# [μ-4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene]bis[(trifluoroacetato)gold(I)] and its dichloromethane 0.58-solvate

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The dinuclear $Au^I$ complex containing the 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) ligand and trifluoroacetate anions exists in a solvent-free form, [μ-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene]bis[(trifluoroacetato)gold(I)], $[Au_2(C_2F_3O_2)_2(C_{39}H_{32}OP_2)]$, (I), and as a dichloromethane solvate, $[Au_2(C_2F_3O_2)_2(C_{39}H_{32}OP_2)]\cdot0.58CH_2Cl_2$, (II). The trifluoroacetate anions are coordinated to the $Au^I$ centres bridged by the xantphos ligand in both compounds. The $Au^I$ atoms are in distorted linear coordination environments in both compounds. The phosphine substituents are in a *syn* arrangement in the xantphos ligand, which facilitates the formation of short aurophilic $Au\cdots Au$ interactions of 2.8966 (8) Å in (I) and 2.9439 (6) Å in (II).

## Comment

Coordination-directed self-assembly of metal centres and multidentate ligands has become a powerful technique for the preparation of large supramolecular structures of defined shapes and sizes (Levin & Stang, 2000). Among these compounds are the $Au^I$–diphosphine complexes, which have attracted much interest because of their photophysical, catalytic and pharmaceutical applications (Keefe *et al.*, 2000). The 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos) ligand was first characterized structurally by Hillebrand *et al.* (1995), and in recent years xantphos and its metal complexes have been used as effective catalysts (Kranenburg *et al.*, 1995). The transition metal complexes [rhodium(I), platinum(II), palladium(II) and nickel(II)] of the xantphos ligand are essential catalysts in hydroformylation, allylic alkylation, amination and hydrocyanation reactions (Kamer *et al.*, 2001). The $Au^I$ complex of xantphos, [AuCl(xantphos)], catalyses the dehydrogenative silylation of alcohols with high chemoselectivity and solvent tolerance (Ito *et al.*, 2005).

The first $Au^I$–xantphos complexes, *viz.* dinuclear [Au₂Cl₂(μ-xantphos)] and mononuclear [Au(xantphos)₂][SbF₆], were

synthesised and structurally characterized a few years ago (Pintado-Alba *et al.*, 2004). We recently reported the synthesis and structural characterization of two novel $Au^I$–xantphos complexes, *viz.* [Au₂(NO₃)₂(μ-xantphos)] (the first example of the crystallization-induced spontaneous resolution of a dinuclear $Au^I$ complex) and [Au₂(μ-xantphos)₂](NO₃)₂ (Deák *et al.*, 2006). As a continuation of our work on $Au^I$ complexes of xanthene-based diphosphine ligands, the dinuclear [Au₂(nixantphos)₂](NO₃)₂ complex [nixantphos is 4,6-bis(diphenylphosphino)phenoxazine] was synthesized and X-ray crystal structure analysis revealed the solvent-assisted spontaneous resolution of the $[Au_2(nixantphos)_2]^{2+}$ metallacycle (Tunyogi *et al.*, 2008).

All reported dinuclear $Au^I$ complexes with xantphos and nixantphos ligands exhibit short intramolecular aurophilic $Au\cdots Au$ interactions ranging from 2.856 (1) to 2.995 (1) Å (Deák *et al.*, 2006; Pintado-Alba *et al.*, 2004; Tunyogi *et al.*, 2008). The $Au\cdots Au$ bond distance in complexes showing aurophilic interactions ranges from 2.70 to 3.30 Å (Schmidbaur, 2000). The strength of this attraction has been determined to be *ca* 7–11 kcal mol$^{-1}$ (1 kcal mol$^{-1}$ = 4.184 kJ mol$^{-1}$) and is comparable with that of hydrogen bonding (Schmidbaur *et al.*, 1988). Very recently, the tricoordinate monomeric [AuCl(xantphos)] complex was prepared and structurally characterized (Ito *et al.*, 2009). The mononuclear [Au(xantphos)₂][SbF₆] and [AuCl(xantphos)] complexes lack any additional aurophilic interactions (Ito *et al.*, 2009; Pintado-Alba *et al.*, 2004).
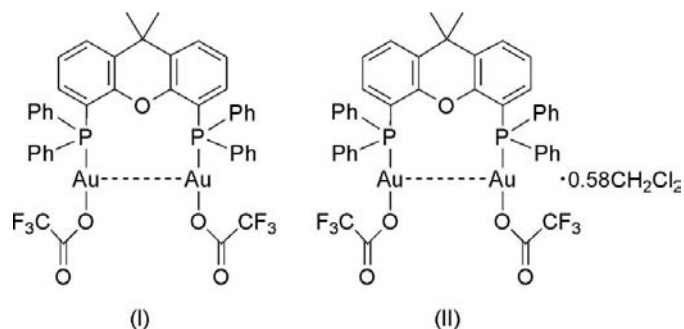


