J. CHEM. SOC., CHEM. COMMUN., 1982

Synthesis and Characterization of an Unsymmetrically Bonded Tetrahydroborato Ruthenium Hydride Complex

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The complex $\text{RuH}(\eta^2-\text{BH}_4)$ (ttp) [ttp = PhP(CH₂CH₂CH₂PPh₂)₂], obtained by treatment of [RuCl₂(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 BH₄ 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 $RuH(\eta^2-BH_4)(ttp)$ (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(η^2 -BH₄)(ttp) complex is the first case where two discrete steps have been observed for the fluxional behaviour of a BH₄⁻ 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 RuH₂(ttp). The i.r. spectrum, however, did not provide a definitive assignment about how the BH_4^- unit was bonded to the metal: v_{max}/cm^{-1} 2390s, 2380s, and 2330s: ν (B-H^t); 1180: δ (B-H^t); 1880m, sharp: ν (Ru-H) rather than v (Ru–H–B) by analogy with other v (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 $\operatorname{RuD}(\eta^2-\operatorname{BD}_4)(\operatorname{ttp})$, obtained from $[\operatorname{RuCl}_2(\operatorname{ttp})]_x$ and excess of NaBD₄ 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: v (Ru-D), but no absorptions that can be assigned unequivocally to the bridging Ru-D-B absorptions.







† 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.

Figure 2. ¹H N.m.r. (¹¹B-decoupled) spectra of (1) in $[{}^{2}H_{8}]$ -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.



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, $v_{\frac{1}{2}}$ ca. 90 Hz), -5.8 (1H, $v_{\frac{1}{2}}$ ca. 85 Hz), and -7.95 (1H, $v_{\frac{1}{2}}$ ca. 90 Hz), and a sharp doublet of triplets at -15.6 [1H, ${}^{2}J(P^{1}-H)$ 39 Hz, ${}^{2}J(P^{2}-H)$

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 some-

what to a broad singlet ($v_{\frac{1}{2}}$ ca. 25 Hz) and a doublet [$v_{\frac{1}{2}}$ ca.

25 Hz, ²J(P-H) 40 Hz], and the resonance at δ 5.1 (v₁ 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

 $\delta - 5.8 (v_{\pm} ca. 40 \text{ Hz}) \text{ and } -7.9 (v_{\pm} ca. 35 \text{ Hz}) \text{ to become broad}$ 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 BH₄⁻, 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 H₄Ru₄(CO)₁₀-(Ph₂PCH₂CH₂PPh₂), 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 $\delta - 15.6$ 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 ${}^{2}J(P-H)$ values (23 and 39 Hz), which are closer to the range of ${}^{2}J(P-H)$ values reported⁶ 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 ³¹P {¹H} n.m.r. spectrum, since we observe an AB₂ ³¹P {¹H} n.m.r. pattern in benzene [δ (P¹) 34.1 p.p.m., δ (P²) 29.8 p.p.m.; ²J(P-P) 40 Hz]. A very broad resonance centred at -14.2 p.p.m. (ν_{\pm} ca. 2000 Hz, referenced to BCl₃ at 47.0 p.p.m.), was observed in the ¹¹B {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)(BH₄)-(PMePh₂)₃.⁷

A variable temperature ¹H {¹¹B} n.m.r. study (Figure 2) of RuH(BH₄)(ttp) in [²H₈]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 BH₄⁻ protons. In the lower-temperature step the Ru-H^a bond is broken allowing free rotation about the Ru-H^b-B linkage and

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equilibration of H^a and H^c before reforming an Ru-H-B bridge; thus, the BH₄⁻ 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* ³¹P-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)]⁺[BH₄]⁻ 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 BH₄⁻ 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 Ru¹¹ complexes.

Owing to the presence of both Ru–H and doubly bridged Ru–BH₄ 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, PPh₃, 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

References

- 1 T. J. Marks and J. R. Kolb, Chem. Rev., 1977, 77, 263.
- 2 J. B. Letts, T. J. Mazanec, and D. W. Meek, J. Am. Chem. Soc., submitted for publication.
- 3 R. J. Uriarte, T. J. Mazanec, K. D. Tau, and D. W. Meek, *Inorg. Chem.*, 1980, **19**, 79.
- 4 D. W. Meek and T. J. Mazanec, Acc. Chem Res., 1981, 14, 266.
- 5 S. I. Richter, Ph.D. Dissertation, University of Illinois at Urbana-Champaign, 1977.
- 6 D. G. Holah, A. N. Hughes, and B. C. Hui, Can. J. Chem., 1976, 54, 320.
- 7 R. H. Crabtree and A. J. Pearman, J. Organomet. Chem., 1978, 157, 335.