A Highly Unsaturated 'A-Frame' Heterobimetallic Trihydride. Preparation, Characterization, and *X*-Ray Crystal Structure of $RuRhH_3(Ph_2PCH_2PPh_2)_2$

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In the very unsaturated 28-electron complex $RuRhH_3(dppm)_2$ (dppm = bisdiphenylphosphinomethane) obtained by the reaction of $RuRhH_2Cl(cod)(dppm)_2$ (cod = cyclo-octa-1,5-diene) with $NaBH_4$ in tetrahydrofuran (thf), thf is not co-ordinated despite the unsaturation of the complex, and the three hydride ligands (one on Ru, one on Rh, one bridging) are rigid at the n.m.r. time-scale; the *X*-ray crystal structure shows the complex to adopt an 'A-frame' configuration with a short metal–metal distance [2.7894(4) Å].

Polyhydride phosphine complexes of transition metals are attracting considerable interest especially because of their rich reactivity in hydrogenation and C–H activation reactions.[1] We recently prepared a series of ruthenium polyhydrides and found that, as previously reported, an 18-electron configuration was achieved in each case.[2,3] Only in one case was a 16-electron intermediate, 'RuH_4P_2,' observed.[4] Ruthenium hydride chemistry was thus found to be somewhat similar to that for rhenium, for example, but not rhodium where unsaturated species of the type $[RhHP_2]_n$ (n = 2 or 3) are known and have been studied.[1a] As the ruthenium dinuclear complexes obtained were found to be particularly unstable, we tried to obtain stable dinuclear polyhydrides using the bridging ligand bisdiphenylphosphinomethane (dppm), known to stabilize homo- and hetero-bimetallic complexes.[5,6] The preparation of ruthenium–rhodium hydrides seemed attractive since we hoped to obtain species containing unsaturated rhodium moieties. We found that $RuRhH_2Cl(cod)(dppm)_2$ (cod = cyclo-octa-1,5-diene),[7] obtained by reaction of $RuH_2(dppm)_2$ with $[RhCl(cod)]_2$, reacts with $NaBH_4$ to afford $RuRhH_3(dppm)_2$, a 28-electron A-frame complex.

We have recently shown that the heterobimetallic complex $RuRhH_2Cl(cod)(dppm)_2$ (**1**) can be conveniently prepared quantitatively from the reaction between $RuH_2(dppm)_2$ and $[RhCl(cod)]_2$. In order to eliminate the chloride ligand from complex (**1**), it was treated with $NaBH_4$ in tetrahydrofuran (thf). The reaction proceeded smoothly at room temperature to give a deep brown solution from which off-white crystals could be isolated (overall yield *ca.* 70%), which could be recrystallized from toluene–pentane. Analytical data were consistent with the formulation $RuRhH_3(dppm)_2$ (**2**). The bimetallic structure of (**2**) was deduced from its ^{31}P n.m.r. spectrum which showed an AA'BB'X pattern as for related compounds[8] (Figure 1) (δ_A 54.0, δ_B 45.8, $J_{B\text{-}Rh}$ 112.3 Hz). The ^1H n.m.r. spectrum at room temperature showed only phenyl groups and a peak for toluene, together with two broad peaks at δ 3.84 and 3.78 for the methylene protons of dppm, and three hydride signals at δ −8.4 (H-3), −8.9 (H-2), and −14.0 (H-1) (integration ratio H-1 : H-2 : H-3 : CH_2 1 : 1 : 1 : 4). The signals for H-3 and H-2 are broad while that for H-1 is a quartet.

$RuRhH_2Cl(cod)(dppm)_2$

(**1**)

$RuRhH_3(dppm)_2$

(**2**)

On lowering the temperature, the chemical shifts did not change whereas the resolution of the signals increased. At 233 K the signal for H-2 remained broad while H-3 showed multiplet structure and H-1 remained a quartet (Figure 2). With complete decoupling, H-3 and H-1 showed coupling to rhodium ($J_{Rh\text{-}H\text{-}1}$ 24.6 Hz, $J_{Rh\text{-}H\text{-}3}$ 13.5 Hz; fortuitously $J_{Rh\text{-}H\text{-}1} = J_{P\text{-}H\text{-}1}$). This was interpreted as H-3 being a bridging hydride with H-3 terminal on ruthenium and H-1 on rhodium. It is remarkable that the complex is rigid on the n.m.r. time-scale and that there is no interconversion between the different hydrides. Since these data led to the proposed formulation

