Tris(dimethylamino)phosphane as a New Ligand in Gold(I) Chemistry: Synthesis and Crystal Structures of $[(Me_2N)_3P]AuCl$, $\{[(Me_2N)_3PAu]_3O\}^+BF_4^-$, $\{[(Me_2N)_3PAu]_3NP(NMe_2)_3\}^{2+}\ \{BF_4^-\}_2$ and the Precursor Molecule $(Me_2N)_3PNSiMe_3$

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[Tris(dimethylamino)phosphane]gold(I) chloride, μ_3-tris-{[tris(dimethylamino)phosphane]gold(I)}oxonium tetrafluoroborate, {μ_3-tris(dimethylamino)phosphaneimidotris[tris(dimethylamino)phosphane]gold(I)}(2+) bis(tetrafluoroborate) and *N*-trimethylsilyltris(dimethylamino)phosphaneimine were prepared using modifications of established procedures. Their structures were determined in single-crystal X-ray diffraction studies. The ligand $(Me_2N)_3P$, here introduced into gold(I) chemistry for the first time, lends high stability to these compounds through efficient steric shielding of the reaction sites and through a balanced electronic substituent effect. The structural details of the $(Me_2N)_3P$ groups are of current interest because of the unusual nonequivalent configuration of the nitrogen atoms in the dimethylamino groups. This behaviour has been observed for most of the $(Me_2N)_3P$ units in the compounds studied in this work.

Tris(dimethylamino)phosphane $(Me_2N)_3P$ is a versatile ligand in coordination chemistry. Its steric requirement is similar to that of triisopropylphosphane $(Me_2CH)_3P$, but the nitrogen compound appears to be much more flexible due to the additional freedom of nitrogen inversion and various degrees of pyramidalization[1]. In addition, the three amino groups offer complementary donor functions and induce a different ligand polarity, including opportunities for hydrogen bonding.

To date, these ligand properties have not been investigated and exploited in gold(I) chemistry. Following work on gold(I) complexes of phosphatriazaadamantane[2], a cage phosphane which has three nitrogen donor functions in β-position to phosphorus, we initiated a study of gold(I) chemistry with the $(Me_2N)_3P$ ligand. The triisopropylphosphane analogues were the subject of two earlier papers[3].

There is also current interest in the conformation of the $(Me_2N)_3P$ unit in the free molecule and its derivatives[1]. Very unexpectedly, this unit has a preference for a low-symmetry (C_s) ground state with grossly nonequivalent dimethylamino groups. Since gold(I) complexes generally provide a nonforcing coordination environment for their ligands, due to the low coordination number and linear geometry at the Au(I) centers, the 1:1 complexes of gold(I) salts in particular should allow the observation of a strain-free ligand structure. The oxonium and ammonium clusters derived therefrom are expected to be important reagents for the synthesis of more complex [tris(dimethylamino)phosphane]gold(I) complexes[4].

Results and Discussion

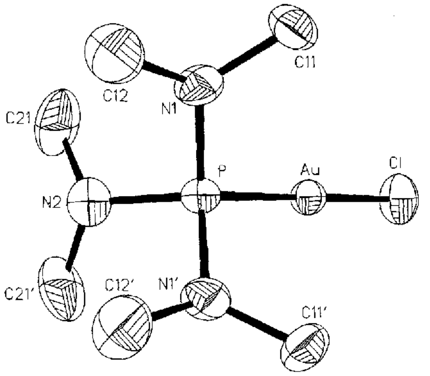
[Tris(dimethylamino)phosphane]gold(I) chloride (**1**) is readily prepared in quantitative yield from equimolar amounts of $(Me_2S)AuCl$[5] and $(Me_2N)_3P$ in tetrahydrofuran. The compound was identified by elemental analysis and mass spectrometry. The parent peak in the field desorption spectra ($CHCl_3$) appears at *m*/*z* = 395 (100%). The NMR spectra are consistent with the proposed formula (see the Experimental Section).

