X-Ray Structure of the Hydrido-tris(triphenylphosphine)-ruthenium(II) ion, $[RuH(PPh_3)_2(\eta\text{-}Ph\text{-}PPh_2)]^+$

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Summary The *X*-ray crystal structure of hydridotris-(triphenylphosphine)ruthenium(II) tetrafluoroborate confirms a previous suggestion based on spectroscopic studies that one of the phenyl rings of one triphenylphosphine group is bound as an arene to the metal; ^{31}P n.m.r. spectra are in accord with the structure but unusual dependence of the low field doublet intensity upon the frequency of the secondary irradiating field at proton resonance frequencies is observed.

DURING further catalytic studies using ionic triphenylphosphine ruthenium complexes,[1] we observed that on heating a suspension of $RuH(CO_2Me)(PPh_3)_3$ in methanol with a large excess of fluoroboric acid, pale yellow needles of the salt, $[RuH(PPh_3)_3]BF_4$, are obtained on cooling. The ^1H n.m.r. spectrum of the cation is similar to that of the ion obtained by Sanders[2] when $[RuH(PPh_3)_4]^+$ is allowed to stand in solution. His suggestion that a phenyl ring was π-bonded to the metal[3] is confirmed by ^{31}P n.m.r. spectra and by *X*-ray crystallography, and the ion is hence $RuH(PPh_3)_2(\eta\text{-}C_6H_5PPh_2)^+$. A similar arene-bonded tetraphenylborate, $RuH(PPh_3)_2(\eta\text{-}C_6H_5BPh_3)$ is known[4] and for BPh_4^-, arene bonding has been crystallographically proved for $Rh[P(OMe)_3]_2BPh_4$.[5]

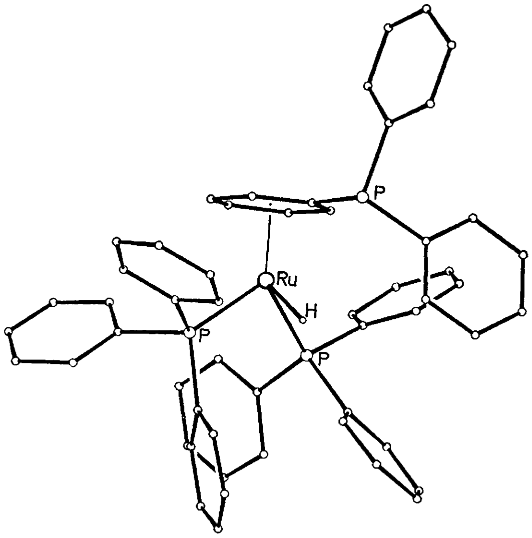

FIGURE 1. The structure of the $RuH(PPh_3)_2(\eta\text{-}PhPPh_2)^+$ ion in the tetrafluoroborate salt.

The crystals† of $[RuH(PPh_3)_3]BF_4$ are monoclinic, with unit-cell dimensions $a = 20{\cdot}755$, $b = 12{\cdot}784$, $c = 18{\cdot}609$ Å, $\beta = 109{\cdot}06°$, $U = 4667{\cdot}0$ Å^3, $Z = 4$, space group $P2_1/c$. *X*-Ray intensity data were collected on a Siemens four-circle diffractometer. Using Cu-K_α radiation a total of 5138 independent reflections were measured (to $\theta = 60°$), of which 480 were judged to be unobserved. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached $R = 0{\cdot}054$.

The crystal structure contains separate $[RuH(PPh_3)_3]^+$ and BF_4^- ions. As shown in Figure 1 the complex cation has one of the PPh_3 groups bonded to the metal atom *via* a η-phenyl group, while the other two PPh_3 ligands bond normally *via* phosphorus atoms. A hydride hydrogen atom completes the co-ordination about the metal atom.

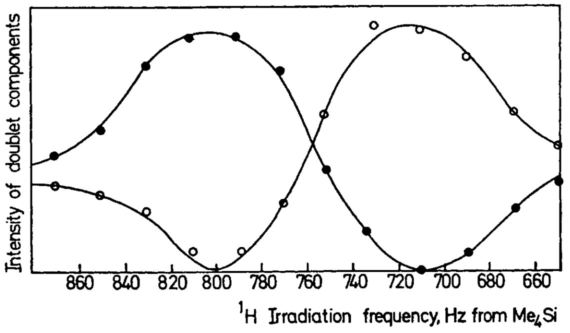

FIGURE 2. The dependence of the low-field ^{31}P doublet line intensities upon the frequency of the secondary irradiating field at ^1H aromatic resonance frequencies: ● = low-field component of a doublet; ○ = high-field component of a doublet.

