ORGANOMETALLICS

Volume 21, Number 6, March 18, 2002

Communications

Isolation of a Stable *ansa*-Chromocene(III) Carbonyl Cation and Characterization of a Transient, Cationic *ansa*-Chromocene(IV) Carbonyl Hydride

David M. J. Foo, Piet-Jan Sinnema, Brendan Twamley, and Pamela J. Shapiro*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

Received December 17, 2001

Summary: Protonation of the metal occurs upon reaction of $Me_4C_2(C_5H_4)_2CrCO$ *with* $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ *at* −70 °C *in thf-*d_8. *The diamagnetic Cr(IV) hydride intermediate was characterized by* ^1H *NMR spectroscopy. Its decomposition to a paramagnetic product mixture upon warming to room temperature is accompanied by the evolution of 0.5 equiv of gas that is 54%* H_2 *and 46% CO. Crystals of the borate salt of the* $17e^-$ *ansa-chromocenium carbonyl cation* $[Me_4C_2(C_2H_4)_2CrCO]^+$ *were isolated from the product mixture for a molecular structure determination.*

The reaction chemistry of bent-sandwich dicyclopentadienylchromium complexes has been conspicuously absent from the literature despite the significant role that early transition metal-containing metallocenes have played and continue to play in our understanding of fundamental organo-transition-metal reactivity and their current prominence as homogeneous catalysts, particularly for olefin polymerization. Some of the earliest investigations into bent-metallocene chemistry involved molybdenocene and tungstenocene, which form a wide variety of derivatives and display a host of thermal and photochemical reactions including [2+2] additions and eliminations, the oxidative addition and reductive elimination of small molecules, α and β migrations and eliminations, and C−H bond activation.[1] The relative paucity of information on bent-chromocene complexes may be traced to a couple of problems. One is the preference of chromocene for the high-spin electronic configuration associated with a parallel ring geometry. This makes the pairing of electrons required for the coordination of ligands such as carbon monoxide thermodynamically unfavorable.[2] Another problem is the lability of chromocene toward the loss of one or both cyclopentadienyl rings in its reaction with small molecules.[1a,3]

Brintzinger and co-workers demonstrated that including an *ansa*-bridge between the rings stabilizes the bent-sandwich chromocene carbonyl derivative so that it can be isolated and structurally characterized.[4] The enhanced thermal stability of the *ansa*-chromocene carbonyl adduct has been confirmed in theoretical calculations by Simpson et al.[5] and by Green and Jardine.[6] These results have encouraged us to pursue

---

[1] (a) Morris, M. J. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Gordon, F., Wilkinson, G., Eds.; Pergamon: Oxford, 1992; Vol. 5, Chapter 7, and references therein. (b) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, Chapters 27.2 and 28.2, and references therein.

[2] (a) Brintzinger, H. H.; Lohr, L. L., Jr.; Tang Wong, K. L. *J. Am. Chem. Soc.* **1975**, *97*, 5146−5155. (b) Wong, K. L. T.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 5143−5146.

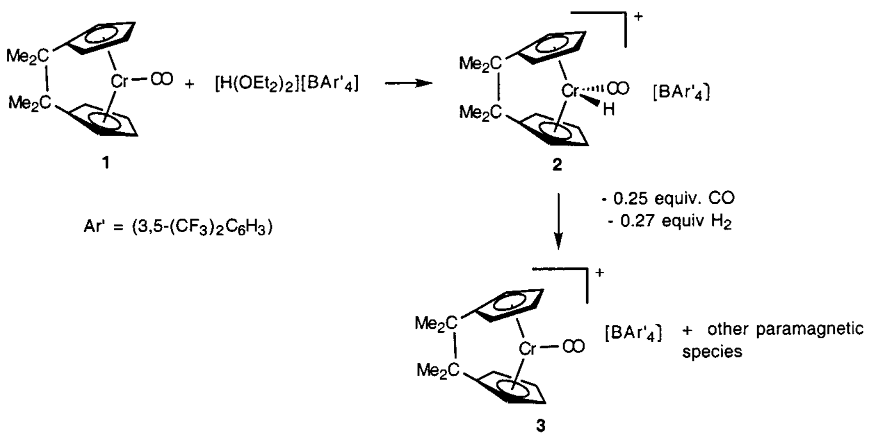
[3] (a) Sneeden, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975. (b) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel., E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, Chapter 26.2, and references therein.

