The Effects of Stereochemistry at Platinum and the Nature of the Organic Group on Carbonyl Insertion at [PtCl(R)(CO)(PMePh$_2$)]

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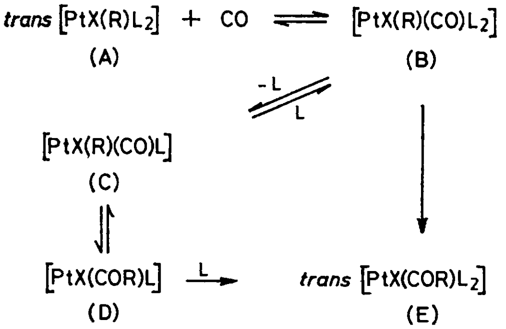
The three geometric isomers of [PtCl(Ph)(CO)(PMePh$_2$)] have been prepared. Only the isomer with Ph *trans* to PMePh$_2$ readily undergoes carbonyl insertion, and produces the halide-bridged acyl complex [Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PMePh$_2$)$_2$], with which it equilibrates in solution. The other isomers are reluctant to undergo CO insertion, and attempts to promote this lead to elimination of carbon monoxide. Replacing the phenyl group by other R groups has a critical effect on the equilibrium position between the acyl and carbonyl complexes, the tendency towards the acyl decreasing in the order R = Et > Ph > Me > CH$_2$Ph ($\simeq$0). These observations are compatible with R migration to CO as the mechanism of acyl formation at platinum(II).

THE reaction of carbon monoxide with platinum(II) complexes [PtX(R)L$_2$] (X = halogen; R = Me, Et, or Ph; L = PEt$_3$) was shown by Booth and Chatt[1] to produce the acyl complexes *trans*-[PtX(COR)L$_2$]. These workers suggested that five- or six-co-ordinate intermediates may be involved.[1a] Kinetic studies by Mawby and his co-workers[2] on the conversion of [PtX(R)(CO)L] into [PtX(COR)L(L′)] by the addition of nucleophiles L′ demonstrated that the rate-determining step, which involved the combination of CO and the organic group R to form an acyl group, was not assisted by either the incoming nucleophile or solvent [Scheme 1; (C) ⟶ (D) ⟶ (E)]. Similar reactions of octahedral iridium(III) complexes [IrCl$_2$R(CO)$_2$L] (R = Me or Et; L = AsPh$_3$ or AsMePh$_2$) were also shown to proceed by carbonyl insertion to form co-ordinatively unsaturated intermediates.[3] Recently, detailed kinetic investigations by Garrou and Heck[4] established the reaction pathways shown in Scheme 1. The predominant pathway involves loss of tertiary phosphine ligand L from the five-co-ordinate intermediate (B), followed by conversion of (C) into the three-co-ordinate acyl species (D). A secondary pathway, direct conversion of (B) into (E), also appears to operate, however.

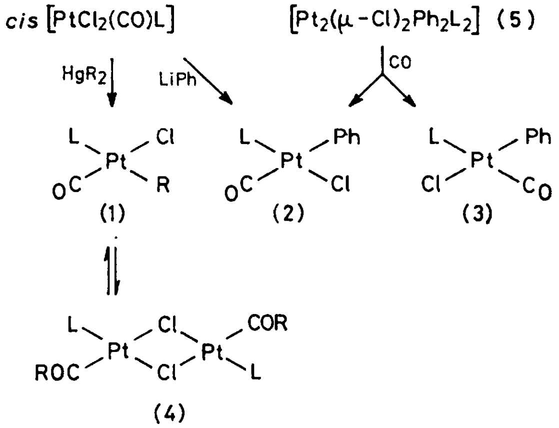
Previously we reported that the arylation of *cis*-[PtCl$_2$(CO)L] by diphenylmercury was accompanied by an insertion reaction from which the halide-bridged acyl complex [Pt$_2$(μ-Cl)$_2$(COPh)$_2$L$_2$] was isolated.[5] Treatment of *cis*-[PtCl$_2$(CO)L] with phenyl-lithium gave no insertion products. We now report the relationship of these acyl complexes [Pt$_2$(μ-Cl)$_2$(COR)$_2$L$_2$] with mononuclear carbonyl derivatives [PtCl(R)(CO)L], and indicate their importance to Scheme 1. A preliminary account of this work has appeared.[6]



