Carbonyl Insertion at [PtX(Ph)(CO)L]: The Effects of varying the Anionic Ligand X and the Neutral Ligand L

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From the reaction of $HgPh_2$ with *cis*-$[PtCl_2(CO)L]$, the benzoyl complexes $[Pt_2(\mu\text{-}Cl)_2(COPh)_2L_2]$ can be isolated when L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, or $P(C_6H_{11})_3$, but when L = $P(C_6H_4Me\text{-}o)_3$, $AsMePh_2$, or $AsPh_3$ only the [PtCl(Ph)(CO)L] complexes are formed. Metathetical replacements of the chloride ions in $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ lead to the corresponding bromide or iodide complexes. Low-temperature n.m.r. studies show that the reaction between $HgPh_2$ and *cis*-$[PtCl_2(CO)L]$ gives first the carbonyl derivative [PtCl(Ph)(CO)L], from which CO insertion proceeds. The equilibrium positions in solution between [PtX(Ph)(CO)L] (each with Ph *trans* to L) and the binuclear benzoyl complexes are reported. The effect of X on the equilibrium position depends on the bridging ability of that group in the benzoyl dimers, stronger bridges favouring the insertion product. The neutral ligands L exert an effect by both electronic and steric factors. The magnitude of the *trans* influence of L directly affects the tendency of the *trans* phenyl group to migrate to CO, unless a critical size of L is exceeded. In these cases, the steric bulk of L favours the mononuclear carbonyl derivative.

PREVIOUSLY we have shown[1] that the isomers of $[PtCl(R)(CO)(PMePh_2)]$ (1; R = Et, Me, Ph, or CH_2Ph) with R *trans* to the tertiary phosphine undergo the carbonyl-insertion reaction (i) and exist in solution in equilibrium with the halide-bridged dimers (4). The

$$\underset{(1)}{2[PtCl(R)(CO)(PMePh_2)]} \rightleftharpoons \underset{(4)}{[(Ph_2MeP)(RCO)Pt(\mu\text{-}Cl)_2Pt(COR)(PMePh_2)]} \quad (i)$$

other two configurations of $[PtCl(R)(CO)(PMePh_2)]$, with R *trans* to CO (2) and Cl (3) respectively, can isomerise readily between themselves and are also slowly converted into (1), but are resistant to attempts to promote carbonyl insertion.

Nucleophile-assisted carbonyl insertion at [PtX(R)(CO)L] (X is halide, L is tertiary phosphine) had earlier been examined kinetically by Mawby and co-workers,[2] and complexes of the same stoicheiometry have been postulated as intermediates in the carbonylation of $[PtX(R)L_2]$ from a mechanistic study by Heck and co-workers.[3] It would appear, therefore, that the complexes featured in both these studies must have had geometry (1).

Changing the organic groups R has a marked effect on the position of the equilibrium between (1) and (4). With 0.02 mol dm^{-3} solutions in chloroform, the amount of (4) decreases from *ca.* 90% (R = Et) to 60% (R = Ph), 17% (R = Me), and 0% (R = CH_2Ph).[1] We report here the effects on this equilibrium of varying the anionic ligand, X, and the neutral ligand, L, and show them to be as critical as the organic group in controlling this carbonyl-insertion reaction.

RESULTS AND DISCUSSION

Formation Reactions.—The reactions between $[PtCl_2(CO)L]$ [L = PEt_3, PMe_2Ph, PPh_3, or $P(C_6H_{11})_3$] and diphenylmercury resembled closely that reported by us between $[PtCl_2(CO)(PMePh_2)]$ and $HgPh_2$.[1] The products were isolated as the crystalline dimeric benzoyl derivatives $[L(PhCO)Pt(\mu\text{-}Cl)_2Pt(COPh)L]$. In chloroform solution, all these compounds were found to be in equilibrium with [PtCl(Ph)(CO)L]. The equilibrium positions and carbonyl-stretching frequencies of each component are listed in Table 1. In every case, the small values of ${}^1J(Pt\text{-}P)$ indicate that the monomers have geometry (1), with Ph *trans* to L (ref. 1) (Table 2).

