Preparation of Arylplatinum(II) Complexes. The Interaction of Dichloro-(η-cyclo-octa-1,5-diene)platinum(II) and Aryltrimethylstannanes

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One or both chloride ligands of [Pt(cod)Cl_2] (cod = cyclo-octa-1,5-diene) can be readily and selectively replaced by aryl groups by treatment of the complex with aryltrimethylstannanes in dichloromethane or *sym*-tetrachloroethane. Use of 1 mol of $SnMe_3R$ usually gives the monoaryl complexes in high yield [*e.g.* R = 2-furyl, 2-thienyl, benzofuran-2-yl, 2-benzothienyl, 1,2-dihydrobenzocyclobuten-3-yl, or C_6H_4X (X = H, *p*-MeO, *p*-Cl, *p*-F, *p*-Me_3Si, or *p*-Me)], but for R = η^6-*p*-$MeC_6H_4Cr(CO)_3$ the diaryl complex is formed. Use of ⩾2 mol of $SnMe_3R$ gives the diaryl complexes in good yield [*e.g.* R as above, plus C_6H_4X (X = *o*-MeO, *m*-MeO, *m*-F_3C, *p*-Br, *m*-F, *m*-Cl, and *p*-O_2N)], but, for steric reasons, with R = $C_6H_2Me_3$-2,4,6 only the monoaryl complex is formed. The reactivity of the $SnMe_3R$ compounds generally parallels the ease of electrophilic substitution at the corresponding R–H bonds. The arylation method has substantial advantages over those using aryl Grignard or lithium reagents. Aryl compounds, MMe_3R, of other Group 4 metals undergo analogous reactions, the reactivity decreasing in the sequence (M =) Pb > Sn ⩾ Ge > Si. While mixed diaryl complexes can sometimes be made in good yield {*e.g.* [Pt(cod)(2-C_4H_3S)(2-C_4H_3O)] from [Pt(cod)(2-C_4H_3S)Cl] and $SnMe_3$(2-C_4H_3O)}, such preparations can be complicated by exchange of aryl groups between platinum centres; *e.g.* (*i*) reaction of [Pt(cod)(2-$C_4H_3S)_2$] with [Pt(cod)Cl_2] followed by addition of 1,2-bis(diphenylphosphino)ethane (dppe) gives [Pt(2-C_4H_3S)Cl(dppe)] in *ca.* 100% yield, (*ii*) [Pt(cod)(2-$C_8H_5O)_2$] and [Pt(cod)(C_6H_4Cl-*m*$)_2$] similarly give some [Pt(2-C_8H_5O)(C_6H_4Cl-*m*)(dppe)], and (*iii*) [Pt(cod)(3-C_8H_7)Cl] and $SnMe_3$(C_6H_4Me-*p*) similarly give some [Pt(3-$C_8H_7)_2$(dppe)] and [Pt(C_6H_4Me-*p*$)_2$(dppe)] (3-C_8H_7 = 1,2-dihydrobenzocyclobuten-3-yl). The olefin ligand is readily displaced from the aryl complexes by neutral ligands, and a wide range of [PtR(Cl)L_2] and [PtR_2L_2] complexes with L = ½ dppe or PPh_3 have been made. The i.r. and ^1H, $^{13}C-\{^1H\}$, and $^{31}P-\{^1H\}$ n.m.r. spectra of the products are discussed. For *cis*-[Pt(C_6H_4X-*p*$)_2(PPh_3)_2$] complexes the values of ^1J(Pt–P) show a good correlation with σ_I constants. The norbornadiene (nbd) complex [Pt(nbd)Cl_2] reacts with $SnMe_3$(2-C_4H_3O) to give [Pt(2-C_4H_3O)(nbd)Cl] in 91% yield, but the corresponding palladium complex [Pd(nbd)Cl_2] reacts with $SnMe_3R$ (R = C_6H_4OMe-*p* or C_6H_4Me-*p*) to give a dimeric chloride-bridged complex in which the aryl group is attached to the organic ligand.

DICHLOROBIS(TRIORGANOPHOSPHINE)PLATINUM complexes [$PtCl_2L_2$] react with $SnMe_3R$ compounds to give complexes [PtCl(R)L_2] (R = CH=CH_2, CF=CF_2, or C≡CPh) or [PtR_2L_2] (R = CF_2=CF_2 or C≡CPh).[1] The ease of reaction increases in the order (R =) CH_2=CH_2 < CF=CF_2 < C≡CPh [and this order applies also to oxidative addition of $SnMe_3$–R species to platinum(0) complexes].[2] No reaction takes place between *cis*-[$PtCl_2(PMe_2Ph)_2$] and $SnMe_3(CH_2SiMe_3)$ even on prolonged refluxing in tetrahydrofuran.[1]

We were interested in the possibility of utilizing aryltin compounds for attaching aryl groups to platinum, and we have found that while $SnMe_3R$ (R = aryl) compounds do not react (or react only very slowly) with bis(phosphine) complexes [$PtCl_2(PR_3)_2$] they do bring about arylation of the cyclo-octa-1,5-diene (cod) complex [Pt(cod)Cl_2], to give [Pt(cod)(R)Cl] and [Pt(cod)R_2].[3] Ligand-replacement reactions can subsequently be used to give the corresponding bis(phosphine) and other complexes.

TABLE 1

Interaction of [Pt(cod)Cl_2] and $SnMe_3R$ in 1 : 1 mol ratio

R	θ_c/°C	Method [a]	Yield (%) of [Pt(cod)(R)Cl] [b]
2-C_4H_3S (2-thienyl)	20	*A* [c]	98
2-C_4H_3O (2-furyl)	20	*A* [c]	71
2-C_8H_5S (2-benzothienyl)	20	*A* [c]	82
2-C_8H_5O (benzofuran-2-yl)	20	*A* [c]	91
Ph	40	*B* [c]	80
C_6H_4OMe-*p*	40	*B* [d]	83
$C_6H_4SiMe_3$-*p*	40	*B* [e]	80
C_6H_4Me-*p*	40	*B* [e]	66
$C_6H_2Me_3$-2,4,6	100	*C* [d]	72
C_6H_4F-*p*	100	*C* [d]	74
C_6H_4Cl-*p*	100	*C* [c]	73
3-C_8H_7 (1,2-dihydrobenzocyclobuten-3-yl)	40	*B* [d]	91
η-*p*-$MeC_6H_4Cr(CO)_3$	40	*B* [e]	*f*

[a] For the meanings of *A*, *B*, and *C*, see Experimental section. Reactions were carried out for 12 h in CH_2Cl_2, except for those at 100 °C which were in $C_2H_2Cl_4$. [b] After recrystallization. [c] Recrystallization from chloroform–diethyl ether. [d] Recrystallization from chloroform–pentane. [e] Recrystallization from benzene–octane. [f] The product was [Pt(cod){η-*p*-$MeC_6H_4Cr(CO)_3\}_2$] (32%).

Aryltrimethylstannanes with a wide range of aryl groups have been shown to react with [Pt(cod)Cl_2] in dichloromethane or, in the case of the less reactive tin compounds, *sym*-tetrachloroethane. The conditions used and results of the reactions are shown in Tables 1 and 2. With one exception, use of a one molar proportion of the aryltrimethylstannane, $SnMe_3R$, gave the monoarylplatinum complex [Pt(cod)(R)Cl] in good yield. Use of two or more molar proportions of $SnMe_3R$, again with one exception, gave the diarylplatinum complexes [Pt(cod)R_2] in good yields. The exceptions arose for: (*i*) R = $Cr(CO)_3$(η-C_6H_4Me-*p*) when use of only one molar proportion of the tin compound gave exclusively the [Pt(cod)R_2] species; and (*ii*) R = $C_6H_2Me_3$-2,4,6 when even with 2.5 mol of the tin compound only the monoarylplatinum species [Pt(cod)(R)Cl] was produced, no doubt because of steric hindrance. (In this case, even the preparation of the monoaryl complex from the

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[1] C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometallic Chem.*, 1973, **60**, C70; C. J. Cardin, D. J. Cardin, and M. F. Lappert, *J.C.S. Dalton*, 1977, 767.

[2] C. Cetinkaya, M. F. Lappert, J. McMeeking, and D. E. Palmer, *J.C.S. Dalton*, 1973, 1202.

[3] C. Eaborn, K. J. Odell, and A. Pidcock, *J. Organometallic Chem.*, 1975, **96**, C38.

mesityltin compound required prolonged reaction at higher temperatures.) It is likely that, in the presence of more than 2 mol of the aryltin reagent, diaryl complexes are usually formed virtually quantitatively, and that the yields of the isolated products are lowered by mechanical losses, since in cases in which 1,2-bis(diphenylphosphino)ethane (dppe) or PPh_3 was added to the reaction mixture from the diarylations and the $^{31}P\text{-}\{^1H\}$ spectra were recorded the expected $[PtR_2L_2]$ species (L = PPh_3 or $\frac{1}{2}$dppe) was usually the only phosphineplatinum complex present in significant amounts. This applied even in the electronically unfavourable case of R = $C_6H_4NO_2$-*p* after reaction for 8 h at 100 °C.

TABLE 2

Interaction of $[Pt(cod)Cl_2]$ and $SnMe_3R$ in 1 : 2 mol ratio

R	θ_c/°C	Method [a]	Yield (%) of $[Pt(cod)R_2]$ [b]
2-C_4H_3S	20	*A* [c]	94
2-C_4H_3O	20	*A* [d]	85
2-C_8H_5O	20	*A* [c]	77
η-*p*-$MeC_6H_4Cr(CO)_3$	20	*A* [e]	50
Ph	40	*B* [c]	84
C_6H_4OMe-*p*	40	*B* [c]	79
C_6H_4OMe-*o*	40	*B* [c]	73
C_6H_4OMe-*m*	40	*B* [c]	94
$C_6H_4SiMe_3$-*p*	40	*B* [e]	58
C_6H_4Me-*p*	100	*C* [d]	70
C_6H_4Br-*p*	40	*B* [c]	73
C_6H_4F-*m*	100	*C* [d]	71
C_6H_4Cl-*m*	40	*B* [c]	87
$C_6H_4CF_3$-*m*	100	*C* [d]	60
3-C_8H_7	40	*B* [d]	67
$C_6H_4NO_2$-*p*	40	*g,h*	
C_6H_4Br-*m*	40	*g,i*	
C_6H_4Cl-*p*	40	*g,i*	
C_6H_4Ph-*p*	40	*g,i*	
$C_6H_3(CF_3)_2$-3,5	40	*g,i*	

[a] For meanings of *A*, *B*, and *C*, see Experimental section. Unless otherwise stated, reactions were carried out for 12 h in CH_2Cl_2, except for those at 100 °C which were in $C_2H_2Cl_4$. [b] After recrystallization. [c] Recrystallization from chloroform–diethyl ether. [d] Recrystallization from chloroform–pentane. [e] Recrystallization from benzene–octane. [f] After 3 h the major product was [Pt(cod)(Ph)Cl]. [g] Reactions for 8 h; the products were not isolated but conversion into the corresponding PPh_3 or dppe complexes, and characterization by $^{31}P\text{-}\{^1H\}$ n.m.r. spectra showed they had been formed in high yield. [h] At 100 °C. [i] At 40 °C.

