Transfer of Cyclopentadienyl Groups between Platinum Atoms

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Replacement of a chloride ion of *cis*-$[PtCl_2(CO)(PR_3)]$ (PR_3 = tertiary phosphine) by a cyclopentadienyl group from $Tl(C_5H_5)$ or $Hg(C_5H_5)_2$ results exclusively in the isomers of $[PtCl(\sigma\text{-}C_5H_5)(CO)(PR_3)]$ with C_5H_5 *trans* to PR_3. The second chloride can be replaced when excess $Tl(C_5H_5)$ is used. The σ-bonded cyclopentadienyl groups of either mono- or di-substituted compounds can readily exchange in solution with a chloride of *cis*-$[PtCl_2(CO)(PR_3)]$ again producing exclusively the same isomers of $[PtCl(\sigma\text{-}C_5H_5)(CO)(PR_3)]$. The cyclopentadienyl groups do not transfer as fast as chloride ions between the same species, but do so considerably faster than any accompanying CO scrambling processes. Cyclopentadienyl groups from the σ-bonded complexes, and from $[Pt(\eta^5\text{-}C_5H_5)(PR_3)_2]Cl$, can also be readily transferred to mercury when treated with $HgCl_2$.

A large number of cyclopentadienyl complexes of platinum are now known. They can be conveniently prepared *via* halide displacement by $C_5H_5^-$ from $Tl(C_5H_5)$ [1-5] or $Hg(C_5H_5)_2$.[5] The products are σ-bonded 16-electron molecules, or η^5-bonded 18-electron molecules, depending on the number and type of other ligands present. Interconversions between the two types have been reported [1,4,5] [equations (1) and (2); cod = cyclo-octa-1,5-diene].

$$[PtMe(\sigma\text{-}C_5H_5)(cod)] \xrightarrow[-cod]{PR_3} [PtMe(\eta^5\text{-}C_5H_5)(PR_3)] \quad (1)$$

$$[\overline{Pt(PBu^t_2CMe_2CH_2})(\eta^5\text{-}C_5H_5)] \xrightarrow{PPh_3} [\overline{Pt(PBu^t_2CMe_2CH_2})(\sigma\text{-}C_5H_5)(PPh_3)] \quad (2)$$

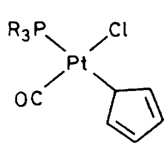
We report here a remarkable stereospecificity in forming σ-bonded cyclopentadienyls from *cis*-$[PtCl_2(CO)(PR_3)]$ (PR_3 = tertiary phosphine), and in the easy intermolecular transfer of C_5H_5 groups between metal atoms.

Results and Discussion

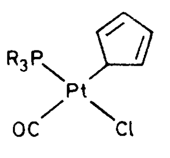
A suspension of *cis*-$[PtCl_2(CO)(PPh_3)]$ and $Tl(C_5H_5)$ in benzene reacted over 1 h to yield $[PtCl(C_5H_5)(CO)(PPh_3)]$ and insoluble TlCl. The cyclopentadienylplatinum complex was crystallized with difficulty from acetone–pentane mixtures to produce an orange powder. Although in the solid phase the compound appears to be indefinitely stable (samples have survived unchanged in air in diffuse light for more than 6 months), decomposition in solution proceeds over several days at ambient temperatures.

The ^{31}P n.m.r. spectrum of the platinum complex revealed a $^{195}Pt-^{31}P$ coupling constant of only 1 780 Hz, typical of complexes with phosphine *trans* to an organic group in compounds of this type.[6] The ^1H n.m.r. signals from the cyclopentadienyl group showed averaged proton signals with $J(PtH)$ 31.0 and $J(PH)$ 4.4 Hz, both in the range expected for a fluxional σ-cyclopentadienyl group *trans* to PR_3.[5] We therefore assign the structure (I) to this compound.

