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Synthesis and characterization of chromocenes containing bulky cyclopentadienyl ligands

Jason S. Overby, Nathan J. Schoell, Timothy P. Hanusa *

Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA

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Abstract

Two equivalents of K[Cp′] (Cp′ = $C_5(i\text{-Pr})_3H_2$, $C_5(i\text{-Pr})_4H$, $C_5(t\text{-Bu})_2H_3$) react with $CrCl_2$ in THF to give the corresponding chromocenes, Cp'_2Cr, in good yield. Despite the presence of bulky substituents on the rings that could affect their properties, the complexes are extremely air- and moisture-sensitive, and possess a low-spin ground state. The low-spin paramagnetic nature of each chromocene was confirmed by magnetic susceptibility measurements. The solid-state structure of $[C_5(i\text{-Pr})_3H_2]_2Cr$ was obtained using single crystal X-ray analysis. It displays rigorously parallel rings, with an average Cr–C(ring) distance of 2.17(1)Å; the chromium resides on a crystallographically imposed inversion center. The orientation of the isopropyl groups minimizes unfavorable steric interactions between the rings. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chromocenes; Chromium; Metallocenes; Crystal Structure

1. Introduction

Metal complexes containing highly alkylated cyclopentadienyl (Cp) rings ($C_5R_nH_{5-n}$; R > Me; $n \geq 3$) are not rare, but apart from work on ferrocene derivatives, relatively few studies have examined in detail the systematic effects of such rings on the structure and bonding of transition metal metallocenes [1,2]. Previous work from our laboratory has included the preparation of middle-to-late transition metal complexes (Mn, Fe, Ru, Co) containing the 1,2,4-triisopropylcyclopentadienyl (Cp^{3i}) and 1,2,3,4-tetraisopropylcyclopentadienyl (Cp^{4i}) ligands [3–5]. Even with a total of six isopropyl groups per complex, little deviation from the properties of the related decamethylmetallocenes is observed. All the $(Cp^{3i})_2M$ complexes, for example, are thermally stable and readily sublimable, and in the solid-state, all are isomorphous with parallel rings. The bulkier tetraisopropylcyclopentadienyl (Cp^{4i}) ligand, however, produces distortions in the solid state structures. The Cp^{4i} rings in the structures of $[(Cp^{4i})_2Fe]PF_6$ and $[(Cp^{4i})_2Co]PF_6$ are no longer parallel, and substantial displacements of the isopropyl substituents out of the ring planes are present. Other differences can be induced as well: for example, the steric bulk of the ligands in $(Cp^{4i})_2Mn$ stabilizes the high-spin ($^6A_{1g}$) state, overriding the effect of the electron-donating *i*-Pr groups [3] and in contrast to $(Cp^{3i})_2Co$, solid samples of $(Cp^{4i})_2Co$ are indefinitely stable in air, a property traced to the 'encapsulation' of the metal center by the rings [4].

Comparatively little work has been reported on the combination of sterically bulky ligands and early transition metals such as vanadium and chromium. Not many substituted chromocenes have been synthesized, and even fewer have been crystallographically characterized; the only structurally authenticated example with substituents larger than methyl groups is octaphenylchromocene, $(C_5PhH_4)_2Cr$, prepared by Trogler et al. [6]. Our interest in exploring the potential for sterically driven manipulation of spin states as a

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* Corresponding author. Tel.: +1 615 3222861; fax: +1 615 3224936; e-mail: hanusat@ctrvax.vanderbilt.edu

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source for stabilized high-spin organometallic building blocks led us to examine combinations of strongly electron-donating Cp ligands with chromium; our initial results are presented here.

2. Experimental details

2.1. General considerations

All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Infrared data were obtained on an ATI Mattson Genesis FT-IR spectrometer. KBr pellets for IR spectroscopy were prepared as previously described [7]. Solution magnetic susceptibility data were obtained in C_6D_6 using the Evans' NMR method [8–11]. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY or by the University of Illinois Microanalytical Laboratory.

2.2. Materials

Chromium(II) chloride was a commercial sample (Aldrich) and was used as received. K[Cp^{3i}] and K[Cp^{4i}] were prepared by literature routes [7]. $K[C_5(t\text{-Bu})_2H_3]$ was prepared from the reaction of $C_5(t\text{-Bu})_2H_4$ [12] and KH in THF. Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. C_6D_6 was vacuum distilled from Na:K (22:78) alloy and stored over 4A molecular sieves.

