

Zwitterionic Ring-Borylated *ansa*-Chromocene Complexes

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

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

Received April 22, 2002

Very little is known about the chemistry of bent-sandwich chromocene complexes.¹ This fact is surprising given the importance of early transition metal-containing bent-metallocene complexes to homogeneous catalysis, particularly alkene polymerization.² High-spin chromocene's recalcitrance toward assuming a bent-sandwich geometry and its propensity toward cyclopentadienyl ring loss are the dominant factors that interfere with the isolation of bent-sandwich derivatives. Theoretical calculations indicate that the interannular bridges stabilize the carbonyl derivatives by destabilizing the 16e⁻ chromocene fragment through enforced bending.³ Brintzinger and co-workers have demonstrated that carbonyl adducts of ethano- and silylene-bridged *ansa*-chromocene complexes are isolable,⁴ unlike Cp₂CrCO, which is unstable to CO loss.⁵ These findings have persuaded us to pursue the synthesis of additional *ansa*-chromocene derivatives⁶ to uncover the previously elusive chemistry of bent-sandwich chromocene and to establish useful catalytic applications for these systems.

Electrophilic addition of B(C₆F₅)₃ to a cyclopentadienyl ring followed by proton transfer to the metal has been demonstrated for a variety of unbridged early transition metal bent-metallocene complexes.⁷ Therefore, as one approach to an unprecedented Cr(4+) hydride derivative of the bent-chromocene system, we examined the reaction between [Me₄C₂(η⁵-C₅H₄)₂CrCO] and B(C₆F₅)₃. The reaction was monitored by ¹H NMR spectroscopy. Complex **1** formed immediately upon mixing the two reagents in toluene-d₈ at -70 °C (Scheme 1).

A characteristic metal hydride signal was observed at δ -7.66, and the remainder of the spectrum was consistent with the assigned structure (see Supporting Information). As the temperature of the sample was raised to 25 °C, the signals for **1** diminished, and a very broad signal grew in at δ -1.6, indicating the formation of paramagnetic species. Toepler pump measurements⁸ revealed no gas evolution at this stage. This was surprising in light of the instability of the related cationic species [Me₄C₂(η⁵-C₅H₄)₂CrH-(CO)]⁺ to the nonselective loss of CO and H₂.^{6c}

X-ray quality crystals of **1** were isolated for a molecular structure determination (Figure 1).⁹ Significantly, this is the first X-ray crystallographic characterization of a chromocene complex with chromium formally in a +4 oxidation state.¹⁰ The gross geometry of the *ansa*-chromocene fragment is very similar to that of the neutral complex Me₄C₂(C₅H₄)₂CrCO^{3a} and the cation in [Me₄C₂(η⁵-C₅H₄)₂CrCO][B(3,5-(CF₃)₂C₆H₃)₄].^{6c} The cyclopentadienyl rings of **1**, with a dihedral angle of 42.5°, are slightly more tilted than those in the other two species (with corresponding angles of 38.5–38.6°). The Cr–CO (1.873(3) Å) and the Cr–O (1.139(4) Å) distances of **1** do not differ substantially from those of the neutral Cr(II) species [Me₄C₂(η⁵-C₅H₄)₂CrCO] (1.85(1) Å, 1.16(1) Å) or the cationic Cr(III) species in [Me₄C₂(η⁵-C₅H₄)₂CrCO][B(3,5-(CF₃)₂C₆H₃)₄] (1.893(6) Å, 1.133(7) Å). The C–O stretching

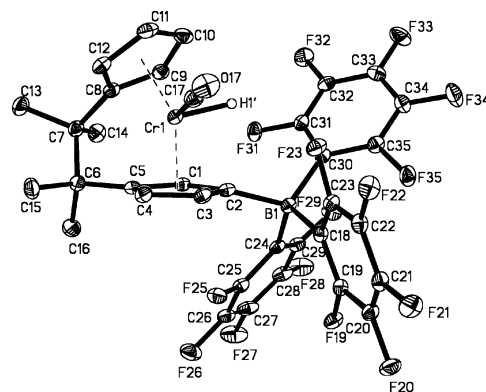
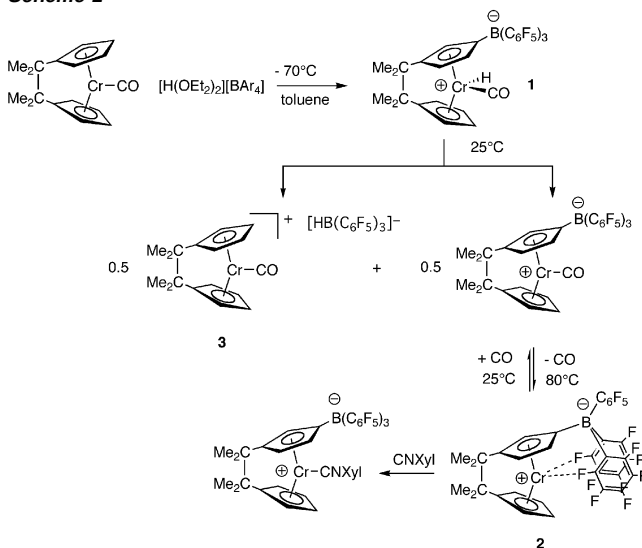


