Bis(styrene)bis(triphenylphosphine)ruthenium(0) and its Reactions with Triphenylphosphine and with Alkenes †

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A complex previously thought to be styrenetris(triphenylphosphine)ruthenium(0) is shown to be bis(styrene)bis-(triphenylphosphine)ruthenium(0). The complex appears to react with aliphatic and aromatic hydrocarbons to form dihydridotetrakis(triphenylphosphine)ruthenium(II), $RuH_2(PPh_3)_4$, but the source of the hydride is shown to be triphenylphosphine.

The reactions of the complex with ethylene and other alkenes have been studied and the products characterised by analysis, i.r., and ^1H and ^{31}P n.m.r. spectra.

New complexes described are: $Ru(C_2H_4)_2(C_8H_8)(PPh_3)_2$, $Ru(C_4H_6)(C_8H_8)(PPh_3)_2$, $Ru(C_4H_6)_2(PPh_3)_2$, $RuH(C_6H_{11})(C_8H_8)(PPh_3)_2$, and $Ru(C_6H_{10})(C_8H_8)(PPh_3)_2$.

ALTHOUGH it was reported [1-3] that the interaction of the dihydro- or tetrahydrido-(triphenylphosphine)ruthenium complexes $RuH_2(PPh_3)_4$ or $RuH_4(PPh_3)_3$ with alkenes gave alkeneruthenium(0) species, we showed [4] that the complex from ethylene is $Ru^{II}H(C_2H_4)(o\text{-}C_6H_4PPh_2)(PPh_3)_2$ while that from pent-1-ene is the pentadiene complex $Ru(C_5H_8)(PPh_3)_3$. Among alkenes, styrene was unique in giving a purple complex formulated,[1] mainly on the basis of carbon and hydrogen analyses, as Ru(styrene)$(PPh_3)_3$. It was also reported [1] that this complex reacts with toluene to regenerate $RuH_2(PPh_3)_4$, the hydrogen evidently coming from the solvent. In view of the fact that in our hands $RuH_2(PPh_3)_4$ also appeared to be formed when saturated hydrocarbons were used, further studies on the styrene complex have been made. The complex has been found to be Ru(styrene)$_2$$(PPh_3)_2$ and the formation of the dihydride has been shown to result from reaction with triphenylphosphine.[5]

Preparation and Synthesis of Bis(styrene)bis(triphenylphosphine)ruthenium(0).—As reported,[1] $RuH_2(PPh_3)_4$ reacts rapidly with styrene to give very deep purple solutions. Diamagnetic purple crystals can be obtained on addition of light petroleum and cooling.

The complex analyses for $Ru(C_8H_8)_2(PPh_3)_2\cdot0.5$sol, where sol is saturated hydrocarbon ‡, and shows no peaks assignable to Ru–H or to an *ortho*-metallated phenyl ring in the i.r., although the C=C stretch of co-ordinated styrene occurs at 1 589 cm^{-1}. *X*-Ray diffraction study [5,6] confirms the bis,bis formulation; the complex is hence the first sixteen-electron complex of ruthenium(0).

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† No reprints available.

‡ G.l.c. and n.m.r. analyses suggest that the lattice solvent consists mainly of pentane and hexane (1 : 1) together with smaller amounts of branched and cyclic pentanes and hexanes.

[1] S. Komiya and A. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 2553.

[2] F. Penella, *Coord. Chem. Rev.*, 1975, **16**, 51.

[3] F. Penella and R. L. Banks, *J. Catalysis*, 1974, **35**, 73.

[4] D. J. Cole-Hamilton and G. Wilkinson, *Nouveau J. Chim.*, 1977, **1**, 141.

[5] B. N. Chaudret, M. A. A. F. de C. T. Carrondo, D. J. Cole-Hamilton, A. C. Skapski, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1978, 463.

[6] M. A. A. F. de C. T. Carrondo, and A. C. Skapski, in preparation.

The instability of the complex in common organic solvents other than styrene precludes detailed n.m.r. characterisation. However, broad peaks at δ 2.7 and 4.3 in the ratio 2 : 1 in the ^1H n.m.r. spectrum measured quickly in benzene or in styrene at room temperature are assigned to the methylene and methine protons of co-ordinated styrene respectively, by analogy with the relative chemical shifts of the protons in $K[PtCl_3(C_8H_8)]$,[7] although in the ruthenium complex the resonances are both to higher field. The complex is stable in toluene below −30 °C and, although insufficiently soluble for acurate ^1H n.m.r. spectra to be obtained, the ^{31}P n.m.r. spectrum at −50 °C (two doublets at 75.5 and 43.3 p.p.m.,* $J_{PP} = 22$ Hz) shows that the complex is rigid on the n.m.r. time scale with *cis*, non-equivalent phosphorus atoms. On warming in the presence of an excess of styrene, these doublets broaden and coalesce until at room temperature the spectrum consists of two broad resonances at δ 60.5 and 55.1 p.p.m. Two new sharp singlet resonances at δ 54.6 and −5.8 of approximately equal intensity are also visible at room temperature and since the −5.8 p.p.m. resonance arises from free PPh_3, the 54.6 frequency probably arises from a compound which contains only one triphenylphosphine, *i.e.* $Ru(C_8H_8)_3(PPh_3)$ formed from interaction of $Ru(C_8H_8)_2(PPh_3)_2$ with an excess of styrene.

Solutions of $Ru(C_8H_8)_2(PPh_3)_2$ in the presence of excess of styrene are red rather than purple but attempts to crystallise $Ru(C_8H_8)_3(PPh_3)$ from them have been unsuccessful, leading only to the isolation of $Ru(C_8H_8)_2(PPh_3)_2$. This suggests that $Ru(C_8H_8)_2(PPh_3)_2$ and $Ru(C_8H_8)_3(PPh_3)$ are in dynamic equilibrium and that the bis-styrene complex is the less soluble of the two.

In the absence of an excess of styrene, extensive decomposition occurs (see below).