TABLE 1

Infrared data * for the system $2[PtX(Ph)(CO)L] \rightleftharpoons [Pt_2(\mu\text{-}X)_2(COPh)_2L_2]$ in $CHCl_3$ solution at 20 °C

L	X	$\nu(CO)/cm^{-1}$		%	%	K_c/
		Monomer	Dimer	Monomer	Dimer	dm^3 mol^{-1}
PEt_3	Cl	2 077	1 628	18	82	690
PMe_2Ph	Cl	2 083	1 631	24	76	650
$PMePh_2$	Cl	2 087	1 635	40	60	160
$PMePh_2$	Br	2 085	1 633	10	90	3 600
$PMePh_2$	I	2 085	1 630	2	98	*ca.* 10^5
PPh_3	Cl	2 087	1 639	63	37	31
$P(C_6H_{11})_3$	Cl	2 072	1 627	83	17	8.0
$P(C_6H_4Me\text{-}o)_3$	Cl	2 083		100	0	0
$AsMePh_2$	Cl	2 084		100	0	0
$AsPh_3$	Cl	2 085		100	0	0

* 0.02 mol dm^{-3} solutions with respect to the monomer.

TABLE 2

Phosphorus-31 n.m.r. data for the system $2[PtX(Ph)(CO)L] \rightleftharpoons [Pt_2(\mu\text{-}X)_2(COPh)_2L_2]$ in $CDCl_3$ at 25 °C

		[PtX(Ph)(CO)L]		$[Pt_2(\mu\text{-}X)_2(COPh)_2L_2]$	
L	X	$\delta(P)$ [a]/ p.p.m.	${}^1J(P\text{-}Pt)$/ Hz	$\delta(P)$/ p.p.m.	${}^1J(P\text{-}Pt)$/ Hz
PEt_3	Cl	18.9	1 407	10.7	5 041
PMe_2Ph	Cl	−5.3	1 381	−15.0	5 180
$PMePh_2$	Cl	6.8	1 402	−3.3	5 321
$PMePh_2$	Br	2.9	1 436	−3.0	5 280
$PMePh_2$	I	*b*		−3.5	5 397
				−4.4	5 016
				−5.1	*ca.* 5 100
PPh_3	Cl	18.9	1 426	11.0	5 495
$P(C_6H_{11})_3$	Cl	31.0	1 437	22.4	5 055
$P(C_6H_4Me\text{-}o)_3$	Cl	17.9	1 366	*b*	

[a] Chemical shifts measured downfield of external H_3PO_4.
[b] Not observable.

A similar reaction takes place between $[PtCl_2(CO)L]$ [L = $P(C_6H_4Me\text{-}o)_3$, $AsPh_3$, or $AsMePh_2$] and diphenylmercury. In these cases, however, only [PtCl(Ph)(CO)L] [geometry (1)] could be observed in solution, i.r. and n.m.r. examination failing to detect any dimer. This situation resembles the formation of the benzyl analogue [PtCl(CH$_2$Ph)(CO)(PMePh$_2$)].[1] The low value of ^1J(Pt–P) in [PtCl(Ph)(CO){P(C$_6$H$_4$Me-*o*)$_3$}] again proves its geometry to be (1). This parameter is not available for the two tertiary arsine complexes, but their values of ν(CO) (Table 1), and δ^{13}C and ^1J(Pt–^{13}C) for ^{13}CO-labelled samples,[4] are typical for complexes with phenyl *trans* to the neutral ligand.

