Use of Aryltin Compounds in the Preparation of Diaryl- and Diaroyl-di-μ-chloro-bis(triorganophosphine)diplatinum(II) Complexes †

By **Colin Eaborn,* Kevin J. Odell,** and **Alan Pidcock,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The complexes *cis*-$[Pt(C_2H_4)Cl_2L]$ (L = triorganophosphine) react with compounds $SnRMe_3$ (R = aryl) (1 mol equivalent) to give the chloride-bridged arylplatinum complexes $[Pt_2R_2Cl_2L_2]$, which exist in solution as mixtures of *cis* and *trans* isomers. The $[Pt_2R_2Cl_2L_2]$ complexes react with ligand species L′ [L′ = NCMe, SBu^t_2, pyridine, NBu^nH_2, $AsPh_3$, PEt_3, PBu^n_3, PPh_3, or $P(OPh)_3$] to give the mononuclear complexes $[PtR(Cl)L(L')]$, and this represents an excellent route to mononuclear complexes having four different ligands on platinum. Cyclo-octa-1,5-diene (cod), however, gives $[PtR(Cl)L_2]$ and $[Pt(cod)R(Cl)]$, while 2,2′-bipyridyl (bipy) gives the salt $[PtR(bipy)L]Cl$. Sodium thiocyanate reacts with $[Pt_2(C_6H_4Me\text{-}p)_2Cl_2(PEt_2Ph)_2]$ to give the thiocyanate-bridged $[Pt_2(C_6H_4Me\text{-}p)_2(PEt_2Ph)_2(\mu\text{-}SCN)_2]$, and $[NEt_4]Cl$ reacts with $[Pt_2(C_6H_4Bu^n\text{-}p)_2Cl_2(PMe_2Ph)_2]$ to give the salt $[NEt_4][Pt(C_6H_4Bu^n\text{-}p)Cl_2(PMe_2Ph)]$. Excess of $SnRMe_3$ causes decomposition of $[Pt_2R_2Cl_2L_2]$ to give the mononuclear complexes $[PtR(Cl)L_2]$. The carbonyl complexes *cis*-$[Pt(CO)Cl_2L]$ react with $SnRMe_3$ to give the binuclear aroyl complexes $[Pt_2(COR)_2Cl_2L_2]$, which also exist in solution as mixtures of *cis* and *trans* isomers. These complexes react with neutral ligand species L′ = NBu^nH_2 or $P(OPh)_3$ to give the mononuclear complexes $[Pt(COR)Cl(L)L']$, but cod reacts with $[Pt_2(COC_6H_4Bu^t\text{-}p)_2Cl_2(PMe_2Ph)_2]$ to give $[Pt(COC_6H_4Bu^t\text{-}p)Cl(PMe_2Ph)_2]$. Again excess of $SnRMe_3$ causes decomposition, to give $[Pt(COR)Cl(L)]$ complexes. Heating of the aroyl complex $[Pt_2(COC_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$ gives some of the corresponding aryl complex $[Pt_2(C_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the complexes have been recorded, and are used extensively in the identification of products.

WE have previously shown that aryltrimethyltin compounds, $SnRMe_3$, react readily with the cyclo-octa-1,5-diene (cod) complex $[Pt(cod)Cl_2]$ to give good yields of $[Pt(cod)R(Cl)]$ or $[Pt(cod)R_2]$ complexes, depending on the ratio of reactants used.[1] We also observed that the bis(phosphine) complexes $[PtCl_2(PR_3)_2]$ do not react with the aryltin compounds. We now describe the results of a study of the reactions of $SnRMe_3$ compounds with the mixed olefin–phosphine and carbonyl–phosphine complexes $[Pt(C_2H_4)Cl_2L]$ and $[Pt(CO)Cl_2L]$ (L = PEt_3, PEt_2Ph or PMe_2Ph), which provides good routes to the halide-bridged aryl or aroyl species $[Pt_2R_2Cl_2L_2]$ and $[Pt_2(COR)_2Cl_2L_2]$.[2]

---

† No reprints available.

[1] C. Eaborn, K. J. Odell, and A. Pidcock, *J.C.S. Dalton*, 1978, 357.

[2] For a brief preliminary account see C. Eaborn, K. J. Odell, and A. Pidcock, *J. Organometallic Chem.*, 1975, **96**, C38.

RESULTS AND DISCUSSION

Addition of a 1 mol equivalent of $SnRMe_3$ [R = Ph, C_6H_4Me-*p*, $C_6H_4Bu^t$-*p*, 2-thienyl ($2-C_4H_3S$), or 2-benzo[*b*]furyl ($2-C_8H_5O$)] to a solution of *cis*-$[Pt(C_2H_4)Cl_2L]$ (L = PEt_3, PEt_2Ph, or PMe_2Ph) in dichloromethane immediately produced a yellow colour and an odour of chlorotrimethyltin. The mixture was left for 1 h at room temperature, the solvent was evaporated, the $SnMe_3Cl$ extracted with pentane, and the residue recrystallized from chloroform–pentane. The products were identified by elemental analysis and by their spectroscopic properties (see below) as the complexes $[PtR_2Cl_2L_2]$ (1) [equation (1)] which exist, at least in solution, as a mixture of *cis* and *trans* isomers. Yields were usually good, but it is important to avoid use of an excess of the aryltin compounds, which causes decomposition of the product to $[PtR(Cl)L_2]$ (see below), and to maintain an excess of the platinum complex by careful dropwise addition of the tin reagent up to slightly less than the stoicheiometric amount. The relatively poor yields of the products when L = PEt_3 can be associated with the fact that in these cases the organotin compound was added in one portion to a suspension of *cis*-$[Pt(C_2H_4)Cl_2(PEt_3)]$.