The stability of the complex in the solid state is presumably a reflection of the steric congestion about the metal atom. This may also account for the relative insensitivity to air—thus the solid may be kept in dry air for several minutes before deterioration occurs. With water in tetrahydrofuran (thf), it reacts to give $RuH(OH)(PPh_3)_2(thf)$ [8]—one of the rare cases of oxidative addition of water as H and OH.[9]

Reactions of $Ru(C_8H_8)_2(PPh_3)_2$ *in Saturated Hydrocarbons*.—(a) *In the absence of added triphenylphosphine.* When $Ru(C_8H_8)_2(PPh_3)_2$ is suspended in saturated hydrocarbons (sol) such as hexane or tetramethylsilane, for several hours at 25 °C, green solids of approximate composition $Ru(C_8H_8)(PPh_3)_2{\cdot}0.5sol$ are formed. Treatment of the hexane material with air, water, aqueous LiOH, H_2SO_4, benzene, or MeI liberated hexane; no deuterium incorporation occurred when D_2O, D_2SO_4, or $LiOD–D_2O$ was used.

The i.r. spectra of the green materials show a weak band of variable intensity at 2 080 cm^{-1} (Ru–H stretch) together with hydrocarbon bands, *e.g.* in the $SiMe_4$ material at 1 248 and 860 cm^{-1}. The n.m.r. spectrum of the $SiMe_4$ material, in addition to phenyl resonances, showed only a resonance due to free $SiMe_4$.

It is clear therefore that oxidative addition of alkenes as H and alkyl has not occurred and the hydrocarbon is evidently merely trapped in the lattice. This is confirmed by the reaction with hexafluorobenzene, which gives a similar green material, $Ru(C_8H_8)(PPh_3)_2{\cdot}0.5C_6F_6$ with an i.r. spectrum similar to the other green materials except that hydrocarbon bands are absent and there are strong sharp peaks at 1 570 [ν(C–F)] and 1 010 cm^{-1} that can be assigned to clathrated C_6F_6. The weak peak at 2 080 cm^{-1} due to Ru–H in the hydrocarbon materials is due to small amounts of '$RuH_2(PPh_3)_4$' † whose presence is confirmed by ^{31}P n.m.r. spectroscopy.

The green materials all decompose in solution in organic solvents to give an orange–brown product. We have been unable to crystallise this material and ^{31}P n.m.r. spectroscopy indicates that it is a mixture; chromatography was unsuccessful.

When $Ru(C_8H_8)_2(PPh_3)_2$ is dissolved in benzene, toluene, or tetrahydrofuran, the initial purple solutions became green then brown and the 'orange species' can be isolated. In contrast to Yamamoto's observation,[1] we obtain $RuH_2(PPh_3)_4$ other than in traces only when an excess of PPh_3 is present (see below).

Finally, if $Ru(C_8H_8)_2(PPh_3)_2$ is refluxed in hydrocarbons the 'orange species' is obtained with very little contamination of $RuH_2(PPh_3)_4$, presumably because the formation of the latter involves a slow reaction.

Since benzene is always found in the solutions it appears that cleavage of a phenyl ring of PPh_3 leading to PPh_2 bridges occurs during the formation of the 'orange species' and low-field ^{31}P n.m.r. lines for the latter are consistent with the presence also of *ortho*-metallated $C_6H_4PPh_2$ groups.

(b) *In the presence of an excess of triphenylphosphine.* When purple $Ru(C_8H_8)_2(PPh_3)_2$ is shaken with three mole equivalents of PPh_3 in hexane, benzene, toluene, tetramethylsilane, *etc.*, at 25 °C for *ca.* 48 h a yellow solid readily identified by i.r. and ^{31}P n.m.r. spectroscopy as '$RuH_2(PPh_3)_4$' is formed in high yield. Small quantities of 'orange species' are also formed according to ^{31}P n.m.r. spectroscopy.

Interaction of $Ru(C_8H_8)_2(PPh_3)_2$ with PPh_3 in C_6D_{14} does not lead to any observable deuterium incorporation (^2D n.m.r. evidence). However, we do not consider that this affords conclusive proof that the solvent is not the source of the hydride ligands since the ready exchange of hydrido hydrogen atoms with the *ortho* hydrogen atoms of the phenyl rings on co-ordinated triphenylphosphine

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* Chemical shifts are in p.p.m. to high frequency of external 85% H_3PO_4.

† Strictly this is a mixed species containing a chelate phosphine, see later.

[7] H. P. Fritz, K. E. Schwarz, and D. Sellman, *J. Organometallic Chem.*, 1966, **6**, 55.

[8] B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr, and G. Wilkinson, *J.C.S. Dalton*, 1977, 1546.

[9] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1977, 838.

is well known.[10] Furthermore, since the reaction was carried out in the presence of an excess of PPh_3, with which the co-ordinated PPh_3 groups of $RuH_2(PPh_3)_4$ readily exchange, the deuterium incorporation, were it occurring, would be such that any deuterium atoms incorporated into the molecule would be spread over many sites. This, together with the splitting of the signals from the D atoms by phosphorus, the dissociative exchange of free and bound PPh_3 at room temperature and the low solubility and high molecular weight of $RuH_2(PPh_3)_4$ render it unlikely that the enrichment would give ^2D resonances which are greater in intensity than that arising from the natural abundance of deuterium in solvent benzene which was not observed in the ^2D n.m.r. experiment.

G.l.c. study of the hexane reaction shows that no hexenes are produced as might have been expected if hexane had undergone oxidation of a C–H bond followed by β-hydride abstraction. Although in separate studies (see later) we showed that the reaction of hexenes with $Ru(C_8H_8)_2(PPh_3)_2$ in the presence of an excess of PPh_3 gives hexadiene complexes, no complexed or uncomplexed hexadienes are present after the reaction in hexane.

In short, the hydrocarbon solvent is not the source of the hydride in ' $RuH_2(PPh_3)_4$ '. This is confirmed by the following observations. When $Ru(C_8H_8)_2(PPh_3)_2$ is warmed to 60 °C in C_6F_6 or hexane containing *two* mole equivalents of PPh_3 a mixture of the ' orange species ' and ' $RuH_2(PPh_3)_4$ ' (together with benzene) is formed, but with a large excess of PPh_3 or in molten PPh_3, the main product is ' $RuH_2(PPh_3)_4$ '.

