Organogold Chemistry:
II Reactions

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Gold forms a variety of organic derivatives, whose preparations and structure were reviewed in Part I. Here the diverse reactions of these compounds are discussed as a prelude to a description in Part III of potential and actual applications of organogolds.
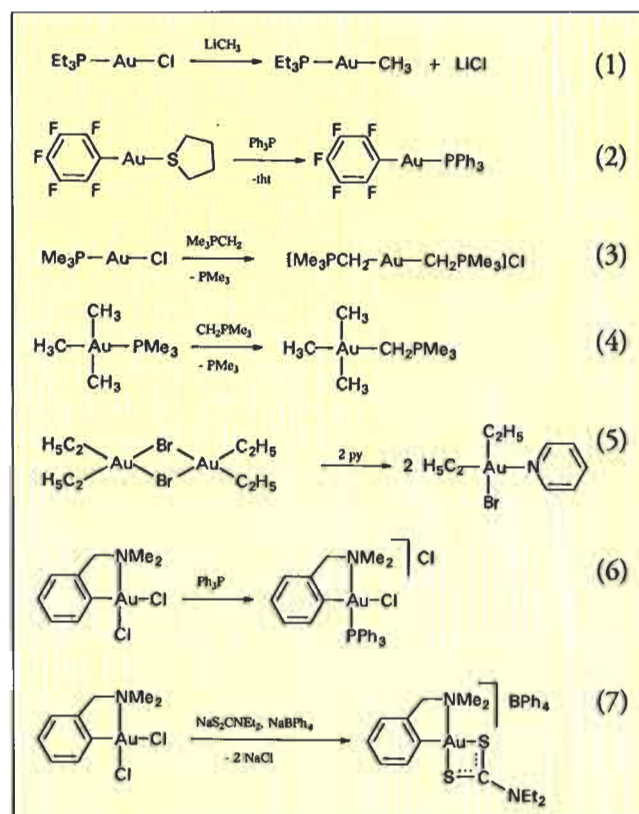
In the previous article (1), the structures and syntheses of organogold compounds and coordination complexes were reviewed, with particular emphasis on relatively modern materials. This contribution treats the chemistry of these compounds, concentrating on reactions which involve the organic groups. In Part III, some recent applications of organogold compounds will be described.

Unfortunately, compounds containing more than one organic group are prone to rearrangement and dissociation, so that many apparently simple reactions are complicated by successive stages, and do not give the expected products. This makes the discussion of separate types of reaction rather difficult, and there is considerable overlap between the sections. The reader's patience is therefore requested for the frequently needed use of 'see below'.
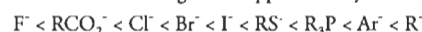
SUBSTITUTION REACTIONS

Both gold(I) and gold(III) are relatively soft Lewis acids which therefore have a preference for soft ligands[1]. Both will undergo facile substitution reactions in which one ligand is replaced by a softer one (Equations 1-7) (2-8):

For both oxidation states, reaction is quite rapid, proceeding by associative mechanisms; for steric reasons, gold(III) reacts a little more slowly than gold(I). If it is desired to replace a ligand by a harder one, *eg* a halide by an O-donor, reaction must be forced. This may be achieved by ensuring that one product is insoluble, for instance, by using silver or thallium salts (Equations 8-10) (9-11).

$$Et_3P-Au-Cl \xrightarrow{LiCH_3} Et_3P-Au-CH_3 + LiCl \qquad (1)$$

$$(2)$$

$$Me_3P-Au-Cl \xrightarrow[-PMe_3]{Me_3PCH_2} [Me_3PCH_2-Au-CH_2PMe_3]Cl \qquad (3)$$

$$(4)$$

$$(5)$$

$$(6)$$

$$(7)$$

An exception to this rule is the recent isolation of alkoxide or phenoxide complexes, obtained by the reaction of an organogold halide complex (Equations 11 and 12) (12,13). These products are useful catalysts (see Part III).
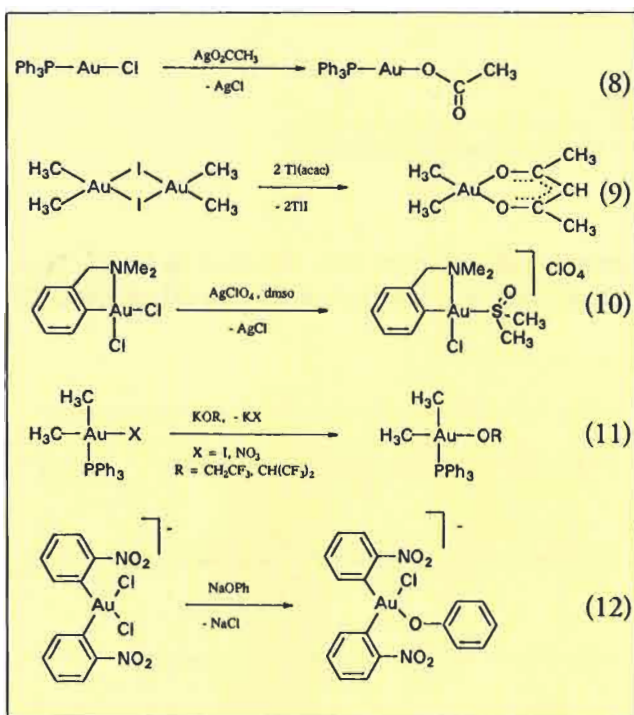
In the case of gold(III), if there is a choice of position for the substitution, the normal *trans*-effect rules would be expected to apply[2]. Generally, this would mean substitution *trans* to an organic group but the stereochemistry of the product rarely conforms to this expectation. Rather, the incoming (soft) ligand is found *cis* to an organic group: this is likely to be the thermodynamically stable configuration (*cf* Equation 6). The two softest ligands are expected to prefer mutually *cis* positions to maximize the bond strength, following the *trans*-influence series[2]. An example of deviation from this behaviour is shown in Equation

