Silylimido and Disilylamido Groups as Clustering Centers for (Phosphane)gold(I) Units: Aurated Silylammonium Cations

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The reaction of hexa*methyl*disilazane with tris[(phosphane)-aurio(I)]oxonium tetrafluoroborates affords the corresponding trinuclear μ_3-trimethylsilylimido compounds of the type $\{[(R_3P)Au]_3NSiMe_3\}^+$ BF_4^- (**1a**–**f**). With (tri*phenyl*silyl)amine and the oxonium reagents the analogous series of Ph_3Si derivatives (**2a**–**f**) is formed (R = Me, Et, *i*Pr; R_3 = Ph_2Me; R = Ph, *o*-Tol). The Et_3P-based oxonium salt and $(Me_3Si)_2NH$ give the dinuclear μ-trimethylsilylamido complex $\{[(Et_3P)Au\}_2N(SiMe_3)_2\}^+$ BF_4^- (**3**) as the main product. The crystal and molecular structures of complexes **2a**, **2e**, and **3** were determined. The trinuclear cations have a pseudo-tetrahedral structure with small Au–N–Au angles and short Au–Au distances for the $SiNAu_3$ units. The Ph_3SiN units in **2a** and **2e** are capping triangles of gold atoms, while in the cation of **3** the $(Me_3Si)_2N$ unit is bridging a pair of gold atoms. In the ^{31}P- and ^{14}N-NMR spectra of compounds **1** and **2** (except for **1f** and **2f**) the coupling $J(^{31}P,^{14}N)$ is observed. This coupling is temperature-dependent, owing to changes in the relaxation characteristics in solution at low temperature. The decomposition of compounds **1** and **2** leads to the formation of pentanuclear dications $\{[(R_3P)Au]_5N\}^{2+}$ for R = Me, Ph.

Mono-, bis-, and tris(silyl)amines are poor bases and weak N donors, and very few silylated amonium salts or donor/acceptor complexes of silylamines are known. It is only in ring- or cage-type molecules with strong electron-acceptor centers (like aluminium) that silylamido groups were occasionally detected as bridging structural units with tetracoordinate nitrogen atoms[1–4].

Therefore, it came as a surprise when it was discovered that the reaction of hexamethyldisilazane $(Me_3Si)_2NH$ with tris[(phosphane)aurio(I)]oxonium salts gave the first examples of mono(silyl)tris[(phosphane)aurio(I)]ammonium salts, in which the silylimido group is capping a triangle of gold atoms[5]. In all previous studies with these reagents only complete desilylation of the nitrogen with formation of tetrakis[(phosphane)aurio(I)]ammonium cations, $[(R_3P)Au]_4N^+$, was observed[6]. These results called for an extensive study aimed at a more comprehensive picture of the novel mixed Si/Au-substituted amines and ammonium salts. These studies were also prompted by recent findings in the chemistry of related carbon compounds, where species of the type $\{[(R'_3Si)_2C[Au(PR_3)]_3\}^+$ with pentacoordinate carbon atoms were encountered[7,8]. For these cations a trigonal-bipyramidal structure with equatorial silyl groups was confirmed by X-ray diffraction studies. The remaining coordination sites are occupied by gold atoms which are clearly drawn together by bonding metal-metal interactions (auriophilicity)[9,10]. Similar phenomena were also expected to occur in the aurated ammonium cations presented in this report.

Preparation of (Triorganosilyl)tris[(phosphane)aurio(I)]ammonium Tetrafluoroborates $\{(R'_3Si)N[Au(PR_3)]_3\}^+$ $(BF_4)^-$

For a thorough investigation of the title compounds with a μ^3-$N(SiR'_3)^{2-}$ unit formally bridging three $(R_3P)Au^+$ units, two series of compounds with R′ = methyl and phenyl at silicon, with R = methyl, ethyl, isopropyl, phenyl, and *o*-tolyl at phosphorus, and R_3P as methyldiphenylphosphane were chosen.

The six compounds of the tri*methyl*silyl series (**1a**–**f**) were obtained from the reaction of $Me_3SiNHSiMe_3$ with the corresponding tris[(phosphane)aurio(I)]oxonium salts according to Eq. (1). The oxonium reagents are readily available following literature procedures or with local variations of these preparations as described in other reports from this laboratory[11–15].

$$[(LAu)_3O]\,BF_4 \xrightarrow{HN(SiMe_3)_2} [(LAu)_3NSiMe_3]\,BF_4 \qquad (1)$$

1a–**f**

$$[(LAu)_3O]\,BF_4 \xrightarrow{H_2NSiPh_3} [(LAu)_3NSiPh_3]\,BF_4 \qquad (2)$$

2a–**f**

1, 2	a	b	c	d	e	f
L	Me_3P	Et_3P	$i Pr_3P$	Ph_2MeP	Ph_3P	o-Tol_3P

$$[(LAu)_3O]\,BF_4 \xrightarrow{HN(SiMe_3)_2} [(LAu)_2N(SiMe_3)_2]\,BF_4 \qquad (3)$$

3, L = Et_3P

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The six analogs from the tri*phenyl*silyl series (**2a**–**f**) were synthesized from (triphenylsilyl)amine Ph_3SiNH_2 and again the corresponding oxonium reagents (Eq. 2).

