Anal. Calcd for $C_6N_2SBrF_{15}$: C, 14.50; N, 5.64. Found: C, 14.69; N, 5.50.

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Reversible Linkage Isomerisms of β-Diketonato Ligands. Oxygen-Bonded and Carbon-Bonded Structures in Gold(III) Acetylacetonate Complexes Induced by Phosphines

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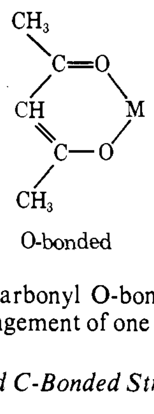
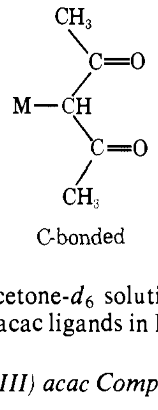
Abstract: Dimethylgold(III) complexes provide a unique opportunity to examine in one system the various linkage isomerisms which are possible with β-diketonato ligands. For example, the reversible rearrangement of an acetylacetonato (acac) ligand from a bidentate O-bonded structure in dimethyl(acetylacetonato)gold(III) to a unidentate C-bonded adduct, dimethyl(acetylacetonato)phosphinegold(III), is induced by phosphines. Rearrangement is promoted by donor phosphines in the order L = $PMe_2Ph > PMePh_2 > PPh_3$. Similarly, with a series of para-substituted triphenylphosphines the formation constants (log K) follow a Hammett correlation with $\rho = -1.6$. The temperature dependence of K yields the thermodynamic parameters, $\Delta H = -11$ kcal mol^{-1} and $\Delta S = -35$ cal deg^{-1}, which are consistent with the associative interaction for triphenylphosphine. The efficacy of PMe_2Ph allows a crystalline C-bonded adduct, *cis*-$(CH_3)_2(acac)AuPMe_2Ph$, to be isolated and characterized. By employing the unsymmetrical benzoylacetonato (ba) ligand, two dynamic processes can be observed separately with $(CH_3)_2(ba)Au$ and L by selective line broadening in the NMR spectra. Associative exchange of phosphine leading to a pre-equilibrium (site-interchange) isomerization of the O-bonded ligand occurs rapidly via a five-coordinate intermediate $(CH_3)_2(ba)AuL$ followed by the slower rearrangement to the four-coordinate C-bonded isomer. The observation of a unidentate O-bonded adduct $(CH_3)_2(acac)AuL$ with L = tricyclohexylphosphine suggests that steric factors play an important role in the rearrangement from *O*-acac to *C*-acac. Trifluoro- and hexafluoroacetylacetonato complexes of dimethylgold(III) are cleaved by phosphines to afford cationic gold species, $Me_2AuL_2^+X^-$ (where X = $CF_3COCHCOCH_3$, $CF_3COCHCOCF_3$). Cleavage of β-diketonates can also be effected by hydrochloric acid and water in both the *O*-acac and *C*-acac complexes of dimethylgold(III). Prior to hydrolysis, a rapid and specific isotopic exchange is observed between D_2O and only the methine proton in the C-bonded $(CH_3)_2(acac)AuPMe_2Ph$.


O-bonded


C-bonded

The widely used β-diketone ligands such as acetylacetone are capable of multiple types of bonding to metals.[1] Acetylacetonato (acac) ligand acting as a bidentate chelate through both oxygen atoms is the most common, but various metal complexes in which a unidentate acac is linked via carbon 3 have been described.[2] However, there are only a few examples of the interconversion of O-bonded and C-bonded acac complexes. Thus, bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedion-5-yl)mercury, $(fod)_2Hg$, in which the central carbon atoms of both fod ligands are initially linked to mercury, has been found by dynamic NMR spectroscopy to undergo stereospecific intramolecular keto-enol tautomerism to the carbonyl O-bonded isomer in acetone-d_6 solutions.[3] Rearrangement of one of the O-bonded acac ligands in Pd(a-

Table I. ^{1}H NMR spectra of Gold^{III}-β-Diketone Complexes in $CDCl_3$

	$Me_2Au(\beta$-diketone) β-diketone	Temp, °C	Me-Au,[a] ppm	β-Diketone ligand,[a] ppm Me	Ph	CH
I	$CH_3COCHCOCH_3$	RT	1.15 (s, 6 H)	2.00 (s, 6 H)		5.35 (s, 1 H)
II	$CH_3COCHCOPh$	RT	1.22 (s, 3 H) 1.27 (s, 3 H)	2.17 (s, 3 H)	7.3-8.0 (m, 5 H)	6.00 (s, 1 H)
III	PhCOCHCOPh	RT	1.32 (s, 6 H)		7.0-8.0 (m, 10 H)	6.65 (s, 1 H)
IV	$CH_3COCHCOCF_3$	RT	1.27 (s, 6 H)	2.17 (s, 3 H)		5.73 (s, 1 H)
		b	1.23 (s, 3 H) 1.27 (s, 3 H)	2.25 (s, 3 H)		5.95 (s, 1 H)
		26[c]	1.25 (s, 6 H)	2.23 (s, 3 H)		5.91 (s, 1 H)
V	$CF_3COCHCOCF_3$[d]	RT	1.43 (s, 6 H)			6.10 (s, 1 H)

[a] The numbers are referred to shifts relative to internal Me_4Si, and the numbers in parentheses indicate the number of protons; s, singlet; m, multiplet. [b] Invariant between 3 to −49 °C in acetone-d_6. [c] In acetone-d_6. [d] Sample prepared from 35.3 mg of $(Me_2AuI)_2$ and 41.0 mg of $Tl(CF_3COCHCOCF_3)$ in situ.

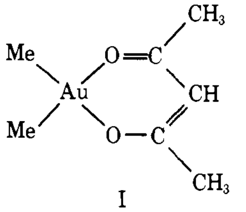
cac)$_2$ to the C-bonded ligand was found to be induced by phosphines and nitrogen bases L during the formation of the adduct, Pd(acac)$_2$L.[4] The irreversible transformation in the latter case precludes a study of the dynamics of the oxygen-to-carbon ligand rearrangement. Indeed, there are no examples to our knowledge of a phosphine induced reversible equilibrium between O-bonded and C-bonded acac. We wish to describe in this report a variety of reversible equilibria and linkage isomerisms of β-diketonato ligands bonded to dimethylgold(III), especially in the presence of tertiary phosphines.

Results and Discussion

Preparation and Dynamic Behavior of Dimethyl(β-diketonato)gold(III) Complexes. Dimethyl(acetylacetonato)gold was prepared from the dimer of dimethylgold iodide

$$(Me_2AuI)_2 + 2Tl(acac) \rightarrow 2Me_2Au(acac) + 2TlI \quad (1)$$

by treatment with a stoichiometric amount of acetylacetonatothallium in a mixture of pentane and ethanol.[5] The sharp singlet resonance in the ^{1}H NMR spectrum of I listed in Table I shows that both methyl groups are equivalent, as expected for a square planar configuration in common with other Au(III) complexes.[6] The acac ligand in I is O-bonded as shown by the characteristic infrared bands at 1520 and 1590 cm^{-1}.


I

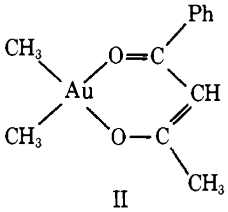
Modification of the procedure by employing the dibenzoylmethane, benzoylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone derivatives[7] of thallium(I) afforded the analogous β-diketonato complexes listed in Table I. The trifluoro- and hexafluoroacetylacetone complexes are unusually volatile, being readily sublimed at atmospheric pressure even at room temperature. The frequency of the carbonyl band in the infrared spectra of these complexes in Table II increased as methyl groups were replaced with trifluoromethyl groups.[8]

The NMR spectrum of dimethyl(benzoylacetonato)gold (II) in $CDCl_3$ showed a sharp singlet for each of the methyl groups bonded to gold due to the unsymmetrical nature of the ligand. No line broadening was observed in the spectrum on increasing the temperature from 25 to 60 °C, which suggests that the complex II like I maintains its rigid square planar configuration in solution.

