

Preparation, Characterization, and X-Ray Crystal Structure of $\text{Ru}_2\text{H}_6\text{N}_2(\text{PPh}_3)_4$, a Compound containing Four Bridging Hydrides and a Ruthenium–Ruthenium Double Bond

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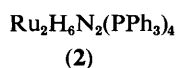
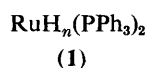
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The compound obtained by recrystallisation under N_2 of the hydrogenation product of $\text{Ru}(\text{styrene})_2(\text{PPh}_3)_2$ has been shown to be $\text{Ru}_2\text{H}_6\text{N}_2(\text{PPh}_3)_4$, a compound containing four bridging hydrides and a short Ru–Ru distance which is consistent with a metal–metal double bond; ^1H and ^{31}P n.m.r. spectra have allowed us to propose that the crude hydrogenation product is a mixture of $\text{RuH}_6(\text{PPh}_3)_2$ and $\text{Ru}_2\text{H}_8(\text{PPh}_3)_4$.

Ruthenium polyhydride complexes have been known for a long time and their importance in catalysis has been well established,¹ but so far only one *dinuclear* complex bridged by three hydrogen atoms has been characterized.² Rhenium polyhydride chemistry has been widely studied³ and $\text{Re}_2\text{H}_8(\text{PET}_2\text{-Ph})_4$ ⁴ has been found to be a unique tetrahydrido bridged complex. We report the facile preparation and the characterization of two tetrahydrido bridged ruthenium complexes $\text{Ru}_2\text{H}_8(\text{PPh}_3)_4$ and $\text{Ru}_2\text{H}_6\text{N}_2(\text{PPh}_3)_4$ together with the X-ray crystal structure of the latter.

The reaction of $\text{Ru}(\text{st})_2(\text{PPh}_3)_2$ (st = styrene)⁵ with hydrogen in hexane produced a pink precipitate which was found to be $\text{RuH}_n(\text{PPh}_3)_2$ (1). This crude product could not be recrystallized under argon but under nitrogen red crystals of the compound $\text{Ru}_2\text{H}_6\text{N}_2(\text{PPh}_3)_4$ (2) were obtained. A crystal obtained from toluene–hexane was mounted on an Enraf–Nonius automatic diffractometer.



Crystal data for (2): $\text{Ru}_2\text{H}_6\text{N}_2(\text{PPh}_3)_4$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 14.7968(21)$, $b = 20.8167(20)$, $c = 21.4421(21)$ Å, $\beta = 96.5791(13)^\circ$, $U = 6561.1$ Å³, $D_c = 1.30$ g cm⁻³. † From 7514 measured reflections (Mo- K_α radiation, λ

$= 0.71069$ Å), 2541 with $F > 6\sigma(F)$ were used for the refinement of the structure with the help of the SHELX program. The crystal was protected by a Lindemann capillary, owing to its air sensitivity. The abundance of weak reflections reduced the amount of data available; all twelve phenyl groups have been refined as rigid groups. This is one of the reasons why we did not achieve a better R value (7.9%). ‡

Figure 1 is a perspective view of compound (2). The molecule represents a structural analogy with $\text{Ru}_2\text{H}_8(\text{PMe}_3)_6$ ⁶. Observed distances range from 2.2 to 2.3 Å for Ru–P bonds. The Ru(2)–N(1) bond length is 1.94(4) Å and N(1)–N(2) 1.11 Å. No phenyl group occupies a co-ordination site as is sometimes the case. It is known that in such compounds the localization of the hydrido atoms is not an easy task and we have not been able to locate them solely on the basis of X-ray investigations. Nevertheless, examination of the geometry around the Ru(2) atom clearly rejects the possibility of a terminal H atom bonded to Ru(2). In contrast, the short Ru–Ru distance [2.556(3) Å] is compatible with the existence of several bridging H atoms and the geometry around Ru(1) with the presence of one or two terminal H atoms on Ru(1). It should be noted that the existence of 4 bridging H atoms and 2 terminal H atoms combined with a Ru–Ru double bond

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

† We were not able to obtain a value for D_m owing to the instability of the compound.

