

Recent Advances in Organogold Chemistry

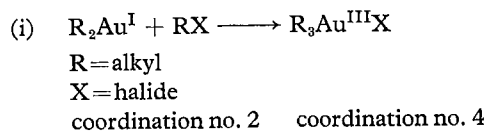
OXIDATIVE-ADDITION AND REDUCTIVE-ELIMINATION REACTIONS

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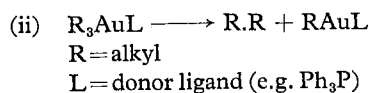
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Although organogold compounds were among the first transition metal alkyls to be discovered their use in synthesis remains limited. This is surprising since in general they are easy to prepare, to purify and to handle, and exhibit high thermodynamic and kinetic stability. In this review some of the reactions of organogold compounds are discussed with reference to recent mechanistic studies which illustrate the importance of organogold chemistry and also to the relationship of organogold systems to those of isoelectronic noble metal ions.

Some of the fundamental properties of gold are of obvious importance in any discussion of its organo-chemistry. Two oxidation states dominate gold chemistry, Au(I) and Au(III); these correspond to the d^{10} and d^8 electronic configurations respectively. Compounds of Au(II) (d^9) are exceedingly rare but are increasingly referred to as reaction intermediates. Gold (IV) (d^7) is unknown in any of its coordination compounds. The coordination numbers of the two important oxidation states are two [Au(I)] and four [Au(III)] although others are attainable. Thus gold is similar to its neighbours in the transition series in that it can readily attain two oxidation states which have a coordination number difference of two. This is clearly seen from the information presented in the table. Not unexpectedly, therefore, complexes of Au(I) undergo **oxidative-addition** reactions of the type:



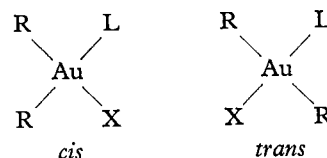
In reaction (i) the aurous ion undergoes oxidation to auric and the coordination number is increased from two to four. Conversely, auric complexes undergo **reductive-elimination**:



These reactions, although common for metals in this area of the Periodic Table, are most easily studied for gold.

The geometries of aurous and auric compounds are linear and square-planar. The square-planar

geometry found for Au(III) is very important in considerations of many of its organic reactions, e.g. reductive elimination as in equation (ii), since for systems of the type R_2AuXL the reaction is dependent upon the geometrical arrangement of the four ligands: *cis* or *trans*; the *cis* more easily undergoing elimination of R.R.



Organogold Bonds

Having discussed the fundamental properties of gold (I) and (III) we will now consider the various bonding types found for organogold systems.

Oxidation States and Coordination Numbers of some d^n ($n=6, 8$ or 10) Metal Ions

Electronic Configuration	Commonly observed Coordination Number			
d^8	(5) Os(0)	(4) Ir(I) Pt(II) Au(III)		
d^6	(6) Os(II) Ir(III) Pt(IV) —			
d^{10}	(4(?)) Os(-II) Ir(-I) Pt(0)			(2) Au(I)
d^8	(5) Os(0)	(4) Ir(I) Pt(II) Au(III)		

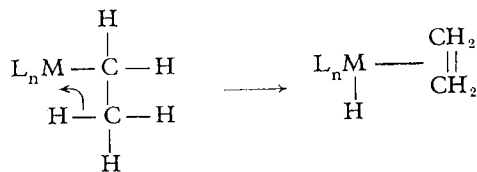
Obviously while these are similar to those of the other noble metals the behaviour they exhibit is not. In many organometallic reactions we are concerned with three bonding types: (a) the metal-olefin bond, (b) the metal-carbon σ -bond and (c) the metal-hydrogen bond. We will consider the relevance of each of these bonding types to organogold chemistry.

Gold-Olefin Bonds

Like the isoelectronic platinum ion Pt(0), Au(I) readily forms π -olefin complexes. Comprehensive lists of these compounds are available. The relative stability of these compounds is easily understood. The comparatively low oxidation state of the aurous ion will encourage π -back donation from the metal to the olefin leading to bond stabilisation but, in contrast to Pt(0), they might be expected to exhibit a lower bond energy and also to show less preference to electrophilic attack. Gold (III) does not form stable π -olefin compounds although they are frequently formulated as reaction intermediates. This is in contrast to the isoelectronic ions Os(0), Ir(I) and Pt(II) which form very stable olefin-derivatives; a good example is Zeise's salt $K[Pt(C_2H_4)Cl_3]H_2O$. In this case the high charge associated with Au(III) minimises π -back donation from the metal to the olefin and, although it favours an increased donation from the olefin to the metal via a σ -donor bond, leads to an overall instability of the Au(III)-olefin system.

