Preparation and Properties of Ditertiary Phosphine Complexes of Ruthenium(0)

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The interaction of bis(styrene)bis(triphenylphosphine)ruthenium, $[Ru(C_8H_8)_2(PPh_3)_2]$, with chelate ditertiary phosphines, $Ph_2P(CH_2)_nPPh_2$ [n = 1 (dppm) or 2 (dppe); (P–P)], leads to ruthenium(0) complexes $[Ru(C_8H_8)(P\text{–}P)_2]$, which for P–P = dppm is extremely stable to heat, light, and the action of potential ligands. $[Ru(C_8H_8)(dppe)_2]$ readily loses styrene and metallates a phenyl ring in toluene at room temperature or on heating and reacts with ligands L = CO or $P(OMe)_3$ to give $[RuL(dppe)_2]$. With $P(OMe)_3$ in refluxing n-octane, or with $P(OPh)_3$, the hydride complex *trans*-$[RuH\{P(O)(OR)_2\}(dppe)_2]$ (R = Me or Ph) is produced. With $Ph_2P(CH_2)_3PPh_2$ (dppp), no ruthenium(0) complex can be isolated from reaction with $[Ru(C_8H_8)_2(PPh_3)_2]$, the main product being $[RuH\{o\text{-}C_6H_4P(Ph)(CH_2)_3PPh_2\}(dppp)]$. The complexes have been characterised by microanalysis and by ^1H and ^{31}P n.m.r. spectra.

Complexes of ruthenium(0) which do not contain CO, fluorinated phosphines, or dienes are unusual, although $[Ru(PPh_3)_3(MeCN)]$,[1] which readily metallates a phosphine, and $[Ru\{P(OMe)_3\}_5]$ [2] have been isolated. Attempts to prepare [3] the fully phosphine-stabilised complex, $[Ru(PMe_3)_5]$, were unsuccessful, metallation of the phosphine readily occurring to give $[RuH(CH_2PMe_2)(PMe_3)_3]$. A similar, although intermolecular metallation of $Me_2PCH_2CH_2PMe_2$ has also been observed.[4,5]

A rare 16-electron complex of ruthenium(0) is the purple $[Ru(C_8H_8)_2(PPh_3)_2]$, obtained [6–8] from reaction of $[RuH_2(PPh_3)_4]$ with styrene (C_8H_8). This complex readily metallates [8] a phosphine ligand on dissolving in hydrocarbon or ethereal solvents whilst reactions with alkenes give [8,9] hydride complexes of ruthenium(II) or diene complexes of ruthenium(0).

We now report on reactions of $[Ru(C_8H_8)_2(PPh_3)_2]$ with diphosphine ligands which give 18-electron zerovalent complexes some of which are remarkably stable.

The ^1H and ^{31}P n.m.r. spectra of the new complexes are given in Tables 1 and 2 and the reactions are summarised in the Scheme.

Results and Discussion

Reactions of $[Ru(C_8H_8)_2(PPh_3)_2]$ *with Diphosphines* (P–P).—$[Ru(C_8H_8)_2(PPh_3)_2]$ reacts with bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe) in styrene (C_8H_8) in the presence of triphenylphosphine to give orange complexes which analyse for $[Ru(C_8H_8)(P\text{–}P)_2]$. The i.r. spectra of the two complexes are fairly similar showing bands arising from the diphosphine and from co-ordinated styrene [ν(C=C) = 1 590 cm^{-1}]. No ν(Ru–H) bands are present and there are no bands from *o*-disubstituted phenyl rings. The ^1H n.m.r. spectrum of $[Ru(C_8H_8)(dppm)_2]$ shows phenyl resonances together with broad peaks at δ 4.05 and 3.05 (ratio 2 : 1) from co-ordinated styrene. The resonance from the methylene protons of the diphosphine is very broad suggesting that the two dppm ligands are not equivalent. $[Ru(C_8H_8)(dppe)_2]$ is insufficiently stable in aromatic solvents other than styrene (see below) for any reliable ^1H n.m.r. data to be obtained. The ^{31}P n.m.r. spectrum of $[Ru(C_8H_8)(dppe)_2]$ measured in styrene consists of two triplets indicating two pairs of equivalent phosphorus atoms. This, together with its reactions (see later) shows it is a genuine complex of ruthenium(0) with structure (I) (see Scheme).

