Hydrido-complexes of Ruthenium and Iron containing Diphenylphosphine Ligands

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The syntheses of *cis*-[$RuH_2(HPPh_2)_4$] and of covalent and ionic monohydrides of ruthenium containing four or five diphenylphosphine ligands, and of analogous iron compounds, are described. Spectroscopic evidence for their configurations, and for intramolecular rearrangements in *cis*-[$FeH_2(HPPh_2)_4$], is presented.

THIS paper describes the preparations of some hydrido-complexes of ruthenium and iron containing diphenylphosphine ($HPPh_2$, which will be written P) ligands. These have been made in order to compare the structures and properties of metal hydrides containing this secondary phosphine ligand with those containing other phosphorus ligands such as mono- and di-tertiary phosphines and phosphites. A preliminary account of some of this work has appeared.[1] Some secondary phosphine complexes of these metals containing various other ligands are known [2-5] and many reactions of iron carbonyl derivatives with secondary phosphines have been carried out.[6-9]

Preparations of Complexes.—Reaction of *trans*- or *cis*-[$RuCl_2P_4$][5] with an excess of lithium methoxide gives *cis*-[RuH_2P_4], which is a light yellow solid, stable to air but light-sensitive. It is soluble in chlorinated solvents and benzene, moderately soluble in ether and insoluble in alcohols—it is slowly decomposed by air in solution.

If this dihydride is treated with alkali-metal salts one hydride ligand is replaced to give *trans*-[$RuHXP_4$] (X = Cl, Br, I, SCN but not F, N_3, NO_2, or CN for which the reaction fails). *trans*-[$RuHClP_4$] May also be made from the reaction of *trans*- or *cis*-[$RuCl_2P_4$] with one equivalent of lithium methoxide or from *cis*-[$RuCl_2P_4$] by treatment with hydrogen and triethylamine; it reacts with stannous chloride giving *trans*-[$RuH(SnCl_3)P_4$]. If the dihydride is treated with hydrogen halides or with alkali-metal salts under severe conditions both hydride ligands are replaced giving *cis*-[RuX_2P_4] (X = Cl, Br, SCN). The complexes in these two series are light yellow or white air-stable solids which are soluble in halogenated solvents but not in alcohols or ether.

Treatment of *trans*-[$RuHClP_4$] with diphenylphosphine

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[1] J. R. Sanders, presented at the Autumn Meeting of the Chemical Society, University of York, September 1971.

[2] K. Issleib and G. Döll, *Z. anorg. Chem.*, 1960, **305**, 1.

[3] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 301.

[4] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 1826.

[5] J. R. Sanders, *J. Chem. Soc.* (*A*), 1971, 2991.

[6] R. G. Hayter, 'Sulfur and Phosphorus-bridged complexes of transition metals,' in 'Preparative Inorganic Reactions,' ed. W. L. Jolly, Interscience, London, 1965, vol. 2, p. 211.

[7] J. G. Smith and D. T. Thompson, *J. Chem. Soc.* (*A*), 1967, 1694.

[8] M. Cooke and M. Green, *J. Chem. Soc.* (*A*), 1968, 1507.

[9] R. C. Dobbie and D. Whittaker, *Chem. Comm.*, 1970, 796.

in the presence of KPF_6 gives $[RuHP_5]^+PF_6$ (ref. 10) which has been obtained from $[RuHCl(PPh_3)_3]$ by treatment with P and KPF_6.[5] When dinitrogen gas was passed for several days through a solution of *trans*-$[RuHClP_4]$ and sodium tetraphenylborane in dichloromethane a material whose i.r. spectrum showed a weak band at 2160 cm^{-1} was obtained. This band was assigned to ν_{N-N} of *trans*-$[RuH(N_2)P_4]^+BPh_4^-$ which could not be obtained pure.

