The First Example of a Gold Bis(diphenylphosphino)methane Cationic Dimer with a Bridging Iodide. The X-ray Crystal Structures of (μ-I)[Au(dppm)]$_2$[I] and [Au(dppm)Br]$_2$

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The reaction of [Au(dppCH)]$_2$, (dppCH, bis(diphenylphosphino)methanido, $Ph_2CHPh_2^-$), with MeI in MeOH gives (μ-I)[Au(dppm)]$_2$[I] (**1**) in which one iodide bridges the two gold centres; while the reaction with $BrCH_2COPh$ in MeOH gives [Au(dppm)Br]$_2$ (**3**) in which one bromide is associated with each gold centre.

While studying the reactivity of [Au(dppCH)]$_2$, (dppCH, bis(diphenylphosphino)methanido, $Ph_2CHPh_2^-$), we characterized the first example of a cationic gold dppm dimer containing a bridging iodide, (μ-I)[Au(dppm)]$_2$[I] (**1**) (Fig. 1).

Crystal Data: $C_{50}H_{44}Au_2I_2P_4 \cdot C_4H_{10}O$ (**1**), orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 13.876(2)$, $b = 15.031(2)$, $c = 26.071(3)$ Å, $Z = 4$, 193 parameters refined, 2469 unique reflections with $I > 3.0\sigma(I)$; $R = 0.0454$, $R_w = 0.0425$. $C_{50}H_{44}Au_2Br_2P_2 \cdot C_2H_4Cl_4$ (**3**), triclinic, space group $P\bar{1}$ (no. 2), $a = 10.970(2)$, $b = 11.332(1)$, $c = 12.343(1)$ Å, $\alpha = 109.54(1)$, $\beta = 107.81(1)$, $\gamma = 97.88(1)°$, $Z = 1$, 121 parameters refined, 2847 unique reflections with $I > 3.0\sigma(I)$, $R = 0.0535$, $R_w = 0.0559$. All calculations were performed using Nicolet SHELXTL crystallographic programs. Data for **1** and **3** were collected on a Nicolet R3m/E four-circle diffractometer. All data were collected at ambient temperature with graphite-monochromated Mo Kα radiation. All data were corrected for Lorentz, decay, polarization and absorption effects.

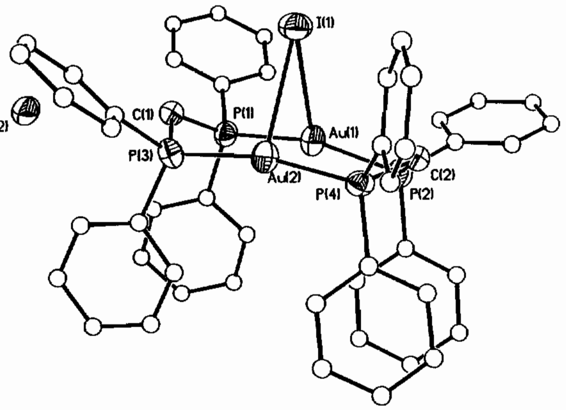

Fig. 1. Molecular structure of (μ-I)[Au(dppm)]$_2$[I] (**1**), hydrogen atoms omitted for clarity, (50% probability displacement ellipsoids). Co-crystallized diethylether is not shown.

Syntheses: Complex **1**: [Au(dppCH)]$_2$ [1] (50.8 mg, 0.0438 mmol) was dissolved in 2 ml methanol; an excess of methyl iodide was added. The solution was allowed to stir for 1 h. Initially the pale yellow solution turned green and after 1/2 h became turbid. The product was isolated by removing the solvent *in vacuo* leaving a pale yellow solid. The solid was dissolved in 1 ml dichloromethane-d$_2$ for ^{1}H NMR study. Yellow crystals (21.3 mg, 32.6% yield, melting point (m.p.) 230 °C) of the isolated product were grown from the dichloromethane solution by vapor diffusion with diethyletheter. Complex **3**: [Au(dppCH)]$_2$ (48.6 mg, 0.0419 mmol) was dissolved in 3.5 ml methanol. The yellow solution became colourless upon the addition of bromoacetophenone (8.2 mg, 0.0412 mmol). After stirring overnight the product was precipitated by the additon of diethylether. The white precipitate was washed twice with diethylether, then was isolated by removing the solvent *in vacuo*. Pale yellow crystals (2.3 mg, 7.5% yield, m.p. 239 °C decomposition) were grown from a dichloromethane solution by vapor diffusion with diethylether.

