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ORGANIC GROUP TRANSFER REACTIONS BETWEEN PLATINUM(II) AND MERCURY(II)

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Summary

Both C_5H_5Tl and $Hg(C_5H_5)_2$ react with $[PtCl(C{\equiv}CR)(CO)L]$ (L is tertiary phosphine, Cl *trans* to L) to produce $[Pt(C_5H_5)(C{\equiv}CR)(CO)L]$ ($C{\equiv}CR$ *trans* to CO). C_5H_5Tl and $[PtClPh(CO)L]$ similarly produce one isomer only (Ph *trans* to CO) of $[Pt(C_5H_5)Ph(CO)L]$. These mixed diorganoplatinum complexes react with $HgCl_2$ or *cis*-$[PtCl_2(CO)L]$ in chloroform to transfer specifically the organic group *trans* to $L(C_5H_5)$ to Hg or Pt, respectively. The reaction between $[PtCl(C_5H_5)(CO)L]$ (C_5H_5 *trans* to L) and $Hg(C{\equiv}CMe)_2$ is complicated, producing initially both $[Pt(C_5H_5)(C{\equiv}CMe)(CO)L]$ and $[PtCl(C{\equiv}CMe)(CO)L]$, but finally *cis*-$[Pt(C{\equiv}CMe)_2(CO)L]$ as the only platinum-containing product. The mechanistic implications of all these reactions, monitored at low temperature by ^{31}P NMR spectroscopy, are discussed.

Introduction

We have examined a variety of ligand exchange reactions between mercury(II) compounds and square planar platinum(II) complexes containing *cis*-carbonyl and phosphine ligands. The difference in character between these ligands has meant that exchange is always specific to the ligand *trans* to tertiary phosphine, L. Equations 1–3 list examples.

(1)

(R = alkyl [1], aryl [2], cyclopentadienyl [3], or ethynyl [4])

Although CO has the greater *trans* effect, tertiary phosphines have the greater bond-weakening *trans* influence [6]. We believe this to be the critical factor, rendering the *trans* ligands more likely to participate in an S_E2 (cyclic) exchange process through transition states of the type **A**. Such electrophilic attack sequences

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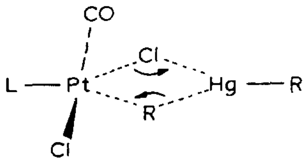
(2)

($R = R' =$ Ph [5] ; $R =$ ethynyl ; $R' =$ ethynyl [4])

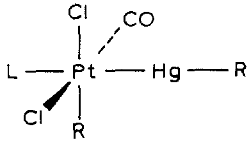
(3)

($R =$ Ph [5] , ethynyl ; $R' =$ Cl ; $R =$ ethynyl ; $R' =$ ethynyl ; $R \neq R'$ [4])

are well documented for mercury(II) [7], and favoured by many authors for exchange reactions of this type at platinum(II) [8–10].



(A)



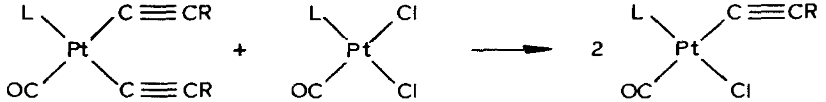
(B)

The reactions could also proceed via oxidative addition/reductive elimination cycles. One of the possible intermediates, **B**, can be regarded as related to transition state **A** by a strong Pt–Hg interaction. The true mechanism may lie between these extremes [4,5,8].

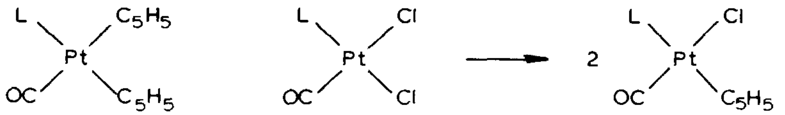
By contrast to the exchange reactions between Hg and Pt, transfer of ligands between two platinum atoms does not always follow the same stereochemical path. Exchange of phenyl and chloride does involve the two sites *trans* to tertiary phosphine, as might be expected (eq. 4) [5].

