An Osmium Tetrahydroborate Complex with Unusual Dynamic Behaviour: *X*-Ray Crystal Structure of $[Os(BH_4)H_3\{P(c\text{-}C_5H_9)_3\}_2]$ ($c\text{-}C_5H_9$ = cyclo-C_5H_9)

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In the complex $[Os(BH_4)H_3\{P(c\text{-}C_5H_9)_3\}_2]$ ($c\text{-}C_5H_9$ = cyclo-C_5H_9), prepared quantitatively from the reaction of $[OsH_6\{P(c\text{-}C_5H_9)_3\}_2]$ with BH_3·thf, (thf = tetrahydrofuran), the tetrahydroborate ligand is bound to the metal by two bridging hydrogen atoms which, at 90 °C, exchange rapidly only with the hydride ligands on osmium.

The common modes of co-ordination of the tetrahydroborate ligand in transition metal complexes involve either two or three hydrogen atoms in bridging positions between boron and the metal.[1] For the majority of these complexes there exists a low energy pathway which allows the interchange of hydrogen atoms between bridging (b) and terminal (t) sites on the boron, although a few exceptionally rigid tetrahydroborate complexes have been reported for some of the second- and third-row transition elements.[2,3] We report here the first osmium tetrahydroborate complexes in which bridging hydrogen atoms exchange with terminal hydride ligands on osmium.

Addition of a stoicheiometric amount of BH_3·thf (thf = tetrahydrofuran) to a stirred solution of $[OsH_6(PR_3)_2]$ [R_3 = $(c\text{-}C_5H_9)_3$ ($c\text{-}C_5H_9$ = cyclo-C_5H_9) or $PhPr^i{}_2$][4] in hexane, results in the evolution of hydrogen and the formation of a yellow solution from which yellow crystals of (**1**) may be obtained at −20 °C (95%) (Scheme 1).

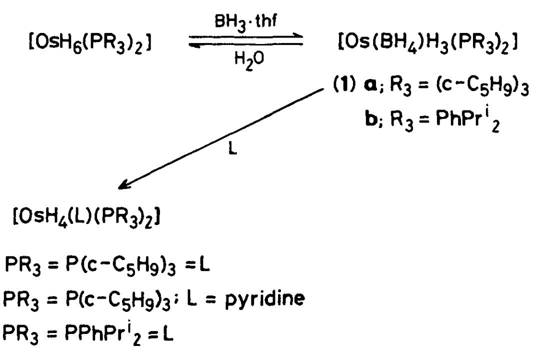
Complexes (**1**) are readily attacked by weak protic acids such as water, regenerating $[OsH_6(PR_3)_2]$, and by Lewis bases such as pyridine and tertiary phosphines affording the tetrahydrido complexes (**2**) (Scheme 1). This route from hexahydride to tetrahydride requires much less vigorous conditions than the direct displacement of H_2 by the Lewis base concerned and may be regarded as an example of acid (BH_3) activation of the hexahydride.

I.r. spectra of (**1a**) revealed absorptions at 2 448, 2 427, 2 130, and 2 112 cm^{-1} (Nujol) suggesting a tetrahydroborate complex with a double hydride bridge but the presence of ν(Os–H) bands is a complicating factor. The bidentate bonding mode was confirmed by a single crystal *X*-ray diffraction study[†] of (**1a**) (Figure 1). The osmium and boron atoms and one of the terminal hydride ligands attached to osmium lie on a crystallographic two-fold rotation axis. All the hydrogen atoms were located except for those associated with a disordered carbon atom, and the pair of symmetry-related terminal hydride ligands attached to osmium. Bond angles for the tetrahydroborate ligand indicate approximate tetrahedral geometry with a normal[1] B–H(t) distance (1.09 Å). The B–H(b) distance of 1.31 Å lies towards the upper limit of observed distances of this type, but the inherent uncertainties suggest that it would be unwise to draw conclusions based on this measurement.

