Complexes of Palladium and Platinum with Tetraethyl Diphosphite and Related Ligands †

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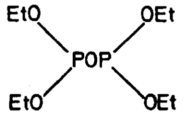
Tetraethyl diphosphite (L^1) forms complexes [$M_2Cl_4L^1_2$] (M = Pd or Pt), [$Pt_2Cl_4L^1(PMe_2Ph)_2$] (2), and [$Pt_2L^1_2(PMe_2Ph)_4$][BPh_4]$_4$ in which it forms bidentate bridges between two metal atoms. Bis(*OO*′-ethylene) diphosphite (L^2) is unidentate in *cis*-[$MCl_2L^2_2$] (M = Pd or Pt) and bridging in (2) and in similar complexes. 1,1,3,3-Tetraethoxy-2-ethyldiphosphazane (L^4) and 2-ethyl-1,1,3,3-tetraphenoxydiphosphazane (L^5) form chelate complexes [MCl_2L] (M = Pt, L = L^4; M = Pd or Pt, L = L^5). Explanations are offered for the differences in stoicheiometry of the complexes formed by these ligands.

THE co-ordination chemistry of ditertiary phosphites $(RO)_2POP(OR)_2$ and the related compounds $(RO)_2PXP(OR)_2$ (X = NR′, $[CH_2]_n$, *etc.*) has apparently not been explored. We have examined the reactions of some of these compounds with transition-metal complexes, and now report the preparation and characterisation of some complexes of palladium(II) and platinum(II).

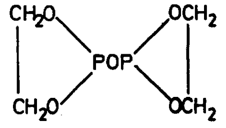
RESULTS AND DISCUSSION

Our initial experiments were conducted with tetraethyl diphosphite (L^1). These showed that uncharacterisable oils were obtained if reaction mixtures were not rigorously protected from moisture or if the reactions displaced chloride (*e.g.* the Church and Mays procedure [1]). In the hope of obtaining less sensitive ligands, we therefore prepared the diphosphites L^2 and L^3, and the nitrogen-bridged compounds (L^4 and L^5) were prepared for comparison. Difficulties were also encountered when the diphosphites were used in reactions expected to liberate chloride and, except in one instance (detailed below), complexes were successfully isolated and characterised only from reactions in which liberation of chloride was deliberately avoided. All the complexes were characterised by microanalysis, molecular-weight determination, and i.r. spectra. At a later date we were able to examine the complexes then available by ^{31}P-{^1H} spectroscopy.

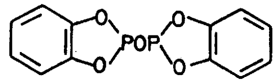
Complexes obtained from cis-[$PtCl_2(SEt_2)_2$] *or* trans-[$PdCl_2(NCPh)_2$].—Terminal Pt–S bonds in complexes of SR_2 with Pt^{II} are known to be long,[2] and we have found that displacement of SEt_2 from *cis*-[$PtCl_2(SEt_2)_2$] or similar complexes proceeds smoothly and is a useful procedure for the preparation of complexes of uncharged donors. Reactions between *cis*-[$PtCl_2(SEt_2)_2$] and 1 : 1 molar proportions of compounds L^1—L^5 were conducted in benzene at ambient temperature. The products were obtained by evaporation of solvent and the complex of L^1 was purified by recrystallisation. The product of L^3 was shown to be impure by microanalysis, and purification by recrystallisation was prevented by its reaction with alcohols or insolubility in other organic solvents. A similar procedure was followed for the preparation of palladium complexes from *trans*-[$PdCl_2(NCPh)_2$], but satisfactory products were obtained only for compounds L^1, L^2, and L^5; the stoicheiometry of each of these products was identical to that of the corresponding platinum complex.



