Primary Amines as Nucleation Centres for Gold Clustering, and the Structural Chemistry of Polygold Ammonium Cations†

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Treatment of *tert*-butylamine and benzylamine with $[Au(PR'_3)]BF_4$ led to the monoauration products $[(R'_3P)AuNH_2R]^+BF_4^-$ (R' = Me, R = Bu^t **1a**; R' = Me, R = CH_2Ph **1b**; R'_3 = Ph_2Me, R = Bu^t **1c**). The salts $[\{Au(PMe_3)\}_3NR]^+BF_4^-$ (R' = Me, R = Bu^t **2a** or CH_2Ph **2b**) derived from the same amines were obtained using the corresponding oxonium salt $[\{Au(PMe_3)\}_3O]^+BF_4^-$. A diauration product $[\{Au(PMe_3)\}_2NH(CH_2Ph)]^+BF_4^-$ **3** was generated upon slow hydrolytic degradation of **2b** in solution. Treatment of $NH(SiMe_3)_2$ with $[\{Au(PMe_3)\}_3O]^+BF_4^-$ afforded both the tris- and tetra-aurated ammonium salts, $[\{Au(PMe_3)\}_3NSiMe_3]^+BF_4^-$ **2c** and $[\{Au(PMe_3)\}_4N]^+BF_4^-$ **4**, depending on the reaction conditions. The cation of **2c** is one of the very rare examples of silylammonium species. Compound **4** was also obtained from the oxonium salt and ammonia. All compounds have been characterized through analytical and spectroscopic data. The crystal structures of **1a**, **1c** and **3** have been determined by X-ray diffraction methods: **1c** is a salt with monomeric gold ammonium cations, but **1a** and **3** show supramolecular aggregation of the cations into dimers with short intercationic Au ··· Au contacts.

The affinity of gold for nitrogen is very low indeed, and most compounds with gold–nitrogen bonds are of limited stability.[1] It is therefore most surprising that this affinity is increased if more than one gold atom is present at a given nitrogen centre: polyauration appears to be much more facile than the introductory step of the metallation at nitrogen.[2] Work in the last two decades has shown that compounds with one, two, three, four, and even five gold atoms at nitrogen can be prepared.[3–15] The stability of these clustering products is found to increase remarkably with the size of the nitrogen-centred metal aggregates. These results have been accumulated from occasional observations during various preparative studies in gold chemistry. It was therefore felt that this field of gold–nitrogen chemistry should now be given a more systematic consideration by developing straightforward synthetic pathways and elucidating more of the molecular structures of the individual species.

Recent investigations have shown that many of the peculiar stoichiometries and properties of gold compounds have their origin in an unusual structural chemistry.[16–18] Most two-co-ordinate compounds of the type L–Au–X have been found to form supramolecular aggregates with Au ··· Au distances of *ca.* 3.0 Å associated with bond energies of *ca.* 8 kcal mol^{-1} (*ca.* 33.47 kJ mol^{-1}).[19–22] This secondary bonding is representing weak forces between the closed-shell metal atoms (Au^I 5d^{10}) originating from significant changes in the energy characteristics of the valence electrons of gold by relativistic effects.[23–25] In the Periodic Table these effects reach a local maximum for gold in the heavy-element region.[26,27]

The strength of the Au ··· Au interactions is influenced also by the electronic effects of the substituents L and X at gold, and some of the experimental findings (above),[28–33] as well as theoretical calculations,[34] have indicated that soft ligands of low group electronegativity should shorten the Au ··· Au distance and increase the bond energy. More recent data have shown, however, that even within the series with X = halide the results are not consistent with this simple picture.[35] On the other hand it is becoming more and more obvious that steric effects are playing a decisive role, since the weak forces associated with the Au ··· Au contacts are easily overruled by steric repulsion and other components such as packing forces. (In solution, it is the solvation by solvent molecules which is overruling the aggregation through Au ··· Au contacts.) In cluster aggregates these Au ··· Au contacts are synergistic and lead to the stabilization mentioned as the key observation.[36–40]

The present study was therefore undertaken also in order to contribute to the open questions regarding the intra- and inter-molecular (supramolecular) aggregation of nitrogen-centred gold cluster cations $[\{Au(PR'_3)\}_nNR_{4-n}]^+$ for different numbers of *n* and different substituents R and R'.