We report here the structures of a dinuclear $Au^I$ complex containing the xantphos ligand and trifluoroacetate anions, in a solvent-free form, [Au₂(O₂CCF₃)₂(μ-xantphos)], (I), and as a dichloromethane 0.58-solvate, (II). In both (I) and (II), the trifluoroacetate anions are coordinated to the $Au^I$ centres bridged by the xantphos ligand (Figs. 1 and 2). In (I), the Au1 atom is disordered over two sites. The $Au^I$ atoms are in distorted linear coordination environments in both compounds, with P—Au—O angles of 159.4 (5), 173.29 (15) and 174.1 (2)° in (I), and 168.40 (14) and 174.18 (14)° in (II). The deviation from linearity of the P—Au—O angles could be the result of an intramolecular aurophilic interaction (Mohamed *et al.*, 2003). The $Au^I$ atom has little affinity for O-donor ligands, and $Au^I$ complexes containing Au—O bonds are generally used as precursors in gold chemistry (Brandys *et al.*, 2000; Deák *et al.*, 2007; Preisenberger *et al.*, 1999).

Gold(I)–phosphine complexes containing the trifluoroacetate anion can be grouped into three broad categories,

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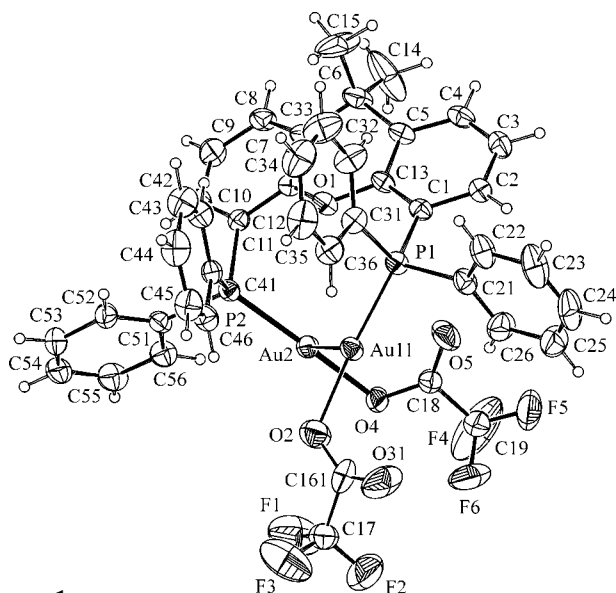


**Figure 1**
A view of the molecular structure of complex (I), showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Only the major components of disordered atoms Au1, O3 and C16 are shown.



**Figure 2**
A view of the molecular structure of complex (II), showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

