Interaction of Organotin Compounds with *trans*-Carbonylchlorobis(triphenylphosphine)platinum(II) Perchlorate †

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The reactions of *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] with aryltrialkyl-, tetra-aryl-, and tetra-alkyl-tin compounds (usually in dichloromethane) have been studied, mainly by ^{31}P-{^{1}H} n.m.r. spectroscopy. Tetramethyltin gives *trans*-[Pt(CO)Me(PPh$_3$)$_2$][ClO$_4$] quantitatively at room temperature. With SnRMe$_3$ compounds (R = aryl) the main product is again *trans*-[Pt(CO)Me(PPh$_3$)$_2$][ClO$_4$], but *trans*-[PtR(Cl)(PPh$_3$)$_2$] is also usually produced, and sometimes *trans*-[Pt(CO)R(PPh$_3$)$_2$][ClO$_4$]. The styryl compound Sn(CH=CHPh)Me$_3$ likewise gives mainly *trans*-[Pt(CO)Me(PPh$_3$)$_2$][ClO$_4$] together with *trans*-[Pt(CH=CHPh)Cl(PPh$_3$)$_2$]. The neutral complexes such as *trans*-[PtR(Cl)(PPh$_3$)$_2$] may arise by loss of CO from *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] to give [Pt$_2$Cl$_2$(PPh$_3$)$_4$][ClO$_4$]$_2$ followed by reaction of the latter with the excess of SnRMe$_3$. The reaction of *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] with Sn(CH$_2$CH=CH$_2$)Me$_3$ gives exclusively [Pt$_2$Cl$_2$(PPh$_3$)$_4$][ClO$_4$]$_2$ and this is also the main product from SnPh$_4$, but substantial amounts of *trans*-[PtPh(Cl)(PPh$_3$)$_2$] and *trans*-[Pt(CO)Ph(PPh$_3$)$_2$][ClO$_4$] are also formed in this case. Tetraethyltin gives initially *trans*-[Pt(CO)Et(PPh$_3$)$_2$][ClO$_4$], but this subsequently decomposes to give finally an unidentified complex. This is also formed from SnREt$_3$, SnRBu$^n{}_3$, and SnPr$^i{}_4$ [and from SnMe$_4$ and Sn(C$_6$H$_4$OMe-*p*)Me$_3$ at higher temperatures], and is suggested to be a carbonyl-bridged platinum cluster complex. In reactions of SnMe$_4$, SnPh$_4$, Sn(C$_6$H$_4$OMe-*p*)Me$_3$, and SnPhMe$_3$, with *trans*-[Pt(CO)ClL$_2$][ClO$_4$]–*cis*-[PtCl$_2$L$_2$] mixtures (L = PEt$_3$ or PMe$_2$Ph), the *cis*-[PtCl$_2$L$_2$] species (which are normally inert to such organotin reagents) are brought into reaction, and this accounts for the substantial formation of *trans*-[PtMe(Cl)L$_2$] from SnMe$_4$. The complex *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] reacts with PbPhMe$_3$ to give *trans*-[Pt(CO)Me(PPh$_3$)$_2$][ClO$_4$], *trans*-[PtMe(Cl)(PPh$_3$)$_2$], and *cis*-[PtMe$_2$(PPh$_3$)$_2$], together with *trans*-[PtPh(Cl)(PPh$_3$)$_2$], and the last complex is the sole product from PbPh$_4$. The reaction with Hg(C$_6$H$_4$Me-*p*)$_2$ gives the neutral aroyl complex *trans*-[Pt(COC$_6$H$_4$-Me-*p*)Cl(PPh$_3$)$_2$] together with *trans*-[Pt(CO)(C$_6$H$_4$Me-*p*)(PPh$_3$)$_2$][ClO$_4$] and *trans*-[Pt(C$_6$H$_4$Me-*p*)Cl(PPh$_3$)$_2$]. Sodium tetraphenylborate gives exclusively *trans*-[Pt(CO)Ph(PPh$_3$)$_2$][ClO$_4$], and is the reagent of choice for this conversion. The GeRMe$_3$ and SiRMe$_3$ compounds examined did not react.