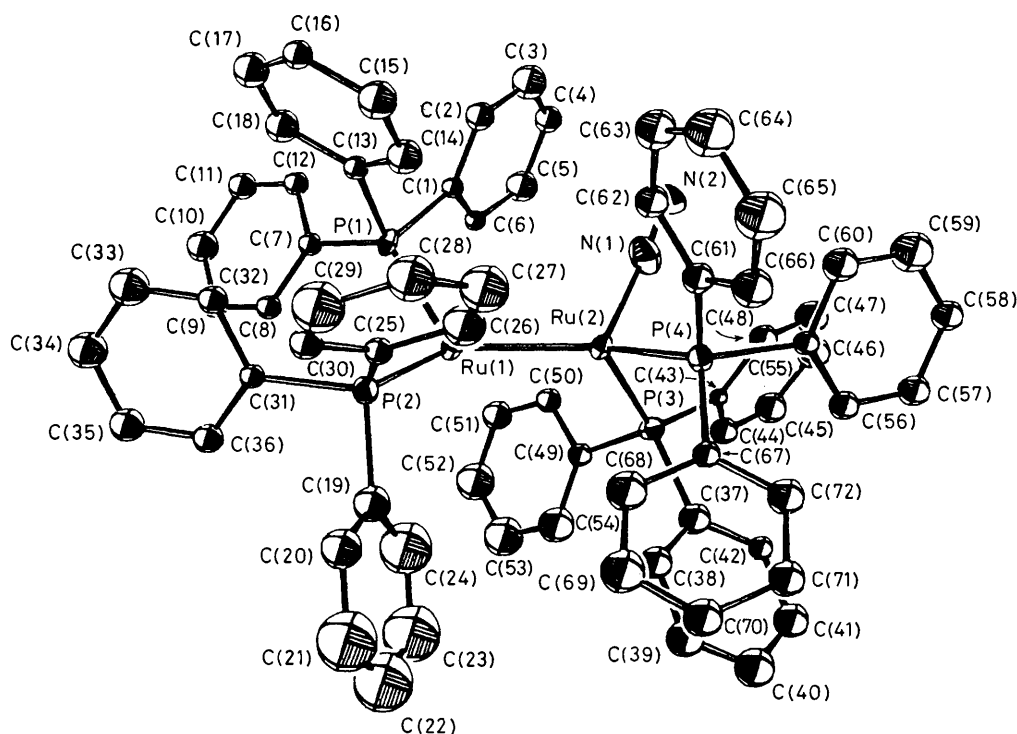


Figure 1. Perspective view and labelling scheme for compound (2). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at a 35% probability level.

gives a formal 18-electron configuration to each metal atom. Several methods of investigation are in progress for locating these hydrido atoms. At present ^1H n.m.r. data give some arguments on which to assess the structure of (2). In addition, the results of localization of the hydrides by molecular mechanics (Orpen's method⁶) are consistent with these results.

The solid state i.r. spectra of (1) and (2) confirm the presence of both terminal [1940m, br. (1), 1940m cm^{-1} (2)] and bridging [1600 v.br. (1), 1650m, 1560m cm^{-1} (2)] hydride ligands. In addition for compound (2), co-ordinated dinitrogen is indicated at 2140 cm^{-1} .

The ^{31}P n.m.r. spectra show two broad peaks for (1) at δ 79.45 and 60.13 p.p.m. (to high frequency of external H_3PO_4), which results in five peaks at -80°C (δ 85.98, 74.96, 64.96, 63.87, and 62.9 p.p.m.), and for (2) a singlet at δ 82 p.p.m. split into four peaks at -80°C . This indicates that the four phosphorus atoms of (2) are equivalent at room temperature which is somewhat surprising when considering the crystal structure. Compound (1) is probably a mixture of two unstable compounds whose relative proportions vary with experimental conditions and which decompose slowly in solution [spectra of (1), when recorded after a prolonged time in solution show a great many peaks].

The ^1H n.m.r. spectra shed more light on the structure of the complexes. Thus, the room temperature ^1H n.m.r. spectrum of (1) shows two broad singlets at δ -7.1 and -10.6 . The former disappears at -80°C (coalescence) whereas the latter is split into four signals of approximately equal intensities: a doublet of broad peaks at δ -8.4 [J_{PH} 65.5 Hz; H(1)], two broad peaks at δ -10.3 [H(2)] and -12.4 [H(3)], and a triplet at -19.2 [J_{PH} 30 Hz; H(4)]. The room temperature high field ^1H n.m.r. of (2) is similar, with three signals of equal intensity: a doublet of broad peaks at δ -8.0 [J_{PH} 64 Hz; H(1)], a quintet at -15.0 [J_{PH} 13 Hz; H(2)], and a triplet at -18.0 [J_{PH} 35 Hz; H(3)] (at -80°C the three peaks broaden and the