The ^{31}P n.m.r. spectrum of $[Ru(C_8H_8)(dppm)_2]$ is more complex but can readily be analysed and shows that all the phosphorus atoms are in different chemical environments. This can only be accommodated if the complex has square-pyramidal geometry, as shown in structure (II) (Figure 1).

With 1,3-bis(diphenylphosphino)propane (dppp), $[Ru(C_8H_8)_2(PPh_3)_2]$ does not give an isolable ruthenium(0) complex. The product contains a hydride ligand [ν(Ru–H) at 1 935 cm^{-1}] and an *o*-metallated phenyl ring [i.r., 1 550 and 1 415 cm^{-1}]; [10,11] ^1H and ^{31}P n.m.r. studies show that the complex has the structure (III) (see Scheme, P–P = dppp). This compound has previously been prepared [12] electrochemically from $[RuCl(dppp)_2]PF_6$.

This difference in behaviour between dppp and the other diphosphines is not fully understood although the ease of metallation correlates with the chelate ring size since $[Ru(C_8H_8)(dppe)_2]$ metallates under mild conditions (see below) whereas $[Ru(C_8H_8)(dppm)_2]$ is stable even in refluxing toluene. Perhaps the longer the backbone, the more flexible is the diphosphine and hence the phosphorus atoms can rotate in such a way that a phenyl ring is brought into close proximity with the metal. For the more rigid dppm ligand, the phenyl rings must be held away from the metal.

Metallation Reactions of $[Ru(C_8H_8)(dppe)_2]$.—The ^{31}P n.m.r. spectrum of $[Ru(C_8H_8)(dppe)_2]$ measured in toluene is quite different from that measured in styrene. Thus, the four phosphorus atoms are non-equivalent and one of them resonates at a very much lower frequency than the other three. This low-frequency shift is characteristic [10] of a phosphorus atom in a four-membered ring containing a metal and suggests that *o*-metallation of a phenyl ring has occurred. Support for this contention comes from the observation that when only the phenyl region of the ^1H n.m.r. spectrum is decoupled, all the phosphorus resonances split further. This confirms the presence of a hydride ligand which, from analysis of the coupling constants is evidently *trans* to P_C. The values of J(PP) (see Table 2) show that the metallated phosphorus atom (P_D) is *trans* to another phosphorus (P_A) and hence that the compound has structure (III) (Scheme).

This complex can be isolated by careful crystallation and i.r. spectra confirm the presence of the hydride (1 950 cm^{-1}) and the *o*-metallated phenyl ring (1 567 cm^{-1}).[10,11] This metallation, which does not occur so readily in styrene, is analogous to that reported [13] for $[Fe(CH_2{=}CH_2)(dppe)_2]$.

If toluene solutions of $[Ru(C_8H_8)(dppe)_2]$ are allowed to stand for longer periods of time (>3 d), another (orange) product can be isolated. This compound has an identical i.r.

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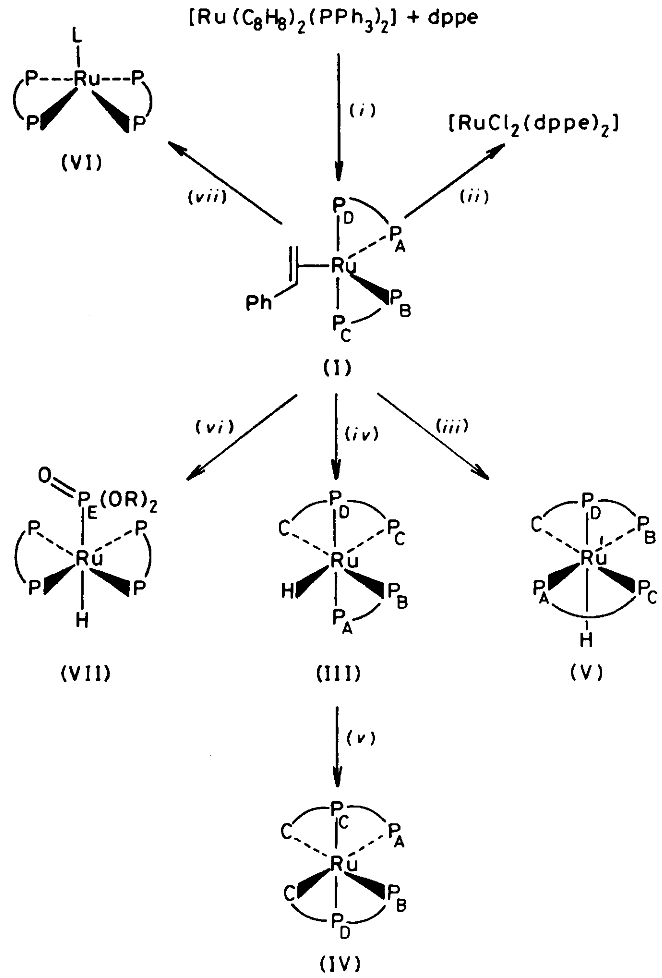
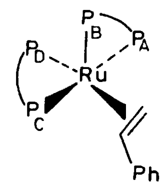


