Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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μ_3-Oxo-tris[(triisopropylphosphine)gold(I)] Tetrafluoroborate

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Abstract

μ_3-Oxo-tris[(triisopropylphosphine)gold(I)] tetrafluoroborate, $[Au_3O(C_9H_{21}P)_3]BF_4$, crystallizes with C_{3v}-symmetrical cations and anions. The cations show intramolecular Au···Au bonding, but any intermolecular aggregation, as detected in other homologues, is prevented by the bulky phosphine ligands.

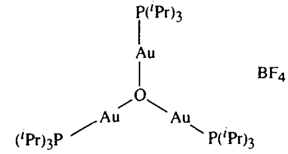
Comment

Trigoldoxonium salts $(LAu)_3O^+.X^-$ are of considerable interest as reagents in gold-cluster chemistry (Ramamoorthy & Sharp, 1990; Perevalova, Smyslova, Dyadchenko, Grandberg & Nesmeyanov, 1980; Zeller, Beruda, Kolb, Bissinger, Riede & Schmidbaur, 1991). Moreover, they provide direct evidence for the influence of Au···Au interactions on the structure of gold(I) compounds. These interactions between closed-shell metal atoms (Au $5d^{10}$) are based largely on relativistic effects (Pyykkö, 1988), which reach a local maximum in the Periodic Table for gold. All previously described structures of trigoldoxonium compounds show a nearly trigonal array of Au atoms, with Au···Au distances close to 3.1 Å, capped by an O atom.

Depending on the size of the phosphine ligands coordinated to the Au atoms, the cations undergo intermolecular aggregation to form dimers of the form $[(R_3PAu)_6O_2]^{2+}$. With the smallest tertiary phosphine ligand Me_3P (*i.e.* R = Me), dications with a tetrahedral Au_4 core are formed, with each bridging Au atom bonded to four neighbouring Au atoms (Angermaier & Schmidbaur, 1994*a*). In contrast, the corresponding oxonium salts having the somewhat larger phosphines Ph_2MeP (R_3 = Ph_2Me) (Yi, Ramamoorthy & Sharp, 1993) and Ph_3P (R = Ph) (Nesmeyanov, Perevalova, Struchkov, Antipin, Grandberg & Dyadchenko, 1980) are less intimately aggregated and form a square Au_4 unit, with each of the Au atoms bonded to only three neighbouring metal atoms. To date, it is only in the complex $[\{(o\text{-tolyl})_3PAu\}_3O]BF_4$, with its more bulky $(o\text{-tolyl})_3P$ ligand, that isolated monomeric cations have been detected (Yi, Ramamoorthy & Sharp, 1993).

Similar results have been obtained for the corresponding sulfonium systems $(LAu)_3S^+.X^-$, where both monocationic as well as oligo- or even polycationic species are observed, but with a different degree and mode of aggregation for a given ligand L (Angermaier & Schmidbaur, 1994*b*; Schmidbaur, Kolb, Zeller, Schier & Beruda, 1993; Jones, Sheldrick & Hädicke, 1980).

The present investigation is part of a more extended study of the influences exerted by the donor ligands, L, on the intermolecular aggregation of mono- or polynuclear gold(I) compounds. $[({}^iPr_3PAu)_3O]BF_4$, (I), crystallizes in the trigonal space group $R\bar{3}$, with the central O atom of the cation and one of the B—F bonds of the anion situated on threefold rotation axes. The anion is found to be disordered, with the B atom located on a centre of inversion, resulting in a split model of two BF_4 ions with site occupancy factors of 0.5.



(I)

In the cations $[({}^iPr_3PAu)_3O]^+$, an Au_3 triangle is capped by an O atom. The coordination geometry of the Au atoms is found to be nearly linear with an O—Au—P angle of 176.4 (2)°. While the Au—O and Au—P distances [2.030 (3) and 2.228 (2) Å, respectively] are in good agreement with literature values, the Au···Au distances [3.198 (1) Å] are remarkably larger than the Au···Au distances found in the only other monomeric $(LAu)_3O^+$ cation, $[\{(o\text{-tolyl})_3PAu\}_3O]BF_4$ (average 3.086 Å). This widening of the Au···Au distance leads to an Au—O—Au angle of 103.7 (2)°, as compared to an average value of 97.8° in the p-tolyl homologue. The bulky ${}^iPr_3P$ ligands thus not only preclude intermolecular Au···Au interactions, but also significantly reduce the intramolecular stabilization of the oxonium cation by direct-cluster bonding.