We have previously discussed the interaction of aryltrimethyltin compounds, SnRMe$_3$, with platinum complexes of the types (*a*) [Pt(cod)Cl$_2$],[1] (*b*) [Pt(C$_2$H$_4$)Cl$_2$L],[2] (*c*) [Pt(CO)Cl$_2$L],[2] and (*d*) [Pt(cod)ClL][BF$_4$] (L = triorganophosphine, cod = cyclo-octa-1,5-diene).[3] In all these cases the greatly predominant reaction was replacement of chloride by aryl ligands to give, respectively, (*a*) [Pt(cod)R(Cl)] or [Pt(cod)R$_2$], (*b*) [Pt$_2$R$_2$Cl$_2$L$_2$], (*c*) [Pt$_2$(COR)$_2$Cl$_2$L$_2$], and (*d*) [Pt(cod)R(L)][BF$_4$]. The bis(phosphine) complexes *cis*-[PtCl$_2$L$_2$] were found not to react with aryltrimethyltin compounds;[1] since the reactions mentioned above are believed to involve electrophilic attack by the platinum centre on the tin–aryl bonds, we thought that the cationic bis(phosphine) complex *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] might undergo this type of interaction much more readily. We describe below the behaviour of this complex towards aryltrimethyltin and other organotin compounds, and show that, while the reactions occur readily, they are different in nature from those previously described, methyl groups being transferred more readily than aryl groups from tin to platinum and several products often being formed.

RESULTS AND DISCUSSION

Reactions with Aryltrimethyltin Compounds.—When a solution of *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] and an excess of *p*-methoxyphenyltrimethyltin in dichloromethane was stirred at room temperature for 2 d the pungent odour which developed was not that of the expected chlorotrimethyltin. It was identified as due to chloro(*p*-methoxyphenyl)dimethyltin. Removal of the solvent and recrystallization of the residue from CH$_2$Cl$_2$–pentane afforded a solid which gave a correct analysis for [Pt(CO)Me(PPh$_3$)$_2$][ClO$_4$]·CH$_2$Cl$_2$. This formulation, with a *trans* configuration, was confirmed by spectroscopy. The i.r. spectrum showed, in addition to characteristic bands of the perchlorate anion at 1 000 and 630 cm^{-1}, a ν(C–O) band at 2 100 cm^{-1}, and no band in the 250—360 cm^{-1} region, characteristic of ν(Pt–Cl). {The starting complex *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] has ν(C–O) and ν(Pt–Cl) bands at 2 121 and 355 cm^{-1}, respectively.} In the ^{1}H n.m.r. spectrum the dichloromethane gave a single resonance at τ 4.80, while the Pt–CH$_3$ protons gave resonances at τ 9.55, split into a 1 : 2 : 1 triplet by the *trans*-phosphine ligands [^3J(PPtCH) 8.5 Hz], together with platinum satellites [^2J(PCH) 59 Hz]. The ^{31}P-{^{1}H} n.m.r. spectrum showed a single resonance at δ 118.7 p.p.m., with platinum satellites [^1J(Pt–P) 2 616 Hz], confirming that the phosphine ligands were *trans* to one another. The molar conductivity of 83 S cm^2 mol^{-1} in nitromethane was consistent with a 1 : 1 electrolyte.

Treatment of *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] with tetramethyltin under the same conditions gave the same product, *trans*-[Pt(CO)Me(PPh$_3$)$_2$][ClO$_4$], in 95% yield. The preparation of the analogous arylplatinum complex *trans*-[Pt(CO)Ph(PPh$_3$)$_2$][ClO$_4$] was more difficult, but it was obtained in 27% yield when a solution of tetraphenyltin and *trans*-[Pt(CO)Cl(PPh$_3$)$_2$][ClO$_4$] in chloroform was heated under reflux for 10 h. Related tetrafluoroborate complexes *trans*-[Pt(CO)R(PPh$_3$)$_2$][BF$_4$] (R = Me, Ph, or H) have been obtained previously from the complexes *trans*-[PtR(Cl)(PPh$_3$)$_2$] by treatment with silver tetrafluoroborate in the presence of carbon monoxide.[4]

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† No reprints available.

