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Hypercoordinate Carbon in Bis(trimethylsilyl)tris[(triphenylphosphine)aurio(I)]methanium Tetrafluoroborate

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Summary: [Bis(trimethylsilyl)methyl](triphenylphosphine)gold(I) has been synthesized according to literature methods and its crystal structure determined. Treatment of this compound with $[(Ph_3P)Au]_3O^+BF_4^-$ *in dichloromethane gives small amounts of the compound* $(Me_3Si)_2C[Au(PPh_3)]_2$ *together with the novel trinuclear complex* $\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+BF_4^-$*. The structure of the cation features the pentacoordinate carbon atom in a distorted-trigonal-bipyramidal environment with two silicon atoms in equatorial positions. Short axial/equatorial Au···Au contacts indicate peripheral metal–metal bonding.*

The discovery[1] of novel boron-, carbon-, nitrogen-, phosphorus-, and arsenic-centered gold(I) clusters of the types $\{[(R_3P)Au]_6C\}^{2+}$ (octahedral Au_6C core[2]), $\{[(R_3P)Au]_4BPR'_3\}^+$, $\{[(R_3P)Au]_5C\}^+$, $\{[(R_3P)Au]_4CR\}^+$, $\{[(R_3P)Au]_5N\}^{2+}$, $\{[(R_3P)Au]_5P\}^{2+}$ (trigonal-bipyramidal Au_5C, Au_5N, and Au_5P cores and square-pyramidal Au_4CC' and Au_4BP cores, respectively[3]), $\{[(R_3P)Au]_6P\}^{3+}$ (distorted-octahedral Au_6P unit[4]), and $\{[(R_3P)Au]_4PR\}^{2+}$ and $\{[(R_3P)Au]_4As\}^+$ (square-pyramidal $RPAu_4$ and Au_4As units,[5] respectively) with hypercoordinate main-group elements has encouraged us to attempt the synthesis of other new types of compounds with hypercoordinate carbon.

Detailed theoretical studies,[6] including relativistic effects,[7] have shown that the aggregation of the new clusters is based both on strong radial interactions between the central atom E and the gold atoms and on significant peripheral Au···Au bonding. The short Au···Au distances of ca. 3.0 Å between closed-shell atoms ($5d^{10}$–$5d^{10}$) and the small Au–E–Au angles commonly encountered are meaningful indicators for this unusual bonding situation. It was also obvious from the results of the calculations that inductive effects of the peripheral phosphine ligands and the nature of the cluster nucleus E play a major role in determining the stability of the cluster species. On the basis of these considerations the auration of poly*silylated* alkylgold(I) compounds was investigated. Suitable precursor compounds have been described in the literature,[8-10] but their acceptor properties for $[LAu]^+$ nucleophiles have not been studied.

[Bis(trimethylsilyl)methyl](triphenylphosphine)gold(I) (1) is readily available and has been fully characterized by analytical and spectroscopic data.[9] In the course of the present study we have also determined its crystal structure,[11] which held no surprises in that all structural parameters proved to be normal (Figure 1). The mononuclear compound 1 thus reflects a fully classical type of structure and bonding.

Treatment of solutions of compound 1 in dichloromethane with tris[(triphenylphosphine)aurio(I)]oxonium tetrafluoroborate[12] in the same solvent at ambient temperature gave a reaction mixture from which small amounts of the dinuclear molecule $(Me_3Si)_2C[Au(PPh_3)]_2$ (2), together with the novel trinuclear complex $\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+BF_4^-$ (3), could be isolated.

Compound 2 was obtained from a benzene extract of the residue after removal of all volatiles under vacuum as the least polar product. It was readily characterized by its spectroscopic data.[13] A structure with a Si_2CAu_2 tetrahedron, slightly distorted to allow for steric effects

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(11) X-ray analysis of 2. Crystal data: $(Me_3Si)_2CHAuPPh_3$ = $C_{25}H_{34}Si_2PAu$, $M_r = 618.66$, monoclinic, space group $P2_1/n$, $a = 12.099(2)$ Å, $b = 14.121(1)$ Å, $c = 15.933(2)$ Å, $\beta = 91.88(1)°$, $V = 2720.69$ Å^3, $Z = 4$. With the use of 6464 measured reflections (5915 unique, 4540 observed with $F_o \geq 4\sigma F_o$) collected at −56 °C with Mo Kα radiation (λ = 0.710 69 Å) on an Enraf-Nonius CAD4 diffractometer, the structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares techniques (SHELX-76) with anisotropic temperature factors for all non-hydrogen atoms (262 parameters) to a final R value of 4.1% ($R_w = 3.8\%$).

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(13) Compound 2: from the benzene extract,[14] colorless crystals; MS (FD, CH_2Cl_2) m/z 1076.0 [M^+, 100%], 1061.2 [$M - Me^+$, 8%]; ^1H NMR ($CDCl_3$, 20 °C) δ 0.168 ppm (s, 18H, Me), 7.3–7.7 ppm (m, 30H, Ph); $^{13}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 39.95 ppm (s).