(4)

Ethynyls [5] and cyclopentadienyl [3] undergo such reactions to produce one isomer only, however (eq. 5 and 6). Whilst a rapid interconversion of one isomer



(5)



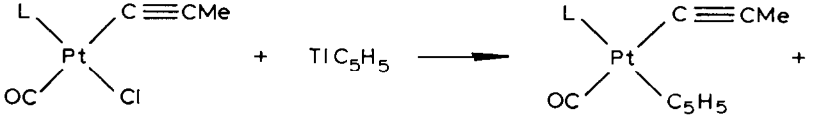
(6)

could not be ruled out in the latter case [3], it seemed unlikely for the ethynyls [5]. Several reactions were followed at low temperatures by ^{31}P NMR spectroscopy, and no intermediates were detected.

We describe here the formation and reactions of several asymmetrically substituted platinum complexes, [PtRR′(CO)L], in a further study of these geometrical variations.

Results and discussion

The reaction between [PtCl(C≡CMe)(CO)L] (L = $PMePh_2$; Cl *trans* to L) and cyclopentadienylthallium proceeds smoothly in $CDCl_3$ to produce [Pt(C_5H_5)(C≡CMe)(CO)L] after 10 min at room temperature. As indicated by ^{31}P NMR spectroscopy, the complex was indefinitely stable in solution at −60°C but slowly decomposed at room temperature, and no attempt was made to isolate it. Its identity was confirmed by ^{1}H NMR spectroscopy. The cyclopentadienyl protons at δ 6.27 ppm and J(PH) 4.5 Hz are typical of a fluxional σ-bonded species *trans* to tertiary phosphine [3]. The ^5J(PH) coupling of the methyl (ethynyl) protons (3.0 Hz) matches values previously found for such groups *cis* to $PMePh_2$ [4].



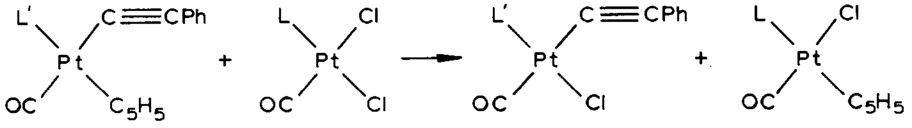
(7)

The same compound is produced by the reaction of [PtCl(C≡Me)(CO)L] and Hg(C_5H_5)$_2$, but the reaction proceeds further to give [PtCl(C_5H_5)(CO)L] (Cl *trans* to CO) and small amounts of *cis*-[Pt(C≡CMe)$_2$(CO)L], presumably from subsequent reactions of the organomercuric halide by-product. (This complication appears in several reactions of organomercurials when two or more organic groups are involved). The chloride of [PtCl(C≡CPh)(CO)L′] (L′ = PMe_2Ph, Cl *trans* to L′) is similarly cleanly replaced by C_5H_5 on treatment with C_5H_5Tl. Spectroscopic parameters for the new platinum compounds are given in the experimental section.

Monitoring by ^{31}P NMR spectroscopy showed that the reaction between [Pt(C_5H_5)(C≡CMe)(CO)L] and $HgCl_2$ in $CDCl_3$ proceeded at −60°C (eq. 8).

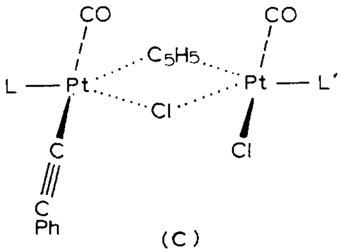
(8)

The reactions of [Pt(C_5H_5)(C≡CPh)(CO)L′] and *cis*-[$PtCl_2$(CO)L] were similar (eq. 9), though transfer was rapid only at room temperature.



