Correlations between Structure, Magnetism, and Polymerization Activity of Paramagnetic Benzylchromium Complexes

Gautam Bhandari, Arnold L. Rheingold, and Klaus H. Theopold*

Abstract: Reaction of $[\{Cp^*Cr(\mu\text{-}Cl)\}_2]$ with benzyllithium yielded $[\{Cp^*Cr(\mu\text{-}Bz)\}_2]$ (**1**), a Cr^{II} alkyl complex with bridging benzyl groups and a Cr–Cr bond, which rearranged at room temperature to $[Cp^*Cr(\eta^1\text{-}Bz)(\mu\text{-}\eta^3{:}\eta^6\text{-}Bz)CrCp^*]$ (**2**), a mixed valent (Cr^I/Cr^{III}) complex with a benzyl ligand coordinating as an η^6-arene ligand to one chromium and as an η^3-allyl ligand to the other one. Upon heating, **2** reductively eliminated bibenzyl and yielded $[(Cp^*Cr)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}Bz\text{-}Bz)]$ (**3**), in which two 17-electron sandwich complexes are linked by an ethano bridge. The crystal structures of **2** and **3** have been determined. Magnetic susceptibility and saturation magnetization measurements showed **2** to be ferromagnetically coupled (ground state $S = 2$, $J = +23(1)\,cm^{-1}$). Of the three isomers, only **2** catalyzed the polymerization of ethylene, presumably because it contains a Cr^{III} alkyl.

Keywords
benzyl ligands · catalysis · chromium compounds · ferromagnetic coupling · polymerization

Introduction

Our continuing investigation of organochromium chemistry[1] is motivated by the notion that paramagnetic organometallic compounds will exhibit interesting physical and chemical properties (e.g., molecular structure, magnetic properties, catalytic reactivity etc.). Neglecting the study of open-shell organometallics for the sake of expediency—namely, straightforward characterization by NMR spectroscopy—obviously leaves whole classes of molecules unscrutinized. A good example is our erstwhile discovery of a class of chromium(III) alkyls that catalyze the polymerization of ethylene in homogenous solution.[2]

Despite the widespread commercial use of chromium-based heterogeneous ethylene polymerization catalysts (e.g., Phillips catalyst, prepared by reduction of chromate deposited on silica, or Union Carbide catalyst, in which Cp_2Cr is supported on silica and variants thereof),[3] the chemical nature of the active site(s) remains the object of wide-ranging speculation. An obvious strategy towards understanding chromium catalysis lies in the synthesis of well-defined homogenous model systems that mimic the supported catalysts. However, given the nature of chromium chemistry, this approach leads into uncharted terrain populated by compounds with unpaired electrons. As part of our efforts in this vein, we have recently prepared and characterized several benzylchromium(III) complexes and determined their activity for ethylene polymerization.[4] To address the widely accepted conjecture that Cr^{II} is the catalytically active oxidation state, we then initiated an investigation of analogous benzylchromium(II) compounds.[5] Herein we describe a series of structural isomers of $[(Cp^*CrBz)_2]$ and their varied activities as catalysts for the polymerization of ethylene. This work has provided us with further insights into the essential requirements for catalytic activity, and, as a bonus, it has led to the discovery of an unusual ferromagnetically coupled organochromium dimer. Given the recent interest in organometallic compounds for the design of novel magnetic materials,[6] we see this as another case in point justifying the exploration of paramagnetic organometallics.

Results and Discussion

Synthesis: By analogy to previous syntheses of chromium(II) alkyls of the type $[\{Cp^*Cr(\mu\text{-}R)\}_2]$ (R = Me, Et, *n*Bu, Ph, CH_2SiMe_3),[7] addition of two equivalents of benzyllithium to a THF solution of $[\{Cp^*Cr(\mu\text{-}Cl)\}_2]$ at $-40\,°C$ resulted in an immediate color change from blue to purple. Subsequent workup and recrystallization from pentane gave brown crystals of $[\{Cp^*Cr(\mu\text{-}Bz)\}_2]$ (**1**, see Scheme 1) in reasonable yield (56%). The ^1H NMR spectrum of **1** was consistent with it being another member of the aforementioned class of bridging alkyl dimers, all of which show a relatively sharp resonance for the two equivalent Cp* rings at around $\delta = 2.3$ (**1**: $\delta = 2.34$, $\Delta\nu_{1/2} = 25$ Hz). The resonances of the *meta* and *para* protons of the bridging benzyl groups were also sharp. The narrow line widths and near absence of isotropic shifts for **1** correspond well with the low magnetic moment ($\mu_{eff} = 1.45\,\mu_B$ per dimer or $1.0\,\mu_B$/Cr at room temperature) found for this dimer. This value is in close agreement with those found for the other complexes of the class $[\{Cp^*Cr(\mu\text{-}R)\}_2]$, several of which have been structurally characterized and feature short Cr–Cr distances (<2.3 Å).[7] Undoubtedly, **1** is a structurally analogous dimer in which the benzylic methylene groups symmetrically bridge the two chromium atoms.