Neither *trans*- nor *cis*-$[FeCl_2P_4]$ is available as a starting point for syntheses of iron hydrides containing diphenylphosphine ligands. However, reaction of anhydrous iron(II) chloride with diphenylphosphine and sodium borohydride at −70° gives *cis*-$[FeH_2P_4]$, a yellow solid less stable to heat, air, and light than its ruthenium analogue but with the same solubility properties. It reacts with an equivalent of hydrogen chloride or carbon tetrachloride giving *trans*-$[FeHClP_4]$ and with ammonium thiocyanate giving *trans*-$[FeH(SCN)P_4]$; since both compounds were very unstable in air, especially in solution, their molecular weights could not be measured; the chloride was not obtained pure and was characterised only by spectroscopic measurements.

The dihydride also reacts with triphenylmethyl tetrafluoroborate in acetonitrile to give *trans*-$[FeH(MeCN)P_4]^+BF_4^-$ by abstraction of one hydride ligand. If this reaction is carried out in dichloromethane $[FeHP_5]^+BF_4^-$ is obtained in low yield and the yield may be increased by using diphenyl(triphenylmethyl)phosphonium tetrafluoroborate instead of Ph_3CBF_4. These iron salts are yellow solids and are quite stable to air.

Spectroscopic Studies.—The configurations of these complexes are established by i.r. and ^1H n.m.r. measurements. The i.r. spectra of both dihydrides have bands assigned to ν_{M-H} (M = Ru or Fe) in the characteristic region for this vibration in *cis*-dihydrido octahedral complexes. In the n.m.r. spectrum of the ruthenium compound the signal assigned to the protons on ruthenium is a complex one. At and below room temperature it consists of three sharp peaks at τ 18·22, 18·47, and 18·71 (the centre peak being rather lower than its neighbours), flanked by broad peaks at τ 17·75, 17·95, 18·95, and 19·13. As the temperature is raised this spectrum remains virtually unchanged in the range 20—115° except that the centre peak becomes higher than its neighbours. The corresponding signal in the spectrum of the iron dihydride at 20° consists of a broad band at τ 22·65 flanked by sharp peaks at τ 21·89 and 23·38. As the temperature is raised the centre peak splits into two and then three broad peaks which are gradually sharpened and elevated relative to the outside peaks until at 85° a 1 : 4 : 6 : 4 : 1 quintet is obtained.

The *trans*-configurations of all the monohydrides are assigned on the basis of the simple quintet signals in their n.m.r. spectrum due to the protons on the metal. The salts of the $[FeHP_5]^+$ cation, like their ruthenium analogues, show two overlapping quintets in this region; these signals remain unchanged over the range 20—55°.

TABLE

Values of ν_{P-H}, ν_{M-H}, and τ (MH) in the spectra of new complexes [a]

Complex	ν_{P-H}/ cm^{-1}	ν_{M-H}/ cm^{-1}	τ(MH)	*J*(HMP)/ Hz
cis-$[RuH_2P_4]$	2281s	1835s	18·47	Complex
trans-$[RuHClP_4]$	2312m	1970s	27·70	18
trans-$[RuHBrP_4]$	2319m	1985s	26·49	18
trans-$[RuHIP_4]$	2312m	1987s	24·08	18
trans-$[RuH(SCN)P_4]$	2316m	1956s	26·23	20
trans-$[RuH(SnCl_3)P_4]$	2323m	1972s	20·15	19
cis-$[RuBr_2P_4]$	2350w [b] 2335w [b] 2328w [b]			
cis-$[Ru(SCN)_2P_4]$	2342w 2336m 2328w [b]			
cis-$[FeH_2P_4]$	2252s	1815s	22·65 22·30 [c]	Complex 37 [c]
trans-$[FeHClP_4]$ [d]	2307m [b]	1891m [b]	37·90	50
trans-$[FeH(SCN)P_4]$	2305m [b]	1877m [b]	38·08	49
$[HPPh_2(CPh_3)]BF_4$	2420m [b]			
trans-$[FeH(MeCN)P_4]BF_4$	2293m [b]	1924w [b]	30·16	45
$[FeHP_5]BF_4$	2310m [b]	1912w [b]	21·07	49 *cis* 19 *trans*
$[FeHP_5]PF_6$	2310m [b]	1905w [b]	21·09	49 *cis* 19 *trans*

[a] In CH_2Cl_2 at room temperature unless otherwise stated. [b] As Nujol mulls. [c] In C_6H_5Cl at 85°. [d] Not obtained pure.