$$(Me_2S)AuCl + (Me_2N)_3P \xrightarrow[-Me_2S]{THF} \underset{\mathbf{1}}{[(Me_2N)_3P]AuCl} \qquad (1)$$

Colourless, orthorhombic crystals of **1**, space group *Pnma*, were grown from $CHCl_3$/hexane (1:1). The crystal structure consists of independent C_s-symmetric molecules without intermolecular Au···Au contacts. There are two equivalent dimethylamino groups (Figure 1) related by a crystallographic mirror plane including the Au, P and N2 positions. The sum of angles at these nitrogen atoms (N1, N1′) is 354.5°. For the third amino group the sum of angles at N2 is only 347.4°, indicating a much more pronounced pyramidal structure. Approximate local C_s symmetry has previously been found in the dicoordinated silver complex $\{[(Me_2N)_3P]_2Ag\}^+BPh_4^-$[6].

Because of the low resolution of the "light atom structure" in **1**, the data do not allow the detection of a shortening of the P–N1 bond [1.651(8) Å] (which involves the planarized sp^2-type nitrogen atom N1) as compared to the P–N2 bond (which involves the more pyramidal atom N2

Figure 1. Molecular structure of compound **1** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity); selected bond lengths (Å) and angles (°): Au–Cl 2.289(4), Au–P 2.222(3), P–N1 1.651(8), P–N2 1.66(1), P–Au–Cl 177.9(1)



of almost sp^3 type). Such an effect has also been observed for the free ligand $(Me_2N)_3P$[1]. The geometry at the gold atom is close to linear [177.9(1)°], and the Au–P and Au–Cl bond lengths are in the expected range.

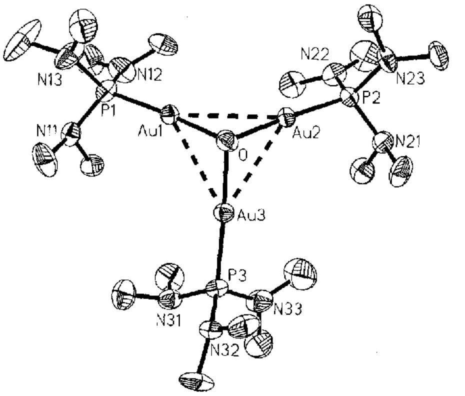
As reported earlier, (triisopropylphosphane)gold(I) chloride also crystallizes orthorhombically[3a], but in space group *Pnm*2$_1$, with only small differences in the cell parameters as compared with those of **1**. The molecular dimensions are very similar to those of $[(Me_2N)_3P]AuCl$ (**1**). The distances Au–P and Au–Cl and the angle P–Au–Cl of (triisopropylphosphane)gold(I) chloride [2.237(2), 2.285(3) Å and 178.4(2)°, respectively] deviate minutely from the corresponding parameters in **1**. There is also no short intermolecular Au···Au contact, obviously for steric reasons. The main difference between the structures of **1** and the isopropyl analogue are the magnitudes of the C–N–C angles compared to the C–C–C angles. The latter are close to the tetrahedral standard, whereas those in **1** are much larger, reaching almost 120° in a few cases. Probably these details are also responsible for the difference in the packing patterns.

$$[(Me_2N)_3P]AuCl \xrightarrow[\text{THF}]{Ag_2O/NaBF_4} \{[(Me_2N)_3PAu]_3O\}^+BF_4^- \quad (2)$$

2

The oxonium salt **2** is accessible following standard literature procedures for analogous compounds[7]. The net composition of the product was confirmed by elemental analysis, mass spectrometry and NMR spectroscopy (see the Experimental Section). According to a single-crystal X-ray diffraction study (colourless, monoclinic crystals from THF/hexane, space group *P*2$_1$/*n*, $Z = 4$), independent trinuclear cations and BF_4^- anions are present in the crystal structure, which contains no solvent molecules (Figure 2). The skeleton of the cations consists of a trigonal OAu_3 pyramid with the oxygen atom in the apical position. The cations have no crystallographically imposed symmetry, but deviations from threefold symmetry are not substantial. Thus the Au···Au distances at the base of the pyramid vary between 3.127(1) and 3.250(1) Å. The coordination geometry at all three gold atoms is close to linear. The conformation of the three $(Me_2N)_3P$ ligands in **2** is similar to that in compound **1**. Each $(Me_2N)_3P$ group contains two nearly planar nitrogen atoms with shorter P–N bonds and one more strongly pyramidal N atom (see Tables 1 and 2). This agreement of geometrical preferences for units within molecules with different electronic structure indicates that the conformational features are an intrinsic property of the $(Me_2N)_3P$ groups, as was further elaborated in a theoretical study[1]. All other bond lengths and angles are as expected.