The tri-*o*-tolylphosphine complex [PtCl(Ph)(CO)-{P(C$_6$H$_4$Me-*o*)$_3$}] was isolated from its solution as a crystalline solid, but the two analogous arsine derivatives decomposed during work-up. In these cases, slow addition of 1 mol of arsine to the complexes produced the aroyl derivatives *trans*-[PtCl(COPh)L$_2$] (L = AsPh$_3$ or AsMePh$_2$) which were isolated and characterised. The complex *trans*-[PtCl(COCH$_2$Ph)(PMePh$_2$)$_2$] was similarly formed by treating [PtCl(CH$_2$Ph)(CO)(PMePh$_2$)] with PMePh$_2$,[1] and all three of these reactions are analogous to Mawby's nucleophile-assisted insertion reactions.[2] It appears therefore that the insertion reaction proceeds, even when the equilibrium between (1) and (4) lies so far to the left that no dimer can be detected in solution.

Interestingly, treatment of [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}] with P(C$_6$H$_{11}$)$_3$, or of [PtCl(Ph)(CO){P(C$_6$H$_4$Me-*o*)$_3$}] with P(C$_6$H$_4$Me-*o*)$_3$, failed to promote the insertion reaction, and the solutions remained unchanged at room temperature. This was surprising, since the platinum complexes were of the correct geometry for insertion, and the tricyclohexylphosphine complex exists in solution in equilibrium with a detectable amount of dimer (Table 1). Presumably the excessive steric demands of these phosphines must prevent attack of another such group at platinum, either on (1) (which would lead to CO loss [1]), (4), or the three-co-ordinate intermediate.

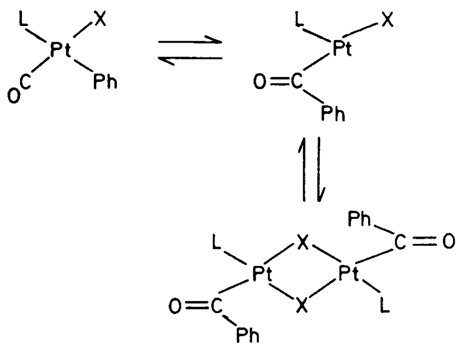
Garrou and Heck [3a] reported isolating two isomers of [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}] after eliminating tricyclohexylphosphine from *trans*-[PtCl(Ph){P(C$_6$H$_{11}$)$_3$}$_2$] by CO over 4 d. These isomers resisted CO insertion, and their isolation was instrumental in establishing the presence of intermediates of the type [PtX(R)(CO)L] in the reaction scheme of *trans*-[PtX(R)L$_2$] with CO. This result is of interest, since the isomer (1) we obtained from the reaction of *cis*-[PtCl$_2$(CO){P(C$_6$H$_{11}$)$_3$}] with HgPh$_2$, whilst resisting reaction with P(C$_6$H$_{11}$)$_3$, did equilibrate with the dimeric benzoyl compound which was obtained as a solid. We therefore repeated the procedure of Garrou and Heck, treating a *sym*-tetrachloroethane solution of *trans*-[PtCl(Ph){P(C$_6$H$_{11}$)$_3$}$_2$] with CO at 70 °C. A similar reaction was carried out using labelled ^{13}CO. Periodic ^{31}P and ^{13}C n.m.r. examinations revealed the reaction to be slower and more complicated than that reported: some starting material remained even after 7 d, and amongst the many products large amounts of *cis*-[PtCl$_2$(CO){P(C$_6$H$_{11}$)$_3$}] [δ(P) 37.1 p.p.m.; ^1J(P–Pt) 2 844 Hz] were always detected. We failed to find any trace of isomer (1) or its related benzoyl, (4), but spectroscopic characteristics clearly typical [1,4] of isomers (2) and (3) of [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}] were observed [(2); δ(P) 27.8, ^1J(P–Pt) 3 725, ^2J(P–C)(CO) 6.8, δ(C) 178.3, ^1J(Pt–C)(CO) 900; (3), δ(P) 15.8, ^2J(P–C)(CO) 141.1 Hz, δ(C) 173.0 p.p.m.]. We thus conclude that the isomers of [PtCl(Ph)(CO){P(C$_6$H$_{11}$)$_3$}] previously isolated [3a] were (2) and (3), which we would not expect [1] to undergo CO insertion.

