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Gold(I) clustering at the triphenylphosphinimine nitrogen atom

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The nitrogen atoms of phosphinimines $R_3P{=}NH$ can function as clustering centers for (ligand)gold(I) units to give di- and trinuclear complex cations. Salts containing these novel cations are best prepared from the reactions of silylated phosphinimines $R_3P{=}NSiR'_3$ ($R = Ph$, $R' = Me$) with the corresponding aliquots of tris[(phosphine)gold]oxonium tetrafluoroborates $[(Ph_3P)Au]_3O^+BF_4^-$ or (phosphine)gold tetrafluoroborates $[(Ph_3P)Au]^+BF_4^-$. Attempts to use a Staudinger reaction of a μ-azido-bis[(phosphine)gold] tetrafluoroborate $[(Ph_3P)Au]_2N_3^+BF_4^-$ with triphenylphosphine as an alternative preparative pathway were unsuccessful and afforded only $[(Ph_3P)_2Au]BF_4$. All products have been characterized by analytical and spectroscopic data. The crystal structures of: (**1**) $\{Ph_3PN[Au(PPh_3)]_2\}^+BF_4^- \cdot THF$; (**2**) $\{Ph_3PN[Au(PPh_3)]_2\}_3^{2+}BF_4^- \cdot THF \cdot 2CH_2Cl_2$; and (**3**) $[(Ph_3P)Au]_2N_3^+BF_4^-$ have been determined. In all three compounds the gold atoms are in close intramolecular contacts indicating significant metal–metal interactions (auriophilicity). Accordingly, the angles at nitrogen are found to be smaller than expected for trigonal planar (**1**), (**3**) or tetrahedral (**2**) coordination. The dication of (**2**) is isoelectronic and isostructural with the triply aurated phosphonium cation $\{Ph_3PC[Au(PPh_3)]_3\}^+$. The isolobality concept relates the cation of compound (**1**) with standard aminophosphonium cations like $Ph_3PNH_2^+$ (H^+/LAu^+). There is no isolobal analogue for the dication in (**2**), however, and this result suggests that the cluster formation of gold contributes significantly to the stability of polyaurated species.

1. Introduction

Phosphine-imines of the type $R_3P{=}NR'$ were discovered at the beginning of this century (Staudinger & Meyer 1919), but only a few classes of organic derivatives were established during the following decades (Johnson 1993). It was only in the late 1960s that these *phosphorus–nitrogen ylides* were introduced as functional groups in organometallic chemistry (Schmidbaur & Wolfsberger 1967; Schmidbaur 1970) and as ligands in coordination chemistry (Schmidbaur & Jonas 1967*a*, 1968; Wolfsberger & Schmidbaur 1969; Schmidbaur *et al.* 1969). This development parallels the history of the classical *phosphorus–carbon ylides* (Johnson 1993) of the type $R_3P{=}CR'_2$, which found application in inorganic chemistry as late as 1960 (Schmidbaur 1975). Both areas of research have since expanded rapidly, and ylide compounds have been obtained with most metals and metalloids in the periodic table (Schmidbaur 1983; Dehnicke & Strähle 1989).

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One of the last triades of elements considered in this context were the coinage metals (Cu, Ag, Au), where information is particularly limited for silver (Schmidbaur *et al.* 1974). This is perhaps not surprising, since organosilver compounds are notoriously unstable, and even with the stabilizing influence of an α-onium centre, the neighbouring Ag—C bonds are quite labile (Noltes & van Koten 1982). By contrast, the chemistry of ylides $R_3P{=}CR'_2$ with gold has grown into a large field of new organometallic chemistry (Schmidbaur 1983), and the corresponding copper chemistry has finally seen at least some progress in recent years (Noltes & van Koten 1982).

The latter is also true with copper compounds of the phosphinimines $R_3P{=}NR'$, as published mainly by Dehnicke and his collaborators (Maurer *et al.* 1988; Meyer zu Köcker *et al.* 1994; Meyer zu Köcker & Dehnicke 1994). This work has provided a series of important standard prototypes, but some intriguing species with puzzling stoichiometries and structures (Meyer zu Köcker & Dehnicke 1994) have also been discovered.

Following some of our studies on ylide-based C-centred gold clusters (Schmidbaur *et al.* 1988), we have therefore turned now to the phosphinimine analogues, which have not previously been considered as coordination centres for gold. The surprising clustering phenomena observed at the nitrogen atoms of a series of quite diverse organic and inorganic compounds (Grohmann *et al.* 1990, 1991; Grohmann & Schmidbaur 1992; Zeller *et al.* 1991; Angermaier & Schmidbaur 1995*a*, *b*; Schmidbuar *et al.* 1991, 1992; Lange *et al.* 1994) suggested that at least trinuclear complexes with strong auriophilic stabilization (Schmidbaur 1990) should be available.

Another important aspect of the study presented here is the isoelectronic relationship between phosphinimines R_3PNH and silanoles R_3SiOH (Schmidbaur 1969, 1970). Silanolates of many metals of the type R_3SiOML_n (M = metal, L = ligand) have been prepared (Schmidbaur 1965; Schindler & Schmidbaur 1967), but gold silanolates with M = Au are still quite rare (Schmidbaur & Bergfeld 1966; Shiotani & Schmidbaur 1970; Bauer *et al.* 1995). The renewed interest in these compounds from the point of view of material science (chemical vapour deposition of gold, production of gold clusters and colloids in silicone matrices $[-R_2SiO-]_n$, etc.) is an incentive for work with gold-containing phosphinimines. Gold-containing phosphazane polymers $[-R_2PN-]_n$ are unprecedented systems (Dash *et al.* 1980).