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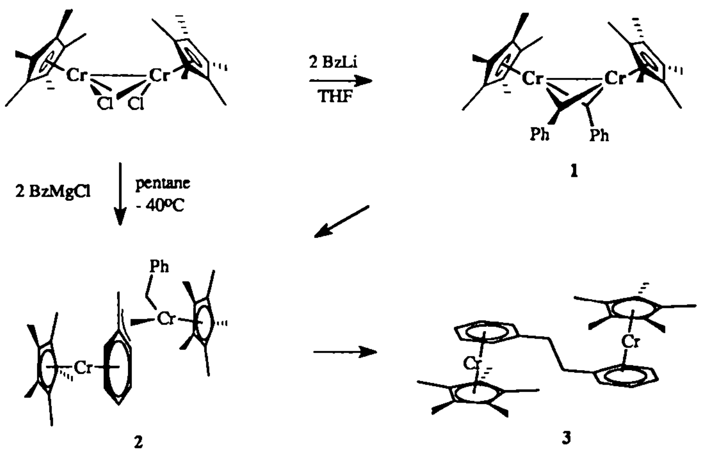

Scheme 1.

Upon monitoring the stability of **1** in solution over the course of several days by ^{1}H NMR, the sharp Cp* resonance slowly disappeared and was replaced by two new resonances at $\delta = 8.0$ and -13.5 in an apparent ratio of 1:1, along with resonances of some other minor reaction products. We have found that this product of the thermal decomposition of **1** (i.e., **2**) can be independently prepared by changing the reaction conditions in the synthesis of the former. Thus, addition of two equivalents of an ether solution of benzylmagnesium chloride to a pentane solution of $[\{Cp^*Cr(\mu\text{-}Cl)\}_2]$ at $-40\,°C$ resulted in a direct color change to brown. Subsequent recrystallization of the solid residue gave $[Cp^*Cr(\eta^1\text{-}Bz)(\mu\text{-}\eta^3{:}\eta^6\text{-}Bz)CrCp^*]$ (**2**) in 75% yield. The molecular structure of **2** was determined by X-ray diffraction, and the result is depicted in Figure 1; Table 1 lists selected interatomic distances and angles.[8] Complex **2** is an isomer of **1**. However, rather than being a chromium(II) alkyl, it is more appropriately described as a mixed-valent Cr^I/Cr^{III} complex. Besides being bonded to the obligate η^5-Cp* ring, Cr(1) forms a σ-bond with a terminal benzyl group and binds a second benzyl ligand in a η^3-fashion. It is of historical interest that the allylic coordination mode of the benzyl moiety to chromium was first anticipated some thirty years ago.[9] However, although the η^3-benzyl motif is now regarded as fairly common, very few examples have been structurally characterized.[10] The Cr–C bonds to the allylic fragment (C(28), C(29), C(30)) range from 2.07 to 2.38 Å in length. The two C–C bond lengths are almost equal (C(28)–C(29), 1.455(8) Å; C(29)–C(30), 1.472(8) Å). While the endocyclic C–C bond is the longest in the six-membered ring ($C\text{–}C_{avg}$, 1.431 Å), the exocyclic C–C bond is shorter than the corresponding bond length in the η^1-benzyl group (C(21)–C(22), 1.494(12) Å); this indicates some multiple bond character. All of these observations are consistent with the η^3-allyl formulation. Cr(1) is the center of a 15-electron $[Cp^*Cr^{III}R_2]$ fragment, intermediate between, for example, $[Cp^*Cr^{III}(CH_2SiMe_3)_2]$[11] and $[CpCr^{III}(\eta^3\text{-}C_3H_5)_2]$.[12] Cr(2), on the other hand, adopts a classical sandwich structure akin to $[CpCr^I(\eta^6\text{-}C_6H_6)]$,[13] and this part of **2** has the structural features expected of such a motif (see also **3** below).