Except for compound **1b**, the products were obtained in good yields as colorless, crystalline solids, which are soluble in polar solvents, preferentially di- and trichloromethane. [Instead of **1b**, the bis-silylated product **3** was generated irrespective of the molar ratio of the reagents (below)].

Single crystals of the $SiPh_3$ compounds **2a** and **2e** could be grown, and the crystal structures could be determined.

In contrast to observations made with the solid compounds, which appear to be quite stable at ambient temperature under inert gas, the solutions are of limited stability. A darkening was soon observed, and the results of NMR control experiments indicated that a complex mixture of products was generated in the decomposition. Surprisingly, the dicationic species $\{[(R_3P)Au]_5N\}^{2+}$ were the only prominent components to be identified. Tetrafluoroborates of such dications have been described for R = Ph in some earlier studies (see also below), while evidence for the species with R = Me was obtained only very recently[16,17].

Preparation of the Bis(triorganosilyl)bis[(phosphane)aurio(I)]ammonium Tetrafluoroborate $\{(Me_3Si)_2N[Au(PEt_3)]_2\}^+ (BF_4)^-$ (3)

The reaction of $Me_3SiNHSiMe_3$ with $\{[(Et_3P)Au]_3O\}^+ (BF_4)^-$ affords only trace amounts of compound **1b** (above), irrespective of the relative molar quantities of the reagents employed. Instead, a colorless bissilylated product (**3**) was obtained in moderate yield, which is soluble in polar solvents and readily crystallizes. It was easily identified by its analytical and spectroscopic data (below), and its crystal structure was determined. It is unclear as yet, why for the particular combination of R′ = Me and R = Et the formation of the bissilylated material **3** is favored compared with the monosilylated product **1b**. It appears that the desilylation of hexamethyldisilazane is particularly slow with the $Au(PEt_3)^+$ reagent, perhaps owing to a specific combined steric and electronic effect.

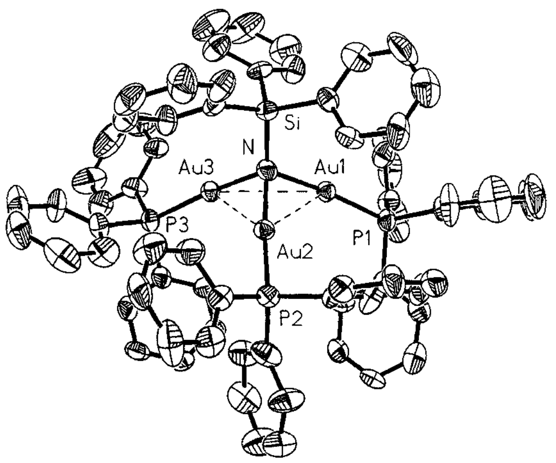
Crystal Structures of Compounds 2a, 2e, and 3

Compound **2e** crystallizes (from chloroform) in the triclinic space group $P\bar{1}$ with two formula units and six molecules of chloroform in the unit cell. The lattice is built from independent tetrafluoroborate anions and silyl-triaurio-ammonium cations. These complex cations (Figure 1) have no crystallographically imposed symmetry, but the skeleton of heavy atoms and the orientation of the phenyl groups deviate only little from the symmetry requirements of point group C_{3v}, with the pseudo-threefold axis coinciding with the Si–N bond and passing through the center of the triangle of gold atoms. The Ph_3SiN group thus has a propeller-type configuration. The SiC_3 group is staggered with respect to the NAu_3 group in an ethane-like conformation.

The triangle of gold atoms in the cation of **2e** is not equilateral, but appears distorted towards an isosceles triangle with one long and two short Au–Au contacts (average 3.0922 Å), corresponding to one large and two small Au–Au–Au angles (see caption of Figure 1). The nitrogen atom lies 0.96(1) Å above the plane of the gold atoms. Its coordination array shows significant distortions from a regular tetrahedral geometry, which are such that the three gold atoms are drawn together, thus opening the Si–N–Au angles at the expense of the Au–N–Au angles. This effect has sample precedent[18,19] and has e.g. also been reported for the corresponding *organo*ammonium analogs of the type $\{RN[Au(PR_3)]_3\}^+$.

Compound **2a** crystallizes without crystal solvent in the monoclinic space group $P2_1$ with 4 formula units in the unit cell. There are two crystallographically independent sets of cations and anions. The dimensions of the two forms are very similar as shown in Figure 2. As already noted for compound **2e**, the gold atoms are arranged in slightly distorted triangles. The Au–Au distances are longer than in **2e**, but still in the region of slightly bonding contacts [average 3.196(3) and 3.194(3) Å, respectively]. The nitrogen atoms are situated 1.01(1) (N1) and 0.80(1) Å (N2) above their individual gold triangles. All other relevant distances and angles are listed in the caption to Figure 2.

