Hypercoordinate Carbon in Trigoldbis(silyl)methanium Cations

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The reactions of organolithium compounds of the type $(R_3Si)_2CHLi$ (R_3 = Me_3 or Me_2Ph) with the gold(I) complex Ph_3PAuCl afford the monoaurated bis(silyl)methanes $(R_3Si)_2CHAuPPh_3$ (**1a**, **b**) in high yield. These compounds are converted into complex salts with hypercoordinate methanium cations $\{(R_3Si)_2C[Au(PPh_3)]_3\}^+BF_4^-$ (**3a**, **b**) by treatment with $\{[(Ph_3P)Au]_3O\}^+BF_4^-$. In the reaction mixtures small amounts of the neutral dinuclear intermediates $\{(R_3Si)_2C[Au(PPh_3)]_2\}$ (**2a**, **b**) have been detected and characterized by their spectroscopic data. Compounds **1a**, **b** and **3a**, **b** have been studied by single crystal X-ray diffraction analyses. While the mononuclear molecules **1a**, **b** have conventional structures with parameters representing classical types of bonding, the novel trinuclear complexes **3a**, **b** feature cations with a pentacoordinate carbon atom in a distorted trigonal-bipyramidal environment of two silicon atoms and one gold atom in equatorial positions and the remaining two gold atoms at the axial vertices of the polyhedra. The main axis of the bipyramid is strongly bent at the central carbon atoms. This distortion leads to short axial/equatorial Au···Au distances indicating peripheral metal-metal bonding.

Aggregation of gold at small interstitial atoms in molecular species is currently attracting considerable interest due to the unusual structural and bonding situations for both the centroid element and the gold atoms in the resulting complexes[1,2]. Polynuclear gold complexes with the hypercoordinate main-group elements boron[3], carbon[4–12], nitrogen[13,14], phosphorus[15–19], and arsenic[17] of the types $\{[(R_3P)Au]_6C\}^{2+}$ (octahedral Au_6C core), $\{[(R_3P)Au]_4BPR'_3\}^+$, $\{[(R_3P)Au]_5C\}^+$, $\{[(R_3P)Au]_5N\}^{2+}$, $\{[(R_3P)Au]_5P\}^{2+}$ (trigonal-bipyramidal Au_5C, Au_5N, and Au_5P cores and square pyramidal Au_4CC' and Au_4BP cores), $\{[(R_3P)Au]_6C\}^{3+}$ (distorted octahedral Au_6P unit) and $\{[(R_3P)Au]_4PR\}^{2+}$ and $\{[(R_3P)Au]_4As\}^+$ (square-pyramidal $RPAu_4$ and Au_4As units) have been discovered and fully characterized. Some of these cationic element-centered clusters had perviously been predicted from theoretical work[20,21], while others were completely unexpected. The ease of formation and the stability of these complexes are attributed to attracitve interactions between closed-shell gold(I) atoms $\{[Xe]4f^{14}5d^{10}\}$, with relativistic effects playing a major role in modifying the energy characteristic of the valence and core electrons[22–25]. Striking non-classical structural principles, as found e. g. in the square-pyramidal (not tetrahedral) tetragoldarsonium cations, the short Au···Au distances of about 3.0 Å and the small Au–E–Au angles observed in the whole family of compounds are indicative of this unusual bonding situation.

From the results of the most advanced theoretical calculations, including the contributions from relativistic effects, it has been concluded that the stability of the cluster species is also influenced by electronic effects of other substituents at the interstitial atom (if any), and by the nature of the peripheral ligands. These aspects prompted us to investigate the auration of *silylated* alkylgold(I) compounds, where silicon substituents would strongly modify the nucleating properties of the central carbon atom. To date only very few heteroleptic carbon-centered gold clusters are known. Full characterization is available for a dimeric (octanuclear) complex with tetragold(oxazolyl)methanium units[4], where the interstitial carbon atom is located in the center of a square pyramid with four gold atoms forming the square base and the oxazolyl group at the apex. A simpler example is present in 1,1,1,1-tetragoldethanium cations of the tetrafluoroborate salt. In this cation the central carbon is thus an *alkylated* example in case. No related *silylated* compounds have been reported.

At least two suitable mononuclear precursor compounds for the target species have already been described[26], but their acceptor properties for $[LAu]^+$ have not been investigated. Our own preliminary results have been published[12] in a communication, which is supplemented here by full data on a more extended basis.

