4370 *Inorg. Chem.* **1992,** *31,* 4370–4375

Synthesis and Structure of Trinuclear and Novel Tetranuclear Gold(I) Complexes Derived from 8-Aminoquinoline

Hubert Schmidbaur,* Andreas Kolb, and Peter Bissinger

Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
W-8046 Garching, Germany

Received February 24, 1992

Treatment of 8-aminoquinoline with 1 mol equiv of μ_3-oxotris[(triphenylphosphine)gold(I)] tetrafluoroborate affords μ_3-[8-quinolinaminato(2−)]tris[(triphenylphosphine)gold(I)] tetrafluoroborate (**1**). This triply N-aurated ammonium salt reacts further with 1 equiv of (triphenylphosphine)gold(I) tetrafluoroborate to give the novel μ_3-[8-quinolinaminato-(2−)]tetrakis[(triphenylphosphine)gold(I)] bis(tetrafluoroborate) (**2**). The structures of both compounds have been determined by single-crystal X-ray diffraction. In the trinuclear complex **1**, the three gold atoms are bound exclusively to the 8-amino nitrogen atom of the quinoline, thus putting this nitrogen at the apex of an NAu_3 pyramid. The pyridine N-atom is not attached to any of the gold atoms, and the quinoline ring has free rotation about the C–N(amino) axis, as shown by NMR spectroscopy. In the tetranuclear complex **2**, the triangle of gold atoms is expanded to give a rhomboidal Au_4 unit, with three Au atoms μ^3-bridged by the amino nitrogen atom and the fourth ligated to the pyridine nitrogen center. In solution the compound appears to be fluxional, with the quinolyl group interacting consecutively with all four gold atoms. In both compounds, the gold atoms show close contacts of 3.0 ± 0.1 Å, indicating significant bonding, which is probably the main driving force for the clustering of seemingly closed-shell (d^{10}) gold(I) metal atoms. Crystal data: $\mathbf{1}\cdot C_4H_8O$ triclinic, $P\bar{1}$ (No. 2), $a = 11.292$ (1) Å, $b = 14.774$ (2) Å, $c = 18.652$ (2) Å, $\alpha = 95.07$ (1)°, $\beta = 104.55$ (1)°, $\gamma = 90.84$ (1)°, $Z = 2$, R (R_w) = 0.026 (0.021); $\mathbf{2}\cdot C_4H_8O$ monoclinic, $P2_1/n$ (No. 14), $a = 13.442$ (2) Å, $b = 21.130$ (2) Å, $c = 28.040$ (4) Å, $\beta = 102.80$ (1)°, $Z = 4$, R (R_w) = 0.036 (0.031).

Introduction

Strongly aurating agents, designed to introduce $[LAu]^+$ at a given nucleophilic center, can "gild" the nitrogen atom of *ammonia* to give not only quaternary ammonium salts of the type $[(LAu)_4N]^+X^-$ (L = tertiary phosphine, X^- = a noncoordinating counterion)[1–4] but also salts with the novel[5] hypercoordinate dianions $[(LAu)_5N]^{2+}2X^-$. These dianions have a trigonal-bipyramidal structure for L = PPh_3, as confirmed by X-ray diffraction studies and other methods.[5] Using similar reagents, like $[(LAu)_3O]^+X^-$ or $[LAu]^+X^-$, *primary amines*[6–9] can also be converted into ammonium salts $[RN(AuL)_3]^+X^-$ with a variety of alkyl or aryl groups R. The cations of these products have the expected tetrahedral structure with a tetracoordinate nitrogen atom in the center.[7–9] However, all attempts to accomplish further auration to give the pentacoordinate species $[RN(AuL)_4]^{2+}2X^-$ have failed.[9]

This negative result is at variance with findings for analogous phosphorus compounds, where both *phosphine*[10] *and primary phosphines*[11] could be aurated to give in the final step nonclassical dications $[(LAu)_5P]^{2+}$ and $[RP(AuL)_4]^{2+}$, respectively. While the structure of the former could not yet be determined,[11] the latter was found to have a square-pyramidal geometry at the central phosphorus atom[11] (L = PPh_3 in both cases, R = *o*-Tol).

