Bis(diphenylphosphino)methane Complexes of Ruthenium(0) and Ruthenium(II)

Bruno Chaudret, Gérard Commenges, and René Poilblanc *
Laboratoire de Chimie de Coordination du C.N.R.S., Associé à l'Université Paul Sabatier, 205, route de Narbonne, 31400, Toulouse, France

[Ru(cod)(cot)] (cod = cyclo-octa-1,5-diene, cot = cyclo-octa-1,3,5-triene) reacts with two equivalents of bis(diphenylphosphino)methane (dppm) to yield [Ru(cod)(dppm)$_2$], a compound containing both a monodentate and a bidentate dppm. This reacts in turn with [Ru(cod)(cot)] to give [Ru$_2$(cod)$_2$(cot)(dppm)$_2$] in the solid state, with CO to give [Ru(CO)(cod)(dppm)] and [Ru(CO)$_2$(cod)(dppm)], and with H_2 to give a 1 : 4 mixture of *trans*- and *cis*-[RuH$_2$(dppm)$_2$]. The reaction of the dihydride with $CHCl_3$ and HBF_4 produces *trans*-[RuHCl(dppm)$_2$] and *trans*-[RuH(dppm)$_2$(H$_2$O)]BF$_4$, respectively. [RuH$_2$(PPh$_3$)$_4$] reacts with dppm to give the mononuclear complex, [RuH$_2$(dppm)(PPh$_3$)$_2$]. The structures of the different complexes were determined mainly using ^{1}H and ^{31}P n.m.r. spectroscopy.

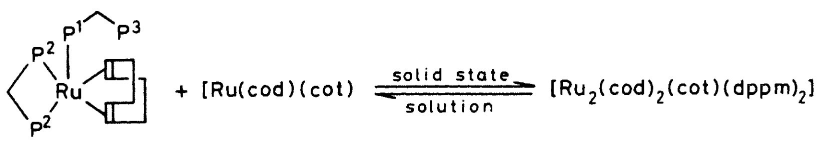
The bis(diphenylphosphino)methane (dppm) chemistry of some platinum metals (Rh,[1a] Ir,[1b] Pd,[1b,c] and Pt[1b,d]) has been extensively studied over the past few years and in particular the chemistry of dinuclear complexes.[1] The possibility of activation of small molecules on two metal centres as well as the possibility of creating and breaking metal–metal bonds were of special interest.[1] Curiously with ruthenium this chemistry has received only little attention.[2,3] This was probably due to the lack of a valuable starting material leading to dinuclear complexes. Thus so far only mononuclear dppm ruthenium complexes have been reported with the exception of carbonyl clusters.[4] Starting from the ruthenium(0) complex [Ru(cod)(cot)][5] (cod = cyclo-octa-1,5-diene and cot = cyclo-octa-1,3,5-triene) which contains very labile ligands we could hope to reach such a di- or poly-nuclear chemistry. We report herein the reactions of [Ru(cod)(cot)] with dppm in the absence or presence of H_2 as well as related reactions. A part of this work is included in a preliminary communication.[6] The same method had been used to prepare a series of dihydridotetrakis(phosphine)ruthenium(II) complexes.[7]

Results and Discussion

1. *Reaction of* [Ru(cod)(cot)] *with Dppm* (*see Scheme*).—We had previously observed that the addition of one or two equivalents of an alkylphosphine to [Ru(cod)(cot)] led to the substitution of one co-ordinated double bond of cot by a phosphine.[6] The results obtained with dppm confirm that cot is substituted first. Thus the reaction of [Ru(cod)(cot)] with one equivalent of dppm produces yellow crystals of a compound analysing for [Ru$_2$(cod)$_2$(cot)(dppm)$_2$] (1). A band at 1 605 cm^{-1} in its i.r. spectrum is attributed to ν(C=C) of a free double bond. A cryoscopic molecular-weight determination suggests the dissociation of this compound in solution {Found, 555; calc., 646 for dissociation of [Ru$_2$(cod)$_2$(cot)(dppm)$_2$]}. Indeed the ^{13}C n.m.r. spectrum is in agreement with this observation and shows the presence of two compounds in solution, [Ru(cod)(cot)] and another compound (2) which can be obtained as pure yellow crystals if the reaction is carried out using two equivalents of dppm. Compound (2) analyses for [Ru(cod)(dppm)$_2$] and exhibits three signals in its ^{31}P-{^{1}H} n.m.r. spectrum (see Table 1): a quartet at δ 35.6 [P^1, *J*(PP) 17 Hz] and two doublets at δ −8.9 [P^2, *J*(PP) 17 Hz] and −25.5 p.p.m. [P^3, *J*(PP) 17 Hz] (intensity ratio, 1 : 2 : 1) (see Scheme). The chemical shift of P^3 is close to that of free dppm (−24.0 p.p.m.) and can be attributed to a free phosphine end. P^1 is coupled on one side to P^2 (spin system AX$_2$) and on the other to P^3 (spin system AY). Fortuitously $J(P^1P^2) = J(P^1P^3)$ which accounts for the quartet pattern. The ^{13}C n.m.r. spectrum of (2) shows, apart from phenyl carbons, two olefinic carbon signals at δ −57.9 and −62.8 p.p.m., two aliphatic signals at δ −92.2 and −95.4 p.p.m., and two triplets due to carbon bound to two phosphorus atoms at δ −79.8 [$J(P^{13}C)$ 18 Hz] and −99.1 p.p.m. [$J(P^{13}C)$ 24 Hz]. These peaks are attributed to the different carbons of cod and to the methylene carbons of the two different dppm ligands, respectively.

