Transition-metal Complexes Containing Phosphorus Ligands. Part IX.[1] Triaryl Phosphite Derivatives of Palladium(II) and Platinum(II) Dihalides

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An extensive series of triaryl phosphite derivatives of palladium(II) and platinum(II) dihalides, $MX_2[P(OAr)_3]_2$ (M = Pd or Pt; X = Cl, Br, or I; Ar = phenyl, *p*-chlorophenyl, *o*-, *m*-, or *p*-tolyl), have been isolated as air-stable crystalline solids by reacting triaryl phosphites, $P(OAr)_3$ and, where appropriate, lithium halides, LiX, with the salts Na_2MCl_4 in ethanol or the neutral complexes MX_2(cyclo-octa-1,5-diene) in benzene solution. The new complexes have been characterised and their stereochemistry investigated by i.r. and n.m.r. spectroscopy. Palladium derivatives containing bulky tri-*o*-tolyl phosphite or iodide ligands were obtained as *trans*-isomers or *cis–trans* mixtures, the remaining complexes occurred predominantly as the *cis*-isomers. An extensive compilation of ^{31}P n.m.r. data is given.

In furtherance of our studies on the *ortho*-metallation of co-ordinated triaryl phosphite ligands we required to synthesise triaryl phosphite derivatives of palladium(II) and platinum(II) dihalides, $MX_2[P(OAr)_3]_2$. These complexes, unlike their triarylphosphine counterparts, have previously attracted little attention, and few syntheses have been recorded in the literature. One complex, $PtCl_2[P(OPh)_3]_2$, has been studied in some detail [2-5] and a few other examples,[6] including the difluoro-derivative $PtF_2[P(OPh)_3]_2$ [7] have been briefly described, however no general study has previously been reported. We have therefore developed the general syntheses described below for the preparation of the class of compounds $MX_2[P(OAr)_3]_2$ and have characterised the products.

The two methods of synthesis employed are based on simple metathetical exchange reactions. One of these, adapted from an earlier synthesis [2] of $PtCl_2[P(OPh)_3]_2$, involves reaction of triaryl phosphite, sodium tetrachloro-palladite(II) or -platinite(II) and, where appropriate, an excess of lithium bromide or iodide in warm ethanol; the other utilises the facile displacement of cyclo-octa-1,5-diene from the complexes $MX_2(C_8H_{12})$ by triaryl phosphite ligands in benzene solution. The latter method, though generally the most convenient, frequently gave products solvated with benzene; this may be removed by recrystallisation of the solvated complexes from dichloromethane–methanol. Difficulty experienced in crystallising some tritolyl phosphite derivatives from the ethanol reaction solutions (first synthetic route) is reflected in the modest yields recorded in several instances.

All the new triaryl phosphite complexes are air-stable, crystalline, solids with very sharp m.p.s, and are very soluble in chloroform and dichloromethane. They vary in colour from white to dark orange-red depending upon the particular metal and halide present; the intensity of colour increases in the expected sequences $Cl < Br < I$ and $Pt < Pd$. The *trans*-isomers are darker coloured than the *cis*-isomers and, unlike the latter, are readily soluble in benzene The stereochemistry of the new triaryl phosphite derivatives was determined by far-i.r. and n.m.r. spectroscopy. The dichloro-derivatives, $MCl_2[P(OAr)_3]_2$ (Ar = phenyl, *m*-tolyl, *p*-tolyl, *p*-chlorophenyl), each show two bands in their i.r. spectra (Table) attributable to *sym* and *asym* vibrations of a *cis*-MCl_2 group and are accordingly assigned as *cis*-

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isomers, in agreement with an earlier conclusion[5] concerning the stereochemistry of $PtCl_2[P(OPh)_3]_2$. The appearance of a third band at *ca.* 360—375 cm^{-1} in the spectra of the corresponding tri-*o*-tolyl phosphite derivatives leads to the formulation of these complexes as *cis–trans*-isomer mixtures. These conclusions were confirmed by ^{31}P n.m.r. spectroscopy; each isomer gives rise to a single ^{31}P resonance with a characteristic chemical shift and, where appropriate, $^{195}Pt–^{31}P$ coupling, thus permitting detection and identification of isomers present. The values of $^{1}J(^{195}Pt–^{31}P)$ recorded for *cis*- and *trans*-isomers are of similar magnitude to those previously recorded for related systems,[5,8] and show the same dependence on the nature of the halide ligands.[8]