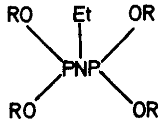
L^1



L^2



L^3



R
L^4 Et
L^5 Ph

The complexes obtained from L^1 had analyses and molecular weights in good agreement with the formula [$M_2Cl_4L^1_2$] [M = Pd or Pt]. Infrared spectra showed bands similar to those of L^1 together with two bands due to ν(M–Cl) [325 and 312 cm^{-1} (M = Pd); 322 and 312 cm^{-1} (M = Pt)] which, since the complexes were non-conductors in acetone, indicates the presence of a *cis*-MCl_2 moiety. The ^{31}P-{^1H} spectrum of the palladium complex was a single line (δ 60.7 p.p.m.) and that of the platinum complex was complicated, but corresponds to a single chemical shift for phosphorus (δ 85.1 p.p.m.). Analysis [3] of the spectrum as a superimposition of A_4, AA′A″A‴X, and AA′A″A‴XX′ spectra corresponding to molecules containing 0, 1, and 2 ^{195}Pt nuclei yielded the parameters ^1J(Pt–P) 5 837, ^3J(Pt–P) −52.7, and J(P–P) 67, 6, and *ca.* 0 Hz. The form of the spectrum, the similarity of ^1J(Pt–P) to that in *cis*-[$PtCl_2\{P(OPh)_3\}_2$] (5 770 Hz),[4] and the absence of a large value (>500 Hz) [5] of J(P–P) show that the phosphorus atoms are *trans* to chloride and establishes the structure (1; M = Pt). The palladium complex is presumed to be similar. The ^1H spectra of complexes (1; M = Pd or Pt) were similar to that of L^1, but the resonances of the methylene groups [M = Pd, τ 5.7, ^3J(HCCH) 7 Hz; M = Pt, τ 5.5,

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† No reprints available

[1] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074.

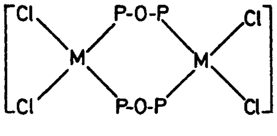
[2] W. A. Spofford III, E. L. Amma, and C. V. Senoff, *Inorg. Chem.*, 1971, **10**, 2309; P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Comm.*, 1968, 31.

[3] K. J. Odell and M. Sivers, personal communication.

[4] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

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

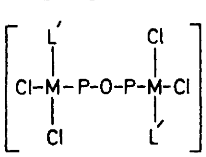
^3J(HCCH) 7 Hz] were less well resolved, probably because of additional coupling to ^{31}P nuclei in the complexes.



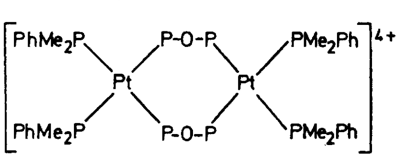
(1) (groups attached to P atoms are omitted)

The complexes obtained from L^2 precipitated directly from the reaction mixtures. They had compositions corresponding to $[MCl_2L^2{}_2]$ and were monomeric in 1,2-dichloroethane. The platinum complex had ν(Pt–Cl) bands at 310 and 280 cm^{-1} indicating a *cis* configuration, and although only one band was observed for the palladium analogue (at 260 cm^{-1}) it probably has a similar configuration. The complexes were insufficiently soluble for n.m.r. spectra to be obtained. The ligand L^2 is evidently unidentate in these complexes.

Complexes obtained from L^4 or L^5 were monomeric in 1,2-dichloroethane and had compositions and ν(M–Cl) bands consistent with the formulation as chelated complexes $[MCl_2L]$ (M = Pd, L = L^5; M = Pt, L = L^4 or L^5). The ^1H n.m.r. spectra of the complexes of L^4 were similar to those of L^4 but were shifted downfield and the methylene protons of the platinum complex displayed coupling to ^{195}Pt. The ^{31}P-$\{^1H\}$ spectra were also consistent with the proposed formulation [Pd, δ 74.4 p.p.m.; Pt, δ 98.3 p.p.m., ^1J(Pt–P) 5 012 Hz], the coupling constant for the platinum complex being of the magnitude expected for a phosphite *trans* to chloride.[4]



(2) (groups attached to P atoms are omitted)



(3)

Thus, although the proportions of the reagents and experimental procedures were closely similar, the stoicheiometry of the products depended strongly on the nature of the phosphorus donor. Although chelate formation is generally favoured for ligands containing two phosphorus-donor sites, this was found only for L^4 and L^5 where initial displacement of one molecule of PhCN (M = Pd) or SEt_2 (M = Pt) is presumably followed rapidly by chelate-ring closure. The compounds L^1 and L^2 evidently have a reduced tendency to form chelate complexes (see below).

Molecular models (Corey–Pauling–Kolthum) show that structure (1) is unstrained for either L^1 or L^2. That L^2 forms products $[MCl_2L^2{}_2]$ is therefore probably due to the rapid precipitation of these complexes. This would prevent further reaction with $[MCl_2L_2]$ (M = Pd, L = PhCN; M = Pt, L = SEt_2) to form products of structure (1). Since L^2 is less flexible than L^1, the formation of the binuclear complex may also be slower for L^2 than L^1.

