Carbonylation of $[PtX(Ph)(PR_3)_2]$. New Intermediates in the CO Insertion Sequence

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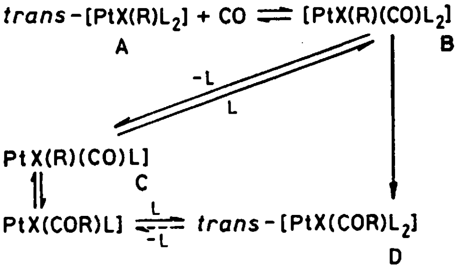
Phosphorus-31 n.m.r. studies of the reaction of *trans*-$[PtX(Ph)(PR_3)_2]$ with carbon monoxide have led to the identification of several new intermediates and reaction pathways involved in the CO insertion process to produce *trans*-$[PtX(COPh)(PR_3)_2]$. Carbonyl addition forms a metastable five-co-ordinate compound in non-polar solvents, which eliminates a halide to form ionic species *trans*-$[Pt(Ph)(CO)(PR_3)_2]X$ in polar solvents. Loss of PR_3 from five-co-ordinate intermediates produces two isomers of $[PtX(Ph)(CO)(PR_3)]$ which convert to the remaining isomer with Ph *trans* to PR_3 before migration of Ph proceeds to form a benzoyl complex. A direct carbonyl insertion route from a five-co-ordinate intermediate also operates, independently of the phosphine elimination pathways, and this becomes the predominant pathway with more nucleophilic PR_3 ligands. The use of elemental sulphur to remove PR_3 from the reaction mixtures was instrumental in identifying some intermediates, and this method has potential synthetic value in replacing PR_3 by weaker ligands at platinum.

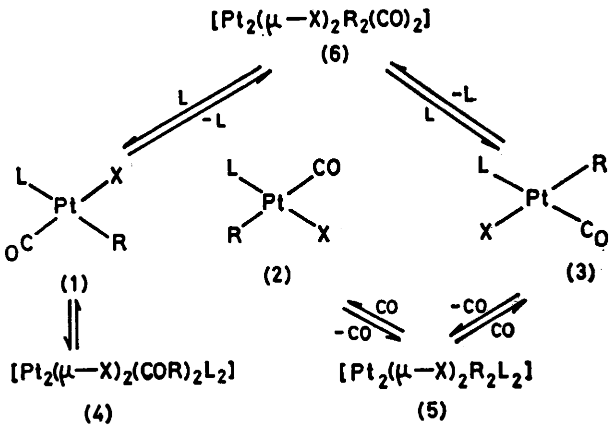
A FEW years ago, Heck and co-workers [1] made a detailed investigation of the insertion of carbon monoxide into *trans*-$[PtX(R)L_2]$ to produce *trans*-$[PtX(COR)L_2]$, and Scheme 1 was proposed as the mechanism. It was supported by kinetic data, the detection in solution of some reaction intermediates, and the following critical observations. (a) One example of a five-co-ordinate intermediate B, $[PtI(Ph)(CO)\{P(C_6H_4NMe_2\text{-}p)_3\}_2]$, was isolated and characterised; (b) one example of intermediate C, $[PtCl(Ph)(CO)\{P(C_6H_{11})_3\}]$, was obtained; (c) the presence of an excess of L inhibited the insertion, but only up to a point, indicating that a minor pathway from B to D also operated; and (d) independent studies by Mawby and co-workers [2] had previously established the pathway from C to D.

We recently reported that of the three isomers of the complex [PtX(R)(CO)L] only isomer (1), with the organic group R *trans* to the tertiary phosphine or arsine L, will readily undergo the carbonyl insertion process.[3] Isomer (1) exists in solution in equilibrium with the halogen-bridged acyl, (4) (Scheme 2), and the reaction almost certainly proceeds by migration of R to CO.[3] Addition of L causes a rapid formation of *trans*-$[PtX(COR)L_2]$ (D of Scheme 1) irrespective of the position of the (1)—(4) equilibrium. Isomers (2) and (3) resist attempts to promote CO insertion. They interconvert readily in solution *via* reversible CO loss to the dimer (5). A much slower isomerisation $\{[PtCl(Ph)(CO)(PMePh_2)]$ takes seven days to proceed 5%, accompanied by CO loss and decomposition$\}$ to (1) [and (4)] also takes place, probably *via* reversible loss of L (Scheme 2).