The unusual structural feature of **1** is a bridging iodide coordinated to both gold centres. We are aware of no other examples in dinuclear gold dppm chemistry of complexes in which the two gold centres are bridged by a single atom. The gold(I) centre is three coordinate and may be described as having a distorted 'Y' geometry. As observed in dimeric dppm A-frame complexes the eight-membered ring adopts an extended boat configuration with the methylene groups displaced towards the bridging atom [2].

We have demonstrated (^{2}H and ^{31}P NMR spectroscopy) that the methylene group of the bridging dppm of [Au(dppm)Cl]$_2$ (**2**) undergoes H/D exchange in CH_3OD/NaOD. As **1** was obtained from the reaction of [Au(dppCH)]$_2$ in a methanol and methyl iodide solution, we suggest that [Au(dppCH)]$_2$ was protonated by the methanol and the iodide counter ions came from the methyl iodide. From ^{1}H NMR studies it appears that another product, tentatively assigned as $[Au(dppCHCH_3)]_2 2I^-$, is also produced in this reaction. The stereochemical nature (*cis* or *trans*) of the alkylated product was not resolved.

Having observed what appears to be an alkylation with methyl iodide we attempted to oxidatively add

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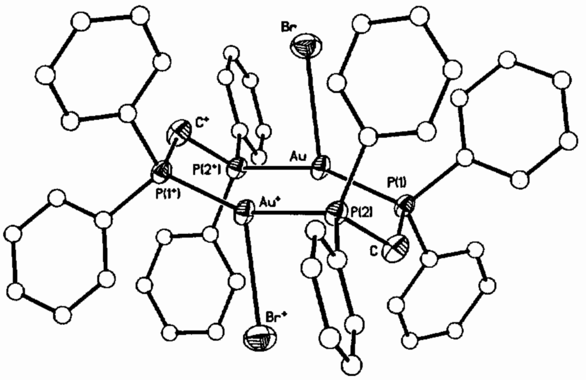
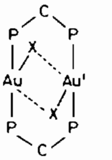


Fig. 2. Molecular structure of $[Au(dppm)Br]_2$ (3), hydrogen atoms omitted for clarity, (50% probability displacement ellipsoids). Co-crystallized dichloromethane is not shown.

TABLE I. Selected Distances (Å) and Angles (°)

		1	2 [4]	3
Distances (Å)				
	Au•••Au'	2.948(2)	2.962(1)	3.015(1)
	Au–X	3.127(2) 3.196(2)	2.771(4)	2.870(1)
	Au'•••X		4.269(1)	4.596(1)
X = I (1) X = Cl (2) X = Br (3)				
Angles (°)				
	P–Au–P	164.1(2) 167.7(2)	155.9(1)	156.5(1)

an alkyl halide to the gold(I) centre of $[Au(dppCH)]_2$ by using a bulkier primary halide which would be less likely to alkylate the dppCH moiety. Since bromoacetophenone forms the unusually stable gold(II) adduct $[Au(CH_2)_2PPh_2]_2(CH_2C(O)Ph)Br$ with $[Au(CH_2)_2PPh_2]_2$ [3], the addition of bromoacetophenone to a methanol solution of $[Au(dppCH)]_2$ was carried out. No oxidative addition occurred (^1H NMR) and the isolated product was $[Au(dppm)Br]_2$ (3) (Fig. 2). The gold centres of 3 are three coordinate, as in $[Au(dppm)Cl]_2$ (2) [4]. However, the bromide atoms do not bridge the two gold centres; one bromide is associated with each gold centre. The eight-membered rings of 2 and 3 adopt an extended chair configuration.

Although the gold to halide distances in **1**, **2** and **3** are long, the gold centre may be described as distorted three coordinate based on the deviation from the linear geometry [5] of the P–Au–P angle generally observed for two coordinate gold(I) centres [6]. Selected distances and angles for **1**, **2** and **3** are listed in Table I. The gold halide distances of **1**, **2** and **3** are 17% (I), 19% (Cl), and 16% (Br) longer than the sum of the covalent radius of the halogen and gold atoms [7]. The nonbridging iodide of **1** is a noninteracting counterion. The closest approach of the nonbridging iodide to a gold centre is 6.57 Å. The closest nonbonding approach of the bridging iodide to a gold centre is 7.34 Å.

Supplementary Material

The atom coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

Acknowledgements

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