Synthesis and Characterization of an Unsymmetrically Bonded Tetrahydroborato Ruthenium Hydride Complex

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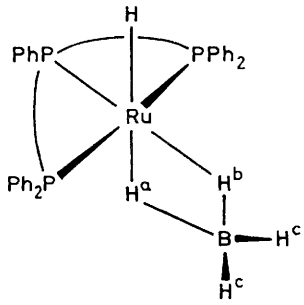
The complex $RuH(\eta^2\text{-}BH_4)(ttp)$ [ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$], obtained by treatment of $[RuCl_2(ttp)]_x$ with excess of sodium tetrahydroborate in refluxing tetrahydrofuran, shows discrete ^1H n.m.r. signals for the Ru–H protons, each of the two Ru–H–B bridging protons, and the two terminal B–H protons at ambient temperature; however, the static BH_4^- group undergoes proton scrambling at higher temperatures in two distinct steps.

In contrast with studies that generally have shown degenerate proton signals for the BH_4^- group in metal complexes,[1] we have found that the BH_4^- group is static at room temperature in the complex $RuH(\eta^2\text{-}BH_4)(ttp)$ (**1**), where ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$. Consequently, the ^1H n.m.r. spectra give discrete signals for all four types of hydrogen atoms in the high-field region, *i.e.*, the metal hydride, each of the two Ru–H–B bridging protons, and the two terminal B–H protons. We also report herein the first example of magnetic coupling between a phosphorus ligand and a bridging proton of the tetrahydroborato ligand in a metal complex. In addition, this $RuH(\eta^2\text{-}BH_4)(ttp)$ complex is the first case where two discrete steps have been observed for the fluxional behaviour of a BH_4^- ligand.

Both the elemental analyses and the i.r. spectrum of (**1**)† suggested that the compound was a mixed ruthenium hydride tetrahydroborate complex, rather than the expected dihydride complex RuH_2(ttp). The i.r. spectrum, however, did not provide a definitive assignment about how the BH_4^- unit was bonded to the metal: ν_{max}/cm^{-1} 2390s, 2380s, and 2330s: ν (B–H^t); 1180: δ (B–H^t); 1880m, sharp: ν (Ru–H) rather than ν (Ru–H–B) by analogy with other ν (Ru–H) absorptions in similar complexes,[2] B–H^b–B absorptions expected in the range 1650—2150 cm^{-1} are either very weak or obscured by ttp(Ph) overtone vibrations, and other BH_4^- i.r. absorptions are indistinguishable from ttp absorptions. The deuteriated complex $RuD(\eta^2\text{-}BD_4)$(ttp), obtained from $[RuCl_2(ttp)]_x$ and excess of $NaBD_4$ shows i.r. absorptions at 1805, 1755, and 1705 cm^{-1}: ν (B–D^t); 1060 cm^{-1}: δ (B–D^t); and 1280 cm^{-1}: ν (Ru–D), but no absorptions that can be assigned unequivocally to the bridging Ru–D–B absorptions.



(**1**)

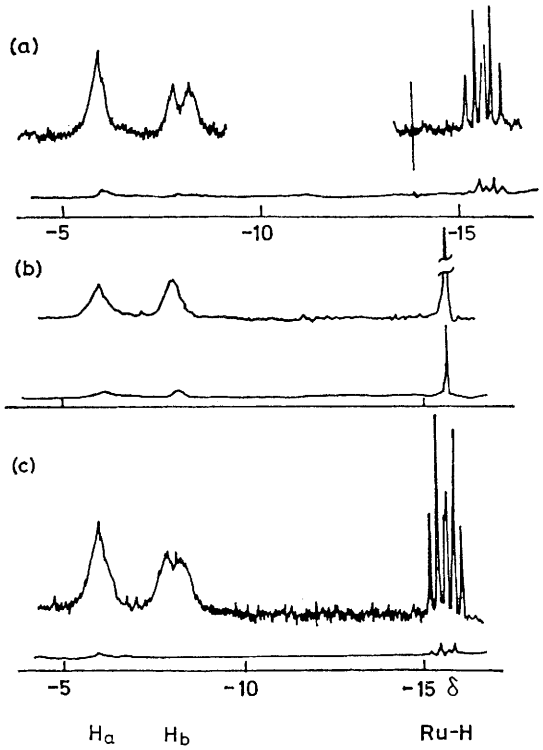


Figure 1. High-field region of the ^1H n.m.r. spectra of $RuH(\eta^2\text{-}BH_4)$(ttp) (**1**) in C_6D_6: (a) with ^{11}B decoupling; (b) with ^{31}P decoupling; (c) with no decoupling.