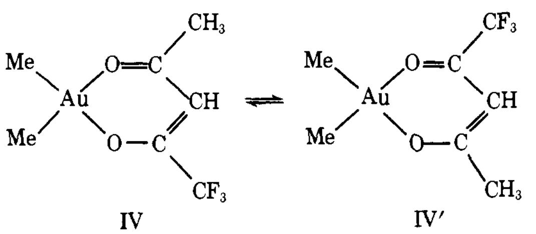
Table II. Infrared Spectra of Gold(III) β-Diketone Complexes

$(CH_3)_2Au$-(β-diketone) β-diketone	Additive	IR bands in the $\nu_{C=O}$ and $\nu_{C=C}$ region, cm^{-1}		
$CH_3COCHCOCH_3$[a]	None	1520 (s)	1540 (sh)	1590 (s)
$CH_3COCHCOCH_3$[b]	$PPhMe_2$	1618 (s)	1653 (sh)	1713 (w)
$CH_3COCHCOPh$[a]	None	1520 (s)	1560 (s)	1590 (m)
PhCOCHCOPh[a]	None	1530 (s)	1545 (s)	1590 (m)
$CH_3COCHCOCF_3$[a]	None	1525 (m)	1540 (sh)	1620 (s)
$CF_3COCHCOCF_3$[c]	None	1535 (w)	1610 (m)	1640 (s)
$CF_3COCHCOCF_3$[d]	PPh_3	1560 (m) 1540 (s) 1550 (sh)	1660 (sh)	1673 (s)

[a] KBr disk. [b] $Me_2Au(C$-acac)PMe_2Ph in KBr disk. [c] NaCl liquid cell in $CDCl_3$. [d] One equivalent of PPh_3 was added to the $CHCl_3$ solution of the hexafluoroacetylacetonato complex: s, strong; m, medium; w, weak; sh, shoulder.


II

By contrast, the NMR spectrum of dimethyl(trifluoroacetylacetonato)gold (IV) in the same solvent consisted of a sharp singlet for both methyl groups bonded to gold, even to temperatures as low as −80 °C. However, the methyl groups are differentiated in acetone-d_6 at the low temperatures indicated in Table I. The collapse of the two singlets at higher temperatures suggests a rapid averaging process of the type described in eq 2. (The lines due to the methyl and methine


(2)

IV IV′

Table III. ^1H NMR Spectra of Gold(III)acac Complexes[a,b]

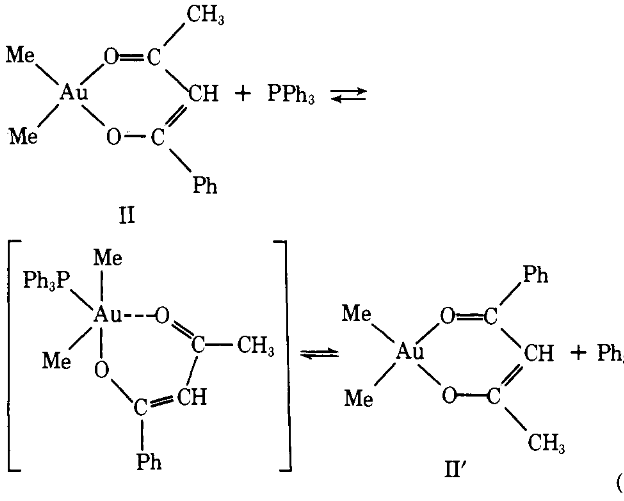
$(CH_3)_2Au(acac)L$		CH_3	CH	CH_3-Au-L		CH_3
	L	(acac)	(acac)	(trans)	(cis)	(L)
VII	$PPh(CH_3)_2$	2,00 (s)	4.60 (12)	1.02 (9)	0.72 (8)	1.97 (10)
VIII	$PPh_2(CH_3)$	2.00 (s)	4.58 (12)	1.10 (9)	0.66 (8)	2.40 (10)
1Xa	PPh_3	1.90 (s)	4.50 (12)	1.17 (9)	0.60 (8)	
b	$P(p\text{-}C_6H_4OCH_3)_3$	1.94 (s)	4.58 (12)	1.10 (9)	0.63 (8)	3.53 (s)
c	$P(p\text{-}C_6H_4CH_3)_3$	1.90 (s)	4.53 (12)	1.13 (9)	0.60 (8)	2.4 (s)
d	$P(p\text{-}C_6H_4CH_3)Ph_2$	1.92 (s)	4.53 (12)	1.16 (9)	0.63 (8)	2.4 (s)
e	$P(p\text{-}C_6H_4Cl)_3$	2.13 (s)		1.40 (9)	0.60 (8)	
X′	$P(c\text{-}C_6H_{11})_3$	2.42 (s) 2.00 (s)	5.38 (s)[c]	0.93 (9)	0.97 (6)	d

[a] $CDCl_3$ at 25 °C. [b] Chemical shifts in parts per million from internal Me_4Si. Numbers in parentheses represent coupling constants (doublets, Hz) to ^{31}P, s = singlet. Aromatic resonances in L (δ 7-8 ppm) not included. [c] Broad, unresolved singlet. [d] Unresolved singlet, c-C_6H_{11}.

protons in the ligand are relatively unbroadened by temperature variations. However, the possibility of intermolecular exchange processes has not been ruled out.) The equilibration in eq 2 probably proceeds via a dissociative process involving initial scission of one of the Au-O bonds. An alternative associative mechanism in which coordination by solvent generates a five-coordinate intermediate does not readily explain why chloroform is more effective than acetone. The complex kinetics relating to other cis-trans stereoisomerisms in O-bonded β-diketonates of various metals, including Al, Si, Cr, Ni, and Au, have been recently described.[9]

Phosphine-Induced Stereoisomerism of β-Diketonato Ligands. Dimethyl(benzoylacetonato)gold shows no dynamic behavior in chloroform solution, judging by the temperature invariance of the proton spectrum described above. However, when a small amount of triphenylphosphine was added to a solution of II, the two resolved Me-Au singlets in the NMR spectrum broadened. The broadening continued as increasing amounts of triphenylphosphine were added, until the resonance finally collapsed to a singlet as shown in Figure 1. The lines associated with the β-diketonato ligand also broadened to a slight extent, but no large change in chemical shifts was observed.

We attribute this phosphine-induced dynamic change in the spectrum of dimethyl(benzoylacetonato)gold to stereoisomerism of the O-bonded ligand in a manner similar to that described in eq 2 for the more labile complex of trifluoroacetylacetonate in the absence of phosphine. A mechanism involving a five-coordinate intermediate VI is proposed below. Similar five-coordinate intermediates have been postulated in associative mechanisms of the well-known isomerizations of other d^8 metal complexes.[10]



II

II′

(3)

VI

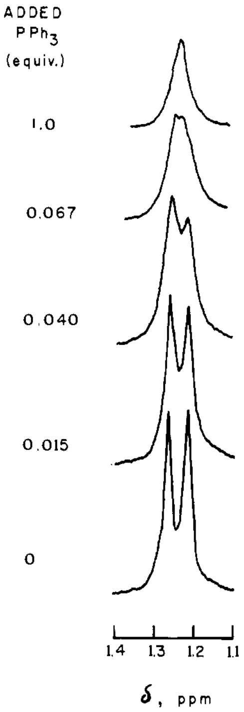
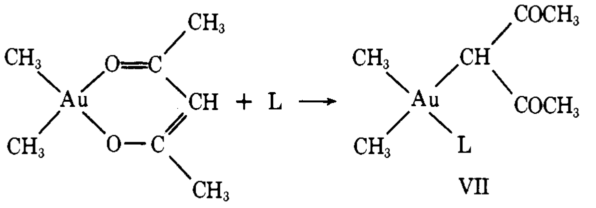


Figure 1. Exchange broadening of the methyl doublets in the ^1H NMR spectrum of 0.12 M dimethyl(benzoylacetonato)gold in $CDCl_3$ induced by various amounts of added triphenylphosphine. Numbers refer to equivalents of PPh_3 relative to the gold complex.

