Transition-metal Cyanotrihydroborate Complexes

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Summary The preparation of several transition-metal cyanotrihydroborate complexes is reported and their physical properties are shown to be consistent with an M–$NCBH_3$ type structure.

THE cyanotrihydroborate ion is a reducing agent of considerable utility in both organic and inorganic chemistry.[1,2] The study of this ion as a ligand for transition-metal complexes was initiated as a result of earlier work in the area of metal borohydride chemistry,[3] from which it appeared that a better understanding of the factors involved in the course of the reaction of the borohydride ion with copper(I) complexes could be gained by modifying BH_4^- itself.

Reactions of the cyanotrihydroborate ion with many of the transition metals (Ti, Zr, Mn, Ni, Cu, Ag) for which stable borohydride complexes are known[4] have been carried out. Some of the complexes which have been synthesized are summarized, along with relevant physical data, in the Table. Compounds (I) and (II) were prepared by addition of an ethanol solution of sodium cyanotrihydroborate to $(Ph_3P)_3MCl$, M=Cu, Ag,[5] dissolved in chloroform. On standing, these solutions developed colourless crystals of the compounds. Their composition $(Ph_3P)_3M(NCBH_3)$ may be contrasted with that of the corresponding borohydrides, $(Ph_3P)_2M(BH_4)$.[3,5] Complex (III) was obtained by heating $Ni(en)_2Cl_2$[6] under reflux with a stoicheiometric quantity of $Na(NCBH_3)$ in tetrahydrofuran for several hours, followed by Sohxlet extraction of the solid residue with the same solvent to yield, upon cooling of the extract, purple crystals. Reaction of $Ni(en)_2Cl_2$ with sodium borohydride produced a black precipitate.

The i.r. spectra of the compounds both in the solid state and in solution, show absorptions in the vicinity of 2350 and 2200 cm^{-1}, which may be assigned to terminal B–H and C≡N stretching vibrations, respectively. Notably absent are bands in the 1900—2100 cm^{-1} region which are usually found in complexes containing M–H–B bridge bonds.[3,4] The C≡N absorption frequency[2] of the free ligand (2179 cm^{-1}) is shifted to higher energy in the complexes (see Table). This result is similar to that commonly obtained in co-ordinated acetonitrile complexes, and is probably of similar origin.[7]

The molar conductivities of (I) and (III) are characteristic of weak electrolytes in acetonitrile solution. Plots of equivalent conductance against the square-root of concentration are strongly curved, and only approach values for completely ionized species at very high dilution. In aqueous solution, however, (III) is completely ionized. Osmometric molecular weight studies of (I) in chloroform over a concentration range shows that dissociation, probably of triphenylphosphine, is taking place. The magnetic moment, μ_{eff}, of (III) is 3·00 B.M. in the solid state at room temperature, as expected[8] for six-co-ordinate Ni^{II}.

The above data strongly suggest that the cyanotrihydroborate ligand is bonded to the metal atoms through the nitrogen atom, rather than forming hydrogen-bridged multicentre bonds. The existence of M–$CNBH_3$ linkages, known to exist in the related $(o\text{-phen})_2Fe(CNBH_3)_2$ complex,[9] would require a structural rearrangement. At present, this possibility[2] cannot be completely eliminated.

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Physical properties

Compound	Colour	M.p.	Molec. weight Calc.	Found[a]	Molec. conductivity[b] (ohm^{-1} cm^2 mole^{-1})
$(Ph_3P)_3Cu(NCBH_3)$ (I)	White	158—159°	890	645	43
$(Ph_3P)_3Ag(NCBH_3),CHCl_3$ (II)[c]	White	202—205	—	—	—
$(en)_2N(NCBH_3)_2,THF$ (III)	Purple	185 (decomp.)	330	[d]	

I.r. spectra in 2000—2500 cm^{-1} *region*

Compound	Absorption frequency (cm^{-1}) Chloroform solution	Nujol mull
(I)	2330, 2190	2330, 2192
(II)	2340, 2180	2330, 2180
(III)	[d]	2370, 2340, 2300, 2225, 2200

[a] By vapour-pressure osmometry at 37° in chloroform at 3·55 × 10^{-2}M.
[b] 6·4 × 10^{-3}M in acetonitrile solution, *ca.* 28°.
[c] Slowly deposits a silver mirror upon standing in solution.
[d] Insufficiently soluble for measurement.

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