Mechanistic Studies of Reactions of Benzenethiol with Methyl Derivatives of Platinum(II) and Gold-(I) and -(III)

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Benzenethiol reacts with the complexes [MeAuL], [Me_3AuL], and *cis*-[$PtMe_2L_2$] (L = PMe_3, PMe_2Ph, $PMePh_2$, or PPh_3) to give methane and [(PhS)AuL], *cis*-[$Me_2Au(SPh)L$], and *trans*-[$PtMe(SPh)L_2$] or *trans*-[$Pt(SPh)_2L_2$] respectively. The reactions with the gold(I) and platinum(II) complexes proceed by free-radical chain mechanisms, but the gold(III) complexes react by a non-radical mechanism. Competitive reactions with benzenethiol show the order of reactivity [$MeAu(PMe_3)$] > [$MeAu(PMePh_2)$] > [$MeAu(PPh_3)$], *cis*-[$PtMe_2(PMe_2Ph)_2$] > *trans*-[$PtMe(SPh)(PMe_2Ph)_2$] $\gg$ [$Me_3Au(PMe_3)$], [$Me_3Au(PMePh_2)$] $\gg$ *cis*-[$Me_2Au(SPh)(PMe_3)$].

THERE has been considerable discussion recently about whether many reactions of transition-metal alkyls take place by free-radical, ionic, or concerted mechanisms.[1-6] Examples include the thermal decomposition of transition-metal alkyls,[3-4] and their reactions with alkenes and alkynes[5,6] and with alkyl halides.[1,2] In some of these reactions a vital step is the attack of a free radical at the transition-metal centre, for example, in oxidative addition of an alkyl halide RX to a transition-metal complex M [equations (1) and (2)].[1] However, little is known about the factors which influence

$$R^{\cdot} + M \longrightarrow RM^{\cdot} \qquad (1)$$

$$RM^{\cdot} + RX \longrightarrow RMX + R^{\cdot} \qquad (2)$$

the reactivity of a transition-metal complex towards this type of reaction, though considerably more is known about similar reactions of main-group metal alkyls.[7] In order to investigate this problem we have studied the reactions of benzenethiol with some methyl-gold(I), -gold(III), and -platinum(II) complexes. Benzenethiol has been shown to react by a free-radical chain mechanism with boron, antimony, and bismuth alkyls,[7] but we find that, although the gold(I) and platinum(II) complexes react by this mechanism, the gold(III) complexes react by a non-radical process. A preliminary report of this work has been published.[8]

RESULTS AND DISCUSSION

The reaction of benzenethiol with *cis*-[$PtMe_2(PMe_2Ph)_2$] took place in two stages. With 1 mol of thiol the reaction of equation (3) occurred and was complete in 30 min at 35 °C in dichloromethane solution. The

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + PhSH \longrightarrow trans\text{-}[PtMe(SPh)(PMe_2Ph)_2] + CH_4 \qquad (3)$$

stereochemistry of the product was easily deduced from its n.m.r. spectrum (Table 1); in particular the peak due to the methylphosphorus protons appeared as an apparent triplet due to coupling with phosphorus,

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typical[9] of complexes containing two mutually *trans* dimethylphenylphosphine ligands. Methane was also identified by its n.m.r. spectrum (δ 0·54 p.p.m.). It is interesting that the reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with hydrogen chloride gives *cis*-$[PtMeCl(PMe_2Ph)_2]$; we could detect no *cis*-$[PtMe(SPh)(PMe_2Ph)_2]$ by n.m.r. spectroscopy at any stage of the reaction with benzenethiol. The complex *trans*-$[PtMe(SPh)(PMe_2Ph)_2]$ reacted with a further mol of benzenethiol according to equation (4). This reaction was complete in *ca.* 1 h at 35 °C in dichloromethane. The same product

$$trans\text{-}[PtMe(SPh)(PMe_2Ph)_2] + PhSH \longrightarrow trans\text{-}[Pt(SPh)_2(PMe_2Ph)_2] + CH_4 \quad (4)$$

was formed by direct reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with 2 mol of benzenethiol. Again the reaction took place in two clear stages with complete conversion to *trans*-$[PtMe(SPh)(PMe_2Ph)_2]$ before any detectable amount of *trans*-$[Pt(SPh)_2(PMe_2Ph)_2]$ was formed.

