Transition-metal Complexes Containing Phosphorus Ligands. Part X.[1] *ortho*-Metallation Reactions Involving Some Triaryl Phosphite Derivatives of Palladium(II) and Platinum(II) Dihalides

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Triaryl phosphite complexes of palladium(II) and platinum(II), $MX_2[P(OAr)_3]_2$ (M = Pd or Pt; X = Cl, Br, or I; Ar = phenyl, *p*-chlorophenyl, *o*-, *m*-, or *p*-tolyl), react in boiling decalin, with elimination of a molecule of hydrogen halide, HX, to afford *ortho*-metallated triaryl phosphite derivatives. The tendency to undergo metallation is dependent upon the anionic ligands present and increases I < Br < Cl. The structures and stereochemistry of these products have been determined by i.r. and n.m.r. spectroscopy. Treatment of the *ortho*-metallated complexes with hydrogen halide in dichloromethane leads to rapid reversal of the *ortho*-palladation reactions and slow reversal of the *ortho*-platination reactions. Mechanistic aspects of the *ortho*-metallation processes are discussed.

As part of our continuing investigation of trialkyl and triaryl phosphite complexes of the platinum metals, we now report our results on the *ortho*-metallation reactions of palladium(II) and platinum(II) triaryl phosphite derivatives. Part of the work described in this paper has been discussed previously in a preliminary communication.[2] Similar studies of ruthenium [3] and iridium [4] triaryl phosphite complexes were reported in previous papers; related investigations involving triaryl phosphite derivatives of the other platinum group metals are in progress, and will be reported elsewhere.[5]

The extensive occurrence of intramolecular *ortho*-metallation reactions, involving activation and cleavage of *ortho*-carbon–hydrogen bonds in aromatic nitrogen and phosphorus donor ligands co-ordinated to transition-metal ions, is now well established, and the substantial body of work published in this field has recently been reviewed.[6,7] Intramolecular metallation reactions, including *ortho*-metallations, show a very strong tendency to form five-membered chelate rings; [6] this behaviour is clearly demonstrated in the reactions of the amines, $Ph(CH_2)_nNMe_2$ ($n = 0$—3), with palladium halides. *NN*-Dimethylbenzylamine alone undergoes metallation, forming a product with a five-membered chelate ring; the other amines all yield simple amine complexes, $PdCl_2[Me_2N(CH_2)_nPh]_2$.[8] Intramolecular *ortho*-metallation of co-ordinated triaryl phosphites affords sterically favoured, five-membered chelate rings; it is therefore not surprising that these ligands undergo metallation relatively readily. Examples of *ortho*-metallation reactions involving triaryl phosphite ligands co-ordinated to ruthenium,[3,9-11] osmium,[5] rhodium,[10] iridium,[4,12,13] palladium,[2] and platinum [2] have now been observed. In addition, exchange of *ortho*-aromatic hydrogen and deuterium provides evidence for the reversible *ortho*-metallation process:

$$CoH[P(OPh)_3]_4 \rightleftharpoons Co[P(OC_6H_4)(OPh)_2][P(OPh)_3]_3 + H_2$$

In this system however the equilibrium lies far to the left and no *ortho*-metallated product has been isolated.[10]

Much of the early work on *ortho*-metallation reactions involved complexes of palladium(II) and platinum(II) containing aromatic nitrogen donor ligands,[6] and interest in these systems has been sustained.[14-16] More recently, the facile metallation of aryl groups in sterically crowded palladium(II) and platinum(II) derivatives containing bulky tertiary phosphine ligands has been reported.[17-19] Palladation and platination reactions involving intramolecular attack on the *o*-methyl groups of co-ordinated *o*-tolylphosphines [17-19] or the terminal methyl groups of triethyl- [20] and *t*-butyl-n-propyl-phosphines [17] have also been described. Prior to the present work, no examples of palladation or platination reactions involving tertiary phosphite ligands had been reported.

We now find that the palladium(II) and platinum(II) triaryl phosphite derivatives,[1] $MX_2[P(OAr)_3]_2$ (M = Pd or Pt; X = Cl, Br, [I]; Ar = phenyl, *p*-chlorophenyl, *o*-, *m*-, or *p*-tolyl),† react in boiling decalin with loss of hydrogen halide, HX, to afford air-stable, white, crystalline complexes. These products are formulated

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† For discussion of stereochemistry of these complexes see preceding paper.

