22] It was therefore of some interest to investigate analogous reactions of chromium(II) alkyls. **3**−**7** were all air sensitive and reacted rapidly with O$_2$. For example, **2** reacted with an excess of O$_2$ to give Cp*Cr^{VI}(O)$_2$CH$_3$ as the major product, accompanied by small amounts of Cp*(CH$_3$)(O)CrOCr(O)(CH$_3$)Cp* (**8**) (eq 3). The latter could be made to predominate if exactly 2 equiv of O$_2$ was used in the reaction. Both compounds had previously been made by oxidation of Cr^{III} precursors;[22] however, the crystal structure of **8** was determined in the course of the work described here. **8** crystallized in the monoclinic space group $P2_1/c$, with unit cell dimensions a = 8.523(9) Å, b = 25.361(29) Å, c = 21.720(23) Å, and β = 96.57(8)°. There were two independent, but structurally similar, molecules in the unit cell. A representation of the molecular structure is given in Figure 6, and selected interatomic distances and angles are listed in Table 5. The structure consists of two pseudooctahedral chromium fragments linked by an essentially linear oxide bridge (Cr−O−Cr angle 173.8°). The known efficacy of the latter in mediating strong antiferromagnetic coupling probably accounts for the diamagnetism of the complex,[23] which contains two chromium atoms in the formal oxidation state V (d^1). The Cr−O and Cr−C bond lengths are similar to known values of comparable molecules.[24]



The reaction of **2** with O$_2$ is not attractive from a preparative viewpoint; the isolated yields were low (<25%), and a host of side products was formed ([Cp*(O)Cr(μ-O)]$_2$,[25] Cp*H, and 2,3,4,5-tetramethylfulvene[26] among them). It is interesting, however, to speculate about the mechanism of formation of Cp*Cr(O)$_2$CH$_3$ in particular, because its formation represents—at least formally—a 4-electron oxidative addition of O$_2$ to Cr^{II}. In this context we were curious whether **8** might be a secondary product of the reaction. Indeed, mixing of independently prepared Cp*Cr(O)$_2$CH$_3$ with a stoichiometric amount of **2** (1/6 equivt) in an NMR tube yielded **8** cleanly. This observation is certainly consistent with Cp*Cr(O)$_2$CH$_3$ being the primary reaction product of the oxidation. Lowering the dioxygen concentrations (2 equiv vs excess; see above) may then allow the secondary reaction of Cp*Cr(O)$_2$CH$_3$ with remaining **2** to compete. The further elucidation of the reaction mechanism would require isotope studies, and we have chosen to look for a cleaner reaction to pursue this question.

Hydrides. To date, the most intriguing reaction of **2** has been the one with hydrogen. Solutions of **2** reacted slowly with H$_2$ (1 atm) at room temperature to give methane (identified by ^{1}H NMR) and a black paramagnetic precipitate. The black precipitate is only very slightly soluble in organic solvents (e.g., diethyl ether, THF, toluene, benzene), ruling out NMR analysis. Infrared spectroscopy indicated the presence of a Cp* ligand and little else. The elemental analysis was consistent with [Cp*CrH$_x$]$_n$ (x = 0−2). The infrared spectrum of the product from a D$_2$ reaction was identical to that obtained with H$_2$, giving no hint of the presence of hydride ligands. Well-formed crystals of the product from the reaction with H$_2$ could be obtained by heating the compound in toluene (ca. 150 °C) in a sealed ampule and then slowly cooling it to room temperature. Unfortunately the crystals suffered from a disorder problem, probably arising from an unresolved superlattice. The space group was triclinic $P1$ with cell dimensions a = 10.617(5) Å, b = 10.845(17) Å, c = 17.895(17) Å, α = 83.00(3)°, β = 82.53(3)°, and γ = 67.33(2)°, V = 1879.3(8) Å^3, and Z = 2. The axial photographs taken along the c axis showed interlayer streaks, suggesting the presence of a superlattice. Insufficient data due to very weak intensity reflections prevented the resolution of the superlattice. Refinement of the sublattice was terminated due to extreme light atom disorder, but a tetrahedral motif of four chromium atoms (Cr−Cr distances of 2.61−2.74 Å) was discernible.

In order to overcome the solubility problem and to prevent crystallographic disorder, we have substituted the tetramethylethylcyclopentadienyl ligand (η^5-EtMe$_4$C$_5$ = Cp″) for the Cp* moiety. The difference in solubility of the Cp* and Cp″ derivatives was indeed remarkable. Both [Cp″Cr(μ-Cl)]$_2$ (**1a**) and [Cp″Cr(μ-CH$_3$)]$_2$ (**2a**) were soluble in pentane to a degree that made their isolation impractical. They were routinely prepared in situ, and used as such for further reactions. Accordingly, hydrogenation of **2a** in pentane solution (1 atm, room temperature,, 5 days) produced a black homogeneous solution, from which a dark brown solid could be isolated. X-ray quality crystals of this material were obtained by cooling a solution in hexamethyldisiloxane to −30 °C. The crystals belonged to the orthorhombic space group $Pnma$ with unit cell dimensions of a = 15.412(4) Å, b = 17.195(4) Å, and c =

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[22] Noh, S.-K.; Heintz, R. A.; Haggerty, B. S.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1992**, *114*, 1892.

[23] (a) Dunitz, J. D.; Orgel, L. E. *J. Chem. Soc.* **1953**, 2594. (b) Figuregis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 91. (c) San Filippo, J., Jr.; Fagan, P. J.; Di Salvo, F. J. *Inorg Chem.* **1977**, *16*, 1016.

[24] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; p 145.

[25] Herberhold, M.; Kremnitz, W.; Razavi, A.; Schöllhorn, H.; Thewalt, U. *Angew. Chem.* **1985**, *97*, 603.

[26] Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686.

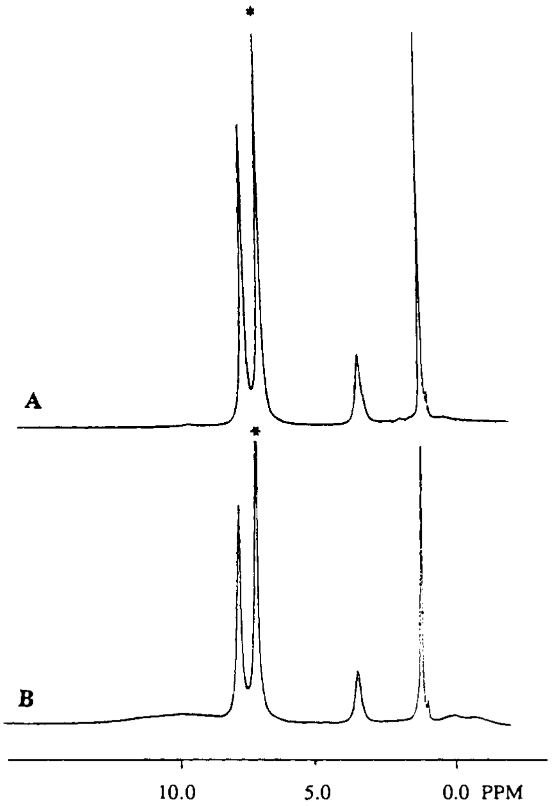
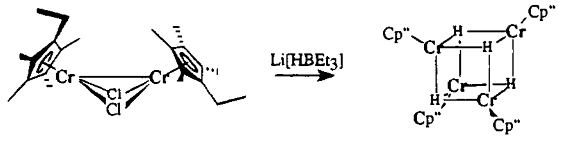


