Hypercoordinate Phosphorus in Gold Clusters: Novel Species $[P(AuL)_6]^{3+}(BF_4^-)_3$

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Treatment of $(Me_3Si)_3P$ with a solution of six equivalents of a (triorganophosphine)gold(I) tetrafluoroborate $LAu^+BF_4^-$ (L = Bu^t_3P, Pr^i_3P) in tetrahydrofuran, in the presence of an excess of KF, leads to high yields of the title compounds 1a, b as stable microcrystalline solids; the products, which contain interstitial six-coordinate phosphorus, have been characterized by a detailed NMR study and on the basis of elemental and mass spectrometric analysis.

As a corroboration of theoretical predictions[1] and a clarification of inconsistencies in earlier experimental work,[2] in a series of recent papers[3–7] the existence of novel carbon-centred octahedral gold clusters of the type $[C(AuL)_6]^{2+}$ (with L = tertiary phosphine) was demonstrated. This work was soon followed by the synthesis of related trigonal-bipyramidal[8–10] or square-pyramidal[11,12] clusters, $[C(AuL)_5]^+$ and $[RC(AuL)_4]^+$, respectively. Complementary results are also available on isoelectronic nitrogen-centred[13] species, $[N(AuL)_5]^{2+}$, and on phosphorus[14,15] analogues, $[P(AuL)_5]^{2+}$ and $[RP(AuL)_4]^{2+}$. Furthermore a novel square-pyramidal structure[16] was discovered for the cations $[As(AuL)_4]^+$, while a classical tetrahedral geometry[17] is present in the ammonium analogue $[N(AuL)_4]^+$. In theoretical models the unusual state of bonding in these clusters with five- and six-coordinate carbon could be rationalized at least in part on the basis of relativistic effects.[18–20]

We now present evidence for a series of related tripositive cations of the general formula $[P(AuL)_6]^{3+}$ with highly electron-deficient six-coordinate phosphorus. The corresponding nitrogen-centred cations were the subject of previous studies,[21] but their existence is not fully confirmed yet.[22]

Treatment of freshly prepared solutions of the reagent $[R_3PAu]^+BF_4^-$ in tetrahydrofuran with a solution of $(Me_3Si)_3P$ in the same solvent (molar ratio 6 : 1), in the presence of finely powdered KF at −78 °C and with protection against bright light, leads to a slurry, from the filtrate of which the products **1a–c** could be obtained according to eqn. (1). Even with a lower relative proportion of gold reagent, no products with a lower degree of auration {*e.g.* $[P(AuL)_5]^{2+}$}[14] were detectable. The yields are highest for complexes with bulky trialkylphosphines (L = Bu^t_3P: 82%; Pr^i_3P: 91.5%), and the solid colourless tetrafluoroborate salts show high thermal stability (**1a**: decomp. >200 °C; **1b**: 198 °C). With Ph_3P as a ligand the yields drop to 70%, and complex **1c**, a yellow-brown solid, is of very limited stability at ambient temperature both as a solid and in solution. With tri(*o*-tolyl)phosphine the product isolated could only be identified by its FAB mass spectrum. Solutions proved to be too unstable for NMR spectra to be recorded even at −40 °C.

$$6\,LAu^+BF_4^- + (Me_3Si)P + 3\,KF \rightarrow$$

$$3\,KBF_4 + 3\,Me_3SiF + [(LAu)_6P]^{3+}\,(BF_4^-)_3 \quad (1)$$

1a: L = Bu^t_3P
1b: L = Pr^i_3P
1c: L = Ph_3P

The complexes **1a–c** are soluble in polar solvents like dichloromethane or tetrahydrofuran, but insoluble in diethyl ether or pentane. Solutions in CD_2Cl_2 give characteristic $^{31}P\{^1H\}$ NMR spectra, each featuring a high-field septet signal for the interstitial phosphorus atom (at δ −211.1, −114.1 and −165.7), and a low-field doublet for six NMR-equivalent peripheral phosphorus atoms (at δ 100.7, 75.8 and 36.7 for **1a–c**), with coupling constants of 185, 145 and 167 Hz for **1a–c**, respectively. These spectra are temperature-dependent for **1a** and **1c**, with line broadening and coalescence of the multiplicity occurring above about −40 °C, owing to rapid ligand exchange. For **1b** well resolved spectra are obtained at ambient temperature. The ^1H and $^{13}C\{^1H\}$ NMR spectra also indicate the equivalence of the ligands L through the appearance of only one set of signals for Bu^t, Pr^i and Ph groups.†