SCHEME 1 L = Tertiary phosphine, X = halide

RESULTS AND DISCUSSION

The reaction between HgPh$_2$ and *cis*-[PtCl$_2$(CO)(PMePh$_2$)] produces [Pt$_2$(μ-Cl)$_2$(COPh)$_2$(PMePh$_2$)$_2$] (4; R = Ph) (Scheme 2). Chloroform solutions of (4; R = Ph) show an i.r. absorption at 2 087 cm^{-1} due to [PtCl(Ph)(CO)(PMePh$_2$)], as well as the aroyl absorptions of (4) at 1 635 cm^{-1}. Hydrogen-1 and ^{31}P n.m.r. spectra of the solutions indicate the presence of three species: two isomers of (4; R = Ph), presumably *cis* and *trans*, and one isomer of [PtCl(Ph)(CO)(PMePh$_2$)] (Table). The geometry of the last isomer is established as (1; R = Ph) (Scheme 2), with Ph *trans* to PMePh$_2$, by the low value of ^1J(Pt–P) (1 402 Hz).[7] The ^{13}C n.m.r. of a sample prepared from enriched ^{13}CO is compatible with this geometry, showing parameters typical of CO *trans* to Cl and *cis* to PR$_3$[8] [δ 162.1, ^1J(Pt–C) 1 947 Hz, ^2J(P–Pt–C) 8.2 Hz].



SCHEME 2 L = PMePh$_2$; R = Me, Et, Ph, or CH$_2$Ph

When solutions of (1) and (4) (R = Ph) are allowed to crystallise only (4) is obtained as a solid. Even rapid removal of the solvent by evaporation yields the aroyl complex (4) almost exclusively. These data suggest that that the species (1) and (4) are in rapid equilibria. This process is analogous to (C) ⇌ (D) of Scheme 1, followed by dimerisation of (D). [Throughout this work, we obtained no evidence of detectable amounts of monomer (D) in solution.] The equilibrium position does not change significantly when chloroform is replaced by benzene or tetrahydrofuran (thf). This is in keeping with the kinetic results of Mawby [2] and Heck,[4] and suggests that the CO insertion (and dimerisation) are not significantly solvent assisted, and that solvation of one species is not markedly greater than that of the others.

The addition of 1 mol equivalent of $PMePh_2$ to solutions containing the equilibrium mixture of (1) and (4) (R = Ph) allowed almost quantitative recovery of the mononuclear aroyl complex *trans*-$[PtCl(COPh)(PMePh_2)_2]$.

Treatment of the halide-bridged complex $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ with $HgPh_2$ produces the binuclear aryl complex $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (5). Cleavage of (5) by carbon monoxide in chloroform solution gives a mixture of isomers (2) and (3) of $[PtCl(Ph)(CO)(PMePh_2)]$. The identity of the isomers is revealed by their n.m.r. spectra (Table); their $^1J(P\text{–}Pt)$ values are typical for phosphines opposite groups of low *trans* influence. The ^{13}C n.m.r. spectrum of a ^{13}CO-enriched sample shows δ 177.4, $^1J(C\text{–}Pt)$ 906 Hz, and $^2J(C\text{–}P)$ 6.1 Hz for (2), and δ 173.3, $^1J(C\text{–}Pt)$ 1 427 Hz, and $^2J(C\text{–}P)$ 157.8 Hz for (3). The $^1J(Pt\text{–}C)$ value for (2) (906 Hz) is consistent with CO being *trans* to the organic group and *cis* to PR_3.[8a] The very large value of $^2J(C\text{–}P)$ for (3) (157.8 Hz) is expected for CO being *trans* to PR_3 * (such species have not previously been studied).