The most likely mechanism for the formation of ' $RuH_2(PPh_3)_4$ ' is the oxidative addition of *ortho* C–H bonds of two phenyl rings followed by elimination of 2,2′-bis(diphenylphosphino)biphenyl, as in Scheme 1. The last step is but an unusual example of the well known elimination reaction from transition-metal bisaryl compounds to give biphenyls.

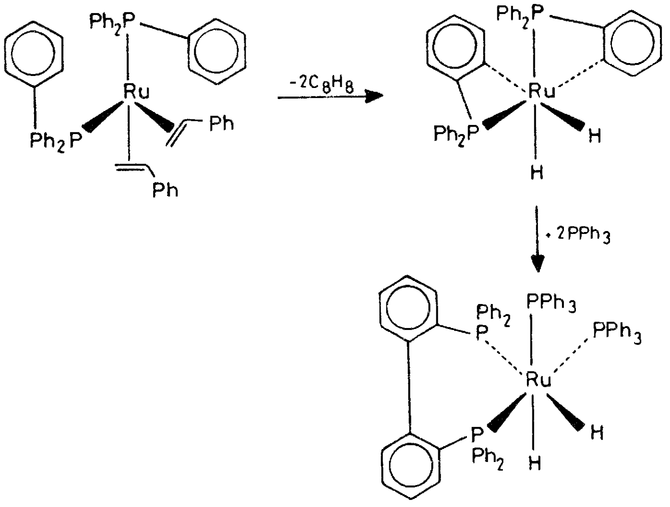
Support for this scheme comes from the reaction of $RuH(o\text{-}C_6H_4PPh_2)(C_2H_4)(PPh_3)_2$ with an excess of PPh_3 in benzene under conditions similar to those used above, which gives ' $RuH_2(PPh_3)_4$ ' in high yield.

Further, mass spectral analysis of the products from the reaction between $Ru(C_8H_8)_2(PPh_3)_2$ and 3 mole equivalents of PPh_3 in hexane, after evaporation to dryness and partial decomposition in air, shows fragmentation patterns of both the mono- and di-oxides of 2,2′-bis(diphenylphosphino)biphenyl.*

Attempts to transfer hydrogen from PPh_3 to styrene catalytically by treating $Ru(C_8H_8)_2(PPh_3)_2$ with an excess of PPh_3 in styrene–hexane were unsuccessful. At first sight this is surprising but a weak peak at 1 550 cm^{-1} (indicative [11] of an *ortho*-disubstituted phenyl ring) is always present in the i.r. spectrum of ' $RuH_2(PPh_3)_4$ ' formed in these reactions. This suggests that the hydride retains the 2,2′-bis(diphenylphosphino)biphenyl as a chelating ligand and that this is not displaced by an excess of PPh_3 (presumably because of the chelate effect). Then, when two such diphosphine ligands are present in the complex, phosphine dissociation and hence further reaction with styrene are inhibited.

In confirmation, the mass spectrum at 250 °C of the ' $RuH_2(PPh_3)_4$ ' from $Ru(C_8H_8)_2(PPh_3)_2$ and a large excess of PPh_3 in C_6F_6 washed several times with petroleum has its major peak at 337 a.m.u. This corresponds to $(biphenyl)Ph_2P^+$, which we assume to be a very stable cation formed from the diphosphine by elimination of Ph_2P. The parent ion for the diphosphine is not observed.

Reactions of $Ru(C_8H_8)_2(PPh_3)_2$ *with Alkenes and Dienes.*—In view of the possibility that dehydrogenation of alkanes could give alkene complexes, and in order to be able to identify such species, we studied the reactions of the styrene complex with various unsaturated hydrocarbons. These reactions are summarised in Scheme 2.



Scheme 1

(a) *Ethylene.* At room temperature petroleum suspensions of $Ru(C_8H_8)_2(PPh_3)_2$ and C_2H_4 give an orange complex $Ru(C_2H_4)_2(C_8H_8)(PPh_3)_2$. The i.r. and ^1H n.m.r. spectra show no Ru–H or $o\text{-}C_6H_4PPh_2$ groups but there is a band due to co-ordinated styrene at 1 595 cm^{-1}; the C=C stretch for ethylene is either too weak to be observed or is masked by other absorptions.

The ^1H n.m.r. spectrum has a series of broad resonances at δ 5.3, 1.9, 1.2, and 0.9, due to olefinic protons, while the ^{31}P spectrum (two doublets δ 67.1, 51.2, $J_{PP} = 9.5$ Hz) shows that the complex has a rigid, five-co-ordinate geometry with mutually *cis*-PPh_3 groups. The J value is similar to those for other five-co-ordinate Ru^0 species [*e.g.* $Ru(C_4H_6)(PPh_3)_3$, $J_{PP} = 4.9$ Hz[4]].

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* In both cases the parent ion is not observed but rather $M - 1$. This is also the case for PPh_3O. This phosphine apparently has not been made although the 3,3′- [B. Chiswell and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 901] and 4,4′- (R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, 1965, **30**, 3860) isomers have.

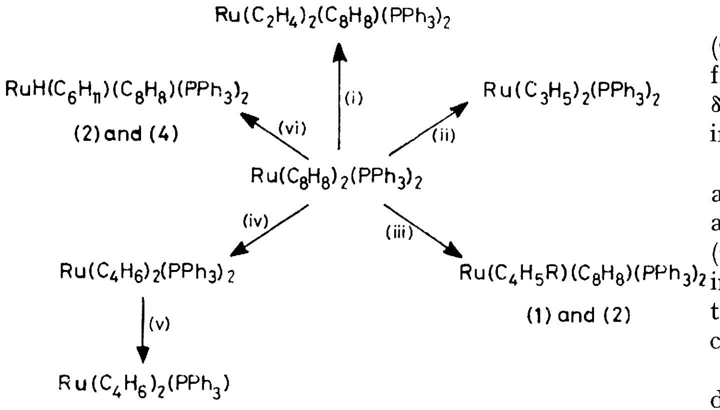
[10] G. W. Parshall in Specialist Periodical Report, ' Catalysis,' Chemical Society, London, 1977, vol. 1, 335,

[11] D. J. Cole-Hamilton and G. Wilkinson, *J.C.S. Dalton*, 1977, 797.