Figure 7. ^{1}H NMR spectra of $[\mathrm{Cp''Cr}(\mu_3\text{-H})]_4$ (**9**) prepared by (A) reaction of $[\mathrm{Cp''Cr}(\mu\text{-Cl})]_2$ with $\mathrm{Li[HBEt_3]}$ and (B) hydrogenolysis (1 atm of H_2) of $[\mathrm{Cp''Cr}(\mu\text{-CH_3})]_2$. The asterisk marks the resonance of C_6D_5H, which coincides with one of the resonances of **9**.

16.221(3) Å. On the basis of the X-ray diffraction measurements and other evidence (see below), we have assigned the formula $[\mathrm{Cp''Cr}(\mu_3\text{-H})]_4$ (**9**) to this compound. *Note: We now believe that this structure determination, the result of which was reported in a preliminary communication,[2] was compromised by cocrystallization of* **9** *with another compound! While the chemical nature of* **9** *was correctly represented, the metrical details of the earlier diffraction study (e.g., average Cr−Cr distance 2.715 Å) were marred with systematic errors.*

The first hint of trouble came with the discovery of an alternate synthesis of **9**, desirable because of the long reaction time required for the hydrogenolysis. Thus, reaction of halide complex **1a** with $\mathrm{Li[HBEt_3]}$ gave **9** rapidly and in acceptable yield (60%, eq 4).



While the spectroscopic properties of the samples produced by the two alternate routes appeared identical at first, the material produced via hydrogenolysis consistently exhibited a higher effective magnetic moment (ca. 5.9(2) μ_B at room temperature) than the metathesis-derived compound (ca. 3.8 μ_B at room temperature). Exposure of the latter to hydrogen gas raised its magnetic moment to values close to those of the products of hydrogenolysis. Instigated by these findings, close comparison of the ^{1}H NMR spectra of the two kinds of samples indeed revealed the presence of two very broad peaks (centered at 9.0 and −0.9 ppm) in the hydrogenolysis product, which were missing in the spectrum of **9** as produced by the hydride route (see Figure 7). As the ^{1}H NMR resonances of **9** were unusually narrow for a paramagnetic complex, the broad resonances of the contaminant had eluded us initially. The contaminant has been identified as another tetranuclear chromium hydride cluster, namely, $\mathrm{Cp''_4Cr_4H_7}$; its structure and fascinating magnetic properties are described elsewhere.[27] Unfortunately, it proved impossible to separate the mixture, once formed, by any method of purification. We conclude that pure **9** must be prepared according to eq 4; all further characterization described below pertains to material made by that route.

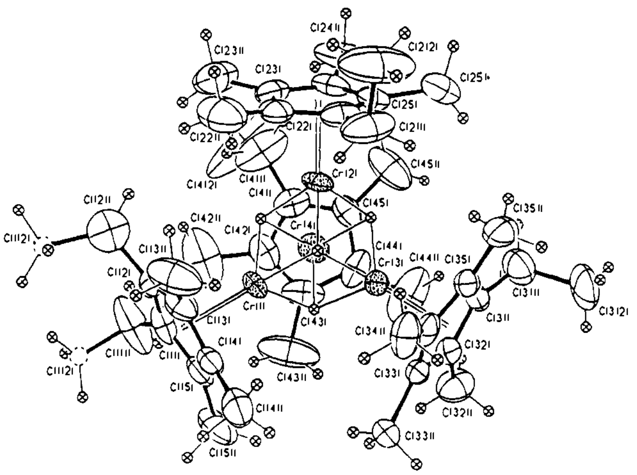


Figure 8. Molecular structure of $[\mathrm{Cp''Cr}(\mu_3\text{-H})]_4$ (**9**). Selected interatomic distances and angles are listed in Table 6.

The crystal structure of **9** was redetermined. This time the compound crystallized in the triclinic space group $P\bar{1}$ with unit cell dimensions a = 11.189(4) Å, b = 12.152(5) Å, c = 18.199(9) Å, α = 88.13(4)°, β = 84.92(4)°, and γ = 63.00(3)°. There were two identical molecules per unit cell. The molecular structure is depicted in Figure 8, and the relevant distances and angles are collected in Table 6. We note that the basic structure of **9** is the same as described before; however, the detailed structural parameters are slightly different. As before, the core of the molecule is a tetrahedron of chromium atoms, each carrying an η^5-cyclopentadienyl moiety. In contrast to the earlier representation, there remains no crystallographically imposed symmetry, however, and all six Cr−Cr distances are different, ranging from 2.612 to 2.681 Å (2.651 Å average). In this context, we note that the Cr−Cr distances in $\mathrm{Cp''_4Cr_4H_7}$ average to 2.765 Å. The previous structure determination of **9** had yielded an intermediate value ($\mathrm{Cr{-}Cr_{av}}$ 2.715 Å); this result is now seen to be caused by the kind of compositional disorder which has led to the controversy about "bond stretch isomerism".[28] One of the $\mathrm{EtMe_4C_5}$ rings exhibited disorder in the location of its ethyl group. This was modeled as a partial occupancy of the two locations indicated by dashed circles in Figure 8. During the final stages of the refinement, electron density was located in the hydride positions shown (μ_3-H), and the positions were refined. **9** may thus also be described as a cubane cluster. Related molecules include diamagnetic $[\mathrm{CpCo}(\mu_3\text{-H})]_4$ ($\mathrm{Co{-}Co_{av}}$ 2.467 Å)[29] and its analog $[\mathrm{Cp''Co}(\mu_3\text{-H})]_4$, which has not been structurally characterized,[30] as well as paramagnetic $[(\mathrm{CpNi})_4(\mu_3\text{-H})_3]$ ($\mathrm{Ni{-}Ni_{av}}$ 2.469 Å),[31] which is missing one of the hydride corners of the cube.

The X-ray diffraction experiment, despite its apparent success in locating the hydride ligands of **9**, is of course not generally a good tool for the unambiguous characterization of metal

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[27] Heintz, R. A.; Wu, P.; Koetzle, T. F.; Rheingold, A. L.; Theopold, K. H. Manuscript in preparation.