Examination of the ^{31}P-$\{^1H\}$ n.m.r. spectra of the solutions obtained by treatment of *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$ with a range of $SnRMe_3$ compounds showed that the reactions were markedly more complex than was indicated by the preparative experiments described above, and a second, and in one case a third, product could be clearly distinguished. Reactions were usually carried out with *ca.* 0.05 g of the platinum complex and an excess of the organotin compound (*ca.* 0.2 cm³) in dichloromethane (1 cm³) at room temperature, and the products, with their relative yields as indicated by the peak heights in the spectrum, are shown in Table 1. It will be seen that the major product under these conditions was always the methylplatinum complex *trans*-$[Pt(CO)Me(PPh_3)_2][ClO_4]$; this formed >84% of the products, except for R = C_6H_4SMe-*p*, when it was formed in 53% yield. (The ability of the sulphur atom to co-ordinate to platinum may possibly have some influence, but it may also be relevant that the reaction was carried on for a rather longer time in this case.) Usually, a single additional product, *trans*-$[PtR(Cl)(PPh_3)_2]$, was formed, but $Sn(C_6H_4SMe$-*p*$)Me_3$ also gave a substantial amount of *trans*-$[Pt(CO)(C_6H_4SMe$-*p*$)(PPh_3)_2][ClO_4]$. There is no obvious pattern in the variation in the yield of the complex *trans*-$[PtR(Cl)(PPh_3)_2]$; certainly, in contrast to the interactions of platinum halides and aryltin compounds which we have previously studied, the ease of electrophilic cleavage of the Sn–R bond seems not to be a major factor, since (2-benzo[*b*]furyl)-trimethyltin, in which the tin–aryl bond is highly activated, and $Sn(C_6H_4F$-*m*$)Me_3$, in which it is markedly deactivated towards attack of electrophiles, both give *trans*-$[Pt(CO)Me(PPh_3)_2][ClO_4]$ in 100% yield. The ease of transfer of methyl compared with aryl groups from tin to platinum also argues strongly against a mechanism involving electrophilic cleavage of the tin–carbon bond.

TABLE 1

Products of interaction of *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$ (1) and $SnRR'_3$ compounds, as indicated by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy.[a] Products: (2), *trans*-$[Pt(CO)Me(PPh_3)_2][ClO_4]$; (3), *trans*-$[Pt(CO)R(PPh_3)_2][ClO_4]$; (4), *trans*-$[PtR(Cl)(PPh_3)_2]$; (5), $[Pt_2Cl_2(PPh_3)_4][ClO_4]_2$;[b] (6), unidentified (see text)

		Conditions[a]		Percentage composition					
R′	R	θ_c/°C	*t*/h	(1)	(2)	(3)	(4)	(5)	(6)
Me	Ph	20	6	49	51				
	Ph	20	9	37	56				
	C_6H_4OMe-*p*	20	24		84		16		
	C_6H_4OMe-*p*	70[c]	12		15	11	45		29
	C_6H_4OMe-*o*	20	24		90		10		
	C_6H_4F-*m*	20	24		100				
	C_6H_4SMe-*p*	20	36		53	25	21		
	2-Benzo(*b*)furyl	20	24		100				
	$CH_2CH{=}CH_2$	20	5					100	
	$CH{=}CHPh$	20	5	26	51		13		
	Me	20	48		100				
	Me	40[d]	4		75				25
Ph	Ph	40[d]	6			30	30	40	
Et	Et	20	16			50			50
	Et	20	80			32			68
	Et	40	12					28[e]	57
	2-Thienyl	20	10	38		31			31
	C_6H_4Me-*p*	20	3	72			7		21
	C_6H_4Me-*p*	20	80				48		52
	C_6H_4Me-*p*	40	6			7	37		56
Pr^i	2-Thienyl	20	40	100					
Pr^i	Pr^i	40	12	33					31[f]
Bu^n	C_6H_4OMe-*p*	20	25	30		8			62

[a] In CH_2Cl_2 unless otherwise indicated; percentage compositions were determined from the peak heights of resonances. [b] ^{31}P-$\{^1H\}$ n.m.r.: δ 124.1 p.p.m., ^1J(Pt–P) 3 982 Hz. [c] After 1 h in CH_2Cl_2 at 20 °C the solvent was replaced by benzene, and reaction then carried on at 70 °C for 12 h. [d] Under reflux. [e] *trans*-$[PtCl(H)(PPh_3)_2]$ (15%) was also formed. [f] *cis*-$[PtCl_2(PPh_3)_2]$ (16%) was also formed.