Scheme. Preparation and reactions of $[Ru(C_8H_8)(dppe)_2]$: (*i*) styrene, 25 °C; (*ii*) $CHCl_3$, 25 °C; (*iii*) toluene, mesitylene or n-octane, reflux; (*iv*) toluene, 25 °C, 24 h; (*v*) toluene, 25 °C, 72 h; (*vi*) $P(OPh)_3$, 25 °C for R = Ph: $P(OMe_3)$, n-octane, reflux for R = Me; (*vii*) L = CO or $P(OMe)_3$, 25 °C. The stereochemistry of (VI) is unknown

spectrum to that of the yellow metallated compound obtained after 24 h (see above) except that the ν(Ru–H) absorption is missing. ^{31}P N.m.r. studies show that there are two sets of two equivalent phosphorus atoms and we conclude that this is the dimetallated complex [structure (IV) in the Scheme]. We have assumed that both metallations do not occur on the same diphosphine ligand and this is supported by the ^{31}P n.m.r. data.

If $[Ru(C_8H_8)(dppe)_2]$ is heated in toluene, mesitylene, or n-octane, a yellow complex may be isolated which again contains a metallated phenyl ring. This compound analyses for $[RuH\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}(dppe)]$ but is a different isomer from that obtained after 24 h at room temperature. Thus, ν(Ru–H) is at 1 915 cm^{-1} and the presence of the metallated phenyl ring is confirmed by absorptions at 1 557 and 1 412 cm^{-1}. The ^{31}P n.m.r. spectrum shows two rather broad resonances in the ratio 3 : 1, with the unique phosphorus atom having a chemical shift typical[11] for a phosphorus atom that holds the metallated phenyl group. Obviously, the other three phosphorus atoms cannot be chemically equivalent so we attribute the apparent simplicity of the spectrum to an accidental degeneracy of their chemical shifts. Measuring the spectrum under conditions in which the coupling to the hydride is present shows that the hydride is *trans* to the unique phosphorus atom. This is confirmed by the ^1H n.m.r. spectrum in which the hydride resonates as a doublet of quartets with the doublet splitting considerably larger than the quartet. The complex thus has structure (V). Molecular weight measurements confirm the monomeric formulation of this complex.



(II)

Figure 1. The structure of $[Ru(C_8H_8)(dppm)_2]$; although P_A and P_C are mutually *trans*, the assignment of the phosphorus atoms is otherwise arbitrary

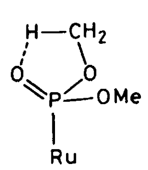


Figure 2. Possible hydrogen bonding in $[RuH\{P(O)(OMe)_2\}(dppe)_2]$

Reactions of $[Ru(C_8H_8)(P\text{–}P)_2]$.—$[Ru(C_8H_8)(P\text{–}P)_2]$ (P–P = dppm or dppe) both react with chloroform to give the known[14] $[RuCl_2(P\text{–}P)_2]$ but otherwise $[Ru(C_8H_8)(dppm)_2]$ is unreactive, being isolated unchanged after refluxing in toluene, photolysis in benzene for 4 d with u.v. light, or reaction with CO in toluene at room temperature.