Results

Mono- and Dinuclear Gold Compounds with Conventional Structures

The starting materials [bis(trimethylsilyl)methyl](triphenylphosphane)gold(I) (**1a**) and [bis(dimethylphenylsilyl)methyl](triphenylphosphane)gold(I) (**1b**) used for the preparation of the title compounds are readily accessible in high yield and pure form by treating (triphenylphosphane)gold(I) chloride with the lithiated disilylmethanes

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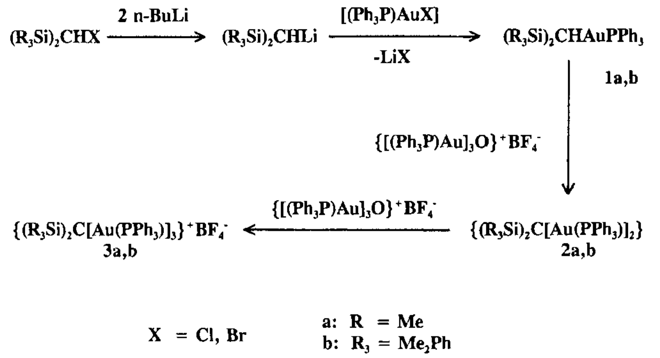
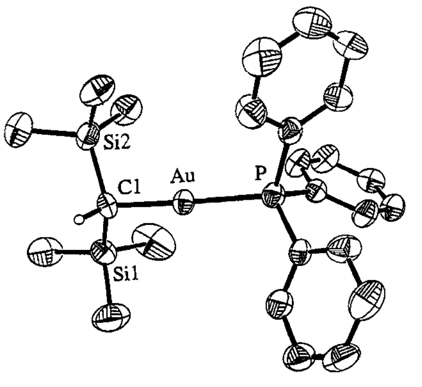
$(R_3Si)_2CHLi$. These reagents can be prepared in situ from the corresponding silylated bromo- or chlorodisilylmethanes and *n*-butyllithium and are treated further with triphenylphosphanegold(I) chloride (Scheme 1). Compound **1a** has previously been fully characterized by its analytical and spectroscopic data[26]. A similar set of data has now become available for **1b** (Experimental). The yields of the reactions (first steps in Scheme 1) are generally higher than 70% for the pure crystalline samples.

Scheme 1



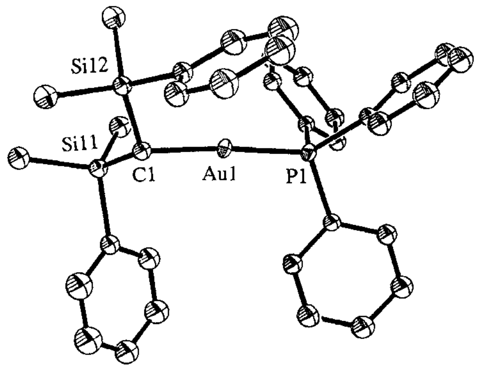
The structures of both compounds have now been determined in order to provide reference data for the structure of the hypercoordinate species (below). The results are shown in Figures 1 and 2. The molecular geometries hold no surprises and represent features of classical bonding with tetrahedral four-coordinate carbon and silicon atoms and linear two-coordinate gold atoms. The distances and angles are comparable in **1a** and **1b** with very little variations induced by steric effects.

Figure 1. Molecular structure of compound **1a** with atomic numbering (ORTEP, 50% probability ellipsoids, methyl and phenyl hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–C1 2.041(6), Au–P 2.271(2), Si1–C1 1.861(7), Si2–C1 1.863(7); C1–Au–P 177.8(2), Au–C1–Si1 108.8(3), Au–C1–Si2 107.7(3), Si1–C1–Si2 119.5(4)



The molecular structure of the precursor of compound **1b**, *bromo*-bis(methyldiphenylsilyl)methane, has also been determined in the course of preparative work on the organosilicon intermediates[27]. It shows surprisingly close similarities, since the steric effects of gold(I) and bromine appear to be not very different. This result is proof that in mononuclear organogold compounds the structure and bonding situation are indeed of "standard quality" readily encompassed by conventional descriptions of electronic and molecular structure. Obviously, structural irregularities arise only as soon as metal aggregation becomes possible in polynuclear species (below).