SCHEME 1 X = halide, L = tertiary phosphine

Intermediate C of Scheme 1 must have geometry (1) (Scheme 2) for the insertion to proceed. We discovered, however, that the example of C isolated by Garrou and Heck [1a] with L = $P(C_6H_{11})_3$ had geometry (2) and (3).[3b]



SCHEME 2 L = tertiary phosphine

This posed the question of whether tricyclohexylphosphine was anomalous because of its size, or whether isomers (2) and/or (3) were produced in every case, in which case an isomerisation to (1) should be added to Scheme 1. We have therefore further examined the relationship between isomers (1), (2), and (3), and the processes described by Garrou and Heck.[1a]

RESULTS AND DISCUSSION

Treatment of chloroform solutions of dimers, (5), by carbon monoxide produces mixtures of (2) and (3). These can be readily identified from their ^{31}P n.m.r. spectra (Table 1). The $^1J(P\text{-}Pt)$ coupling constants of isomers (2) are always higher by *ca.* 350 Hz than those of (3). We have previously reported ^{13}C n.m.r. data for some of these complexes.[4] Isomer (3), with carbon monoxide *trans* to tertiary phosphine, appears to be produced preferentially {almost exclusively, for example, from treatment of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ at −60 °C}, but equilibration with (2) at room temperature is complete in *ca.* 2 h, and (2) then predominates. For the iodide complex [PtI(Ph)(CO)(PMePh$_2$)], only isomer (2) could be detected in solution at equilibrium.

The nature of the tertiary phosphine plays a large part in determining the rate of isomerisation to (1). Whereas [PtCl(Ph)(CO)(PMePh$_2$)] [(2) and (3)] take seven days at room temperature to produce *ca.* 5% of (1) [and (4)], the triarylphosphine complexes [PtCl(Ph)(CO)(PPh$_3$)] [(2) and (3)] convert substantially to (1) and (4) in 24 h, during which time little decomposition had occurred. Complexes of P(C$_6$H$_{11}$)$_3$,[3b] PEt$_3$, and PMe$_2$Ph on the other hand, produced no detectable amounts of (1) or (4) over several days.

TABLE 1

Phosphorus-31 n.m.r. parameters for the complexes [PtX(Ph)(CO)(PR$_3$)] [isomers (2) and (3)] [a]

		Isomer (2)		Isomer (3)	
X	PR$_3$	δ(P) [b]/ p.p.m.	^1J(Pt–P)/ Hz	δ(P) [b]/ p.p.m.	^1J(Pt–P)/ Hz
Cl	PEt$_3$	12.5	3 700	12.1	3 337
Cl	PMePh$_2$	−1.7	3 920	5.7	3 481
Cl	PPh$_3$	10.2	4 071	20.1	3 561
Br	PMe$_2$Ph	−14.4	3 770	−10.1	3 359
I	PMePh$_2$	−1.6	3 699	Not observed	

[a] Spectra were recorded in CDCl$_3$ solution at 25 °C. [b] Chemical shifts are measured downfield of external H$_3$PO$_4$.

The more rapid conversion of (2) and (3) into (1) in the complexes of the less nucleophilic triarylphosphines supports the isomerisation mechanism proposed in Scheme 2 and suggests that an isomerisation step in Scheme 1 might indeed be possible with these ligands. Although isomer (2) could be isolated when the tertiary phosphine, L, was PMePh$_2$,[3a] rapid CO loss prevented isolation with L = PEt$_3$ or PMe$_2$Ph, and isomerisation was too fast to allow isolation of (2), L = PPh$_3$. The addition of tertiary phosphines or arsines to (2) or (3) caused replacement of CO in every case,[3,5] and no carbonyl insertion.

The problem in examining the nature of C in Scheme 1 is that the tertiary phosphine released in its formation prevents any appreciable concentration developing. Isomers (2) or (3) revert to A, whereas (1) is converted to D. This difficulty was overcome by carrying out the reactions between *trans*-[PtX(Ph)L$_2$] and CO in the presence of sulphur [equation (1)]. This removed the

$$trans\text{-}[\mathrm{PtX(Ph)L_2}] + \mathrm{CO} + \tfrac{1}{8}\mathrm{S_8} \longrightarrow [\mathrm{PtX(Ph)(CO)L}] + \mathrm{LS} \quad (1)$$

released phosphine as its sulphide. In 22 h in CDCl$_3$ solution, *trans*-[PtCl(Ph)(PPh$_3$)$_2$] produced PPh$_3$S [δ(P) 43.3 p.p.m.] and isomers (2) and (3) of [PtCl(Ph)(CO)(PPh$_3$)] in 4 : 1 ratio. Some *trans*-[PtCl(COPh)(PPh$_3$)$_2$] [δ(P) 19.9 p.p.m.; ^1J(P–Pt) 3 381 Hz] was also produced.