Figure 1. Molecular structure and of the cation $\{[(Ph_3P)Au]_3NSiPh_3\}^+$ in the tetrafluoroborate salt **2e** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1–Au2 3.008(1), Au1–Au3 3.278(1), Au2–Au3 2.991(1), N–Au1 2.03(1), N–Au2 2.043(8), N–Au3 2.032(8), N–Si 1.750(8); Au1–Au2–Au3 66.3(1), Au2–Au1–Au3 56.6(1), Au2–Au3–Au1 57.1(1), Au1–N–Au2 95.3(4), Au1–N–Au3 107.7(4), Au2–N–Au3 94.5(3), Si–N–Au1 118.1(4), Si–N–Au2 117.7(5), Si–N–Au3 118.8(5)



Compound **3** crystallizes in the orthorhombic space group *Cmcm* with 4 formula units in the unit cell. As for **2a** and **2e**, the cations and anions are separated, and no crystal solvent is present in the lattice. The cation has two crystallographic mirror planes passing through the triatomic units NSi_2 and NAu_2, respectively. The Au–Au′ distance is 3.071(1) Å, the Au–N–Au′ angle as small as 93.1(5)°, complemented by a large angle Si–N–Si′ of 127.0(8)°. The quality of the structure solution suffers from disorder of an ethyl group and of the BF_4^- anion (Experimental). The structure of the cation is shown in Figure 3, with selected distances and angles in the caption.

Figure 2. Molecular structure and atomic numbering of the two crystallographically independent cations $\{[(Me_3P)Au]_3NSiPh_3\}^+$ in the tetrafluoroborate salt **2a** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: a) Au1−Au2 3.210(3), Au1−Au3 3.119(3), Au2−Au3 3.259(3), N1−Au1 2.20(1), N1−Au2 2.08(2), N1−Au3 2.05(2), N1−Si1 1.61(2). Au1−Au2−Au3 57.7(1), Au2−Au1−Au3 62.0(1), Au2−Au3−Au1 60.4(1), Au1−N1−Au2 96.9(6), Au1−N1−Au3 94.4(6), Au2−N1−Au3 104.3(7), Si1−N1−Au1 113.7(8), Si1−N1−Au2 115(1), Si1−N1−Au3 127(1). − b) Au4−Au5 3.209(3), Au4−Au6 3.112(3), Au5−Au6 3.260(3), N2−Au4 1.91(1), N2−Au5 2.06(2), N2−Au6 2.07(2), N2−Si2 1.83(2). Au4−Au5−Au6 57.5(1), Au5−Au4−Au6 62.1(1), Au5−Au6−Au4 60.4(1), Au4−N2−Au5 108.0(8), Au4−N2−Au6 102.9(8), Au5−N2−Au6 104.4(7), Si2−N2−Au4 118.1(9), Si2−N2−Au5 108.1(9), Si2−N2−Au6 114.4(9)

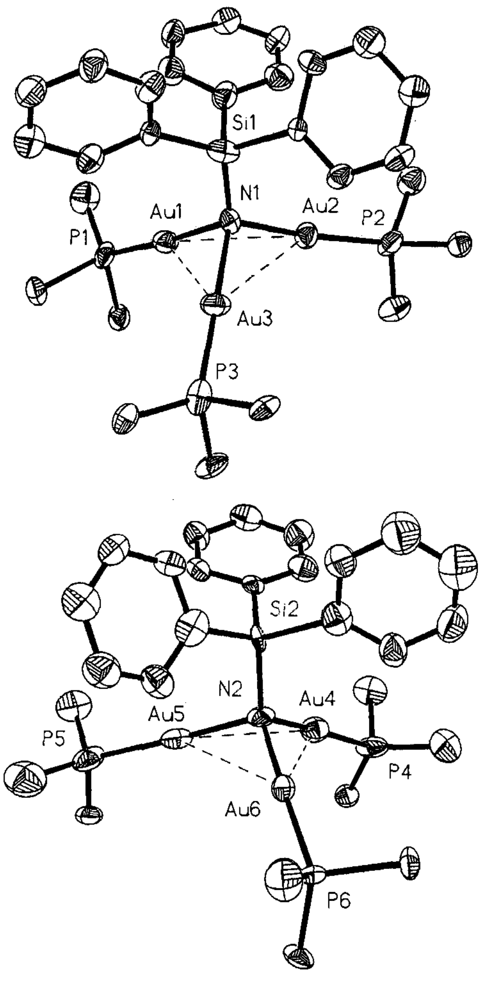
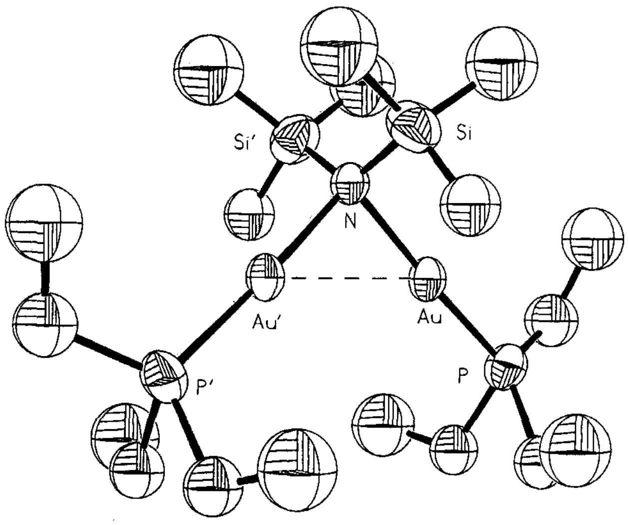


