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Isolation and structural characterization of the first thermally robust and air stable Cr(4+) bent-metallocene complex†

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The first thermally robust and air stable bent-sandwich chromocene complex with chromium in the +4 oxidation state has been isolated and fully characterized.

The chemistry of chromocene has remained elusive due to the metallocene's reluctance to adopt a bent-sandwich geometry and its susceptibility to ring loss. The strategy that we have employed to override these tendencies and gain access to bent-sandwich chromocene complexes is to introduce an interannular bridge between the cyclopentadienyl rings of the chromocene that is too short to span a parallel ring geometry.[1,2] Brintzinger and coworkers demonstrated the effectiveness of this approach with their synthesis of $Me_4C_2(\eta^5\text{-}C_5H_4)_2CrCO$,[3] which is thermally stable, unlike $(\eta^5\text{-}C_5H_4)_2CrCO$, which undergoes CO loss to form the more stable 16e- $(\eta^5\text{-}C_5H_5)_2Cr$.[4] Recently we reported the first bent metallocene complexes of Cr(3+) and Cr(4+).[5] Whereas the 3+ oxidation state is quite prevalent in organochromium chemistry, the 4+ oxidation state is rare and, prior to our examples, unknown for chromocene.[6] The 18e-, diamagnetic Cr(4+) species **1**[5a] and **2**[5b] (Fig. 1) that we reported previously are only meta-stable, decomposing above −25 °C to form paramagnetic species, some of which have been structurally characterized. One decomposition product formed by **2** is the 15e-, zwitterionic complex $[Me_4C_2(\eta^5\text{-}C_5H_4)\{\eta^5\text{-}C_5H_3B(C_6F_5)_3\}]Cr$ (**3**).[5b] Complex **3** reacts with various σ-donating ligands like CO, isocyanides and phosphines to give the 17e-complexes $[Me_4C_2(\eta^5\text{-}C_5H_4)\{\eta^5\text{-}C_5H_3B(C_6F_5)_3\}]CrL$. In this communication we highlight one of these species, the xylylisocyanide (CNXyl) complex $[Me_4C_2(\eta^5\text{-}C_5H_4)\{\eta^5\text{-}C_5H_3B(C_6F_5)_3\}]CrCNXyl$ (**4**), which is oxidized by AgCN to form the first *thermally robust* and *air-stable* Cr(4+) bent-metallocene complex, $[Me_4C_2(\eta^5\text{-}C_5H_4)\{\eta^5\text{-}C_5H_3B(C_6F_5)_3\}]Cr(CN)CNXyl$ (**5**).

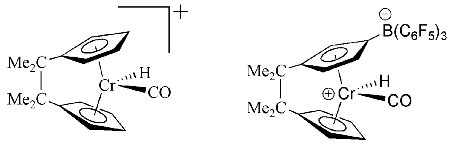


Fig. 1 Meta-stable Cr(4+) *ansa*-metallocene complexes.

The combination of green, high-spin ($\mu_{\text{eff}} = 3.85\ \mu_B$) **3** with one equivalent of xylyl isocyanide produces brown, low-spin ($\mu_{\text{eff}} = 1.75\ \mu_B$) **4** (Scheme 1). The X-ray crystal structure of **4** was determined. An ORTEP drawing of the complex is shown in Fig. 2.§ A particularly interesting feature of the structure is a π-stacking interaction between the isocyanide ligand and one of the C_6F_5 rings of the boryl group, with a distance of 3.331 Å from the centroid of the arene ring plane to the center of the CN bond. The C_6F_5 ring is practically coplanar with the xylyl ring, with a dihedral angle of 2.4° between the two ring planes. Although there are now several examples of early transition metal bent-metallocene complexes bearing an anionic $B(C_6F_5)_3$ substituent on one of the cyclopentadienyl rings[7] this is the first time an intramolecular π-stacking interaction between the $B(C_6F_5)_3$ group and a ligand on the metal has been identified.

