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SOME REACTIONS OF METHYLPLATINUM AND METHYLGOLD COMPOUNDS WITH PHENYLSELENOL, DIPHENYLPHOSPHINE, DIPHENYLARSINE, *N*-BROMOSUCCINIMIDE AND 2-NITROPHENYLSULPHENYL CHLORIDE

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Summary

Phenylselenol, diphenylphosphine and diphenylarsine react with methyl derivatives of platinum(II), gold(I) and gold(III) to cleave the methyl—metal bond, but *N*-bromosuccinimide and 2-nitrophenylsulphenyl chloride oxidise methylplatinum(II) complexes to methylplatinum(IV) complexes without cleavage of the methyl—platinum bonds.

Introduction

Benzenethiol has been shown to cleave the methyl—metal bond in methylgold(I) or methylplatinum(II) complexes by a free-radical chain mechanism [1], and in methylgold(III) complexes by a non-radical mechanism to give the products of eq. 1—3.

$$[\mathrm{AuMeL}] + \mathrm{PhSH} \rightarrow [\mathrm{Au(SPh)L}] + \mathrm{CH_4} \quad (1)$$

$$[\mathrm{AuMe_3L}] + \mathrm{PhSH} \rightarrow cis\text{-}[\mathrm{AuMe_2(SPh)L}] + \mathrm{CH_4} \quad (2)$$

$$cis\text{-}[\mathrm{PtMe_2L_2}] + \mathrm{PhSH} \rightarrow trans\text{-}[\mathrm{PtMe(SPh)L_2}] + \mathrm{CH_4} \quad (3)$$

(L = tertiary phosphine)

We have now examined reactions of methylgold and methylplatinum complexes with other reagents which are known to take part in free-radical reactions, with the aim of establishing whether this duality of mechanism is a general effect.

Reactions with phenylselenol

The reactions with phenylselenol parallel very closely those with benzenethiol reported previously [1]. The reaction with *cis*-$[PtMe_2L_2]$ took place in two stages as shown in eq. 4 and 5.

$$\textit{cis}\text{-}[PtMe_2L_2] + PhSeH \rightarrow \textit{trans}\text{-}[PtMe(SePh)L_2] + CH_4 \qquad (4)$$

$$\textit{trans}\text{-}[PtMe(SePh)L_2] + PhSeH \rightarrow \textit{trans}\text{-}[Pt(SePh)_2L_2] + CH_4 \qquad (5)$$

$(L = PMe_2Ph \text{ or } PMePh_2)$

Thus with 1 mol of PhSeH only *trans*-$[PtMe(SePh)L_2]$ was formed, and this with a further mol of PhSeH gave *trans*-$[Pt(SePh)_2L_2]$, which could also be formed by the reaction of *cis*-$[PtMe_2L_2]$ and PhSeH in a 1 : 2 mol ratio. All of these reactions were very fast at room temperature in both dichloromethane and carbon disulphide as solvents. It was impossible to follow the course of the reactions by NMR spectroscopy in the way used previously for the slower reactions with benzenethiol therefore because the reactions were complete before the first spectrum could be recorded.

The formation of only *trans*-$[PtMe(SePh)L_2]$ in the reactions of *cis*-$PtMe_2L_2$ and PhSeH in a 1 : 1 mol ratio shows that the reaction of eq. 4 is much faster than that of eq. 5. If this were not the case, then significant quantities of *trans*-$[Pt(SePh)_2L_2]$ and unreacted *cis*-$[PtMe_2L_2]$ would be expected. An exchange reaction does take place between *cis*-$[PtMe_2L_2]$ and *trans*-$[Pt(SePh)_2L_2]$ according to eq. 6, but this takes 20 h when $L = PMe_2Ph$, and ca. 2 weeks when $L = PMe_2Ph_2$ to reach completion. This reaction is therefore much too slow to invalidate the conclusions reached above.

$$\textit{cis}\text{-}[PtMe_2L_2] + \textit{trans}\text{-}[Pt(SePh)_2L_2] \rightarrow 2\ \textit{trans}\text{-}[PtMe(SePh)L_2] \qquad (6)$$

The large difference in rate for the reaction of eq. 6 when $L = PMe_2Ph$ and $PMePh_2$ is noteworthy since the rates of the similar exchange reactions of *cis*-$PtMe_2L_2$ and PtX_2L_2 when X = halogen are very similar for these two ligands L [2]. This could be due to steric hindrance in the 5 co-ordinate transition state for the exchange reaction [2] being dominant for the bulky phenylseleno complexes but not for the halides.