Only a 15% yield of *trans*-$[Pt(CO)Me(PPh_3)_2][ClO_4]$ was obtained when the reaction involving $Sn(C_6H_4Me$-*p*$)Me_3$ was carried out in dichloromethane at 20 °C for 1 h, the solvent removed and replaced by benzene, and the mixture heated at 70 °C for 12 h. Since *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$ is virtually insoluble in benzene the reaction in this solvent may involve considerable interaction of the excess of the aryltin compound with the initial products. The major final product (45% yield) was *trans*-$[Pt(C_6H_4OMe$-*p*$)Cl(PPh_3)_2]$, but *trans*-$[Pt(CO)(C_6H_4OMe$-*p*$)(PPh_3)_2][ClO_4]$ also appeared, together with a substantial amount of a further, unidentified, product (A) (see below).

The unexpected formation of the neutral *trans*-$[PtR(Cl)(PPh_3)_2]$ species requires consideration. A possible route to this type of product would be *via* the chloride-bridged binuclear species $[Pt_2Cl_2(PPh_3)_4][ClO_4]_2$ formed by dissociation of *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$ [equation (1)]. {This dissociation is assisted by heating,

$$2\ trans\text{-}[Pt(CO)Cl(PPh_3)_2][ClO_4] \rightleftharpoons [Pt_2Cl_2(PPh_3)_4][ClO_4]_2 + 2CO \quad (1)$$

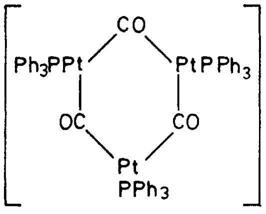
which would explain the increase in the proportion of the $[PtRCl(PPh_3)_2]$ product at higher temperatures.} Support for this proposal comes from the observation that the binuclear complex is sometimes found in the products from interaction of organotin compounds and *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$; *e.g.* it is formed in 40% yield from $SnPh_4$ at 40 °C, and in 100% yield from $Sn(CH_2CH{=}CH_2)Me_3$ at 20 °C (Table 1). When formed, the complex $[Pt_2Cl_2(PPh_3)_4][ClO_4]_2$ will react with the $SnRMe_3$ compounds (R = aryl) to give exclusively *trans*-$[PtR(Cl)(PPh_3)_2]$.[5]

Reactions with SnR_4 *and Other* $SnRR'_3$ *Compounds.*—Table 1 also shows the results of a ^{31}P-$\{^1H\}$ n.m.r. study of treatment of *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$ with $SnPh_4$ and with several SnR'_4 and $SnRR'_3$ compounds (R = aryl, R′ = alkyl). Tetraphenyltin at 40 °C gives $[Pt_2Cl_2(PPh_3)_2][ClO_4]_2$ in 40% yield, with *trans*-$[PtPh(Cl)(PPh_3)_2]$ and *trans*-$[Pt(CO)R(PPh_3)_2][ClO_4]$ each in 30% yield. The compound $Sn(CH{=}CHPh)Me_3$ reacts relatively rapidly, to give mainly the usual methylplatinum product, *trans*-$[Pt(CO)Me(PPh_3)_2][ClO_4]$, and some *trans*-$[Pt(CH{=}CHPh)Cl(PPh_3)_2]$. As noted above, the allyl compound $Sn(CH_2CH{=}CH_2)Me_3$ rapidly gave exclusively binuclear $[Pt_2Cl_2(PPh_3)_4][ClO_4]_2$, which surprisingly did not react further with the excess of the organotin compound, possibly because the total reaction time was relatively short in this case.

Tetramethyltin after 48 h at 20 °C gives exclusively *trans*-$[Pt(CO)Me(PPh_3)_2][ClO_4]$, but when the reaction is carried out at 40 °C for 4 h the unidentified product (A) is also formed, in 25% yield.