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[2] The *trans*-effect is based on kinetic behaviour during reactions, where the ligand highest in the *trans*-effect series appears to direct an incoming ligand to the position *trans* to itself. The *trans*-influence is seen in the properties of an isolated molecule: a ligand high in the *trans*-influence series weakens the metal bond *trans* to itself (seen also in bond lengths, infrared stretching frequencies, NMR coupling constants, *etc*). This series is similar in order to the softness series; the two series broadly follow each other; the principal exceptions are π-accepting ligands (*eg* carbonyl, η^2-alkenes) which have a high *trans* effect but quite a small *trans* influence. An ylide ligand appears intermediate between a tertiary phosphine and an aryl group.

10. Presumably, the substitution initially conforms to the *trans*-effect, but is followed by an isomerization. The mechanism of this second stage is not known. In platinum(II) chemistry isomerism is commonly triggered by catalytic amounts of a free ligand (usually a phosphine), and occurs by association. This could occur simultaneously with the substitution reaction, if the latter were slow enough.

Substitution reactions never result in replacement of a σ-bonded organic group, although an ylide may sometimes be displaced (but see the section below on elimination reactions). There are two principal reasons for this: (a) the organic groups are amongst the softest known ligands, so that other ligands would be substituted in preference; (b) it is not possible for an organic group to be displaced as a free carbanion (displacement as a radical would involve quite different chemistry, and seems not to occur even for thermal decomposition). When loss of an organic group does occur, there has to be a co-reagent which can bind it, rather in the way that silver(I) binds a halide ion. For instance the *trans*-metallation reaction, which is often used to produce organo-gold compounds, may be reversible: a gold-bound organic group can be exchanged for a halide bound to mercury(II) or thallium(III) (Equations 13, 14) (14). Such reactions are driven by the overall change in bond energies of all the compounds involved.
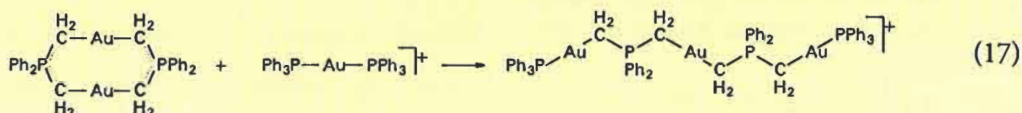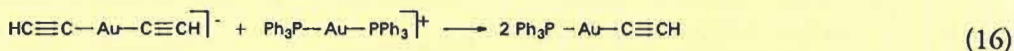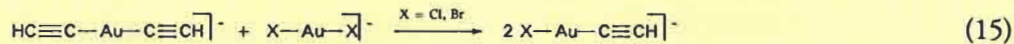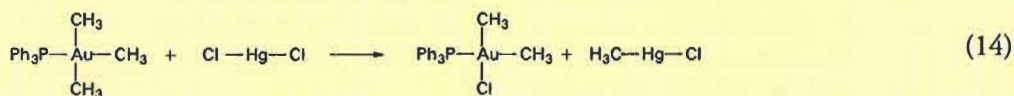
The *trans*-metallation reaction can be used to introduce further organic groups into an organogold(III) complex; this is effectively substitution of a halide by a carbanion (15).

It is also possible to transfer organic groups from one gold atom to another, as in the comproportionation reactions of bis-alkenyl complexes (Equations 15 and 16) (16) or the ring-opening reactions of cyclic ylides (Equation 17) (17).

OXIDATION OF GOLD(I)

In the organometallic chemistry of transition metals, oxidation is usually synonymous with oxidative addition, *ie* a reaction in which the oxidant becomes bound to the metal. This normally involves cleavage of the oxidant, *eg* a halogen molecule becomes two halide ligands. Thus, both the oxidation state and the coordination number of the metal increase by two units. In the present context, such reactions are possible only for gold(I).