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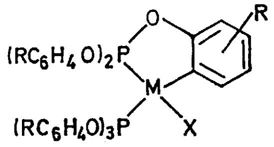
[20] S. Bresadola, P. Rigo, and A. Turco, *Chem. Comm.*, 1968, 1205.

(see below) as metal-*ortho* carbon bonded derivatives of palladium(II) and platinum(II) (I). In accord with previous usage[4] phosphite ligands are designated (P) and the chelate ligands derived from them by metallation are represented by (P–C). The structure (I) is therefore abbreviated to MX(P–C)P in the text.



(I)

(M = Pd or Pt; X = Cl, Br, or [I]; R = H, Cl, or Me)

The gaseous hydrogen halide, 1 mol per mol of reacted complex, liberated during these reactions was collected and estimated as silver halide. The rate of metallation decreases in the sequence Cl > Br > I and Pt > Pd for a given phosphite ligand; thus the platinum dichloride complexes, $PtCl_2[P(OAr)_3]_2$, react to completion in 2 h while the platinum and, in particular, palladium di-iodo derivatives $MI_2[P(OAr)_3]_2$ afford only traces of desired product after reaction times of 4—6 h. Prolonged reactions (2—4 days) of the platinum complexes, $PtI_2[P(OAr)_3]_2$ in boiling decalin lead to evolution of hydrogen iodide (*ca.* 0·6 mol per mol of complex) and formation of an intractable white solid residue. However attempts to isolate and crystallise the desired metallated complexes from these reaction products were unsuccessful. The palladium complexes, $PdX_2[P(OAr)_3]_2$, undergo some decomposition in boiling decalin; thus their *ortho*-metallation reactions are accompanied by deposition of palladium metal. These metallation reactions are not suited to kinetic study and no attempt has been made to establish a relationship between reaction rate and the structure of the triaryl phosphite ligands. Our qualitative observations concerning the rates of *ortho*-metallation are discussed further in the section on mechanism (see below). Attempts to form di-metallated products, $M(P-C)_2$, by boiling the metallated complexes, MCl(P–C)P, in decalin for periods of 2—3 days were unsuccessful.

The *ortho*-palladated compounds, PdCl(P–C)P (P = triphenyl or tri-*o*-tolyl phosphite) react rapidly with hydrogen chloride in cold dichloromethane to regenerate the parent dichloride complexes; similar reactions involving the *ortho*-platinated species, PtCl(P–C)P, proceed slowly over a period of 24 h. Cleavage of platinum–carbon bonds by hydrogen chloride has previously been observed to occur with the non-chelated complexes *cis*- and *trans*-$PtRCl(PR'_3)_2$ (R = alkyl or aryl)[21,22] and with the chelate species, $PtCl[CH(Me)C_6H_4PPh_2][PPh_2(o\text{-vinylphenyl})]$.[23] However, Cheney *et al.* were unable to cleave the platinum–carbon bonds in their mono-metallated tertiary phosphine derivatives, and tentatively attributed the inert character of these complexes to steric factors and/or the stability of the chelate ring.[17,18] The relatively facile de-platination of the bulky co-ordinated tri-*o*-tolyl phosphite ligands, observed in the present work, is perhaps rather surprising in view of the conclusions of Cheney *et al.* that steric congestion is important in promoting metallation within these systems.[17–19]

Attempts to isolate *ortho*-metallated products from the reaction of the platinum(0) complex, $Pt[P(OPh)_3]_4$ in boiling decalin were inconclusive; the intractable reaction product showed i.r. evidence for the presence of small quantities of metallated material but none could be isolated.