Rearrangement of β-Diketonates from O-Bonded to C-Bonded Ligands. 1. Acetylacetonato Complexes. When dimethyl(acetylacetonato)gold is treated with a stoichiometric amount of dimethylphenylphosphine in either benzene or deuteriochloroform solution at room temperature, the ^1H NMR spectrum of I is immediately replaced by that of VII



I

VII

(4)

(where L = $P(CH_3)_2Ph$). Adduct VII can be readily isolated as a colorless, crystalline solid in excellent yield simply by removing the solvent in vacuo. It was recrystallized from a mixture of n-pentane and toluene and was identified by its IR and NMR spectra (Table III) together with the elemental

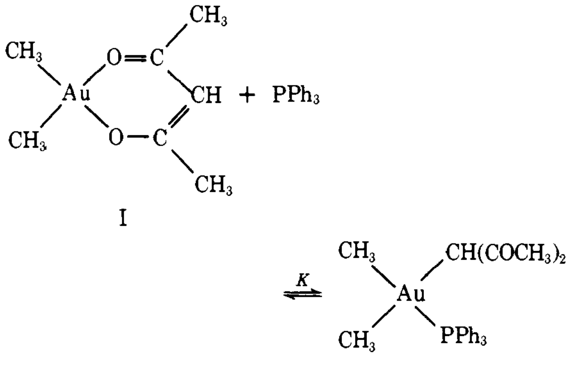
Table IV. $^{31}P\{^1H\}$ NMR Parameters of $Me_2Au(acac)L$ in $CDCl_3$

		Chemical shift^a (half-width, Hz)	
L	Temp, °C	(coordinated ligand)	(free ligand)
$PPh_3{}^b$	−21.2	−33.9 (1.8)	+6.5 (1.8)
	10.3	−33.9 (5.3)	+5.8 (7.8)
	33.8	−33.8 (3.6)	+4.9 (15.8)
$PPhMe_2{}^c$	36.3	+6.6 (~2)	

[a] From external H_3PO_4. [b] Me_2Au acac (0.077 mmol); PPh_3 (0.153 mmol) in 0.5 mL of $CDCl_3$. [c] $Me_2Au(acac)$ (0.077 mmol); $PPhMe_2$ (0.078 mmol) in 0.5 mL of $CDCl_3$.

analysis. The presence of C-bonded acac in VII is shown by the characteristic doublet splitting (12 Hz) of the methine proton by phosphorus in the NMR spectrum as well as the diagnostic infrared bands at 1618, 1653, and 1713 cm^{-1} (see Experimental Section). As expected for square planar VII, the methyl groups are no longer equivalent, but they maintain their cis relationship as shown in the NMR spectrum by the pair of doublets similar to those in the related trimethyl(phosphine)gold and dimethyl(aniono)phosphinegold complexes.[11] An analogous adduct VIII is readily formed from dimethyl(acac)gold and methyldiphenylphosphine.

On the other hand, if dimethyl(acetylacetonato)gold is treated with triphenylphosphine, the ^{1}H NMR spectrum of the solution consists of the *superposition* of the spectrum of I as well as that of the adduct IX (L = PPh_3). The same spectrum is obtained from a solution of *cis*-dimethyliodo(triphenylphosphine)gold after treatment with thallous acetylacetonate followed by the immediate separation of the thallous iodide precipitate. As expected, the ^{31}P NMR spectrum of the mixture (Table IV) showed a sharp singlet for IX (δ −34 ppm) as well as a singlet for free PPh_3 at δ +5.8 ppm. The latter, however, is shifted slightly downfield relative to that of PPh_3 alone (δ +8.5 ppm). A rapid associative preequilibrium of the type described above in eq 3 preceding the rearrangement in eq 5 can be readily accommodated by this observation.



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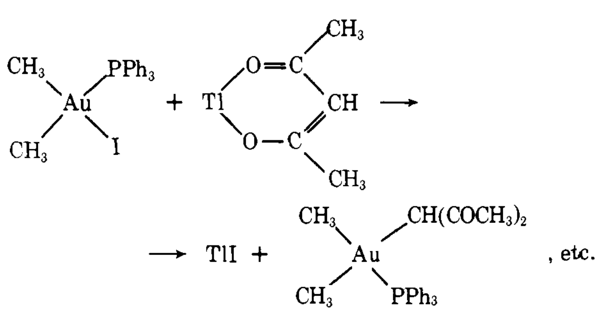


(6)

The relative concentrations of I and IX in eq 5 can be altered by either adding various amounts of triphenylphosphine or varying the temperature of the solution. In both cases, equilibrium is established according to the relationship $K = [IX]/[I][PPh_3]$. The temperature dependences of K derived from the analyses of both the proton and the phosphorus NMR spectra of dimethyl(acetylacetonato)gold and triphenylphosphine are in good agreement as shown in Figure 2.

Table V. Structural and Temperature Dependences of the Equilibrium Constants for the Rearrangement of $(CH_3)_2Au(acac)$ with Phosphines in $CDCl_3$

L	Temp, °C	K L mol^{-1}	$\Sigma\sigma^a$
$P(CH_3)_2Ph$	RT	>100	
$P(CH_3)Ph_2$	RT	>100	
$P(p\text{-}C_6H_4OCH_3)_3$	16	135	−0.804
	38	45.8	
	63	7.6	
$P(p\text{-}C_6H_4CH_3)_3$	16	83.9	−0.510
	38	25.3	
	63	3.1	
$P(p\text{-}C_6H_4CH_3)Ph_2$	16	18.0	−0.170
	38	4.7	
	63	0.8	
PPh_3	14	13.7	0
	37	2.7	
	62	1.0	
	14^b	0.5	
	37^b	0.2	
	62^b	0.1	
$P(p\text{-}C_6H_4Cl)_3$	−30	2.7	0.671
	30	0.4	

[a] Sum of Hammett constants in the para positions of triphenylphosphine. [b] In benzene.

Table VI. Thermodynamic Parameters for the Rearrangement-Adduct Formation of $Me_2Au(acac)L^{a,b}$

Phosphine L	$\Delta F°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal deg^{-1} mol^{-1}
$P(p\text{-}C_6H_4Cl)_3$	−0.8	−11	−41
PPh_3	1.1	−11	−35
$P(p\text{-}C_6H_4CH_3)Ph_2$	1.3	−13	−39
$P(p\text{-}C_6H_4CH_3)_3$	2.2	−13	−36
$P(p\text{-}C_6H_4OCH_3)_3$	2.7	−13	−35

[a] 25 °C in $CDCl_3$. [b] The estimated errors: $\Delta F°$, ±0.1; $\Delta H°$, ±1; $\Delta S°$, ±5.

The electronic properties of triphenylphosphine were systematically altered with a series of para substituents listed in Table V. The equilibrium constants for the phosphine-induced rearrangements show a reasonably linear Hammett correlation in Figure 3. The ρ value of −1.6 indicates that electron-rich phosphines are the most effective in promoting the rearrangement.[12] The variations in the equilibrium constants with different triarylphosphines, however, reflect changes in contributions from both enthalpy as well as entropy terms (Table VI). The steric properties of the added ligand L should also be taken explicitly into account in their effect on K, since their effectiveness increases in the order $PPh_3 < PPh_2(CH_3) < PPh(CH_3)_2$, which parallel a trend in decreasing cone angle of the phosphines.[14,15] (Unfortunately, this series also includes changes in electronic properties, and more appropriate phosphines must be examined for steric effects alone.)

Tricyclohexylphosphine (PCy_3) induced a change which is unique among the phosphines studied with dimethyl(acetylacetonato)gold. Thus, no NMR signal attributable to a C-bonded adduct X was obtained (see Table III). Instead, two

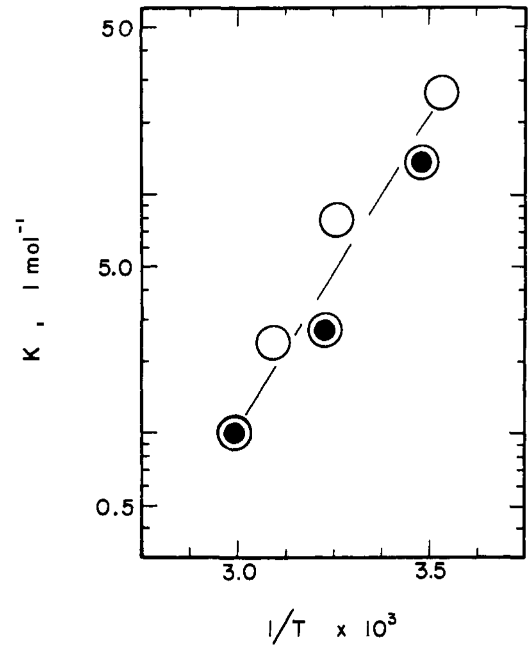
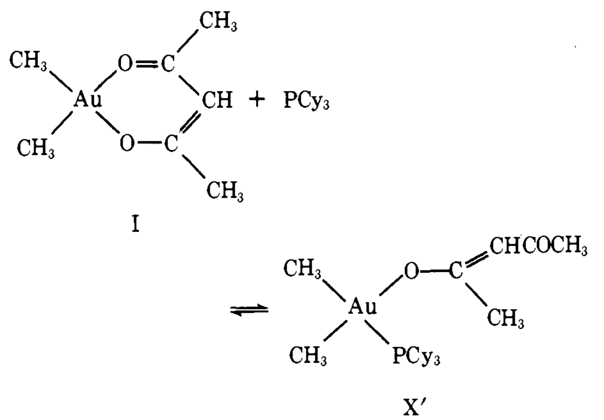