Treatment of [Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PMePh$_2$)$_2$] (4) with LiBr or LiI forms the analogous bromide- or iodide-bridged dimers. Like the chloride, these exist in solution in equilibria with [PtX(Ph)(CO)(PMePh$_2$)], and the ^{31}P n.m.r. spectra of the latter compounds again show Ph to lie *trans* to PMePh$_2$. Data are in Tables 1 and 2.

The halide-bridged acyl or aroyl complexes exist in solution as mixtures of *cis* and *trans* isomers. The chloride derivatives interconvert rapidly on the n.m.r. time scale at room temperature, leading to broadened or coalesced signals. These can be resolved at low temperature.[4] The bromide and iodide complexes isomerise more slowly and both isomers can be detected by ^{31}P n.m.r. at ambient temperatures. There is now considerable evidence that binuclear complexes [Pt$_2$(μ-X)$_2$Y$_2$L$_2$] (X = halide; Y = X, alkyl, aryl, acyl, or aroyl) exist in solution as both *cis* and *trans* isomers.[1,4–7] When Y is halide, *trans* isomers predominate, but *cis* configurations become more common with terminal organic groups. In the case of [Pt$_2$(μ-Cl)$_2$Me$_2$(PMe$_2$Ph)$_2$] only the *cis* isomer was observed.[8]

The values of ^1J(^{195}Pt–^{31}P) in the halide-bridged organic derivatives are unusually large,[5] ranging up to *ca.* 5 495 Hz in [Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PPh$_3$)$_2$] (Table 2). We have reported the *X*-ray analysis of *trans*-[Pt$_2$(μ-Cl)$_2$-(COEt)$_2$(PMe$_2$Ph)$_2$] and shown that the abnormal coupling constants are not reflected in excessively short Pt–P bond lengths.[5]

Although well proven examples are still quite rare, the accepted mechanism for carbonyl insertion is by organic group migration.[9] Our evidence is compatible with this mechanism, with isomers (1), having their organic groups *trans* to the bond-weakening [10] tertiary phosphine or arsine ligands, being the only ones to undergo insertion. The cumulative data from our studies [1] and the kinetic studies by Mawby,[2] Heck,[3] and their co-workers suggest that equation (ii) reflects the true situation. Many cases have now been reported of the



(ii)

existence of 'T-shaped' 14-electron intermediates in platinum chemistry,[11] and the potential importance of halide-bridge formation in the carbonyl-insertion reaction at second- and third-row transition elements has been emphasised.[12] The equilibria between 'T-shaped' intermediates and the halide-bridged dimer [equation (ii)] represents a possible isomerisation mechanism for the dimer, although others have been suggested.[13]

The question remains whether the carbonyl complex (1) or the acyl (4) is the initial product from the reaction between *cis*-$[PtCl_2(CO)L]$ and HgR_2. Some years ago [14] we suggested the possibility that the reaction proceeded *via* oxidative addition of the mercury compound to platinum, and that CO insertion could take place at the six-co-ordinate intermediate. More recently Eaborn *et al.*[7] suggested the same mechanism to account for the isolation of $[Pt_2(\mu\text{-}Cl)_2(COR)_2L_2]$ from the reaction between *cis*-$[PtCl_2(CO)L]$ and $SnMe_3R$ (R = aryl).* We have now studied the course of the reaction between diphenylmercury and *cis*-$[PtCl_2(CO)(PMePh_2)]$ by ^{31}P n.m.r. spectroscopy at low temperature. Deuteriochloroform solutions of the reactants were mixed at −60 °C, at which temperature no reaction occurred. At −40 °C, the presence of $[PtCl(Ph)(CO)(PMePh_2)]$ [isomer (1)] was clearly observable, virtually no benzoyl derivative (4) being detected. On warming, the reaction proceeds and (1) and (4) equilibrate, (4) predominating. Thus, although it is possible that the reaction proceeds *via* oxidative addition, the primary product is (1), and it is unlikely that insertion occurs at a platinum(IV) intermediate.