Results and Discussion

Preparative Results.—*tert*-Butylamine and benzylamine were chosen as substrates because it should be possible to follow the stepwise auration at nitrogen most easily. The steric effect of the Bu^t group was expected to hinder quick and complete auration, whereas benzyl was expected to give products with good crystallization properties for all steps. For small and simple alkyl and aryl groups it has already been demonstrated in previous experiments that complete auration to give tri(gold)-ammonium cations is virtually instantaneous.[2]

Treatment of NH_2Bu^t with a solution of equimolar quantities of (trimethylphosphine)gold(I) tetrafluoroborate {prepared *in situ* from $[Au(PMe_3)Cl]$ and $AgBF_4$ in tetrahydrofuran} gives high yields of the monoaurated ammonium salt **1a** (Scheme 1).

$$[Au(PR'_3)]^+BF_4^- \xrightarrow{NH_2R} [(R'_3P)AuNH_2R]^+BF_4^-$$

1a R' = Me, R = Bu^t
1b R' = Me, R = CH_2Ph
1c R'_3 = Ph_2Me, R = Bu^t

Scheme 1

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† *Supplementary data available:* details of the crystal structure determinations are available from Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the names of the authors, the journal citation, and the CSD number 58808.

Even if an excess of the aurating agent is used only this primary product is obtained. This result has been confirmed in the reaction of the same amine with (methyldiphenylphosphine)-gold(I) tetrafluoroborate, which consistently gave only the analogous product **1c**. In a similar way, $NH_2(CH_2Ph)$ was converted into the mononuclear complex salt **1b**. It therefore appears that $[Au(PR'_3)]^+BF_4^-$ reagents quite generally lead to monoauration products only. No more highly aurated by-products have been observed in the reaction mixtures by NMR spectroscopy.

By contrast, with μ_3-oxo-tris[(trimethylphosphine)gold(I)] tetrafluoroborate the two amines, NH_2Bu^t and $NH_2(CH_2Ph)$, are triply aurated immediately even at low temperature and with stoichiometric or sub-stoichiometric quantities of the reagent. The products **2a**, **2b** are generated in high yields and with very satisfactory purity. This behaviour is in agreement with the findings of NH_2Me, NH_2Et, NH_2Ph and other simple mono- or di-functional primary amines (like ethylenediamine or diaminobenzenes).

$$[\{Au(PMe_3)\}_3O]^+BF_4^- \xrightarrow{NH_2R} [\{Au(PMe_3)\}_3NR]^+BF_4^-$$

2a $R = Bu^t$
2b $R = CH_2Ph$

Scheme 2

Although the pure crystalline compounds are stable at ambient temperature in an inert atmosphere (below), slow degradation is observed in solution, most notably if humidity is allowed to enter into the storage vessel. The benzyl compound **2b** has been found to undergo hydrolysis thereby (in moist dichloromethane) which leads to the crystalline primary degradation product with only two gold atoms left at the nitrogen atom $[\{Au(PMe_3)\}_2NH(CH_2Ph)]^+BF_4^-$ **3**. Compound **2a** also shows this solvolysis, as monitored by NMR spectroscopy, but no pure crystalline material could be isolated.

Hexamethyldisilazane $(Me_3Si)_2NH$ is known to react with $[\{Au(PR'_3)\}_3O]^+$ salts to give salts of the type $[\{Au(PR'_3)\}_4N]^+BF_4^-$. As shown, *e.g.* for the case with R = Ph, no partially aurated cations are detected in this reaction: both trimethylsilyl groups are replaced by (phosphine)gold units, and the imino hydrogen atom is also lost in the quaternization. In the reaction with $[\{Au(PMe_3)\}_3O]^+BF_4^-$ we were now able to isolate a triply aurated cation still bearing one trimethylsilyl group at the nitrogen centre $[\{Au(PMe_3)\}_3NSiMe_3]^+BF_4^-$ **2c**. The reaction was found to proceed further if humidity is allowed to enter the reaction mixture, or if moist tetrahydrofuran is used as a solvent. Under these conditions, the quadruply aurated salt $[\{Au(PMe_3)\}_4N]^+BF_4^-$ **4** is the sole product. This compound is also available from the oxonium salt and ammonia, as suggested by previous work. Compound **2c** can be converted into **4** by reaction with another mole of the oxonium reagent, preferably in moist solvent.

No attempts have yet been made to aurate further the cation of **4** aiming at the generation of the five-co-ordinate salt of the type $[\{Au(PMe_3)\}_5N]^{2+}2BF_4^-$. It is expected that future work will confirm the existence of this Me_3P analogue of the known Ph_3P complex.[15]

General Properties and Spectroscopic Data.—All new complexes have been obtained as colourless (or pale yellow) crystalline materials, except for **1b** which has been obtained as an oil, which are soluble in polar solvents, preferably di- and tri-chloromethane or tetrahydrofuran. These solutions are not very stable, and decomposition is observed after a few hours or days at room temperature. However, samples of the dry, pure solid materials are stable in dry air at ambient temperature. Their composition has been confirmed by elemental analysis. The cations of the compounds have been registered as parent ions in the mass spectra of these solutions (field desorption, fast atom bombardment, or chemical ionization techniques).