The new complexes, isolated from the reactions of the dihalide derivatives, $MX_2[P(OAr)_3]_2$, in boiling decalin, are formulated as the metal *ortho*-carbon bonded species (I) on the basis of the evidence described below. The presence of the *ortho*-metallated chelate ligands (P–C) was established by the appearance of characteristic i.r. bands[3] at 1100, 900, and 800 cm^{-1} (P = triphenyl phosphite) and at 1120, 900, and 750 cm^{-1} (P = tri-*p*-tolyl phosphite). The i.r. spectra of the *ortho*-metallated products obtained from the palladium(II) and platinum(II) derivatives of tri-*o*-tolyl, tri-*m*-tolyl, and tri-*p*-chlorophenyl phosphites show similar characteristic bands, these are listed in Table 1. The band at 1120 cm^{-1} characteristic of *o*-metallated tri-*p*-tolyl phosphite is often of low intensity;[3] we find that the presence of this chelate group is more convincingly diagnosed by the appearance of a strong band at 900 cm^{-1}. ^1H N.m.r. spectra of the parent tri-*o*-tolyl, tri-*m*-tolyl, and tri-*p*-tolyl phosphite complexes, *cis*- or *trans*-$MX_2[P(OC_6H_4Me)_3]_2$ each show a single sharp resonance at τ *ca.* 7·6—8·2, attributable to six equivalent methyl groups.[1] However, integrated n.m.r. spectra of the *ortho*-metallated products derived from these tritolyl phosphite complexes each show three bands of relative intensity 1 : 2 : 3 at τ *ca.* 7·6—8·2 attributable to a total of six methyl groups in three different chemical environments (a, b, c) (II; Table 2).

TABLE 1

Infrared data[a] for metallated complexes, MX(P–C)P; bands[b] associated with metallated ligands

Triphenyl phosphite	*ca. 1105*m, 1030m, *900*m, *800*m
Tri-*o*-tolyl phosphite	1395w, 1250w, *1063*w, *ca. 835*m, *775*m
Tri-*m*-tolyl phosphite	*1030*m, *810*m, *740*m
Tri-*p*-tolyl phosphite	*1120*w, *900*m, *850*w, *ca. 755*m, 662m
Tri-*p*-chlorophenyl phosphite	1115vw, *1030*m, 905m, *780*m, *709*m

[a] Recorded from Nujol mulls, in cm^{-1}. [b] Diagnostically most useful bands in italic.

None of these spectra provides any evidence for the presence of metallated methylene groups; we therefore conclude that the intramolecular metallation reactions occur at an *ortho* aromatic site in each complex. The structure of the products derived from the tri-*o*-tolyl phosphite complexes, $MX_2[P(OC_6H_4Me)_3]_2$ is particularly interesting. Intramolecular metallation of *ortho*-tolyl

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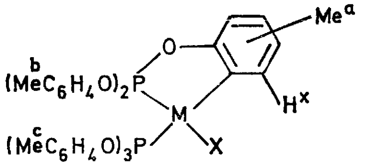
TABLE 2

^{1}H n.m.r.[a] and far-i.r.[b] data for *ortho*-metallated complexes, MX(P–C)P

M	X	Phosphite	τ(tolyl-Me) a	b	c	ν(M–Cl)
Pd	Cl	Triphenyl				325
Pd	Cl	Tri-*o*-tolyl	7·80	7·88	8·02	335
Pd	Br	Tri-*o*-tolyl	7·76	7·88	8·00	
Pd	Cl	Tri-*m*-tolyl	8·06	8·12	8·03	320
Pd	Cl	Tri-*p*-tolyl	8·07	8·11	7·96	315
Pt	Cl	Triphenyl				330
Pt	Cl	Tri-*p*-chlorophenyl				310
Pt	Cl	Tri-*o*-tolyl	7·79	7·85	7·96	310
Pt	Br	Tri-*o*-tolyl	7·78	7·86	7·98	
Pt	Cl	Tri-*m*-tolyl	8·08	8·13	8·02	310
Pt	Cl	Tri-*p*-tolyl	8·05	8·09	7·93	310
Pt	Br	Tri-*p*-tolyl	8·06	8·10	7·92	

[a] N.m.r. spectra recorded at 100 MHz in deuteriobenzene solution; spectra taken in deuteriochloroform show different ordering of the methyl resonances. All spectra show complex resonance patterns (*ca.* τ 2·3—3·5) arising from aryl protons.
[b] Far-i.r.spectra recorded from Nujol mulls.

groups in co-ordinated *ortho*-tolylphosphines[17-19,24] and tri-*o*-tolyl phosphite[2] have now been shown to occur at the *ortho*-methyl and *ortho*-aromatic sites respectively to afford products containing five-membered chelate rings.



(II)

No evidence for the formation of four- or six-membered chelate rings by metallation of these ligands at the alternative sites has been observed to date. It appears therefore, that the electronic features of those carbon–hydrogen bonds available for attack are subordinate to steric factors in directing the course of intramolecular metallation reactions.