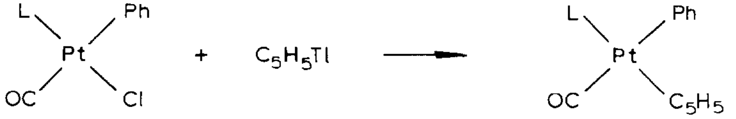
(9)

In all these reactions the groups *trans* to tertiary phosphine on platinum are involved in the exchange, the expected result of S_E2(cyclic) mechanisms. The most plausible transition state for eq. 9 is shown by C.



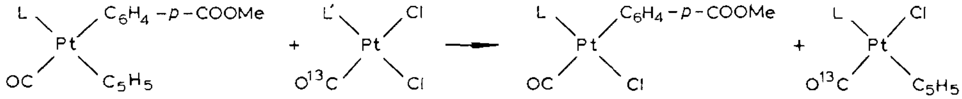
(C)

Cyclopentadienylthallium and [PtClPh(CO)L] (Ph *trans* to CO) also react readily at room temperature, the chloride on platinum being replaced by C_5H_5 (NMR data in experimental.) A small amount of *cis*-[$PtPh_2$(CO)L] [5] was also evident amongst the products, however.



(10)

The *p*-carbomethoxyphenyl complex, [PtCl(C_6H_4-*p*-COOMe)(CO)L] reacts with C_5H_5Tl in a similar manner to afford [Pt(C_5H_5)C_6H_4-*p*-COOMe(CO)L]. This latter material reacts smoothly at room temperature with *cis*-[$PtCl_2$(^{13}CO)L′] (eq. 11).



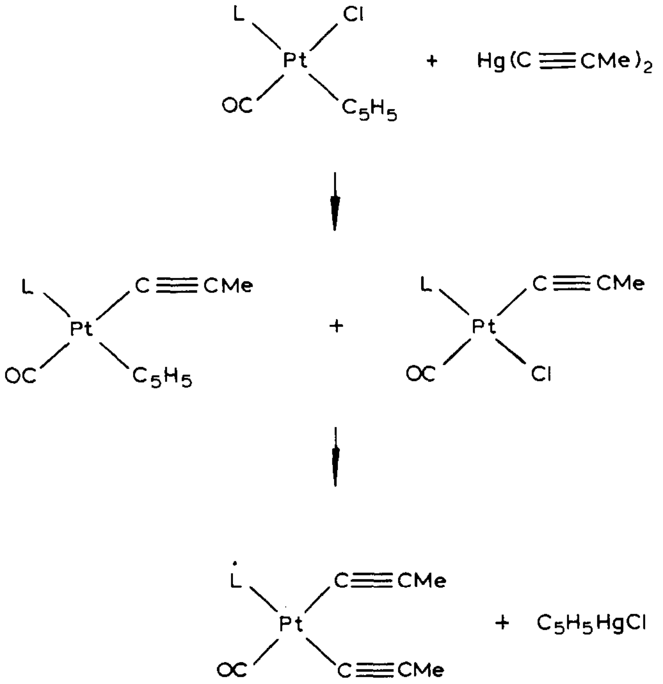
(11)

The use of different phosphines, and ^{13}C-labelled carbon monoxide show unambiguously that once again the sites *trans* to tertiary phosphine are involved in the transfer, and a transition state similar to **C** again appears appropriate.

The reactions of alkynylmercury compounds, $Hg(C{\equiv}CR)_2$, with organoplatinum complexes were more complicated. [PtCl(C_5H_5)(CO)L] (Cl *trans* to CO) reacted with $Hg(C{\equiv}CMe)_2$ at −60°C to produce the same isomer of [Pt(C≡CMe)(C_5H_5)(CO)L] as did the reaction between [Pt(C≡CMe)Cl(CO)L] (Cl *trans* to L) and $Hg(C_5H_5)_2$, but a similar amount of [Pt(C≡CMe)Cl(CO)L] appeared simultaneously. Followed by ^{31}P NMR spectroscopy, the reaction continued until finally only *cis*-[Pt(C≡CMe)$_2$(CO)L] and C_5H_5HgCl were apparent (eq. 12).