2.3. Synthesis of bis(triisopropylcyclopentadienyl) chromium(II), $(Cp^{3i})_2Cr$

Chromium(II) chloride (0.22 g, 1.8 mmol) and K[Cp^{3i}] (0.83 g, 3.6 mmol) were dissolved in 30 ml of THF in a 125 ml Erlenmeyer flask containing a magnetic stirring bar. The initially green mixture turned red-violet after 1 h. After being stirred overnight, it was evaporated to dryness and extracted with 30 ml of hexanes. Removal of precipitated KCl through a medium glass frit left an orange-red filtrate that was subsequently evaporated to dryness. The resulting solid was fractionally sublimed (100–120°C, 10^{-6} torr) to give red-orange $(Cp^{3i})_2Cr$ (0.61 g, 78% yield), m.p. 154–156°C. Anal. Calc. for $C_{28}H_{46}Cr$: C 77.37, H 10.67. Found: C 77.17, H 10.19%. Principal IR bands (KBr, cm^{-1}): 2963 (vs), 2873 (s), 1458 (s), 1371 (s), 1315 (sh), 1267 (s), 1095 (s), 1025 (s), 805 (s), 568 (m). Magnetic susceptibility: $\mu_{corr} = 3.17\ \mu_B$. X-ray quality crystals were grown by slow evaporation from a saturated hexane:toluene (50:50) solution.

2.4. Synthesis of bis(tetraisopropylcyclopentadienyl)-chromium(II), $(Cp^{4i})_2Cr$

In a procedure similar to that for $(Cp^{3i})_2Cr$, a 125 ml Erlenmeyer flask containing a magnetic stirring bar was charged with chromium(II) chloride (0.06 g, 0.46 mmol) and K[Cp^{4i}] (0.25 g, 0.92 mmol). THF (30 ml) was added and the mixture was stirred overnight, after which it was evaporated to dryness. Extraction of the residue with 30 ml of hexanes and filtration through a medium glass frit gave a burgundy filtrate. The filtrate was evaporated to dryness, leaving a dark red-brown solid. Brick-red $(Cp^{4i})_2Cr$ was isolated upon fractional sublimation at 120–140°C/10^{-6} torr (0.17 g, 72% yield), m.p. 225–227°C. Anal. Calc. for $C_{34}H_{58}Cr$: C 78.71, H 11.27. Found: C 78.48, H 11.19%. Principal IR bands (KBr, cm^{-1}): 2964 (vs), 2874 (m), 1559 (w), 1458 (m), 1370 (m), 1320 (w), 1260 (m), 1174 (w), 1095 (vs), 1024 (vs), 936 (w), 859 (w), 804 (vs), 557 (w). Magnetic susceptibility: $\mu_{corr} = 2.94\ \mu_B$.

2.5. Synthesis of bis(di-t-butylcyclopentadienyl)-chromium(II), $[C_5(t\text{-Bu})_2H_3]_2Cr$

In a procedure similar to that used for $(Cp^{3i})_2Cr$, chromium(II) chloride (0.14 g, 1.2 mmol), $K[C_5(t\text{-Bu})_2H_3]$ (0.50 g, 2.3 mmol) and THF (30 ml) were added to a 125 ml Erlenmeyer flask containing a magnetic stirring bar. The mixture was stirred overnight, after which it was evaporated to dryness. Extraction of the residue with 30 ml of hexanes followed by filtration through a medium glass frit gave an orange-brown residue. The filtrate was evaporated to dryness, leaving an orange-brown solid. Fractional sublimation (110–125°C/10^{-6} torr) of the solid gave burnt-orange $[C_5(t\text{-Bu})_2H_3]_2Cr$ (0.30 g, 64% yield), m.p. 182–184°C. Anal. Calc. for $C_{26}H_{42}Cr$: C 76.80, H 10.42. Found: C 76.89, H 10.15%. Principal IR bands (KBr, cm^{-1}): 2969 (vs), 2867 (s), 1704 (s), 1560 (m), 1466 (s), 1393 (m), 1364 (s), 1252 (m), 1210 (m), 1059 (m), 1022 (m), 808 (m), 442 (m). Magnetic susceptibility: $\mu_{corr} = 3.13\ \mu_B$.