[4] (a) Schaper, F.; Rentzsch, M.; Prosenc, M. H.; Rief, U.; Schmidt, K.; Brintzinger, H.-H. *J. Organomet. Chem.* **1997**, *534*, 67−79. (b) Schwemlein, H.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *256*, 285−289.

[5] Simpson, K. M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1992**, *11*, 4363−4364.

10.1021/om011066l CCC: $22.00 © 2002 American Chemical Society
Publication on Web 02/16/2002

Scheme 1



the *ansa*-chromocene derivatives as a means of gaining entry into the chemistry of the elusive bent-sandwich chromocene system. The development of a more convenient and higher-yielding synthetic route to *ansa*-chromocene carbonyl and isocyanide derivatives in our laboratory[7] has allowed us to prepare the complexes in sufficient quanitities for further chemical investigation. Described herein is the first structurally characterized bent-metallocene complex of Cr(III) and the NMR characterization of its Cr(IV) hydride precursor, which are formed through the protonation and subsequent one-electron oxidation of the neutral, 18 e$^-$ Cr(II) carbonyl derivative.

Brønsted acids have been employed previously for the one-electron oxidation of neutral Cp_2M complexes to form the corresponding parallel-ring metallocenium ions.[8] Since reversible electrochemical oxidation of *ansa*-chromocene carbonyl and isonitrile complexes has been demonstrated,[7a,9] this appeared to be a straightforward chemical approach to the corresponding cations. Indeed, reaction of $Me_4C_2(C_5H_4)_2CrCO$ (**1**) with the oxonium acid $[H(Et_2O)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$[10] afforded crystals of the Cr(III) species $[Me_4C_2(C_5H_4)_2CrCO][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (**3**), the structure of which was determined by X-ray crystallography.[11]

An ORTEP drawing of the *ansa*-chromocenium carbonyl portion of salt **3** is shown in Figure 1. The geometry of the cation is similar to that of the neutral species, **1**. The centroid−Cr−centroid angles for **1** and **3** are 143.3(5)° and 142.2(2)°, respectively, with associated dihedral angles between the Cp ring planes of 38.5° and 38.6°, respectively. The average Cr−Cp centroid distance of 1.808(5) Å for **3** is close to that of **1** (1.78(1) Å). The longer Cr−CO distance in **3** (1.893(6) vs 1.85(1) Å in **1**) and shorter CrC−O distance (1.133(7) vs 1.16(1) Å in **1**) reflect the higher oxidation state of the chromium center in **3**. The only other chromocene carbonyl cations that have been isolated and structurally characterized, $Cp(2,4\text{-}C_7H_{11})CrCO^+$ and $Cp^*(3\text{-}C_6H_9)CrCO^+$, contain an open η^5-pentadienyl ligand in place of one of the cyclopentadienyl rings.[12] Accurate structural details could only be obtained for the Cp* complex, for which the Cr−CO distance (1.858(7) Å) was slightly longer and the CrC−O distance (1.145(7) Å) slightly shorter than the corresponding distances in **3**, in keeping with the greater electron-releasing properties of the Cp* ring relative to Cp.

The intermediacy of a diamagnetic chromium(IV) hydride derivative (**2**) in the formation of **3** (Scheme 1) was established by monitoring the reaction by ^1H NMR spectroscopy. The ^1H NMR spectrum of the C_1-symmetric chromocenium carbonyl hydride derivative[13] is observed immediately upon mixing the reagents at −70 °C in thf-d_8. Complex **2** is stable in solution at −70 °C for at least 14 h and at −40 °C for at least 9 h. Upon warming the NMR sample above −25 °C, the signals

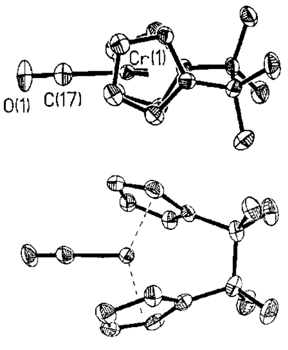


Figure 1. Top and side views of the cation portion of the molecular structure of **3**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths and angles (Å, deg): Cr−C(17) = 1.893(6); C(17)−O(1) = 1.133(7); Cr−cent (av) = 1.808(5); Cr−C(17)−O(1) = 178.8(5); cent−Cr−cent = 142.2(2).

