X-Ray Molecular Structure and Reactions of Bis(styrene)bis(triphenylphosphine)ruthenium(0); the First Sixteen-electron Ruthenium(0) Species†

By Maria A. A. F. de C. T. Carrondo, Bruno N. Chaudret, David J. Cole-Hamilton, Andrzej C. Skapski,* and Geoffrey Wilkinson*

(*Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London* SW7 2AY)

Summary The complex originally formulated as Ru(styrene)$(PPh_3)_3$ has been shown by *X*-ray study to be Ru(styrene)$_2(PPh_3)_2$, (containing solvent); the formation of dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$, on interaction of the complex with hydrocarbons has been studied and the source of hydride attributed to triphenylphosphine.

Various yellow compounds obtained by interaction of the hydridotriphenylphosphine ruthenium compounds, $RuH_4(PPh_3)_3$ or $RuH_2(PPh_3)_4$, with alkenes were not, as originally believed,[1] ruthenium(0) complexes, but ruthenium(II) alkene hydrido, orthometallated phosphine or ruthenium(0) diene species.[2] The product formulated[1] as Ru(styrene)$(PPh_3)_3$ was anomalous in being purple. In view of our interest in purple species[3] and the reported[1] reactions with hydrocarbons to re-form $RuH_2(PPh_3)_4$ the complex and its reactions have been studied again.

The complex is a 16-electron ruthenium(0) species but it is Ru(styrene)$_2(PPh_3)_2$ as shown by *X*-ray study, n.m.r. spectroscopy, and analysis. The complex $RuCl(NO)(PPh_3)_2$[4] could be considered as a 16-electron complex of Ru^0, but under present convention it is a Ru^I complex; $Ru(Me_2PCH_2CH_2PMe_2)_2$[5] has been postulated in solution.

A crystal obtained from styrene–light petroleum (mainly C_5 and C_6 hydrocarbons) was mounted in a Lindemann tube on a Siemens automatic diffractometer, and a total of 6022 independent reflexions were measured to θ = 40°. The crystals are triclinic, and a morphologically convenient unit cell‡ a = 21·666, b = 17·549, c = 16·332 Å, α = 80·19, β = 113·52, γ = 118·20° was used; space group is $P\bar{1}$ and Z = 4. Patterson and Fourier methods were used to solve the structure, and the least-squares refinement has reached R = 0·074.§

Two crystallographically independent complex molecules are found in the structure, with some disordered aliphatic solvent molecules loosely packed between them. There are

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† No reprints available.

‡ The Delaunay reduced cell is a = 16·332, b = 17·549, c = 20·446 Å, α = 110·95, β = 106·06, γ = 99·81°.

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

no significant differences between the complex molecules and mean values of bond lengths and angles are used. Figure 1 shows the molecular structure in which the ruthenium atom is bound to two triphenylphosphine molecules (∠P–Ru–P, 107·8°) and to the vinylic double bonds of two styrene groups. The co-ordination geometry around ruthenium can best be described in terms of a highly distorted tetrahedron (with angles in the range 92—138°) if one considers the Ru–styrene links as single to the midpoints of the double bonds. As a result of this bonding the C=C distances are appreciably lengthened (1·40—1·42 Å) compared with those found for exocyclic C=C bonds (*ca.* 1·35 Å).[6] The two Ru–P bonds are markedly different: Ru–P(2), which together with the two double bonds forms an approximate plane, is long (2·411 Å), while Ru–P(1), which is approximately normal to this plane is short (2·216 Å).

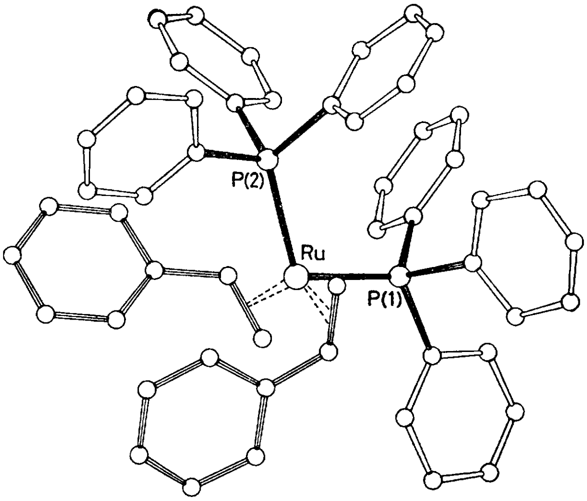

FIGURE 1. Molecular structure of Ru(styrene)$_2$(PPh$_3$)$_2$.

