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A NEW TYPE OF ORGANOGOLD COMPOUND

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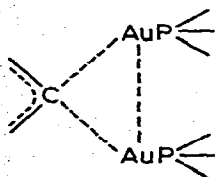
Summary

Organogold complexes of the type $[R(AuPPh_3)_2]^+ BF_4^-$ (I) containing a univalent gold atom and an Au—Au fragment have been synthesised. They are formed by the interaction of $RAuPPh_3$ with tetrafluoroboric acid or organomercury compounds with CH_3AuPPh_3 and HBf_4 . Their structures have been identified through 1H NMR, ^{31}P NMR, IR, UV (and X-ray for $[C_5H_5-FeC_5H_4(AuPPh_3)_2]^+ BF_4^-$). When acted upon by nucleophilic reagents, the complexes liberate the cation $AuPPh_3^+$. Organometallic compounds promote an exchange of organic ligands.

Introduction

Organogold compounds reported in the literature to date belong to one of two types, $LAuR$ (where L is a phosphine, amine or isocyanide ligand) or (olefin)· $AuCl$. These structures are typical of organometallic derivatives of transition metals.

The present paper reports a new type of organogold compound, in which there are two gold atoms per molecule, and these atoms bonded with one another directly*:



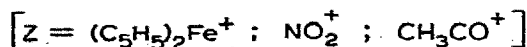
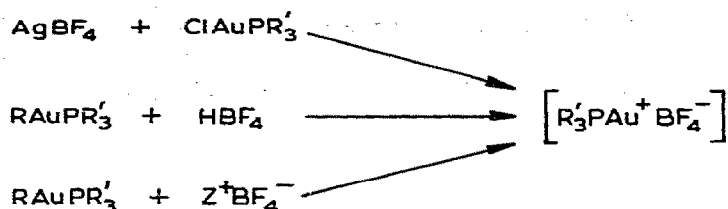
Complexes synthesised have the general formula $[R(AuPR'_3)_2]^+ BF_4^-$ (I) where R is C_6H_5 , $p-CH_3C_6H_4$, $CH_2=CH$, $C_5H_5FeC_5H_4$, $C_5H_5FeC_5H_3Cl$, $C_5H_5FeC_5H_3OCH_3$ or $C_5H_5FeC_5H_3CH_2N(CH_3)_2$.

* A similar structure has been identified recently [1], in an X-ray study of rather inaccessible osmium and copper cluster compounds.

Results and discussion

Preparation

Compounds containing two gold atoms per molecule are formed when the reactive, coordinatively unsaturated moiety $+AuPR'_3$ is generated in a solution containing the organogold compound $RAuPR'_3$. The counterion was BF_4^- in almost all cases. In principle, any anions which form no covalent bond with the univalent gold cation may be used*. The reactive entity $AuPR'_3$ was generated as follows:



The most convenient route of the synthesis of complexes (I) is by the action of tetrafluoroboric acid on the respective organogold derivative:



The yields are close to quantitative.

Structures

IR, UV and NMR spectroscopic evidence has been used. An X-ray study of the very stable ferrocenyl complex $[C_5H_5FeC_5H_4(AuPPh_3)_2]^+BF_4^-$ (II) has been made by Struchkov, Andrianov and Rosinskaya and the structure and some of the parameters are shown in Fig. 1.

The existence of a gold-gold bond is verified by the fact that the Au—Au distance in (II) is shorter (2.77 Å) than that in metallic gold (2.88 Å) while the angle $Au_1C_1Au_2$ is appreciably less than the tetrahedral angle. The aromatic ferrocene system in the complex acts as a bridge between the two gold atoms. The distances $Au_1—C_1$ and $Au_2—C_1$ are close to each other and to the sum of covalent radii of the atoms, 2.2 Å. The plane of the triangle $C_1—Au_1—Au_2$ is approximately perpendicular to that of the cyclopentadienyl ring**.

The X-ray and ^{31}P NMR data obtained for (II) show that the $AuPR'_3$ groups are not equivalent, being positioned unsymmetrically with respect to the ferrocenyl ring. The ^{31}P NMR spectrum of (II) exhibits two signals of the same intensity due to the two non-equivalent phosphorus atoms ($\delta -36.4$ ppm and $\delta -38.2$ ppm; in acetone with H_3PO_4 as external standard). The non-equ-

*Thus we have synthesised [2] the sulphate $[C_5H_5FeC_5H_4(AuPPh_3)_2]_2^+SO_4^{2-}$

**The unexpectedly short Au—Fe distance (2.82 Å) should be noted. The Au—Fe interaction may constitute a chemical bond although it does not appreciably distort the ferrocene system: the dihedral angle formed by the cyclopentadienyl planes being merely 13° while the Fe—C bond lengths are close to those in ferrocene, i.e. 2.08 Å. The Au—Fe interaction does not perturb the electronic properties of the Fe atom significantly, the Mössbauer parameters (isomer shift δ 0.77 mm/s, quadrupole splitting ΔQ 2.30 mm/s at 80 K) being typical of ferrocene and its derivatives.

