

Notes

Addition of the Iminium Salt $[\text{Me}_2\text{N}=\text{CMe}_2][\text{BF}_4]$ to the Reductively Activated Benzene in $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ Jian Bao, Sang-Hee Ko Park, Steven J. Geib,[†] and N. John Cooper*

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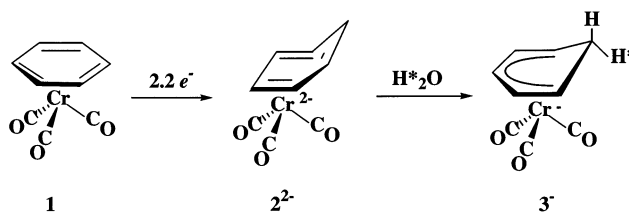
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Summary: The iminium salt $[\text{Me}_2\text{N}=\text{CMe}_2][\text{BF}_4]$ (**4BF₄**) adds to the reductively activated η^4 -benzene ligand in $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ (**2²⁻**) to give the aminoalkyl-substituted η^5 -cyclohexadienide Cr(0) complex $[\text{Cr}(\eta^5\text{-C}_6\text{H}_6)(\text{CMe}_2\text{NMe}_2)(\text{CO})_3]^-$ (**5⁻**). The unusual upfield chemical shift in NMR spectra of the methyl protons and carbons, which are positioned right above the cyclohexadienide ligand by an exo-addition, suggests a magnetic shielding effect indicative of a modest ring current despite the open conjugation of the cyclohexadienyl ligand. The analogous Mn(1) complex $[\text{Mn}(\eta^5\text{-C}_6\text{H}_6)(\text{CMe}_2\text{NMe}_2)(\text{CO})_3]$ (**6**) has been crystallographically characterized.

Introduction

Reactions of arene metal tricarbonyl complexes have been intensively studied with a view to their potential applications in organic synthesis,¹ and the electrophilicity of the “M(CO)₃” moiety in $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]$ (**1**), for example, facilitates reactions such as nucleophilic attack and proton abstractions on the arene ligand.²

Complex **1** also, however, undergoes two-electron reduction to give the dianion $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ (**2²⁻**), in which the reactivity of the arene ligand has been reversed and the arene is highly activated toward electrophiles, including mild proton sources such as water and other weak acids (Scheme 1).³ Our group reported earlier that the carbon-centered electrophile carbon dioxide adds to **2²⁻** to give $[\text{Cr}(\eta^5\text{-C}_6\text{H}_6\text{CO}_2)(\text{CO})_3]^{2-}$, with the carboxylate group as an endo-substituent of the cyclohexadienyl ligand;⁴ given the steric bulk of the coordinated metal, we have interpreted the observation that both protons and CO₂ add to the endo-position on the arene ring as a consequence of metal-mediated reaction pathways. In sharp contrast, when **2²⁻** reacts with benzyl halides, the product $[\text{Cr}(\eta^5\text{-C}_6\text{H}_6\text{-}$

Scheme 1. Reductive Activation of Benzene Coordinated to “[Cr(CO)₃”

$\text{CH}_2\text{Ph})(\text{CO})_3]^-$ was formed by an exo addition: this excludes a metal-mediated mechanism and is consistent with a sterically controlled radical addition mechanism.

Reductive activation of benzene by “[Cr(CO)₃]²⁻” could be a useful strategy for the modification of aromatic ligands, but we have had difficulty in identifying adducts other than CO₂ and benzyl halides that add to **2²⁻**: the major reason for this is that dianionic **2²⁻** is a powerful reductant and participates in rapid electron transfer to most electrophiles. Iminium salts are valuable electrophilic reagents that react with many nucleophiles and reducing reagents,⁵ and as part of our efforts to develop the synthetic potential of **2²⁻**, we now wish to report that the dianionic complex **2²⁻** adds to the iminium cation $[\text{Me}_2\text{N}=\text{CMe}_2]^+$ (**4⁺**) to give the monoanionic adduct $[\text{Cr}(\eta^5\text{-C}_6\text{H}_6)(\text{CMe}_2\text{NMe}_2)(\text{CO})_3]^-$ (**5⁻**). The analogous Mn(1) complex $[\text{Mn}(\eta^5\text{-C}_6\text{H}_6)(\text{CMe}_2\text{NMe}_2)(\text{CO})_3]$ (**6**) has also been prepared by addition of **4⁺** to $[\text{Mn}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^-$ (**7⁻**), and this has allowed us to establish crystallographically that the addition occurs with exo stereochemistry.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen by means of standard Schlenk techniques or a Vacuum Atmospheres Drybox as described in recent publications from this group.⁶

All solvents were freshly distilled under nitrogen before use. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were predried over sodium ribbon. THF was distilled from potassium, and

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[†] Address crystallographic correspondence to this author.