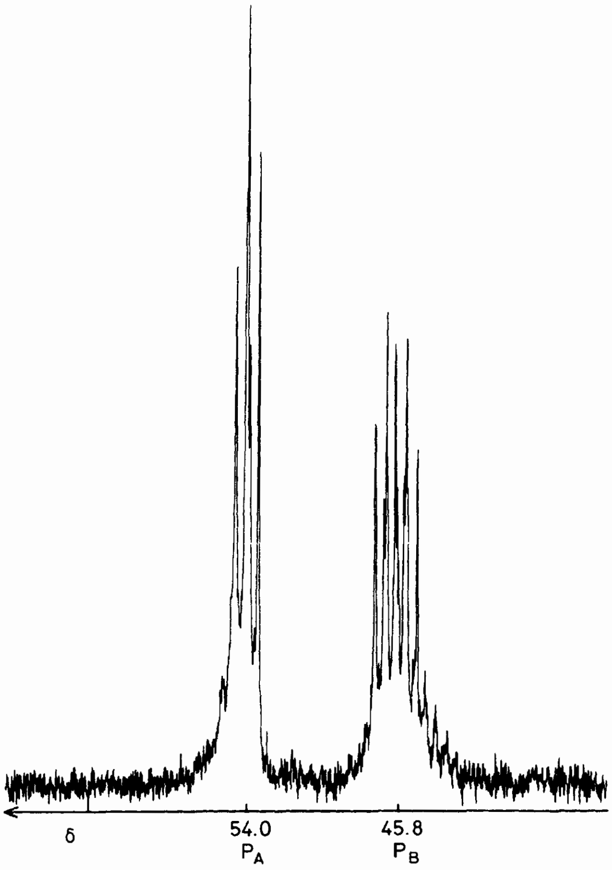

Figure 1. ^{31}P N.m.r. spectrum of (**2**).

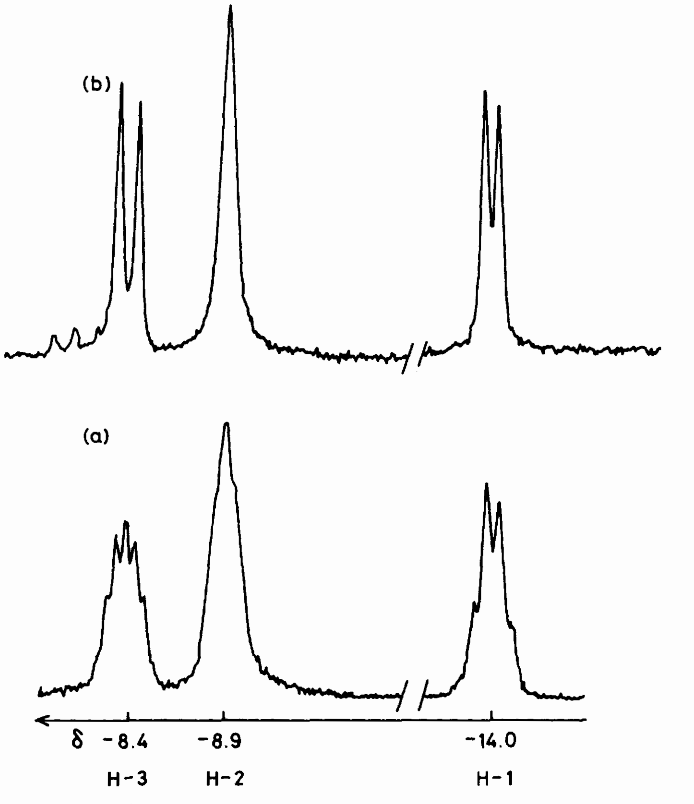

Figure 2. (a) High-field ^{1}H n.m.r. spectrum of (**2**) at 233 K; (b spectrum with complete phosphorus decoupling.