The most commonly used oxidants are the halogens. The reaction may be complicated, and its course depends

$$Ph_3P\text{---}Au\text{---}C_2H_5 \ + \ Cl\text{---}Hg\text{---}Cl \ \longrightarrow \ Ph_3P\text{---}Au\text{---}Cl \ + \ H_5C_2\text{---}Hg\text{---}Cl \tag{13}$$

$$Ph_3P\text{---}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Au}}\text{---}CH_3 \ + \ Cl\text{---}Hg\text{---}Cl \ \longrightarrow \ Ph_3P\text{---}\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{Au}}\text{---}CH_3 \ + \ H_3C\text{---}Hg\text{---}Cl \tag{14}$$

$$HC\equiv C\text{---}Au\text{---}C\equiv CH\big]^- \ + \ X\text{---}Au\text{---}X\big]^- \ \xrightarrow{X = Cl, Br} \ 2\ X\text{---}Au\text{---}C\equiv CH\big]^- \tag{15}$$

$$HC\equiv C\text{---}Au\text{---}C\equiv CH\big]^- \ + \ Ph_3P\text{---}Au\text{---}PPh_3\big]^+ \ \longrightarrow \ 2\ Ph_3P\text{---}Au\text{---}C\equiv CH \tag{16}$$

$$Ph_2P\underset{C\text{---}Au\text{---}C}{\overset{\overset{H_2}{\underset{H_2}{C\text{---}Au\text{---}C}}}{}}PPh_2 \ + \ Ph_3P\text{---}Au\text{---}PPh_3\big]^+ \ \longrightarrow \ Ph_3P^{Au}\underset{P}{\overset{H_2}{\underset{Ph_2}{C}}}\underset{P}{\overset{H_2}{\underset{H_2}{C}}}Au\underset{C}{\overset{Ph_2}{\underset{H_2}{C}}}P\underset{C}{\overset{}{\underset{}{}}}\!\!{}^{Au}\!PPh_3\big]^+ \tag{17}$$
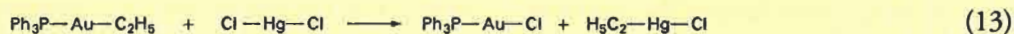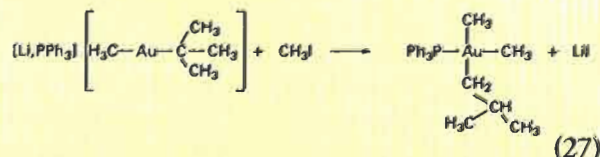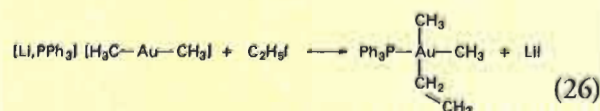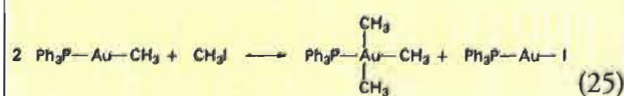
critically on the nature of the organic groups and sometimes on the halogen. Straightforward oxidative addition often occurs for perhaloaryl derivatives (Equations 18-20) (18-20). In other cases there is cleavage of the Au-C bond, and the final products are an organic halide and a gold(I) complex (Equations 21 and 22) (18, 21). Such reactions may occur by oxidative addition followed by elimination of the organic halide, but there are also side reactions which result in organic coupling products (see also below).

$$Ph_3As\text{---}Au\text{---}C_6Cl_5 \ + \ X_2 \ \xrightarrow{X = Cl, Br, I} \ Ph_3As\text{---}\underset{\underset{X}{|}}{\overset{\overset{C_6Cl_5}{|}}{Au}}\text{---}X \tag{18}$$

$$Ph_3P\text{---}Au\text{---}C_6F_5 \ + \ Br_2 \ \longrightarrow \ Ph_3P\text{---}\underset{\underset{Br}{|}}{\overset{\overset{C_6F_5}{|}}{Au}}\text{---}Br \tag{19}$$

$$C_6F_5\text{---}Au\text{---}Cl\big]^- \ + \ Cl_2 \ \longrightarrow \ C_6F_5\text{---}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Au}}\text{---}Cl\big]^- \tag{20}$$

$$Ph_3As\text{---}Au\text{---}C_6F_5 \ + \ I_2 \ \longrightarrow \ Ph_3As\text{---}Au\text{---}I \ + \ C_6F_5I \tag{21}$$

$$Ph_3P\text{---}Au\text{---}C_6H_5 \ + \ Br_2 \ \longrightarrow \ Ph_3P\text{---}Au\text{---}Br \ + \ C_6H_5Br \tag{22}$$

$$Cl\text{---}Au\text{---}\underset{\underset{PPh_3}{\diagdown}}{\overset{\overset{O\diagup^R}{\diagup C}}{CH}} \ + \ Cl_2 \ \longrightarrow \ Cl\text{---}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Au}}\text{---}\underset{\underset{PPh_3}{\diagdown}}{\overset{\overset{O\diagup^R}{\diagup C}}{CH}} \tag{23}$$