Complexes obtained from sym-trans-$[M_2Cl_4L'_2]$ (M = Pd, L′ = PMe_2Ph; M = Pt, L′ = PMe_2Ph *or* PBu_3).—Addition of L^1 or L^2 (1 or 2 mol) to suspensions or solutions of *sym-trans*-$[M_2Cl_4L'_2]$ (M = Pd, L′ = PMe_2Ph; M = Pt, L′ = PMe_2Ph or PBu_3) (1 mol) in benzene led to the isolation of products $[M_2Cl_4LL'_2]$ (L = L^1, L′ = PMe_2Ph, M = Pt; L = L^2, L′ = PMe_2Ph, M = Pd or Pt; L = L^2, L′ = PBu_3, M = Pt) which are non-electrolytes in acetone and have two ν(M–Cl) bands in the i.r. spectra indicating the presence of *cis*-MCl_2 moieties. The ^1H n.m.r. spectrum indicates that the CH_3P groups are equivalent and that the CH_3CH_2O groups are equivalent in the complex with L = L^1, L′ = PMe_2Ph, so the products are assigned structure (2). The greater tendency toward chelate formation by L^5 is further illustrated by the formation of $[PtCl_2L^5]$ from *sym-trans*-$[Pt_2Cl_4(PMe_2Ph)_2]$ (1 mol) and L^5 (2 mol) under conditions similar to those used for L^1 and L^2.

When the reaction between L^1 and *sym-trans*-$[Pt_2Cl_4(PMe_2Ph)_2]$ (1 mol) was carried out in ethanol in the presence of $Na[BPh_4]$ (2 mol),[1] a precipitate of NaCl was formed. The complex isolated from the reaction mixture is formulated as $[Pt_2L^1{}_2(PMe_2Ph)_4][BPh_4]_4$ [structure (3)] on the basis of analyses, absence of ν(Pt–Cl) bands in the i.r. spectrum, and conductivity in acetone (366 S cm^2 mol^{-1}). In this system, initial cleavage of the chloride bridge by L^1 could be followed by intra- or inter-molecular displacement of chloride by the free end of L^1. The structure of the product provides further evidence that the intramolecular reaction with chelate-ring formation is unfavourable for ligands of diphosphite structure.

Conclusions.—Reactions in which chelate rings would normally be produced have been shown to lead to bridged structures (1)—(3) or products with unidentate ligands when the ligands are of the diphosphite type (L^1 and L^2). Similar results have been obtained with transition-metal carbonyls as substrates.[6] In diphosphites the angle at the central oxygen atom is probably 140—160°.[7] If the bond lengths M–P 2.25 Å and P–O 1.76 Å are used to calculate the geometry of a hypothetical chelate structure based on P–O–P angles of 140 and 160°, the maximum angles M–P–O are 62 and 50° with corresponding P–M–P angles of 95 and 140°. It is, therefore, impossible for diphosphite-type ligands to adopt normal approximately tetrahedral M–P–O angles and to retain the large P–O–P angle. This contrasts with chelate structures for ligands containing the systems P–N(R)P or P–CH_2–P, where the angles at the central atom are approximately tetrahedral (or smaller), and allow normal M–P–(N or C) angles of *ca.* 100°.[8] Since the angles P–X–P probably

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[6] A. L. Du Preez, I. L. Marais, R. J. Haines, A. Pidcock, and M. Safari, unpublished work.

[7] D. E. J. Arnold and D. W. H. Rankin, *J. Fluorine Chem.*, 1973, **2**, 405.

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increase in the order C < N < O in the free ligands, it is therefore evident that the diphosphites will have the least tendency towards chelation and the greatest tendency towards bridge formation as in (1)—(3).

EXPERIMENTAL

Infrared spectra were recorded with a Perkin-Elmer 457 grating spectrophotometer (250—4 000 cm^{-1}) as Nujol mulls. Hydrogen-1 n.m.r. spectra were obtained for deuteriochloroform solutions with Varian HA100, A60A, or T60 spectrometers. A JEOL PFT100 spectrometer, which became available after completion of the synthetic work, was used to obtain $^{31}\text{P-}\{^{1}\text{H}\}$ spectra of available complexes in dichloromethane. A capillary of P(OMe)_3 in deuteriodichloromethane was used to provide the ^{31}P reference (positive shifts are to high field of the reference) and the spectrometer lock signal. Conductivities of *ca.* 1×10^{-3} mol dm^{-3} solutions in acetone were measured with a Portland P310 conductivity bridge. Molecular weights in 1,2-dichloroethane were obtained by vapour-pressure osmometry.

Manipulations were in a dry-nitrogen atmosphere and solvents were dry and air-free. Microanalyses were by the microanalytical laboratory of this School or by Bernhardt Laboratories (West Germany).