Figure 3. Molecular structure of the cation $\{[(Et_3P)Au]_2N(SiMe_3)_2\}^+$ in the tetrafluoroborate salt **3** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity; the disorder of the ethyl groups is not shown). Two mirror planes pass through the nitrogen atom. Selected bond lengths [Å] and angles [°]: Au−Au' 3.071(1), N−Au 2.115(9), N−Si 1.759(7); Au−N−Au' 93.1(5), Si−N−Au 107.9(2), Si−N−Si' 127.0(8)



NMR Spectroscopic and Mass Spectrometric Data of the Compounds

All compounds described in this paper were characterized by their *multinuclear solution NMR spectra*. The data are summarized in the experimental section, and only few of the NMR parameters require further comments. A note concerning the unusual splitting of the ^{31}P resonances of compounds of the series **1** and **2** (except for **1f** and **2f**) by ^{31}P-^{14}N coupling should be made. In all of these (^{1}H-decoupled) spectra the resonance of the three equivalent phosphorus atoms appears as a 1:1:1 triplet with J values of about 21 Hz. The corresponding quartet splitting with the same J value is observed in the ^{14}N-NMR spectrum of compound **2b** as a representative example. It appears that the full C_{3v} symmetry of the cations reduces the electric field gradient at the nitrogen center and thus allows detection of ^{14}N coupling with spin 1/2 nuclei. This assumption is in agreement with the detection of ^{14}N splittings in other species of high rotational symmetry. It is intriguing, however, that the spectra of both tri-*o*-tolylphosphane complexes (**1f**, **2f**) do not exhibit ^{31}P-^{14}N splitting. The lowering of the ligand symmetry from C_{3v} (all other R_3P ligands) or C_s ($MePh_2P$!) to C_3 may be sufficient to quench the coupling.

The ^{31}P-^{14}N coupling was also found to be temperature-dependent. Full resolution into the 1:1:1 triplet was only obtained at ambient and elevated temperatures, while upon cooling of the samples coalescence to a broad singlet resonance was observed (−60 °C). This phenomenon can be ascribed to a change in relaxation behavior arising from the increase in the viscosity of the solution at low temperature, but also from the longer lifetime of ion pairs with lower symmetry at low temperature.

In the *mass spectra* (cations in FAB) of the compounds of the series **1**, **2**, and **3** the molecular ions of the cationic units $R'_3SiN[Au(PR_3)]_3$ are detected in all cases. A main fragmentation pathway (Table 1) leads to the ions $\{R'_2Si{=}N[Au(PR_3)]_2\}^+$ through loss of one substituent R' from the silicon and one unit $Au(PR_3)$ from the nitrogen atoms. In the negative ion spectra, only the BF_4^- anions are encountered.

Decomposition Products

Compounds **1**−**3** decompose slowly in chloroform or dichloromethane solution at ambient temperature even under inert gas, and more rapidly if water or other protic

Table 1. Mass spectral data (*m/z*, relative intensity in parentheses) for salts of the type $[(LAu)_3NSiR'_3]^+$ BF_4^-, **1a–f**, **2a–f**. Parent cations and main fragmentation products $[(LAu)_2NSiR'_2]^+$ (FAB, NBA as solvent)

	$[(LAu)_3NSiR'_3]^+$	$[(LAu)_2NSiR'_2]^+$
1a	906 (100 %)	618 (73 %)
2a	1092 (100 %)	742 (85 %)
1b	1032 (29 %)	702 (9 %)
2b	1218 (100 %)	826 (51 %)
1c	1159 (100 %)	787 (27 %)
2c	1344 (100 %)	910 (40 %)
1d	1280 (17 %)	867 (11%)
2d	1464 (100 %)	990 (51 %)
1e	1467 (100 %)	992 (31 %)
2e	1650 (100 %)	1114 (48 %)
1f	1590 (100 %)	1074 (22 %)
2f	1776 (100 %)	1198 (30 %)

agents are present. A mixture of products is formed, which give rise to a large number of ^1H, ^{13}C, and ^{31}P resonances in the NMR spectra. Apart from hexamethyldisiloxane and triphenylsilanol only the dications with five gold atoms at the nitrogen atom were identified for systems with the ligands PMe_3 and PPh_3[16,17]. The latter was observed previously, and the crystal structure of a monoclinic tetrafluoroborate modification has been determined.

In the present study another modification of this compound was crystallized. Its unit cell dimensions [a = 34.345(4), b = 15.301(2), c = 53.369(1) Å, β = 107.19(1)°, V = 26792 Å^3, monoclinic, space group $P2_1/c$, Z = 12, T = −41 °C] and a diffraction data set were collected, but the structure could not be solved and refined completely. The preliminary results leave no doubt that three dications of the formula $\{[(Ph_3P)Au]_5N\}^{2+}$ are again present, which have a trigonal-pyramidal NAu_5 core with dimensions similar to those of the known monoclinic modification.

A set of NMR data could be assigned to the dications $\{[(Me_3P)Au]_5N\}^{2+}$, but simple binary salts of this unit could not be crystallized. In the course of parallel studies of this system an adduct with two molecules of Me_3PAuCl could be crystallized and its structure solved and refined[17]. It shows the expected NAu_5 core with five PMe_3 units attached to the gold atoms. These findings taken together are good proof of the identity of the surmised products and their surprisingly high stability.

