Dinuclear Gold Complexes of Two Simple but Underutilized Dicarbanionic Ligand Types

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday in recognition of his numerous contributions to inorganic and organometallic chemistry

Both *mono-* and *bis*ylide zwitterionic complexes of gold(I), $[(C_6F_5)\{PhCH(PPh_3)\}Au]$ (**4**), $[(C_6F_5)_2(C_6H_4\text{-}p)\{CH(PPh_3)\}_2Au_2]$ (**5**) and $[(C_6F_5)_2(C_6H_4\text{-}m)\{CH(PPh_3)\}_2Au_2]$ (**6**) were prepared by THT substitution in $[C_6F_5(THT)Au]$ (THT = tetrahydrothiophene) using deprotonated *mono-* and *bis*-phosphonium salts. Lithiation of 4,4′-dibromo-2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl and transmetallation with $[Cl(Ph_3P)Au]$ produced a dinuclear gold complex of octafluoro-substituted biphenyl $[[(PPh_3)_2(C_6F_4\text{-}C_6F_4)_2Au_2]]$ (**8**).

Key words: Gold(I), *Bis*ylide Complexes, Octafluorobiphenyl, Ylide Structures,
Dinuclear Gold(I) Complexes

Introduction

For more than three decades ylide ligands have been used by gold chemists to prepare a large variety of complexes [1 – 3]. Groups that have featured prominently are those of Schmidbaur [4], the Laguna brothers [5], Fackler [6] and Vicente [7]. More recently, phosphonium ylide complexes of gold (and other late as well as early transition elements) have been used as sources of carbene complexes [8], and in a recent *Dalton Perspective*, Urriolabeitia [9] addresses the bonding as well as redox properties of, amongst others, gold ylide complexes from theoretical as well as practical viewpoints. As far as we could ascertain, no dinuclear gold complexes bearing phosphine *bis*ylides have been reported and, with certainty, no crystal structures of such compounds or of any transition metals have been authenticated.

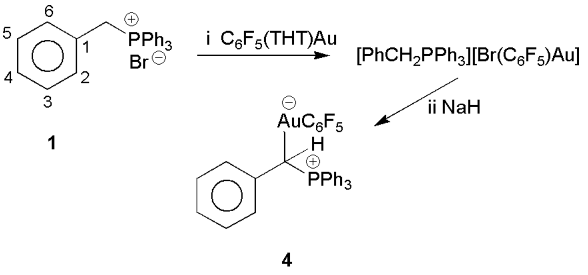
Pentafluorophenyl is an important spectator ligand in gold chemistry [10], and it is surprising that its extended 4,4′-dianionic variant, 2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl, although synthetically useful in organic chemistry and reported to form a gold(I) complex [11], has been described as a ligand in only one crystal structure determination wherein nickel is the metal of choice [12].

In this communication we report on the preparation and structure of dinuclear gold complexes employing, firstly, zwitterionic phosphonium *bis*ylides and, secondly, a dianionic fluorosubstituted biphenyl ligand. For comparative purposes, three other and somewhat related new crystal structures are also described.

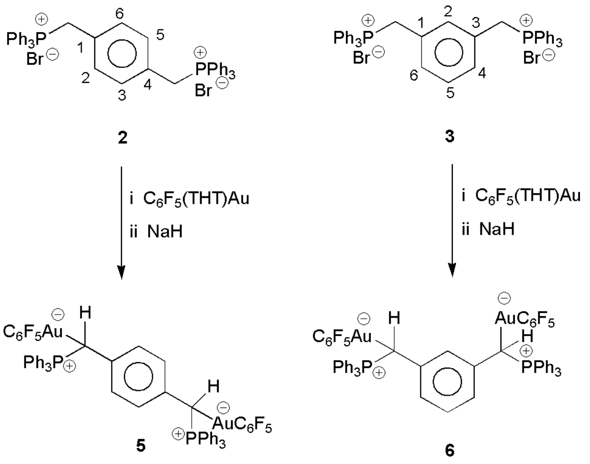
Results and Discussion

Synthetic procedures

Colorless precursor phosphonium salts (**1**, **2** and **3**, Schemes 1 and 2) were formed by alkylation reactions between *mono-* and *bis*(bromoalkyl)benzene and triphenylphosphine [13, 14]. The choice of solvent is very important for the formation of the *bis*phosphonium



Scheme 1.



Scheme 2.

salts since strongly polar solvents such as nitrobenzene, acetonitrile (used by us) and dimethylformamide keep the formed *mono*phosphonium salts in solution allowing reaction with a second molar equivalent of triphenylphosphine. Deprotonation effected ylide formation.

Various methods were compared in our attempts to prepare dinuclear ylide complexes of gold from *bis*phosphonium salts. The biggest problem experienced when successively deprotonating with *n*-BuLi [15] and also when employing the Ag_2O-method, previously used for the preparation of carbene complexes [16], was the formation of by-products that could not easily be separated from the targeted compounds. A similar complication emerged with $[(acac)(Ph_3P)Au]$ [17], and the known compound $[\{Me(CO)\}_2C(Ph_3PAu)_2]$ [18] was formed along with the desired product and other mononuclear (acac)gold and (ylide)gold compounds. The most successful protocol in our hands turned out to be one based on developmental work by Usón and coworkers [19]. The approach is illustrated for both monoylide (in Scheme 1) and diylide formation (in Scheme 2). The ylide ligand substitutes Br^- in $[Br(C_6F_5)Au]$ upon formation from the phosphonium salts. Complex **4** represents the first example of a neutral gold compound stabilized by C_6F_5 while also comprising an aromatic group adjacent to the ylide carbon atom. Using the same principles, the method was extended to include the formation of the unique dinuclear complexes **5** and **6**. Unreacted phosphonium salt was removed from the residue after stripping off the solvent by multiple extractions with diethyl ether. An attempt to isolate only a mononuclear complex by first converting the *bis*phosphonium bromide into *bis*phosphonium tetrafluoroborate and then deprotonating with one molar quantity of *n*-BuLi before reaction with $[C_6F_5(THT)Au]$, was unsuccessful. It produced a mixture of compounds from which solely the salt **7** [20] (Fig. 1) was crystallized. The cationic fragments in compounds **2** and **3** and **5** and **6**, respectively, differ only therein that two hydrogen atoms in the former two are replaced by two isolobal C_6F_5Au units in the latter two complexes.