The reactions of the analogous P(*p*-tolyl)$_3$ and P(*p*-anisyl)$_3$ complexes were much faster and the *trans*-[PtCl(COPh)(PR$_3$)$_2$] insertion product was not obtained. The reaction of *trans*-[PtCl(Ph){P(C$_6$H$_4$OMe-*p*)$_3$}$_2$] with CO in the presence of sulphur proceeded almost quantitatively in 3.5 h to produce P(C$_6$H$_4$OMe-*p*)$_3$S [δ(P) 40.9 p.p.m.] and [PtCl(Ph)(CO){P(C$_6$H$_4$OMe-*p*)$_3$}] [isomer (2): δ(P) 5.9 p.p.m.; ^1J(Pt–P) 4 052 Hz]. Similar treatment of *trans*-[PtCl(Ph){P(C$_6$H$_4$Me-*p*)$_3$}$_2$] resulted in a slightly slower reaction, but after 4 h *ca.* 70% reaction had occurred to produce P(C$_6$H$_4$Me-*p*)$_3$S [δ(P) 42.4 p.p.m.] and [PtCl(Ph)(CO){P(C$_6$H$_4$Me-*p*)$_3$}] [isomer (2): δ(P) 8.2 p.p.m.; ^1J (Pt–P) 4 056 Hz]. In these latter two reactions isomer (3) was not detected.

The carbonylation of *trans*-[PtCl(Ph){P(C$_6$H$_{11}$)$_3$}$_2$] in tetrachloroethane at 70 °C was previously shown to produce [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}] [(2) and (3)] and *cis*-[PtCl$_2$(CO){P(C$_6$H$_{11}$)$_3$}].[3b] When this reaction was repeated in the presence of sulphur only P(C$_6$H$_{11}$)$_3$S [δ(P) 61.2 p.p.m.] and *cis*-[PtCl$_2$(CO){P(C$_6$H$_{11}$)$_3$}] [δ(P) 36.9 p.p.m.; ^1J (Pt–P) 2 847 Hz] were produced after 42 h. It appears, therefore, that loss of P(C$_6$H$_{11}$)$_3$ from [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}], and subsequent P(C$_6$H$_{11}$)$_3$S formation, is at least as fast as the reaction of *trans*-[PtCl(Ph){P(C$_6$H$_{11}$)$_3$}$_2$] with carbon monoxide, as no isomers of [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}] were detected in solution. Interestingly, prolonged exposure of the triphenylphosphine complexes [PtCl(Ph)(CO)(PPh$_3$)] [isomers (2) and (3)] to sulphur in CDCl$_3$ led to the production of more PPh$_3$S, adding some support to the hypothesis that reversible loss of phosphine is responsible for the isomerisation to isomer (1) (Scheme 2). In none of these experiments, when free phosphine would be scavenged by the sulphur, was any isomer (1) detected.

It thus appears that the four-co-ordinate complexes [PtX(R)(CO)L] of Scheme 1 are the isomers (2) and (3), and isomerisation to (1) would be necessary before migration of R can proceed by this route.

No reaction took place between the sulphur and any of the complexes *trans*-[PtX(Ph)L$_2$] or *trans*-[PtX(COPh)-L$_2$] in the absence of carbon monoxide. It would seem that the reactions described above might have considerable synthetic value for the replacement of strongly bonded tertiary phosphines by weaker ligands at platinum.

TABLE 2

Phosphorus-31 n.m.r. data for the complexes [a] *trans*-[Pt(Ph)(CO)(PR$_3$)$_2$][CF$_3$SO$_3$]

PR$_3$	δ(P) [b]/p.p.m.	^1J(Pt–P)/Hz
P(C$_6$H$_{11}$)$_3$	25.2	2 263
PMePh$_2$	3.9	2 560
PPh$_3$	15.6	2 656
P(C$_6$H$_4$Me-*p*)$_3$	14.1	2 605
P(C$_6$H$_4$OMe-*p*)$_3$	12.3	2 572
P(C$_6$H$_4$NMe$_2$-*p*)$_3$	10.4	2 450

[a] Spectra were recorded in CDCl$_3$ solution at 25 °C. [b] Downfield of external H$_3$PO$_4$.