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It is noteworthy that the homologous sulfur compound, tris[(triisopropylphosphine)gold(I)]sulfonium tetrafluoroborate, also crystallizes in space group $R\bar{3}$, with analogous symmetry criteria for the cations and anions (Angermaier & Schmidbaur, 1994*b*). This is the first case that for a given ligand *L* and anion *X* the same structural principles are verified for related trigoldoxonium and sulfonium salts.

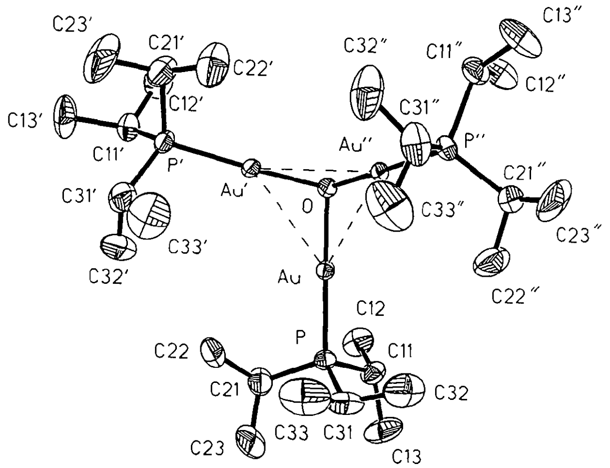

Fig. 1. Structure of the $[(^iPr_3PAu)_3O]^+$ cation in the lattice of the tetrafluoroborate salt (*ORTEP*; Johnson, 1965), shown with 50% probability ellipsoids and H atoms omitted for clarity.

Experimental

$[(^iPr_3PAu)_3O]BF_4$ was prepared in high yields from the reaction of $Au(^iPr_3P)Cl$, Ag_2O and $NaBF_4$ in tetrahydrofuran as described for related compounds by Nesmeyanov, Perevalova, Struchkov, Antipin, Grandberg & Dyadchenko (1980). Crystals suitable for X-ray analysis were obtained by crystallization of the product from CH_2Cl_2/Et_2O.

Crystal data

$[Au_3O(C_9H_{21}P)_3]BF_4$
$M_r = 1174.42$
Trigonal
$R\bar{3}$
$a = 13.622$ (1) Å
$c = 36.470$ (2) Å
$V = 5860.9$ (4) Å^3
$Z = 6$
$D_x = 2.00$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17–20°$
$\mu = 11.4$ mm^{-1}
$T = 211$ K
Prism
0.30 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans
$T_{min} = 0.497$, $T_{max} = 0.999$
6040 measured reflections
2762 independent reflections

2385 observed reflections $[F > 4\sigma(F)]$
$R_{int} = 0.0475$
$\theta_{max} = 27°$
$h = 0 \rightarrow 17$
$k = -17 \rightarrow 0$
$l = -46 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 5.3%

Refinement

Refinement on F
$R = 0.0309$
$wR = 0.0344$
$S = 0.89$
2385 reflections
111 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.001330F_o^2]$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.66$ e Å^{-3}
$\Delta\rho_{min} = -1.36$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for disordered B, F; $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{eq}/U_{iso}
Au	0.67585 (2)	0.47304 (2)	0.11612 (1)	0.023 (1)
P	0.6863 (2)	0.6305 (1)	0.09401 (5)	0.029 (1)
O	2/3	1/3	0.1395 (2)	0.026 (1)
C11	0.7666 (7)	0.7478 (6)	0.1268 (2)	0.041 (1)
C12	0.7057 (9)	0.7188 (8)	0.1635 (3)	0.057 (1)
C13	0.797 (1)	0.8667 (7)	0.1129 (3)	0.071 (1)
C21	0.5443 (7)	0.6154 (7)	0.0889 (3)	0.050 (1)
C22	0.4547 (9)	0.4967 (9)	0.0776 (3)	0.075 (1)
C23	0.541 (1)	0.702 (1)	0.0628 (5)	0.110 (1)
C31	0.7627 (9)	0.6746 (8)	0.0505 (2)	0.056 (1)
C32	0.883 (1)	0.702 (1)	0.0552 (4)	0.084 (1)
C33	0.705 (1)	0.586 (1)	0.0217 (3)	0.096 (1)
B	0	0	0	0.060
F1	0	0	0.0383 (7)	0.093
F2	0.047 (1)	0.111 (1)	0.0154 (4)	0.098

Table 2. *Selected geometric parameters* (Å, °)