$[Ru(C_8H_8)(dppe)_2]$, on the other hand, reacts with CO at room temperature to give the known[15] $[Ru(CO)(dppe)_2]$. The value of $\nu(C\equiv O)$ in this complex is very low (1 835 cm^{-1}) consistent with there being a high electron density on the ruthenium atom and hence a large amount of π back donation.

A similar reaction is observed with $P(OMe)_3$ and in both cases ^{31}P studies at room temperature show that the four dppe phosphorus atoms are equivalent. For $[Ru\{P(OMe)_3\}(dppe)_2]$, low-temperature studies show that this equivalence arises from fluxionality; coalescence is at *ca.* −50 °C but the low-temperature limiting spectrum is not reached even at −80 °C. This compound is sometimes contaminated with small amounts of an impurity which has a hydride resonance [doublet of quintets, J(PH) = 19.0, $J(P_EH)$ = 90 Hz] at δ −9.4. This impurity can be isolated by carrying out the reaction between $[Ru(C_8H_8)(dppe)_2]$ and $P(OMe)_3$ in refluxing n-octane. The white solid which is a diamagnetic non-electrolyte has ν(Ru–H) at 1 830 cm^{-1}. By analogy with $[RuH\{P(O)(OPh)_2\}(dppe)_2]$, see below, we tentatively assign this impurity as $[RuH\{P(O)(OMe)_2\}(dppe)_2]$. However, there are no bands in the i.r. spectrum around 1 200 cm^{-1} (1 225 and 1 200 cm^{-1} for the diphenyl phosphonate complex) which can be assigned to ν(P=O). The absorption at 1 018 cm^{-1}, which is not present in the trimethyl phosphite complex is tentatively assigned to ν(P=O) and its low energy can be attributed to hydrogen-bond formation between a methyl hydrogen and the oxido-oxygen atom in a sterically favoured five-membered ring (see Figure 2). The value of ν(P=O) in these types of complexes is unusually *ca.* 1 120 cm^{-1} but it can be as low as 1 010 cm^{-1} when hydrogen bonding is known to be important.[16]

Reaction of $P(OPh)_3$ with $[Ru(C_8H_8)(dppe)_2]$ surprisingly

Table 1. Hydrogen-1 n.m.r. data for hydride resonances of ruthenium complexes at 25 °C. For assignments see structures (I)—(VII)

			Coupling constants (Hz)				
Complex	Structure	δ/p.p.m.	HP_A	HP_B	HP_C	HP_D	HP_E
[RuH{*o*-$C_6H_4P(Ph)(CH_2)_2PPh_2$}(dppe)] [a]	(V)	−8.9	18.0	18.0	18.0	80.0	—
[RuH{*o*-$C_6H_4P(Ph)(CH_2)_3PPh_2$}(dppp)] [a]	(III)	−6.0	19.0 [b]	19.0 [b]	80.0	24.6 [b]	—
[RuH{P(O)$(OPh)_2$}$(dppe)_2$] [c]	(VII)	−9.7	19.4	19.4	19.4	19.4	95.0
[RuH{P(O)$(OMe)_2$}$(dppe)_2$] [a]	(VII)	−9.4	19.0	19.0	19.0	19.0	90.0

[a] In toluene. [b] Arbitrary assignments. [c] In $CDCl_3$.

Table 2. Phosphorus-31 n.m.r. data for some ruthenium complexes at 25 °C

		Chemical shifts [a]				Coupling constants (Hz)					
Complex	Structure	P_A	P_B	P_C	P_D	P_AP_B	P_AP_C	P_AP_D	P_BP_C	P_BP_D	P_CP_D
[Ru(C_8H_8)$(dppe)_2$] [b]	(I)	63.2		58.8			20.7	20.7	20.7	20.7	
[Ru(C_8H_8)$(dppm)_2$] [c]	(II)	1.2	−4.7	−5.2	−10.1	32.1	293.8	39.8	40.4	32.5	24.6
[RuH{*o*-$C_6H_4P(Ph)(CH_2)_2PPh_2$}(dppe)] [c]	(III)	73.7	71.1	46.3	7.4	18.8	6.4	255.6	7.0	23.8	5.5
[RuH{*o*-$C_6H_4P(Ph)(CH_2)_2PPh_2$}(dppe)] [c,d]	(V)	73.2	73.2	73.2	−5.2						
[Ru{*o*-$C_6H_4P(Ph)(CH_2)_2PPh_2$}$_2$]	(IV)	65.9		39.7			19.0	19.0	19.0	19.0	
[RuH{*o*-$C_6H_4P(Ph)(CH_2)_3PPh_2$}(dppp)] [c]	(III)	31.4	31.2	−6.7	−38.7	27.5	23.6	240.0	8.3	27.4	27.4
[Ru(CO)$(dppe)_2$] [c]	(VI)	69.1									
[Ru{P$(OMe)_3$}$(dppe)_2$] [c,e]	(VI)	68.3									
trans-[RuH{P(O)$(OPh)_2$}$(dppe)_2$] [f]	(VII)	66.3									
trans-[RuH{P(O)$(OMe)_2$}$(dppe)_2$] [g]	(VII)	70.4									