A dramatic effect of the borate substituent on the redox properties of the *ansa*-chromocene complex is revealed in cylic voltammetry measurements on **4**. The complex exhibits a reversible $Cr^{2+/3+}$ couple at −1523 mV, which, significantly, is 350 mV lower than that of $[Me_2C_4(\eta^5\text{-}C_5H_4)_2CrCN^tBu$,[2] a non-borylated analog. Complex **4** also exhibits a reversible $Cr^{3+/4+}$ couple at +24 mV. $[Me_4C_4(\eta^5\text{-}C_5H_4)_2CrCN^tBu$, by contrast, exhibits an irreversible anodic peak at +200 mV. This prompted us to investigate the

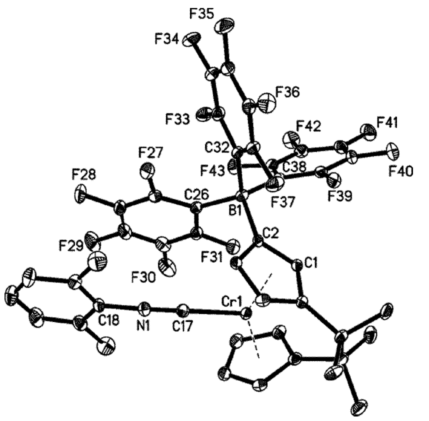
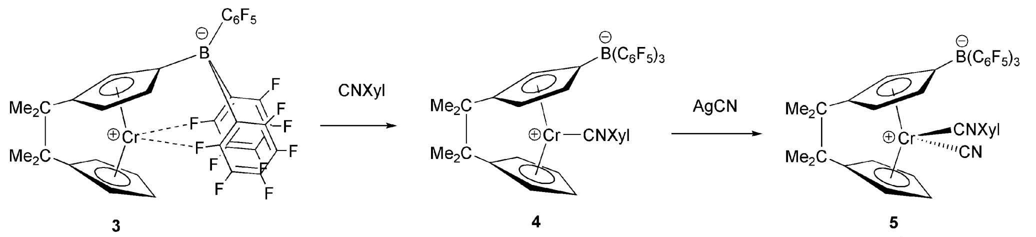


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°). Cr1–Cent(C1-5) 1.834(3), Cr1–Cent(C8-12) 1.830(3), Cr1–C17 1.944(3), C17–N1 1.171(4), C2–B1 1.635(4), Cp < Cp 43.5, Cent-Cr1-Cent 142.7, Cr–C17–N1 178.6(3).



Scheme 1 Preparation of complexes **4 and 5** from complex **3**.

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† Electronic supplementary information (ESI) available: details of synthesis and characterization for **4** and **5**. See http://www.rsc.org/suppdata/cc/b3/b311352c/

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chemical oxidation of **4**. Refluxing a solution of **4** in THF with excess AgCN for 24 h resulted in the deposition of metallic silver and the formation of complex **5**, which was isolated as a dark orange-red solid in 73% yield (Scheme 1). Alternatively, **3** reacts readily with AgCN at room temperature to form a paramagnetic, reddish brown species, which reacts slowly with CNXyl to form **5** in 54% yield. Efforts to identify the paramagnetic intermediate formed in the reaction between **3** and AgCN are in progress. We presume it to be a dimer or higher aggregate of the 16e-*ansa*-chromocene cyanide derivative.

An 18e-complex, **5** is diamagnetic, thermally robust (stable when heated for 16 h at 70 °C in THF) and stable in air for at least 1 h. We have characterized it thoroughly by ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopy and determined its molecular structure by X-ray crystallography. An ORTEP drawing of the molecule is shown in Fig. 3.§ Significantly, the boryl group is positioned over the much bulkier xylyl isocyanide ligand, with which it retains its π-stacking interaction. The same arrangement of ligands results when the CN^- and CNXyl ligands are introduced in reverse order onto chromium (*i.e.* by reacting **3** with AgCN prior to introducing CNXyl). A comparison of the Cp–Cp dihedral angles (**5**: 44.6° **4**: 43.5°; **2**: 42.5°; **3**: 36.9°) and Cp–Cr–Cp angles (**5**: 133.6° **4**: 142.7°; **2**: 140.0°; **3**: 149.3°) shows that introducing more ligands on chromium results in greater tilting of the cyclopentadienyl rings away from the equatorial wedge.