---

(6) Green, J. C.; Jardine, C. N. *J. Chem. Soc., Dalton Trans.* **1999**, 3767−3770.

(7) (a) Foo, D. M. J.; Shapiro, P. J. *Organometallics* **1995**, *14*, 4957−4959. (b) Matare, G. J.; Foo, D. M.; Kane, K. M.; Zehnder, R.; Wagener, M.; Shapiro, P. J. *Organometallics* **2000**, *19*, 1534−1539.

(8) (a) Curphey, T. J.; Sater, J. O.; Rosenblum, M.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5249−5250. (b) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1972**, *40*, C29−C32. (c) Bitterwolf, T. E.; Ling, A. C. *J. Organomet. Chem.* **1973**, *57*, C15−C18. (d) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325−4329.

(9) van Raaij, E. U.; Mönkeberg, S.; Kiesele, H.; Brintzinger, H. H. *J. Organomet. Chem.* **1988**, *356*, 307−314.

(10) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920−3922.

(11) Crystallographic data for **3**: monoclinic, space group $P2_1$; a = 9.9402(9) Å, b = 16.4924(14) Å, c = 15.1391(13) Å, b = 105.4240(10)° at 203(2) K; V = 2392.5(4) Å^3; Z = 2; D_{calc} = 1.604 Mg/m^3, m_{abs} = 0.371 mm^{-1}, $F(000)$ = 1158, reflns collected = 14 377, indep reflns = 7487, R1 = 0.0534 ($I > 2\sigma(I)$, wR2 = 0.1427). Anal. Calcd for $C_{49}H_{36}BCrOF_{24}$: C, 50.74; H, 3.13. Found: C, 50.43; H, 3.28.

(12) Shen, J. K.; Freeman, J. W.; Hallinan, N. C.; Rheingold, A. L.; Arif, A. M.; Ernst, R. D.; Basolo, F. *Organometallics* **1992**, *11*, 3215−3224

(13) ^1H NMR (THF-d_8, −70 °C, 500 MHz): δ 7.90, 7.50 (2s, aryl-B, 12H), 6.00, 5.82, 5.80, 5.53 (4s, 8H, C_5H_4), 1.31, 1.26 (2s, 12H, $(CH_3)_4C_2$), −7.99 (1H, Cr-*H*).

due to **2** disappear, leaving only the signals for the borate counteranion and a new, very broad signal at -1.5 ppm.

Toepler pump measurements[14] showed the evolution of 0.5 ± 0.02 equiv of a noncondensable gas per chromium when the reaction was performed in toluene; however, IR analysis of the gas indicated that it contained a substantial amount of carbon monoxide. Oxidation of the gas to CO_2 and H_2O over a heated column of CuO revealed that the gas was 46% CO and 54% H_2. Thus, other paramagnetic species are formed along with **3**, possibly the 16e$^-$ chromocenium hydride ion and/or the 15e$^-$ chromocenium cation.[15] As a result, the reaction product exhibits a higher magnetic moment[16] ($\mu_{\mathrm{eff}} = 2.85\ \mu_B$) than that expected for a low-spin, 17e$^-$ complex. One-electron oxidation of **1** by $[CPh_3][B(C_6F_5)_4]$[17] in toluene affords the *ansa*-chromocene carbonyl salt $[Me_4C_2(C_5H_4)_2CrCO][B(C_6F_5)_4]$ (**4**) with only a small amount of CO gas evolution (0.08 equiv per Cr). The X-ray crystal structure of **4** was also determined. The geometric features of the chromocenium carbonyl cation fragment are very similar to that of **3** and will be reported elsewhere. The frequency of the carbonyl stretch in **4** (2002 cm^{-1}) is 100 cm^{-1} higher than that of neutral **1** (1905 cm^{-1}). A similar increase in C−O stretching frequencies is observed upon one-electron oxidation of half-open chromocene carbonyl complexes. A $\mu_{\mathrm{eff}} = 1.83\ \mu_B$ was measured for **4**, consistent with the spin-only value expected for a low-spin, 17e$^-$ species. Both **3** and **4** exhibit normal Curie magnetic behavior from 188 to 300 K and are ESR active at room temperature with *g* values close to 2.