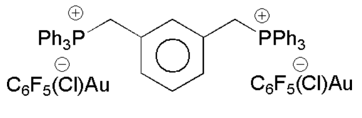
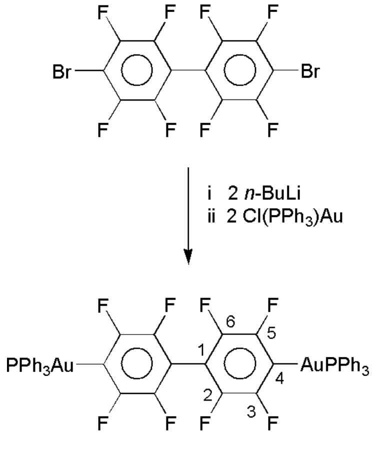


Fig. 1.



Scheme 3.

To prepare compound **8** (Scheme 3) commercial 4,4′-dibromo-2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl was lithiated with *n*-BuLi at low temperature and the product then transmetallated *in situ* with $[Cl(Ph_3P)Au]$. Product **8** was obtained in pure form by crystallization from the crude mixture and recrystallization with diethyl ether to afford suitable crystals for structure determination by X-ray diffraction. Dinuclear **8** was also characterized by NMR measurements, elemental analysis and mass spectrometry.

Spectrometric and spectroscopic characterization

Fragments observed in the EI-MS of **1** and ES-MS of **2**, **3** and **6** confirmed the formation of the proposed products. The molecular ions of **4**, **5** and **8** were observed in their ES-MS spectra. For the latter, a scrambling of the gold ligands occurs in the mass spectrometer to form the homoleptic product $(Ph_3P)_2Au^+$.

It is interesting to note that the chemical shifts for the ylide carbon atoms in **4**, **5** and **6** adopt essentially the same values, δ = 35.4, δ = 34.9 and 35.3 and δ = 35.6. The same carbon atoms in the precursor salts for the preparation of these three complexes resonate upfield at δ = 30.7 and 29.6 (**5** and **6**).

A single signal for the P atoms in compounds **1**, **2** and **3** in their ^{31}P NMR spectra confirms that the multiplets observed for the carbons of the PPh_3 groups of **2** and **3** result from the magnetic inequivalence of these carbons (AA′XX′ spin system with $J_{XX'} = 0$ [21]) and not from the presence of impurities. The chemical shifts of **2** and **3** were unequivocally assigned from ^{1}H-^{13}C gHSQC NMR measurements.

In contrast to single resonances for **4** and **6**, the two singlet signals in the ^{31}P NMR spectrum of **5** indicate, like the ^{13}C NMR spectra mentioned above, the formation of diastereomeric compounds. Diastereomeric structures are possible as a result of the two different conformations (*R* and *S*) that each of the two chiral centers (the two ylidic carbons) allow. These diastereomers give two different but very similar sets of NMR signals for each type of carbon, proton or phosphorus atom in the applicable spectra. The *RR* and *SS* isomers are responsible for one set of signals and the *meso RS* and *SR* isomers for another set. From the NMR spectra (^{13}C, ^{1}H and ^{31}P) it is evident that one set of diastereomers is preferably formed (60 %) to the other (40 %). The ^{13}C NMR spectra of **5** and **6** are again complicated by the magnetic inequivalence of the carbon atoms of the PPh_3 groups similar to the spectra of **2** and **3**. The signals corresponding to the Ph_3PAu fragments in **4**, **5**, **6** and **8** are normal.

The C_6F_5Au group in the ^{13}C NMR spectrum of **4** exhibits similar signals to those of the starting material $[(C_6F_5)(THT)Au]$ [22], but the multiplets are of low intensity due to multiple J_{CF} couplings. As a result of this the signals for C1 and C4 in the spectrum of compound **8** could not be observed, and in the spectra of **5** and **6** no signals were visible.

Molecular structures

Compound **2** crystallizes with two equivalents of ethanol (Fig. 2) in the body-centered tetragonal space group $I4_1/a$. The solvent molecules form hydrogen bonds to bromide anions. The bromide Br1 is further stabilized by C–H···Br contacts (H7A···Br1 distance 2.69 Å) involving pro-ylidic methylene groups. While both bromide anions and the ethanol molecule that contains O1 are well-defined, the other ethanol molecule exhibits strong thermal motion and could not be modeled satisfactorily. The dication is asymmetric, and both CH_2PPh_3 groups at the central benzene ring are in a UU configuration, meaning that they face the same direction in respect of the C_6 plane of the ring. This orientation allows a short $\pi\cdots\pi$ contact of 3.570 Å between the two benzene rings related by a center of inversion (symmetry operator: $3/2-x, 3/2-y, 1/2-z$). Other crystal structures that contain the same dication as **2** are known to exhibit both UU [23] and UD [24] orientations, and sometimes both arrangements are observed in a single crystal [25]. Most molecular structures in the UU orientation exhibit $\pi\cdots\pi$ interactions of the central benzene ring with centroid distances between 3.623 and 3.701 Å [23a], markedly longer than in $\mathbf{2}\cdot 2C_2H_6O$.

