

Phosphite and Phosphonate Complexes. Part I. Synthesis and Structures of Dialkyl and Diphenyl Phosphonate Complexes of Palladium and Platinum

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Reactions of chloro-complexes of palladium and platinum with dialkyl and diphenyl phosphonates and their sodium and silver salts give complexes of types [(I)–(VI)]: $[M\{(RO)_2PO\}_2\{(RO)_2POH\}_2]$ (I) ($M = Pd$ and Pt), *trans*- $[Pt\{(RO)_2PO\}_2L_2]$ (II) ($L = Et_3As$, Et_3P , and C_6H_5N), $[MCl\{(RO)_2PO\}\{(RO)_2POH\}L]$ (III), *trans*- $[PtCl\{(RO)_2PO\}_2L_2]$ (IV) ($L = R_3P$ and Et_3As), $[Pt\{(RO)_2PO\}_2(diphos)]$ (V), $[PdCl\{(PhO)_2PO\}\{(PhO)_2POH\}]$ (VI) (probably dimeric). The complex (IV) ($R = Ph$; $L = Et_3As$) was also obtained by heating *cis*- $[PtCl_2-(Et_3As)_2]$ with [(I); $M = Pt$; $R = Ph$], and the complex [(III); $M = Pt$, $R = Me$; $L = Et_3P$] was obtained from *cis*- $[PtCl_2(Et_3P)_2]$ and [(I); $M = Pt$; $R = Me$]. The complex [(III); $M = Pd$; $R = Ph$; $L = Ph_3P$] was obtained from (VI) and triphenylphosphine. Reaction of [(I); $M = Pt$; $R = Ph$ or Me] with 1,2-bisdiphenylphosphinoethane also gave [(V); $R = Ph$ or Me]. Metathetical reactions with complex [(III); $M = Pt$; $R = Ph$; $L = Bu_3P$] with sodium or silver salts of X gave the complexes $[PtX\{(PhO)_2PO\}(Bu_3P)_2]$ ($X = Br$, I , NO_2 , NCO , N_3 , NCS , CN , NO_3 , and AcO) and the modes of co-ordination of the anionic ligands have been established. Structures have been derived from 1H and ^{31}P n.m.r. and from i.r. spectra.

DIALKYL PHOSPHONATES exhibit a variety of modes of co-ordination in complexes with metals, since the proton attached to the phosphorus may be retained or lost, and the neutral and anionic forms can co-ordinate to metal atoms through either (i) the phosphorus atom, (ii) a terminal oxygen atom, or (iii) both the phosphorus atom and a terminal oxygen atom. Class (a) or hard acceptors from Groups IA and IIA form compounds in which the phosphorus atom has been shown to be trivalent by ^{31}P n.m.r. spectroscopy.¹ The structures can be represented by $(RO)_2P-O-M^+$, but the high solubility of these compounds in hydrocarbon solvents indicates that further association occurs. Rather surprisingly the Class (b) acceptors Ag^+ and Cu^+ appear on the basis of i.r. spectra to be best formulated as $(RO)_2P-O-M$ in the solid state,² but the insolubility of

the silver compounds in organic solvents prevented us from obtaining ^{31}P n.m.r. spectra. The phosphorus chemical shifts and the phosphorus-hydrogen coupling constants of dialkyl phosphonate solutions change slightly on addition of uranyl nitrate and this is believed to be due to the formation of complexes which contain the linkage $(RO)_2(H)P=O \rightarrow U$.³ Complexes which contain phosphorus bonded to the acceptor atom are known only for the strongly Class (b) acceptors mercury(II),⁴ palladium(II),⁵ and platinum(II),⁶ and this contrasts for example with the ability of the sulphur atom in the thiocyanate anion to co-ordinate to a much wider range of metals which includes silver(I).⁷

We describe here several new palladium and platinum complexes and the structures of these and some previously known compounds. The principal difficulty in this work was the very high solubility of the complexes;

¹ K. Moedritzer, *J. Inorg. Nuclear Chem.*, 1961, **22**, 19.

² L. W. Daasch, *J. Amer. Chem. Soc.*, 1958, **80**, 5301; T. D. Smith, *J. Inorg. Nuclear Chem.*, 1960, **15**, 95.

³ J. L. Burdett and L. L. Burger, *Canad. J. Chem.*, 1966, **44**, 111.

⁴ F. K. Butcher, B. E. Deuters, W. Gerrard, E. F. Mooney, R. A. Rothenbury, and H. A. Willis, *Spectrochim. Acta*, 1964, **20**, 759.

⁵ G. A. Levishina, A. D. Troitskaya, and R. R. Shagidullin, *Russ. J. Inorg. Chem.*, 1966, **11**, 985.

⁶ A. A. Grinberg and A. D. Troitskaya, *Bull. Acad. Sci. USSR*, 1944, 178 (*Chem. Abs.*, 1945, **39**, 1064). T. N. Itskovich and A. D. Troitskaya, *Trudy Kazan khim. Teknol. Inst. S. M. Kivova*, 1953, **18**, 59.

⁷ I. Lindqvist, *Acta Cryst.*, 1957, **10**, 29.

in several instances this prevented the isolation of compounds in a satisfactorily pure state. A detailed account of the ^{31}P n.m.r. spectra is given in the following paper,⁸ but certain features necessary for the assignment of structures are given here. Thus, the large platinum-phosphorus coupling constants imply direct Pt-P bonding in all the platinum complexes.

Platinum Complexes.—Troitskaya *et al.*⁶ have obtained bis(dialkyl phosphonato)bis(dialkyl phosphite)platinum(II) complexes $[\text{Pt}\{(\text{RO})_2\text{PO}\}_2\{(\text{RO})_2\text{POH}\}_2]$ ($\text{R} = \text{Me}$ and Et) from tetrachloroplatinate(II) and trialkyl phosphite in aqueous solution or dialkyl phosphonate in alcohol. We found that the compound with $\text{R} = \text{Ph}$ was obtainable in only 20% yield after 5 days from diphenylphosphonate and sodium tetrachloropalladate(II) in alcohol but that reactions of the phosphonate with $[\text{PtCl}_2(\text{MeCN})_2]$ or $[\text{PtCl}_2(\text{Et}_2\text{S})_2]$ were much more convenient.

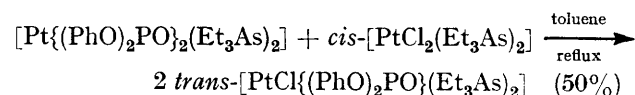
All the phosphorus atoms in each complex are equivalent in the ^{31}P n.m.r. spectra implying that proton exchange occurs in solution. In contrast to previous workers,⁶ we could find no direct evidence for the POH group in the i.r. spectra. These complexes, which have only phosphonate groups in the co-ordination sphere, are the only complexes of platinum of this type we obtained and this contrasts with palladium which forms two kinds of complex with this feature.

