Metal β-Diketone Complexes. Part VI.† Some β-Diketone Complexes of Copper(I), Silver(I), and Gold(I)

By **D. Gibson, B. F. G. Johnson,** and **J. Lewis,*** Department of Chemistry, University College, London W.C.1

Two classes of β-diketone complexes of Cu^I, Ag^I, and Au^I have been prepared *viz.*: class (i) L_2M(β-diketone), M = Cu, L = Ph_3P, β-diketone = conjugate base of acetylacetone (acac), benzoylacetone (ba), trifluoroacetylacetone (tfa), or hexafluoroacetylacetone (hfa), and M = Ag, L = Ph_3P, β-diketone = ba or hfa; and class (2) LM(β-diketone), M = Ag, L = Ph_3P, β-diketone = acac or tfa, and M = Au, L = Ph_3P, Ph_2EtP, Et_3P, $(Ph{\cdot}Me)_3P$, or Ph_3As, β-diketone = acac or ba. On the basis of molecular-weight data, and i.r. and n.m.r. spectral studies the complexes of Cu^I and Ag^I are shown to contain oxygen-bonded β-diketones irrespective of their composition, whereas those of Au^I contain carbon-bonded ligands in all cases. The stereochemical consequences of these observations are discussed.

THE ability of β-diketones to co-ordinate to metals through either their C-3 atom or their two oxygen atoms has been clearly demonstrated.[1-8] The formation and stability of those complexes containing β-diketones bonded through their C-3 atoms has been related to similar methyl derivatives, the stability of which is known to increase with increasing atomic weight of the metal. It therefore seemed desirable to examine some β-diketone complexes of the metals of a given transition-metal triad. We have, prepared and investigated the bonding of the β-diketone in some β-diketone complexes of copper(I), silver(I), and gold(I). Stable alkylgold complexes containing tertiary phosphines have been reported.[9]

In this work two classes of compound have been prepared *viz.*: class (1) those of formula L_2M(β-diketone) where M = Cu, L = Ph_3P, β-diketone = conjugate base of acetylacetone (acac), benzoylacetone (ba), trifluoroacetylacetone (tfa), and hexafluoroacetylacetone (hfa), and M = Ag, L = Ph_3P, β-diketone = ba or hfa, and class (2) those of formula LM(β-diketone), M = Ag, L = Ph_3P, β-diketone = acac or tfa, and M = Au, L = Ph_3P, Ph_2EtP, Et_3P, $(Ph{\cdot}Me)_3P$, or Ph_3As, β-diketone = acac or ba. This classification depends only upon the composition of the compound since we have established that the complexes of Cu^I and Ag^I contain oxygen-bonded β-diketones irrespective of their composition whereas those of Au^I always contain carbon-bonded β-diketone groups. This work has already been reported briefly.[5]

Reaction of Ph_3PCuCl with the appropriate thallium(I) β-diketonate in benzene gave the complexes $(Ph_3P)_2Cu$(β-diketone). In the corresponding reactions with Ph_3PAgCl the product obtained depended upon the β-diketone employed. Thus with acetyl- or trifluoroacetyl-acetone compounds of the type Ph_3PAg(β-diketone) were obtained whereas with benzoyl- or hexafluoro-acetylacetone the complexes $(Ph_3P)_2Ag$(β-diketone) which are similar to those described for copper were isolated. In similar reactions with LAuCl only one product, LAu(β-diketone), where L = Ph_3P, Ph_2EtP, Et_3P, or Ph_3Au, β-diketone = acac or ba, was isolated. Attempts to prepare the related complexes using dibenzoylmethane, trifluoroacetylacetone, or hexafluoroacetylacetone were unsuccessful. From all reactions white crystalline products were obtained. All compounds were non-electrolytes and those of class (2) (see before) were monomeric in either benzene or chloroform. However, the copper complexes [class (1)] dissociate in these solvents giving rise to low molecular-weight values. We consider that the equilibrium existing is:

$$L_2Cu(\beta\text{-diketone}) \rightleftharpoons LCu(\beta\text{-diketone}) + L$$

In chloroform the copper complexes are oxidised by the air to $Cu(\beta\text{-diketone})_2$.