2.6. X-ray crystallography of $(Cp^{3i})_2Cr$

A suitable crystal of the compound was located and sealed in a glass capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer with graphite monochromated Cu–K_α ($\lambda = 1.54178$ Å) radiation. Relevant crystal and data collection parameters for the present study are given in Table 1.

Cell constants and orientation matrices for data collection were obtained from systematic searches of limited hemispheres of reciprocal space; sets of diffraction maxima were located whose setting angles were refined by least squares. The space group $P\bar{1}$ was determined from consideration of unit cell parameters and a statistical analysis of intensity distribution. Subsequent solution and refinement of the structure confirmed the choice.

Data collection was performed using continuous $\omega-2\theta$ scans with stationary backgrounds (peak:background counting time = 2:1). Data were reduced to a unique set of intensities and associated sigma values in the usual manner. The structure was solved by direct methods (SHELXS-86, DIRDIF) and Fourier techniques. All non-H atoms were refined anisotropically. All but four H atoms (on one of the isopropyl groups) were located and refined isotropically. The remaining H atoms were inserted in calculated positions based on packing considerations and $d(\text{C–H}) = 0.95$ Å. The positions were fixed for the final cycles of refinement. A final difference map was featureless. Fractional coordinates and isotropic thermal parameters for all atoms are listed in Table 2; selected bond distances and angles are listed in Table 3.

3. Results and discussion

3.1. Synthesis and properties of the chromocenes

Using as a basis a literature preparation for a Cr(II) precursor [13], our initial attempts at synthesizing the isopropyl-substituted chromocenes employed the zinc reduction of chromium(III) chloride followed by reaction with either K[Cp^{3i}] or K[Cp^{4i}] in THF. However, upon workup of the reaction mixtures, no chromium-containing compounds were isolated; the related zincocenes $(Cp^{3i})_2Zn$ and $(Cp^{4i})_2Zn$ were recovered instead [14].

Table 1
Crystal data and summary of X-ray data collection for $(Cp^{3i})_2Cr$

Formula	$C_{28}H_{46}Cr$
F_w	434.67
Crystal color	Orange–red
Crystal dimensions (mm)	0.60 × 0.35 × 0.25
Space group	$P\bar{1}$
Lattice parameters	
a (Å)	9.146(4)
b (Å)	9.406(3)
c (Å)	8.811(4)
α (°)	100.08(3)
β (°)	117.15(3)
γ (°)	75.98(3)
V (Å^3)	652.6(5)
Z	1
$D_{calc.}$ (g cm^{-3})	1.106
Radiation type	Cu–K$_\alpha$
μ (cm^{-1})	37.0
Transmission factors	0.56–1.00
Scan speed (° min^{-1})	4.0
Scan width	$1.52+0.30\tan\theta$
Limits of data collection (°)	$20\leq 2\theta \leq 120$
Total reflections	2082
Unique reflections	1943
No. with $I>3.0\sigma(I)$	1612
$R(F)$, $R_w(F)$	0.041, 0.051
Goodness-of-fit	1.84
Max Δ/σ in final cycle	0.06
Max/min difference peak and hole (e Å^{-3})	0.21, −0.22

Table 2
Fractional coordinates and equivalent isotropic thermal parameters for $(Cp^{3i})_2Cr$