Figure 2. Temperature dependence of the formation constant K for dimethyl(acac)phosphinegold from $Me_2(acac)Au$ and PPh_3 in $CDCl_3$ solution determined by ○ $^{31}P\{^1H\}$ (uncorrected for the nuclear Overhauser effect) and ⊙ ^1H NMR spectroscopy.

separate resonances were observed at δ 2.00 (s) and 2.42 (s) for the methyl groups on the acac ligand, together wth two methylgold doublets at δ 0.97 (d, 9 Hz) and 0.93 (6 Hz). The two sets of doublets are consistent with a square planar *cis*-dimethylgold configuration described earlier, but the different chemical shifts for the two methyl groups associated with acac suggest that the ligand is bonded to gold via only one oxygen as in X′. Acac bonded to gold(III) as a unidentate O-bonded

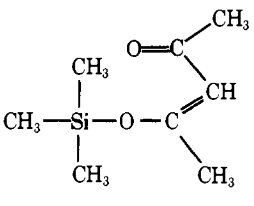


I

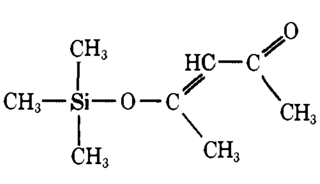
(7)

X′

ligand in X′ can be considered as an open chain enol ether structure in which the uncoordinated oxygen is ketonic.[16] Indeed, coordination of acac in this manner has been recently described for a four-coordinate silicon derivative, $(CH_3)_3Si$-acac[17] (XIa,b), the chemical shifts and coupling constants of which are remarkably similar to those of X′.[18]



XIa



XIb

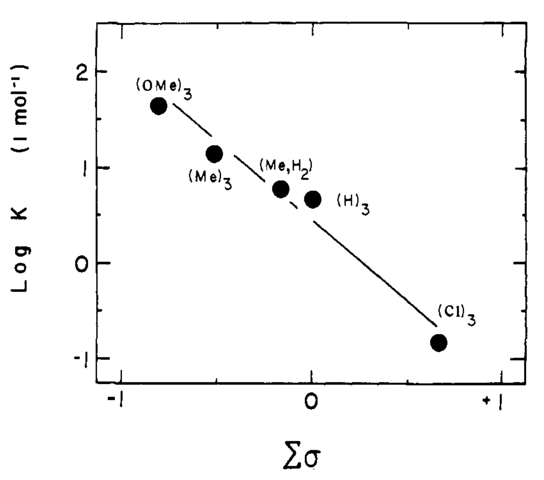
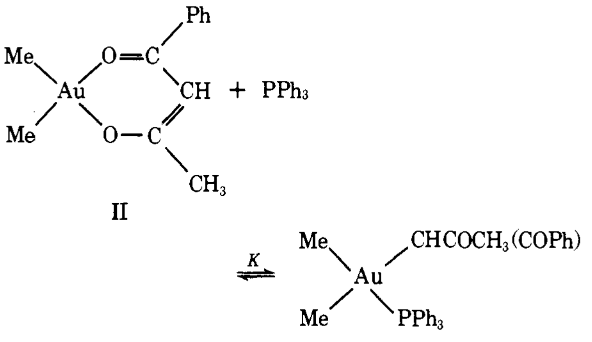


Figure 3. Hammett correlation of the extent of acac rearrangement (measured by K) for dimethyl(acac)gold and various para-substituted triphenylphosphines. Substituents denoted in parentheses.

The disparate modes of acac bonding in the dimethyl(acetylacetonato)gold adducts IX and X′ derived from triarylphosphines and tricyclohexylphosphine, respectively, correlate mostly with differences in the steric properties of these phosphines. Thus, the cone angle θ of tricyclohexylphosphine (170°) is significantly larger than that in triphenylphosphine (145°). Electronic factors do not appear to be as important. (Although the electronic parameter ν of tricyclohexylphosphine is 2056 cm^{-1} compared to 2069 cm^{-1} for triphenylphosphine,[15] dimethylphenylphosphine, which has an intermediate value of ν (2065 cm^{-1}) and the smallest θ (122°), forms a C-bonded adduct VII which is even more stable than that (IX) derived from triphenylphosphine.)

2. Benzoylacetonate Complexes. Replacement of a single methyl group in acac with a phenyl group leaves the resulting benzoylacetonato complex II only slightly less prone to rearrange. Thus, addition of an equimolar amount of triphenylphosphine to *cis*-dimethyl(benzoylacetonato)gold not only induces the rapid cis–trans stereoisomerism of O-bonded isomers described in eq 3, but it also causes the partial rearrangement of II to the C-bonded complex XI. The latter is observed by the presence of its characteristic *cis*-Me_2Au resonances [δ 0.56 (d, 8 Hz) and-δ 1.23 (d, 8 Hz)] in the ^1H NMR spectrum together with those of II. An eightfold excess of triphenylphosphine is required to shift the equilibrium in eq 8 to heavily favor the C-bonded complex XI; and from the line intensities we estimate K to be 2.2 L mol^{-1}. It is noteworthy that the rate of the attainment of the equilibrium in eq 8 is not



II

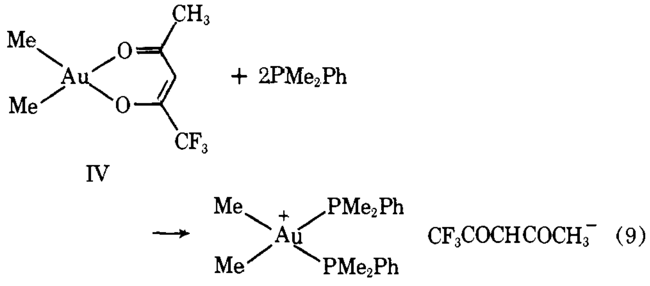
(8)

XI

sufficiently rapid on the NMR time scale to obliterate the phosphorus splittings of the methyl protons in XI.

3. Dibenzoylmethido Complexes. Judging by the temperature invariance of its sharp singlet CH_3Au resonance, dimethyl(dibenzoylmethido)gold exists in solution as a stable, square planar complex much like the acetylacetonato and benzoylacetonato complexes. However, III differs significantly from both I and II, particularly the latter, in that no transformation to a C-bonded adduct could be detected even in the presence of a sevenfold excess of triphenylphosphine. Only a slight line broadening was observed in the NMR spectrum, and we conclude that the equilibrium constant is less than 0.1 L mol^{-1}. Furthermore, the addition of the more strongly coordinating ligand, PMe$_2$Ph, in equimolar amounts led to extensive line broadening in the NMR spectrum of III. The presence of the C-bonded adduct could not be clearly discerned due to the broad unresolved MeAu and MeP resonances (compare Table III) in the spectra.

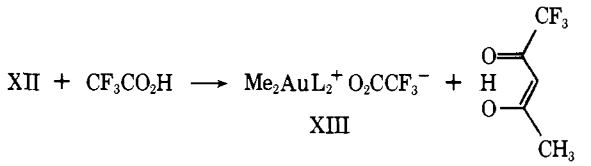
4. Trifluoro- and Hexafluoroacetylacetonato Complexes. The lability of the β-diketonato ligand to cis–trans isomerization in O-bonded dimethyl(trifluoroacetylacetonato)gold IV was described in eq 2. The addition of 2 equiv of dimethylphenylphosphine to IV induced the formation of the ion pair XII. The ^{1}H NMR spectrum of XII consists of the superposition of the spectrum of the cationic dimethylgold species Me$_2$AuL$_2^+$ on that of the trifluoroacetylacetonate ion. Tobias and co-workers[19] have isolated and fully characterized a series of stable salts in which the cation Me$_2$AuL$_2^+$ (L = PMe$_2$Ph) always shows a characteristic A$_3$XX′A$_3$ multiplet in the NMR spectrum. The latter is identical with that obtained in XII. It is noteworthy that the trifluoroacetylacetonato counterion as shown in XII is rather unique in that it is formulated in an uncoordinated form; and its ^{1}H NMR spectrum shows the two singlets at δ 5.25 and 2.40 ppm for the methine and methyl proton, respectively, shifted relative to those in the free ligand (trifluoroacetylacetone enol: CH$_3$ δ 2.21, CH 5.88, OH, 11.70 ppm). The latter can be liberated quantitatively from the ion pair XII by the addition of 1 equiv of strong acid, e.g.,



IV

XII

(9)