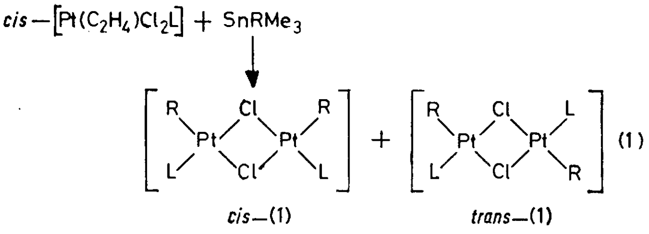


TABLE 1

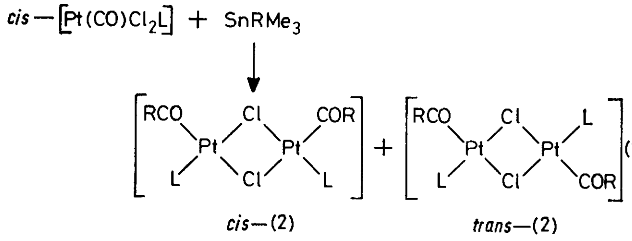
Analytical and physical data for complexes $[Pt_2R'_2Cl_2L_2]$ [R′ = aryl (R) or COR] isolated from reactions between $SnRMe_3$ and $[Pt(C_2H_4)Cl_2L]$ or $[Pt(CO)Cl_2L]$

R′	L	Yield (%)	M.p. [a] (θ_c/°C)	Analysis (%) [b] C	Analysis (%) [b] H	I.r. data (cm^{-1}) [c] ν(Pt–Cl)	I.r. data (cm^{-1}) [c] ν(CO)
Ph	PEt_3	44	160	33.8 (33.85)	4.7 (4.7)	285 (260)	
C_6H_4Me-*p*	PEt_3	41	209—210	35.5 (35.5)	5.0 (5.0)	279 (255)	
C_6H_4Me-*p*	PEt_2Ph	81	197—199	41.5 (41.8)	4.6 (4.5)	279 (256)	
$C_6H_4Bu^t$-*p*	PMe_2Ph	87	191	42.0 (43.0)	4.7 (4.8)	281 (255)	
2-Thienyl	PMe_2Ph	66	175	31.9 (31.9)	3.2 (3.1)	281 (260)	
2-Benzo[*b*]furyl	PMe_2Ph	80	209—213	40.3 (38.6)	3.4 (3.3)	290 (264)	
$COC_6H_4Bu^t$-*p*	PMe_2Ph	67	249—250	42.8 (43.1)	4.6 (4.6)	278	1 640, 1 602
COC_6H_4Me-*p*	PEt_3	70	125—130	35.1 (34.3)	4.7 (4.9)	280	1 620, 1 599
COC_6H_4OMe-*p*	PEt_3	87	145	34.3 (34.75)	4.8 (4.6)	276	1 620, 1 595

[a] With decomposition. [b] Calculated values are given in parentheses. [c] Nujol mulls. The values in parentheses refer to shoulders to the main, intense, broad Pt–Cl band.

Similar treatment of the carbonyl complex *cis*-$[Pt(CO)Cl_2L]$ (L = PEt_3 or PMe_2Ph) with $SnRMe_3$ gives not aryl but aroyl complexes, (2) [equation (2)]; again, decomposition occurs if an excess of the $SnRMe_3$ is present. It is not necessary to isolate the complexes *cis*-$[Pt(CO)Cl_2L]$ since good results were obtained by adding the tin compound to the solutions obtained by bubbling carbon monoxide through solutions of $[Pt_2Cl_4L_2]$. The analyses and some physical constants of the products are shown in Table 1.

These reactions provide useful routes to complexes of types (1) and (2). Cross and Wardle [3] have previously made the benzoyl complexes of type (2) (*i.e.* R = Ph) by treatment of *cis*-$[Pt(CO)Cl_2L]$ (L = PPh_3 or PBu_3) with diphenylmercury, but the yield was low because of decomposition of the benzoyl complex during removal of the chloro(phenyl)mercury(II) by sublimation. Aryl complexes of type (1) do not undergo such decomposition, and we obtained a 44% yield of $[Pt_2Ph_2Cl_2(PEt_3)_2]$ by treatment of *cis*-$[Pt(C_2H_4)Cl_2(PEt_3)]$ with $HgPh_2$. In this case use of $SnMe_3Ph$ gave only a similar yield, because of the mixing procedure we used (see above), but even for comparable yields the ease of work-up makes $SnRMe_3$ much more convenient reagents than HgR_2.



We found that tetramethyltin does not react with *cis*-$[Pt(C_2H_4)Cl_2(PEt_3)]$ at room temperature, and at reflux only decomposition of the complex occurred to give $[Pt_2Cl_4(PEt_3)_2]$ (*cf.* ref. 4). We did not examine the reaction of $SnMe_4$ with *cis*-$[Pt(CO)Cl_2L]$ species, but Cross and Wardle [3] obtained a small yield of *cis*-$[Pt_2(COMe)_2Cl_2L_2]$ by use of dimethylmercury.

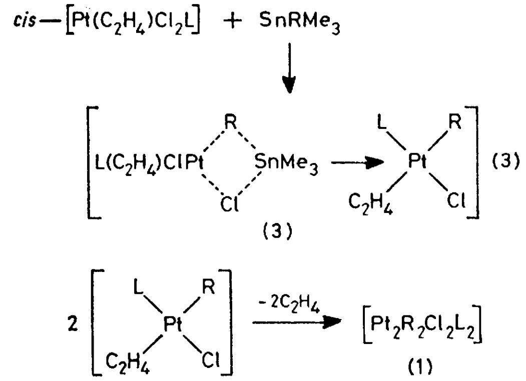
It is noteworthy that, for X = Br or I, Chatt and Davidson [5] obtained $[Pt_2Ph_2X_2(PPr_3)_2]$ complexes in 20—30% yield by treatment of bridged complexes $[Pt_2X_4(PPr_3)_2]$ with phenyl-lithium, but for X = Cl they isolated only *trans*-$[PtR_2(PPr_3)_2]$ and concluded, wrongly in view of our results, that $[Pt_2Ph_2Cl_2(PR_3)_2]$ species are unstable. It seems reasonable to write the reaction between the ethylene complex *cis*-$[Pt(C_2H_4)Cl_2L]$ and $SnRMe_3$ compounds as involving initial formation of the species $[Pt(C_2H_4)R(Cl)L]$ (3) in a bimolecular process, *e.g.* that shown in equation (3), having characteristics of an

[3] R. J. Cross and R. Wardle, *J. Chem. Soc.* (*A*), 1970, 840.

[4] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.