[28] Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455.

[29] Huttner, G.; Lorenz, H. *Chem Ber.* **1975**, *108*, 973.

[30] Schneider, J. J. *Z. Naturforsch.* **1994**, *49b*, 691.

[31] (a) Müller, J.; Dorner, H.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1005. (b) Koetzle, T. F.; Müller, J.; Tipton, D. L.; Hart, D. W.; Bau, R. *J. Am. Chem. Soc.* **1979**, *101*, 5631.

Table 6. Interatomic Distances and Angles for $[Cp''Cr(\mu_3\text{-}H)]_4$ (**9**)

	Distances (Å)		
Cr(1)−Cr(2)	2.681(2)	Cr(1)−Cr(3)	2.678(2)
Cr(1)−Cr(4)	2.676(3)	Cr(1)−C(11)	2.258(9)
Cr(1)−C(12)	2.280(13)	Cr(1)−C(13)	2.297(13)
Cr(1)−C(14)	2.313(11)	Cr(1)−C(15)	2.263(10)
Cr(1)−H(1)	1.805(17)	Cr(1)−H(2)	1.801(29)
Cr(1)−H(3)	1.802(29)		
Cr(2)−Cr(3)	2.623(2)	Cr(2)−C(4)	2.612(2)
Cr(2)−C(21)	2.271(9)	Cr(2)−C(22)	2.263(12)
Cr(2)−C(23)	2.275(9)	Cr(2)−C(24)	2.281(11)
Cr(2)−C(25)	2.275(10)	Cr(3)−Cr(4)	2.635(2)
Cr(2)−H(1)	1.803(26)	Cr(2)−H(2)	1.806(23)
Cr(2)−H(4)	1.803(25)		
Cr(3)−C(31)	2.262(10)	Cr(3)−C(32)	2.279(9)
Cr(3)−C(33)	2.258(8)	Cr(3)−C(34)	2.264(8)
Cr(3)−C(35)	2.268(7)	Cr(3)−H(1)	1.801(34)
Cr(3)−H(3)	1.802(16)	Cr(3)−H(4)	1.799(16)
Cr(4)−C(41)	2.244(10)	Cr(4)−C(42)	2.280(9)
Cr(4)−C(43)	2.265(10)	Cr(4)−C(44)	2.265(13)
Cr(4)−C(45)	2.239(13)	Cr(4)−H(2)	1.800(32)
Cr(4)−H(3)	1.804(29)	Cr(4)−H(4)	1.803(23)
	Angles (deg)		
Cr(2)−Cr(1)−Cr(3)	58.6(1)	Cr(2)−Cr(1)−Cr(4)	58.4(1)
Cr(3)−Cr(1)−Cr(4)	59.0(1)	Cr(1)−Cr(2)−Cr(3)	60.6(1)
Cr(1)−Cr(2)−Cr(4)	60.7(1)	Cr(3)−Cr(2)−Cr(4)	60.4(1)
Cr(1)−Cr(3)−Cr(2)	60.8(1)	Cr(1)−Cr(3)−Cr(4)	60.5(1)
Cr(2)−Cr(3)−Cr(4)	59.6(1)	Cr(1)−Cr(4)−Cr(2)	60.9(1)
Cr(1)−Cr(4)−Cr(3)	60.5(1)	Cr(2)−Cr(4)−Cr(3)	60.0(1)
H−Cr(1)−H (av)	83.8	H−Cr(2)−H (av)	85.6
H−Cr(3)−H (av)	85.4	H−Cr(4)−H (av)	85.6
Cr−H(1)−Cr (av)	95.1	Cr−H(2)−Cr (av)	94.9
Cr−H(3)−Cr (av)	95.3	Cr−H(4)−Cr (av)	93.5

hydrides (witness the problem described above). Indeed, the presence of hydride ligands coupled with paramagnetism of a molecule under scrutiny still poses a difficult problem of chemical identification, resulting in the occasional misassignment.[32] Fortunately, we have several independent pieces of evidence which support the formulation of **9** as a tetrahydride, if not its detailed structure. First, reaction of **9** with an excess of gaseous HCl liberated 5.9(2) equiv of H_2, as measured with a Töpler pump. The only chromium-containing product of this reaction was identified as $[Cp''CrCl_2]_2$, apparently formed in quantitative yield. Of the total H_2 produced, 4 equiv were attributed to four hydrides in the cluster combining with an equal number of protons, and the other 2 equiv presumably resulted from oxidation of four Cr^{II} centers to Cr^{III}. To test the latter notion, **1** was reacted with excess HCl; it indeed gave $[Cp^*CrCl_2]_2$ and 0.89(3) equiv of H_2.

The second line of evidence confirming the presence of four hydrides in paramagnetic **9** came, somewhat surprisingly, from an NMR experiment. As luck would have it, rapid electronic relaxation led to the observation of relatively narrow, and only marginally shifted, resonances in both the ^1H and ^{13}C NMR spectra of **9** (no hydride resonances were observed, however!).[33] This coincidence facilitated the observation of an unusual isotope effect on its chemical shifts. The effect (an example of paramagnetic isotope effects on chemical shifts, PIECS) has been described in detail elsewhere;[34] it will be summarized here only in so far as it speaks to the number of hydride ligands in **9**. We have found that H/D exchange of **9** with D_2 or C_6D_6 produced a statistical mixture of isotopomers of the type $[Cp''_4Cr_4(H)_{n-x}(D)_x]$ (n = ?). The room temperature ^{13}C NMR spectrum of such a mixture showed that each of the seven resonances of **9** had split up into a set of five clearly separated peaks. We have further shown,that each isotopomer gave rise to one distinct set of resonances, and as there were five such sets observed, the number of exchangeable hydrides must be four ($n = 4$), i.e., **9** is indeed $[Cp''CrH]_4$.

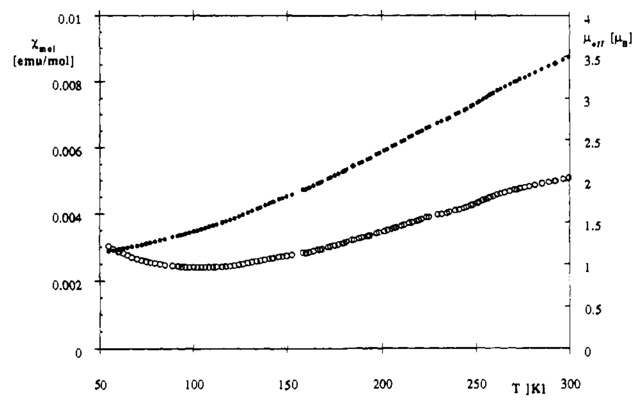

Figure 9. Temperature dependencies of the molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, solid circles) of $[Cp''Cr(\mu_3\text{-}H)]_4$ (**9**). The line represents the theoretical fit (see text).

