The First Complexes of Tetragoldmethane CAu₄

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Treatment of [B(OMe)₄] with four equivalents of a (tert-phosphine)gold(I) chloride LAuCl with L = Pr(C₅H₅)₃ or (2-MeC₆H₄)₂P in the presence of CsF in hexamethylphosphoronic triamide (HMPT) affords the first complexes of the type (LAu)₄C. The product is formed together with salts (LAu)₅Cₓ⁺BF₄⁻ as the by-product for L = tricyclohexylphosphine, from which it can be separated by fractional crystallisation. With Ph(2-MeC₆H₄)₂P only the hexacoordinate species (LAu)₄Cₓ₂⁺BF₄⁻ is obtained, while with Ph(2-MeC₆H₄)₂P a mixture of (LAu)₅Cₓ⁺ and (LAu)₆C²⁺ salts is generated. The title compounds are stable, colourless solids readily identified by standard analytical and spectroscopic techniques, including ¹³C NMR of ¹³C-enriched material.

All previous attempts to generate a species CAu₄ or its complexes, e.g. C(AuL)₄ with L a donor ligand, have met with failure [1–3]. Initially these negative results came as a surprise, since 1) analogous mercury compounds of the type C(HgX)₄ have been known in the literature for a long time [4, 5], and 2) since aurated ammonium cations of the type N(AuL)₄⁺ are well established [6–10].

Careful investigation of the auration of suitable functional methane precursors like poly(boryl)methane has recently shown, however, that complete auration of carbon does in fact take place, but is transgressing the stage of C(AuL)₄ molecules leading instead to hypercoordinate cationic species of the types C(AuL)₅⁺ and even C(AuL)₆⁺. These cations contain penta- and hexacoordinate carbon atoms with trigonal bipyramidal and octahedral geometry, respectively [11–15]. Molecules C(AuL)₄ were thus recognized to be “aurophilic” and function as strong nucleophiles towards LAu⁺ units in the reaction medium. This unprecedented phenomenon has meanwhile been rationalized on the basis of sophisticated theoretical calculations including relativistic effects [16–20].

Notwithstanding, there remained the challenge to synthesize the elusive C(AuL)₄ species. The introduction of reagents which prevented auration of carbon beyond tetra-coordination through bulky substituents at phosphorus appeared to be the most obvious concept.

Since the reaction of (triphenylphosphine)gold(I) chloride with tetrakis(dimethoxyboryl)methane in the presence of CsF in hexamethylphosphoramic triamide [6] leads to [(Ph₃PAu)₆C]²⁺, in a first series of experiments the phenyl substituents were gradually exchanged by sterically more demanding o-tolyl groups. While the mono(o-tolyl)diphenylphosphine ligand (2-MeC₆H₄)₂PPh and (2-MeC₆H₄)₃P induced the expected reduction in the coordination number of carbon in the product from six to five, and finally to four:

⁴Ph(2-MeC₆H₄)₃PAuCl C[B(OMe)₄]₄, CsF, HMPT
[(Ph₃PAu)₆C]²⁺ 2BF₄⁻
Ph(2-MeC₆H₄)₃PAuCl → [Ph(2-MeC₆H₄)₃PAu]C⁺BF₄⁻, [Ph(2-MeC₆H₄)₃PAu]C₆BF₄⁻
(2-MeC₆H₄)₃PAuCl → [(2-MeC₆H₄)₃PAu]C₆BF₄⁻

The preparation yields a mixtures of products with different stages of carbon auration for L = d(o-tolyl)phenylphosphine, which are difficult to separate due to facile exchange of LAu⁺ units. Though identification of the components of the mixture is readily accomplished, mainly by NMR spectroscopy (Exp. Section), isolation of analytically pure samples is extremely tedious.

In further experiments, therefore, tricyclohexylphosphine was used as a ligand, which owing to its still larger cone angle should favour more strongly
the tetracoordination of carbon, and reduce ligand exchange rates.

\[(c-C_6H_{11})_3PAuCl \rightarrow [(c-C_6H_{11})_3PAu]_5C^+BF_4^- \]

Though penta-auration was again not fully suppressed, and the reaction mixture contained both the penta- and tetra-aurated species, separation of the components presented no problem in this system.