Treatment of *trans*-$[Pt(CO)Cl(PPh_3)_2][ClO_4]$ with $SnEt_4$ in dichloromethane at room temperature immediately produced a strong smell of $SnEt_3Cl$, and gave an orange colour, which darkened during several hours to deep red. Attempts to isolate the product gave only intractable red oils. When the progress of the reaction was monitored by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy it was observed that a single product was initially formed, and slowly underwent conversion into the unidentified species (A). The initially produced complex is thought, on the basis of spectroscopic data, to be the simple replacement product, *trans*-$[Pt(CO)Et(PPh_3)_2][ClO_4]$; thus in the i.r. it shows a ν(C–O) band at 2 095 cm^{-1} (compare 2 100 cm^{-1} for the analogous methyl derivative), while the ^{31}P-$\{^1H\}$ n.m.r. spectrum comprises a single phosphorus resonance with platinum satellites, δ 119.9 p.p.m. [^1J(Pt–P) 2 837 Hz]. The subsequently formed product, (A), when taken up in chloroform after removal of the dichloromethane, gave a sharp i.r. band at 2 042 and a broad band at 1 815 cm^{-1}, and an unusual ^{31}P-$\{^1H\}$ n.m.r. spectrum consisting of a single resonance at δ 117.3 p.p.m., with platinum satellites which are doublets of equal intensity and equal splitting; the frequency difference between the inner pair of satellite lines is 2 800 Hz, and that between the outer pair 2 836 Hz. Such a pattern could arise from the presence of two complexes having identical chemical shifts but slightly different couplings, but this seems unlikely since they would have to be produced in equivalent amounts. This product, (A), is also formed from SnR'_4 and $SnRR'_3$ compounds (R′ = Et, Pr^i, or Bu^n) as well as from $SnMe_4$ and $Sn(C_6H_4OMe$-*p*$)Me_3$ when these are used at higher temperatures.* From the results obtained with $SnEt_4$ the complex seems most likely to be a decomposition product of the initially formed, rather unstable, cationic alkylplatinum complexes *trans*-$[Pt(CO)R'(PPh_3)_2][ClO_4]$. An obvious candidate was the hydrido-complex *trans*-$[Pt(CO)H(PPh_3)_2][ClO_4]$, which could be formed readily by β-elimination from the corresponding ethyl-, isopropyl-, and n-butyl-platinum complexes, and possibly also formed from the methyl complex at higher temperatures. When this known hydrido-complex[6] was prepared it was found to have quite different ^{31}P-$\{^1H\}$ n.m.r. [δ 117.1 p.p.m., ^1J(Pt–P) 2 554 Hz] and solution i.r. spectra [ν(Pt–H) at 2 170, ν(C–O) at 2 078 cm^{-1}]. While it was stable in dichloromethane, on addition of $SnEt_4$ it was rapidly converted into complex (A), and so it may well be an intermediate in the formation of (A) in the reactions listed in Table 1.

The i.r. band at 1 815 cm^{-1} given by product (A) could arise from a bridging carbonyl ligand, and the value of ^1J(Pt–P) would be reasonably consistent with a carbonyl-bridged platinum(0) cluster compound. The trimeric complex $[Pt_3(CO)_3(PPh_3)_4]$ has previously been obtained from *trans*-$[Pt(CO)H(PPh_3)_2][BF_4]$[7] and other hydridoplatinum complexes in the presence of carbon monoxide,[8] and is described as an orange solid which is very soluble in most organic solvents to give a deep red solution [ν(C–O) at 1 839 and 1 784 cm^{-1}] which contains the very stable species $[Pt_3(CO)_3(PPh_3)_3]$ (B), formed by loss of one of the phosphine ligands. As reported for complex (B), our complex (A) on treatment with 1,2-bis(diphenylphosphino)ethane, dppe, gave immediate evolution of carbon monoxide and a yellow solution from which $[Pt(dppe)_2]$ was isolated. It seems that (A) and (B) are probably related, but a formulation of type (B) would not explain the i.r. band at 2 042 cm^{-1} given by (A). This could arise from either a Pt–H bond or a terminal carbonyl group, and the latter seems more likely because the ^1H n.m.r. spectrum show no Pt–H resonances in the τ 15—30 region; we cannot rule out the possibility that this band arises from the presence of a second component, since it is conceivable that two phosphine-containing entities could be present but give only one set of signals because of rapid phosphine-ligand exchange. We treated complex (A) with pyridine in dichloromethane in the hope that this would cleave the carbonyl bridges while leaving the phosphine ligands attached, but the ^{31}P-$\{^1H\}$ spectrum of the yellow solution formed indicated



(B)

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* The very low reactivity of $SnPr^i_3(2$-$C_4H_3S)$, which can be attributed to steric hindrance, is noteworthy.

that four products, all still unidentified, were formed: (*i*) (*ca.* 60%), δ 112.3 p.p.m., ^1J(Pt–P) 3 232 Hz; (*ii*) (*ca.* 20%), δ 122.8 p.p.m., ^1J(Pt–P) 3 855 Hz; (*iii*) (*ca.* 10%), δ 109.7 p.p.m., ^1J(Pt–P) 2 947 Hz; (*iv*) (*ca.* 10%), δ 114.4 p.p.m., ^1J(Pt–P) 3 046 Hz.