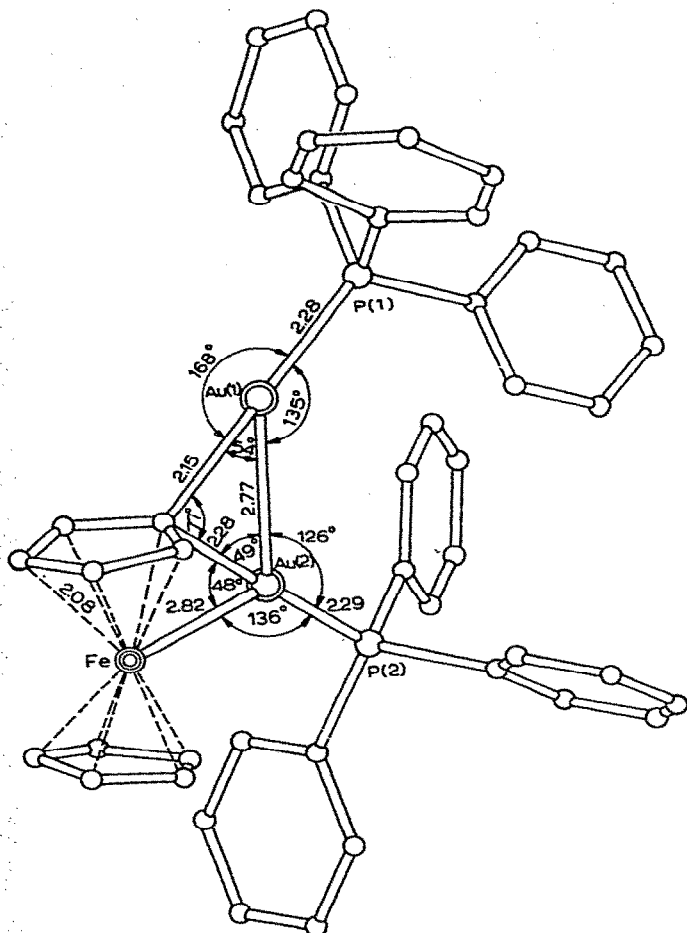


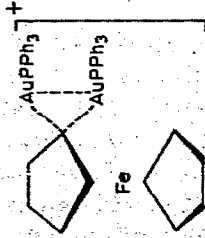
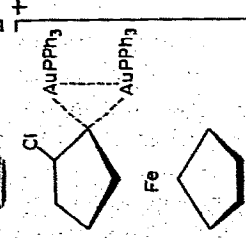
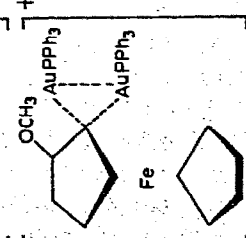
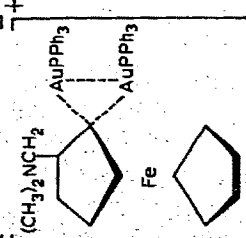
Fig. 1. The structure of $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4(\text{AuPPh}_3)_2]^+\text{BF}_4^-$.

ivalence vanishes in the tolyl compounds, the spectrum of $[\text{CH}_3\text{C}_6\text{H}_4(\text{AuPPh}_3)_2]^+\text{BF}_4^-$ (VI) taken at -80 to $+25^\circ$ containing only one signal (δ -35.2 ppm at -80° , in acetone, -37.0 ppm at $+25^\circ$ in CH_2Cl_2 , with H_3PO_4 as external standard in both cases) while the PMR data for $[\text{CH}_3\text{C}_6\text{H}_4(\text{AuPPh}_2\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)_2]^+\text{BF}_4^-$ (VII) show that the ferrocenylphosphine groups are identical (see Table 1).

The interaction of the carbon C_1 with the two gold atoms is, in our opinion, a three-centre two-electron bond formed at the expense of the electron pair of the $\text{Au}-\text{C}$ bond which was present in the initial organogold derivative. The UV and IR spectra of (VI) and (VII) display no alterations usually associated with the benzenonium ion formation and assigned to the disturbance of aromaticity, which justifies our suggestion as to the nature of the bond between C_1 and the two gold atoms. This bond alone, however, could hardly make the complexes so stable for although Al_2Ph_6 , for example, is dimeric in the crystalline state it readily dissociates in solution [3]. We believe that the high stability of (I) is due to the formation of a gold-gold bond. Recently [1]

(continued on p. 136)

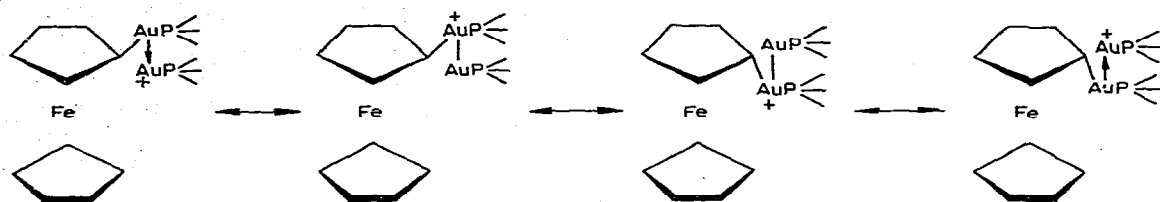
TABLE I
PMR SPECTRA OF ORGANOGOLD COMPOUNDS

N	Compound	Proton chemical shifts ^d		Solvent		
		C ₅ H ₅	C ₅ H _{5-n}			
(II)		4.55 (s)	H ₂ , H ₅ 4.17 (t)	CH ₃	CHCl ₃	
(III)		4.58 (s)	H ₅ 4.10 (m)	—	CHCl ₃	
(IV)		4.59 (s)	H ₅ 3.83 (m)	3.65 (s)	CHCl ₃	
(V)		4.48 (s)	H ₅ 4.22 (m)	H ₃ 5.23 (m) H ₄ 5.07 (t)	2.30 (s)	CHCl ₃