The ^1H, ^{13}C, ^{29}Si and ^{31}P NMR spectra of the halogenocarbon solutions show the expected patterns. The number of resonances and their relative intensities are consistent with the proposed composition. In a few selected cases the tetrafluoroborate anions have been registered separately by ^{19}F and ^{11}B NMR spectroscopy, as well as by their IR absorptions and negative-ion mass spectra. Details are given in the Experimental section. While most chemical shift values and (where applicable) coupling constants do not need special comments, it is interesting to mention a more unusual observation in the ^{31}P NMR spectrum of compound **2c**: the $^{31}P-\{^1H\}$ resonance of this cation is a triplet signal with a clear $^{31}P-^{14}N$ coupling ($J = 22.8$ Hz). We suggest that the three-fold symmetry of the cation leads to a very small field gradient at the nuclei thus eliminating the quadrupolar broadening of the resonance.

Compound **2c** is noteworthy in other respects as well. Its cation is one of the few examples of silylated ammonium species. Silylamines, disilazanes and trisilylamines are all exhibiting very low basicity, and hence quaternization is generally not a common process. If it occurs, it is often followed by desilylation leaving behind again only triply bonded nitrogen compounds. It is only in systems stabilized by chelation that silylated, quadruply bonded nitrogen is observed, preferably in fused rings or cages.[41] In the present case (**2c**) the system appears to be stabilized by the intimate aggregation of the three gold atoms in a tightly bound metal triangle. Units $[(AuL)_3NR]^+$ have been structurally characterized for several substituents R and phosphine ligands L. Their geometrical details are proof for the above assumption of NAu_3 aggregation through bonding Au···Au contacts.[2] Small Au–N–Au angles and short Au···Au distances are diagnostic for the bonding situation in these clusters.

Crystal Structures of Selected Compounds (**1a**, **1c** *and* **3**).—Single crystals were obtained for compounds **1a**, **1c** and **3**. All are ionic materials, with well separated cations and anions in the lattices. The individual cations of **1a** and **1c** have the expected configuration, with the primary amines as donor ligands to gold(I). The metal atoms are linearly two-co-ordinate with a tertiary phosphine as the second ligand (Figs. 1 and 2). Groups N–Au–P are not very common, and it was only very recently that complexes of this type could be confirmed by structural data.

In agreement with results reported for related compounds, the cations of compound **1c** are not associated in the crystal, because steric effects of the bulky Bu^t and $MePh_2P$ groups prevent the intimate approach required for metal–metal contacts. In the lattice of compound **1a**, however, the cations are associated into pairs to give a short intermolecular Au···Au distance of 3.047(1) Å. The smaller Me_3P ligand (as compared

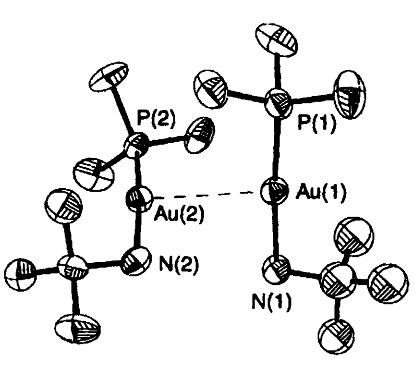

Fig. 1 Dimeric structure of compound **1a**. Selected bond lengths (Å) and angles (°): Au(1)···Au(2) 3.047(1), Au(1)–P(1) 2.236(4), Au(1)–N(1) 2.13(1), Au(2)–P(2) 2.235(3), Au(2)–N(2) 2.11(1); N(1)–Au(1)–P(1) 175.7(4), N(2)–Au(2)–P(2) 174.8(3), N(1)–Au(1)–Au(2) 86.6(3), P(1)–Au(1)–Au(2) 96.8(1), N(2)–Au(2)–Au(1) 86.6(3), P(2)–Au(2)–Au(1) 97.8(1)

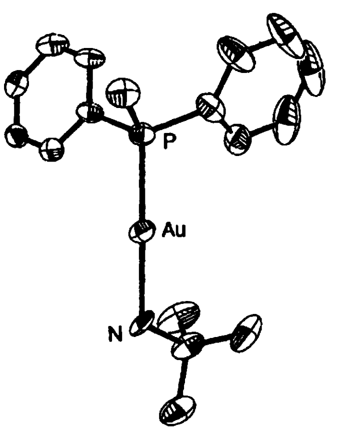

Fig. 2 Monomeric structure of compound **1c**. Selected bond lengths (Å) and angles (°): Au–N 2.105(8), Au–P 2.235(3); N–Au–P 176.4(2)

to $MePh_2P$) allows a closer aggregation, which is typical for many LAuX complexes with sterically non-demanding ligands L. Compound **1a** is probably the first case, however, where an amine and a phosphine form the ligand sphere of the metals.