This new arylation procedure is especially attractive because the other product, chlorotrimethylstannane, is soluble in solvents such as diethyl ether and pentane, and any traces of it are readily removed, together with any unchanged $SnMe_3R$, by appropriate washing of the platinum complex. It is considerably better than the usual use of Grignard or organolithium reagents, because the latter are less selective, and tend to give substantial amounts of the $[Pt(cod)R_2]$ complexes even when used in less than stoicheiometric proportion, and in order to make the monoaryl complex it is usual to prepare the diaryl complex and then cleave off one aryl group with hydrogen chloride.[4] Furthermore, work-up of the product from reactions involving Grignard or organolithium reagents usually involves a hydrolysis step to destroy any residual reagents, and this can cause complications.[5] Especially important is that aryltin compounds can be used in cases in which the corresponding Grignard or lithium reagents are not available. Three examples in our study were: (*a*) R = $C_6H_4NO_2$-*p*, for which MgRX or LiR species are unobtainable; * (*b*) R = $Cr(CO)_3(\eta\text{-}C_6H_4Me\text{-}p)$ for which MgRX or LiR species are again unknown; and (*c*) R = 1,2-dihydrobenzocyclobuten-3-yl (3-halogeno-1,2-dihydrobenzocyclobutenes, the precursors of MgRX or LiR, are obtainable only with great difficulty, while metallation of 1,2-dihydrobenzocyclobutene gives a complex mixture of organolithium species [6]).†

From the times and temperatures needed for the reactions it is clear that the most reactive $SnMe_3R$ compounds are those with R = 2-furyl, 2-thienyl, benzofuran-2-yl, and 2-benzothienyl. Furthermore, within the $SnMe_3(C_6H_4X)$ series, electron release by X facilitates, and electron withdrawal by X retards, reaction; thus when $[Pt(cod)Cl_2]$ was treated for 1 h in dichloromethane with 2.5 mol of $SnMe_3(C_6H_4X)$ (X = *p*-OMe, H, or *m*-CF_3), the diaryl complex $[Pt(cod)(C_6H_4X)_2]$ was formed in 80% yield for X = *p*-OMe and the monoaryl complex [Pt(cod)(Ph)Cl] in 70% yield for X = H, while no product was obtained for X = *m*-CF_3. Prolonged reaction at higher temperature gave the diaryl species in 60% yield for X = *m*-CF_3.

The sequence of reactivity is wholly consistent with the hypothesis that replacement of the aryl–tin by the aryl–platinum bond can be regarded as an electrophilic aromatic substitution (aromatic platinodestannylation), as can be confirmed by comparison with the known reactivity sequences in, say, acid-catalyzed protodetritiation,[7] protodesilylation,[8] and protodestannylation,[9] and (except when there is steric hindrance, as with R = $C_6H_2Me_3$-2,4,6, for which a very high reactivity would be expected on electronic grounds) the reactivities of other $SnMe_3R$ compounds in the platinum arylation can usually be confidently predicted.

Also consistent with the view that the reaction may be regarded as an electrophilic aromatic substitution are the results (Table 3) of a brief study of the reactivities of $[Pt(cod)Cl_2]$ towards a range of MMe_3R compounds (M = Si, Ge, or Pb) present in a *ca.* 4 mol proportion.

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* Because only a small amount of trimethyl(*p*-nitrophenyl)stannane was available we did not attempt to isolate $[Pt(cod)(C_6H_4NO_2\text{-}p)_2]$ but instead converted it into the corresponding bis(phosphine) derivative $[Pt(C_6H_4NO_2\text{-}p)_2(PPh_3)_2]$, which was examined in solution only.

† 1,2-Dihydrobenzocyclobutene is the IUPAC name for the compound usually called benzocyclobutene.

[4] U. Belluco, 'Organometallic and Coordination Chemistry of Platinum,' Academic Press, London and New York, 1974, pp. 224—225; F. R. Hartley, 'Chemistry of Platinum and Palladium,' Applied Science Publishers, London 1973, pp. 325—327; R. J. Cross, *Organometallic Chem. Rev.*, 1967, **2**, 97.

[5] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[6] C. Eaborn, A. A. Najam, and D. R. M. Walton, *J.C.S. Perkin I*, 1972, 2481.

[7] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

[8] C. Eaborn, Z. Lasocki, and J. A. Sperry, *J. Organometallic Chem.*, 1972, **35**, 245.

[9] C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542.

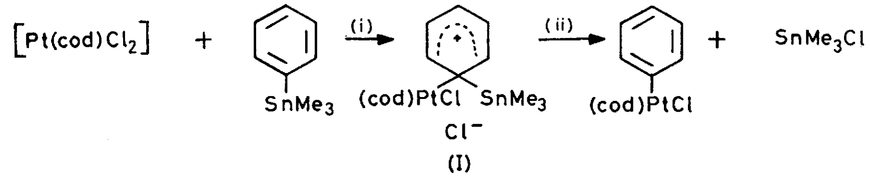
For M = Si, only the most active aryl groups are transferred to platinum; thus even after 30 h at 90 °C, no product was obtained for R = C_6H_4OMe-*p*, but for R = 2-thienyl a 15% yield of the monoarylplatinum complex was obtained. For M = Ge and R = 2-furyl, a little monoaryl product was formed in 40 h even at 20 °C, but 23 h at 90 °C were required to give a good yield of the diaryl product. In contrast, for M = Pb, even with R = Ph, precipitation of chlorotrimethylplumbane seemed complete within a few minutes at 20 °C, and after 1 h the diaryl product was isolated in good yield. These results, together with those in Table 2, show that the reactivity sequence for MMe_3R compounds is Pb > Sn ≫ Ge > Si, in agreement with that for reactions with other electrophiles, *e.g.* acids.[10]

TABLE 3

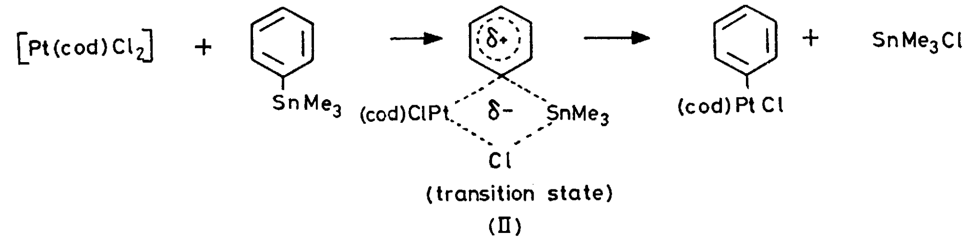
Interaction of $[Pt(cod)Cl_2]$ and MMe_3R in 1 : 4 mol ratio

M	R	Conditions	Product	Yield (%)
Si	C_6H_4OMe-*p*	$C_2H_2Cl_4$, 90 °C, 30 h		*
Si	2-C_4H_3S	$C_2H_2Cl_4$, 90 °C, 30 h	[Pt(cod)(R)Cl]	15
Ge	2-C_8H_5O	CH_2Cl_2, 20 °C, 40 h	[Pt(cod)(R)Cl]	10
Ge	2-C_8H_5O	$C_2H_2Cl_4$, 90 °C, 23 h	$[Pt(cod)R_2]$	68
Pb	Ph	CH_2Cl_2, 20 °C, 1 h	$[Pt(cod)R_2]$	85

* No detectable reaction.



(1)



(2)

We also found that diphenylmercury (2.7 mol) gave a precipitate of phenylmercury(II) chloride within 20 min at room temperature, and after 2 h this compound was isolated in 96% yield and the monoarylplatinum complex in 74% yield, indicating that $HgPh_2$ is comparable in reactivity to $PbMe_3Ph$. When sodium tetraphenylborate (1.66 mol) was used for arylation in dichloromethane–tetrahydrofuran (thf) at 60 °C some sodium chloride was precipitated within 5 min, and after 2 h $[Pt(cod)Ph_2]$ was isolated in 41% yield, suggesting that the borate is roughly comparable in reactivity to $SnMe_3Ph$.

Reaction mechanisms involving initial oxidative addition of the aryl and $SnMe_3$ moieties to platinum are conceivable but very unlikely, since such additions occur only slowly even with platinum(0) species, and, furthermore, there is no reason to believe that such reactions would follow a sequence appropriate to electrophilic aromatic substitution as the aryl group is varied. We suggest that the arylation can be regarded as analogous to, say, aromatic halogenomercuration or (halogenomercuri)de-silylation or -stannylation. Thus it may proceed through a Wheland intermediate (I) as in sequence (1), but it is impossible to make a firm choice between this and a concerted four-centre process (2) in which a substantial degree of positive charge lies on the aromatic ring in the transition state (II), especially since in the media used the chloride obtained in step (i) of route (I) would probably remain within an ion pair and leave with the $SnMe_3$ group in step (ii). These proposals are also in keeping with the fact that the second Pt–Cl bond is normally replaced markedly less readily than the first, since electron withdrawal by the chlorine atoms will make the platinum centre more electrophilic in $[Pt(cod)Cl_2]$ than in [Pt(cod)(R)Cl], although steric effects are probably also important.

The high reactivity of $[Cr(CO)_3(\eta\text{-}p\text{-}MeC_6H_4SnMe_3)]$ in the platinum arylation is of interest, since $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ is usually regarded as very unreactive towards electrophilic substitution in the aromatic ring:[11,12] *e.g.* acid-catalyzed hydrogen exchange is said to be much slower in $[Cr(CO)_3(\eta\text{-arene})]$ complexes than in the corresponding free arenes.[11,12] The validity of some of the evidence was questioned by Brown and Hughes,[13] in the light of theoretical calculations by Brown and Raju[14] which predict that the $Cr(CO)_3$ group should be able to facilitate electrophilic (as well as nucleophilic)

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[13] D. A. Brown and F. J. Hughes, *Inorg. Chim. Acta*, 1967, **1**, 448.

[14] D. A. Brown and J. R. Raju, *J. Chem. Soc.* (*A*), 1966, 40; D. A. Brown, *J. Chem. Soc.*, 1963, 4389.

substitution. It is known that carbonium ions in which the positive centre is adjacent to the aromatic ring, as in $[Cr(CO)_3(\eta\text{-}C_6H_4\overset{+}{C}\!:)]$ are strongly stabilized,[15] and stability of a side-chain carbonium ion $R\overset{+}{C}\!:$ usually goes together with ease of substitution at the corresponding RH bond (*i.e.* with stabilization of the Wheland intermediate RHE^+). However, the stabilization in the case of $[Cr(CO)_3(\eta\text{-}C_6H_4\overset{+}{C}\!:)]$ may be of a special type, involving direct interaction of the metal and the carbonium-ion centre,[15,16] which would not necessarily imply stabilization of a corresponding Wheland intermediate. Certainly, we cannot take the high reactivity of $[Cr(CO)_3(\eta\text{-}p\text{-}MeC_6H_4SnMe_3)]$ in our reaction as confirming Brown and Raju's view that the complexed $Cr(CO)_3$ group should facilitate electrophilic aromatic substitutions, since there may be some special factors operating, *e.g.* direct interaction between the chromium atom and the incoming electrophile $[Pt(cod)Cl_2]$.