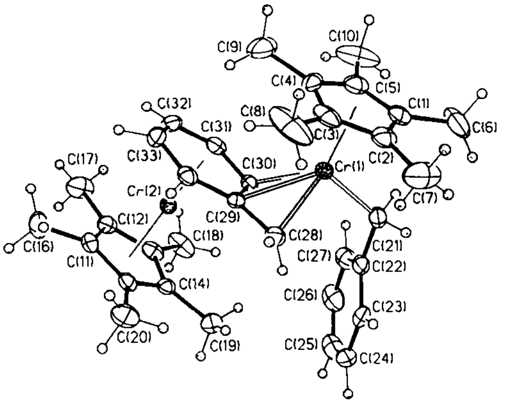

Fig. 1. The molecular structure of **2**. Selected interatomic distances and angles are listed in Table 1.

Table 1. Selected interatomic distances (Å) and angles (°) for **2**.

Cr(1)-Cr(2)	4.196	Cr(1)-C(21)	2.132(7)
Cr(1)-C(28)	2.071(7)	Cr(1)-C(29)	2.275(7)
Cr(1)-C(30)	2.381(6)	Cr(1)-C_{Cp*}(av)	2.2584
Cr(2)-C_{Cp*}(av)	2.1688	Cr(2)-C_{Bz}(av)	2.1053
C(21)-Cr(1)-C(28)	95.9(3)	C(21)-Cr(1)-C(30)	95.6(3)
C(28)-Cr(1)-C(29)	38.7(2)	C(30)-Cr(1)-C(29)	36.8(2)
Cr(1)-C(28)-C(29)	78.2(3)	Cr(1)-C(21)-C(22)	124.7(5)

While formed by a thermal rearrangement of **1**, **2** is merely an intermediate in a cascade of reactions that ultimately produces a third isomer of the same composition. When **2** was heated in solution to 50 °C for 42 hours, it was cleanly transformed into $[(Cp^*Cr)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}Bz\text{-}Bz)]$ (**3**), which was characterized by a very broad ^{1}H NMR resonance at $\delta = -12.5$. No loss of any diamagnetic organic fragments or formation of any other paramagnetic products was observed by ^{1}H NMR spectroscopy. Translucent orange crystals of **3** were grown by slow evaporation of toluene. The result of a crystal structure determination of **3** is shown in Figure 2, and Table 2 lists selected interatomic distances and angles.[8] Complex **3** possesses a center of inversion between C(17) and C(17A). The coordination environment about chromium is essentially identical to the sandwich fragment of **2**, with the two arene rings linked by an ethano bridge. The formal oxidation state of both equivalent chromium atoms is now + I. Complex **3** is the product of a reductive elimination of the benzyl groups in **2**.

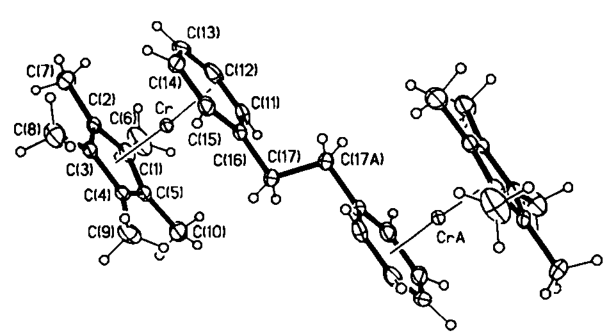

Fig. 2. The molecular structure of **3**. Selected interatomic distances and angles are listed in Table 2.

Table 2. Selected interatomic distances (Å) and angles (°) for **3**.

Cr–C_{Ph}(av)	2.099	Cr–C_{Cp*} (av)	2.160
Cr–Cr(a)	7.908	C(16)–C(17)	1.502(4)
C(17)–C(17a)	1.545(6)	C(16)-C(17)-C(17a)	111.7(3)

Magnetism: Compounds with unpaired electrons can exhibit various magnetic properties, depending on the nature and extent of coupling between the individual magnetic moments.[14]

If the moments do not interact appreciably (i.e., in "magnetically dilute" compounds), random thermal agitation counteracts the alignment of the moments with the external field; this results in Curie-type behavior, that is, the molar magnetic susceptibility is inversely proportional to the temperature ($\chi_m = C/T$) and the effective magnetic moment (μ_{eff}) is independent of temperature and characteristic of the number of unpaired electrons. Compound **3**, with its widely separated chromium atoms (Cr–Cr A = 7.9 Å) linked only by a saturated hydrocarbon bridge, is expected to behave in this way. Accordingly, its room temperature moment was measured to be $\mu_{eff} = 1.7(1)\ \mu_B$ per Cr, that is, close to the expected spin-only moment of a first-row transition metal with one unpaired electron (low-spin d^5 configuration, $S = {}^1/_2$).

