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Synthesis and Structure of $[Au_5(C_6H_4PPh_2)_4]^+$: A Cycloaurated Cation Containing a Pair of *Ipso*-Carbon−Digold Interactions

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Introduction

Phosphorus bis(ylides), $[R_2P(CH_2)_2]^-$ [R_2 = Ph_2, Me_2, Et_2, PhMe, $(CH_2)_4$][1,2] and [bis(2-organo)phosphino]phenyl, *o*-C_6H_4-PR_2 (R = Ph, Et),[3,4] belong to a large family of 1,3-bifunctional ligands that form stable binuclear gold(I) complexes whose metal atoms ($5d^{10}-5d^{10}$) are separated by only 2.8−3.1 Å. The weak attraction that is thought to exist between the gold atoms in such compounds has been termed aurophilicity.[5] Both sets of compounds characteristically undergo two-center, two-electron oxidative addition[6] at the dimetal unit with reagents such as halogens and dibenzoyl peroxide to give binuclear gold(II)−gold(II) ($5d^9-5d^9$), metal−metal-bonded complexes containing an $X-Au^{II}-Au^{II}-X$ unit.[1,2,4,7] Methyl iodide and methyl bromide also add reversibly to $Au_2\{\mu\text{-}(CH_2)_2PR_2\}_2$ to give the unsymmetrical digold(II) complexes $Au_2(X)(CH_3)\{\mu\text{-}(CH_2)_2PR_2\}_2$ (X = I, Br).[8−11] Two compounds of this class, having R = Me, X = I[9] and R = Ph, X = Br,[10,11] have been characterized by X-ray crystallography, the Au−Au distances being 2.695(4) and 2.674(1) Å, respectively. The methyl iodide adduct of $Au_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ could be detected by ^{31}P NMR spectroscopy, but attempts to isolate it were frustrated by formation of the diiodide. This type of behavior is often observed in the reactions of alkyl bromides and alkyl iodides with low-valent metal complexes as a consequence of radical chain processes. Formation of the corresponding diiodide also vitiated early attempts to isolate $Au_2(I)(CH_3)\{\mu\text{-}(CH_2)_2PPh_2\}$, apparently because of the photosensitivity of this compound.[9−11]

The addition of methyl halides to $Au_2\{\mu\text{-}(CH_2)_2PR_2\}_2$ is thought to be an S_N2 process.[6] We therefore tried the reaction of $Au_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ with methyl triflate, hoping to obtain the (triflato)methyldigold(II) complex $Au_2(OTf)(CH_3)\{\mu\text{-}o\text{-}C_6H_4PPh_2\}_2$ (OTf = OSO_2CF_3). The unexpected result of this experiment is described here.

Experimental Section

General Procedures and Starting Materials. Reactions were carried out under dry nitrogen with use of standard Schlenk techniques, but the solid product could be filtered off in air. The following instruments were used for spectroscopic measurements: JEOL FX-60 (^1H at 60 MHz, ^{31}P at 24.3 MHz), Varian XL-200E (^1H at 200 MHz, ^{31}P at 80.96 MHz), VG ZAB-2SEQ (FAB mass spectra), and Perkin-Elmer 683 (IR spectra as KBr disks or Nujol mulls). Elemental analyses were carried out in-house. The compounds $Au(OTf)(PPh_3)$ and $Au(BF_4)(PPh_3)$ were made by treating $AuX(PPh_3)$ (X = Cl, Br) with the appropriate silver salt in THF according to literature references for related compounds containing monodentate O-donor ligands.[13] After removal of THF in vacuo, the resulting white solids were used immediately. The very hygroscopic triflate showed a singlet ^{31}P NMR resonance at δ 28.5. The complex $Au_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ (**1**) was prepared as described previously.[3,4]