[5] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1964, 2433.

electrophilic aromatic substitution, as discussed previously for the interaction of $[Pt(cod)Cl_2]$ and $SnRMe_3$.[1]



Electron donation by the *trans*-aryl ligand in (3) would weaken the $Pt-C_2H_4$ bond, and ethylene would be readily lost to give the dimeric product (1). However, it is less likely that the reaction of the carbonyl complex *cis*-$[Pt(CO)Cl_2L]$ involves initial formation of $[Pt(CO)R(Cl)L]$. In the first place the alkyl complexes $[Pt(CO)Me(I)(PPh_3)]$ and $[Pt(CO)Et(Cl)(AsPh_3)]$ are known to be stable, and to show no tendency to form acyl complexes,[6] though the corresponding aryl complexes could be markedly more labile. Secondly, if $[Pt(CO)R(Cl)L]$ were formed with CO *trans* to R, which would be expected as a consequence of the large *trans* effect of CO, the configuration would be unfavourable for carbonyl migration to give the aroyl group, although it is conceivable that such migration could follow conversion into the isomer having the carbonyl ligand *cis* to R. Oxidative addition of the $SnRMe_3$ followed by carbonyl migration to form a five-co-ordinate species and reductive elimination of $SnMe_3Cl$ to form the bridged complex is a reasonable alternative [equation (4)].

$$cis\text{-}[Pt(CO)Cl_2L] + SnRMe_3 \longrightarrow [Pt(CO)RCl_2(SnMe_3)L] \quad (4)$$

$$[Pt_2(COR)_2Cl_2L_2] \xleftarrow{-SnMe_3Cl} [Pt(COR)Cl_2(SnMe_3)L]$$

Spectroscopic Properties of $[Pt_2R_2Cl_2L_2]$ *and* $[Pt_2(COR)_2Cl_2L_2]$.—*Infrared spectra.* The complexes $[Pt_2R_2Cl_2L_2]$ and $[Pt(COR)_2Cl_2L_2]$ show two bands in the 250—300 cm^{-1} region. A strong band at *ca.* 280 cm^{-1} is assigned to the bridge stretching vibration ν(Pt–Cl) associated largely with the bond *trans* to L in the *trans* complexes; a shoulder on the low-frequency side may be due to the ^{37}Cl isotope.[7] A less-intense band at *ca.* 260 cm^{-1} may be at too high a frequency to arise from ν(Pt–Cl) *trans* to R; the n.m.r. spectra (see below) show that in solution *cis* and *trans* isomers are present and, if these are also present in the solid, bands arising from ν(Pt–Cl) *trans* to L could be expected from the *cis* isomer. There are no clear bands in the 200—250 cm^{-1} region, and so it is possible that no band for ν(Pt–Cl) *trans* to R or COR is detected; in view of the high *trans* influences of aryl and benzoyl[8] ligands this band may be at <200 cm^{-1}.

The aroyl complexes show two bands in the range 1 600—1 640 cm^{-1}, a region similar to that in which the carbonyl-stretching bands of mononuclear benzoyl complexes are usually found. Again the appearance of two bands is consistent with the presence of *cis* and *trans* isomers. A weaker band at *ca.* 1 570 cm^{-1} is given also by the aryl complexes, and can be assigned to the aromatic ring.

N.m.r. spectra. The ^{31}P-{^1H} n.m.r. parameters of complexes (1) and (2) are listed in Table 2. The presence of two components, believed to be *cis* and *trans* isomers, is evident; the chemical shifts are very similar and in some cases coincident, but the coupling constants ^1J(Pt–P) differ by 50—100 Hz. The larger coupling constant is tentatively assigned to the *trans* isomer by comparison with the spectra of the complexes $[Pt_2Cl_4L_2]$, for which the two isomers can be unambiguously identified.[9] On this basis the *cis* isomer almost always predominates, as was observed for the related bromide-bridged complex $[Pt_2Br_2Ph_2(PPr_3)_2]$ from dipole-moment studies.[5] The coupling constants ^1J(Pt–P) in the *cis* and *trans* isomers of the PEt_3 complexes (Table 2) are much larger than that for PEt_3 *trans* to bridging chlorine in *sym-trans*-$[Pt_2Cl_4(PEt_3)_2]$ (3 845 Hz).[9] This is probably mainly due to the presence of an aryl or aroyl ligand *cis* to phosphorus, but there may also be some weakening of the chlorine bridge bonds due to the high *trans* influence of the aryl and aroyl ligands.[9]

The presence of two isomeric forms is also evident as a slight splitting of the ^1H n.m.r. resonances from the protons of the X groups in the complexes $[Pt_2(C_6H_4X\text{-}p)_2Cl_2L_2]$ (X = Me, OMe, or Bu^t). This splitting is less marked for the corresponding aroyl complexes.

Reactions of $[Pt_2R_2Cl_2L_2]$ *and* $[Pt_2(COR)_2Cl_2L_2]$.—(*a*) *With neutral species.* Treatment of the bridged complexes $[Pt_2R'_2Cl_2L_2]$ [R' = aryl (R) or COR] with neutral unidentate ligands L' [L' = MeCN, SR''_2, C_5H_5N, $NBu^n H_2$, $SbPh_3$, PR''_3, or $P(OR'')_3$] readily brings about bridge splitting to give mononuclear complexes $[PtR(Cl)L(L')]$ [equation (5)]. This reaction, which provides an excellent route to mononuclear platinum(II) complexes containing four different ligands, occurs markedly more readily than the corresponding reaction of $[Pt_2Cl_4L_2]$ complexes, presumably because of the high *trans* effect of the R or COR groups; *e.g.* $AsPh_3$ or pyridine react immediately to give a colourless solution, while complete reaction with corresponding dimeric tetrachloro-species often requires refluxing.[10] Only the products $[Pt(C_6H_4Me\text{-}p)Cl(NC_5H_5)(PEt_3)]$ and [Pt-

$$[Pt_2R_2Cl_2L_2] + 2L' \longrightarrow 2[PtR(Cl)L(L')] \quad (5)$$

---

[6] C. J. Wilson, M. G. Green, and R. J. Mawby, *J.C.S. Dalton*, 1974, 421; R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 1971, **10**, 854.

[7] D. M. Adams and P. J. Chandler, *J. Chem. Soc. (A)*, 1969, 588.