Ligands.—Tetraethyl diphosphite (L^1) was obtained commercially (Aldrich). Established methods were used for the synthesis of bis(*OO'*-ethylene)diphosphite (L^2),[9] b.p. 102—104 °C (5 mmHg) * (Found: C, 23.9; H, 4.0. Calc. for $\text{C}_4\text{H}_8\text{O}_5\text{P}_2$: C, 24.2; H, 4.0%), 1,1,3,3-tetraethoxy-2-ethyldiphosphazane (L^4),[10] b.p. 112 °C (0.25 mmHg) (Found: C, 41.9; H, 8.7; N, 4.9. $\text{C}_{10}\text{H}_{25}\text{NO}_4\text{P}_2$ requires C, 42.0; H, 8.7; N, 4.9%), and 2-ethyl-1,1,3,3-tetraphenoxydiphosphazane (L^5),[10] b.p. 216—220 °C (0.05 mmHg) (Found: C, 65.3; H, 5.0; N, 2.9. $\text{C}_{26}\text{H}_{25}\text{O}_4\text{P}_2$ requires C, 65.4; H, 5.2; N, 2.9%).

Complexes obtained from cis-$[\text{PtCl}_2(\text{SEt}_2)_2]$ *or* trans-$[\text{PdCl}_2(\text{NCPh})_2]$.—*Di-μ-(tetraethyl diphosphite)-bis[dichloroplatinum*(II)*].* A solution of *cis*-dichlorobis(diethyl sulphide)platinum(II) (0.45 g) and tetraethyl diphosphite (0.28 g) in benzene was stirred at ambient temperature for 30 min. Evaporation of the solvent under reduced pressure gave a white precipitate which was recrystallised from benzene to give $[\text{Pt}_2\text{Cl}_4\{(\text{EtO})_2\text{POP(OEt)}_2\}_2]$ as white crystals, m.p. 149—150 °C (Found: C, 18.3; H, 3.8; Cl, 13.1. $\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{O}_{10}\text{P}_4\text{Pt}_2$ requires C, 18.3; H, 3.8; Cl, 13.5%), *M* 1 046 (calc.: 1 048).

Similarly prepared were: cis-*bis[bis*(OO'*-ethylene) diphosphite]dichloroplatinum*(II) (precipitated from reaction mixture), m.p. 100 °C (decomp.) (Found: C, 14.9; H, 2.6; Cl, 9.7. $\text{C}_8\text{H}_{16}\text{Cl}_2\text{O}_{10}\text{P}_2\text{Pt}$ requires C, 14.5; H, 2.4; Cl, 10.7%), insoluble in organic solvents; cis-*dichloro*(2-*ethyl*-1,1,3,3-*tetraphenoxydiphosphazane*)*platinum*(II), m.p. 202 °C (Found: C, 42.1; H, 3.3; Cl, 9.6; N, 1.9. $\text{C}_{26}\text{H}_{25}\text{Cl}_2\text{NO}_4\text{P}_2\text{Pt}$ requires C, 42.0; H, 3.3; Cl, 9.5; N, 1.9%), *M* 742 (calc.: 743); and cis-*dichloro*(1,1,3,3-*tetraethoxy*-2-*ethyldiphosphazane*)*platinum*(II), in very small yield, m.p. 160 °C (Found: C, 21.8; H, 4.6; N, 2.6. $\text{C}_{10}\text{H}_{25}\text{Cl}_2\text{NO}_4\text{P}_2\text{Pt}$ requires C, 21.8; H, 4.6; N, 2.5%), *M* 563 (calc.: 551). Obtained by a similar procedure from *trans*-$[\text{PdCl}_2(\text{NCPh})_2]$ were: *di-μ-(tetraethyl diphosphite)-bis[dichloropalladium*(II)*]*, recrystallised from benzene–light petroleum as off-white crystals, m.p. 102—103 °C (Found: C, 22.3; H, 4.7; Cl, 16.0. $\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{O}_{10}\text{P}_4\text{Pd}_2$ requires C, 22.1; H, 4.6; Cl, 16.3%), *M* 884 (calc.: 870); *bis[bis*(OO'*-ethylene) diphosphite]dichloropalladium*(II) (precipated from the reaction mixture), m.p. *ca.* 100 °C (decomp.) (Found: C, 16.0; H, 2.9; Cl, 11.4. $\text{C}_8\text{H}_{16}\text{Cl}_2\text{O}_{10}\text{P}_4\text{Pd}$ requires C, 16.7; H, 2.8; Cl, 12.4%), cis-*dichloro*(2-*ethyl*-1,1,3,3-*tetraphenoxydiphosphazane*)*palladium*(II), m.p. 180 °C (decomp.) (Found: C, 47.8; H, 3.9; Cl, 10.9; N, 2.2. $\text{C}_{26}\text{H}_{25}\text{Cl}_2\text{NO}_4\text{P}_2\text{Pd}$ requires C, 47.7; H, 3.8; Cl, 10.8; N, 2.1%), *M* 680 (calc.: 654).