Benzeneselenol also reacted very rapidly with $[AuMe(PMe_2Ph)]$ according to eq. 7, but the reaction with $[AuMe_3(PMe_2Ph)]$ was slower, being complete in

$$[AuMe(PMe_2Ph)] + PhSeH \rightarrow [Au(SePh)(PMe_2Ph)] + CH_4 \qquad (7)$$

40 min at 35°C in dichloromethane solution to give the products of eq. 8.

$$[AuMe_3(PMe_2Ph)] + PhSeH \rightarrow \textit{cis}\text{-}[AuMe_2(SePh)(PMe_2Ph)] + CH_4 \qquad (8)$$

Within several days at room temperature the initial product *cis*-$[AuMe_2(SePh)(PMe_2Ph)]$ decomposed to give $[Me_2Au(\mu\text{-}SePh)_2AuMe_2]$, which could also be prepared [3] by the reaction of benzeneselenol with $[AuMe_3(OEt_2)]$ at −80°C.

The products isolated were all white or pale yellow solids which were characterised by elemental analysis, and by their NMR spectra which are given in Table 1.

TABLE 1

NMR SPECTRA OF THE COMPLEXES IN DICHLOROMETHANE SOLUTION

Compound	$\delta(CH_3P)$ [a] (ppm)	$^2J(PH)$ (Hz)	$^3J(PtH)$ (Hz)	$\delta(CH_3M)$ [a] (ppm)	$^2J(PH)$ (Hz)	$^2J(PtH)$ (Hz)
trans-$[PtMe(SePh)(PMe_2Ph)_2]$	1.73(t)	6.5	30.1	0.21(t)	6.6	69.7
trans-$[PtMe(SePh)(PMePh_2)_2]$	2.13(t)	7.3	29.5	—0.07(t)	6.5	71.3
trans-$[Pt(SePh)_2(PMe_2Ph)_2]$	1.74(t)	7.0	27.3			
trans-$[Pt(SePh)_2(PMePh_2)_2]$	2.17(t)	7.1	29.4			
$[Au(SePh)(PMe_2Ph)]$	1.78(d)	10.1				
cis-$[AuMe_2(SePh)(PMe_2Ph)]$	1.83(d)	9.9		0.79(d) 0.69(d)	8.5 8.8	
$[Au_2Me_4(\mu\text{-}SePh)_2]$				0.95(s)		
$[Au_2Me_4(\mu\text{-}PPh_2)_2]$				0.68(d)	1.8 [b]	

[a] Chemical shifts downfield from internal TMS, M = Au or Pt, t = triplet, d = doublet, s = singlet.
[b] $^3J(PH) + {}^3J(P'H)$.

The reactions of *cis*-$[PtMe_2(PMe_2Ph)_2]$ and $[AuMe(PMe_2Ph)]$ with benzeneselenol were also conducted in sealed ESR tubes in the presence of the radical trap t-BuNO. In each case the ESR spectrum of t-BuMeNO$^\bullet$ radicals was obtained, showing that methyl radicals were formed during the reaction. In the similar reaction with $[AuMe_3(PMe_2Ph)]$ no such radicals could be detected indicating that no methyl radicals were formed in this case. Attempts were also made to inhibit the reactions by adding the radical scavenger galvinoxyl to the reacting mixtures. However this did not inhibit the reactions, which were still extremely fast for reactions with *cis*-$[PtMe_2(PMe_2Ph)_2]$ and $[AuMe(PMe_2Ph)]$. This could be taken as evidence that the reactions are not free-radical chain processes, but, in view of the very fast reaction rates observed, it is also possible that the propagation steps in the radical chain process are faster than the rate of scavenging of radicals by galvinoxyl. Rather more convincing is the lack of inhibition in the reaction of benzeneselenol with $[AuMe_3(PMe_2Ph)]$ which is a considerably slower reaction, and hence would be expected [1] to be retarded by added galvinoxyl if a free-radical chain mechanism did operate. Together with the spin-trapping experiments described above and with the similar data obtained for reactions of $[AuMe_3(PMe_2Ph)]$ with benzenethiol [1], this is strong evidence that the reactions of $[AuMe_3(PMe_2Ph)]$ with PhSH and PhSeH do not take place by a free-radical mechanism.