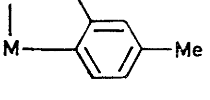
TABLE 3

^{31}P N.m.r.[a] data for *ortho*-metallated triaryl phosphite complexes of palladium and platinum, *cis*-MX(P–C)P

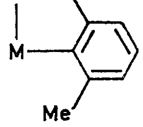
			Unmetallated phosphite (P)			Metallated phosphite (P–C)		
M	X	Phosphite	δ	^{1}J(Pt–P)	^{4}J(P–H)	δ	^{1}J(Pt–P)	^{2}J(P–P)
Pd	Cl	Triphenyl	−109·4		13·0	−128·1		56·0
Pd	Cl	Tri-*o*-tolyl	−109·1		12·0	−126·8		54·0
Pd	Cl	Tri-*p*-tolyl	−109·6		12·0	−128·2		52·0
Pt	Cl	Triphenyl	−112·8	3229	12·0	−100·5	6371	29·0
Pt	Cl	Tri-*o*-tolyl	−112·7	3201	12·0	−99·6	6409	30·0
Pt	Cl	Tri-*p*-tolyl	−112·9	3214	12·0	−100·4	6407	30·0
Pt	Br	Tri-*o*-tolyl	−112·0	3200	12·0	−96·5	6371	30·0

[a] Spectra recorded at 36·43 MHz in deuteriochloroform solution with field–frequency lock provided by deuteriochloroform. Chemical shifts are given relative to 85% H_3PO_4 (±0·2 p.p.m.); *J*-values are ±2 Hz.

The ^{1}H n.m.r. spectra of the *ortho*-metallated complexes all contain a well-resolved multiplet pattern, total intensity 1·0, centred at *ca.* τ 1·0—1·5. This resonance, which is absent from the spectra of the non-metallated parent complexes, lies on the low-field side of other aromatic proton resonances; its τ value is typical of aryl protons *ortho* to a metal–carbon bond and deshielded by the magnetic anisotropy associated with this bond.[25] We assign this resonance to the unique proton, H^x (II), present in the *ortho*-metallated products. The fine structure may be attributed to coupling of this *ortho*-proton with adjacent ring protons, the *trans*-phosphorus nucleus (see below) and, in the platinum complexes, the ^{195}Pt nucleus. Similar low-field resonances have been attributed to protons *ortho* to the metal–ligand bond in metallated derivatives of azobenzene[26] and 8-methylquinoline.[15] The presence of this low-field resonance pattern in the ^{1}H n.m.r. spectra of the metallated tri-*m*-tolyl phosphite complexes permits positive assignment of the sterically favoured structure (IIIa) rather than the alternative (IIIb) for the *ortho*-metallated *m*-tolyl group. In contrast Cheney *et al.* report[17] that the proton *ortho* to the platinum–carbon bond in PtBr(P′–C)P′ [P′ = P(*p*-tolyl)$_2$Bu^t] resonates at *higher* field (τ 4·35) than the other aryl protons present. This anomalous chemical shift may arise from the position, relative to the metal atom, imposed on the *ortho* proton by the highly strained, four-membered chelate ring structure.



(IIIa)



(IIIb)

The stereochemistry about the metal centre in the *ortho*-metallated products, MX(P–C)P, has been elucidated by ^{31}P n.m.r. spectroscopy. The first-order spectrum observed for each of these complexes comprises a pair of doublets indicative of coupling ^{2}J(P–P) between two non-equivalent ^{31}P nuclei. The magnitudes of the coupling constants, ^{2}J(P–P) (Table 3) are consistent with coupling between mutually *cis*-phosphorus ligands[27] and thus establish the *cis*-stereochemistry previously suggested for these metallated products. In each spectrum the doublet arising from the phosphorus

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[26] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3204.
[27] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

