Cyanotrihydroborato- and Tetrahydroborato-complexes of Rhodium and Iridium

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Summary The synthesis and properties of air-stable hydroborato-complexes, *trans*-$[MA(CO)(R_3P)_2]$ [M = Ir, Rh; A = $BH_3(CN)$, BH_4; R_3P = tertiary phosphine] are reported; the co-ordination of $BH_3(CN)^-$, probably through the –NC group, is the first example of this anion acting as a ligand.

IN the course of attempts to prepare some new hydrido-complexes of rhodium and iridium by the standard method of using borohydrides, we have unexpectedly isolated compounds containing BH_4^- or $BH_3(CN)^-$ co-ordinated to these metals (Table). While the ligation of tetrahydroborate (BH_4^-) to d^0 (*e.g.* Zr^{IV}), and d^{10} (Cu^I) metal centres has been well established in recent years,[1] there is only one previous account on molecular BH_4^- complexes of transition metals with partly filled *d* shells (Ni^{II} and Pd^{II}).[2] No cyanohydroborato-complexes have been reported before, although they have been postulated as intermediates in the reduction of certain metal ions by $BH_3(CN)^-$.[3]

The new compounds listed in the Table are best prepared by the metathesis depicted in equation 1.[†][‡] The crystalline complexes are stable in air; in solution, the BH_4^- derivatives

$$\textit{trans}\text{-}[\mathrm{M(OClO_3)(CO)L_2}]^{4} + \mathrm{NaX} \rightarrow \textit{trans}\text{-}[\mathrm{MX(CO)L_2}] + \mathrm{NaClO_4} \qquad (1)$$

$$\mathrm{M = Rh,\ Ir;\ X = BH_4,\ BH_3(CN);\ L = Ph_3P;\ (C_6H_{11})_3P.}$$

decompose rapidly, while the $BH_3(CN)^-$ complexes are recovered unchanged. In general, the stability and/or inertness of these compounds show these sequences: Rh > Ir; $BH_3(CN) > BH_4$; $(C_6H_{11})P > Ph_3P$.

We have also studied the reactions between the two hydroborates and various other derivatives of *trans*-$[MA(CO)L_2]$, and found that the nature of the product depends on the metal (Ir, Rh), the electronic and steric properties of the ligands (A, L), as well as the borate. For example, $[IrA(CO)(Ph_3P)_2]$ (A = Cl or $OClO_3$) give *mer*-$[IrH_3(CO)(Ph_3P)_2]$ with $NaBH_4$, but $[IrH(CO)(Ph_3P)_3]$ with $NaBH_3(CN)$. However, when A = $OClO_3$ and L = $(C_6H_{11})_3P$, co-ordination of the borate results [equation 1, Table (**3**), (**4**)]. The corresponding rhodium complexes, *on* the other hand, behave differently, see Table.[‡] All these observations suggest that the well-known synthesis of metal hydrido-complexes by reaction with BH_4^- [and now also with $BH_3(CN)^-$] is likely to proceed *via* metal–hydroborato-intermediates.

The i.r. spectra of (**1**)—(**3**) (Table) suggest that the BH_4^- is co-ordinated through a double hydrogen bridge, MH_2BH_2, by analogy with related copper complexes.[5] The cyanotrihydroborate, however, appears to be *N*-bonded $M-NCBH_3$, as inferred from the vibrational spectra of (**4**) and (**5**): the terminal ν_{BH} peaks are hardly shifted from the ν_{BH} in the free ion, and the complex formation is accompanied by a small increase in the ν_{CN}, which is consistent with a cyano-bridged species.[6]

The carbonyl stretching frequencies (ν_{CO}, Table) convey important information on the electronic properties of the two borates as ligands. The ν_{CO} in (**1**) has essentially the same value as the ν_{CO} in the corresponding fluoro complex, $[RhF(CO)(Ph_3P)_2]$ [1956 (Nujol), 1971 ($CHCl_3$) cm^{-1}], which, according to a previous suggestion, shows that BH_4^- is, as expected, unable to act as a π-acceptor; "total electronegativity", $x[BH_4(T)] = 4{\cdot}0$.[7] On the other hand, the

TABLE

Infrared spectral data (cm^{-1})[a] *for hydroborato-complexes*

	Complex	ν_{BH}[b]	δ_{BH}[b]	ν_{CO}	ν_{CN}
(**1**)	$[Rh(H_2BH_2)(CO)(Ph_3P)_2]$	2452m 2416m	1149	1955	
(**2**)	$[Rh(H_2BH_2)(CO)\{(C_6H_{11})_3P\}_2]$[c]	2460m 2402m	1174	1931	
(**3**)	$[Ir(H_2BH_2)(CO)\{(C_6H_{11})_3P\}_2]$[d]	2485m 2425m		1916	
(**4**)	$[Ir(NCBH_3)(CO)\{(C_6H_{11})_3P\}_2]$	2375sb	1113	1957	2200
(**5**)	$[Rh(NCBH_3)(CO)(Ph_3P)_2]$	2360sb	1109	1997	2192
(**6**)	$Na[NCBH_3]$	2360sb	1130		2182

[a] Nujol mulls. δ_{BH}, m-ms; ν_{CO}, vs; ν_{CN}, s. [b] Terminal BH_2. [c] $\nu(RhH_2B)$, 1960 cm^{-1} (mb). This ring-expansion vibration has not been observed in the spectra of (**1**) and (**3**); it may be obscured by the intense ν_{CO} absorption. [d] Not isolated in pure state; obtained in a mixture with an unidentified hydrido-complex.

[†] The complexes are obtained by mixing saturated ethanolic solutions of the reagents: yellow [(**3**) is colourless] products precipitate immediately in 40—80% yields. All compounds show correct elemental analyses.

[‡] Compound (**2**) is synthesized from the chloro-complex, $[RhCl(CO)\{(C_6H_{11})_3P\}_2]$, by treating a hot benzene solution of the latter with $NaBH_4$ in EtOH and then cooling the mixture to 0°.

ν_{CO} in the $BH_3(CN)^-$ complex (**5**), 2000 cm^{-1} in $CHCl_3$ ($x[BH_3(CN)(T)] = 4{\cdot}82$), is comparable to those shown by the analogous –CN, –NCSe and –NO_2 derivatives, implying that all these ligands have similar π-acidities.[7]

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[1] B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, 1970, **11**, 99.

[2] M. L. H. Green and H. Munakata, *J. Chem. Soc.* (*A*), 1971, 469.

[3] J. R. Berschield, jun., and K. F. Purcell, *Inorg. Chem.*, 1970, **9**, 624.

[4] J. Peone, jun., and L. Vaska, *Angew. Chem. Internat. Edn.*, 1971, **10**, 511.

[5] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 1967, **6**, 2223; S. J. Lippard and D. A. Ucko, *ibid.*, 1968, **7**, 1051.

[6] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd edn., Wiley–Interscience, New York, 1970, p. 185.

[7] L. Vaska and J. Peone, jun., *Chem. Comm.*, 1971, 418.