Metal-Carbon σ -Bonds

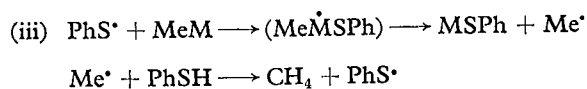
Both gold (I) and gold (III) form unusually stable metal-carbon σ -bonds and a wide variety of alkyl and aryl complexes have been prepared. A feature of Au(III)-carbon σ -bonds is their kinetic stability. With other noble metal systems the metal-ethyl moiety, for example, is kinetically labile. This may be attributed to one of several decomposition pathways but one of the more general is the so-called β -elimination. Here H-migration from the β -carbon of the bound alkyl to the metal occurs and a metal-hydrido-olefin complex is generated:



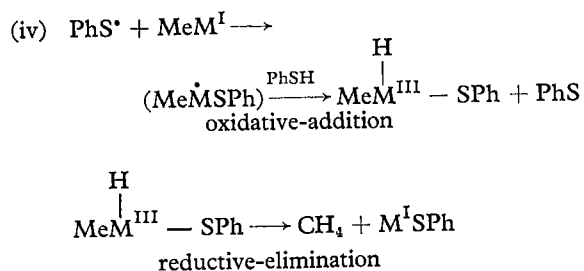
Such complexes are commonly recognised as intermediates in olefin isomerisations using noble metal complexes as catalysts. For gold (III), however, β -elimination is not so commonly observed but hydrido-olefin species are considered intermediates in isomerisation reactions.

The reactions of transition metal alkyls have involved much speculation and discussion. A number

of mechanisms by which reactions, such as thermal decomposition, addition of alkenes and alkynes, and with alkyl halides, may take place have been considered; these include free radical, ionic or concerted processes. Recent work (1) has shown that MeAuL (L=tertiary phosphine ligand) complexes undergo reaction with benzene thiol, PhSH , via a free radical chain mechanism but that reaction with Me_3AuL proceeds via a non-radical mechanism:



Reaction (iii) is similar to the behaviour shown by many main group alkyls. Displacement of the methyl radical may be concerted or may involve the formation of a paramagnetic Au(II) (d^9) intermediate. Alternatively the reaction may proceed via an oxidative-addition reaction:



The formation of Me^\bullet during the course of the reaction was established although the authors of the work stress that this does not necessarily rule out mechanism (iv).

In contrast, the gold (III) complex Me_3AuL reacts via a non-radical pathway. It has been argued that whereas the reaction with Au(I) involves the formation of a Au(II) species which have been previously identified; the Au(III) system would be required to produce an unlikely Au(IV) intermediate. The inaccessibility of this oxidation state is generally recognised and the free radical mechanism is therefore not important.

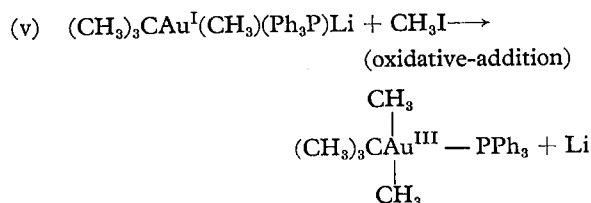
Gold-Hydrogen Bonds

In keeping with the high kinetic stability of Au(III)-alkyls, Au(III)-H complexes have not been isolated. This may merely reflect lack of interest in the production of such species rather than any inherent instability. However, very recent work would imply that such bonds are produced in intermediates formed during olefin isomerisation reactions in the presence of Au(III).

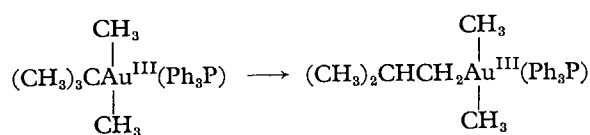
With these points in mind we will now consider some of the reactions that organogold complexes undergo.