(VI)		2.49 (s)				CH ₂ Cl ₂
(VII)		2.50				CH ₂ Cl ₂
(VIII)	C ₅ H ₅ FeC ₅ H ₄ AuPPh ₃	4.06	(s) H ₂ , H ₃ , H ₄ , H ₅ ^b	4.23 (t) two protons	4.60 (t) two protons	CCl ₄
(IX)	C ₅ H ₅ FeC ₅ H ₃ (Cl)AuPPh ₃	4.03	(s) H ₂ , H ₃ , H ₄ , H ₅ ^b	3.90 (t) two protons	4.16 (t) two protons	CHCl ₃
(X)	C ₅ H ₅ FeC ₅ H ₃ (OCH ₃)AuPPh ₃	4.18	(s) H ₃ , H ₄ , H ₅ ^b	3.93(m)	4.09(m)	CHCl ₃
(XI)	C ₅ H ₅ FeC ₅ H ₃ (CH ₂ N(CH ₃) ₂)AuPPh ₃	4.24	(s) H ₃ , H ₄ , H ₅ ^b	3.77 (m)	3.93 (t)	CHCl ₃
(XII)	p-CH ₃ C ₆ H ₄ AuPPh ₃	4.10	(s) H ₃ , H ₄ , H ₅ ^b	4.06 (m)	4.23 (t)	CH ₂ Cl ₂
(XIII)	p-CH ₃ C ₆ H ₄ AuP(Ph) ₂ C ₅ H ₄ FeC ₅ H ₅	4.36	(s) H ₂ , H ₃ , H ₄ , H ₅ ^b	4.46 (t) two protons	4.60 (t) protons	CHCl ₃
(XIV)	C ₅ H ₅ FeC ₅ H ₅ SAuPPh ₃	4.06	(s) H ₂ , H ₃ , H ₄ , H ₅ ^b	4.00 (t) two protons	4.26 (t) two protons	CH ₂ Cl ₂
(XV)	[C ₅ H ₅ FeC ₅ H ₄ S(AuPPh ₃) ₂] ⁺ BF ₄ ⁻	4.16	(s) H ₂ , H ₃ , H ₄ , H ₅ ^b	4.24 ^c	4.43 ^c	CH ₂ Cl ₂

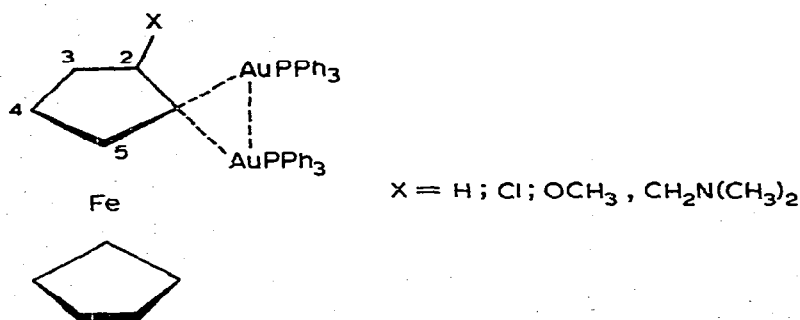
a₅ = singlet; t = triplet; m = multiplet. bThe proton signals of the substituted cyclopentadienyl were not assigned. cPoorly resolved.

such three-centre two-electron bonds involving metal—metal bonds were found in an X-ray study of multicomponent osmium and copper clusters. In terms of canonical structures, the structure of (II) may be written as follows:



In this way, compounds of the type (I) may be regarded as complexes of the univalent gold cation containing two stabilising ligands, PR'_3 and RAuPR'_3 .

When discussing PMR spectra of (I), a comparison with the initial compounds RAuPR'_3 is useful. The most convenient quantities for comparison are the methyl proton chemical shifts in the tolyl derivatives ($\text{R} = \text{CH}_3\text{C}_6\text{H}_4$) and the cyclopentadienyl proton chemical shifts in the ferrocenyl derivatives [$\text{R} = \text{C}_5\text{H}_5\text{FeC}_5\text{H}_3\text{X}$ where $\text{X} = \text{H}, \text{Cl}, \text{OCH}_3, \text{CH}_2\text{N}(\text{CH}_3)_2$]. The ^1H NMR proton signals of the substituent R are markedly shifted downfield when RAuPR'_3 is replaced by the complex cation (I) indicating that the acceptor properties of the substituent are significantly increased (see Table 1). Also, PMR spectra of the ferrocenyl complexes are very similar to the spectra of α -ferrocenylcarbonium ions since, (a) the proton signals of the unsubstituted cyclopentadienyl are shifted unusually strongly downfield in contrast to many other substituted ferrocenes and (b) the mutual arrangement of the proton signals in the substituted cyclopentadienyl are similar. As with α -ferrocenylcarbonium ions (and in contrast to other derivatives), the H_3 and H_4 signals in (I) are situated at the lowest field values (Table 1, Fig. 2) while the H_2 and H_5 signals occur at higher fields.



This assignment is based on the fact that when a substituent is introduced in a position adjacent to the gold atom the spectrum exhibits two proton signals which are always located at lower fields. These correspond to H_3 (a multiplet at lowest field) and H_4 (a triplet with two vicinal constants, $J(3-4)$ and $J(4-5) 2.4$ Hz). At the same time, just the H_5 signal is observed in the substituted complexes at higher fields. To explain the spectral similarities displayed by the ferrocenyl derivatives, the canonical structures mentioned above may be employed.

