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Iridium and Rhodium Dihydride–Hydroborate Complexes of the Type $[MH_2(BH_4)L_2]$†

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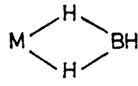
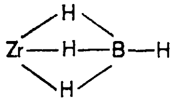
Summary Complexes of the type $[IrH_2(BH_4)L_2]$ are described (L = bulky tertiary phosphine) and are the first examples of metal–hydroborate complexes in which the BH_4 ligand is not fluxional; an analogous rhodium complex shows some fluxionality.

MANY metal–hydroborate (M–BH_4) complexes are known and some of their structures have been determined by electron- or single crystal *X*-ray-diffraction, *e.g.*, $Al(BH_4)_3$,[1] $Me_3N.Al(BH_4)_3$.[2] $Cu(BH_4)(PPh_3)_2$,[3] $[CoH(BH_4)\{P(cyclohexyl)_3\}_2]$[4] and $Zr(BH_4)_4$. The first four have doubly hydrogen-bridged structures (I) but the zirconium hydroborate has a triply-bridged structure (II). There are several complexes for which the hydroborate has been assigned as a doubly hydrogen-bridging ligand on the basis of careful analysis of the i.r. absorption spectrum. These include $[Cp_2M(BH_4)_2]$ (M = Ti, Zr or Hf), $[Cp_2ZrH(BH_4)]$[6–8] and $[MH(BH_4)(PR_3)_2]$ (M = Ni or Pd, R = Pr^i or cyclohexyl).[9]

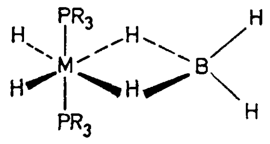
All diamagnetic metal–hydroborate complexes previously described are fluxional, *i.e.* some rapid intramolecular process is occurring which makes the four hydroborate hydrogens magnetically equivalent (the paramagnetic cobalt complex may also be fluxional). Thus n.m.r. spectroscopy has been of little use in assigning structure.[6a,7,9,10] In some cases, *e.g.* $[Cp_2Zr(BH_4)_2]$[7] and $[Zr(BH_4)_4]$[8] the complexed BH_4 ligand gives a 1:1:1:1 quartet (^1H) and a 1:4:6:4:1 quintet (^{11}B) pattern. In others, *e.g.* the nickel or palladium complexes of type $[MH(BH_4)(PR_3)_2]$, the resonance of the BH_4 protons could not be observed because of quadrupole broadening by ^{10}B or ^{11}B.[9] In these cases the fluxionality of the BH_4 ligand was shown by the MH resonance pattern, *e.g.* with $[NiH(BH_4)(PPr^i_3)_2]$ this is a triplet of 1:4:6:4:1 quintets. For $[Cu(BH_4)(PPh_3)_2]$ the ^1H n.m.r. pattern for the BH_4 hydrogen is extremely broad at 298 K but sharpens to a broad singlet at lower temperatures due to 'thermal' decoupling of the boron quadrupole nucleus.[10]



(I)



(II)



(III)

We now describe complexes of the type $[IrH_2(BH_4)(PR_3)_2]$ which are not fluxional and for which the ^1H resonances for the bridging hydrogens (IrH_2B) and the terminal hydrogens (BH_2) have been observed for the first time.

Treatment of $[IrHCl_2(PBu^t_2Me)_2]$[11] with sodium borohydride in ethanol at 0 °C gives the pale yellow $[IrH_2(BH_4)(PBu^t_2Me)_2]$ (III) (M = Ir). At higher reaction temperatures (*e.g.* 25 °C) some $[IrH_5(PBu^t_2Me)_2]$ is also formed and this pentahydride is gradually produced by decomposition of $[IrH_2(BH_4)(PBu^t_2Me)_2]$ in dry deuterio-toluene solution at

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† No reprints available.