[8] S. P. Dent, C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1972, **46**, C68.

[9] K. J. Odell, D. Phil. Thesis, University of Sussex, 1976.

$(AsPh_3)(2\text{-}C_8H_5O)Cl(PMe_2Ph)]$ were isolated and the other products were identified in the reaction mixtures by their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra (Table 3). For $L' = PR_3$ exactly 2 mol equivalents of the ligand were added, but in the other cases a slight excess of L′ was used; the spectra were recorded within 1 h. Except for L′ = amine, a single isomer was produced; since the coupling constants $^1J(Pt\text{-}P)$ follow a sequence corresponding to that of the *trans* influences of the ligands L′ (*viz.* MeCN < SBu^t_2 < amine < $SbPh_3$ < $AsPh_3$ < PR_3), it is very

TABLE 2

Hydrogen-1 and $^{31}P\text{-}\{^1H\}$ n.m.r. data for the complexes $[Pt_2R'_2Cl_2L_2]$ [R′ = aryl (R) or COR]

			$^{31}P\text{-}\{^1H\}$			
R′	L	Isomer (proportion in %)	δ/p.p.m.	$^1J(Pt\text{-}P)$/Hz	^1H for X in C_6H_4X (τ)	Notes
$2\text{-}C_8H_5O$	PMe_2Ph	*cis* (52)	152.3	4 477		*a,b*
		trans (48)	152.6	4 495		*a,b*
$C_6H_4Bu^t\text{-}p$	PMe_2Ph	*cis* (73)	153.9	4 885	7.80	*c*
		trans (27)	153.9	4 951	7.84	*d*
$2\text{-}C_4H_3S$	PMe_2Ph	*cis* (45)	153.8	4 567		*a,e*
		trans (55)	154.4	4 578		*a,e*
$C_6H_4Me\text{-}p$	PEt_3	*cis* (80)	130.8	4 755	7.89	
		trans (20)	131.4	4 828	7.92	
Ph	PEt_3	*cis* (73)	130.8	4 734		
		trans (27)	131.4	4 780		
$C_6H_4SnMe_3\text{-}p$	PEt_3	*cis* (69)	130.7	4 651		
		trans (31)	131.2	4 680		
$C_6H_4Me\text{-}p$	PEt_2Ph	*cis* (69)	132.8	4 863	7.99	*f*
		trans (31)	132.8	4 915	8.02	
$C_6H_4OMe\text{-}p$	PPr_3	*cis* (72)	139.2	4 712		
		trans (28)	139.7	4 746		
$COC_6H_4Bu^t\text{-}p$	PMe_2Ph	*cis* (75)	155.1	5 208	8.82	*a,g*
		trans (25)	155.1	5 332		*a,g*
$COC_6H_4Me\text{-}p$	PEt_3	*cis* (70)	129.5	5 049	7.70	*a*
		trans (30)	129.5	5 149		*a*
$COC_6H_4Me\text{-}p$	PEt_3	*cis* (69)	129.5	5 059	6.21	*a*
		trans (31)	129.5	5 159		*a*

[a] Hydrogen-1 n.m.r. spectra of *cis* and *trans* isomers not resolved. [b] In ^1H n.m.r.: $^2J(PCH)$ 11 and $^3J(PtPCH)$ 50 Hz; $\tau(PCH_3)$ 8.41. [c] In ^1H n.m.r.: $^2J(PCH)$ 11 and $^3J(PtPCH)$ 53 Hz; $\tau(PCH_3)$ 8.57. [d] In ^1H n.m.r.: $^2J(PCH)$ 11 and $^3J(PtPCH)$ 54 Hz; $\tau(PCH_3)$ 8.53. [e] In ^1H n.m.r.: $^2J(PCH)$ 11 and $^3J(PtPCH)$ 49 Hz; $\tau(PCH_3)$ 8.48. [f] In $^{31}P\text{-}\{^1H\}$ n.m.r.: $^2J(PtClPt)$ 110, $^3J(PPtClPt)$ −5; and $^4J(PPtClPtP)$ <3 Hz. [g] In ^1H n.m.r.: $^2J(PCH)$ 11 and $^3J(PtPCH)$ 59 Hz; $\tau(PCH_3)$ 8.42.

TABLE 3

Some $^{31}P\text{-}\{^1H\}$ n.m.r. data for products of the interaction of $[Pt_2R_2Cl_2L_2]$ complexes with neutral species L′