The reaction between the tris(*p*-dimethylaminophenyl)phosphine complex, *trans*-[PtI(Ph){P(C$_6$H$_4$NMe$_2$-*p*)$_3$}$_2$], and CO proceeded only as far as the CO adduct [PtI(Ph)(CO)L$_2$], B, as reported by Garrou and Heck.[1a] The complex isolated was identical to that described.[1] The same ^{31}P n.m.r. characteristics were found when the reaction was carried out on the chloride or bromide complex, however, and these coincided with the parameters for the ionic complex *trans*-[Pt(Ph)(CO){P(C_6H_4-NMe_2-*p*)$_3$}$_2$][CF_3SO_3], prepared by treating *trans*-[PtCl-(Ph){P($C_6H_4NMe_2$-*p*)$_3$}$_2$] with CO in the presence of Ag-[CF_3SO_3]. Table 2 lists the ^{31}P n.m.r. data for a number of similarly obtained ionic complexes.

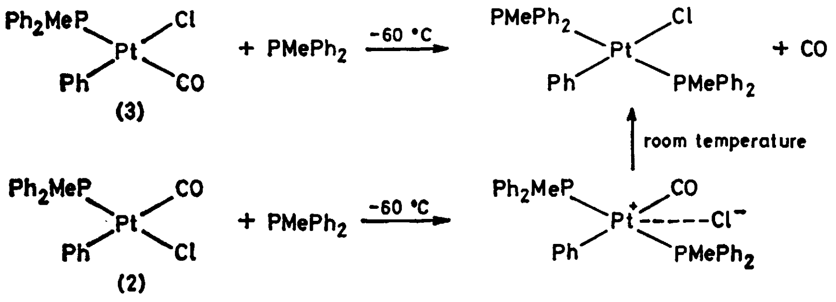
TABLE 3

Phosphorus-31 n.m.r. data for the intermediate species in the carbonylation of *trans*-[PtI(Ph)(PR_3)$_2$] [a]

	R = C_6H_4OMe-*p*		R = C_6H_4Me-*p*		R = Ph	
Solvent mixture	δ(P) [b]/p.p.m.	^1J(Pt–P)/Hz	δ(P)/p.p.m.	^1J(Pt–P)/Hz	δ(P)/p.p.m.	^1J(Pt–P)/Hz
C_6D_6 (+ trace $C_2H_2Cl_4$)	3.8	*c*				
C_6D_6 (+10% $C_2H_2Cl_4$)	7.1	2 743	6.7	2 850	12.4	2 742
C_6D_6–$C_2H_2Cl_4$ (1 : 1)	9.8	2 641	12.1	2 661		
C_6D_6–$C_2H_2Cl_4$–MeOH (1 : 1 : 1)	12.1	2 559				
$C_2H_2Cl_4$ (+ trace C_6D_6)	11.4	2 584	13.6	2 609		

[a] Spectra were recorded at −10 °C at concentrations *ca.* 0.05 mol dm^{-3}. No dependence of δ or ^1J on concentration was detected in any solvent. [b] Downfield of external H_3PO_4. [c] Too weak to be observed.

Thus the example of intermediate B (Scheme 1) which was previously isolated is clearly ionic, and not five-co-ordinate as claimed.[1a] The situation for complexes of P(C_6H_4OMe-*p*)$_3$ and P(C_6H_4Me-*p*)$_3$ is more complicated, however. In chloroform solution the ^{31}P n.m.r. parameters of [PtX(Ph)(CO)L_2] are again independent of X, and identical to those of the respective ionic complexes of Table 2. When the polarity of the solvent is reduced by employing various mixtures of C_6D_6 and $C_2H_2Cl_4$, the chemical shift decreases and the coupling constant increases. Moreover, the values are then dependent on the nature of the halide, as reported by Garrou and Heck.[1a] A similar situation prevails for the PPh_3 analogue, reported for the first time. Data are presented in Table 3.