† Complex (**1**) was obtained by treatment of $[RuCl_2(ttp)]_x$ with excess of sodium tetrahydroborate in refluxing tetrahydrofuran as yellow microcrystals in 75% yield.

The ^1H n.m.r spectrum of (**1**) in C_6D_6 showed multiplet patterns typical of the ttp ligand[3,4] centred at δ 7.3 (25H) and 1.8 (12H) which are assigned to the phenyl and methylene protons, broad absorptions at 5.1 (2H, $\nu_{\frac{1}{2}}$ *ca.* 90 Hz), −5.8 (1H, $\nu_{\frac{1}{2}}$ *ca.* 85 Hz), and −7.95 (1H, $\nu_{\frac{1}{2}}$ *ca.* 90 Hz), and a sharp doublet of triplets at −15.6 [1H, $^2J(P^1\text{–}H)$ 39 Hz, $^2J(P^2\text{–}H)$ 23 Hz]. The high-field region of this spectrum is illustrated in Figure 1(c). Broad-band decoupling of the boron nucleus causes the resonances at δ −5.8 and −7.9 to sharpen somewhat to a broad singlet ($\nu_{\frac{1}{2}}$ *ca.* 25 Hz) and a doublet [$\nu_{\frac{1}{2}}$ *ca.* 25 Hz, ^2J(P–H) 40 Hz], and the resonance at δ 5.1 ($\nu_{\frac{1}{2}}$ *ca.* 25 Hz) to sharpen; boron decoupling has little effect on the pattern at δ −15.6, as illustrated in Figure 1(a). Moreover, phosphorus-31 decoupling [Figure 1(b)] causes the pattern at δ −15.6 to collapse to a sharp singlet, and the absorptions at

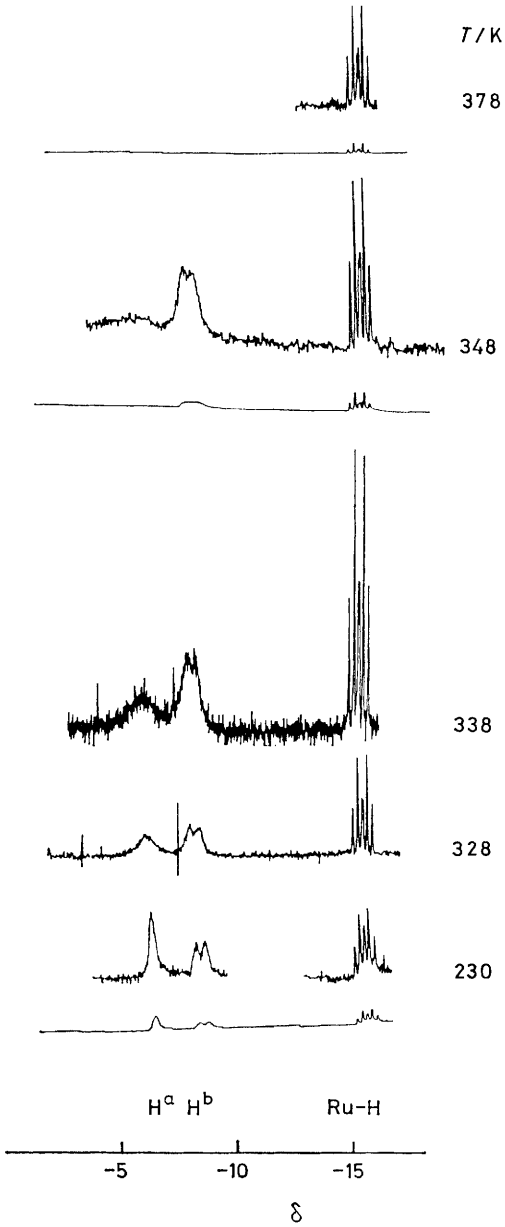


Figure 2. ^1H N.m.r. (^{11}B-decoupled) spectra of (**1**) in $[^2H_8]$-toluene for the temperature range 230—378 K. Note that the resonance for H^a begins to collapse in the temperature range 338—348 K, whereas the resonance of H^b remains. Both H^a and H^b resonances have collapsed at 378; however, the multiplet resonance for the Ru–H remains sharp throughout the temperature range.