Reactions with Other Arylmetal Compounds.—A ^{31}P-{^{1}H} n.m.r. study was made of the reaction of *trans*-[Pt(CO)Cl(PPh_3)$_2$][ClO_4] with some compounds containing aryl–silicon, –germanium, –boron, –mercury, or –lead bonds, and the compositions of the product mixtures are shown in Table 2. Tetraphenyl-lead slowly gave *trans*-[PtPh(Cl)(PPh_3)$_2$] {probably *via* [Pt_2Cl_2(PPh_3)$_4$][ClO_4]$_2$}, while $PbPhMe_3$ reacted much more readily to give this product together with substantial amounts of *trans*-[Pt(CO)Me(PPh_3)$_2$][ClO_4], *trans*-[PtMe(Cl)(PPh_3)$_2$], and *cis*-[$PtMe_2$(PPh_3)$_2$], methyl predominating over aryl transfer from lead to platinum. The mercury compound Hg(C_6H_4Me-*p*)$_2$ also readily gave *trans*-[Pt(C_6H_4Me-*p*)Cl(PPh_3)$_2$] as the major product, together with *trans*-[Pt(CO)(C_6H_4Me-*p*)(PPh_3)$_2$][ClO_4], and also *trans*-[Pt(COC_6H_4Me-*p*)Cl(PPh_3)$_2$], the structure of which was assigned by comparison of its ^{31}P-{^{1}H} n.m.r. spectrum [δ 120.5 p.p.m., ^1J(Pt–P) 3 398 Hz] with that of analogous complexes and on the basis of the appearance of a band at 1 620 cm^{-1} in the solution ($CHCl_3$) i.r. spectrum corresponding to an aroyl carbonyl-stretching mode; this is the only case in which an aroyl complex was observed. Sodium tetraphenylborate in tetrahydrofuran–dichloromethane gave exclusively the simple replacement product *trans*-[Pt(CO)Ph(PPh_3)$_2$][ClO_4], and is clearly the reagent of choice for this transformation. The aryltrimethyl-germane and -silane used gave no reaction.

TABLE 2

Products of interaction of *trans*-[Pt(CO)Cl(PPh_3)$_2$][ClO_4] (1) and various organometallic reagents as indicated by ^{31}P-{^{1}H} n.m.r. spectroscopy.[a] Products: (2)—(4) as in Table 1; (7), *trans*-[PtMe(Cl)(PPh_3)$_2$]; (8), *cis*-[$PtMe_2$(PPh_3)$_2$]; (9), *trans*-[Pt(COR)Cl(PPh_3)$_2$]

		Percentage composition						
Reagent	*t*/h [a]	(1)	(2)	(3)	(4)	(7)	(8)	(9)
$PbPhMe_3$	5		30		35	20 [b]	15	
$PbPh_4$	24	57			43			
Hg(C_6H_4Me-*p*)$_2$	5			26	47			27 [c]
Na[BPh_4]	48 [d]			100				
Ge(2-benzo[*b*]furyl)Me_3	240	100						
Si(2-furyl)Me_3	240	100						

[a] See footnote *a* to Table 1. [b] ^{31}P-{^{1}H} n.m.r.: δ 112.7 p.p.m., ^1J(Pt–P) 1 897 Hz. [c] ^{31}P-{^{1}H} n.m.r.: δ 120.5 p.p.m., ^1J(Pt–P) 3 398 Hz. [d] In tetrahydrofuran–CH_2Cl_2.