$$\underset{Ph_3P}{\overset{R\diagdown_{C}\diagup O}{}}HC\text{---}Au\text{---}CH\underset{PPh_3}{\overset{O\diagdown_{C}\diagup R}{}}\big]^+ \ + \ Cl_2 \ \longrightarrow \ \underset{Ph_3P}{\overset{R\diagdown_C\diagup O}{}}HC\text{---}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Au}}\text{---}CH\underset{PPh_3}{\overset{O\diagdown_C\diagup R}{}}\big]^+ \tag{24}$$
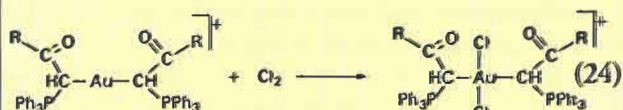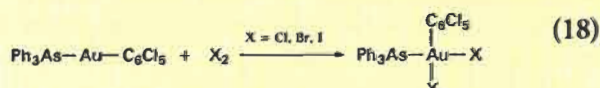
Simple ylide complexes seem to react cleanly with halogens (Equations 23 and 24) (22); in this respect they are comparable to complexes of other neutral ligands, such as tertiary phosphines.

It is also possible to use organic halides as oxidants and this is a good way of obtaining complexes containing different organic groups. However, the products may be unstable to elimination or rearrangement reactions (see below), and the products are not always those expected (Equations 25-27) (23-25)[3].

$$2\ Ph_3P\text{---}Au\text{---}CH_3 \ + \ CH_3I \ \longrightarrow \ Ph_3P\text{---}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Au}}\text{---}CH_3 \ + \ Ph_3P\text{---}Au\text{---}I \tag{25}$$

$$[Li, PPh_3] \ [H_3C\text{---}Au\text{---}CH_3]I \ + \ C_2H_5I \ \longrightarrow \ Ph_3P\text{---}\underset{\underset{CH_2}{|}}{\overset{\overset{CH_3}{|}}{Au}}\text{---}CH_3 \ + \ LiI \\ \diagdown_{CH_3} \tag{26}$$

$$[Li, PPh_3] \left[H_3C\text{---}Au\text{---}\underset{\diagdown_{CH_3}}{\overset{\diagup^{CH_3}}{C}\text{---}CH_3} \right] \ + \ CH_3I \ \longrightarrow \ Ph_3P\text{---}\underset{\underset{CH_2}{|}}{\overset{\overset{CH_3}{|}}{Au}}\text{---}CH_3 \ + \ LiI \\ H_3C\overset{\diagup^{CH}}{\diagdown_{CH_3}} \tag{27}$$
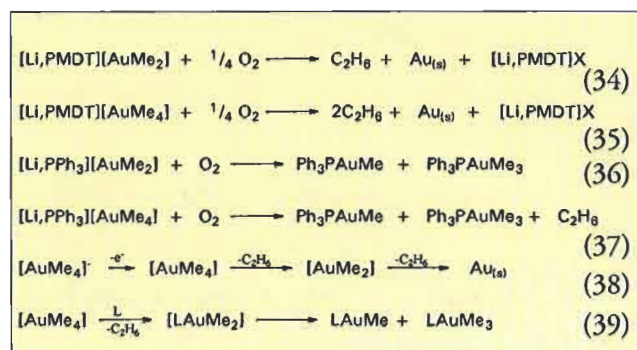

The oxidation of cyclic di-gold ylide complexes has been widely studied, partly because the reactions may occur in two well-defined stages. Reaction with one molar equivalent of a halogen often leads to isolable gold(II) complexes which contain a gold-gold bond (Equation 28) (4); oxidation to gold(III) may be completed by addition of a second equivalent (Equation 29). As with mononuclear complexes, alkyl halides may also be used as oxidants (Equation 30), but the reaction is sometimes reversible (26), leading to catalytic halogen exchange reactions. When a dihaloalkane is used as oxidant, bridged di-gold(III) complexes result (Equations 31-33) (27, 28). Much effort has been devoted to trying to understand the course of these reactions (29).
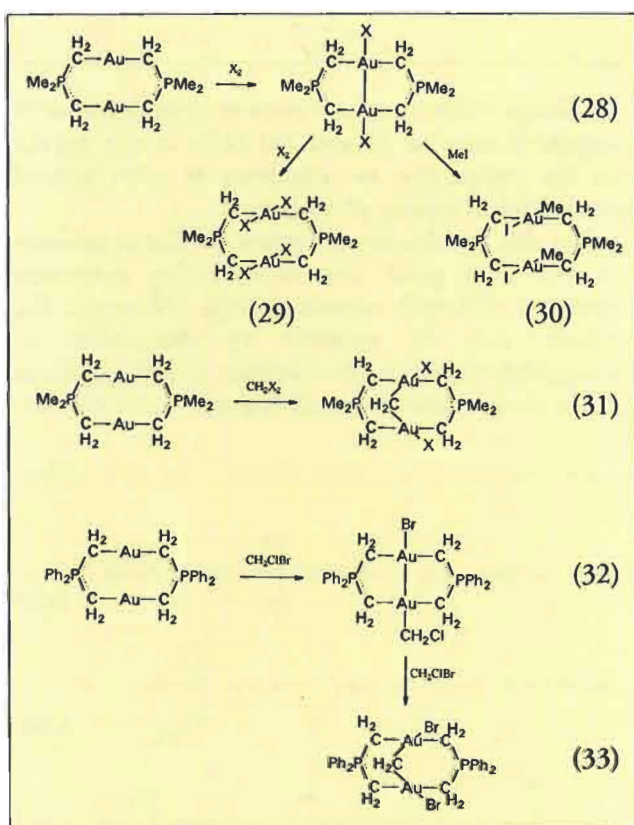
In contrast to other precious metals, there is no evidence of oxidative addition of hydrogen halides to gold(I), although protonation reactions do occur (see below).