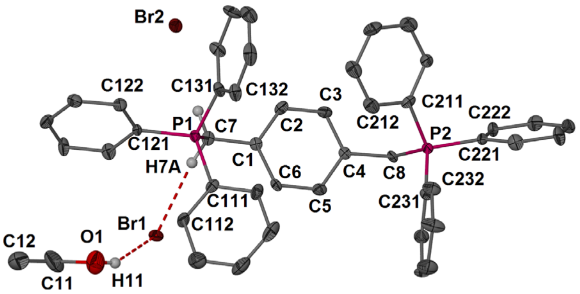


Fig. 2. Molecular structure of **2**; selected bond lengths and angles (Å, deg): O1···Br1 3.328(5), O1–H11···Br1 155.5, C7···Br1 3.687(5), C7–H7A···Br1 172.9.

Compound **3** (Fig. 3), the *meta*-substituted isomer of **2**, also crystallizes as $\mathbf{3}\cdot 3C_2H_6O$, with a unique dication in the UU orientation and three

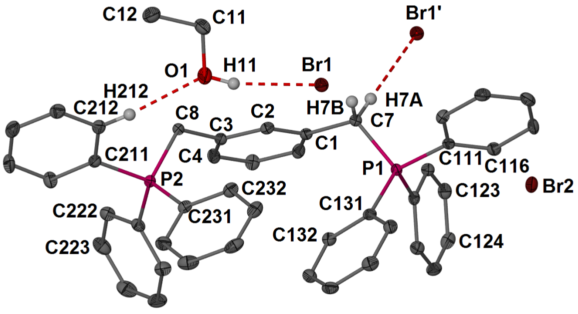


Fig. 3. Molecular structure of **3**. Two ethanol molecules forming hydrogen bonds to Br2 have been omitted for clarity; selected bond lengths and angles (Å, deg): O1···Br1 3.266(2), O1–H11···Br1 165.5, O2···Br2 3.362(2), O2–H21···Br2 175.6, O3···Br2 3.314(2), O3–H31···Br2 156.9, C212···O1 3.324(3), C212–H212···O1 172.7, C7···Br1′ 3.691(2), C7–H7A···Br1′ 171.9.

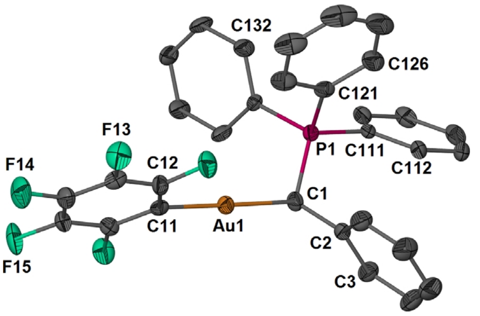


Fig. 4. Molecular structure of **4**; selected bond lengths and angles (Å, deg): Au1–C1 2.098(3), Au1–C11 2.034(3), Au1 ··· H112 2.73, C1–Au1–C11 178.45(14).

ethanol molecules in the asymmetric unit. The chloro(pentafluorophenyl)aurate salt of this dication, **7**, (Fig. 1) has been reported [20]. Two ethanol solvent molecules form hydrogen bonds with Br2 while the ethanol that contains O1 forms a hydrogen bond to Br1 and associates *via* its oxygen atom with an aromatic C–H unit (H212 ··· O1 2.38 Å). The PPh_3 moiety of P1 forms a six-fold phenyl embrace (6PE) [26] with its symmetry-generated image (P1 ··· P1′ 6.055 Å, symmetry operator ′: $1-x$, $2-y$, $1-z$). As in the molecular structure of $\mathbf{2}\cdot 2C_2H_6O$, a C–H ··· Br contact is observed (H7A ··· Br1′ 2.71 Å, symmetry operator ′: $1-x, 1-y, 1-z$).

Complex **4** (Fig. 4) crystallized in the orthorhombic crystal system, space group $P2_12_12_1$. No aurophilic interactions are present. The C11–Au1–C1 angle is practically linear [177.7(5)°] as expected for Au(I) compounds. The Au(I)-aryl bond (to C_6F_5) is significantly (0.05 Å) shorter than the Au(I)-ylide bond. This complex represents the simplest example of a coordinated triphenylphosphonium ylide with an aromatic side-chain and is also the first example of a mononuclear gold ylide complex that contains $C_6F_5^-$ as an auxiliary ligand. The most important difference between the free [27] and coordinated ylide ligand is seen in the C–P separation that is 0.09 Å shorter in the free ylide owing to more double-bond character in this bond. H112 exhibits a short contact to Au1 measuring 2.73 Å.