Pure tetrakis(tricyclohexylphosphinegold)methane (1) was obtained in a 23% isolated yield as a colourless, polycrystalline solid, which is soluble in di- and trichloromethane, tetrahydrofuran, benzene, and toluene, but only very sparingly soluble in diethylether and pentane. For solutions in CD$_2$Cl$_2$ the $^{31}$P resonance appears at $\delta = 48.4$ ppm. The $^1$H NMR spectrum shows only a multiplet at $\delta = 1.14-2.07$ ppm for the cyclohexyl groups, but with the CH quartet resonance clearly distinguished at $\delta = 1.47$. For $^{13}$C NMR spectroscopy, a sample $^{13}$C-enriched in the center of the molecule was prepared following a procedure described elsewhere [14] for other poly(auro)methanium compounds. This labeled material shows a resonance for the interstitial carbon atom at $\delta = 99.3$ ppm as a 1:4:6:4:1 quintet with $2(J(CAuP)) = 61.0$ Hz. (The same splitting can be extracted from the satellites in the $^{31}$P spectrum of the enriched material.) C1–C4 of the C$_6$H$_{11}$ groups are located at 34.5 ($J = 23.7$ Hz), 27.9 ($J = 12.2$ Hz), 26.7, and 30.9 ppm. The field desorption mass spectrum shows a parent peak at $m/e = 1921.5$.

All attempts to grow single crystals of one of the tetragoldmethane complexes were unsuccessful. For the present cases there is little doubt that the CAu$_4$ cores of the molecules have a tetrahedral structure. However, this prediction is only valid for complexes with bulky ligands, where inter-ligand repulsion prevents any structural reorganization which could bring the gold atoms closer together. It should be remembered that tetra(auro)-arsonium salts have been shown to have a square pyramidal Au$_4$As$^+$ core [10]. This violation of the classical Le Bel/vant'Hoff and Lewis concepts (which require arsonium cations with an octet of electrons at arsenic to be tetrahedral) is a consequence of strong intramolecular Au···Au attractions which lead to a reduction of the Au–As–Au angles from the tetrahedral 109° to ca. 80° in the (LAu)$_4$As$^+$ cation. Tetra(auro)methanes with small ligands L are also expected to be strongly distorted, and this unusual structural feature is to be taken as one of the reasons for the hypercoordination phenomena observed in the corresponding system.

**Experimental**

All experiments were routinely carried out in an atmosphere of dry, purified nitrogen. Glassware was oven-dried and filled with nitrogen, and solvents were purified, dried and saturated with nitrogen. NMR: Jeol GX 270 and GX 400 spectrometers; MS: Finngen MAT 90 spectrometer, in field desorption or fast atom bombardement mode.

The tertiary phosphines and their AuCl complexes were obtained using standard methods [21–24]:

- (2-MeC$_6$H$_4$)Ph$_2$PAuCl: m.p. 201–205 °C, $^{31}$P NMR (CD$_2$Cl$_2$): $\delta P = 26.9$ ppm.
- (2-MeC$_6$H$_4$)$_2$PhPAuCl: m.p. 202–205 °C, $\delta P = 17.5$ ppm.
- (2-MeC$_6$H$_4$)$_3$PAuCl: m.p. 212–215 °C, $\delta P = 8.7$ ppm.
- (c-C$_6$H$_{11}$)$_3$PAuCl: m.p. 221–223 °C, $\delta P = 54.9$ ppm.