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Et₂O was distilled from sodium/benzophenone ketyl. *n*-Pentane was stirred over concentrated H₂SO₄ for more than 24 h, neutralized with K₂CO₃, and distilled from CaH₂. Deuterated NMR solvents were purchased from Cambridge Isotope Labs and used as received. Chromium carbonyl [Cr(CO)₆] was purchased from Strem Chemicals and used as received.

Metal naphthalenide solutions [M(C₁₀H₈)] (M = Li, K) were prepared by dissolution of freshly cut metal (Aldrich) in a solution (0.2 M) of naphthalene (1.0 equiv) in THF. The mixture was stirred for 8 h at room temperature, and naphthalenide solutions were stored at -80 °C. Solutions of KNap are dark blue, and solutions of LiNap are dark green.

Samples of [Cr(η⁶-C₆H₆)(CO)₃] (**1**) were prepared from [Cr(CO)₆] in 70% yield by a local modification of the literature procedure;⁷ samples of [Me₂N=CMe₂][BF₄] were prepared by condensation of anhydrous acetone and [H₂N=CMe₂][BF₄] in 54% yield by a variation of the Paukstelis procedure.⁸ Samples of [Mn(η⁶-C₆H₆)(CO)₃]PF₆ (**8**PF₆) were prepared by a variation of the method described by Wilkinson and co-workers⁹ as previously described.⁶

Instrumental Analysis. Infrared spectra were recorded on a Perkin-Elmer Model 783 spectrophotometer. IR spectra of low-temperature reactions were recorded at room temperature within 2 min of removing samples from -78 °C reaction mixtures. ¹H NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz. ¹³C NMR spectra were recorded on a Bruker AC 300 at 75 MHz. Microanalyses were performed by Atlantic Microlab, Norcross, GA. Crystals for X-ray diffraction studies were coated with fluorolube, then mounted on a glass fiber and coated with epoxy. X-ray data were collected on a Siemens P3 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Data processing and graphics were done with the Siemens SHELXTL package program. All non-hydrogen atoms were located and refined anisotropically.

Preparation of K[Cr(η⁵-C₆H₆CMe₂NMe₂)(CO)₃] (K5**) by Addition of [Me₂N=CMe₂]⁺ to K₂[Cr(η⁴-C₆H₆)(CO)₃] (**K2**).** A 2.2 M solution of freshly prepared KNap in THF (7.68 mL, 1.54 mmol) was added by syringe to a vigorously stirred solution of **1** (0.15 g, 0.7 mmol) in THF at -78 °C. IR spectra showed that ν_{C=O} absorption bands at 1810 (m), 1665 (s, br) cm⁻¹ (assigned to **2**²⁻) replaced the 1965 (s), 1890 (s) cm⁻¹ bands of complex **1**, indicating that complete reduction had occurred. The solution was kept at -78 °C, and [Me₂N=CMe₂][BF₄] (**5**[BF₄]) (0.277 g, 0.7 mmol) was added. The color of the solution changed instantly from deep blue to dark red, and the ν_{C=O} absorptions shifted to 1891 (s), 1790 (m), 1742 (m) cm⁻¹. The reaction was kept at -78 °C for 2 h before it was allowed to warm to 25 °C. After being stirred for another 3 h, the solid (KBF₄) was filtered, and the solvent was removed under reduced pressure. The material was then washed with pentane (50 mL × 3) and ether (30 mL × 2), then the residue was placed under vacuum overnight, to leave a red-orange powder of **K5** (0.119 g, 0.35 mmol, 50%). ¹H NMR (CD₃COCD₃, 297 K): δ 4.22 (t, J = 5 Hz, 1H, H_a), 3.91 (t, J = 6 Hz, 2H, H_b), 1.61 (m, 2H, H_c), 2.61 (t, J = 6 Hz, 1H, H_d), 1.44 (s, 6H, H_f), -0.05 (s, 6H, H_g). ¹³C NMR (CD₃CN, 297K): δ 243.90 (s, C_{CO}), 76.40 (d, C_a), 98.00 (d, C_b), 54.80 (d, C_c), 18.45 (d, C_d), 62.83 (s, C_e), 40.67 (q, C_f), 2.33 (q, C_g) (for numbering system, see Figure 1).