The complexes *cis*-$[PtX_2(CO)(PR_3)]$ (X = Cl, PR_3 = $PMePh_2$, PMe_2Ph, or PEt_3; X = Br, PR_3 = PMe_2Ph) also reacted with one equivalent of $Tl(C_5H_5)$ to produce quantitative yields of complexes with structure (I). The same materials were produced when $Tl(C_5H_5)$ was replaced by $Hg(C_5H_5)_2$ (X = Cl, PR_3 = $PMePh_2$ or PMe_2Ph); the by-product in these cases was the soluble $HgCl(C_5H_5)$. These compounds (I) appear to be somewhat less stable than their PPh_3 analogue. Although they survive in solution for up to 24 h attempted isolation tended to lead to decomposition. The complex $[PtCl(\sigma\text{-}C_5H_5)(CO)(PMe_2Ph)]$ was finally obtained as an impure yellow solid; no attempts were made to isolate the others, and they were examined in solution after TlCl had been removed by filtration. Spectroscopic parameters are listed in the Table. The compounds are not affected by O_2, H_2O, CO, CO_2, or light.



(I)



(II)

The formation of (I) with C_5H_5 *trans* to PR_3 was expected from the reaction of the organomercurial. Numerous reactions with other organomercury compounds have produced just this geometry.[6-8] Nucleophilic attack by anions on *cis*-$[PtX_2(CO)(PR_3)]$ usually displaces the halide *trans* to CO, however,[6] so the isomer with C_5H_5 *trans* to CO [structure (II)] might have been expected from the reaction of $Tl(C_5H_5)$. The non-appearance of this isomer is interesting, and might indicate the operation of a non-ionic reaction mode for $Tl(C_5H_5)$, an anomalous reaction of $C_5H_5^-$ compared to other carbanions, or a rapid rearrangement of (II) to (I) (see later).

With other organic groups, the isomers analogous to (I) readily undergo migration–insertion reactions to produce acyl derivatives.[6-8] We have found no evidence for carbonyl insertion in any of the cyclopentadienyl complexes described, either spontaneously in solution ($CHCl_3$, C_6H_6, or Me_2CO) or on treatment with tertiary phosphine or halide.

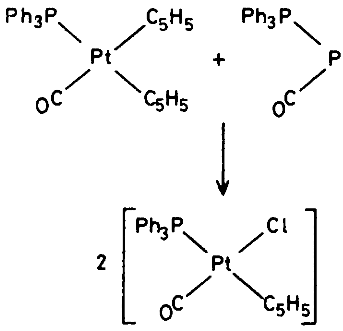
The reaction of *cis*-$[PtCl_2(CO)(PPh_3)]$ with excess $Tl(C_5H_5)$ leads to the formation of the bis(cyclopentadienyl) complex, *cis*-$[Pt(\sigma\text{-}C_5H_5)_2(CO)(PPh_3)]$. This decomposed much more readily than the mono-cyclopentadienyls, and could not be isolated. Spectroscopic data are shown in the Table. As with compounds (I), bis-cyclopentadienyl complexes of the other phosphines appear to be even less stable, and relatively small amounts were obtained in solution before decomposition products became apparent.

Transfer Reactions.—When $CDCl_3$ solutions of *cis*-$[PtCl_2(CO)(PPh_3)]$ and *cis*-$[Pt(\sigma\text{-}C_5H_5)_2(CO)(PPh_3)]$ were mixed at ambient temperatures, a rapid redistribution reaction took place leaving only (I) in solution [equation (3)]. A similar result was obtained from mixtures of *cis*-$[Pt(\sigma\text{-}C_5H_5)_2(CO)(PMe_2Ph)]$ and *cis*-$[PtBr_2(CO)(PMe_2Ph)]$; when complexes of different phosphines were employed, geometry (I) was observed for both products [equation (4)].