The cations of compound **3** feature a benzylamino group bearing two Me_3PAu substituents at the quaternary nitrogen centre. As expected for element-bridged dinuclear gold(I) compounds, the angle Au–N–Au 99.9(3)° is much smaller than the standard tetrahedral angle of 109°, clearly indicating Au ··· Au bonding. This situation resembles that in cations $[(AuL)_2OR]^+$, $[(AuL)_2SR]^+$ and $[(AuL)_2SeR]^+$ which are (valence) isoelectronic.[42–45] The individual cationic units of compound **3** are associated into centrosymmetrical dimers, as shown in Fig. 3. The two intramolecular Au ··· Au bonds [Au(1) ··· Au(2) 3.171(1)] and the two intermolecular contacts [Au(1) ··· Au(2′) 3.143(1)] form the edges of the rectangular skeleton of gold atoms in the dication. This type of aggregation to give a rectangle of gold atoms is again analogous to the configuration of the related oxonium and sulfonium cations (above). It is only for very small ligands that an even more intimate clustering is observed, where the gold atoms join up to form a tetrahedron.[46]

There is no evidence for hydrogen bonding originating from the NH groups in the aggregate of compound **3**, and from the NH_2 groups in compounds **1a** and **1c**. The bond distances and angles of the ligands L and the amino groups $RNH_{(2)}$ of all three compounds show no anomalies. Selected data are given in the figure captions.

Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves in a nitrogen atmosphere. The NMR spectra were recorded in $CDCl_3$ as solvent, with $SiMe_4$ as internal standard for ^1H, ^{29}Si and ^{13}C-{^1H}, H_3PO_4 (85%) as external standard for ^{31}P-{^1H}, on JEOL GX 270 and GX 400 spectrometers. Mass spectra were obtained on a Varian MAT 90 spectrometer.

(tert-*Butylamine*)(*trimethylphosphine*)*gold*(I) *Tetrafluoroborate* **1a**.—To a solution of $[Au(PMe_3)]BF_4$ {freshly prepared from $[Au(PMe_3)Cl]$ (0.17 g, 0.55 mmol) and $AgBF_4$ (0.11 g, 0.56 mmol)} in tetrahydrofuran (20 cm^3) was added NH_2Bu^t (0.1 cm^3) at 0 °C. After stirring the solution for 2 h the crude product was precipitated with pentane. Compound **1a** was purified from a dichloromethane solution by carefully precipitating with diethyl ether. Colourless crystals, yield 0.17 g (77%), decomp. 152 °C (Found: C, 20.60; H, 5.60; N, 3.90. $C_7H_{20}AuBF_4NP$ requires C, 20.90; H, 5.00; N, 3.50%). NMR: ^1H, δ 1.3 (CCH_3, s), 1.6 [PCH_3, d, $J(PH) = 11.0$] and 3.7 (NH_2, s); ^{13}C-{^1H}, δ 14.9 [PCH_3, d, $J(PC) = 41.4$ Hz], 31.4 (CCH_3, s) and 53.8 (CCH_3, s); ^{31}P-{^1H}, δ −9.7 (s). FAB mass spectrum: m/z = 346.4 (100%).

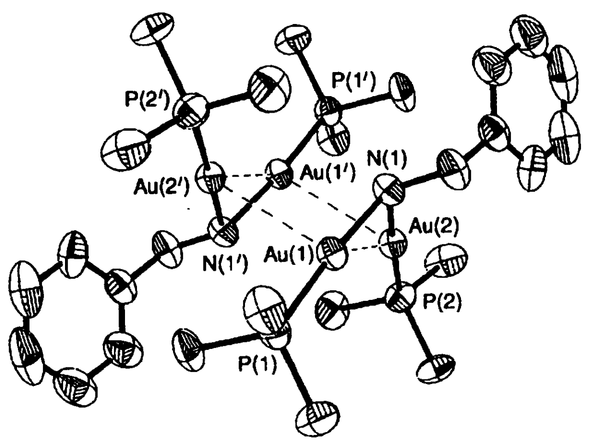

Fig. 3 Dimeric structure of compound **3**. Selected bond lengths (Å) and angles (°): Au(1) ··· Au(2) 3.171(1), Au(1) ··· Au(2′) 3.143(1), Au(1)–N 2.071(8), Au(2)–N 2.073(8), Au(1)–P(1) 2.246(3), Au(2)–P(2) 2.248(3); Au(1)–Au(2)–Au(1′) 91.3(1), Au(2)–Au(1)–Au(2′) 88.7(1), Au(1)–N–Au(2) 99.9(3)