The formation of the diaryl complex from $[Cr(CO)_3(\eta\text{-}p\text{-}MeC_6H_4SnMe_3)]$ (1 mol) is also difficult to rationalize. The $Cr(CO)_3$ group normally withdraws electrons strongly from the arene to which it is complexed,[17] and thus the platinum centre in $[Pt(cod)\{Cr(CO)_3(\eta\text{-}p\text{-}MeC_6H_4)\}Cl]$ should be markedly more electrophilic than in most of the other [Pt(cod)(R)Cl] complexes, but it should still not be as electrophilic as that in $[Pt(cod)Cl_2]$. We cannot rule out the possibility that in this case the disproportionation of the initially formed monoarylplatinum complex to the dichloro and diaryl complexes (see below) is rapid and lies well over to the products.

Alkylation of $[Pt(cod)Cl_2]$.—If the reactions described above do, indeed, involve electrophilic cleavage of the carbon–tin bond, alkyl–tin bonds would also be expected to enter the reaction, although much less readily. Although a sensitive method of analysis was used (involving addition of PPh_3 or dppe followed by examination of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum), no methylplatinum products were detected under our conditions from the reactions of the $SnMe_3R$ compounds,* but $SnMe_3[C(SiMe_3)_3]$ gave [Pt(cod)(Me)Cl] in 30% yield during 80 h at 100 °C, while $SnMe_3(CH_2C_6H_4Me\text{-}p)$ gave $[Pt(cod)(CH_2C_6H_4Me\text{-}p)Cl]$ in 39% and [Pt(cod)(Me)Cl] in 15% yield during 15 h at 100 °C. Thus the reactivities of Sn–R species fall in the sequence aryl $\gg$ CH_2Ph > Me, which parallels the behaviour towards other electrophiles,[19] *e.g.* in cleavage by aqueous methanolic perchloric acid.[20] For the benzyl and methyl transfers a process of type (1) is, of course, impossible, and a four-centre mechanism related to process (2) seems very likely in these cases. {In comparable interactions involving bis(phosphine) complexes, *e.g.* *cis*-$[PtCl_2(PMe_2Ph)_2]$, the high reactivity of $SnMe_3(CF{=}CF_2)$ [1] shows that reactions of this general type cannot always be satisfactorily regarded as involving electrophilic substitution at the Sn–C bond.}

Interchange of Aryl Groups between Platinum Nuclei.—The mixed diaryl complex $[Pt(cod)(2\text{-}C_4H_3O)(2\text{-}C_4H_3S)]$ was isolated in 68% yield from the reaction between $[Pt(cod)(2\text{-}C_4H_3S)Cl]$ and $SnMe_3(2\text{-}C_4H_3O)$, and $[Pt(cod)(2\text{-}C_8H_5O)(C_6H_4Me\text{-}p)]$ in 65% yield from the reaction between $[Pt(cod)(2\text{-}C_8H_5O)Cl]$ and $SnMe_3(C_6H_4Me\text{-}p)$. However, it became clear that such preparations of mixed diaryl species could be complicated by aryl–aryl and aryl–chloride exchanges between platinum centres. This was revealed when the mixtures obtained from [Pt(cod)(R)Cl]–$SnMe_3R'$ interactions were treated with PPh_3 or dppe, and the composition of the resulting phosphine complexes examined by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. The results are shown in Table 4, and it will be seen, for example, that when the mixture from $[Pt(cod)(2\text{-}C_4H_3O)Cl]$ (1 mol) and $SnMe_3(2\text{-}C_4H_3S)$ (2 mol) was treated with dppe (1 mol) the expected $[Pt(2\text{-}C_4H_3O)(2\text{-}C_4H_3S)(dppe)]$ comprised only 56% of the product mixture, while $[Pt(2\text{-}C_4H_3O)_2(dppe)]$ and $[Pt(2\text{-}C_4H_3S)_2(dppe)]$ comprised *ca.* 18 and 26%, respectively. Interaction of $[Pt(cod)(C_6H_4Me\text{-}p)Cl]$ and $SnMe_3(2\text{-}C_8H_5O)$ ($2\text{-}C_8H_5O$ = benzofuran-2-yl) followed by treatment with PPh_3 gave $[Pt(C_6H_4Me\text{-}p)(2\text{-}C_8H_5O)(PPh_3)_2]$ and $[Pt(2\text{-}C_8H_5O)_2(PPh_3)_2]$ in *ca.* 2 : 1 ratio. However, from $[Pt(cod)(3\text{-}C_8H_7)Cl]$ ($3\text{-}C_8H_7$ = 1,2-dihydrobenzocyclobuten-3-yl) and $SnMe_3(2\text{-}C_4H_3S)$ only $[Pt(3\text{-}C_8H_7)(2\text{-}C_4H_3S)(PPh_3)_2]$ was obtained. We cannot be sure that the equilibrium compositions are not substantially changed by the addition of the phosphines, but the ^1H n.m.r. spectra of the initial mixtures of cod complexes were roughly consistent with compositions corresponding to those noted for the derived phosphine complexes, and in the discussion below we assume for simplicity that the exchanges involve the cod complexes only, not the subsequently formed phosphine complexes. From the limited range of results, the tendency of the aryl group in [Pt(cod)(R)Cl] to migrate (either directly to another platinum atom or *via* tin) seems to increase with the ease of electrophilic attack at the corresponding R–H bond.

Interchange of aryl groups also takes place between $[Pt(cod)R_2]$ and $[Pt(cod)Cl_2]$, and even between $[Pt(cod)R_2]$ and $[Pt(cod)R'_2]$, as Table 4 shows. {For the $[Pt(cod)R_2]$–$[Pt(cod)Cl_2]$ interactions, the results are again consistent with the assumption that the ease of

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* It was recently found that when a solution of $[Pt(cod)Cl_2]$ and $SnMe_3(C_6H_4F\text{-}p)$ (*ca.* 0.5 mol) in *sym*-tetrachloroethane was kept at 90 °C for 48 h, [Pt(cod)(Me)Cl] and $[Pt(cod)(C_6H_4F\text{-}p)Cl]$ were formed in roughly equal amounts. Furthermore, the interaction of $[Pt(cod)Cl_2]$ with $SnMe_4$ gave [Pt(cod)(Me)Cl] in 59% yield after 16 h at 100 °C; the reaction is faster in dimethyl sulphoxide, and can give $[Pt(cod)Me_2]$.[18]

[15] M. Acampora, A. Ceccon, M. D. Farra, G. Giacometti, and G. Rigatti, *J.C.S. Perkin II*, 1977, 483 and refs. therein.

[16] R. S. Bly and R. L. Veazey, *J. Amer. Chem. Soc.*, 1969, **91**, 4221.

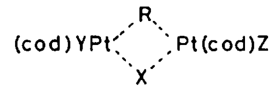
[17] See P. J. Dossor, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1974, **71**, 207 and refs. therein

[18] Z. Dawoodi, B.Sc. Thesis, University of Sussex, 1977.

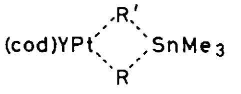
[19] J. G. A. Luijten and G. J. M. Van der Kerk, in 'Organometallic Compounds of the Group IV Elements,' vol. I, ed. A. G. MacDiarmid, Marcel Dekker, New York, 1968, part 2, pp. 140—157.

[20] R. Alexander, M. T. Attar-Bashi, C. Eaborn, and D. R. M. Walton, *Tetrahedron*, 1974, **30**, 899.

migration increases with the ease of electrophilic attack on the carbon atom of the aryl–metal bond, but we cannot be confident that the product compositions reflect the rate of migration rather than the positions of equilibria.} It seems reasonable tentatively to regard the migrations as involving a four-centre process, such as that depicted in (III), analogous to that proposed for the much slower interchange of methyl groups between *cis*-$[PtMe_2(PMePh_2)_2]$ and *cis*-$[PtCl_2(PMePh_2)_2]$.[21] We have not established whether, in the $[Pt(cod)(R)Cl]$–$SnMe_3R'$ interactions, the aryl groups migrate from platinum to tin as well as from platinum to platinum and tin to platinum, but process (IV) seems likely. The absence of any $[Pt(cod)(C_6H_4Me\text{-}p)_2]$ product from the reaction of $[Pt(cod)(C_6H_4Me\text{-}p)Cl]$ with $SnMe_3(2\text{-}C_8H_5O)$ is consistent with such an exchange, since if $[Pt(cod)(2\text{-}C_8H_5O)Cl]$ and $SnMe_3(C_6H_4Me\text{-}p)$ are formed both the $[Pt(cod)(2\text{-}C_8H_5O)Cl]$ and $[Pt(cod)(C_6H_4Me\text{-}p)Cl]$ will react rapidly with the remaining $SnMe_3(2\text{-}C_8H_5O)$, but only slowly with $SnMe_3(C_6H_4Me\text{-}p)$.



(III) X = Cl or R'



(IV)

In view of the seeming ease of the equilibration reaction $[Pt(cod)R_2] + [Pt(cod)Cl_2] \longrightarrow [Pt(cod)(R)Cl]$, the possibility arises that formation of $[Pt(cod)(R)Cl]$ from $[Pt(cod)Cl_2]$ and $SnMe_3R$ (1 mol) initially proceeds through to $[Pt(cod)R_2]$ which then undergoes relatively rapid redistribution with unchanged $[Pt(cod)Cl_2]$. If this route were followed, however, there would be no reason why reaction of the second mol of $SnMe_3R$ should be so much slower than that of the first, and so we can rule out this route as a general one, although it might occur for certain aryl groups.

While mixed diaryl complexes $[Pt(cod)(R)R']$ may sometimes be formed in high yield from $[Pt(cod)(R)Cl]$ and $SnMe_3R'$ [*e.g.* $R = 3\text{-}C_8H_7$, $R' = 2\text{-}C_4H_3S$ (see Table 4)], or isolated in good yield from the product mixture by fractional crystallization [*e.g.* $R = 2\text{-}C_4H_3S$, $R' = 2\text{-}C_4H_3O$; $R = 2\text{-}C_8H_5O$, $R' = C_6H_4Me\text{-}p$ (see above)], the occurrence of the redistributions noted above means that these reactions are unlikely always to provide a good route to such diaryl species. However, such redistributions will arise to a greater or lesser extent in treatment of a $[PtR(Cl)L_2]$ complex with any organometallic reagent containing a different aryl group.