nucleus of the non-metallated phosphite is further split by coupling ${}^4J$(P–H) with the *ortho* proton, H^x, of the metallated aryl group situated in the *trans*-position (II). Broad band proton decoupling experiments confirm that this splitting originates from a phosphorus–hydrogen coupling interaction. The occurrence of the coupling ${}^4J$(P–H) has been observed in the ${}^1H$ n.m.r. spectra of the metallated aryl group (see above); its appearance in the ${}^{31}P$ spectra permits unambiguous assignment of ${}^{31}P$ resonances for the metallated and unmetallated phosphite ligands (Table 3). The ${}^{31}P$ n.m.r. data recorded for our metallated triaryl phosphite complexes are compatible with those previously reported for similar palladium(II) and platinum(II) triaryl phosphite derivatives.[27] The 'δ' values (*ca.* -110 p.p.m.) recorded for the unmetallated phosphite ligands are virtually independent of the central metal atom, M; those of the metallated phosphite ligands occur at *ca.* -127 p.p.m. (M = Pd) and at *ca.* -100 p.p.m. (M = Pt). In each of the platinated complexes the phosphorus nucleus *trans* to the halide resonates at higher field and has larger coupling constant ${}^1J$(Pt–P) than that *trans* to the aryl group. The coupling constants ${}^2J$(P–P) are dependent upon the central metal ion, M, and decrease in the order Pd > Pt; a similar trend has recently been observed for the complexes *trans*-$MX_2(PBu_3)[P(OPh)_3]$ and $MCl[(PhO)_2PO][PhO)_2POH](PR_3)$.[27]

The far-i.r. spectra of our metallated complexes, MCl(P–C)P each show a medium intensity band *ca.* 310—325 cm^{-1} attributable to ν(M–Cl); these values are typical of chlorine *trans* to phosphorus in square-planar palladium and platinum complexes, and thus confirm the *cis*-stereochemistry. Many of the corresponding bromo-derivatives, MBr(P–C)P, were not isolated in sufficient quantity for ${}^{31}P$ n.m.r. spectroscopy, and their far-i.r. spectra could not be interpreted with confidence, we have therefore been able to establish *cis*-stereochemistry for only one of these products.

The *cis*-configuration observed for our *ortho*-metallated triaryl phosphite derivatives contrasts with the *trans*-configuration reported by Cheney *et al.* for their related products derived from tertiary phosphine platinum(II) dihalide complexes.[18,19] This difference confirms the strong tendency [1] for triaryl phosphite ligands to adopt mutually *cis*-positions in their square planar palladium(II) and platinum(II) derivatives.

Mechanism of ortho-*Metallation*.—The recent literature contains numerous examples of intramolecular metallation reactions involving co-ordinated, aromatic nitrogen or phosphorus donor ligands; however very little positive information has been reported, concerning the mechanisms of these reactions. Tentative mechanisms advanced to date invoke electrophilic attack by the metal on the aromatic ring, and/or oxidative addition of the carbon–hydrogen bond across the metal centre. We tentatively suggest that the *ortho*-metallation processes described in the present paper are initiated by electrophilic attack on the aromatic ring by the metal atom, and may proceed by an oxidative addition and reductive elimination sequence similar to those proposed by Hodges *et al.*[28,29] for their platinum catalysed benzene and alkane deuteriation reactions.

Substituent effects found in the kinetics of metallation of azobenzenes [30] and triarylphosphines [31] suggest that electrophilic attack by the central metal ion on the aromatic ring is the rate-determining step in these particular reactions. In the present study the conditions required to induce metallation deterred us from measuring accurately the relationship between the rate of metallation and the nature or position of substituents on the metallated ring. However, observations that the rates of reaction in our metallation processes and in the isotope exchange reactions of Hodges *et al.*[32] are dependent upon the nature of the co-ordinated halide, and decrease in the sequence Cl > Br > I, support our suggestion that a common rate-determining step, involving electrophilic attack on the hydrocarbon moiety, is operative in both systems. In contrast, Cheney *et al.*[17] report that the rate of metallation of bulky tertiary phosphines, L, in the platinum(II) halide complexes PtX_2L_2 *increases* in the sequence Cl < Br < I; this order, which is the reverse of that discussed above, is consistent with a rate determining step involving oxidative addition across the metal atom. However, stereochemical factors, which are considered to be of prime importance in the complexes studied by Cheney *et al.*,[17-19] also predict the observed order of halide dependence. Finally, in the present study and in the work of Cheney *et al.*,[17-19] on the metallation of tertiary phosphine ligands, the tendency to undergo metallation depends upon the identity of the central metal ion and decreases in the order Pt > Pd. However, other workers report that co-ordinated tertiary amines [8] or azobenzenes [33] undergo palladation more readily than platination. We note these very intriguing differences in behaviour; however, in the absence of detailed kinetic data we prefer not to speculate further concerning their interpretation.

EXPERIMENTAL

Palladium(II) and platinum(II) triaryl phosphite complexes, $MX_2[P(OAr)_3]_2$, were prepared as previously described.[1] Laboratory grade solvents were used as purchased. All reactions were performed under a nitrogen atmosphere.