Factors affecting the (1), (4) *Equilibria.*—The equilibrium positions between the carbonyl and aroyl complexes are listed in Table 1.

The variations caused by changing the anionic group X can be readily explained in terms of the bridge strengths of Cl, Br, and I. The softer halides are more compatible with the soft acid Pt^{II} and form stronger bridges in (4). Bromide and iodide readily replace Cl in bridging positions,[17] and dimer formation will be energetically favoured by these groups.

The effects of the neutral ligands, L, are not so straightforward, and both steric and electronic factors must be considered. The effective sizes of the ligands can be estimated from the cone angles subtended at the metal atom, and an extensive series has been computed by Tolman,[18] mainly from measurements on models. Although it has been shown that this angle is somewhat dependent on the system involved,[19] it is clear that $P(C_6H_{11})_3$ and $P(C_6H_4Me\text{-}o)_3$ are particularly bulky, and will favour the less sterically crowded side of an equilibrium. These ligands favour (1), rather than (4) (Table 1), presumably because CO in the *cis* position in (1) is less sterically demanding than COPh in (4), or in the 'T-shaped' intermediate.

Steric factors cannot explain the remainder of the sequence, however, and the correlation between equilibrium position and cone angle [18] is poor. The arsines in particular, with small cone angles due to longer Pt–L bonds, are obviously in an anomalous position. Clearly the bond-weakening *trans* influence of L would be expected to be important in promoting the migration of the *trans* aryl groups. Tolman's 'electronic parameter' gives a reasonable fit with our observed equilibria for PEt_3, PMe_2Ph, $PMePh_2$, and PPh_3 [although not, of course, for $P(C_6H_{11})_3$ or $P(C_6H_4Me\text{-}o)_3$], but no data on arsines were reported, and in any case the data were derived from tetrahedral molecules.[20] Spectroscopic [21] and kinetic [22] data on phosphine and arsine complexes suggest that the *trans* influence does follow our observed pattern of equilibria for the less bulky ligands in Table 1, but data for our complete series have not been published. We therefore accurately measured ν(Pt–Cl) for the series *cis*-$[PtCl_2L_2]$ (Table 3). The values fit the *trans*-influence series $PEt_3 > PMe_2Ph > PMePh_2 > PPh_3 > AsMePh_2 > AsPh_3$, which matches our equilibrium sequence for these ligands exactly. *cis*-Dihalides for the bulky $P(C_6H_{11})_3$ and $P(C_6H_4Me\text{-}o)_3$ ligands are not available, but the ν(Pt–Cl) values for *cis*-$[PtCl_2(CO)L]$, as well as Tolman's values,[20] suggest that these ligands fall in an exceptional position in the equilibrium series, with $P(C_6H_{11})_3$ electronically resembling PEt_3, and $P(C_6H_4Me\text{-}o)_3$ being similar to PPh_3.

TABLE 3

Infrared spectra of the complexes *cis*-$[PtCl_2L_2]$ and *cis*-$[PtCl_2(CO)L]$, recorded as CsI discs

	ν(Pt–Cl)/cm⁻¹	
L	*cis*-$[PtCl_2L_2]$	*cis*-$[PtCl_2(CO)L]$
PEt_3	303, 280	353, 304
PMe_2Ph	308, 286	349, 301
$PMePh_2$	316, 292	348, 304
PPh_3	318, 293	353, 312
$P(C_6H_4Me\text{-}o)_3$		349, 312 (KBr disc)
$P(C_6H_{11})_3$		345, 303
$AsMePh_2$	320, 299	350, 308
$AsPh_3$	338, 325 (sh)	341, 315

We thus conclude that the *trans* influences of the neutral ligands, L, dominate the equilibrium positions up to a critical size {cone angle greater than 145° (for PPh_3), but less than 170° [for $P(C_6H_{11})_3$] [18]}, when steric effects become more important.