The phosphonate ligands in these complexes, which are expected to be labilised by the *trans* phosphorus atoms, are surprisingly difficult to displace. Although the complexes with $\text{R} = \text{Me}$ and Ph reacted immediately in benzene with 1,2-bisdiphenylphosphinoethane (diphos), only starting materials were recovered after the complex was heated under reflux with 1,2-bisdiphenylarsinoethane, 1,10-phenanthroline, *o*-phenylenediamine, or 1,4-diphenylthioethane. Although these reagents were used in excess, it is possible that the failure to observe reaction may be due to thermodynamic factors. The product of the reaction with bisdiphenylphosphinoethane had an analysis consistent with the formula $[\text{Pt}\{(\text{PhO})_2\text{PO}\}_2(\text{diphos})]$, but the compound with $\text{R} = \text{Me}$ was too unstable for satisfactory analysis or for a ^{31}P n.m.r. spectrum to be obtained. The phenyl derivative was rather insoluble in dichloromethane and this prevented an entirely satisfactory ^{31}P n.m.r. spectrum from being obtained even after enhancement by spectrum accumulation. It was, however, clear that the spectrum was not simple and this is consistent with the formulation given, for which an A_2B_2 pattern (with additional splitting from ^{195}Pt) is expected.

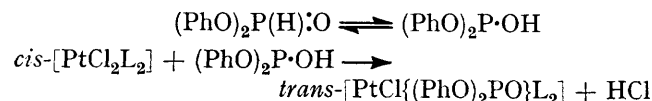
The complex $[\text{Pt}\{(\text{PhO})_2\text{PO}\}_2(\text{diphos})]$ was also obtained from dichloro(1,2-bis-diphenylphosphinoethane)-platinum and silver diphenyl phosphonate in benzene heated under reflux. The low yield (10%) is attributable to the insolubility of both reactants.

The complexes *trans*- $[\text{Pt}\{(\text{RO})_2\text{PO}\}_2\text{L}_2]$ were obtained from sodium dialkyl phosphonates and *cis*- $[\text{PtCl}_2(\text{R}'_3\text{P})_2]$, but for $\text{R} = \text{Ph}$, it was necessary to use silver (diphenyl phosphonate) to cause replacement of both chlorine ligands in *cis*- $[\text{PtCl}_2\text{L}_2]$ ($\text{L} = \text{Et}_3\text{P}$, Et_3As , and $\text{C}_5\text{H}_5\text{N}$). The complexes are stable and monomeric in benzene and give nonconducting solutions in nitrobenzene. The *trans*-stereochemistry is established by the ^{31}P n.m.r. spectra which are of A_2X_2 form with $|^2J(\text{PPtP}')|$ *ca.* 30 Hz, which is characteristic of *cis* placed phosphorus ligands.⁹ Complexes of *cis*-configuration are expected to give A_2B_2 spectra with $|^2J(\text{PPtP}')|$ *ca.* 700 Hz.⁹ Since the chemical shift of the phosphonate ligand and the coupling $|^1J(\text{Pt-P})|$ are both sensitive to the nature of the ligand in the *trans*-position, the close similarity of these parameters in the complexes with $\text{L} = \text{Et}_3\text{As}$, pyridine to those in $[\text{Pt}\{(\text{PhO})_2\text{PO}\}_2(\text{R}_3\text{P})_2]$ enables all the compounds to be assigned to the *trans* configuration.

Reaction of *cis*- $[\text{PtCl}_2(\text{Et}_3\text{P})_2]$ with $(\text{PhO})_2\text{PONa}$ gave a small amount of *trans*- $[\text{Pt}\{(\text{PhO})_2\text{PO}\}_2(\text{Et}_3\text{P})_2]$ but the compound in which only one chloride had been replaced was obtained in about 40% yield. This compound is also monomeric and nonionic, and the ^{31}P n.m.r. spectrum shows the phosphines to be equivalent and the resonance of the phosphonate is split by phosphorus-phosphorus coupling into a symmetrical triplet. This compound has, therefore, the structure *trans*- $[\text{PtCl}\{(\text{PhO})_2\text{PO}\}(\text{Et}_3\text{P})_2]$ and we have obtained a large number of compounds of this type. The analogous complex of Et_3As was made by the following interesting reaction before we discovered a simpler route. These complexes are best obtained by heating *cis*- $[\text{PtCl}_2\text{L}_2]$ ($\text{L} = \text{R}_3\text{P}$ or Et_3As)



under reflux with phosphonate (1 mole) in an organic solvent under nitrogen. The reaction presumably involves the following sequence, and the hydrogen chloride liberated is readily detected. The tautomerism



of the phosphonate to the phosphite form is probably involved also in the reactions of phosphonates with $[\text{PtCl}_4]^{2-}$ and with *sym,trans*- $[\text{Pt}_2\text{Cl}_4\text{L}_2]$ which we describe later. Since the chemical shift and coupling to platinum of the phosphonate group in the complex with $\text{L} = \text{Et}_3\text{As}$ are very similar to the values in the phosphine complexes, it also must have the *trans*-configuration.

Metathetical reactions of the chloro-complex were used to obtain the complexes *trans*- $[\text{PtX}\{(\text{PhO})_2\text{PO}\}(\text{Bu}_3\text{P})_2]$ ($\text{X} = \text{Br}$, I , N_3 , NO_2 , NCO , NCS , CN , NO_3 , and AcO), but it was not possible to obtain the cyano- and

⁸ F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.*, following paper.