Figure 2. Molecular structure of compound **2** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). The trinuclear monocation has no crystallographic symmetry; selected bond lengths (Å) and angles (°): Au1–Au2 3.250(1), Au1–Au3 3.127(1), Au2–Au3 3.152(1), Au1–O 2.024(7), Au2–O 2.031(7), Au3–O 2.047(7), Au1–P1 2.220(3), Au2–P2 2.220(2), Au3–P3 2.216(3), P1–Au1–O 175.9(2), P2–Au2–O 176.1(2), P3–Au3–O 176.6(2)



The isoelectronic complex $[(i\text{-}Pr_3P)Au]_3O^+BF_4^-$, where the isopropyl groups replace the dimethylamino units, is not isomorphous to compound **2** but crystallizes in the trigonal space group $R\bar{3}$. The Au–O–Au bond angles in its cations are 103.7(2)° as compared to an average of 102.7° in compound **2**. This leads to Au···Au' contacts of 3.193(1) Å, again close to the average in **2** (3.208 Å). The Au–O and Au–P distances and the O–Au–P angles [2.030(3), 2.228(2) Å and 176.4(2)°, respectively] show even smaller differences from the data of **2** [averages of 2.034, 2.218 Å and 176.2°]. The individual units of the $CHMe_2/NMe_2$ analogues are therefore very similar in structure and differ only in the packing of the molecules in the lattice, which is generally most sensitive to subtle changes in the geometric details and polarizability.

We have recently shown[8] that tris[(phosphane)gold]oxonium salts react with silylphosphaneimines of the type $R_3PNSiMe_3$ to give di- and trinuclear (phosphane)gold(I) phosphaneimido complexes. This reaction has now been probed with $(Me_2N)_3PNSiMe_3$ (**5**)[9] and the parent gold(I) complex **2** (above) in order to get access to the corresponding polynuclear species uniformly covered with $(Me_2N)_3P$ ligands in all positions.

$$2/3\ \{[(Me_2N)_3PAu]_3O\}^+BF_4^- + (Me_2N)_3PNSiMe_3 \xrightarrow[CH_2Cl_2]{NaBF_4} \{[(Me_2N)_3PAu]_2NP(NMe_2)_3\}^+BF_4^- \quad (3)$$

3

The product obtained from this reaction, in a molar ratio of 2:3 in the presence of an excess of $NaBF_4$, is a colourless, crystalline material (70% yield), readily identified as the dinuclear complex **3** by elemental analysis. The $^{31}P\{^1H\}$-NMR spectrum exhibits triplet and doublet resonances at $\delta = 57.1$ and $\delta = 114.2$, respectively, with an intensity ratio of 1:2 ($^3J_{PP} = 15.2$ Hz), and the field desorption mass spectra (CH_2Cl_2) show the parent peak of the monocation at m/z = 897 (56%). Unfortunately, only twinned crystals of this compound could be grown, but the structure is expected to be similar to that of the analogous PPh_3 complex, the structure of which has recently been determined[8].

$$\{[(Me_2N)_3PAu]_3O\}^+BF_4^- + (Me_2N)_3PNSiMe_3 \xrightarrow[CH_2Cl_2]{NaBF_4} \{[(Me_2N)_3PAu]_3NP(NMe_2)_3\}^{2+}\{BF_4^-\}_2 \quad (4)$$