Table. Spectroscopic data

Compound	$\delta(C_5H_5)^a$/ p.p.m.	J(PtH)/ Hz	J(PH)/Hz	$\delta(P)^b$/p.p.m.	J(PtP)/Hz	$J(P^{13}C)$/Hz	$\nu(CO)^c$/ cm^{-1}
$[PtCl(C_5H_5)(CO)(PPh_3)]$	6.21	31.0	4.4	18.6	1 780	10.0	2 085
$[PtCl(C_5H_5)(CO)(PMePh_2)]$	6.25	30.5	4.5	6.3	1 760	10.5	2 080
$[PtCl(C_5H_5)(CO)(PMe_2Ph)]$	6.18	30.0	4.5	−5.0	1 733	10.5	2 080
$[PtCl(C_5H_5)(CO)(PEt_3)]$	6.17	29.0	4.3	21.3	1 763		2 075
$[PtBr(C_5H_5)(CO)(PMe_2Ph)]$	6.23	30.0	4.5	−8.7	1 749	9.5	2 080
$[PtBr(C_5H_5)(CO)(PMePh_2)]$				2.9	1 780		
cis-$[Pt(C_5H_5)_2(CO)(PPh_3)]$	5.90	33.0	3.5	20.0	2 127		2 075
	5.45	33.0	5.0				
cis-$[Pt(C_5H_5)_2(CO)(PMePh_2)]$				3.0	2 107		
cis-$[Pt(C_5H_5)_2(CO)(PMe_2Ph)]$				−9.8	2 095		
$[Pt(\eta^5\text{-}C_5H_5)(PPh_3)_2]Cl$	5.39	11.5	1.5	3.9	4 736		
$[Pt(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2]Cl$	6.05	11.0	1.5	−28.2	4 498		
$[Pt(\eta^5\text{-}C_5H_5)(PMePh_2)_2]Cl$	5.55	12.0	1.5	−14.1	4 578		
$[Pt(\eta^5\text{-}C_5H_5)(CO)(PMe_2Ph)][SO_3CF_3]^d$	6.15	13.3	1.3	−25.2	3 724		2 065

[a] In $CDCl_3$ at 25 °C, downfield from internal $SiMe_4$. [b] In $CDCl_3$ at 25 °C, downfield from 85% H_3PO_4. [c] $CHCl_3$ solution. [d] $[Pt(\eta^5\text{-}C_5H_5)(CO)(PPh_3)][ClO_4]$ has been reported by Kurosawa *et al.*[3]



(3)

$$[Pt(C_5H_5)_2(CO)(PMePh_2)] + [PtCl_2(CO)(PMe_2Ph)] \longrightarrow (I;\ PR_3 = PMePh_2) + (I;\ PR_3 = PMe_2Ph) \quad (4)$$

Intermolecular exchange of cyclopentadienyl with chloride also occurred when (I) reacted with *cis*-$[PtX_2(CO)(PR'_3)]$. Thus n.m.r. investigations revealed that solutions of *cis*-$[PtCl_2(CO)(PPh_3)]$ and $[PtCl(\sigma\text{-}C_5H_5)(CO)(PMe_2Ph)]$ equilibrated with *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ and $[PtCl(\sigma\text{-}C_5H_5)(CO)(PPh_3)]$ in less than 30 min at ambient temperatures. This and related systems [see equations (5)—(7)] revealed that at equilibrium the C_5H_5 group showed a preference for the platinum atom with the less basic phosphine (or that with the smaller *trans* influence[7]). Equilibrium constants for reactions (5)—(7) were approximately 0.3, 0.2, and 0.45, respectively.