We have again employed n.m.r. and i.r. spectral data in order to establish the bond-type adopted by the β-diketone. The n.m.r. spectra are recorded in Table 1. As often observed in the n.m.r. spectra of complexes of this type the 3H chemical shift varies considerably. For the acetylacetone complexes only one sharp methyl resonance is observed, implying a symmetrical environment of the acetylacetone group in every case. The i.r. spectra of the complexes in the carbonyl stretching region (1500—1700 cm.$^{-1}$) are shown in Table 2. Nakamoto and his co-workers[10] have shown that for an oxygen-bonded acetylacetone group two frequencies are expected in this range; these arise from the CO and C=C stretching modes which are coupled and normally occur at about 1600 and 1520 cm.$^{-1}$. Whilst two frequencies are observed with the copper and silver complexes, only one (the higher) is observed with the gold complex suggesting an absence of double-bond C–C character in the ligand. The 3H out-of-plane bonding frequency,

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† Part V is ref. 8.

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TABLE 1

N.m.r. spectra of β-diketone complexes of copper(I), silver(I), and gold(I) *

Compound	Peak (c./sec.)	Intensity	Assignment
$(Ph_3P)_2Cu(acac)$	435	30	C_6H_5
	305	1	3H
	106	6	Me
$(Ph_3P)_2Cu(ba)$	440	35	C_6H_5
	348	1	3H
	117	3	Me
$(Ph_3P)_2Cu(tfa)$	442	30	C_6H_5
	CH not observed		
	117	3	Me
$(Ph_3P)_2Cu(hfa)$	437	—	C_6H_5
	CH not observed		
$(Ph_3P)Ag(acac)$	438	15	C_6H_5
	312	1	3H
	115	6	Me
	327 †	1	3H
	124 †	6	Me
$(Ph_3P)Ag(tfa)$	442	15	C_6H_5
	332	1	3H
	121	3	Me
$(Ph_3P)_2Ag(ba)$	444	30	C_6H_5
	351	1	3H
	120	3	Me
$(Ph_3P)_2Ag(hfa)$	441	30	C_6H_5
	344	1	3H
$(Ph_3P)Au(acac)$	456	15	C_6H_5
	280	1	3H
	144	6	Me
$(Ph_3As)Au(acac)$	446	15	C_6H_5
	277	1	3H
	139	6	Me
$(Ph_3P)Au(ba)$	493	2	C_6H_5
	456	18	C_6H_5
	326	1	3H
	165	3	Me

* All spectra are recorded for solutions in deuteriochloroform unless otherwise stated. Chemical shifts are relative to tetramethylsilane as internal standard.

† In solution in benzene.

TABLE 2

I.r. spectra of the β-diketone complexes of copper(I), silver(I), and gold(I) in the range 1500—1700 cm.$^{-1}$ *

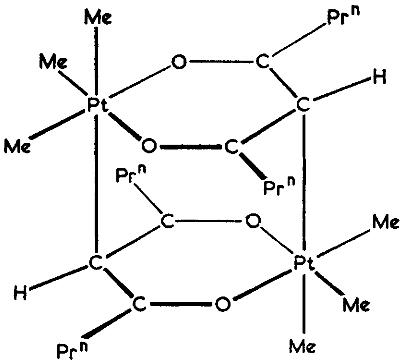
$(Ph_3P)_2Cu(acac)$	1596s, 1583sh, 1506s
$(Ph_3P)_2Cu(tfa)$	1660sh, 1626s
$(Ph_3P)_2Cu(ba)$	1600s, 1571s, 1509s
$(Ph_3P)_2Cu(hfa)$	1647s, 1542m, 1503s
$(Ph_3P)_2Ag(hfa)$	1663s, 1514s, 1505s
$(Ph_3P)_2Ag(ba)$	1603s, 1570m, 1504s
$(Ph_3P)Ag(acac)$	1614s, 1599s, 1543w, 1500m
$(Ph_3P)Ag(tfa)$	1658sh, 1633s
$(Ph_3P)Au(acac)$	1664s, 1651s, 1585w
$(Ph_3P)Au(ba)$	1651s, 1630s, 1573w
$(Ph_2Et)PAu(acac)$	1659s, 1642s
$(Et_3P)Au(acac)$	1658s, 1640s
$(Ph_3As)Au(acac)$	1649s
$(Ph_2Et)PAu(ba)$	1651s, 1630s
$[(p\text{-tolyl})_3P]Au(acac)$	1664s, 1644s