(*Benzylamine*)(*trimethylphosphine*)*gold*(I) *Tetrafluoroborate* **1b**.—Procedure as described for compound **1a**, a solution of $[Au(PMe_3)]BF_4$ {freshly prepared from $[Au(PMe_3)Cl]$ (0.15 g, 0.49 mmol) and $AgBF_4$ (0.10 g, 0.54 mmol)} in tetrahydrofuran (20 cm^3) being treated with $NH_2(CH_2Ph)$ (0.1 cm^3). Colourless oil, yield 0.13 g (57%) (Found: C, 25.70; H, 3.35; N, 3.10. $C_{10}H_{18}AuBF_4NP$ requires C, 25.70; H, 3.90; N, 3.00%). NMR: ^1H, δ 1.5 [PCH_3, d, $J(PH) = 11.6$], 3.7 (NH_2, s), 4.2 (CH_2, s) and 7.3–7.5 (aryl, m); ^{13}C-{^1H}, δ 14.6 [PCH_3, d, $J(PC) = 41.4$ Hz], 48.9 (CH_2, s), 128.3 (C^5, s), 128.8 ($C^{4,6}$, s), 129.1 ($C^{3,7}$, s) and 138.4 (C^2, s); ^{31}P-{^1H}, δ −10.5 (s). FAB mass spectrum: m/z = 380.3 (100%).

(tert-*Butylamine*)(*methyldiphenylphosphine*)*gold*(I) *Tetrafluoroborate* **1c**.—Procedure as described for compound **1a**, a solution of $[Au(PPh_2Me)]BF_4$ {freshly prepared from $[Au(PPh_2Me)Cl]$ (0.31 g, 0.72 mmol) and $AgBF_4$ (0.14 g, 0.72 mmol)} in tetrahydrofuran (30 cm^3) being treated with NH_2Bu^t (0.1 cm^3). Colourless crystals, yield 0.37 g (92%), decomp. 175 °C (Found: C, 36.60; H, 4.45; N, 2.05. $C_{17}H_{24}AuBF_4NP$ requires C, 36.65; H, 4.35; N, 2.50%). NMR: ^1H, δ 1.3 (CCH_3, s), 2.1 [PCH_3, d, $J(PH) = 10.6$], 4.3 (NH_2, s) and 7.4–7.6 (aryl, m); ^{13}C-{^1H}, δ 14.0 [PCH_3, d, $J(PC) = 43.4$ Hz], 31.9 (CCH_3, s), 54.1 (CCH_3, s) and 129.5–132.9 (aryl, m); ^{31}P-{^1H}, δ 16.0 (s). FAB mass spectrum: m/z = 470.2 (35%).

μ-*Benzylamido-bis*[(*trimethylphosphine*)*gold*(I)] *Tetrafluoroborate* **3**.—Slow removal of the solvent from a solution of compound **2b** in humid dichloromethane within 5 d afforded **3** as a colourless crystalline product. ^{31}P-{^1H} NMR: δ −10.6 (s). FAB mass spectrum: m/z = 652.2 (22%).

μ_3-tert-*Butylimido-tris*[(*trimethylphosphine*)*gold*(I)] *Tetrafluoroborate* **2a**.—To a solution of $[\{Au(PMe_3)\}_3O]^+BF_4^-$ (0.12 g, 0.13 mmol) in dichloromethane (20 cm^3) was added NH_2Bu^t (0.05 cm^3). The solution was initially kept at 0 °C for 1 h, then allowed to warm to room temperature and stirred for 3 h. After reducing the volume to 10 cm^3 in a vacuum, diethyl ether was added to precipitate the solids. The pure, crystalline product was obtained at −25 °C from a dichloromethane solution by carefully adding pentane. Colourless crystals, yield 0.06 g (47%), decomp. 135 °C (Found: C, 15.90; H, 3.45; N, 1.75. $C_{13}H_{36}Au_3BF_4NP_3$ requires C, 16.00; H, 3.70; N, 1.45%). NMR: ^1H, δ 1.3 (CCH_3, s) and 1.6 [PCH_3, d, $J(PH) = 10.0$]; ^{13}C-{^1H}, δ 15.5 [PCH_3, d, $J(PC) = 37.7$ Hz], 43.4 (CCH_3, s) and 63.7 (CCH_3, s); $^{31}P-\{^1H\}$, δ −11.2 (s). FAB mass spectrum: m/z = 890.6 (61.2%).