In marked contrast, **1** exhibited a much reduced moment, despite its higher number of unpaired electrons per chromium (d^4, $S = 1$, two unpaired electrons expected by analogy to related mononuclear complexes, e.g., [Cp*Cr(dmpe)Me][2b]). Its room temperature moment measured $\mu_{eff} = 1.0(1)\ \mu_B$ per Cr (1.4 μ_B per dimer). The former value is very close to those measured for other molecules of the type $[\{Cp^*Cr(\mu\text{-}R)\}_2]$, which ranged from 0.7 to 1.0 μ_B per Cr.[7] We have previously shown that these dimers feature strong metal–metal interactions, which may be described as metal–metal bonding or strong antiferromagnetic coupling ($J > -400\ cm^{-1}$). Either way, antiparallel alignment of the electronic spins on adjacent chromium atoms results in lowered effective magnetic moments, which further decrease upon lowering the temperature. While we have not actually carried out variable temperature susceptibility measurements on **1**, there remains little doubt that its behavior parallels that of all other representatives in its class.

Both types of magnetic behavior described so far are common in transition metal chemistry. However, the unusual structure of **2** and its mixed-valent character, juxtaposing a Cr^I ($S_1 = {}^1/_2$) and a Cr^{III} ($S_2 = {}^3/_2$) center linked by a conjugated polyene ligand, prompted us to study its magnetic behavior. Figure 3 shows the temperature dependencies of the molar magnetic susceptibility and the effective magnetic moment of **2** as measured with a Faraday balance. Notably, at room temperature $\mu_{eff} = 4.3\ \mu_B$ per dimer, and lowering the temperature led to an increase in the moment, which reached $\mu_{eff} = 4.9\ \mu_B$ at 50 K! This unusual behavior is that expected of a *ferromagnetically coupled* dinuclear complex.[15] More specifically, it appears that the ground state of **2** has the two spins coupled in parallel, resulting in a molecule with four unpaired electrons ($S = 2$, spin only moment 4.9 μ_B). The state featuring antiparallel alignment of S_1 and S_2 ($S = 1$) is of slightly higher energy, and is appreciably populated only when the thermal energy of the system (kT) becomes comparable to the difference in energy between the two spin states ($\Delta E = |4J|$). Indeed, analysis of the temperature dependence of χ_m allows the determination of the coupling constant J of the spin–spin interaction. Application of the Heisenberg–Dirac–van Vleck model yields Equation (1),[16] which

$$\chi_m = \frac{Ng^2\mu_B^2}{3kT}\frac{(6 + 30\,e^{4J/kT})}{(3 + 5\,e^{4J/kT})} \qquad (1)$$

may be used to fit the experimental data. For **2**, this resulted in a coupling constant of $J = +23(1)\ cm^{-1}$; the plus sign signalizes the ferromagnetic nature of the interaction (note that by convention J is negative for antiferromagnetic interactions, see above).

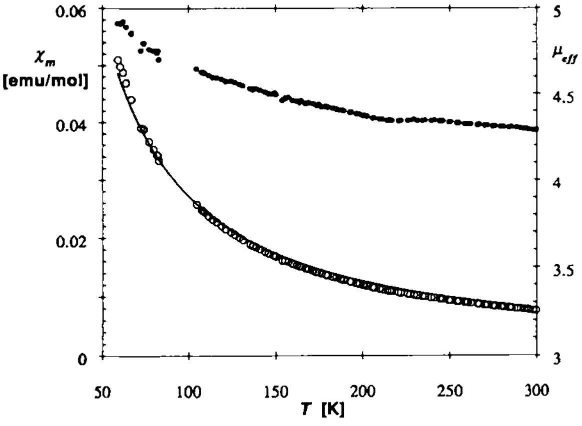

Fig. 3. Temperature dependencies of molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, solid circles) of **2**. Line represents fit with Equation (1); $J(2) = +23(1)\ cm^{-1}$.