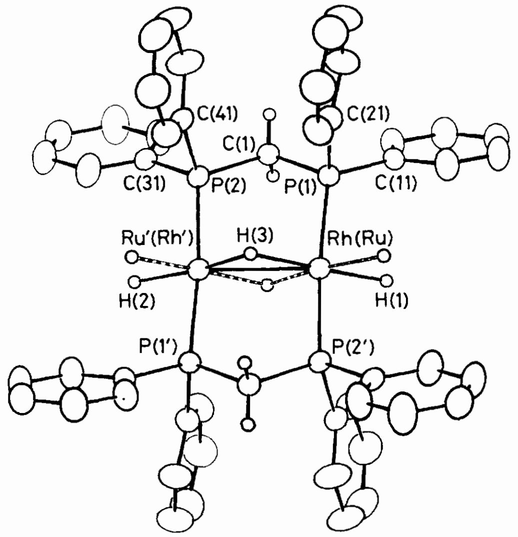

Figure 3. Perspective view of (**2**) showing the atom numbering scheme and the crystallographic disorder. Hydrogen atoms except H(1), H(2), H(3), and methylene protons are omitted for clarity. Principal bond lengths (Å) and angles (°): Rh–Ru' 2.7894(4), Rh–P(2') 2.282(1), Rh–H(3) 1.79(5), Ru'–H(3) 1.89(5), Rh–P(1) 2.283(1), Rh–H(1) 1.60(5), Ru'–H(2) 1.40(5); Ru'–Rh–P(1) 92.8(1), Ru'–Rh–H(1) 138(2), P(1)–Rh–P(2') 174.6(1), P(1)–Rh–H(3) 91(1), P(2')–Rh–H(3) 93(1), Rh–Ru'–H(2) 154(2), P(1')–Ru'–H(2) 87(2), P(2)–Ru'–H(2) 88(2), H(2)–Ru'–H(3) 164(2), Rh–H(3)–Ru' 99(1), Ru'–Rh–P(2') 92.5(1), Ru'–Rh–H(3) 42(1), P(1)–Rh–H(1) 86(2), P(2')–Rh–H(1) 90(2), H(1)–Rh–H(3) 177(2), Rh–Ru'–H(3) 39(1), P(1')–Ru'–H(3) 94(1), P(2)–Ru'–H(3) 91(1).

$RuRhH_3(dppm)_2$, a 28-electron complex, an *X*-ray crystallographic determination was carried out.[†]

[†] *Crystal data:* $RhRuP_4C_{50}H_{47} \cdot 2C_7H_8$: $M_r = 1160.09$, monoclinic, $a = 12.803(3)$, $b = 14.137(3)$, $c = 16.733(3)$ Å, $\beta = 108.89(2)°$, $U = 2866(1)$ Å^3, space group $P2_1/n$, $Z = 2$, $D_c = 1.344$ g cm^{-3}, $F(000) = 1188$, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 6.88$ cm^{-1}.

Intensity data were collected on a crystal coated with epoxy resin of dimensions 0.24 × 0.28 × 0.30 mm using θ–2θ scans ($3.2 < 2\theta < 50°$) with a variable scan speed of 2.93—29.3° min^{-1} and a scan width of 0.8° below $K_{\alpha1}$ to 0.8° above $K_{\alpha2}$ on a Syntex P2$_1$ diffractometer. From a total of 5072 measured reflections, 3555 had $I > 3\sigma(I)$ and were used in the structure solution and refinement. Two standard reflections (600, 25$\bar{7}$) monitored after every 100 measurements showed no change in intensity over the course of the data collection. With $\mu = 6.88$ cm^{-1} for these atoms no absorption correction was deemed necessary.

The heavy atom position was derived from a Patterson synthesis. With $Z = 2$, the molecule is required to sit across a centre of symmetry with the metal site occupied 50% by rhodium, 50% by ruthenium. The remaining atomic positions including the toluene solvate were located from a Fourier synthesis. Refinement of all non-hydrogen atoms with isotropic thermal parameters gave an R value of 0.075. With anisotropic thermal parameters, R was reduced to 0.045. A difference map at this stage allowed all non-solvent hydrogen atoms to be located, and these were included in subsequent refinements. The structure converged at $R = 0.034$ and $R_w = 0.040$ ($R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w^{-1} = 1.73 - 0.0176|F_o| + 0.00032|F_o|^2$). A final difference map was featureless with maximum residuals of 0.38 e Å^{-3} in the solvent vicinity. Scattering factors used were taken from the International Tables[9] and for hydrogen, the data of Stewart *et al.*[10] An average of the scattering factors for rhodium and ruthenium including anomalous dispersion corrections was used for the heavy atom. Computer programs used have been described elsewhere.[11]

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.

The molecular structure is shown in Figure 3 together with the atom numbering scheme. It is a classical example of an 'A-frame' complex with square-planar ruthenium and rhodium moieties. The structure can be compared with that of the similar platinum complexes $[Pt_2H(Me)_2(dppm)_2]^+$ or $[Pt_2H_3(dppm)_2]^+$.[12—14] While the ruthenium–rhodium complex is 28-electron, the platinum examples are 30-electron complexes. The Ru–Rh distance is shorter than that for the platinum complexes {2.933 Å for $[Pt_2H(Me)_2(dppm)_2]^+$} and simple electron counting indicates some multiplicity of the metal–metal bonding. Indeed, the T-shaped fragments[15] '$RuHP_2$' and '$RhHP_2$' with one and two electrons, respectively, in their HOMO may be combined, together with the bridging hydrogen atom, to provide a two-electron metal–metal bond and a three-centre Ru–H–Rh two-electron bond. The electron deficiency of this complex is very surprising especially since only one 16-electron ruthenium complex containing only hydride and phosphine ligands had been observed before and since the reaction proceeds in thf. The co-ordination deficiency around ruthenium is also unusual and indicates that the complex should have a high reactivity.

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