[a] In p.p.m. downfield from external 85% H_3PO_4. For assignment of phosphorus atoms see structures (I)—(VII). [b] In styrene. [c] In toluene. [d] Coupling not resolved. [e] P$(OMe)_3$: δ(P) = 155.8 p.p.m., *J*(PP) = 37.4 Hz. [f] In $CDCl_3$; δ(P_E) = 118.3 p.p.m., *J*(PP) = 39 Hz. [g] P_E Not observed; *J*(P_AP_E) = 36.2 Hz.

gives *trans*-[RuH{P(O)$(OPh)_2$}$(dppe)_2$] [structure (VII) in the Scheme] and ^{31}P n.m.r. spectra of crude reaction solutions show that this is the only ruthenium-containing product.

Similar rearrangements of trialkyl phosphites have been observed,[17,18] usually in the presence of nucleophiles, but the fate of the alkyl or aryl group and the source of the hydride ligand is uncertain in our examples. Presumably the driving force for these reactions is the lowering of the electron density on the highly electron-rich metal centres, although steric factors are probably also important.

Experimental

Microanalyses were by Butterworth Laboratories Ltd. and Elemental Micro-Analysis Ltd. I.r. spectra were recorded in Nujol mulls between KBr plates on Perkin-Elmer 457 and 597 grating spectrophotometers. N.m.r. spectra were recorded on Perkin-Elmer R12 and R32 (^1H), Bruker WM250 (^{31}P), and Varian Associates XL 100 and EM390 (^1H and ^{31}P) spectrometers. Phosphorus-31 n.m.r. spectra were recorded in the Fourier-transform mode with proton noise decoupling. Simulation of second-order spectra was carried out using a PANIC program on the Bruker WM250 Aspect 2000 computer.

Melting points were measured on an Electrothermal melting point apparatus in tubes sealed under an argon atmosphere and are uncorrected.

[Ru$(C_8H_8)_2$$(PPh_3)_2$] was synthesised by a published method.[8]

All solvents were dried and degassed before use, whilst other reagents were reagent grade and were used without further purification. The light petroleum used had a boiling point range of 40—60 °C. All manipulations were carried out under argon using standard Schlenk line and catheter tubing techniques.

*Bis[bis(diphenylphosphino)methane-*P,P′*](styrene)ruthenium.*—[Ru$H_2$$(PPh_3)_4$] (1 g) was stirred in styrene (6 cm³) for 20 min. To the purple solution was added dppm (0.7 g). After 1 h, light petroleum (30 cm³) was added. The orange solid was collected, washed with light petroleum, and dried *in vacuo*. Recrystallisation was from toluene–light petroleum. Yield *ca.* 60%, m.p. 190 °C (decomp.) (Found: C, 71.6; H, 5.5; P, 12.6. $C_{58}H_{52}P_4Ru$ requires C, 71.5; H, 5.3; P, 12.7%). I.r. ($\tilde{v}_{max.}$): 3 060m, 1 590s, 1 572w, 1 490 (sh), 1 484s, 1 435vs, 1 308w, 1 292vw, 1 275vw, 1 227m, 1 178w, 1 160vw, 1 146w, 1 102m, 1 083s, 1 070m, 1 030w, 994w, 933vw, 912w, 874w, 775m, 768m, 747s, 730vs, 698vs, 678w, 656w, 620vw, 554w, 540m, 510vs, 485s, 440s, and 415s cm⁻¹.

