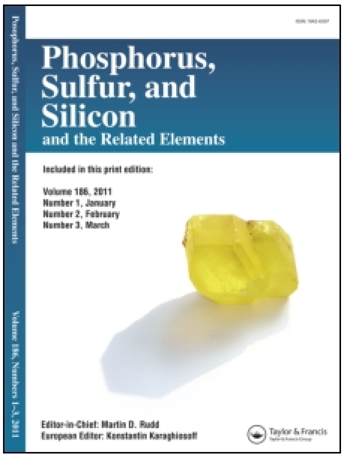

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H. Schmidbaur[a]; H. Beruda[a]; E. Zeller[a]
[a] Anorganisch-chemisches Institut der Technischen Universität München, Garching, Germany

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HYPER-COORDINATE PHOSPHORUS ATOMS IN A GOLDEN HOUR-GLASS[#]

H. SCHMIDBAUR,* H. BERUDA and E. ZELLER

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching,
Germany

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Treatment of phosphine, PH_3, or bis(pivaloyl)phosphine, $(^{t}BuCO)_2PH$, with {tris[(triphenylphosphine)gold]oxonium} tetrafluoroborate $(Ph_3PAu)_3O^+ BF_4^-$ in tetrahydrofuran at -60°C affords small amounts of a tricationic nona-nuclear gold complex $\{Au[P(AuPPh_3)_4]_2\}^{3+}(BF_4^-)_3$. The low temperature $\{^1H\}$ ^{31}P NMR spectra of this product exhibit an $(A_4M)_2$ spin system indicating a highly symmetrical species of D_{4d} or D_{4h} symmetry in solution. The D_{4h} structure, resembling a golden hour-glass, has been confirmed by an X-ray diffraction analysis of single crystals (tetragonal space group I4/mmm, Z = 2, a = 16.878(2), c = 30.320(3) Å). The trication contains two square pyramidal $P(AuPPh_3)_4^+$ units P-coordinated to the central Au^+ cation.

Key words: Gold clusters; Hypercoordinate phosphorus; NMR spectroscopy; X-ray crystallography.

[#] Dedicated to Professor Alan H. Cowley on the occasion of his 60th birthday.

INTRODUCTION

Recent work has shown that many Main Group Elements can function as coordination centers for gold(I).[1],[2] The compounds obtained show many unusual types of structure and bonding. Hypercoordination with electron-deficient bonding and non-classical coordination geometries are common features, with prominent examples already available for boron,[3] carbon,[4-10] nitrogen[11] and arsenic.[12] For the two pnicogen elements the situation regarding the structure of the cations $N(AuL)_4^+$ and $As(AuL)_4^+$ is particularly intriguing: While the tetragold-ammonium cation follows other ammonium cations in exhibiting a tetrahedral structure,[13-15] the analogous tetragold-arsonium cations have been found to be square-pyramidal.[12] Regarding structural details, it has also been noted that the $N(AuL)_4^+$ cations are clearly destorted,[13-15] and that the $As(AuL)_4^+$ cations have rather small Au-As-Au angles.[12]

These structural parameters indicate significant Au···Au interactions between seemingly closed-shell Au(I) centers with their d^{10} configuration of electrons.[1],[2],[16] And in fact, recent computational treatments, of these systems have lead to the conclusion, that metal-metal interaction do play a decisive role in the determination of the structures of the polyhedra.[16],[17]

From these calculations the prediction has also been made that the analogous tetragold-phosphonium cation should also sho a non-standard square planar structure,[18] which is at variance with classical models of structure and bonding based e.g. on the LeBel - van't Hoff rule or on the theory of hybride orbitals (sp^3) for elements with an octet of electrons.

Initially, all attempts to synthesize salts containing isolated $P(AuL)_4^+$ cations, where L is representing a standard tertiary phosphine ligand, have failed.[19] It was only when ligands L = PR_3 were chosen with very bulky groups R, that at least one example (with R = ^tBu) could be obtained.[20] Owing to the steric requirements of the ligands, the structure of this cation, was found to be (distorted) tetrahedral, but it was obvious that the dimension of the four phosphine ligands actually prevented the compound from becoming square planar. In the experiments carried out with L = PPh_3 the isolated cations $P(AuPPh_3)_4^+$ have not been observed, but in one case an addition compound with $Au(PPh_3)_2^+$ has been isolated.[21] The stoichiometry of the resulting dication, written as $[(Ph_3PAu)_4P{\cdot}Au(PPh_3)_2]^{2+}$, is indicative of the two components, but the structure is extremely irregular and does not allow to draw any conclusion regarding the structure of the independent units.