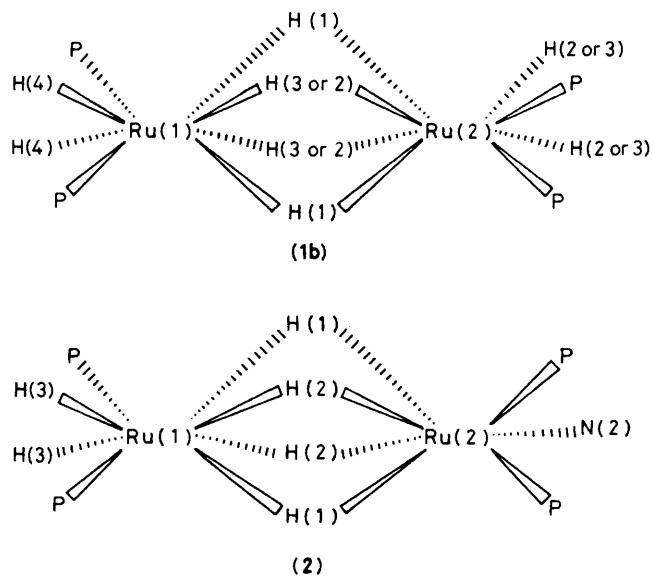


Figure 2. Structures of $\text{Ru}_2\text{H}_8(\text{PPh}_3)_4$ (1b) and $\text{Ru}_2\text{H}_6\text{N}_2(\text{PPh}_3)_4$ (2).

quintet pattern disappears). A comparison of these two spectra allowed us to propose that each peak represents two protons. The ^1H and ^{31}P n.m.r. spectra suggest that (1) is a mixture of two complexes, (1a) and (1b). Complex (1a) is a fluxional compound which can be transformed into (2) by recrystallization under nitrogen. It could be the unstable hexahydride $\text{RuH}_6(\text{PPh}_3)_2$ which is similar to that isolated from the reaction between $\text{Ru}(\text{cod})(\text{cot})(\text{cod} = \text{cyclo-octadiene}, \text{cot} = \text{cyclo-octatriene})$, $\text{P}(\text{C}_6\text{H}_{11})_3$, and hydrogen (^1H n.m.r. δ -7.7 s).⁷ It is clear on consideration of the spectra obtained for (1b) and

(2) that these are parent compounds. The high field triplet in (1b) [H(4)] and (2) [H(3)] probably represents two terminal protons on Ru(1) coupled to two equivalent *cis* phosphorus atoms. It is difficult to assign the other peaks but the two broad doublets [(1b): H(1) and (2): H(1)] could be due to bridging hydrides *trans* to phosphorus whereas the quintet [(2): H(2)] should be due to bridging hydrides which see four equivalent phosphorus atoms.

We propose two static formula for (1b) and (2) (see Figure 2) but since the compounds are fluxional [the four phosphorus atoms are equivalent at room temperature in compounds (1b) and (2)] we cannot unambiguously establish the hydride positions. The similar ^{31}P n.m.r. chemical shifts of (1b) and (2) (79.45 and 82 p.p.m.) and the ^1H n.m.r. spectra suggest that (1b) is $\text{Ru}_2\text{H}_8(\text{PPh}_3)_4$ which can lose two hydrogen atoms which are replaced by dinitrogen to give (2). Like (2), (1b) is probably dissymmetrical as four hydride signals were obtained but the exact structure is not known, particularly the position of the hydrides on Ru(2) (see Figure 2).

Structures containing four hydrides bridging a multiple metal-metal bond have only been found previously in Re_2H_8 -

$(\text{PEt}_2\text{Ph})_4$ but seem easy to obtain for ruthenium complexes.⁷ It is interesting to note that the presence of dinitrogen has allowed the study of this system by giving a more stable and rigid complex.

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References

- 1 E.g. B. R. James, *Inorg. Chim. Acta, Rev.*, 1970, 73.
- 2 R. A. Jones, G. Wilkinson, I. J. Colquhoun, W. McFarlane, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1980, 2480.
- 3 D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 1982, **224**, 363 and references therein.
- 4 R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, 1977, **99**, 3872.
- 5 B. Chaudret, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 1739.
- 6 G. A. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.
- 7 B. Chaudret, G. Commenges, and R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, 1982, 1388.