*Bis[1,2-bis(diphenylphosphino)ethane-*P,P′*](styrene)-ruthenium.*—[Ru$H_2$$(PPh_3)_4$] (1 g) was stirred in styrene (6 cm³) for 20 min; dppe (0.7 g) was added to the purple solution and then light petroleum (30 cm³). The solution was filtered and the orange solid collected, washed with light petroleum, and dried *in vacuo*. Yield *ca.* 60%, m.p. 125 °C (decomp.) (Found: C, 72.4; H, 5.2; P, 11.9. $C_{60}H_{56}P_4Ru$ requires C, 72.0; H, 5.6; P, 12.4%). I.r. ($\tilde{v}_{max.}$): 3 060m, 1 597 (sh), 1 590s, 1 570w, 1 488s, 1 435vs, 1 310w, 1 296w, 1 268w, 1 230m, 1 179w, 1 157w, 1 100 (sh), 1 090m, 1 030w, 995w, 970vw, 940vw, 920vw, 880w, 805m, 780vw, 743s, 698vs, 662s, 652m, 643m, 620w, 570vw, 540m, 530s, 520s, 505m, 488m, 470w, 455w, 439m, 412s, and 380s cm⁻¹.

*[1,2-Bis(diphenylphosphino)ethane-*P,P′*]{*o*-[(2-diphenylphosphinoethyl)phenylphosphino]phenyl-*C^β*,P,P′}hydrido-ruthenium*(II)*: Structure* (III).—[Ru(C_8H_8)$(dppe)_2$] (0.5 g) was stirred in toluene (15 cm³) until dissolved and kept at room temperature for 24 h. The volume of solution was reduced, by vacuum pumping, to 2 cm³. After 1 d at room temperature the yellow crystals were collected, washed with light petroleum, and

dried *in vacuo*. Yield *ca.* 20%, m.p. 180 °C (decomp.) (Found: C, 68.7; H, 5.5. $C_{52}H_{48}P_4Ru$ requires C, 69.6; H, 5.4%). I.r. ($\tilde{\nu}_{max.}$): 3 045m, 1 950m, 1 600vw, 1 582vw, 1 567vw, 1 490 (sh), 1 480s, 1 430vs, 1 310vw, 1 270vw, 1 188w, 1 155vw, 1 090m, 1 025w, 995vw, 875w, 810m, 740s, 725s, 693vs, 668m, 640w, 615vw, 520vs, 508s, 493m, 480w, 460w, 440vw, and 410w cm^{-1}.

Bis{o-[(*2-diphenylphosphinoethyl*)*phenylphosphino*]*phenyl*-C$^{\beta}$,P,P′}*ruthenium*(II): *Structure* (IV).—The residual solution from the preceding preparation was allowed to stand at room temperature for 3 d and the orange crystals were collected, washed with light petroleum and dried *in vacuo*. Yield *ca.* 60% {relative to the initial [Ru(C_8H_8)(dppe)$_2$]}, m.p. 147—150 °C (Found: C, 70.6; H, 5.73. $C_{52}H_{46}P_4Ru$ requires C, 69.7; H, 5.1%). I.r. ($\tilde{\nu}_{max.}$): 3 040m, 1 600vw, 1 585w, 1 570w, 1 495 (sh), 1 480s, 1 433vs, 1 420 (sh), 1 333w, 1 312w, 1 270w, 1 190m, 1 155w, 1 098s, 1 070w, 1 028m, 998w, 970vw, 875m, 820s, 788vw, 775vw, 743vs, 735s, 728s, 698vs, 675s, 657w, 640w, 617w, 523vs, 511s, 500vs, 462m, 452vw, 442w, and 415m cm^{-1}.

[1,2-*Bis*(*diphenylphosphino*)*ethane*-P,P′]{o-[(*2-diphenylphosphinoethyl*)*phenylphosphino*]*phenyl*-C$^{\beta}$,P,P′}*hydridoruthenium*(II): *Structure* (V).—(*a*) [Ru(C_8H_8)(dppe)$_2$] (0.2 g) was refluxed in toluene (5 cm^3) for 1 h. Light petroleum (4 cm^3) was added to the filtered solution. After 24 h at room temperature, the yellow crystals formed were collected, washed with light petroleum and dried *in vacuo*. Yield *ca.* 70%.