* All spectra measured for Nujol and hexachlorobutadiene mulls between sodium chloride plates.
s = Strong, m = medium, sh = shoulder.

normally found as a sharp peak in acetylacetone complexes at 800 cm.$^{-1}$ is also absent in the gold complexes although it is observed in the silver and copper complexes at 765 and 775 cm.$^{-1}$ respectively. Thus the i.r. spectra of all the copper adducts in the carbonyl region shows peaks in the range associated with oxygen-bonded ligands [10] and the complexes may be formulated as involving a tetrahedral arrangement of ligands around the central copper(I) ion with a bidentate oxygen structure for the β-diketone group. Similarly, the i.r. frequencies in the carbonyl region in the silver acetyl- and benzoylacetone complexes are within the range associated with conventional oxygen-bonded ligands but for the tri- and hexa-fluoroacetylacetone complexes the observed frequencies are higher than any previously observed and the possibility of a carbon bonded structure must be considered in these cases.

The structures of these silver complexes are unknown. The simple phosphine halide complexes R_3PAgCl are tetrameric [11,12] with approximately tetrahedral co-ordination about each silver atom whereas three-co-ordinate silver is apparently observed in the complexes $(R^1R^2{}_2P)AgI$ [13] and $Ag(thiourea)_3Cl$.[14] Thus, the new complexes L_2Ag(β-diketone), may adopt either a pseudo-tetrahedral structure as considered for the analogous copper compounds and involving an oxygen-bonded β-diketone group or a three-co-ordinate structure related to $(R^1R^2{}_2P)_2AgI$ and involving a carbon-bonded β-diketone group. In view of the change in the i.r. spectrum from the benzoyl- to the hexafluoroacetylacetone derivative it is possible that both forms exist.

The structures of the second class of silver compound, *viz.* Ph_3PAg(β-diketone), are unlikely to be similar to those of gold which have the same basic formulation, since their i.r. spectra are different. The spectrum of $Ph_3PAg(acac)$ is, however, very similar to that of $Me_3Pt(acac)$ [2] and it is possible that the structures are similar at least in the solid state. The related platinum complex (I) is dimeric and involves the co-ordination of acetylacetone by both the two oxygens atoms and the C-3 atom so that it forms a bridging group (I). This



(I)

dimeric formulation persists in solution, whereas the silver complex is monomeric. This may simply reflect the relative stabilities of Pt–C and Ag–C σ-bonds.

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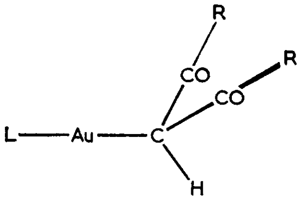
Although the stoicheiometry of certain of the silver and gold complexes is the same, a comparison of the i.r. spectra indicates different structures for these compounds. Although other co-ordination numbers are known for univalent gold, the most usual is two in which the two bonds are co-linear. Thus, while the phosphine–metal halides of copper and silver are tetramers those of gold are monomeric linear molecules. The equivalence of the methyl protons, as indicated by the ^1H n.m.r. spectrum points to a symmetrical environment for the ligand, which rules out any structure based on unidentate acetylacetone bonded *via* one oxygen atom. Previously, we outlined the properties of β-diketone adducts of metals bonded solely *via* the C-3 atom of the ligand (carbon-bonded). This type of bonding leads to much higher carbonyl stretching frequencies than are observed when the ligand is oxygen-bonded and to an absence of the 3H out-of-plane bending mode. Both features are observed in the spectrum of the gold complexes. This, together with the ^1H n.m.r. data and stereochemical considerations lead us to suggest a structure of the type shown in (II), for these complexes.