TABLE 1

N.m.r. spectra of the complexes in dichloromethane solution

Complex	δ(MeP)[a] p.p.m.	^2J(PH) Hz	^3J(PtH) Hz	δ(MeM)[a] p.p.m.	^3J(PH) Hz	^2J(PtH) Hz
$[MeAu(PMe_3)]$	1·75 (d)	9·0		0·58 (d)	8·0	
$[MeAu(PMePh_2)]$	2·36 (d)	8·8		0·76 (d)	8·4	
$[MeAu(PPh_3)]$				0·90 (d)	8·6	
$[Au(SPh)(PMe_3)]$	1·90 (d)	10·1				
$[Au(SPh)(PMePh_2)]$	2·45 (d)	9·4				
$[Me_3Au(PMe_3)]$	1·90 (d)	10·2		0·45 (d)[b]	7·4	
				1·12 (d)[c]	9·6	
$[Me_3Au(PMePh_2)]$	2·50 (d)	9·4		0·42 (d)[b]	7·2	
				1·38 (d)[c]	9·2	
cis-$[Me_2Au(SPh)(PMe_3)]$	1·75 (d)	11·0		1·06 (d)	9·6	
				0·90 (d)	9·8	
cis-$[Me_2Au(SPh)(PMePh_2)]$	2·65 (d)	10·2		1·10 (d)	9·2	
				1·27 (d)	9·6	
cis-$[Me_2Pt(PMe_2Ph)_2]$	1·92 (d)	7·5[d]	20·4	0·90 (c)		67·3
trans-$[MePt(SPh)(PMe_2Ph)_2]$	2·10 (t)	6·8[d]	31·8	0·55 (t)	6·8	62·4
trans-$[Pt(SPh)_2(PMe_2Ph)_2]$	2·10 (t)	7·0[d]	28·5			

[a] From external $SiMe_4$; d = doublet, t = triplet, c = complex multiplet. [b] *trans* to carbon. [c] *trans* to phosphorus. [d] $^2J(PH) + {}^4J(P^1H)$.

The gold(I) complexes [MeAuL] (L = PMe_3, $PMePh_2$, or PPh_3) reacted with benzenethiol according to equation (5), the reactions being complete in 30—60 min at 35 °C in dichloromethane solution. However, the

$$[MeAuL] + PhSH \longrightarrow [(PhS)AuL] + CH_4 \quad (5)$$

gold(III) complexes $[Me_3AuL]$ (L = PMe_3 or $PMePh_2$) reacted considerably more slowly with benzenethiol. The reaction with $[Me_3Au(PMe_3)]$ took place cleanly according to equation (6), and was complete in 2 d

$$[Me_3Au(PMe_3)] + PhSH \longrightarrow cis\text{-}[Me_2Au(SPh)(PMe_3)] + CH_4 \quad (6)$$

at 35 °C in dichloromethane. The stereochemistry of the product follows from its n.m.r. spectrum (Table 1) which contained two peaks due to methylgold protons each split into a doublet by coupling with phosphorus; the *trans*-isomer would contain only one such peak.

The reaction of benzenethiol with $[Me_3Au(PMePh_2)]$ was even slower (several weeks under similar conditions) and the product was a mixture of *cis*-$[Me_2Au(SPh)(PMePh_2)]$, identified by its n.m.r. spectrum (Table 1), and the thio-bridged complex $[Me_2Au(\mu\text{-}SPh)_2AuMe_2]$[10] and Ph_2MePS [δ(CH_3P) 2·25 p.p.m., doublet, ^2J(PH) 13·5 Hz]. The methyldiphenylphosphine sulphide may be formed after dissociation of the phosphine according to equation (7).[11] Approximately equal amounts of *cis*-$[Me_2Au(SPh)(PMePh_2)]$

$$Ph_2MeP + PhSH \longrightarrow Ph_2MePS + C_6H_6 \quad (7)$$

and $[Me_2Au(\mu\text{-}SPh)_2AuMe_2]$ were formed, and since some of the thiol was consumed in reaction with phosphine some $[Me_3Au(PMePh_2)]$ remained also. An attempt to separate the products by chromatography led to complete elimination of the phosphine and only $[Me_2Au(\mu\text{-}SPh)_2AuMe_2]$ could be isolated. The remaining methylgold bonds in *cis*-$[Me_2Au(SPh)(PMe_3)]$ and $[Me_2Au(\mu\text{-}SPh)_2AuMe_2]$ were inert to reaction with benzenethiol.