Preparation of [Mn(η⁵-C₆H₆CMe₂NMe₂)(CO)₃] (6**) by Addition of [Me₂N=CMe₂]⁺ to K[Mn(η⁴-C₆H₆)(CO)₃] (**K7**).** Fast addition of 2.2 equiv of KNap to a slurry of 0.4 g (1.1 mmol) of [Mn(η⁶-C₆H₆)(CO)₃]PF₆ (**8**PF₆) in THF at -78 °C resulted in an immediate change from a yellow slurry to an orange-brown solution and finally to an orange-brown slurry. IR spectra of new ν_{C=O} bands (IR, THF: 1940 (s), 1885 (s),

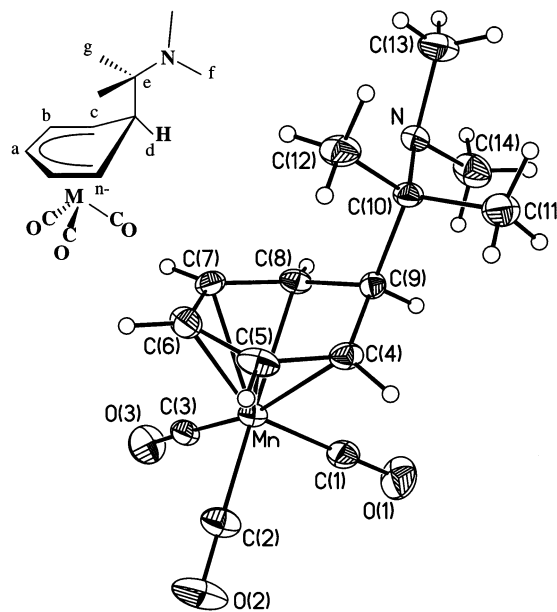


Figure 1. ORTEP drawing of [Mn(η⁵-C₆H₆)(CMe₂NMe₂)(CO)₃] (**6**) (35% probability ellipsoids).

and 1820 (s) cm⁻¹) assigned to [Mn(η⁴-C₆H₆)(CO)₃]K. The solution was then transferred into a 20 mL CH₂Cl₂ solution of [Me₂N=CMe₂][BF₄] (**4**[BF₄]) (0.19 g, 1.1 mmol) at -78 °C. IR spectra showed that ν_{C=O} absorptions at 2020 (s), 1940 (s, br) cm⁻¹ replaced the original bands. The reaction was warmed to 25 °C and stirred overnight. The solid (KBF₄) was filtered, and the solvent was removed under reduced pressure. The orange-brown residue was then extracted into pentane (60 mL × 3) and purified by silica gel flash chromatography, with pentane/ether as eluent. Bright yellow crystals of **6** were obtained by recrystallization from pentane solution at -80 °C. The crystals yielded 0.04 g of product (0.13 mmol, 12%). IR (ν_{C=O}, *n*-pentane): 2025 (vs), 1955 (s), 1945 (s) cm⁻¹. ¹H NMR (C₆D₆, 297 K): δ 4.83 (t of t, J_{Ha-Hb} = 5, J_{Ha-Hc} = 1 Hz, 1H, H_a), 4.17 (t, J = 6 Hz, 2H, H_b), 2.71 (m, 3H, H_{c,d}), 1.89 (s, 6H, H_f), 0.34 (s, 6H, H_g). ¹³C NMR (C₆D₆, 297K): δ 223.4 (s, C_{CO}), 97.1 (d, C_b), 77.7 (d, C_a), 61.2 (s, C_e), 59.1 (d, C_d), 42.1 (d, C_d), 38.2 (q, C_f), 18.19 (q, C_g) (for numbering system, see Figure 1). Anal. Calcd for C₁₄H₁₈MnNO₃: C, 55.45; H, 5.98; N, 4.64. Found: C, 54.73; H, 5.86; N 4.38. MS (CI⁻, CH₄): *m/z* 303 (100, M⁻); 275 (429, [M - CO]⁻); 218 (2.3, 7⁻).