4

The reaction of equimolar amounts of **2** and $(Me_2N)_3PNSiMe_3$ (**5**) leads to good yields (65%) of a stable, colourless, crystalline product, which was identified as the trinuclear complex **4** by standard analytical methods and X-ray crystallography. The $^{31}P\{^1H\}$-NMR spectrum shows a quartet at $\delta = 56.3$ and a doublet at $\delta = 103.9$ ($^3J_{PP} =$ 7.1 Hz) with an overall intensity ratio of 1:3. In the field desorption mass spectra (CH_2Cl_2) the peak of the dication is found at its half mass, i.e. m/z = 628.5. The elemental analysis is in good agreement with the proposed composition (see the Experimental Section).

Monoclinic crystals, space group $P2_1/n$, were grown by slow evaporation of the solvent from a solution of **4** in $CHCl_3$/hexane (1:1). The crystal structure was shown by X-ray crystallography to be built from independent trinuclear dications and BF_4^- counterions. The structure of the dication consists of a trigonal pyramid with three gold atoms at the base and the nitrogen atom in the apical position (Figure 3), closely resembling the core of the cation in compound **2**. The dication has no crystallographically imposed symmetry, but the arrangement of the heavy atoms approaches C_3 symmetry. Probably induced by the bulky $(Me_2N)_3P$ group at the central nitrogen atom, the Au–N–Au angles in **4** are smaller than the Au–O–Au angles in **2**, leading also to shorter Au···Au distances [3.034(1) to 3.153(1) Å]. The linear coordination at the gold atoms shows little change, but the Au–N bond lengths (2.09 Å on average) are longer than the Au–O bonds in **2**. The geometry of the $(Me_2N)_3P$ ligands bound to Au reflects the situation in compounds **1** and **2** (see Tables 1 and 2), each with one pyramidal and two planar nitrogen atoms. The conformation of the $(Me_2N)_3P$ unit in the phosphaneimido group of **4** is significantly different, however. All three dimethylamino groups appear to adopt virtually planar coordination geometries at their nitrogen atoms, with the sums of angles being 356.4°, 359.0° and 359.1° (Tables 1, 2). The P4–N bond [1.608(7) Å] is short, indicating a high bond order for the phosphaneimine function. The remaining three P4–N41 (N42, N43) bonds (average length 1.625 Å) provide an internal standard, allowing a direct comparison.

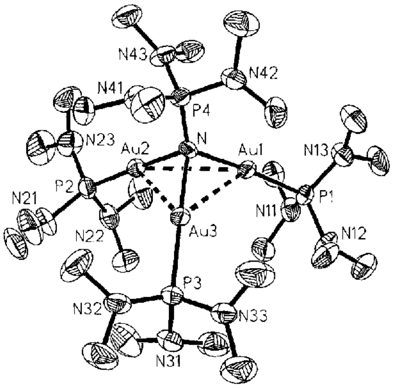


Figure 3. Molecular structure of compound **4** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity); the trinuclear dication has no crystallographically imposed symmetry; selected bond lengths (Å) and angles (°): Au1–Au2 3.153(1), Au1–Au3 3.102(1), Au2–Au3 3.034(1), Au1–N 2.075(6), Au2–N 2.101(7), Au3–N 2.093(6), Au1–P1 2.236(2), Au2–P2 2.231(2), Au3–P3 2.233(2), P4–N 1.608(7); P1–Au1–N 175.9(2), P2–Au2–N 177.6(2), P3–Au3–N 176.2(2)

Table 1. Sums of angles [°] at the nitrogen atoms of the dimethylamino groups of compounds **1**, **2**, **4** and **5**

Atom	**1**	**2**	**4**	**5**
N11 (N1)	354.5	340.1	341.0	358.8
N12 (N2)	347.4	355.2	354.4	358.2
N13 (N1', N3)	354.5	359.2	355.5	345.4
N21	–	339.2	359.2	–
N22	–	357.7	341.0	–
N23	–	358.6	355.7	–
N31	–	343.2	342.7	–
N32	–	352.3	359.4	–
N33	–	359.6	358.4	–
N41	–	–	356.4	–
N42	–	–	359.0	–
N43	–	–	359.1	–