Mechanism of Reaction.—In preliminary studies of the reaction of $[MeAu(PMe_3)]$ with benzenethiol, we observed long induction periods before reaction began in the solvents benzene or carbon disulphide. In didichloromethane or $(D_3C)_2CO$ there was often no induction period but sometimes short induction periods of *ca.* 10 min were observed, and the rates of reaction were not reproducible. Reactions could often be started by vigorous shaking of the n.m.r. tube containing the reactants. Such behaviour is typical of free-radical chain reactions, with the induction periods presumably being due to adventitious presence of free-radical scavengers and the initiation on shaking caused by reaction of the thiol with oxygen.

In order to confirm this we studied the effect of adding the free-radical scavenger galvinoxyl or the initiator

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azobis(isobutyronitrile) (aibn) to the reaction mixtures. A typical result is shown in Figure 1. Addition of 1·0% galvinoxyl to the reaction mixture of [MeAu($PMePh_2$)] and benzenethiol caused complete inhibition of the reaction until the colour of the galvinoxyl was discharged. Addition of aibn caused a rapid acceleration in the rate of reaction. These effects were also seen in reactions of *cis*-[$PtMe_2(PMe_2Ph)_2$] and of *trans*-[PtMe(SPh)($PMe_2Ph)_2$] with benzenethiol, showing that a free-radical chain mechanism is operative. However, addition of 2·0% galvinoxyl or aibn (20%) to the reaction mixture of [$Me_3Au(PMe_3)$] and benzenethiol had no effect on the rate of reaction. It seems clear that this reaction does not take place by a free-radical chain mechanism.

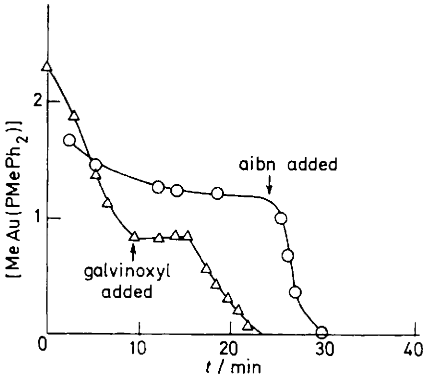

FIGURE 1 Effects of galvinoxyl and azobis(isobutyronitrile) on the reaction of [$MeAu(PMePh_2)$] with benzenethiol

We have considered two mechanisms for the free-radical chain reactions. The first is shown in equations (8) and (9) (M = Au^{I} or Pt^{II}). The mechanism, which

$$PhS^{\cdot} + MeM \longrightarrow (Me\dot{M}SPh) \longrightarrow MSPh + Me^{\cdot} \quad (8)$$

$$Me^{\cdot} + PhSH \longrightarrow CH_4 + PhS^{\cdot} \quad (9)$$

we call (*i*), is the same as that proposed for reaction of benzenethiol with main-group metal alkyls.[7,8] The vital step [equation (8)] involves attack of a thiyl radical at the metal centre with displacement of a methyl radical.[12] The displacement may be concerted (S_H2 concerted mechanism [7]) or may involve formation of a gold(II) or platinum(III) intermediate formed by addition of the thiyl radical (S_H2 stepwise mechanism [7]).

However both gold(I) and platinum(II) can undergo oxidative-addition reactions to give gold(III) or platinum(IV) complexes respectively, and this leads to another possible mechanism, (*ii*), shown in equations (10) and (11). The same gold(II) or platinum(III) intermediate is formed as in mechanism (*i*), but it reacts with benzenethiol directly to give the hydridomethyl-gold(III) or -platinum(IV) complex which undergoes intramolecular concerted reductive elimination of methane. The first step [equation (10)] may be compared with the free-radical mechanism of

$$PhS^{\cdot} + MeM \longrightarrow (Me\dot{M}SPh) \xrightarrow{PhSH} Me\overset{H}{\overset{|}{M}}SPh + PhS^{\cdot} \quad (10)$$

$$Me\overset{H}{\overset{|}{M}}SPh \longrightarrow CH_4 + MSPh \quad (11)$$

oxidative addition of alkyl halides to iridium(I) complexes,[1] and the second step [equation (11)] has ample precedent in related systems.[13] It is surprising though that oxidative addition of benzenethiol to iridium(I) takes place by a concerted rather than a free-radical mechanism.[14]