The experiments were therefore continued,[22] and in one new variation of the reaction components and conditions yet another adduct of the elusive $P(AuL)_4^+$ cation has been discovered. Fortunately the structure of this aggregate is of very high symmetry and suggests that the proposal of a square pyramidal structure for the $P(AuL)_4^+$ is indeed valid.[23]

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RESULTS

Treatment of a slurry of tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate in tetrahydrofuran with bis(pivaloyl)phosphine $(^tBuCO)_2PH$ at -60°C leads to a reaction mixture, which contains several polynuclear gold cluster cations as their tetrafluoroborate salts. The product distribution is not unlike the mixtures obtained from the analogous reactions with phosphine gas PH_3 (in thf at -78°C in the presence of excess $NaBF_4$). Removal of all volatile components from the reaction mixtures in a vacuum leaves yellow solid residues, from which three crystalline products can be isolated upon extraction with dichloromethane and fractional crystallization from dichloromethane/diethylether/pentane mixed solvents. The title compound appears as the last fraction in about 25% yield after the main products have been removed, i.e. after $\{[(Ph_3P)_2Au]P[Au(PPh_3)]_4\}^{2+}(BF_4^-)_2$ and $\{[(Ph_3P)Au]_5P\}^{2+}(BF_4^-)_2$.

$$(^tBuCO)_2PH + [(Ph_3P)Au]_3O^+\ BF_4^- \longrightarrow$$
$$\longrightarrow\ ^tBuCOOH + \{Au[P(AuPPh_3)_4]_2\}^{3+}\ (BF_4^-)_3$$

The product is a pale-yellow crystalline solid, which is stable in air and water. It is readily dissolved in di- and trichloromethane or acetonitrile. In an inert atmosphere decomposition starts at 185°C with deposition of a gold mirror at the walls of the glass capillary.

Solutions in dichloromethane-d_2 at ambient temperature show $\{^1H\}^{31}P$ NMR spectra which are characterized by a large doublet at δ = 40.6 ppm, J(P,P) = 185 Hz (relative intensity 4), and a broad resonance at δ = -105.0 ppm (relative intensity 1). Cooling of the sample to -70°C leads to an improved resolution revealing fine structure in both multiplets.

The signal pattern could be reproduced by calculation of a 10 spin system of the type $(A_4M)_2$ with the following set of parameters: δA = 38.25, δM = −106.2 ppm; J(M,M') = −309, J(A,M) = −189, J(A,M') = −11.0, and J(A,A') = 0.0 Hz (Figure 1). It thus appears that the cation of the salt is of high symmetry with eight chemically equivalent ligand phosphorus atoms and two equivalent centroid phosphorus atoms. At low temperature extended P,P-couplings give rise to magnetical non-equivalence and second order splittings. At elevated temperature, however, dynamic processes lead to a break-down of some of these couplings, leaving intact only the "primary" couplings of the individual pyramid components (below). The NMR spectra require a high symmetry for the trication, best represented by point groups D_{4d} or D_{4h}.