The Ru–C bond lengths shown in Figure 2 are comparable to those for Ru π-bonds to C=C.[7] There is, however, a significant difference between the two styrene ligands. In one case the phenyl ring points away from the metal atom, while in the other one it appears to be pulled slightly towards the metal atom. This difference can best be seen by comparing Ru····C(1) and Ru····C(1′) distances, 3·179 and 2·750 Å, respectively. Slight variations of the Ru–C bond distances are consistent with this difference. Thus while the centre of gravity of the Ru to C$_\alpha$=C$_\beta$ bond is slightly towards the terminal β carbon, in the other styrene the centre of gravity is marginally towards the inner α' carbon. While an Ru····C(1′) distance of 2·750 Å does not constitute a bonding distance, the overall geometry is suggestive of a slight overspill of double-bond character onto C(1′)–C$_{\alpha'}$.

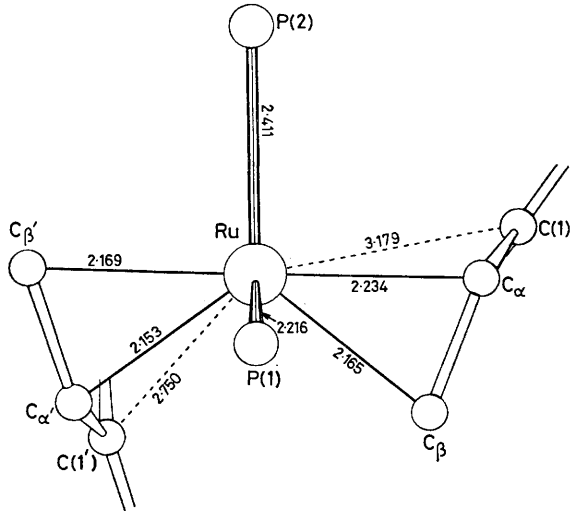

FIGURE 2. Co-ordination about the ruthenium atom. View is normal to the Ru–P(2) bond, and midpoints of the vinylic double bonds are fractionally below the plane of paper. For sake of clarity phenyl rings have been omitted except for the C(1) and C(1′) atoms on the two styrene groups. E.s.d.s are: Ru–P, 0·004; Ru–C, 0·013 Å.

There is no spectroscopic evidence for the presence of hydride ligands and low temperature ^{31}P n.m.r. study (doublets at δ 75·5 and 43·3 p.p.m., J_{PP} = 22 Hz) shows that the complex retains the solid state structure in solution, but on warming the two doublet resonances broaden and coalesce. The spectra are difficult to obtain due to ready reaction of the complex in solvents other than styrene, in which an equilibrium between Ru(styrene)$_2$(PPh$_3$)$_2$ and Ru(styrene)$_3$(PPh$_3$) is established.

In the presence of an excess of PPh$_3$ (although not in its absence as reported[1]) we confirmed the formation of RuH$_2$(PPh$_3$)$_4$ using a wide range of solvents including saturated hydrocarbons. Regrettably, however, the source of hydride is triphenylphosphine and not the solvent. Thus on warming Ru(styrene)$_2$(PPh$_3$)$_2$ in hexafluorobenzene or hexane containing two moles of PPh$_3$, the product is largely the same as that obtained by warming in any hydrocarbon in the absence of added PPh$_3$, namely an orange material evidently a mixture and probably containing diphenylphosphido groups. With a large excess of PPh$_3$ in C$_6$F$_6$, the main product is RuH$_2$(PPh$_3$)$_4$.

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