These data allow us to propose that (2) is a five-co-ordinate ruthenium(0) complex containing one bidentate and one monodentate dppm group. Complexes of palladium and platinum showing some similarities, and in particular containing monodentate dppm groups, are known and have been recently used to prepare heterobimetallic complexes.[8] The chemical shift of the free phosphine end in such complexes is, as in our case, close to that of free dppm.

When only one equivalent of dppm is added to [Ru(cod)(cot)], complex (2) is formed by substitution of cot; this complex can then act as a bulky phosphine and be added reversibly to excess [Ru(cod)(cot)]. This equilibrium is



(2) (1)

Scheme. Proposed structure of [Ru(cod)(dppm)$_2$] (2) and its reaction with [Ru(cod)(cot)]

Table 1. ^{31}P-{^{1}H} N.m.r. data for the new ruthenium complexes

Compound	Solvent	δ [a] (multiplicity [b])[J(PP) [c]]
(2) [Ru(cod)(dppm)$_2$]	C_6D_6–C_6H_6 (1 : 2)	35.6 (q) [17], −8.9 (d) [17], −25.5 (d) [17]
(3) [Ru(CO)(cod)(dppm)]	C_6D_6–C_6H_6 (1 : 2)	0.24 (s)
(4) [Ru(CO)$_2$(cod)(dppm)]	C_6D_6–C_6H_6 (1 : 2)	23.1 (d) [51], −28.5 (d) [51]
(5) [RuH$_2$(dppm)$_2$]	CD_2Cl_2	12.9 (t) [30], 8.6 (s), 0.3 (t) [30]
(6) [RuHCl(dppm)$_2$]	CD_2Cl_2	−2.2 (s)
(8) [RuH$_2$(dppm)(PPh$_3$)$_2$]	C_6D_6–C_6H_6 (1 : 2)	60.9 (d t), 51.7 (q), 14.7 (d d d), −5.4br
(9) [RuCl$_2$(dppm)$_2$]	CH_2Cl_2–CD_2Cl_2 (1 : 1)	0.1 (t) [36], −25.7 (t) [36]
(7) [RuH(dppm)$_2$(H$_2$O)]BF$_4$	$(CH_3)_2CO$–$(CD_3)_2CO$ (2 : 1)	0.0 (s)

[a] δ/p.p.m. to high frequency of external H_3PO_4 in D_2O. [b] s = Singlet, d = doublet, t = triplet, q = quartet, br = broad. [c] In Hz.

Table 2. Infrared and ^{1}H n.m.r. data for new diphosphine ruthenium hydride complexes

Compound	ν(Ru–H)/cm^{-1}	Solvent	δ [a] (multiplicity [b])[J/Hz]
(5) [RuH$_2$(dppm)$_2$]	1 830vs	C_6D_6	−4.7 (quin) [J(PH) 19.7], −7.4 (dq) [J(P^{1}H) 72.8, J(P^{2}H) 18.7]
(6) [RuHCl(dppm)$_2$]	1 970m	CD_2Cl_2	−14.05 (quin) [J(PH) 19.7]
(8) [RuH$_2$(dppm)(PPh$_3$)$_2$]	1 990m, 1 865s	C_6D_6	−7.8 (m), −9.6 (m) [c]
(7) [RuH(dppm)$_2$(H$_2$O)]BF$_4$	1 960w br	$(CD_3)_2CO$	−18.8 (quin) [J(PH) 19.1]

[a] δ/p.p.m. relative to SiMe$_4$. [b] d = Doublet, q = quartet, quin = quintet, m = multiplet. [c] For coupling constants, see Table 3.

responsible for the formation of complex (1) in the solid state (see Scheme).