⁹ R. J. Goodfellow, *Chem. Comm.*, 1968, 114; A. Pidcock, *ibid.*, p. 92.

acetato-complexes in a pure state, although apparently satisfactory n.m.r. spectra were obtained. The modes of co-ordination of the groups NO₂, NCO, NCS, NO₃, and AcO were established by i.r. spectroscopy (Table 1), and confirmed in some instances by special features

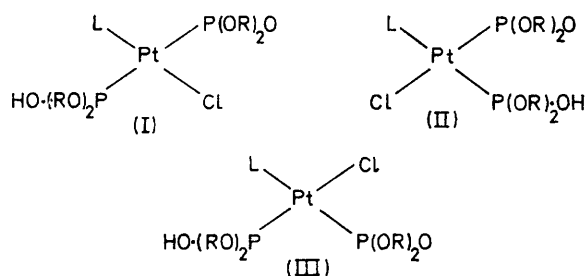
Assignment of i.r. spectral bands associated with anionic ligands in *trans*-[PtX{(PhO)₂PO}(Bu₃P)₂]

Ligand	Frequency (cm. ⁻¹) ^a	Assignment
Pt·O·NO ₂ ^b	1475	NO ₂ asym. stretch
	1270	NO ₂ sym. stretch
	990	NO stretch
	800	out-of-plane rock
Pt·NO ₂ ^c	1300	NO ₂ sym. stretch
	812	NO ₂ bend
	2237	CN stretch
Pt·NCO ^d	1335	CO stretch
	2100	CN stretch
Pt·NCS ^d	840	CS stretch
	1630	asym. stretch
Pt·O·CO·CH ₃ ^d	1315	sym. stretch

^a In Nujol. ^b C. C. Addison and N. Logan, 'Adv. Inorg. Chem. Radiochem.', 1965, **6**, 71. ^c D. M. Adams, 'Metal Ligand and Related Vibrations,' Arnold, 1967. ^d K. Nakamoto, 'IR Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1963.

of the ³¹P n.m.r. spectra which are discussed in detail in the following paper.⁸ The co-ordination of the thiocyanate group through nitrogen to platinum appears to occur when the group is *trans* to other groups of high *trans*-influence such as R₃P,¹⁰ Me,¹¹ and H, although in solution the sulphur-bonded form is present to the extent of about 30% when *trans* to hydride.¹²

The bridged complex *sym,trans*-[Pt₂Cl₄(Et₃As)₂] reacts with (PhO)₂P(H)·O to give a monomeric nonionic complex which has an analysis consistent with the formulation [PtCl{(PhO)₂PO}{(PhO)₂POH}L] (L = Et₃As) for which structures (I)–(III) are possible. The



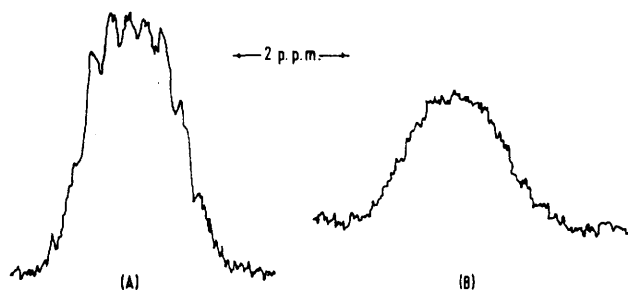
³¹P spectrum shows the presence of equal amounts of two chemically shifted phosphorus nuclei coupled to each other [²J(PPtP') = 32.5 Hz]. Structure (I) is therefore eliminated as proton exchange would probably cause the phosphorus ligands to appear equivalent in the spectrum and also a value of [²J(PPtP')] > 500 Hz would be expected.⁹ The ¹H n.m.r. spectrum confirms the formulation of the complex. The hydroxy-proton appears at τ -4.9 and the integrated spectrum gives the ratio hydroxy : aromatic : aliphatic protons as 1 : 19.4 : 15 in good agreement with the calculated ratio 1 : 20 : 15. The resonance of the CH₂ protons (at τ 7.92) is split by coupling from the methyl groups [³J(HCCH)] = 1.5 Hz,

and from the *trans* phosphorus nucleus [⁴J(PPtAsCH)] = 2.5 Hz.

The ¹H n.m.r. spectrum of [PtCl{(MeO)₂PO}{(MeO)₂POH}(Et₃As)] has a similar spectrum of the Et₃As group and the hydroxylic proton resonates at τ -4.9. The spectrum of the methoxy-protons consists of four equally intense lines (two doublets from POCH coupling) which are partly resolved into *ca.* 1:4:1 triplets due to coupling with ¹⁹⁵Pt. Since there is a small difference in the values of [⁴J(PtPOCH)] for the two phosphorus ligands, the shifts and coupling constants can be assigned as follows:

τ	[³ J(POCH)](Hz)	[⁴ J(PtPOCH)](Hz)
6.19	13.1	1.0
6.35	12.6	1.6

The parameters for a methylphosphonato-group, τ 6.42 [³J(POCH)] = 11.8 Hz, and [⁴J(PtPOCH)] = 1.4 Hz, determined from the spectrum of *trans*-[PtCl{(MeO)₂PO}(Bu₃P)₂] are similar to those of the higher-field methoxy-protons in [PtCl{(MeO)₂PO}{(MeO)₂POH}(Et₃As)], which is therefore tentatively assigned to the unprotonated form of the ligand. The possibility that the proton is mainly associated with one of the phosphonate groups is also suggested by the ³¹P spectrum of [PtCl{(MeO)₂PO}{(MeO)₂POH}(Et₃As)]. This has resonances due to non-equivalent phosphorus atoms, but coupling due to [²J(PPtP')] is not observed because the phosphorus nuclei are also coupled to six protons in the methoxy-groups. However, fine structure due to [³J(POCH)] is observed in the spectrum of only one of the phosphonate ligands (Figure). Since the values of [³J(POCH)] are known



Line shapes of ³¹P n.m.r. resonances at 24.29 MHz for the phosphonate groups in [PtCl{(MeO)₂PO}{(MeO)₂POH}(Et₃As)]. A = high-field resonance; B = low-field resonance

to be very similar in the two ligands from the ¹H n.m.r. spectrum and the same splitting due to [²J(PPtP')] occurs in each resonance, it is probable that the fine structure is obscured in the higher-field resonance by coupling to the hydroxylic proton [²J(POH)]. Addition of hydrogen chloride to the sample collapses the fine structure of the lower-field resonance, presumably by protonation of the (MeO)₂PO⁻ group, so the higher field resonance appears to be associated with the phosphite

¹⁰ A. Turco and C. Pecile, *Nature*, 1961, **191**, 66.

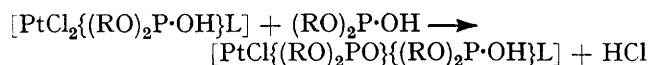
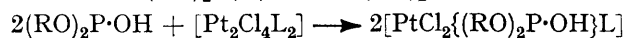
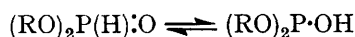
¹¹ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

¹² J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879.

form of the ligand. The coupling $[^2J(\text{POH})]$ is not resolved in the ^1H n.m.r. spectrum because the line is somewhat broadened by exchange.