EXPERIMENTAL

The complexes *cis*-$[PtCl_2(CO)L]$ (L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, $AsMePh_2$, or $AsPh_3$) were prepared by passing carbon monoxide through suspensions of $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ in benzene, the complexes being obtained as colourless crystals.[23]

Solution i.r. spectra were recorded in chloroform on a Perkin-Elmer 577 instrument using NaCl cells of 0.5 mm path length. Infrared spectra of solid materials were obtained for CsI or KBr discs on a Perkin-Elmer 580

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* We previously observed that $SnPh_4$ reacts with *cis*-$[PtCl_2(CO)L]$ to produce the aroylplatinum dimer.[15] The obvious similarity between these reactions and the arylation of $[PdCl_2(CNR)L]$ to $[Pd_2(\mu\text{-}Cl)_2\{C(R')NR\}_2L_2]$ (R′ = aryl) by a variety of organometallic arylating agents [16] suggests that overall the process is very versatile.

spectrophotometer. Phosphorus-31 and ^{13}C n.m.r. spectra were recorded in $CDCl_3$ solution using a Varian XL-100 spectrometer in the Fourier-transform mode.

cis-*Carbonyldichloro(tricyclohexylphosphine)platinum*.—The compound dichloro(norbornadiene)platinum (0.256 g, 0.72 mmol) was stirred in chloroform (40 cm^3). Carbon monoxide was passed through the suspension for 2 h and tricyclohexylphosphine (0.200 g, 0.71 mmol) was added. After 1 h the solvent was removed, the residue stirred with charcoal in benzene, and the solution filtered. Addition of light petroleum (b.p. 40—60 °C) caused precipitation of a white solid (0.125 g, 31%), which was recrystallised from chloroform-diethyl ether to give colourless crystals of *cis*-$[PtCl_2(CO)\{P(C_6H_{11})_3\}]$, ν(CO) at 2 099 cm^{-1} in $CHCl_3$ solution (Found: C, 39.65; H, 5.95. Calc. for $C_{19}H_{33}Cl_2OPPt$: C, 39.7; H, 5.80%).

Similarly prepared was *cis*-$[PtCl_2(CO)\{P(C_6H_4Me\text{-}o)_3\}]$, ν(CO) at 2 110 cm^{-1} in $CHCl_3$ solution (Found: C, 44.2; H, 3.65. Calc. for $C_{22}H_{21}Cl_2OPPt$: C, 44.15; H, 3.55%).

The following compounds were prepared by the method previously described[1] for dibenzoyl-di-μ-chloro-bis(diphenylmethylphosphine)diplatinum. *Dibenzoyl-di-μ-chloro-bis(triethylphosphine)diplatinum*, m.p. 153 °C (Found: C, 34.35; H, 4.4. Calc. for $C_{26}H_{40}Cl_2O_2P_2Pt_2$: C, 34.4; H, 4.45%); *dibenzoyl-di-μ-chloro-bis(dimethylphenylphosphine)diplatinum*, m.p. 166—168 °C (decomp.) (Found: C, 37.9; H, 3.30. Calc. for $C_{30}H_{32}Cl_2O_2P_2Pt_2$: C, 38.0; H, 3.4%); *dibenzoyl-di-μ-chloro-bis(triphenylphosphine)diplatinum*, m.p. 287—291 °C (decomp.) (Found: C, 50.25; H, 3.25. Calc. for $C_{50}H_{40}Cl_2O_2P_2Pt_2$: C, 50.2; H, 3.35%); *dibenzoyl-di-μ-chloro-bis(tricyclohexylphosphine)diplatinum*, m.p. 192—194 °C. This solid material also contains $[PtCl(Ph)(CO)\{P(C_6H_{11})_3\}]$ [isomer (1)] which was not separated by crystallisation (Found: C, 48.65; H, 6.20. Calc. for $C_{50}H_{76}Cl_2O_2P_2Pt_2$: C, 48.75; H, 6.20%).