We have also studied the relative reactivities of various methylplatinum and methylgold complexes towards benzeneselenol by allowing mixtures of two complexes to compete for a limited quantity of benzeneselenol. The series of reactivities obtained was:

$$
\begin{aligned}
&[AuMe(PMe_2Ph)] > [AuMe(PPh_3)] > cis\text{-}[PtMe_2(PMe_2Ph)_2] \\
&\quad > cis\text{-}[PtMe_2(PMePh_2)_2] > trans\text{-}[PtMe(SePh)(PMePh_2)_2] \\
&\quad > [AuMe_3(PMe_2Ph)] \gg cis\text{-}[AuMe_2(SePh)(PMe_2Ph)]
\end{aligned}
$$

This is completely consistent with the reactivity series obtained for the similar reactions with benzenethiol [1]. Thus, although we have been unable to prove conclusively that the reactions of benzeneselenol with methylgold(I) and methylplatinum(II) complexes are free-radical chain reactions, the similarity in the results of the spin-trapping experiments and in the reactivity series with the benzenethiol reactions for which the evidence for a radical chain mechanism is very strong suggests that such a mechanism operates.

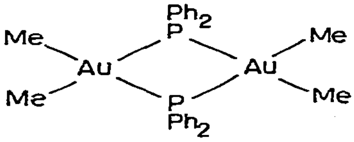
Reactions with diphenylphosphine and diphenylarsine

These reagents with [$AuMe(PMe_2Ph)$] gave highly insoluble precipitates of [$(AuPPh_2)_n$] or [$(AuAsPh_2)_n$] and methane. These are presumably polymeric compounds with PPh_2 or $AsPh_2$ groups bridging between gold atoms, and were insoluble even in donor solvents. A slower reaction took place between [$AuMe_3(PMe_2Ph)$] and Ph_2PH according to eq. 9, this being complete in 2 days at 40°C.

$$2\ AuMe_3(PMe_2Ph) + 2\ Ph_2PH \rightarrow [Au_2Me_4(\mu\text{-}PPh_2)_2] + 2CH_4 + 2\ PMe_2Ph \qquad (9)$$

Again the PMe_2Ph is displaced from gold and bridging diphenylphosphide groups are formed, but in this case a dimer rather than a polymer results. Diphenylarsine did not react with [$AuMe_3(PMe_2Ph)$] at 40°C.

A slow reaction took place between Ph_2PH and *cis*-[$PtMe_2(PMe_2Ph)_2$] to give methane and a product which analysed as $PtMe(PPh_2)(PMe_2Ph)$. This is likely to be a dimer with bridging PPh_2 groups, [$Pt_2Me_2(\mu\text{-}PPh_2)_2(PMe_2Ph)_2$], but, owing to, its low solubility in common organic solvents, we have been unable to characterise it fully. Again diphenylarsine failed to react with *cis*-[$PtMe_2(PMe_2Ph)_2$]. Since the reactions are generally slow and are complicated by displacement of phosphine from platinum or gold to give dimeric or polymeric products, we have not attempted to study the mechanisms of reaction in detail. However the following general observations have been made. The reactions with diphenylphosphine follow the rate sequence [$AuMe(PMe_2Ph)$] $\gg$ [$AuMe_3(PMe_2Ph)$] $>$ *cis*-[$PtMe_2(PMe_2Ph)_2$], and were considerably faster than similar reactions with diphenylarsine. These results can be contrasted with the reactions with PhSH and PhSeH, where the selenol reacted much faster than the thiol, and the reactivity sequence was [$AuMe(PMe_2Ph)$] $>$ *cis*-[$PtMe_2(PMe_2Ph)_2$] $\gg$ [$AuMe_3(PMe_2Ph)$]. Thus it is likely that different mechanisms operate in the two cases. Together with the observation that whenever Ph_2PH or Ph_2AsH reacted a tertiary phosphine ligand was displaced from the metal, the evidence suggests a mechanism in which Ph_2PH or Ph_2AsH first displaces a tertiary phosphine ligand from platinum or gold, followed by intramolecular loss of methane from the resulting species [$MeM(YPh_2H)$] where M = Au or Pt and Y = P or As. Thus the reactivity series gold(I) $\gg$ gold(III) $>$ platinum(II) parallels the reactivity towards ligand substitution reactions, and the greater reactivity of Ph_2PH over Ph_2AsH parallels the expected ability of these ligands to displace a tertiary phosphine ligand from platinum or gold.