For *arsine*[1] and *primary arsines*,[11] only tetracoordinate gold derivatives could be observed, with cations of the type $[(LAu)_4As]^+$ exhibiting the completely unexpected square-pyramidal configuration at arsenic.[1] The structure of cations $[RAs(AuL)_3]^+$ has not yet been determined[11] but is expected to have a tetrahedral geometry, as also confirmed[10] for the *phosphorus analogues* $[RP(AuL)_3]^+$.

This body of synthetic and structural information has been interpreted on the basis of novel metal–metal bonding effects ("aurophilicity") in the clusters:[12] Since gold(I) centers with a closed-shell (d^{10}) electronic configuration are not a priori expected to participate in direct metal–metal bonding, the observed phenomena first have to be rationalized in terms of relativistic effects,[12–15] which lead to a strong mixing of $5d^{10}$ and 6s states,[16] thus "breaking up" the $5d^{10}$ block for Au···Au bonding. The ideal interatomic distance for gold–gold interactions appears to be ca. 3.0 Å, as witnessed by a plethora of structural data.[12,17] In all of the above cases of gold clustering around a central element this distance is retained wherever structurally possible.

On the basis of these arguments, the failure of auration experiments with $[RN(AuL)_3]^+$ to give $[RN(AuL)_4]^{2+}$ species must be explained[9] by the small radius of nitrogen (as compared to phosphorus), which does not allow the assembly of a square of gold atoms topped by an RN apex (as found[10] with RP in $[RP(AuL)_4]^{2+}$). Considering that a primary ammonium nitrogen atom thus cannot be sufficient to induce the clustering of four

---

(1) Zeller, E.; Beruda, H.; Kolb, A.; Bissinger, P.; Riede, J.; Schmidbaur, H. *Nature* **1991**, *352*, 141–143.
(2) Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *277*, 143–146.
(3) Perevalova, E. G.; Smyslova, E. I.; Dyadchenko, V. P.; Grandberg, K. I.; Nesmeyanov, A. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1455.
(4) Kress, W. Diss., Univ. Erlangen-Nürnberg, 1983. Brodbeck, A. Diss., Univ. Tübingen, 1990.
(5) Grohmann, A.; Riede, J.; Schmidbaur, H. *Nature* **1990**, *345*, 140–142.
(6) Perevalova, E. G.; Grandberg, K. I.; Smyslova, E. I.; Kuz'mina, L. G.; Korsunskii, V. I.; Kravtsov, D. N. *Organomet. Chem. USSR* **1989**, *2*, 523–526.
(7) Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1990**, *29*, 3336–3341.
(8) Grohmann, A.; Riede, J.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1991**, 783–787.
(9) Grohmann, A. Diss., Techn. Univ. Munich, 1991.
(10) Schmidbaur, H.; Weidenhiller, G.; Steigelmann, O. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 433–435.
(11) Schmidbaur, H.; Zeller, E.; Weidenhiller, G.; Steigelmann, O.; Beruda, H. *Inorg. Chem.* **1992**, *31*, 2370-2376.
(12) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11–21.
(13) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563–578.
(14) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187–2195.
(15) Rösch, N.; Görling, A.; Ellis, D. E.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1357–1359.
(16) Rösch, N.; Görling, A.; Ellis, D. E.; Schmidbaur, H. *Inorg. Chem.* **1991**, *30*, 3986–3994.
(17) Jones, P. G. *Gold Bull.* **1981**, *14*, 102–109; **1981**, *14*, 159–165; **1983**, *16*, 114–119; **1986**, *19*, 46–52.

0020-1669/92/1331-4370$03.00/0

gold atoms in a square, it was decided to introduce at nitrogen a substituent tailor-made to provide auxiliary donor capacity assisting in the bonding of the fourth gold atom. The substituent chosen was the 8-aminoquinolinyl group.

Experimental Section

General Methods. All reactions were carried out in oven-dried glassware using standard inert-atmosphere techniques. All solvents were dried, saturated with nitrogen, and distilled before use. Exposition to direct daylight was avoided if possible.