(*b*) [Ru(C_8H_8)(dppe)$_2$] (0.2 g) was stirred in mesitylene (5 cm^3) at 130 °C for 1 h. Yellow crystals were formed from the filtered solution at room temperature after 12 h. These were collected, washed with light petroleum and dried *in vacuo*. Yield *ca.* 60%.

(*c*) [Ru(C_8H_8)(dppe)$_2$] (0.13 g) was refluxed in n-octane (20 cm^3) for 1 h. The boiling solution was filtered and kept at room temperature for 6 h. The yellow-orange crystals were collected, washed with n-octane and dried *in vacuo*. Yield *ca.* 70%, m.p. 205 °C (decomp.). Molecular weight (cryoscopically in benzene) 802; required 897 (Found: C, 68.8; H, 5.5; P, 13.2. $C_{52}H_{48}P_4Ru$ requires C, 69.6; H, 5.4; P, 13.8%). I.r. ($\tilde{\nu}_{max.}$): 3 050m, 1 915m br, 1 588w, 1 572w, 1 557w, 1 483s, 1 432vs, 1 412m, 1 406 (sh), 1 307w, 1 280w, 1 269w, 1 231w, 1 180w, 1 155w, 1 122w, 1 095s, 1 068m, 1 030m, 1 000w, 986vw, 872m, 845vw, 805s, 740s, 728s, 720m, 700vs, 663s, 648m, 638m, 618vw, 527vs, 510vs, 488s, 438s, and 385s cm^{-1}.