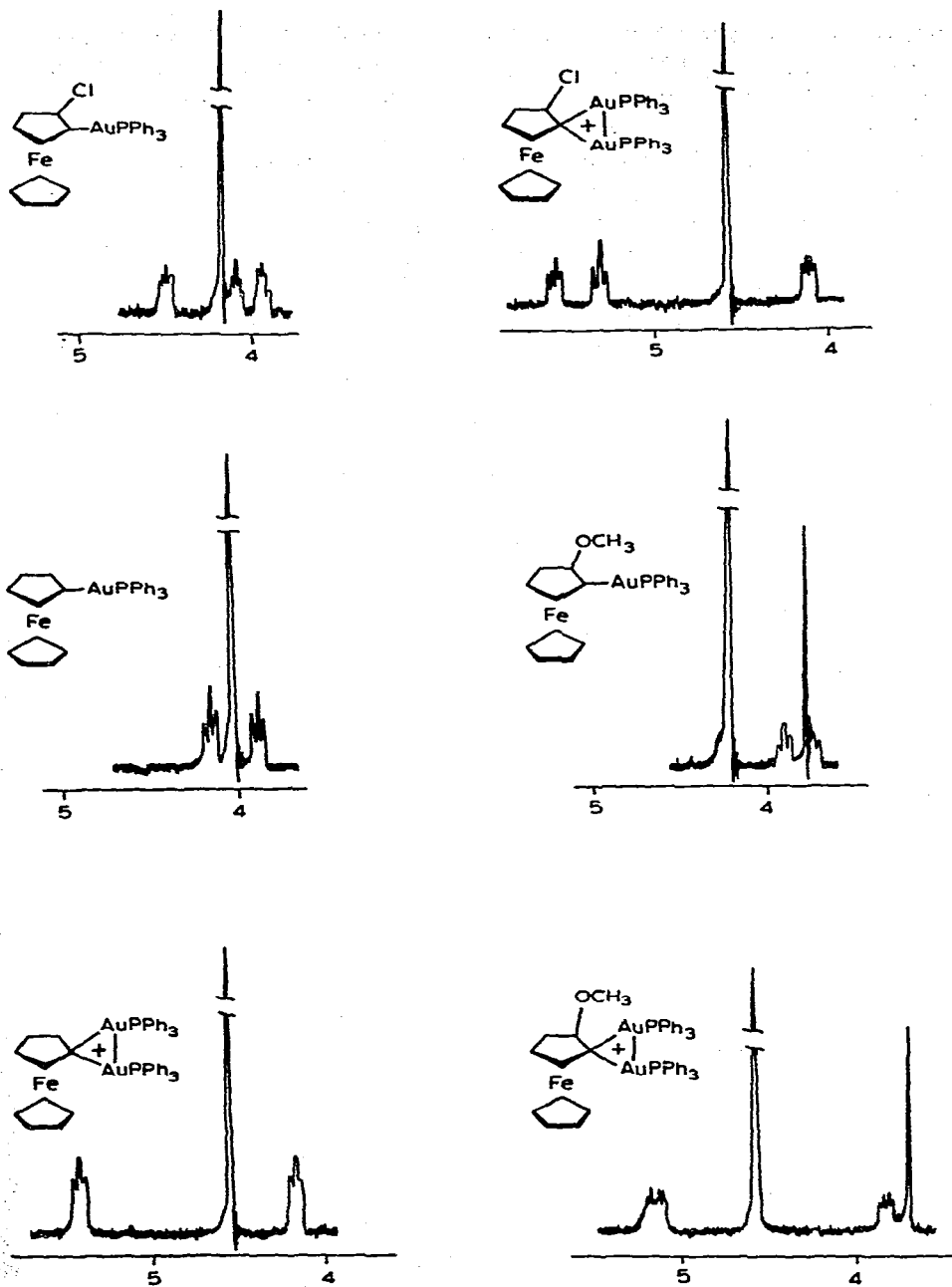


Fig. 2. PMR spectra of some organogold ferrocene derivatives and related complexes.

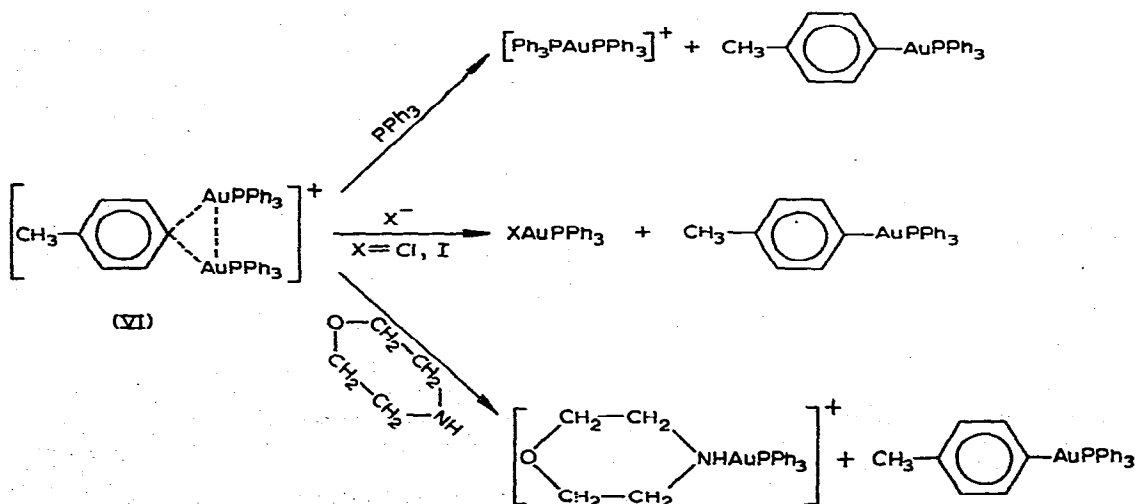
The stability series found for the organogold complexes (I) coincides with that for the carbonium ions RCH_2^+ . Thus, the ability to stabilise the adjacent cation site, a characteristic feature of ferrocene, results in greater stability for the ferrocenyl complexes in comparison with the aryl complexes.

In addition to PMR, UV spectra have been used to characterise the acceptor properties of a substituent in the group R. At 350 - 550 nm, the $d-d$ iron transitions are shifted markedly towards longer wavelengths when the initial organogold compounds are replaced by the complex cations (II) - (V). The spectra of complexes (II) - (V) resemble the spectra of ferrocene derivatives containing strong electron-withdrawing substituents (nitro, benzoyl).