N.m.r. and i.r. spectral data [a]

Complex	Phosphine methyl			δ(P) [c]	$^1J(Pt\text{–}P)$/Hz	$\tilde{\nu}(CO)$/cm^{-1}
	$\delta(CH_3)$ [b]	$^2J(PH)$/Hz	$^3J(Pt\text{–}H)$/Hz			
cis-$[PtCl_2(CO)(PMePh_2)]$	2.48	12.3	33.5	−0.21	2 946	2 115
(1; R = Ph)	2.28	9.8	15.2	6.76	1 402	2 087 [d]
(2; R = Ph)	1.69	11.4	50.8	−1.72	3 920	2 106
(3; R = Ph)	1.71	10.7	40.0	5.71	3 481	2 116
$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMePh_2)_2]$ [e]	1.84	11.1	63	−3.32	5 321	1 635 [d]
(1; R = CH_2Ph)	2.18	10.2	15.8	8.41	1 414	2 077
(1; R = Et)				12.13	1 449	2 075
$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMePh_2)_2]$ [e]	1.99	11.1	63	−1.24	5 559	1 662
(1; R = Me)	2.21	9.3	15.3	12.12	1 449	2 079
$[Pt_2(\mu\text{-}Cl)_2(COMe)_2(PMePh_2)_2]$	2.00	11.1		−1.21	*f*	1 660

[a] Spectra were recorded in $CDCl_3$ solution at ambient temperatures. [b] Chemical shifts measured downfield of $SiMe_4$. [c] Chemical shifts measured downfield of external H_3PO_4. [d] In C_6H_6 solution, values of 2 080 and 1 642 cm^{-1} are obtained, while in thf solution absorbances occur at 2 079 and 1 643 cm^{-1}. [e] These complexes exist as two, presumably *cis* and *trans*, isomers which may be distinguished at low temperatures. [f] Satellites too weak to be observed.

By cooling such a solution to −60 °C within 10 min of CO addition it was found that (2) and (3) were present in the ratio 1 : 2. After standing at ambient temperature for another 21 h, (2) and (3) were present in the ratio 5.5 : 1. Isomer (2) was obtained as a crystalline solid from a benzene solution of these isomers [ν(Pt–Cl) at 308 cm^{-1}, indicative of Cl *trans* to PR_3 [9]], but on redissolving in chloroform a small amount of (3) was also apparent after *ca.* 1 h [the ratio of (2) to (3) was 6.6 : 1]. It thus appears that (2) and (3) isomerise slowly to form an equilibrium mixture of ratio *ca.* 6 : 1. Neither isomer (1) nor its associated aroyl complex (4) was detected in these solutions on standing for 21 h. It is thus apparent that (2) and (3) do not undergo rapid CO insertion analogous to isomer (1), and the isomerisation process linking (2) and (3) does not convert them into (1).

When solutions of (2) and (3) were heated at 50 °C for 2 h however, small amounts (*ca.* 5%) of isomer (1) and its accompanying aroyl complex (4) were detected, although such treatment predominantly caused loss of carbon monoxide to regenerate (5). Similarly, allowing solutions of (2) and (3) to stand at ambient temperatures for 7 d produced some (1) and (4) (R = Ph), but CO loss and other decomposition processes leading to unidentified products predominated.

Attempts to promote carbonyl insertion at isomers (2) and (3) were unsuccessful. The slow addition of 1 mol equivalent of $PMePh_2$ caused elimination of CO, and the main reaction product was *trans*-$[PtCl(Ph)(PMePh_2)_2]$.

Whilst we cannot rule out the possibility that the small amounts of (1) and (4) produced on standing or by heating solutions of (2) and (3) may be formed by a slow carbonyl-insertion reaction of (2) and/or (3), our failure to promote such an insertion by the addition of tertiary phosphine makes this seem unlikely. Instead we favour a slow isomerisation to (1), and hence (4), as an explanation. Cleavage of (5) by CO produces only (2) and (3), so reversible loss of CO from (2) or (3) can provide an isomerisation route between these two species. Similarly, a reversible loss of tertiary phosphine {involving $[Pt_2(\mu\text{-}Cl)_2Ph_2(CO)_2]$, (6), as an intermediate} would provide a process of isomerisation for (1) and (3) (Scheme 3). Such a process would be expected to be slower than isomerisation of (2) and (3), since phosphines are more nucleophilic and more strongly held than carbon monoxide.