2. *Reaction of* [Ru(cod)(dppm)$_2$] (2) *with* CO.—Complex (2) reacts with CO to give a yellow ruthenium(0) complex, [Ru(CO)(cod)(dppm)] (3), by substitution of the monodentate dppm ligand. Spectroscopic data [ν(CO) at 1 875s (Vaseline), 1 885 cm^{-1} (CH_2Cl_2); δ(^{31}P), 0.24 p.p.m. (s)] are in agreement with a symmetrical five-co-ordinate structure.

In the presence of excess CO, another ruthenium(0) complex is formed, [Ru(CO)$_2$(cod)(dppm)] (4), which contains two *cis* carbonyl groups and a monodentate dppm ligand as indicated by spectroscopic data {i.r., 1 960s and 1 880s cm^{-1}; ^{31}P-{^{1}H} δ, 23.1 [d, J(PP) 51 Hz] and −28.5 p.p.m. [d, J(PP) 51 Hz]}. Although (4) has not been isolated pure and is always mixed with (3), these observations are of interest since they show that dppm is more easily substituted than cod which is quite surprising.

3. *Reaction of* [Ru(cod)(cot)] *with Dppm in the Presence of* H$_2$.—When the reaction is performed under hydrogen in toluene, a pale yellow powder which can be recrystallized from toluene–hexane precipitates (5), which analyses for [RuH$_2$(dppm)$_2$] and shows a very strong Ru–H band at 1 830 cm^{-1} in its i.r. spectrum. The n.m.r. spectra (^{1}H and ^{31}P-{^{1}H}) of this product are rather puzzling, indicating the presence of both a *trans* dihydride {^{1}H n.m.r.: δ −4.7 p.p.m. [quintet, J(P–H) 19.7 Hz]; ^{31}P-{^{1}H} n.m.r.: δ 8.6 p.p.m. (s)} and a *cis* dihydride {^{1}H n.m.r.: δ −7.4 p.p.m. [doublet of quartets, J(P–H) *trans* 72.8, J(P–H) *cis* 18.7 Hz]; ^{31}P-{^{1}H} n.m.r. (A_2X_2): δ 1.29 (t) and 0.3 p.p.m. [t, J(PP) 30 Hz]} (see Figures 1 and 2) whatever the preparations and the recrystallisations.

The integration ratio measured at three different temperatures (203, 300, and 323 K) is constant and equal to the *trans* dihydride : *cis* dihydride ratio of 1 : 4 (^{31}P n.m.r., 2 : 1 : 2; ^{1}H n.m.r., hydride region, 1 : 4) (see Figure 1). The relationship between the peaks attributed to the *cis* and *trans* dihydrides was confirmed by a double-resonance experiment. Thus, irradiation of P^2 changes the quintet signal for H^1 into a singlet, whereas irradiation of P^3 does not change H^1 but transforms the H^2 signal into a triplet by loss of the large P–H *trans* and of a small P–H *cis* coupling. Complex (5) is soluble (although not very much) in toluene and benzene but not in polar solvents like acetone or methanol. It is soluble in, but reacts with, CH_2Cl_2 (see below). These data led us to propose a polynuclear formulation,[6] which we have since shown to be erroneous. Thus, despite the low solubility of the complex we performed a cryoscopic molecular-weight determination in benzene which did not reveal any evidence for dissociation or decomposition. The values obtained (750 and 980) are close enough to the theoretical value (871) and suggest the mononuclearity of the complex.

The observation of the methylene groups of dppm in the ^{1}H n.m.r. spectra is also in favour of a mixture of mononuclear isomers. Thus three broad multiplets are observed at 250 MHz (two at 90 MHz) integrating for 2 : 1 : 2 (see Figure 2). When all the phosphorus nuclei are decoupled the spectrum is simplified into an ABX spectrum [inequivalence of the two protons of a methylene group, J(AB) 15 Hz] and a pseudo-triplet [J(HH) 2 Hz]. One part of the AB spectrum shows an extra coupling constant (4 Hz) attributed to H–H through-space coupling between the methylene atom and a hydride proton. Similarly the other peak is split into a pseudo-triplet [J(H–H) 2 Hz] by the same kind of coupling.