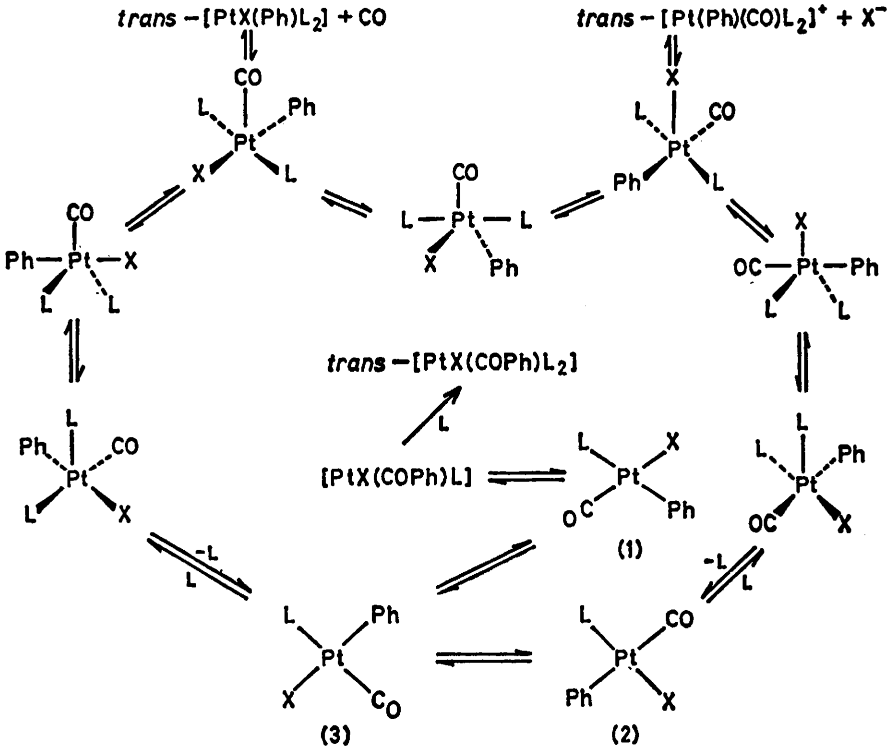


The nature of these intermediates is clearly dependent on both the solvent and the tertiary phosphine ligand. More polar solvents favour the formation of ionic species, as do electron-donating substituents on the phosphines, presumably by stabilising the cation. The order Ph < *p*-tolyl < *p*-anisyl < *p*-$Me_2NC_6H_4$ is observed, and with the latter substituent on phosphorus only the ionic material was formed even in low-polarity solvents.

A precedent for this relationship between ionic four-co-ordinate and non-ionic five-co-ordinate platinum complexes can be found in the nature of the intermediates in the nucleophile-catalysed *cis–trans* isomerisations of [PtX_2L_2] compounds. In polar solvents these take the form [$PtXL_3$]$^+X^-$, condensing to associated ion pairs then covalent adducts as the polarity is reduced.[6,7] A number of analogous five-co-ordinate complexes of palladium and platinum have been isolated and structurally characterised.[8] These have a geometry close to square pyramidal with a halide in the apical position, as would be expected from an association of ions. The five-co-ordinate species observed in the present study probably have a similar geometry.

It is apparent that many of the steps involved in this system can easily be reversed. Addition of $PMePh_2$ to a $CDCl_3$ solution [PtCl(Ph)(CO)($PMePh_2$)] [isomers (2) and (3)] at −60 °C resulted in a quantitative reaction of each isomer; (3) by CO replacement to *trans*-[PtCl-(Ph)($PMePh_2$)$_2$] [δ(P) 9.3 p.p.m.; ^1J(P–Pt) 2 987 Hz] and (2) to the ion pair *trans*-[Pt(Ph)(CO)($PMePh_2$)$_2$]Cl [δ(P) 1.3 p.p.m.; ^1J(P–Pt) 2 702 Hz]. On warming, the complex produced from (2) also converted to *trans*-[PtCl(Ph)($PMePh_2$)$_2$].

Scheme 3 shows the relationships of the newly discovered pathways and intermediates. The phosphine eliminations to produce (2) and/or (3) are probably the slowest steps, though the isomerisations of the four-co-ordinate intermediates may also be slow. It is not possible to state whether both pathways for phosphine elimination operate, since in the time scale of the reactions (2) and (3) would equilibrate. The reverse reactions do operate independently, however. The addition of iodide ions to solutions of the ionic species *trans*-[Pt(Ph)(CO){P(C_6H_4OMe-*p*)$_3$}$_2$][CF_3SO_3] produces both *trans*-[PtX(Ph)L_2] and *trans*-[PtX(COPh)L_2]. When the reaction is performed in the presence of sulphur, P(C_6H_4OMe-*p*)$_3$S is produced, but when carried out whilst bubbling N_2 through the solution, all the CO is lost to produce only *trans*-[PtX(Ph)L_2].