[1,3-*Bis*(*diphenylphosphino*)*propane*-P,P′]{o-[(*3-diphenylphosphinopropyl*)*phenylphosphino*]*phenyl*-C$^{\beta}$,P,P′}*hydridoruthenium*(II): *Structure* (III).—[$RuH_2(PPh_3)_4$] (0.5 g) was stirred in styrene (4 cm^3) for 20 min; dppp (0.4 g) was added to the purple solution and stirred for 15 h. Light petroleum (15 cm^3) was added and the solution filtered and left at -20 °C for 24 h. The pale yellow crystals were collected, washed with light petroleum and dried *in vacuo*. The volume of the residual solution was reduced by vacuum pumping to 2 cm^3 and light petroleum (10 cm^3) added to obtain more crystals by cooling for 24 h. Yield 65%, m.p. 220 °C (decomp.) (Found: C, 70.6; H, 6.0; P, 13.2. $C_{54}H_{52}P_4Ru$ requires C, 70.1; H, 5.6; P, 13.4%). I.r. ($\tilde{\nu}_{max.}$): 3 070 (sh), 3 020m, 1 935m, 1 582w, 1 550w, 1 480s, 1 432vs, 1 415m, 1 305w, 1 265w, 1 180w br, 1 150m, 1 120vw, 1 090m, 1 053vw, 1 025w, 998vw, 965m, 920vw, 850w, 837s, 800m, 788s, 750s, 740vs, 720s, 695vs 670w, 650 (sh), 640s, 615vw, 528w, 512vs, 500s, 495s, 485s, 457m, 437w, 420vw, 410m, and 402m cm^{-1}.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonylruthenium*.—Carbon monoxide was bubbled through [Ru(C_8H_8)(dppe)$_2$] (0.25 g) dissolved in toluene (20 cm^3) for 2 h. The volume of the orange filtrate was reduced to 5 cm^3, light petroleum (3 cm^3) added and the solution cooled to -20 °C. After 24 h the yellow-orange crystals were collected, washed with light petroleum and dried *in vacuo*. Yield *ca.* 75%, m.p. 253 °C (decomp.) (Found: C, 69.6; H, 5.2; P, 12.9. $C_{53}H_{48}OP_4Ru$ requires C, 68.8; H, 5.2; P, 13.4%). I.r. ($\tilde{\nu}_{max.}$): 3 075m, 1 835vs, 1 788w, 1 604vw, 1 585w, 1 575w, 1 497w, 1 482m, 1 435s, 1 416w, 1 307w, 1 280w, 1 180w, 1 156w, 1 102m, 1 088s, 1 070 (sh), 1 030m, 1 002w, 880m, 845vw, 800m, 755m, 738s, 697vs, 675m, 667m, 640m, 618w, 535vs, 522s, 510vs, 485w, 470w, 445m, 435w, 415w, and 384s cm^{-1}.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*](*trimethyl phosphite*)*ruthenium*.—Trimethyl phosphite (0.3 g) was refluxed with [Ru(C_8H_8)(dppe)$_2$] (0.35 g) in toluene (5 cm^3) for 1 h. Light petroleum (20 cm^3) was added to the orange solution and, after cooling for 24 h at -20 °C, the crystals (red and white) were collected. They were dissolved in hot toluene (8 cm^3). After filtration, the solution was treated with light petroleum (20 cm^3) and allowed to stand at room temperature for 24 h. The red crystals of the complex were collected, washed with tetrahydrofuran (2 cm^3) and dried *in vacuo*. More crystals of the complex were obtained by cooling the mother-liquors to -20 °C for 48 h. Yield *ca.* 60%, m.p. 125 °C (decomp.) (Found: C, 64.5; H, 5.6. $C_{55}H_{57}O_3P_5Ru$ requires C, 64.6; H, 5.6%). I.r. ($\tilde{\nu}_{max.}$): 3 050m, 1 590w, 1 485m, 1 435s, 1 415vw, 1 330vw, 1 310w, 1 275w br, 1 183m, 1 155vw, 1 098m, 1 070s, 1 040vs, 1 023s, 910vw, 880m, 850vw, 825m, 815m, 750s, 740vs, 730s, 695vs, 680 (sh), 665s, 637w, 547w, 520s, 515s, 500 (sh), 497s, 463w, 405s, and 383s cm^{-1}.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*](*dimethyl phosphonato*)*hydridoruthenium*(II).—[Ru(C_8H_8)(dppe)$_2$] (0.2 g) and P(OMe)$_3$ (0.6 cm^3) were refluxed in n-octane (10 cm^3) for 1 h. The cream coloured solid that had separated on cooling was collected and dissolved in hot toluene (5 cm^3). The resulting solution was treated with light petroleum (5 cm^3), filtered, and allowed to stand at room temperature for 1 h. The white crystals were collected, washed with light petroleum and dried *in vacuo*. A further crop of white crystals of the product was obtained on cooling the mother-liquors to -20 °C for 1 d. Yield *ca.* 60%, m.p. 290—293 °C (decomp.) (Found: C, 65.7; H, 5.95. $C_{54}H_{54}O_3P_5Ru$ requires C, 65.7; H, 5.5%). I.r. ($\tilde{\nu}_{max.}$): 3 040w, 3 010w, 1 830m, 1 590vw, 1 575vw, 1 485m, 1 435s, 1 310vw, 1 275vw, 1 185w, 1 170w, 1 155w, 1 115 (sh), 1 098 (sh), 1 090m, 1 075s, 1 037vs, 1 025 (sh), 1 018s, 998w, 970vw, 880w, 812m, 800 (sh), 740s, 732s, 690vs, 665 (sh), 640w, 612vw, 582w, 520m, 505w, 492w, 478vw, and 462vw cm^{-1}.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*](*diphenyl phosphonato*)*hydridoruthenium*(II).—[Ru(C_8H_8)(dppe)$_2$] (0.30 g) and P(OPh)$_3$ (90.5 cm^3) were dissolved in styrene (4 cm^3) and stirred for 1 h. Light petroleum (20 cm^3) was added and the filtered solution kept at room temperature for 3 d. The pale yellow crystals were collected, washed with light petroleum and dried *in vacuo*. Yield *ca.* 60%, m.p. 217 °C (decomp.) (Found: C, 67.2; H, 5.4; P, 12.7. $C_{64}H_{59}O_3P_5Ru$ requires C, 67.9; H, 5.2; P, 13.7%). I.r. ($\tilde{\nu}_{max.}$): 3 060m, 1 897m, 1 877m, 1 598s, 1 580 (sh), 1 490vs, 1 435vs, 1 315vs, 1 285m, 1 240 (sh), 1 225vs, 1 200s, 1 163m, 1 143vw, 1 095vs, 1 070m, 1 022w, 998w, 890vw, 865vs, 845s, 830 (sh), 803m, 770m, 750 (sh), 740vs, 690vs, 670s, 640w, 615w, 600vw, 520s, 500m, 490m, 460m, 427vw, and 410w cm^{-1}.

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