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Crystal structure of tris(2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl-κ*P*)-μ-oxoethenylidene-*triangulo*-trigold(I) bis(trifluoromethanesulfonyl)imide

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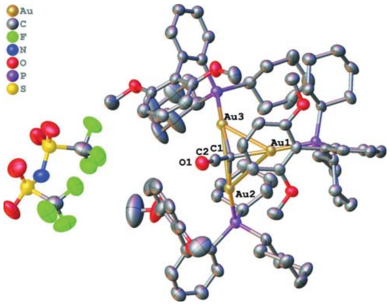
The title ketenylidene, $[Au_3(C_2O)(C_{26}H_{35}O_2P)_3](C_2F_6NO_4S_2)$, was obtained upon exposure of [2-(dicyclohexylphosphino)-2′,6′-dimethoxy-1,1′-biphenyl]-gold(I) bis(trifluoromethanesulfonyl)imide to acetic anhydride at elevated temperature. The ketenylidene bridge caps the tri-gold cluster. The title compound has provided crystals that upon analysis represent the first tri-gold ketenylidene with atomic distances indicative of bonding interaction between the gold atoms.



1. Chemical context

Metal clusters containing ketenylidenes are of interest for their wide range of applications. For instance, ketenylidenes are useful for facilitating C—C bond formation and cleavage (Went *et al.*, 1987), metal cluster building (Sailor & Shriver, 1985), and as potential intermediates for carbon monoxide chemistry (Jensen & Shriver, 1992). One of the first transition-metal ketenylidene complexes described was a tricobalt cluster reported by Seyferth *et al.* in 1974 (Seyferth *et al.*, 1974). Since then, the scope of ketenylidene clusters has been expanded to include metals such as osmium (Went *et al.*, 1987), ruthenium (Sailor & Shriver, 1985), molybdenum (Ramalakshmi *et al.*, 2015), and manganese (Crespi & Shriver, 1986) to name a few.

However, relatively few ketenylidenes involving gold have been reported. Work by Green and co-workers uncovered a surface-bound gold ketenylidene [Au_2CCO], which serves as a reactive intermediate in the aerobic oxidation of acetic acid on Au/TiO_2 surfaces (Green *et al.*, 2012). More recently, Daugherty and co-workers reported the first instance of a tri-gold ketenylidene (Daugherty *et al.*, 2017). In that case, the Au···Au distances suggest that there is no bonding interaction between the metal atoms.

Herein, we describe the first crystal structure analysis of a tri-gold ketenylidene in which the atomic distances suggest a bonding interaction between the gold atoms

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. Four molecules are present in the unit cell ($Z = 4$) and there is one component in the asymmetric unit. The title

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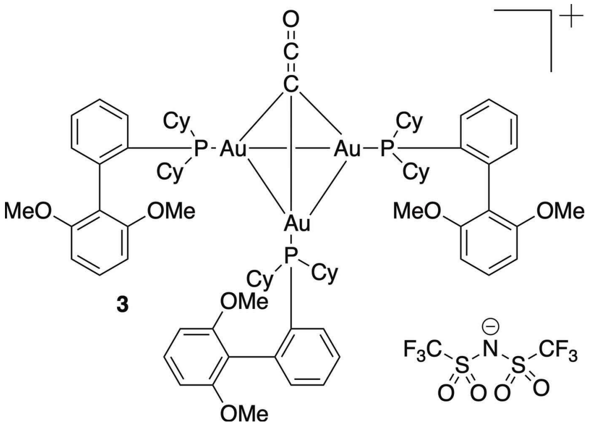
compound consists of three molecules of (2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl)gold(I) bis(trifluoromethanesulfonyl)imide capped by a ketenylidene unit (C=C=O) to form a tri-gold cluster. The tri-gold cluster has an overall charge of +1, with trifluoromethanesulfonylimide serving as the counter-ion. As shown in Fig. 1, the ketenylidene atoms (C=C=O) form an angle of 88.1 (5)° with the mean Au1—Au2—Au3 gold plane.