The formation of [Pt(C_5H_5)(C≡CMe)(CO)L] can be accounted for by a direct replacement of the S_E2(cyclic) type. Although the halide replaced is *trans* to CO, it is the only halide present. The formation of [PtCl(C≡CMe)(CO)L] probably involves more than one step, though it is possible to produce this material from a single specific oxidative addition of $Hg(C{\equiv}CMe)_2$ to platinum, followed by reductive elimination of Hg(C≡CMe)(C_5H_5). Both Hg(C≡CMe)Cl and Hg(C≡CMe)(C_5H_5) are presumably also present at the intermediate stages of this reaction, so a variety of steps are possible for the final processes.

$Hg(C{\equiv}CMe)_2$ reacts rapidly at room temperature with [PtClPh(CO)L] (Ph *trans* to CO) to form mainly [PtPh(C≡CMe)(CO)L], the NMR characteristics of which indicate that Ph is *trans* to CO (eq. 13). Here, too, there were complications, however, and some *cis*-[Pt(C≡CMe)$_2$(CO)L] was also produced, with, later, some



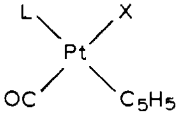
(12)

trans-[$PtClPhL_2$]. The reaction between Hg(C≡CMe)$_2$ and [$PtCl(C_6H_4$-*p*-COOMe)(CO)L] proceeded similarly, but with lesser amounts of side products, though they were still apparent.

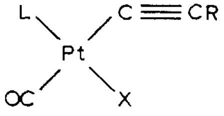
(13)

Whilst it is clear that the majority of these reactions fall into the pattern expected for the operation of the S_E2(cyclic) mechanism, the appearance of minor products, the production of some of which require more than one step must introduce a note of caution. Mechanistic interpretations of this type rely on being able to observe the species formed from each bimolecular exchange step. It is apparent that this cannot always be done, even with continuous NMR monitoring of the reaction mixtures at the lowest temperatures at which the reactions proceed. This in turn throws some doubt on all the sequences observed. It is well established that the rates of such reactions are very dependent on the ligands involved, and reaction times can vary from a few seconds [3] to several days [9] at room temperature. If the initial exchange processes are very much slower than subsequent ones, it may prove impossible to observe the intermediate species between reactants and products, irrespective of conditions. This could be the case with eq. 5 and 6, which do not fit the expected sequence.

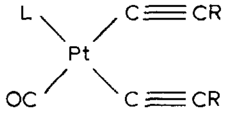
It is also apparent from the nature of the final products that different substituents prefer different geometrical arrangements about platinum. Tertiary phosphine and carbonyl are nearly always found mutually *cis*, and compounds with *trans* R_3P and CO usually isomerise rapidly [11]. Complexes of stoicheiometry [PtRX(CO)L] (with *cis* L and CO) are normally found in geometry **D** when R is C_5H_5 [3], but as **E**, when R is ethynyl [4].



(D)



(E)



(F)

With R = aryl, **D** is favoured, but only marginally [1,2,5]. Finally, the *cis*-bis-ethynyl complexes, **F**, appear to have a special stability, featuring often as the end products of multiple exchange steps in compounds of the type under discussion. It may well be that processes which would produce initially compounds in other than these preferred geometries will be prone to rapid multistep rearrangements.

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).

The starting materials $Tl(C_5H_5)$, $Hg(C_5H_5)_2$, $Hg(C\equiv CR)_2$, $HgAr_2$, *cis*-$[PtCl_2(CO)(PR_3)]$ and *cis*-$[PtCl_2(C_2H_4)(PMePh_2)]$ were prepared by standard methods [12–15].

Reactions

Solutions of $[PtCl(C\equiv CR)(CO)L]$, Cl *trans* to L (R = Me, L = $PMePh_2$; R = Ph, L = PMe_2Ph) and $[PtCl(Ar)(CO)(PMePh_2)]$, Cl *trans* to $PMePh_2$, (Ar = Ph, $C_6H_4CO_2Me$-*p*) were prepared in situ as follows [4].

