# 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.[1] In the ensuing years, a variety of these borane adducts have been reported,[2] and the issue of linkage isomerism has been explored.[3] 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.[4,5]

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.[2a] 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 $[Cr^{III}(CN)_6]^{3-}$.

Treatment of a solution of $[Et_4N]_3[Cr^{III}(CN)_6]$ with excess $BPh_3$ in refluxing acetonitrile produced a salmon-colored solution from which the pink solid, $[Et_4N]_3[Cr^{III}(NCBPh_3)_6]\cdot 5CH_3CN$ (**1**), was isolated in high yield.†

The pink product was characterized by elemental analysis,[6] and by infrared spectroscopy which is a powerful tool for the structural determination of cyanoborate complexes.[7] Compound **1** exhibits a single, intense $\nu_{C\equiv N}$ stretch at 2205 $cm^{-1}$, which is shifted by +96 $cm^{-1}$ as compared to the $[Et_4N]_3[Cr^{III}(CN)_6]$ 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 **1** 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 **1** 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 **1** range from 2.004(3)–2.043(3) Å which are significantly shorter that those found in $K_3[Cr^{III}(CN)_6]$,

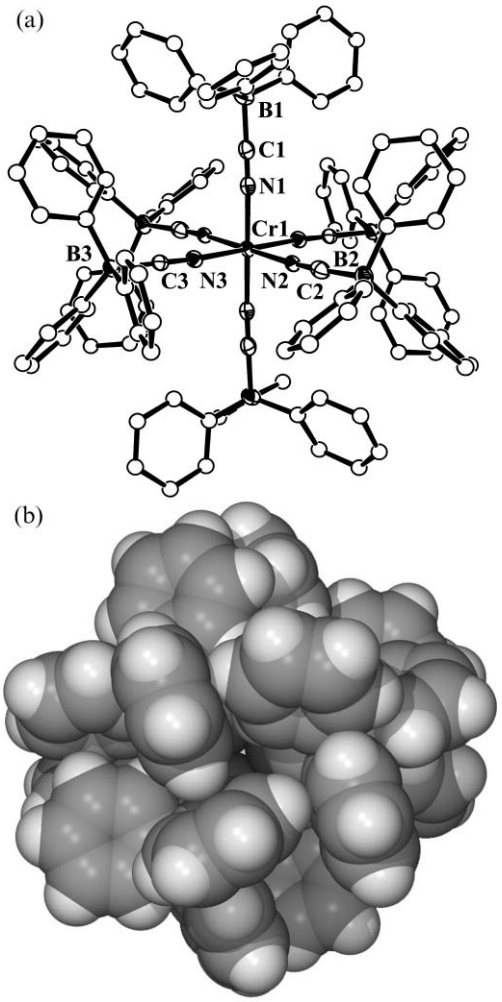


**Fig. 1** (a) Thermal ellipsoid plot of the molecular anion of **1** at the 50% probability level. Phenyl carbons are depicted as spheres of arbitrary radius. Selected bond distances and angles: Cr1–N1 2.010(3), Cr1–N2 2.043(3), Cr1–N3 2.004(3), N1–C1 1.127(5), N2–C2 1.100(5), N3–C3 1.150(5), C1–B1 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–N1–C1 174.8(3), Cr1–N2–C2 175.4(3), Cr1–N3–C3 173.5(3), N1–C1–B1 178.9(4), N2–C2–B2 176.8(4), N3–C3–B3 179.8(5). (b) Space filling diagram of the molecular anion of **1** looking down the 3-fold axis illustrating the steric demand of the N≡C–$BPh_3$ ligand set.

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[2.075(7), 2.057(12) and 2.100(10) Å], or $[Cr^{III}(CNPh)_6][SbCl_6]_3$, [2.060(10), and 2.085(13)],[8] and are consistent with nitrile coordination based on a comparison to $[Cr^{III}(CH_3CN)_6][BF_4]_3$, which exhibits $Cr^{III}$–N distances of 1.9959(12)–2.0040(11) Å.[9] Literature values of B–N distances in the triphenylcyanoborate moiety (B–N 1.567(3)–1.608(8) Å)[10] are generally shorter than those observed for the B–C isomer (B–C 1.616(2)–1.64(2) Å).[11] The B–C distances observed in the structure of **1** [1.610(6)–1.637(6) Å] clearly fall within the range of reported B–C, rather than B–N distances. Finally, the C≡N distances in **1** are 1.127(5), 1.100(5), and 1.150(5) Å, which are generally shorter than those reported for $K_3[Cr(CN)_6]$ [1.141(9), 1.167(17), 1.099(22) Å].[8] The decrease in the C≡N distances is due to donation of the $\sigma^*$ anti-bonding lone pair on the nitrogen atom.

The $^{11}$B-NMR spectrum of **1** in $CD_3CN$ contains broad, featureless resonances at +21.8 and −5.5 ppm with a shoulder at −16.0 ppm, indicative of coordinated borane but insufficient to substantiate assignment of the absolute configuration of the nitrogen-bound cyanoborate ligand.[5] The fact that the peaks are broad is not surprising, given that the compound is paramagnetic.