Curiously, oxidation by molecular oxygen of dimethylaurate(I) or tetramethylaurate(III) leads to the production of metallic gold, at least when the counterion is a strongly complexed Li⁺; the organic groups appear as ethane (Equations 34 and 35; PMDT is $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$). However, in the presence of PPh_3, methylgold(I) and

trimethylgold(III) complexes are formed (Equations 36 and 37). A mechanism has been suggested (30), based on the oxidation of the anions by dioxygen to neutral methylgold intermediates which either decompose or are trapped by the phosphine (Equations 38 and 39).

$$[Li,PMDT][AuMe_2] + \tfrac{1}{4}O_2 \longrightarrow C_2H_6 + Au_{(s)} + [Li,PMDT]X \quad (34)$$

$$[Li,PMDT][AuMe_4] + \tfrac{1}{4}O_2 \longrightarrow 2C_2H_6 + Au_{(s)} + [Li,PMDT]X \quad (35)$$

$$[Li,PPh_3][AuMe_2] + O_2 \longrightarrow Ph_3PAuMe + Ph_3PAuMe_3 \quad (36)$$

$$[Li,PPh_3][AuMe_4] + O_2 \longrightarrow Ph_3PAuMe + Ph_3PAuMe_3 + C_2H_6 \quad (37)$$

$$[AuMe_4]^- \xrightarrow{-e^-} [AuMe_4] \xrightarrow{-C_2H_6} [AuMe_2] \xrightarrow{-C_2H_6} Au_{(s)} \quad (38)$$

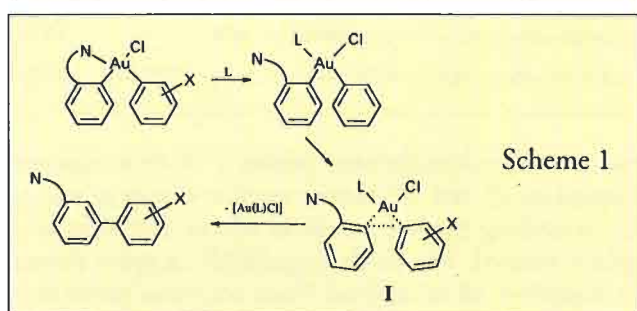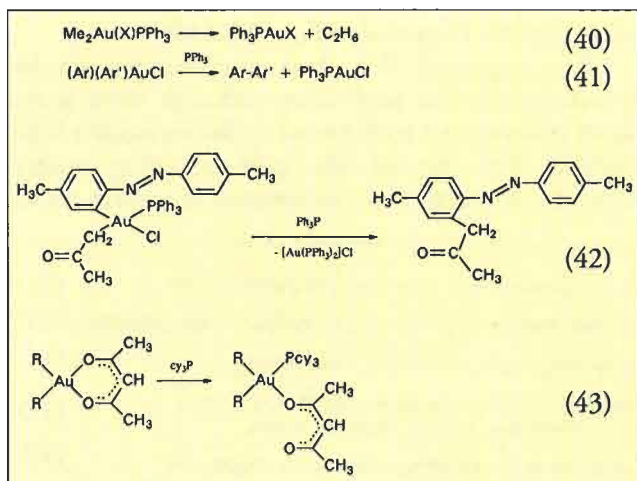$$[AuMe_4] \xrightarrow[-C_2H_6]{L} [LAuMe_2] \longrightarrow LAuMe + LAuMe_3 \quad (39)$$

ELIMINATION, THERMAL DECOMPOSITION

As indicated above, the elimination of an organic halide from a gold(III) complex appears to occur reasonably readily (Equations 21 and 22). However, more commonly for a gold(III) complex containing two or more organic groups, a hydrocarbon is lost. This may occur spontaneously or on gentle heating, and it appears to be a conventional reductive elimination reaction, with two groups in *cis* positions becoming coupled together and the metal being reduced to gold(I) (Equation 40) (30).