Analytical, i.r.,[a] and ^{31}P n.m.r.[b] data of platinum(II) and palladium(II) derivatives, $MX_2[P(OAr)_3]_2$

						cis			*trans*		
M	X	Aryl (Ar)	C (%) *	H (%) *	Other (%) *	δ	^{1}J(PtP)	M–Cl	δ	^{1}J(PtP)	M–Cl
Pt	Cl	Phenyl	48·65 (48·75)	3·5 (3·4)	Cl, 8·25 (8·0)	−59·33	5793	310, 335			
		o-Tolyl	52·15 (51·95)	4·45 (4·35)	Cl, 7·0 (7·3)	−57·04	5859	315, 340	−74·86	4405	360
		m-Tolyl	51·85 (51·95)	4·25 (4·35)	Cl, 7·6 (7·3)			310, 335			
		p-Tolyl	51·6 (51·95)	4·35 (4·35)	Cl, 7·5 (7·3)	−58·71	5840	310, 330			
		p-Chlorophenyl[c]	42·7 (43·05)	2·6 (2·6)		−61·29	5746	310, 335			
	Br	Phenyl	44·8 (44·35)	3·2 (3·1)	Br, 16·0 (16·35)	−59·17	5728				
		o-Tolyl	47·9 (47·6)	4·0 (4·0)	Br, 15·65 (15·1)	−57·44	5840				
		m-Tolyl	47·85 (47·6)	4·1 (4·0)	P, 6·1 (5·85)						
		p-Tolyl	47·65 (47·6)	4·0 (4·0)	Br, 14·95 (15·1)	−59·33	[d]				
		p-Chlorophenyl	36·65 (36·55)	2·05 (2·05)	P, 5·2 (5·25)	−61·13	5668				
		Phenyl	40·6 (40·45)	3·0 (2·85)	I, 23·5 (23·75)	−59·2	5600				
		o-Tolyl	43·85 (43·75)	3·75 (3·65)	I, 21·55 (22·0)	−57·86	5602				
		m-Tolyl	43·6 (43·75)	3·9 (3·65)	I, 22·35 (22·0)[e]	−58·24	5650				
		p-Tolyl	43·45 (43·75)	3·75 (3·65)	I, 22·3 (22·0)	−59·49	5519				
		p-Chlorophenyl	34·15 (33·85)	2·1 (1·9)	P, 5·15 (4·85)	−60·8	5442				
Pd	Cl	Phenyl	54·15 (54·2)	3·85 (3·8)	Cl, 8·65 (8·9)	−83·42		300, 335—340			
		o-Tolyl	56·9 (57·2)	4·8 (4·8)	Cl, 8·3 (8·05)[f]	−84·88		300, 335	−86·81		375
		m-Tolyl	57·45 (57·2)	4·85 (4·8)	Cl, 7·95 (8·05)			310, 335			
		p-Tolyl	57·0 (57·2)	4·6 (4·8)	Cl, 7·9 (8·05)	−83·52		310, 335			
		p-Chlorophenyl[c]	45·95 (46·6)	2·95 (2·8)	Cl, 25·65 (26·2)	−84·66		308, 327			
	Br	Phenyl	49·1 (48·75)	3·55 (3·4)	Br, 18·45 (18·0)	−82·37					
		o-Tolyl	51·7 (51·95)	4·3 (4·35)		−84·7			−90·3		
		m-Tolyl	51·75 (51·95)	4·5 (4·35)	Br, 17·0 (16·45)[g]	−81·55					
		p-Tolyl	51·75 (51·95)	4·5 (4·35)		−82·86					
		p-Chlorophenyl	39·6 (39·55)	2·15 (2·2)	P, 5·45 (5·65)	−83·52			−87·44		
		Phenyl	44·0 (44·1)	3·3 (3·1)	P, 6·1 (6·3)	−82·24			−93·6		
		o-Tolyl	47·8 (47·35)	4·05 (4·0)	P, 5·4 (5·8)				−92·7		
		m-Tolyl	47·5 (47·35)	4·3 (4·0)	P, 6·0 (5·8)	−81·36			−92·7		
		p-Tolyl	46·9 (47·35)	3·85 (4·0)	P, 6·1 (5·8)	−82·87			−93·68		
		p-Chlorophenyl	36·65 (36·4)	2·25 (2·0)	P, 5·5 (5·2)				−95·12		

[a] I. r. spectra recorded from Nujol mulls. [b] P N.m.r. spectra recorded at 36·43 MHz in deuteriochloroform solution with field-frequency lock provided by deuteriochloroform. Chemical shifts (±0·2 p.p.m.) are given relative to 85% H_3PO_4; *J* values ±2 Hz. [c] Benzene adducts $MCl_2[P(OC_6H_4Cl)_3]_2–C_6H_6$. [d] Resolution insufficient to premit accurate measurement of ^{1}J(PtP). [e] P, 5·65 (5·35)%. [f] P, 6·9 (7·0)%. [g] P, 6·05 (6·4)%.
* Calculated values in parentheses.