$$(I;\ PR_3 = PPh_3) + cis\text{-}[PtCl_2(CO)(PMePh_2)] \rightleftharpoons (I;\ PR_3 = PMe_2Ph) + cis\text{-}[PtCl_2(CO)(PPh_3)] \quad (5)$$

$$(I;\ PR_3 = PPh_3) + cis\text{-}[PtCl_2(CO)(PMe_2Ph)] \rightleftharpoons (I;\ PR_3 = PMe_2Ph) + cis\text{-}[PtCl_2(CO)(PPh_3)] \quad (6)$$

$$(I;\ PR_3 = PMe_2Ph) + cis\text{-}[PtCl_2(CO)(PEt_3)] \rightleftharpoons (I;\ PR_3 = PEt_3) + cis\text{-}[PtCl_2(CO)(PMe_2Ph)] \quad (7)$$

That the migrating groups in these reactions were C_5H_5 and Cl, and not PR_3, was established by using samples labelled with ^{13}CO [equation (8)]. Phosphorus-31 n.m.r. spectra easily identified the coupling of ^{13}C to P as of *cis* geometry,[9] showing that these parts of the molecules retained their integrity in the time of scrambling C_5H_5 and Cl (<30 min). Over 24 h, however, a slower reaction was also observed, leading to scrambling of the CO (or PR_3) groups.

$$[PtCl(C_5H_5)(^{13}CO)(PMePh_2)] + cis\text{-}[PtCl_2(CO)(PPh_3)] \rightleftharpoons cis\text{-}[PtCl_2(^{13}CO)(PMePh_2)] + [PtCl(C_5H_5)(CO)(PPh_3)] \quad (8)$$

Experiments on compounds with different halides indicated that reactions of the type (5)—(8) were accompanied by exchange of halides. Thus, ^{31}P n.m.r. spectroscopic examination of the reaction between $[PtCl(C_5H_5)(CO)(PMe_2Ph)]$ and *cis*-$[PtBr_2(CO)(PMe_2Ph)]$ showed that it reached equilibrium in less than 10 min, producing $[PtBr(C_5H_5)(CO)(PMe_2Ph)]$ and one isomer of $[PtClBr(CO)(PMe_2Ph)]$ [δ 8.1 p.p.m., *J*(PPt) 2 832 Hz: the coupling constant suggests that a halide is *trans* to PMe_2Ph [9]]. This isomer is presumably the thermodynamically stable one since it is the only one produced when solutions of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ and *cis*-$[PtBr_2(CO)(PMe_2Ph)$ are mixed.* Phosphorus-31 n.m.r. examination of the reactions between $[PtBr(\sigma\text{-}C_5H_5)(CO)(PMe_2Ph)]$ and *cis*-$[PtCl_2(^{13}CO)(PMe_2Ph)]$ revealed that all the materials contained ^{13}CO after only 15 min. Since it is unlikely [from equation (8)] that CO exchange would have progressed this far in such a short time, the scrambling must originate from rapid halide and C_5H_5 migration. Mixing $[PtCl(\sigma\text{-}C_5H_5)(CO)(PMePh_2)]$ and *cis*-$[PtBr_2(CO)(PMe_2Ph)]$ resulted in rapid (<10 min) conversion of half of the cyclopentadienyl complex to its bromide analogue *before* C_5H_5 had been transferred to any great extent to the other platinum. Halide exchange in these systems appears to be two or three times faster than cyclopentadienyl exchange.

These C_5H_5 transfer reactions appear to proceed quite rapidly compared to other organic radical transfers. Exchange reactions of methyl and aryl groups between platinum(II) bisphosphine complexes have been reported to take anything up to a month for completion, for example.[10] This comparison may be misleading, however, as the nature of the other ligands might exert as big an influence on the transfer rate as the organic groups themselves. We detected no reactions between $[PtCl(\sigma\text{-}C_5H_5)(CO)(PMe_2Ph)]$ and *cis*-$[PtCl_2(PR_3)_2]$ (PR_3 = PMe_2Ph or PPh_3) or $[PtCl(\sigma\text{-}C_5H_5)(CO)(PPh_3)]$ and $[PtCl(C_2Cl_3)(CO)(PMePh_2)]$ (Cl *trans* to CO) in 24 h. Also, although the aryl group of $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMe_2Ph)]$

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* If it were the kinetic product resulting from a single exchange of two halide ions, it would mean the involvement of different specific sites on each Pt. The similarity of Cl and Br makes this unlikely.