The complex is unstable in solvents other than styrene giving an orange material or, in presence of an excess of PPh_3, ' $RuH_2(PPh_3)_4$ '.

(b) *Propene*. There is only a slow reaction in petroleum at room temperature so that after 15 h the product is mostly the green $Ru(C_8H_8)(PPh_3)_2 \cdot 0.5sol$, but at 60 °C in heptane the reaction is smooth giving the previously characterised[4] bis-allyl complex, *cis*-$Ru(\eta\text{-}C_3H_5)_2(PPh_3)_2$.

(c) *But-*1-*ene; buta-*1,3-*diene*. Interaction of but-1-ene with $Ru(C_8H_8)_2(PPh_3)_2$ in petroleum gives a yellow powder recrystallisable from toluene or deuteriobenzene as crystalline solvates $Ru(C_4H_6)(C_8H_8)(PPh_3)_2 \cdot sol$. The same compound is formed from buta-1,3-diene in styrene in presence of an excess of PPh_3. We have previously observed[4] the dehydrogenation of but-1-ene to give the diene complex in the reaction with $RuH_4(PPh_3)_3$ and the present reaction presumably goes *via* a similar path.



SCHEME 2 Reactions of $Ru(C_8H_8)_2(PPh_3)_2$ with alkenes. *Reagents:* (i) C_2H_4–petroleum, 25 °C; (ii) C_3H_6–petroleum, 60 °C; (iii) C_4H_8–petroleum, 25 °C (R = H); C_4H_6–styrene, 25 °C (R = H); 2-C_6H_{12}, 25 °C (R = C_2H_5); (iv) C_4H_6–petroleum, 25 °C; (v) C_6H_6, 25 °C; (vi) 1-C_6H_{12}, 25 °C

The presence of co-ordinated styrene in the complex is confirmed by the i.r. peak at 1 592 cm^{-1} and broad ^1H resonances at δ 5.7 (CH) and 3.2 (CH_2) while ^1H resonances of co-ordinated *cis*-buta-1,3-diene are at δ 4.3, 1.6, and −0.5.

Although in the solid state, the complex appears to have only one isomer, in solutions it forms an equilibrium mixture of two isomeric forms in each of which the PPh_3 groups are equivalent since the ^{31}P n.m.r. spectra shows two singlets at 60.9 and 40.5 p.p.m. of relative intensity *ca.* 1 : 1.2. There also appears to be a small amount of $Ru(C_4H_6)(PPh_3)_3$[4] present according to the ^{31}P n.m.r. data. Crystallisation gives the original complex, which on re-dissolution gives the two ^{31}P resonances.

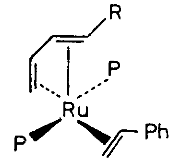
The separation between the peaks is too large to be attributable to the type of isomers suggested[4] for $Ru(C_4H_6)(PPh_3)_3$ at low temperatures, hence we suggest that the structures are (1) and (2), based on a distorted square pyramidal geometry; the 60.9 resonance can be assigned to the *cis* and the 40.5 resonance to the *trans*-isomer.[12]

In petroleum, the reaction with buta-1,3-diene gives white $Ru(C_4H_6)_2(PPh_3)_2$ which on dissolution in aromatic hydrocarbons rapidly gives $Ru(C_4H_6)_2PPh_3$.[4] The i.r. spectrum of $Ru(C_4H_6)_2(PPh_3)_2$ has strong, sharp bands at 1 610 (C=C) and 860 cm^{-1} (δ CH_2). The former is close to the position of ν(C=C) of the unco-ordinated double bond in $[(\eta\text{-}C_5H_5)Fe(CO)_2(1\text{—}2\text{-}\eta\text{-}C_4H_6)]PF_6$[13] and in $Fe(CO)_4(1\text{—}2\text{-}\eta\text{-}C_4H_6)$,[14] indicating that buta-1,3-diene co-ordinates through only one double bond and that the complex has a structure similar to the other complexes of general formula $Ru(C_4H_6)(PPh_3)_2L$ (L = PPh_3[4] or C_8H_8).

Although the complex readily decomposes to $Ru(C_4H_6)_2PPh_3$ in solution the ^1H n.m.r. spectrum of a fresh solution in C_6D_6 shows broad resonances from δ −0.5 to 6.4 suggesting that the two diene groups are inequivalent.

(d) *Hex-*1-*ene*. With hex-1-ene neat or in petroleum a yellow complex is obtained which, after recrystallisation from toluene, has stoicheiometry $RuH(C_6H_{11})(C_8H_8)(PPh_3)_2 \cdot C_7H_8$. Although no Ru–H stretch appears in the i.r. spectrum, the ^1H n.m.r. shows two high-field triplets. The C=C stretch for styrene appears at 1 592 cm^{-1}.

The fully decoupled ^{31}P n.m.r. spectrum shows three doublets, δ 64.9, 64.8, and 51.3 all with J_{PP} = 18 Hz, relative ratios 1 : 1 : 2. On allowing coupling to *H*–Ru each doublet splits into a further doublet, J_{PH} = 27 Hz, so that together with the high-field ^1H spectrum this means that there are two metal centres each with a hydride and two phosphine groups in a *fac*-configuration. The resonances from one of the P atoms on each metal have identical chemical shifts while the shifts of the other P atoms differ by 0.1 p.p.m. This information coupled with the general similarity of the ^1H spectrum to that of



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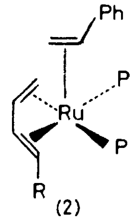

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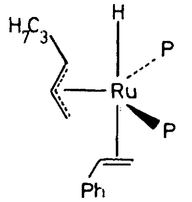

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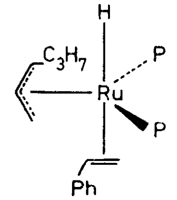

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[12] P. R. Hoffmann and R. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221.