Further confirmation of the ferromagnetic interaction of the chromium centers in **2** was provided by saturation magnetization measurements at low temperature. Figure 4 shows the field dependence of the magnetization of **2** at 5, 10, and 15 K. Fitting of the data with Brillouin functions (assuming $g = 2.0$) gave three independent values of the spin quantum number S of the ground state, averaging to $S = 2.08(12)$. This experiment thus supports the notion that **2**, in its ground state, is a high-spin molecule with four unpaired electrons. That said, we find it difficult to provide a convincing explanation for the ferromagnetic interaction. A popular model proposes orthogonality of the "magnetic orbitals" (i.e., those orbitals occupied by the unpaired electrons) as the condition for ferromagnetic coupling.[17] However, the unpaired electrons on the two chromium atoms reside in d orbitals which engage in π backbonding to the same bridging benzyl ligand. As the empty π* levels of the η^6-arene and η^3-allyl moieties, respectively, are linear combinations of the same atomic orbitals (i.e., C 2p), it is not obvious how they could fail to mix, thereby providing a mechanism for antiferromagnetic exchange. However, the experimental result is unambiguous, and we reserve further speculation on the underlying reasons for a later date.

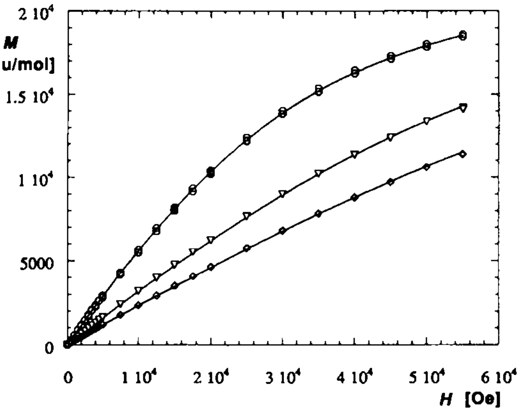

Fig. 4. Saturation magnetization measurements on **2** at 5 K (circles), 10 K (triangles), and 15 K (diamonds). Lines represent fits with Brillouin functions (assuming $g = 2$): $S(5\ K) = 1.95$, $S(10\ K) = 2.08$, $S(15\ K) = 2.19$.

Polymerization Catalysis: Solutions of **1**, **2**, and **3** were exposed to excess ethylene at ambient temperature and atmospheric pressure. While neither **1** nor **3** showed any catalytic activity toward the formation of polyethylene under these mild reaction conditions, a solution of **2** (30 mg in pentane) reacted with ethylene and produced 115 mg of insoluble polymer. GPC (gel permeation chromatography) analysis of the latter gave average molecular weights of $M_n = 3140$ and $M_w = 5120$ and polydispersity of $M_w/M_n = 1.63$. The molecular weights are very low, even by comparison with other homogeneous chromium catalysts studied in our laboratory,[2, 4] but the important point is the observation of polymerization catalysis for one and only one of the three isomeric complexes. Notably, the sole catalytically active compound is the one that contains a chromium(III) alkyl.

Conclusions

We have prepared and characterized three isomeric organochromium complexes containing benzyl groups. The formal oxidation states of chromium in these compounds are $Cr^{II}Cr^{II}$, $Cr^{I}Cr^{III}$, and $Cr^{I}Cr^{I}$, and the complexes feature various degrees of metal–metal interaction. The mixed valent complex **2** contains an unusual bridging benzyl ligand, and its two chromium atoms are ferromagnetically coupled. This complex is also the only one that catalyzes the polymerization of ethylene. Once again, a direct comparison of the reactivity of chromium alkyls of different oxidation states has thus shown chromium(III) to be the active valence state. While we will continue to test this notion, the weight of available evidence would appear to discount chromium(II) as a catalytically competent oxidation state in ethylene polymerization.

Experimental Section

General Techniques: All manipulations of compounds were carried out by standard Schlenk, vacuum, and glove-box techniques. Pentane, diethyl ether, tetrahydrofuran, and toluene were distilled from purple Na benzophenone/ketyl solutions. C_6H_6, $[D_6]$benzene and $[D_8]$THF were all pre-dried with Na and stored under vacuum over Na/K alloy. $CrCl_2$ (anhydrous) was purchased from Strem, and $C_6H_5CH_2MgCl$ from Aldrich as a 2 M solution in ether or THF. 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. LiCp* [18] and $[Cp^*CrCl]_2$ [7] were synthesized by literature procedures. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer, and FTIR spectra 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, N. Y. 13492. Characterization of polyethylene samples was conducted at Chevron Chemical Company, Kingwood, TX.