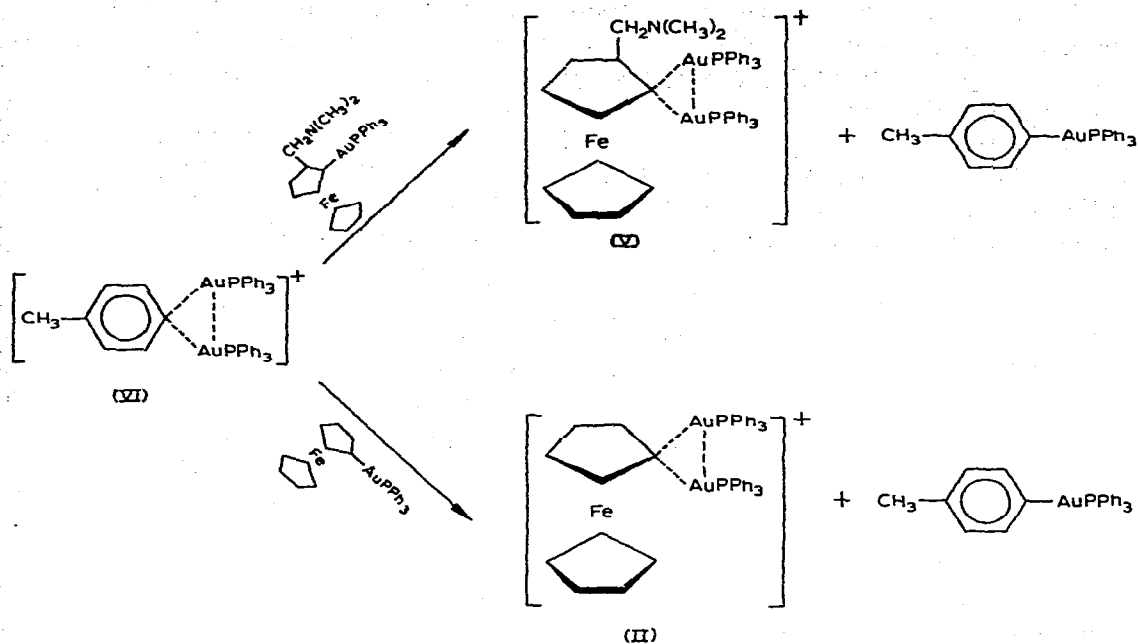
NMR has also been used for solving structural problems when the reactive $^+AuPR'_3$ moiety could be coordinated to a heteroatom rather than to the gold atom in $RAuPR'_3$, the heteroatom supplying its electron pair for binding the univalent gold cation. Thus it was found, for example, that the dimethylaminoferrocenyl complex (XIII) has a similar structure to (I) since the cyclopentadienyl proton chemical shifts are close to those of the complex (II) while the $(CH_3)_2N$ methyl chemical shifts remain practically unaffected.

Reactions

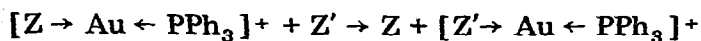
The novel organogold derivatives described in this paper undergo reactions involving either one, or both, of the $AuPR'_3$ groups. Thus complexes (I) very readily undergo $^+AuPR'_3$ transfer reactions. These include regeneration of the initial $RAuPR'_3$, a reaction which may be regarded as the reverse of the synthesis of (I). This occurs readily in the presence of nucleophiles such as phosphines, amines and halides:



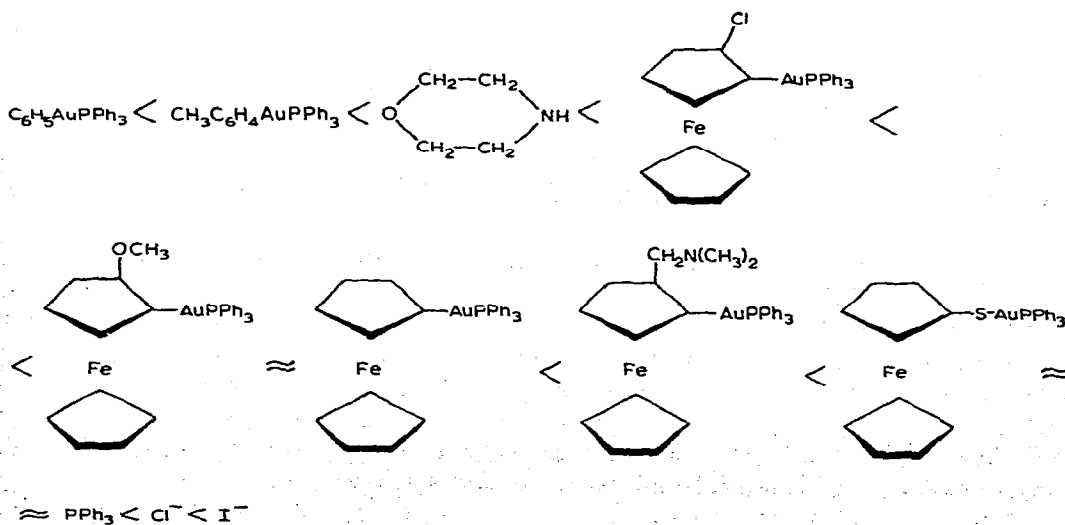
The $^+AuPR'_3$ moiety may also be transferred to other organogold compounds.



More than half of the new organogold compounds described here were synthesised through AuPPh_3^+ transfer reactions. A number of other exchanges have also been carried out involving exchange of a gold-containing ligand for one more strongly bonded.