Equipment. Jeol GX 400 and GX 270 NMR spectrometers (deuterated solvents as internal standards, converted to TMS, for ^{1}H; external aqueous H_3PO_4 for ^{31}P) and a MAT 90 mass spectrometer (*f*ield *d*esorption) were used. Melting points (sealed capillaries in a Büchi apparatus) are uncorrected. Elemental analyses were performed in the microanalytical laboratory of this Institute.

Reagents. μ_3-Oxotris[(triphenylphosphine)gold(I)] tetrafluoroborate[18] and (triphenylphosphine)gold(I) tetrafluoroborate[18] were prepared by following the literature procedures. 8-Aminoquinoline is commercially available.

μ_3-[8-Quinolinaminato(2–)]tris[(triphenylphosphine)gold(I)] Tetrafluoroborate (1). To a suspension of $[Ph_3PAu]_3O^+BF_4^-$ (600 mg, 0.41 mmol) in tetrahydrofuran (30 mL) was added a solution of 8-aminoquinoline (120 mg, 0.83 mmol) in the same solvent (15 mL). The reaction mixture was stirred for 2 h at 20 °C. On addition of the same volume of diethyl ether to the resulting yellow solution a precipitate was obtained, which was filtered out, dried in a vacuum, and recrystallized from dichloromethane/tetrahydrofuran (1:5): yield 620 mg (94%) of pale yellow crystals; mp 169–175 °C dec.

^{1}H NMR (CD_2Cl_2, 20 °C, assignment following standard numbering of quinoline): δ 8.26 ppm (dd, ^3J(HH) = 4.15 Hz, ^4J(HH) = 1.47 Hz, 1 H, H2), 7.91 (dd, ^3J(HH) = 8.30 Hz, ^4J(HH) = 1.46 Hz, 1 H, H4), 7.76 ("dd", N = 6.34, H5), 7.31–6.69 (m, 48 H, C_6H_5 + H3 + H6 + H7). {^{1}H}^{31}P NMR (CD_2Cl_2, 20 °C): δ 28.89 ppm, s. MS (FD, CH_2Cl_2): m/z = 1519.6 [M^+ (cation of **1**)] (100%), 1377.4 [$(Ph_3PAu)_3^+$] (3%), 1061 [$M^+ - Ph_3PAu$] (2%). Anal. Found: C, 47.09; H, 3.20; N, 1.74. Calcd for $C_{63}H_{51}Au_3BF_4N_2P_3$ (1606.75): C, 47.00; H, 3.28; N, 1.82; F, 4.77.

μ_3-[8-Quinolinaminato(2–)]tetrakis[(triphenylphosphine)gold(I)] Bis(tetrafluoroborate) (2). A solution of **1** (400 mg, 0.25 mmol) in tetrahydrofuran (15 mL) was treated with a freshly prepared solution of $Ph_3PAu^+BF_4^-$ (from 124 mg of Ph_3PAuCl and 48 mg of $AgBF_4$, 0.25 mmol each in 15 mL of the same solvent). After the reaction mixture was stirred at 20 °C for 1 h, the yellow precipitate was filtered out, dried in a vacuum, and recrystallized from dichloromethane/tetrahydrofuran (1:5): yield 360 mg (67%) of yellowish-green crystals; mp 150–155 °C dec.

^{1}H NMR (CD_2Cl_2, 20 °C): δ 9.46 ppm (dd, ^3J(HH) = 4.88 Hz, ^4J(HH) = 1.22 Hz, 1 H, H2), 8.72 (dd, ^3J(HH) = 8.54 Hz, ^4J(HH) = 1.22 Hz, 1 H, H4), 8.65 ("d", N = 7.33 Hz, 1 H, H5); 8.10 (dd, ^3J(HH) = 8.54 Hz, ^4J(HH) = 4.86 Hz, 1 H, H3); 7.84 ("t", N = 7.93 Hz, 1 H, H7), 7.75 ("d", N = 7.94 Hz, 1 H, H6), 7.41–7.11 (m, 60 H, C_6H_5). {^{1}H}^{31}P NMR (CD_2Cl_2, 20 °C): δ 27.65 ppm, s. {^{1}H}^{31}P NMR (CD_2Cl_2, –70 °C): δ 26.8 ppm, s. MS (FD, CH_2Cl_2): m/z = 989.7 [M^{2+} (dication of **2**)] (100%), 1061.2 [$M^+ - Ph_3PAu$] (4%). Anal. Found: C, 45.20; H, 3.09; N, 1.30; F, 7.06. Calcd for $C_{81}H_{66}Au_4B_2F_8N_2P_4$ (2152.80): C, 45.4; H, 3.34; N, 1.01; F, 7.04.