μ_3-*Benzylimido-tris*[(*trimethylphosphine*)*gold*(I)] *Tetrafluoroborate* **2b**.—Procedure as described for compound **2a**, $[\{Au(PMe_3)\}_3O]^+BF_4^-$ (0.24 g, 0.26 mmol) being treated with $NH_2(CH_2Ph)$ (0.07 cm^3). Colourless crystals, yield 0.26 g (79%), decomp. 146 °C (Found: C, 18.90; H, 3.45; N, 1.45. $C_{16}H_{34}Au_3BF_4NP_3$ requires C, 19.00; H, 3.40; N, 1.40%). NMR: ^1H, δ 1.5 [PCH_3, d, J(PH) = 10.4], 4.8 [CH_2, q, J(PH) = 4.9], 7.2–7.3 (C^{4-6}, m) and 7.5 [$C^{3,7}$, d, J(HH) = 6.1]; $^{13}C-\{^1H\}$, δ 15.4 [PCH_3, d, J(PC) = 38.6 Hz], 67.9 (CH_2, s), 126.7 (C^5, s), 128.4 ($C^{4,6}$, s), 129.4 ($C^{3,7}$, s) and 151.0 (C^2, s); $^{31}P-\{^1H\}$, δ −11.9 (s). FAB mass spectrum: m/z = 924.1 (89%).

μ_3-*Trimethylsilylimido-tris*[(*trimethylphosphine*)*gold*(I)] *Tetrafluoroborate* **2c**.—Procedure as described for compound **2a**, $[\{Au(PMe_3)\}_3O]^+BF_4^-$ (0.30 g, 0.32 mmol) being treated with $NH(SiMe_3)_2$ (0.05 cm^3). Colourless crystals. NMR: ^1H, δ 1.5 [PCH_3, d, J(PH) = 10.7] and 0.1 ($SiCH_3$, s); $^{13}C-\{^1H\}$, δ 8.1 ($SiCH_3$, s) and 15.7 [PCH_3, d, J(PC) = 39.1]; ^{29}Si, δ 6.4 [$SiCH_3$, dct, J(SiH) = 7.4]; $^{31}P-\{^1H\}$, δ −12.1 [PAuN, t, J(PN) = 22.8 Hz]. FAB mass spectrum: m/z = 906.3 (100) and 618.2 (73%).

μ_4-*Nitrido-tetrakis*[(*trimethylphosphine*)*gold*(I)] *Tetrafluoroborate* **4**.—(*a*) To a solution of $[\{Au(PMe_3)\}_3O]^+BF_4^-$ (0.22 g, 0.24 mmol) in dichloromethane (30 cm^3) was added NH_3 (0.10 cm^3). The solution was initially kept at −55 °C for 3 h, then

Table 1 Crystallographic data for compounds **1a**, **1c** and **3**

	1a	**1c**	**3**
Formula	$C_7H_{20}AuBF_4NP$	$C_{17}H_{24}AuBF_4NP$	$C_{13}H_{26}Au_2BF_4NP_2$
M	432.99	557.12	739.03
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$C2/c$ (no. 15)	$Pccn$ (no. 56)	$P2_1/n$ (no. 14)
a/Å	18.242(2)	12.246(2)	9.783(1)
b/Å	11.058(1)	16.577(1)	13.512(1)
c/Å	28.902(4)	20.215(2)	15.759(1)
β/°	106.05(2)	90	92.38(1)
U/Å^3	5602.9	4103.6	2081.4
D_c/g cm^{-3}	2.04	1.80	2.36
Z	16	8	4
μ(Mo-Kα)/cm^{-1}	106.3	72.8	142.6
Crystal dimensions/mm	0.18 × 0.25 × 0.35	0.30 × 0.45 × 0.45	0.07 × 0.08 × 0.40
T/°C	−62	−68	25
Absorption correction	Empirical	Empirical	None
T_{min}, T_{max} (%)	55.96, 99.80	66.89, 99.96	—
Scan mode	ω	θ–θ	θ–θ
Scan range θ/°	3–26	2–27	2–27
hkl ranges	0–22, 0–13, ±35	0–15, 0–21, 0–25	±12, 0–17, 0–20
Measured data	5952	4858	4680
Unique data	4743	3864	3951
Observed data [$F_o \geqslant 4\sigma(F_o)$]	3535	3065	3154
No. of parameters	207	200	204
R	0.051	0.053	0.038
R'	0.047	0.051	0.036
Weighting scheme, w	$[\sigma^2(F_o) + 0.000\,100\,F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.000\,245\,F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.000\,379\,F_o^2]^{-1}$
Residual electron density/e Å^{-3}	1.42, −2.07	1.84, −1.21	1.78, −0.80

$R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/wF_o^2]^{\frac{1}{2}}$.