Reactions involving Mixtures of trans-[Pt(CO)ClL_2][ClO_4] *and cis*-[$PtCl_2L_2$] (L = PEt_3 *or* PMe_2Ph).—With the intention of observing the effects of changes in the triorganophosphine ligand, we examined some reactions involving *trans*-[Pt(CO)ClL_2][ClO_4] (L = PEt_3 or PMe_2Ph). However, in each case we used a solution containing almost an equal quantity of the corresponding precursor, *cis*-[$PtCl_2L_2$], which had not been fully converted into the carbonyl complex. Since *cis*-[$PtCl_2L_2$] complexes are known not to react with $SnMe_4$ or $SnRMe_3$ compounds we assumed that they would not participate in the reactions, but the ^{31}P-{^{1}H} n.m.r. spectrum showed that they disappeared together with the *trans*-[Pt(CO)Cl(L)][ClO_4] species. The formation of substantial amounts of *trans*-[PtMe(Cl)L_2] (L = PEt_3 or PMe_2Ph) from $SnMe_4$ (see Table 3) almost certainly arises from the presence of the *cis*-[$PtCl_2L_2$] species; the explanation given above for the formation of *trans*-[PtR(Cl)(PPh_3)$_2$] from *trans*-[Pt(CO)R(PPh_3)$_2$][ClO_4] cannot apply, since, in contrast to $SnRMe_3$ species, $SnMe_4$ does not react with [Pt_2Cl_2(PPh_3)$_4$][ClO_4]$_2$. We suggest that transfer of organic ligands between platinum centres [1,8] brings the *cis*-[$PtCl_2L_2$] into the reaction, *e.g.* as in (2). In spite of this complication it seems fairly

$$\textit{trans}\text{-[Pt(CO)R}L_2\text{][ClO}_4\text{]} + \textit{cis}\text{-[PtCl}_2L_2\text{]} \longrightarrow \textit{trans}\text{-[Pt(CO)Cl}L_2\text{][ClO}_4\text{]} + \textit{trans}\text{-[PtR(Cl)}L_2\text{]} \quad (2)$$

safe to conclude from the results in Table 3 that aryl transfer from tin to platinum, at the expense of methyl transfer, is increasingly favoured on going from *trans*-[Pt(CO)Cl(PPh_3)][ClO_4] to the corresponding complexes containing PEt_3 and PMe_2Ph ligands, steric effects possibly being mainly responsible.

TABLE 3

Products of reaction of $SnRMe_3$ compounds with a mixture of *trans*-[Pt(CO)ClL_2][ClO_4] (1′) and *cis*-[$PtCl_2L_2$] (*ca.* 1 : 1) in dichloromethane at 20 °C, as indicated by ^{31}P-{^{1}H} n.m.r. spectroscopy.* Products: (2′), *trans*-[Pt(CO)MeL_2][ClO_4]; (3′), *trans*-[Pt(CO)RL_2][ClO_4]; (4′), *trans*-[PtR(Cl)L_2]

			Percentage composition			
L	R	*t*/h	(1′)	(2′)	(3′)	(4′)
PEt_3	C_6H_4OMe-*p*	13		34		66
	Ph	9	63			37
	Me	18		49		51
PMe_2Ph	C_6H_4OMe-*p*	13			22	78
	Ph	20			20	80
	Me	12		40		60

* See footnote [a] to Table 1

EXPERIMENTAL

Dry oxygen-free solvents were used, and all the reactions were carried out under dry nitrogen. The ^{31}P-{^{1}H} n.m.r. spectra (see text and Tables 4 and 5) were recorded at 40.48 MHz on a JEOL PFT 100 Fourier-transform instrument. The field was locked to the ^{2}H resonance of the external reference solution of trimethyl phosphite in C_6D_6; positive shifts are to high field of the reference. Infrared spectra were recorded with Nujol mulls unless otherwise indicated.

Preparations.—Reagents. The complex *trans*-[Pt(CO)Cl(PPh_3)$_2$][ClO_4] was prepared by passing carbon monoxide into a 1 : 1 mixture of *cis*-[$PtCl_2(PPh_3)_2$] and Na[ClO_4] in acetone;[9] it had m.p. 230—235 °C (decomp.), ν(Pt–Cl) at 355, ν(CO) at 2 105 cm^{-1}, and ^{31}P-{^1H} n.m.r. parameters of δ 120.9 p.p.m. and ^1J(Pt–P) 1 992 Hz. A sample of *trans*-[Pt(CO)Cl(PEt_3)$_2$][ClO_4] was made analogously, and had m.p. 180—192 °C (decomp.), ν(Pt–Cl) at 350 (lit.,[9] 344 cm^{-1}), ν(CO) at 2 100 cm^{-1} (lit.,[9] 2 109 cm^{-1} in $CHCl_3$), and ^{31}P-{^1H} n.m.r. parameters of δ 112.9 p.p.m. and ^1J(Pt–P) 1 819 Hz; however, for the reactions indicated in Table 3, a *ca.* 1 : 1 mixture of *cis*-[$PtCl_2(PEt_3)_2$] and *trans*-[Pt(CO)Cl(PEt_3)$_2$][ClO_4] was used. The corresponding mixture was also used in the case of *trans*-[Pt(CO)Cl(PMe_2Ph)$_2$][ClO_4]; the latter [ν(Pt–Cl) in $CHCl_3$ at 2 105 cm^{-1}] gave a ^{31}P-{^1H} n.m.r. resonance at 141.3 p.p.m. [^1J(Pt–P) 1 897 Hz].