It should be possible to distinguish between these mechanisms since only (*i*) leads to formation of methyl radicals. The reactions of *cis*-[$PtMe_2(PMe_2Ph)_2$] and [$MeAu(PMe_3)$] with benzenethiol were carried out in an e.s.r. tube in the presence of the radical trap Bu^tNO. Within 30 min an e.s.r. spectrum of the radical $Bu^tMeNO^{\cdot}$ was observed, showing that methyl radicals had been formed during the reaction. No such radicals were observed in the absence of benzenethiol. This shows that the reaction proceeds at least in part by mechanism (*i*), but other evidence suggests that (*ii*) is dominant. Thus Bu^tNO, which is an efficient scavenger of methyl radicals but not of thiyl radicals,[15] had little effect on the overall rates of reaction. Also, we observed no CIDNP effects in the n.m.r. spectra of reacting mixtures, again more consistent with mechanism (*ii*) in which the final products are not formed directly from free radicals. Eaborn *et al.* have shown that cleavage of optically active silyl groups from the complexes *cis*-[$PtH(*SiR_3)(PPh_3)_2$] and *trans*-[$PtCl(*SiR_3)(PMe_2Ph)_2$] [R_3Si* = Me(1-$C_{10}H_7$)PhSi] with benzenethiol takes place with 92 and 75% retention of configuration at silicon respectively.[16] The mechanism of these reactions is not known, but if they take place by a free-radical chain mechanism then a mechanism of type (*ii*) must predominate. If the two reaction paths are in competition the proportion of reaction taking place by mechanism (*ii*) should be proportional to the concentration of benzenethiol; we plan to investigate this possibility using chiral alkylplatinum(II) complexes.

The reaction of [$Me_3Au(PMe_3)$] with benzenethiol in the presence of Bu^tNO gave no e.s.r. signal due to $Bu^tMeNO^{\cdot}$ radicals as expected for a non-radical reaction. The only signal observed was due to $Bu^t_2NO^{\cdot}$ which is formed by slow decomposition of the radical trap even in the absence of other reagents. It is interesting that trimethylgold formed by reaction of gold(III) bromide with methyl-lithium in diethyl ether reacts rapidly at −80 °C with benzenethiol to give [$Me_2Au(\mu\text{-}SPh)_2AuMe_2$] [10] whereas, when stabilised by co-ordination of tertiary phosphine, the reactions proceed

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only slowly at room temperature. The former reaction is likely to take place by intramolecular elimination of methane from the complex $[Me_3Au(SHPh)]$ which is expected to be formed rapidly when the only competing ligand is diethyl ether, and the same mechanism could apply to the latter reactions in which displacement of a phosphine ligand by benzenethiol would be much slower. Alternatively, electrophilic cleavage without prior dissociation of a phosphine ligand is possible. Gregory and Ingold have shown that electrophilic cleavage of methyl groups from methyl-gold(I) and -gold(III) complexes by mercury(II) chloride takes place at similar rates,[17] so that, if the free-radical mechanism were not available, the methylgold(I) complexes would probably react with benzenethiol as slowly as do the trimethylgold(III) complexes.

The most likely explanation for the gold(III) complexes reacting by a non-radical mechanism is related to the stability of the proposed intermediates. Addition of a thiyl radical to gold(I) or platinum(II) gives gold(II) or platinum(III) which have been identified as reaction intermediates in other systems,[18,19] but gold(III) would give the unknown gold(IV) species. Thus the free-radical mechanism is expected to be unfavourable for gold(III) complexes if the S_H2 stepwise mechanism or (*ii*) above operates, though there is no obvious reason why the S_H2 concerted mechanism should be less favoured than with the gold(I) and platinum(II) complexes (perhaps suggesting that this mechanism is not important for these complexes).