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The Au—Au bond distances suggest aurophilic interaction (Schmidbaur & Schier, 2012). The shortest Au—Au bond length is 3.1910 (5) Å (Au1-Au3), which is significantly shorter than the sum of two van der Waals radii (Bondi, 1964). The Au2—Au3 bond length of 3.2101 (5) Å also indicates a significant Au—Au interaction, although the complex is not entirely symmetrical, with the Au1—Au2 bond length measuring 3.3005 (5) Å. Other bond lengths within the cluster are more highly conserved within each subunit of the trimeric structure [*e.g.* Au—C1 distances: 2.090 (7) to 2.098 (7) Å; Au—P distances: 2.273 (2) to 2.281 (2) Å].

3. Supramolecular features

In the crystal structure of the title compound, the discrete complexes are arranged into columns along the *b* axis (Fig. 2). Within these columns, the ketenylidene atoms alternate between the +*a* and −*a*-axis directions. The only other similar cluster with Au was reported by Daugherty and co-workers (Daugherty *et al.*, 2017), and it does not show this alternating arrangement. However, in this earlier case, the Au atoms are all bonded to the carbon of *N*-heterocyclic carbene ligands, rather than to phosphines. As such, the title compound is the first trimetallic ketenylidene cluster of any metal that involves the metal bound to only phosphine and the ketenylidiene bridge, rather than the more common C=O ligand found in most trimetallic metal complexes in the CSD.

4. Database survey

The Cambridge Structural Database (CSD, Version 5.42, February 2021; Groom *et al.*, 2016) contains 12 unique struc-

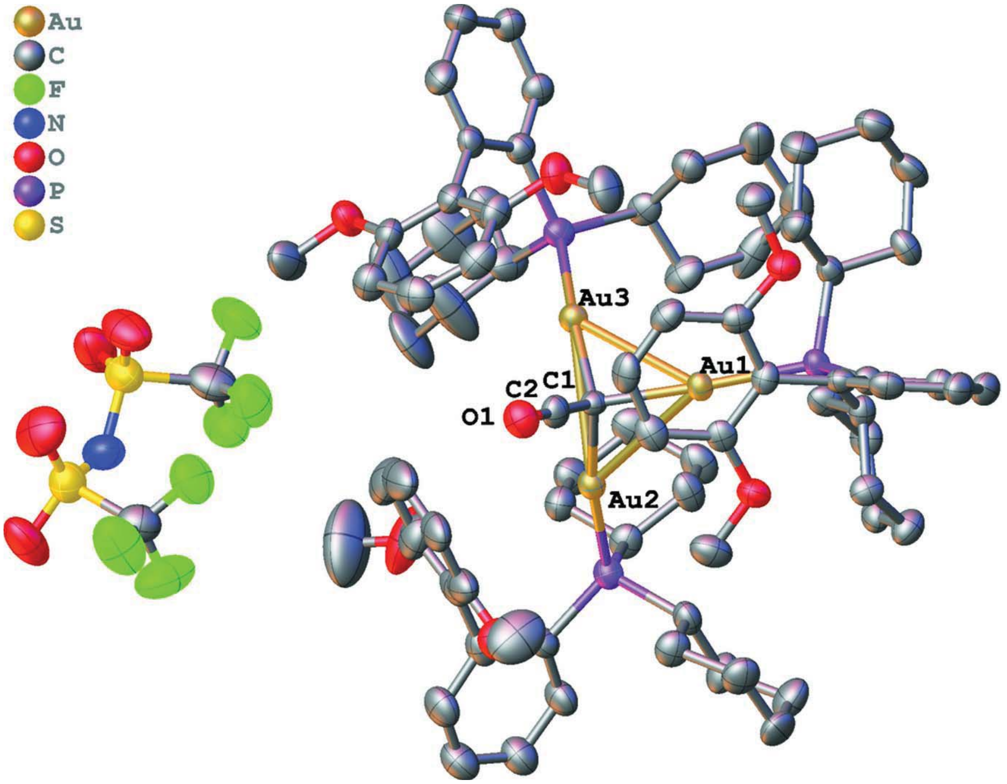

Figure 1
The molecular structure of the title compound with select atom labeling. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity reasons.