Crystal Structure Determination. A suitable crystal of compound **1** (**2**) was sealed under argon at dry ice temperature into a glass capillary and examined directly on the diffractometer. Reduced cell calculation did not indicate any higher symmetry. The measured 13 085 (15 921) reflections were corrected for Lorentz and polarization effects and empirically for absorption effects. From 13 027 (15 153) independent structure factors 11 159 (11 657) with $F_o \geq 2.0\sigma(F_o)$ ($4.0\sigma(F_o)$) were taken as "observed" and used for all calculations. The structures were solved by direct methods (SHELXS-86) and completed by difference Fourier syntheses (SHELX-76). All non-hydrogen atoms were refined by using anisotropic thermal displacement parameters; the hydrogen atoms were included in the structure factor calculations with fixed atomic contributions (U_{iso} = 0.05 Å^2). The final R and R_w values were calculated for 730 (890) refined parameters, with residual electron density +0.70/–0.93 e/Å^3 (+3.47/–1.19 e/Å^3). Crystal data are listed in Table I. The fractional atomic coordinates and equivalent isotropic displacement parameters are presented in Tables II and III.

Table I. Crystal Data

	$1 \cdot C_4H_8O$	$2 \cdot C_4H_8O$
formula	$C_{63}H_{51}Au_3BF_4N_2P_3 \cdot C_4H_8O$	$C_{81}H_{66}Au_4B_2F_8N_2P_4 \cdot C_4H_8O$
molecular mass	1678.857	2224.923
temp (°C)	–41	–40
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	11.292 (1)	13.442 (2)
b (Å)	14.774 (2)	21.130 (2)
c (Å)	18.652 (2)	28.040 (4)
α (deg)	95.07 (1)	90
β (deg)	104.55 (1)	102.80 (1)
γ (deg)	90.84 (1)	90
V (Å^3)	2997.9	7766.3
ρ_{calc} (g cm^{-3})	1.860	1.903
Z	2	4
$F(000)$ (e)	1612	4544
μ(Mo Kα) (cm^{-1})	74.3	76.6
transm coeff	0.819–0.999	0.867–0.999
radiation (λ = 0.710 69 Å) graphite monochromator)	Mo Kα	Mo Kα
$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.026	0.036
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.021	0.031
k, with $w = k(\sigma^2(F_o) + F_o^2)$	1.8557	2.2193

Results

Synthesis and Structure of μ_3-[8-Quinolinaminato(2–)]tris[(triphenylphosphine)gold(I)] Tetrafluoroborate (1). Treatment of a suspension of μ_3-oxotris[(triphenylphosphine)gold(I)] tetrafluoroborate in tetrahydrofuran with 1 equiv (or an excess) of 8-aminoquinoline leads to a complete substitution of the N-bound hydrogen atoms of the amine by (triphenylphosphine)gold(I) groups. The product (**1**) is obtained, in high yield (94%), as a pale yellow, crystalline, air-stable material (eq 1).

$$(8\text{-}C_9H_6N)NH_2 + [(Ph_3PAu)_3O]^+BF_4^- \rightarrow H_2O + \underset{\mathbf{1}}{[(8\text{-}C_9H_6N)N(AuPPh_3)_3]^+BF_4^-} \quad (1)$$

The compound is readily identified by it elemental analysis, by mass spectrometry, and by NMR spectroscopy. In the mass spectrum (by field desorption from dichloromethane) the cation of the salt is registered as the parent peak in high intensity, associated with fragment ions of the expected pattern. In the ^{1}H NMR spectrum (in dichloromethane-d_2) some of the quinoline hydrogen signals are clearly resolved, while others are obscured by the phenyl multiplet resonances. The ^{31}P spectrum exhibits only a single line for three equivalent phosphorus atoms. This result suggests that all three phosphorus atoms are attached to the amino nitrogen atom, with the quinolinyl donor site not yet engaged in gold coordination.