Electronic absorption spectral measurements on an acetonitrile solution of **1** revealed transitions located at 20,650 ($\varepsilon$ = 3.55), 35,030 (shoulder, $\varepsilon$ = 920), 36,970 ($\varepsilon$ = 3600), 37,960 ($\varepsilon$ = 4690), 38,330 (shoulder, $\varepsilon$ = 4440), 38,840 (shoulder, $\varepsilon$ = 4160) and 39,990 $cm^{-1}$ ($\varepsilon$ = 3530 $M^{-1}$ $cm^{-1}$). The feature at 20,650 $cm^{-1}$ is assigned to the *d–d* transition $^4A_2 \rightarrow {}^4T_2$ which corresponds to the value of $\Delta_o$. The higher energy bands are clearly charge transfer transitions. The reported $\Delta_o$ values for $[Cr^{III}(NCCH_3)_6][BF_4]_3$ ($\Delta_o$ = 20,160 $cm^{-1}$)[9] and $K_3Cr(CN)_6$ ($\Delta_o$ = 26,600 $cm^{-1}$)[12] indicate the $Cr^{III}$ ion in **1** is experiencing a *weak* crystal field similar to the nitrile environment of the metal ion in $[Cr^{III}(NCCH_3)_6][BF_4]_3$. These data corroborate our assignment of the positions of the C and N atoms in the X-ray refinement.

The fact that the ligands in **1** are nitriles rather than isocyanides even after being exposed to refluxing conditions indicates that **1** is the thermodynamic product of the reaction between $[Et_4N]_3[Cr^{III}(CN)_6]$ and $BPh_3$. Initially, the formation of a N-bound isomer as the thermodynamic product was surprising, given the literature reports of the C-bound products *trans*-$HPt^{II}[P(C_2H_5)_3]_2CNBR_3$ (R = $C_6H_5$, *p*-tolyl, $CH_2C_6H_5$, *o*-tolyl, 1-naphthyl)[3a] and $[Rh^{I}(CNBPh_3)(PPh_3)_3]$.[3b] In retrospect, however, the outcome is quite reasonable. The relative size and "soft" nature of the low-valent Rh and Pt metal ions promotes a π-backbonding interaction with the C-end of the cyanide ligand, whereas the metal–ligand interaction with the much harder $Cr^{III}$ ion in **1** is mostly of the σ-type which favors the stability of the nitrile derivative, **1**. Indeed, the $Fe^{II}$–$Cr^{III}$ Prussian Blue also undergoes the same type of linkage isomerism when prepared from hexacyanochromate, with the thermodynamically favored product being the $Cr^{III}$ bound to the N-end of the cyanide ligands.[13]

Finally, in considering the preferred formation of **1**, it is also important to consider the energy of the B–C bond *versus* the B–N interaction. Despite several attempts to prepare the B–N isomer, $[Et_4N]_3[Cr^{III}(CNBPh_3)_6]$ by performing the reaction of $[Et_4N]_3[Cr^{III}(CN)_6]$ with triphenylborane at low temperatures (−40 °C or −73 °C in $CH_3CN$ or $CH_2Cl_2$ respectively), the M–C≡N–B isomer was never observed, as judged by infrared spectroscopy.

The isolation and structure of the metal-nitrogen-bound product, **1**, 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 $Cr^{III}$ product as it is stable in the presence of other metal ions even under refluxing conditions. This is actually quite interesting, as it may be possible to use $[Cr(NCBPh_3)_6]^{3-}$ 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 $[Et_4N]_3[Cr(NCBPh_3)_6]\cdot 5CH_3CN$ (**1**): to a mixture of $[Et_4N]_3[Cr(CN)_6]$ (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 $CH_3CN$ with stirring. The resulting clear 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 × 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 $[Et_4N]_3[Cr(NCBPh_3)_6]\cdot 5CH_3CN$ (**1**): $C_{148}H_{122}B_6CrN_{14}$, $M$ = 2213.46, monoclinic, $P2_1/c$ (No. 14), $a$ = 28.879(6), $b$ = 17.256(4), $c$ = 27.838(6) Å, $\beta$ = 110.62(3)°, $V$ = 12984(5) Å$^3$, $T$ = 25 K, $Z$ = 4, $\mu$ = 0.144 $cm^{-1}$, 55336 reflections (18561 unique, $R_{int}$ = 0.0403) with $2\theta$ = 46.60°, 1665 variables, $R$ = 0.0756, $wR(F_0^2)$ = 0.2132 [13914 data, $I > 2\sigma(I)$], $GooF$ = 1.069. The structure was solved and refined using SHELXL97[15] with the graphical interface X-SEED.[16] Disorder of two $[Et_4N]^+$ ions, as well as some slight disorder of the borane phenyl groups was not modeled, which is responsible for the slightly high $R$ factors. CCDC 251359. See http://www.rsc.org/suppdata/cc/b4/b414262d/ for crystallographic data in .cif or other electronic format.

‡ An assignment of the primary atoms of the $Cr^{III}$ 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, $wR(F_0^2)$ = 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.

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