Unexpected conversion of a hexacyanometallate to a homoleptic nitrile complex with triphenylborane substituents

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The homoleptic, triphenylborane adduct of the hexacyanochromate anion was structurally characterized and found to be a product in which all six cyanide ligands have undergone isomerization to nitrile groups.

The formation of a dative bond between the Lewis basic nitrogen end of the cyanide ligand and Lewis acidic boranes has been known since the seminal reports by Shriver of boron trifluoride adducts of cyanometallate anions. In the ensuing years, a variety of these borane adducts have been reported, and the issue of linkage isomerism has been explored. Recently, this chemistry has been extended to more general studies of the structures and properties of perfluoronated borane adducts of cyanide compounds due, primarily, to the interest in these compounds as weakly-coordinating anions.

Our particular interest in the chemistry of boranes is related to a desire to passivate the cyanide ligand in order to retard reactions of metal cations with cyanometallate anions that lead to rapid precipitation of Prussian-blue cubic phases. To this end we are pursuing reactions of triphenylborane with paramagnetic cyanometallates, chemistry that has led to the isolation of a highly stable, six-coordinate borane adduct of $\text{[Cr}^\text{III}(\text{CN})_6]_2$. Treatment of a solution of $\text{[Et}_4\text{N]_3[Cr}^\text{III}((\text{NCBPh}_3)_6]$ with excess BPh$_3$ in refluxing acetonitrile produced a salmon-colored solution from which the pink solid, $\text{[Et}_4\text{N]_3[Cr}^\text{III}(\text{NCBPh}_3)_6]_2.5\text{CH}_3\text{CN (I)}$, was isolated in high yield.

The pink product was characterized by elemental analysis, and by infrared spectroscopy which is a powerful tool for the structural determination of cyanoborate complexes. Compound I exhibits a single, intense $\nu_\text{C=N}$ stretch at 2205 cm$^{-1}$, which is shifted by $+96$ cm$^{-1}$ as compared to the $\text{[Et}_4\text{N]_3[Cr}^\text{III}((\text{CN})_6]$ starting material (2109 cm$^{-1}$). This shift to higher energy is consistent with coordination of BPh$_3$ to the cyanide ligand, and the fact that it is a single stretch indicates substitution at all six sites.

The single-crystal X-ray structure of I confirmed that all six cyanide ligands are capped by BPh$_3$ groups (Fig. 1a), which is somewhat surprising given the steric demands of the BPh$_3$ group (see Fig. 1b). A close inspection of the metrical parameters of the anion led to the conclusion that the immediate coordination sphere of the Cr$_{III}$ ions consists of nitrogen rather than carbon atoms, i.e., an isomerism of the M–CN linkage has occurred. The results of the two possible refinement models for the Cr$_{III}$ ligand environment [specifically the thermal parameters of N versus C atoms bound directly to the Cr$_{III}$ ion] as well as a comparison of the M–N and C–B bond distances in I with hexacyanochromate, isocyanide and nitrile complexes of Cr$_{III}$ and other cyanoborates support the conclusion that the N atoms are bound to the metal atom. The Cr$_{III}$–N distances in I range from 2.004(3)–2.043(3) Å which are significantly shorter that those found in K$_3[\text{Cr}^\text{III}(\text{CN})_6]$.

Fig. 1 (a) Thermal ellipsoid plot of the molecular anion of I at the 50% probability level. Phenyl carbons are depicted as spheres of arbitrary radius. Selected bond distances and angles: Cr1–N1 2.010(3), Cr1–N2 2.043(3), Cr1–N3 2.004(3), C1–N2 1.127(5), C2–N1 1.100(5), C3–N3 1.150(5), C1–B1 1.619(6), C2–B2 1.637(6), C3–B3 1.610(6), N1–Cr1–N2 90.15(11), N1–Cr1–N3 89.27(12), N2–Cr1–N3 91.33(11), Cr1–Cr1–N3 90.15(11), Cr1–Cr1–N3 89.27(12), N2–Cr1–N3 91.33(11), Cr1–Cr1–N3 174.8(3), Cr1–Cr1–N3 176.8(4), Cr1–Cr1–N3 179.8(5). (b) Space filling diagram of the molecular anion of I looking down the 3-fold axis illustrating the steric demand of the N=C–BPh$_3$ ligand set.