SCHEME 3 L = tertiary phosphine

This would suggest that equilibrium (2) is rapidly achieved. When CO is removed, the reactions are displaced to the left, but when CO remains in solution, the slower reactions to produce aroyl complexes can proceed. When chloride ions are added to the ionic material *trans*-[Pt(Ph)(CO){P(C_6H_4OMe-*p*)$_3$}$_2$][CF_3SO_3], only *trans*-[PtCl(Ph)L_2] results, even in the absence of a N_2 stream. This is in keeping with the observations that the reactions between CO and *trans*-[PtCl(Ph)L_2] are much slower than with the iodide analogues.[1a]

$$\textit{trans}\text{-}[\mathrm{PtX(Ph)L_2}] + \mathrm{CO} \rightleftharpoons \textit{trans}\text{-}[\mathrm{Pt(Ph)(CO)L_2}]\mathrm{X} \qquad (2)$$

Garrou and Heck [1] suppressed the phosphine elimination steps by adding an excess of ligand to the system, and observed a slower, direct carbonyl insertion route, presumably from a five-co-ordinate species. We have further evidence for the operation of this second route. When the reaction between CO and *trans*-[PtCl(Ph)-($PMePh_2$)$_2$] is carried out in the presence of sulphur, no phosphine sulphide is produced, indicating that, as expected, the more nucleophilic phosphine is not eliminated. Nevertheless *trans*-[PtCl(COPh)($PMePh_2$)$_2$] is slowly produced, obviously by a route not involving phosphine loss. Further evidence can be derived from the fact that some *trans*-[PtCl(COPh)(PPh_3)$_2$] is produced during the reaction of [PtCl(Ph)(PPh_3)$_2$] and CO in the presence of sulphur. This, too, is most likely to proceed by a direct route, since eliminated PPh_3 would react with sulphur and would not be available to form the final product. Four of the five-co-ordinate intermediates of Scheme 3 have CO and Ph mutually *cis* at 90° or 120° angles, and any of these might be responsible for the direct carbonylation. The metastable five-co-ordinate species observed in solution are most probably square pyramidal with *trans* phosphines and apical halide.

TABLE 4

Analytical and ^{31}P n.m.r. [a] data for the complexes *trans*-[PtX(Ph)(PR_3)$_2$]

			Analysis [c] (%)	
X	PR_3	δ(P) [b][^1J(P–Pt)/Hz]	C	H
Cl	P(C_6H_{11})$_3$	17.2 [2 792]	57.85 (58.1)	8.05 (8.25)
Cl	$PMePh_2$	8.7 [3 010]		
Cl	PPh_3	24.5 [3 153]	60.35 (60.6)	4.20 (4.25)
Cl	P(C_6H_4Me-*p*)$_3$	22.7 [3 124]	63.45 (62.9)	5.85 (5.15)
Cl	P(C_6H_4OMe-*p*)$_3$	21.1 [3 103]	56.9 (56.95)	4.70 (4.70)
Cl	P($C_6H_4NMe_2$-*p*)$_3$	19.4 [3 037]	56.6 (59.5)	6.00 (6.00)
Br	P($C_6H_4NMe_2$-*p*)$_3$	19.0 [3 027]		
I	PPh_3	21.7 [3 094]		
I	P(C_6H_4Me-*p*)$_3$	19.9 [3 064]		
I	P(C_6H_4OMe-*p*)$_3$	18.3 [3 044]		
I	P($C_6H_4NMe_2$-*p*)$_3$	16.6 [2 984]		

[a] In $CDCl_3$ at 25 °C. [b] In p.p.m. downfield from external H_3PO_4. [c] Calculated values are given in parentheses.

EXPERIMENTAL

The complexes [PtCl(Ph)L_2] were prepared by phosphine displacement of cod from [PtCl(Ph)(cod)] (cod = cycloocta-1,5-diene),[9] or by the reaction of $HgPh_2$ with [$PtCl_2L_2$].[10]

Analogous iodides or bromides were prepared by metathetical displacements. Analytical and ^{31}P data not reported elsewhere[1] are presented in Table 4. Phosphorus-31 n.m.r. spectra were recorded on a Varian XL-100 spectrometer in the Fourier-transform mode. In a typical experiment using sulphur to trap displaced PR_3, the complex *trans*-$[PtX(Ph)(PR_3)_2]$ (*ca.* 25 mg) in $CDCl_3$ (0.5 cm^3) was stirred with 30 mol equivalents of sulphur crystals under a CO atmosphere. After the desired reaction time the sulphur was filtered off and the ^{31}P n.m.r. spectrum recorded.

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