Double-resonance experiments show that the protons of the methylene group exhibiting the AB spectrum are coupled with the doublet of quartet hydride (H^2) whereas the protons of the pseudo-triplet CH$_2$ are coupled with the quintet hydride (H^1). Since the ratio is again four methylene groups of *cis* dihydride to one methylene group of a *trans* dihydride, these results are completely consistent with a mixture of two mononuclear dihydride complexes. There is probably a rapid temperature-independent equilibrium between the two isomeric forms of the complex (but slow on the n.m.r. time-scale). Confirmation can be found in reactivity experiments, where only the *trans* isomer is obtained (see later).

4. *Reactivity of* [RuH$_2$(dppm)$_2$] (5).—[RuH$_2$(dppm)$_2$] does not react at room temperature and pressure with N_2, C_2H_4, or CO which is quite surprising when compared with the reactivity of [RuH$_2$(PPh$_3$)$_4$].[9–11] However, this is probably due to the lack of a vacant site in solution. Prolonged u.v. irradiation only causes some decomposition.

Nevertheless [RuH$_2$(dppm)$_2$] (5) reacts with chlorinated solvents (slowly with CH_2Cl_2, almost instantaneously with

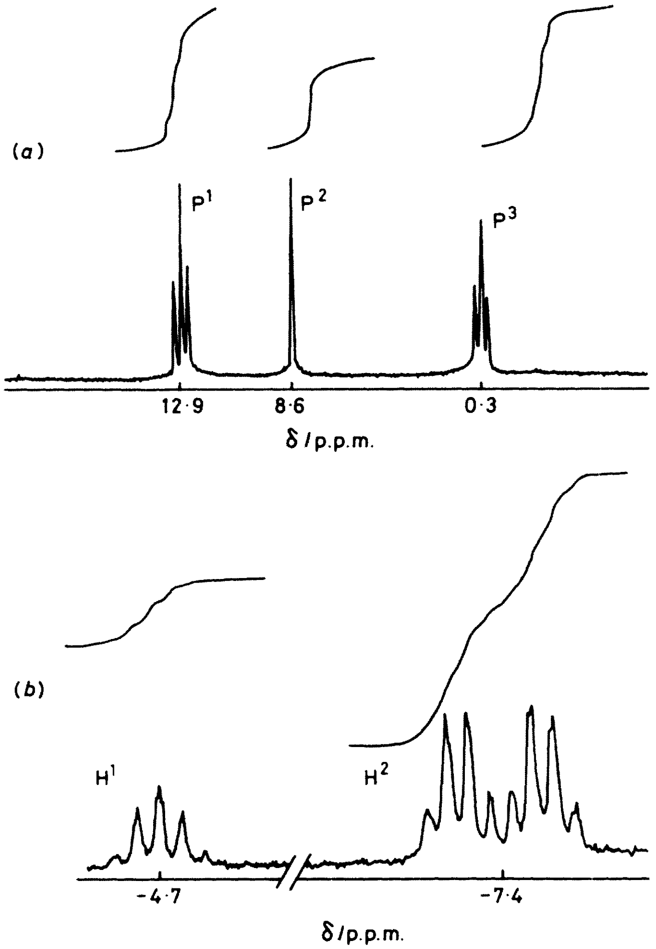


Figure 1. ^{31}P N.m.r. (*a*) and ^{1}H n.m.r. in the hydride region (*b*) of $[RuH_2(dppm)_2]$ (5)

$CHCl_3$) to give after recrystallization yellow crystals of $[RuHCl(dppm)_2]$ (6), similar to the known $[RuHCl(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane].[12] Its i.r. spectrum shows a medium intensity ν(Ru–H) band at 1 970 cm^{-1}. A weak absorption at 270 cm^{-1} could be attributed to the Ru–Cl stretching mode. The ^{1}H n.m.r. spectrum shows a quintet at δ −14.05 [*J*(PH) 19.7 Hz] and the ^{31}P-{^{1}H} n.m.r. spectrum a singlet at δ −2.2 p.p.m. This is in agreement with a *trans* hydrido-chloride formulation with two equivalent dppm groups.

Similarly protonation of $[RuH_2(dppm)_2]$ by HBF_4 in methanol leads to pale yellow microcrystals of a compound analysing for $[RuH(dppm)_2(H_2O)]BF_4$ (7). A broad band at 1 960 cm^{-1} could be due to Ru–H but nevertheless the presence of a hydride is attested by a quintet at δ −18.8 p.p.m. [*J*(PH) 19.1 Hz] in the ^{1}H n.m.r. spectrum; in addition it shows an ABX_2 pattern for the CH_2 protons of dppm [δ (H^a) 4.64, δ(H^b) 5.20, *J*(H^aH^b) 11.5 Hz, *J*(PH^a) = *J*(PH^b) = 3.5 Hz]. These data show that the compound is again symmetrical which is confirmed by the observation of a singlet at δ 0.0 in the ^{31}P n.m.r. spectrum. The hydride is then *trans* to the water molecule (see Figure 3).