TABLE 4

Transfer of aryl groups between platinum nuclei

	Reactants	Conditions *	L	Product composition	(%)
1 : 1	$[Pt(cod)(2\text{-}C_4H_3S)_2]$ $+[Pt(cod)Cl_2]$	12 h, 20 °C	½ dppe	$[Pt(2\text{-}C_4H_3S)(Cl)L_2]$	100
1 : 1	$[Pt(cod)(C_6H_4Cl\text{-}m)_2]$ $+[Pt(cod)Cl_2]$	12 h, 60 °C	PPh_3	$[Pt(C_6H_4Cl\text{-}m)_2L_2]$	22
				$[Pt(C_6H_4Cl\text{-}m)(Cl)L_2]$	55
				$[PtCl_2L_2]$	21
			½ dppe	$[Pt(C_6H_4Cl\text{-}m)_2L_2]$	28
				$[Pt(C_6H_4Cl\text{-}m)(Cl)L_2]$	49
				$[PtCl_2L_2]$	22
1 : 1	$[Pt(cod)(2\text{-}C_8H_5O)_2]$ $+[Pt(cod)(C_6H_4Cl\text{-}m)_2]$	20 h, 20 °C	½ dppe	$[Pt(2\text{-}C_8H_5O)(C_6H_4Cl\text{-}m)L_2]$	23
				$[Pt(2\text{-}C_8H_5O)_2L_2]$	38
				$[Pt(C_6H_4Cl\text{-}m)_2L_2]$	39
1 : 2	$[Pt(cod)(3\text{-}C_6H_7)Cl]$ $+SnMe_3(2\text{-}C_4H_3S)$	20 h, 20 °C	PPh_3	$[Pt(3\text{-}C_8H_7)(2\text{-}C_4H_3S)L_2]$	100
			½ dppe	$[Pt(3\text{-}C_8H_7)(2\text{-}C_4H_3S)L_2]$	95
				$[Pt(3\text{-}C_8H_7)_2L_2]$	5
1 : 2	$[Pt(cod)(3\text{-}C_8H_7)Cl]$ $SnMe_3(C_6H_4Me\text{-}p)$	20 h, 60 °C	½ dppe	$[Pt(3\text{-}C_8H_7)(2\text{-}C_4H_3S)L_2]$	37
				$[Pt(3\text{-}C_8H_7)_2L_2]$	12
				$[Pt(C_6H_4Me\text{-}p)_2L_2]$	51
1 : 2	$[Pt(cod)(C_6H_4Me\text{-}p)Cl]$ $+SnMe_3(2\text{-}C_8H_5O)$	18 h, 20 °C	PPh_3	$[Pt(2\text{-}C_8H_5O)(C_6H_4Me\text{-}p)L_2]$	66
				$[Pt(2\text{-}C_8H_5O)_2L_2]$	34
			½dppe	$[Pt(2\text{-}C_8H_5O)(C_6H_4Me\text{-}p)L_2]$	60
				$[Pt(2\text{-}C_8H_5O)_2L_2]$	40
1 : 2	$[Pt(cod)(2\text{-}C_4H_3S)Cl]$ $+SnMe_3(2\text{-}C_4H_3O)$	30 h, 20 °C	½ dppe	$[Pt(2\text{-}C_4H_3O)(2\text{-}C_4H_3S)L_2]$	56
				$[Pt(2\text{-}C_4H_3O)_2L_2]$	18
				$[Pt(2\text{-}C_4H_3S)_2L_2]$	26

* Reactions in CH_2Cl_2, with subsequent addition of dppe or PPh_3.

Displacement of the Diolefin of $[Pt(cod)(R)Cl]$ *and* $[Pt(cod)R_2]$ *Complexes by Neutral Ligands*.—Neutral ligands of high *trans* influence readily replace the diolefin ligand of the mono- and di-aryl cyclo-octa-1,5-dieneplatinum complexes. Kistner *et al.*[22] used somewhat forcing conditions (0.5—2 h at 138 and 80 °C, respectively) for triphenylphosphine displacement of cod from $[Pt(cod)(C_6H_4Me\text{-}p)I]$ and $[Pt(cod)(C_6H_4Me\text{-}p)_2]$, but we found that with 2 mol of PPh_3 or dppe the reaction in CH_2Cl_2 was normally complete at room temperature within 0.5 h. However, the reaction between $[Pt(cod)(C_6H_4OMe\text{-}o)_2]$ and PPh_3 was only *ca.* 40% complete after 18 h at room temperature, presumably for steric reasons, but went to completion during 1 h at reflux (*ca.* 40 °C). Refluxing for 2 h in CH_2Cl_2 was necessary even for unhindered aryl groups, for the displacement of cod by $AsPh_3$, $SbPh_3$, or bipy (2,2'-bipyridyl). Characterization data for the complexes isolated are

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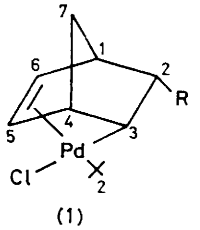
[21] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, 1975, 1810; *J. Organometallic Chem.*, 1976, **120**, C51.

[22] C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, 1963, **2**, 1255.

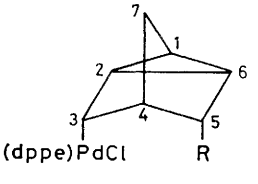
shown in Table 10. Many other dppe or bis(triphenylphosphine) complexes were generated from the cod complexes only in solution and the $^{31}P-\{^1H\}$ spectra were recorded (see Table 8). With PPh_3 ligands present, except for R = $C_6H_2Me_3$-2,4,6, the monoaryl complexes all had predominantly (>85%) *trans* configurations in solution, whereas the diaryl complexes all had exclusively *cis* configurations. Presumably, the initial displacement of cod gives *cis* products in both cases, but the monoaryl species normally readily isomerize to the thermodynamically more stable *trans* complexes in the presence of free phosphine ligand. In the case of [Pt($C_6H_2Me_3$-2,4,6)Cl(PPh_3)$_2$] in which the *cis* isomer was obtained exclusively, the bulk of the aryl group presumably hinders the isomerization.

Reactions of $SnMe_3R$ *with* [Pd(diolefin)Cl_2].—In an attempt to extend the use of the organotin reagents to arylation of palladium, [Pd(diolefin)Cl_2] complexes (diolefin = cyclo-octa-1,5-diene or dicyclopentadiene) were treated with $SnMe_3R$ (R = Ph, C_6H_4Me-*p*, or C_6H_4F-*m*) in dichloromethane at room temperature. The mixture immediately turned red then black, a black precipitate or metallic mirror of palladium metal separated, and the characteristic smell of $SnMe_3Cl$ developed. When [Pd(cod)Cl_2] and $SnMe_3Ph$ were mixed in dichloromethane at −78 °C there was no apparent decomposition and no smell of $SnMe_3Cl$, but when the mixture was allowed to warm slowly towards room temperature palladium metal again separated. G.l.c. showed that no cyclo-octadiene remained in the mixture, and revealed the presence of at least four organic derivatives.

In contrast, when a suspension [Pd(nbd)Cl_2] (nbd = norbornadiene) in dichloromethane was treated at room temperature with 1 mol of $SnMe_3R$ (R = C_6H_4OMe-*p* or C_6H_4Me-*p*), the palladium complex rapidly dissolved to give an orange solution, the smell of $SnMe_3Cl$ developed, and there was no sign of decomposition. After some hours, pentane was added and the orange solids separating were identified as the dimeric chloride-bridged complexes (1), which have the aryl group attached (in the *endo* mode) to the organic ligand. The identification was simple because Maitlis and his co-workers [23] have shown that complex (1; R = Ph) is formed from [Pd(nbd)Cl_2] and $HgPh_2$ or, better, Na[BPh_4]. Addition of dppe to complex (1; R = C_6H_4OMe-*p*) gave the corresponding nortricyclenyl derivative (2), again as described by Maitlis for the reaction with pyridine of (1; R = Ph).



(1)



(2)

The $SnMe_3R$ compounds seem superior to the corresponding HgR_2 species for these arylations; thus for R = C_6H_4OMe-*p* we obtained a 92% yield of product (1) from the tin and only a 25% yield from the mercury compound. However, Maitlis and his co-workers obtained a 75% yield of (1; R = Ph) from Na[BPh_4], and it is not clear whether the tin compounds would be generally better than boron compounds, although there will undoubtedly be cases in which $SnMe_3R$ are more readily available than the corresponding Na[BR_4] reagents.

The formation of (1) is believed to involve initial arylation at palladium followed by migration of the aryl group.[23] In contrast, the platinum complex [Pt(nbd)Cl_2] reacts with $HgPh_2$ to give the stable [Pt(nbd)(Ph)Cl] complex (and, with further HgR_2, the corresponding diarylplatinum species).[23] Consistently, we obtained [Pt(nbd)(2-C_4H_3O)Cl] in 81% yield on treatment of [Pt(nbd)Cl_2] with $SnMe_3$(2-C_4H_3O) (1 mol) in dichloromethane at room temperature.

Infrared Spectra.—The two Pt–Cl stretching frequencies of [Pt(cod)Cl_2], at 316 and 328 cm^{-1}, are replaced by a single frequency at 319—328 cm^{-1} in [Pt(cod)(R)Cl] (see Table 8). The band at 479ms cm^{-1} of [Pt(cod)Cl_2] assigned to the metal–olefin stretching frequency is shifted to lower wavenumber, *viz.* 460 cm^{-1}, in [Pt(cod)R_2], in accord with the greater *trans* influence of the aryl groups. The bands at *ca.* 480 and 440 cm^{-1} of the [Pt(cod)(R)Cl] complexes can be assigned to metal–olefin stretching modes influenced by *trans*-Cl and *trans*-R groups, respectively.

The ν(Pt–C) bands of *cis*-[PtR(Cl)L_2] and *cis*-[PtR_2L_2] (R = alkyl or aryl, L = triorganophosphine) have been reported to lie in the range 480—600 cm^{-1}, the diaryl complexes having two i.r.-active vibration modes and the monoaryl only one. However, the position is not clear for cod complexes; *e.g.* for [Pt(cod)Me_2] bands at 563 and 548 cm^{-1} were assigned to $\nu(Pt-C_{Me})$ by Kistner *et al.*,[22] while Fritz and Selman [24] say that the two stretching modes are degenerate, giving a single band at 550 cm^{-1}. We cannot identify ν(Pt–C) bands in our spectra. For several of the diaryl complexes a medium-strong doublet of separation 15 cm^{-1} appears in the 510—560 cm^{-1} range, but for some complexes (*e.g.* R = $C_6H_4CF_3$-*m*, Ph, or 2-C_4H_3S) there are no bands at 500—600 cm^{-1}, suggesting that the ν(Pt–aryl) bands are weak, and that the bands which do appear in the 510—560 cm^{-1} region may in some cases be associated with additional platinum–olefin modes or with the aromatic rings or their substituents.

The ν(C–O) values of [Cr(CO)$_3$(η-*p*-$MeC_6H_4SnMe_3$)] at 1 970 and 1 910 cm^{-1} are lowered to 1 937 and 1 869 cm^{-1} in the platinum complex [Cr(CO)$_3${η-*p*-MeC_6H_4Pt(cod)R}] suggesting that replacement of $SnMe_3$ by Pt(cod)R increases the electron density at the chromium atom.

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[23] A. Segnitz, E. Kelly, S. H. Taylor, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **124**, 113; A. Segnitz, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1973, 698.

[24] H. Fritz and L. Selman, *Z. Naturforsch.*, 1967, **B22**, 20.

Hydrogen-1 *N.M.R. Spectra*.—Details of the ^1H n.m.r. spectra of the [Pt(cod)(R)Cl] complexes are given in Table 5. The olefin protons give two distinct broad resonances each with satellites due to coupling with ^{195}Pt (34% natural abundance). The peaks associated with ^2J(Pt–CH) values of 71—78 Hz are assigned to the protons *trans* to the chloride ligand, and those (usually at lower field) associated with ^2J(Pt–CH) values of 31—34 Hz to the protons *trans* to the aryl group. The methylene proton resonances of the cyclo-octadiene moiety, centred at *ca.* τ 7.6, were complex and no attempt was made to assign platinum coupling constants.