XIII

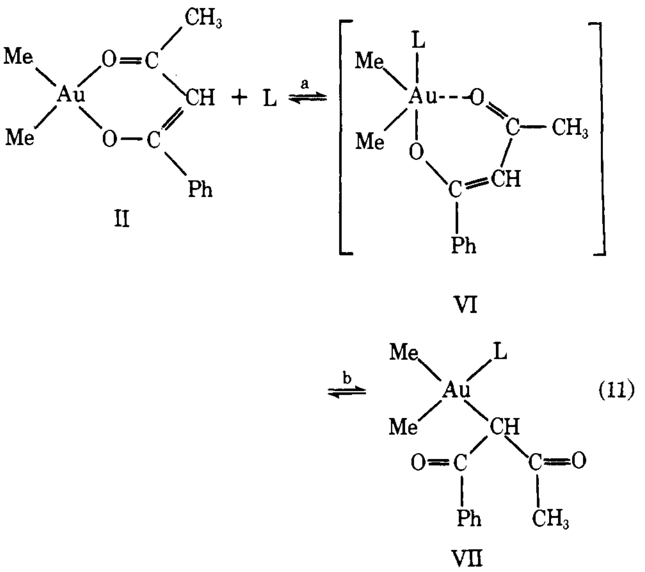
(10)

The new ion pair XIII is directly related to the salts prepared by Tobias et al.,[19] its NMR spectrum showing the same A$_3$XX′A$_3$ multiplet.[20] If less than 2 equiv of PMe$_2$Ph are added to IV, a proportionately smaller amount of ion pair XII is formed (judging from the relative intensities of the spectra of IV and XII in the presence of various amounts of phosphine). No additional resonance lines due to the expected C-bonded adduct Me$_2$(tfacac)AuL were observed.[21] Furthermore, the use of L = triphenylphosphine was not helpful, since the resonance lines were severely broadened and the species in solution not clearly identifiable (see Experimental Section).

Dimethyl(hexafluoroacetylacetonato)gold V showed a pair of characteristic singlets in the NMR spectrum at δ 1.43 and 6.10 ppm which are expected for equivalent cis methyl groups and the single methine proton on the ligand, respectively. The addition of 0.9 equiv of triphenylphosphine to this solution led to shifting (δ 1.17 ppm) and severe broadening of the resonance due to the methyl groups.[22] The methine singlet was also shifted (δ 5.63) but only slightly broadened. Thus, the phosphine induced changes in the ^{1}H NMR spectrum of V are similar to those observed overall with the trifluoroacetylacetonato complex IV. The intermediate stages were not observed.

5. Dynamic Processes in the Phosphine-Induced Rearrangement of β-Diketonatogold(III) Complexes. The dynamics of at least four distinct rate processes can be clearly distinguished in the NMR spectra of various β-diketonate complexes of dimethylgold(III). Two of these processes observed upon the addition of triphenylphosphine to dimethyl(benzoylacetonato)gold relate directly to the rearrangement of the O-bonded ligand to the C-bonded linkage isomer. First, the associative exchange leading to the isomerization of the O-bonded benzoylacetonato ligand described in eq 3 is rapid. Second, the rearrangement of O-bonded benzoylacetonate in II to the C-bonded ligand in XI is facile (eq 8), but not sufficiently rapid to lead to NMR line broadening.[23] These separately observed processes can be interrelated by a common mechanism in Scheme I which includes the five-coordinate species as an intermediate in the rearrangement.

Scheme I



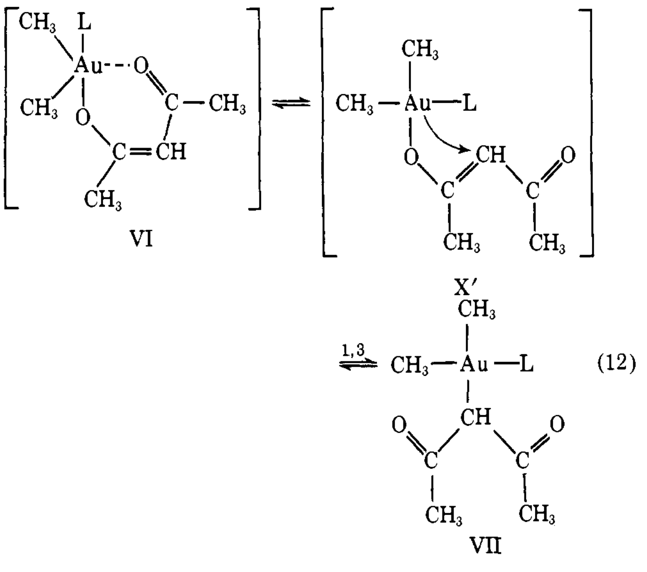
II

VI

VII

(11)

Scheme II



VI

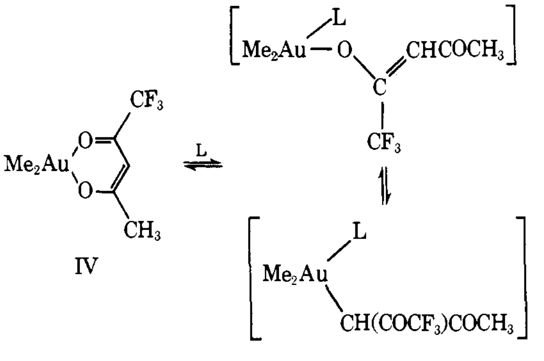
X′

VII

(12)

The observation of intermediate X′ in which the β-diketonate ligand is unidentate and O-bonded as an enol ether (compare eq 7) suggests that step 11b occurs by dissociation followed by a 1,3-enolate rearrangement of gold(III), e.g., see Scheme II.

The presence of α-trifluoromethyl groups in the ligand generally causes metal β-diketonate complexes to be more labile to substitution than the acac analogues.[9] In accord with this expectation, two additional effects have been observed with the fluoroacetylacetonato complexes of dimethylgold(III). First, the isomerization of dimethyl(trifluoroacetylacetonato)gold IV is rapid in eq 2, and it occurs spontaneously without the benefit of added phosphine (in contrast to the more stable benzoylacetonato analogue II in eq 3). More importantly, trifluoroacetylacetonate is *displaced* quantitatively from the dimethylgold(III) complex IV by dimethylphenylphosphine according to eq 9. The absence of the C-bonded adduct in significant amounts may be attributed to the equilibria in eq 13 which favor the ion pair XII. A similar process is probable with the hexafluoroacetylacetonate complex V, but the analysis of the NMR spectral changes was obscured by severe line broadening. However, we hope that further studies of the temperature dependence of the line broadening behavior, particularly in the trifluoro- and hexafluoroacetylacetonato complexes IV and V, will provide detailed information on these dynamic changes.



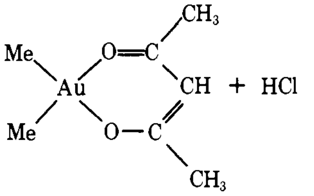
$$\xrightleftharpoons{L} \mathrm{Me_2AuL_2^+\,CH_3COCHCOCF_3^-} \quad (13)$$

XII

6. C-Bonded β-Diketonates in metal Complexes. The formation of C-bonded β-diketonato complexes can be likened to the formation of alkylmetals, in which the most stable transition metal complexes are generally found among the heavier elements with the highest electronegativities.[24] The formation of C-bonded β-diketonato ligands in dimethylgold(III) complexes is thus akin to related linkages in Pt, Pd, Rh, and Ir β-diketonates.[2,25]

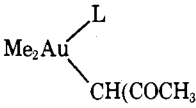
The *driving force* provided by phosphine for acac rearrangement can be ascribed to electronic as well as steric factors in adduct formation. The electronic effects of phosphine coordination are clearly shown by the Hammett correlation in Figure 3, which underscores the importance of base strengths (i.e., $\rho = -1.6$) of phosphines.[26] If gold(III) is to maintain its square planar coordination upon phosphine coordination, acac is forced to become unidentate, and the C-bonded linkage is the most stable when steric effects are minimal.[27] Unidentate O-bonding only obtains when bulky ligands such as tricyclohexylphosphine are present in the adducts, since the enol ether structure involves less steric encumbrance around gold than the isomeric C-bonded diketo structure (compare X′ and VII in eq 12). Adduct formation without concomitant rearrangement of acac suggests that the change from O-bonding to C-bonding is a consequence of phosphine coordination to dimethylgold(III). Although phosphine coordination may provide the principal driving force for acac rearrangement, steric effects in linking a unidentate O-bonded or C-bonded β-diketonate to gold must also be considered. Thus, the absence of adduct formation (and rearrangement) when dimethyl(dibenzoylmethido)gold III is treated with triphenylphosphine can be attributed mainly to steric factors.[29]