Results and Discussion

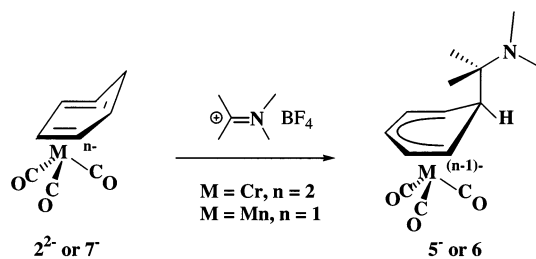
Complex [Cr(η⁶-C₆H₆)(CO)₃] (**1**) can be conveniently activated toward electrophiles through naphthalenide (M₂NaP) reduction.¹⁰ After addition of 2 equiv of KNap to a THF solution of **1** at -78 °C, the IR absorptions assigned to ν_{C=O} bands shifted from the original 1965 (s), 1890 (s) cm⁻¹ to 1810 (m), 1665 (m, br) cm⁻¹. These bands are assigned to dianionic [Cr(η⁴-C₆H₆)(CO)₃]²⁻ (**2**²⁻) and are consistent with complete two-electron reduction. Under a flow of N₂, 1 equiv of 1,1-dimethyl *N,N*-dimethyliminium fluoborate ([Me₂N=CMe₂][BF₄]) (**4**BF₄) was added, the color of the solution changed instantly from dark green to brown, and a new set of ν_{C=O} bands appeared at 1891 (s), 1790 (m), 1742 (m)/cm⁻¹: their position is consistent with oxidation of the metal center relative to **2**²⁻. The reaction was allowed to run at -78 °C for 1 h and was then stirred overnight

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Scheme 2. Iminium Salt Addition to Activated Benzene Ligand**Table 1. Crystal Data and Structure Refinement for 6**

empirical formula	C ₁₄ H ₁₈ MnNO ₃
fw	203.23
temp, wavelength	293(2) K, 0.71073 Å
cryst syst, space group	monoclinic, P2 ₁ /c
unit cell dimens	a = 11.963(3) Å, α = 90° b = 11.923(2) Å, β = 111.45° c = 10.627(3) Å, γ = 90°
volume	1410.8(6) Å ³
Z, calcd density	3, 1.428 Mg/m ³
abs coeff	0.938 mm ⁻¹
F(000), cryst size	632, 0.21 × 0.22 × 0.34 mm
θ range for data collection	2.50–27.49°
limiting indices	–15 ≤ h ≤ 14, –15 ≤ k = 0, 0 ≤ l ≤ 13
reflns collected, unique	3409, 3247 [R _{int} = 0.0297]
refinement method	full-matrix least-squares on F ²
data/restraints/params	3247/0/245
goodness-of-fit on F ²	1.052
final R indices [I > 2σ(I)]	R1 = 0.0487, wR2 = 0.1144
R indices (all data)	R1 = 0.0710, wR2 = 0.1296
extinct coeff	0.016(2)
largest diff peak and hole	1.244 and –0.434 e Å ⁻³

at ambient temperature before the product was purified. The resulting complex is a red-orange solid, characterized as K[Cr(η^5 -C₆H₆)(CMe₂NMe₂)(CO)₃] (K5) by IR and ¹H, ¹³C NMR, as shown in the Experimental Section (Scheme 2).