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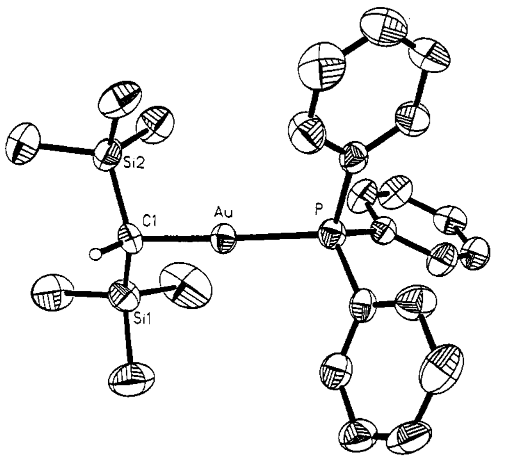

Figure 1. Molecular structure of compound 1 (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Au–C1 = 2.041(6), Au–P = 2.271(2), Si1–C1 = 1.861(7), Si2–C1 = 1.863(7); C1–Au–P = 177.8(2), Au–C1–Si1 = 108.8(3), Au–C1–Si2 = 107.7(3), Si1–C1–Si2 = 119.5(4).

$$\underset{\mathbf{1}}{(Me_3Si)_2CHAu(PPh_3)} \xrightarrow{\{[(Ph_3P)Au]_3O\}^+BF_4^-} \underset{\mathbf{2}}{(Me_3Si)_2C[Au(PPh_3)]_2} + \underset{\mathbf{3}}{\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+BF_4^-}$$

of the silyl groups and for short Au···Au contacts, is proposed for this molecule. In the structure of 1 (Figure 1) the proton at the central carbon atom has been substituted by a $[Au(PPh_3)]^+$ cation in the auration process.

The main product 3 (40% yield; colorless, air-stable crystals; mp 192–194 °C with decomposition) was isolated from the tetrahydrofuran extract.[14] It is insoluble in nonpolar solvents but soluble in tri- and dichloromethane. The positive and negative ion field-desorption mass spectra of such solutions are proof for the presence of the parent ions $\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+$ (M, *m/z* 1534.6) and BF_4^- (*m/z* 86.9), respectively. Major fragments are $[M - Me]^+$ (*m/z* 1060.6), $[Au(PPh_3)_2]^+$ (*m/z* 720.7), and $[Au]^-$ (*m/z* 196.7). The BF_4^- counterion has also been identified by its ^{19}F and ^{11}B NMR signals (in CD_2Cl_2: δ −73.7 (relative to CF_3COOH) and −1.4 ppm (relative to $(MeO)_3B$), respectively).

The $^{31}P\{^1H\}$ NMR spectrum (25 °C, CD_2Cl_2) shows two resonances, in the intensity ratio 2:1, at δ 32.0 and 34.8 ppm (relative to H_3PO_4), and the ^1H NMR spectrum features one singlet in the alkyl region (δ 0.44 ppm, 18H) and a multiplet in the aryl region (δ 7.0–7.5 ppm, 45H). In keeping with the ^{31}P NMR data, the $^{13}C\{^1H\}$ NMR spectrum—under the same experimental conditions—shows only one signal for the Me_3Si carbon atoms but two sets of signals for the Ph groups (intensity ratio 2:1), suggesting equivalent Me_3Si groups and inequivalent Ph_3PAu groups (2:1).

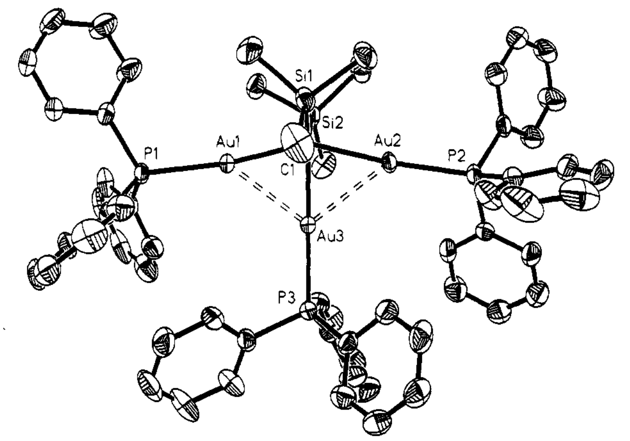

Figure 2. Molecular structure of the cation in compound 3 (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Au1–Au3 = 2.720(1), Au2–Au3 = 2.720(1), Au1–C1 = 2.220(6), Au2–C1 = 2.208(7), Au3–C1 = 2.190(6), Au1–P1 = 2.262(2), Au2–P2 = 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 3 crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell.[15] 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 of the lattice. In the cations pentacoordinate carbon atoms are located in the center of a distorted trigonal bipyramid, with the two silyl groups in equatorial positions and the three Ph_3PAu units in the two axial and the remaining equatorial position (Figure 2). The interstitial 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° value 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 becoming 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)°)) and from the remarkably short distances Au1–Au3 (2.720(1) Å) and Au2–Au3 (2.720(1) Å). The axial Au–C bonds are larger than the equatorial Au–C bond but well within the established range of Au–C distances. The Si–C(center) bonds are significantly longer than the Si–C(Me) bonds, probably reflecting the different hybridization states of the tetra- and pentacoordinate carbon atoms involved.