(Cl *trans* to CO) was appreciably transferred to the platinum of *cis*-[PtCl$_2$(CO)(PPh$_3$)] after 1 h (about three times slower than for C$_5$H$_5$ transfer), the *ortho*-substituted aryl of [PtCl(C$_6$H$_4$Me-*o*)(CO)(PMe$_2$Ph)] showed no substantial movement to the same dichloroplatinum complex until *ca.* 12 h had elapsed. Interestingly, the exchange of C$_6$H$_4$Cl-*o* for Cl in the reaction between [PtCl(C$_6$H$_4$Cl-*o*)(CO)(PMe$_2$Ph)] and *cis*-[PtCl$_2$(^{13}CO)(PPh$_3$)], which also required longer than 12 h, was not accompanied by ^{12}CO–^{13}CO scrambling in this time. Such scrambling would be appreciable in the analogous cyclopentadienyl system [*e.g.* reaction (8)], suggesting the possibility of a link between the various transfers.

The reaction of cyclopentadienylthallium with *cis*-[PtCl$_2$(PR$_3$)$_2$] (PR$_3$ = PPh$_3$, PMePh$_2$, or PMe$_2$Ph) produced the η^5-bonded complexes [Pt(η^5-C$_5$H$_5$)(PR$_3$)$_2$]Cl. Proton n.m.r. parameters were typical of compounds of this type[5] (see Table). Replacement of the chlorides by SO$_3$CF$_3$$^-$ from Ag(SO$_3$CF$_3$) created no change in the n.m.r. parameters, indicating no close association of Cl$^-$ with the cation in CDCl$_3$. Silver salts also abstracted halide from complexes (I) to yield η^5-bonded materials [equation (9)].

$$\text{(I; PR}_3 = \text{PMe}_2\text{Ph)} + \text{Ag(SO}_3\text{CF}_3\text{)} \xrightarrow{-\text{AgCl}} [\text{Pt}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{PMe}_2\text{Ph})][\text{SO}_3\text{CF}_3] \quad (9)$$

The complex [Pt(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$]Cl reacts rapidly with HgCl$_2$ by C$_5$H$_5$ transfer [equation (10)]. Mercury(II) chloride also rapidly cleaves C$_5$H$_5$ from (I) [equation (11)]. It is possible that the transfer reaction in equation (10) may be preceded by a $\eta^5 \longrightarrow \sigma$ conversion of C$_5$H$_5$. Transfer of η^5-C$_5$H$_5$ between cobalt atoms has been reported, however, although the mechanism is unknown.[11]

$$[\text{Pt}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)_2]\text{Cl} + \text{HgCl}_2 \longrightarrow \text{HgCl(C}_5\text{H}_5) + cis\text{-[PtCl}_2(\text{PR}_3)_2] \quad (10)$$

$$\text{(I; PR}_3 = \text{PMe}_2\text{Ph)} + \text{HgCl}_2 \longrightarrow \text{HgCl(C}_5\text{H}_5) + cis\text{-[PtCl}_2(\text{CO})(\text{PMe}_2\text{Ph})] \quad (11)$$

Finally, we note that the rapid transfer of σ-cyclopentadienyl between platinum atoms, or the easy conversions between η^5- and σ-bonding of these groups, offer the possibility that isomer (I) is universally obtained simply because it may be the thermodynamic isomer. Thus if isomer (II) (where C$_5$H$_5$ is *trans* to CO) was the initial product from Tl(C$_5$H$_5$) and *cis*-[PtCl$_2$(CO)(PR$_3$)] [and/or included in the products from equations (3) and (4)] it could be converted rapidly into (I) by intermolecular transfers,* or reversible conversion to an η^5-bonded compound. Attempts were made to detect intermediates during the formation of (I) by n.m.r. spectroscopic investigation at low temperatures. None was observed, however: the first detectable products from Tl(C$_5$H$_5$) and [PtCl$_2$(CO)(PR$_3$)] were (I). Thus if such isomerisations are part of the preparative routes to (I), they must be faster than the initial formation of the precursor to (I).