Attempted Reaction of $Au_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ (1) with Methyl Triflate. A suspension of **1** (130 mg, 0.14 mmol) in dichloromethane (20 mL) was cooled to −70 °C, and methyl triflate (31.9 mg, 22 μL, 0.19 mmol) was added from a syringe. The mixture was allowed to warm to room temperature and stirred overnight while being shielded from light. Solvent was evaporated in vacuo from the pale yellow solution, and the solid residue was washed with hexane. Recrystallization from dichloromethane−ether and cooling to 0 °C gave pale yellow microcrystals of $[Au_5(C_6H_4PPh_2)_4]CF_3SO_3$ [**2**-OTf], which were isolated by filtration, washed with ether, and air-dried. The yield was 75 mg (50%). Crystals suitable for X-ray analysis were grown by slow evaporation of a dichloromethane−ether solution. $^{31}P\{^1H\}$ NMR ($CDCl_3$, FX-60): δ 43.5 (d), 40.6 (d) ($^2J_{PP}$ = 1.6 Hz). Anal. Calcd for $C_{38}H_{31}Au_2F_3O_3P_2S$ [$Au_2(OTf)(CH_3)(C_6H_4PPh_2)_2$]: C, 42.24; H, 2.89. Found: C, 41.67; H, 2.47.

Reaction of 1 with $Au(OTf)(PPh_3)$. A stirred suspension of **1** (100 mg, 0.11 mmol) in dichloromethane (10 mL) in a flask shielded from light was cooled to 0 °C and treated with solid $Au(OTf)(PPh_3)$ (64 mg, 0.11 mmol). A clear, pale yellow solution was formed after a few minutes. After 1 h, the solvent was removed in vacuo and the residue was taken up in a small volume of dichloromethane. Addition of ether gave **2**-CF_3SO_3 as pale yellow microcrystals, which were dried by heating for 3 h at 60 °C in vacuo. The yield was 65 mg (55%). ^1H NMR ($CDCl_3$): δ 8.0−6.2 (m, 56 H, arom), 1.63 (s, 2 H, H_2O). The peak at δ 1.63 broadens and disappears on addition of D_2O. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, XL 200E): δ 43.7 (d), 41.0 (d) ($^2J_{PP}$ = 1.6 Hz). FAB-MS: *m/z* 2030, 1571, 1113, 915, 719, 579, 457, 337. Anal. Calcd for $C_{73}H_{56}Au_5F_3O_3P_4S$: C, 40.24; H, 2.59. Found: C, 40.03; H, 2.46.

The BF_4 salt was prepared similarly in 88% yield from **1** and $Au(BF_4)(PPh_3)$.

Crystallography. Crystal and refinement data are summarized in Table 1. Data reduction and refinement computations were performed with the XTAL 2.6 package.[14] Anisotropic displacement parameters were used for Au, S, P, F, and O atoms. The isotropic form was used for C atoms because of the limited number of reflections that could be observed. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from a standard compilation.[15]

Results and Discussion

Methyl triflate reacted slowly with a suspension of $Au_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ (**1**) in dichloromethane to give a clear solution from which a pale yellow microcrystalline solid was isolated. The analytical data (C, H) were in fair agreement with those

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Table 1. Crystal and Refinement Data for $[Au_5(C_6H_4PPh_2)_4]CF_3SO_3 \cdot 4H_2O$ (**2**-OTf)

empirical formula	$C_{73}H_{64}Au_5F_3O_7P_4S$	V (Å^3)	14715(17)
fw	2251.09	D_c (g cm^{-3})	2.032
cryst system	monoclinic	Z	8
space group	$C2/c$	λ(Mo Kα) (Å)	0.710 69
unit cell dimens		T (K)	298
a (Å)	35.209(11)	μ (cm^{-1})	100.7
b (Å)	23.354(7)	R(obsd data) (%)	5.4
c (Å)	23.802(7)	R_w(obsd data) (%)[a]	6.8
β (deg)	131.25(2)	GOF	1.71