Table 2. P–N bond lengths [Å] of compounds **1**, **2**, **4** and **5**

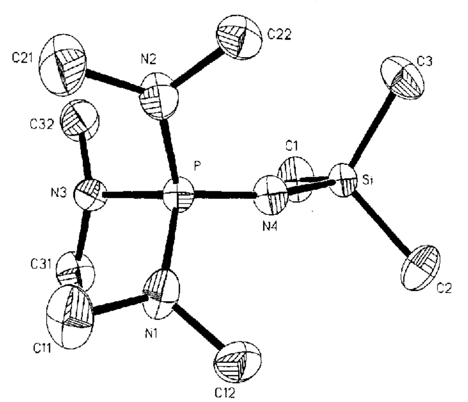
Atom	**1**	**2**	**4**	**5**
P1–N11 (N1)	1.65(1)	1.67(2)	1.67(1)	1.656(2)
P1–N12 (N2)	1.66(1)	1.65(2)	1.65(1)	1.653(2)
P1–N13 (N1', N3)	1.65(1)	1.63(2)	1.65(1)	1.670(2)
P2–N21	–	1.68(2)	1.62(1)	–
P2–N22	–	1.64(1)	1.68(2)	–
P2–N23	–	1.63(1)	1.63(2)	–
P3–N31	–	1.65(2)	1.67(2)	–
P3–N32	–	1.65(2)	1.63(1)	–
P3–N33	–	1.65(1)	1.63(1)	–
P4–N41	–	–	1.62(1)	–
P4–N42	–	–	1.62(2)	–
P4–N43	–	–	1.64(2)	–
P4–N	–	–	1.61(1)	1.514(2)

It is noteworthy that in the dication of compound **4** the neighbouring atoms P4 and N(central) both bear a positive formal charge, which could be expected to give rise to Coulombic repulsion. This is not borne out by the short P4–N distance and therefore the structure may be taken as evidence for efficient charge redistribution on the part of the amino substituents (at P4) and of the trinuclear cluster at N with its strongly electronegative gold atoms.

The $(Me_2N)_3P$ group including the phosphaneimine phosphorus atom P4 is in a staggered conformation relative to the NAu_3 unit, but the P4–N axis is significantly tilted away from the hypothetical threefold axis of the NAu_3 pyramid. There is no obvious reason for this distortion, and packing forces resulting from cation/anion interaction are the most likely origin. Figure 3 shows the efficient shielding of the NAu_3 core by four $(Me_2N)_3P$ groups; this does not constitute severe crowding, however. The high flexibility of the twelve Me_2N groups (through P–N rotation and variable N-pyramidalization) clearly provides plenty of opportunities for geometrical adaptation to a changing environment.

For further comparison the crystal structure of the precursor molecule $(Me_2N)_3PNSiMe_3$ (**5**) has also been determined. A colourless crystal of **5** was grown from the melt in situ on the diffractometer. It belongs to the triclinic system, space group $P\bar{1}$. Despite the fact that the molecule has no crystallographically imposed symmetry, the conformation of the $(Me_2N)_3P$ unit quite closely approaches local C_s symmetry. The P–N4 bond [1.514(2) Å] is extremely short compared for example to the triphenyl analogue $Ph_3PNSiMe_3$ [1.542(2) Å][10] and the non-silylated $tBu_3P{=}NH$ [1.652(11) Å], the structure of which has been determined by electron diffraction in the gas phase[11]. The crystal structure of another (trimethylsilyl)iminophosphorane with three nitrogen substituents at the phosphorus atom, $(i\text{-}Pr_2N)$(tetramethylpiperidino)$\{[(i\text{-}Pr_2N)_3P{=}N)]\text{-}P{=}NSiMe_3\}$, shows a P–N bond length of 1.526(3) Å and a P–N–Si angle of 160.6(2)° in the PNSi unit. Both values are in good agreement with those of **5** [P–N4–Si angle: 160.0(2)°], indicating that packing forces are not important. By contrast, the P–N–Si angles in the bis(trimethylsilylimino)phosphorane $(Me_3Si)_2NP({=}NSiMe_3)_2$ [148.6(3)° at 18 °C and 146.8(2)° at −130 °C][13] and other related compounds[14] are much more acute, indicating a more marked electronic influence of other substituents at the phosphorus atom.