TABLE 5

Hydrogen-1 n.m.r. data for [Pt(cod)(R)Cl] complexes [a]

	Vinyl protons		τ for protons of		
R	τ, ^2J(Pt–CH)/Hz	τ, ^2J(Pt–CH)/Hz	CH_2	aryl	others
2-C_4H_3S	4.36, 41	4.96; 72	7.59	2.5—3.6	
2-C_4H_3O	4.43, 39	4.43, 74	7.56	2.6—3.9 [b]	5.6
2-C_8H_5S	4.28, 37	4.89, 72	7.58	2.3—3.2	
2-C_8H_5O	4.42, 37	4.42, 71	7.60	2.3—3.0	
Ph	4.19, 34	5.40, 76	7.34	2.5—3.2	
C_6H_4OMe-*p*	4.17, 36	5.32, 77	7.42	2.4—3.2	6.21 [c]
C_6H_4Me-*p*	4.36, 31	5.51, 73	7.63	2.6—3.3	7.81 [d]
C_6H_4Cl-*p*	4.34, 35	5.51, 73	7.63	2.6—3.3	
$C_6H_4SiMe_3$-*p*	4.29, 31	5.46, 74	7.60	2.6—3.2	9.79 [e]
$C_6H_2Me_3$-2,4,6	4.49, 35	5.72, 73	7.52	3.3—3.5 [f]	8.87, 8.68 [d]
3-C_8H_7	4.26, 33	5.34, 75	7.56	3.2—3.6	

[a] In $CDCl_3$, with $SiMe_4$ as internal reference. [b] τ 2.72 (H^3), 3.37 (H^4), and 3.80 (H^5). [c] OCH_3. [d] CH_3. [e] $SiMe_3$. τ 2.78 (H^3)[^4J(Pt-H) 6 Hz].

Details of the ^1H n.m.r. spectra of the [Pt(cod)R_2] complexes are given in Table 6 (see also ref. 25). A single olefin resonance is observed, with ^2J(Pt–CH) 34—61 Hz, and a methylene resonance at *ca.* τ 7.5, with ^3J(Pt–CH) 16 Hz. The value of ^2J(Pt–CH) for the olefin protons *trans* to the aryl group changes little as the aryl ligand is varied, and there is no obvious pattern to the small changes which do occur.

TABLE 6

Hydrogen-1 n.m.r. data for [Pt(cod)R_2] complexes [a]

		τ for protons of		
R	Vinyl protons τ, ^2J(Pt–CH)	CH_2 [b]	aryl	aryl substituents
2-C_4H_3S	4.56, 41	7.49	2.5—3.8	
2-C_4H_3O	4.36, 40	7.50	2.5—4.1 [c]	
2-C_8H_5O	4.18, 38	7.42	2.2—4.0 [d]	
η-*p*-$MeC_6H_4Cr(CO)_3$	4.50, 39	7.39	4.6—5.2 [e]	7.91 (CH_3)
3-C_3H_7	4.94, 39	7.56	2.4—3.7	7.12 (CH_2)
Ph	4.98, 37	7.78	2.2—3.6	
C_6H_4OMe-*o*	5.00, 42 [f]	7.60 [g]	2.8—3.7	6.28 (OCH_3)[h]
C_6H_4OMe-*m*	4.98, 39	7.59	2.4—3.9	6.39 (OCH_3)
C_6H_4OMe-*p*	5.04, 37 [i]	7.47 [j]	2.3—3.6	6.28 (OCH_3)[k]
$C_6H_4CF_3$-*m*	4.96, 38	7.48	2.4—3.2	
$C_6H_4SiMe_3$-*p*	5.00, 37	7.55	2.3—3.6	9.82 ($SiMe_3$)
C_6H_4Br-*p*	5.06, 39	7.56	2.3—3.8	
C_6H_4F-*m*	4.90, 40 [l]	7.50 [m]	2.6—3.6	
C_6H_4Cl-*m*	5.00, 38	7.51	2.2—3.5	
C_6H_4Me-*p*	4.98, 38 [n]	7.57 [o]	2.3—3.6	7.86 (CH_3) [p]
$C_6H_4Bu^t$-*p*	5.00, 36	7.54	2.4—3.6	8.90 (CMe_3)

[a] In $CDCl_3$ with $SiMe_4$ as internal reference. [b] ^3J(Pt–CCH) 16 Hz. [c] τ 2.69 (H^3), 3.82 (H^4), and 4.02 (H^5). [d] τ 3.37 (H^3) [^3J(Pt–CCH) 19 Hz]. [e] *o*- and *m*-protons give quartet, τ 4.62 (H_m) and 5.14 (H_o) [$J(H_mH_o)$ 6.1 Hz]. [f] Lit.,[25] τ 4.48, 43 Hz. [g] Lit.,[25] τ 7.11. [h] Lit.,[25] τ 5.79. [i] Lit.,[25] τ 4.41, 38 Hz. Lit.,[25] τ 7.05. [k] Lit.,[25] τ 5.85. [l] Lit.,[25] τ 4.45, 39 Hz. [m] Lit.,[25] τ 7.00. [n] Lit.,[25] τ 4.44, 39 Hz. [o] Lit.,[25] τ 7.07. [p] ^6J(Pt–H) 4.0 Hz; lit.,[25] τ 7.37, ^6J(Pt–H) 4.2.

Carbon-13 *N.M.R. Spectra*.—Details of the ^{13}C-{^1H} n.m.r. spectra of some of the [Pt(cod)(R)Cl] and [Pt(cod)R_2] complexes are shown in Table 7. The signals from the olefin carbon atoms of the cyclo-octadiene ligands are readily distinguished by their chemical shifts from those arising from the methylene carbon atoms. The monoaryl complexes show two distinct resonances for each pair of olefin groups and also for each of the methylene carbon atoms. The chemical shifts and ^2J(Pt–C) coupling constants for the methylene signals are very close in each case, and we have not separately assigned them. The resonances from olefin carbons *trans* to chloride appear at high field with ^1J(Pt–C) 188—210 Hz, while those from the olefin carbons *trans* to aryl groups appear at low field with ^1J(Pt–C) 27—50 Hz. The diaryl complexes, as expected, show only a single olefin carbon resonance, with ^1J(Pt–C) 49—66 Hz; no coupling was observed between the ^{195}Pt atom and the methylene carbon.

Assignments of the aryl carbon resonances are based on additivity relations and comparison with values of δ(^{13}C) and $J(^{117}Sn–^{13}C)$ for a series of $SnMe_3R$ compounds, or, in the case of heterocyclic aryl groups, by comparison with chemical-shift data for the unco-ordinated monosubstituted species and the relative magnitudes of the Pt–C coupling constants.

Clark and his co-workers [26] recently reported J(Pt–C) values for [Pt(cod)(Ph)Cl] but could not observe the platinum satellites for the carbon atom (C^1) of the platinum–aryl bond. We also observed no Pt–C^1 coupling at the normal pulse repetition time of 1 s, although the signals from the other carbon atoms were all fully resolved. The C^1 signal appeared at a low intensity but with no Pt satellites. However, when for some complexes the pulse-repetition time was increased to 10 s, or when [Cr(pd)$_3$] (pd = pentane-2,4-dionate) was added,

[25] N. Chaudhury and R. J. Puddephatt, *J. Organometallic Chem.*, 1975, **84**, 105.

[26] M. M. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 1973, **95**, 8574.

TABLE 7

^{13}C-{^1H} N.m.r. data for [Pt(cod)(R)X] complexes [a]

								cod carbons [c]			
		Aryl carbons [b,c]						vinyl		methylene	
R	X	C^1	C^2	C^3	C^4	C^5	C^6	*trans*-aryl	*trans*-Cl	*trans*-aryl	*trans*-Cl
2-C_4H_3S	Cl	137.2	127.3	127.1	129.1			113.3	90.0	28.5	31.9
		(1 060)	(61)	(35)	(37)			(50)	(188)	(18)	(19)
2-C_4H_3O	Cl	*d*	115.5	110.2	143.8			112.1	89.6	28.6	31.7
								(50)	(188)	(18)	(19)
2-C_8H_5O [e]	Cl	*d*	112.1	129.0	120.7	121.9	122.9	113.5	90.4	28.4	31.8
								(50)	(186)	(18)	(19)
3-C_8H_7 [f]	Cl	148.8	145.4	137.3	118.6	127.3	131.5	115.8	86.2	27.9	32.2
		d		(46)		(46)	(12)	(30)	(206)	(24)	(26)
C_6H_4Me-*p* [g]	Cl	140.0	133.5	129.2	133.5	129.2	133.4	115.5	87.1	27.9	32.1
								(27)	(210)	(23)	(24)
Ph [h]	Cl	143.4	133.4	127.8	123.7	127.8	133.4	115.2	87.1	27.5	31.7
		d	(12)	(50)	(8)	(50)	(12)	(28)	(208)	(24)	(26)
2-C_4H_3S	2-C_4H_3S	145.7	126.9	126.4	130.7			104.4		29.9	
		(1 186)	(82)	(56)	(59)			(66)		(<3)	
2-C_4H_3O	2-C_4H_3O	164.1	117.2	109.9	143.5			103.2		29.9	
		d	(162)	(53)	(59)			(66)		(<3)	
2-C_8H_5O [h]	2-C_8H_5O	168.3	113.9	129.7	119.8	121.5	122.1	105.2		29.9	
		d						(64)		(<3)	
C_6H_4OMe-*o* [i]	C_6H_4OMe-*o*	141.8	161.0	120.9	123.3	110.4	135.5	102.0		29.9	
		(1 077)	(17)	(76)		(37)	(24)	(57)		(<3)	
C_6H_4Cl-*m* [j]	C_6H_4Cl-*m*	156.7	132.7	133.5	123.1	128.7	133.8	105.3		29.9	
		(1 086)	(31)	(97)	(11)	(86)	(37)	(49)		(<3)	
C_6H_4Br-*p* [k]	C_6H_4Br-*p*	153.3	136.0	130.5	117.0	130.5	136.0	105.1		29.9	
		d	(40)	(81)		(81)	(40)	(49)		(<3)	

[a] In $CDCl_3$ with $SiMe_4$ as internal reference. Frequency range 6 250 Hz, resolution 1.52 Hz. [b] Ring numbers are based on Pt at C^1. [c] δ/p.p.m.; *J*(Pt–C)/Hz in parentheses. [d] Not observed. [e] δ 110.0 (C^7), 156.7 p.p.m. (C^8). [f] C^2 and C^3 are bridge carbons. δ 30.7 (C^7), 28.6 p.p.m. (C^8). [g] *p*-Me carbon has δ 20.7 p.p.m. [h] δ 110.1 (C^7), 157.0 p.p.m. (C^8). [i] MeO is at C^2. For OMe carbon, δ 55.6 p.p.m. [j] Cl is at C^3. [k] Br is at C^4.