R	L	L′	Product	δ/p.p.m.	$^1J(Pt\text{-}P)$/Hz	L *trans* to	Notes
$C_6H_4Me\text{-}p$	PEt_3	NCMe	$[PtR(Cl)L(L')]$	131.3	4 307	MeCN	
		SBu^t_2	$[PtR(Cl)L(L')]$	130.3	4 111		
		NC_5H_5	$[PtR(Cl)L(L')]$	136.7	4 048	py	
		Piperidine	$[PtR(Cl)L(L')]$	135.4	4 048	Cl	
				137.6	3 938	$C_5H_{11}N$	
		NBu^nH_2	$[PtR(Cl)L(L')]$	136.8	4 009	Cl	
				135.5	3 894	NBu^nH_2	
		$SbPh_3$	$[PtR(Cl)L(L')]$	128.5	3 933	$SbPh_3$	
		$AsPh_3$	$[PtR(Cl)L(L')]$	127.6	3 736	$AsPh_3$	
		PEt_3	$[PtR(Cl)L_2]$	126.0	2 800	PEt_3	
		cod	$[PtR(Cl)L_2]$	126.0	2 800	PEt_3	
		$P(OPh)_3$	*trans*-$[PtR(Cl)L(L')]$	126.5	2 983	$P(OPh)_3$	*a*
		PPh_3	*trans*-$[PtR(Cl)L(L')]$	113.5	2 832	PPh_3	*b*
		PBu^n_3	*trans*-$[PtR(Cl)L(L')]$	123.7	2 791	PBu^n_3	*c*
		$MeC_6H_4SnMe_3\text{-}p$	$[PtR(Cl)L_2]$	126.0	2 800	PEt_3	
$C_6H_4Bu^t\text{-}p$	PMe_2Ph	bipy	$[PtR(L)(L')]Cl$	153.4	4 082	½bipy	
		NBu^nH_2	$[PtR(Cl)L(L')]$	157.5	3 909	NBu^nH_2	
		cod	$[PtR(Cl)L_2]$	145.3	2 874	PMe_2Ph	
		$BiPh_3$	$[PtR(Cl)L_2]$	145.4	2 866	PMe_2Ph	
$C_6H_4Me\text{-}p$	PEt_2Ph	cod	$[PtR(Cl)L_2]$	126.5	2 881	PEt_2Ph	
$2\text{-}C_8H_5O$	PMe_2Ph	$AsPh_3$	$[PtR(Cl)L(L')]$	147.4	3 437	$AsPh_3$	
$COC_6H_4Me\text{-}p$	PEt_3	NBu^nH_2	$[PtR(Cl)L(L')]$	135.0	4 175	Cl	
				136.8	3 887	NBu^nH_2	
$COC_6H_4Bu^t\text{-}p$	PMe_2Ph	cod	*trans*-$[PtR(Cl)L_2]$	148.2	3 076	PMe_2Ph	*d*
			cis-$[PtR(Cl)L_2]$	150.4	1 609	R	
				150.7	4 243	Cl	
$COC_6H_4Me\text{-}p$	PEt_3	$P(OPh)_3$	*trans*-$[PtR(Cl)L(L')]$	126.5	3 203	$P(OPh)_3$	*e*
$COC_6H_4Me\text{-}p$	PEt_3	$MeC_6H_4SnMe_3\text{-}p$	*trans*-$[PtR(Cl)L_2]$	126.7	2 998	PEt_3	
$COC_6H_4Bu^t\text{-}p$	PMe_2Ph	$Bu^tC_6H_4SnMe_3\text{-}p$	*trans*-$[PtR(Cl)L_2]$	148.1	3 066	PMe_2Ph	
$COC_6H_4Bu^t\text{-}p$	PMe_2Ph	$MeOC_6H_4SnMe_3\text{-}p$	*trans*-$[PtR(Cl)L_2]$	148.2	3 072	PMe_2Ph	
			trans-$[Pt(C_6H_4OMe\text{-}p)ClL_2]$	145.3	2 854	PMe_2Ph	

[a] For $P(OPh)_3$ *trans* to L : δ 41.2 p.p.m.; $^1J(Pt\text{-}P)$ 4 985 and $^2J(PPtP)$ 652 Hz. [b] For PPh_3 *trans* to L : δ 127.3 p.p.m.; $^1J(Pt\text{-}P)$ 2 900 and $^2J(PPtP)$ 432 Hz. [c] For PBu_3 *trans* to L : δ 136.5 p.p.m.; $^1J(Pt\text{-}P)$ 2 786 and $^2J(PPtP)$ 420 Hz. [d] $^2J(PPtP)$ 17 Hz. [e] For $P(OPh)_3$ *trans* to L : δ 41.2 p.p.m.; $^1J(Pt\text{-}P)$ 5 435 and $^2J(PPtP)$ 562 Hz.

likely that L and L′ are *trans* to one another. Formation of the two isomers might be expected, and it is possible that this does, indeed, occur, but that isomerization to give a single isomer then occurs, catalyzed by an excess of L′. It is noteworthy that for $[Pt(C_6H_4Me\text{-}p)Cl(PEt_3)L']$ (L′ = amine) the isomer with the amine *trans* to the aryl group predominates (*ca.* 82%) for L′ = pyridine, whereas with the more basic n-butylamine the isomer with the amine *trans* to PEt_3 predominates (*ca.* 76%).

When carbon monoxide was passed for 2 h through a solution of $[Pt(C_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$ in dichloromethane, and the solvent then removed, the pale yellow solid obtained had an i.r. spectrum almost identical with that of the starting material, and there were no bands at 1 600—1 700 cm^{-1} typical of aroyl carbonyl-stretching modes, but new weak bands at 2 068 and 2 059 cm^{-1} indicated the formation of trace amounts of a product having terminal carbonyl ligands.

The complex $[Pt_2(C_6H_4Bu^t\text{-}p)_2Cl_2(PMe_2Ph)_2]$ reacted with an excess of 2,2′-bipyridyl (bipy) to give the salt $[Pt(C_6H_4Bu^t\text{-}p)(bipy)(PMe_2Ph)]Cl$. A route analogous to that proposed for the corresponding reactions of $[Pt_2Cl_4L_2]$ complexes with bidentate amine or phosphine ligands [11] can be postulated [equation (6)]. In contrast, unsymmetrical bridge cleavage occurred when a solution of $[Pt_2R_2Cl_2L_2]$ (R = C_6H_4Me-*p*, L = PEt_3; or R = $C_6H_4Bu^t$-*p*, L = PMe_2Ph) was heated under reflux with an excess of cod for several hours, and roughly equimolar quantities of $[PtR(Cl)L_2]$ and $[Pt(cod)R(Cl)]$ were isolated [equation (7)]. The corresponding products from treatment of $[Pt_2(COC_6H_4Bu^t\text{-}p)_2Cl_2(PMe_2Ph)_2]$ with cod could not be satisfactorily separated, but the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed the presence of *cis*- and *trans*-$[Pt(COC_6H_4Bu^t\text{-}p)Cl(PMe_2Ph)_2]$. An unsymmetrical cleavage of $[Pt_2Br_6]^{2-}$ by cod to give $[PtBr_2(cod)]$ and $[PtBr_4]^{2-}$ has been noted.[12]

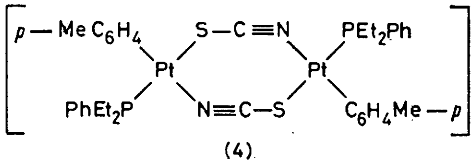
$$\begin{array}{c} [Pt_2R_2Cl_2L_2] + bipy \longrightarrow [PtR(bipy)L][PtRCl_2L] \\ \Big\downarrow\Big\uparrow \text{bipy} \\ 2[PtR(bipy)L]Cl \end{array} \qquad (6)$$

$$[Pt_2R_2Cl_2L_2] + cod \rightleftharpoons [Pt(cod)(R)Cl] + [Pt(R)ClL_2] \qquad (7)$$