[a] Weighting scheme: $w = [\sigma^2(F) + 0.0004F^2]^{-1.}$

calculated for the expected formulation $Au_2(OTf)(CH_3)(C_6H_4PPh_2)_2$, and the ^1H NMR spectrum showed a singlet at δ 1.63 that could have been ascribed to the methyl protons. However, although the $^{31}P\{^1H\}$ NMR spectrum showed the expected pair of doublets in a 1:1 ratio (at δ 43.5 and 40.6), the coupling constant was only about 2 Hz. Digold(II) complexes of the type $Au_2(X)(Y)(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ containing different anionic ligands X and Y have a coupling constant $^3J_{PP}$ of about 75 Hz for X,Y = Cl, Br, I, or O_2CPh, and for the tentatively identified compound $Au_2(I)(CH_3)(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$ formed during the reaction of **1** with methyl iodide, the value is 54 Hz.[4] Single-crystal X-ray structural analysis (see below) showed that the compound is $[Au_5(C_6H_4PPh_2)_4]CF_3SO_3$ (**2**-OTf); the same compound was isolated in 55% yield by treatment of **1** with an excess of $Au(OTf)(PPh_3)$.

Complex **2** is readily identified by its FAB mass spectrum, which shows an intense parent peak for the cation at *m*/*z* 2030 and a less intense peak at *m*/*z* 1571 arising from the loss of $[Au(C_6H_4PPh_2)]^+$ or $[Au(PPh_3)]^+$. The IR spectrum contains strong bands at 1150 and 1270 cm^{-1} assignable to ionic triflate,[16] and the peak at δ 1.63 in the ^1H NMR spectrum is due to water, which cannot be removed completely even after the sample has been heated at 60 °C in vacuo for 3 h.

We supposed initially that the presence of small amounts of triflic acid in the ester might be responsible for the formation of **2** from **1** and methyl triflate, a plausible sequence being that shown in eqs 1 and 2. Treatment of **1** with triflic acid in a 5:1

$$Au_2(C_6H_4PPh_2)_2 + 2CF_3SO_3H \rightarrow 2Au(CF_3SO_3)(PPh_3) \quad (1)$$

$$2Au_2(C_6H_4PPh_2)_2 + Au(CF_3SO_3)(PPh_3) \rightarrow [Au_5(C_6H_4PPh_2)_4]CF_3SO_3 + PPh_3 \quad (2)$$

molar ratio in CD_2Cl_2 did indeed give **2** over a period of days, as shown by ^{31}P NMR spectroscopy, though only as a minor product; the main product was an unidentified species having a singlet at δ 41.9. Moreover, **2** was still formed on treatment of **1** with methyl triflate that had been freshly distilled from P_4O_{10}. Monitoring of the reaction by ^{31}P NMR spectroscopy in CD_2Cl_2 showed the development of the peaks due to **2** together with an unidentified singlet at δ 38.0. The ^1H NMR spectrum of the solid obtained after solvents had been removed in vacuo contained a sharp singlet at δ 2.6, which could be due to an *o*-tolyl methyl group, *cf.* $\delta(CH_3)$ for free $Ph_2(o\text{-}MeC_6H_4)P$ = 2.34.[14,15] This singlet was not observed in the reactions of **1** with triflic acid or $Au(OTf)(PPh_3)$. We conclude tentatively that in the first step methyl triflate attacks a gold–carbon bond of **1** to generate a cationic gold species containing $Ph_2P(o\text{-}MeC_6H_4)$; however, the subsequent steps remain unclear. In the reaction of **1** with $Au(OTf)(PPh_3)$, monitoring by ^{31}P NMR spectroscopy failed to detect the free PPh_3 required by eq 2, and the peaks due to **2** were accompanied by other singlets in the region δ 40–45. Attempts to separate and identify the other products of these reactions have been unsuccessful.

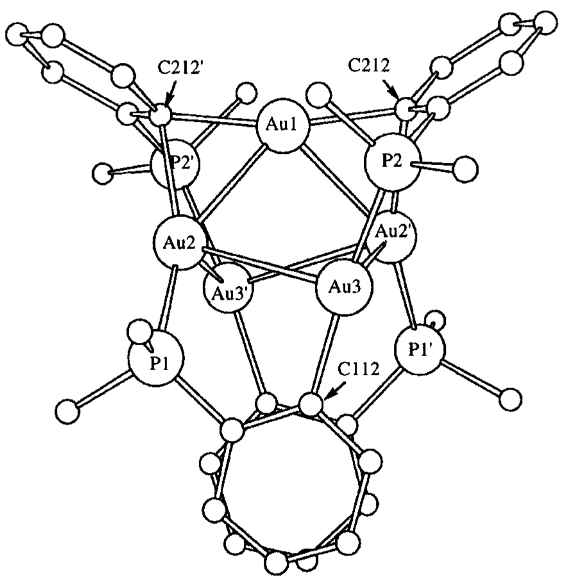

Figure 1. Molecular structure of the cation in $[Au_5(C_6H_4PPh_2)_4]OTf$ (**2**-OTf)