TABLE 8

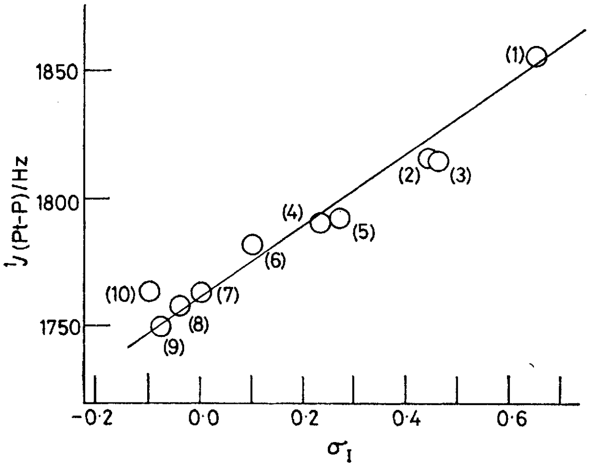
^{31}P-{^1H} N.m.r. data for [PtR(X)L_2] complexes [a]

		[PtR(X)(dppe)]		*cis*-[PtR(X)$(PPh_3)_2$]		*trans*-
R	X	*trans*-aryl	*trans*-Cl	*trans*-aryl	*trans*-Cl	[PtR(X)$(PPh_3)_2$]
2-C_4H_3S	Cl	97.1, 1 973	101.4, 3 929	*b*		117.6, 2 900
2-C_8H_5S	Cl	97.4, 1 968	200.9, 3 889	*b*		117.5, 2 888
2-C_4H_3O	Cl	97.6, 1 875	99.7, 3 986	*b*		118.6, 2 917
2-C_8H_5O	Cl	97.5, 1 887	99.4, 3 940	*b*		118.7, 2 886
C_6H_4Cl-*m*	Cl	102.0, 1 716	102.0, 4 067	*c*		115.6, 3 084
C_6H_4Cl-*p*	Cl	99.8, 1 699	102.3, 4 089	*c*		116.4, 3 093
C_6H_4F-*p*	Cl	100.0, 1 694	102.4, 4 114	*c*		
3-C_8H_7	Cl	98.4, 1 697	100.5, 4 166	119.7, 1 609	122.8, 4 465 [d]	115.8, 3 123
C_6H_4OMe-*p*	Cl	99.7, 1 670	102.8, 4 166	119.5, 1 582	122.8, 4 502 [d]	115.8, 3 142
Ph	Cl	100.4, 1 663	102.9, 4 165	119.5, 1 560	122.8, 4 500 [d]	115.6, 3 157
$C_6H_4SiMe_3$-*p*	Cl			119.8, 1 560	122.8, 4 497 [d]	115.4, 3 164
C_6H_4Me-*p*	Cl	99.9, 1 650	103.0, 4 177	119.4, 1 548	123.0, 4 521 [d]	115.9, 3 169
2-C_4H_3S	2-C_4H_3S	98.4, 2 031		122.8, 2 056		
2-C_8H_5S	2-C_8H_5S	97.4, 2 016				
2-C_4H_3O	2-C_4H_3O	96.9, 1 975		122.8, 2 014		
2-C_8H_5O	2-C_8H_5O	96.4, 1 975		121.8, 2 014		
η-*p*-Me$C_6H_4Cr(CO)_3$	η-*p*-Me$C_6H_4Cr(CO)_3$	97.8, 1 948				
$C_6H_4CF_3$-*m*	$C_6H_4CF_3$-*m*	97.9, 1 770		122.3, 1 826		
$C_6H_3(CF_3)_2$-3,5 [e]	$C_6H_3(CF_3)_2$-3,5	96.8, 1 831		123.1, 1 887		
$C_6H_4NO_2$-*p*	$C_6H_4NO_2$-*p*	97.4, 1 785		122.9, 1 855		
C_6H_4Br-*m* [e]	C_6H_4Br-*m*	97.9, 1 770		122.2, 1 836		
C_6H_4Br-*p*	C_6H_4Br-*p*	98.2, 1 758		122.2, 1 816		
C_6H_4Cl-*m*	C_6H_4Cl-*m*	98.0, 1 774		122.0, 1 831		
C_6H_4Cl-*p*	C_6H_4Cl-*p*	98.2, 1 758		122.2, 1 816		
3-C_8H_7	3-C_8H_7	100.1, 1 748		122.6, 1 809		
C_6H_4OMe-*o*	C_6H_4OMe-*o*	101.4, 1 912		124.8, 2 012		
C_6H_4OMe-*m*	C_6H_4OMe-*m*	99.4, 1 704		121.5, 1 775		
C_6H_4OMe-*p*	C_6H_4OMe-*p*	99.3, 1 721		123.0, 1 792		
C_6H_4SMe-*p* [f]	C_6H_4SMe-*p*	98.9, 1 743		122.0, 1 790		
C_6H_4Ph-*p* [e]	C_6H_4Ph-*p*	99.3, 1 721		121.9, 1 782		
Ph	Ph	99.4, 1 704		121.7, 1 763		
$C_6H_4SiMe_3$-*p*	$C_6H_4SiMe_3$-*p*	100.3, 1 699		121.6, 1 763		
C_6H_4Me-*p*	C_6H_4Me-*p*	99.5, 1 704		121.8, 1 758		
$C_6H_4Bu^t$-*p*	$C_6H_4Bu^t$-*p*	101.0, 1 702		121.7, 1 750		

[a] In CH_2Cl_2 relative to $P(OMe)_3$. δ/p.p.m. followed by ^1J(Pt–P)/Hz. [b] No significant amount of *cis* isomer was present. [c] Not resolved; <20% of *cis* isomer present. [d] ^2J(P–P) 15 Hz. [e] The [Pt(cod)R_2] complex was not isolated, but converted directly into the phosphine complexes. [f] The formation of this complex will be described elsewhere.

the usual 1 : 4 : 1 triplet pattern appeared for the C^1 resonances. The large magnitude of ^1J(Pt–C) {*e.g.* 1 086 Hz for *cis*-[Pt(cod)(C_6H_4Cl-*m*)$_2$]} reflects the low ***trans*** influence of the olefin ligand. {Compare the ^1J(Pt–C) value of 817 Hz for *cis*-[$PtPh_2(PEt_3)_2$].}

^{31}P-{^1H} *N.M.R. Spectra.*—Details of the ^{31}P-{^1H} n.m.r. spectra of mono- and di-aryl complexes containing dppe or PPh_3 ligands are shown in Table 8. For the *cis*-diaryl complexes [Pt(C_6H_4X-*p*)$_2L_2$] (L = PPh_3 or $\frac{1}{2}$ dppe; X = NO_2, Br, Cl, OMe, SMe, H, $SiMe_3$, Me, or Bu^t) the values of ^1J(Pt–P) show a poor correlation with σ_p or $\sigma_p{}^0$ constants, but a good correlation with σ_I constants;[27] the line shown in the Figure is the best least-squares line (correlation coefficient, 0.987) omitting the point for the *p*-$SiMe_3$ group, which seems anomalous. Evidently the ***trans*** influence[28] of the C_6H_4X ligand decreases with increasing inductive electron withdrawal by X. This is in accord with *trans*-influence theory,[29] in that magnitude of the *s* component of the Pt–P bonds will increase with decreasing σ-electron density on the attached carbon atom of the *trans* ligand.



Plot of ^1J(Pt–P) against σ_I for *cis*-[Pt(C_6H_4X-*p*)$_2(PPh_3)_2$] complexes. X = NO_2 (1), Br (2), Cl (3), SMe (4), OMe (5), Ph (6), H (7), Me (8), Bu^t (9), and $SiMe_3$ (10)

It is noteworthy that in each of the [Pt{$C_6H_3(CF_3)_2$-3,5}$_2L_2$] complexes the effects of the two CF_3 groups are additive; *e.g.* for [Pt(C_6H_4X)$_2(PPh_3)_2$] the value of ^1J(Pt–P) is 63 Hz larger for X = *m*-CF_3 than for H, and introduction of a second *m*-CF_3 group raises the value by a further 61 Hz.

EXPERIMENTAL

The preparations of the organotin compounds have been described.[6,30] The complexes [Pt(cod)Cl_2] and [Pt(nbd)Cl_2] were prepared by published methods.[31,32] Reference in Tables 1 and 2 to recrystallization from, *e.g.*, chloroform–diethyl ether, means that the product was dissolved in chloroform, ether was added until turbidity appeared, and the mixture was set aside, with cooling if necessary.

Reactions of [Pt(cod)Cl_2] *with* $SnMe_3R$ *Compounds.*—*Method A.* To a solution of [Pt(cod)Cl_2] (usually 1—4 mmol) in dichloromethane (20—40 cm^3) was added the aryltrimethylstannane in one or two molar proportions. The solution was stirred for 12 h at room temperature, the solvent was removed *in vacuo*, and diethyl ether added to precipitate a white or pale yellow solid. This was filtered off and recrystallized from the solvent mixture indicated in Table 1 or 2.

Method B. The reaction mixture was made up as in *A*, but was heated under reflux for 12 h. The solvent was evaporated off *in vacuo* to leave a solid, which was washed with pentane (5—10 cm^3) and recrystallized from the solvent mixture indicated in Tables 1 or 2.

Method C. A mixture was made up as in *A*, but in *sym*-tetrachloroethane. This was kept at 100 °C for 12 h, the solvent and the $SnMe_3Cl$ were removed *in vacuo* (90 °C, 2 mmHg),* and the dark residue was dissolved in chloroform (5—10 cm^3). The solution was stirred with charcoal overnight, then filtered through Celite and reduced in volume *in vacuo*. Dropwise addition of pentane gave the pure product.

For the preparation of [Pt(cod)($C_6H_4CF_3$-*m*)$_2$] by this method the compound $SnEt_3$($C_6H_4CF_3$-*m*) was used and the reaction was carried out at 100 °C for 14 h. Subsequent work-up was as above.

Yields of products obtained by all the three methods are listed in Tables 1 and 2, and the analyses, colour, and physical constants in Tables 5—7 and 9. In certain cases (Table 2) the [Pt(cod)R_2] complexes were not isolated but converted into the corresponding triorganophosphine derivatives (see below) and characterized by ^{31}P-{^1H} n.m.r. spectra. In these cases the reaction was carried out for only 8 h at 40 °C, except for R = *p*-$NO_2C_6H_4$ for which 100 h was used, but the ^{31}P-{^1H} spectra ultimately obtained showed that reaction was effectively complete.

In the reaction between [Pt(cod)Cl_2] and $SnMe_3$[η-*p*-$MeC_6H_4Cr(CO)_3$] in 1 : 1 mol ratio by method *A*, after 3 h at room temperature the solvent was removed to leave a pale green solid, the i.r. spectrum of which was recorded immediately and showed the characteristic ν(Pt–Cl) bands of [Pt(cod)Cl_2] at 338 and 316 cm^{-1}, but no other ν(Pt–Cl) band, indicating the absence of any [Pt(cod)(R)Cl]. Recrystallization from benzene–octane gave [Pt(cod)R_2] in 32% yield. In a separate experiment, after 3 h at room temperature as above, dppe was added. The ^{31}P-{^1H} n.m.r. spectrum showed that only [$PtCl_2$(dppe)] and [PtR_2(dppe)] were present.

Relative Reactivities of $SnMe_3(C_6H_4X)$ *Compounds.*—A dichloromethane solution of [Pt(cod)Cl_2] and $SnMe_3(C_6H_4X)$ (X = H, *p*-OMe, or *p*-CF_3) in 1 : 2.5 mol ratio was stirred at room temperature for 1 week. Subsequent work-up as in method *A* above gave [Pt(cod)(C_6H_4OMe-*p*)$_2$] in 80% and [Pt(cod)(Ph)Cl] in 70% yield, while no product was isolated for X = *p*-CF_3.