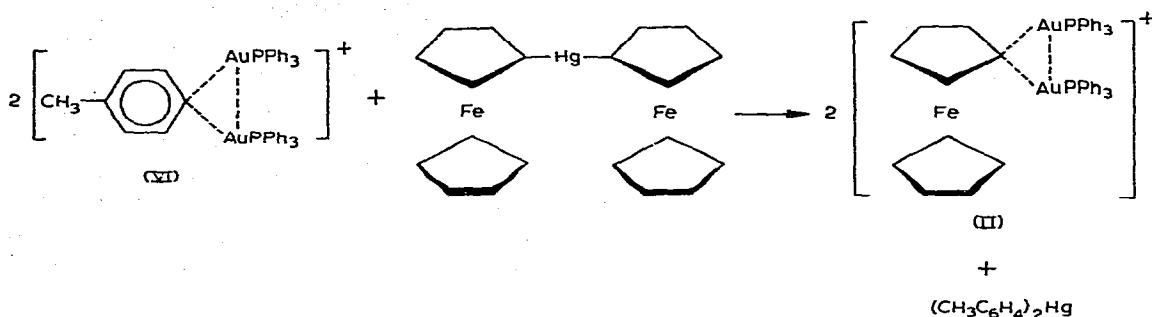
In this way, a donor strength series has been determined for ligands relative to AuPPh_3^+ , i.e.



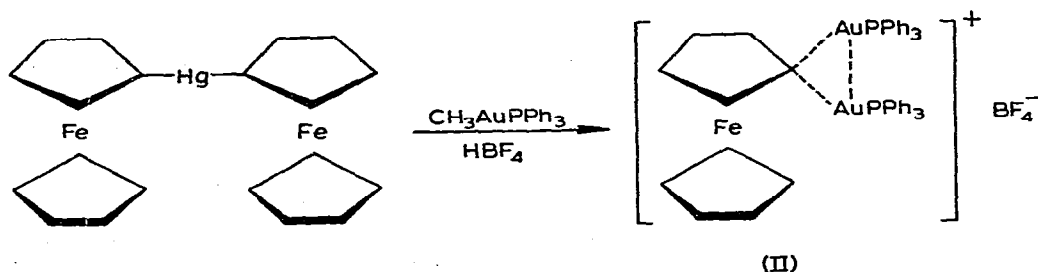
In this series, the Z—Au bond strength in the complex $[\text{Z} \rightarrow \text{Au} \leftarrow \text{PPh}_3]^+ \text{BF}_4^-$ increases from left to right, the stability of the complexes in the solid state or

in solution increasing in the same sequence. Mild reaction conditions and high product yields allow the use of these reactions for the synthesis of new organogold complexes containing various organoelement ligands (including further organogold ligands).

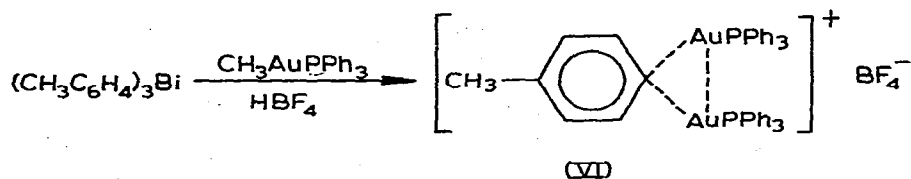
Another type of transformation is represented by the reactions of complex (I) with organometallic compounds, in which both the AuPPh_3 groups are affected. Thus, the tolyl complex (VI) reacts with diferrocenylmercury to give a high yield of ditolylmercury and the ferrocenyl complex (II):



The reaction consists in an interchange of organic radicals between the organometallic compounds. The tolyl complex (VI) also reacts with ferrocenylmercury chloride in a similar manner, although in this case the process is somewhat obscured by the chloride-induced partial decomposition of the complex. Complexes of type (I) are also formed when a mixture of methylgold and an organomercury compound is used in the reaction with HBF_4^* :



The latter reaction has been also carried out with organobismuth compounds.



Reactions of this type are a promising tool for the synthesis of new organogold complexes containing two gold atoms in a molecule.

* Methylgold does not react with HBF_4 in the absence of organometallics.

Experimental

Analytical data for the new compounds are collected in Table 2.

Synthesis of $[R(AuPPh_3)_2]^+ BF_4^-$ (I)

A solution of HBF_4 in ether was added to tolyl(triphenylphosphine)gold [4] (0.40 g, 0.73 mmol) until the white crystalline solid precipitated completely. The precipitate was filtered and carefully washed with ether to give 0.38 g (95%) of (VI) which was slowly reprecipitated from acetone with hexane/ether (1/2).

A similar technique allowed us to convert the respective organogold compounds [5 - 7] into the complexes (II) - (IV), (VII), (XVI) and (XVII). Their melting points and elemental analyses are listed in Table 2. As a rule, the complexes are moderately soluble in acetone, chloroform, methylene chloride and acetonitrile, and practically insoluble in ether, benzene and tetrahydrofuran. The complexes (XVI) and (XVII) are extremely unstable in solution.

Synthesis of $[C_5H_5FeC_5H_4(AuPPh_3)_2]_2SO_4$ (IIa)

Compound (IIa) was synthesised using the same conditions as those employed for the synthesis of (II) through the action of an ether solution of H_2SO_4 upon ferrocenyl(triphenylphosphine)gold. The yield obtained was 93%, see Table 2. The UV as well as PMR spectra of (IIa) and (II) are identical.