Proton Transfer and Exchange in Acac–Gold(III) Complexes. Dimethyl(acetylacetonato)gold I and its dimethylphenylphosphine adduct VII were examined with strong acid, alcohol, and water. Acidolysis of I with hydrochloric acid produced no methane (or ethane), but only free acetylacetone in 80% yield. Similarly the C-bond adduct VII also gave only acetylacetone and no methane. The preferential cleavage of acac, especially in VII, arises from the strong trans-activating effect of the methyl group. In the absence of such activation, electrophilic cleavage of a carbon–gold bond is expected to occur at the less hindered methyl site.[30,31] The C-bonded adduct VII is even susceptible to hydrolysis and will slowly liberate free acetylacetone even from a chloroform solution, unless it is scrupulously dried and protected from air. Moreover, hydrolysis of VII is preceded by an exceptionally rapid and selective isotopic exchange of only the methine proton. Thus, the resonance of the methine proton at δ 4.60 disappeared immediately when D_2O was added to a chloroform solution of $Me_2(acac)AuPMe_2Ph$, and no other immediate change was detected in the NMR spectrum. Since the parent O-bonded $Me_2(acac)Au$ I does not undergo exchange under the same conditions, it is likely that the deuterium exchange proceeds directly via prototropic keto–enol tautomerism of the C-bonded adduct, e.g.,

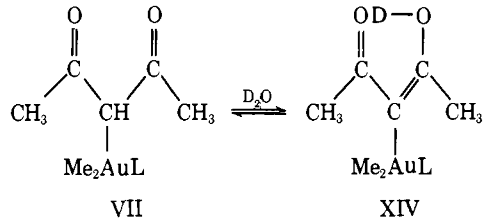


I

$$\longrightarrow \tfrac{1}{2}[\mathrm{Me_2AuCl}]_2 + \text{acacH} \quad (14)$$



$$+ \mathrm{H_2O} \longrightarrow \mathrm{Me_2Au(OH)L} + \mathrm{CH_3COCH_2COCH_3} \quad (16)$$



(17)

The subsequent hydrolysis is too rapid to allow sufficient concentrations of XIV to develop. However, structures analogous to XIV (in which the β-diketonato ligand is a C-bonded enol) have been presented for a series of hexafluoro- and trifluoroacetylacetonato complexes of manganese(I) carbonyls.[32]

Experimental Section

Materials. The phosphines $P(C_6H_5)_3$, $P(p\text{-}C_6H_4CH_3)_3$, $P(p\text{-}C_6H_4CH_3)(C_6H_5)_2$, $P(p\text{-}C_6H_4Cl)_3$, and $P(p\text{-}C_6H_4CH_3)_2(C_6H_5)$ were obtained from M and T Chemicals, Inc., and recrystallized from ethanol before use. $P(c\text{-}C_6H_{11})_3$, PPh_2Me, and $P(p\text{-}C_6H_4OCH_3)_3$ were prepared from phosphorus trichloride and the corresponding Grignard reagents in ether. The various β-diketonatothallium(I) complexes were synthesized either from thallous ethoxide or thallous carbonate and the free β-diketone followed by recrystallization from the appropriate solvent.[7] Acetylacetone, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, and hexafluoroacetylacetone were obtained from Eastman Organic Chemicals. Dimethylgold iodide was prepared from $AuCl_3py$ and methylmagnesium iodide.[5]

Dimethyl(acetylacetonato)gold. The preparative procedure by Brian and Gibson was followed,[5] using 2.95 g of $(Me_2AuI)_2$ and 3.00 g of Tl(acac). The subject compound was obtained in 88% yield, and readily purified by sublimation in vacuo as colorless needles, mp 81–82 °C.

Dimethyl(dibenzoylmethido)gold. A solution of $(Me_2AuI)_2$ (100 mg) in 5 mL of *n*-pentane was treated with a solution of Tl(dbm) (121 mg) in ethanol (5 mL) to give an immediate yellow precipitate. The TlI was removed by filtration and the slightly yellow solution evaporated in vacuo to give a crude product, yield 84 mg. The compound was recrystallized from *n*-pentane to afford a colorless crystal, mp 118 °C. Anal. Calcd for $C_{17}H_{17}O_2Au$: C, 45.34; H, 3.80. Found: C, 45.60; H, 3.90.

Dimethyl(benzoylacetonato)gold. A solution of $(Me_2AuI)_2$ (100 mg) in benzene (2 mL) was added to a solution of thallium benzoylacetonate (103 mg) in benzene (2 mL) to give an immediate yellow precipitate (TlI). After filtration, the solvent was removed under reduced pressure to give white crystals which were recrystallized from *n*-pentane, yield 62 mg, mp 40–41 °C. Anal. Calcd for $C_{12}H_{15}O_2Au$: C, 37.12; H, 3.89. Found: C, 37.31; H, 4.00.

Dimethyl(trifluoroacetylacetonato)gold. A solution of $(Me_2AuI)_2$ (243 mg) in acetone-d_6 (1 mL) was mixed with thallium trifluoroacetylacetonate (250 mg) to give a yellow precipitate which was removed by filtration. The resultant solution was transferred by trap to trap distillation using a liquid nitrogen cold bath. After repetition several times, the NMR spectrum of the solution indicated the presence of dimethyl(trifluoroacetylacetonato)gold [AuMe, δ 1.27 (s, 6 H); CH_3C, δ 2.17 (s, 3 H); CH, δ 5.73 (s, 1 H)]. Colorless crystals could be obtained from the acetone solution by carefully removing the solvent. The complex sublimes in vacuo at room temperature and has a strong characteristic odor. Sublimation occurred too readily for a reliable elemental analysis. Calcd for $C_7H_{10}F_3O_2Au$, mol wt 380. Mass spectrum *m/e* (rel intensity) 380 (6.5), 350 (1.9), 335 (1.1), 311 (2.1), 281 (5.5), 239 (4.2), 227 (5.0), 225 (5.9), 154 (9.0), 153 (12.3), 139 (2.7), 125 (2.5), 119 (2.6), 91 (1.7), 86 (3.4), 85 (43.9), 69 (19.1), 43 (100), 41 (3.3), 29 (6.5), 28 (15.8), 18 (64.7).

Dimethyl(hexafluoroacetylacetonato)gold. $(Me_2AuI)_2$ (35 mg) in $CDCl_3$ (1.0 mL) was treated with thallium hexafluoroacetylacetonate (41 mg) to give a yellow precipitate. Filtration afforded a clear solution, showing two proton NMR resonances for AuMe at δ 1.43 (s, 6 H) and $\geq$CH at δ 6.10 (s, 1 H). The subject compound has a strong odor similar to that of the trifluoroacetylacetonato complex. Isolation was not possible due to its ready sublimation. It codistilled even with low boiling solvents.

Reaction of Dimethyl(β-diketonato)gold Complexes with Phosphines. Acetylacetonato (acac) Complexes. $Me_2Au(acac)$ (25.0 mg) was placed in an NMR tube and dissolved with $CDCl_3$ (0.5 mL). A known amount of PPh_3 was added. The ^1H NMR spectrum of the solution showed resonances attributable to both $Me_2Au(acac)$ (δ 1.15 ppm (s), 2.00 (s), 5.35 (s)) and $Me_2Au(acac)PPh_3$ (δ 0.60 ppm (d, 8 Hz), 1.17 (d, 9 Hz), 1.90 (s), 4.50 (d, 12 Hz)). The dependence of the ratio of the intensities of these species under various conditions is listed in Table V. Other reactions of the dimethyl(β-diketonato)gold complexes with triphenylphosphine were carried out in a similar manner.

Benzoylacetonato (ba) Complexes. When $Me_2Au(C_6H_5COCHCOCH_3)$ (18.0 mg) was mixed with PPh_3 (12.1 mg) in $CDCl_3$, the original pair of separate AuMe singlets coalesced (cf. Figure 1) at 1.25 ppm. The other resonances showed slight broadening. In the presence of excess PPh_3 (95 mg), new lines attributable to the C-bonded ba complex were observed. ^1H NMR δ 0.56 ppm (d, 8 Hz) for cis AuMe; δ 1.23 (d, 8 Hz) for trans AuMe; δ 2.47 (s) for β-diketone-Me; δ 5.50 (d, 12 Hz) for methine proton; δ 7.3–8 (m) for Ph and PPh_3. The equilibrium constant K was estimated as 2.2 L mol^{-1} at room temperature.