The i.r. spectra of the complexes also show bands assigned to ν_{P-H} in the 2350—2250 cm^{-1} region. The complexes $[RuBr_2P_4]$ and $[Ru(SCN)_2P_4]$ are tentatively assigned a *cis*-configuration because of the similarity of their mull spectra in this and other regions to that of *cis*-$[RuCl_2P_4]$ (whose dipole moment has been measured [5]) and because of the similarity of the methods of their preparation from *cis*-$[RuH_2P_4]$ to that of *cis*-$[RuCl_2P_4]$.

Complexes containing SCN or MeCN ligands, BF_4^- and PF_6^- anions, or methanol of crystallization show bands in their i.r. spectra and signals (of the correct intensity relative to phenyl-group signals) in their n.m.r. spectra which may be assigned to these groups. The values of ν_{P-H}, ν_{M-H}, and τ(MH) for all the new complexes are given in the Table.

DISCUSSION

Jesson and his colleagues have examined the temperature dependence of the n.m.r. spectra of several molecules of formula $[FeH_2P_4]$ (P = various phosphines, phosphonites, and phosphonates) and find that they are stereochemically non-rigid and that the signals due to the protons on iron become simple quintets at high temperatures, showing the equivalence of the phosphorus atoms relative to these protons on the n.m.r. time scale. They propose that the FeP_4 system is a distorted tetrahedron and rearrangement occurs by hydride ligands traversing between tetrahedral faces.[11,12]

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[10] G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2146.

[11] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1971, **93**, 4701.

[12] P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 3482.

It seems clear that $[\mathrm{FeH}_2P_4]$ is undergoing a similar process because of the similarity of its spectrum to those determined by Jesson *et al.* At low temperatures it has a distorted *cis*-structure—there is no evidence for a *trans*-isomer.[12] The analogous ruthenium compounds undergo the same process but the barriers to rearrangement are higher and the compounds decompose before the simple quintet spectrum is reached.

The structures of both dihydrides and monohydrides support the hypothesis [5] that the products from reactions of transition-metal compounds with diphenylphosphine will resemble those formed from similar reactions with chelating ditertiary phosphines but not in general from reactions with monotertiary phosphines. For example, ferrous chloride and sodium borohydride react with diphenylphosphine or 1,2-bis(diphenylphosphino)ethane [13] (or with triethyl phosphite [14]) giving iron dihydrides with four phosphorus atoms bound to the metal but they react with ethyldiphenylphosphine giving the tetrahydride $[\mathrm{FeH}_4(\mathrm{PEtPh}_2)_3]$.[13] Because the hydrogen atom on phosphorus does not take up much space, diphenylphosphine may be less sterically demanding as a ligand than tertiary phosphines, and this may account for the different stoicheiometries of its complexes.

The preparation of transition-metal hydride complexes by treatment of the corresponding chlorides with alkoxide ion is well known. *trans*-$[\mathrm{RuCl}_2P_4]$ Reacts with various alkoxides to give *cis*-$[\mathrm{RuH}_2P_4]$ (lithium methoxide being chosen for ease of isolation of the product) but does not react with t-butoxide ion. This supports the theory that the source of the hydride ligand is a hydrogen atom bound to the carbon atom that carries the oxygen in the alkoxide ion.