This assumption was confirmed by a single-crystal X-ray analysis of the compound. Crystals of $1 \cdot C_4H_8O$ (from CH_2Cl_2/THF) are triclinic, space group $P\bar{1}$, with Z = 2 formula units in the unit cell. The structure is built from independent μ_3-[8-quinolinaminato(2–)]tris[(triphenylphosphine)gold(I)] cations and tetrafluoroborate anions. The cations have the expected pseudotetrahedral configuration with the amino nitrogen atom in the center of the trigonal pyramid, three gold atoms at the base, and the *peri* carbon atom of the quinoline ring at the apex (Figure 1a).

The quinoline plane is roughly perpendicular to the plane of the gold triangle, and the conformation is such that the heterocycle is not eclipsed with any of the three N–Au–P groups. The quinoline donor atom (N2) is thus not oriented toward one of the gold atoms, and its distance from the nearest gold neighbor (Au1) is 2.805 (4) Å, not suggesting any significant donor/acceptor interaction (Figure 1b). By contrast (and as internal references)

---

(18) Nesmeyanov, A. N.; Perevalova, A. G.; Struchkov, Yu. T.; Antipin, M. Yu.; Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* **1980**, *201*, 343.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $1 \cdot C_4H_8O$[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
Au1	0.16474 (1)	0.43568 (1)	0.25968 (1)	0.023
Au2	0.06936 (1)	0.36395 (1)	0.09457 (1)	0.024
Au3	−0.05058 (1)	0.52874 (1)	0.17162 (1)	0.022
P1	0.2011 (1)	0.36817 (7)	0.36514 (6)	0.025
P2	0.0298 (1)	0.21935 (7)	0.04624 (6)	0.027
P3	−0.22719 (9)	0.57842 (7)	0.19168 (6)	0.025
N1	0.1150 (3)	0.4860 (2)	0.1566 (2)	0.023
N2	0.2411 (4)	0.1685 (2)	0.2667 (3)	0.041
B	0.3773 (5)	0.0163 (4)	0.7462 (4)	0.045
F1	0.2590 (3)	0.0436 (2)	0.7254 (2)	0.061
F2	0.4408 (3)	0.0387 (2)	0.6953 (2)	0.070
F3	0.3784 (3)	−0.0761 (2)	0.7479 (2)	0.073
F4	0.4370 (4)	0.0579 (3)	0.8138 (2)	0.091
C1	0.1886 (4)	0.5558 (3)	0.1387 (3)	0.025
C2	0.2003 (4)	0.5606 (3)	0.0677 (3)	0.036
C3	0.2694 (6)	0.6317 (4)	0.0498 (4)	0.045
C4	0.3283 (5)	0.6980 (4)	0.1032 (5)	0.044
C5	0.3199 (4)	0.6958 (3)	0.1767 (4)	0.037
C6	0.3755 (6)	0.7626 (4)	0.2333 (6)	0.058
C7	0.3671 (7)	0.7545 (4)	0.3022 (6)	0.063
C8	0.2969 (6)	0.6821 (4)	0.3185 (4)	0.060
C9	0.2505 (4)	0.6241 (3)	0.1961 (3)	0.031
C111	0.3519 (4)	0.3209 (3)	0.3935 (2)	0.028
C112	0.4510 (4)	0.3774 (3)	0.4326 (3)	0.037
C113	0.5661 (4)	0.3433 (4)	0.4528 (3)	0.050
C114	0.5845 (5)	0.2540 (4)	0.4318 (4)	0.053