Complexes obtained from sym-trans-$[\text{Pt}_2\text{Cl}_4\text{L'}_2]$.—*μ-(Tetraethyl diphosphite)-bis[dichloro(dimethylphenylphosphine)platinum*(II)*].* To a suspension of di-μ-chloro-bis[chloro(dimethylphenylphosphine)platinum(II)] (0.40 g) in benzene, was added L^1 (0.15 g) and the mixture was stirred at room temperature for 1 h. Evaporation of solvent gave white crystals which were washed with hexane and dried *in vacuo*. Recrystallisation from dichloromethane–hexane gave $[\text{Pt}_2\text{Cl}_4\{(\text{EtO})_2\text{POP(OEt)}_2\}(\text{PMe}_2\text{Ph})_2]$, m.p. 152 °C (Found: C, 27.0; H, 4.0; Cl, 13.4. $\text{C}_{24}\text{H}_{42}\text{Cl}_4\text{O}_5\text{P}_4\text{Pt}_2$ requires C, 27.0; H, 4.0; Cl, 13.3%), *M* 1 096 (calc.: 1 066).

Similarly prepared were: μ-[*bis*(OO'*-ethylene) diphosphite*]-*bis[dichloro(dimethylphenylphosphine)platinum*(II)], m.p. 149—150 °C (decomp.) (Found: C, 23.6; H, 3.0; Cl, 14.1 $\text{C}_{20}\text{H}_{30}\text{Cl}_4\text{O}_5\text{P}_4\text{Pt}_2$ requires C, 23.8; H, 3.0; Cl, 14.1%), *M* 996 (calc.: 1 066); μ-[bis(*OO'*-ethylene) diphosphite]-bis[dichloro(tributylphosphine)platinum(II)], recrystallised from benzene–light petroleum as white crystals, m.p. 145—146 °C (decomp.) (Found: C, 29.7; H, 5.5; Cl, 13.4. $\text{C}_{28}\text{H}_{62}\text{Cl}_4\text{O}_5\text{P}_4\text{Pt}_2$ requires C, 29.6; H, 5.5; Cl, 12.5%), *M* 1 104 (calc.: 1 134); μ-[bis(*OO'*-ethylene) diphosphite]-bis[dichloro(dimethylphenylphosphine)palladium(II)], m.p. 135 °C (decomp.) (Found: C, 29.6; H, 3.7; Cl, 16.7. $\text{C}_{20}\text{H}_{30}\text{Cl}_4\text{O}_5\text{P}_4\text{Pd}_2$ requires C, 29.9; H, 3.6; Cl, 17.1%), *M* 848 (calc.: 828).

Di-μ-(tetraethyl diphosphite)-bis[(dimethylphenylphosphine)platinum(II)*] Tetrakis(tetraphenylborate).*—The complex $[\text{Pt}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_2]$ (0.20 g) and sodium tetraphenylborate (0.17 g) were dissolved in a minimum volume of ethanol. An excess of L^1 in ethanol was added dropwise and very slowly to the mixture. A white precipitate formed which was centrifuged from the pale yellow solution. The solid was found to be NaCl. Evaporation of the solvent from the solution gave a white precipitate which was washed with hexane and dried *in vacuo* to give $[\text{Pt}_2\{(\text{EtO})_2\text{POP(OEt)}_2\}(\text{PMe}_2\text{Ph})_2][\text{BPh}_4]_4$ as a white solid, m.p. 141—142 °C (Found: C, 58.9; H, 6.6. $\text{C}_{144}\text{H}_{182}\text{B}_4\text{O}_{20}\text{P}_{10}\text{Pt}_2$ requires C, 58.1; H, 6.2%), Λ 366 S cm^2 mol^{-1}. The complex is insoluble in organic solvents. *cis*-Dichloro(2-ethyl-1,1,3,3-tetraphenoxydiphosphazane)platinum(II), with properties (m.p., analysis, and i.r. spectrum) identical to those given above, was obtained as a precipitate from *sym-trans*-$[\text{Pt}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_2]$ (0.2 g) and the diphosphazane L^5 (0.25 g) in benzene.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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