[13] E. O. Fischer and K. Fichtel, *Chem. Ber.*, 1962, **95**, 2063.

[14] H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, 1962, **45**, 1156.

the mixture of *syn*- and *anti*-isomers of (1—3-η-C_5H_9)-Co$(CO)_3$ [15] then suggests that we have a mixture of *syn*- and *anti*-RuH(1—3-η-C_6H_{11})$(C_8H_8)(PPh_3)_2$, (3) and (4). Since both species always appear to be present in equimolar amounts, we cannot, however, rule out the possibility that the complex is dimeric with bridging allyl groups. The chemical shifts of the hydride resonances suggest that they are *trans* to styrene moieties.[4] A 1—3-η-hexenyl complex of cobalt is known.[16]

TABLE 1

^{31}P N.m.r. data for ruthenium complexes in C_6H_6 at 28 °C

Compound	Stereo-chemistry	Chemical shifts [a] P_A	P_B	$J(P_AP_B)$/Hz
$Ru(C_2H_4)_2(C_8H_8)(PPh_3)_2$		67.2(d)	51.2(d)	9.6
$Ru(C_4H_6)(C_8H_8)(PPh_3)_2$	(1)	40.50		
$Ru(C_4H_6)(C_8H_8)(PPh_3)_2$	(2)	60.91		
$RuH(C_6H_{11})(C_8H_8)(PPh_3)_2$	(3)	64.87	51.35	40 [b]
$RuH(C_6H_{11})(C_8H_8)(PPh_3)_2$	(4)	64.77	51.35	40 [b]
$Ru(C_6H_{10})(C_8H_8)(PPh_3)_2$	(1)	43.62		
$Ru(C_6H_{10})(C_8H_8)(PPh_3)_2$	(2)	54.37		

[a] In p.p.m. to high frequency of external 85% H_3PO_4. [b] $J(P_AH) = J(P_BH) = 29$ Hz.

TABLE 2

Analytical data for ruthenium complexes

Compound	Colour	M.p.[c] (θ_c/°C)	Found (%) C	H	P	Other	Required (%) C	H	P	Other
$Ru(C_8H_8)_2(PPh_3)_2\cdot0.5sol$[a]	Purple	86d	75.3	5.6	6.7		75.4	5.9	7.1	
$Ru(C_8H_8)(PPh_3)_2\cdot0.5SiMe_4$	Green-grey		72.9	6.4	7.2	Si: 1.9	71.4	5.7	8.0	Si: 1.8
$Ru(C_8H_8)(PPh_3)_2\cdot0.5C_5H_{12}$ [b]	Green		72.4	5.5	8.4		72.9	5.7	8.1	
$Ru(C_8H_8)(PPh_3)_2\cdot0.5C_6H_{14}$	Green		72.9	5.5	8.5		73.1	5.8	8.0	
$Ru(C_8H_8)(PPh_3)_2\cdot0.5C_6F_6$	Green	60d	67.25	4.7	7.4		68.6	4.6	7.5	
$Ru(C_2H_4)_2(C_8H_8)(PPh_3)_2$	Orange	121	73.0	6.5	7.6		73.4	5.9	7.9	
$Ru(C_4H_6)(C_8H_8)(PPh_3)_2\cdot C_7H_8$	Pale yellow	147	74.75	6.4	7.4		75.4	6.0	7.1	
$Ru(C_4H_6)(C_8H_8)(PPh_3)_3\cdot C_6D_6$	Pale yellow		74.4		7.1		74.7		7.2	
$Ru(C_4H_6)_2(PPh_3)_2$	Creamy white	106d	72.0	5.8	8.6		72.0	5.7	8.5	
$RuH(C_6H_{11})(C_8H_8)(PPh_3)_2$	Yellow	119	74.2	6.3	7.4		73.8	6.2	7.6	
$RuH(C_6H_{11})(C_8H_8)(PPh_3)_2\cdot0.5C_7H_8$	Yellow		74.7	6.2			74.7	6.3		
$Ru(C_6H_{10})(C_8H_8)(PPh_3)_2$	Yellow	122	73.6	6.0	7.8		74.0	5.9	7.6	

[a] Mixture of C_5 and C_6 hydrocarbons. [b] Isopentane. [c] d = Decomposes.

In addition there is a weak ^1H resonance at δ −0.35 and singlet ^{31}P resonances at δ 58.2 and 43.9 that can be ascribed to the presence of a hexadiene complex [although not that obtained from $Ru(C_8H_8)_2(PPh_3)_2$ and *cis* + *trans*-hex-2-ene] formed by loss of hydrogen from $RuH(C_6H_{11})(C_8H_8)(PPh_3)_2$ and indeed these resonances slowly increase in intensity with time.

(e) cis- + trans-*Hex-2-ene* (87 : 13). Interaction of $Ru(C_8H_8)_2(PPh_3)_2$ with hex-2-enes either neat or in petroleum gives a complex $Ru(C_6H_{10})(C_8H_8)(PPh_3)_2$. While the i.r. spectrum is very similar to that of RuH-$(C_6H_{11})(C_8H_8)(PPh_3)_2$, the n.m.r. spectra show that it is a hexadiene complex of ruthenium(0). As with the analogous butadiene complex there are two isomers in solution giving two ^{31}P singlets. The ^1H resonances at δ 2.7 (v.br. multiplet) and δ 1.0 (triplet with increased intensity on low-field side) clearly indicate the presence of an ethyl group and hence that hexa-1,3-diene, rather than hexa-2,4-diene, is bound to the metal. Broad resonances at δ −0.2 and −0.9 suggest that the C_2H_5 group is *exo* with respect to the metal [*cf.* (1) and (2)]. The conclusions are confirmed by g.l.c. analyses of solutions of the complex decomposed either thermally or by reaction with carbon monoxide, which show only one hexadiene peak from *trans*-hexa-1,3-diene.