Because of the contrasting endo and exo stereochemistry of CO₂ and benzyl halide addition to **2**²⁻, it was important to determine the stereochemistry of addition of **4**⁺ to **2**²⁻, and we attempted to grow crystals of K5. Unfortunately, the anionic complex **5**⁻ is very sensitive toward air and moisture, and attempts to grow high-quality crystals were not successful and did not even generate analytically pure samples. We therefore prepared the Mn analogue, [Mn(η^5 -C₆H₆)(CMe₂NMe₂)(CO)₃] (**6**), which as a neutral species is likely to be more stable than **5**⁻. Complex [Mn(η^6 -C₆H₆)(CO)₃]PF₆ (**8**PF₆) was reduced with 2.2 equiv of KNap at –78 °C to give [Mn(η^4 -C₆H₆)(CO)₃]⁻ (**7**⁻). The $\nu_{C=O}$ IR absorption bands of **7**⁻ appeared at 1940 (s), 1885 (s), and 1820 (s) cm⁻¹. One equivalent of **4**BF₄ was then added, the color of the solution changed instantly from red-brown to orange, and a new set of $\nu_{C=O}$ bands appeared at 2020 (s) and 1940 (s, br) cm⁻¹ assigned to complex **6**. The product was isolated as a bright yellow crystalline solid and characterized as **6** by IR, ¹H and ¹³C NMR, elemental analysis, and MS, as reported in the Experimental Section. Slow cooling of a pentane solution of **6** to –78 °C gave us crystallographic grade crystals, which we used for X-ray diffraction data that established the structure shown in Figure 1 with the crystallographic data in Table 1; selected bond lengths and bond angles are listed in Table 2.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

Mn–C(1)	1.795(4)	Mn–C(2)	1.805(3)
Mn–C(3)	1.800(3)	Mn–C(4)	2.232(3)
Mn–C(5)	2.133(3)	Mn–C(6)	2.127(3)
Mn–C(7)	2.143(7)	Mn–C(8)	2.229(3)
O(1)–C(1)	1.144(4)	O(2)–C(2)	1.138(4)
O(3)–C(3)	1.143(4)	N–C(10)	1.486(4)
N–C(14)	1.460(5)	N–C(13)	1.454(4)
C(4)–C(5)	1.370(5)	C(5)–C(6)	1.415(5)
C(4)–C(9)	1.505(4)	C(9)–C(10)	1.561(4)
C(6)–C(7)	1.412(5)	C(7)–C(8)	1.386(4)
C(12)–C(10)	1.523(4)	C(8)–C(9)	1.510(4)
C(1)–Mn–C(3)	92.5(2)	C(2)–Mn–C(1)	94.1(2)
C(3)–Mn–C(2)	89.2(2)	O(1)–C(1)–Mn	179.1(3)
O(2)–C(2)–Mn	179.3(3)	O(3)–C(3)–Mn	178.0(3)

Comparison of ¹H NMR spectra of **5**⁻ with those of **6** indicated that the molecules contain cyclohexadienyl ligands with the same exo stereochemistry for the iminium addition. The splitting pattern observed for the endo protons of cyclohexadienyl compounds in ¹H NMR spectra features characteristic coupling of 6 Hz to the protons on vicinal carbon C_c; this feature was observed in the ¹H NMR spectrum of **5**⁻ and supports the proposed exo-addition stereochemistry.^{3,11} The structure of **6** is exceptional: the cyclohexadienyl ligand has the expected η^5 -coordination with the aminoalkyl addend in the exo position. The molecule has C_i symmetry with one CO ligand underneath C_d, consistent with the CO stretch pattern: the three IR absorption bands for $\nu_{C=O}$ are assigned to two asymmetric stretches and one symmetric stretch. The bond length of C(9)–C(10) for **6** is slightly longer than a C–C single bond at 1.561 Å, indicative of the steric hindrance around quaternary carbon C(10). The dihedral angle between planes C_c–C_d–C_c and C_a–C_b–C_c in **6** (an important parameter in determining the electronic structure of **6**¹²) is 34.4° and is smaller than the 43° in C₆H₇Mn(CO)₃.¹³

A significant counterion effect was observed in addition reactions to **2**²⁻. Addition of **4**BF₄ to K₂**2** is complete, as monitored by IR, within 1 h at –78 °C, but when lithium naphthalenide (LiNap) is employed as the reducing reagent (to give Li₂**2** as the Cr substrate), the electrophilic addition of **4**⁺ to Li₂**2** is very slow. After the iminium salt has been mixed with the reduced substrate and the solution had been stirred for more than 4 h under –78 °C, Li₂**2** remained as the major carbonyl complex in solution, as shown by IR spectra. Warming of the reaction mixture to a higher temperature resulted in decomposition of the dianionic species and left a poor yield of K5 (<5%). The dependence of **4**⁺ additions on the alkali metal counterion for **2**²⁻ can be explained if the Li⁺ counterion forms contact ion pairs with **2**²⁻; this is consistent with the position and complexity of $\nu_{C=O}$ in IR spectra¹⁴ of Li₂**2**, and contact ion pairing would reduce the nucleophilicity of **2**²⁻.¹⁵