In compound **6** (Fig. 5), the ylide substituents now exhibit UD orientation relative to the central benzene ring, but the whole molecule remains unique, and a possible symmetry with a two-fold rotation axis is not realized. No aurophilic contacts are formed by the gold atoms due to steric requirements of the bulky triphenylphosphine groups that lie on opposite sides of the aromatic ring and C atoms attached thereto, thus placing the C_6F_5Au units on either side of this plane, too far removed from each other for aurophilic interactions to occur. The gold atom Au2 engages in a Au ··· H interaction to H8′ (symmetry operator: $1-x$, $1-y$, $1-z$) measuring 2.94 Å, effectively forming dimers in the solid state. Additionally, there are close contacts between the *ortho*-hydrogen atoms of a PPh_3 phenyl group and the gold centers (Au1 ··· H126 2.80 Å, Au2 ··· H236 2.68 Å). Contacts showing similar distances have been observed in thione complexes of Au(I) as well [28]. No 6PE interactions are formed by either PPh_3 group in **6**. Only two other gold(I) ylide complexes with AuC_6F_5 groups have been reported by Usón *et al.*, and they exhibit comparable geometries [29]. The C8–Au2–C21 and C7–Au1–C11 bond angles deviate very slightly from linearity by 4° and 5°, respectively. The phosphorus atoms in the triphenylphosphonium units have tetrahedral symmetry. π-Stacking of the pentafluorophenyl groups (distance C14–C16′ 3.371 Å, symmetry operator: $1-x$, $-y$, $1-z$) determine the lattice arrangement.

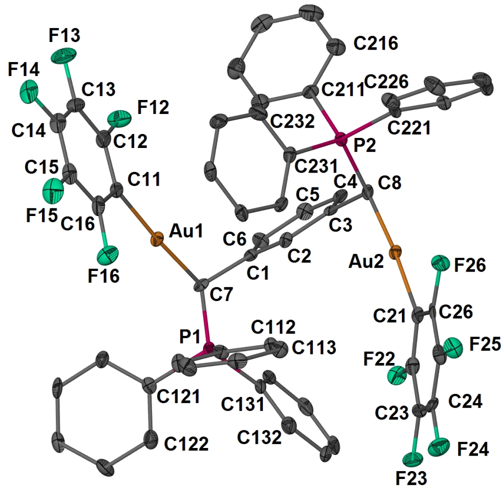


Fig. 5. Molecular structure of **6**; selected bond lengths and angles (Å, deg): Au1–C7 2.104(5), Au1–C11 2.038(6), Au2–C8 2.079(6), Au2–C21 2.024(6), Au1 ··· H126 2.78, Au2 ··· H8′ 2.94 (symmetry transformations applied to generate equivalent atoms: $1-x$, $1-y$, $1-z$), Au2 ··· H236 2.68, Au2 ··· H8′–C8′ 170.6.

Corresponding interatomic separations in all the new ylide complexes [**2**, **3**, **4**, **6**, **7** [20] and **9** (Fig. 6, [30])] of gold are remarkably similar (Table 1), and representative values are displayed in Fig. 7.

Compound **8** (Fig. 8), the first gold and only the second dinuclear transition metal complex [12] of

	$\mathbf{2}^a$	$\mathbf{3}^a$	$\mathbf{4}^b$	$\mathbf{6}^b$	$\mathbf{7}^a$	$\mathbf{9}^b$
Distances						
C_6H_n–CP	1.507(7), 1.506(7)	1.516(3), 1.520(3)	1.508(4)	1.518(8), 1.514(8)	1.507(5)	1.522(6)
C_6H_nC–P	1.808(5), 1.813(5)	1.811(2), 1.816(2)	1.789(3)	1.777(6), 1.781(6)	1.814(3)	1.788(4)
C_6F_5–Au			2.034(3)	2.038(6), 2.024(6)	2.008(4), 2.3024(12)	2.0040(4)
Au–CP			2.098(3)	2.104(5), 2.079(6)		
Angles						
C_6F_5–Au–CP			178.75(14)	176.0(2), 175.1(2)		
C_6H_n–C–P	113.8(4), 112.1(4)	115.91(14), 116.52(15)	113.0(2)	116.9(4), 112.2(4)	115.0(2)	114.6(3)
Dihedral angles						
C_6F_5–Au–C–P			70.9	155(3), 119(3)		78.4
C_6F_5–Au–C–C_6H_n			56.3	27(4), −10(3)		−7.1

Table 1. Selected bond lengths (Å) and angles (deg) in **2**–**4**, **6**, **7**, and **9** with estimated standard deviations in parentheses.

[a] Phosphonium salt;
[b] ylide compound.

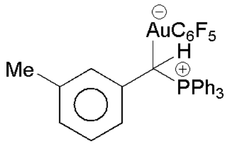


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Fig. 6.

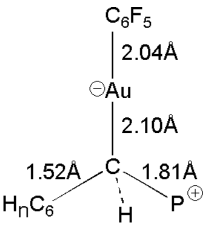

Fig. 7. Representative values for bond lengths.

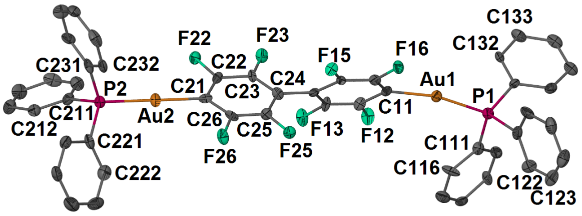

Fig. 8. Molecular structure of **8**; selected bond lengths and angles (Å, deg): Au1–P1 2.269(3), Au1–C11 2.04(1), P1–Au1–C11 167.4(3), Au2–P2 2.275(3), Au2–C21 2.02(2), P2–Au2–C21 177.8(3).

the 4,4′-substituted 2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl ligand to be characterized by X-ray diffraction, exhibits a considerably distorted C11–Au1–P1 angle of 167.4(3)° which can be assigned to packing forces rather than close sub-van der Waals contacts to Au1. The tetrafluorophenylene unit containing C11 engages in an off-center $\pi\cdots\pi$ contact with its symmetry-generated image (symmetry operator: $2-x$, $-y$, $-z$) and the other tetrafluorophenylene group forms contacts to the PPh_3 phenyl substituent containing C131. These π-stacking interactions are only made possible by bending the P1–Au1–C11 angle considerably. The best planes for the two benzene rings of the octafluorobiphenyl linker are at an angle of 62.1(3)°. The rod-like molecules all arrange parallel to the [$\bar{1}$ 1 1] line in the crystal. The related compound [$(PPh_3)(C_6F_5)Au$] [31] exhibits similar Au–P and Au–C distances.