In the presence of an excess of PPh_3 both hex-1-ene and hex-2-enes give a mixture of $RuH_2(PPh_3)_4$ and $Ru(C_6H_{10})(C_8H_8)(PPh_3)_2$. The reaction is noticeably slower with hex-1-ene, suggesting that isomerisation to hex-2-enes occurs as the first step.

(f) *Other reactions.* In neat cyclopentadiene there is a rapid reaction to give RuH(η-C_5H_5)$(PPh_3)_2$ [17] identified by ^1H n.m.r. and i.r. spectroscopy. The reaction with cyclohexene is complicated and is reported separately. With carbon monoxide $Ru(C_8H_8)_2(PPh_3)_2$ in styrene containing PPh_3 rapidly gives a yellow solution from which $Ru(CO)_3(PPh_3)_2$ [18] can be isolated.

EXPERIMENTAL

Microanalyses by Pascher, Butterworth, and Imperial College Microanalytical Laboratories. I.r. spectra were obtained in Nujol mulls between caesium iodide plates on a Perkin–Elmer PE457 grating spectrophotometer, n.m.r. spectra using Perkin–Elmer R12 (60 MHz) and Varian Associates XL-100-12 (^{31}P) spectrometers, the latter operating in the Fourier transform mode with proton noise decoupling. Mass spectra were recorded on an V.G. 7070, double-focussing mass spectrometer. Melting points were measured on an Electrothermal melting point apparatus in closed capillaries under argon and are uncorrected.

All solvents were thoroughly degassed and dried over sodiobenzophenone ketyl (toluene, diethyl ether, tetrahydrofuran) or sodium (petroleum, boiling range 40—60 °C, and heptane). Hexane was shaken with 99% sulphuric acid, washed with water, dried with anhydrous Na_2SO_4, and distilled from sodium.

Hex-1-ene and hex-2-ene were purified by shaking with acidified solutions of ferrous ammonium sulphate, and drying by passage through an alumina column.

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Hexafluorobenzene was dried over molecular sieves.

(1) *Bis(styrene)bis(triphenylphosphine)ruthenium*(0)–*petroleum* (1/0.5).—$RuH_2(PPh_3)_4$ (1.15 g, 1 mmol) was dissolved in styrene (12 ml). The colour changed immediately from yellow to purple. After 1 h petroleum (40 ml) was added and the solution filtered and cooled to −15 °C to afford deep red-purple crystals of the *complex* (yield, *ca.* 75%). The crystallisation time was found to be variable (3 days—4 weeks). However, by seeding the solution with previously obtained crystals of $Ru(C_8H_8)_2(PPh_3)_2$ crystallisation is complete within 16 h. I.r. (cm^{-1}) spectrum: 3 140vw, 3 050m, 3 010w, 1 590ms, 1 580m, 1 570w, 1 430s, 1 310w, 1 300w, 1 285w, 1 220m, 1 200m, 1 180m, 1 165m, 1 155w, 1 080ms, 1 025m, 995m, 935w, 900w, 850vw, 770w,sh, 760w,sh, 750s, 740s, 720w, 700s, 690vs, 620m, 590w, 540s, 530s, 515vs, 500ms, 480m, 450m, 435m, and 410w.

(2) *Reactions of* $Ru(C_8H_8)_2(PPh_3)_2$ *in Saturated Hydrocarbons*.—$Ru(C_8H_8)_2(PPh_3)_2$ (0.4 g, 0.48 mmol) was stirred in alkane (40 ml) (Me_4Si, isopentane, hexane, *etc.*) for 24 h (72 h in the case of tetramethylsilane). The green powder which separated was collected, washed with alkane (10 ml), and dried *in vacuo*; yield, *ca.* 90%. The complex was identified as mainly $Ru(C_8H_8)(PPh_3)_2 \cdot 0.5RH$ contaminated with a small amount of $RuH_2(PPh_3)_4$ [ν(Ru–H) = 2 080 cm^{-1}]. I.r. (cm^{-1}) spectrum: 3 130vw, 3 050m, 2 080w, 1 590m, 1 580m, 1 570m, 1 430s, 1 305w, 1 210m, 1 180m, 1 150w, 1 080ms, 1 020m, 995w, 910w, 850w, 800m, 780vw, 740vs, 720w, 690vs, 615w, 515s, 505vs, 440m, and 410m.

For RH = $SiMe_4$ extra absorptions at 1 245m and 860s are observed. For RH = C_6F_6 there is no absorption at 2 080 cm^{-1} but extra absorptions at 1 525s and 1 010s cm^{-1}. When the above reaction was carried out under reflux an orange–brown material was obtained. It did not contain $RuH_2(PPh_3)_4$ and is hereafter referred to as the ' orange-species '. It is probably a mixture of clusters. I.r. spectrum of ' orange species ' (cm^{-1}): 3 140vw, 3 050m, 1 590m, 1 580m, 1 570m, 1 500w, 1 430s, 1 305w, 1 330vw, 1 215m, 1 180m, 1 150w, 1 110w, 1 080m, 1 065w, 1 020m, 995m, 980w, 800m, 750s, 740w, 720w, 695vs, 680w, 615w, 530vs, 505s, 490m, 455w, and 420m; ^{31}P n.m.r. spectrum δ −17.4 (d, J = 5 Hz), −8.4(s), 24.3(s), 53.3(s), 56.8 (complex multiplet) and 60.8 (complex multiplet). The spectrum does not alter when coupling to any hydrides present is introduced.

(3) *Reactions of* $Ru(C_8H_8)_2(PPh_3)_2$ *in Alkanes in the Presence of* PPh_3.—(a) Hexane (10 ml) was added to $Ru(C_8H_8)_2(PPh_3)_2$ (0.25 g, 0.3 mmol) and PPh_3 (0.24 g, 0.92 mmol) and the suspension shaken for 3 d at room temperature. The resulting orange solution was filtered free from the yellow solid which was identified as ' $RuH_2(PPh_3)_4$ ' by its i.r. spectrum. A ^{31}P n.m.r. spectrum of the orange solution containing some yellow solid evaporated to dryness showed resonances attributable to ' $RuH_2(PPh_3)_4$ ', PPh_3 and the ' orange species '. G.l.c. analysis of the solution showed the presence of a mixture of C_5 and C_6 hydrocarbons, hexane, styrene, and small amounts of ethylbenzene and benzene.