By comparison with the dimeric alkyls $[Cp^*Cr(\mu\text{-}R)]_2$ (i.e., **2**−**8**), the Cr−Cr distances in **9** are relatively long, and there arises the question of metal−metal bonding. The value of 2.65 Å is certainly inside the range of known Cr−Cr bonds, but it is significantly longer than the interatomic distance in chromium metal (2.50 Å). The bonding in $Cp_4M_4H_n$ (M = Co, Ni; n = 3, 4) has been the subject of a theoretical analysis, and these "saturated" clusters have been described as having M−M single bonds due to occupation of a set of molecular orbitals derived largely from metal s and p orbitals.[35] **9** has a much lower electron count, however (i.e., 48 instead of 60 for $[CpCo(\mu_3\text{-}H)]_4$), and if the same MO diagram is used, only levels described as "descendants of the octahedral t_{2g} set" which "are primarily d in character and interact little with neighboring metal atoms" are partially filled. Within the framework of this analysis, little or no metal−metal bonding would be expected. Relevant to this discussion is the magnetochemistry of **9**, shown in Figure 9. The effective magnetic moment decreased with temperature from a value of 3.50 μ_B (1.75 μ_B/Cr) at 299 K to 1.15 μ_B (0.58 μ_B/Cr) at 55 K. Such behavior is consistent with antiferromagnetic coupling between the Cr atoms of the Cr_4 tetrahedron. However, attempts at fitting the magnetic susceptibility data to a Heisenberg−Dirac−Van Vleck (HDVV) model for intracluster magnetic exchange in a tetrahedral arrangement of four triplet metal ions ($S = 1$)[36] were not successful. In particular, the increase of χ_m at low temperature indicates a more complicated magnetic behavior. On balance, we prefer to think of **9** as not exhibiting significant metal−metal bonding, but as in other borderline cases, there may not be a simple, unambiguous answer to the question.

Conclusions

The fortuitous discovery of the simple starting material $[Cp^*Cr(\mu\text{-}Cl)]_2$ has allowed the preparation of a new series of paramagnetic organochromium(II) compounds containing the Cp* (or Cp″) ligand. The alkyl complexes $[Cp^*Cr(\mu\text{-}R)]_2$ feature metal−metal bonds, as indicated by short Cr−Cr distances, low magnetic moments, and attenuated reactivity. Their reactions include Lewis base induced cleavage of the Cr−

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[32] (a) Schneider, J. J.; Goddard, R.; Werner, S.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1124. (b)Kersten, J. L.; Rheingold, A. L.; Theopold, K. H.; Casey, C. P.; Widenhoefer, R. A.; Hop, C. E. C. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1341.

[33] Bertini, I.; Luchinat, C. *NMR of Paramagnetic molecules in Biological Systems*; Benjamin/Cummings: Menlo Park, CA, 1986.

[34] Heintz, R. A.; Neiss, T. G.; Theopold, K. H. *Angew. Chem.*, in press.

[35] Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *100*, 6088.

[36] Bertrand, J. A.; Ginsberg, A. P.; Kaplan, R. I.; Kirkwood, C. E.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1971**, *10*, 240.

Cr bond, aromatic C−H activation, and reaction with O_2 to yield high-valent chromium oxo alkyls. No ethylene polymerization activity or even reaction with ethylene was observed. Reaction of $[Cp''Cr(\mu\text{-Cl})]_2$ with $Li[HBEt_3]$ is the preferred way to prepare pure samples of the hydride cluster $[Cp''Cr(\mu_3\text{-H})]_4$. The structural characterization of this complex has been a reminder of the special difficulties associated with the investigation of paramagnetic metal hydrides. There are indications that chromium holds in store a fascinating variety of hydride chemistry. The investigation of the structures, magnetic properties, and reactivities of such hydrides will be pursued in this laboratory.

Experimental Section

General Considerations. All manipulations of compounds were carried out by standard Schlenk, vacuum, and glovebox techniques. Pentane, diethyl ether, tetrahydrofuran, toluene, and hexamethyldisiloxane were distilled from purple sodium benzophenone/ketyl solutions. C_6H_6, C_6D_6, and C_6D_{12} were all predried with Na and stored under vacuum over Na/K alloy. CCl_4 was dried with P_2O_5 and stored under vacuum over 3 Å molecular sieves. $CrCl_3$(anhydrous) and $CrCl_2$(anhydrous) were purchased from Strem Chemical Co. L-Selectride, CH_3Li, EtMgBr, *n*-butyllithium, phenyllithium, HCl, Super-Hydride, Super-Deuteride, and 1,2-bis(dimethylphosphino)ethane (dmpe) were all purchased from Aldrich Chemical Co. and used as received. [(Trimethylsilyl)methyl]lithium was purchased from Aldrich Chemical Co. as a 1 M solution in pentane, but was crystallized from solution at −30 °C and isolated as a white crystalline solid. High-purity H_2 gas was purchased from Airco. $CrCl_3(THF)_3$ was prepared by a literature procedure.[37] LiCp* was synthesized by a literature procedure[38] and $EtMe_4C_5Li$ by a modification of the procedure using ethyl propionate instead of ethyl acetate.[39]

NMR spectra were taken on a Bruker AM-250 or WM-250 spectrometer and were referenced to the residual protons of the solvent (C_6D_5H, 7.15 ppm; $C_6D_{11}H$, 1.38 ppm). FTIR spectra were taken on a Mattson Alpha Centauri spectrometer with a resolution of 4 cm^{-1}. UV/vis/NIR spectra were recorded using a Bruins Instruments Omega 20 spectrophotometer. Mass spectra were performed by the University of Delaware Mass Spectrometry Facility. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY 13492. H_2 gas from the Töpler pump experiments was identified by circulating the gas through a CuO tube that was heated to 350 °C to oxidize the H_2 to H_2O.[40]

Room temperature magnetic susceptibilities were determined using a Johnson Matthey magnetic susceptibility balance which utilizes a modification of the Gouy method.[41] The variable temperature magnetic susceptibilities were determined using a Faraday magnetic susceptibility balance. Molar magnetic susceptibilities were corrected for diamagnetism using Pascal constants.[42] Magnetic susceptibilites determined with the Faraday balance were also corrected for ferromagnetic impurities through a Honda-Owens analysis,[43] and for temperature independent paramagnetism (TIP) where appropriate.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)bis(μ-chloro)-dichromium(II), $[Cp^*Cr(\mu\text{-Cl})]_2$ (1). Cp*Li (1.000 g, 7.04 mmol) was added to a stirred suspension of $CrCl_2$ (0.870 g, 7.08 mmol) in 5 mL of THF. After the mixture was stirred for 12 h the THF was evaporated, and the solid residue was extracted with pentane. The green-brown solution was filtered and concentrated. Cooling of this pentane solution to −30 °C yielded 1.010 of **1** (2.27 mmol, 65%). ^1H NMR (C_6D_6): δ 10.8 (br s) ppm. IR (KBr): 2959 (s), 2909 (s), 2857 (s), 1441 (m), 1377 (s), 1069 (w), 1022 (m), 799 (w), 523 (w) cm^{-1}. μ_{eff}(280 K): 1.63 μ_B (see Figure 3). Anal. Calcd for $C_{20}H_{30}Cr_2Cl_2$: C, 53.94; H, 6.79; Cl, 15.92. Found: C, 54.21; H, 6.60; Cl, 15.73.

