Trimethylamine–Isocyanoborane Derivatives and their Complexes with Metal Compounds

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Summary The synthesis of the boron isocyanide Me_3N–BH_2NC and some of its metal and transition-metal complexes is reported; salts of the cyanide-bridged cation $(Me_3NBH_2)CN^+$ have also been synthesised.

The preparation of the trimethylamine–cyanoborane adduct has been reported,[1] and recently derivatives with a variety of amines have been synthesised.[2]

A similar procedure for preparing adducts of isocyanoborane did not seem feasible since the required BH_3NC^- salt is available only in a mixture with the more stable BH_3CN^- ion.[3] We now report the synthesis of the Me_3N–BH_2NC adduct and some of its metal and transition-metal complexes,[4] and a synthesis of the $(Me_3NBH_2)_2CN^+$ cation.

The reaction of Me_3N–BH_2I (33·4 mmol), prepared *in situ*,[5] with $KAg(CN)_2$ (16·9 mmol) in CH_2Cl_2 gave a residue (3·84 g) which was filtered off. When the filtrate was left overnight, $(Me_3NBH_2)_2CNAg_2I_3$ (I) (0·07 g) precipitated; m.p. 165—167 °C, ν_{CN} 2270 cm^{-1}.[‡] Compound (I) was not observed using an eight-fold excess Me_3N–BH_2I. The residue (5·22 g) left on evaporation of the remaining solution yielded Me_3N–BH_2NC (II) (0·20 g), m.p. 46—47 °C; ν_{NC} 2135 cm^{-1}; δ (Me) 2·63; δ (^{11}B) 28·5 p.p.m. (t); J_{B-H} 118 Hz, and a mixture of (II) and the isomeric cyanide Me_3N–BH_2CN (III), ν_{CN} 2195 cm^{-1}; δ (Me) 2·70; δ (^{11}B) 33·3 p.p.m. (t); J_{B-H} 108 Hz, upon sublimation at 65 and 110 °C, respectively. Extraction of the non-sublimable solids with hot water and addition of NH_4PF_6 precipitated $(Me_3NBH_2)_2CNPF_6$ (IV) (1·00 g), m.p. 155—156 °C (lit.[6] 143—144 °C), ν_{CN} 2275 cm^{-1}; δ (Me) 2·73 and 2·80 (br.); δ (^{11}B) 28·5 p.p.m. (br.m). This salt could also be obtained by heating (I) in water, filtering, and precipitation with NH_4PF_6 or by treatment of (I) or the non-sublimable solids above with H_2S followed by filtration and precipitation with NH_4PF_6 (yield 59%).

$Me_3NBH_2NCAgCN$ (V), m.p. 60—63 °C, ν_{CN} 2170 (bridging) and 2134 (terminal) cm^{-1}; δ (Me) 2·68; δ(^{11}B) 25·7 p.p.m., was obtained in 77% yield from the reaction of Me_3NBH_2I (22·0 mmol) with AgCN (112 mmol) in CH_2Cl_2 at 0 °C after filtration followed by treatment of the filtrate with KCN (2·7 g) and precipitation with Et_2O–heptane (1:1). Compound (V) was also obtained in 78% yield by direct mixing of excess of AgCN with (II) in CH_2Cl_2; its conductivity was <5% of that of Bu_4NI in CH_2Cl_2. It added B_2H_6 to give $Me_3NBH_2NCAgCNBH_3$ (VI), m.p. 102—110 °C (decomp.); ν_{CN} 2245 and 2205 ($CNBH_3$) cm^{-1}.

Structural assignments were based on analytical and i.r. and n.m.r. spectral data. The lower CN i.r. absorption in (II) than in (III) is consistent with similar differences in the isomeric BH_3CN^- and BH_3NC^- ions[3] or that observed for nitriles and isonitriles.[7] The ^{11}B n.m.r. spectra show the expected triplets and a smaller chemical shift in (II) than in

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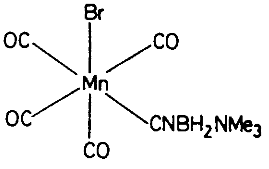
[‡] Satisfactory elemental analyses were obtained for all compounds isolated. N.m.r. and i.r. spectra were recorded for solutions in CH_2Cl_2 unless otherwise stated. ^1H n.m.r. shifts are downfield from Me_4Si and ^{11}B shifts are relative to $B(OMe)_3$.

(III) [*cf.* $BH_3(CN)^{-3}$]. The spectra of (IV) are in good agreement with literature values.[6] The spectrum of (V) shows the presence of bridging and terminal CN groups, whereas the n.m.r. spectrum shows only one kind of aminoborane grouping. Similar arguments apply to (VI). The i.r. spectrum of (I) is very similar to that of (IV) and the complex argentate ion has been reported before.[8]

$[Mn(CO)_5]Br$[9] (4·18 mmol) and $Me_3N\text{–}BH_2NC$ (4·17 mmol) were stirred in CH_2Cl_2 at room temperature for 3 h, to yield a solution with a single n.m.r. resonance (Me) at δ 2·72 and i.r. bands at 2195 and 2175 (ν_{CN}) and 2100, 2030, 2055, 1990, 1970, and 1930 cm^{-1} (ν_{CO}). The yellow solid, m.p. 92—93 °C, obtained after evaporation gave two ^1H resonances in benzene solution at δ 1·73 and 1·87 (ratio 1·3 : 1), but its i.r. spectrum was identical to that just described. Starting materials were not present, as shown by the absence of their i.r. and n.m.r. absorptions. The single ^1H n.m.r. absorption in CH_2Cl_2 was unchanged after 1 month at room temperature, but after 1 month in benzene solution the more intense band (δ 1·73) had disappeared, leaving the singlet at δ 1·87. In the i.r. spectrum only the ν_{CN} band at 2195 cm^{-1} and 3 ν_{CO} bands at 2055, 1990, and 1930 cm^{-1} remained.

We have assigned structure (VII) to the final product on the basis of the foregoing spectral data, elemental analyses, its osmometric molecular weight in $CHCl_3$, its mass spectrum, and its very low equivalent conductance. The i.r. spectrum precludes a bridging isocyanide group,[10] and the 3 CO vibrations show that substitution had taken place *cis* to Br. The ^1H n.m.r. signal and the $C\equiv N$ i.r. absorption indicate that B–N bonding is retained in the complexed ligand.



(VII)

The intermediate in the initial stages of the reaction is not a mixture of Me_3NBH_2Br and $Mn(CO)_5CN$, as shown by the absence of a $C\equiv N$ i.r. absorption at 2145 cm^{-1},[12] and we tentatively suggest a structure in which the $N\equiv C$ group is π-bonded, followed by rearrangement into (VII). There is precedent for this type of rearrangement.[13]

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