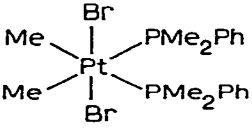


(I)

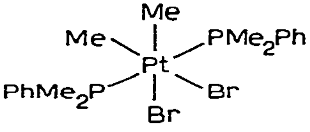
The NMR spectrum of the complex [$Au_2Me_4(PPh_2)_2$] which is expected to have structure I is of some interest. Each $(CH_3)_2AuP_2$ unit is expected to give an $A_3A'_3XX'$ spin system due to coupling of chemically identical but magnetically non-equivalent methyl protons and phosphorus atoms. The NMR spectrum gave a 1 : 1 doublet for the methylgold resonance, with peaks separated by $[^3J(PH) + {}^3J(P'H)] = 1.8$ Hz. Since typical coupling constants $^3J(PH)$ in methylgold phosphine complexes fall in the region 6—10 Hz whether the phosphorus and methyl groups are mutually *cis* or *trans*, this indicates that $^3J(PH)$ and $^3J(P'H)$ are of opposite sign. This situation has previously been established for *cis*-$AuMe_2(CF_3)(PMe_3)$ for which $^3J(PH)$ was +8.5 Hz and —8.9 Hz for the methyl groups *cis* and *trans* to phosphorus respectively [4].

Reactions with *N*-bromosuccinimide and 2-nitrophenyl-sulphenyl chloride

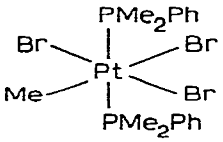
N-Bromosuccinimide is known to react with organotin compounds by a free-radical mechanism [5,6] and we were interested to see if this mechanism also operates in reactions with transition metal alkyls. However the reactions which we have studied are complex. Thus *N*-bromosuccinimide reacts with *cis*-[$PtMe_2(PMe_2Ph)_2$] within 1 h at room temperature, but the initial products are complex and we have been unable to characterise them. However after 24 h the complexes [$PtBr_2Me_2(PMe_2Ph)_2$], as a mixture of isomers II and III, were formed and were positively identified by their NMR spectra and were subsequently isolated from the reaction mixture. Free succinimide was also formed. It seems likely that the initial fast reaction may give a simple oxidative addition of the N—Br bond to the platinum complex, followed by decomposition of the resulting succinimidoplatinum(IV) complex to give the final products. Attempts to isolate the initial products were unsuccessful however so that this conclusion must remain tentative. The overall reaction is to oxidise platinum(II) to platinum(IV) rather than to cleave the methyl—platinum bonds.



(II)



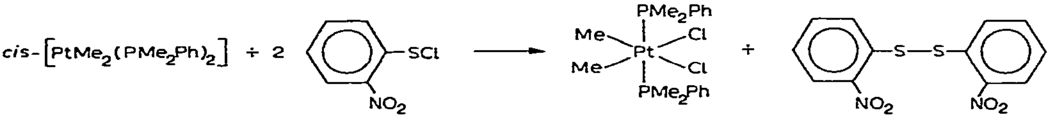
(III)



(V)

A similar reaction took place with 2-nitrophenylsulphenyl chloride which acted as a chlorinating agent according to eq. 10. Again the reaction was not a clean one and other unidentified products were formed in low yield.

N-Bromosuccinimide also acted as a brominating agent towards *trans*-[$PtBrMe(PMe_2Ph)_2$] and [$AuBr(PMe_2Ph)$] to give V and [$AuBr_3(PMe_2Ph)$] respectively.



(IV)

(10)

In the reaction with [$AuBr(PMe_2Ph)$] considerable decomposition to gold took place and a complex [$AuBr_3(PMe_2Ph)_2$] was also isolated.