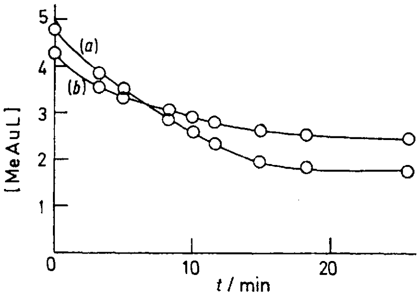

FIGURE 2 Competition of $[MeAu(PMe_3)]$ (*a*) and $[MeAu(PMePh_2)]$ (*b*) for benzenethiol

Relative-reactivity Studies.—The course of the above reactions was easily followed by n.m.r. spectroscopy, and we have used this technique to study the relative reactivity of the methyl transition-metal complexes towards benzenethiol by allowing two methyl transition-metal complexes to compete for a limited quantity of thiol. The relative amounts of reagents consumed and products formed were determined from the relevant peak heights in the n.m.r. spectra (Figure 2). The results are summarised in Table 2, in which $\bar{P}$ is defined as $\log (a_0/a_t)\log (b_0/b_t)$ where a_0 and a_t are the concentrations of the reacting transition-metal alkyl (A) at time zero and t, and b_0 and b_t are the analogous concentrations of the competing metal alkyl (B). These $\bar{P}$ values give the ratio of the rate constants for attack of phenylthiyl radicals on complexes (A) and (B) respectively if the following conditions are met:[20], (1) attack of thiyl radicals on the complexes (A) and (B) is not reversible; and (2) exchange reactions do not take place after the initial cleavage reactions. In fact two types of exchange can be shown to take place in these systems. For the gold(I) complexes reaction probably takes place by phosphine for phosphine exchange, which is known to be rapid.[21] Thus reaction of $[Au(SPh)(PMe_3)]$ and $[MeAu(PMePh_2)]$ gave a random mixture of the products shown in equation (12) within 10 min at 35 °C.

TABLE 2

Competition reactions with benzenethiol at 35 °C in dichloromethane solution

Complex (A)	Complex (B)	[PhSH] [a]	$\bar{P}$
$[MeAu(PMe_3)]$	$[MeAu(PMePh_2)]$	0·8	1·47 ± 0·01
$[MeAu(PMe_3)]$	*cis*-$[PtMe_2(PMe_2Ph)_2]$	0·8	2·83 ± 0·11
$[MeAu(PMe_3)]$	*cis*-$[PtMe_2(PMe_2Ph)_2]$	2·0	3·58 ± 0·34
cis-$[PtMe_2(PMe_2Ph)_2]$	$[MeAu(PMePh_2)]$	0·8	1·36 ± 0·20
cis-$[PtMe_2(PMe_2Ph)_2]$	$[MeAu(PMePh_2)]$	2·0	0·97 ± 0·11
cis-$[PtMe_2(PMe_2Ph)_2]$	$[MeAu(PMePh_2)]$	3·0	0·79 ± 0·05
$[MeAu(PMePh_2)]$	$[MeAu(PPh_3)]$	0·8	1·12 ± 0·24
$[MeAu(PMePh_2)]$	$[MeAu(PPh_3)]$	2·0	1·18 ± 0·14
$[MeAu(PMePh_2)]$	*trans*-$[PtMe(SPh)(PMe_2Ph)_2]$	0·8	4·08 ± 0·40
$[MeAu(PMePh_2)]$	$[Me_3Au(PMePh_2)]$	1·0	5·87 ± 0·27 [b]

[a] mol per mol (A) = mol per mol (B). [b] The complex $[Me_3Au(PMePh_2)]$ reacts by a different mechanism.

$$[Au(SPh)(PMe_3)] + [MeAu(PMePh_2)] \rightleftharpoons [MeAu(PMe_3)] + [Au(SPh)(PMePh_2)] \qquad (12)$$

However, the reaction was suppressed in the presence of benzenethiol, perhaps by reaction of the traces of free phosphine which catalyse such reactions [21] with the thiol. Phosphine exchange did not take place in the other systems studied, but methyl groups could exchange with thiyl groups. Thus *cis*-$[PtMe_2(PMe_2Ph)_2]$ with $[(PhS)Au(PMePh_2)]$ gave *trans*-$[PtMe(SPh)(PMe_2Ph)_2]$ and $[MeAu(PMePh_2)]$, the reaction being 20% complete in 40 min and 25% complete in 90 min at 35 °C. Since the competition reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ and $[MeAu(PMePh_2)]$ with benzenethiol was complete in 30 min, this exchange reaction could have a moderate influence on the $\bar{P}$ values obtained. The values of $\bar{P}$ obtained at high thiol concentration should be most reliable since the cleavage rate was increased under these conditions, whilst the rate of the subsequent exchange reaction was not. High thiol concentrations should also minimise the reversibility of the reaction in which thiyl radical adds to the initial

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transition-metal alkyl,[20] so that the reactivity [MeAu(PMePh$_2$)] > *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] obtained at high thiol concentration is considered more reliable than the reverse *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] > [MeAu(PMePh$_2$)] obtained at low thiol concentration.