A similar result was obtained from $Ru(C_8H_8)_2(PPh_3)_2$ (0.29 g, 0.35 mmol), PPh_3 (0.33 g, 1.3 mmol) and hexane (3 ml) in a sealed tube under argon (0.5 atm), and from $Ru(C_8H_8)_2(PPh_3)_2$ (0.28 g, 0.34 mmol), PPh_3 (0.31 g, 1.2 mmol) in $SiMe_4$ (10 ml) with a reaction time of 2 weeks.

(b) $Ru(C_8H_8)_2(PPh_3)_2$ (0.1 g, 1.2 mmol) and PPh_3 (0.063 g, 0.24 mmol) were stirred in hexane (2 ml) with warming to 60 °C. The purple suspension rapidly dissolved to give an orange solution from which an amorphous orange powder precipitated. After cooling this solid was collected and identified as a mixture of the ' orange species ' and ' $RuH_2(PPh_3)_4$ '.

(4) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with* C_6F_6.—This reaction was carried out as in (2) above but using hexafluorobenzene (10 ml) in place of alkane. The green product was collected, dried *in vacuo*, and identified as $Ru(C_8H_8)_2(PPh_3)_2 \cdot 0.5C_6F_6$; it contained no '$RuH_2(PPh_3)_4$'; yield *ca.* 90%.

Under reflux the ' orange species ' was again obtained in high yield.

(5) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with* C_6F_6 *in the Presence of* PPh_3.—(a) No reaction was observed on shaking $Ru(C_8H_8)_2(PPh_3)_2$ (0.27 g, 0.32 mmol) with PPh_3 (0.31 g, 1.2 mmol) in C_6F_6 (3 ml) for 3 weeks in a sealed tube under 0.5 atm of argon.

(b) $Ru(C_8H_8)_2(PPh_3)_2$ (0.11 g, 0.13 mmol) and PPh_3 (0.07 g, 0.26 mmol) were stirred in C_6F_6 (2 ml) with warming to 60 °C. After 3 h, the orange precipitate was collected, dried *in vacuo*, and identified as a mixture of ' $RuH_2(PPh_3)_4$ ' and the ' orange species '.

(c) $Ru(C_8H_8)_2(PPh_3)_2$ (0.11 g, 0.13 mmol) and PPh_3 (1 g, 3.8 mmol) were stirred in C_6F_6 (2 ml) with warming to 60 °C for 3 h. The yellow powder which precipitated from the red solution was collected, washed with petroleum (2 × 5 ml) to remove PPh_3, and dried *in vacuo*. It was identified as ' $RuH_2(PPh_3)_4$ ' from its i.r. spectrum.

(6) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with Triphenylphosphine*.—$Ru(C_8H_8)_2(PPh_3)_2$ (0.1 g, 0.12 mmol) was added to molten PPh_3 (1 g) at 85 °C and the resulting red solution stirred for 1 h. After cooling and extraction with petroleum (3 × 5 ml) the yellow solid was identified as ' $RuH_2(PPh_3)_4$ ' from its i.r. spectrum.

(7) *Bis(ethylene)styrenebis(triphenylphosphine)ruthenium*(0).—Ethylene was passed through a stirred suspension of $Ru(C_8H_8)_2(PPh_3)_2$ (0.4 g, 0.48 mmol) in petroleum (50 ml) for 5 h at room temperature. The *complex* separated as an orange powder which was collected and dried *in vacuo*; yield *ca.* 80%. I.r. (cm^{-1}) spectrum: 3 140vw, 3 050m, 1 595m,sh, 1 580m,sh, 1 570m, 1 430s, 1 355w, 1 310w, 1 290w, 1 260w, 1 1195m, 1 180m, 1 160mw, 1 155mw, 1 115w, 1 080ms, 1 025m, 1 015w, 995m, 975w, 930w, 915w, 905w, 880w, 850m, 835w, 750s, 740s, 720w, 695vs, 620w, 600w, 530s, 510vs, 475m, 455m, 440w, 430m, 400m, and 275w. The ^{1}H n.m.r. spectrum showed broad resonances at δ 0.95, 1.3, 1.95, and 5.3.

(8) *Butadienestyrenebis(triphenylphosphine)ruthenium*(0).—The reaction was carried out as in (7) from but-1-ene; yield *ca.* 90%. The complex was also prepared by passing buta-1,3-diene through a solution of $RuH_2(PPh_3)_4$ (0.5 g, 0.435 mmol) in styrene (10 ml) for 5 min; addition of petroleum (40 ml) and cooling gave the complex; yield *ca.* 60%. Recrystallisation from toluene (2 ml) or C_6D_6 (1 ml) gave the complex as 1 : 1 solvates. I.r. spectrum of C_6D_6 solvate (cm^{-1}): 3 050m, 2 280w, 1 595m, 1 585m, 1 570m, 1 495m, 1 480w, 1 475w, 1 430s, 1 330w, 1 310w, 1 290vw, 1 235m, 1 200m, 1 188m, 1 182m, 1 160m, 1 115m, 1 080m, 1 070w, 1 040w, 1 025m, 1 000m, 950w, 900w, 880w, 850w, 810mw, 790w, 750s, 740s, 730w, 720w, 700vs, 680w, 620w, 550w, 540w, 528s, 515s, 508s, 490m, 450m, and 410m; ^{1}H n.m.r. spectrum: δ −0.45, 1.55, 3.2, 4.3, and 5.7 (all broad).