The mean Ru–C distance is 2·28 Å and the distance of the metal atoms to the centroid of the η-phenyl ring is 1·78 Å. This is rather shorter than the equivalent distance (1·86 Å) in $Rh[P(OMe)_3]_2BPh_4$,[5] but longer than that in $(C_6H_6)Cr(CO)_3$ (1·72 Å).[6] The two Ru–P distances are 2·332(2) and 2·311(2) Å, and the angle between them is 98·7(1)°. These distances compare most closely with a mean of 2·326 Å found in $Ru(PPh_3)_2(pyS)_2$,[7] a six-co-ordinate complex with *cis*-PPh_3 groups and a similar P–Ru–P angle.

Although the full procedure[8] for optimising the hydride hydrogen position has not yet been applied, the highest remaining peak in a difference Fourier is near the expected position at a distance of *ca.* 1·7 Å as found in $RuHCl(PPh_3)_3$[9] and $RuH(CO_2Me)(PPh_3)_3$.[10] The hydride hydrogen is approximately symmetrically placed with respect to the two metal-bonded P atoms, with H–Ru–P angles of *ca.* 78°. Thus the presence of a large flat ligand close to the Ru atom pushes the other three ligand atoms together to give less than tetrahedral angles between them.

Proton-noise decoupled ^{31}P n.m.r. spectra of a $(CD_3)_2CO$ solution (*ca.* 75 mg per ml) were recorded at 40·505 MHz using a Varian XL100-12 spectrometer operating in Fourier transform mode. The spectrum showed a doublet (relative intensity 2, J_{P-P} 0·8 Hz) at 48·91 p.p.m. to low field and a triplet (relative intensity 1, J_{P-P} 0·8 Hz) at 5·77 p.p.m. to high field of external H_3PO_4 reference.

Selective irradiation at the ^1H absorption frequency of the aromatic protons (*ca.* 7·6 p.p.m. to low field of Me_4Si)

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† The crystals originally contain one methanol molecule of solvation, as shown by n.m.r. spectroscopy in solutions, but this is readily lost *in vacuo* and the structure determination revealed only ill defined traces of it in the lattice.

led to the observation of a major doublet splitting on each of these lines due to coupling with the hydride proton (low field line, J_{P-H} 33·3 Hz, high field line J_{P-H} 5·8 Hz). Best results were obtained using a limited amount of noise modulation of the proton frequency (*ca.* 850 Hz bandwidth) and *ca.* 5 W indicated power.

The appearance of this partially decoupled ^{31}P spectrum is critically dependent upon the centre frequency of the secondary irradiating field in the broad, unresolved aromatic region of the ^{1}H spectrum. The doublet line positions do not change significantly if this frequency is altered, but the relative intensity of the components varies greatly; one line may disappear completely while the other doubles in intensity. Figure 2 illustrates this by plotting the intensities of the components of the low field doublet (J_{P-H} 33·3 Hz) *vs.* the centre-frequency of the secondary irradiating field; the high field doublet shows parallel behaviour at slightly different frequencies.

The phenomenon probably arises from an Overhauser effect involving the redistribution of the populations of nuclear magnetic energy levels of phosphorus which are common to both aromatic and hydride proton spins. It is to be widely expected whenever off-resonance heteronuclear decoupling experiments are carried out on complex spin systems, and could be very misleading; similar effects have been noted while observing ^{13}C resonance while irradiating at off-resonance ^{1}H frequencies.[11]

The ^{31}P n.m.r. spectrum is consistent with the structure in Figure 1. The chemical shift of phosphorus in the arene-bonded ligand, ($\delta - 5·77$ p.p.m. from H_3PO_4) is close to that in free triphenylphosphine [$\delta - 6·34$ p.p.m. added to the solution of complex in $(CD_3)_2CO$] which confirms that bonding is not *via* phosphorus since the two conventionally bonded ligands resonate at $\delta + 48·91$ p.p.m. The observation of spin-spin coupling between the non-equivalent P nuclei, and between the single P and the hydridic proton, indicates that there is substantial electron delocalisation from P into the aromatic π-system and on to Ru. The arene-bonded complex is catalytically inactive towards hydrogenation of alkenes; it is presumably formed by intramolecular electrophilic attack of the co-ordinatively unsaturated ruthenium atom in a normal intermediate tris-species probably with synchronous breaking of the Ru–P bond in one PPh_3 group.

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