5. *Reaction of* $[RuH_2(PPh_3)_4]$ *with Dppm.*—As the direct reaction of dppm on a 'ligand free' ruthenium complex did not lead to a dinuclear ruthenium dppm chemistry we investigated another route: the substitution of PPh_3 by dppm. Thus the reaction of dppm on $[RuH_2(PPh_3)_4]$ leads, whatever the amount of dppm used (stoicheiometric or excess), to a compound analysing for $[RuH_2(dppm)(PPh_3)_2]$ (8). A cryoscopic molecular-weight determination indicates that the complex is mononuclear (found, 936; calc., 1 011). The i.r. spectrum shows two Ru–H bands at 1 990m and 1 865s cm^{-1} characteristic of a *cis* dihydride. The four phosphorus atoms as well as the two hydrides are inequivalent which leads to 15 coupling constants which have all been identified (see Table 3). The ^{31}P-{^{1}H} n.m.r. spectrum at 258 K consists of four signals: a doublet of triplets at δ 60.9 (P^1), a quartet at 51.7 (P^2), a doublet of doublets of doublets at 14.7 (P^3), and a broad peak at −5.4 p.p.m. (P^4) (integration ratio 1 : 1 : 1 : 1). The large P^1–P^3 coupling constant indicates a *trans* configuration for these two phosphorus atoms. By decoupling selectively P^1, P^2, P^3, and P^4 and observing the results on the dppm methylene protons using ^{1}H n.m.r., we deduced that P^1 and P^4 are phosphorus atoms of the PPh_3 groups whereas P^2 and P^3 belong to dppm (see Figure 4). The high-field ^{1}H n.m.r. spectrum consists of two complex multiplets at δ −7.8 and −9.6 (see Figure 5). By decoupling selectively P^1, P^2, P^3, P^4, and the groups P^1–P^2 and P^3–P^4, we reached a certain number of coupling constants, the values of which were refined by a calculation (see Table 3). The geometry of the molecule thus has been solved, since this experiment showed that H^1 is *trans* to P^2 [*J*(PH) 60 Hz] and that H^2 is

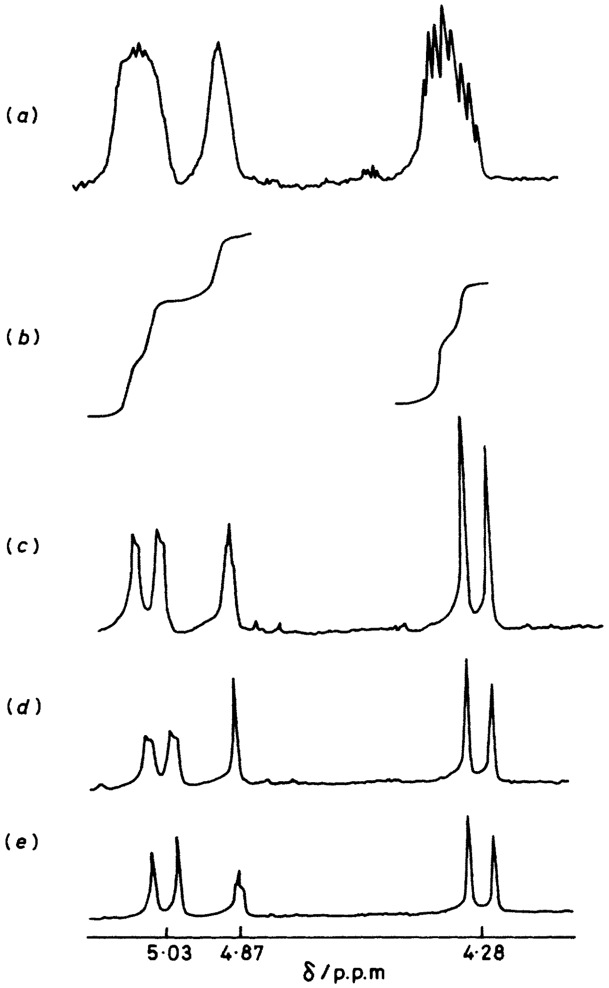
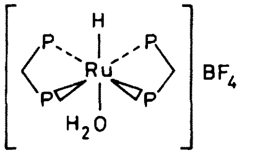