^{1}H and ^{13}C NMR spectra of **5** reflect the lack of symmetry in the compound; all of the cyclopentadienyl ring carbons and hydrogens are inequivalent, as are all four methyl groups along the ethanediyl bridge. A variable temperature ^{19}F NMR study revealed restricted rotation of the $–B(C_6F_5)_3$ substituent in the complex (ESI†). At 25 °C the three C_6F_5 rings appear equivalent, showing only three resonances for the *o*, *m* and *p*-fluorines. At −34 °C, the resonance for the *p*-fluorines at −163 ppm decoalesces into three resonances. Line shape analysis gave $\Delta H^{\ddagger} = 7.6 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = 11 \pm 3$ eu for the three site exchange. The decoalescence patterns of the *o*- and *m*-fluorines are more complex since they are affected by two processes, the Cp-Boryl rotation and the rotation of the individual C_6F_5 rings. Ultimately, at −94 °C all 15 inequivalent fluorine atoms are distinguishable.

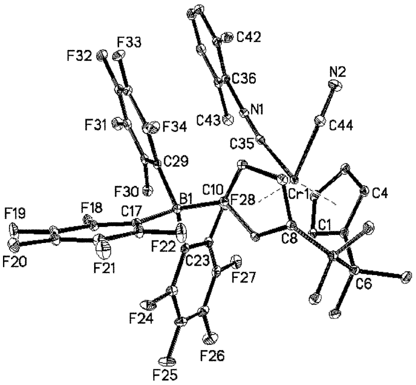

Fig. 3 Molecular structure of **5**. Selected bond lengths (Å) and angles (°). Cr1–Cent(C1-5) 1.853(2), Cr1–Cent(C8-12) 1.864(2), Cr1–C44 2.0136(16), C35–N1 1.1556(19), C10–B1 1.649(2), Cp < Cp 44.6, Cent-Cr1-Cent 133.6, Cr–C35–N1 171.66(13).

In summary, we have prepared and fully characterized the first thermally robust, air stable bent metallocene complex of Cr(4+). The electron releasing properties of the anionic $–B(C_6F_5)_3$ substituent was key to achieving this result by lowering the redox potential of the chromium and stabilizing the unusual Cr(4+) oxidation state. A similar effect of the anionic boryl group on the redox properties of metallocene complexes of other early transition metals may be expected.

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Notes and references

§ *Crystal data:* **4** + C_6H_6: $C_{49}H_{34}BCrF_{15}N$, M = 984.58, triclinic, space group $P\bar{1}$ (#2), a = 11.864(3), b = 12.943(3), c = 15.545(2) Å, α = 72.61, β = 73.68(1), γ = 71.90(2)°, V = 2118.1(8) Å^3, Z = 2, D_c = 1.544 g cm^{-3}, μ(Mo–Kα) = 37.4 cm^{-1}, F(000) = 998. An orange parallelpiped of dimensions 0.19 × 0.11 × 0.07 mm^3 was used. **5** + 1.5C_6H_6: $C_{53}H_{37}BCrF_{15}N_2$, M = 1049.66, monoclinic, space group $P2(1)/n$ (#14), a = 13.975(3), b = 19.331(4), c = 16.878(3) Å, β = 90.30(3), V = 4559.6(16) Å^3, Z = 4, D_c = 1.529 g cm^{-3}, μ(Mo–Kα) = 35.4 cm^{-1}, F(000) = 2132. A red block of dimensions 0.44 × 0.33 × 0.20 mm^3 was used. 27874 (60130) reflections were collected at 203(2) K (83(2) K) on a Bruker SMART APEX diffractometer with Mo–Kα radiation using ω scans for **4** (**5**), respectively. The structures were solved by direct methods. All atoms were refined anisotropically using full materix least squares based on F^2 to give R_1 = 0.0645 (0.0445), wR_2 = 0.1205 (0.1030) for 9713 (13043) independent reflections [$|F_o| > 2\sigma(|F_o|)$, $2\theta \leq 55(60)°$] and 610 (655) parameters for **4** (**5**), respectively. CCDC reference numbers 219696 and 219697. See http://www.rsc.org/suppdata/cc/b3/b311352c/ for crystallographic files in .cif format.

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