$[PtCl(C\equiv CMe)(CO)(PMePh_2)]$ (Cl trans to $PMePh_2$). The complex *cis*-$[PtCl_2(CO)(PMePh_2)]$ (20.0 mg; 0.0405 mmol), $[NEt_4]Cl$ (3.3 mg, 0.0202 mmol) and $Hg(C\equiv CMe)_2$ (5.7 mg, 0.0202 mmol) were dissolved together in 0.5 ml $CDCl_3$. A clear yellow solution and a silver grey precipitate formed. The precipitate, $[Et_4N]_2[Hg_2Cl_6]$, was filtered off. ^{31}P NMR investigation of the solution showed the presence of a single product, $[PtCl(C\equiv CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$).

$[PtCl(C\equiv CPh)(CO)(PMe_2Ph)]$(Cl trans to PMe_2Ph). $[PtCl(C\equiv CPh)(CO)(PMe_2Ph)]$ was produced as above.

$[PtCl(Ph)(CO)(PMePh_2)]$ (Cl trans to $PMePh_2$). *cis*-$[PtCl_2(C_2H_4)(PMePh_2)]$ (20.0 mg, 0.0405 mmol) and $HgPh_2$ (14.4 mg, 0.0405 mmol) were mixed in $CDCl_3$ solution (0.5 ml) and allowed to react for 1 h. The solution was filtered and a ^{31}P NMR spectrum showed it to be a *cis/trans* mixture of $[Pt_2Cl_2Ph_2(PMePh_2)_2]$ [1] (^{31}P NMR at −60°C. $\delta(P)$ 0.0 ppm, $^{1}J(PtP)$ 4940 Hz and $\delta P = +0.1$ ppm, $^{1}J(PtP)$ 4993 Hz) in a ratio of 10/3. Carbon monoxide was bubbled through the solution, followed by N_2, and then the solution was allowed to stand at room temperature until ^{31}P NMR spectroscopic examination showed that it was pure $[PtCl(C_6H_5)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) ($\delta(P)$ −1.2 ppm, $^{1}J(PtP)$ 3928 Hz at −60°C).

$[PtCl(C_6H_4CO_2Me)(CO)(PMePh_2)]$ (Cl trans to $PMePh_2$). *cis*-$[PtCl_2(C_2H_4)(PMePh_2)]$ (20.0 mg, 0.0405 mmol) and $Hg(C_6H_4CO_2Me$-*p*$)_2$ (19.1 mg, 0.0405

mmol) were allowed to react in 0.5 ml $CDCl_3$ for several hours. The solution was filtered and a ^{31}P NMR spectrum showed it to be $[Pt_2Cl_2(C_6H_4CO_2Me\text{-}p)_2(PMePh_2)_2]$. ($^{31}P$ NMR at −60°C $\delta(P)$ −1.4 ppm, $^1J(PtP)$ 4901 Hz and $\delta(P)$ −1.2 ppm, $^1J(PtP)$ 4930 Hz). Carbon monoxide was bubbled through the solution, followed by N_2, and then it was allowed to stand at room temperature until ^{31}P NMR spectroscopic examination revealed it to be the correct isomer of $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ ($\delta(P)$ −2.6 ppm, $^1J(PtP)$ 3826 Hz at −60°C).

$[Pt(\eta^1\text{-}C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (C_5H_5 trans to $PMePh_2$). A solution of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) (0.0607 mmol) in 0.5 ml $CDCl_3$ was allowed to react with $Tl(C_5H_5)$ (16.4 mg, 0.0607 mmol) for 10 min at room temperature. Spectroscopic investigation of the solution revealed it to be pure $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (^{31}P NMR at 25°C: $\delta(P) = -2.2$ ppm, $^1J(PtP)$ 1848 Hz. ^1H NMR at 25°C: $\delta(C_5H_5)$ +6.27 ppm, $J(PtH)$ 35.5 Hz, $J(PH)$ 4.5 Hz, $\delta(C{\equiv}Me)$ +1.91 ppm, $J(PtH)$ 16.0 Hz, $J(PH)$ 3.0 Hz; $\delta(PMePh_2)$ 2.33 ppm, $J(PtH)$ 28.5 Hz, $J(PH)$ 10.5 Hz).