Table 2 Positional parameters for the non-hydrogen atoms of compound **1a**

Atom	x	y	z
Au(1)	−0.073 95(3)	−0.151 03(6)	−0.599 16(2)
Au(2)	0.008 88(3)	−0.355 00(6)	−0.634 74(2)
P(1)	−0.086 3(2)	−0.028 7(4)	−0.662 4(1)
P(2)	0.127 4(2)	−0.283 0(4)	−0.606 9(1)
N(1)	−0.070 4(7)	−0.263(1)	−0.538 8(4)
N(2)	−0.098 7(6)	−0.439(1)	−0.659 9(4)
C(21)	0.138 7(9)	−0.169(2)	−0.563 2(6)
C(22)	0.164 4(9)	−0.218(2)	−0.662 3(5)
C(23)	0.192 7(9)	−0.399(2)	−0.580 5(7)
C(24)	−0.110 4(7)	−0.522(1)	−0.701 4(5)
C(25)	−0.048 0(9)	−0.612(1)	−0.693 6(5)
C(26)	−0.187 4(9)	−0.585(1)	−0.707 1(6)
C(27)	−0.114 8(8)	−0.446(1)	−0.745 3(5)
C(11)	−0.096(1)	−0.106(1)	−0.718 3(5)
C(12)	−0.168(1)	0.066(2)	−0.673 0(5)
C(13)	−0.009(1)	0.068(1)	−0.659 8(6)
C(141)[a]	−0.120(1)	−0.240(2)	−0.511 7(7)
C(151)[a]	−0.116(1)	−0.328(2)	−0.471 5(7)
C(161)[a]	−0.200(1)	−0.243(2)	−0.546 5(7)
C(171)[a]	−0.103(1)	−0.112(2)	−0.490 8(7)
C(142)[b]	−0.094(1)	−0.188(2)	−0.500 3(7)
C(152)[b]	−0.167(1)	−0.123(2)	−0.514 1(7)
C(162)[b]	−0.033(1)	−0.092(2)	−0.478 6(7)
C(172)[b]	−0.100(1)	−0.278(2)	−0.461 1(7)
B(1)	0.815(2)	0.195(3)	0.181(1)
F(1)	0.738 7(7)	0.218(1)	0.184 8(4)
F(2)	0.859 9(8)	0.169(1)	0.220 4(5)
F(3)	0.830 1(8)	0.318(1)	0.167 8(5)
F(4)	0.811 9(9)	0.118(1)	0.146 1(6)
B(21)[c]	0.144(1)	0.325(2)	0.035 9(7)
F(11)[c]	0.171(1)	0.227(2)	0.016 8(7)
F(21)[c]	0.150(1)	0.303(2)	0.083 4(7)
F(31)[c]	0.185(1)	0.427(2)	0.031 9(7)
F(41)[c]	0.069(1)	0.341(2)	0.011 0(7)
B(22)[d]	0.110 6(6)	0.359(1)	0.046 7(4)
F(12)[d]	0.084 6(6)	0.451(1)	0.069 7(4)
F(22)[d]	0.089 4(6)	0.250(1)	0.061 7(4)
F(32)[d]	0.188 5(6)	0.364(1)	0.057 5(4)
F(42)[d]	0.079 8(6)	0.370(1)	−0.002 0(4)

[a] Split atom (s.o.f. = 0.48). [b] Split atom (s.o.f. = 0.52). [c] Split atom (s.o.f. = 0.25). [d] Split atom (s.o.f. = 0.75).

Table 3 Positional parameters for the non-hydrogen atoms of compound **1c**

Atom	*x*	*y*	*z*
Au	0.090 31(3)	0.120 73(2)	0.350 66(2)
P	0.179 3(2)	0.103 7(2)	0.446 2(1)
N	0.014 9(6)	0.133 3(5)	0.257 6(4)
C(11)	0.323 9(8)	0.123 4(6)	0.434 5(5)
C(12)	0.399 3(9)	0.102 4(7)	0.482 3(5)
C(13)	0.509 0(9)	0.118 0(7)	0.473 0(5)
C(14)	0.544 5(9)	0.153 8(6)	0.414 0(6)
C(15)	0.469 5(9)	0.173 7(6)	0.365 9(5)
C(16)	0.360 0(9)	0.159 9(6)	0.377 4(5)
C(21)	0.171 3(8)	0.000 5(7)	0.474 2(6)
C(22)	0.165(1)	−0.020 0(9)	0.540 4(7)
C(23)	0.164(1)	−0.099(1)	0.559(1)
C(24)	0.165(1)	−0.160(1)	0.516(1)
C(25)	0.169(1)	−0.139 6(8)	0.448(1)
C(26)	0.173(1)	−0.060 1(7)	0.427 6(7)
C(3)	0.135 8(9)	0.167 5(7)	0.512 6(6)
C(41)	−0.002 2(9)	0.055 3(7)	0.220 1(5)
C(42)	−0.052(1)	0.079 2(9)	0.153 5(6)
C(43)	−0.077(1)	0.004 3(9)	0.258 4(7)
C(44)	0.108(1)	0.016 3(9)	0.210 7(7)
B(1)	0.25	0.25	0.184 7(8)
B(2)	0.25	0.75	0.237(1)
F(1)	0.204(1)	0.190(1)	0.146 9(8)
F(2)	0.173(1)	0.277(1)	0.229 3(8)
F(3)	0.168(1)	0.780(1)	0.276(1)
F(4)	0.207(1)	0.691(1)	0.196(1)