It appears that these competition experiments cannot give a quantitative comparison of the relative reactivities of transition-metal alkyls towards thiyl radicals, but a reliable qualitative reactivity series can be deduced to be [MeAu(PMe$_3$)] > [MeAu(PMePh$_2$)] > [MeAu(PPh$_3$)], *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] > *trans*-[PtMe(SPh)(PMe$_2$Ph)$_2$] $\gg$ [Me$_3$Au(PMe$_3$)], [Me$_3$Au(PMePh$_2$)]. The following trends can be observed.

(1) For the gold(I) complexes, substitution of phenyl for the methyl groups in the phosphine ligand causes a decrease in reactivity. This could be either due to a steric effect of the bulkier phenyl groups or an electronic effect due to the greater electronegativity of the phenyl group decreasing electron density at gold and so reducing the reactivity towards the electrophilic thiyl radical.[20]

(2) For a given ligand L the reactivity series is [MeAuL] > *cis*-[PtMe$_2$L$_2$] > *trans*-[PtMe(SPh)L$_2$] > [Me$_3$AuL]. Increasing the oxidation state of the metal reduces the reactivity, and substitution of a phenylthiyl for a methyl group decreases the reactivity. Again it seems that a high electron density on the metal centre (and hence an easily oxidised metal complex) leads to high reactivity. It is perhaps not surprising therefore that the reactivity series resembles similar series obtained for oxidative-addition reactions and for reactions with alkenes and alkynes (in which the reactive intermediates may be formed by oxidative addition).[22-25] The only exception appears to be in the competition reaction of benzenethiol with *trans*-[PtMe(Cl)(PMe$_2$Ph)$_2$] and *trans*-[PdCl(Me)(PMe$_2$Ph)$_2$] in which the palladium complex reacted more quickly; however the mechanism of reaction with the palladium complex has not been established.

EXPERIMENTAL

The complexes *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$][9] and [MeAu(PMe$_3$)][26] were prepared by literature methods.

Bromo(methyldiphenylphosphine)gold(I).—This complex was prepared by reaction of AuBr$_3$ in ethanol with PMePh$_2$ (2 mol) and was recrystallised from warm ethanol, m.p. 117—119 °C (lit.[27] 118—119 °C). N.m.r. spectrum in CH$_2$Cl$_2$: δ(CH$_3$P) 2·60 p.p.m., doublet, ^2J(PH) 10·7 Hz (Found: C, 33·0; H, 2·75. Calc. for C$_{13}$H$_{13}$AuBrP: C, 32·8; H, 2·75%).

Methyl(methyldiphenylphosphine)gold(I).—This was prepared by treating [AuBr(PMe$_2$Ph)] with methyl-lithium in diethyl ether at -78 °C under nitrogen. After hydrolysis the product was obtained from the dried organic layer as colourless crystals, m.p. 69—70 °C (Found: C, 41·05; H, 4·20. Calc. for C$_{14}$H$_{16}$AuP: C, 40·75; H, 3·90%).

Trimethyl(methyldiphenylphosphine)gold(III).—This complex was prepared by treating [AuBr(PMePh$_2$)] with methyl-lithium (2 mol) in diethyl ether in the presence of excess of methyl iodide.[28] Isolation as above gave colourless crystals, m.p. 63—65 °C (Found: C, 43·65; H, 5·20. Calc. for C$_{16}$H$_{22}$AuP: C, 43·5; H, 5·00%).