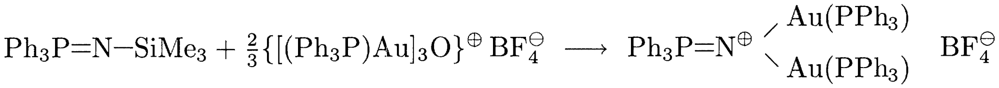
2. Preparative results

Mononuclear gold derivatives of phosphinimines of the type $R_3P{=}N{-}AuL_n$ were not the target of our initial studies, because it had been observed previously that primary auration of a given nitrogen-functional system is rapidly followed by formation of higher nuclearity clusters (auriophilicity) (Grohmann *et al.* 1990; Grohmann & Schmidbaur 1992; Zeller *et al.* 1991; Schmidbaur *et al.* 1991, 1992; Lange *et al.* 1994; Angermaier & Schmidbaur 1995*a*, *b*). The stoichiometry of the preparative experiments was therefore oriented towards di- and trinuclear compounds.

Phosphinimido complexes of metals are available via a very general route, which involves the use of free phosphinimines $R_3P = NH$ (Birkhofer *et al.* 1963; Birkhofer & Kim 1964; Birkhofer & Ritter 1965; Schmidbaur & Jonas 1967*c*) or a whole range of their metalation products $[R_3P = N]^- M^+$. M can represent a ligand-free metal (Li, Na) or an organometallic group (Me_3Si, Me_3Sn, etc.). These reagents are available (Schmidbaur & Jonas 1967*b*) through N-metalation of the phosphinimine $R_3P = NH$

employing the metal or its alkyl or hydride (e.g. Li, LiR, LiH) (Schmidbaur & Jonas 1968; Cristau *et al.* 1988, 1989; Johnson 1993), or from the (organo)metal azides and a phosphine in the Staudinger reaction (Schmidbaur & Wolfsberger 1967; Johnson 1993).

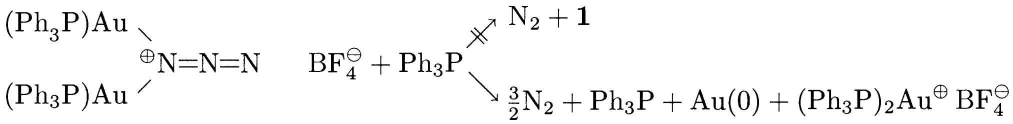
For the preparation of the gold complexes, the silyl-phosphinimines are the most convenient starting materials. The reaction of *N*-trimethylsilyl-triphenylphosphinimine (Birkhofer *et al.* 1963) with tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate (Nesmeyanov *et al.* 1980) in the presence of excess sodium tetrafluoroborate in dichloromethane gives high yields (89%) of the expected dinuclear phosphinimonium salt **1** (equation (2.1)). The solid decomposes at 185–189 °C.



$$\mathrm{Ph_3P{=}N{-}SiMe_3} + \tfrac{2}{3}\{[(\mathrm{Ph_3P})\mathrm{Au}]_3\mathrm{O}\}^{\oplus}\,\mathrm{BF}_4^{\ominus} \longrightarrow \mathrm{Ph_3P{=}N}^{\oplus}\begin{array}{l}\diagup\ \mathrm{Au(PPh_3)}\\ \diagdown\ \mathrm{Au(PPh_3)}\end{array}\quad \mathrm{BF}_4^{\ominus}$$

1 (2.1)

An alternative synthesis for compound **1** could start from a corresponding dinuclear azide complex $\{[(\mathrm{Ph_3P})\mathrm{Au}]_2\mathrm{N}_3\}^{+}\mathrm{X}^{-}$, with $\mathrm{X} = \mathrm{BF}_4^{-}$ (**3**) for an anion match with the specific example **1**, as a substrate for a Staudinger reaction with triphenylphosphine. Such an azido-bridged complex is available in the literature (Uson *et al.* 1976), but its characterization was not comprehensive. The compound has therefore been prepared, some complementary spectroscopic data collected, and its crystal structure determined by single crystal X-ray diffraction (below and experimental part). The complex was then reacted with triphenylphosphine in toluene. As the temperature was increased towards reflux, effervescence was observed, and the decomposition of $(\mathrm{Ph_3PAu})_2\mathrm{N}_3^{+}\mathrm{BF}_4^{-}$ became evident from the formation of insoluble colloidal gold metal. Upon cooling of the reaction mixture to room temperature, a colourless precipitate was formed, which was identified spectroscopically as $(\mathrm{Ph_3P})_2\mathrm{Au}^{+}\mathrm{BF}_4^{-}$. The solution was found to contain only triphenylphosphine. This result shows that the employed azido complex is unsuitable for a Staudinger reaction, since its thermal treatment in the presence of excess triphenylphosphine results in the formation of gold metal, $(\mathrm{Ph_3P})_2\mathrm{Au}^{+}\mathrm{BF}_4^{-}$ and nitrogen (equation (2.2)).