Figure 2. ^{1}H N.m.r. spectrum of $[RuH_2(dppm)_2]$ (5) in the methylene region: (*a*) observed (250 MHz), (*b*) integration, (*c*) with phosphorus decoupled, (*d*) with phosphorus and H^1 decoupled, and (*e*) with phosphorus and H^2 decoupled

trans to P^4 [J(PH) 77 Hz] (see Figure 5). The other data are summarized in Table 3. When all the phosphorus atoms are decoupled, the hydride signals consist of two broad doublets [$J(H^1H^2)$ 4 Hz] whereas the CH_2 group of dppm shows an AB resonance pattern at δ 4.75 and 4.59 p.p.m. [J(HH) 14 Hz]. Again this method did not allow the preparation of a dinuclear complex.

6. *Other Reactions.*—Although the complex $[RuCl_2(dppm)_2]$ has been known for a long time we thought that an alternative experiment using $[RuCl_2(dmso)_4]$ (dmso = dimethyl sulphoxide) [12] could lead to a dinuclear complex. Thus substituting dppm (at 80 °C) in toluene for dmso, we obtained *cis*-$[RuCl_2(dppm)_2]$ (9) with a yield better than 95% (see Table 1). Interestingly, the *cis* isomer is obtained whereas the *trans* isomer is usually more readily available.[3]



(7)

Figure 3. Proposed structure of $[RuH(dppm)_2(H_2O)]BF_4$ (7)

Table 3. Coupling constants for $[RuH_2(dppm)(PPh_3)_2]$ (8) * (see Figures 4 and 5)

	H^2	P^1	P^2	P^3	P^4
H^1	4	18	60	22	18
H^2		13	25	15	77
P^1					
P^2		20.5			
P^3		249	20.5		
P^4		20.5	20.5	13	

* The values are still approximate (±3 Hz) because of the difficulty of obtaining completely selective phosphorus decoupling.

Our study shows again that surprisingly no dinuclear bis(diphenylphosphino)methane complex of ruthenium was obtained; dppm acts as a chelating rather than a bridging ligand. It must be noted that dppm complexes of iron are mononuclear.[13]

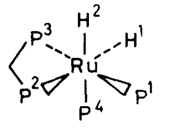
Experimental

Microanalyses were performed by the Centre d'Analyse du C.N.R.S. and by Mlle. Magna in this laboratory. Infrared spectra were obtained as Nujol mulls using Perkin-Elmer PE 577 or PE 225 grating diffractometers and n.m.r. spectra using Brucker WH90 (90 MHz) or WM250 (250 MHz) spectrometers operating in the Fourier-transform mode with proton-noise decoupling when recording ^{31}P n.m.r. spectra.

All solvents were thoroughly degassed before use and all operations were carried out in a nitrogen or argon atmosphere.

The complexes [Ru(cod)(cot)] [5] and $[RuH_2(PPh_3)_4]$ [14] were prepared according to published methods. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey Ltd, dppm and dppe from Alfa. Analytical data for the new complexes are summarized in Table 4.

(*a*) $[Ru^0_2(cod)_2(cot)(dppm)_2]$ (1).—[Ru(cod)(cot)] (0.3 g, 0.95 mmol) was added to a solution of (dppm) (0.37 g, 0.96



(8)

Figure 4. Structure of $[RuH_2(dppm)(PPh_3)_2]$ (8)