Our ability to isolate and structurally characterize **3** and **4** is remarkable in light of the instability of neutral Cp_2CrCO (let alone its one-electron oxidation product) and highlights the influence of the *ansa*-bridge in stabilizing derivatives that are not isolable with the parent, unbridged chromocene system.[18] Detection of the diamagnetic Cr(IV) hydride intermediate **2** is also significant since it means that bent-sandwich chromocene(IV) derivatives of potential catalytic utility are chemically accessible. The only other dicyclopentadienylchromium(IV) derivatives that have been reported to date were formed by oxidative addition of XCN (X = halide), $(CN)_2$, and $(SCN)_2$ to Cp_2Cr.[19] These pseudohalide derivatives are paramagnetic and have not been crystallographically characterized.

In summary, we have isolated and structurally characterized the first stable chromocene carbonyl cation, which is formed by one-electron oxidation of the neutral chromocene carbonyl species by either a Brønsted acid or a trityl salt. The diamagnetic, cationic Cr(IV) hydride intermediate that is formed en route to **3** is a rare example of a bent-sandwich bis(cyclopentadienyl)chromium(IV) derivative and demonstrates that this oxidation state can play a role in the reaction chemistry of these systems. We are currently examining further the physical properties and reactivity of these bent-sandwich derivatives of Cr(III) and Cr(IV) and exploring their potential application to homogeneous catalysis.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (grant No. CHE-9816730), and the Department of Energy EPSCoR program (grant no. DE-FG02-98ER45709) for their generous financial support. The establishment of a Single-Crystal X-ray Diffraction Laboratory and the purchase of a 500 MHz NMR spectrometer were supported by the M. J. Murdock Charitable Trust of Vancouver, WA, the National Science Foundations, and the NSF-Idaho EPSCoR Program. The authors thank Dr. Alex Blumenfeld (University of Idaho) for his assistance with the NMR experiments, Professor Roger Willett (Washington State University) for the use of his ESR spectrometer, and Ms. Suh-Jane Lee for preparing the $[H(Et_2O)_2][B(3,5-(CF_3)_2C_6H_3)_4]$ and $[CPh_3][B(C_6F_5)_4]$.

Supporting Information Available: Crystallographic data for **3**, NMR spectra of **2**, ESR spectra of **3** and **4**, and synthetic and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM011066L

---

[14] Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1985; Chapter 4.

[15] Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882−1893.

[16] Magnetic susceptibility measurements were performed by the Evan's NMR method; see: Girolami, G. S.; Rauchfuss, T. B.; Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry*; University Science Books: Sausolito, 1999; pp 120−126.

[17] Ihara, E.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277−8278, Supporting Information, page 3.

[18] For more examples of the *ansa* effect see: (a) Churchill, D. G.; Bridgewater, B. M.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 178−179. (b) Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403−2406. (c) Shin, J. H.; Parkin, G. *Chem. Commun.* **1999**, 887−888. (d) Lee, H.; Desrosier, P. J.; Guzei, I.; Rheingold, A. L.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 3255−3256. (e) Conway, S. L. J.; Dijkstra, T.; Doerrer, L. H.; Green, J. C.; Green, M. L. H.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1998**, 2689−2695. (f) Chernega, A.; Cook, J.; Green, M. L. H.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225−3243. (g) Labella, L.; Chernega, A.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 395−399. (h) Heinekey, D. M.; Radzewich, C. E. *Organometallics* **1999**, *18*, 3070−3074.

[19] (a) Morán, M.; Fernández, V. *J. Organomet. Chem.* **1979**, *165*, 215−223. (b) Moràn, M.; Gayoso, M. *Z. Naturforsch.* **1983**, *38b*, 177−180.