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at 30% probability. Selected bond distances (Å) and angles (deg): av Cp–Cr 1.823(2); Cr1–C17O17 1.873(3); Cr1C17–O17 1.139(4); Cr1–H1' 1.44(3); Cr1–F23 3.735(2); Cp–Cr–Cp 140.0(3); Cp–Cp dihedral 42.5(3).

Scheme 1



frequencies of the three complexes (1992, 1905, 1990 cm⁻¹, respectively), on the other hand, are quite sensitive to variations in the electronic properties of the metal center.

Upon being heated from room temperature to 80 °C, the red-brown toluene solution containing the paramagnetic decomposition products of **1** turned green and evolved 0.48 ± 0.02 equiv of carbon monoxide gas. The thermolysis product consisted of two new species, one green and the other red, both of which were separated by selective crystallization and structurally characterized. The green species is the zwitterionic ring-borylated Cr(III) complex, {Me₄C₂(η⁵-C₅H₄)(η⁵-C₅H₃B(C₆F₅)₃)Cr} (**2**). The red species is the ionic Cr(III) complex, [Me₄C₂(η⁵-C₅H₄)₂CrCO][HB(C₆F₅)₃] (**3**). X-ray crystal structures of both **2**¹¹ and **3** were obtained. An ORTEP

* To whom correspondence should be addressed. E-mail: shapiro@uidaho.edu.

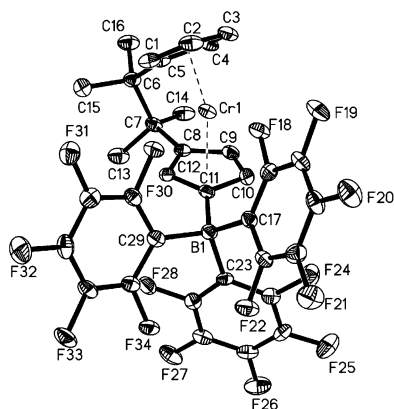


Figure 2. Molecular structure of **2**. Thermal ellipsoids are shown at 30% probability. Selected bond distances (Å) and angles (deg): Cp–Cr1 1.851(5); BCp–Cr1 1.821(5); Cr–F18 2.675(4); Cr–F30 3.173(4); Cp–Cr–Cp 149.3(3); Cp–Cp dihedral 36.9(3).

drawing of the molecular structure of **2** is shown (Figure 2). Compound **3** is related to an *ansa*-chromocenium carbonyl salt whose structure has been reported.^{6c} Details about its structure are provided in the Supporting Information. The structure of **2** is reminiscent of that of a related zwitterionic boryl-titanocene complex, (η^5 -C₅H₅)(η^5 -[C₅H₄B(C₆F₅)₃])Ti.^{7c} As in the titanium complex, there are close contacts between the metal center in **2** and two *ortho*-fluorine atoms on the pendant boryl group (Cr–F18 2.675(4) Å; Cr–F30 3.173(4) Å) that are shorter than the sum of the van der Waal radii for both elements (Cr–F = 3.47 Å).¹² These distances are substantially longer than those in the titanocene complex (2.248(2) Å and 2.223(3) Å), even though the single-bonded metallic radius of Ti (1.32 Å) is larger than that of Cr (1.19 Å).¹³ This is probably due to the fact that the titanium complex has only one unpaired electron in its frontier orbitals, whereas the high-spin chromium complex has three unpaired electrons ($\mu_{\text{eff}} = 3.8 \mu_B$).

Experiments in toluene-*d*₈ exclude the involvement of the solvent in the formation of the hydroborate anion of **3**, indicating that the hydride must originate from a cyclopentadienyl ring. Loss of CO in the formation of **2** is reversible, and exposure of a solution of **2** in toluene-*d*₈ to either an atmosphere of CO or an equivalent of xylol isocyanide (XylNC) at room temperature produces the corresponding adducts, the structures and properties of which will be described in a full paper.

In summary, complex **1** represents the first structurally characterized bent-metallocene complex of Cr(4+). This species is metastable and decomposes thermally in toluene to species that contain Cr in its preferred +3 oxidation state. The chirality conferred to complexes **1** and **2** by the boryl substituent poises them for application in the asymmetric catalysis of reactions such as the Nozaki–Hiyama–Kishi reaction, for which Cp₂Cr¹⁴ and our *ansa*-chromocene derivatives¹⁵ have demonstrated activity.