Conclusion

Although practically ignored thus far in coordination chemistry, *bis*ylides derived from *m*- or *p*-phenylene-*bis*-[(triphenylphosphonio)methane] have now been shown to form thermodynamically stable complexes with the C_6F_5Au complex fragment. The isolation and characterization of a 4,4′-dinuclear complex of 2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl indicates that gold, and certainly other metals as well, could make use of this ligating binding unit to form a variety of compounds in which more than one metal feature.

Experimental Section

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, *n*-pentane from sodium and CH_2Cl_2 and methanol from CaH_2. Melting points were determined on a

Stuart Scientific Melting Point Apparatus SMP3 and are uncorrected. Mass spectra were recorded on a VG Quattro (ESI, 70 eV) or AMD 604 (EI, 70 eV) instrument, the infrared spectra on a Perkin-Elmer 1600 Series FTIR instrument and NMR spectra on a Varian 300 FT or INOVA 600 MHz spectrometer (δ reported relative to the solvent resonance or external reference 85 % H_3PO_4). Elemental analyses were carried out by the Department of Chemistry, University of Cape Town. Gold(I) starting materials, $[(C_6F_5)(THT)Au]$ [32–34], $[Cl(PPh_3)Au]$ [35] were prepared according to literature methods. All the other starting materials are commercially available and were used without further purification.

Benzyltriphenyphosphonium bromide (**1**)

Triphenylphosphine (16.9 g, 64.3 mmol, 10 % excess) in 75 mL of diethyl ether was stirred until all the triphenylphosphine had dissolved. Benzyl bromide (9.99 g, 58.5 mmol) in 30 mL of diethyl ether was added dropwise to this solution. The solution became cloudy and was stirred for 5 h at r. t. The suspension was left for two days to precipitate. The precipitate (6.32 g, 30 %) was filtered off and dried *in vacuo*. The salt was recrystallized from hot ethanol. Special precautions were taken to destroy all benzyl bromide left in the flasks and funnel with ammonium hydroxide since benzyl bromide is a powerful lachrymator. M. p. 294–296 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.70 (m, 3 H, *p*-Ph), 7.63 (m, 6 H, *o*-Ph), 7.55 (m, 6 H, *m*-Ph), 7.14 (m, 1H, H4), 7.03 (m, 2 H, H2 and H6), 7.01 (m, 2 H, H3 and H5), 5.22 (d, ^2J = 14.1 Hz, 2 H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 134.9 (d, ^4J = 2.5 Hz, *p*-Ph), 134.1 (d, ^3J = 9.7 Hz, *m*-Ph), 131.2 (d, ^3J = 5.6 Hz, C2 and C6), 130.0 (d, ^2J = 12.6 Hz, *o*-Ph), 128.6 (d, ^4J = 3.3 Hz, C3 and C5), 128.2 (d, ^5J = 3.8 Hz, C4), 126.9 (d, ^2J = 8.8 Hz, C1), 117.5 (d, ^1J = 85.8 Hz, *i*-Ph), 30.7 (d, ^1J = 46.2 Hz, CH_2). – ^{31}P NMR ($CDCl_3$): δ = 23.8 (s, PPh_3). – MS (EI, 70 eV): *m/z* (%) = 353 (22) $[PhCH_2PPh_3]^+$, 262 (100) $[PPh_3]^+$, 183 (66) $[PPh_2]^+$, 108 (22) $[PPh]^+$, 91 (9) $[PhCH_2]^+$. – $C_{25}H_{22}BrP$ (433.32): calcd. C 69.29, H 5.12; found C 69.38, H 5.00.

1,4-Bis[(triphenylphosphonio)methyl]benzene dibromide (**2**)

Triphenylphosphine (11.7 g, 44.8 mmol, 25 % excess) in acetonitrile (100 mL) was boiled under reflux (80 °C) until all the PPh_3 had dissolved, and 1,4-*bis*(bromomethyl)-benzene (5.28 g, 20.1 mmol) in acetonitrile (100 mL) was added [13, 14]. The solution became cloudy and was boiled under reflux for 40 h. The colorless precipitate that formed was filtered off and dried *in vacuo* (12.4 g, 80 %). These colorless crystals were recrystallized from hot chloroform and dried again *in vacuo*. M. p. 330–332 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.69 (m, 6 H, *p*-Ph), 7.53 (m, 12 H, *m*-Ph), 7.43 (m, 12 H, *o*-Ph), 6.65 (s, 4 H, H2, H3, H5 and H6), 4.62 (d, ^2J = 13.6 Hz, 4 H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 135.4 (br s, *p*-Ph), 133.9 (m, *m*-Ph), 131.7 (br s, C2, C3, C5 and C6), 130.3 (m, *o*-Ph), 127.8 (m, C1 and C4), 117.1 (d, ^1J = 86.9 Hz, *i*-Ph), 29.6 (dm, ^1J = 52.3 Hz, CH_2). – ^{31}P NMR ($CDCl_3$): δ = 28.1 (s, PPh_3). – MS ((+)-ESI): *m/z* (%) = 365 (49) $[PPh_3CHC_6H_4CH_2]^+$, 314 (100) $[P_2Ph_3Na\text{–}2H]^{2+}$, 262 (12) $[PPh_3]^+$. – $C_{44}H_{38}Br_2P_2$ (788.56): calcd. C 67.02, H 4.86; found C 67.31, H 4.92.