Figure 2. Molecular structure of compound **1b** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Only one of the two crystallographically independent molecules (A, B) is shown. Selected bond lengths [Å] and angles [°] for A [B]: Au–C1 2.095(3) [2.092(3)], Au–P 2.284(1) [2.273(1)], Si1–C1 1.860(4) [1.844(4)], Si2–C1 1.844(4) [1.846(4)]; C1–Au–P 174.4(1) [177.5(1)], Au–C1–Si1 105.8(2) [106.2(2)], Au–C1–Si2 112.7(2) [106.6(2)], Si1–C1–Si2 120.8(2) [120.5(2)]



Compounds **1a, b** are colorless, air-stable crystalline solids which are readily soluble in common organic solvents of medium polarity. Treatment of these solutions (in CH_2Cl_2) with one or more equivalents of the oxonium reagent $\{[(Ph_3P)Au]_3O\}^+BF_4^-$ at room temperature leads to the formation of novel *tri*nuclear complexes $\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+BF_4^-$ and $\{(Me_2PhSi)_2C[Au(PPh_3)]_3\}^+BF_4^-$ (**3a, b**), respectively, which can be isolated as colorless, airstable, crystalline solids (Scheme 1 and below). As *byproducts* of the auration reactions, the corresponding neutral *di*nuclear molecules $\{(R_3Si)_2C[Au(PPh_3)]_2\}$ (**2a, b**) can be obtained in small quantities and in a somewhat impure form from benzene extracts of the solid residues left after evaporation of the solvents. The solubility properties of the two classes of products distinguish them as polar (**2a, b**) and non-polar species (**3a, b**): The latter remain after benzene extraction and can be taken up in polar solvents. Regardless of the stoichiometric ratio of the reagents employed, the *tri*nuclear products **3a, b** are obtained as the main products (below).

Compounds **2a, b** – obviously formed by substitution of the single proton at the central carbon atom in **1a** and **b** by a $[AuPPh_3]^+$ cation in the auration process – have been characterized only by their spectroscopic data. No single crystals could be grown, and hence the structural details are still unknown. There are good reasons, however, to predict that the molecules have tetrahedral structures with slightly distorted Si_2CAu_2 cores to allow for steric effects of the silyl groups and for short Au···Au contacts.

Structural data are also available in this case for the corresponding silane precursor, *dibromo*-bis(methyldiphenylsilyl)methane[27]. Referring again to the analogy with **2b**, based on similar steric effects of Au(I) and Br, we can use the structure of $(MePh_2Si)_2CBr_2$ as a model regarding the overall solid state configuration and conformation. A narrowing of the Au–C–Au angle is to be expected, however, as compared to the Br–C–Br angle of 106.0(2)° observed in the dibromide.

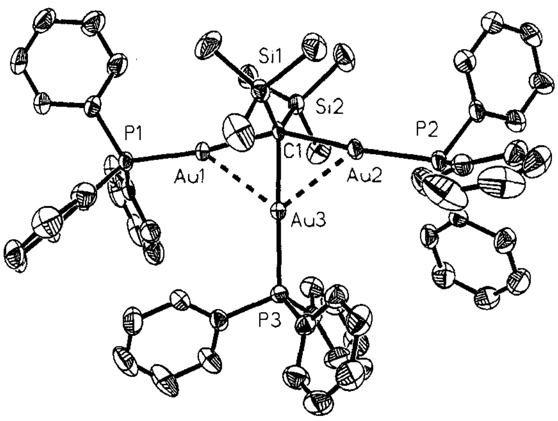
Trinuclear Compounds with Hypercoordinate Carbon Atoms

As shown in Scheme 1, treatment of compounds **1a** and **1b** with the oxonium reagent in dichloromethane at ambient temperature affords the trinuclear species **3a** and **3b**, respectively, in ca. 50% isolated yield. The compounds are colorless crystalline materials of high thermal stability, decomposition occuring only upon heating at temperatures as high as 150 and 192°C, respectively. Crystalline samples are not sensitive to air and water and can be recrystallized from hot ethanol (**3a**) or diethyl ether/dichloromethane (**3b**). Solutions in di- and trichloromethane are stable at room temperature for a limited period of time if protected against light. Elemental analyses of samples dried in vacuo give satisfactory data for the solvate-free composition.

In the fast atom bombardment *cation* mass spectra, the parent cations (neglecting the BF_4^- anions) are observed as the peaks of highest mass and intensity [m/z = 1659.1 for **3b**, 1534.6 for **3a**], followed by fragmentation products as suggested by the formula and structure (Experimental). FAB mass spectrometry for *anions* features the tetrafluoroborate group (m/z = 86.9, 100%) and gold anions (m/z = 197.1 for Au^-).