C115	0.4888 (5)	0.1985 (4)	0.3909 (4)	0.053
C116	0.3705 (4)	0.3209 (3)	0.3720 (3)	0.041
C121	0.0924 (4)	0.2748 (3)	0.3596 (2)	0.028
C122	0.0542 (4)	0.2525 (3)	0.4217 (3)	0.036
C123	−0.0308 (5)	0.1816 (3)	0.4153 (3)	0.042
C124	−0.0767 (5)	0.1312 (3)	0.3486 (3)	0.042
C125	−0.0374 (5)	0.1520 (4)	0.2875 (3)	0.049
C126	0.0460 (5)	0.2231 (4)	0.2925 (3)	0.042
C131	0.1897 (4)	0.4454 (3)	0.4444 (2)	0.026
C132	0.2389 (4)	0.4261 (3)	0.5182 (2)	0.032
C133	0.2234 (4)	0.4858 (3)	0.5764 (3)	0.040
C134	0.1576 (4)	0.5635 (3)	0.5620 (3)	0.037
C135	0.1101 (4)	0.5833 (3)	0.4892 (3)	0.038
C136	0.1267 (4)	0.5239 (3)	0.4310 (2)	0.032
C211	−0.1221 (4)	0.1752 (3)	0.0438 (2)	0.027
C212	−0.1866 (4)	0.1132 (3)	−0.0135 (3)	0.035
C213	−0.2998 (4)	0.0764 (3)	−0.0113 (3)	0.039
C214	−0.3459 (4)	0.0984 (3)	0.0489 (3)	0.043
C215	−0.2842 (5)	0.1607 (4)	0.1054 (3)	0.047
C216	−0.1722 (4)	0.1998 (3)	0.1029 (3)	0.042
C221	0.0505 (4)	0.1897 (3)	−0.0459 (2)	0.025
C222	−0.0114 (4)	0.2387 (3)	−0.1034 (2)	0.028
C223	−0.0042 (4)	0.2151 (3)	−0.1752 (2)	0.034
C224	0.0679 (4)	0.1444 (3)	−0.1909 (2)	0.032
C225	0.1328 (4)	0.0975 (3)	−0.1336 (3)	0.032
C226	0.1227 (4)	0.1191 (3)	−0.0611 (2)	0.031
C231	0.1352 (4)	0.1504 (3)	0.1075 (2)	0.026
C232	0.0954 (4)	0.0736 (3)	0.1340 (2)	0.033
C233	0.1798 (4)	0.0238 (3)	0.1815 (3)	0.038
C234	0.3027 (5)	0.0506 (3)	0.2025 (3)	0.040
C235	0.3411 (4)	0.1271 (3)	0.1759 (3)	0.043
C236	0.2589 (4)	0.1777 (3)	0.1297 (3)	0.037
C311	−0.3260 (4)	0.4894 (3)	0.2085 (2)	0.027
C312	−0.4501 (4)	0.5025 (3)	0.2033 (3)	0.035
C313	−0.5200 (4)	0.4354 (4)	0.2231 (3)	0.041
C314	−0.4688 (5)	0.3564 (3)	0.2474 (3)	0.042
C315	−0.3469 (5)	0.3416 (3)	0.2512 (3)	0.043
C316	−0.2748 (4)	0.4076 (3)	0.2318 (3)	0.036
C321	−0.2019 (4)	0.6614 (3)	0.2719 (2)	0.029
C322	−0.0821 (4)	0.6840 (3)	0.3129 (2)	0.034
C323	−0.0602 (5)	0.7510 (3)	0.3721 (3)	0.041
C324	−0.1571 (6)	0.7945 (3)	0.3903 (3)	0.045
C325	−0.2754 (5)	0.7702 (3)	0.3515 (3)	0.046
C326	−0.2984 (4)	0.7042 (3)	0.2933 (3)	0.040
C331	−0.3177 (4)	0.6331 (3)	0.1133 (2)	0.028
C332	−0.3394 (4)	0.7240 (3)	0.1151 (3)	0.037
C333	−0.4021 (5)	0.7616 (4)	0.0506 (3)	0.047
C334	−0.4409 (5)	0.7083 (4)	−0.0144 (3)	0.048
C335	−0.4185 (6)	0.6178 (4)	−0.0159 (3)	0.056
C336	−0.3577 (5)	0.5788 (4)	0.0467 (3)	0.049
O	0.1872 (4)	0.8963 (3)	0.4609 (3)	0.080
C1F	0.2284 (9)	0.9713 (5)	0.5140 (4)	0.087
C2F	0.3028 (8)	1.0316 (5)	0.4790 (5)	0.093
C3F	0.268 (1)	0.9991 (6)	0.3999 (5)	0.102
C4F	0.1696 (8)	0.9263 (5)	0.3887 (4)	0.09