Addition of $SnRMe_3$ to the complexes $[Pt_2R_2Cl_2L_2]$ in dichloromethane immediately gave a black precipitate, indicating extensive decomposition, and the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the supernatant solution showed the presence of only a single Pt–P complex, identified as $[PtR(Cl)L_2]$. On treatment of $[Pt_2(COC_6H_4Bu^t\text{-}p)_2Cl_2(PMe_2Ph)_2]$ with $Sn(C_6H_4OMe\text{-}p)Me_3$, containing a different aryl group, two products *trans*-$[Pt(COC_6H_4Bu^t\text{-}p)Cl(PMe_2Ph)_2]$ and *trans*-$[Pt(C_6H_4OMe\text{-}p)Cl(PMe_2Ph)_2]$ were observed, but when $Sn(C_6H_4Bu^t\text{-}p)Me_3$ was used only *trans*-$[Pt(COC_6H_4Bu^t\text{-}p)Cl(PMe_2Ph)_2]$ was detected, and no *trans*-$[Pt(C_6H_4Bu^t\text{-}p)Cl(PMe_2Ph)_2]$.

(*b*) *With anionic species.* Monitoring of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed that tetraethylammonium chloride reacts with $[Pt_2(C_6H_4Bu^t\text{-}p)_2Cl_2(PMe_2Ph)_2]$ to give the salt $[NEt_4][Pt(C_6H_4Bu^t\text{-}p)Cl_2(PMe_2Ph)]$; analogous bridge splitting is known to occur with $[Pt_2Cl_4L_2]$ complexes.[13]

In contrast, sodium thiocyanate reacted with $[Pt_2(C_6H_4Me\text{-}p)_2Cl_2(PEt_2Ph)_2]$ to give $[Pt_2(C_6H_4Me\text{-}p)_2(PEt_2Ph)_2(\mu\text{-}SCN)_2]$; the spectrum of the product at room temperature showed a single, clearly resolved, resonance, with well defined platinum satellites, δ 130.7 p.p.m. [^1J(Pt–P) 4 111 Hz]. Since there is no evidence of $^{31}P\text{–}^{14}N$ interaction configuration (4) is tentatively assigned. The iodide-bridged complex $[Pt_2(COC_6H_4OMe\text{-}p)_2I_2(PEt_3)_2]$ was isolated from the reaction between sodium iodide and the aroyl complex $[Pt(COC_6H_4OMe\text{-}p)_2Cl_2(PEt_3)_2]$; the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum indicated that effectively equal amounts of *cis* and *trans* isomer were present in the solution in $CDCl_3$.



(4)

(*c*) *Decarbonylation of* $[Pt_2(COC_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$. When the aroyl complex $[Pt_2(COC_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$ was heated at 130 °C (0.01 mmHg) * extensive decomposition occurred, but the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the soluble products showed that some of the corresponding aryl complex $[Pt_2(C_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$ had been formed.

The Reaction of trans-$[Pt(COC_6H_4Me\text{-}p)Cl(PEt_3)_2]$ *with* $SFO_2(OMe)$.—An interesting example of migration of an aryl ligand to platinum with retention of the platinum–carbonyl linkage occurred when *trans*-$[Pt(COC_6H_4Me\text{-}p)Cl(PEt_3)_2]$ (prepared by adding PEt_3 to the corresponding binuclear aroyl complex) was treated with an excess of methyl fluorosulphate. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of the reaction mixture showed a single Pt–P species to be present [δ 126.8 p.p.m., ^1J(Pt–P) 3 000 Hz], and the i.r. spectrum showed a strong band at 2 102 cm^{-1} in place of the ν(CO) of the aroyl group of the starting material. These spectral characteristics are similar to those of the cationic complexes *trans*-$[Pt(CO)RL_2][ClO_4]$,[9] and it seems that halide abstraction by the methyl fluorosulphate [14] promotes aryl migration from carbon to platinum, to give *trans*-$[Pt(CO)RL_2][SFO_3]$.

EXPERIMENTAL

All the solvents were dry and oxygen-free, and reactions were carried out under nitrogen. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded at 40.48 MHz on a JEOL PFT 100

---

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

[10] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 3858.

[11] U. Belluco, ' Organometallic and Coordination Chemistry of Platinum,' Academic Press, New York, 1974, p. 78.

[12] M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta*, 1970, **4**, 565.

[13] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc. (A)*, 1970, 545.

[14] C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J.C.S. Dalton*, 1976, 58.

instrument. Solutions in dichloromethane in 8-mm outside-diameter tubes were used. The field was locked to the ^{2}H resonance of a solution of trimethyl phosphite in CD_2Cl_2, which served as external reference. Isomer proportions were inferred directly from the relative peak heights in the $^{31}P-\{^1H\}$ n.m.r. spectra. The starting platinum complexes were made by published methods;[15,16] some physical data are given in Table 4. The preparations of the tin compounds have been described.[17]

Reactions of cis-$[Pt(C_2H_4)Cl_2L]$ (L = PEt_3, PMe_2Ph, *or* PEt_2Ph) *with Aryltrimethyltin Compounds*.—(*a*) Trimethyl-*p*-tolyltin (0.37 g, 1.4 mmol) in dichloromethane (10 cm^3) was added dropwise with stirring during 0.5 h to a solution of *cis*-$[Pt(C_2H_4)Cl_2(PEt_2Ph)]$ (0.65 g, 1.4 mmol) in dichloromethane (20 cm^3). A yellow colour appeared after 5 min, and the odour of $SnMe_3Cl$ was detectable. The mixture was stirred at room temperature for another 2 h, and the solvent removed *in vacuo* to leave a pale yellow solid, which was washed with diethyl ether and dried. The i.r. spectrum (Nujol) of the crude product had a strong band at 274 cm^{-1}, and the bands at 295 and 331 cm^{-1} given by the starting material were absent. The solid was dissolved in hot chloroform, diethyl ether was added until a turbidity persisted, and the mixture was set aside at 5 °C to give colourless crystals of *di-μ-chloro-bis*[(*diethylphenylphosphine*)p-*tolylplatinum*(II)] (0.56 g, 81%) (see Table 1).