Atom	x/a	y/b	z/c	U_{eq} (Å^2)[a]
Cr(1)	0.5	0.5	0.5	3.67(4)
C(2)	0.2694(4)	0.5526(4)	0.2681(4)	4.4(1)
C(3)	0.2342(4)	0.5073(4)	0.3919(4)	4.5(1)
C(4)	0.3176(4)	0.3610(4)	0.4290(4)	4.2(1)
C(5)	0.4088(4)	0.3123(4)	0.3275(4)	4.2(1)
C(6)	0.3774(4)	0.4316(4)	0.2307(4)	4.5(2)
C(7)	0.2028(5)	0.6976(5)	0.1873(5)	5.8(2)
C(8)	0.177(1)	0.6844(9)	0.0125(9)	16.0(6)
C(9)	0.0590(9)	0.7865(7)	0.213(1)	13.1(4)
C(10)	0.2974(5)	0.2690(5)	0.5406(5)	5.1(2)
C(11)	0.1403(7)	0.2027(7)	0.4400(8)	7.5(3)
C(12)	0.2918(7)	0.3535(7)	0.7008(6)	7.2(3)
C(13)	0.5051(5)	0.1610(4)	0.3095(5)	5.2(2)
C(14)	0.3897(8)	0.0648(6)	0.1718(7)	7.4(3)
C(15)	0.6511(7)	0.1627(7)	0.2721(8)	7.7(3)
H(1)	0.162(4)	0.565(3)	0.438(4)	5.0(8)
H(2)	0.425(4)	0.428(3)	0.165(4)	4.1(7)
H(3)	0.719(5)	0.062(5)	0.267(5)	8(1)
H(4)	0.734(7)	0.228(6)	0.345(7)	10(1)
H(5)	0.611(8)	0.202(6)	0.176(7)	11(1)
H(6)	0.449(5)	−0.028(5)	0.164(5)	7(1)
H(7)	0.347(5)	0.111(4)	0.065(5)	7(1)
H(8)	0.298(8)	0.058(6)	0.175(8)	12(1)
H(9)	0.548(4)	0.121(4)	0.408(4)	4.8(8)
H(10)	0.386(4)	0.195(3)	0.574(4)	3.6(7)
H(11)	0.139(5)	0.144(5)	0.517(5)	8(1)
H(12)	0.143(6)	0.142(5)	0.341(6)	8(1)
H(13)	0.034(7)	0.285(6)	0.405(6)	10(1)
H(14)	0.287(5)	0.290(4)	0.766(5)	7(1)
H(15)	0.184(6)	0.439(5)	0.666(6)	10(1)
H(16)	0.390(6)	0.390(5)	0.764(5)	8(1)
H(17)	0.294(7)	0.757(6)	0.232(7)	11(1)
H(18)	0.156(6)	0.776(6)	−0.035(7)	10(1)
H(19)	0.213(8)	0.618(7)	−0.041(8)	12(1)
H(20)	0.0710	0.6591	−0.0601	19.2
H(21)	0.0825	0.7911	0.3300	15.7
H(22)	0.0389	0.8829	0.1799	15.7
H(23)	−0.0366	0.7430	0.1451	15.7

[a] $U_{eq} = \frac{8\pi^2}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$

The need for a reducing agent such as zinc was eliminated by using a divalent chromium precursor. $(Cp^{3i})_2Cr$, $(Cp^{4i})_2Cr$ and $[C_5(t\text{-Bu})_2H_3]_2Cr$ were prepared in good yield (> 60%) by the metathetical reaction of K[Cp^{3i}], K[Cp^{4i}] and K[$C_5(t\text{-Bu})_2H_3$], respectively, with $CrCl_2$ in THF (Eq. 1):

$$2KCp' + CrCl_2 \rightarrow Cp'_2Cr + 2KCl\downarrow \text{ (where } Cp' = Cp^{3i}, Cp^{4i}, C_5(t\text{-Bu})_2H_3) \quad (1)$$

The metallocenes were isolated by hexanes extraction of the reaction mixtures, and each was purified using fractional sublimation under high vacuum. Like Cp_2Cr [15] and Cp^*_2Cr [16], $(Cp^{3i})_2Cr$, $(Cp^{4i})_2Cr$ and $[C_5(t\text{-Bu})_2H_3]_2Cr$ are highly air- and moisture-sensitive. This behavior exists despite the presence of multiple isopropyl and *t*-butyl substituents, and suggests that they do not effectively shield the metal centers from attack by oxygen or water.