It is noteworthy that the decomposition of the carbon analogs of the present silicon compounds, i.e. salts of the type $\{[(R_3P)Au]_3NR'\}^+$ X^-, follows a completely different pathway. No pentanuclear nitrogen-centered dications were found for these systems, and a stepwise *de*auration is the dominant process[5]. In contrast to the Si–N bond, the R–N bond is not easily cleaved, and no further replacement of substituents at the nitrogen atom by $(R_3P)Au$ groups can take place.

Attempts to further aurate the cations of the types **1**–**3** by using $[(R_3P)Au]^+$ BF_4^- or an excess of oxonium reagent without cleavage of Si–N bonds failed. Species of the formula $\{[(R_3P)Au]_3N(SiR'_3)_2\}^{2+}$ or $\{[(R_3P)Au]_4NSiR'_3\}^{2+}$, which are isoelectronic with analogous carbon[20], boron[21], and phosphorus compounds[22] remain elusive up to the present time.

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Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves under nitrogen. – NMR: $CDCl_3$ as solvent, TMS as internal standard for ^1H, $^{29}Si\{^1H\}$, and $^{13}C\{^1H\}$, H_3PO_4 (85%) as external standard for $^{31}P\{^1H\}$, CH_3NO_2 as external standard for ^{14}N, Jeol GX 270, Jeol GX 400. – MS: Varian MAT 90.

General Procedure: To a solution of the tris[(phosphane)aurio(I)]oxonium tetrafluoroborate in dichloromethane (20 ml) hexamethyldisilazane or (triphenylsilyl)amine was added, and the mixture was allowed to react for 2 h at 0 °C. The volume of the mixture was reduced to a few ml in vacuo, and diethyl ether was added to precipitate all the products. Pure products were obtained by carefully adding diethyl ether to a dichloromethane solution. For **1a** see ref.[5].

μ_3-(Trimethylsilylimido)tris[(triethylphosphane)gold(I)] Tetrafluoroborate (**1b**): Obtained in small yields (<1%) as a by-product in the preparation of **3** from 0.18 g (0.17 mmol) of tris[(trimethylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.04 g (0.25 mmol) of hexamethyldisilazane. – $C_{21}H_{54}Au_3BF_4NP_3Si$ (1119.5): MS (FAB), *m/z* (%): 1032 (29), (M – $[Et_3PAu + CH_3]$) 702 (9). – $^{31}P\{^1H\}$ NMR: δ = 29.4 [t, J(PN) = 20.7 Hz].

μ_3-(Trimethylsilylimido)tris[(triisopropylphosphane)gold(I)] Tetrafluoroborate (**1c**): From 0.20 g (0.17 mmol) of tris[(triisopropylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.04 g (0.25 mmol) of hexamethyldisilazane; yield 0.17 g (0.14 mmol, 80%) of **1c**, dec. temp. 110 °C. – $C_{30}H_{72}Au_3BF_4NP_3Si$ (1245.7): calcd. C 28.93, H 5.83, N 1.12; found C 28.64, H 5.72, N 0.98. – ^1H NMR: δ = 0.1 ($SiCH_3$, s), 1.3 [CCH_3, dd, J(PH) = 15.9, J(HH) = 7.3 Hz], 2.2 [CH, dsept, J(PH) = 7.3, J(HH) = 7.3 Hz]. – $^{13}C\{^1H\}$ NMR: δ = 7.8 ($SiCH_3$, s), 20.3 (CCH_3, s), 23.7 [PC, d, J(PC) = 29.4 Hz]. – $^{31}P\{^1H\}$ NMR: δ = 59.7 [t, J(PN) = 20.7 Hz]. – MS (FAB), *m/z* (%): 1159 (100), (M – [*i*$Pr_3PAu + CH_3$]) 787 (27).

μ_3-(Trimethylsilylimido)tris[(methyldiphenylphosphane)gold(I)] Tetrafluoroborate (**1d**): From 0.25 g (0.19 mmol) of tris[(methyldiphenylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.04 g (0.25 mmol) of hexamethyldisilazane; yield 0.16 g (0.12 mmol, 61%) of **1d**, dec. temp. 121 °C. – $C_{42}H_{48}Au_3BF_4NP_3Si$ (1365.7): calcd. C 36.94, H 3.54, N 1.03; found C 37.29, H 3.20, N 0.87. – ^1H NMR: δ = 0.2 ($SiCH_3$, s), 2.1 [PCH_3, d, J(PH) = 9.2 Hz], 7.3–7.6 [Aryl H, m]. – $^{13}C\{^1H\}$ NMR: δ = 8.1 ($SiCH_3$, s), 14.3 [PCH_3, d, J(PC) = 38.6 Hz], 129.2 [C-3,5, d, J(PC) = 11.0 Hz], 131.3 [C-1, d, J(PC) = 58.8 Hz], 131.7 [C-4, s], 132.5 [C-2,6, d, J(PC) = 13.8 Hz]. – $^{31}P\{^1H\}$ NMR: δ = 13.7 [t, J(PN) = 21.8 Hz]. – MS (FAB), *m/z* (%): 1280 (17), (M – $[Ph_2MePAu + CH_3]$) 867 (11).