Reaction of $[Cp^*CrCl_2]_2$ with $Li[HBEt]_3$. To a stirred suspension of 0.530 g (1.41 mmol) of $CrCl_3(THF)_3$ in 4 mL of THF was added 0.200 g (1.41 mmol) of Cp*Li. The solution was allowed to stir for 2 h and was then degassed thoroughly. The blue solution was cooled to −78 °C, and 1.4 mL of degassed L-Selectride solution (1 M in THF) was added via a side arm addition tube. The solution was then allowed to warm to room temperature. During warming, the solution color turned from blue to brown and gas evolution was observed. The H_2 gas evolved (0.47(2) equiv, 0.66(3) mmol) was collected and measured using a Töpler pump. The THF was removed by rotoevaporation and the resulting solid extracted with pentane and filtered. The brown-green pentane solution was concentrated and cooled (−30 °C) to give 0.160 g (0.359 mmol, 51%) of **1**.

Synthesis of Bis-(η^5-pentamentylcyclopentadienyl)bis(μ-methyl)-dichromium(II), $[Cp^*Cr(\mu\text{-}CH_3)]_2$ (2). Cp*Li (1.000 g, 7.04 mmol) was added to a suspension of $CrCl_2$ (0.870 g, 7.08 mmol) in 50 mL of THF. After the mixture was stirred for 12 h, 5.0 mL (7.0 mmol) of MeLi (1.4 M in Et_2O) was added. The THF was evaporated, and the resulting solid residue was extracted with pentane and filtered. Concentration and cooling (−30 °C) of the brown pentane solution gave 0.850 g of **2** (2.1 mmol, 60%). ^1H NMR (C_6D_6): δ 14.9 (br s, 3H), 2.51 (s, 15H) ppm. IR (KBr): 2960 (s), 2909 (s), 2857 (s), 1435 (m), 1375 (s), 1165 (w), 1111 (w), 1022 (w), 937 (m), 824 (w), 475 (w) cm^{-1}. μ_{eff}(286 K): 0.65 μ_B (see Figure 4). Anal. Calcd for $C_{22}H_{36}Cr_2$: C, 65.32; H, 8.97. Found: C, 64.10; H, 8.66.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)bis(μ-ethyl)-dichromium(II), $[Cp^*Cr(\mu\text{-}C_2H_5)]_2$ (3). To a stirred solution of 0.950 g of **1** (2.13 mmol) in 50 mL of diethyl ether was added 2.1 mL (4.2 mmol) of EtMgBr (2 M in diethyl ether). The solution was stirred for 20 min and then was filtered. The diethyl ether was removed by rotoevaporation, and the resulting solid was dissolved in pentane. Cooling (−30 °C) of the brown pentane solution gave 0.580 g of **3** (1.34 mmol, 63%). ^1H NMR (C_6D_6): δ 2.91 (br s, 3H), 2.28 (s, 15H) ppm. IR (KBr): 2903 (s), 2852 (s), 2719 (w), 1437 (s), 1375 (s), 1109 (m), 1022 (m), 950 (w), 565 (m) cm^{-1}. μ_{eff} (286 K): 1.2(1) μ_B. Anal. Calcd for $C_{24}H_{40}Cr_2$: C, 66.64; H, 9.32. Found: C, 66.77; H, 9.48.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)bis(μ-^{n}butyl)-dichromium(II), $[Cp^*Cr(\mu\text{-}C_4H_9)]_2$ (4). To a stirred solution of 0.900 g of **1** (2.02 mmol) in 50 mL of pentane was added 1.3 mL of *n*-butyllithium (3.2 M in hexanes). The brown solution was then filtered and concentrated. Cooling the pentane solution to −30 °C gave 0.560 g of **4** (1.14 mmol, 56%). ^1H NMR (C_6D_6): δ 3.01 (br s, 2H), 2.35 (s, 15H), 1.73 (br s, 2H), 1.32 (s, 3H) ppm. IR (KBr): 2953 (s), 2916 (s), 2864 (s), 1454 (m), 1375 (m), 1107 (m), 1022 (m), 937 (m), 800 (m), 545 (m) cm^{-1}. μ_{eff} (297 K): 1.0(1) μ_B. Anal. Calcd for $C_{28}H_{48}Cr_2$: C, 68.82; H, 9.90. Found: C, 68.57; H, 9.90.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)bis(μ-phenyl)-dichromium(II), $[Cp^*Cr(\mu\text{-}C_6H_5)]_2$ (5). To a stirred suspension of 0.433 g of $CrCl_2$ (3.52 mmol) in 50 mL of THF was added 0.500 g (3.52 mmol) of Cp*Li. This was stirred for 3 h, and then 2.0 mL (3.6 mmol) of phenyllithium was added (1.8 M in cyclohexane/diethyl ether, 70/30). The solution was then stirred for an additional 20 min, and the THF was removed by rotoevaporation. The resulting solid was extracted with pentane, and then the brown pentane solution was filtered. The solution was concentrated and upon cooling to −30 °C yielded 0.562 g (1.00 mmol, 57%) of **5**. ^1H NMR (C_6D_6): δ 7.33 (br s, 3H), 4.15 (br s, 2H), 3.59 (br s, 15H) ppm. IR (KBr): 3049 (s), 2962 (s), 2904 (s), 2854 (s), 2721 (w), 1558 (m), 1431 (s), 1375 (s), 1045 (m), 1020 (s), 700 (s), 578 (m), 434 (s) cm^{-1}. MS (EI): *m/e* 528 (M^+, 100). μ_{eff} (295 K): 1.4(1) μ_B. Anal. Calcd for $C_{32}H_{40}Cr_2$: C, 72.70; H, 7.63. Found C, 72.87; H, 7.69.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)bis(μ-trimethylsilyl)methyl]dichromium(II), $[Cp^*Cr(\mu\text{-}CH_2Si(CH_3)_3)]_2$ (6). A 0.380 g sample of [(trimethylsilyl)methyl]lithium was slowly added to a stirring solution of 0.900 g (2.02 mmol) of **1** in 60 mL of THF. The THF was removed by rotoevaporation, and the solid was extracted with pentane and filtered. The brown pentane solution was concentrated and cooled to −30 °C to give 0.560 g of **6** (1.02 mmol, 50%). ^1H NMR (C_6D_6): δ 2.67 (s, 15H), 0.98 (s, 9H) ppm. IR (KBr): 2945 (s), 2904 (s), 2858 (s), 2723 (w), 1435 (m), 1377 (m), 1240 (s), 1022 (m), 970 (m), 852 (s), 825 (s), 736 (s), 678 (m), 545 (m) cm^{-1}. μ_{eff} (294

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[37] Herwig, W.; Zeiss, H. H. *J. Org. Chem.* **1958**, *23*, 1404.