The product ratio of such isomerisations would be dependent on a number of factors, including the geometric ratios (*cis* to *trans*) of intermediates (5) and (6). We have not detected any tendency of isomer (1) to convert into (2) or (3) however, so it seems probable that this is the thermodynamically most stable form. Interestingly, the observation that the addition of tertiary

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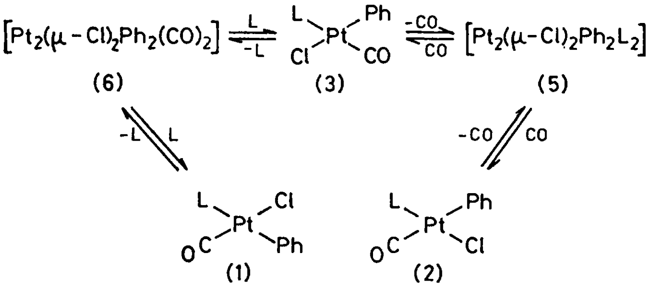
* Similar large values have been found for other ligands, *e.g.* hydrides, when *trans* to phosphine.[8b]

phosphines to solutions of $[Pt_2(\mu\text{-}Cl)_2R_2(CO)_2]$ (R = octyl) causes both insertion and elimination of carbon monoxide[10] fits our interpretation. Moreover, the fact that insertion is favoured by the less basic PPh_3, or by slower addition of the phosphine, can also be accounted for since these conditions would allow more isomerisation of species analogous to (3) into geometry (1), and thus the acyl complex.

The detailed mechanism of carbonyl insertion has been elucidated in only a few cases, and involves migration of the organic group to a neighbouring CO ligand already present in the metal co-ordination sphere.[11] This route has not been proved to operate in platinum complexes, but it is fully consistent with the isomeric constraints we have observed. In isomer (1) the organic group lies opposite the tertiary phosphine ligand. This has a large bond-labilising *trans* influence,[12] which should promote migration of the organic group. In isomer (3) the organic group lies *trans* to chloride and would not be labilised. Isomer (2) does not have the necessary *cis* arrangement of R and CO.



SCHEME 3 L = $PMePh_2$

The reaction of phenyl-lithium with *cis*-$[PtCl_2(CO)(PMePh_2)]$ in diethyl ether is complicated, and always produces a large variety of products from which it is difficult to isolate any. Phosphorus-31 n.m.r. investigations of the products show the presence of (2), however, and the complete absence of (1) or (4) (R = Ph). This indicates that the chloride which is displaced by LiPh is that *trans* to CO, whereas $HgPh_2$ replaces the chloride *trans* to tertiary phosphine. Obviously a different mechanism must operate in the two cases and phenyl-lithium seems most likely to act *via* a carbanion attack to produce a five-co-ordinate intermediate.[13] The kinetic *trans* effect of CO[12] will stabilise this intermediate with the entering and leaving groups in the same trigonal plane as itself, thus ensuring loss of the Cl^- *trans* to it. Diphenylmercury, on the other hand, is more likely to react *via* an electrophilic attack on Hg–C (S_E2) or by an oxidative-addition reductive-elimination sequence.[5,14] The high *trans* influence of tertiary phosphine[12] will weaken the Pt–Cl bond *trans* to it, favouring its elimination.

When *cis*-$[PtCl_2(CO)(PMePh_2)]$ reacts with $HgMe_2$, $HgEt_2$, or $Hg(CH_2Ph)_2$ a reaction analogous to that with $HgPh_2$ takes place, but the position of the equilibrium between (1) and (4) varies markedly. For reaction (1) the equilibrium constants, K_c, decrease in the order R = Et (13.9) > Ph (0.43) > Me (0.01) > CH_2Ph (*ca.* 0) (all values in 10^3 dm^3 mol^{-1}).

$$2[PtCl(R)(CO)(PMePh_2)] \rightleftharpoons [Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2] \quad (1)$$

When R = Me, Et, or Ph the acyl derivatives (4) are isolated as solids from the equilibria. With R = CH_2Ph, however, no acyl complex could be detected in solution and (1) was isolated as a crystalline solid. Hydrogen-1 and ^{31}P n.m.r. spectroscopy were again used to establish the geometry of each of these mononuclear platinum carbonyls as (1) (Table).