Interactions.—[Pt(nbd)Cl_2] *and* $SnMe_3(C_4H_3O$-2). 2-Furyltrimethylstannane (0.16 g, 0.70 mmol) was added to a

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

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stirred suspension of [Pt(nbd)Cl_2] (0.25 g, 0.70 mmol) in dichloromethane (25 cm^3) at room temperature. A yellow colour developed immediately, and within 0.5 h all the complex had dissolved to give a green-yellow solution. The mixture was stirred for 12 h at room temperature, and the solvent was taken off under reduced pressure. Diethyl ether (10 cm^3) was added to give a yellow powder, which was filtered off, washed with pentane (5 cm^3), and recrystallized from chloroform–diethyl ether to give yellow crystals of chloro(2-furyl)(norbornadiene)platinum(II) (0.22 g, 81%), m.p. 120 °C (decomp.), ν(Pt–Cl) at 329 cm^{-1}; τ 4.59 (vinylic H) [^2J(Pt–CH) 34], 4.73 (vinylic H) [^2J(Pt–CH) 76 Hz], 8.27 (CH_2), 2.78 (H^3 of C_4H_3O), 3.61 (H^4 of C_4H_3O), 3.81 (H^5 of C_4H_3O), and 5.60 (bridgehead H of nbd).

TABLE 9

Elemental analyses and physical properties of [Pt(cod)(R)X] complexes

R	X	M. p.[a] (θ_c/°C)	Analysis (%)[b] C	H	ν(Pt–Cl)/cm^{-1}	Notes
2-C_4H_3S	Cl	158—160	34.2 (34.2)	3.5 (3.6)	319	*c*
2-C_4H_3O		135—137	35.5 (35.5)	3.7 (3.7)	320	*d*
2-C_8H_5S		177	40.8 (40.6)	3.7 (3.6)	322	*c*
2-C_8H_5O		147—151	41.6 (42.1)	3.9 (4.0)	322	*d*
3-C_8H_7		194—196	43.8 (43.5)	4.4 (4.3)	328	*e*
Ph		164—165[f]	40.4 (40.4)	4.5 (4.1)	318	*e,g*
C_6H_4OMe-*p*		124—127	40.2 (40.4)	4.3 (4.7)	316	*e*
C_6H_4Cl-*p*		173—178	37.3 (37.0)	3.6 (3.4)	326	*e*
$C_6H_4SiMe_3$-*p*		184—187	41.2 (41.8)	5.2 (5.2)	323	*e*
C_6H_4Me-*p*		168—171	41.7 (41.9)	4.6 (4.5)	322	*e*
C_6H_4F-*p*		171—177	37.9 (38.8)	3.2 (3.7)	324	*e*
$C_6H_2Me_3$-2,4,6		203—205	43.8 (44.6)	5.0 (5.1)	328	*e*
2-C_4H_3S	2-C_4H_3S	154	40.8 (40.9)	3.9 (3.9)		*c*
2-C_4H_3O	2-C_4H_3O	140—146	43.8 (43.9)	4.1 (4.15)		*c*
2-C_8H_5O	2-C_8H_5O	203—206	53.8 (53.6)	4.1 (4.1)		*c*
η-$C_6H_4Cr(CO)_3$	η-*p*-$MeC_6H_4Cr(CO)_3$	178	44.1 (44.4)	3.5 (3.5)		*c*
3-C_8H_7	3-C_8H_7	180	56.6 (56.6)	5.1 (5.1)		*e*
Ph	Ph	155—156[h]	52.1 (52.5)	4.9 (4.8)		*e*
C_6H_4OMe-*o*	C_6H_4OMe-*o*	167—170[i]	51.1 (51.1)	5.0 (5.1)		*e*
C_6H_4OMe-*m*	C_6H_4OMe-*m*	148—150	50.7 (51.1)	5.1 (5.1)		*e*
C_6H_4OMe-*p*	C_6H_4OMe-*p*	134[j]	50.4 (51.1)	4.8 (5.1)		*e*
$C_6H_4CF_3$-*m*	$C_6H_4CF_3$-*m*	158	44.6 (44.5)	3.5 (3.4)		*e*
$C_6H_4SiMe_3$-*p*	$C_6H_4SiMe_3$-*p*	173	51.9 (51.9)	6.8 (6.4)		*e*
C_6H_4Me-*p*	C_6H_4Me-*p*	169—170[k]	53.6 (54.4)	5.3 (5.4)		*e*
$C_6H_4Bu^t$-*p*	$C_6H_4Bu^t$-*p*	152	58.7 (59.0)	6.6 (6.7)		*e*
C_6H_4Br-*p*	C_6H_4Br-*p*	180—182	39.3 (39.1)	3.4 (3.3)		*e*
C_6H_4F-*m*	C_6H_4F-*m*	177—179[l]	48.7 (48.7)	4.0 (4.1)		*e*
C_6H_4Cl-*m*	C_6H_4Cl-*m*	186	45.4 (45.6)	3.9 (3.8)		*e*
2-C_4H_3O	2-C_4H_3S	132—135	42.3 (42.4)	3.8 (4.0)		*c*
2-C_8H_5O	C_6H_4Me-*p*	172	53.7 (53.9)	4.8 (4.9)		*c*

[a] With decomposition. [b] Calculated values are given in parentheses. [c] Yellow. [d] Pale yellow. [e] White. [f] Lit.,[31] 166—168 °C. [g] *M* 428 (Calc.: 416). [h] Lit.,[22] 152 °C. [i] Lit.,[25] 105—110 °C. [j] Lit.,[25] 110—125 °C. [k] Lit.,[25] 167—170 °C. [l] Lit.,[25] 174—176 °C.

[Pt(cod)(R)Cl] *and* $SnMe_3R'$. A solution of [Pt(cod)(2-C_4H_3S)Cl] and $SnMe_3$(2-C_4H_3O) in 1 : 1 mol ratio in dichloromethane was stirred for 12 h at room temperature. The solvent was removed *in vacuo*, and the residue was recrystallized three times from chloroform–diethyl ether to give a yellow solid (68%), m.p. 132—135 °C; τ 4.77 (vinylic H) [^2J(Pt–CH) 38 Hz], 4.60 (vinylic H) [^2J(Pt–CH) not resolved], 7.50 (CH_2), and 2.2—4.5 (aryl H) (Found: C, 42.3; H, 3.8. $C_{16}H_{18}OPtS$ requires C, 42.4; H, 4.0%). In spite of the satisfactory analysis we suspect that the product contained trace amounts of the other possible diaryl complexes, since the ^1H n.m.r. spectrum was not as clean as expected. However, the corresponding phosphine complex [Pt(2-C_4H_3O)(2-C_4H_3S)(dppe)] was obtained pure (see Table 10), as shown by its ^{31}P-{^1H} n.m.r. spectrum.

The reactions between equimolar amounts of [Pt(cod)(C_6H_4Me-*p*)Cl] and $SnMe_3$(2-C_8H_5O) under the same conditions gave [Pt(cod)(2-C_8H_5O)(C_6H_4Me-*p*)] (65%), m.p. 172 °C (decomp.); τ 3.95 (vinylic H) [^2J(Pt–CH) not resolved], 5.02 (vinylic H) [^2J(Pt–CH) 43], 7.48 (CH_2), 2.2—4.5 (aryl H), and 7.72 (CH_3) [^6J(Pt–H) 4 Hz] (Found: C, 53.7; H, 4.8. $C_{23}H_{24}OPt$ requires C, 53.9; H, 4.9%). Again, from the appearance of the ^1H n.m.r. spectrum, we suspect that the product was not wholly free from the other possible diaryl complexes, but again the dppe complex was obtained pure (see Table 10).

[Pt(cod)Cl_2] *and* $SnMe_3[C(SiMe_3)_3]$. A solution of [Pt(cod)Cl_2] (0.5 g, 1.3 mmol) and $SnMe_3[C(SiMe_3)_3]$ [33] (1.1 g, 3.3 mmol) in *sym*-tetrachloroethane was kept at 100 °C for 100 h. Solvent was distilled off under reduced pressure, diethyl ether (10 cm^3) added to the residue, and the solution filtered. n-Pentane was added to the filtrate to give [Pt(cod)(Me)Cl] (0.15 g, 31%), m.p. 166—170 °C (lit.,[32] 166—167 °C), ν(Pt–Cl) at 318 cm^{-1}; τ 4.58 [^2J(Pt–CH) 35], 5.59 [^2J(Pt–CH) 77], 7.76 (CH_2), and 9.1 (Pt–CH_3) [^2J(Pt–CH) 72 Hz] (Found: C, 30.3; H, 4.2. Calc. for $C_9H_{15}ClPt$: C, 30.6; H, 4.3%).

[Pt(cod)Cl_2] *and* $SnMe_3(CH_2C_6H_4Me$-*p*). A solution of [Pt(cod)Cl_2] (0.6 g, 1.6 mmol) and $SnMe_3(CH_2C_6H_4Me$-*p*) (1.3 g, 4.8 mmol) in *sym*-tetrachloroethane (25 cm^3) was kept at 100 °C for 20 h (during which considerable decomposition occurred). Solvent was distilled off at low pressure, the residual dark oil was taken up in dichloromethane (10 cm^3), and the solution was stirred overnight with charcoal. Filtration through Celite gave a pale

[33] M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 529.

yellow solution. Evaporation of some of the solvent followed by addition of n-hexane gave plates of [Pt(cod)($CH_2C_6H_4Me$-*p*)Cl] (0.28 g, 39%), m.p. 145—147 °C (decomp.), ν(Pt–Cl) at 316 cm^{-1} (Found: C, 42.8; H, 4.7. $C_{26}H_{21}ClPt$ requires C, 43.3; H, 4.8%). The mother liquor was taken to dryness, benzene (10 cm^3) was added, and the solution filtered. Evaporation left a yellow oil; this was taken up in dichloromethane and dppe (0.1 g) was added. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the solution indicated the presence of two components (*ca.* 2 : 1) which were identified, respectively, as [PtMe(Cl)(dppe)], δ(*trans*-RPt*P*) 96.2 [^1J(Pt–P) 1 736] and δ(*trans*-ClPt*P*) 97.4 p.p.m. [^1J(Pt–P) 4 216 Hz], and [Pt($CH_2C_6H_4Me$-*p*)Cl(dppe)], δ(*trans*-RPt*P*) 97.5 [^1J(Pt–P) 1 773] and δ(*trans*-ClPt*P*) 99.5 p.p.m. [^1J(Pt–P) 4 373 Hz].

Analogous use of PPh_3 gave the corresponding $^{31}P-\{^1H\}$ n.m.r. spectrum: (*i*) *cis*-[PtMe(Cl)$(PPh_3)_2$] δ(*trans*-RPt*P*) 113.8 [^1J(Pt–P) 1 726] and δ(*trans*-ClPt*P*) 118.5 p.p.m. [^1J(Pt–P) 4 475, ^2J(PPtP) 12 Hz] (no *trans*-isomer was present); (*ii*) *cis*-[Pt($CH_2C_6H_4Me$-*p*)Cl$(PPh_3)_2$] δ(*trans*-RPt*P*) 113.9 [^1J(Pt–P) 1 714] and δ(*trans*-ClPt*P*) 118.5 p.p.m. [^1J(Pt–P) 4 470, ^2J(PPtP) 12 Hz]; (*iii*) *trans*-[Pt($CH_2C_6H_4Me$-*p*)$_2$Cl$(PPh_3)_2$] δ 113.3 p.p.m. [^1J(Pt–P) 3 298 Hz].