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The isolation and structure of the metal-nitrogen-bound product, I, demonstrates the feasibility of preparing stable, homoleptic cyanoborate adducts of hexacyanometallates. Regarding the earlier stated goal of obtaining new Prussian Blue crystalline phases from borane capped cyanide precursors, clearly this is not feasible with the present CrIII product as it is stable in the presence of other metal ions even under refluxing conditions. This is actually quite surprising, as it may be possible to use \([\text{Cr}(\text{NCBPh}_3)_6]\)^{1-2} in reactions that require “non-coordinating” anions. Given the large number of available cyanometallate anions, we plan to investigate other 3d metal ions to probe isomerization and spin state changes as part of a general effort to develop a family of octahedral anions with different borane Lewis acid capping groups.

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Notes and references

† Synthesis of \([\text{Et}_4\text{N}]_2[\text{Cr}(\text{NCBPh}_3)_6]_2\cdot \text{CH}_3\text{CN} \) (I): to a mixture of \([\text{Et}_4\text{N}]_2[\text{Cr}(\text{CN})_6] \) (0.10 g, 0.17 mmol) and BPh\(_3\) (0.33 g, 1.38 mmol, 8 eq.) in a pear-shaped Schlenk flask under a N\(_2\) atmosphere was added 15 mL of dry CH\(_3\)CN with stirring. The resulting yellow solution was refluxed, and within ~30 min, the color of the solution had changed from yellow to salmon. The solution was refluxed for 12 h and the volume was reduced to a minimum in vacuo. The solution was treated with 40 mL of dry diethyl ether, which resulted in the precipitation of a pink solid. The clear, colorless supernatant was removed and the pink solid was washed with 3 \(\times\) 20 mL diethyl ether and dried in vacuo. The product was collected and stored in a N\(_2\) atmosphere dry box. Yield 0.22 g, 64\%. Crystal Data for \([\text{Et}_4\text{N}]_2[\text{Cr}(\text{NCBPh}_3)_6]_2\cdot \text{CH}_3\text{CN} \) (I): \(C_{72}H_{132}N_{18}Cr_{16} \cdot \text{N}_2 \) \(M = 2213.46\), monoclinic, \(P2_1/c\) (No. 14), \(a = 28.8786(4), b = 17.2564(4), c = 27.8386(3) \text{ Å}, \beta = 110.62(3)\), \(V = 1928.54(5) \text{ Å}^3\), \(T = 25\) K, \(Z = 4\), \(\mu = 0.144 \text{ cm}^{-1}\), 5536 reflections (1856 unique, \(R_{int} = 0.0403\)) with \(\Delta \theta = 46.60\), 1665 variables, \(R = 0.0756, wR(\overline{F}^2) = 0.2132[1394\text{ data}], J > 2\sigma (J)\). \(GooF = 1.069\). The structure was solved and refined using SHELXL97 with the graphical interface X-SEED.8\(^{\dagger}\) Disorder of two \([\text{Et}_4\text{N}]_2\) ions, as well as some slight disorder of the boron phenyl groups was not modeled, which is responsible for the slightly high \(R\) factors. CCDC 251359. See http://www.ccdc.cam.ac.uk/suppdata/cc/c/c/b/b414262d/ for crystallographic data in cif or other electronic format.

‡ An assignment of the primary atoms of the CrIII coordination sphere as ‘carbon’ and the secondary atoms as ‘nitrogen’ led to non-positive definite carbon atoms and unusually large thermal ellipsoids for the nitrogen atoms. Moreover, the values of \(R = 0.0820, wR(\overline{F}^2) = 0.2282\), and \(GooF = 1.146\) are higher than for the other model. This method, with high quality single-crystal X-ray data, has been used to successfully evaluate primary coordination modes of the cyanide ligand. As early as 1965, the absolute configuration of the cyanide ligand was determined with the use of X-ray diffraction. See reference 14.

6 Anal. Calc’d. for I, C₁₃₈H₁₁₀N₆B₆Cr: C, 80.79; H, 7.37; N, 6.14; B, 3.16; Cr, 2.53. Found: C, 80.41; H, 6.95; N, 6.20.
15 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.