Addition of tertiary phosphine to the (1) $\rightleftharpoons$ (4) equilibria was shown (by ^{13}C n.m.r. spectroscopy) to produce *trans*-$[PtCl(COR)(PMePh_2)_2]$ for R = Me or Et. The complex *trans*-$[PtCl(COCH_2Ph)(PMePh_2)_2]$ was isolated after the slow addition of $PMePh_2$ to (1; R = CH_2Ph), but in this case rapid addition caused loss of CO instead. We take this to indicate that (1; R = CH_2Ph) is in equilibrium with its acyl complex, (4), and that this, like the other acyls, is readily attacked by tertiary phosphine to produce the mononuclear acylbis(phosphine)platinum complexes. [The attack could be on the three-co-ordinate intermediate, (D) of Scheme 1, which, although not detected by us, is presumably part of the equilibrium sequence.] When (4) [or (D)] is in low concentration compared to the amount of phosphine, a slower nucleophilic attack of the phosphine on (1) successfully competes and leads to CO elimination. Similar effects of the rate of addition of phosphine have been reported by Mawby[2] and Wright,[10] who also noted that more basic phosphines (or arsines) tended to favour CO elimination against insertion. These observations also fit our interpretation.

The decrease in the extent of insertion along the series Et > Ph > Me > CH_2Ph remains unexplained at present, although we note that several similar series have emerged from kinetic studies of insertions and decarbonylations at other metals.[11]

We conclude that intermediate (C) of Scheme 1 should have geometry (1) (Scheme 2). The effect of tertiary phosphine on the other isomers would not be to promote CO insertion, but could enhance their isomerisation to (1) *via* (B) and perhaps (A). The requirement of geometry (1) is consistent with R migration to CO being the mechanism of acyl formation at platinum(II).

EXPERIMENTAL

Solution i.r. spectra were recorded on a Perkin-Elmer 577 instrument using NaCl cells of 0.5 mm path length. Infrared spectra of solid materials were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer. Proton n.m.r. spectra were recorded in $CDCl_3$ solution using a Perkin-Elmer R32 spectrometer (90 MHz), ^{13}C and ^{31}P n.m.r. spectra in $CDCl_3$ solution using a Varian XL-100 spectrometer. Carbon-13 n.m.r. spectra were recorded for samples prepared, by the methods described, from isotopically labelled CO (90.5 atom % ^{13}C) (Merck, Sharp and Dohme).

Di-μ-chloro-bis[benzoyl(methyldiphenylphosphine)platinum(II)] (4; R = Ph).—The complex *cis*-[$PtCl_2$(CO)-($PMePh_2$)] (1.965 g, 3.98 mmol) was dissolved in chloroform (100 cm^3) under nitrogen, and diphenylmercury (1.413 g, 3.98 mmol) was added. The solution became yellow and a fine colourless solid precipitated. The solution was stirred for 4 h and the precipitate of HgCl(Ph) (0.959 g) was filtered off. After the solvent had been evaporated, the remaining HgCl(Ph) was removed by sublimation at 80 °C (0.001 Torr) * for 7 h. The residue was recrystallised from benzene–light petroleum to yield [Pt_2(μ-Cl)$_2$(COPh)$_2$(PMe-Ph_2)$_2$] as colourless crystals (1.02 g, 48%), m.p. 232—235 °C (decomp.) (Found: C, 44.65, H, 3.35. Calc. for $C_{40}H_{36}Cl_2O_2P_2Pt_2$: C, 44.8; H, 3.40%).

The following complexes were prepared similarly, except that the reactions were carried out in benzene under a CO atmosphere, with heating to 50 °C for 1 h in the case of dimethylmercury: *di-μ-chloro-bis[(methyldiphenylphosphine)propionylplatinum*(II)] (4; R = Et), m.p. 153—157 °C (Found: C, 39.3; H, 3.50. Calc. for $C_{32}H_{36}Cl_2O_2$-P_2Pt_2: C, 39.4; H, 3.70%), yield 63% from 0.6 mmol; *di-μ-chloro-bis[acetyl(methyldiphenylphosphine)platinum*(II)] (4; R = Me), m.p. 151—153 °C (decomp.) (Found: C, 37.75; H, 3.30. Calc. for $C_{30}H_{32}Cl_2O_2P_2Pt_2$: C, 38.0; H, 3.40%).