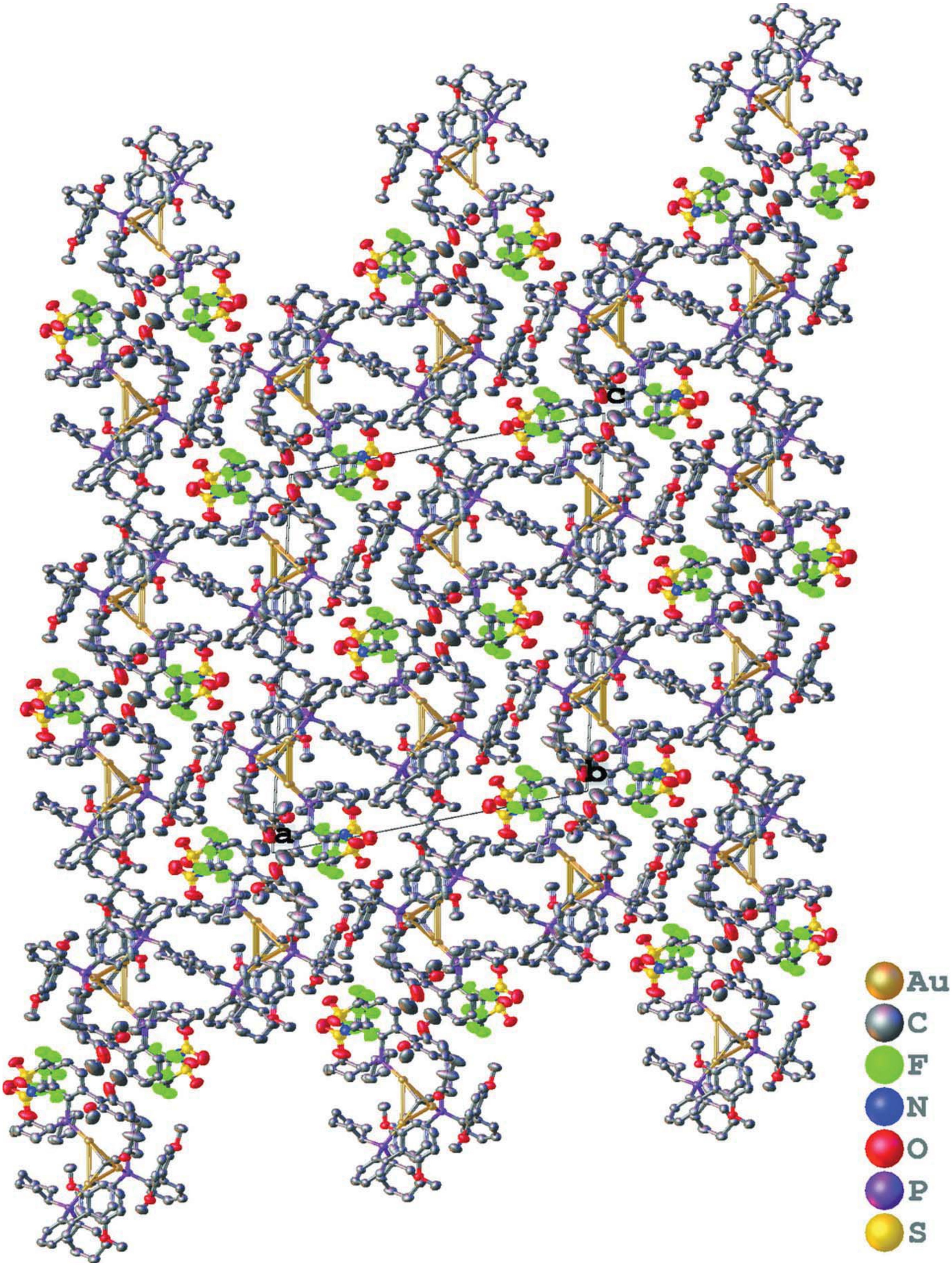

Figure 2
Packing diagram of the title compound along the *b* axis.

tures of ketenylidene-bridged metal clusters. Of these, ten contain clusters of three metal atoms, including: all iron (CAXVAY, Kolis *et al.*, 1983; GEFPIQ, Bogdan *et al.*, 1988), all ruthenium (DELSAO, Sailor & Shriver, 1985; FONWAG, Sailor *et al.*, 1987), all osmium (FONYEM, Went *et al.*, 1987), and all gold(I) (LEBFOQ, Daugherty *et al.*, 2017) and various combinations of iron, cobalt, manganese, molybdenum, and ruthenium (DUHDIT, Crespi & Shriver, 1986 and Crespi *et al.*, 1988; GAHBIA, Ching *et al.*, 1988; HUQBIG, Ramalakshmi *et al.*, 2015; KALVAU, Ching *et al.*, 1989). Two additional structures of this type with central clusters of four metal atoms, either three ruthenium and one copper (PAJWOM, Gunale *et al.*, 1992) or three iron and one copper (KINFOC10, Gunale *et al.*, 1992) have also been reported. Within this group, only one 2Fe/1Co cluster bears a phosphine ligand (KALVAU, Ching *et al.*, 1989) similar to the reported title compound; however, even in this case, the reported cluster is much simpler than the title compound, as all of the remaining positions are occupied by CO.