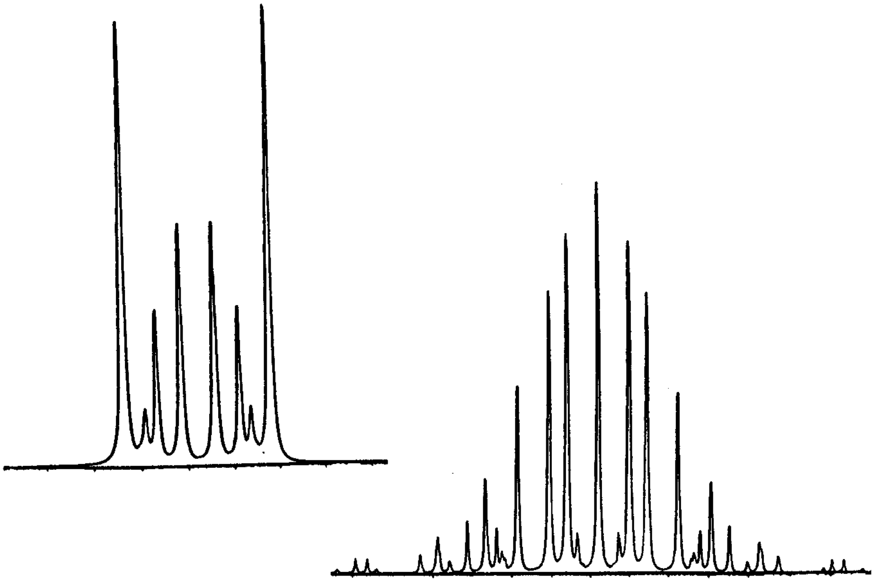

FIGURE 1 $\{^1H\}^{31}P$ NMR spectrum of the title compound (in dichloromethane-d_2 at −70°C). The spectrum represents a $(A_4M)_2$ ten-spin system. A- and M-part are shown seperately, with relative intensities not to scale.

The fast atom bombardment mass spectrometric studies indicated the presence of the component $[P(AuPPh_3)_4]^+$ at m/z = 1868.1, but ions of higher mass could not be observed owing to fragmentation processes. The ions $AuPPh_3^+$ (m/z = 459.3) and $(Ph_3P)_2Au^+$ (m/z = 721.4) are also indicators for rather extensive fragmentation.

Crystals of the title compound obtained from CH_2Cl_2/Et_2O are tetragonal, space group I4/mmm with two formula units in the unit cell. [a = 16.878(2), b = 30.320(3) Å, V = 8637.2 Å^3, M = 4193.3]. The lattice contains nona-nuclear trications $[(LAu)_4P\text{-}Au\text{-}P(AuL)_4]^{3+}$ and independent tetrafluoroborate anions. These anions are partially disordered and meet the crystal symmetry only by employing appropriate site occupancy factors.

The heavy atom skeleton of the trication is shown in Figure 2. This partial structure has D_{4h} symmetry. It is composed of two square pyramids $AuPAu_4$ sharing a common vertice (Au2). By symmetry, the gold atoms at the square bases (Au1) are in an eclipsed conformation. The central gold atom Au2 is linearly two-coordinate with distances

Au2-P1 at 2.293(7) Å. The phosphorus atoms P1 in the center of the $AuPAu_4$ pyramids are equidistant from the four basal gold atoms Au1 at distances Au1-P1 of 2.369(3) Å. The angles Au1-P1-Au1a are as small as 76.6(1)°, which leads to short contacts Au1···Au1a of 2.9355(8) Å.

These dimensions of the two $P1(Au1)_4$ pyramids are very similar to those of the corresponding arsonium cations[12] $As(AuL)_4^+$, also with L = PPh_3, where the angles Au-As-Au are 71° (average) and the Au···Au contacts are 2.896 Å (average). For both structural units significant Au-Au bonding is to be considered as the main origin of the non-tetrahedral (square pyramidal) geometry of the cations. In the title compound the two PAu_4 pyramids are not isolated, but linked through the central gold cation (Au2), which functions as the acceptor site for the phosphorus donor functions of the two pyramids. It appears therefore that cations $P(AuL)_4^+$ are potent donor ligands, which are readily attached to metal acceptors.

There is a parallel for this donor activity of $P(AuL)_4^+$ pyramids in the dication $[PAu_5(PPh_3)_6]^{2+}$, where the gold atom of a cation $[Au(PPh_3)_2]^+$ serves as the acceptor site.