The analysis of the ^{31}P n.m.r. spectrum of $[\text{PtCl}\{(\text{MeO})_2\text{PO}\}(\text{MeO})_2\text{POH}(\text{Et}_3\text{P})]$ is complicated by the presence of an extra phosphorus atom (see following paper⁸), but it is clear that the nucleus in the phosphine ligand is coupled very strongly to the phosphite form of the ligand, since fine structure due to $[^3J(\text{POCH})]$ is only observed in the spectrum of the other phosphonate ligand which is itself coupled only weakly to the other two phosphorus nuclei. Very large values of $[^2J(\text{PPtP})]$ are expected from ligands placed mutually *trans*,⁹ so the phosphine complex must have structure [(II); $\text{L} = \text{Et}_3\text{P}$] in solution. Since the chemical shifts are very similar in the arsine complex, it can be safely assumed that the structure is also similar.

A brief investigation by u.v. spectrophotometry of the mode of formation of these complexes indicated a two-step process with comparable rates for each step. This suggests the following scheme in which also the phosphite



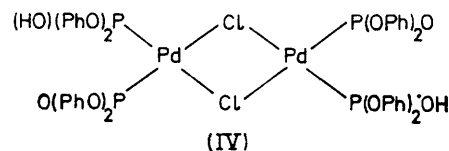
complex produced initially probably also rearranged from *trans* to *cis* before the final stage.

The complexes with $\text{R} = \text{Me}$ were also obtained by heating stoichiometric amounts of $[\text{Pt}\{(\text{MeO})_2\text{PO}\}_2\{(\text{MeO})_2\text{POH}\}_2]$ with *cis*- $[\text{PtCl}_2\text{L}_2]$ at 110° in toluene for 30 min. For $\text{L} = \text{Et}_3\text{P}$ a yield of 90% was obtained, but the greater solubility of the complex with $\text{L} = \text{Et}_3\text{As}$ limited the yield to *ca.* 60%. This method failed for $\text{L} = \text{py}$, probably because of the insolubility of $[\text{PtCl}_2(\text{py})_2]$.

Several attempts were made to synthesise diphenyl phosphonate complexes of platinum(IV). Treatment of $[\text{Pt}\{(\text{PhO})_2\text{PO}\}_2\{(\text{PhO})_2\text{POH}\}_2]$ and of *trans*- $[\text{PtCl}\{(\text{PhO})_2\text{PO}\}(\text{Bu}_3\text{P})_2]$ in carbon tetrachloride with chlorine changed the initially colourless solutions to golden. Oils were obtained after removal of solvent and their ^{31}P n.m.r. spectra showed the presence of $(\text{PhO})_2\text{P}(\text{H})\text{:O}$ and some of its chlorinated derivatives. The spectrum of the phosphine complex indicated, in addition, the presence of $[\text{PtCl}_4(\text{Bu}_3\text{P})_2]$. Neither spectrum showed peaks which may be attributed to phosphonate or phosphite complexes.

Palladium Complexes.—Troitskaya *et al.*⁵ isolated two complexes formulated as $[\text{Pd}\{(\text{EtO})_2\text{PO}\}_2]$ and $[\text{PdCl}\{(\text{EtO})_2\text{PO}\}\{(\text{EtO})_2\text{POH}\}]$ from the reaction between $\text{K}_2[\text{PdCl}_4]$ and $(\text{EtO})_3\text{P}$ in water. The second complex was the only product from the reaction of $\text{K}_2[\text{PdCl}_4]$ and $(\text{EtO})_2\text{P}(\text{H})\text{:O}$ in water. No structural formulae were proposed, although the authors appear to have assumed the presence of the $(\text{EtO})_2\text{PO}^-$ bridging group.

We have studied the reaction between $\text{Na}_2[\text{PdCl}_4]$ and $(\text{PhO})_2\text{PHO}$ in water and in ethanol. In water two complexes are formed which have analyses consistent with the formulae $[\text{Pd}\{(\text{PhO})_2\text{PO}\}_2\{(\text{PhO})_2\text{POH}\}_2]$ and $[\text{PdCl}\{(\text{PhO})_2\text{PO}\}\{(\text{PhO})_2\text{POH}\}]$ although the first complex was obtained only once in spite of many attempts with varying conditions. The second complex was the only product of the reaction in alcohol. Both complexes have only a single ^{31}P resonance. This is expected for $[\text{Pd}\{(\text{PhO})_2\text{PO}\}_2\{(\text{PhO})_2\text{POH}\}_2]$, but it suggests strongly that $[\text{PdCl}\{(\text{PhO})_2\text{PO}\}\{(\text{PhO})_2\text{POH}\}]$ has structure (IV) rather than one involving $(\text{PhO})_2\text{PO}$ bridges.



The complex reacts with diethylamine to give a highly insoluble product and with pyridine to give an oil. These products could not be characterised, but reaction of the bridged compound with triphenylphosphine gave $[\text{PdCl}\{(\text{PhO})_2\text{PO}\}\{(\text{PhO})_2\text{POH}\}(\text{Ph}_3\text{P})]$. The ^{31}P n.m.r. spectrum of this complex indicated its similarity to the platinum compounds of the same type, and, consistent with this, we obtained the analogous palladium complex of PhMe_2P from four moles of $(\text{PhO})_2\text{PHO}$ and one mole of *sym,trans*- $[\text{Pd}_2\text{Cl}_4(\text{PhMe}_2\text{P})_2]$.

Several attempts were made to prepare the complexes $[\text{PdCl}\{(\text{PhO})_2\text{PO}\}_2\text{L}_2]$ and $[\text{Pd}\{(\text{PhO})_2\text{PO}\}_2\text{L}_2]$ ($\text{L} = \text{R}_3\text{P}$), but only intractable oils were obtained. The ^{31}P n.m.r. spectra of some of the oils indicated that some complex formation had taken place but free $(\text{PhO})_2\text{P}(\text{H})\text{:O}$ was also present.