[38] Threlkel, R. S.; Bercaw, J. E.; Seidler, P. F.; Stryker, J. M.; Bergman, R. G. *Org. Synth.* **1987**, *65*, 42.

[39] Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

[40] Guldner, W. G. In *Standard Methods of Chemical Analysis*, 6th ed., v 2B; Welcher, F. J., Ed.; Van Nostrand: Princeton, NJ, 1963; p 1522.

[41] Johnson Matthey Fabricated Equipment Catalytic Systems Divison, 436 Devon Park Dr., Wayne, PA 19087; 1990.

[42] *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*; Hellwege, K. H., Hellwege, A. M., Eds.; Landolt-Börnstein Series; Springer-Verlag: Berlin, 1981; Vol. 11.

[43] Bates, L. F. *Modern Magnetism*, 4th ed.; Cambridge University Press: London, 1961; p 133.

K): 1.2(1) μ_B. Anal. Calcd for $C_{28}H_{52}Cr_2Si_2$: C, 61.27; H, 9.55. Found C, 61.36; H, 9.33.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)(μ-ethyl)(μ-phenyl)dichromium(II), [(Cp*Cr)$_2$(μ-C_6H_5)(μ-C_2H_5)] (7). A 0.300 g of sample **3** (0.69 mmol) was placed in a glass ampule, and dry C_6H_6 was vacuum distilled in. The ampule was flame sealed and heated in an oil bath at 50 °C for 66 h. The ampule was opened, and the C_6H_6 was removed by rotoevaporation. The solid was then dissolved in a minimum amount of pentane and cooled to −30 °C. This yielded 0.210 g of **7** (0.44 mmol, 60%). ^{1}H NMR (C_6D_6): δ 8.15 (br s, 3H), 6.07 (br s, 2H), 3.53 (br s, 3H), 2.59 (br s, 30H) ppm. IR (KBr): 3044 (m), 2961 (s), 2911 (s), 2855 (s), 1730 (w), 1445 (s), 1377 (s), 1022 (m), 801 (m), 546 (m) cm^{-1}. MS (EI): *m*/*e* 480 (M$^+$, 26.6), 453 (48.5), 452 (62.4), 294 (19.3), 293 (16.5), 266 (40.8), 265 (100.0). μ_{eff} (293 K): 1.4(1) μ_B. Anal. Calcd for $C_{28}H_{40}Cr_2$: C, 69.97; H, 8.39. Found: C, 70.14; H, 8.50.

Synthesis of (Cp*Cr)$_2$(μ-C_6D_5)(μ-C_2H_4D) (7-*d*$_6$). A 0.030 g sample of **3** was placed in an NMR tube fitted with a 14/20 glass joint. C_6D_6 was vacuum distilled into the tube, and the tube was flame sealed. The reaction mixture was heated in an oil bath at 50 °C for 66 h. The tube was then cracked open and the C_6D_6 removed by rotoevaporation. The resulting solid was characterized by infrared spectroscopy and mass spectroscopy. IR (KBr): 2961 (s), 2911 (s), 2855 (s), 2241 (w), 1730 (w), 1445 (m), 1377 (m), 1022 (m), 801 (m), 546 (m) cm^{-1}. MS (EI): *m*/*e* 459 (26.9), 458 (67.6), 457 (75.3), 300 (9.9), 299 (8.2), 271 (36.7), 270 (66.5). ^{1}H NMR (C_6D_6): δ 3.53 (br s, 6H), 2.59 (br s, 30H) ppm.

Reaction of 2 with dmpe. **2** (0.203 g, 0.502 mmol) was dissolved in 30 mL of pentane, and a solution of 0.150 g (0.999 mmol) of 1,2-bis(dimethylphosphino)ethane (dmpe) in 5 mL of pentane was added. The reaction was allowed to stir for 2−3 h, and during this time the solution slowly turned dark orange. The pentane was removed by rotoevaporation, and the solid was dissolved in a minimum of pentane. The pentane solution was cooled to −30 °C to give 0.231 g of Cp*Cr(dmpe)(CH_3) (66% yield). ^{1}H NMR(C_6D_6): δ 5.8 (br , 15H), −15.9 (br, 12H) ppm.[11]

Reaction of 2 with Ethylene. A 0.031 g sample of **2** (0.077 mmol) was placed in an NMR tube fitted with a 14/20 joint. C_6D_6 was vacuum distilled into the tube. A 0.3 mmol sample of ethylene was condensed into the tube, and the tube was flamed sealed. By ^{1}H NMR, no apparent reaction had taken place even after a week at room temperature.

Synthesis of Bis(η^5-pentamethylcyclopentadienyl)dimethyldioxo(μ-oxo)dichromium(V), [Cp*Cr(CH_3)(O)]$_2$-(μ-O) (8). A 0.200 g sample of **2** (0.495 mmol) was dissolved in 10 mL of pentane. The solution was degassed and then cooled to 0 °C. To the cold solution was added 1 equiv of O_2 per chromium. O_2 (281 mmHg) in a volume of 32.4 mL at 295 K was admitted to the solution. The solution was stirred for 1 h and then allowed to warm to room temperature. The solution was degassed by three freeze/pump/thaw cycles and then filtered. The pentane was removed by rotoevaporation. The red solid was dissolved in pentane and run down a silica column using 20% (by volume) diethyl ether in pentane as the solvent. The product eluted from the column as a bright red band. The solvent was removed by rotoevaporation, and the resulting solid was dissolved in pentane and cooled to −30 °C to yield 0.062 g of **8** (0.137 mmol, 28%). ^{1}H NMR (C_6D_6): δ 1.78 (s, 15H); 1.21 (s, 3H) ppm. IR (KBr): 2986 (s), 2910 (s), 2860 (s), 2725 (w), 1435 (m), 1377 (s), 1109 (m), 1020 (m), 937 (s), 825 (s) cm^{-1}. MS (EI, 40 eV): *m*/*e* 453 (6.4), 452 (14.2), 423 (7.8), 422 (16.3), 235 (12.9), 234 (55.2), 219 (12.5), 218 (54.5), 204 (82.6), 203 (100.0). Anal. Calcd for $C_{22}H_{36}Cr_2O_3$: C, 58.39; H, 8.02. Found: C, 57.76; H, 8.21.