This reaction is a useful way of obtaining diaryl compounds; in particular, clean coupling of two different groups to give the unsymmetrical diaryl can be achieved simply, and at room temperature (Equation 41) (31). The elimination is triggered by reaction with a ligand such as Ph_3P or even a chloride ion (Scheme 1); Ar is an aromatic group bearing a chelating substituent, *eg* $C_6H_4N=NPh$, which allows the formation of a stable bis-aryl complex. The function of the added ligand is to 'unlatch' the chelating group, freeing its ring to move perpendicular to the coordination plane, and parallel to the second ring. It is presumed that, as suggested for the related platinum(II) complexes (32), reaction proceeds *via* a four-electron three-centre intermediate, **I**. This process is stoichiometric, and not catalytic, but it would be possible to economize by recycling the gold (31).

The scope of the reaction may be wider than indicated above, since coupling has also been observed between an aryl and a ketonyl group (Equation 42)

$$Me_2Au(X)PPh_3 \longrightarrow Ph_3PAuX + C_2H_6 \qquad (40)$$

$$(Ar)(Ar')AuCl \xrightarrow{PPh_3} Ar\text{-}Ar' + Ph_3PAuCl \qquad (41)$$

(42)

(43)

Scheme 1

(33). This clearly raises the possibility of obtaining unusual alkylbenzenes or other substituted aromatics.

The cyclic ylide complexes in which gold(III) bears two alkyl groups undergo similar elimination reactions (34). Although these materials normally have *trans* geometry, the system is flexible enough to allow isomerization (35).

Tri-alkyl gold(III) complexes, R_3AuL, and tetralkylaurates(III), $[R_4Au]^-$, undergo thermal decomposition at modest temperatures, the latter being the more stable. Detailed studies have established that *cis* elimination occurs here too, but it is preceded for R_3AuL by dissociation (36, 37). The greater stability of complexes in which L is an ylide is attributed to lessened tendency for dissociation (38). With mixed-ligand complexes, a mixture of coupling products is usually obtained, because isomerization and redistribution reactions occur more rapidly than the elimination reaction. Calculations show that the lowest-energy form of the three-coordinate intermediate should retain the initially formed **T**-shape, but this readily rearranges via a symmetrical **Y**-shaped molecule (Scheme 2). The latter is unstable, and must either reform a **T** (isomerization) or distort to an elongated **Y**, from which elimination occurs. In mixed systems, R_3AuL + R'_3AuL, cross-coupling (to give R-R') is also observed, showing that the two

different intermediates can become associated. Elimination is very rapid and no scrambling of alkyl groups between the two gold(III) centres occurs. The way in which this could happen has not been defined, but it presumably involves dinuclear species in which the two gold centres are linked by one or more alkyl groups and/or gold-gold bonds.

Scheme 2
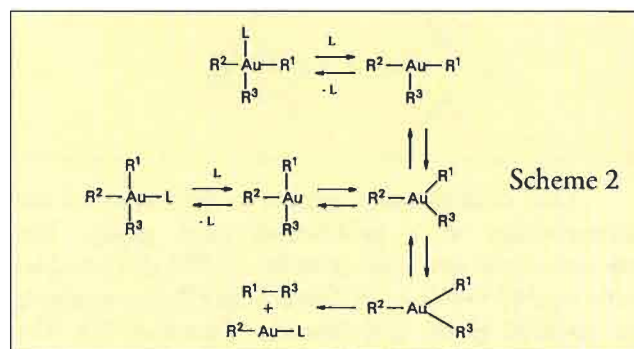
Alkylgold(I) complexes, LAuR, also undergo thermal decomposition (39). Primary alkyls predominantly give the straightforward coupling product R-R. Branched derivatives give also some of the products of disproportionation: the hydrocarbon RH and the alkene (R-H). For R = Me, reaction again appears to occur by dissociation of the ligand followed by attack of 'AuCH$_3$' on $LAuCH_3$, but the pathway has not been further defined.

It is notable that in none of these elimination reactions is there any evidence for the involvement of organic radicals.

In contrast with other transition-metal systems, there is very little definitive evidence for ß-elimination reactions of gold-bound alkyl groups to produce an alkene; this is probably due to the inability of gold to form hydride complexes.
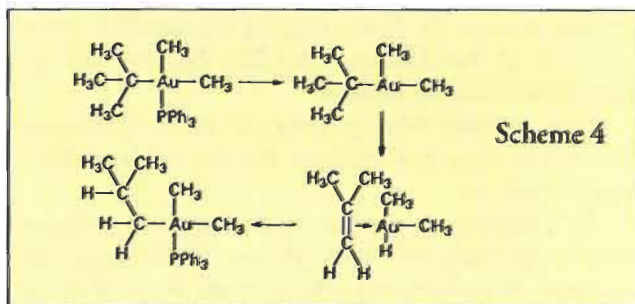
ISOMERIZATION

The mixed alkyl complexes $Me_2RAu(PPh_3)$ and $[Me_2AuR_2]^-$ undergo rapid isomerization in solution (37, 40). It follows the pathway discussed above and shown in Scheme 2. It was possible to make these studies because the elimination reaction is strongly retarded by the addition of a trace of the ligand, while the isomerization is much less inhibited.