The only other known all gold(I) cluster (LEBFOQ, Daugherty *et al.*, 2017) differs from both the reported title compound as well as the other structures in the CSD, as it bears *N*-heterocyclic carbene ligands attached to gold, rather than either phosphines or carbon monoxide ligands. Additionally, the gold(I) atoms in this previously reported cluster were too far apart from each other to have any metal–metal bonding interaction.

Thus, the reported ketenylidene cluster differs from similar compounds in the CSD in both the title cluster's unique phosphine ligands and the short Au—Au bonding interactions.

5. Synthesis and crystallization

The title compound was observed during scope studies related to the gold(I)-catalyzed synthesis of trisubstituted indolizine **2** from 2-propargyloxypyridine **1** (Rossler *et al.*, 2019). While initial studies had shown that treatment of pyridine **1** with methyl ketones in the presence of alcohols and (2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl)gold(I) bis(trifluoromethane-sulfonyl)imide could provide trisubstituted indolizines **2** in moderate to good yields, when the methyl ketone was replaced with acetic anhydride, an unknown organic product and the title ketenylidene cluster **3** were observed (Fig. 3). In an attempt to determine the organic product of the reaction, crystals were grown by the slow evaporation of a concentrated ethanol solution over several weeks at room temperature. Using this method, a few tiny yellow needle-shaped crystals, suitable for X-ray diffraction, were obtained and analyzed. However, rather than revealing the structure of the organic product as expected, the X-ray structure revealed the title ketenylidene-bridged tri-gold cluster **3**. Subsequent studies aimed at the independent synthesis of cluster **3** and related species stoichiometrically were unsuccessful.

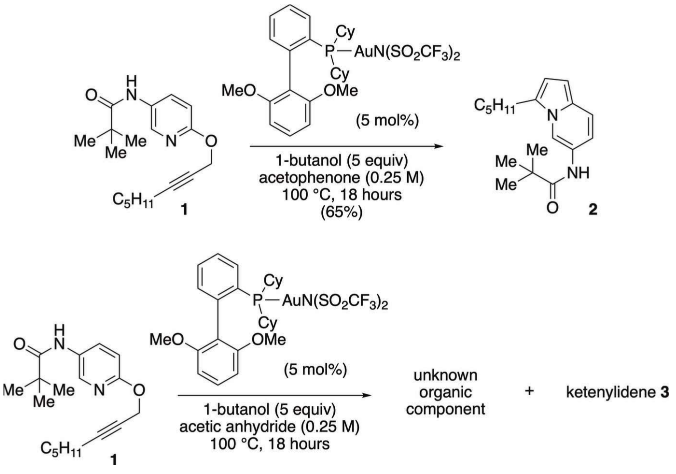

Figure 3
Reaction scheme. The title ketenylidene **3** was discovered as an unexpected by-product of a reaction exploring the gold(I)-catalyzed rearrangement of 2-propargyloxypyridine **1**.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Au_3(C_2O)(C_{26}H_{35}O_2P)_3]$-$(C_2F_6NO_4S_2)$
M_r	2142.59
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	173
a, b, c (Å)	24.0018 (3), 12.4867 (1), 28.4299 (3)
β (°)	103.7669 (8)
V (Å^3)	8275.75 (15)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	11.42
Crystal size (mm)	0.2 × 0.05 × 0.03
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.321, 0.735
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	73587, 15716, 11064
R_{int}	0.110
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.120, 1.01
No. of reflections	15716
No. of parameters	979
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.77, −0.95

Computer programs: *COSMO* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection, and refinement details are collected in Table 1. All non-hydrogen atoms were refined anisotropically. Hydrogen-atom positions were calculated geometrically (C—H = 0.95–1.00 Å) and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(C-methyl).

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