Experimental

Nuclear magnetic resonance spectra were recorded in CDCl$_3$ solutions on a Varian XL100 spectrometer operating in the Fourier transform mode (^{31}P) or on a Perkin-Elmer R32 90-MHz continuous-wave spectrometer (^{1}H). Infrared spectra were recorded on a Perkin-Elmer 580 or 257 spectrophotometer as KBr discs (for solid materials) or as 0.02 mol dm^{-3} CHCl$_3$ solutions in NaCl cells (0.5 mm path length).

The starting materials Tl(C$_5$H$_5$), Hg(C$_5$H$_5$)$_2$, *cis*-[PtCl$_2$(CO)(PR$_3$)], and *cis*-[PtCl$_2$(PR$_3$)$_2$] were prepared and purified by standard methods.[13–15]

Preparations.—[PtCl(σ-C$_5$H$_5$)(CO)(PPh$_3$)]. *cis*-Carbonyldichloro(triphenylphosphine)platinum(II) (293 mg, 0.53 mmol) and cyclopentadienylthallium (146 mg, 0.54 mmol) were stirred together in benzene (5 cm^3) under a nitrogen atmosphere for 1 h. After removal of TlCl by filtration, the solvent was removed under vacuum leaving an orange semi-solid which was dissolved in acetone (3 cm^3). Addition of pentane (10 cm^3) precipitated the *product*, [PtCl(σ-C$_5$H$_5$)(CO)(PPh$_3$)] as an orange powder, m.p. 106—108 °C, yield 181 mg, 59% (Found: C, 49.35; H, 3.5. Calc. for C$_{24}$H$_{20}$ClOPPt: C, 49.2; H, 3.4%).

[PtCl(C$_5$H$_5$)(CO)(PMe$_2$Ph)]. The complex *cis*-[PtCl$_2$(CO)(PMe$_2$Ph)] (306 mg, 0.71 mmol) and Tl(C$_5$H$_5$) (193 mg, 0.72 mmol) were stirred together in benzene (5 cm^3) for 45 min. Removal of TlCl and the solvent left a sticky orange semi-solid. Attempts to crystallise the orange material from several solvents led to decomposition and formation of brown or black solids or oils. Finally, the remaining material was dissolved in a minimum of benzene and the *product* precipitated as a slightly impure yellow powder on addition of pentane: m.p. 73—79 °C, yield 64 mg, 20% (Found: C, 35.5; H, 3.0. Calc. for C$_{14}$H$_{16}$ClOPPt: C, 36.4; H, 3.5%).

Solutions of [PtCl(σ-C$_5$H$_5$)(CO)(PMe$_2$Ph)] were stable in various solvents (CHCl$_3$, C$_6$H$_6$, or Me$_2$CO) indefinitely at −60 °C, and no decomposition products were detected by ^{31}P n.m.r. at ambient temperatures for several hours. Decomposition in solution was not accelerated by light, oxygen, moisture, or CO, but proceeded rapidly on attempted crystallisations: it may therefore be a bimolecular process. No attempts were made to isolate other examples of these monocyclopentadienyls. Solutions were prepared *in situ* for examination of their reactions. Spectroscopic parameters are listed in the Table.

cis-[Pt(σ-C$_5$H$_5$)$_2$(CO)(PPh$_3$)]. The complex *cis*-[PtCl$_2$(CO)(PPh$_3$)] (32.2 mg, 0.06 mmol) and Tl(C$_5$H$_5$) (63 mg, 0.23 mmol) were stirred together in CDCl$_3$ solution (0.5 cm^3) under a nitrogen atmosphere. The reaction was monitored by ^{1}H and ^{31}P n.m.r. spectrometry. Resonances assigned to [Pt(C$_5$H$_5$)$_2$(CO)(PPh$_3$)] (Table) grew in strength, as those due to [PtCl(C$_5$H$_5$)(CO)(PPh$_3$)] diminished. Increasing quantities of decomposition products were also apparent in solution after 2 h, and the bis-cyclopentadienyl complex could not be obtained in a pure state.