The paramagnetic nature of the chromocenes was confirmed by magnetic susceptibility measurements with the Evans' NMR method in C_6D_6 solution. The experimentally determined values of 3.17, 2.94 and 3.13 μ_B for $(Cp^{3i})_2Cr$, $(Cp^{4i})_2Cr$ and $[C_5(t\text{-Bu})_2H_3]_2Cr$, respectively, are higher than the spin-only value of 2.83 μ_B, but are typical for chromocenes (e.g. Cp_2Cr 2.97 [17], Cp^*_2Cr, 3.01 [16], $(C_5Ph_4H)_2Cr$ 2.90 μ_B [6]). With 16-electrons and high axial symmetry, chromocene itself should have an orbitally-degenerate ground state. An orbital angular momentum contribution is then possible that will raise the magnetic moment above the spin-only value [18]. Some of the degeneracy will be removed in a D_{5d} symmetry environment, and the angular momentum should be completely quenched in a low symmetry chromocene such as $(Cp^{3i})_2Cr$ (C_i). In $(C_5Ph_4H)_2Cr$ (which also possesses C_i symmetry), the energy difference between the levels is estimated to be small, and the symmetry emulates the effect of the Jahn–Teller-distorted $^3E_{2g}$ ground state of Cp_2Cr [6]; similar energy level differences may be present in $(Cp^{3i})_2Cr$, $(Cp^{4i})_2Cr$ and $[C_5(t\text{-Bu})_2H_3]_2Cr$.

The addition of electron-donating isopropyl and *t*-butyl groups to the Cp ring does not change the low-spin ground state of the corresponding chromocene. This is different from the behavior with the related manganocenes [3]. $(Cp^{3i})_2Mn$ exists in a low-spin/high-spin equilibrium, whereas $(Cp^{4i})_2Mn$, despite the presence of additional electron-donating groups, is entirely high-spin from room temperature down to 10 K. The fact that the $(Cp^{3i})_2Cr/(Cp^{4i})_2Cr$ pair does not exhibit similar behavior indicates that the high-spin/low-spin energy gap is greater in the chromocene systems, and cannot be readily perturbed by steric effects.

Table 3
Selected bond distances (Å) and angles (°) for $(Cp^{3i})_2Cr$

Bond distances (Å)			
Cr(1)–C(2)	2.187(3)	C(2)–C(3)	1.423(5)
Cr(1)–C(3)	2.157(3)	C(2)–C(6)	1.414(5)
Cr(1)–C(4)	2.169(3)	C(3)–C(4)	1.416(5)
Cr(1)–C(5)	2.177(3)	C(4)–C(5)	1.434(4)
Cr(1)–C(6)	2.165(3)	C(5)–C(6)	1.423(5)
Cr(1)–Cent[a]	1.803	C(ring)–CH (av)	1.50(1)
$CH–CH_3$ (av)	1.50(2)		
Bond angles (°)			
$CH_3–CH–CH_3$ (av)	110.8(8)	Cent–Cr(1)–Cent	180
Norm[b]–Cr(1)–Norm	180		

The average displacement of methine carbon from ring plane was 0.10 Å and the planarity of rings was within 0.002 Å.

[a] Cent, ring centroid. [b] Norm, ring normal.

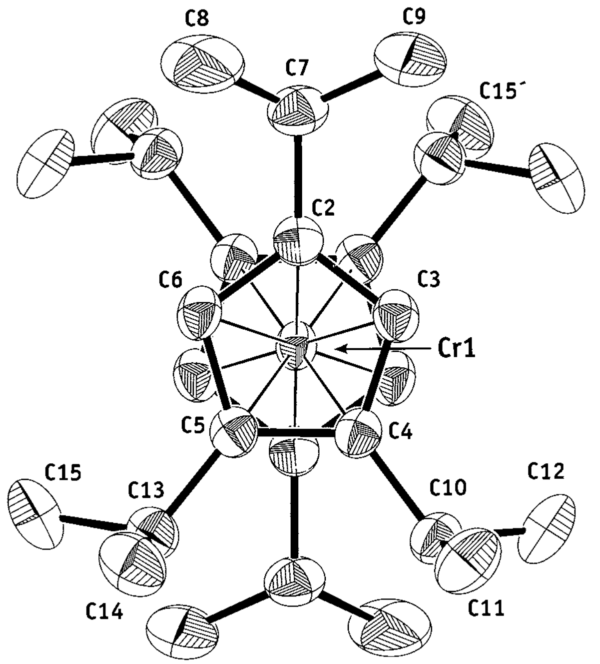

Fig. 1. ORTEP diagram of the non-H atoms of $(Cp^{3i})_2Cr$, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level.