Rhodium Complex.—By analogy with the reaction of $(\text{PhO})_2\text{P}(\text{H})\text{:O}$ with *cis*- $[\text{PtCl}_2\text{L}_2]$, we attempted to replace the chlorine *trans* to phosphorus in *mer*- $[\text{RhCl}_3(\text{Et}_3\text{P})_3]$ by heating it under reflux with an excess of $(\text{PhO})_2\text{P}(\text{H})\text{:O}$ in dry benzene under nitrogen. The oil on removal of solvent smelled strongly of triethylphosphine and since the ^{31}P n.m.r. spectrum in the phosphonate region was a pair of 1 : 2 : 1 triplets there is a strong inference that the product was $[\text{RhCl}_3(\text{Et}_3\text{P})_2\{(\text{PhO})_2\text{POH}\}]$. The resonance from the Et_3P groups was obscured by free $(\text{PhO})_2\text{P}(\text{H})\text{:O}$. The similarity of the n.m.r. spectral parameters to those of *mer*- $[\text{RhCl}_3(\text{Bu}_3\text{P})_2\{(\text{PhO})_3\text{P}\}]$ suggests that the configuration of the complex is also meridional.⁸

DISCUSSION

Although i.r. spectra in the $\nu(\text{P}-\text{O})$ region were useful for the initial examination of reaction products since they depended significantly on the nature of the *trans*-ligand, positive identification of bands associated with the terminal $\text{P}-\text{O}$ group could not be made, so it was not possible to investigate electronic effects by this means. However, protonation of the phosphonate *trans* to

phosphine or arsine in $[\text{PtCl}\{(\text{RO})_2\text{PO}\}\{(\text{RO})_2\text{POH}\}\text{L}]$ ($\text{L} = \text{Et}_3\text{P}$ or Et_3As) may be the result of electronic effects. Because the *trans*-influence of Et_3P or Et_3As groups is greater than that of chloride, the phosphonate *trans* to Et_3P or Et_3As will be less strongly bound to the metal than the group *trans* to chlorine. Weaker binding of the phosphorus atom to the metal will reduce its affinity for the p_π -electrons of the terminal oxygen atom and since there will be much less P–O multiple bonding in the protonated ligand, less energy will be required to protonate the more weakly bound phosphonate group.

If the chlorine-bridged structure postulated for the complex $[\text{PdCl}\{(\text{PhO})_2\text{PO}\}\{(\text{PhO})_2\text{POH}\}]$ is correct, none of the complexes described here involve M–P–O–M bridges, whereas the bridges were very stable in platinum complexes of Ph_2PO^- .¹³ Electronegative RO groups in the phosphonates will reduce the basicity of the terminal oxygen, but it is possible that phosphonate-bridges in platinum complexes could be made by other methods.

The 'scrambling' reaction of *cis*- $[\text{PtCl}_2(\text{Et}_3\text{As})_2]$ with $[\text{Pt}\{(\text{PhO})_2\text{PO}\}_2(\text{Et}_3\text{As})_2]$ to give $[\text{PtCl}\{(\text{PhO})_2\text{PO}\}(\text{Et}_3\text{As})_2]$ (50%) could be the result of a random redistribution of ligands (ignoring isomers), but the reaction of *cis*- $[\text{PtCl}_2(\text{Et}_3\text{P})_2]$ with $[\text{Pt}\{(\text{MeO})_2\text{PO}\}_2\{(\text{MeO})_2\text{POH}\}_2]$ gave a 90% yield of $[\text{PtCl}\{(\text{MeO})_2\text{PO}\}\{(\text{MeO})_2\text{POH}\}(\text{Et}_3\text{P})]$. This system is not sufficiently labile for this to result from the isolation procedure, so it appears that this product is favoured by the enthalpy of reaction. The reasons for the special stability of this complex are not clear, and in view of the complexity of the n.m.r. spectrum of the individual complex, a detailed study of the equilibrium mixture was not attempted.

EXPERIMENTAL

Dimethyl and dibutyl phosphonates were obtained from Albright and Wilson Ltd., and diethyl and diphenyl phosphonates from Aldrich Chemical Co. Inc. All were used without purification. I.r. spectra were recorded with a Perkin-Elmer model 337 spectrophotometer as Nujol mulls. The ^1H n.m.r. spectra were obtained at 60 MHz with a Varian A60A spectrometer. The measurement of the ^{31}P n.m.r. spectra is described in the following paper.⁸ Molecular weights were determined osmotically in a Mechrolab vapour pressure osmometer. Melting points, determined on a Kofler hot stage, are corrected. Microanalyses were by A. G. Olney of this laboratory.

Phosphonate Salts.—Solutions of sodium diethyl phosphonate were prepared by an adaptation of the method of Kosolapoff.¹⁴ Diethyl phosphonate was added dropwise to sodium wire (50% excess) in a known volume of dry tetrahydrofuran. The mixture was then heated under reflux until evolution of hydrogen ceased. Estimation of the concentration of the solution by titration with standard acid gave inconsistent results due probably to the presence of acidic monoesters produced by the excess sodium. Titration of the bromide liberated after reaction of the solution of the sodium salt with 1-bromobutane indicated 67% conversion of the phosphonate; this agreed well with

the measured volume of hydrogen liberated during the preparation.

Sodium diphenyl phosphonate was obtained in similar yield, but is insoluble in tetrahydrofuran. Volumes of the vigorously stirred fine suspension were withdrawn by pipette for reaction with complexes.

The methods previously used for the preparation of silver dialkyl phosphonates² gave impure products when applied to the diphenyl compound. Treatment of diphenyl phosphonate in diethyl ether with a stoichiometric amount of silver acetate in the absence of light gave a white precipitate of silver diphenyl phosphonate. This was washed with a large volume of diethyl ether to remove acetic acid and was then dried *in vacuo*. The white powder was stable in a desiccator protected from light for up to four days.

Complexes: $[\text{Pt}\{(\text{RO})_2\text{PO}\}_2\{(\text{RO})_2\text{POH}\}_2]$ ($\text{R} = \text{Me}$ or Ph).—*Bis(dimethyl phosphonato)bis(dimethyl phosphite)platinum(II)*. Trimethyl phosphite (1.51 g., 12 mmoles) was added to sodium tetrachloroplatinate(II) (1.38 g., 3 mmoles) in methanol (20 ml.) and water (5 ml.); discharge of colour was immediate. The mixture was warmed to 50° for 5 min.; the white precipitate which formed when the mixture was cooled was washed with diethyl ether and dried. Recrystallisation from chloroform-ether gave needles (0.9 g., 48%), m.p. 175–178° (lit.,⁶ 163°) (Found: C, 15.3; H, 4.3. Calc. for $\text{C}_8\text{H}_{24}\text{O}_{12}\text{P}_4\text{Pt}$: C, 15.2; H, 3.8%).

Bis(diphenyl phosphonato)bis(diphenyl phosphite)platinum(II). This was obtained by methods (a)–(c) of which (a) was the most convenient.

(a) Diphenyl phosphonate (6.0 g.) was heated with *cis*-dichlorobis(acetonitrile)platinum(II)¹⁵ (1.31 g.) under nitrogen until the complex had dissolved. The mixture was cooled, diethyl ether (40 ml.) was added to it, and the product was allowed to crystallise. Recrystallisation from benzene gave prisms (2.02 g., 47%), m.p. 166–166.5° (Found: C, 51.1; H, 3.8. $\text{C}_{48}\text{H}_{42}\text{O}_{12}\text{P}_4\text{Pt}$ requires C, 51.0; H, 3.7%).