Experimental

Methylplatinum and methylgold complexes were prepared by literature methods [1,2,7,8]. The course of the reactions was usually followed first by NMR spectroscopy, and a typical procedure is given below. Particular care to exclude oxygen was taken in the reactions with Ph_2PH and Ph_2AsH.

trans-[Pt(SePh)Me(PMe$_2$Ph)$_2$] with PhSeH

A solution of *trans*-$[Pt(SePh)Me(PMe_2Ph)_2]$ (0.103 g, 0.16 mmol) in dichloromethane (0.5 ml) in an NMR tube was degassed by several freeze-pump-thaw cycles, PhSeH (0.017 ml, 0.16 mmol) was added and the NMR tube was sealed under vacuum. The NMR spectrum was recorded immediately after warming to room temperature and showed the products to be methane and *trans*-$[Pt(SePh)_2(PMe_2Ph)_2]$ only. The tube was opened, the solvent was evaporated and the residual yellow oil was recrystallised from dichloromethane/ether to give *trans*-$[Pt(SePh)_2(PMe_2Ph)_2]$ as yellow crystals, m.p. 210—215°C (Found: C, 42.8; H, 4.5. $C_{28}H_{32}P_2PtSe_2$ calcd.: C, 42.9; H, 4.1%).

trans-[Pt(SePh)Me(PMe$_2$Ph)$_2$]

To a solution of *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0.43 g, 0.86 mmol) in dichloromethane (5 ml) was added PhSeH (0.091 ml, 0.86 mmol). After 15 min the solvent was evaporated and the yellow oil which remained was washed with pentane and then crystallised from dichloromethane/ether as yellow crystals (0.5 g, 92%), m.p. 103—105°C (Found: C, 42.4; H, 4.95. $C_{23}H_{30}P_2PtSe$ calcd.: C, 43.0; H, 4.7%).

Prepared similarly were *trans*-$[Pt(SePh)Me(PMePh_2)_2]$ as a yellow solid which was very difficult to crystallise, but which was identified by its NMR spectrum, and *trans*-$[Pt(SePh)_2(PMePh_2)_2]$, m.p. 208—210°C (lit. [9] 195—196°C), yield 69%.

[Au(SePh)(PMe$_2$Ph)]

This was prepared from $[AuMe(PMe_2Ph)]$ (0.029 g) with PhSeH (0.006 ml) in dichloromethane (0.5 ml). Reaction to give methane and $[Au(SePh)(PMe_2Ph)]$ was instant as shown by the NMR spectrum. The product was isolated as above, m.p. 118°C (dec.) (Found: C, 34.4; H, 3.4. $C_{14}H_{16}AuPSe$ calcd.: C, 34.2; H, 3.3%).

cis-[AuMe$_2$(SePh)(PMe$_2$Ph)]

This was obtained from $[AuMe_3(PMe_2Ph)]$ and PhSeH in ether solution, and was isolated and purified as above, m.p. 111—115°C (Found: C, 36.6; H, 3.9. $C_{16}H_{22}AuPSe$ calcd.: C, 36.85; H, 4.2%).

[Au$_2$Me$_4$(μ-SePh)$_2$]

This was obtained by reaction of $[AuMe_3(OEt_2)]$ [3] (from Au_2Br_6 (0.97 g) and methyllithium (3.5 ml of 2.3 *M* solution in ether) in ether (25 ml) at —78°C) with PhSeH (0.3 ml) at —78°C. The mixture was allowed to warm to room temperature, then hydrolysed with water and the product was isolated from the dried ether, and recrystallised from dichloromethane/petroleum spirit, m.p. 131—132°C (Found: C, 25.1; H, 3.1; Au, 49.5. $C_{16}H_{22}Au_2Se_2$ calcd.: C, 25.1; H, 2.9; Au, 51.4%),

ESR experiments

PhSeH (0.014 ml) was added to a solution of *cis*-[$PtMe_2(PMe_2Ph)_2$] (0.065 g) and t-BuNO (0.001 g) in benzene (0.5 ml) in an ESR tube. The tube was sealed under vacuum, the mixture was allowed to warm to room temperature and the ESR spectrum was recorded. The spectrum of t-Bu(Me)NO$^\bullet$ was obtained [10] as a 1 : 1 : 1 triplet of 1 : 3 : 3 : 1 quartets with A_N 15.6 G and A_H 11.7 G.