3.2. Solid state structure of $(Cp^{3i})_2Cr$

Crystals of $(Cp^{3i})_2Cr$ were grown by slow evaporation of a saturated hexane:toluene (50:50) solution and studied with X-ray diffraction. The molecule displays a classic sandwich geometry with rigorously parallel rings by virtue of a crystallographically-imposed inversion center at the chromium atom. As a result, $(Cp^{3i})_2Cr$ is isomorphous and isostructural with both $(Cp^{3i})_2Fe$ and $(Cp^{3i})_2Co$ [4]. An ORTEP view of the molecule displaying the numbering scheme used in the tables is provided in Fig. 1.

The average Cr–C distance of 2.17(1) Å is intermediate between the 2.151(4) distance of $(C_5H_5)_2Cr$ [19] and the 2.197(5) Å length found in $(C_5PhH_4)_2Cr$ [6]. The range of Cr–C distances in $(Cp^{3i})_2Cr$ is 2.157(3)–2.187(3) ($\Delta = 0.030$ Å), is essentially the same as in $(C_5H_5)_2Cr$, (2.136(3)–2.171(4), $\Delta = 0.035$ Å) but notice-

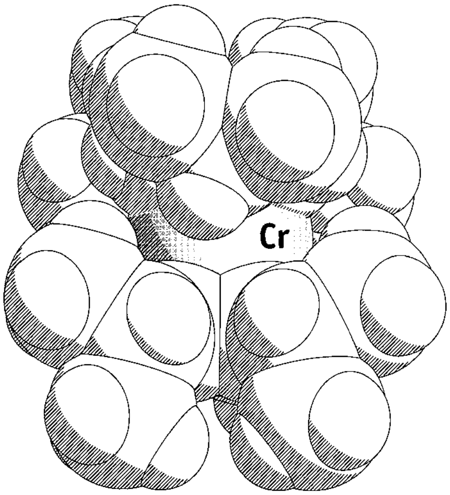

Fig. 2. Space-filling model of $(Cp^{3i})_2Cr$, illustrating the manner in which the isopropyl orientations minimize close inter-ring contacts.

ably less than the range in $(C_5HPh_4)_2Cr$ (2.141(5)–2.234(5), $\Delta = 0.093$ Å). The larger range of metal-ring carbon distances of $(C_5HPh_4)_2Cr$ is probably a result of the steric requirements of eight phenyl groups, whereas the six isopropyl substituents of $(Cp^{3i})_2Cr$ necessitate only small adjustments to the metal-ring carbon distances.

To minimize inter-ring contacts between ring substituents in $(Cp^{3i})_2Cr$, the rings adopt a perfectly staggered orientation with the isopropyl groups exhibiting angles of 18.6, 70.8 and 65.0° (involving C(2), C(4), and C(5), respectively) in relation to the Cp ring plane. A result of these orientations is that the metallocene is largely strain-free (Fig. 2). Some displacement of the isopropyl methine carbons out of the ring plane (av 0.10 Å) occurs, but the closest inter-ring contact involving the isopropyl groups is 4.09 Å (between C(9) and C(15)′), which is outside the sum of the van der Waals radii for two methyl groups (ca. 4.0 Å) [20].

4. Conclusions

The preparation of $(Cp^{3i})_2Cr$, $(Cp^{4i})_2Cr$ and $[C_5(t\text{-}Bu)_2H_3]_2Cr$ is accomplished by straightforward halide elimination reactions from chromium(II) chloride, although in the case of the isopropyl-substituted metallocenes, the zinc-mediated reduction of a Cr(III) precursor led instead to the formation of zincocenes. This indicates that the formation of chromocenes with sterically bulky ligands may be sensitive to the synthetic approach used, although once the compounds are formed, their physical and structural properties may be similar to unsubstituted chromocene.

Note added in proof: After the submission of this article, Sitzmann et al. (H. Sitzmann, M. Schlär, E. Dormann, M. Kelemen, Z. Anorg. Allg. Chem. 623 (1997) 1850–1852) reported an alternate synthesis of $(Cp^{4i})_2Cr$. In the solid state, it displays a gradual low-spin/high-spin transition on warming to 300 K, in contrast to the solution behavior described here.

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