The observation that **4**BF₄ adds to the hydrocarbon ligand in the η^4 -benzene complexes is quite surprising,

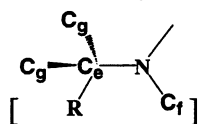
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(14) Li₂**2** in THF showed $\nu_{C=O}$ absorption bands at 1665 (w), 1740 (m), 1816 (w), 1845 (m), 1896 (w) cm⁻¹, more complicated than the simple 1810 (s), 1665 (m, br) cm⁻¹ absorptions of K₂**2** in THF solution.

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Table 3. Electronic Effects of the Substituents on the Tetramethyl Amine

δ ppm	R			
	Ph-	CH ₃ -	[Mn(η^5 -C ₆ H ₆)(CO) ₃]	[Cr(η^5 -C ₆ H ₆)(CO) ₃] ⁻
H _g	1.43	1.10	0.34	-0.05
H _f	2.27	2.27	1.89	1.44
C _g	28.4	28.5	18.2	2.33
C _f	36.1	36.2	38.2	40.7
C _e	64.3	57.6	61.2	62.8

especially in the case of **2**²⁻, which is extremely basic and reacts with H₂O instantly. The endo stereochemistry observed for deuteration of **2**²⁻ and **7**⁻ has established that the metal centers are the most basic sites in both anionic η^4 -benzene complexes; therefore, we had anticipated that proton abstraction of the acidic α -H in **4**BF₄ would occur in preference to ligand addition. Successful iminium addition to the benzene ligand may reflect steric inhibition of approach of **4**⁺ to the metal center.

Surprisingly, our attempts to add iminium salts other than **4**⁺ (including [Ph₂C=NMe₂]⁺, [H₂C=NMe₂]⁺, and [cyclohexyl₂C=NMe₂]⁺) to **2**²⁻ were not successful and generally ended with direct oxidation of **2**²⁻ to **1** by the iminium salt. Iminium salt addition to **7**⁻ was first reported by Park et al.¹⁶ and appears to be a general reaction in the manganese case. In that system evidence was presented that suggested that the reaction did not involve a single electron transfer (SET) mechanism;

(16) Park, S. K.; Geib, S. J.; Cooper, N. J. *J. Am. Chem. Soc.* **1997**, *119*, 8365.

when [Ph₂C=NMe₂]⁺ was mixed with a cold THF solution of **2**²⁻, however, the color of the solution turned to the distinctive blue violet that indicates the formation of radical [Ph₂CNMe₂][•]. This observation suggests that SET might occur in the Cr system, and the addition of **4**⁺ to the isoelectronic complexes **7**⁻ and **2**²⁻ may involve different mechanisms.

One of the most intriguing aspects of NMR spectra of **5**⁻ involves the unusually high-field shift of the methyl groups on the α -carbon (see Table 3). The contrast with the corresponding data for organic amines is marked and raises the possibility that there is electronic communication between those carbon atoms at the end of cyclohexadienyl ligand in **5**⁻ that gives rise to a significant ring current, a possibility that has been discussed in the case of the corresponding cycloheptatriene complex [$\{M(\text{CO})_3\}_2\{\mu-(\eta^6\text{-C}_7\text{H}_7\text{-}\eta^6\text{-C}_7\text{H}_7)\}$] (M = Cr, Mo, W).¹⁷ Since the methyl groups are located right above the cyclohexadienyl rings in **5**⁻ and **6**, these will be sensitive markers for ring current effects.

In conclusion, we have determined that iminium salt addition to reductively activated arene ligands can be extended from the Mn(-1) system to the Cr(-2) system, though the reaction was disappointingly restricted to date to permethylated **4**⁺.

Acknowledgment. This work was financially supported by the NSF through grant numbers CHE 9632202 (N.J.C.).

Supporting Information Available: Complete X-ray crystallographic data for **6** and NMR spectra for **K5** are available at <http://pubs.acs.org>.

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