Reactions.—*cis*-[Pt(C$_5$H$_5$)$_2$(CO)(PPh$_3$)] *with* *cis*-[PtCl$_2$(CO)(PPh$_3$)]. The complex *cis*-[PtCl$_2$(CO)(PPh$_3$)] (27.7 mg, 0.05 mmol) and Tl(C$_5$H$_5$) (49.3 mg, 0.18 mmol) were stirred together in CDCl$_3$ (400 μl) under nitrogen for 2 h. After filtration, ^{1}H n.m.r. investigation of the orange solution revealed the main product to be *cis*-[Pt(C$_5$H$_5$)$_2$(CO)(PPh$_3$)] (55%). A solution of *cis*-[PtCl$_2$(CO)(PPh$_3$)] (15.2 mg, 0.027 mmol) in CDCl$_3$ (100 μl) was added. Proton n.m.r. investigation now revealed [PtCl(C$_5$H$_5$)(CO)(PPh$_3$)] as the main, and only cyclopentadienyl-containing product.

[PtCl(C$_5$H$_5$)(CO)(PMe$_2$Ph)] *with* *cis*-[PtCl$_2$(CO)(PPh$_3$)]. A solution of [PtCl(C$_5$H$_5$)(CO)(PMe$_2$Ph)] was prepared from the reaction of *cis*-[PtCl$_2$(CO)(PMe$_2$Ph)] (30.7 mg, 0.07 mmol) and Tl(C$_5$H$_5$) (19.8 mg, 0.075 mmol) in CDCl$_3$ (350 μl) and filtered. To it was added a solution of *cis*-[PtCl$_2$(CO)(PPh$_3$)] (18.2 mg, 0.033 mmol) in CDCl$_3$ (150 μl). Phosphorus-31 n.m.r. investigation of the solution revealed the presence of

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* This does not happen with [PtCl(R″)(CO)(PR$_3$)] (R″ = aryl). The isomer with aryl *trans* to CO converts only very slowly into that with Cl *trans* to CO and by a dissociative route.[6] Neither is any reaction observed between [PtCl(R″)(CO)(PR$_3$)] (R″ *trans* to CO; R″ = C≡CMe or C≡CPh) and *cis*-[PtCl$_2$(CO)(PR$_3$)] to produce the isomer with Cl *trans* to CO.[12]

cis-[PtCl$_2$(CO)(PMe$_2$Ph)], [PtCl(C$_5$H$_5$)(CO)(PMe$_2$Ph)], [PtCl(C$_5$H$_5$)(CO)(PPh$_3$)], and *cis*-[PtCl$_2$(CO)(PPh$_3$)]. A similar mixture was obtained starting from *cis*-[PtCl$_2$(CO)(PMe$_2$Ph)] and [PtCl(C$_5$H$_5$)(CO)(PPh$_3$)]. Integration of the ^{31}P signals allowed the equilibrium constant to be calculated.