TABLE 10

Elementary analyses and physical constants for [PtR(X)L_2] complexes

L_2	R	X	M.p. (θ_c/°C)	Analysis (%) [a] C	H	Notes
$(PEt_2Ph)_2$	C_6H_4Me-*p*	Cl	78—79	49.5 (49.6)	5.9 (5.7)	*b*
bipy	2-C_4H_3S	Cl	151	35.2 (35.8)	2.6 (2.4)	*c*
dppe	2-C_4H_3S	Cl	258—271	52.6 (53.7)	4.0 (4.0)	*d*
dppe	2-C_4H_3S	2-C_4H_3O	260—265	53.4 (54.8)	4.1 (4.1)	
$(PPh_3)_2$	C_6H_4Br-*p*	C_6H_4Br-*p*	129—132	39.0 (39.0)	3.2 (3.3)	
dppe	C_6H_4OMe-*m*	C_6H_4OMe-*m*	215—222	59.3 (59.5)	4.8 (4.7)	*e*
$(AsPh_3)_2$	C_6H_4OMe-*m*	C_6H_4OMe-*m*	150—151	58.5 (58.8)	4.5 (4.3)	*f*
$(SbPh_3)_2$	C_6H_4OMe-*m*	C_6H_4OMe-*m*	109	53.0 (53.8)	3.8 (4.0)	*g*

[a] Calculated values are given in parentheses. [b] ν(Pt–Cl) at 333 cm^{-1}; τ 7.86 (CH_3). [c] Orange; N 5.6 (Calc.: 6.0%); ν(Pt–Cl) at 346 cm^{-1}. [d] ν(Pt–Cl) at 305 cm^{-1}. [e] τ 6.64 (OCH_3). [f] τ 6.80 (OCH_3). [g] τ 6.67 (OCH_3).

Reactions of [Pt(cod)Cl_2] *with* MMe_3R (M = Si, Ge, *or* Pb), HgR_2, *and* Na[BPh_4].—(*a*) A solution of [Pt(cod)Cl_2] (0.3 g, 0.8 mmol) and an excess of 2-furyltrimethylsilane (1 cm^3) in *sym*-tetrachloroethane (20 cm^3) was kept at 90 °C for 30 h. Removal of the solvent at low pressure left a yellow oil, and addition of benzene gave a solid which was shown from its i.r. spectrum to be [Pt(cod)Cl_2] (0.22 g, 73%). The benzene mother liquor was reduced in volume and n-pentane was added, giving yellow crystals of [Pt(cod)(2-C_4H_3O)Cl] (0.049 g, 15%), m.p. 140—142 °C, ν(Pt–Cl) at 320 cm^{-1} (Found: C, 35.5; H, 3.7. $C_{12}H_{15}ClOPt$ requires C, 35.5; H, 3.7%).

(*b*) A reaction involving (*p*-methoxyphenyl)trimethylsilane under the same conditions gave only unchanged starting materials.

(*c*) A solution of [Pt(cod)Cl_2] (0.4 g, 1.1 mmol) and an excess of (benzo[*b*]furan-2-yl)trimethylgermane (0.5 cm^3) in *sym*-tetrachloroethane (20 cm^3) was kept at 90 °C for 23 h. The solvent was removed at low pressure, and the residue was extracted with benzene. The benzene solution was filtered, and the solvent removed. The residue was recrystallized from chloroform–diethyl ether to give [Pt(cod)(2-C_8H_5O)$_2$] (0.4 g, 68%), m.p. 207—210 °C (decomp.) (Found: C, 53.4; H, 4.2. $C_{24}H_{22}O_2Pt$ requires C, 53.6; H, 4.1%). When an identical reaction mixture was kept at room temperature (*ca.* 21 °C) for 5 d the only product was [Pt(cod)(2-C_8H_5O)Cl] (10%), m.p. 152—156 °C (decomp.), ν(Pt–Cl at 322 cm^{-1} (Found: C, 41.6; H, 3.9. $C_{16}H_{18}ClOPt$ requires C, 42.1; H, 3.9%).

(*d*) Trimethyl(phenyl)lead (0.52 g, 1.6 mmol) was added to a solution of [Pt(cod)Cl_2] (0.33 g, 0.63 mmol) in dichloromethane (20 cm^3) at room temperature. After 0.5 h a substantial amount of precipitate had formed, but the mixture was stirred for 12 h and the solvent was then removed. Extraction with benzene (15 cm^3) and filtration left chlorotrimethyl-lead (0.24 g). The filtrate was reduced in volume and dropwise addition of n-pentane gave [Pt(cod)Ph_2] (0.19 g, 66%) (see Table 9).

(*e*) A suspension of [Pt(cod)Cl_2] (0.3 g, 0.8 mmol) and Na[BPh_4] (0.55 g, 1.6 mmol) in a mixture of thf (30 cm^3) and dichloromethane (10 cm^3) was warmed at 60 °C. The reactants dissolved, and a substantial precipitate of sodium chloride appeared within 5 min. The mixture was heated under reflux for 2 h (some black decomposition products appeared), the solvent was removed under reduced pressure, and the residual dark oil was dissolved in chloroform. The solution was stirred with charcoal for 1 h, then filtered through Celite. Diethyl ether was added dropwise to the filtrate to give [Pt(cod)Ph_2] (0.15 g, 41%) which had identical properties to those of the product described in (*d*).

(*f*) A solution of [Pt(cod)Cl_2] (1.0 g, 2.7 mmol) and $HgPh_2$ (0.95 g, 2.7 mmol) in dichloromethane (35 cm^3) was stirred at room temperature. After 20 min a white precipitate suddenly separated. After 2 h the solid was filtered off and identified as chloro(phenyl)mercury(II) (0.35 g, 41%), m.p. 268—272 °C. Solvent was removed under reduced pressure and chloroform (12 cm^3) was added to give additional HgPhCl (0.46 g, 55%), which was filtered off. Diethyl ether was added to the filtrate, and cooling gave [Pt(cod)(Ph)Cl] (0.835 g, 74%), m.p. 164 °C (decomp.), ν(Pt–Cl) at 321 cm^{-1}.

Displacement of cod by Neutral Ligands.—Typical procedures were as follows. (*a*) A solution of [Pt(cod)(R)X] (X = Cl or aryl) with 2 mol of PPh_3 or PEt_2Ph or 1 mol of 1,2-bis(diphenylphosphino)ethane (dppe) in dichloromethane was stirred at room temperature for 2 h. The solvent was removed, then the residue was washed with a little pentane and recrystallized from dichloromethane–diethyl ether. The properties of the products are listed in Table 10. In the reaction of [Pt(cod)(C_6H_4OMe-*o*)$_2$] the product was isolated in only *ca.* 40% yield after 18 h at room temperature, but in good yield after 1 h under reflux.

(*b*) A solution of 2,2′-bipyridyl (bipy) (0.09 g, 0.60 mmol) and [Pt(cod)(2-C_4H_3S)Cl] (0.25 g, 0.59 mmol) in dichloromethane (20 cm^3) was boiled under reflux for 3 h. On cooling orange crystals separated. Diethyl ether was added to complete the precipitation, and the solution kept at 0 °C for several hours. The solid was filtered off, washed with hexane, and shown to be [Pt(2-C_4H_3S)Cl(bipy)] (0.19 g, 67%) (see Table 10). When this reaction was carried out at room temperature for 30 h the product was obtained in only 20% yield.

(*c*) A solution of $AsPh_3$ (0.22 g, 0.72 mmol) and [Pt(cod)-(C_6H_4OMe-*m*)$_2$] (0.19 g, 0.35 mmol) in dichloromethane (10 cm^3) was stirred at room temperature for 30 h. Removal of solvent left an oil, which was dissolved in diethyl ether (15 cm^3). Slow evaporation of the ether gave a solid, which was filtered off, washed with a little ethanol, dried *in vacuo*, and shown to be [Pt(C_6H_4OMe-*m*)$_2$($AsPh_3$)$_2$] (0.28 g, 78%) (see Table 10).

Reactions of [Pd(nbd)Cl_2].—(*a*) When $SnMe_3$(C_6H_4OMe-*p*) (1.0 g, 3.9 mmol) was added to a stirred suspension of [Pd(nbd)Cl_2] [34] (1.0 g, 3.8 mmol) in dichloromethane (40 cm^3) the complex slowly dissolved to give an orange solution. After 2 h the solvent was removed under reduced pressure and the residue was washed with pentane (30 cm^3) and recrystallized from dichloromethane–pentane to give orange *di-μ-chloro-bis*{[5—6-η-2-(p-*methoxyphenyl*)*norbornen*-3-*yl*)]-*palladium*(II)}, (1) (1.2 g, 92%), m.p. 167—170 °C (decomp.), ν(Pd–Cl) at 296 and 261 cm^{-1} (Found: C, 48.9; H, 4.5. $C_{28}H_{30}Cl_2O_2Pd_2$ requires C, 49.3; H, 4.4%); τ 3.98 (t, width 14.5 Hz) (H^5), 4.13 (dt, width 16.5 Hz) (H^6), 6.56 (s, width 20.0 Hz) (H^1), 6.98 (s, width 13.0 Hz) (H^2), 7.14 (s, width 17.0 Hz) (H^4), 7.50 (dd, width 19.0 Hz) (H^3), 7.71—8.30 (m, probably H^{7a} and H^{7b}), 6.14 (s) and 6.26 (s) (OCH_3), and 2.58—3.25 (m) (C_6H_4).

A sample (0.2 g, 0.3 mmol) of the *p*-methoxyphenyl complex obtained above was suspended in dichloromethane and dppe (0.24 g, 0.6 mmol) was added. The pale yellow solution was stirred at room temperature for 3 h, the solvent was reduced in volume to *ca.* 3 cm^3, and n-hexane (6 cm^3) was added. Cooling gave yellow crystals (0.28 g, 61%), m.p. 168—173 °C [ν(Pd–Cl) at 285 cm^{-1}; ^{31}P-{^1H} n.m.r. in CH_2Cl_2: δ 86.6 and 111.6 p.p.m., ^2J(PPdP) 42 Hz], believed to be *cis*-[1,2-bis(diphenylphosphino)ethane]chloro[5-(*p*-methoxyphenyl)nortricyclen-3-yl]palladium(II) containing 0.3 CH_2Cl_2 molecules of crystallization (Found: C, 63.1; H, 5.2. Calc. for $C_{40.3}H_{39.6}Cl_3OP_2Pd$: C, 63.3; H, 5.2%); τ 7.44—7.63 (m) (H^{1-3}), 8.60—9.20 (m) (H^{4-8}), 6.57 (s) (OCH_3), 3.77—2.50 (m) (C_6H_4, C_6H_5), 7.95—8.50 (dt) (PCH_2), and 4.80 (s) (CH_2Cl_2).

(*b*) The analogous reaction between [Pd(nbd)Cl_2] and $SnMe_3$(C_6H_4Me-*p*) similarly gave orange di-μ-chloro-bis{[5—6-η-2-(*p*-tolyl)norbornen-3-yl]palladium(II)} (85%), m.p. 178—180 °C (decomp.), ν(Pd–Cl) at 296 and 261 cm^{-1} (Found: C, 51.7; H, 4.7. $C_{28}H_{30}Cl_2Pd_2$ requires C, 51.7; H, 4.65%).

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