(*b*) A similar procedure starting from $Sn(C_6H_4Bu^t$-*p*$)Me_3$ and *cis*-$[Pt(C_2H_4)Cl_2(PMe_2Ph)]$ gave fine needles of *di-μ-chloro-bis*[(*dimethylphenylphosphine*)(p-*t-butylphenyl*)*platinum*(II)] in 87% yield (see Table 1).

(*c*) Trimethyl(*p*-tolyl)tin (1.3 g, 4.9 mmol) was added directly in one portion to a suspension of *cis*-$[Pt(C_2H_4)Cl_2(PEt_3)]$ (2.0 g, 4.9 mmol) in dichloromethane (10 cm^3). A yellow colour appeared and gas was slowly evolved. After 0.5 h the solution, which had become red, was evaporated to half its volume, benzene (5 cm^3) was added, and the white solid which separated was filtered off and identified as unchanged *cis*-$[Pt(C_2H_4)Cl_2(PEt_3)]$ (0.73 g, 37%) from its i.r. spectrum. The red solution was stirred with charcoal for 0.5 h and filtered through Celite. The pale yellow filtrate was evaporated *in vacuo* and the resulting oil crystallized from dichloromethane–pentane to give white plates of *di-μ-chloro-bis*[p-*tolyl*(*triethylphosphine*)*platinum*(II)] (0.88 g, 41%; 65% based on unrecovered starting material) (see Table 1). The $^{31}P-\{^1H\}$ spectrum of the mother liquor showed the presence of another product, δ 125.9 p.p.m. [^1J(Pt–P) 2 800 Hz], identified by comparison with an authentic sample as *trans*-$[Pt(C_6H_4Me$-*p*$)Cl(PEt_3)_2]$.

TABLE 4

Physical and spectroscopic properties of *cis*-$[Pt(C_2H_4)Cl_2L]$ and *cis*-$[Pt(CO)Cl_2L]$ complexes

Complex	M.p. (θ_c/°C)	I.r. data (cm^{-1})[a] ν(Pt–Cl)	ν(CO)	$^{31}P-\{^1H\}$ n.m.r.[b] δ/p.p.m.	^1J(Pt–P)/Hz	Notes
$[Pt(C_2H_4)Cl_2(PEt_3)]$	130—134	280, 322		127.4	3 042	*c*
$[Pt(C_2H_4)Cl_2(PPr_3)]$	139—143	295, 335		136.2	3 025	*d*
$[Pt(C_2H_4)Cl_2(PMe_2Ph)]$	230—234	303, 341		150.6	3 081	*e*
$[Pt(C_2H_4)Cl_2(PEt_2Ph)]$	164—170	295, 331		131.1	3 079	*f*
$[Pt(CO)Cl_2(PEt_3)]$	136	310, 357	2 100	117.6	2 781	*g*
$[Pt(CO)Cl_2(PMe_2Ph)]$	188—191		2 108	150.4	2 839	*h*

[a] Nujol mulls, except for $[Pt(CO)Cl_2(PMe_2Ph)]$ in $CHCl_3$. [b] In CH_2Cl_2, relative to $P(OMe)_3$ in C_6D_6. [c] In ^{1}H n.m.r. in $CHCl_3$: τ 5.86 ($PtCH_2$), $^2J(PtCH_2)$ 61.8 Hz. [d] In ^{1}H n.m.r. in $CHCl_3$: τ 5.68 ($PtCH_2$), $^2J(PtCH_2)$ 67.0 Hz (lit.,[15] m.p. 138—141 °C). [e] Not sufficiently soluble in $CHCl_3$ for ^{1}H n.m.r. spectra. [f] In ^{1}H n.m.r.: τ 5.93 ($PtCH_2$), $^2J(PtCH_2)$ 61 Hz. [g] Lit.,[15] m.p. 134—136 °C; ν(CO) at 2 100 cm^{-1}. [h] In ^{1}H n.m.r.: τ 7.76 (*trans*-P–CH_3); $|^2J(PtCH) + {}^4J(PPtPCH)|$ 12.3 and ^3J(PtPCH) 36.0 Hz (lit.,[16] m.p. 184—191 °C).

Reaction of cis-$[Pt(C_2H_4)Cl_2(PEt_3)]$ *with Diphenylmercury*.—Addition of diphenylmercury (0.77 g, 2.2 mmol) to a suspension of *cis*-$[Pt(C_2H_4)Cl_2(PEt_3)]$ (0.47 g, 2.15 mmol) in dichloromethane (15 cm^3) immediately produced a yellow solution. The solution was stirred at room temperature for 5 h, during which time a precipitate of chloro(phenyl)mercury(II) appeared. Filtration, evaporation of the solvent, and removal of the remaining HgPhCl by sublimation at 90 °C (0.01 mmHg) gave a residue, which was dissolved in chloroform. The solution was stirred with charcoal for 0.5 h and filtered. Addition of pentane gave white *di-μ-chloro-bis*[*phenylbis*(*triethylphosphine*)*platinum*(II)] (0.215 g, 44%), m.p. 160 °C (decomp.), ν(Pt–Cl) at 286 cm^{-1} (Found: C, 33.8; H, 4.7. Calc. for $C_{24}H_{40}Cl_2P_2Pt_2$: C, 33.85; H, 4.7%). The $^{31}P-\{^1H\}$ n.m.r. spectrum indicated the presence of both the *cis* (85%), δ 130.8 p.p.m. [^1J(Pt–P) 4 780 Hz], and the *trans* isomer (15%), δ 131.4 p.p.m. [^1J(Pt–P) 4 734 Hz].

Reactions of cis-$[Pt(CO)Cl_2L]$ (L = PEt_3 *or* PMe_2Ph) *with Aryltrimethyltin Compounds*.—(*a*) (*p*-Methoxyphenyl)trimethyltin (0.26 g, 0.97 mmol) in dichloromethane (10 cm^3) was added dropwise with stirring to a solution of *cis*-$[Pt(CO)Cl_2(PEt_3)]$ (0.40 g, 0.97 mmol) in dichloromethane (15 cm^3). The resulting yellow solution was stirred at room temperature for 2 h, and the solvent was removed to leave an orange wax which was crystallized from chloroform–pentane to give pale yellow *di-μ-chloro-bis*[(p-*methoxybenzoyl*)(*triethylphosphine*)*platinum*(II)] (0.41 g, 87%) (see Table 1).