The cation of 3 thus represents one of the few examples[3] of pentacoordinate carbon in a nonforced structure.

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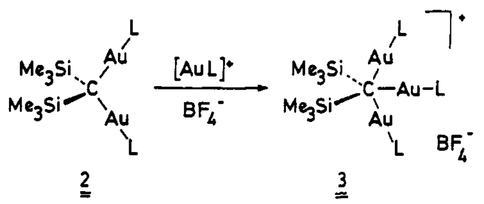
(14) Compound 3: compound 1 (0.35 g, 0.55 mmol) and the oxonium reagent (0.54 g, 0.36 mmol) were reacted in CH_2Cl_2 (20 mL) at 20 °C for 15 h. Thereafter, all volatiles were removed under vacuum, and the brown residue was extracted with benzene (2 × 5 mL) and with tetrahydrofuran (2 × 5 mL). From the latter extract, complex 3 was isolated through evaporation of the solvent and crystallization from ethanol (0.35 g, 40%); colorless crystals (from ethanol). Anal. Calcd for $C_{61}H_{63}Au_3BF_4P_3Si_2$ (1622.98): C, 45.14; H, 3.91. Found: C, 45.50; H, 3.94. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 10.0 ppm [s, Me]; 129.14 [d, *J*(P,C) = 58.6 Hz, C1], 129.16 [d, *J*(P,C) = 10.9 Hz, C3], 131.46 [d, *J*(P,C) = 2.5 Hz, C4], and 133.67 [d, *J*(P,C) = 13.6 Hz, C2] for equatorial Ph_3P; 129.26 [d, *J*(P,C) = 57.9 Hz, C1], 129.38 ["t", AXX′, *N* = 5.8 Hz, C3], 131.92 [s, C4], and 133.8 ["t", AXX′, *N* = 6.8 Hz, C2] for axial Ph_3P.

(15) X-ray analysis of 3. Crystal data: $\{(Me_3Si)_2C[Au(PPh_3)]_3\}^+BF_4^- = C_{61}H_{63}Au_3P_3Si_2BF_4$, $M_r = 1622.98$, triclinic, space group $P\bar{1}$, $a = 13.912(3)$ Å, $b = 14.318(2)$ Å, $c = 17.696(2)$ Å, $\alpha = 90.52(1)°$, $\beta = 98.29(1)°$, $\gamma = 108.76(1)°$, $V = 3296.97$ Å^3, $Z = 2$. With the use of 14 344 measured reflections (13 256 unique, 11 486 observed with $F_o \geq 4\sigma F_o$) collected at −56 °C with Mo Kα radiation ($\lambda = 0.710\,69$ Å) on an Enraf-Nonius CAD4 diffractometer, the structure was solved by direct methods (SHELXTL-Plus) and refined by full-matrix least-squares techniques (SHELX-76) with anisotropic temperature factors for all non-hydrogen atoms, except the B and F atoms of the anion (622 parameters), to a final *R* value of 3.18% (R_w = 3.18%).

Scheme I



Clearly this structure formally originates from an electrophilic attack of a $[(Ph_3P)Au]^+$ unit at the central carbon atom via the Au···Au edge of the neutral molecule 2. The incoming gold atom is forcing the two gold atoms of the substrate apart, and the system is reaching an energy minimum when adopting a distorted trigonal-bipyramidal configuration (3) with two short meridional Au···Au contacts (Scheme I). This process is an important variant of the formation[3] of $\{[(Ph_3P)Au]_5C\}^+$ from (hypothetical) $[(Ph_3P)Au]_4C$ and of $\{[(Cy_3P)Au]_4CMe\}^+$ from the (equally hypothetical) $[(Cy_3P)Au]_3CMe$.[3] The three examples illustrate the unique potential of gold(I) to stabilize hypercoordinate carbon species largely through peripheral Au···Au interactions.[6,7]

Simple molecular orbital diagrams[3] (idealized C_{2v} symmetry) can account for the diamagnetic ground state of the (colorless) cation in 3, which has no electronic transition in the visible region. Four bonding orbitals are occupied by the eight core electrons available for bonding, which leaves the Si_2CAu_3 unit electron-deficient. The present results have a bearing on a whole series of AB_5 electron-octet species, most of which are only considered high-energy intermediates or transition states, with CH_5^+ perhaps being the most widely discussed prototype. Note that H^+ and LAu^+ (and Me_3Si) are to be considered isolobal!

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for 1 and 3 (21 pages). Ordering information is given on any current masthead page.

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