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $[Au_5(C_6H_4PPh_2)_4]CF_3SO_3 \cdot 4H_2O$ (**2**-OTf)[a,b]

Au(1)–Au(2)	2.709(2)	Au(4)–Au(5)	2.701(2)
Au(1)–C(212)	2.10(4)	Au(4)–C(412)	2.11(3)
Au(2)–P(1)	2.263(8)	Au(5)–P(3)	2.264(9)
Au(2)–C(212)′	2.26(2)	Au(5)–C(412)′	2.25(3)
Au(3)–P(2)	2.306(8)	Au(6)–P(4)	2.297(9)
Au(3)–C(112)	2.01(3)	Au(6)–C(312)	2.06(3)
Au(2)–Au(1)–Au(2)′	95.32(7)	Au(5)–Au(4)–Au(5)′	91.05(7)
Au(2)–Au(1)–C(212)	140.6(7)	Au(5)–Au(4)–C(412)	137.4(9)
Au(2)–Au(1)–C(212)′	54.3(7)	Au(5)–Au(4)–C(412)′	54.2(9)
C(212)–Au(1)–C(212)′	164(1)	C(412)–Au(4)–C(412)′	168(1)
Au(1)–Au(2)–P(1)	148.4(3)	Au(4)–Au(5)–P(3)	149.3(3)
Au(1)–Au(2)–C(212)′	49(1)	Au(4)–Au(5)–C(412)	49.5(7)
P(1)–Au(2)–C(212)′	161(1)	P(3)–Au(5)–C(412)	157.1(7)
P(2)–Au(3)–C(112)	168.5(7)	P(4)–Au(6)–C(312)	170(1)
Au(2)–P(1)–C(111)	115(1)	Au(5)–P(3)–C(311)	116.4(9)
Au(1)···Au(3)	3.487(2)	Au(4)···Au(6)	3.590(2)
Au(2)···Au(3)	3.186(2)	Au(5)···Au(6)	3.225(3)
Au(2)···Au(2)′	4.005(3)	Au(5)···Au(5)′	3.855(2)
Au(2)···Au(3)′	3.158(3)	Au(5)···Au(6)′	3.101(3)
Au(3)···Au(3)′	4.679(2)	Au(6)···Au(6)′	4.758(3)

[a] Primes indicate atoms related by the symmetry operation ($-x$, y, $0.5 - z$) to those given in the table of atomic coordinates (see Supporting Information and Figure 1). [b] The third and fourth columns refer to the second independent molecule in the unit cell.

The unit cell of **2**-OTf contains two independent cations, which do not differ significantly in their geometries and metrical parameters. In the following discussion, the data cited refer to one of these cations. There are also two triflate anions, whose metrical data are unexceptional, and four ill-defined solvent molecules, which exist in pairs with atomic separations of about 2.7 Å. These are assumed to be water molecules on the basis of the NMR data (see above), but they could equally well be CH_2Cl_2 molecules of half-occupancy; peaks consistent with bridging half-carbon atoms were observed in the $\Delta\rho$ map.