I.r. spectra (4000—200 cm^{-1}) were recorded on a Perkin-Elmer 621 grating spectrometer using samples mulled in Nujol. ${}^1H$ N.m.r. spectra were measured in deuteriobenzene with T.M.S. as internal reference, using a Varian

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[31] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[32] R. J. Hodges, D. E. Webster, and P. B. Wells, personal communication.

[33] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

HA100 spectrometer, phosphorus-31 n.m.r. spectra were recorded in deuteriochloroform using a Bruker HFX90 spectrometer and Fourier transform accessory. M.p.s (corrected) were taken on a Kofler hot-stage apparatus. Microanalyses by Dr. Strauss, Oxford. Molecular weight data were recorded on a Hitachi–Perkin-Elmer osmometer using benzene solutions at 43°. Evolved hydrogen halides were collected in acidified silver nitrate solution and estimated gravimetrically as silver halide.

Platination Reactions

Chloro[triphenyl phosphito(2C,P)*](triphenyl phosphite)-platinum*(II) $PtCl[(PhO)_2P(OC_6H_4)][P(OPh)_3]$.—Dichlorobis-(triphenyl phosphite)platinum (0·3 g) was heated under reflux in decalin (4—6 ml) for 3 h. Hydrogen chloride (*ca.* 1 mol) was evolved during the reaction. The reaction solution was cooled overnight at room temperature and the resultant precipitate filtered off then washed successively with *n*-hexane, water, ethanol, and *n*-hexane to give the required product (0·22 g, 80%). Recrystallisation from dichloromethane–methanol gave white microcrystals (m.p. 160°) (Found: C, 50·75; H, 3·35; P. 7·6; Cl, 4·1%; *M*, 905. $C_{36}H_{29}ClO_6P_2Pt$ requires C, 50·85; H, 3·45; P. 7·3; Cl, 4·15%; *M*, 850).

The following were similarly prepared from the appropriate triaryl phosphite complexes. *Chloro[tri-*o*-tolyl phosphito*(2C,P)*](tri-*o*-tolyl phosphite)platinum*(II) as white microneedles, 80%, m.p. 195—196° (Found: C, 54·15; H, 4·5; P, 6·7; Cl, 4·05. $C_{42}H_{41}ClO_6P_2Pt$ requires C, 54·0; H, 4·4; P, 6·65; Cl, 3·8%). *Chloro[tri-*m*-tolyl phosphito-*(2C,P)*](tri-*m*-tolyl phosphite)platinum*(II) as white microcrystals, 80% (Found: C, 53·85; H, 4·6; P, 6·85; Cl, 4·05. $C_{42}H_{41}ClO_6P_2Pt$ requires C, 54·0; H, 4·4; P, 6·65; Cl, 3·8%). *Chloro[tri-*p*-tolyl phosphito*(2C,P)*](tri-*p*-tolyl phosphite)platinum*(II) as a white powder, 80%. This product was not crystallised (Found: C, 54·15; H, 4·65; P, 7·0; Cl, 4·05. $C_{42}H_{41}ClO_6P_2Pt$ requires C, 54·0; H, 4·4; P, 6·65; Cl, 3·8%). *Chloro[tri-*p*-chlorophenyl phosphito-*(2C,P)*](tri-*p*-chlorophenyl phosphite)platinum*(II) as white microneedles, 85%, m.p. 174—175° (Found: C, 41·2; H, 2·4; P, 5·95; Cl, 23·4%; *M*, 1031. $C_{36}H_{23}Cl_7O_6P_2Pt$ requires C, 40·9; H, 2·2; P, 5·85; Cl, 23·5; *M*, 1056). *Bromo[triphenyl phosphito*(2C,P)*](triphenyl phosphite)-platinum*(II) as a white microcrystalline powder, 55%, m.p. 155—170° (Found: C, 48·45; H, 3·4; P, 6·8; Br, 8·7. $C_{36}H_{29}BrO_6P_2Pt$ requires C, 48·35; H, 3·25; P, 6·9; Br, 8·95%). *Bromo[tri-*o*-tolyl phosphito*(2C,P)*](tri-*o*-tolyl phosphite)platinum*(II) as white microneedles, 80%, m.p. 199—200° (Found: C, 51·7; H, 4·05; P, 6·6; Br, 7·9. $C_{42}H_{41}BrO_6P_2Pt$ requires C, 51·55; H, 4·2; P, 6·35; Br, 8·15%). *Bromo[tri-*p*-tolyl phosphito*(2C,P)*](tri-*p*-tolyl phosphite)platinum*(II) as white lustrous microcrystals, 80%, m.p. 178—180° (Found: C, 51·9; H, 4·35; P, 6·25; Br, 8·1%; *M*, 981. $C_{42}H_{41}BrO_6P_2Pt$ requires C, 51·55; H, 4·2; P, 6·35; Br, 8·15%; *M*, 978).