1,3-Bis[(triphenylphosphonio)methyl]benzene dibromide (**3**)

Triphenylphosphine (9.88 g, 37.7 mmol, 25 % excess) in acetonitrile (100 mL) was boiled under reflux until all the triphenylphosphine had dissolved [13, 14]. To this clear solution (3.97 g, 15.0 mmol) 1,3-*bis*(bromomethyl)benzene in acetonitrile (100 mL) was added. The solution remained clear and was boiled under reflux for 24 h. A white precipitate (3.86 g, 36 %) formed which was filtered off and washed with diethyl ether (3 × 20 mL) and dried under vacuum. The precipitate was recrystallized from hot ethanol. M. p. 237–239 °C. – ^{1}H NMR (CD_2Cl_2): δ = 7.77 (m, 6 H, *p*-Ph), 7.71 (m, 12 H, *m*-Ph), 7.60 (m, 12 H, *o*-Ph), 7.53 (m, 1 H, H5), 7.00 (m, 2 H, H4 and H6), 6.88 (d, $^4J_{PH}$ = 7.7 Hz, 1 H, H2), 5.23 (d, ^2J = 15.1 Hz, 4 H, CH_2). – ^{13}C NMR (CD_2Cl_2): δ = 135.5 (m, ^4J = 1.3 Hz, *p*-Ph), 135.2 (m, ^4J = 6.2 Hz, C5), 134.9 (m, ^3J = 10.2 Hz, *m*-Ph), 131.8 (m, ^3J = 8.6 Hz, C4 and C6), 130.5 (m, ^2J = 13.1 Hz, *o*-Ph), 129.2 (m, ^2J = 9.9 Hz, C1 and C3), 129.0 (m, ^3J = 3.2 Hz, C2), 118.0 (d, ^1J = 86.3 Hz, *i*-Ph), 29.6 (d, ^1J = 47.5 Hz, CH_2). – ^{31}P NMR (CD_2Cl_2): δ = 23.4 (s, PPh_3). – MS ((+)-ESI): *m/z* (%) = 707 (70) $[Br][Ph_3PCH_2C_6H_4CH_2PPh_3]^+$, 627 (70) $[Ph_3P{=}CHC_6H_4CH_2PPh_3]^+$, 315 (100) $[P_2Ph_3Na\text{–}H]^{2+}$. – $C_{44}H_{38}Br_2P_2$ (788.56): calcd. C 67.02, H 4.86; found C 67.22, H 5.07.

(Benzyl-triphenyl-λ^5-phosphorane)(pentafluorophenyl)gold (**4**)

Benzyltriphenylphosphonium bromide (0.890 g, 2.10 mmol) and $[(C_6F_5)(THT)Au]$ (0.920 g, 1.90 mmol) were suspended in 20 mL of THF and stirred for 40 min at r. t. NaH (0.240 g, 10.0 mmol) in 10 mL of THF was added to deprotonate the phosphonium salt to the corresponding ylide. The suspension was stirred for 3 h at r. t. and filtered through celite. The solvent was removed *in vacuo* and the residue extracted first with diethyl ether and subsequently with dichloromethane. Both fractions were dried *in vacuo*, yielding 1.08 g, 70 % of product. Crystals suitable for single crystal X-ray diffraction were obtained from a solution of **5** in CH_2Cl_2 at −20 °C. M. p. 128 °C (decomp.). – ^{1}H NMR ($CDCl_3$): δ = 7.75 (m, 6 H, *o*-Ph), 7.63 (m, 3 H, *p*-Ph), 7.50 (m, 6 H, *m*-Ph), 7.00 (m, 5 H, CHC_6H_5), 3.92 (d, ^2J = 13.6 Hz, 1 H, $C\mathit{H}C_6H_5$). – ^{13}C NMR ($CDCl_3$): δ = 148.9 (ddm, ^1J = 225.8 Hz, ^3J = 26.2 Hz, *o*-C_6F_5), 138.7 (dm, ^1J = 244.3 Hz, *p*-C_6F_5), 137.1 (dm, ^1J = 232.2 Hz, *m*-C_6F_5), 134.2 (d, ^3J = 8.9 Hz, *m*-Ph), 134.0 (d, ^4J =

7.3 Hz, C4), 133.3 (d, ^4J = 2.9 Hz, *p*-Ph), 132.3 (m, *i*-C_6F_5), 130.2 (d, ^3J = 8.0 Hz, C2 and C6), 129.4 (d, ^2J = 11.7 Hz, *o*-Ph), 128.6 (d, ^4J = 2.9 Hz, C3 and C5), 125.2 (d, ^1J = 84.1 Hz, *i*-Ph), 124.9 (d, ^2J = 3.8 Hz, C1), 35.4 (dm, ^1J = 31.6 Hz, *C*HC_6H_5). – ^{31}P NMR ($CDCl_3$): δ = 26.2 (s, PPh_3). – MS (EI, 70 eV): *m/z* (%) = 716 (3) $[M]^+$, 459 (3) $[AuPPh_3]^+$, 352 (100) $[PhCHPPh_3]^+$, 275 (6) $[PPh_3CH_2]^+$, 262 (40) $[PPh_3]^+$, 183 (60) $[PPh_2]^+$, 167 (38) $[C_6F_5]^+$, 91 (24) $[PhCH_2]^+$. – $C_{31}H_{21}F_5AuP$ (716.10): calcd. C 51.97, H 2.95; found C 51.86, H 2.78.