The action of sodium chloride upon complexes (I)

A solution of (II) (0.20 g, 0.17 mmol) in CH_2Cl_2 was shaken for 5 min with a solution of NaCl in water when the red organic layer turned yellow. The organic layer was separated, dried over potassium carbonate and diluted with fourfold excess of hot hexane to give $ClAuPPh_3$, 0.078 g (94%), m.p. 242 - 244° (lit. [8] m.p. 243 - 244°). The filtrate was cooled down intensely to give ferrocenyl(triphenylphosphine)gold, 0.124 g (95%) which decomposes above 150° (lit. [5]: dec. > 150°).

The complexes (VI) and (XVII) react with sodium chloride in a similar manner giving yields of the respective organogold derivatives $RAuPPh_3$ and $ClAuPPh_3$ which were close to quantitative. The products could be separated via chromatography on alumina.

Action of triphenylphosphine or diphenylferrocenylphosphine on complexes (I)

A solution of (VI) (0.10 g, 0.09 mmol) in acetone was added to a solution of PPh_3 (0.024 g, 0.09 mmol) in ether. The solvent was removed in vacuo and the residue extracted with cold benzene to give tolyl(triphenylphosphine)gold, 0.05 g (quantitative yield), m.p. 160 - 161°, (lit. [4] m.p. 160 - 161°). The residue after the benzene extraction was $[(Ph_3P)_2Au]^+ BF_4^-$, 0.08 g (quantitative yield). This was crystallised from a hexane/ether/methanol mixture. M.p. 224 - 226° (lit. [9] 234 - 236°). Analysis found: C, 53.33; H, 3.83; Au, 23.71%. $C_{36}H_{20}P_2AuBF_4$ calcd.: C, 53.48; H, 3.75; Au, 24.36%.

The reactions of (II) and (XVII) with PPh_3 and (VII) with diphenylferrocenylphosphine were carried out in a similar manner.

TABLE 2
ANALYTICAL DATA FOR NEW ORGANOGOLD COMPOUNDS

N	Compound ^d	M.p.(°C)	Found (calcd.) (%)		
			C	H	Au
(II)	C ₄₆ H ₃₉ Au ₂ P ₂ FeBF ₄	161 - 163 (dec)	46.56 46.20 (46.45)	3.36 3.32 (3.30)	33.66 (33.25)
(IIa)	C ₉₂ H ₇₈ Au ₄ P ₄ Fe ₂ SO ₄	160	46.81	3.44	33.19
(III)	[C ₅ H ₅ FeC ₅ H ₄ (AuPPh ₃) ₂] ₂ SO ₄ C ₄₆ H ₃₈ Au ₂ P ₂ FeBF ₄ Cl	(dec.) 156 - 159	(47.94) 44.85 44.77	(3.41) 3.47 3.30	(34.23) 31.18 31.92
(IV)	C ₄₇ H ₄₁ Au ₂ P ₂ FeOBF ₄	149 - 153	(45.10) 46.13 46.34	(3.19) 3.63 3.50	(31.27) 32.20 31.77
(V)	C ₄₉ H ₄₆ Au ₂ P ₂ FeNBF ₄	119 - 121	(46.25) 47.56 47.74	(3.36) 4.00 3.81	(32.30) 31.40 31.18
(VI)	C ₄₃ H ₃₇ Au ₂ P ₂ BF ₄	175 - 176	(47.15) 46.80	(3.69) 3.02	(31.59) 36.05
(VII)	C ₅₁ H ₄₅ Au ₂ P ₂ Fe ₂ BF ₄	127 - 129	(47.10) 46.88	(3.40) 3.55	(35.93) 29.30
(XV)	C ₄₆ H ₃₉ Au ₂ P ₂ FeSBF ₄	186	(46.67) 45.10 45.39	(3.46) 3.38 3.43	(30.02) 32.06 31.95
(XVI)	C ₄₂ H ₃₅ Au ₂ P ₂ BF ₄	151 - 154	(45.20) 46.90	(3.22) 3.16	(32.32) 36.47
(XVII)	[C ₆ H ₅ (AuPPh ₃) ₂] ⁺ BF ₄ ⁻ C ₃₈ H ₃₃ Au ₂ P ₂ BF ₄	153	(46.64) 44.21	(3.17) 3.22	(36.43) 38.16
(XVIII)	[CH ₂ =CH(AuPPh ₃) ₂] ⁺ BF ₄ ⁻ C ₄₇ H ₅₄ P ₂ Au ₂ NB ₂ F ₈ O ₃	(dec.) 166 - 168	(44.60) 42.46 (42.61)	(3.55) 4.55 (4.11)	(38.20)
	[O ₂ CH ₂ CH ₂ NH(AuPPh ₃) ⁺ BF ₄ ⁻ ·1/4(CH ₃) ₂ CO				

^dFor structures of (II) to (VIII), and (XV), see Table 1.

Action of morpholine on (VI)

A few drops of morpholine were added to a solution of (VI) (0.100 g, 0.69 mmol) in acetone. The mixture was diluted by an equal amount of an ether/hexane mixture (3/1) and the morpholine(triphenylphosphine)gold (XVIII) which precipitated was separated, yield 0.06 g (quantitative). The crystals of this compound contained solvated acetone and the structure is $[\text{O}(\text{CH}_2\text{CH}_2)_2\text{NHAuP}(\text{C}_6\text{H}_5)_3]^+ \text{BF}_4^- \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$ (Table 2) as verified by IR and PMR spectroscopy.

Reactions of (III), (VI), (XVII) and (XVIII) with ferrocenyl(triphenylphosphine)gold (VIII)

The compound (VIII) (0.060 g, 0.09 mmol) was added to a solution of (VI) (0.100 g, 0.09 mmol) in acetone, and the yellow solution turned red. The mixture was diluted with an equal amount of an ether/hexane (2/1) mixture and the red crystals of (II) formed were separated. The yield was 0.11 g (quantitative). After removing the solvent from the mother liquor, tolyl(triphenylphosphine)gold was isolated, 0.050 g (quantitative yield), m.p. 160 - 161°.