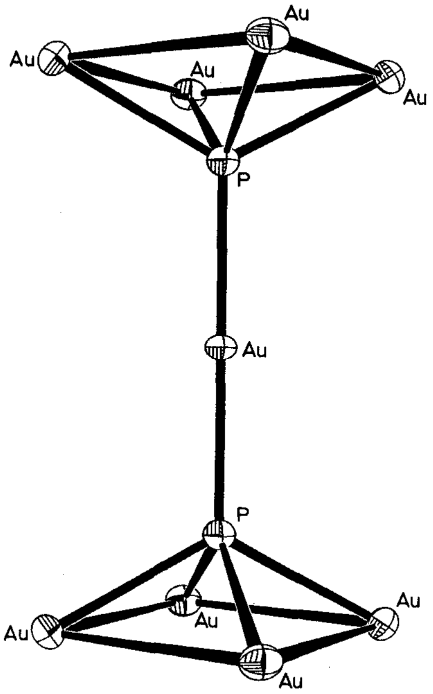

FIGURE 2 $Au_4PAuPAu_4$ core of the trication in crystals of $\{[(Ph_3P)Au]_4PAuP[Au(PPh_3)]_4\}^{3+}(BF_4^-)_3$. The peripheral Ph_3P ligands have been omitted.

These results thus provide evidence that phosphonium cations $[P(AuL)_4]^+$ are indeed components of the reaction mixtures obtained from PH_3, $P(SiMe_3)_3$, or pivaloylphosphines like $(^tBuCO)_2PH$ or $(^tBuCO)_3P$ with aurating agents, and that these cations are pyramidal with a high apical donor capacity. This leads to aggregates with various other components, the title component being an example with Au^+. The stoichiometry of the trication of the title compound is then straightforward as represented by the formula $\{(LAu)_4P^+, Au^+, (LAu)_4P^+\}$.

The gold atoms at the basal planes of the two small pyramids bear one phosphine ligand L each, with angles P1-Au1-P2 at 178.5(2)° and distances Au1-P2 at 2.287(4) Å, as expected from standard data. Figure 3 shows the extended skeleton, again not unlike the frame of an hour-glass, this symbol being of course chosen for the occasion[#]. The dimensions and relative orientations of the ligand phenyl groups follow the usual pattern.

DISCUSSION

The description of bonding in the title complex can follow model systems of similar stoichiometry and symmetry. The closest analogy, the relation to the arsenic compounds, has already been mentioned.[12] Less obvious, but even more interesting, is the parallel to be found in the square pyramidal methanium cations $RC(AuL)_4{}^+$, which also obey C_{4v} symmetry for the $CC(AuP)_4$ skeleton.[24] Under this point group the valence orbitals of the central carbon atom, the atom in the apical position, and the four gold atoms can be combined to give a set of three bonding orbitals for the CAu_4 cluster indicating delocalized, electron-deficient bonding for this unit, and a localized bonding of the apical atom. The diamagnetic ground state thus arrived at by computational methods is compatible with the general properties of all compounds obtained to date.

Similar structural features have been found finally for a <u>boronium</u> <u>cation</u> $L{-}B(AuL)_4{}^+$, which also exhibits a square pyramidal skeleton.[3]

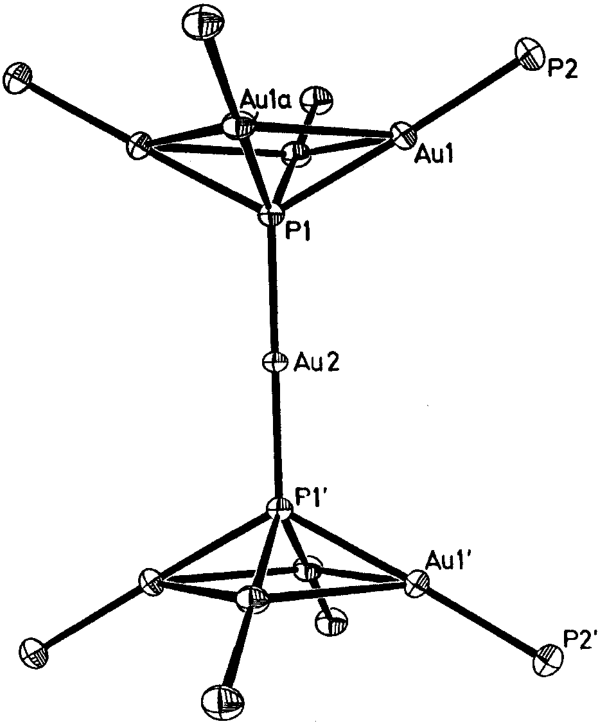

FIGURE 3 $[(PAu)_4PAuP(AuP)_4]^{3+}$ skeleton of the trication with atomic numbering (point group D_{4h}). Phenyl groups have been omitted.