Magnetic measurements: Room temperature magnetic susceptibilities were determined by the Evans method [19]. Variable-temperature magnetic susceptibilities were determined by means of a Faraday magnetic susceptibility balance. Magnetic susceptibilities determined by the Faraday balance were corrected for ferromagnetic impurities by the method of Honda and Owens [20]. Saturation magnetization experiments were performed on a Quantum Design MPMS-5 SQUID magnetometer. The magnetic fields applied were in the range of 0 to 55 kOe. The temperature accuracy of the instrument is ±0.05 K and ±0.1% for the applied field. Molar magnetic susceptibilities were corrected for diamagnetism using Pascal's constants.

Bis(η^5-pentamethylcyclopentadienyl)-bis(μ:η^1-benzyl)-dichromium (II) (1): A THF solution (50 mL) of $[(Cp^*CrCl)_2]$ (0.333 g, 0.75 mmol) was cooled to −40 °C. To this solution was added dropwise BzLi (3.3 mL, 0.45 M in Et_2O). The color of the solution rapidly changed to purple. This mixture was then warmed to room temperature and allowed to stir for an additional 45 min. The solvent was then removed and the residue extracted with pentane. Crystallization yielded 0.234 g (56%) of **1**. ^1H NMR (250 MHz, $[D_6]$Benzene, 22 °C) $\delta = 2.34$ (30 H), 6.82 (2 H), 7.31 (4 H), 11.38 (br, 4 H). IR (KBr): $\tilde{\nu} = 3063$ (w), 3011 (m), 2962 (m), 2908 (s), 2857 (s), 1596 (s), 1485 (s), 1447 (m), 1376 (s), 1197 (m), 1085 (m), 1025 (m), 742 (s), 692 (s), 528 (w), 501 (w) cm^{-1}. UV/Vis (Et_2O): λ_{max} (ε) = 407 (1650 $M^{-1}cm^{-1}$), 516 nm (690 $M^{-1}cm^{-1}$). M.p. 128 °C. $\mu_{eff} = 1.45\ \mu_B$ (294 K). Anal. calcd. for $C_{34}H_{44}Cr_2$: C, 73.35; H, 7.97; N, 0. Found: C, 72.07 ; H, 7.80; N, 0. MS (70 eV, EI): m/z (%): 556 (37) [M^+], 465 (10) [$M^+ - C_7H_7$], 369 (30) [$M^+ - Cp^*Cr$].

Bis(η^5-pentamethylcyclopentadienyl)-(η^1-benzyl)-(μ-η^3:η^6-benzyl)-dichromium(I,III) (2): $[(Cp^*CrCl)_2]$ (0.375 g, 0.84 mmol) was dissolved in pentane (50 mL) and cooled to −40 °C. Benzylmagnesium chloride (1.68 mL, 1 M in Et_2O; 2 equiv. 1.68 mmol) was slowly added to this solution. This reaction was allowed to stir for 4 h and then filtered to remove the $MgCl_2$ formed. Crystallization from a mixture of Et_2O and pentane gave 0.349 g (75% yield) of **2** as brown needles. ^1H NMR (250 MHz, $[D_6]$Benzene, 22 °C): $\delta = 41.86$ (v br, 2 H), 32.47 (br, 1 H), 7.97 (br, 15 H), 1.85 (br, 2 H), −10.80 (br, 2 H), −13.45 (br, 15 H). IR (KBr): $\tilde{\nu} = 2939$ (m), 2904 (s), 2854 (s), 1591 (m), 1481 (m), 1450 (m), 1427 (w), 1379 (m), 1215 (w), 1026 (m), 972 (m), 744 (m), 698 (m), 464 (m) cm^{-1}. UV/Vis (Et_2O): λ_{max} (ε) = 481 (2078 $M^{-1}cm^{-1}$), 935 nm (580 $M^{-1}cm^{-1}$). M.p. 122 °C. $\mu_{eff} = 4.3\ \mu_B$ (290 K). Anal. calcd. for $C_{34}H_{44}Cr_2$: C, 73.35; H, 7.97; N, 0. Found: C, 73.51; H, 8.06; N, 0. MS (12 eV, EI): m/z (%): 556 (5) [M^+], 369 (22) [$M^+ - Cp^*Cr$], 279 (5) [$M^+ - Cp^*Cr(C_7H_8)$].