The room-temperature high-resolution NMR spectra of solutions of **3a**/**3b** in CD_2Cl_2 or $CDCl_3$ show the ^{11}B and ^{19}F signals of the tetrafluoroborate anion as referenced in the literature. Singlet ^{29}Si resonance lines for the cations indicate the equivalence of the two silyl groups in the cations of both compounds, as is also confirmed by a single set of hydrogen and carbon resonances of the Me_3Si and $MePh_2Si$ groups, respectively. The signals of the three Ph_3P groups in each of the cations (**3a**/**3b**) show a splitting in the intensity ratio 2:1, which suggests non-equivalent binding of one $AuPPh_3$ group as distinguished from the other two. This is particularly obvious in the $^{31}P\{^1H\}$ spectra, where only two singlet lines in the intensity ratio 2:1 are present. In keeping with this observation, the phenyl P signals are also split into two sets (^1H, ^{13}C). Owing to the low intensity and the likely overlap with the aryl resonances, the signal of the central carbon atom could not be detected. It should be pointed out that for other polyaurated hypercoordinate carbon atoms the resonance of the interstitial atom has been observed (after isotopic enrichment and at extremely high magnetic field strengths) in the region of the signals of aryl carbon atoms (at δ ca. 135)[7]. The position of the signals of compounds **3a**/**3b** is difficult to predict. Current theoretical calculations for compounds with very heavy atoms (like gold) are not sufficiently reliable to concentrate on a specific region in the spectra. Complex **3a** crystallizes in the triclinic space group *P*$\bar{1}$ with two formula units in the unit cell. The crystals are composed of discrete cations $\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+$ with no crystallographically imposed symmetry, and BF_4^- anions disordered in two positions in the lattice. In the cations *penta*coordinate carbon atoms are located in the center of a distorted trigonal bipyramid, with two silyl groups in equatorial positions and three $AuPPh_3$ units in the two axial and the remaining equatorial position (Figure 3). The interstitial, hypercoordinate carbon atom is coplanar with the two silicon atoms and the equatorial gold atom (Au3), and the Si–C–Si angle [123.0(3)°] is close to the 120° angle expected for adjacent equatorial sites. The axis Au1–C–Au2 [152.1(3)°] deviates strongly from linearity, however, which clearly indicates attractive forces between Au1, Au2, and Au3. Such interactions are also obvious from the bending of the units P1–Au1–C [172.3(2)°] and P2–Au2–C [173.0(2)°], but not of P3–Au3–C [179.1(2)°]. The distances Au1–Au3 = 2.720(1) and Au2–Au3 = 2.702(1) Å are remarkably short, a clear manifestation of direct metal-metal interactions[1]. The Au-C distances in the electron-deficient core (Si_2CAu_3) are longer than standard two-center-two-electron Au–C bonds.

Figure 3. Molecular structure of the cation of compound **3a** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–Au3 2.720(1), Au2–Au3 2.720(1), Au1–C1 2.220(6), Au2–C1 2.208(7), Au3–C1 2.190(6), Au1–P1 2.262(2), Au2–P2 2.268(2), Au3–P3 2.270(2), Si1–C1 1.887(7), Si2–C1 1.898(7); P1–Au1–C1 172.3(2), P2–Au2–C1 173.0(2), P3–Au3–C1 179.1(2), Au1–C1–Au3 76.1(2), Au2–C1–Au3 76.4(2), Au1–C1–Au2 152.1(3), Si1–C1–Si2 123.0(3), Au3–C1–Si1 121.9(3), Au3–C1–Si2 115.1(3)



Complex **3b** crystallizes in the orthorhombic space group *Pca*2_1 with four formula units in the unit cell. As for **3a**, the crystals are again composed of discrete cations $\{(Me_2PhSi)_2C[Au(PPh_3)]_3\}^+$ with no crystallographically imposed symmetry and BF_4^- anions which in this case are not disordered. The heavy-atom skeleton of the cations is very similar to that found for **3a** (above), with differences only arising from the variation in the substitution pattern at the silicon atoms (Figure 4). There ist only minor disorder of one phenyl group of one of the three PPh_3 ligands. The $P_3Au_3CSi_2$ cores are virtually superimposible for **3a** and **3b**, and the description of the structure of **3a** (above) is also valid for **3b**.