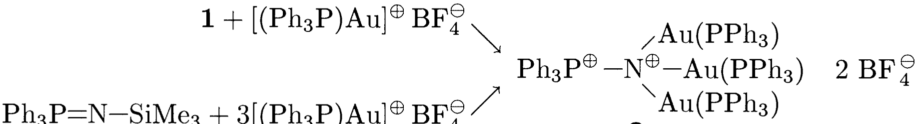


$$\begin{array}{l}(\mathrm{Ph_3P})\mathrm{Au}\ \diagdown\\ \qquad\qquad\ {}^{\oplus}\mathrm{N{=}N{=}N}\\ (\mathrm{Ph_3P})\mathrm{Au}\ \diagup\end{array}\quad \mathrm{BF}_4^{\ominus} + \mathrm{Ph_3P}\begin{array}{l}\nearrow\!\!\!\!\!\!\times\ \mathrm{N_2} + \mathbf{1}\\ \\ \searrow\ \tfrac{3}{2}\mathrm{N_2} + \mathrm{Ph_3P} + \mathrm{Au(0)} + (\mathrm{Ph_3P})_2\mathrm{Au}^{\oplus}\,\mathrm{BF}_4^{\ominus}\end{array}$$

3 (2.2)

Compound **1** from the reaction according to equation (2.1) has been identified by its elemental analysis and by its mass spectra. Fast atom bombardement spectra (4-nitrobenzyl alcohol matrix) showed the parent peak of the cation $\{\mathrm{Ph_3PN[Au(PPh_3)]_2}\}^{+}$ (m/z = 1194, 100%), and fragments $[\mathrm{Ph_3PNAuPPh_3}]^{+}$, $[\mathrm{Ph_3PAu}]^{+}$, and $[\mathrm{Ph_3PN}]^{+}$. The presence of the $[\mathrm{BF_4}]^{-}$ anion was confirmed by its IR absorption bands. Colourless single crystals of the product with one molecule of tetrahydrofuran per formula unit could be grown from a mixed solvent (tetrahydrofuran/toluene/hexane—5:1:10 [vol]). Compound **1** is freely soluble in di- and trichloromethane. The ^{31}P NMR spectra [$\{^1\mathrm{H}\}$, 25 °C] of these solutions show two singlet resonances in the intensity ratio 2:1, and the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ and ^{1}H NMR spectra have two sets of phenyl resonances (experimental part).

The dinuclear compound **1** can be aurated further at the nitrogen atom by reaction with one equivalent of (triphenylphosphine)gold(I) tetrafluoroborate in tetrahydrofuran. An excess of $NaBF_4$ should be present in the reaction mixture. A trinuclear complex (**2**) is obtained in 68% yield. The same product is generated in a direct reaction of N-trimethylsilyl-triphenylphosphinimine with three equivalents of $[(Ph_3P)Au]BF_4$ and excess $NaBF_4$, without isolation of the dinuclear intermediate. This direct route affords a 62% yield of colourless crystals, which decompose at 176–180 °C.



$$\mathbf{1} + [(\mathrm{Ph_3P})\mathrm{Au}]^{\oplus}\,\mathrm{BF_4^{\ominus}} \searrow \qquad (2.3)$$

$$\mathrm{Ph_3P^{\oplus}{-}N^{\oplus}}\begin{array}{l}\diagup\,\mathrm{Au(PPh_3)}\\ -\mathrm{Au(PPh_3)}\\ \diagdown\,\mathrm{Au(PPh_3)}\end{array}\quad 2\,\mathrm{BF_4^{\ominus}}$$

$$\mathrm{Ph_3P{=}N{-}SiMe_3} + 3[(\mathrm{Ph_3P})\mathrm{Au}]^{\oplus}\,\mathrm{BF_4^{\ominus}} \nearrow \qquad (2.4)$$

2

Compound (**2**) was identified by its elemental analysis and its mass spectra. Cation field desorption experiments showed the dication at $m/z = 826$ (100%), but also the dication associated with one tetrafluoroborate anion ($m/z = 1739$, 16%), together with other fragments as observed for **1** (above).

Solutions in di- or trichloromethane showed two ^{31}P NMR singlet resonances in the intensity ratio 1:3, and two sets of phenyl resonances in the ^{13}C and ^{1}H spectra. Single crystals could be grown from a mixture of dichloromethane/tetrahydrofuran/toluene = 5:1:1 [vol].

Further auration of compound **2** by $[(Ph_3P)Au]BF_4$ to give clusters of higher nuclearity appears to be possible according to the results of preliminary experiments, but no final details are available as yet.

3. Structural results

(*a*) *The structure of the μ-azido compound* **3**

For the μ-azido complex $[(Ph_3P)Au]_2N_3^+BF_4^-$ a structure with a (1, 1)-coordination of the azide anion has been proposed in earlier studies (Uson *et al.* 1976), and this configuration has now been confirmed in the present work. Colourless crystals of the compounds could be grown from dichloromethane/hexane. The crystals are monoclinic, space group $C2/c$, with four formula units in the unit cell (table 1). The most interesting structural feature of the cation of compound **3** is a crystallographically imposed linearity of the azido group, with a two-fold axis passing through the three nitrogen atoms. The two symmetry-related gold atoms have a distance of $Au \cdots Au' = 3.428(1)$ Å, and form an angle Au—N1—Au′ of 112.6(5)° at nitrogen (figure 1). By symmetry, the configuration of this nitrogen atom is planar, which would suggest an Au—N—Au′ angle of 120°. The observed angle of 112.6(5) is thus smaller than this reference value, and the distortion can be attributed to weak $Au \cdots Au'$ attraction. The coordination of the gold atoms is almost linear (P—Au—N1 175.8(3)°), with Au—N and Au—P distances in the expected range. In the lattice the cations are packed in strings parallel to the z-axis, as shown in figure 2. No discrete cation–anion interactions are observed.