$[Pt(\eta^1\text{-}C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (C_5H_5 trans to PMe_2Ph). A similar reaction was performed using $[PtCl(C{\equiv}CPh)(CO)(PMePh_2)]$ Cl *trans* to PMe_2Ph) (0.0393 mmol) and $Tl(C_5H_5)$ (12.2 mg, 0.0453 mmol) to produce $[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (^{31}P NMR at 25°C $\delta(P)$ −14.4 ppm, $^1J(PtP)$ 1799 Hz).

$[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ and $Hg(C_5H_5)_2$. A $CDCl_3$ solution of $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) (0.0405 mmol) and a $CDCl_3$ solution of $Hg(C_5H_5)_2$ (13.4 mg, 0.0405 mmol) were mixed at −60°C and allowed to react at room temperature. Initially the complex $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (identified by ^{31}P NMR) was produced, but subsequent reactions led to the production of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ [3]; (C_5H_5 *trans* to $PMePh_2$) ($\delta(P)$ +6.4 ppm, $^1J(PtP)$ 1784 Hz at −60°C), and a small amount of *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ ($\delta(P)$ −3.2 ppm, $^1J(PtP)$ 2120 Hz at −60°C).

$[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ and $HgCl_2$. $HgCl_2$ (25.0 mg, 0.093 mmol) was added to a solution of $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (0.0405 mmol) in 0.5 ml $CDCl_3$ at −60°C. A ^{31}P NMR investigation showed that within 45 min this had reacted to produce $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$).

$[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ and cis-$[PtCl_2(CO)(PMePh_2)]$. A solution of *cis*-$[PtCl_2(CO)(PMePh_2)]$ (13.8 mg, 0.0279 mmol) in 0.2 ml $CDCl_3$ was mixed with a solution of $[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (0.0393 mmol) at room temperature. ^{31}P NMR investigation of the mixture revealed the presence of $(PtCl(C{\equiv}CPh)(CO)(PMe_2Ph)]$ (Cl *trans* to PMe_2Ph), $[PtCl(C_5H_5)(CO)(PMePh_2)]$ [3] (C_5H_5 *trans* to $PMePh_2$), $[Pt(C_5H_5)(C{\equiv}CPh)(CO)(PMe_2Ph)]$, and *cis*-$[PtCl_2(CO)(PMePh_2)]$.

$[Pt(C_5H_5)Ph(CO)(PMePh_2)]$, ($C_5H_5$ trans to $PMePh_2$). TlC_5H_5 (11.5 mg, 0.0427 mmol) was added to a solution of $[PtCl(Ph)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) (0.0405 mmol) in 0.5 ml $CDCl_3$. After 15 min at room temperature, spectroscopic examination showed that the major product was $[Pt(C_5H_5)Ph(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$). (^{31}P NMR at 25°C: $\delta(P)$ 0.0 ppm, $^1J(PtP)$ 2296 Hz. ^1H NMR at 25°C: $\delta(C_5H_5)$ +6.14 ppm, $J(PtH)$ 39.5 Hz, $J(PH)$ 4.0 Hz). A minor byproduct was identified by ^{31}P NMR spectroscopy as *cis*-$[PtPh_2(CO)(PMePh_2)]$ (^{31}P NMR at 25°C, $\delta(P)$ +2.5 ppm, $^1J(PtP)$ 1611 Hz [5]).

$[Pt(C_5H_5)(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ (C_5H_5 trans to $PMePh_2$). A similar reaction was carried out between TlC_5H_5 (10.9 mg, 0.0405 mmol) and

$[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ (0.0405 mmol) to produce $[Pt(C_5H_5)(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$). (^{31}P NMR at −60°C: $\delta(P)$ −0.7 ppm, $^1J(PtP)$ 2272 Hz).