The ^1H n.m.r. spectra of complexes (**1**) are temperature

[†] *Crystal data* for (**1a**): $C_{30}H_{61}BOsP_2$, $M = 674.0$, monoclinic, space group *C2/c*, $a = 14.113(8)$, $b = 18.444(9)$, $c = 12.950(4)$ Å, $\beta = 108.86(4)°$, $U = 3190(3)$ Å^3 (220 K), $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1\,416$, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 41.2$ cm^{-1}. Data were collected on a Nicolet P3/m diffractometer; $R(R') = 0.038$ (0.040) for 2 306 unique reflections [$I > 2\sigma(I)$].

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1

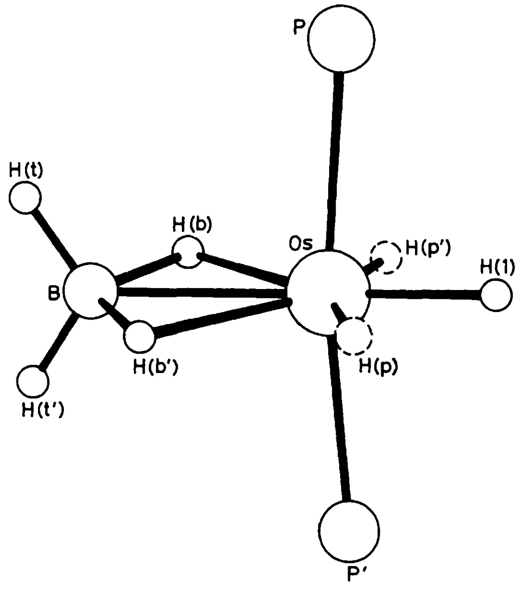


Figure 1. Co-ordination sphere of osmium in complex (**1a**) including postulated hydride positions [H(p)]. Selected distances:‡ Os–P 2.346(2); Os–B 2.30(1), Os–H(b) 1.90, Os–H(1) 1.57, B–H(b) 1.31, B–H(t) 1.09(7) Å. Selected angles: H(t)–B–H(t') 111(7), H(b)–B–H(b') 111, P–Os–H(1) 85.8, P–Os–H(b) 88.2, H(1)–Os–H(b) 145, P–Os–P' 171.5(1)°.

dependent. In addition to signals arising from the PR_3 ligand they exhibit three resonances [(**1a**), $-80\,°C$] at δ 9.05 (br. 2 H), -6.83 (2 H), and -12.69 (3 H) assigned to hydrogen atoms terminal on boron, bridging, and terminal on osmium [H(Os)], respectively. These assignments are consistent with those made previously for the tetrahydroboratohydrido complexes[2,3] $[Ir(BH_4)H_2(PBu^t_3)_2]$ and $[Ru(BH_4)H(ttp)]$ [ttp = $PPh(CH_2CH_2CH_2PPh_2)_2$]. As the temperature is increased the two high-field signals coalesce whereas that at δ 9.05 broadens but hardly moves (a result of coupling to the quadrupolar ^{11}B nucleus). At 90 °C there are resonances at δ *ca.* 8.8 (v br.) and -10.19, implying rapid exchange between H(b) and H(Os) without involvement of H(t). In comparison, $[Ir(BH_4)H_2(PBu^t_3)_2]$ is reported not to undergo any rapid exchange process, whereas in $[Ru(BH_4)H(ttp)]$ normal H(t)/H(b) exchange is observed at 105 °C without influence on the signal of the hydride bound to ruthenium.

It is apparent that previous generalizations about the fluxional behaviour of the co-ordinated hydroborate ligand are applicable only to those complexes in which a degree of ionic character is retained in the metal–hydroborate bond. Second- and third-row transition elements from Groups 6—8 are known to form strong covalent bonds to hydrogen and this is presumably the cause of the unusual n.m.r. behaviour of complexes (**1**).

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‡ No e.s.d.'s are given for some hydrogen atom parameters as these were not refined in the final refinement quoted.