(*b*) *The structure of the dinuclear complex* **1** · THF

Crystals of the tetrahydrofuran solvate **1** · THF are triclinic, space group P$\bar{1}$, with two formula units in the unit cell (table 1). The lattice consists of independent

Table 1. *Crystal data, data collection, structure solution and refinement for compounds* **1**, **2** *and* **3**. *DM denotes direct methods.*

	1 · THF	**2** · THF · **2** CH_2Cl_2	**3**
formula	$C_{58}H_{53}NOP_3Au_2BF_4$	$C_{78}H_{72}NOP_4Au_3B_2F_8Cl_4$	$C_{36}H_{30}N_3P_2Au_2BF_4$
M_r	1353.74	2069.67	1047.35
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ [No. 2]	$P2_1/n$ [No. 14]	$C2/c$ [No. 15]
a (Å)	8.886(1)	20.229(2)	18.420(2)
b (Å)	14.630(2)	16.413(2)	17.437(2)
c (Å)	20.531(3)	23.705(2)	12.552(2)
α (°)	99.05(1)	90	90
β (°)	94.20(1)	105.00(1)	118.08(1)
γ (°)	101.67(1)	90	90
V (Å^3)	2565.8	7643.7	3557.0
ρ_{calc} (g cm^{-3})	1.752	1.970	1.877
Z	2	4	4
$F(000)$ (e)	1320	4324	1984
$\mu(Mo-K_\alpha)$ (cm^{-1})	58.7	79.2	83.46
absorption correct.	empirical	empirical	empirical
$T_{\min}/T_{\max}$ (%)	72.91/99.97	54.23/99.90	77.14/99.91
T (°C)	−62	−62	−62
diffractometer	Enraf Nonius CAD4		
radiation	Mo–K_α	Mo–K_α	Mo–K_α
$\lambda(Mo-K_\alpha)$	0.71069, graphite monochromator		
scan mode	ω	$\omega-\theta$	ω
hkl range	$\pm 11, \pm 18, +26$	$\pm 24, +20, +27$	$\pm 20, +22, +15$
$\sin(\theta/\lambda)_{\max}$ (Å^{-1})	0.64	0.62	0.66
measured refl.	11 160	15 832	4520
unique refl.	10 212	12 965	3676
observed refl.	8757	10 026	2856
$F_0 \geqslant$	$4\sigma(F_0)$	$4\sigma(F_0)$	$4\sigma(F_0)$
refined parameters	606	701	221
structure solution	DM	DM	DM
H atoms (found/calcd.)	0/45	0/60	0/30
R^{a}	0.0299	0.0531	0.0358
$R_{\mathrm{w}}^{\mathrm{b}}$	0.0333	0.0571	0.0376
(shift/error)$_{\max}$	0.001	0.001	0.001
ρ_{fin}(max / min) (eÅ^{-3})	$+1.86/-1.46^{\mathrm{c}}$	$+2.21/-1.54^{\mathrm{c}}$	$+1.18/-1.19^{\mathrm{c}}$

[a] $R = \Sigma(\|F_0\| - \|F_c\|)/\Sigma|F_0|$.

[b] $R_{\mathrm{w}} = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2}$. $w = 1/\sigma^2(F_0)$.

[c] Residual electron densities located at Au atoms (**1**, **3**) and Cl atoms (**2**), respectively.

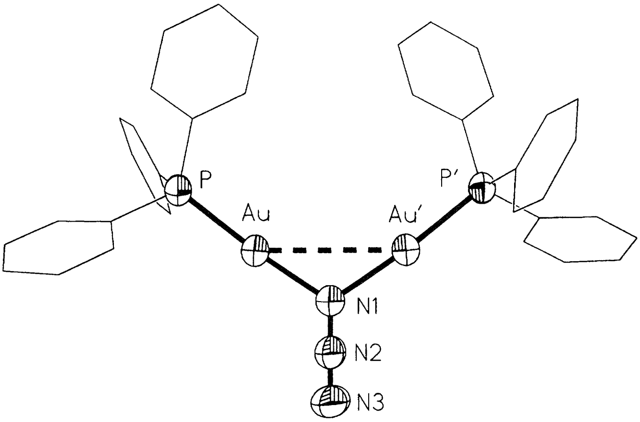


Figure 1. Molecular structure of the cation of compound **3** with atomic numbering (phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au$\cdots$Au′ 3.428(1), Au—P 2.228(2), Au—N1 2.061(6), N1—N2 1.20(2), N2—N3 1.13(2); Au—N1—N2 123.7(3), Au—N1—Au′ 112.6(5), P—Au—N1 175.8(3).

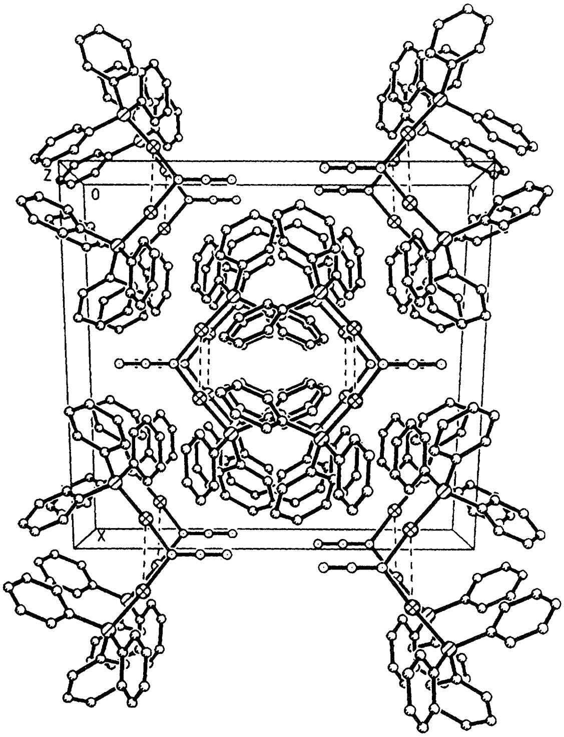


Figure 2. Crystal packing of the cation in the unit cell of **3** showing the strings of pairs of gold atoms parallel to the z-axis.

cations and anions with no sub-van-der-Waals interionic contacts, and of disordered uncoordinated tetrahydrofuran molecules. There is a stacking of the bulky cations parallel to the x-axis to give a string of pairs of gold atoms (figure 3).