(b) Diphenyl phosphonate (2.68 g.) was added to a saturated solution of sodium tetrachloroplatinate(II) in ethanol. The white precipitate was extracted with chloroform and the solution was evaporated to dryness under reduced pressure. Recrystallisation from ethyl methyl ketone gave prisms (0.5 g., 20%), m.p. 165–166°.

(c) A mixture of diphenyl phosphonate (2.73 g.) and *cis*- and *trans*-dichlorobis(diethyl sulphide)platinum(II)¹⁶ (1.25 g.) in benzene (20 ml.) was heated briefly and the clear solution obtained was evaporated under reduced pressure to remove solvent and diethyl sulphide. The solid residue was recrystallised from benzene to give prisms (2.67 g., 85%), m.p. 165–166°.

cis-Bis(diphenyl phosphonato)(1,2-bisdiphenylphosphinoethane)platinum(II). (a) *Bis(diphenyl phosphonato)bis(diphenyl phosphite)platinum(II)* (0.5 g.) in benzene (30 ml.) was treated with 1,2-bisdiphenylphosphinoethane (0.177 g.) and a white precipitate was immediately formed. Recrystallisation of this from chloroform-ether gave needles (0.38 g., 80%), m.p. 214–216° (Found: C, 56.8; H, 4.4; P, 11.8%. $\text{C}_{50}\text{H}_{44}\text{O}_6\text{P}_4\text{Pt}$ requires C, 56.6; H, 4.2; P, 11.7%).

(b) Silver diphenyl phosphonate (1.02 g.) and *cis*-dichlorobis(1,2-bisdiphenylphosphinoethane)platinum(II)¹⁷

¹⁵ R. A. Walton, *Spectrochim. Acta*, 1965, **21**, 1795.

¹⁶ K. A. Jensen, *Z. anorg. Chem.*, 1935, **225**, 115.

¹⁷ R. S. Nyholm, M. J. Hudson, and M. H. B. Stiddard, *J. Chem. Soc. (A)*, 1968, 40.

¹³ J. Chatt and B. T. Heaton, *J. Chem. Soc. (A)*, 1968, 2745.

¹⁴ G. M. Kosolapoff, *J. Amer. Chem. Soc.*, 1945, **67**, 1180.

(0.901 g.) in benzene (20 ml.) were stirred and heated under reflux for 15 min.; the mixture was then filtered through Celite. Evaporation of the filtrate under reduced pressure gave a white solid which, recrystallised as above, gave the product (0.14 g., 10%), m.p. 214—216°.

cis-Bis(dimethyl phosphonato)(1,2-bisdiphenylphosphinoethane)platinum(II), m.p. 276—277° was obtained in a similar manner from $[\text{Pt}\{(\text{MeO})_2\text{PO}\}_2\{(\text{MeO})_2\text{POH}\}_2]$ but the analysis was not entirely satisfactory (Found: C, 42.3; H, 4.3; P, 15.2. $\text{C}_{30}\text{H}_{36}\text{O}_6\text{P}_4\text{Pt}$ requires C, 44.4; H, 4.4; P, 15.3%).

Complexes *trans*- $[\text{Pt}\{(\text{RO})_2\text{PO}\}_2\text{L}_2]$.—(a) *trans*-Bis(diethyl phosphonato)bis(tributylphosphine)platinum(II). Sodium diethyl phosphonate (1.0 g., in tetrahydrofuran) was added to a solution of *cis*-dichlorobis(tributylphosphine)platinum(II) (1.3 g.) in tetrahydrofuran and the mixture was heated under reflux for 30 min. The yellow suspension was evaporated to dryness under reduced pressure and the residue was extracted with chloroform. The extract was washed twice with water and was then dried and evaporated to dryness to give a pale yellow solid; this crystallised from acetone as colourless prisms (1.56 g., 60%), m.p. 190—192° (Found: C, 44.1; H, 8.3; P, 14.4. $\text{C}_{32}\text{H}_{74}\text{O}_6\text{P}_4\text{Pt}$ requires C, 44.0; H, 8.5; P, 14.2%).

trans-Bis(diethyl phosphonato)bis(triethylphosphine)platinum(II) [oily crystals (50%) from *cis*-dichlorobis(triethylphosphine)platinum(II)] and *trans*-bis(dibutyl phosphonato)bis(tributylphosphine)platinum(II) [m.p. 173—175° (Found: C, 49.0; H, 9.1; P, 12.4. $\text{C}_{40}\text{H}_{90}\text{O}_6\text{P}_4\text{Pt}$ requires C, 48.7; H, 9.1; P, 12.6%), from *cis*-dichlorobis(tributylphosphine)platinum(II) and sodium dibutyl phosphonate in light petroleum]¹⁴ were obtained similarly.

(b) *trans*-Bis(diphenyl phosphonato)bis(triethylphosphine)platinum(II). Silver diphenyl phosphonate (1.5 g., 4.5 mmoles) was added to *cis*-dichlorobis(triethylphosphine)platinum(II) (1.0 g., 2 mmoles) in ethanol (20 ml.) under nitrogen and the mixture was heated under reflux for 15 min. It was then filtered through Celite and the filtrate was evaporated to dryness to give a grey residue; this was extracted with chloroform. The extract was boiled with charcoal to remove silver and then filtered. Evaporation of the solvent left a white solid which, recrystallised from acetone-ether, gave needles (1.61 g., 34%), m.p. 166—168° (Found: C, 48.2; H, 5.7. $\text{C}_{36}\text{H}_{50}\text{O}_6\text{P}_4\text{Pt}$ requires C, 48.2; H, 5.6%). A small amount of more soluble material was obtained and this was identified as *trans*-chloro(diphenyl phosphonato)bis(triethylphosphine)platinum(II) by its i.r. spectrum and m.p. *trans*-Bis(diphenyl phosphonato)bis(triethylarsine)platinum(II) was obtained similarly from *cis*-dichlorobis(triethylarsine)platinum(II) and was recrystallised from benzene-light petroleum (40—60°); it had m.p. 143—145° (Found: C, 43.7; H, 5.2; P, 6.1. $\text{C}_{36}\text{H}_{50}\text{As}_2\text{O}_6\text{P}_2\text{Pt}$ requires C, 43.9; H, 5.1; P, 6.3%). Also, *trans*-bis(diphenyl phosphonato)bis(pyridine)platinum(II) was obtained from *cis*-dichlorobis(pyridine)platinum(II)¹⁸ as brown plates from chloroform-ether, m.p. 175—176° decomp. (Found: C, 49.7; H, 3.8; N, 3.2; P, 7.5. $\text{C}_{34}\text{H}_{36}\text{N}_2\text{O}_6\text{P}_2\text{Pt}$ requires C, 49.8; H, 3.7; N, 3.4; P, 7.6%).