The *cis*-influence of the diphenylphosphine ligand on the metal–hydrogen bond may be compared with that of other phosphines by comparing $\nu_{\mathrm{Ru-H}}$ in *trans*-$[\mathrm{RuHCl}P_4]$ and in a series of complexes [15] *trans*-$[\mathrm{RuHCl(P-P)}_2]$ (P–P = various chelating phosphines) with the same geometry. Diphenylphosphine has approximately the same *cis*-influence as the phenyl-substituted chelating phosphine $\mathrm{Ph_2PCH_2PPh_2}$ ($\nu_{\mathrm{Ru-H}}$ = 1970 cm^{-1} with P ligands and 1978 cm^{-1} with the chelate ligands) but when P–P is $\mathrm{Me_2PCH_2CH_2PMe_2}$ then $\nu_{\mathrm{Ru-H}}$ is much lower at 1891 cm^{-1}. This suggests that there is no special electronic effect associated with the hydrogen atom on phosphorus in a P ligand.

In the series *trans*-$[\mathrm{RuHX}P_4]$(X = Cl, Br, I, SCN, $\mathrm{SnCl_3}$), the values of $\nu_{\mathrm{Ru-H}}$ give an order of *trans*-influence for X. This is weakest for X = iodide, followed by bromide, trichlorostannate, chloride, and thiocyanate. This order is the same as that found for the series *trans*-$[\mathrm{RuHX(Me_2PCH_2CH_2PMe)_2}]$.[15]

The values of $\nu_{\mathrm{P-H}}$ for covalent ruthenium complexes in solution fall into three groups. This absorption comes at 2280 cm^{-1} in *cis*-$[\mathrm{RuH}_2P_4]$, in the 2320—2310 cm^{-1} region in the monohydrides and in the 2340—2320 cm^{-1} region for *cis*-$[\mathrm{Ru(SCN)}_2P_4]$ (and also for *cis*- and *trans*-$[\mathrm{RuCl}_2P_4]$). This change possibly occurs because as the more electronegative halide ligands replace hydrides the metal acquires more positive charge which is transferred to the phosphorus atoms. In agreement with this, $\nu_{\mathrm{P-H}}$ occurs at 2280 cm^{-1} in free diphenylphosphine but near 2400 cm^{-1} in phosphonium salts.

EXPERIMENTAL

Preparations, analyses, and spectroscopic measurements were carried out as described.[5] All compounds melted *in vacuo* with decomposition.

cis-*Dihydridotetrakis(diphenylphosphine)ruthenium*(II).—A suspension of *trans*-$[\mathrm{RuCl}_2P_4]$ (2·0 g) in a solution of lithium methoxide in methanol (0·2M; 50 ml) was heated to reflux temperature for 15 h and then cooled to 20°. The light yellow precipitate which was obtained was recrystallised from dichloromethane–methanol in 60% yield and dried at 60°, m.p. 150—153° [Found: C, 67·3; H, 5·3%; *M* (in benzene), 841. $\mathrm{C_{48}H_{46}P_4Ru}$ requires C, 68·0; H, 5·5%; *M*, 847].

trans-*Hydridochlorotetrakis(diphenylphosphine)ruthenium*(II).—(*a*) Hydrogen was passed through a solution of *cis*-$[\mathrm{RuCl}_2P_4]$ (5·0 g) in dichloromethane (20 ml), benzene (200 ml), and triethylamine (10 ml) at 20°. The solution became dark yellow and a white precipitate formed. After 3 days solvent was removed *in vacuo* and the residue was recrystallized from dichloromethane–methanol (60% yield) and dried at 100°, m.p. 230—240° (Found: C, 66·1; H, 5·5%; *M*, 817. $\mathrm{C_{48}H_{45}ClP_4Ru}$ requires C, 65·4; H, 5·1%; *M*, 882).