δ −5.8 ($\nu_{\frac{1}{2}}$ *ca.* 40 Hz) and −7.9 ($\nu_{\frac{1}{2}}$ *ca.* 35 Hz) to become broad singlets. We conclude from these observations that the resonance at δ 5.1 is due to the two terminal B–H nuclei of the bonded BH_4^-, and the two resonances at δ −5.8 and −7.9 are due to two *nonequivalent* Ru–H–B bridges, the one at δ −7.9 being *trans* to the central phosphorus atom of the ttp ligand [indicated by the ^2J(P–H) coupling]. The observed *trans* P–H coupling (40 Hz) is of comparable magnitude to the ^2J(P–H^b) values reported for the compound $H_4Ru_4(CO)_{10}$-($Ph_2PCH_2CH_2PPh_2$), in which ^2J(P–H^b) (*trans*) = 28—30 Hz and ^2J(P–H^b) (*cis*) *ca.* 9—18 Hz.[5] [The *cis*-couplings in (**1**) are not resolved.]

The proton resonance at δ −15.6 is assigned to the hydrogen that is bonded directly to ruthenium; that hydrogen is *cis* to all three phosphorus atoms of the ttp ligand. This assignment is based on the magnitudes of the ^2J(P–H) values (23 and 39 Hz), which are closer to the range of ^2J(P–H) values reported[6] for a *cis*-geometry (6—32 Hz) than for a *trans*-geometry (73 Hz).

The structure proposed for (**1**) is a distorted octahedral arrangement around ruthenium with a meridianal arrangement of ttp and with the bidentate BH_4^- ligand spanning honequivalent sites, *i.e.*, (**1**). The proposed C_s symmetry of (**1**) is supported by the $^{31}P\{^1H\}$ n.m.r. spectrum, since we observe an AB_2 $^{31}P\{^1H\}$ n.m.r. pattern in benzene [δ (P^1) 34.1 p.p.m., δ (P^2) 29.8 p.p.m.; ^2J(P–P) 40 Hz]. A very broad resonance centred at −14.2 p.p.m. ($\nu_{\frac{1}{2}}$ *ca.* 2000 Hz, referenced to BCl_3 at 47.0 p.p.m.), was observed in the $^{11}B\{^1H\}$ n.m.r. spectrum. The signal was invariant with broad-band decoupling of the phosphorus nuclei. The structure of (**1**) is similar to that proposed by Crabtree for Ru(H)(BH_4)-($PMePh_2$)$_3$.[7]

A variable temperature $^1H\{^{11}B\}$ n.m.r. study (Figure 2) of RuH(BH_4)(ttp) in [$^2H_8$]toluene showed that the resonances at δ −5.8 and 5.1 (not shown in Figure 2) begin to collapse first, and at 348 K they disappeared into the baseline. A further increase of 10 K caused the resonance at δ −7.9 to collapse, but the doublet of triplets at δ −15.6 remained sharp up to 388 K, the safety limit of the solvent. These exchange steps are reversible. The dynamic ^1H n.m.r. results are interpreted in terms of a two-step process which causes scrambling of the bridging and terminal BH_4^- protons. In the lower-temperature step the Ru–H^a bond is broken allowing free rotation about the Ru–H^b–B linkage and equilibration of H^a and H^c before reforming an Ru–H–B bridge; thus, the BH_4^- group goes from bidentate to monodentate co-ordination. Note that H^b retains its stereochemical integrity in this first step; the presence of this Ru–H^b–B bridge is supported by the retention of the *trans* ^{31}P–^1H coupling in the temperature range 338—348 K. The second step equilibrates H^b with H^a and H^c, either by Ru–H^b bond rupture to give the ion pair [RuH(ttp)]$^+$[BH_4]$^-$ or by a fluxional process in which the Ru–H^b–B bridge breaks, equilibrating H^b and H^c by rotation about the remaining Ru–H^a–B bridge. A sequence of these two steps results in complete scrambling of the BH_4^- protons. The slightly lower energy required to break the Ru–H^a bond may reflect the slightly higher *trans*-labilizing effect of a hydride *vs.* a phosphine ligand in octahedral Ru^{II} complexes.

Owing to the presence of both Ru–H and doubly bridged Ru–BH_4 linkages in (**1**), addition of acid or base in the presence of neutral ligands L produces two different series of products, *i.e.*, monohydride cations of the type [Ru(H)$(L)_2$(ttp)]$^+$ [L = CO, MeCN, and P(OMe)$_3$] and dihydride neutral complexes of the type RuH_2(L)(ttp) [L = CO, PPh_3, and P(OMe)$_3$]. The syntheses, structures, and spectra of these two series of ruthenium hydride complexes will be reported later in a full paper.[2]

We gratefully acknowledge the loan of $RuCl_3.3H_2O$ by Johnson, Matthey Co. Ltd., a John Simon Guggenheim Fellowship to D. W. M., and a Lubrizol Fellowship to J. B. L. for 1981—1982.

Received, 27th October 1981; Com. 1261

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