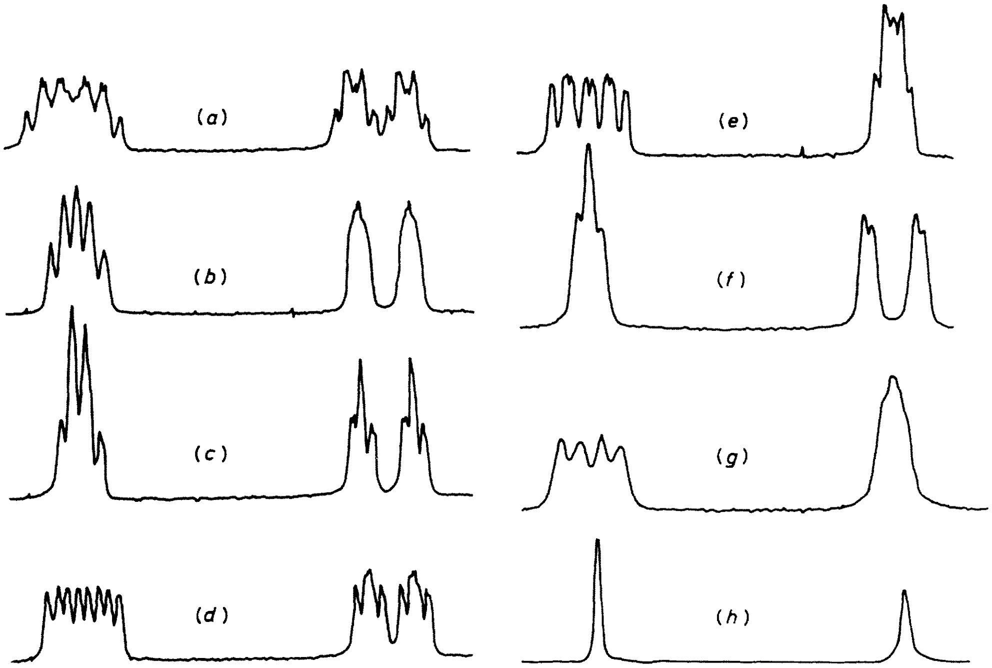


Figure 5. High-field ^1H n.m.r. spectra of $[RuH_2(dppm)(PPh_3)_2]$ (8): normal (*a*), and with selective decoupling of P^1 (*b*), P^2 (*c*), P^3 (*d*), P^4 (*e*), P^1—P^2 (*f*), P^3–P^4 (*g*), and all phosphorus atoms (*h*)

Table 4. Analytical data for the new ruthenium complexes

	Found (%)			Calculated (%)		
Compound	C	H	P	C	H	P
(1) $[Ru_2(cod)_2(cot)(dppm)_2]$	68.9	5.7	9.6	68.7	6.0	9.6
(2) $[Ru(cod)(dppm)_2]\cdot C_6H_5Me$	72.3	5.8	11.7	72.9	5.9	11.6
(3) $[Ru(CO)(cod)(dppm)]$	65.8	5.5	9.9	65.7	5.5	9.9
(5) $[RuH_2(dppm)_2]$	68.7	5.1	13.7	68.9	5.3	14.2
(6) $[RuHCl(dppm)_2]\cdot CH_2Cl_2$ *	61.7	4.9	11.9	61.8	4.8	12.5
(8) $[RuH_2(dppm)(PPh_3)_2]$	72.2	5.5	12.1	72.4	5.3	12.3
(7) $[RuH(dppm)_2(H_2O)]BF_4\cdot H_2O$	59.4	4.8	12.7	59.3	5.0	12.3

* Found: Cl, 10.5. Calc.: 10.7%.

mmol) in toluene (20 cm^3). The mixture was stirred at room temperature for 16 h after which time the volume of the solution was reduced to *ca.* 5 cm^3. Hexane (10 cm^3) was added and the solution was cooled to −15 °C affording yellow crystals of complex (1) (yield *ca.* 60%).

(*b*) $[Ru^0(cod)(dppm)_2]$ (2).—This complex was obtained as for (*a*) above but using 0.75 g (1.95 mmol) of dppm. Yellow crystals were obtained (yield *ca.* 85%). ^{1}H N.m.r.: δ 7—8 (br, phenyl), 4.5 (m, methylene of dppm), and 4—2.5 p.p.m. (cod).

(*c*) *Reaction of* $[Ru(cod)(dppm)_2]$ (2) *with Carbon Monoxide.*—$[Ru(cod)(dppm)_2]$ (2) (0.5 g, 0.51 mmol) was dissolved in toluene (20 cm^3) and the solution placed in a CO atmosphere. Evaporation to *ca.* 5 cm^3 and addition of hexane afforded yellow crystals of $[Ru(CO)(cod)(dppm)]$ (3) (yield *ca.* 50%). If CO was bubbled through the solution and the reaction prolonged for 15 h, i.r. and $^{31}P-\{^1H\}$ n.m.r. spectra showed the presence of another compound, $[Ru(CO)_2(cod)(dppm)]$ (4), which was obtained mixed with $[Ru(CO)(cod)(dppm)]$ (3) by recrystallization from toluene–hexane.

(*d*) $[Ru^{II}H_2(dppm)_2]$ (5).—$[Ru(cod)(cot)]$ (0.3 g, 0.95 mmol) was added to a solution of dppm (0.75 g, 1.95 mmol), in toluene (20 cm^3). Hydrogen was passed through the solution for 1 h and the mixture left for 15 h under a hydrogen atmosphere. A pale yellow powder precipitated which was filtered off. Addition of hexane to the solution caused further precipitation. The powder was analytically pure but could be recrystallized by dissolution in warm toluene and cooling to −15%. Total yield of powder *ca.* 80%.