Isomerisation of Alkyl Groups σ -Bonded to Gold(III)

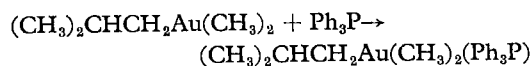
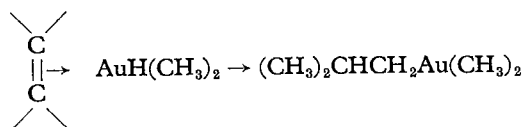
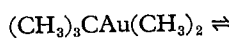
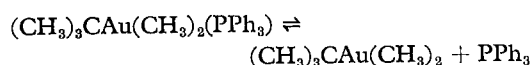
Tamaki and his co-workers (2) have examined the isomerisation of *trans*-butylmethyl(triphenylphosphine) gold prepared from the reaction of lithium *tert*-butylmethyl(triphenylphosphine)gold(I) and methyl iodide in diethyl ether at -78°C .



They found that even under moderate conditions this *tert*-butyldimethyl derivative underwent spontaneous conversion to the isomeric *trans*-isobutyldimethylgold(III) analogue:

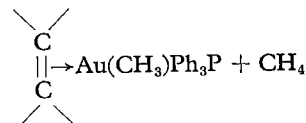
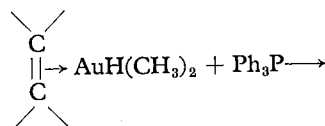


The kinetics of isomerisation in DME solution were first order in *tert*-butyldimethyl(triphenylphosphine)gold and the rearrangement was not markedly affected by the presence of a threefold excess of propylene or a 25-fold excess of 1-butene. However the first-order rate constantly decreased with increasing amounts of added triphenylphosphine. On the basis of these results the following mechanism was proposed:



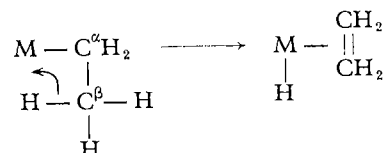
In this scheme, which is similar to those formulated for isomerisation occurring with other d^8 systems e.g. Rh(I), Ir(I), Pd(II) and Pt(II), an intermediate involving an isopropylene-gold bond and a hydrido-gold bond is postulated. However, as the authors of this work correctly point out, attempts to generate π -complexed hydridogold species from dimethylaurate(I) have been unsuccessful. In fact there is no

direct evidence for a Au-H species and a feature of this reaction is the absence of a competing reductive elimination reaction to produce methane:



π -complexed gold(III) complexes are not expected to be stable; the stability of π -complexes decreasing with increase in oxidation state of the coordinating metal ion, although they would be expected to be extremely susceptible to nucleophilic attack (H^-) since the nucleophilicity of olefin-metal is also very dependent on the metal oxidation state diminishing rapidly across the $\text{Au(III)} > \text{Pt(II)} \gg \text{Ir(I)} > \text{Os(0)}$; in fact Ir(I) and Os(0) show a pronounced electrophilicity. Considerable importance is attached to this behaviour of Pt(II) in industrial processes, and although Au(III)-H bonds have not been observed the formation of metal-hydrogen links dominates the chemistry of alkyl derivatives of the other noble metals.

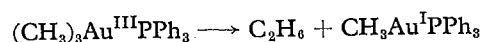
The so-called β -elimination of H from bound ethyl group is responsible for the lability of many such alkyl derivatives:



Gold is unusual in that it does not show this reactivity and both gold(I) and gold(III) form stable ethyl compounds. It has been argued that the β -elimination is brought about largely from steric considerations, in which case elimination from a *n*-butyl group is expected to be more readily accomplished than from an ethyl moiety.

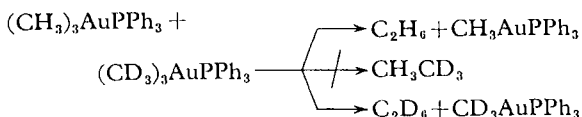
Reductive-Elimination

Coates and Parkin (3) established that trimethyl-(triphenylphosphine)gold undergoes reductive-elimination of ethane:



Decomposition has been shown to be intramolecular. Thus, Tamaki, Magennis and Kochi studied the decomposition of an equimolar mixture of $(\text{CH}_3)_3\text{AuPPh}_3$ and $(\text{CD}_3)_3\text{AuPPh}_3$. They found that C_2H_6 and C_2D_6 were produced in roughly equal

amounts but that less than 5 per cent of the cross-over product CH_3CD_3 was formed:



Conclusions

Organogold chemistry is in its infancy. It offers many attractions and recent work has shown that it is of significant interest to organometallic chemists not only because of the wide range of compounds available but also because their reaction mechanisms are easily studied.