Figure 4. Molecular structure of compound **5** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity); the molecule has no crystallograpically imposed symmetry; selected bond lengths (Å) and angles (°): P–N1 1.656(2), P–N2 1.653(2), P–N3 1.670(2), P–N4 1.514(2), Si–N4 1.664(2), P–N4–Si 160.0(2)



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Experimental Section

All experiments were carried out under dry, pure nitrogen. Solvents were dried and saturated with nitrogen. $(Me_2S)AuCl$[5] and $(Me_2N)_3PNSiMe_3$[6] were prepared according to literature procedures. All other reagents were commercially available. Conventional equipment was used throughout. NMR chemical shifts are reported in ppm referenced to internal TMS for ^1H and ^{13}C and to external H_3PO_4 (85%) for ^{31}P.

[Tris(dimethylamino)phosphane]gold(I) Chloride (**1**): To a slurry of $(Me_2S)AuCl$ (2.76 g, 9.4 mmol) in 20 ml of THF was added $(Me_2N)_3P$ (1.53 g, 9.4 mmol). The resulting clear solution was stirred for 1 h at ambient temperature. The product was precipitated by addition of pentane. Crystallization from chloroform/hexane (1:1) yielded 3.71 g of **1** (100%); m.p. 167 °C (decomp.). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ = 110.7 (s). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.57 (d, $^3J_{HP}$ = 11.7 Hz). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ = 37.5 (d, $^2J_{CP}$ = 9.4 Hz). – $C_6H_{18}AuClN_3P$ (395.62): calcd. C 18.22, H 4.59, N 10.62; found C 18.20, H 4.62, N 10.72. – MS (FD, $CHCl_3$): *m/z* = 395 (M^+, 100%).

μ_3-Tris{[tris(dimethylamino)phosphane]gold(I)}oxonium Tetrafluoroborate (**2**): Compound **2** was synthesized from $[(Me_2N)_3P]AuCl$ (**1**) (1.10 g, 2.8 mmol), $NaBF_4$ (2.13 g, 19.5 mmol) and freshly prepared Ag_2O (3.0 g, 13.0 mmol) in 100 ml of tetrahydrofuran using a procedure analogous to that in the literature[7] for this class of compounds. Crystallization from THF/hexane (1:1) afforded a colourless product in 94% yield; 3.11 g, m.p. 179 °C (decomp.). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ = 100.9 (s). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.59 (d, $^3J_{HP}$ = 11.2 Hz). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ = 37.3 (d, $^2J_{CP}$ = 8.3 Hz). – $C_{18}H_{54}Au_3BF_4N_9OP_3$ (1183.32): calcd. C 18.27, H 4.60, N 10.65; found C 18.35, H 4.64, N 10.84. – MS (FAB, 4-nitrobenzyl alcohol): *m/z* = 1096 (M^+, 100%).

[Tris(dimethylamino)phosphoranylidene]bis{[tris(dimethylamino)phosphane]gold(I)}ammonium Tetrafluoroborate (**3**): To a solution of **2** (0.35 g, 0.29 mmol) in 10 ml of CH_2Cl_2 were added $NaBF_4$ (0.20 g, excess) and $(Me_2N)_3PNSiMe_3$ (**5**) (0.11 g, 0.44 mmol). The mixture was stirred for 5 h at room temperature. The product **3** was precipitated by addition of hexane. Slow concentration of a solution of **3** in $CHCl_3$/hexane (1:1) gave 0.30 g (70%) of crystalline material; m.p. 158 °C (decomp.). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ = 57.1 (t, $^3J_{PP}$ = 15.2 Hz, 1 P), 114.2 (d, $^3J_{PP}$ = 15.2 Hz, 2 P). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.56 (d, $^3J_{HP}$ = 11.6 Hz; 36H), 2.63 (d, $^3J_{HP}$ = 9.8 Hz; 18H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ = 37.3 (d, $^2J_{CP}$ = 9.2 Hz, 12 C), 37.6 (d, $^2J_{CP}$ = 2.8 Hz, 6 C). – $C_{18}H_{54}Au_2BF_4N_{10}P_3$ (984.34): calcd. C 21.96, H 5.53, N 14.23; found C 21.83, H 5.67, N 14.44. – MS (FAB, 4-nitrobenzyl alcohol): *m/z* = 897 (M^+, 56%).