Phenylthio(trimethylphosphine)gold(I).—This was obtained by treating [MeAu(PMe$_3$)] (0·035 g, 0·122 mmol) in dichloromethane (0·4 cm^3) with benzenethiol (0·009 cm^3, 0·122 mmol). After 15 min the solvent was removed *in vacuo* and the *product* was washed thoroughly with isopentane and dried *in vacuo*, yield 96%, m.p. 92—94 °C (Found: C, 27·6; H, 3·9. Calc. for C$_9$H$_{14}$AuPS: C, 28·3; H, 3·7%). *(Methyldiphenylphosphine)phenylthiogold*(I) was prepared similarly, yield 95%, m.p. 89—91 °C (Found: C, 45·1; H, 3·6. Calc. for C$_{18}$H$_{18}$AuPS: C, 45·0; H, 3·6%). *Phenylthio(triphenylphosphine)gold*(I) was prepared similarly, yield 93%, m.p.154—156 °C (Found: C, 50·8; H, 3·5. Calc. for C$_{24}$H$_{40}$AuPS: C, 50·7; H, 3·5%).

cis-*Dimethyl(phenylthio)(trimethylphosphine)gold*(III).—This complex was prepared by reaction of [Me$_3$Au(PMe$_3$)] with PhSH (1 mol) in dichloromethane for 45 h, and isolated as above, yield 88%, m.p. 71—73 °C (Found: C, 32·3; H, 5·2. Calc. for C$_{11}$H$_{20}$AuPS: C, 32·1; H, 4·9%).

Di-μ-phenylthio-bis[dimethylgold(III)].—The complex [Me$_3$Au(PMePh$_2$)] was treated with PhSH (1 mol) in dichloromethane solution. After 1 month, the solution was chromatographed through silica gel, eluting with dichloromethane and then methanol. The methanol eluted first methyldiphenylphosphine sulphide, identified by comparison with an authentic specimen prepared by reaction (7).[11] Then [Me$_2$Au(μ-SPh)$_2$AuMe$_2$] was eluted, m.p. 129—131 °C (lit.[10] 132—133 °C). N.m.r. spectrum in CH$_2$Cl$_2$: δ(CH$_3$Au) 1·30 p.p.m., singlet. The product was identical with an authentic specimen prepared by the method of Gilman and Woods.[10]

trans-*Bis(dimethylphenylphosphine)methyl(phenylthio)platinum*(II).—This complex was prepared by reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] in dichloromethane with benzenethiol (1 mol). After 45 min, the solvent was evaporated to give the pale yellow *product*, yield 95%, m.p. 113—115 °C (Found: C, 46·7; H, 5·3. Calc. for C$_{23}$H$_{30}$PPtS: C, 46·4; H, 5·08%).

trans-*Bis(dimethylphenylphosphine)bis(phenylthio)platinum*(II).—This was prepared by treating *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with benzenethiol (2 mol) as above. After 80 min the solvent was removed to give the product as pale yellow *crystals*, yield 90%, m.p. 170—177 °C (lit.[29] 181—182 °C) (Found: C, 48·4; H, 4·9. Calc. for C$_{28}$H$_{32}$PPtS: C, 48·7; H, 4·6%).

Effect of Galvinoxyl and aibn.—To a solution of [MeAu(PMePh$_2$)] (0·099 mmol) in dichloromethane (0·4 cm^3) in an n.m.r. tube was added PhSH (0·099 mmol). The course of the reaction was followed by monitoring the n.m.r. spectrum for 10 min, then galvinoxyl (2×10^{-4} mmol) in dichloromethane (0·02 cm^3) was added and further n.m.r. spectra were obtained until the reaction was complete. The concentration of [MeAu(PMePh$_2$)] was measured at each point from the height of the methylgold peak

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using the high-field ^{13}C satellite of dichloromethane as internal standard. Other experiments with additives were carried out in a similar way.

Competition Experiments.—To a mixture of [MeAu(PMe$_3$)] (0·160 mmol) and [MeAu(PMePh$_2$)] (0·160 mmol) in dichloromethane (0·4 cm^3) in an n.m.r. tube was added PhSH (0·128 mmol). The course of the reaction was followed by monitoring the n.m.r. spectrum as described above. Other experiments are summarised in Table 2.

E.S.R. Experiments.—A mixture of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] (0·058 mmol) and Bu^{t}NO (*ca.* 0·005 g) in dichloromethane (0·4 cm^3) was added to PhSH (0·058 mmol) in dichloromethane (0·4 cm^3) in an e.s.r. tube. The tube was degassed by several freeze–pump–thaw cycles. After 0·5 h the e.s.r. spectrum of Bu^t(Me)NO$^\bullet$ was obtained [30] as a 1 : 1 : 1 triplet of 1 : 3 : 3 : 1 quartets with a_N 15·0 and a_H 11·5 G. No intensification of the signal was observed after 3 h. Other experiments were carried out similarly.

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