The treatment of the metal-metal bonding between the gold atoms (d^{10} blocks !) to be invoked for the small pyramids with their short edges in all of these examples and in the new hyper-coordinate phosphorus compounds needs much more sophisticated theoretical approaches. Work dedicated to these phenomena is in progress, and preliminary results have been communicated. The significance of relativistic effects for these theoretical treatments has been stressed in a series of relevant papers. It is probably from this direction, that progress in the understanding of the new phenomena is most imminent.

SUPPLEMENTARY MATERIAL

Experimental details of this work can be extracted from the PhD Theses of the Holger Geruda and Edgar Zeller. Crystal and structure solution have been deposited. Related work will be the subject of forthcoming publications.

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REFERENCES

1. H. Schmidbaur, Gold Bull. 23, 11 (1990)
2. H. Schmidbaur, Interdisc. Sci. Rev. 17, 213, (1992); Pure & Appl. Chem. 65, 691 (1993).
3. A. Blumenthal, H. Beruda, H. Schmidbaur, J. Chem. Soc., Chem. Commun. 1993, 1005.
4. F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 27, 1544 (1988).
5. F. Scherbaum, A. Grohmann, G. Müller, H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 28, 463 (1989).

6. O. Steigelmann, P. Bissinger, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl. 29*, 1399 (1990).
7. H. Schmidbaur, B. Brachthäuser, O. Steigelmann, *Angew. Chem. Int. Ed. Engl. 30*, 1488 (1991).
8. H. Schmidbaur, B. Brachthäuser, O. Steigelmann, H. Beruda, *Chem. Ber. 125*, 2705 (1992).
9. H. Schmidbaur, O. Steigelmann, *Z. Naturforsch. 47b*, 1721 (1992).
10. H. Schmidbaur, B. Brachthäuser, S. Gamper, A. Schier, O. Steigelmann, *Z. Naturforsch. 47b*, 1725 (1992).
11. A. Grohmann, J. Riede, H. Schmidbaur, *Nature 345*, 140, (1990).
12. E. Zeller, H. Beruda, A. Kolb, P. Bissinger, J. Riede, H. Schmidbaur, *Nature 352*, 141 (1991).
13. E. G. Perevalova, E. I. Smyslova, V. P. Dyadchenko, K. I. Grandberg, A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR Ser. Khim. 1980*, 1455.
14. Y. L. Slovokhotov, Y. T. Struchkov, *J. Organometal. Chem. 277*, 143 (1984).
15. A. Brodbeck, J. Strähle, *Acta Crystallogr. Sect. A, 46*, C-232(1990).
16. A. Görling, N. Rösch, D. E. Ellis, H. Schmidbaur, *Inorg. Chem. 30*, 3986 (1991); N. Rösch, A. Görling, D. E. Ellis, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl. 28*, 1357 (1989).
17. P. Pyykkö, Y.-F. Zhao, *Chem. Phys. Lett. 177*, 103 (1991); P. Pyykkö, Y.-F. Zhao, *Angew. Chem. Int. Ed. Engl. 30*, 604 (1991).
18. J. Li, P. Pyykkö, *Inorg. Chem. 32*, 2630 (1993). J. Li, P. Pyykkö, *Chem. Phys. Lett. 197*, 586 (1992).
19. H. Schmidbaur, G. Weidenhiller, O. Steigelmann, *Angew. Chem. Int. Ed. Engl. 30*, 433 (1991).
20. E. Zeller, H. Beruda, H. Schmidbaur, *Chem. Ber. 126*, 2033 (1933).
21. H. Beruda, E. Zeller, H. Schmidbaur, *Chem. Ber. 126*, 2037 (1993).
22. E. Zeller, H. Beruda, *Diss.*, Techn. Univ. Munich 1993.
23. E. Zeller, H. Schmidbaur, *J. Chem. Soc., Chem. Commun. 1993*, 69.
24. O. Steigelmann, P. Bissinger, H. Schmidbaur, *Z. Naturforsch. 48b*, 72 (1993); F. Scherbaum, B. Huber, G. Müller, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl. 27*, 1542 (1988).