The individual cation has no crystallographic symmetry (figure 4). The nitrogen atom is the centre of aggregation of the two gold atoms, which have a distance

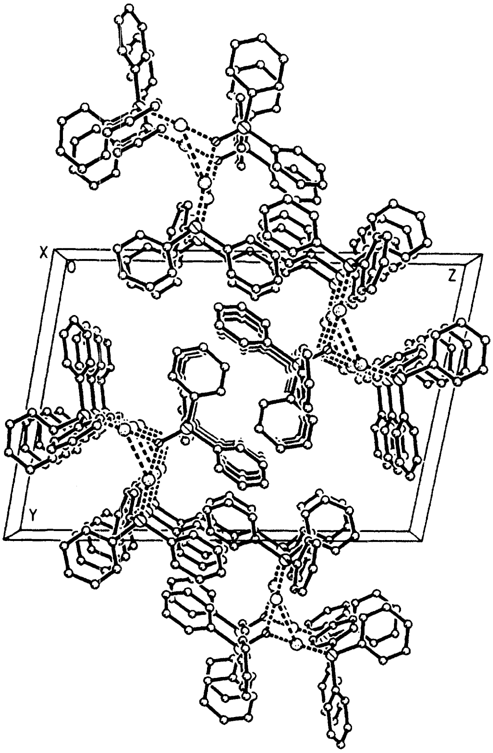


Figure 3. Crystal packing of the cation in the unit cell of **1** showing the strings of pairs of gold atoms parallel to the x-axis.

Au1—Au2 = 3.249(1) Å. The irregularly three-coordinate nitrogen atom is in an almost planar configuration with angles Au—N—Au2 107.2(2)°, Au1—N—P3 115.9(3)°, and Au2—N—P3 133.9(3)°. The sum of these angles is thus 357.0°. There is no obvious reason for such strong distortion from a more symmetrical array of the three ligands at nitrogen, and therefore crystal packing may be the most likely origin of the phenomenon. Energy profiles of the distortion of the geometry at three-coordinate nitrogen with third-row atoms (like silicon or phosphorus) are known (Mitzel *et al.* 1993, 1994*a*, *b*) to be very flat, and therefore the structure found in the cation of **1** can arise even from minor intermolecular forces. The Au—N—Au angle compression is of course readily ascribed to auriophilicity, but the interpretation of the difference of the two Au—N—P angles is less straightforward. The tilting of the P—N connection line away from the possible two-fold axis (or mirror plane) is quite severe and certainly not caused by intracationic phenyl repulsion (figure 3).

The P—N distance of 1.599(5) Å is surprisingly short and represents a P—N bond with a high bond order, probably close to that in free phosphinimines with two-coordinate nitrogen. The reference value in $Me_3SiNPPh_3$ is P=N 1.542(2) Å (Weller *et al.* 1995). This result suggests a formulation as drawn in equation (2.1), with a P=N double bond, and indicates that the bonding characteristics of the phosphinimine function are not grossly changed by double auration.

The coordination at the two gold atoms is linear, and the Au—P and Au—N distances are normal. It should be noted, however, that the structure of complex **1** and that of the azido complex (above) **3** are the first compounds to feature two gold atoms at planar nitrogen centers.

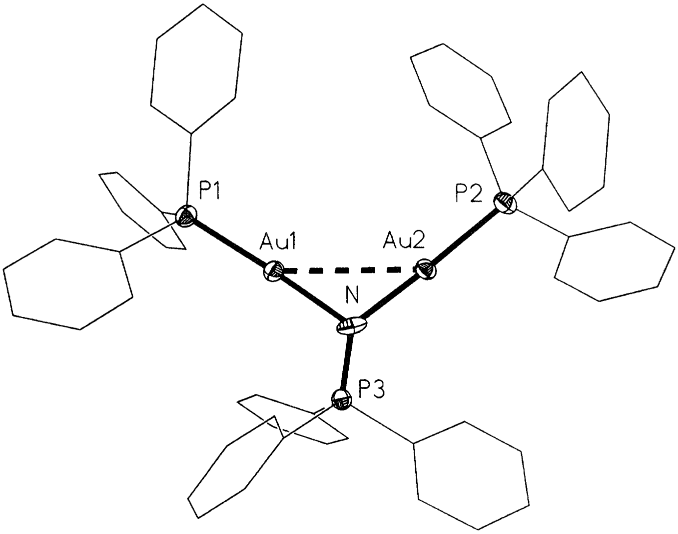


Figure 4. The molecular structure of the cation of compound **1** with atomic numbering (phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1 ··· Au2 3.249(1), Au1—P1 2.233(2), Au1—N 2.041(5), Au2—P2 2.234(2), Au2—N 1.994(5), P3—N 1.599(5); P1—Au1—N 176.6(1), P2—Au2—N 176.9(2), Au1—N—Au2 107.2(2), Au1—N—P3 115.9(3), Au2—N—P3 133.9(3).