Complexes *trans*- $[\text{PtCl}\{(\text{RO})_2\text{PO}\}_2\text{L}_2]$.—The complex *trans*-chloro(diphenyl phosphonato)bis(triethylphosphine)platinum(II) was obtained by two methods:

Method A. Sodium diphenyl phosphonate (1.02 g., suspension in tetrahydrofuran) was added to *cis*-dichlorobis(triethylphosphine)platinum(II) (1.0 g.) in tetrahydro-

furan (20 ml.) and the mixture was heated under reflux for 20 min. The yellow oil obtained on evaporation of the solvent was dissolved in chloroform and washed with water. Evaporation of solvent gave a yellow solid which was recrystallised from ethyl methyl ketone to give grey plates (0.61 g., 47%), m.p. 129—131° (Found: C, 41.6; H, 5.9. $\text{C}_{24}\text{H}_{40}\text{ClO}_3\text{P}_3\text{Pt}$ requires C, 41.2; H, 5.7%).

Method B. Diphenyl phosphonate (0.47 g., 2 mmoles) was added to *cis*-dichlorobis(triethylphosphine)platinum(II) (1.0 g., 2 mmoles) in dimethyl sulphoxide (5 ml.) and the mixture was maintained at ca. 60° for 2 hr. Removal of solvent under high vacuum gave a green residue which was extracted with ether (3 × 10 ml.) to leave a residue of starting material. Evaporation of the ether and recrystallisation from benzene-light petroleum (40—60°) gave the product (0.39 g., 26%), m.p. 130—131°.

Method B was also used to obtain the following complexes: *trans*-chloro(diphenyl phosphonato)bis(tributylphosphine)platinum(II) (70%), from *cis*-dichlorobis(tributylphosphine)platinum(II), after heating under reflux in benzene-acetone (2:1); as colourless needles, m.p. 94—96°, from methanol-water (Found: C, 49.8; H, 7.7. $\text{C}_{36}\text{H}_{64}\text{O}_3\text{P}_3\text{ClPt}$ requires C, 49.8; H, 7.4%), *trans*-chloro(diphenyl phosphonato)bis(triethylarsine)platinum(II) (77%), from *cis*-dichlorobis(triethylarsine)platinum(II) after heating under reflux for 3½ hr. in benzene-acetone (2:1), as plates, m.p. 111—113°, from methanol (Found: C, 36.7; H, 5.0. $\text{C}_{24}\text{H}_{40}\text{PClAsPt}$ requires C, 36.6; H, 5.1%); *trans*-chloro(dimethyl phosphonato)bis(tributylphosphine)platinum(II), from *cis*-dichlorobis(tributylphosphine)platinum(II) and dimethyl phosphonate in benzene-acetone (2:1) as an oil, with satisfactory n.m.r. spectra.

trans-Chloro(diphenyl phosphonato)bis(triethylarsine)platinum(II) was also obtained by heating a mixture of *cis*-dichlorobis(triethylarsine)platinum(II) (1.123 g., 0.2 mmole) and *trans*-bis(diphenyl phosphonato)bis(triethylarsine)platinum(II) (0.204 g., 0.2 mmole) in toluene (2 ml.) at 110° for 30 min. Evaporation of solvent gave an oil which crystallised as plates, m.p. 109—111° (0.15 g., 50%), from diethyl ether.

Metathetical Reactions.—The complexes *trans*- $[\text{PtX}\{(\text{PhO})_2\text{PO}\}_2(\text{Bu}_3\text{P})_2]$ (X = Br, I, N₃, NO₂, NCO, or NCS) were obtained from *trans*-chloro(diphenyl phosphonato)bis(tributylphosphine)platinum and the appropriate sodium salt (2:1 excess of salt) in either acetone or methanol. Recrystallisation was from aqueous methanol except where stated: *bromo-complex* as needles (76%), m.p. 99.5—101.5° (Found: C, 47.9; H, 7.6. $\text{C}_{36}\text{H}_{64}\text{BrO}_3\text{P}_3\text{Pt}$ requires C, 47.4; H, 7.0%); *iodo-complex* from light petroleum (b.p. 40—60°) as flocculent needles (44%), m.p. 115—116.5° (Found: C, 45.3; H, 7.2. $\text{C}_{36}\text{H}_{64}\text{IO}_3\text{P}_3\text{Pt}$ requires C, 45.0; H, 7.0%); *azido-complex* as a mixture of plates and needles (82%) with identical i.r. spectra and m.p. 129—130° (Found: C, 49.4; H, 7.8. $\text{C}_{36}\text{H}_{64}\text{N}_3\text{O}_3\text{P}_3\text{Pt}$ requires C, 49.4; H, 7.3%); *nitro-complex* as plates (68%), m.p. 123—125° (Found: C, 49.1; H, 7.6; N, 1.5. $\text{C}_{36}\text{H}_{64}\text{NO}_3\text{P}_3\text{Pt}$ requires C, 49.2; H, 7.3; N, 1.6%); *cyanato-complex* as needles (73%), m.p. 150.5—152° (Found: C, 50.8; H, 7.6; N, 1.8. $\text{C}_{37}\text{H}_{64}\text{NO}_4\text{P}_3\text{Pt}$ requires C, 50.9; H, 7.3; N, 1.6%); *thiocyanato-complex* as needles (87%), m.p. 166—166.5° (Found: C, 50.1; H, 7.7; N, 1.7. $\text{C}_{37}\text{H}_{64}\text{NO}_3\text{P}_3\text{PtS}$ requires C, 49.9; H, 7.2; N, 1.6%). The *nitrate-complex* was obtained as needles (72%), m.p. 148—151° (Found:

¹⁸ G. B. Kauffman, *Inorg. Synth.*, VII, 250.

C, 48.9; H, 7.5; N, 1.7. $C_{36}H_{64}NO_6P_3Pt$ requires C, 48.3; H, 7.2; N, 1.6%) by use of the stoichiometric amount of silver nitrate. The *cyano-complex* was obtained as an intractable oil by use of potassium cyanide and the *acetato-complex* was obtained from silver acetate in benzene as a white solid that could not be purified by recrystallisation. Both the cyano- and the acetato-complexes gave apparently satisfactory i.r. and ^{31}P n.m.r. spectra.

