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Zwitterionic Ring-Borylated *ansa*-Chromocene Complexes

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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 Cp_2CrCO, which is unstable to CO loss.[5] These findings have persuaded us to pursue the synthesis of additional *ansa*-chromocene derivatives[6] to uncover the previously elusive chemistry of bent-sandwich chromocene and to establish useful catalytic applications for these systems.

Electrophilic addition of $B(C_6F_5)_3$ 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 $[Me_4C_2(\eta^5\text{-}C_5H_4)_2CrCO]$ and $B(C_6F_5)_3$. The reaction was monitored by ^1H NMR spectroscopy. Complex **1** formed immediately upon mixing the two reagents in toluene-d_8 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 measurements[8] revealed no gas evolution at this stage. This was surprising in light of the instability of the related cationic species $[Me_4C_2(\eta^5\text{-}C_5H_4)_2CrH(CO)]^+$ to the nonselective loss of CO and H_2.[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 $Me_4C_2(C_5H_4)_2CrCO$[3a] and the cation in $[Me_4C_2(\eta^5\text{-}C_5H_4)_2CrCO][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$.[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 CrC−O (1.139(4) Å) distances of **1** do not differ substantially from those of the neutral Cr(II) species $[Me_4C_2(\eta^5\text{-}C_5H_4)_2CrCO]$ (1.85(1) Å, 1.16(1) Å) or the cationic Cr(III) species in $[Me_4C_2(\eta^5\text{-}C_5H_4)_2CrCO][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (1.893(6) Å, 1.133(7) Å). The C−O stretching 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.

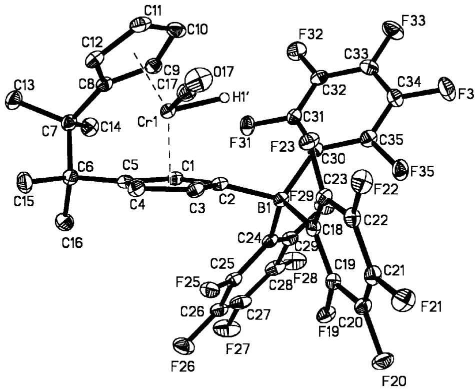
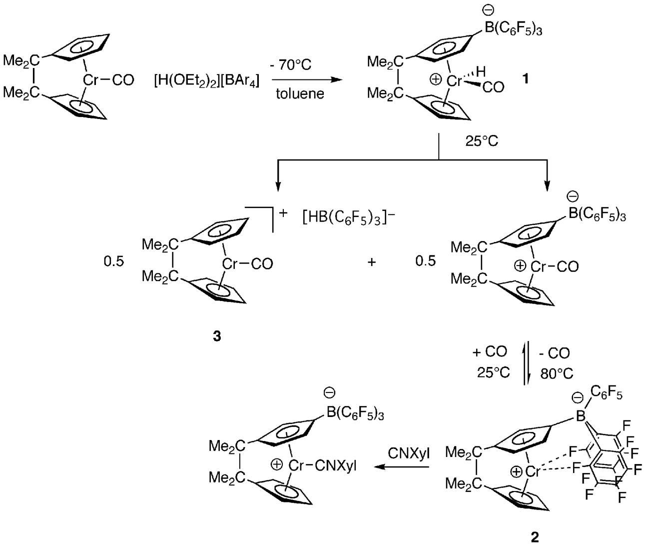


Figure 1. Molecular structure of **1**. Thermal ellipsoids are shown at 30% probability. Selected bond distances (Å) and angles (deg): av Cp−Cr 1.823(2); Cr1−C17O17 1.873(3); Cr1C17−O17 1.139(4); Cr1−H1′ 1.44(3); Cr1−F23 3.735(2); Cp−Cr−Cp 140.0(3); Cp−Cp dihedral 42.5(3).

Scheme 1



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, $\{Me_4C_2(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3B(C_6F_5)_3\}Cr$ (**2**). The red species is the ionic Cr(III) complex, $[Me_4C_2(\eta^5\text{-}C_5H_4)_2CrCO][HB(C_6F_5)_3]$ (**3**). X-ray crystal structures of both **2**[11] and **3** were obtained. An ORTEP

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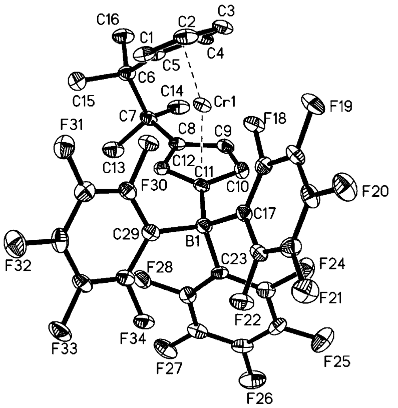

Figure 2. Molecular structure of **2**. Thermal ellipsoids are shown at 30% probability. Selected bond distances (Å) and angles (deg): Cp−Cr1 1.851(5); BCp−Cr1 1.821(5); Cr−F18 2.675(4); Cr−F30 3.173(4); Cp−Cr−Cp 149.3(3); Cp−Cp dihedral 36.9(3).

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-C_5H_5)(η^5-[$C_5H_4B(C_6F_5)_3$])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 ($\mu_{\mathrm{eff}} = 3.8\ \mu_{\mathrm{B}}$).

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 xylyl 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 Cp_2Cr[14] and our *ansa*-chromocene derivatives[15] have demonstrated activity.

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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.

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(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) $Å^3$; Z = 2; D_{calc} = 1.595 Mg/m^3, μ_{abs} = 0.417 mm^{-1}, $F(000)$ = 904, refl. collected = 23 214, indep. refl. = 8550, R1 = 0.0671 ($I > 2\sigma(I)$, wR2 = 0.1259). Anal. Calcd for $C_{42}H_{28}BCrF_{15}O$: 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.

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(11) Crystallographic data for **2**: monoclinic, space group *P*2(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) $Å^3$; Z = 4; D_{calc} = 1.716 Mg/m^3, μ_{abs} = 0.502 mm^{-1}, $F(000)$ = 1548, refl. collected = 25 522, indep. refl. = 5287, R1 = 0.0651 ($I > 2\sigma(I)$, wR2 = 0.1116). Anal. Calcd for $C_{34}H_{19}BCrF_{15}$: C, 52.67; H, 2.47. Found: C, 52.40; H, 2.52.

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