(II)



These can be viewed as substituted methyl complexes equivalent to the phosphine gold alkyls reported by Coates *et al.*[9] Attempts to assign a gold–carbon stretching frequency in the low-frequency region of the i.r. spectrum of the triaryl phosphine complexes has not been possible because of the presence of strong obscuring bands arising from phenyl groups. However, in the triethyl phosphine compound, a band at 530 cm.$^{-1}$ is in the region previously associated with gold–carbon stretching frequencies.[9,15] It has been pointed out [16] that the stability of metal–carbon bonds would be expected to increase (*a*) on going from the first to the second to the third row of the transition series, (*b*) with an increase in the π-bonding capacity of other ligands around the metal atom, and (*c*) with increasing electronegativity of substituents on the carbon atom. From the point of view of (*c*) we should expect the stability of the gold complexes to be: Me < acac < ba < tfa < hfa. However, the reaction of thallium(I) trifluoroacetylacetone with triphenylphosphine gold chloride in benzene produces only a small amount of thallium(I) chloride, and no gold trifluoroacetylacetone complex can be isolated.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer and n.m.r. spectra on a Perkin-Elmer R10.

Melting Points were recorded on a Gallenkamp apparatus.

Bis(triphenylphosphine)acetylacetonatocopper(I).—Thallium(I) acetylacetonate (1 mole) in benzene was shaken with triphenylphosphinecopper(I) chloride (1 mole) for 2 hr. The precipitated thallium(I) chloride was filtered off, the solution evaporated and, the residue recrystallised from benzene–ether to give the white crystalline *complex*. Other β-diketone complexes were similarly prepared from the corresponding thallium(I) β-diketonate [Found: C, 71·9; H, 5·4; P, 9·0%; *M* ($CHCl_3$) 337, (C_6H_6) 350. $C_{41}H_{37}CuO_2P_2$ requires C, 71·9; H, 5·4; P, 9·1%; *M*, 686. *M* ($CHCl_3$) for the hfa derivative, 801; calc. *M*, 795)].

Triphenylphosphineacetylacetonatosilver(I).—Thallium(I) acetylacetonate (1 mole) in benzene was shaken with triphenylphosphinesilver chloride (1 mole) for 1 hr. in the dark. The solution was rapidly filtered and the solvent evaporated without heating. The residue was recrystallised rapidly from benzene to give white light-sensitive crystals of the *complex*. The other complexes were obtained similarly. The bisphosphine complexes did not appear to be light sensitive and this property is possibly due to the disproportionation of the monophosphine complexes to give the very light-sensitive silver acetylacetonate {Found: C, 58·0; H, 4·8; P, 6·6%; *M* ($CHCl_3$), 459. $C_{23}H_{22}AgO_2P$ requires C, 58·6; H, 4·5; P, 6·6%; *M*, 469 Found [for $(Ph_3P)Ag(tfa)$]: C, 53·2; H, 3·3. $C_{23}H_{19}AgF_3O_2P$ requires C, 53·0; H, 3·6%. Found [for $(Ph_3P)_2Ag(ba)$]: C, 69·8; H, 4·9. $C_{46}H_{39}AgO_2P$ requires C, 69·8; H, 5·1%. Found [for $(Ph_3P)_2Ag(hfa)$]: C, 59·6; H, 4·0 *M*, (C_6H_6), 844. $C_{41}H_{31}AgF_6O_2P$ requires C, 58·7; H, 3·8%; *M*, 840}.

Triphenylphosphineacetylacetonatogold(I).—Thallium(I) acetylacetonate (1 mole) was mixed with a solution of triphenylphosphinegold chloride (1 mole). The precipitated thallium(I) chloride was filtered off, the solvent evaporated and the residue recrystallised from benzene–ether to give white crystals of the *complex*. Other complexes were obtained similarly from the appropriate phosphinegold halide and the thallium(I) β-diketonate {Found: C, 49·5; H, 4·2; P, 5·3%; *M* ($CHCl_3$), 537. $C_{23}H_{22}AuO_2P$ requires C, 49·5; H, 4·0; P, 5·6%; *M* 558). Found [for $Ph_3AsAu(acac)$]: C, 45·2; H, 3·6. $C_{23}H_{22}AsAuO_2$ requires C, 45·5; H, 3·6%. Found [for $Ph_3PAu(ba)$]: C, 53·4; H, 3·9; P, 4·8. $C_{28}H_{24}AuO_2P$ requires C, 54·2; H, 3·9; P, 5·0%.

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