Kochi and his co-workers have shown for instance the usefulness of gold as a catalyst for mechanistic studies since reactions are readily probed by nmr studies in solution and intermediates identified.

Much of the chemistry of Au(I) and Au(III) organo-complexes would appear to be similar to that of other metal ions possessing the d^{10} and d^8 configurations but there are differences in the thermodynamic and kinetic stabilities of such complexes.

References

- 1 A. Johnson and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1975, (2), 115
- 2 A. Tamaki, S. A. Magennis and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, (19), 6140, and references therein
- 3 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, Pt. I, 421

Inlay-Clad Gold Alloys for Telephone Contacts

The use of inlay-clad gold alloys as an alternative to electrodeposited gold is progressing in a number of electrical and electronic applications, and is currently proving of interest to the Bell Telephone System. The analysis of a number of gold alloys in inlay form recently compiled by R. J. Russell (*Gold Bull.*, 1976, **9**, (1), 2-6) showed that this approach offered possibilities for the contacts in a TRIMLINE telephone hand-set, and a paper presented to the 8th Annual Connector Symposium held at Cherry Hill, New Jersey in October last year reports on a detailed assessment of inlaid gold for this application.

The paper, by M. U. Rao and A. J. Molchan of Bell Telephone Laboratories, Indianapolis, and R. J. Russell of Technical Materials, Lincoln, Rhode Island, shows that over a three-month evaluation a 6 per cent nickel-gold alloy for this specific contact spring application gave acceptable properties in terms of porosity, wear, arc erosion and ease of forming and was comparable to a cobalt-hardened electrodeposited gold in use for the past eight years, with appreciable savings in cost.

The switch is expected to withstand at least 50,000 operations over a life of about 20 years. The normally closed contacts carry between 20 and 200 mA, the normal force required to separate the contacts being 150g minimum. Five hand-sets from the Western Electric production line were fitted with the prototype gold-inlay contacts and were tested for 300,000 operations—far exceeding the likely service life—alongside five normal hand-sets with the electrodeposited gold contacts. All ten sets were then submitted to the Western Electric procedure for initial testing and all were found to be acceptable.

The hardness of the 6 per cent nickel-gold alloy in its rolled inlay form was 220 KHN as against 140 to 180 KHN for the electrodeposited hard gold, which showed a greater degree of smearing in the wear tests.

The contacts of the switch under investigation are in series with the telephone line and must meet telephone system requirements for speech transmission, and a further series of tests was used to operate the contacts through 50,000 make and break cycles under 48 volts DC with a high level of inductive loading.

The contact resistance was measured before and after the test runs. An increase from around 10 m Ω to less than 30 m Ω was found. (Noise in a telephone set generally appears at around 60 m Ω .) Arc erosion on both the inlaid and the electrodeposited contacts was much the same in these intentionally severe conditions.

The 6 per cent nickel-gold alloy was chosen for the inlay since its hardness, wear characteristics and contact resistance data showed the likelihood of its acceptability as a substitute for electroplated hard gold. Other alloys are to be investigated later.

The authors conclude that the clad-inlay approach offers the best route to substantial cost savings at present production levels when compared with alternatives such as selective plating or welded-on contacts. Replacement of the electroplated springs with inlay contact springs would not alter assembly procedures, while the expense of the one-off re-tooling would be offset by economies in the cost of production.

Constitution of Gold Alloy Electrodeposits

The constitution of a gold alloy in electrodeposited form—usually quite different from that of the same alloy in cast or wrought form—is of importance in determining its resistance to oxidation or corrosion in service, but so far very little information is available on this subject.

An X-ray study by H. Grossman and F. Horn of DODUCO, Pforzheim, carried out with H. Bauer of the University of Giessen, on the structure of hard gold deposits from a sulphite bath (*J. Less-Common Metals*, 1975, **43**, 291-294) shows that while a deposit containing 0.3 per cent cobalt virtually retains the lattice parameter of pure gold, two highly alloyed deposits, one having 15 per cent nickel and the other 35 per cent copper, show the presence of a new face-centred cubic phase with almost all the alloying elements in solid solution.