[μ^3-Tris(dimethylamino)phosphaneimido]tris{[tris(dimethylamino)phosphane]gold(I)}(2+) Bis{tetrafluoroborate} (**4**): To a solution of **2** (0.47 g, 0.40 mmol) in 15 ml of CH_2Cl_2 were added $NaBF_4$ (0.30 g, excess) and $(Me_2N)_3PNSiMe_3$ (**5**) (0.10 g, 0.40 mmol). The mixture was stirred for 6 h at room temperature and the product **4** precipitated by addition of hexane. Slow concentration of a solution of **4** in $CHCl_3$/hexane (1:1) gave 0.37 g (65%) of colourless crystals; m.p. 154 °C (decomp.). – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 109.3 MHz): δ = 56.3 (q, $^3J_{PP}$ = 7.1 Hz, 1 P), 114.2 (d, $^3J_{PP}$ = 7.1 Hz, 3 P); ^1H NMR ($CDCl_3$, 270 MHz): δ = 2.66 (d,

$^3J_{HP}$ = 12.2 Hz; 54 H), 2.87 (d, $^3J_{HP}$ = 10.3 Hz; 18 H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz): δ = 37.4 (d, $^2J_{CP}$ = 8.8 Hz, 18 C), 38.2 (d, $^2J_{CP}$ = 3.3 Hz, 6 C). – $C_{24}H_{72}Au_3B_2F_8N_{13}P_4$ (1431.34): calcd. C 20.14, H 5.07, N 12.72; found C 20.40, H 4.97, N 13.11. – MS (FD, CH_2Cl_2): m/z = 628.5 ($M^+/2$, 43%).

Crystal Structure Determinations: Suitable single crystals of **1**, **2** and **4** were sealed into glass capillaries and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for the compounds. Diffraction intensities were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F (**1**)[15] and F^2 (**2**, **4**)[16], respectively. The thermal motion of all non-hydrogen atoms was treated anisotropically except for the highly disordered BF_4^- anion of compound **2**. The disorder was resolved into 12 split fluorine positions (s.o.f. of 1/3 for each F atom) with idealized geometry (DFIX). The hydrogen atoms of compounds **1**, **2** and **4** were calculated in idealized positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)}$ = 0.08 Å^2 for **1** and **2**), or their isotropic thermal parameters were tied to those of the adjacent carbon atoms by a factor of 1.5 (for **4**).

A cylindrical crystal of compound **5** was grown from the melt in a sealed capillary mounted on a Stoe Stadi-4 diffractometer with an Oxford Cryosystems low-temperature device[17], by cooling the sample from 255.5 to 253 K at a rate of 30 K h^{-1} after growing a seed crystal. Details of the crystal data, data collection and structure refinement are summarized in Tables 3 and 4. The refinement followed the same procedure as described above. The hydrogen positions were calculated in idealized positions, the angles were fixed and the C–H bond lengths and isotropic thermal parameters were refined groupwise for each of the CH_3 units. Selected interatomic distances and angles are given in Tables 1 and 2 and in the corresponding figure captions. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59385, the names of the authors, and the full journal citation.