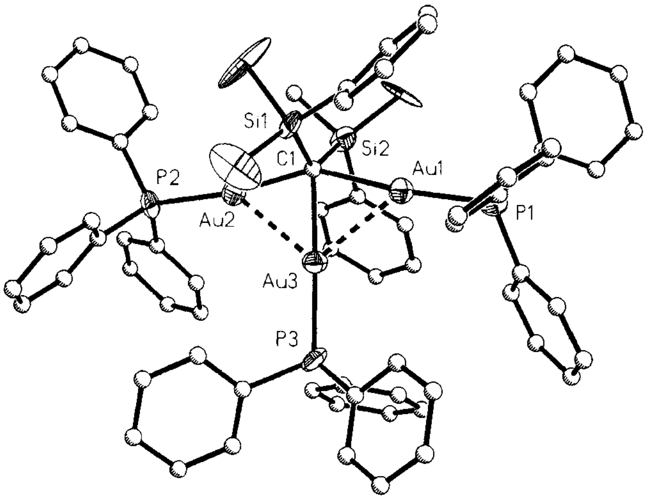


Figure 4. Molecular structure of the cation of compound **3b** with atomic numbering (ORTEP, 50% probability ellipsoids for the anisotropically refined atoms, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–Au3 2.739(3), Au2–Au3 2.723(3), Au1–C1 2.32(3), Au2–C1 2.15(3), Au3–C1 2.21(1), Au1–P1 2.22(1), Au2–P2 2.29(1), Au3–P3 2.273(4), Si1–C1 1.93(1), Si2–C1 1.84(1); P1–Au1–C1 173.2(6), P2–Au2–C1 171.7(6), P3–Au3–C1 177.2(9), Au1–C1–Au3 74.8(8), Au2–C1–Au3 77.4(7), Au1–C1–Au2 151.7(6), Si1–C1–Si2 124.0(7), Au3–C1–Si1 118.2(6), Au3–C1–Si2 116.9(6)

The cations of compounds **3a** and **3b** thus represent two of the few examples of pentacoordinate carbon in a non-forced structure, i. e. not assisted by ring formation or other constraints. The structure originates from an electrophilic attack of a $[(Ph_3P)Au]^+$ unit at the central carbon atoms via the Au–Au edge of the dinuclear neutral molecules **2a** or **2b**. This process is an important variant of the formation[5] of $\{[(Ph_3P)Au]_5C\}^+$ from (hypothetical) $[(Ph_3P)Au]_4C$ and of $\{[(Cy_3P)Au]_4CMe\}^+$ from equally hypothetical $[(Cy_3P)Au]_3CMe$[11]. The three examples illustrate the unique potential of gold(I) to stabilize hypercoordinate carbon species by radial and peripheral Au-Au interactions. It should be pointed out that the isolobal relationship between LAu^+, Me_3Si^+, and the proton H^+ connects fundamental species like CH_5^+ with the new polynuclear gold clusters reported in the present studies.

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Experimental

All experiments were carried out in dry and pure N_2. Solvents were dried, distilled, and saturated with N_2. Glassware was oven-dried and filled with N_2. The apparatus were protected against light. – NMR: Bruker WP100SY, Jeol-GX 400, Jeol GX 270. – MS: Varian MAT 311 A.

$\{[(Ph_3P)Au]_3O\}^+BF_4^-$[28], Ph_3PAuCl[29], and $(Me_3Si)_2CHAuPPh_3$[26] (**1a**) have been prepared according to literature.

Preparation of Compound **1b**: A solution of $(Me_2PhSi)_2CHBr$ (1.22 g, 3.4 mmol), obtained by the reaction of *n*-butyllithium with a mixture of $Me_2PhSiCl$ and $CHBr_3$, in hexane is treated with a solution of 1.6 M *n*BuLi in the same solvent (2.1 ml, 3.4 mmol) at −78°C[30]. The mixture is allowed to warm to −10°C within 1 h, and a solution of Ph_3PAuCl in THF (1.0 g, 2.0 mmol) is added. After warming to room temp. over a period of 1 h the mixture is hydrolyzed with ice, the phases are separated, and the organic layer is dried with $MgSO_4$. The volatile components are removed in vacuo, and treatment of the residue with $EtOH/C_6H_6$ affords colorless crystals of **1b**, yield 0.90 g (61%), m.p. 86°C. – ^1H NMR ($CDCl_3$, 20°C): $\delta = 6.9-7.9$ (m, PPh_3); 0.95 [d, $^3J(PH) = 6.4$ Hz, CH]; 0.63 (s, CH_3); 0.57 (s, CH_3'). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 146.2$ [d, $^1J(CSi) = 47.8$ Hz, Ph-C_1(Si)]; 134.1 [s, Ph-$C_{2/6}$(Si)]; 127.8 [s, Ph-C_4(Si)]; 127.6 [s, Ph-$C_{3/5}$(Si)]; 134.0 [d, $^2J(CP) = 13.4$ Hz, Ph-$C_{2/6}$]; 131.6 [d, $^1J(CP) = 48.7$ Hz, Ph-C_1]; 131.0 [d, $^4J(CP) = 2.7$ Hz, Ph-C_4]; 129.0 [d, $^3J(CP) = 10.7$ Hz, Ph-$C_{3/5}$]. – ^{29}Si NMR ($CDCl_3$, 20°C): $\delta = -5.2$ (m). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 43.7$ (s). – $C_{35}H_{38}AuPSi_2$ (742.8): calcd. C 56.60, H 5.16, Au 26.50, Si 7.60; found C 57.22, H 5.51, Au 25.53, Si 7.77. – MS (FAB), *m/z*: 742 [M^+], 727 [$M^+ - 15$], 665 [$M^+ - 77$], 459.1 $[AuPPh_3]^+$, 135.1 $[SiMe_2Ph]^+$.