μ_3-(Trimethylsilylimido)tris[(triphenylphosphane)gold(I)] Tetrafluoroborate (**1e**): From 0.17 g (0.11 mmol) of tris[(triphenylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.04 g (0.25 mmol) of hexamethyldisilazane; yield 0.11 g (0.07 mmol, 62%) of

Table 2. Crystallographic data for compounds **2a**, **2e** · 3 $CHCl_3$ and **3**

	2a	**2e·3CHCl$_3$**	**3**
Formula	$C_{27}H_{42}Au_3BF_4P_3SiN$	$C_{75}H_{63}Au_3BCl_9F_4P_3SiN$	$C_{18}H_{48}Au_2BF_4P_2Si_2N$
Mw	1179.3	2096.0	877.4
Cryst. system	monoclinic	triclinic	orthorhombic
Space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	Cmcm (No. 63)
a [Å]	17.477 (2)	12.765 (1)	12.950 (1)
b [Å]	11.870 (1)	15.921 (2)	17.726 (2)
c [Å]	17.924 (2)	20.119 (2)	14.117 (1)
α [°]	90	89.08 (1)	90
β [°]	95.99 (1)	73.29 (1)	90
γ [°]	90	89.80 (1)	90
D_c [g cm^{-1}]	2.12	1.78	1.80
Z	4	2	4
μ (Mo-K_α) [cm^{-1}]	120.7	60.4	92.4
Cryst. dim. [mm]	0.20/0.25/0.30	0.30/0.40/0.55	0.15/0.20/0.60
T [°C]	-62	-56	-62
Abs. correction	empirical	empirical	empirical
$T_{min.}/T_{max.}$ (%)	71.58/99.77	75.90/99.96	88.49/99.79
scan mode	ω	ω	θ
scan range (θ) [°]	3 - 27	3-27	3-27
hkl range	±22/15/22	±16/±20/25	18/22/18
measured data	8632	16992	3752
unique data	7361	15369	3349
observed data	5426	13161	1552
No. of parameters	670	782	60
Obs. criterion	$F \geq 4\sigma(F_o)$	$F \geq 4\sigma(F_o)$	$F \geq 4\sigma(F_o)$
R*	0.0355	0.0562	0.0373
R_w**	0.0331	0.0728	-
Weighting scheme	$w = [\sigma^2(F) + 0.000244\,F_o^2]^{-1}$	$w = [\sigma^2(F_o) + 0.070904\,F_o^2]^{-1}$	Unit Weights
Res. density [e Å^{-3}]	1.23/-1.08	3.18/-2.47	2.11/-1.31

$* R = [\sum\|F_o| - |F_c\|]/\sum|F_o|$. - $** R_w = [\sum w(|F_o| - |F_c|)^2/[wF_o^2]]^{1/2}$.

1e, dec. temp. 134 °C. – $C_{57}H_{54}Au_3BF_4NP_3Si$ (1551.9): calcd. C 44.12, H 3.51, N 0.90; found C 43.87, H 2.98, N 1.08. – ^{1}H NMR: δ = 0.3 ($SiCH_3$, s), 7.2–7.62 (Aryl H, m). – $^{13}C\{^1H\}$ NMR: δ = 8.0 ($SiCH_3$, s), 129.2 [C-1, d, *J*(PC) = 58.8 Hz], 129.3 [C-3,5, d, *J*(PC) = 11.9 Hz], 132.0 (C-4, s), 133.8 [C-2,6, d, *J*(PC) = 13.8 Hz]. – $^{31}P\{^1H\}$ NMR: δ = 29.2 [t, *J*(PN) = 21.8 Hz]. – MS (FAB), *m/z* (%): 1467 (100), (M – [Ph_3PAu + CH_3]) 992 (31).

μ_3-(Trimethylsilylimido)tris[(tri-o-tolylphosphane)gold(I)] Tetrafluoroborate (**1f**): From 0.21 g (0.13 mmol) of tris[(tri-*o*-tolylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.03 g (0.19 mmol) of hexamethyldisilazane; yield 0.15 g (0.09 mmol, 69%) of **1f**, dec. temp. 128 °C. – ^{1}H NMR: δ = 0.1 ($SiCH_3$, s), 2.3 (CCH_3, s), 6.8 [6-H, dd, *J*(PH) = 12.7, *J*(HH) = 7.3 Hz], 7.2 (3,5-H, m], 7.5 [4-H, t, *J*(HH) = 7.3 Hz]. – $^{13}C\{^1H\}$ NMR: δ = 6.7 ($SiCH_3$, s), 22.6 [CCH_3, d, *J*(PC) = 13.2 Hz], 126.7 [C-1, d, *J*(PC) = 60.8 Hz], 126.9 [C-5, d, *J*(PC) = 10.3 Hz], 132.1 (C-4, s), 132.3 [C-3, d, *J*(PC) = 10.1 Hz], 133.4 [C-6, d, *J*(PC) = 9.2 Hz], 142.2 [C-2, d, *J*(PC) = 11.9 Hz]. – $^{31}P\{^1H\}$ NMR: δ = 7.6 (s). – MS (FAB), *m/z* (%): 1590 (100), (M – [*o*-Tol_3PAu + CH_3]) 1074 (22).