*1,4-Bis[(triphenylphosphonio)methanido]benzene bis(pentafluorophenyl)gold (**5**)*

A suspension of phosphonium salt **2** (0.820 g, 1.04 mmol, 1 % excess) and $[(C_6F_5)(THT)Au]$ (0.930 g, 2.06 mmol) in 20 mL of THF was stirred for 1 h at r. t. NaH (0.250 g, 10.4 mmol) in 10 mL of THF was added, and the mixture stirred for 5 h at r. t., after which it was filtered through celite. A brown filtrate was obtained and dried *in vacuo*. The residue was extracted sequentially with diethyl ether and dichloromethane, filtered through anhydrous $MgSO_4$ and dried *in vacuo*. A brown solid stayed behind on the $MgSO_4$, which was insoluble in CH_2Cl_2, diethyl ether or THF and was discarded. From the NMR spectra it was evident that the dichloromethane extract contained the desired compound, yield 1.29 g, 40 %. M. p. 135 °C (decomp.). – ^{1}H NMR ([D$_8$]THF): δ = 7.83 (m, 24 H, *m*-Ph), 7.66 (m, 12 H, *p*-Ph), 7.52 (m, 24 H, *o*-Ph), 6.72, 6.68 (2 × br s, 2 × 4 H, H2, H3, H5 and H6), 4.04, 4.00 (2×d, ^1J = 13.5, 13.4 Hz, 2 × 2 H, AuCH). – ^{13}C NMR ([D$_8$]THF): δ = 137.2, 137.0 (2 × m, C2, C3, C5 and C6), 135.3 (m, *m*-Ph), 134.1 (br s, *p*-Ph), 131.4, 131.2 (2 × m, C1 and C4), 130.2 (m, *o*-Ph), 126.4, 126.5 (2 × dd, ^1J = 85.3 Hz, ^9J = 1.5 Hz, *i*-Ph), 35.3, 34.9 (2 × m, AuCH). – ^{31}P NMR ([D$_8$]THF): δ = 26.1, 26.3 (2× s, PPh_3). – MS ((+)-ESI): *m/z* (%) = 1354 (15) $[M]^+$, 991 (100) $[Ph_3PCH(AuC_6F_5)C_6H_4CH_2PPh_3]^+$, 314 (15) $[P_2Ph_3Na{-}2H]^+$. – $C_{56}H_{36}F_{10}Au_2P_2$ (1354.77): calcd. C 49.65, H 2.68; found C 49.55, H 2.81.

*1,3-Bis[(triphenylphosphonio)methanido]benzene bis(pentafluorophenyl)gold (**6**)*

The phosphonium salt **3** (0.810 g, 1.00 mmol) and $[(C_6F_5)(THT)Au]$ (1.10 g, 2.40 mmol) were suspended in 20 mL of THF and stirred for 1 h at r. t. A clear solution formed to which NaH (0.250 g, 10.3 mmol) in 10 mL of THF was added. The mixture became light-yellow, and after stirring for 1 h the suspension became bright-orange. The mixture was stirred overnight as it was believed that the orange color resulted from free ylide. The next morning the suspension was light-yellow again and was filtered over celite to obtain a clear light-yellow filtrate. The solvent was removed *in vacuo*. The residue was extracted sequentially with diethyl ether and dichloromethane, filtered through anhydrous $MgSO_4$ and dried *in vacuo*. The diethyl ether layer contained the proposed compound (1.98 g, 60 %), and crystals suitable for single crystal X-ray diffraction studies were obtained from a solution of **6** in CH_2Cl_2, layered with pentane and stored at −10 °C. M. p. 120 °C (decomp.). – ^{1}H NMR (CD_2Cl_2): δ = 7.70 (m, 12 H, *o*-Ph), 7.60 (m, 6 H, *p*-Ph), 7.46 (m, 12 H, *m*-Ph), 6.74 (m, 2 H, H2 and H5), 6.61 (m, 2 H, H4 and H6), 3.77 (d, ^2J = 13.9 Hz, 2 H, AuCH). – ^{13}C NMR (CD_2Cl_2): δ = 140.4 (t,^4J = 4.8 Hz, C5), 134.5 (m, *m*-Ph), 133.7 (m, *p*-Ph), 132.3 (m, C4 and C6), 129.8 (m, *o*-Ph), 129.1 (m, C1 and C3), 126.9 (t, ^3J = 5.5 Hz, C2), 125.4 (d, ^1J = 84.4 Hz, *i*-Ph), 35.6 (d, ^1J = 36.0 Hz, AuCH). – ^{31}P NMR (CD_2Cl_2): δ = 25.6 (s, PPh_3). – MS ((+)-ESI): *m/z* (%) = 372 (100) $[Ph_3PCHC_6H_4CHPPh_3 + CHCl_3]^{2+}$, 358 (18) $[Ph_3PCH_2C_6H_4CH_2{+}3H]^+$. – $C_{56}H_{36}F_{10}Au_2P_2$ (1354.77): calcd. C 49.65, H 2.68; found C 49.57, H 2.80.