Attempted Reaction of Di-iodobis(triphenyl phosphite)-platinum(II) *in Boiling Decalin.*—The complex (0·3 g) was heated under reflux in decalin for 4 h. Only trace amounts of hydrogen iodide were eliminated and, on cooling the reaction mixture at 0° overnight, unchanged di-iodobis-(triphenyl phosphite)platinum was recovered (0·24 g, 80%) (Found: C, 40·6; H, 2·95; I, 23·55. $C_{36}H_{30}I_2O_6P_2Pt$ requires C, 40·45; H, 2·95; I, 23·75%).

Di-iodobis(tri-*o*-tolyl phosphite)platinum(II) was similarly recovered unchanged and in 80% yield after heating under reflux in decalin for 4 h (Found: C, 43·55; H, 3·8; I, 21·35. $C_{42}H_{42}I_2O_6P_2Pt$ requires C, 43·75; H, 3·65; I, 21·95%).

Prolonged Reaction of Di-iodobis(triphenyl phosphite)-platinum.—The complex (0·3 g) was heated under reflux in decalin for 72 h; hydrogen iodide (0·6 mol) was evolved. The reaction mixture was cooled at 0° overnight and the pale yellow solid (0·2 g) deposited was collected by filtration and washed with n-hexane. This solid product was identified by spectroscopic methods as a mixture of $PtI_2[P(OPh)_3]_2$ and the metallated derivative $PtI[(PhO)_2P(OC_6H_4)]$-$[P(OPh)_3]$.

Attempted Dimetallation of Dichlorobis(triphenyl phosphite)platinum.—Dichlorobis(triphenyl phosphite)platinum (0·7 g) was heated under reflux in decalin (8 ml). Hydrogen chloride evolution (*ca.* 1 mol) occurred during the first 12 h and virtually ceased thereafter. After 5 days the reaction solution was cooled at 0° overnight, and the resultant precipitate (0·4 g, 60%) filtered off and washed with n-hexane. The product was identified spectroscopically as the mono-metallated derivative.

Deplatination Reactions.—Chloro[tri-*o*-tolyl phosphito-(2*C*,*P*)](tri-*o*-tolyl phosphite)platinum (0·20 g) dissolved in dichloromethane (35 ml) was saturated with hydrogen chloride gas for 10 min, then sealed and set aside for 24 h. The solution was partially evaporated then diluted with n-hexane (20 ml) to induce crystallisation. The white crystalline product (0·17 g, 82% based on platinated complex) was washed with n-hexane, dried *in vacuo* and characterised as dichlorobis(tri-*o*-tolyl phosphite)platinum by i.r. and ^1H n.m.r. spectroscopy.

Under similar conditions chloro[triphenyl phosphito-(2*C*,*P*)](triphenyl phosphite)platinum reacted to give dichlorobis(triphenyl phosphite)platinum (77%), characterised by i.r. spectroscopy.

Palladation Reactions

Chloro[triphenyl phosphito(2C,P)*](triphenyl phosphite)-palladium*(II).—Dichlorobis(triphenyl phosphite)palladium (0·4 g, 0·0005 mol) was heated in decalin under reflux for 3 h. The hot solution was filtered to remove precipitated palladium metal then cooled overnight at room temperature. The precipitate was washed thoroughly with n-hexane then dried *in vacuo* to give the required product (0·18 g, 50%). Recrystallisation from dichloromethane–methanol gave white microcrystals (m.p. 143°) (Found: C, 57·1; H, 3·75; P, 7·9; Cl, 4·45%; *M*, 694. $C_{36}H_{29}ClO_6P_2Pd$ requires C, 56·8; H, 3·85; P, 8·15; Cl, 4·65%; *M*, 761).