It is interesting, however, that all NMR spectra (^{31}P, ^{13}C and ^1H of **1a**) show further splitting below −80 °C, which finally indicates non-equivalence of the six LAu groups at very low temperatures. We offer the following explanation for this phenomenon. In a regular PAu_6 octahedron with PAu bond lengths of *ca.* 2.30 Å, the Au–Au edges are calculated to be 3.25 Å long. This distance exceeds the ideal Au···Au distance of *ca.* 3.0 Å which allows bonding interactions ('auriophilicity')[3–5] by 0.25 Å. Any distortion of the Au–P–Au angles from the idealized geometry will lead to more strongly bonding contact for at least some of the gold atoms, however, and we hold such distortions responsible for the reduction of symmetry observed in the NMR experiments.

The mass spectra of the three compounds (FAB from 4-nitrobenzyl alcohol matrix and CH_2Cl_2 as a solvent) show the $[(LAu)_4P]^+$ cations as the parent peaks and L_2Au^+ as the base peaks. Of greatest diagnostic value are ions $[(LAu)_5PAu]^{3+}$ (*e.g. m/z* 670.9 for **1b**) most likely containing six gold atoms attached to a central phosphorus atom. The stoichiometry is further supported by elemental analyses.

Unfortunately no well ordered single crystals could be grown for any of the three complexes, and therefore the assignment of the most plausible (distorted) octahedral structure is only tentative. An attempted crystal structure determination for **1a** gave preliminary results consistent with a PAu_6 core of point group C_{2v} symmetry, but problems with the X-ray data set and/or refinement of disorder precluded definite conclusions.

The new six-coordinate tripositive cations can be clearly distinguished from related five- and four-coordinate species at least in the case of the family with L = Bu^t_3PAu, for which all three cations could be identified. Salts with the dication $[(Bu^t_3PAu)_5P]^{2+}$ are obtained through reaction of $(Me_3Si)_3P$ with the milder aurating agent $[(Bu^t_3PAu)_3O]^+\,BF_4^-$ and are characterized in their ^{31}P NMR spectra by a sextet–doublet pattern with chemical shifts (δ −103.5 and 95.8) and a coupling constant (J_{PP} 168.8 Hz) quite distinct from the data for **1a**. Through adjusting the stoichiometry of the auration experiment, salts of the four-coordinated monocation $[(Bu^t_3PAu)_4P]^+$ could also be obtained. Their NMR data again differ quite significantly from those of the six- and five-aurated species (δ −71.0, quintet; δ 95.6, doublet; J_{PP} 206.6 Hz). Through these complementary data all conclusions regarding the existence and structure of the title compounds have gained further support leaving little doubt about the validity of the overall concept.

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† **1a**: ^1H NMR (CD_2Cl_2, 25 °C): δ 1.99 (d, Me, *J* 14.16 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 32.25 (s, Me) and 40.35 (d, CP, *J* 13.97 Hz); MS (FAB, CH_2Cl_2, 4-nitrobenzyl alcohol matrix): *m/z* 740.8 $[(M - Bu^t_3P)^{3+}]$ and 1628.8 $[(Bu^t_3PAu)_4P^+]$.

1b: ^1H NMR (CD_2Cl_2, 325 °C): δ 1.36 (m, 6H, Me, $[A_6BX]_n$) and 2.50 (m, 1H, CH, $[A_6BX]_n$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.04 (s, Me) and 25.34 (d, CH, *J* 28.09 Hz); MS (*vide supra*): *m/z* 517.1 $[(Pr^i_3P)_2Au^+]$, 670.9 $[(M - Pr^i_3P)^{3+}]$ and 1459.1 $[(Pr^i_3PAu)_4P^+]$.

The bonding in the PAu_6 core can be described by a simple molecular orbital diagram,[1,4] which leads to a set of four strongly bonding orbitals to be filled with the eight electrons available to give a diamagnetic ground state not readily excited by low-energy electromagnetic radiation. This is consistent with the observed diamagnetism of the compounds and the absence of absorption in the visible region. Any distortions of the octahedron will lead to splitting of the degenerate levels, but without grossly affecting the bond order of the P–Au interactions. For a description of Au···Au bonding[3] more sophisticated calculations are required,[18–20] but there is little doubt that these interactions will contribute strongly to the overall stability of the clusters.

This work has been supported by Deutsche Forschungsgemeinschaft (Leibniz-Programme), by Fonds der Chemischen Industrie, and, through the donation of chemicals, by Hoechst AG, Degussa AG, and Heraeus GmbH. We thank Professor F. R. Kreissl for obtaining the mass spectra.

Received, 18th September 1992; Com. 2/05004H

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