Au—P	2.228 (2)	C11—C12	1.52 (1)
Au—O	2.030 (3)	C11—C13	1.54 (2)
Au···Au′	3.198 (1)	C21—C22	1.52 (2)
P—C11	1.85 (1)	C21—C23	1.53 (2)
P—C21	1.850 (7)	C31—C32	1.49 (1)
P—C31	1.83 (1)	C31—C33	1.49 (2)
Au···Au′···Au″	60.0	C12—C11—C13	112.7 (9)
O—Au—P	176.4 (2)	P—C21—C22	112.7 (7)
O—Au···Au′	38.2 (1)	P—C21—C23	114.1 (7)
Au—O—Au′	103.7 (2)	C22—C21—C23	109.5 (9)
P—Au···Au′	143.9 (1)	P—C31—C32	110.7 (7)
P—C11—C12	109.6 (8)	P—C31—C33	111 (1)
P—C11—C13	115.2 (6)	C32—C31—C33	110.5 (9)

The structure was solved by direct methods, with all non-H atoms located by difference Fourier syntheses. All H atoms were included in idealized fixed positions with $U_{iso} = 0.08$ Å^2.

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: local programs. Programs used to solve and refine structure: *SHELXTL-Plus* (Sheldrick, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,1′-Bis(trimethylsilyl)ferrocenium Tetrachloroaluminate(1−), 1,1′-Bis(trimethylsilyl)ferrocene and 1,1′-Dimethylferrocene

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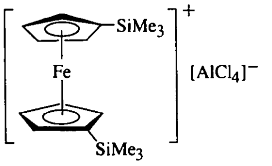
Abstract

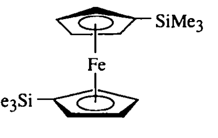
The structures of two substituted ferrocene compounds and one substituted ferrocenium compound have been determined. In compound (1), 1,1′-bis(trimethylsilyl)ferrocenium tetrachloroaluminate(1−), $[Fe\{(CH_3)_3Si\text{-}\eta^5\text{-}C_5H_4\}_2]AlCl_4$, the cyclopentadienyl rings are staggered by 17.7 (2)°. They are also tilted by 4.9 (6)° from parallelism, possibly due to steric interaction between the bulky trimethylsilyl groups, which are intermediate between *cis* and *trans*. The parallel cyclopentadienyl rings in the centrosymmetric molecule of 1,1′-bis(trimethylsilyl)ferrocene, $[Fe\{(CH_3)_3Si\text{-}\eta^5\text{-}C_5H_4\}_2]$, (2), are ideally staggered and the trimethylsilyl groups are *trans* to each other. In 1,1′-dimethylferrocene, $[Fe(CH_3\text{-}\eta^5\text{-}C_5H_4)_2]$, (3), the rings are virtually eclipsed and the methyl groups have a *cis* conformation.

Comment

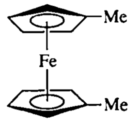
The interest in preparing polymers containing skeletal transition metals is driven by the possibility of unusual and novel electrochemical, magnetic and preceramic properties for these materials (Sheats, Carraher & Pittman, 1985; Manners, 1994). We have recently reported that high molecular weight poly(ferrocenylsilanes) in the presence of an oxidizing agent such as I_2 will convert to a partially oxidized material containing both ferrocene and ferrocenium moieties in the polymer backbone (Foucher, Tang & Manners, 1992; Rulkens, Lough & Manners, 1994; Foucher, Ziembinski, Rulkens, Nelson & Manners, 1994; Lough, Manners & Rulkens, 1994). The syntheses and determination of the structures of 1,1′-bis(trimethylsilyl)ferrocenium tetrachloroaluminate, (1), 1,1′-bis(trimethylsilyl)ferrocene, (2), and 1,1′-dimethylferrocene, (3), were undertaken in order to provide structurally characterized models for oligoferrocenylsilanes and poly(ferrocenylsilanes).



(1)



(2)



(3)

Many structures of ferrocenium salts have been determined to date but a search of the October 1994 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed that (1) was the first to contain an $AlCl_4^-$ anion. Compound (1) crystallizes as two discrete ionic moieties; the shortest carbon-to-chlorine distance between the anion and cation is 3.582 (3) Å for C(3)···Cl(1). In (1), the trimethylsilyl groups are intermediate between *cis* and *trans* with a C(1)···Cp(centroid)···Cp(centroid)···C(6) dihedral angle of 89.1 (2)°, and the cyclopentadienyl rings are staggered by 17.7 (2)° [this angle is defined by the torsion angle C(1)···Cp(centroid)···Cp(centroid)···C(10)]. In (2), however, the Fe atom lies on an inversion center, the trimethylsilyl substituents are fully *trans* and the Cp rings have an ideally staggered conformation. The geometry about the Si atoms in (1) and (2)