The following were similarly prepared. *Chloro[tri-*o*-tolyl phosphito*(2C,P)*](tri-*o*-tolyl phosphite)palladium*(II) as white microneedles, 50%, m.p. 154—155° (Found: C, 59·85; H, 4·65; P, 7·1; Cl, 4·4. $C_{42}H_{41}ClO_6P_2Pd$ requires C, 59·65; H, 4·9; P, 7·35; Cl, 4·2%). *Chloro[tri-*m*-tolyl phosphito-*(2C,P)*](tri-*m*-tolyl phosphite)palladium*(II) as white microneedles, 50%, m.p. 193—194° (Found: C, 59·75; H, 4·8; P, 7·1; Cl, 4·5. $C_{42}H_{41}ClO_6P_2Pd$ requires C, 59·65; H, 4·9; P, 7·35; Cl, 4·2%). *Chloro[tri-*p*-tolyl phosphito-*(2C,P)*](tri-*p*-tolyl phosphite)palladium*(II) as white microcrystals, 50%, m.p. 138—141° (Found: C, 59·75; H, 5·05; P, 7·0; Cl, 4·45. $C_{42}H_{41}ClO_6P_2Pd$ requires C, 59·65; H, 4·9; P, 7·35; Cl, 4·2%). *Chloro[tri-*p*-chlorophenyl phosphito*(2C,P)*](tri-*p*-chlorophenyl phosphite)palladium*(II) as white microneedles, 80% (Found: C, 44·8; H, 2·3; Cl, 25·2. $C_{36}H_{23}Cl_7O_6P_2Pd$ requires C, 44·65; H, 2·4; Cl, 25·6%).

*Bromo[tri-*o*-tolyl phosphito*(2C,P)](*tri-*o*-tolyl phosphite*)*palladium*(II).—Dibromobis(tri-*o*-tolyl phosphite)palladium (0·3 g) was heated under reflux for 3 h in decalin (5 ml). The hot solution was filtered to remove precipitated palladium metal, then cooled overnight at room temperature. Well formed crystals of required product (pale yellow) and unchanged starting material (orange) were isolated from the mother liquor, washed by decantation, then separated manually. Yield 20% (m.p. 151°) (Found: C, 56·45; H, 4·7; P, 7·0; Br, 8·8. $C_{42}H_{41}BrO_6P_2Pd$ requires C, 56·7; H, 4·65; P, 6·95; Br, 9·0%).

Other palladium(II) dibromo complexes $PdBr_2[P(OAr)_3]_2$ reacted under similar conditions to give mixtures of product and starting material. These were identified by ^1H n.m.r. spectroscopy but could not be separated by crystallisation.

*Attempted Palladation of Di-iodobis(tri-*p*-tolyl phosphite)palladium*(II) *in Boiling Decalin*.—The complex (0·2 g) was heated in decalin under reflux for 4 h, only trace amounts of hydrogen iodide were evolved. The hot solution was filtered to remove metallic palladium, then cooled to room temperature overnight. Unchanged di-iodobis(tri-*p*-tolyl phosphite)palladium precipitated from the solution and was recovered (0·18 g, 90%) (Found: C, 47·6; H, 3·95; I, 23·0. $C_{42}H_{42}I_2O_6P_2Pd$ requires C, 47·35; H, 4·0; I, 23·8%).

Depalladation Reaction.—Chloro[tri-*o*-tolyl phosphito-(2*C*,*P*)](tri-*o*-tolyl phosphite)palladium(II) (0·20 g) dissolved in dichloromethane (35 ml) was saturated with hydrogen chloride gas for 10 min. The colourless solution rapidly turned deep yellow, the characteristic colour of $PdCl_2[P(OAr)_3]_2$ complexes in dichloromethane solution. The solution was concentrated by evaporation, then diluted with n-hexane (15 ml) to induce crystallisation. The yellow crystalline product (0·185 g, 88% yield based on palladated complex) was washed with n-hexane, dried *in vacuo* and characterised as dichlorobis(tri-*o*-tolyl phosphite)palladium by i.r. and ^1H n.m.r. spectroscopy.

Under similar conditions chloro[triphenyl phosphito-(2*C*,*P*)](triphenyl phosphite)palladium(II) (0·20 g) reacted to give dichlorobis(triphenyl phosphite)palladium (0·15 g, 72%), characterised by i.r. spectroscopy.

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