The framework of one cation is shown in Figure 1; selected interatomic distances and angles for both independent units are listed in Table 2. The cation consists of a butterfly arrangement of four gold atoms [Au(2), Au(2)′, Au(3), Au(3)′], the primed and unprimed atoms being related by a 2-fold rotation axis on

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which the remaining gold atom [Au(1)] is located. The C_6H_4-PPh_2 groups fall into two distinct classes, thus accounting for the observed ^{31}P NMR spectrum. Atoms Au(2) and Au(3) (and Au(2)′ and Au(3)′) are each bridged by a $C_6H_4PPh_2$ group similar to that in **1**. The separation between the gold atoms of each pair [3.186(2) Å] is, however, significantly greater than that in **1** [2.8594(3) Å].[3] Atoms Au(1), Au(2), and Au(3)′ are bridged by a $C_6H_4PPh_2$ group, the phosphorus atom being coordinated to Au(3)′ and the aryl carbon atom [C(212)′] bridging atoms Au(1) and Au(2) in an asymmetrical, three-center, two-electron (3c, 2e) interaction. A similar connectivity is evident for atoms Au(1), Au(2)′, Au(3), and C(212). The geometry and metrical parameters in this Au−C−Au unit are very similar to those observed in the bridging ferrocenyl salt [μ-($CpFeC_5H_4$)$Au_2(PPh_3)_2$]BF_4 (**3**)[19] and in mesitylgold(I) pentamer Au_5(μ-$C_6H_2Me_3$-2,4,6)$_5$ (**4**).[20,21] Thus, the gold−gold distances are 2.709(2) Å (**2**-OTf), 2.768(2) Å, (**3**) and 2.697(1) Å (**4**), the gold−carbon distances are 2.10(4), 2.26(2) Å (**2**-OTf), 2.12(4), 2.25(4) Å (**3**), and 2.13(3), 2.20(2) Å (**4**), and the Au−C−Au angles are 77(1)° (**2**-OTf), 78(1)° (**3**), and 75.9(7)° (**4**). Gold atom Au(1) is unique in bearing no tertiary phosphine, being bound only to gold atoms Au(2) and Au(2)′ and to carbon atoms C(212)′ and C(212) with an angle C(212)′−Au−C(212) of 164(1)°. This fragment could be regarded as a linearly coordinated diarylaurate, slightly perturbed by the interactions with Au(2) and Au(2)′. Possible additional weak attractive interactions between Au(2) and, respectively, Au(3)′ [separation = 3.158(3) Å] and Au(3) [separation = 3.186(2) Å] may be partly responsible for the deviations from linearity at Au(3) [angle P(2)−Au(3)−C(112) = 168.5(7)°] and Au(2) [angle C(212)′−Au(2)−P(1) = 161(1)°]. Not surprisingly, the Au−C bond in the bidentate bridging $C_6H_4PPh_2$ group [Au(3)−C(112) = 2.01(3) Å] is significantly shorter than the two gold to bridging carbon bonds of the tridentate $C_6H_4PPh_2$ group (see above).

Complexes such as **3** and its *p*-tolyl analogue [μ-(*p*-MeC_6H_4)-$Au_2(PPh_3)_2$]$^+$, which contain a Au−C(*ipso*)−Au interaction, are formed by treatment of the appropriate neutral Au(η^1-organyl)-(PPh_3) complex with acid or other electrophiles,[22] and the formation of **2**-OTf is clearly an extension of this type of reaction. The complex is another member of the limited number of pentanuclear gold clusters, which display a remarkable range of geometries, e.g. Au_5(μ-$C_6H_2Me_3$-2,4,6)$_5$ (approximately pentagonal),[20,21] [$C_6F_5Au_2$\{μ-$(CH_2)_2PPh_2$\}$_2$]$_2$\{(μ-$Au(C_6F_5)_2$\} (linear),[23] [$CAu_5(PPh_3)_5$]$^+$ (trigonal bipyramidal),[24] [$NAu_5(PPh_3)_5$]$^{2+}$ (trigonal bipyramidal),[25] [Au_5(N-*t*-Bu)$_2$(PPh_3)$_4$]$^+$ (two triangular units in a bow-tie arrangement),[26] and [Au_5L_3(μ-Ph_2PCH_2-PPh_2)$_2$]$^{2+}$ (LH = quinoline-2-thiol; three Au atoms approximately linear).[27]

Supporting Information Available: Thermal ellipsoid diagrams for both cations in the unit cell and listings of crystallographic data, atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and selected least-squares planes (17 pages). Ordering information is given on any current masthead page.

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