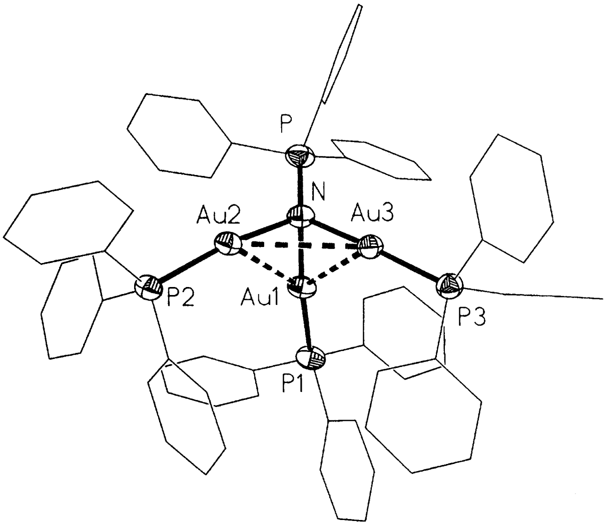


Figure 5. The molecular structure of the dication of compound **2** with atomic numbering (phenyl hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au1 ··· Au2 3.043(1), Au1 ··· Au3 2.958(1), Au2 ··· Au3 3.294(1), Au1—N 2.09(1), Au2—N 2.085(9), Au3—N 2.083(8), P—N 1.62(1), Au1—P1 2.236(4), Au2—P2 2.235(3), Au3—P3 2.238(3); Au1—N—Au2 93.5(4), Au1—N—Au3 90.2(4), Au2—N—Au3 104.4(4), P—N—Au1 118.0(5), P—N—Au2 119.9(5), P—N—Au3 123.5(5), N—Au1—P1 175.1(2), N—Au2—P2 169.7(3), N—Au3—P3 175.6(3).

(*c*) *The structure of the trinuclear complex* **2**

The dication of compound **2** is isoelectronic with the cationic triply aurated phosphonium mono-cation $Ph_3P{-}C(AuPPh_3)_3^+$. The two structures (Schmidbaur *et al.*

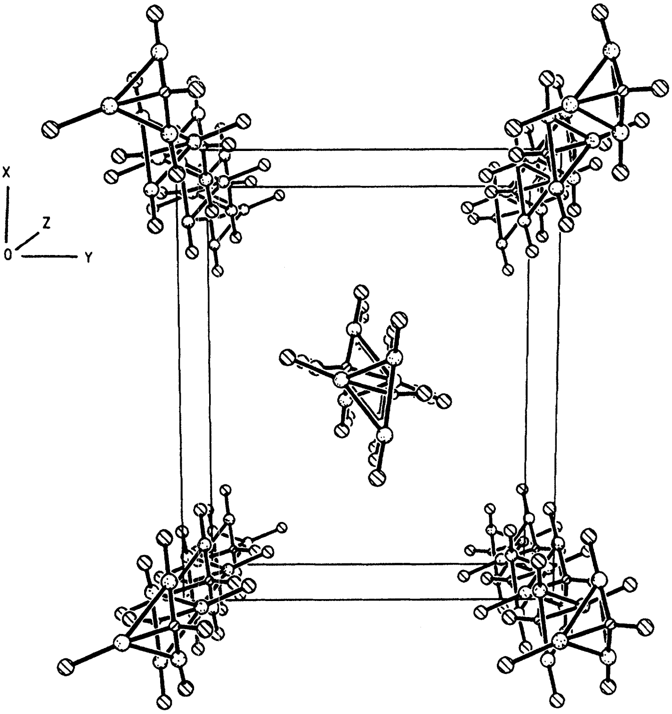


Figure 6. Crystal packing of the dicationic core in the unit cell of compound **2** parallel to the z-axis (phenyl rings omitted for clarity).

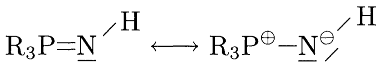
1988) are very similar in virtually all of their dimensions, as expected for such closely related species. Compound **2** crystallizes together with one molecule of tetrahydrofuran and two molecules of methylenechloride in the monoclinic space group $P2_1/n$ (table 1). The dication, which has no crystallographically imposed symmetry, shows no discrete contacts to the anions and the solvent molecules. The three gold atoms are roughly equidistant from the common nitrogen atom. Pairwise they form angles with the central nitrogen atom which are significantly smaller than the tetrahedral angle of 109° (figure 5), indicating again $\mathrm{Au}\cdots\mathrm{Au}$ attraction, with $\mathrm{Au}\cdots\mathrm{Au}$ distances of 3.043(1), 2.958(1) and 3.294(1) Å. Accordingly, the P–N–Au angles are larger than 109°. The N–Au–P axes deviate only slightly from linearity. The surprisingly short P—N distance in the dication of **2** of 1.62(1) Å is comparable to the corresponding distance in the dinuclear complex **1** and to the P—C distance in the triply aurated phosphonium mono-cation $\mathrm{Ph_3P{-}C(AuPPh_3)_3^+}$ (Schmidbaur *et al.* 1988). All other bond lengths and angles are in the expected ranges. The stacking of the dications in the unit cell leads to strings of $\mathrm{Au_3}$ triangles parallel to the z-axis (figure 6).

4. Gold clustering at nitrogen and the isolobal principle

The isolobal principle (Hoffmann 1982) puts the proton $[\mathrm{H}]^+$ and carbenium and silicenium cations, $[\mathrm{R_3C}]^+/[\mathrm{R_3Si}]^+$, into the same category with donor-complexed gold(I) cations $[\mathrm{LAu}]^+$. The common characteristics of the frontier orbitals suggest similar bonding relations with a wide variety of partners. Like the concept of isoelectronic and isosteric compounds (Schmidbaur 1969, 1970), this isolobal relation turned out to be a very useful heuristic principle, and this is particularly true for the rapidly developing chemistry of univalent gold.