Table 3. Crystal data, data collection, and structure refinement for compounds **1** and **2**

	1	**2**
Crystal data		
Formula	$C_6H_{18}AuClN_3P$	$C_{18}H_{54}Au_3BF_4N_9OP_3$
M_r	395.62	1183.32
Crystal system	orthorhombic	monoclinic
Space group	*Pnma*	$P2_1/n$
Crystal dimensions (mm)	0.17 × 0.33 × 0.45	0.15 × 0.30 × 0.45
a (Å)	14.724(2)	10.850(1)
b (Å)	11.440(1)	25.829(2)
c (Å)	7.148(1)	12.858(1)
α (°)	90	90
β (°)	90	97.94(1)
γ (°)	90	90
V (Å^3)	1203.9(2)	3568.8(4)
ρ_{calc} (gcm^{-3})	2.182	2.20
Z	4	4
F(000) (e)	744	2224
μ (Mo-K_α) (cm^{-1})	125.3	125.0
Data collection		
Diffractometer	Enraf Nonius CAD4	
Radiation	Mo-K_α, 0.71073 Å, graphite monochromator	
T (°C)	–68	–68
Scan mode	ω	ω
hkl range	+14/+13/±8	+13/+32/±16
Measured refl.	2312	8159
Unique refl.	1096	7759
Used refl.	1007 [$F_o \geq 4\,\sigma F_o$]	7736
Absorption correction	empirical	DIFABS[18]
T_{min}/T_{max} (%)	0.1781/0.9986	0.1800/1.0000
Refinement		
Refined parameters	61	307
H atoms (found/calcd.)	0/18	0/54
R / $R1$[a]	0.0318/–	–/0.0442
R_w[a]/$wR2$[b]	0.0368/–	–/0.1443
ρ_{fin}(max/min) (eÅ^{-3})	+1.93/–1.60[c]	+1.39/–2.07[c]

[a] $R, R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. – $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. – $w = 1/\sigma^2(F_o)$. – [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$. – $w = 1/2\sigma^2(F_o^2) + (ap)^2 + bp; p = (F_o^2 + 2F_c^2)/3$. – a = 0.0743, b = 16.2152 (**2**). – [c] Residual electron densities located close to the Au atoms.

Table 4. Crystal data, data collection, and structure refinement for compounds **4** and **5**

	4	**5**
Crystal data		
Formula	$C_{24}H_{72}Au_3B_2F_8N_{13}P_4$	$C_9H_{27}N_4PSi$
M_r	1431.35	250.41
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	*P*1bar
Crystal dimensions (mm)	0.25 × 0.35 × 0.45	0.80 × 0.39 × 0.39
a (Å)	12.365(1)	8.4168(9)
b (Å)	16.659(1)	9.6828(12)
c (Å)	23.449(2)	10.7303(12)
α (°)	90	100.491(5)
β (°)	97.53(1)	94.273(6)
γ (°)	90	114.589(6)
V (Å^3)	4788.6(6)	770.8(2)
ρ_{calc} (gcm^{-3})	1.985	1.079
Z	4	2
F(000) (e)	2744	276
μ (Mo-K_α) (cm^{-1})	93.7	21.72
Data collection		
Diffractometer	Enraf Nonius CAD4	Stoe Stadi-4
Radiation	Mo-K_α, 0.71073 Å, graphite monochr.	Cu-K_α, 1.54184 Å graphite monochr.
T (°C)	–68	–163
Scan mode	ω	ω – 2θ
hkl range	±15/+20/+28	±9/±10/0→+12
Measured refl.	8664	2421
Unique refl.	8373	2231
Used refl.	8360	2231
Absorption correction	empirical	empirical
T_{min}/T_{max} (%)	0.7171/0.9997	0.3950/0.7590
Refinement		
Refined parameters	487	165
H atoms (found/calcd.)	0/72	0/27
R / $R1$[a]	–/0.0369	–/0.0527
R_w[a]/$wR2$[b]	–/0.0895	–/0.1530
ρ_{fin}(max/min) (eÅ^{-3})	+1.33/–1.25[c]	+0.49/–0.60

[a,b] See Table 3. – a = 0.0587/0.1068, b = 8.0508/0.6417 (**4**/**5**). – [c] Residual electron densities located close to the Au atoms.

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