The same result was obtained in the similar reaction with [$AuMe(PMe_2Ph)$] but with [$AuMe_3(PMe_2Ph)$] no such radicals were formed, nor were the radicals formed from the methylplatinum or methylgold compounds with t-BuNO in the absence of PhSeH.

Competition reactions

A representative example only is given. A solution of [$AuMe(PMe_2Ph)$] (0.12 mmol) and *cis*-[$PtMe_2(PMe_2Ph)_2$] (0.12 mmol) in dichloromethane (0.8 ml) in an NMR tube was treated with PhSeH (0.10 mmol). Reaction took place instantly and the NMR spectrum showed that approximately 0.059 mmol of [$AuMe(PMe_2Ph)$] and 0.041 mmol of *cis*-[$PtMe_2(PMe_2Ph)_2$] had been consumed. Hence the gold compound is the more reactive.

[$(AuPPh_2)_n$]

Diphenylphosphine (0.02 ml) was added to a solution of [$AuMe(PMe_2Ph)$] (0.04 g) in dichloromethane (0.5 ml). A very pale green precipitate of the product was formed rapidly. This was filtered off, washed with ether and dried under vacuum, m.p. 250°C (dec.) (Found: C, 37.5; H, 2.8; Au, 52.0. $(C_{12}H_{10}AuP)_n$ calcd.: C, 37.7; H, 2.6; Au, 51.7%). It was insoluble in common organic solvents.

[$Au_2Me_4(\mu\text{-}PPh_2)_2$]

This was prepared by reaction of [$AuMe_3(PMe_2Ph)$] (0.06 g) with Ph_2PH (0.06 ml) in dichloromethane (0.6 ml) in a sealed tube. The tube was heated to 40°C for 2 days. The tube was opened and the solvent was evaporated to give the product as a white solid, m.p. 175°C (dec.) (Found: C, 41.1; H, 4.0; Au, 44.9. $C_{28}H_{32}Au_2P_2$ calcd.: C, 40.8; H, 3.9; Au, 47.8%). The complex gave a peak in the mass spectrum at *m/e* 825 ± 2, corresponding to the expected parent ion of 824, confirming that the product was dimeric.

[$(AuAsPh_2)_n$]

This was prepared from [$AuMe(PMe_2Ph)$] (0.045 g) with Ph_2AsH (0.023 ml) in dichloromethane (0.5 ml) at 50°C in a sealed tube. After 2 h the precipitate of [$(AuAsPh_2)_n$] was collected and purified as above. (Found: C, 33.9; H, 2.4; Au, 43.6. $C_{12}H_{10}AsAu$ calcd.: C, 33.8; H, 2.35; Au, 46.25%).

cis-[$PtMe_2(PMe_2Ph)_2$] with Ph_2PH

A solution of *cis*-[$PtMe_2(PMe_2Ph)_2$] (0.22 g) and Ph_2PH (0.077 ml) in acetone (25 ml) was heated under reflux for 10 h under an atmosphere of nitrogen. The solvent was removed under vacuum, and the remaining oil, which contained some unreacted *cis*-[$PtMe_2(PMe_2Ph)_2$], was chromatographed over a column of silica using benzene eluent. This gave a white crystalline product which melted over a wide temperature range of 110—180°C, and was tentatively characterised as [$Pt_2Me_2(\mu\text{-}PPh_2)_2(PMe_2Ph)_2$] (Found: C, 47.3; H, 4.9. $C_{42}H_{48}P_4Pt_2$ calcd.: C, 47.3; H, 4.5%). The complex was only sparingly soluble in common organic solvents so that a satisfactory NMR spectrum could not be obtained.

trans-PtBrMe(PMe₂Ph)₂ with N-bromosuccinimide

N-Bromosuccinimide (0.071 g) was added to a solution of *trans*-$PtBrMe(PMe_2Ph)_2$ (0.22 g) in dichloromethane (5 ml). After 2 h, the solvent was evaporated, the residue was washed with ether and recrystallised from dichloromethane/methanol to give [$PtBr_3Me(PMe_2Ph)_2$] (V), as yellow crystals (Found: C, 28.3; H, 3.6. $C_{17}H_{25}Br_3P_2Pt$ calcd.: C, 28.1; H, 3.45%). NMR in $CHCl_3$: δ(MePt) 0.96 (t, ^3J(PH) 5.2 Hz, ^2J(PtH) 65.5 Hz), δ(MeP) 2.28 (t, $^2J + {}^4J$(PH) 8.2 Hz, ^3J(PtH) 16 Hz) in good agreement with the literature data [7].