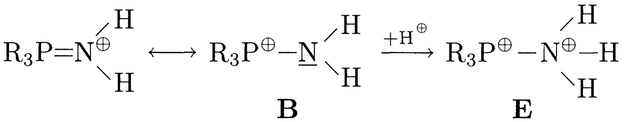
With isolobality as a guideline, unusual stoichiometries and structures as for example in $[(LAu)_5C]^+$ or $[(LAu)_5N]^{2+}$ could be rationalized (Grohmann *et al.* 1990; Scherbaum *et al.* 1989) and put into perspective as related to the existing $[CH_5]^+$ and the non-existing $[NH_5]^{2+}$ species.

The present compounds therefore are of considerable interest regarding their protic, alkyl or silyl analogues as derived from phosphinimines. Phosphinimines (**A**) which have become mono-protonated are well established (Johnson 1993) and can be classified as aminophosphonium cations (**B**). Homologous alkylated, arylated or silylated phosphinimines (**C**, **D**) are equally well documented (Cristau *et al.* 1989). It should be noted, however, that no multiple-protonation (-alkylation, -arylation or -silylation) has been observed, which would produce dications (**E**, **F**, **G**) or species with even higher charges to be classified either as P-analogues of doubly protonated (alkylated...) hydrazines, $[R_3P{-}NR_3]^{2+}$ versus $[H_3N{-}NH_3]^{2+}$, or as (tertiary) amine complexes of R_3P-dications, i.e. $[R_3P]^{2+} + NH_3/NR_3$. (Such an interaction with tri(silyl)amines is ruled out, however, by the exceedingly low donor properties of silylated amines (Mitzel *et al.* 1992, 1995).) The non-existence of the dications of this type is to be attributed generally to the destabilizing effect of neighbouring positive charges (localized at P and N).



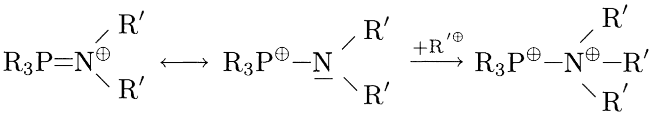
$$R_3P{=}\underline{N}{-}H \longleftrightarrow R_3P^{\oplus}{-}\underline{N}^{\ominus}{-}H$$

A



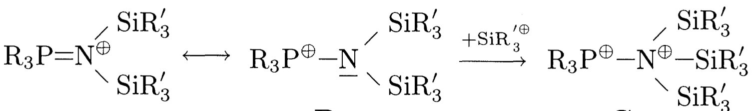
$$R_3P{=}N^{\oplus}H_2 \longleftrightarrow R_3P^{\oplus}{-}\underline{N}H_2 \xrightarrow{+H^{\oplus}} R_3P^{\oplus}{-}N^{\oplus}H_3$$

B **E**



$$R_3P{=}N^{\oplus}R'_2 \longleftrightarrow R_3P^{\oplus}{-}\underline{N}R'_2 \xrightarrow{+R'^{\oplus}} R_3P^{\oplus}{-}N^{\oplus}R'_3$$

C **F**



$$R_3P{=}N^{\oplus}(SiR'_3)_2 \longleftrightarrow R_3P^{\oplus}{-}\underline{N}(SiR'_3)_2 \xrightarrow{+SiR'^{\oplus}_3} R_3P^{\oplus}{-}N^{\oplus}(SiR'_3)_3$$

D **G**

Compounds **1** and **2** are isolobal analogues of mono- and bis-protonated phosphinimines, respectively. Therefore, while the former (**1**) is just a H/R/AuL congener, the latter (**2**) is novel in that none of the isolobal species have ever been detected. As in previous H/R/LAu isolobal cases, this result is proof that the clustering of $[LAu]^+$ units at a given metalloid centre is going well beyond the limits observed for protonation or alkylation (silylation) (Bommers *et al.* 1995). Clearly the auriophilicity phenomenon is not only stabilizing the cluster units, but also reduces the repulsive Coulomb forces at a given coordination centre. This observation is an incentive to probe other classes of low-coordinate nitrogen compounds, such as carbodiimines or Schiff-bases, as nucleation centres for gold clustering.

5. Experimental part

(*a*) *General*

All experiments were carried out in an atmosphere of dry purified nitrogen. Glassware and solvents were dried and filled/saturated with nitrogen. All apparatus was protected against directly incandescent light. NMR spectrometers: Jeol GX 400 and 270; TMS as an internal standard (^{1}H, ^{13}C), aqueous phosphoric acid as an external standard (^{31}P); spectra were recorded at ambient temperature in deuterated solvents. Mass spectrometer: Varian MAT 90, with FAB and FD sources. Microanalyses: in-house elemental analysers (by combustion and atomic absorption techniques). Chemicals: $Ph_3P{=}N{-}SiMe_3$ (Birkhofer *et al.* 1963), $[(Ph_3P)Au]^+BF_4^-$ (Puddephatt 1987), Ph_3PAuN_3 (Ziolo *et al.* 1972) and $[(Ph_3P)Au]_3O^+BF_4^-$ (Nesmeyanov 1980) were prepared following published procedures; all other compounds were commercially available.

(*b*) *Bis[(triphenylphosphine)gold]amino-triphenylphosphonium tetrafluoroborate* (**1**)

$Ph_3P{=}N{-}SiMe_3$ (0.23 g, 0.66 mmol) was reacted with $[(Ph_3P)Au]_3O^+BF_4^-$ (0.65 g, 0.44 mmol) at ambient temperature in a slurry of excess $NaBF_4$ (1.0 g) in dichloromethane (45 mL) for 2 d. The reaction mixture was filtered and the product precipitated by slow addition of pentane (15 mL) to the filtrate. A colourless solid was obtained in 89% yield, m.p. 185–189 °C with decomposition.