(9) (1—2-η-*Butadiene*)(1—4-η-*butadiene*)*bis*(*triphenyl*-

phosphine)ruthenium(0).—This reaction was carried out as in (7) from butadiene to give an off-white powder; yield *ca.* 80%. I.r. (cm^{-1}) spectrum: 3 140vw, 3 060vw, 3 040m, 3 020w, 1 610s, 1 580m, 1 510m, 1 430s, 1 330w, 1 310w, 1 285w, 1 210m,sh, 1 200m, 1 185m, 1 175w, 1 105w, 1 080m, 1 040w, 1 025w, 1 015w, 1 000m, 950w, 920w, 910w, 890w, 870w, 860s, 850w, 845w, 780vw, 750m, 740s, 720w, 695vs, 675w, 615w, 550w, 525s, 515s, 495s, 450ms, 430m, 420m, and 405m; ^{1}H n.m.r. spectrum: δ −0.5, 1.5, 2.1, 2.5, 4.7, 5.2, and 5.4 (all broad). Recrystallisation from C_6D_6–petroleum gave $Ru(C_4H_6)_2(PPh_3)$ (identified by its i.r. and ^{1}H n.m.r. spectra) as pale yellow crystals.

(10) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with Propene.*—Propene was passed through a suspension of $Ru(C_8H_8)_2(PPh_3)_2$ (0.4 g, 0.48 mmol) in heptane (50 ml) at 60 °C for 5 h. The off-white powder obtained was collected and recrystallised from benzene (2 ml) to give orange crystals of *cis*-$Ru(C_3H_5)_2(PPh_3)_2$ [4] identified by its i.r. and ^{1}H n.m.r. spectra.

(11) 1—3-η-*Hexenyl(hydrido)styrenebis(triphenylphosphine)ruthenium*(II)-*Toluene* (1/0.5).—(a) $Ru(C_8H_8)_2(PPh_3)_2$ (0.4 g, 0.48 mmol) was stirred with hex-1-ene (3 ml) for 15 h at room temperature, during which time a yellow solid precipitated; this was collected and recrystallised from toluene–petroleum to give yellow *crystals*; yield after recrystallisation *ca.* 20%.

(b) This reaction was carried out similarly, but with hex-1-ene (2 ml) in petroleum (15 ml). I.r. (cm^{-1}): 3 050m, 1 590m, 1 580m, 1 570m, 1 490m, 1 430s, 1 310w, 1 250vw, 1 230m, 1 220w, 1 185m, 1 180w, 1 155w, 1 075ms, 1 025m, 995m, 975w, 945m, 920w, 880w, 860m, 850w, 840w, 750s, 740s, 720w, 700vs, 678w, 660w, 620w, 560m, 550m, 535m, 525s, 515s, 500s, 490m, 450m, 430w, 410w, and 405m; ^{1}H n.m.r. spectrum: δ −12.3 (t, $J_{PH} = 27$ Hz), −10.5 (t, $J_{PH} = 27$ Hz), −0.35, 0.85, 1.6, 4.35, 4.9, 5.55 (all broad for $\delta > -2$).

(12) *Hexa*-1,3-*dienestyrenebis(triphenylphosphine)-ruthenium*(0).—This compound was prepared as described above from *cis,trans*-hex-2-ene; it was a yellow powder (yield *ca.* 80%). It is also obtained along with $RuH_2(PPh_3)_4$ from the reaction between $Ru(C_8H_8)_2(PPh_3)_2$ and hex-1-ene or hex-2-ene in petroleum in the presence of an excess of PPh_3 (^{31}P n.m.r. evidence). I.r. spectrum (cm^{-1}): 3 050m, 1 590m, 1 580m, 1 570m, 1 490m, 1 430s, 1 305w, 1 230m, 1 220w, 1 195w, 1 185m, 1 150w, 1 115w, 1 075ms, 1 020w, 995w, 940w, 900w, 850m, 745s, 740s, 720w, 690vs, 620vw, 558w, 550m, 535m, 525m, 510s, 500s, 490m, 450m, 430w, and 405m; ^{1}H n.m.r. spectrum: δ −1.0, −0.2, 1.0, 1.7, 5.1, and 5.5 (all broad).

(13) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with Cyclopentadiene.*—$Ru(C_8H_8)_2(PPh_3)_2$ (0.3 g, 0.36 mmol) was dissolved in freshly distilled cyclopentadiene (5 ml). Addition of petroleum (30 ml) to the yellow solution obtained after 15 min afforded a yellow powder identified as $RuH(C_5H_5)(PPh_3)_2$ from its i.r. and ^{1}H n.m.r. spectra.

(14) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with* CO.—$RuH_2(PPh_3)_4$ (0.3 g, 0.36 mmol) was stirred in styrene (4 ml) for 30 min at room temperature. CO was then passed through the purple solution for 30 min, during which time the colour changed to pale yellow. On addition of petroleum (40 ml), $Ru(CO)_3(PPh_3)_2$, identified by its i.r. spectrum, separated as pale yellow microcrystals.

(15) *Reaction of* $Ru(C_8H_8)_2(PPh_3)_2$ *with Water.*—$Ru(C_8H_8)_2(PPh_3)_2$ (0.2 g, 0.24 mmol) was stirred with tetrahydrofuran (4 ml) containing water (1.5 ml) for 10 h at room temperature, during which time the colour of the suspension changed from purple to red. The red solid was collected, dried *in vacuo*, and identified as $RuH(OH)(PPh_3)_2(C_4H_8O)$ by its i.r. spectrum.

(16) *Reaction of* $RuH(C_2H_4)(o\text{-}C_6H_4PPh_2)(PPh_3)_2$ *with an excess of* PPh_3.—Ethylene was bubbled through a suspension of $RuH_2(PPh_3)_4$ (0.2 g) in benzene (3 ml) for 30 min at room temperature; ^{1}H n.m.r. studies showed complete conversion to $RuH(C_2H_4)(o\text{-}C_6H_4PPh_2)(PPh_3)_2$.[4] PPh_3 (0.2 g) was added and the solution heated to 60 °C for 2 h. On cooling, yellow crystals formed. These were collected and identified as ' $RuH_2(PPh_3)_4$ ' from their i.r. spectrum.

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