(*b*) A suspension of *cis*-$[\mathrm{RuH}_2P_4]$ (1·0 g) in a solution of lithium chloride (1·0 g) in ethanol (40 ml) was heated to reflux for 15 h and then cooled, giving the *trans*-hydridochloride which was recrystallized from dichloromethane–methanol in 20% yield.

trans-*Hydridobromotetrakis(diphenylphosphine)ruthenium*(II).—This compound was obtained using reaction (*b*) above with lithium bromide instead of lithium chloride and refluxing for 2 h only; yield 50%, m.p. 241—244° (Found: C, 62·7; H, 5·9%; *M*, 959. $\mathrm{C_{48}H_{45}BrP_4Ru}$ requires C, 62·2; H, 4·9%; *M*, 926).

trans-*Hydridoiodotetrakis(diphenylphosphine)ruthenium*(II).—This compound was prepared in a similar way, using sodium iodide, in 50% yield, m.p. 241—244° (Found: C, 59·1; H, 5·6%; *M*, 972. $\mathrm{C_{48}H_{45}IP_4Ru}$ requires C, 59·2; H, 4·6%; *M*, 973).

trans-*Hydrido(thiocyanato)tetrakis(diphenylphosphine)ruthenium*(II).—This compound was prepared in a similar way using ammonium thiocyanate at 20° for 15 h, in 60% yield, m.p. 190—192° (Found: C, 65·4; H, 5·1%; *M*, 908. $\mathrm{C_{49}H_{45}NP_4RuS}$ requires C, 65·2; H, 5·0%; *M*, 904).

trans-*Hydrido(trichlorostannato)tetrakis(diphenylphosphine)ruthenium*(II).—A suspension of *trans*-$[\mathrm{RuHCl}P_4]$ (0·4 g) in a solution of stannous chloride (1·0 g) in ethanol (30 ml) was warmed to 60° for 15 min and then cooled. The resulting white precipitate was recrystallized from dichloromethane–methanol (40% yield) and dried at 100°, m.p. 235—237° (Found: C, 53·3; H, 4·8; Cl, 10·3%; *M*, 1190. $\mathrm{C_{48}H_{45}Cl_3P_4RuSn}$ requires C, 53·3; H, 4·2; Cl, 10·0%; *M*, 1070).

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[13] M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1971, **5**, 115.

[14] W. Kruse and R. H. Atalla, *Chem. Comm.*, 1968, 921.

[15] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 2605.

cis-*Dibromotetrakis*(*diphenylphosphine*)*ruthenium*(II).—*cis*-[RuH$_2P_4$] (1·0 g) and hydrobromic acid (48%, 5 ml) were heated to reflux in ethanol (30 ml) for 3 h and then cooled to 20°. The yellow precipitate formed was recrystallized from dichloromethane–methanol (90% yield) and dried at 100°, m.p. 270—274° (Found: C, 56·8; H, 4·8. $C_{48}H_{44}$-Br_2P_4Ru requires C, 57·2; H, 4·5%). The compound was too insoluble in chloroform for its molecular weight to be measured.

cis-*Dichlorotetrakis*(*diphenylphosphine*)*ruthenium*(II).—This compound was formed by reaction of *cis*-[RuH$_2P_4$] with hydrogen chloride at 25°, and identified by its m.p. and i.r. spectrum.[5]

cis-*Di*(*thiocyanato*)*tetrakis*(*diphenylphosphine*)*ruthenium*-(II).—*cis*-[RuH$_2P_4$] (0·82 g) and ammonium thiocyanate (2·5 g) in ethanol (30 ml) were heated to reflux for 15 h and then cooled. The resulting yellow precipitate was recrystallized from dichloromethane–methanol (65% yield) and dried at 100°, m.p. 273—277° (Found: C, 62·4; H, 4·7%; *M*, 989. $C_{50}H_{44}N_2P_4RuS_2$ requires C, 62·5; H, 4·6%; *M*, 961).