Hydrogenolysis of 2. In a large ampule (50 mL) was placed 0.800 g of **2** (1.98 mmol) and 5 mL of pentane. The solution was degassed and then charged with 1 atm of H_2 gas. The ampule was closed and the solution stirred at room temperature for 6 days. During this time a black powder precipitated from solution. The solution was filtered and the black solid collected. The solid was washed with pentane and THF and then dried under vacuum. The reaction yielded 0.510 g of [Cp*$_4$Cr$_4$H$_x$] (*x* = 4?) (0.68 mmol, 68%). IR (KBr): 2982 (s), 2903 (s), 2852 (s), 2714 (w), 1435 (m), 1369 (s), 1020 (m), 549 (s) cm^{-1}. μ_{eff}(298 K): 5.7 μ_B. Anal. Calcd for $C_{40}H_{64}Cr_4$: C, 63.81; H, 8.57. Found: C, 63.53; H, 8.39. μ_{eff}(298 K) = 5.7 μ_B Note that **5** may be contaminated with other chromium hydrides (see Results and Discussion).

Synthesis of Tetrakis(η5-ethyltetramethylcyclopentadienyl)-tetrakis(μ_3-hydrido)tetrachromium(II), [(Cp″)Cr(μ_3-H)]$_4$ (9). Method A. To a stirred suspension of 1.001 g of $CrCl_2$ (8.14 mmol) in 6 mL of THF was added 1.269 g of ($EtMe_4C_5$)Li (8.12 mmol). The solution was stirred for 2 h, and then 5.4 mL of MeLi (1.5 M in diethyl ether) was added slowly via syringe. The solution color changed from dark purple to dark brown. The reaction was allowed to stir for 30 min more, and then the THF was removed by rotoevaporation. The resulting brown oil was extracted with pentane and filtered. The pentane was removed by rotoevaporation, and the resulting brown oil was dissolved in 5 mL of pentane and filtered again directly into a 50 mL reaction ampule. The solution was degassed, and the ampule was charged with 1 atm of H_2 gas. The reaction was allowed to stir for 6 days. The solution was then filtered and the pentane removed by rotoevaporation. The resulting sticky brown solid was recrystallized from pentane to give 0.880 g (1.10 mmol, 54%) of a mixture of **9** and Cp″$_4$Cr$_4$H$_7$ (up to 20% by NMR integration) (see Figure 7).

Method B. To a stirred suspension of 1.004 g (8.17 mmol) of $CrCl_2$ in 60 mL of THF was added 1.271 g (8.14 mmol) of ($EtMe_4C_5$)Li. The reaction was allowed to stir for 2 h at room temperature. To this solution was added 8.1 mL (8.1 mmol) of Super-Hydride ($LiHBEt_3$, 1 M in THF) slowly via syringe. The reaction was allowed to stir for an additional 30 min, and then the THF was removed by rotoevaporation. The resulting sticky brown solid was extracted with pentane and filtered. The pentane solution was concentrated and cooled to −30 °C to give 0.991 g (1.22 mmol, 60%) of **9**. ^{1}H NMR (C_6D_6): δ 7.9 (br s, 6H), 7.3 (br s, 6H), 3.4 (br s, 2H), 1.1 (br s, 3H) ppm (see Figure 7). ^{13}C NMR (C_6D_6): δ 119.7, 114.7, 111.0, 94.0, 91.7, 84.5, 37.9 ppm. IR (KBr): 2960 (s), 2901 (s), 2868 (s), 2714 (w), 1448 (s), 1365 (s), 1303 (w), 1018 (m), 945 (w), 551 (s) cm^{-1}. μ_{eff}(299 K): 3.50 μ_B (1.75 μ_B/Cr) (see Figure 9). Anal. Calcd for $C_{44}H_{72}Cr_4$: C, 65.65; H, 8.97. Found: C, 65.55; H, 8.88.

Reaction of 9 (Made by Method A, See Above) with H_2 (1 atm). A 0.500 g sample of **9** (μ_{eff}(294 K) = 3.7(1) μ_B, made following method B (see above)) was placed in a 50 mL reaction ampule. The solid was dissolved with 6 mL of pentane. The solution was degassed well, and then the flask was filled with 1 atm of H_2. The reaction was allowed to stir at room temperature for 5 days. The solution was then degassed and the pentane removed by rotoevaporation. The resulting solid was dissolved in a minimum of pentane and was recrystallized at −30 °C. A 0.430 g sample of solid was collected, and in addition to the normal ^{1}H NMR resonances of **9** two very small and very broad peaks could be seen at 9 and −1 ppm (see Figure 7). The effective magnetic moment of the sample was much higher (μ_{eff}(294 K) = 6.7(1) μ_B). Repeated recrystallizations of the solid failed to remove the additional peaks or significantly alter the effective magnetic moment.

Synthesis of Tetrakis(η^5-ethyltetramethylcyclopentadienyl)-tetrakis(μ_3-deuterio)tetrachromium(II) (9-*d*$_4$). The procedure was the same as method B above except that Super-Deuteride (95% D) was used instead of Super-Hydride. This gave a sample containing 80% of ($EtMe_4C_5Cr$(μ_3-D)$_4$ (**9**-*d*$_4$) and 20% of what appeared to be ($EtMe_4C_5Cr$)$_4$(μ_3-D)$_3$(μ_3-H) (**9**-*d*$_3$) by ^{1}H and ^{13}C NMR. ^{1}H NMR (C_6D_6) of **9**-*d*$_4$: δ 6.8 (br s), 6.2 (br s), 3.1 (br s) 1.1 (br s) ppm. ^{13}C NMR (C_6D_6) of **9**-*d*$_4$: δ 108.9, 103.7, 100.5, 95.4, 93.4, 87.6, 33.7 ppm. ^{1}H NMR (C_6D_6) of **9**-*d*$_3$: δ 7.0 (br s), 6.4 (br s), 3.1 (br s) 1.1 (br s) ppm. ^{13}C NMR (C_6D_6) of **9**-*d*$_3$: δ 111.7, 106.7, 103.2, 95.1, 93.0, 86.8, 34.8 ppm.

Reaction of 9 with HCl. 0.084 g sample of **9** (0.104 mmol) was dissolved in 40 mL of pentane. The solution was degassed (freeze/pump/thaw) three times, and then 1.17 mmol of HCl gas was added (663 mmHg, 32.4 mL, 295 K) to the stirred solution. The solution turned blue, and a blue solid precipitated. A 0.616 mmol (151 mmHg, 75.1 mL, 295 K) sample of H_2 gas was collected using a Topler pump. The pentane was removed under vacuum to give a blue solid. The blue solid was identified as [($EtMe_4C_5$)Cr(μ-Cl)(Cl)]$_2$ (0.102 g, 90%). ^{1}H NMR (C_6D_6): δ −0.8 (br s, 3H); −20.9 (br s, 2H); −47.2 (br s, 12H) ppm. MS (EI, 7 eV): *m*/*e* 544 (M$^+$, 5.9), 542 (3.1), 273 (78.2), 271 (100.0).