*4,4′-Bis-(triphenylphosphine)gold(I)-μ-2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl (**8**)*

A suspension of 4,4′-dibromo-2,3,5,6,2′,3′,5′,6′-octafluoro-1,1′-biphenyl (0.750 g, 1.60 mmol, 2 % excess) in 20 mL of diethyl ether was cooled down to −75 °C, and 1.6 M *n*-BuLi (1.60 mL, 3.70 mmol) was added dropwise. The mixture was stirred at −75 °C for 10 min, whereafter the $[Cl(Ph_3P)Au]$ (1.57 g, 3.17 mmol) was added. The mixture was stirred at −75 °C for another 10 min before the temperature was slowly (over 1 h) raised to r. t. The suspension was filtered through $MgSO_4$ and the solvent removed *in vacuo*. Compound **8** was recrystallized from a solution of the crude mixture in diethyl ether, yielding, 1.09 g, 60 %. M. p. 106.7 °C (decomp.). – ^{1}H NMR (CD_2Cl_2): δ = 7.70 (m, 12 H, *m*-Ph), 7.60 (m, 6 H, *p*-Ph), 7.54 (m, 12 H, *o*-Ph). – ^{13}C NMR (CD_2Cl_2): δ = 149.8 (dm, ^1J = 228.4 Hz, C3 and C5), 144.7 (dm, ^1J = 257.9 Hz, C2 and C6), 135.0 (d, ^3J = 13.8 Hz, *m*-Ph), 132.3 (d, ^4J = 2.5 Hz, *p*-Ph), 130.5 (d, ^1J = 55.1 Hz, *i*-Ph), 130.0 (d, ^2J = 11.3 Hz, *o*-Ph). – ^{31}P NMR (CD_2Cl_2): δ = 42.4 (s, PPh_3). – MS ((+)-ESI): *m/z* (%) = 1673 (10) $[M + AuPPh_3]^+$, 1215 (15) $[M{+}H]^+$, 721 (100) $[(Ph_3P)_2Au]^+$, 459 (18) $[AuPPh_3]^+$. – $C_{48}H_{30}Au_2F_8P_2$ (1214.64): calcd. C 47.47, H 2.49; found C 47.41, H 2.38.

X-Ray structure determinations

Intensity data of **2**, **3**, **6**, and **8** were collected at 100 K with a Bruker SMART Apex diffractometer [36], intensity data of **4** were collected at 173 K with a Nonius Kappa CCD diffractometer [37]. All experiments were conducted with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Intensities were measured using the ω-scan mode (Nonius Kappa CCD: φ- and ω-scan mode) and were corrected for Lorentz and polarization effects. The structures

Table 2. Crystal structure data for **2 – 4**, **6** and **8**.

	2	**3**	**4**	**6**	**8**
Formula	$C_{44}H_{38}Br_2P_2 \cdot 2C_2H_6O$	$C_{44}H_{38}Br_2P_2 \cdot 3C_2H_6O$	$C_{31}H_{21}AuF_5P$	$C_{56}H_{36}Au_2F_{10}P_2$	$C_{48}H_{30}Au_2F_8P_2$
M_r	880.64	926.71	716.41	1354.7	1214.6
Crystal size, mm^3	$0.25 \times 0.15 \times 0.07$	$0.27 \times 0.21 \times 0.11$	$0.12 \times 0.09 \times 0.08$	$0.27 \times 0.25 \times 0.19$	$0.21 \times 0.15 \times 0.11$
Crystal system	tetragonal	triclinic	orthorhombic	triclinic	triclinic
Space group	$I4_1/a$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
a, Å	36.774(4)	10.6152(7)	9.761(2)	13.319(2)	11.935(3)
b, Å	36.774(4)	11.8454(8)	15.390(3)	13.530(2)	12.132(3)
c, Å	12.672(3)	18.686(2)	17.025(3)	14.453(2)	15.224(3)
α, deg	90	98.000(1)	90	104.022(2)	107.103(3)
β, deg	90	93.938(1)	90	107.468(2)	97.704(4)
γ, deg	90	99.380(1)	90	99.837(2)	100.494(4)
V, Å^3	17136(5)	2285.6(3)	2557.4(9)	2325.4(6)	2030.0(8)
Z	16	2	4	2	2
D_{calcd}, g cm^{-3}	1.36	1.35	1.86	1.93	1.9
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	2.0	1.9	5.9	6.4	7.4
$F(000)$, e	7264	960	1384	1300	1156
hkl range	−47 to 48, −46 to 47, −16 to 13	±13, ±15, −23 to 24	±12, ±19, ±22	±17, ±17, ±19	±15, ±16, ±19
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6673	0.6664	0.6492	0.6666	0.6664
Refl. measured	45641	26630	5837	26439	22415
Refl. unique	9445	10552	5837	10600	9206
R_{int}	0.1754	0.0343	0.0000	0.0505	0.0895
Param. refined	461	519	343	631	541
$R(F)/wR(F^2)$[a] (all refl.)	0.1369 / 0.1659	0.0493 / 0.0912	0.0337 / 0.0375	0.0657 / 0.0880	0.1075 / 0.1335
Weighting factors a, b	0, 0	0.0484, 0.1316	0.0154, 0	0.0389, 0	0.0466
GoF (F^2)[b]	0.706	1.028	1.026	0.999	0.990
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.953 / −0.445	0.793 / −0.297	0.823 / −0.990	2.477 / −1.419	2.048 / −0.248

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

were solved by Direct Methods and refined by full-matrix least-squares or F^2 using the SHELX-97 software package within the X-Seed environment [38]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogens were placed in calculated positions. The figures are drawn with displacement ellipsoids at the 50 % probability level; hydrogens not involved in close contacts are omitted for clarity. Data and parameters of the crystal structure determinations are shown in Table 2.

In the crystal structure of **2** $\cdot$ $2C_2H_6O$ the disordered solvent could not be modeled satisfactorily and was removed using the SQUEEZE routine in the PLATON set of programs [39]. The anisotropic displacement parameters of atoms C21, C25 and C26 in the crystal structure of **8** were restrained with a DELU instruction.

CCDC 749855 – 749859 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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