Hydridopentakis(*diphenylphosphine*)*ruthenium*(II) *Hexafluorophosphate*.—This compound was prepared in 75% yield by treating *trans*-[RuHClP_4] (1·0 g) with *P* (0·3 g) in methanol (20 ml) at 60° for 5 min, adding KPF_6 (0·5 g) to the solution to obtain a white precipitate, and recrystallising the latter from dichloromethane–methanol. It was identified by its m.p. and i.r. spectrum.[5]

cis-*Dihydridotetrakis*(*diphenylphosphine*)*iron*(II).—Sodium borohydride (2·0 g) was added in small portions to a vigorously stirred solution of ferrous chloride (2·0 g) and diphenylphosphine (12·0 g) in methanol (150 ml) at −70°. A red precipitate and red solution formed. This was stirred at −70° for 2 h and then allowed to warm to room temperature. During this process effervescence occurred and the precipitate became a red oil which became a yellow solid after being stirred for 5 h at room temperature. It recrystallized from dichloromethane–methanol (45% yield), m.p. 138—140° (Found: C, 71·7; H, 5·6. $C_{48}H_{46}FeP_4$ requires C, 71·8; H, 5·7%). Osmometric determinations of the molecular weight of this compound in benzene consistently gave values in the range 1000—1100.

trans-*Hydridochlorotetrakis*(*diphenylphosphine*)*iron*(II).—Carbon tetrachloride (0·1 g) was added to a stirred suspension of *cis*-[FeH$_2P_4$] (0·47 g) in ethanol (30 ml) and ether (10 ml). After 30 min the red solid was recrystallized from dichloromethane–methanol, but could not be obtained pure (Found: C, 64·6; H, 5·0. $C_{48}H_{45}ClFeP_4$ requires C, 68·9; H, 5·2%).

trans-*Hydrido*(*thiocyanato*)*tetrakis*(*diphenylphosphine*)-*iron*(II).—This compound was prepared in 60% yield in the same way as its ruthenium analogue as orange crystals containing one molecule of methanol, m.p. 181—184° (Found: C, 67·0; H, 5·1. $C_{50}H_{49}FeNOP_4S$ requires C, 67·3; H, 5·4%).

Diphenyl(*triphenylmethyl*)*phosphonium Tetrafluoroborate*.—Diphenylphosphine (0·72 g, slight excess) in dichloromethane (5 ml) was added to triphenylmethyl tetrafluoroborate (1·0 g) in dichloromethane (10 ml). Ether was added to the resulting colourless solution to precipitate a white solid which recrystallized from dichloromethane–ether (70% yield) and dried at 100°, m.p. 201—203° (Found: C, 71·6; H, 5·2. $C_{31}H_{26}BF_4P$ requires C, 72·1; H, 5·0%).

trans-*Hydrido*(*acetonitrile*)*tetrakis*(*diphenylphosphine*)*iron*-(II) *Tetrafluoroborate*.—Ph_3CBF_4 (0·29 g) was added to *cis*-[FeH$_2P_4$] (0·70 g) in acetonitrile (10 ml). A dark red solution was formed with some effervescence. Dichloromethane (10 ml) was added to the solution which was then filtered; methanol was then added until a yellow solid crystallized (60% yield); it was dried at 100°, m.p. 176—180° (Found: C, 64·9; H, 5·2%; Ω, 143. $C_{50}H_{48}BF_4FeNP_4$ requires C, 64·6; H, 5·2%).

Hydridopentakis(*diphenylphosphine*)*iron*(II) *Tetrafluoroborate*.—[HPPh$_2$(CPh$_3$)]$^+$ BF$_4^-$ (0·44 g) was added to *cis*-[FeH$_2P_4$] (0·68 g) in dichloromethane (4 ml) to produce a yellow solution with some effervescence. Methanol was added to the solution until a yellow solid crystallized out (75% yield); it was dried at 100°, m.p. 180—190° (Found: C, 66·3; H, 5·4%; Ω, 134. $C_{60}H_{56}BF_4FeP_5$ requires C, 67·0; H, 5·2%).

The corresponding *hexafluorophosphate* was made in the same way as its ruthenium analogue, in 50% yield, m.p. 185—190° (Found: C, 63·8; H, 5·2%; Ω, 139. $C_{60}H_{56}F_6$-FeP_6 requires C, 63·6; H, 5·0%).

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