Bis(η^5-pentamethylcyclopentadienyl)(μ-η^6:η^6-bibenzyl)dichromium(I) (3): Compound **2** (0.275 g) was dissolved in toluene (20 mL). The solution was then sealed in an ampoule fitted with a Teflon tap. The ampoule was then heated to 50 °C in an oil bath for 2 d. Over this period the color of the solution changed from brown to orange. The ampoule was then opened and the toluene removed by evaporation under reduced pressure. By NMR the product was found to be pure **3**. Translucent orange crystals (0.71 mg) for X-ray analysis were grown from this powder by the slow evaporation of toluene over 2 d. ^1H NMR (250 MHz, $[D_6]$Benzene, 22 °C): $\delta = -12.58$ (v br). IR (KBr): $\tilde{\nu} = 3052$ (m), 2936 (m), 2900 (m), 2852 (m), 1599 (w), 1481 (w), 1448 (m), 1380 (s), 1069 (w), 1026 (m), 971 (m), 762 (s), 698 (w), 471 (m) cm^{-1}. UV/Vis (Et_2O): λ_{max} (ε) = 353 nm (3390 $M^{-1}cm^{-1}$). $\mu_{eff} = 2.42\ \mu_B$ (296 K). Anal. calcd. for $C_{34}H_{44}Cr_2$: C, 73.35; H, 7.97; N, 0. Found: C, 73.43; H, 7.79: N, 0. MS (70 eV, EI): m/z (%): 556 (100) [M^+], 421 (5) [$M^+ - Cp^*$], 369 (31) [$M^+ - Cp^*Cr$].

Crystal Structure Determinations for 2 and 3 [8]: Crystallographic data are collected in Table 3. Both samples were mounted in glass capillary tubes and flame sealed. From photographic evidence, both compounds were shown to possess 2/*m* symmetry, and in both cases the space groups were uniquely determined from systematic absences in the diffraction data. Data were corrected for *Lp* and minor absorption effects (variation in transmission < 10%, ψ scan data, six reflections). Both structures were solved by direct methods, and completed from subsequent difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined, and hy-

Table 3. Crystallographic data for **2** and **3**.

	2	**3**
formula	$C_{34}H_{44}Cr_2$	$C_{34}H_{44}Cr_2$
formula weight	556.7	556.7
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a/Å	11.115(3)	9.521(5)
b/Å	17.521(5)	9.702(4)
c/Å	15.849(4)	16.001(7)
β/°	107.94(2)	105.66(4)
volume/Å^3	2936.5(14)	1423(1)
Z	4	2
crystal dimen./mm	0.30 × 0.35 × 0.35	0.28 × 0.34 × 0.36
crystal color	brown-black	orange
D_{calcd}/g cm^{-3}	1.259	1.299
$\mu(Mo_{K\alpha})$/cm^{-1}	7.41	7.84
T/K	233	216
diffractometer	Siemens P4	Siemens P4
monochromator	graphite	graphite
radiation (Å)	$Mo_{K\alpha}$ ($\lambda = 0.71073$)	$Mo_{K\alpha}$ ($\lambda = 0.71073$)
scan mode	Wyckoff	Wyckoff
2θ/°	4–48	4–60
data collected (h,k,l)	±12, +20, +18	±13, +13, +22
reflections collected	4784	4259
independent	4603	4124
observed ($F_0 > n\sigma(F_0)$)	2756 ($n = 5$)	2818 ($n = 5$)
standard refl.	3/197	3/197
var. in stand. refl./%	< 1	< 1
program	Siemens SHELXTL PLUS	Siemens SHELXTL PLUS
solution	direct methods	direct methods
refinement method	full-matrix least-squares	full-matrix least-squares
no. parameters refined	325	163
hydrogen atoms	riding model fixed isotropic U	riding model fixed isotropic U
$R(F)$/%	5.29	4.81
$R(wF)$/%	6.97	6.09
$(\Delta/\sigma)_{max}$	0.032	0.04
$\Delta(\rho)$/e Å^{-3}	0.51	0.41
N_o/N_v	8.5	17.3
GOF	1.24	1.25

drogen atoms were treated as idealized, updated contributions. All computer programs are contained in the SHELXTL library (Version 4.4, G. Sheldrick, Siemens XRD, Madison, WI).

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