Benzyl(carbonyl)chloro(methyldiphenylphosphine)platinum(II)] (1; R = CH_2Ph).—The complex *cis*-[$PtCl_2$(CO)-($PMePh_2$)] (0.52 g, 1.06 mmol) and dibenzylmercury (0.406 g, 1.06 mmol) were stirred in benzene (60 cm^3) at 45 °C, under a CO atmosphere, for 48 h. The solvent was removed and the residue treated with benzene (8 cm^3) and n-pentane (40 cm^3) causing deposition of a grey solid. This was filtered off and colourless crystals precipitated from the filtrate. The crystals were removed and treated at 70 °C (0.005 Torr). Benzylmercury(II) chloride sublimed out, leaving [PtCl(CH_2Ph)(CO)($PMePh_2$)] as a near-colourless solid (193 mg, 33%), m.p. 106—109 °C (Found: C, 45.8; H, 3.85. Calc. for $C_{21}H_{20}ClOPPt$: C, 45.85; H, 3.65%).

Di-μ-chloro-bis[(methyldiphenylphosphine)phenylplatinum(II)].—The complex [Pt_2Cl_4($PMePh_2$)$_2$] (2.13 g, 2.29 mmol) was suspended in benzene (120 cm^3) under nitrogen, and $HgPh_2$ (1.62 g, 4.56 mmol) was introduced. The suspension was stirred for 4.5 h after which HgCl(Ph) (1.07 g) was filtered off. The volume was reduced causing further precipitation of HgCl(Ph). This was filtered off and the remaining solvent was evaporated. The residue was crystallised from methylene chloride–diethyl ether to give [Pt_2(μ-Cl)$_2Ph_2$($PMePh_2$)$_2$] as colourless crystals (1.33 g, 57%), m.p. 239—240 °C (Found: C, 45.0; H, 3.45. Calc. for $C_{38}H_{36}Cl_2P_2Pt_2$: C, 44.95; H, 3.55%).

Carbonylchloro(methyldiphenylphosphine)phenylplatinum(II).—The complex [Pt_2(μ-Cl)$_2Ph_2$($PMePh_2$)$_2$] (0.177 g, 0.175 mmol) was dissolved in methylene chloride (30 cm^3) and carbon monoxide was passed through the solution for 2 h. The solvent was removed without heating to leave a pale brown solid. This was dissolved in benzene (5 cm^3), through which CO was passed for 1 min, and the solution was then filtered. Addition of light petroleum caused precipitation of [PtCl(Ph)(CO)($PMePh_2$)] as colourless crystals. These were treated at 70—80 °C (0.15 Torr) for 2 h to drive off residual benzene (Found: C, 45.0; H, 3.35. Calc. for $C_{20}H_{18}ClOPPt$: C, 44.8; H, 3.40%).

Reactions of [PtCl(Ph)(CO)($PMePh_2$)].—(*a*) *Addition of* $PMePh_2$. One mol equivalent of $PMePh_2$ in $CDCl_3$ solution was added dropwise to a $CDCl_3$ solution of [PtCl(Ph)(CO)-($PMePh_2$)] over *ca.* 1 h. Almost complete loss of the carbonyl absorption was noted in the i.r. spectrum, although a very weak band at 1 620 cm^{-1}, indicative of an aroyl derivative, was observed. After solvent removal the i.r. spectrum indicated the main product to be *trans*-[PtCl-(Ph)($PMePh_2$)$_2$], by comparison with the spectrum of an authentic sample.

(*b*) *Heating in* $CDCl_3$ *solution*. When a 0.01 mol dm^{-3} solution of [PtCl(Ph)(CO)($PMePh_2$)] was warmed to 50 °C for 2 h the solution i.r. spectrum showed almost total loss of the carbonyl absorption at *ca.* 2 100 cm^{-1}. The i.r. spectrum of the solid residue after solvent removal showed a weak acyl band at 1 638 cm^{-1}, but the main product was identified as [Pt_2(μ-Cl)$_2Ph_2$($PMePh_2$)$_2$] by comparison with the i.r. spectrum of an authentic sample.