Digold(III) cyclic ylide complexes $[R_2P(CH_2AuX_2CH_2)_2PR_2]$ can be obtained in both the conventional *trans-trans* and the unusual *cis-cis* geometries, and the isomerizations *trans-trans* to *cis-trans* and *cis-trans* to *cis-cis* have been reported (35). A

mechanism has been proposed involving a halide-bridged species (Scheme 3).

Scheme 3
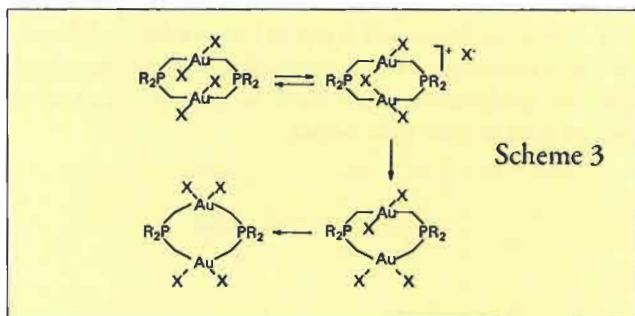
One example only appears to be known of the isomerization of a gold-bound alkyl group. The reaction of the *tert*-butyl complex [Li,PPh$_3$]['BuAuMe] with methyl iodide gives ^{i}BuAuMe$_2$(PPh$_3$) containing an *iso*-butyl group (25) (see also Equation 27). The initial product is the *tert*-butyl derivative which undergoes spontaneous isomerization in a reaction which is inhibited by added triphenylphosphine. It has to be presumed that a three-coordinate ^{t}BuAuMe$_2$ intermediate is formed which undergoes ß-hydrogen elimination to form an isobutene complex (Scheme 4).

Scheme 4

Another example of isomerization of a ligand is the change of a ß-diketonate from O,O-bonded to O-bonded when an extra ligand is coordinated (10, 13). If the incoming ligand is particularly bulky (Pcy$_3$), the diketone switches to an unusual mono-dentate enolate O-bonding mode (Equation 43)(10).

The probable isomerization of C,N-chelated arylgold(III) complexes during substitution reactions has been mentioned above.

HYDROLYSIS, ACIDOLYSIS

Most gold(III) compounds containing three or more methyl groups react with water, a protic acid or even an alcohol to liberate the corresponding organic compound (Equations 44-48) (36, 38, 41, 42); dimethylaurate(I)

reacts similarly (Equations 49 and 50) (36).

It is suggested that these reactions proceed by protonolysis at the gold atom, although there is no direct evidence and such formal oxidation seems a little unlikely. The fate of the gold-containing moiety depends on the presence or absence of ligands which
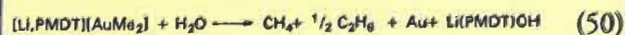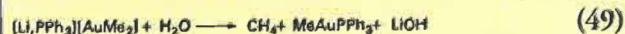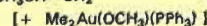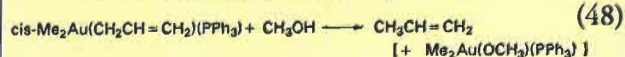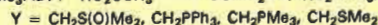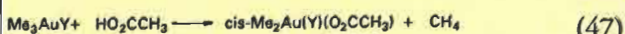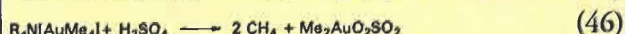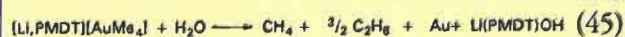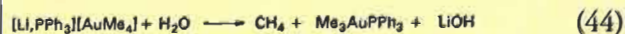
can trap the demethylated product. In their absence (Equations 45 and 50) further reaction occurs to release the remaining methyl groups as ethane and elemental gold is formed. The methoxy-gold(III) complex shown in Equation 48 is inferred from reactions performed after the methanolysis (see below) (42).
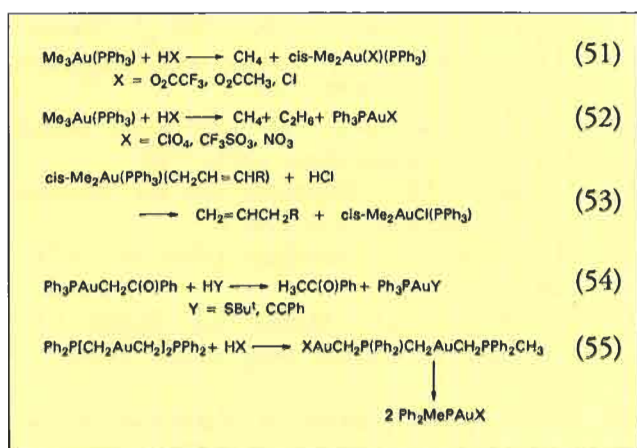
Under anhydrous conditions, similar reactions occur (Equation 51) except that the dimethylgold(III) complex may again undergo spontaneous further reaction (Equation 52), depending on the nature of X in HX. The weakest acids react most slowly, showing that proton transfer is an important stage of the reaction (30).