**General synthetic procedure**

A suspension of the (phosphine)gold(I) chloride and an excess of cesium fluoride in hexamethylphosphoric triamide (ca. 30 ml) is treated at room temperature and with stirring with a solution of the stoichiometric amount of tetrakis(dimethoxymethyl)borylmethane in 10 ml of HMPT. The reaction mixture is stirred for 24 h and then filtered. Pentane is slowly added to the filtrate to give a precipitate, which is washed with pentane and recrystallized from dichloromethane/pentane or tetrahydrofuran/diethylether.
Hexakis[(o-tolyl)dipheny1phosphine-gold(I)]methanium(2+)/bis(tetrafluoroborate)

1.05 g (2.06 mmol) 2-MeC₆H₄PH₂PAuCl; 0.16 g (0.53 mmol) [(MeO)₂B]₄C; 5.10 g (33.7 mmol) CsF. Yield 0.20 g (20%), m.p. 155°C (decomp.).

\[\text{CsF. Yield 0.20 g (20%), m.p. 155°C (decomp.).}\]

\[\text{(0.56 mmol) [(MeO)₂B]₄C; 4.82 g (31.9 mmol) CsF. Yield 0.31 g of a mixture of both products.}\]

\[\text{31P NMR (CD₂Cl₂): 2.20 and 2.32 (Me); 6.82-7.63, Aryl.}\]

\[\text{13C NMR (CD₂Cl₂): 22.5, Me; 128.6 (J = 23.4 ppm), 133.6 (J = 7.9), 132.4 (J = 3.0), 133.6 (J = 3.8) (Cl-C6 of o-tolyl); 129.2 (J = 57.2), 134.4 (J = 1.5).}\]

\[\text{1H NMR (CD₂Cl₂): 2.04, Me; 6.79-7.44 (o-tolyl, phenyl).}\]

\[\text{MS (FAB, p-nitrobenzylalcohol): m/e = 1425.1 [10%, M²⁺(cation)].} \]

\[\text{31P NMR (CD₂Cl₂): δ = 24.8 and 25.4.} \]

\[\text{1H NMR (CD₂Cl₂): 2.20 and 2.32 (Me); 6.82-7.63, Aryl.}\]

\[\text{MS (FAB): 1921.5 [59%, M⁺(cation)]; 1961.2 [18%, (M)⁻].} \]

Tetrakis[(di(o-tolyl)pheny1phosphine-gold(I)]methane

1.2 g (2.24 mmol) (MeC₆H₄)₂PAuCl; 0.17 g (0.56 mmol) [(MeO)₂B]₄C. 4.82 g (31.9 mmol) CsF. Yield 0.26 g (23%), m.p. 162°C (decomp.).

\[\text{MS (FD, CH₂Cl₂): m/e = 2018.2 (7%, M⁺). 31P NMR (CD₂Cl₂): δ = 23.0. 13C NMR (CD₂Cl₂): 23.1 (J = 9.8, Me), 128.0 (J = 49.4), 143.4 (J = 12.2), 132.4 (J = 7.9), 131.5, 126.8 (J = 9.8), 134.1 (J = 9.2).}\]

\[\text{1H NMR (CD₂Cl₂): 2.15, Me; 6.86-7.35, Aryl.} \]

Pentakis[tricyclohexylphosphine-gold(I)]methanium (+/1)tetrafluoroborate and tetrakis[tricyclohexylphosphine-gold(I)]methane (I)

1.42 g (2.77 mmol) ((c-C₆H₄)₃PAuCl; 0.22 g (0.72 mmol) [(MeO)₂B]₄C. 15°C (enriched in the position indicated), 5.22 g (34.5 mmol) CsF. Yield 0.80 g of a mixture of both products. The methanium salt has the following spectroscopic data taken from solutions of this mixture: 31P NMR (CD₂Cl₂): δ = 50.9, doublet (J = 60.3). 13C NMR (CD₂Cl₂): δ = 185.3, quintet (J = 60.3). MS (FD): m/e = 2398.3 [100%, M⁺(cation)]. Extraction of the mixture with benzene and reprecipitation with pentane gives pure tetraauromethane I, yield 0.31 g (23.3%).

\[\text{C₁₅H₁₀2Au₄P₆ (1921.62)} \]

\[\text{Caled C 45.66 H 3.40%, Found C 44.97 H 3.51%.} \]

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