cis-[PtMe₂(PMe₂Ph)₂] with N-bromosuccinimide

N-Bromosuccinimide (0.07 g) was added to a solution of *cis*-[$PtMe_2(PMe_2Ph)_2$] (0.2 g) in acetone (25 ml). After 24 h at room temperature the acetone was evaporated under vacuum, and the remaining oil was crystallised from methanol to give white crystals of [$PtBr_2Me_2(PMe_2Ph)_2$], configuration III, m.p. 182—183°C (lit. [7] 184—186°C) (Found: C, 32.9; H, 4.1; Pt, 33.5. $C_{18}H_{28}Br_2P_2Pt$ calcd.: C, 32.7; H, 4.3; Pt, 32.9%). The NMR spectrum was identical with that reported in the literature [7].

In other experiments conducted in $(CD_3)_2CO$, CH_2Cl_2 or $CDCl_3$ in NMR tubes, the presence of [$PtBr_2Me_2(PMe_2Ph)_2$] of configuration II was proved from the characteristic NMR spectrum [7] but was not isolated.

[AuBr(PMe₂Ph)] with N-bromosuccinimide

N-Bromosuccinimide (0.318 g) was added to a solution of [$AuBr(PMe_2Ph)$] (0.74 g) in dichloromethane (10 ml). Ether was added and red-brown crystals of [$AuBr_3(PMe_2Ph)$] precipitated and were identified by the NMR spectrum [2]. Some metallic gold was also deposited. Further crystals were obtained as a mixture of red crystals, m.p. 60—80°C, identified as $AuBr_3(PMe_2Ph)_2$ (Found: C, 26.4; H, 3.1. $C_{16}H_{22}AuBr_3P_2$ calcd.: C, 26.9; H, 3.1%), NMR in CH_2Cl_2: $\delta(CH_3P)$ 1.99 (d, ^2J(PH) 13.2 Hz), and white crystals, m.p. 166—169°C, identified as $AuBr(PMe_2Ph)_2$ (Found: C, 34.3; H, 3.7. $C_{16}H_{22}AuBrP_2$ calcd.: C, 34.7; H, 4.0%).

cis-[PtMe₂(PMe₂Ph)₂] with 2-NO₂C₆H₄SCl

Initial NMR studies showed that 2 mol of 2-$NO_2C_6H_4SCl$ was required to react with 1 mol of *cis*-[$PtMe_2(PMe_2Ph)_2$], and [$PtCl_2Me_2(PMe_2Ph)_2$] (IV) was identified as the major platinum-containing product by its NMR spectrum [7]. Examination by thin layer chromatography showed the presence of 5 compounds the major ones being IV and (2-$NO_2C_6H_4S)_2$. Only IV could be crystallised from the mixture.

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References

1 A. Johnson and R.J. Puddephatt, J. Chem. Soc. Dalton Trans., (1975) 115.
2 R.J. Puddephatt and P.J. Thompson, J. Chem. Soc. Dalton Trans., (1975) 1810.
3 H. Gilman and L.A. Woods, J. Amer. Chem. Soc., 70 (1948) 550.
4 J.D. Kennedy, W. McFarlane and R.J. Puddephatt, J. Chem. Soc. Dalton Trans., (1976) 745.
5 A.G. Davies, B.P. Roberts and J.M. Smith, J. Chem. Soc. Dalton Trans., (1972) 2221.
6 P.M. Digiacomo and H.G. Kuivila, J. Organometal. Chem., 63 (1973) 251.
7 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2801.
8 A. Johnson and R.J. Puddephatt, J. Organometal. Chem., 85 (1975) 115.
9 K. Kawakami, Y. Ozaki and T. Tanaka, J. Organometal. Chem., 69 (1974) 151.
10 M.J. Perkins, P. Ward and A. Horsfield, J. Chem. Soc. B, (1970) 395.