Occurrence of appreciable concentrations of *trans*-isomers in the tri-*o*-tolyl phosphite derivatives may be attributed to steric factors arising from the bulky nature of this particular ligand. We were unable to assign the rather complex far-i.r. spectra obtained for the bromo- and iodo-derivatives, and therefore base our stereochemical assignments for these products on ^{31}P n.m.r. data alone. These indicate that the complexes are predominantly *cis*, except for the palladium derivatives containing bulky tri-*o*-tolyl phosphite and/or iodide ligands which occur as *trans*-isomers or *cis–trans* mixtures. Confirmation of stereochemical assignments for the tritolyl phosphite derivatives was provided by ^{1}H n.m.r. data. Pure isomers give rise to single resonances (*ca.* τ 7·6—7·9, *o*-tolyl; *ca.* τ 8·0—8·15, *m*- or *p*-tolyl) attributable to the methyl protons of the tolyl groups; *cis–trans*-isomer mixtures give rise to two singlets of differing intensity in the same region. Our stereochemical assignments for the palladium derivatives are in agreement with an earlier report,[9] that in some related tertiary phosphine complexes, $PdX_2(PR_3)_2$ the tendency to adopt a *trans*-configuration is halide dependent and increases in the order Cl ~ Br < I.[9]

EXPERIMENTAL

Sodium chloropalladite was used as purchased; sodium chloroplatinite was obtained by careful evaporation of a 10% aqueous solution (Johnson Matthey). Triphenyl and tri-*p*-tolyl phosphites were used as purchased, other triaryl phosphites were prepared and purified by literature methods.[10]

I.r. spectra (4000—200 cm^{-1}) were recorded on a Perkin-Elmer 621 grating spectrometer using samples mulled in Nujol. ^{1}H N.m.r. spectra were measured in deuteriobenzene with T.M.S. as internal reference using a Varian HA 100 spectrometer. Phosphorus-31 n.m.r. spectra were recorded in deuteriochloroform using a Bruker HFX 90 spectrometer and Fourier transform accessory. M.p.s (corrected) were taken on a Kofler hot-stage apparatus. Microanalyses by Dr. Strauss, Oxford.

Dichlorobis(triphenyl phosphite)platinum(II).—Cold solutions of triphenyl phosphite (0·62 g, 0·002 mol) in ethanol (4 ml) and sodium tetrachloroplatinite tetrahydrate (0·4 g, 0·001 mol) in ethanol (8 ml) were mixed. The mixture was gently warmed for 30 s, shaken at room temperature for 10 min, then cooled at 0°; after 30 min the colourless precipitate was filtered off, washed with ethanol, 50% aqueous ethanol, ethanol, and n-hexane, then dried *in vacuo* to give the required product (0·7 g, 80%). Recrystallisation from dichloromethane–methanol gave white crystals (m.p. 187—189°).

Similarly prepared using the appropriate triaryl phosphites were: *dichlorobis(tri-o-tolyl phosphite)platinum*(II) as

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[9] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[10] G. M. Kosolapoff, 'Organophosphorus Compounds,' Wiley, New York, 1950, pp. 180—210.

white microprisms, yield 80%, m.p. 195—196°; *dichlorobis(tri-*m*-tolyl phosphite)platinum*(II) as white microneedles, yield 75%, m.p. 151—152°; *dichlorobis(tri-*p*-tolyl phosphite)-platinum*(II) as white microcrystals, yield 75%, m.p. 182—184°.

*Dichlorobis(tri-*p*-chlorophenyl phosphite)platinum*(II).—Tri-*p*-chlorophenyl phosphite (0·82 g, 0·002 mol) was added to a suspension of $PtCl_2(C_8H_{12})$ (0·37 g, 0·001 mol) (C_8H_{12} = cyclo-octa-1,5-diene) in benzene (8 ml). After gentle warming for a few minutes the mixture was filtered, diluted with *n*-hexane, cooled at 0° for 30 min, then allowed to stand at room temperature until crystallisation was complete. The resultant white precipitate was filtered off, washed with n-hexane, and dried *in vacuo* as a benzene solvate, $PtCl_2[P(OC_6H_4Cl)_3]_2,C_6H_6$. Yield 0·8 g, 73%. Recrystallisation from dichloromethane–methanol gave white crystals of solvent-free product (m.p. 195—196°).