Dibenzoylmethido (dbm) Complexes. $Me_2Au(C_6H_5COCHCOC_6H_5)$ (10.0 mg) was mixed with PPh_3 (41.0 mg) in $CDCl_3$. Only slight broadening of each line was observed in the same spectrum. No lines attributable to a C-bonded dbm compound were found. The equilibrium constant K is estimated to be less than 0.1 L mol^{-1}. The complex changes in the ^1H NMR spectrum accompanying the addition of PMe_2Ph to $Me_2(dbm)Au$ are summarized in the text.

Trifluoroacetylacetonato (tfacac) Complexes. Th ^1H NMR spectrum of $Me_2Au(tfacac)$ (30.0 mg) dissolved in $CDCl_3$ showed three singlets at 1.27, 2.17, and 5.73 ppm attributable to Me_2Au, CH_3, and CH of the trifluoroacetylacetone (tfacac) ligand, respectively. When less than 2 equiv of PMe_2Ph was added to this solution, new signals attributable to $Me_2Au(PMe_2Ph))_2{}^+$ tfacac$^-$ appeared, together with the original peaks of $Me_2Au(tfacac)$. The intensities of these new lines increased at the expense of the lines due to $Me_2(tfac)Au$ when increasing amounts of PMe_2Ph were added. Finally, the NMR spectrum of a 1:2 mixture of $Me_2Au(tfacac)$ and PMe_2Ph showed only the resonances due to the new species. ^1H NMR δ 1.18 (m) for MeAu and 1.77 ppm (d, 10 Hz) for PMe_2Ph due to a $A_3XX'A_3$ multiplet;[19] and δ 2.40 (s) and 5.25 ppm (s) for CH_3 and CH of the trifluoroacetylacetonato ligand as well as δ 7.5 ppm (m) for the phenyl group in PMe_2Ph. The addition of more PMe_2Ph (4 equiv) caused the methyl doublet coordinated to a PMe_2Ph to shift slightly to higher fields (~1.57 ppm) and the coupling constant to become smaller (~6 Hz). The MeAu multiplet coincidentally became a sharp singlet. However, no further change was observed for the trifluoroacetylacetonato moiety.

In a similar manner, the reaction of $Me_2Au(tfacac)$ (30.0 mg) with PPh_3 (0–6 equiv) also showed behavior analogous to that observed above. However, most of the lines in the spectrum were broader than those obtained with PMe_2Ph. All of the original signals broadened progressively with increasing amounts of added PPh_3, and a new broad resonance assignable to a MeAu species appeared at 1.1 ppm. When 1.5 equiv of PPh_3 was added, only three very broad peaks remained centered at 1.2, 2.3, and 5.4 ppm. In the presence of more PPh_3 (2–2.7 equiv), a broad signal for MeAu was observed at 1.2 ppm together with two relatively sharp singlets for the trifluoroacetylacetonato group at 2.53 and 5.37 ppm. (This spectrum is tentatively assigned to $[Me_2Au(PPh_3)_2{}^+]$tfacac$^-$. The difference in chemical shifts for the β-diketonato anion in the PPh_3 and PMe_2Ph complexes may be attributable to a strong Coulombic interaction within the ion pair.)

The reaction of $[Me_2Au(PPhMe_2)_2]^+$tfacac$^-$ with CF_3COOH (excess) showed no apparent change in ^1H NMR spectrum, except for shifts in the trifluoroacetylacetonato resonances to that of free trifluoroacetylacetone at 2.2 and 5.9 ppm.[33]

Hexafluoroacetylacetonato (hfacac) Complexes. $Me_2Au(CF_3COCHCOCF_3)$ was prepared in situ from $(Me_2AuI)_2$ (35.3 mg) and $Tl(CF_3COCHCOCF_3)$ (41.0 mg) in $CDCl_3$. After filtration of TlI, the NMR spectrum of the clear solution showed sharp resonances at δ 1.43 (s) and 6.10 (s). When PPh_3 (26.2 mg) was added to the solution, the original signals disappeared and new broad peaks appeared at 1.17 ppm for the AuMe groups and a singlet at 5.63 ppm for the methine proton in hfacac.

Isolation of Dimethylacetylacetonato(dimethylphenylphosphine)gold. $Me_2Au(acac)$ (200 mg) in benzene was treated with dimethylphenylphosphine (85 μL) to give a colorless solution. The solvent was removed under reduced pressure to afford a white solid which was recrystallized from the mixture of toluene and *n*-pentane at −20 °C, yield 165 mg (58%), mp 95 °C. Anal. Calcd for $C_{15}H_{24}PO_2Au$: C, 38.80; H, 5.21; P, 6.67. Found: C, 38.82; H, 5.32; P, 6.78. The infrared spectrum in a KBr disk showed three bands in the carbonyl region at 1618 (vs), 1653 (m), and 1713 cm^{-1} (w). However, in chloroform solution only a broad band showing definite maxima at 1630 and 1660 cm^{-1} was observed, together with a shoulder at approximately 1590 cm^{-1}. (Although C-bonded dichlorobis(acac)platinate(II) shows only two bands at 1650 and 1626 cm^{-1} due to symmetric and antisymmetric C=O stretching bands (G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 440 (1967)), more than two bands may be possible in other C-bonded acac complexes, since several conformational isomers are known.[27b] Alternatively, some XIV may be present in the solid.)

Reaction of $Me_2(acac)(PPhMe_2)Au$ with HCl. $Me_2(acac)(PPhMe_2)Au$ (25.0 mg) dissolved in benzene (1.0 mL) was placed in a round-bottom flask and sealed with a serum cap under vacuum. Concentrated hydrochloric acid (14 μL) was added through the serum cap. No gas was evolved. The presence of free acetylacetone (80% yield) in solution was determined by gas chromatography and ^1H NMR analysis. The gold containing product was assigned as *cis*-$Me_2AuClPPhMe_2$ from its ^1H NMR spectrum[30] (0.93 ppm (d, J = 8 Hz) for cis AuMe, 1.67 ppm (d, 9 Hz) for trans AuMe, 1.45 ppm (d, J = 10 Hz) for PMe, and 7–8 ppm for PhP (in benzene relative to internal Me_4Si)).

Reaction of $Me_2Au(acac)$ with HCl. $Me_2Au(acac)$ (60.0 mg) in benzene (1.0 mL) was treated with concentrated HCl aqueous solution

(47 μL). No gas was evolved. Equal amounts of free acetylacetone and $(Me_2AuCl)_2$ were detected by NMR. By removing all the solvent under reduced pressure, $(Me_2AuCl)_2$ was recovered as a white solid: ^1H NMR δ 1.27 ppm (s, AuMe) in CCl_4; mp 80 °C dec (lit. δ 1.28 (s), mp 79–80 °C).[6]

Thermal Decomposition of Dimethylgold Compounds. Me_2(acac)-AuPPhMe_2 (43.0 mg) was placed in a round-bottom flask, which was evacuated and sealed. The flask was heated to 140 °C whereupon a brown oil and white crystals were deposited on the walls. Trace amounts of methane, ethane, and 3-methylpentane-2,4-dione (~0.005 mmol) were detected by gas chromatography.

Me_2Au(acac) in the solid state could not be decomposed under vacuum owing to its ready sublimation. Furthermore, in benzene solution, each compound did not undergo decomposition at 70 °C for a day. The starting material was recovered.

Reaction of Dimethylacetylacetonato(dimethylphenylphosphine)gold with Water, Deuterium Oxide, and Ethanol. A solution of Me_2(acac)-AuPPhMe_2 (25.0 mg) in purified $CDCl_3$ or $CHCl_3$ (see below) contained in a sealed NMR tube in vacuo showed no spectral change for 2 days at room temperature. However, when commercial $CDCl_3$ or reagent $CHCl_3$ (with 0.75% EtOH as a preservative) was used as a solvent, the compound was hydrolyzed by trace amounts of water or ethanol within 24 h at room temperature to afford free acetylacetone (^1H NMR CH_3, δ 2.07 (s), CH, δ 5.50 (s), and OH, δ 15.6 (br) for the enol form and CH_3, 2.20 (s) and CH_2, 3.60 ppm (s) for the keto form) and a gold compound (see below). In separate experiments, it could be shown that protonolysis was enhanced by the addition of ethanol or water, the ^1H NMR spectrum of authentic free acetylacetone in $CHCl_3$ solution showing resonances at 2.07 (s), 5.50 ppm (s) for the enol form and 2.20 (s) and 3.60 ppm (s) for the keto form. The hydroxyl resonance was not observed due to the fast exchange with H_2O or EtOH. In $CDCl_3$ solution, no resonance for the methine proton was detected: instead the $CHCl_3$ impurity increased. The gold species obtained on protonolysis may be identified as a *cis*-Me_2Au(P-Me_2Ph)X species (where X = OH or OEt) from its ^1H NMR spectrum.[30] ^1H NMR 0.55 ppm (d, J = 9 Hz) for cis MeAu, 1.25 ppm (d, J = 9 Hz) for trans MeAu, 1.90 ppm (d, J = 10 Hz) for PPhMe_2, and 7.5 ppm (m) for PMe_2Ph. $^{31}P\{^1H\}$ NMR +1.6 ppm from H_3PO_4 (external). Similar changes were also observed when L = PMePh_2 and PPh_3 were used. (Use of excess PPh_3 was necessary with the latter complex.) ^1H NMR 0.33 (9 Hz) and 1.34 ppm (8 Hz) for the PPh_3 complex and 0.37 (9 Hz) and 1.27 ppm (8 Hz) for the PMePh_2 complex.