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.

Supporting Information Available: Crystallographic data for **1**, **2**, and **3** (CIF) and synthetic and experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For reviews on the chemistry of chromocene, see: (a) 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. (b) Morris, M. J. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Gordon, F., Wilkinson, G., Eds.; Pergamon: Oxford, 1992; Vol. 5, Chapter 7.
- (2) (a) *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999. (b) *Ziegler Catalysts*; Fink, G., Mühlaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995.
- (3) (a) Brintzinger, H. H.; Lohr, L. L., Jr.; Tang Wong, K. L. *J. Am. Chem. Soc.* **1975**, *97*, 5146–5155. (b) Simpson, K. M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1992**, *11*, 4363–4364. (c) Green, J. C.; Jardine, C. N. *J. Chem. Soc., Dalton Trans.* **1999**, 3767–3770.
- (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) Wong, K. L. T.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1975**, *97*, 5143–5146.
- (6) (a) Foo, D. M. J.; Shapiro, P. J. *Organometallics* **1995**, *14*, 4957–4959. (b) Matere, G. J.; Foo, D. M.; Kane, K. M.; Zehnder, R.; Wagener, M.; Shapiro, P. J. *Organometallics* **2000**, *19*, 1534–1539. (c) Foo, D. M. J.; Sinnema, P.-J.; Twamley, B.; Shapiro, P. J. *Organometallics* **2002**, *21*, 1005–1007.
- (7) (a) Liu, S.; Liu, F.-C.; Renkes, G.; Shore, S. G. *Organometallics* **2001**, *20*, 5717–5723. (b) Burlakov, V. V.; Pellny, P.-M.; Arndt, P.; Baumann, W.; Spannenberg, A.; Shur, V. B.; Rosenthal, U. *Chem. Commun.* **2000**, 241–242. (c) Burlakov, V. V.; Troyanov, S. I.; Letov, A. V.; Strunkina, L. I.; Minacheva, M. K.; Furin, G. G.; Rosenthal, U.; Shur, V. B. *J. Organomet. Chem.* **2000**, *598*, 243–247. (d) Doerrer, L. H.; Graham, A. J.; Haussinger, D.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **2000**, 813–820. (e) Ruwwe, J.; Erker, G.; Frölich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80–82.
- (8) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, D.C., 1985; Chapter 4.
- (9) Crystallographic data for **1**·toluene: triclinic, space group P-1; *a* = 11.0780(11) Å, *b* = 12.1571(12) Å, *c* = 16.0434(16) Å, α = 106.75(1)°, β = 101.15(1)°, γ = 108.26(1)° at 203(2)K; *V* = 1866.8(3) Å³; *Z* = 2; *D*_{calc} = 1.595 Mg/m³, μ_{abs} = 0.417 mm⁻¹, *F*(000) = 904, refl. collected = 23 214, indep. refl. = 8550, *R*1 = 0.0671 (*I* > 2 σ (*I*), *wR*2 = 0.1259). Anal. Calcd for C₄₂H₂₆BCrF₁₅O: C, 56.27; H, 3.15. Found: C, 54.66; H, 2.89. We attribute the low carbon value to the presence of less than a stoichiometric amount of toluene in the analytical sample.
- (10) Although paramagnetic complexes of the type Cp₂CrXY (X = halide, CN, NCSe, NCS; Y = CN, NCSe, NCS) were previously reported and characterized by elemental analysis, ESR, and magnetic susceptibility, X-ray structural confirmation was not obtained: (a) Morán, M.; Fernández, V. *J. Organomet. Chem.* **1979**, *165*, 215–223. (b) Morán, M.; Gayoso, M. Z. *Naturforsch.* **1983**, *38b*, 177–180.
- (11) Crystallographic data for **2**: monoclinic, space group P2(1)/c; *a* = 15.952(3) Å, *b* = 8.9873(15) Å, *c* = 21.434(4) Å, β = 102.47(3)° at 203(2)K; *V* = 3000.5(9) Å³; *Z* = 4; *D*_{calc} = 1.716 Mg/m³, μ_{abs} = 0.502 mm⁻¹, *F*(000) = 1548, refl. collected = 25 522, indep. refl. = 5287, *R*1 = 0.0651 (*I* > 2 σ (*I*), *wR*2 = 0.1116). Anal. Calcd for C₃₄H₁₉BCrF₁₅: C, 52.67; H, 2.47. Found: C, 52.40; H, 2.52.
- (12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–551.
- (13) Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000; p 32.
- (14) Fürstner, A. *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357.
- (15) Shapiro, P. J.; Höhn, B.; Sinnema, P.-J.; Bandini, M.; Cozzi, P. G. *Abstracts of Papers*, 221st National Meeting of the American Chemical Society, San Diego, CA; American Chemical Society: Washington, D.C., 2001; ORGN 603.

JA026633Q