allowed to warm to 0 °C and stirred for 3 h. After reducing the volume to 10 cm^3 in a vacuum, diethyl ether was added to precipitate the solids. Pure product was obtained from an acetonitrile solution by carefully adding pentane.

(*b*) Compound **4** was also obtained by reacting **2c** with $[\{Au(PMe_3)\}_3O]^+BF_4^-$ for 20 h at room temperature in humid tetrahydrofuran, but in lower yields compared with route (*a*). Colourless. Yield 0.11 g (51%) [route (*a*)], decomp. 122 °C (Found: C, 12.30; H, 3.15; N, 1.00. $C_{12}H_{36}Au_4BF_4NP_4$ requires C, 12.05; H, 3.05; N, 1.15%). NMR: ^1H, δ 1.6 [PCH_3, d, *J*(PH) = 10.8]; $^{13}C-\{^1H\}$, δ 15.8 [PCH_3, d, *J*(PC) = 37.2 Hz]; $^{31}P-\{^1H\}$, δ −15.1 (s). FAB mass spectrum: m/z = 1106.0 (84%).

Crystal Structure Determinations.—All samples were mounted in glass capillaries. Graphite-monochromated Mo-Kα radiation was used. The structures were solved by direct methods (SHELXTL PLUS).[47] That of compound **1a** was complicated by disorder of Bu^t and BF_4 groups. These distributions were accounted for by using split models of rigid groups with site occupation factors (s.o.f.s) of 0.25 and 0.75 for one BF_4 group and 0.48 and 0.52 for one Bu^t group. Rigid-group refinement was also used for the BF_4 in **1c**. An empirical absorption correction was not carried out after data collection for compound **3** because of some decomposition of the crystal during the measurements of the intensity data. Hydrogen atoms of non-disordered groups were included in idealized, fixed positions. The final unit-cell parameters and specific data collection parameters are summarized in Table 1; atomic coordinates are given in Tables 2–4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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Table 4 Positional parameters for the non-hydrogen atoms of compound **3**

Atom	*x*	*y*	*z*
Au(1)	0.074 40(4)	0.841 98(3)	0.507 11(2)
Au(2)	0.199 74(4)	1.052 88(3)	0.552 18(2)
P(1)	0.081 1(3)	0.728 5(2)	0.403 2(2)
P(2)	0.331 6(3)	1.170 0(2)	0.495 8(2)
N(1)	0.084 8(9)	0.942 5(6)	0.606 4(5)
C(11)	−0.007(1)	0.762 0(9)	0.304 1(7)
C(12)	0.011(1)	0.609 4(8)	0.433 2(8)
C(13)	0.255(1)	0.698(1)	0.371 6(8)
C(21)	0.255(1)	1.229(1)	0.402 4(8)
C(22)	0.373(1)	1.268 3(9)	0.572 3(9)
C(23)	0.498(1)	1.128 3(9)	0.465 4(8)
C(1)	0.141(1)	0.898 8(8)	0.688 1(7)
C(2)	0.165(1)	0.977 9(8)	0.756 5(7)
C(3)	0.290(1)	1.029 2(9)	0.761 5(9)
C(4)	0.312(2)	1.102(1)	0.821(1)
C(5)	0.215(2)	1.124(1)	0.878(1)
C(6)	0.090(2)	1.070(1)	0.876 5(8)
C(7)	0.064(1)	0.995(1)	0.813 1(8)
B	0.683(2)	0.037(1)	0.718(1)
F(1)	0.613(1)	−0.050 8(6)	0.727 8(6)
F(2)	0.790(1)	0.024(1)	0.673 0(8)
F(3)	0.712(2)	0.074(1)	0.792 3(9)
F(4)	0.591(1)	0.096(1)	0.676 0(9)

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