μ_3-(Triphenylsilylimido)tris[(trimethylphosphane)gold(I) *Tetrafluoroborate* (**2a**): From 0.12 g (0.13 mmol) of tris[(trimethy phosphane)aurio(I)]oxonium tetrafluoroborate and 0.05 g (0.1 mmol) of (triphenylsilyl)amine; yield 0.13 g (0.11 mmol, 85%) **2a**, dec. temp. 158 °C. – ^{1}H NMR: δ = 1.5 [PCH_3, d, *J*(PH) 10.7 Hz], 7.3 [3,5-H, t, *J*(HH) = 7.1 Hz], 7.3 [4-H, t, *J*(HH) = 7. Hz], 7.8 [2,6-H, d, *J*(HH) = 7.1 Hz]. – $^{13}C\{^1H\}$ NMR: δ = 15 [PCH_3, d, *J*(PC) = 39.1 Hz], 127.1 (C-2,6, s), 128.8 (C-1, s), 134 (C-3,5, s], 141.0 (C-4, s). – $^{31}P\{^1H\}$ NMR: δ = –12.6 [t, *J*(PN) 22.1 Hz]. – MS (FAB), *m/z* (%): 1092 (100), (M – [Me_3PAu Ph]) 742 (85).

μ_3-(Triphenylsilylimido)tris[(triethylphosphane)gold(I)] Tetr *fluoroborate* (**2b**): From 0.17 g (0.16 mmol) of tris[(triethylpho phane)aurio(I)]oxonium tetrafluoroborate and 0.06 g (0.22 mmo of (triphenylsilyl)amine; yield 0.12 g (0.09 mmol, 57%) of **2b**, de temp. 128 °C. – $C_{36}H_{60}Au_3BF_4NP_3Si$ (1305.6): calcd. C 33.12, 4.63, N 1.07, Si 2.15; found C 33.27, H 4.60, N 0.96, Si 1.85. – NMR: δ = 1.0 [CH_3, dt, *J*(PH) = 18.3, *J*(HH) = 7.3 Hz], 1.7 [CH dq, *J*(PH) = 10.4, *J*(HH) = 7.3 Hz], 7.3 [3,5-H, t, *J*(HH) = 7.

Hz], 7.3 [4-H, t, *J*(HH) = 7.3 Hz], 7.8 [2,6-H, d, *J*(HH) = 7.3 Hz]. – ^{13}C{^{1}H} NMR: δ = 9.2 (CH_3, s), 18.2 [CH_2, d, *J*(PC) = 33.1 Hz], 128.0 (C-2,6, s), 129.6 (C-1, s), 135.1 (C-3,5, s), 142.2 (C-4, s). – ^{31}P{^{1}H} NMR: δ = 29.5 [t, *J*(PN) = 20.7 Hz]. – ^{14}N NMR: δ = −299.1 [q, *J*(PN) = 20.7 Hz]. – MS (FAB), *m/z* (%): 1218 (100), (M – [Et_3PAu + Ph]) 826 (51).

μ₃-(Triphenylsilylimido)tris[(triisopropylphosphane)gold(I)] Tetrafluoroborate (**2c**): From 0.17 g (0.14 mmol) of tris[(triisopropylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.05 g (0.18 mmol) of (triphenylsilyl)amine; yield 0.17 g (0.12 mmol, 82%) of **2c**, dec. temp. 158°C. – $C_{45}H_{78}Au_3BF_4NP_3Si$ (1431.9): calcd. C 37.75, H 5.49, N 0.98; found C 38.11, H 5.53, N 1.02. – ^{1}H NMR: δ = 1.1 [CH_3, dd, *J*(PH) = 15.9, *J*(HH) = 7.3 Hz], 2.1 [CH, dsept, *J*(PH) = 7.3, *J*(HH) = 7.3 Hz], 7.2 [3,5-H, t, *J*(HH) = 7.2 Hz], 7.3 [4-H, t, *J*(HH) = 7.2 Hz], 7.8 [2,6-H, d, *J*(HH) = 7.2 Hz]. – ^{13}C{^{1}H} NMR: δ = 20.1 (CH_3, s), 23.5 [CH, d, *J*(PC) = 30.3 Hz], 127.2 (C-2,6, s), 128.8 (C-1, s), 135.1 (C-3,5, s), 141.2 (C-4, s). – ^{31}P{^{1}H} NMR: δ = 59.9 [t, *J*(PN) = 18.5 Hz]. – MS (FAB), *m/z* (%): 1344 (100), (M – [*i*Pr_3PAu + Ph]) 910 (40).

μ₃-(Triphenylsilylimido)tris[(methyldiphenylphosphane)gold(I)] Tetrafluoroborate (**2d**): From 0.17 g (0.13 mmol) of tris[(methyldiphenylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.09 g (0.33 mmol) of (triphenylsilyl)amine; yield 0.16 g (0.10 mmol, 79%) of **2d**, dec. temp. 147°C. – ^{1}H NMR: δ = 2.0 [PCH_3, d, *J*(PH) = 9.3], 7.1–7.8 (Aryl H, m). – ^{13}C{^{1}H} NMR: δ = 13.3 [CH_3, d, *J*(PC) = 39.7 Hz], 127.7 [C-2,6(Si), s], 129.6 [C-1(Si), s], 134.9 [C-3,5(Si), s], 140.3 [C-4(Si), s], 128.8 [C-3,5(P), d, *J*(PC) = 11.0 Hz], 129.6 [C-4(P), s], 130.6 [C-1(P), d, *J*(PC) = 60.4 Hz], 132.3 [C-2,6(P), d, *J*(PC) = 8.8 Hz]. – ^{31}P{^{1}H} NMR: δ = 12.6 [t, *J*(PN) = 19.3 Hz]. – ^{29}Si{^{1}H} NMR: δ = 9.9 (s). – MS (FAB), *m/z* (%): 1464 (100), (M – [Ph_2MePAu + Ph]) 990 (51).