Dibenzoyl-di-μ-bromo-bis(methyldiphenylphosphine)diplatinum.—The compound $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ (0.304 g, 0.52 mmol) was stirred with lithium bromide (*ca.* 1.0 g, 11.5 mmol) in acetone (50 cm^3) under nitrogen for 18 h, then heated briefly to 50 °C. The solvent was removed and the oily residue treated with water–chloroform (4 : 1). The chloroform layer was withdrawn, dried over anhydrous $Mg[SO_4]$, and filtered. Diethyl ether addition caused precipitation of colourless crystals of $[Pt_2(\mu\text{-}Br)_2(COPh)_2(PMePh_2)_2]$, m.p. 165—170 °C (decomp.) (Found: C, 41.25; H, 3.35. Calc. for $C_{40}H_{36}Br_2O_2P_2Pt_2$: C, 41.4; H, 3.15%).

Dibenzoyl-di-μ-iodo-bis(methyldiphenylphosphine)diplatinum.—Treatment of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ with lithium iodide, in a manner analogous to that described above, gave yellow crystals of $[Pt_2(\mu\text{-}I)_2(COPh)_2(PMePh_2)_2]$, m.p. 243—244 °C (Found: C, 38.15; H, 2.90; I, 20.1. Calc. for $C_{40}H_{36}I_2O_2P_2Pt_2$: C, 38.3; H, 2.90; I, 20.3%).

*Carbonylchloro(phenyl)(tri-*o*-tolylphosphine)platinum*.—The compound *cis*-$[PtCl_2(CO)\{P(C_6H_4Me\text{-}o)_3\}]$ (65.7 mg, 0.11 mmol) and $HgPh_2$ (39.0 mg, 0.11 mmol) were stirred in benzene (5 cm^3) under nitrogen for 8 h. Phenylmercury(II) chloride was filtered off, and addition of light petroleum (b.p. 40—60 °C) caused precipitation of colourless crystals of $[PtCl(Ph)(CO)\{P(C_6H_4Me\text{-}o)_3\}]$, m.p. 171—172 °C (Found: C, 52.5; H; 4.45. Calc. for $C_{28}H_{26}ClOPPt$: C, 52.55; H, 4.10%).

trans-*Benzoylchlorobis(methyldiphenylarsine)platinum*.—The compound *cis*-$[PtCl_2(CO)(AsMePh_2)]$ (0.115 g, 0.21 mmol) was suspended in benzene (10 cm^3) under nitrogen. Diphenylmercury (0.076 g, 0.21 mmol) was added, and the mixture was stirred for 2 h. A small amount of charcoal was added to the brown suspension and stirring continued for 15 min. To the pale yellow solution, after filtration, was added, over 2 h, a solution of $AsMePh_2$ (41 μl, 0.21 mmol) in benzene (2 cm^3). The solution was again filtered and addition of light petroleum caused precipitation of colourless crystals of *trans*-$[PtCl(COPh)(AsMePh_2)_2]$, m.p. 163—165 °C (Found: C, 48.05; H, 3.95. Calc. for $C_{33}H_{31}As_2ClOPt$: C, 48.1; H, 3.80%). trans-*Benzoylchlorobis(triphenylarsine)platinum* was prepared similarly, m.p. 243—245 °C (Found: C, 54.4; H, 3.80. Calc. for $C_{43}H_{35}As_2ClOPt$: C, 54.45; H, 3.70%).

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