Preparation of Compound **3a**: Compound **1a** (0.34 g, 0.55 mmol) and the oxonium reagent (0.54 g, 0.36 mmol) are allowed to react in CH_2Cl_2 (20 ml) at 20°C for 15 h to give an orange solution. All volatile components are removed in vacuo. The brown residue is washed twice with 5 ml of benzene, then extracted with THF (2 × 5 ml). From the combined extracts **3a** is isolated by evaporation of the solvent and crystallization of the residue from EtOH; colorless crystals, yield 0.35 g (40%), m.p. 192–194°C (dec.). – ^1H NMR (CD_2Cl_2, 20°C): $\delta = 0.44$ (s, CH_3); 7.0–7.5 (m, Ph). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20°C): $\delta = 32.0$ [s, Ph(P_{eq})]; 34.8 [s, Ph(P_{ax})]. – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20°C): $\delta = 10.0$ (s, CH_3); 129.1 [d, $^1J(CP) = 58.6$ Hz, Ph-$C_1(P_{eq})$]; 129.3 [d, $^1J(CP) = 57.9$ Hz, Ph-$C_1(P_{ax})$]; 129.2 [d, $^3J(CP) = 10.9$ Hz, Ph-$C_3(P_{eq})$]; 129.4 ["t", AXX', $N = 5.8$ Hz, Ph-$C_3(P_{ax})$]; 131.5 [d, $^4J(CP) = 2.5$ Hz, Ph-$C_4(P_{eq})$]; 131.9 [s, Ph-$C_4(P_{ax})$]; 133.7 [d, $^2J(CP) = 13.6$ Hz, P-$C_2(P_{eq})$]; 133.8 ["t", AXX', $N = 6.8$ Hz, Ph-$C_2(P_{ax})$]. – $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 20°C): $\delta = -1.4$ (s). – $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 20°C): $\delta = -73.74$ (s); −73.79 (s) ratio 1:4. – $C_{61}H_{63}Au_3BF_4P_3Si_2$ (1623.0): calcd. C 45.14, H 3.91; found C 45.50, H 3.94. – MS (FAB), *m/z* (%): 196.7 [Au^-]; 86.9 [BF_4^-] (100).

Preparation of Compound **3b** according to the same procedure as described for **3a** with 0.10 g (0.55 mmol) of **1b** and 0.36 g (0.24 mmol) of $\{[Ph_3PAu]_3O\}^+BF_4^-$. Colorless, microcrystalline samples of **3b** are obtained from CH_2Cl_2/Et_2O, m.p. 146°C (dec.). – ^1H NMR ($CDCl_3$, 20°C): $\delta = 7.3-8.0$ (m, Ph); 0.66 (s, CH_3). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 31.2$ (s, P_{eq}), 34.8 (s, P_{ax}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 145.8$ [s, Ph-C_1(Si)]; 133.5 [s, Ph-$C_{2/6}$(Si)]; 128.5 [s, Ph-C_4(Si)]; 127.7 [s, Ph-$C_{3/5}$(Si)]; 133.7 ["t", AXX', $N = 6.4$ Hz, Ph-$C_{2/6}(P_{ax})$]; 133.4 [d, $^2J(CP) = 12.8$ Hz, Ph-$C_{2/6}(P_{eq})$]; 131.9 [s, Ph-$C_4(P_{ax})$]; 131.5 [d, $^4J(CP) = 1.8$ Hz, Ph-$C_4(P_{eq})$]; 129.3 ["t", AXX', $N = 5.0$ Hz, Ph-$C_{3/5}(P_{ax})$]; 129.0 [d, $^3J(CP) = 11.0$ Hz, Ph-$C_{3/5}(P_{eq})$]. – ^{29}Si NMR ($CDCl_3$, 20°C): $\delta = -9.2$ (s). – $^{11}B\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = -1.17$ (s). – $C_{71}H_{67}Au_3BF_4P_3Si_2$ (1747.1): calcd. C 48.80, H 3.87, Au 33.79; found C 47.35, H 3.90, Au 32.76. – MS (FAB), *m/z*: 1659.1 [M^+], 721 $[Au(PPh_3)_2]^+$, 459.1 $[Au(PPh_3)]_3^+$, 135 $[Me_2PhSi]^+$.