(*c*) *Standing at ambient temperature in* $CDCl_3$ *solution*. A solution of [PtCl(Ph)(CO)($PMePh_2$)] was allowed to stand in air at ambient temperature for 7 d. After this time the ^{31}P n.m.r. spectrum showed the presence of small amounts of [PtCl(Ph)(CO)($PMePh_2$)] (1; R = Ph) and [Pt_2(μ-Cl)$_2$-(COPh)$_2$($PMePh_2$)$_2$], although the main components of the mixture were still [PtCl(Ph)(CO)($PMePh_2$)], (2) and (3) (R = Ph).

trans-*Benzoylchlorobis(methyldiphenylphosphine)platinum*(II).—The complex [Pt_2(μ-Cl)$_2$(COPh)$_2$($PMePh_2$)$_2$] (0.127 g, 0.119 mmol) was dissolved in CH_2Cl_2 (20 cm^3) under nitrogen and $PMePh_2$ (44.1 μl, 0.238 mmol) was added. The solution was stirred for 4 h, the solvent removed, and the residue crystallised from CH_2Cl_2–Et_2O to give *trans*-[PtCl(COPh)($PMePh_2$)$_2$] as pale yellow crystals, m.p. 165 °C (Found: C, 53.9; H, 4.65. Calc. for $C_{33}H_{31}ClOP_2Pt$: C, 53.85; H, 4.25%). The ^{13}C n.m.r. spectrum of a ^{13}CO-enriched sample showed δ 212.9, ^1J(C–Pt) 1 007 Hz, and ^2J(C–P) 6.1 Hz.

Similarly, addition of 1 mol equivalent of $PMePh_2$ to solutions of ^{13}CO-enriched [Pt_2(μ-Cl)$_2$(COEt)$_2$($PMePh_2$)$_2$] or [Pt_2(μ-Cl)$_2$(COMe)$_2$($PMePh_2$)$_2$] caused formation of the corresponding *trans*-acylbis(phosphine)platinum complexes: *trans*-[PtCl(COEt)($PMePh_2$)$_2$], δ 218.0, ^1J(C–Pt) 928 Hz, and ^2J(C–Pt) *ca.* 5 Hz; *trans*-[PtCl(COMe)($PMePh_2$)$_2$], δ 216.9, ^1J(C–Pt) 928 Hz, and ^2J(C–P) *ca.* 5 Hz.

trans-*Chlorobis(diphenylmethylphosphine)phenylacetylplatinum*(II).—The complex [PtCl(CH_2Ph)(CO)($PMePh_2$)] (1; R = CH_2Ph) (53.2 mg, 0.097 mmol) was dissolved in benzene (5 cm^3) under nitrogen. A solution of $PMePh_2$ (17.9 μl, 0.097 mmol) in benzene (5 cm^3) was prepared under nitrogen, and added dropwise to the former solution over a period of 4 h. The solution was filtered and light petroleum added, causing precipitation of *trans*-[PtCl($COCH_2$Ph)-($PMePh_2$)$_2$] as colourless crystals (35 mg, 48%), m.p. 158—159 °C (Found: C, 54.4; H, 4.00. Calc. for $C_{34}H_{33}ClOP_2$-Pt: C, 54.45; H, 4.45%).

trans-*Chlorobis(methyldiphenylphosphine)phenylplatinum*(II).—The complex *cis*-[$PtCl_2$($PMePh_2$)$_2$] (0.377 g, 0.566 mmol) and $HgPh_2$ (0.201 g, 0.566 mmol) were heated under reflux in ethanol (50 cm^3) under nitrogen for 24 h.[5] The solvent was removed and the residue treated at 90 °C (0.001 Torr) for 12 h. Phenylmercury(II) chloride (0.146 g, 85%) was thus obtained by sublimation, and the residue was crystallised from benzene–light petroleum to give *trans*-[PtCl(Ph)($PMePh_2$)$_2$] as colourless crystals (221 mg, 55%), m.p. 185 °C (Found: C, 54.4; H, 4.30. Calc. for $C_{32}H_{31}$-ClP_2Pt: C, 54.3; H, 4.40%).

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

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