namely those having no aurophilic interactions, those with intermolecular Au···Au interactions, and those with intramolecular Au···Au interactions. Complexes in the first category, e.g. [Au(O$_2$CCF$_3$)(Ph$_3$P)], are mononuclear and contain a monophosphine ligand with bulky substituents on P, and the formation of an Au···Au interaction is precluded by steric restraints (Zhang *et al.*, 1988). Gold(I) compounds in the second category contain either monophosphine or diphosphine ligands. Complexes of monophosphine ligands, *e.g.* [Au(O$_2$CCF$_3$)(Me$_3$P)], form trimers *via* intermolecular Au···Au interactions when the substituents on P are not too bulky (Preisenberger *et al.*, 1999). Complexes of diphosphine ligands having phosphine substituents linked by conformationally flexible backbones, *e.g.* [Au$_2$(O$_2$CCF$_3$)$_2$($\mu$-dppb)] [dppb is 1,4-bis(diphenylphosphino)butane] (Brandys *et al.*, 2000) and [Au$_2$(O$_2$CCF$_3$)$_2$($\mu$-dppf)] [dppf is 1,1′-bis(diphenylphosphino)ferrocene] (Low *et al.*, 1997), also exhibit intermolecular Au···Au interactions. In these compounds, the formation of any intramolecular aurophilic interaction is precluded by the *anti* arrangement of the phosphine substituents. Gold(I) complexes in the third category exhibit intramolecular Au···Au interactions as a result of their rigid phosphine backbone, which preorganizes the Au$^I$ centres in a *syn* configuration. In the [Au$_2$(O$_2$CCF$_3$)$_2$($\mu$-dppbz)] complex [dppbz is 1,2-bis(diphenylphosphino)benzene], the rigid backbone of the diphosphine advances the formation of an intramolecular aurophilic interaction of 2.908 (1) Å (Deák *et al.*, 2007). Complexes (I) and (II) also exhibit short aurophilic interactions of 2.8966 (8) Å in (I) and 2.9439 (6) Å (II). In (I) and (II), the xantphos ligand backbone is folded and tilted [by 53.9 (1)° in (I) and 52.8 (1)° in (II)] with respect to the main Au···Au axis, most likely to accommodate the two Au$^I$ atoms at a close distance.
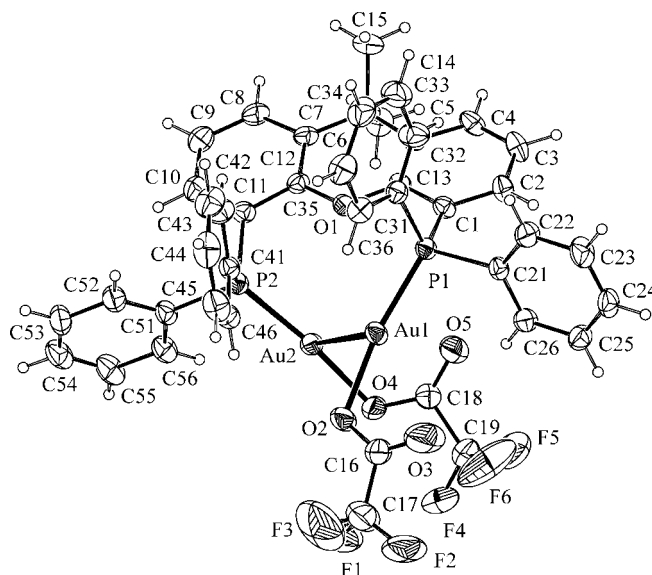
The Au—P bond lengths are 2.2208 (19) and 2.2113 (18) Å in (I), and 2.2133 (16) and 2.2202 (17) Å in (II). The observed P1···P2 distances in (I) [4.687 (2) Å] and (II) [4.742 (2) Å] are significantly longer than that in the free ligand [4.045 (1) Å; Hillebrand *et al.*, 1995]. The trifluoroacetate ions in both (I) and (II) coordinate to the Au$^I$ atom through only one O atom, with Au—O = 2.060 (5) and 2.100 (7) Å in (I), and 2.071 (5) and 2.094 (5) Å in (II). For comparison, in the acetate structure [Au(O$_2$CMe)(Ph$_3$P)] (Jones, 1984), the Au—O distance is 2.063 (6) Å.

In (I) and (II), the orientation of the coordinated trifluoroacetate anions can be defined by the values of the O2—Au1—Au2—O4 torsion angles [−74.2 (3)° in (I) and −67.6 (2)° in (II)]. In both complexes, the CF$_3$ group has high thermal motion consistent with some unresolved rotational disorder, as is often found in other trifluoroacetate compounds (Kia *et al.*, 2005; Rodrigues *et al.*, 2000, 2001). In (II), the anisotropic displacement parameters of atoms O3 and C17 are also large, however, the data quality did not enable an adequate model to be developed for this possible disorder of the trifluoroacetate group.

A variety of dinuclear Au$^I$–diphosphine complexes have been reported to be luminescent in solution and in the solid state under ambient conditions (King *et al.*,1989; Pawlowski *et al.*,2004; Pintado-Alba *et al.*, 2004). Complex (I) is non-emissive in dichloromethane solution at room temperature. The solid-state emission spectrum of (I) at room temperature exhibits a broad band at 416 nm and two shoulders at 450 and 560 nm when excited at 340 nm.

## Experimental

Compound (I) was prepared starting from [Au$_2$Cl$_2$($\mu$-xantphos)] (Deák *et al.*, 2006). A solution of [Au$_2$Cl$_2$($\mu$-xantphos)] (1 mmol) in

dichloromethane (20 ml) was added to a suspension of silver(I) trifluoroacetate (2 mmol) in dichloromethane (5 ml). After stirring for 45 min shielded from light, the AgCl precipitate was filtered through Celite. Diethyl ether (10 ml) was added to the colourless filtrate and shiny crystals of (I) were obtained by slow evaporation of this solution.