TABLE 4

The ^{31}P-{^1H} n.m.r. parameters of products *trans*-[Pt(CO)(X)L_2][ClO_4] in dichloromethane

L	X	δ/p.p.m.	^1J(Pt–P)/Hz
PPh_3	Me	118.7	2 617
	Et	119.9	2 837
	Ph	124.9	2 654
	H	117.1	2 554
	C_6H_4SMe-*p*	124.7	2 627
	C_6H_4OMe-*p*	124.6	2 637
	C_6H_4Me-*p*	124.7	2 656
PEt_3	Me	121.1	2 314
	C_6H_4Cl-*p*	124.3	2 266
PMe_2Ph	Me	146.1	2 458
	Ph	149.8	2 459
	C_6H_4OMe-*p*	149.4	2 441

TABLE 5

The ^{31}P-{^1H} n.m.r. parameters of products *trans*-[PtCl(X)L_2] in dichloromethane

L	X	δ/p.p.m.	^1J(Pt–P)/Hz
PPh_3	Ph	115.3	3 152
	C_6H_4SMe-*p*	112.0	2 991
	C_6H_4OMe-*o*	116.5	3 130
	C_6H_4OMe-*p*	115.9	3 169
	H	117.7	3 008
	Cl	126.3	3 679
PEt_3	Me	124.2	2 820
	Ph	126.0	2 793
	C_6H_4Cl-*p*	126.1	2 744
	Cl	131.0	3 508
PMe_2Ph	Me	142.4	2 891
	Ph	145.6	2 869
	C_6H_4OMe-*p*	145.2	2 857
	Cl	154.9	3 550

trans-*Carbonylmethylbis*(*triphenylphosphine*)*platinum*(II) *perchlorate*. (*i*) An excess of *p*-methoxyphenyltrimethyltin (0.4 cm^3) was added to a solution of *trans*-[Pt(CO)Cl(PPh_3)$_2$]-[ClO_4] (0.28 g) in dichloromethane (10 cm^3), and the mixture was stirred at room temperature for 2 d. Solvent was removed to leave a pale orange oil, which was recrystallized from CH_2Cl_2–n-pentane to give the required *product* containing one molecule of CH_2Cl_2 of crystallization (0.205 g, 67%), m.p. 208—209 °C (decomp.), ν(CO) at 2 100 cm^{-1}. N.m.r. spectra: ^1H in $CDCl_3$, τ 9.55 [t, PtMe, ^2J(Pt–CH) 59 Hz, ^3J(PPtCH) 8.5 Hz] and 4.80 (s, CH_2Cl_2); ^{31}P-{^1H}, δ 118.7 p.p.m., ^1J(Pt–P) 2 616 Hz (Found: C, 49.6; H, 3.8. $C_{39}H_{35}Cl_3O_5P_2Pt$ requires C, 49.5; H, 3.7%).

(*ii*) A similar procedure starting from tetramethyltin gave the same product in 95% yield.

trans-*Carbonylphenylbis*(*triphenylphosphine*)*platinum*(II) *perchlorate*. A solution of *trans*-[Pt(CO)Cl(PPh_3)$_2$][ClO_4] (0.26 g, 0.29 mmol) and tetraphenyltin (0.15 g, 0.35 mmol) in chloroform (25 cm^3) was heated under reflux for 10 h. The cooled solution was filtered through Celite, and solvent was removed *in vacuo*. The yellow oil was recrystallized from dichloromethane–hexane to give the required *product* (0.072 g, 27%), m.p. 203—206 °C (decomp.), ν(CO) at 2 103 cm^{-1}; ^{31}P-{^1H} n.m.r., δ 124.5 p.p.m., ^1J(Pt–P) 2 646 Hz (Found: C, 56.0; H, 3.9. $C_{43}H_{35}ClO_5PtP$ requires C, 55.9; H, 3.8%).

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.

[8/355 *Received*, 27*th February*, 1978]

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