μ₃-(Triphenylsilylimido)tris[(triphenylphosphane)gold(I)] Tetrafluoroborate (**2e**): From 0.21 g (0.14 mmol) of tris[(triphenylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.07 g (0.25 mmol) of (triphenylsilyl)amine; yield 0.23 g (0.13 mmol, 93%) of **2e**, dec. temp. 153°C. – $C_{72}H_{60}Au_3BF_4NP_3Si$ (1738.1): calcd. C 49.76, H 3.45, N 0.81; found C 50.56, H 3.66, N 0.79. – ^{1}H NMR: δ = 7.1–7.5 (Aryl H, m). – ^{13}C{^{1}H} NMR: δ = 127.5 [C-2,6(Si), s], 129.2 [C-1(Si), s], 135.2 [C-3,5(Si), s], 140.6 [C-4(Si), s], 128.1 [C-1(P), d, *J*(PC) = 56.4 Hz], 129.2 [C-3.5(P), d, *J*(PC) = 11.0 Hz], 131.9 [C-4(P), s], 133.8 [C-2,6(P), d, *J*(PC) = 8.8 Hz]. – ^{31}P{^{1}H} NMR: δ = 29.4 [t, *J*(PN) = 19.8 Hz]. – MS (FAB), *m/z* (%): 1650 (100), (M – [Ph_3PAu + Ph]) 1114 (48).

μ₃-(Triphenylsilylimido)tris[(tri-o-tolylphosphane)gold(I)] Tetrafluoroborate (**2f**): From 0.16 g (0.10 mmol) of tris[(tri-*o*-tolylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.04 g (0.15 mmol) of (triphenylsilyl)amine; yield 0.15 g (0.08 mmol, 80%) of **2f**, dec. temp. 164°C. – $C_{81}H_{78}Au_3BF_4NP_3Si$ (1864.3): calcd. C 52.18, H 4.22, N 0.75; found C 52.86, H 4.37, N 0.85. – ^{1}H NMR: δ = 2.0 (CH_3, s), 6.6–7.56 (Aryl H, m). – ^{13}C{^{1}H} NMR: δ = 22.1 [CH_3, d, *J*(PC) = 10.5 Hz], 127.4 [C-2,6(Si), s], 129.1 [C-1(Si), s], 135.5 [C-3.5(Si), s], 138.7 [C-4(Si), s], 125.0 [C-1(P), d, *J*(PC) = 58.4 Hz], 126.9 [C-5(P), d, *J*(PC) = 9.9 Hz], 132.2 [C-4(P), s], 132.2 [C-3(P), d, *J*(PC) = 13.2 Hz], 133.3 [C-6(P), d, *J*(PC) = 8.8 Hz], 142.2 [C-2(P), d, *J*(PC) = 12.1 Hz]. – ^{31}P{^{1}H} NMR: δ = 7.0 (s). – MS (FAB), *m/z* (%): 1776 (100), (M – [Ph_3PAu + Ph]) 1198 (30).

μ-[Bis(trimethylsilyl)amido]bis[(triethylphosphane)gold(I)] Tetrafluoroborate (**3**): From 0.18 g (0.17 mmol) of tris[(triethylphosphane)aurio(I)]oxonium tetrafluoroborate and 0.04 g (0.25 mmol) of hexamethylsilazane; yield 0.07 g (0.08 mmol, 47%) of **3**, dec. temp. 145°C. – $C_{18}H_{48}Au_2BF_4NP_2Si_2$ (877.4): calcd. C 24.64, H 5.51, N 1.60, Si 6.40; found C 24.59, H 5.44, N 1.68, Si 6.06. – ^{1}H NMR: δ = 0.3 ($SiCH_3$, s), 1.2 [CH_3, dt, *J*(PH) = 19.6, *J*(HH) = 7.6 Hz], 1.9 [CH_2, dq, *J*(PH) = 10.4, *J*(HH) = 7.6 Hz]. – ^{13}C{^{1}H} NMR: δ = 6.8 ($SiCH_3$, s), 9.4 (CH_3, s), 17.9 [CH_2, d, *J*(PC) = 37.7 Hz]. – ^{31}P{^{1}H} NMR: δ = 32.1 (s). – ^{29}Si{^{1}H} NMR: δ = 38.9 (s). – MS (FAB), *m/z*: 790 (100%).

X-Ray Structure Determinations: All samples were mounted in glass capillaries. Graphite-monochromated Mo-K_α radiation was used. The structures were solved by direct methods (program SHELXTL-PC). Hydrogen atoms of non-disordered groups were included in idealized, fixed positions. The structure of **3** was complicated by disorder of ethyl and BF_4 groups. These distributions were accounted for by using split models with SOF = 0.5/0.5 for both groups. Rigid-group refinement was used for the BF_4 and $CHCl_3$ groups of the structures of **2a** and **2e**. The final cell parameters and specific data collection parameters are summarized in Table 2. – Details of the X-ray structure determinations were deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the depository number CSD-59008.

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