Reaction of 1 with HCl. **1** (0.296 g, 0.665 mmol) was dissolved in 5 mL of pentane. The solution was degassed thoroughly. To this solution was added 1.34 mmol of HCl (203 mmHg, 12 mL, 295 K). A blue solid precipitated from solution. A 0.592 mmol sample of H_2 gas (145 mmHg, 75.1 mL, 295 K) was collected using a Töpler pump.

Table 7. Crystallographic Data for [Cp*Cr(μ-Cl)]$_2$ (**1**), [Cp*Cr(μ-Me)]$_2$ (**2**), [(Cp*Cr)$_2$(μ-Et)(μ-Ph)] (**7**), [(Cp*Cr(O)Me)$_2$(μ-O)] (**8**), and [Cp″Cr(μ_3-H)]$_4$ (**9**)

	1	**2**	**7**	**8**	**9**
Crystal Parameters					
formula	$C_{20}H_{30}Cr_2Cl_2$	$C_{22}H_{36}Cr_2$	$C_{28}H_{39}Cr_2$	$C_{44}H_{72}Cr_4O_6$	$C_{44}H_{72}Cr_4$
formula weight	445.58	402.50	479.6	905.0	809.0
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	*Pnma*	*Pnma*	$P2_12_12_1$	$P2_1/c$	$P1$
a (Å)	20.860(5)	20.172(12)	13.551(5)	8.523(9)	11.189(4)
b (Å)	14.768(3)	14.714(8)	8.925(5)	25.361(29)	12.152(5)
c (Å)	7.2274(14)	7.537(4)	21.916(11)	21.720(23)	18.199(9)
α (deg)					88.13(4)
β (deg)				96.57(8)	84.92(4)
γ (deg)					63.00(3)
Z	4	4	4	4	2
crystal dimens (mm)	0.38 × 0.32 × 0.22	0.55 × 0.31 × 0.36	0.30 × 0.32 × 0.36	0.20 × 0.38 × 0.42	0.32 × 0.40 × 0.42
crystal color	dark red	deep purple/black	black	red	brown
D(calc) (g cm^{-3})	1.329	1.195	1.207	1.289	1.224
μ(Mo Kα) (cm^{-1})	11.96	9.49	8.35	9.49	9.9
T (K)	296	296	299	298	298
Data Collection					
diffractometer	Nicolet R3m	Nicolet R3m	Siemens P4	Siemens P4	Siemens P4
monochromator	graphite	graphite	graphite	graphite	graphite
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
2θ scan range (deg)	4.0−45.0	4.0−45.0	4.0−45.0	4.0−45.0	4.0−48.0
data collected (*h*,*k*,*l*)	+25,+16,+8	+22,+16,+9	+14,+9,+23	±9,+27,+23	±12,±13,−20
rns collected	1937	1821	1992	6279	7080
indep rfns	1722	1535	1992	6092	6838
obsd rfns ($F_o > n\sigma(F_o)$)	1065 ($n = 5$)	861 ($n = 5$)	1431 ($n = 4$)	3145 ($n = 4$)	3993 ($n = 4$)
std rfns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns	3 srd/197 rflns	3 std/197 rflns
var in stds (%)	<1	<1	<1	<1	<1
Refinement					
R(*F*) (%)	4.91	7.16	8.68	6.17	7.45
R(*wF*) (%)	5.42	7.66	10.63	6.51	9.08
Δ/σ(max)	0.001	0.007	1.652 (0.010 mean)	0.004	0.095
$\Delta(\varrho)$ (e Å^{-3})	0.421	0.988	0.65	0.44	0.70
N_o/N_v	9.0	7.3	8.3	6.4	9.1
GOF	1.371	1.417	1.64	1.19	1.40

The pentane was removed from the solid under vacuum and the solid collected to give 0.292 g (0.566 mmol, 85%) of [Cp*Cr(μ-Cl)(Cl)]$_2$. ^{1}H NMR (C_6D_6): δ −47 (br s) ppm.[3]

Reaction of 9 with C_6D_6 (H/D Exchange). **9** (0.450 g, 0.556 mmol) was placed in a 10 mm NMR tube. C_6D_6 (approximately 4 mL) was vacuum distilled into the NMR tube, and the tube was flame sealed. The reaction was then heated in an oil bath at 50 °C for 18 days during which time NMR spectra were taken periodically to follow the progress. After 18 days of heating, the tube was cracked open and the C_6D_6 removed by rotoevaporation. The solid was dissolved in pentane and cooled to −30 °C to yield 0.350 g of a mixture of isotopomers of **9**, i.e., [(EtMe$_4$C$_5$Cr)$_4$(μ_3-H)$_{4-x}$(μ_3-D)$_x$] (x = 0−4).

Reaction of 9-*d*$_4$ with H$_2$. A 0.300 g sample of **9**-*d*$_4$ (0.369 mmol) was placed in a 50 mL reaction ampule. The solid was dissolved with 5 mL of pentane. The solution was degassed, and then the ampule was filled with 1 atm of H$_2$. The reaction was allowed to stir for 6 days at room temperature. The solution was then degassed, and the pentane was removed by rotoevaporation. The resulting solid was recrystallized from pentane at −30 °C to give 0.205 g (0.253 mmol, 69%) of **9** as shown by ^{1}H NMR. ^{1}H NMR (C_6D_6): δ 7.9 (br s, 6H), 7.3 (br s, 6H), 3.4 (br s, 2H), 1.1 (br s, 3H) ppm.

Reaction of 9 with D$_2$. A 0.300 g sample of **9** (0.371 mmol) was dissolved in 5 mL of pentane and added to a 50 mL reaction ampule. The solution was degassed, and then the ampule was filled with 1 atm of D$_2$. The reaction mixture was allowed to stir for 5 days, and then the solution was degassed and the pentane removed by rotoevaporation. The resulting solid was dissolved in a minimum of pentane and recrystallized at −30 °C to give 0.210 g (0.260 mmol, 70%) of **9**-*d*$_4$. ^{1}H NMR (C_6D_6): δ 6.8 (br s, 6H), 6.2 (br s, 6H), 3.1 (br s, 2H) 1.1 (br s, 3H).

X-ray Crystallography, General Comments. All crystals were mounted in 0.5 mm X-ray capillary tubes in a drybox, and the tubes were flame sealed. Table 7 contains information on the structure determination, data collection, and solution. The structures were solved with direct methods and refined by a full-matrix least-squares method. All computations used SHELXTL software (various versions) (G. Sheldrick, Siemens XRD, Madison, WI).

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Supplementary Material Available: Tables giving the positional and thermal parameters for **1**, **2**, and **7**−**9** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.