(*e*) $[Ru^{II}HCl(dppm)_2]$ (6).—$[RuH_2(dppm)_2]$ (5) (0.3 g) was added to $CHCl_3$ (10 cm^3) and the mixture was stirred for 1 h after which time the clear yellow solution was evaporated to dryness (reaction completed as shown by ^{1}H n.m.r.). Recrystallization from CH_2Cl_2–Et_2O afforded yellow crystals of complex (6) (yield *ca.* 80%).

(*f*) $[Ru^{II}H(dppm)_2(H_2O)]BF_4$ (7).—To $[RuH_2(dppm)_2]$ (5) (0.4 g) was added HBF_4 (1 cm^3) in methanol (10 cm^3) and the mixture stirred for 15 min. The pale yellow microcrystalline precipitate was filtered off, washed with methanol and diethyl ether, and dried *in vacuo* (yield *ca.* 65%). The complex could be recrystallized from acetone.

(*g*) $[Ru^{II}H_2(dppm)(PPh_3)_2]$ (8).—$[RuH_2(PPh_3)_4]$ (0.5 g, 0.43 mmol) and dppm (0.17 g, 0.44 mmol) were added to toluene (40 cm^3). The solution was stirred for 15 h after which time the toluene solution was reduced to *ca.* 10 cm^3 and hexane added. Yellow crystals of complex (8) were obtained (yield *ca.* 40%). The crystallization proved difficult, evaporation to dryness of the solution and recrystallization from acetone–hexane gave a better yield of the complex (*ca.* 75%).

(*h*) $[Ru^{II}Cl_2(dppm)_2]$ (9).—$[RuCl_2(dmso)_4]$ (1 g, 2.07 mmol) was added to a solution of dppm (1.6 g, 4.17 mmol) in toluene (100 cm^3). The suspension was stirred at 80 °C for 15 h during which time the colour changed from golden yellow to lemon yellow. The analytically pure precipitate was filtered off and washed with toluene and diethyl ether (yield *ca.* 100%). The crude product could be recrystallized from dichloromethane–diethyl ether to afford light yellow crystals of *cis*-$[RuCl_2(dppm)_2]\cdot 0.5CH_2Cl_2$.

References

1 See, for example, (*a*) J. T. Mague and S. H. Devries, *Inorg. Chem.*, 1982, **21**, 1632; J. T. Mague and A. R. Sanger, *ibid.*, 1979, **18**, 2060; C. P. Kubiak, C. Woodcock, and R. Eisenberg, *ibid.*, 1982, **21**, 2119; M. Cowie and S. K. Dwight, *J. Organomet. Chem.*, 1981, **214**, 233; M. Cowie and T. G. Southern, *Inorg. Chem.*, 1982, **21**, 246; (*b*) A. R. Sanger, *J. Chem. Soc., Dalton Trans.*, 1977, 1971; (*c*) C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 1641; (*d*) G. K. Anderson, H. C. Clark, and J. A. Davies, *J. Organomet. Chem.*, 1981, **210**, 135; R. J. Puddephatt and M. A. Thompson, *Inorg. Chem.*, 1982, **21**, 725; and refs. therein.

2 J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1972, **11**, 2714.

3 G. Smith, D. J. Cole-Hamilton, A. C. Gregory, and N. C. Gooden, *Polyhedron*, 1982, **1**, 97.

4 F. A. Cotton and B. E. Hanson, *Inorg. Chem.*, 1977, **16**, 3369; G. Lavigne, N. Lugan, and J. J. Bonnet, *Organometallics*, 1982, **1**, 1040.

5 P. Pertici, G. Vitulli, M. Paci, and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.

6 B. Chaudret, G. Commenges, and R. Poilblanc, *J. Chem. Soc., Chem. Commun.*, 1982, 1388.

7 P. Pertici, G. Vitulli, W. Porzio, and M. Zocchi, *Inorg. Chim. Acta*, 1979, **37**, L521.

8 P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 581, 956.

9 R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. C. Yuen, *J. Organomet. Chem.*, 1973, **54**, 259.

10 T. V. Ashworth and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1976, 705 and refs. therein.

11 D. J. Cole-Hamilton and G. Wilkinson, *Nouv. J. Chim.*, 1977, **1**, 141.

12 A. R. Al-Ohaly, R. A. Head, and J. F. Nixon, *J. Organomet. Chem.*, 1981, **205**, 99.

13 J. P. Evans, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204.

14 R. Young and G. Wilkinson, *Inorg. Synth.*, 1977, **17**, 75.

Received 11*th May* 1983; *Paper* 3/749