If the organic group is larger than methyl, *eg* allyl or crotyl, attack may occur directly at a γ-carbon atom, as in Equation 53. This is analogous to other organometallic systems (43).

Gold(I)-ketonyl derivatives react similarly (Equation 54) (44). Cyclic ylide complexes behave like methyl complexes, with ring opening, possibly in two stages (Equation 55) (45).

INSERTION REACTIONS

The common insertion reactions of transition-metal organometallics, with alkenes or carbon monoxide, seem not to occur for gold compounds. However, Au-C(O)OR derivatives can be obtained from reactions of gold(III) complexes with carbon monoxide under conditions where alkoxy complexes may be expected as intermediates (Equations 56 and 57) (46).

$$Me_3Au(PPh_3) + HX \longrightarrow CH_4 + cis\text{-}Me_2Au(X)(PPh_3) \quad (51)$$
$$X = O_2CCF_3, O_2CCH_3, Cl$$

$$Me_3Au(PPh_3) + HX \longrightarrow CH_4 + C_2H_6 + Ph_3PAuX \quad (52)$$
$$X = ClO_4, CF_3SO_3, NO_3$$

$$cis\text{-}Me_2Au(PPh_3)(CH_2CH=CHR) + HCl$$
$$\longrightarrow CH_2=CHCH_2R + cis\text{-}Me_2AuCl(PPh_3) \quad (53)$$

$$Ph_3PAuCH_2C(O)Ph + HY \longrightarrow H_3CC(O)Ph + Ph_3PAuY \quad (54)$$
$$Y = SBu^t, CCPh$$

$$Ph_2P[CH_2AuCH_2]_2PPh_2 + HX \longrightarrow XAuCH_2P(Ph_2)CH_2AuCH_2PPh_2CH_3 \quad (55)$$
$$\downarrow$$
$$2\ Ph_2MePAuX$$

Insertion of an aldehyde into a gold(III)-allyl bond has been suggested (42) as a key step in the reaction of cis-$Me_2Au(CH_2CH=CH_2)(PPh_3)$ with benzaldehyde (Equation 58). The intermediate alkoxo-gold complex has been identified by NMR; it reacts with compounds RH, containing an active hydrogen, to release an alcohol (Equation 59). Clean reactions are obtained when R = $CH(CN)_2$; in the absence of added RH, excess benzaldehyde acts as the protonating reagent, but the resultant phenoxo-complex undergoes further reactions. The corresponding gold(III) crotyl and methallyl complexes give the corresponding homoallyl alcohols with high stereospecificity (42).
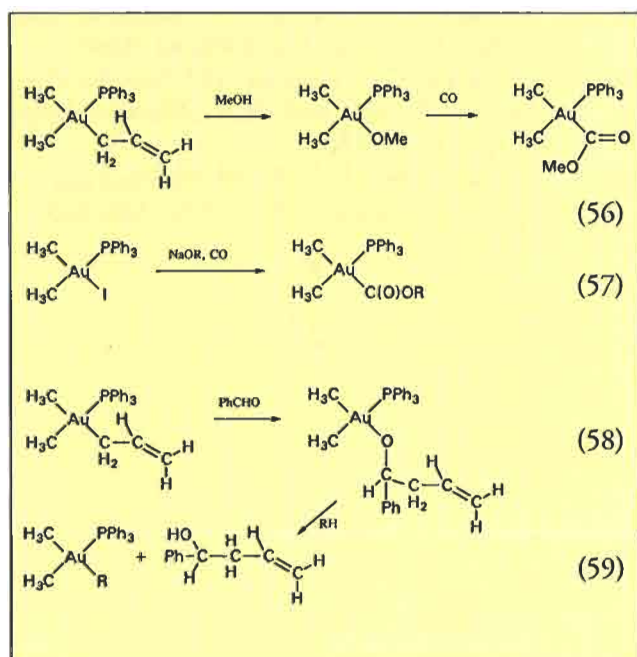
CONCLUSION

Organogold compounds undergo a variety of types of reactions. The principal differences between these and the reactions undergone by analogous compounds of other transition metals derive largely from the inability of gold to form stable hydride complexes, and to the facile elimination of cis-pairs of organic groups.

ABOUT THE AUTHOR

Dick Parish is Reader in Chemistry at UMIST and has a long-standing interest in the chemistry of gold, particularly of compounds with actual or potential medicinal interest, and in the application of Mössbauer spectroscopy to coordination chemistry, including that of gold.

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