$[Pt(C_5H_5)(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ and cis-$[PtCl_2(^{13}CO)(PMe_2Ph)]$. A solution of $[Pt(C_5H_5)(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$) (0.0405 mmol) in 0.3 ml $CDCl_3$ was mixed with a solution of *cis*-$[PtCl_2(^{13}CO)(PMe_2Ph)]$ (14.3 mg, 0.0330 mmol) in 0.3 ml $CDCl_3$ at room temperature. After 15 min, ^{31}P NMR spectroscopic examination of the solution revealed the presence of equal amounts of $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ (Cl *trans* to $PMePh_2$) and $[PtCl(C_5H_5)(^{13}CO)(PMe_2Ph)]$ [3] (C_5H_5 *trans* to PMe_2Ph) (^{31}P NMR at room temperature $\delta(P)$ −5.0 ppm, $^1J(PtP)$ 1733 Hz $^2J(CP)$ 10.3 Hz).

$[PtCl(C_5H_5)(CO)(PMePh_2)]$ (C_5H_5 trans to $PMePh_2$) and $Hg(C{\equiv}CMe)_2$. *cis*-$[PtCl_2(CO)(PMePh_2)]$ (20 mg, 0.0405 mmol) and TlC_5H_5 (10.9 mg, 0.0405 mmol) were allowed to react in $CDCl_3$ solution for 30 min. The solution was filtered and ^{31}P NMR investigation showed that it was $[PtCl(C_5H_5)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$) [3]. To this solution was added a $CDCl_3$ solution of $Hg(C{\equiv}CMe)_2$ (11.3 mg, 0.0405 mmol) at −60°C. Initially equal amounts of $[Pt(C_5H_5)(C{\equiv}CMe)(CO)(PMePh_2)]$ (C_5H_5 *trans* to $PMePh_2$) and $[PtCl(C{\equiv}CMe)(CO)(PMePh_2)]$ were produced, (^{31}P NMR spectra), but eventually the major products were *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ [4] (identified by ^{31}P NMR), and $HgCl(C_5H_5)$ (identified by ^1H NMR $\delta(C_5H_5)$ +6.16 ppm).

$[PtCl(C_6H_5)(CO)(PMePh_2)]$ (Cl trans to $PMePh_2$) and $Hg(C{\equiv}CMe)_2$. $[PtCl(C_6H_5)(CO)(PMePh_2)]$ (0.0405 mmol) and $Hg(C{\equiv}CMe)_2$ (11.4 mg, 0.0405 mmol) reacted rapidly in 0.5 ml $CDCl_3$ at room temperature to produce $[Pt(C{\equiv}CMe)Ph(CO)(PMePh_2)]$ ($C{\equiv}CMe$ *trans* to $PMePh_2$). (^{31}P NMR at −60°C: $\delta(P)$ +1.1 ppm, $^1J(PtP)$ 2450 Hz. However large amounts of *cis*-$[Pt(C{\equiv}CMe)_2(CO)(PMePh_2)]$ [4] and some *trans*-$[PtCl(Ph)(PMePh_2)_2]$ were detectable by ^{31}P NMR later.

$[PtCl(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ (Cl trans to $PMePh_2$) and $Hg(C{\equiv}CMe)_2$. $[PtCl(C_6H_4CO_2Me\text{-}p)(CO)PMePh_2)]$ (0.0405 mmol) and $Hg(C{\equiv}CMe)_2$ (11.4 mg, 0.0405 mmol) reacted similarly in $CDCl_3$ to produce $[Pt(C{\equiv}CMe)(C_6H_4CO_2Me\text{-}p)(CO)(PMePh_2)]$ ($C{\equiv}CMe$ *trans* to $PMePh_2$). (^{31}P NMR at −60°C; $\delta(P)$ + 0.1 ppm, $^1J(PtP)$ 2418 Hz). Some *trans*-$[PtCl(C_6H_4\text{-}CO_2Me\text{-}p)(PMePh_2)_2]$ was also produced.

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