Similar reactions were carried out between [PtCl(C$_5$H$_5$)(^{13}CO)(PMePh$_2$)] and *cis*-[PtCl$_2$(CO)(PPh$_3$)]; [PtCl(C$_5$H$_5$)(CO)(PEt$_3$)] and *cis*-[PtCl$_2$(CO)(PMe$_2$Ph)]; [PtCl(C$_5$H$_5$)(CO)(PPh$_3$)] and *cis*-[PtCl$_2$(CO)(PMePh$_2$)]; [PtCl(C$_5$H$_5$)(CO)(PMe$_2$Ph)] and *cis*-[PtBr$_2$(CO)(PMe$_2$Ph)]; [PtBr(C$_5$H$_5$)(CO)(PMe$_2$Ph)] and *cis*-[PtCl$_2$(^{13}CO)(PMe$_2$Ph)]; and [PtCl(C$_5$H$_5$)(CO)(PMePh$_2$)] and *cis*-[PtBr$_2$(CO)(PMe$_2$Ph)]. No reactions were observed between [PtCl(C$_5$H$_5$)(CO)(PMe$_2$Ph)] and either *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] or *cis*-[PtCl$_2$(PPh$_3$)$_2$].

[Pt(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$]Cl. The complex *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (30.2 mg, 0.054 mmol) and Tl(C$_5$H$_5$) (16.9 mg, 0.063 mmol) were stirred together suspended in CDCl$_3$ (0.5 cm^3) for 2 h under a nitrogen atmosphere. The orange-yellow solution was filtered [to remove TlCl and unreacted Tl(C$_5$H$_5$)] into an n.m.r. tube. Phosphorus-31 and ^{1}H n.m.r. spectra (Table) indicated the presence in solution of only [Pt(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$]Cl.

[Pt(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$]Cl *with* HgCl$_2$. A solution of [Pt(η^5-C$_5$H$_5$)(PMe$_2$Ph)$_2$]Cl in CDCl$_3$ (0.5 cm^3) was prepared as above from *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (30.1 mg, 0.054 mmol) and Tl(C$_5$H$_5$) (15.1 mg, 0.056 mmol). To this was added HgCl$_2$ (8.4 mg, 0.032 mmol) and the solution examined by ^{1}H n.m.r. spectroscopy. As well as unreacted η^5-C$_5$H$_5$ starting material, resonances were observed from HgCl(C$_5$H$_5$) (δ 6.1 p.p.m.) and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] [phosphine methyl resonance: δ 1.76 p.p.m., *J*(PtH) 34.5, *J*(PH) 11.0 Hz].

[PtCl(R$''$)(CO)(PMe$_2$Ph)] (R$''$ = *aryl*) *with cis*-[PtCl$_2$(CO)(PPh$_3$)]. Solutions of various [PtCl(R$''$)(CO)(PMe$_2$Ph)] (Cl *trans* to CO) in CDCl$_3$ were prepared by standard methods [6,8] and characterised by their ^{31}P n.m.r. spectroscopic parameters [R$''$ = C$_6$H$_6$OMe-*o*, δ(P) − 5.4 p.p.m., *J*(PtP) 1 487 Hz; R$''$ = C$_6$H$_4$Cl-*o*, δ(P) −7.5 p.p.m., *J*(PtP) 1 541, *J*(PC) 8.5 Hz; R$''$ = C$_6$H$_4$CO$_2$Me-*p*, δ(P) −5.8 p.p.m., *J*(PtP) 1 410 Hz]. To each solution was added one mol equivalent of *cis*-[PtCl$_2$(CO)(PPh$_3$)$_2$] in CDCl$_3$, and the reactions followed by ^{31}P n.m.r. spectroscopy. Transfer of the aryl group to produce [PtCl(R$''$)(CO)(PPh$_3$)] (Cl *trans* to CO) took 1 h to reach detectable concentrations of [PtCl(C$_6$H$_4$CO$_2$Me-*p*)(CO)(PPh$_3$)] [δ(P) + 18.3 p.p.m., *J*(PtP) 1 483 Hz], but greater than 12 h in the other two cases [R$''$ = C$_6$H$_4$OMe-*p*, δ(P) 18.8 p.p.m., *J*(PtP) 1 552 Hz; R$''$ = C$_6$H$_4$Cl-*o*, δ(P) 16.4 p.p.m., *J*(PtP) 1 607 Hz].

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