25 °C. The ^1H (90 MHz) n.m.r. spectrum of this iridium–hydroborate complex in deuteriotoluene at 300 K shows t-butyl- and methyl- virtually coupled triplets, corresponding to mutually *trans*-phosphines, an iridium hydride resonance at δ −19·5 consisting of a doublet of triplets (2H), and a very broad singlet at *ca.* δ −6·87 (2H, $w_{\frac{1}{2}}$ 94 Hz). The ^{11}B resonance is a broad singlet δ 13·1 (BF_3,H_2O in C_6D_6 as the standard), $w_{\frac{1}{2}}$ 350 Hz, which is sharpened by broad-band proton decoupling to $w_{\frac{1}{2}}$ 150 Hz. Moreover ^1H-{^{11}B} double resonance sharpens the peak at *ca.* −6·87 ($w_{\frac{1}{2}}$ 23 Hz) and a new singlet appears at δ 6·86 (2H, $w_{\frac{1}{2}}$ 23 Hz). The broadening effect of boron quadrupoles may also be reduced by 'thermal decoupling' without double resonance.[10] Thus at 222 K the singlet at δ −6.79 (previously *ca.* −6·87, above) has sharpened ($w_{\frac{1}{2}}$ 28 Hz) and the low field resonance δ 7·05 (not observable at 300 K without ^{11}B coupling) has $w_{\frac{1}{2}}$ 34 Hz. The iridium hydride resonance pattern at δ −19·5 does not change over the temperature range of 222–300 K. Homonuclear double resonance establishes that the protons resonating at −6·87 are coupling to the protons resonating at −19·5 (terminal Ir–H) the resonance of which then collapses to a 1:2:1 triplet ^2J(PH) 15·4 Hz. The corresponding complexes $[IrH_2(BH_4)(PBu^t_3)_2]$ and $[IrH_2(BD_4)(PBu^t_3)_2]$ were similarly synthesized by treatment of $[IrH_2Cl(PBu^t_3)_2]$ with $NaBH_4$ or $LiBD_4$ respectively. These hydroborate complexes show all the i.r. absorptions one would expect for doubly bridged metal–BH_4 complexes.[7,9] The complexes thus have structure (III) and are the first examples of non-fluxional metal hydroborates. The double resonance studies establish that the absorption at *ca.* δ −6·5 is due to bridging IrH_2B hydrogens and the absorption at lower field (6·8–7·8) is therefore due to terminal BH_2 hydrogens. We have also made the iridium–hydroborate complexes $[IrH_2(BH_4)(PBu^t_2Br^n)_2]$ and $[IrH_2(BH_4)(PBu^t_2Ph)_2]$ but sodium borohydride reduction of $[IrHCl_2(AsBu^t_2Pr^n)_2]$ gives $[IrH_5(AsBu^t_2Pr^n)_2]$ and we could not isolate an intermediate hydroborate complex. $[IrH_2(BH_4)(PBu^t_3)_2]$ in benzene solution at 20 °C is stable showing no tendency to decompose into $[IrH_5(PBu^t_3)_2]$. Bulky tertiary phosphines were of course used by Green and his co-workers to stabilize the complexes of type $[MH(BH_4)(PR_3)_2]$ (M = Ni or Pd) mentioned above. Sodium borohydride reduction of $[RhHCl_2(PBu^t_2Me)_2]$ gives $[RhH_2(BH_4)(PBu^t_2Me)_2]$ for which terminal Rh–H (δ −16·85), bridging RhH_2B (−4·53) and terminal BH (3·9) were identified in a similar fashion to the iridium complexes. In this case, however, the terminal Rh–H resonance pattern is complex and changes with temperature. We cannot interpret these changes but they suggest some fluxional behaviour. The static structure is almost certainly of type (III) however (i.r. evidence).

A referee has drawn our attention to a brief report[11] regarding the existence of compounds of the type $[MH_2(BH_4)L_3]$ (M = Rh or Ir). In view of our work this formulation may be wrong

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