Preparation of Compounds **2a** *and* **2b**: These compounds can be isolated from the corresponding reaction mixtures of **3a**, **b** in low yields by extracting the mixtures with benzene and removing the solvent from the extract in vacuo to give microcrystalline, colorless

Table 1. Crystal and structure solution and refinement data for compounds **1a**, **b**, **3a**, **b**

	1a	**1b**	**3a**	**3b**
formula	$C_{25}H_{34}AuPSi_2$	$C_{35}H_{38}AuPSi_2$	$C_{61}H_{63}Au_3BF_4P_3Si_2$	$C_{71}H_{78}Au_3BF_4P_3Si_2$
M_r	618.66	742.80	1622.98	1758.13
crystal system	monoclinic	triclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pca2_1$
a [Å]	12.099(2)	10.617(1)	13.912(3)	24.045(1)
b [Å]	14.121(1)	15.208(1)	14.318(2)	9.241(1)
c [Å]	15.933(2)	22.498(2)	17.696(2)	31.198(2)
α [°]	90	105.99(1)	90.52(1)	90
β [°]	91.88(1)	97.14(1)	98.29(1)	90
γ [°]	90	105.71(1)	108.76(1)	90
V [Å^3]	2720.7	3283.3	3297.0	6932.9
ρ_{calc} [gcm^{-3}]	1.510	1.500	1.635	1.685
Z	4	4	2	4
F(000) [e]	1224	1480	1560	3420
μ(Mo-K_α) [cm^{-1}]	55.4	46.0	67.9	64.9
T [°C]	-56	-62	-56	+23
diffractometer		Enraf Nonius CAD4		
radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
λ(Mo-K_α) [Å]		0.71069, graphite monochromator		
scan mode	ω	θ-θ	θ-θ	ω
hkl range	$\pm15, +18, +20$	$\pm13, \pm18, +28$	$\pm17, \pm18, +22$	$+28/\pm10/\pm38$
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.64	0.64	0.64	0.62
measured refl.	6464	14227	14344	12040
unique refl.	5915	14220	13256	11656
observed refl.	4540	10025	11486	7316
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$
absorptions corr.	empirical (Ψ-scans)	empirical (Ψ-scans)	empirical (Ψ-scans)	empirical (DIFABS)
t_{max}/t_{min}	0.99/0.75	1.00/0.67	0.99/0.59	1.00/0.46
refined parameters	262	703	622	261
structure solution	direct methods	direct methods	direct methods	direct methods
H atoms (f/c)	0/34	0/76	0/63	0/78
R	0.0414[a]	0.0232[a]	0.0318[a]	0.0632[a]
R_w	0.0383[b]	0.0255[b]	0.0318[b]	0.2212[c]
(shift/error)$_{max}$	0.001	0.001	0.001	0.001
ρ_{fin}(max/min) [eÅ^{-3}]	+2.80,-2.00[d]	+0.94/-0.34	+1.79,-0.78[d]	+2.62/-2.26

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. – [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. – [c] $R = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$ (all data); $w = q/\sigma^2(F_o^2) + (ap)^2 + bp)$, $p = \max(f_o,0) + 2F_c^2/3$, $a = 0.1057$, $b = 92.564$. – [d] Residual electron densities located at Au atoms.

solids. – **2a**: ^1H NMR ($CDCl_3$, 20°C): $\delta = 0.17$ (s, CH_3), 7.3–7.5 (m, Ph). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 39.95$ (s). – MS (FD), *m/z* (%): 1076.0 [M^+] (100), 1061.2 [$M - CH_3$]$^+$ (8). – **2b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 40.1$ (s).

Crystal Structure Determinations: Suitable crystals of compounds **1a**, **b** and **3a**, **b** were sealed under argon at dry-ice temperature into glass capillaries and examined directly by means of the diffractometer. Intensity data were corrected for Lorentz, polarization, and for absorption effects [Ψ scans (**1a**, **b**, **3a**) and DIFABS (**3b**)]. Structures were solved by direct methods and refined by full-matrix least-squares calculations against F (**1a**, **b**, **3a**) and F^2 (**3b**). For **1a**, **b** and **3a**, the thermal motion was treated anisotropically for all non-hydrogen atoms except the B and F atoms of the anion in **3a**, which was disordered in split positions with site occupation factors of 0.6/0.4 for B1 and B2, respectively. The B and F atoms of the anion of **3b** were located and refined isotropically in idealized geometry. The phenyl rings in **3b** were refined isotropically as idealized six-membered rings. All hydrogen atoms of all compounds were calculated in idealized positions and allowed to ride on their carbon atom. Compound **1b** has two crystallographically independent molecules (A, B) in the asymmetric unit, which show only marginal differences of the dimensions. More detailed information on solution and refinement procedures are given in Table 1. Further information on the X-ray structure determinations may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58498, the names of the authors, and the journal citation.