Analysis. Found C 50.61, H 3.54, P 7.25, F 5.93, N 1.09 and Au 30.74. $C_{54}H_{45}Au_2BF_4NP_3$ (1281.62) requires C 50.90, H 3.55, P 6.80, F 5.83, N 1.16, Au 30.41. MS (FAB, $4{-}NO_2C_6H_4CH_2OH$): m/z 1194, 100%, M^+; 735, 77%, $Ph_3PNAuPPh_3^+$; 459, 67%, Ph_3PAu^+; 276, 16%, Ph_3PN^+. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 31.59 (s, 2P, PAu); 39.18 (s, 1P, PN). ^{1}H NMR ($CDCl_3$): δ 7.32 (m), 7.51 (m). ^{13}C {^{1}H} NMR ($CDCl_3$), δ [ppm]/J[Hz]: 128.8(61.1), 133.8(13.8), 129.3(11.6), 132.0(2.2) [C ipso, ortho, meta, and para for PhPAu], 134.1(98.6), 132.1(9.9), 128.8(12.1), 132.4(2.8) [for PhPN], respectively.

(*c*) *μ-Azido-bis[(triphenylphosphine)gold] tetrafluoroborate* (**3**)

To a cooled solution (−78 °C) of Ph_3PAuN_3 (0.165 g, 0.33 mmol) in THF (5 mL) was added a THF solution (5 mL) of $Ph_3PAu^+BF_4^-$ (generated in situ by the reaction of Ph_3PAuCl (0.163 g, 0.33 mmol) and $AgBF_4$ (0.065 g, 0.33 mmol)). The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The precipitate was isolated by filtration and dissolved in CH_2Cl_2 (4 mL). Slow diffusion of hexane into the solution resulted in the formation of a crystalline product in 55% yield, m.p. 140 °C with decomposition.

Analysis. Found C 41.17, H 2.95, N 4.12, Au 37.90, F 7.36. $C_{36}H_{30}Au_2BF_4N_3P_2$ (1047.35) requires C 41.29, H 2.89, N 4.01, Au 37.61, F 7.26. $^{31}P\ \{^1H\}$ NMR ($CDCl_3$): δ 30.2 (s). ^1H NMR ($CDCl_3$): 7.40–7.65 (m). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ [ppm]/J[Hz]: 126.6 (66.1), 129.8 (12.7), 132.9 (2.8), 133.9 (13.2) (C ipso, meta, para, and ortho for Ph_3PAu, respectively). IR ($CHCl_3$ solution): ν (N_3) 2137 cm^{-1}.

(*d*) *Tris[(triphenylphosphine)gold]ammonio-triphenylphosphonium bis(tetrafluoroborate)* (**2**)

(a) Compound **1** (0.28 g, 0.22 mmol) was dissolved in tetrahydrofuran (25 mL, containing ca. 1.0 g of $NaBF_4$), and reacted with a solution of 0.22 mmol of $[(Ph_3P)Au]BF_4$ in the same solvent (freshly prepared from the chloride and $AgBF_4$) at 0 °C. After 1 h the reaction mixture was allowed to warm to room temperature and stirred for 2 d at 25 °C. After filtration the clear solution was diluted with hexane to precipitate the product. Colourless crystals were obtained in 68% yield, m.p. 176–180 °C with decomposition.

(b) $Ph_3P{=}N{-}SiMe_3$ (0.19 g, 0.55 mmol) was dissolved in a slurry of $NaBF_4$ (1.0 g in 45 mL) in tetrahydrofuran and reacted with three equivalents of $[(Ph_3P)Au]BF_4$ at 0 °C for 3 h. The mixture was filtered and the product precipitated from the filtrate by addition of hexane (62% yield). MS (cation FD): m/z 1739, 16%, $[M\,BF_4]^+$; 1194, 37%, M^+ of **1**; 826, 100%, M^{2+}; 735, 11%, $Ph_3PNAuPPh_3^+$. $^{31}P\ \{^1H\}$ NMR ($CDCl_3$): δ 28.93 (s, 3P, PAu); 57.42 (s, 1P, PN). ^1H NMR ($CDCl_3$): 7.11 (m), 7.30 (m), 7.57 (m), 7.91 (m). $^{13}C\ \{^1H\}$ NMR ($CDCl_3$), δ/J: 126.2(65.3), 133.2(13.8), 129.6(12.0), 132.9(2.8) (C ipso, ortho, meta, and para for CPAu), 128.6(99.3), 131.9(11.0), 130.0(12.0), 135.0(2.8) (for CPN), respectively.

6. Crystal structure determinations

Suitable crystals of **1**, **2** and **3** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection. Diffraction intensities were corrected for decay, Lp, and absorption effects. The THF molecule in the lattice of compound **1** was disordered, with the oxygen position not unambigously identified. The solvent molecule was treated isotropically, and its H atoms were neglected. The same is true for the solvent THF and CH_2Cl_2 molecules in the lattice of compound **2**. The phenyl rings of the $AuPPh_3$ units in **2** were treated as rigid groups, as were the two BF_4 anions. The thermal motion of all other nonhydrogen atoms was treated anisotropically. Phenyl hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom with fixed istotropic contributions ($U_{\mathrm{iso(fix)}} = 0.08$ Å^2). Structures were solved by direct methods and refined by full-matrix least-squares calculations (Sheldrick 1989). Further information on crystal data, data collection, structure solution and refinement are given in table 1. Important interatomic distances and angles are summarized in the corresponding figure captions. Anisotropic thermal parameters, tables of interatomic distances and angles, and tables of observed and calculated structure factors have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting the CDS number.

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