The reactions of (III), (XVII), and (XVIII) with (VIII) proceed similarly and the yields are close to quantitative.

Interaction of (III) with 2-methoxyferrocenyl(triphenylphosphine)gold (X). Interaction of (II) with 2-N,N-dimethylaminoferrocenyl(triphenylphosphine)gold (XI) or with triphenylphosphinegold thioferrocenate (XIV)

The above method when applied to (III) (0.200 g, 0.162 mmol) and (X) (0.120 g, 0.178 mmol) gave (IV), 0.192 g (96%), and (XI), 0.120 g (quantitative yield), m.p. 164 - 168°, (lit. [6] m.p. 164 - 168°).

Similarly, the reactions of (XI) or (XIV) with (II) gave (V) and (VIII) quantitatively or the sulphonium salt (XV) and (VIII), respectively (see Tables 1 and 2). The sulphonium compound (XV) was obtained in quantitative yield from (XIV) and a solution of HBF_4 in ether. The procedure used was similar to that employed with (VI). The structure of (XV) was verified [10] by its PMR and ^{31}P NMR spectra.

Reactions of complexes (I) with organometallic compounds

(VI) and diferrocenylmercury. The compound (VI) (0.40 g, 0.35 mmol) was added to a solution of diferrocenylmercury (0.10 g, 0.17 mmol) in CHCl_3 and the solution became red in colour. The solvent was removed in vacuo, and the residue was washed carefully with ether. The solvent-free mixture was extracted with a small amount of acetone to give 0.40 g (92%) of (II). The residual ditolylmercury was chromatographed on an alumina column using CHCl_3 as eluant to give 0.06 g (98%) of di-*p*-tolylmercury, m.p. 234 - 236°, (lit. [11] m.p. 237 - 238°).

(VI) and ferrocenylmercury chloride. The above technique when applied to ferrocenylmercury chloride (0.12 g, 0.27 mmol) and (VI) (0.32 g, 0.28 mmol) gave (II) (0.13 g (40%)), $\text{ClAuP}(\text{C}_6\text{H}_5)_3$ (0.05 g (30%), m.p. 243 - 244°) and *p*-tolylmercury chloride, (0.052 g (57%), m.p. 230 - 232°, lit. [12] m.p. 232 - 233°).

Reactions of methyl(triphenylphosphine)gold with organo-mercury and -bismuth compounds in the presence of HBF₄

Diferrocenylmercury and CH₃AuPPh₃. A solution of HBF₄ in ether (0.68 ml of the 2.5 N solution) was added to a solution of diferrocenylmercury (0.24 g, 0.42 mmol) and CH₃AuPPh₃ (0.80 g, 1.68 mmol) in 50 ml of chloroform. The yellow reaction mixture rapidly turned red. The solvent was removed in vacuo and the residue was washed with ether and extracted with acetone to give 0.55 g (78%) of (II).

Tris(p-tolyl)bismuth and CH₃AuPPh₃. A solution of HBF₄ in ether (0.11 ml of the 2 N solution) was added to a solution of tris(p-tolyl)bismuth (0.10 g, 0.21 mmol) and CH₃AuPPh₃ (0.10 g, 0.21 mmol) in ether. After 5 h at 45°, the reaction mixture was treated to give 0.09 g (85%) of (VI).

Interaction of diferrocenylmercury with ClAuPPh₃ and AgBF₄

A solution of ClAuPPh₃ (0.10 g, 0.20 mmol) and AgBF₄ (0.04 g) in acetone was added to a solution of diferrocenylmercury (0.10 g, 0.17 mmol) in benzene. The solvent was removed in vacuo and the residue extracted with acetone to give 0.08 g (73%) of (II).

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References

- 1 C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland and R. Mason, *Chem. Commun.* (1972) 87;
A.J. Deeming, R.S. Nyholm and M. Underhill, *Chem. Commun.*, (1972) 224;
J.M. Guss, R. Mason and K.M. Thomas, *J. Organometal. Chem.* 40 (1972) C79.
- 2 E.G. Perevalova, D.A. Lemenovskii, K.I. Grandberg and A.N. Nesmeyanov, *Doklady Akad. Nauk. SSSR* 202 (1972) 93.
- 3 J.F. Malone and V.S. McDonald, *Chem. Commun.*, (1967) 444.
- 4 E.G. Perevalova, T.V. Baukova, K.I. Grandberg and A.N. Nesmeyanov, *Doklady Akad. Nauk SSSR* 206 (1972) 1355.
- 5 A.N. Nesmeyanov, E.G. Perevalova, D.A. Lemenovskii, A.N. Kosina and K.I. Grandberg, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1969) 2030.
- 6 E.G. Perevalova, D.A. Lemenovskii, O.B. Afanassova, V.P. Dyatchenko, K.I. Grandberg and A.N. Nesmeyanov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1972) 2594.
- 7 A.N. Nesmeyanov, E.G. Perevalova, V.V. Krivykh, A.N. Kosina, K.I. Grandberg and Ye.I. Smyslova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1972) 653.
- 8 C. Kowala and J.M. Swan, *Aust. J. Chem.* 19 (1966) 547.
- 9 A.D. Westland, *Can. J. Chem.* 47 (1969) 4135.
- 10 E.G. Perevalova, D.A. Lemenovskii, K.I. Grandberg and A.N. Nesmeyanov, *Doklady Akad. Nauk SSSR* 203 (1972) 1320.
- 11 P.R. Austin, *J. Amer. Chem. Soc.* 54 (1932) 3726.
- 12 O. Dimroth, *Chem. Ber.* 32 (1899) 758.