(*b*) A similar procedure using trimethyl(*p*-t-butylphenyl)tin and *cis*-$[Pt(CO)Cl_2(PMe_2Ph)$ gave pale yellow *di-μ-chlorobis*[(*dimethylphenylphosphine*)(p-*t-butylbenzoyl*)*platinum*(II)] (67%) (see Table 1).

(*c*) In several cases the *cis*$[Pt(CO)Cl_2L]$ complexes were not isolated; carbon monoxide was passed through the solution of $[Pt_2Cl_4L_2]$ until reaction was complete, and the $SnRMe_3$ compound was then added as above.

Reaction of $[Pt_2(C_6H_4Me$-*p*$)_2Cl_2(PEt_2Ph)_2]$ *with cod*.—A solution of $[Pt_2(C_6H_4Me$-*p*$)_2Cl_2(PEt_2Ph)_2]$ (0.20 g, 0.205 mmol) and an excess of cod (0.4 cm^3) in chloroform (10 cm^3) was heated under reflux for 9 h then set aside overnight. Solvent was removed *in vacuo* and pentane (5 cm^3) was added to give a white solid, which was filtered off, washed with

---

[15] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.

[16] A. C. Smithies, M. Rychek, and M. Orchin, *J. Organometallic Chem.*, 1968, **12**, 199.

[17] C. Eaborn, H. L. Hornfeld, and D. R. M. Walton, *J. Organometallic Chem.*, 1967, **10**, 529.

pentane, and identified as *chloro*(*cyclo-octadiene*)(p-*tolyl*)-*platinum*(II) 0.082 g, 0.19 mmol), m.p. 173—176 °C (decomp.), ν(Pt–Cl) at 322 cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 4.36 [t, olefin protons *trans* to R, ^2J(Pt–CH) 31 Hz], 5.51 [t, olefin protons *trans* to Cl, ^2J(Pt–CH) 73 Hz], 7.63 (m, CH_2), 7.81 (s, CH_3), and 2.60—3.33 (m, C_6H_4) (Found: C, 41.7; H, 4.6. $C_{15}H_{19}ClPt$ requires C, 41.9; H, 4.6%). The pentane mother liquors were evaporated to give a colourless oil, which was crystallized from water–methanol to give needles of trans-*chlorobis*(*diethylphenylphosphine*)(p-*tolyl*)*platinum*(II) (0.091 g, 0.14 mmol), m.p. 83 °C, ν(Pt–Cl) at 275 cm^{-1}. N.m.r. spectra: ^1H in $CDCl_3$, τ 7.86 (s, CH_3); $^{31}P\{^1H\}$ in CH_2Cl_2, δ 126.5 p.p.m., [^1J(Pt–P) 2 881 Hz] (Found: C, 49.6; H, 5.9. $C_{27}H_{37}ClP_2Pt$ requires C, 49.6; H, 5.7%).

Reaction of $[Pt_2(2\text{-}C_8H_5O)_2Cl_2(PMe_2Ph)_2]$ *with Triphenylarsine.*—Triphenylarsine (0.055 g, 0.18 mmol) was added to a suspension of $[Pt_2(2\text{-}C_8H_5O)_2Cl_2(PMe_2Ph)_2]$ (0.085 g, 0.087 mmol) in benzene (15 cm^3). The complex dissolved within 1 min to give a colourless solution which was left at room temperature for 0.5 h. The solvent volume was reduced *in vacuo* and pentane was added to give colourless crystals of trans-(2-*benzo*[b]*furyl*)*chloro*(*dimethylphenylphosphine*)(*triphenylarsine*)*platinum*(II) (0.09 g, 65%), m.p. 205—215 °C (decomp.), ν(Pt–Cl) at 303 cm^{-1} (Found: C, 52.1; H, 4.0. $C_{34}H_{31}AsClOPPt$ requires C, 51.6; H, 3.95%).

Reaction of $[Pt_2(C_6H_4Me\text{-}p)_2Cl_2(PEt_3)_2]$ *with Pyridine.*—A procedure analogous to that of the preceding experiment gave *chloro*(*pyridine*)(p-*tolyl*)(*triethylphosphine*)*platinum*(II) (76%), m.p. 133 °C (decomp.), ν(Pt–Cl) at 278 (Cl *trans* to C_5H_5N) and 265 cm^{-1} (Cl *trans* to PEt_3)(Found: C, 42.0; H, 5.2. $C_{18}H_{27}NPPt$ requires C, 41.7; H, 5.2%).

Reaction of $[Pt_2(COC_6H_4OMe\text{-}p)_2Cl_2(PEt_3)_2]$ *with Sodium Iodide.*—When an excess of sodium iodide (0.1 g) was added to the yellow solution of $[Pt_2(COC_6H_4OMe\text{-}p)_2Cl_2(PEt_3)_2]$ (0.15 g, 0.165 mmol) in acetone (25 cm^3) the colour immediately darkened and a fine white precipitate appeared. This was filtered off, and the filtrate was evaporated to leave an orange solid, which was washed with water, dried, and dissolved in chloroform. The solution was filtered through Celite and pentane was added to give orange crystals of *di-μ-iodo-bis*[(p-*methoxybenzoyl*)(*triethylphosphine*)-*platinum*(II)] (0.165 g, 92%), m.p. 155—156 °C (decomp.), ν(CO) at 1 612 cm^{-1}. N.m.r. spectra: ^1H in $CDCl_3$, τ 6.17 (s, OMe); $^{31}P\text{-}\{^1H\}$ in CH_2Cl_2, (*i*) *trans* isomer (*ca.* 51%), δ 133.8 p.p.m., [^1J(Pt–P) 4 912 Hz]; (*ii*) *cis* isomer (*ca.* 49%), 133.8 p.p.m. [^1J(Pt–P) 4 858 Hz] (Found: C, 29.1; H, 3.9. $C_{13}H_{22}IOPPt$ requires C, 29.2; H, 3.85%).

We thank the S.R.C. for the award of a Research Studentship (to K. J. O.), and Chugoku Marine Paints Ltd. for a gift of dichlorodimethyltin.

[7/2077 *Received, 25th November*, 1977]