Dibromobis(triphenyl phosphite)platinum(II).—Solutions of lithium bromide (1·42 g) in ethanol (10 ml) and triphenyl phosphite (0·62 g, 0·002 mol) in ethanol (4 ml) were added to a cold solution of sodium tetrachloroplatinite tetrahydrate (0·4 g, 0·001 mol) in ethanol (8 ml). The mixture was warmed gently for *ca.* 30 s, shaken at room temperature for 10 min, then cooled at 0° for 45 min. The resultant precipitate was filtered off, washed successively with ethanol, 50% aqueous ethanol, ethanol, and n-hexane, then dried *in vacuo*. Yield 0·53 g, 50%. Recrystallisation from dichloromethane–methanol gave white microprisms (m.p. 187—188°).

Similarly prepared using the appropriate triaryl phosphite and lithium halide were: *dibromobis(tri-*o*-tolyl phosphite)-platinum*(II) as white microcrystals, yield 55%, m.p. 194—195°; *dibromobis(tri-*m*-tolyl phosphite)platinum*(II) as white microprisms, yield 50%, m.p. 173—174°; *dibromobis-(tri-*p*-tolyl phosphite)platinum*(II) as white microneedles, yield 50%, m.p. 209—210°; *di-iodobis(triphenyl phosphite)-platinum*(II) as yellow microprisms, yield 60%, m.p. 185—187°; *di-iodobis(tri-*o*-tolyl phosphite)platinum*(II) as yellow microcrystals, yield 60%, m.p. 170—171°; *di-iodobis(tri-*m*-tolyl phosphite)platinum*(II) as yellow microprisms, yield 10%, m.p. 168—169°. The following were prepared from the appropriate cyclo-octa-1,5-diene complex, $PtX_2(C_8H_{12})$ as described above: *dibromobis(tri-*p*-chlorophenyl phosphite)platinum*(II) as white flaky crystals, yield 77%, m.p. 189—190°; *di-iodobis(tri-*p*-chlorophenyl phosphite)platinum*(II) as canary-yellow crystals, yield 78%, m.p. 174°; *di-iodobis(tri-*p*-tolyl phosphite)platinum*(II) as canary-yellow crystals, yield 58%, m.p. 185—186°.

The palladium complexes were prepared from sodium tetrachloropalladite tetrahydrate or, where stated, from dihalogeno(cyclo-octa-1,5-diene)palladium by methods similar to those employed to synthesise their platinum analogues. Palladium derivatives isolated and characterised were: *dichlorobis(triphenyl phosphite)palladium*(II) as white microcrystals, yield 85%, m.p. 175—180°; *dichlorobis(tri-*o*-tolyl phosphite)palladium*(II) as white microcrystals, yield 80%, m.p. 171—174°; *dichlorobis(tri-*m*-tolyl phosphite)palladium-*(II) as white microcrystals, yield 80%, m.p. 147—148°; *dichlorobis(tri-*p*-tolyl phosphite)palladium*(II) as white microprisms, yield 80%, m.p. 179°; *dichlorobis(tri-*p*-chlorophenyl phosphite)palladium*(II) from dichloro(cyclo-octa-1,5-diene)-palladium as benzene solvated white microprisms, yield 80%, m.p. 154—155°; *dibromobis(triphenyl phosphite)-palladium*(II) as yellow microplates, yield 80%, m.p. 176—178°; *dibromobis(tri-*o*-tolyl phosphite)palladium*(II) as orange-red microcrystals, yield 75%, m.p. 152—153°; *dibromobis(tri-*m*-tolyl phosphite)palladium*(II) as yellow microneedles, yield 70%, m.p. 162—163°; *dibromobis(tri-*p*-tolyl phosphite)palladium*(II) as yellow microneedles, yield 70%, m.p. 161—162°; *dibromobis(tri-*p*-chlorophenyl phosphite)palladium*(II) from dibromo(cyclo-octa-1,5-diene)-palladium as yellow-orange flaky crystals, yield 78%, m.p. 212—214°; *di-iodobis(triphenyl phosphite)palladium*(II) as dark orange microprisms, yield 50%, m.p. 189—191°; *di-iodobis(tri-*o*-tolyl phosphite)palladium*(II) as red microprisms, yield 50%, m.p. 164—165°; *di-iodobis(tri-*m*-tolyl phosphite)palladium*(II) as dark red prismatic needles, yield 30%, m.p. 129—130°; *di-iodobis(tri-*p*-tolyl phosphite)-palladium*(II) as orange microcrystals, yield 50%, m.p. 204—205°; *di-iodobis(tri-*p*-chlorophenyl phosphite)-palladium*(II) from di-iodo(cyclo-octa-1,5-diene)palladium as orange-red flaky crystals, yield 72%, m.p. 198—199°.

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