Complexes $[PtCl\{(RO)_2PO\}\{(RO)_2POH\}L]$.—Phosphonate (>4 mmoles) was added to a solution of the appropriate chlorine-bridged complex *sym-trans*- $[Pt_2Cl_4L_2]$ ($L = Et_3P$, Bu_3P , or Et_3As) (1 mmole) and the mixture was warmed in order to discharge the colour. Evaporation of the solvent followed by recrystallisation of the residue from benzene–light petroleum (b.p. 40–60°) gave the following as prisms: *chloro(diphenyl phosphonato)(diphenyl phosphite)(triethylphosphine)platinum(II)* (80%), m.p. 126–128° (Found: C, 44.4; H, 4.5; Cl, 4.4; P, 11.6. $C_{30}H_{36}ClO_6P_3Pt$ requires C, 44.1; H, 4.4; Cl, 4.4; P, 11.4%); *chloro(diphenyl phosphonato)(diphenyl phosphite)(triethylarsine)platinum(II)* (74%), m.p. 120–121.5° (Found: C, 42.2; H, 4.3. $C_{30}H_{36}AsClO_6P_2Pt$ requires C, 41.9; H, 4.2%); *chloro(dimethyl phosphonato)(dimethyl phosphite)(triethylphosphine)platinum(II)* (76%), m.p. 102–104° (Found: C, 21.5; H, 5.2; Cl, 6.8. $C_{10}H_{28}ClO_6P_3Pt$ requires C, 21.2; H, 4.9; Cl, 6.3%); *chloro(dimethyl phosphonato)(dimethyl phosphite)(triethylarsine)platinum(II)* (67%, from diethyl ether–light petroleum), m.p. 80–82° (Found: C, 19.7; H, 4.7. $C_{10}H_{28}AsClO_6P_2Pt$ requires C, 19.6; H, 4.6%). The complex with $R = Ph$, $L = Bu_3P$ could not be crystallised.

The reaction between $[Pt\{(MeO)_2PO\}_2\{(MeO)_2POH\}_2]$ (0.5 mmoles) and *cis*- $[PtCl_2L_2]$ ($L = Et_3P$ or Et_3As) (0.5 mmoles) in toluene at 110° for 5 min. gave *chloro(dimethyl phosphonato)(dimethyl phosphite)(triethylphosphine)platinum(II)* (91%), m.p. 101–103°, and *chloro(dimethyl phosphonato)(dimethyl phosphite)(triethylarsine)platinum(II)* (56%), m.p. 80.5–82°.

Palladium Complexes.—*Bis(diphenyl phosphonato)bis(diphenyl phosphite) palladium(II)* was obtained from diphenyl phosphonate (0.96 g., 4 mmoles) and sodium tetrachloropalladate(II) in concentrated aqueous solution containing a few drops of ethanol to assist mixing. The mixture was shaken for 5 hr. and the grey precipitate formed was filtered off and dried. Extraction with chloroform and boiling with charcoal gave a colourless solution on filtration. Evaporation of the solvent under reduced pressure followed by recrystallisation from chloroform–ether gave *prisms* (0.435 g., 21%), m.p. 141–143° (Found: C, 55.8; H, 4.4; P, 11.6. $C_{48}H_{42}O_{12}P_4Pd$ requires C, 55.4; H, 4.0; P, 11.9%).

Chloro(diphenyl phosphonato)(diphenyl phosphite)palladium(II) was obtained by two methods. (a) Diphenyl phosphonate (1.91 g., 8 mmoles) was added to sodium tetrachloropalladate(II) (1.42 g., 4 mmoles) dissolved in the

minimum amount of alcohol, and the mixture was shaken for 12 hr. The pink precipitate was filtered off, washed with diethyl ether, and dried. The crude solid was recrystallised in poor yield from chloroform–ether to give the *product* (0.34 g., 14%), m.p. 155–170° (Found: C, 47.5; H, 3.7; Cl, 5.7; P, 10.4. $C_{24}H_{21}ClO_6P_2Pd$ requires C, 47.3; H, 3.5; Cl, 5.8; P, 10.2%).

(b) Diphenyl phosphonate (2.35 g., 10 mmoles) was added to a stirred suspension of dichlorobis(acetonitrile)palladium(II) 15 (1.3 g., 5 mmoles) in benzene (40 ml.). The solution was warmed and a few drops of phosphonate was added to compete the discharge of colour. The *product* was obtained as prisms, m.p. 170–195°, after the mixture had been heated with charcoal.

Chloro(diphenyl phosphonato)(diphenyl phosphite)(triphenylphosphine)palladium(II). Triphenylphosphine (0.26 g., 1 mmole) was added to *chloro(diphenyl phosphonato)(diphenyl phosphite)palladium(II)* (0.61 g., 1 mmole) in benzene (50 ml.) and the mixture was stirred for 1 hr. Removal of the solvent followed by crystallisation of the residue from benzene–light petroleum (40–60°) gave the *product* (0.56 g., 65%) as large prisms, m.p. 106–108° (Found: C, 60.4; H, 4.5. $C_{42}H_{36}ClO_6P_3Pd$ requires C, 57.9; H, 4.1%).

Chloro(diphenyl phosphonato)(diphenyl phosphite)(dimethylphenylphosphine)palladium(II). Diphenyl phosphonate (0.48 g., 2 mmoles) was added to *sym,trans*-di- μ -chloro-dichlorobis(dimethylphenylphosphine)dipalladium(II) (0.31 g., 0.5 mmole) in 2:1 acetone–benzene (20 ml.) and left for 2 hr. Evaporation of the solvent gave an oil that solidified on prolonged pumping under high vacuum. The crude solid (0.57 g.) recrystallised from benzene–light petroleum (40–60°) as needles (0.36 g., 48%), m.p. 107–109°, that were not analytically pure, but which gave satisfactory n.m.r. spectra.

Reactions of Diphenyl Phosphonate with Rhodium Compounds.—Although colour changes indicated that reactions had occurred, we were unable to obtain products of satisfactory purity from the action of diphenyl phosphonate on rhodium trichloride in ethanol or $[Rh_2Cl_6(Et_3P)_4]$ 19 in chloroform. Reaction with *mer*-trichlorotris(triethylphosphine)rhodium(III) 19 in oxygen-free dry benzene followed by removal of solvent gave an oil. The ^{31}P n.m.r. spectrum suggested that the product was *mer*- $[RhCl_3(Et_3P)_2\{(PhO)_2POH\}]$ contaminated with diphenyl phosphonate.

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19 J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.