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[1] H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11–21.

[2] H. Schmidbaur, *Interdisc. Sci. Rev.* **1992**, *17*, 213–220.

[3] A. Blumenthal, H. Beruda, H. Schmidbaur, *J. Chem. Soc., Chem. Commun.* **1993**, 1005–1006.

[4] F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem.* **1988**, *100*, 1602–1604; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1544–1546.

[5] F. Scherbaum, A. Grohmann, G. Müller, H. Schmidbaur, *Angew. Chem.* **1989**, *101*, 464–466; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 463–465.

[6] O. Steigelmann, P. Bissinger, H. Schmidbaur, *Angew. Chem.* **1990**, *102*, 1473–1475; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1399–1340.

[7] H. Schmidbaur, B. Brachthäuser, O. Steigelmann, *Angew. Chem.* **1991**, *103*, 1552–1553; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1488–1490.

[8] H. Schmidbaur, B. Brachthäuser, O. Steigelmann, H. Beruda, *Chem. Ber.* **1992**, *125*, 2705–2710.

[9] H. Schmidbaur, O. Steigelmann, *Z. Naturforsch., Teil B*, **1992**, *47*, 1721–1724.

[10] H. Schmidbaur, B. Brachthäuser, S. Gamper, A. Schier, O. Steigelmann, *Z. Naturforsch., Teil B*, **1992**, *47*, 1725–1735.

[11] O. Steigelmann, P. Bissinger, H. Schmidbaur, *Z. Naturforsch., Teil B*, **1993**, *48*, 72–78.

[12] N. Dufour, A. Schier, H. Schmidbaur, *Organometallics* **1993**, *12*, 2408–2410.

[13] A. Grohmann, J. Riede, H. Schmidbaur, *Nature* **1990**, *345*, 140–142.

[14] A. Grohmann, J. Riede, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1991**, 783–787.

[15] H. Schmidbaur, G. Weidenhiller, O. Steigelmann, *Angew. Chem.* **1991**, *103*, 442–444; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 433–435.

[16] H. Schmidbaur, E. Zeller, G. Weidenhiller, O. Steigelmann, H. Beruda, *Inorg. Chem.* **1992**, *31*, 2370–2376.

[17] E. Zeller, H. Beruda, A. Kolb, P. Bissinger, J. Riede, H. Schmidbaur, *Nature* **1991**, *352*, 141–143.

[18] H. Beruda, E. Zeller, H. Schmidbaur, *Chem. Ber.* **1993**, *126*, 2037–2040.

[19] E. Zeller, H. Schmidbaur, *J. Chem. Soc., Chem. Commun.* **1993**, 69–70.

[20] D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.* **1976**, 1163–1170.

[21] D.M.P. Mingos, T. Slee, L. Zhenyang, *Chem. Rev.* **1990**, *90*, 383–396.

[22] N. Rösch, A. Görling, D. E. Ellis, H. Schmidbaur, *Angew. Chem.* **1989**, *101*, 1410–1412; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1357–1359.

[23] A. Görling, N. Rösch, D. E. Ellis, H. Schmidbaur, *Inorg. Chem.* **1991**, 3986–3994.

[24] P. Pyykkö, Y. Zhao, *Angew. Chem.* **1991**, *103*, 622–624; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 611–613.

[25] P. Pyykkö, Y. Zhao, *Chem. Phys. Lett.* **1991**, *177*, 103–107.

[26] F. Glockling, V. H. Mahale, *J. Chem. Res.* **1978**, 170–176.

[27] H. Schmidbaur, S. Bommers, H. Beruda, *Z. Naturforsch.*, in preparation.

[28] A. N. Nesmeyanov, E. G. Perevalova, Yu. T. Struchkov, M. Yu. Antipin, K. I. Grandberg, V. P. Dyadchenko, *J. Organomet. Chem.* **1980**, *201*, 343–351.

[29] A. K. Al-Sa'ady, C. A. McAuliffe, R. V. Parish, J. A. Sandbank, *Inorg. Synth.* **1985**, *23*, 191–194.

[30] N. Wiberg, G. Wagner, *J. Organomet. Chem.* **1984**, *271*, 381.

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