Crystals of (II) were obtained by layering the filtrate with *n*-hexane. Shiny crystals of (I) and (II) were collected by filtration, washed with *n*-hexane and dried under vacuum. Absorption–emission and excitation data for (I) (Hitachi F-2500 fluorescence spectrophotometer, nm): 280 and 340 ($CH_2Cl_2$, $10^{-5}$ *M* at room temperature); $\lambda_{ex}$ = 340 nm, $\lambda_{max}$ (nm) = 416 (*br*), 450 (*sh*), 560 (*sh*); $\lambda_{em}$ = 420 nm, $\lambda_{max}$ (nm) = 270, 315 (*sh*) (solid, room temperature).

## Compound (I)

### Crystal data

| | |
|---|---|
| [Au$_2$(C$_2$F$_3$O$_2$)$_2$(C$_{39}$H$_{32}$OP$_2$)] | $\gamma$ = 70.353 (6)° |
| $M_r$ = 1198.56 | $V$ = 2090.0 (6) Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z$ = 2 |
| $a$ = 10.2311 (15) Å | Mo $K\alpha$ radiation |
| $b$ = 13.041 (2) Å | $\mu$ = 7.16 mm$^{-1}$ |
| $c$ = 17.344 (3) Å | $T$ = 295 K |
| $\alpha$ = 73.969 (6)° | 0.45 × 0.34 × 0.31 mm |
| $\beta$ = 88.123 (6)° | |

### Data collection

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 66358 measured reflections |
| | 7370 independent reflections |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005) | 6387 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.085 |
| $T_{min}$ = 0.067, $T_{max}$ = 0.109 | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.041 | 5 restraints |
| $wR(F^2)$ = 0.108 | H-atom parameters constrained |
| $S$ = 1.03 | $\Delta\rho_{max}$ = 1.65 e Å$^{-3}$ |
| 7370 reflections | $\Delta\rho_{min}$ = −1.06 e Å$^{-3}$ |
| 542 parameters | |

## Compound (II)

### Crystal data

| | |
|---|---|
| [Au$_2$(C$_2$F$_3$O$_2$)$_2$(C$_{39}$H$_{32}$OP$_2$)]·· 0.58CH$_2$Cl$_2$ | $\beta$ = 100.253 (11)° |
| $M_r$ = 1247.60 | $V$ = 4370 (2) Å$^3$ |
| Monoclinic, $P2_1/c$ | $Z$ = 4 |
| $a$ = 10.548 (3) Å | Mo $K\alpha$ radiation |
| $b$ = 17.028 (4) Å | $\mu$ = 6.92 mm$^{-1}$ |
| $c$ = 24.724 (7) Å | $T$ = 295 K |
| | 0.64 × 0.50 × 0.43 mm |

### Data collection

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 99529 measured reflections |
| | 7703 independent reflections |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005) | 6972 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.081 |
| $T_{min}$ = 0.021, $T_{max}$ = 0.050 | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.037 | 526 parameters |
| $wR(F^2)$ = 0.092 | H-atom parameters constrained |
| $S$ = 1.08 | $\Delta\rho_{max}$ = 1.04 e Å$^{-3}$ |
| 7703 reflections | $\Delta\rho_{min}$ = −1.26 e Å$^{-3}$ |

In complex (I), the disorder of atom Au1 was refined over two positions with the displacement parameters constrained to be equal [refined site-occupancy factors are 0.834 (8) and 0.166 (8)]. Carboxyl atoms O3 and C16 were also determined to be disordered over two positions. Between the disordered components [refined site-occupancy factors are 0.65 (3) and 0.35 (3)], all equivalent C—O and C—C distances were restrained to be equal. The displacement parameters for atoms C161 and C162 atoms were also constrained to be equal. Planarity was also restrained for the disordered C17/C161/O2/O31 and C17/C162/O2/O32 carboxyl systems. The anisotropic displacement parameters of atoms C14 and C15 are large for methyl C atoms, which may be due to large thermal motion and/or disorder.

In (II), the dichloromethane solvent molecule was not sufficiently resolved in the electron-density map, and therefore it could not be modelled with disordered atoms. Accordingly, the residual electron density was removed using the SQUEEZE routine in *PLATON* (Spek, 2009). The total volume available for solvent molecules was 529 Å$^3$, which is distributed over four voids. The residual electron count was 97 electrons per unit cell, which corresponds to 2.31 dichloromethane molecules per unit cell. This means that 0.58 of a dichloromethane molecule could be accommodated in each void.

The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å), with $U_{iso}$(H) = 1.5$U_{eq}$(C), but were allowed to rotate freely about their C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.93 Å), and constrained to ride on their parent atoms, with $U_{iso}$(H) = 1.2$U_{eq}$(C).

For both compounds, data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON*, *SHELXL97*, *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

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