Reagent grade chloroform (Mallinckrodt, Analytical Reagent) was shaken vigorously with concentrated sulfuric acid and washed several times with water. It was dried over calcium chloride and then refluxed over phosphorus pentoxide for several hours in the dark under nitrogen. After distillation (61 °C), it was stored in a Schlenk tube in the dark over P_2O_5 and transferred by bulb-to bulb distillation in vacuo as needed.

The C-bonded acac complex Me_2(acac)AuPMe_2Ph is quite stable in benzene solution, remaining unchanged for 6 days at room temperature. In the presence of ethanol, however, it slowly hydrolyzed as mentioned above.

A solution of Me_2Au(acac)PMe_2Ph (25 mg) in $CDCl_3$ was treated with D_2O (0.1 mL) and the NMR spectrum recorded immediately. Only slight hydrolysis occurred, but the resonance at δ 4.60 (d) due to the methine proton disappeared completely. No other changes were observed. Similarly, no spectral change was observed when Me_2Au(acac) (25.0 mg) was treated with D_2O (0.1 mL) in $CDCl_3$ under the same conditions.

Spectral Measurements. The ^1H NMR spectra were recorded on a Varian EM-360, Varian XL-100 FT, or a Varian HR-220 spectrometer. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-100 FT spectrometer. Infrared spectra were recorded on a Perkin-Elmer 467 spectrometer and calibrated with a polystyrene film. Mass spectra were obtained on a Varian CH7 spectrometer. Gas chromatographic analyses were carried out with (2 ft) Porapak Q and (10 ft) Apiezon columns.

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(21) Interestingly both lines (CH_3 and CH) due to trifluoroacetylacetonate in the ion pair XII show greater broadening (but unshifted) than others in a solution containing 0.5 equiv of PMe_2Ph.

(22) The formation of adduct may be indicated by the change in the infrared spectrum attendant on the addition of triphenylphosphine (see Table II).

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(27) (a) For keto–enol tautomerism in β-diketones, substitution of electron-donor groups on the central carbon lowers the enthalpy change whereas electron-acceptor groups increase it.[28] With this interpretation in mind (barring steric effects and metal coordination), Me_2AuL is a better donor than Me_2Au if only electronic effects are stressed. (b) Two principal conformations are known for C-bonded acac in crystals. (For summary see M. Horike, Y. Kai, N. Yasuoka, and N. Kasai, *J. Organomet. Chem.*, **72**, 441 (1974).) Interconversion between these conformers is probably fast in solution (compare E. A. Noe and M. Raban, *J. Chem. Soc., Chem. Commun.*, 165 (1976) even for interconversion between *Z,Z* and *E,Z* forms of the hindered ions).

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Low-Temperature Infrared Studies of Some Chloroethylene–Ozone Reactions

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Abstract: The reactions of ozone with the haloethylenes C_2Cl_4, CH_2CCl_2, *cis*- and *trans*-CHClCHCl, and CH_2CHCl have been examined by low temperature infrared spectroscopy. An unstable primary ozonide was detected only from vinyl chloride. It did not rearrange into a secondary ozonide but decomposed instead into HCOOH, HCl, CO_2, polymer, and presumably CO and O_2. Two isomeric forms of the primary ozonide were present. Other solid chloroethylenes gave unstable π complexes, characterized by a weak infrared band at 1030 cm^{-1}, which reverted to the reactants or produced other products upon warming. The present results support a non-Criegee mechanism as a dominant path of ozonolyses of chloroethylenes except in the case of vinyl chloride, where both the ozonide and nonozonide reaction paths are nvolved.

An earlier report[1] from this laboratory described how a low temperature infrared spectroscopic technique can be used to gain mechanistic information on reactions of ozone with simple olefins. In particular, when these reactions were carried out at temperatures near the boiling point of liquid nitrogen, many gave two unstable primary products. One product was identified as a π complex on the basis of its decomposition back to the reactants upon warming and since its O_3-group frequencies and the temperature dependence of such bands were similar to those observed with the yellow-colored O_3–toluene π complex. The second product was a primary ozonide (1,2,3-trioxolane) which on warming isomerized into the better known and more stable secondary ozonide (1,2,4-trioxolane) or decomposed into acids, carbonyl products, and polymers.

In the present investigation the above spectroscopic method was used to examine the reactions of ozone with C_2Cl_4, CH_2CCl_2, *cis*- and *trans*-CHClCHCl, and CH_2CHCl. Studies of the gas phase ozonolysis of C_2Cl_4,[2] CH_2CCl_2,[3] and CHClCHCl[4] have already been reported from our laboratory and a preliminary note on the CH_2CHCl reaction[5] has appeared. Also, Williamson and Cvetanović[6] have reported the ozonolyses of chloroethylenes in CCl_4 solutions.

Experimental Section

The liquid chloroethylenes C_2Cl_4 (J. T. Baker Co.), CH_2CCl_2 (Fisher Scientific Co.), and CHClCHCl (Aldrich Chemical Co.) were degassed several times and distilled in a vacuum line into storage vessels. The stated purity of each isomeric CHClCHCl was better than 98% and was satisfactory for our infrared studies. The infrared spectra of C_2Cl_4 and CH_2CCl_2 also showed no impurity absorption bands under our experimental conditions. Matheson Co. was the source of CH_2CHCl which was distilled in the vacuum line at reduced temperatures and pressures to give a sample with no apparent impurities. Pressures of the haloethylenes were measured with an oil manometer containing Kel-F No. 3 oil (3M Co.). A Tesla coil discharge of purified oxygen gas cooled to liquid nitrogen temperature gave ozone for each experiment. Excess oxygen in an ozone sample was removed by pumping on the mixture at liquid nitrogen temperature with a glass single-stage oil diffusion pump.

Our Pyrex glass low temperature infrared cells were similar to that used previously.[1] A copper–constantan thermocouple attached to the window holder frame permitted estimation of the sample window temperatures. Generally, the olefin in excess was condensed on the low temperature window first, and then ozone was added to the cell. Under normal experimental conditions, ozone did not condense on the window but accumulated instead on the copper section of the cold finger which was in direct contact with the liquid nitrogen. When the liquid nitrogen refrigerant was removed, however, the ozone distilled over to the low temperature window and imparted a blue color to it. Recooling of the cell, however, caused the ozone to distill back to the colder copper sections of the cell. In addition to the initial spectrum taken before the first warming of the sample, spectra were recorded repeatedly after warming to various temperatures and recooling each time to liquid nitrogen temperature. The infrared spectra were taken on Perkin-Elmer Model 225 and 521 grating spectrophotometers.

Results

C_2Cl_4. When solid C_2Cl_4 at liquid nitrogen temperature was exposed to ozone, a new infrared band which was weak but sharp appeared at 1030 cm^{-1}. On warming the solid this band grew weaker until it disappeared at temperatures near −130 °C. By appropriately controlling the temperature of the sample window the 1030-cm^{-1} band could be made to appear or disappear reversibly. Other absorption bands in the spectrum remained unchanged during this warming process. No evidence of an ozonolysis reaction was observed on further warming of the solid to about −80 °C where the sample started to sublime off the low temperature window. Neither was an ozonide observed from the liquid phase reaction of C_2Cl_4 with ozone. The products in this case were similar to those observed from the gas phase reaction[2] and consisted mostly of CCl_2O and CCl_3CClO with a smaller amount of $\overline{CCl_2CCl_2O}$. Traces of HCOOH and an explosive solid residue were also detected.

CH_2CCl_2. As in the tetrachloro compound, the 1030-cm^{-1} band was the only new feature in the initial spectrum of solid CH_2CCl_2 after it was exposed to ozone at liquid nitrogen temperature. This new band grew weaker on warming and was no longer observable at temperatures near the melting point