[a] $U(\mathrm{eq}) = (U1U2U3)^{1/3}$, where $U1$, $U2$, and $U3$ are the eigenvalues of the U(*ij*) matrix. Esd's are in parentheses.

the three N–Au distances to the central nitrogen atom (N1) are much shorter, with values of 2.071 (3), 2.040 (3), and 2.059 (3) Å for gold atoms Au1, Au2, and Au3, respectively. Coordination of the quinoline nitrogen N1 to Au1 is also ruled out by the quasi-linearity of the N1–Au1–P1 triplet [173.1 (1)°], which does not differ from the situation at N1–Au2–P2 [169.7 (1)°] and at N1–Au3–P3 [177.9 (1)°].

It should be remembered here that the ^{31}P NMR data for **1** indicate free rotation of the quinolinyl group about the C–N1 axis, also ruling out "static" N2–Au coordination.

It must be taken as the most significant result, however, that the Au–N–Au angles within the tetrahedron are all much smaller than the tetrahedral standard of 109.4°: Au1–N1–Au2 = 97.1 (1), Au2–N1–Au3 = 102.9 (1), and Au1–N1–Au3 = 93.1 (1)°. Through these small angles short Au···Au contacts of Au1···Au2 = 3.081 (1), Au2···Au3 = 3.207 (1), and Au1···Au3 = 2.998 (1) Å are secured at the basis of the pyramid. It thus appears that Au···Au interactions are strongly influencing the structure of this triaurioammonium salt, as previously observed in all other compounds of this type.[7–8] It is therefore also not surprising that the reaction according to eq 1 does not yield *partially* aurated quinolinylamines, even if a molar excess of this amine is added to the reaction mixture. The triply aurated species is clearly the most favored product. Selected bond distances and angles for **1** are summarized in Table IV.

Synthesis and Structure of μ_3-[8-Quinolinaminato(2–)]tetrakis[(triphenylphosphine)gold(I)] Bis(tetrafluoroborate) (2). Treatment of **1** with 1 equiv of $[Ph_3PAu]^+BF_4^-$ in tetrahydrofuran affords the 1:1 addition compound in good yield (67%) as yellowish-green, air-stable crystals (eq 2). The stoichiometry of

$$(C_9H_6N)N[AuPPh_3]_3{}^+BF_4^- + [Ph_3PAu]^+BF_4^- \rightarrow \{(C_9H_6N)N[AuPPh_3]_4\}^{2+}(BF_4^-)_2 \quad (2)$$

2

this product is established by elemental analysis and *f*ield *d*esorption *m*ass *s*pectrometry. FD-MS (from CH_2Cl_2) shows the *di*cation at $m/z = 989.7$ as the parent peak in high intensity.

The proton NMR spectrum (in CD_2Cl_2) features some of the quinoline protons well separated from the multiplet of the phenyl resonances, but assignments are only tentative owing to the complexity of the pattern (Experimental Section). The proton-decoupled ^{31}P spectrum exhibits only one line both at room temperature and at −70 °C (δ = 27.2 ± 0.4 ppm). This result suggests the presence of four structurally equivalent Ph_3PAu groups, but virtual equivalence owing to rapid site exchange in solution with a very low activation barrier cannot be ruled out. Limited solubility precluded experiments at temperatures below −70 °C.

The crystal structure analysis clarified this point at least for the solid state. The compound crystallizes from CH_2Cl_2/THF with one molecule of crystal tetrahydrofuran. Crystals of $2 \cdot C_4H_8O$ are monoclinic, space group $P2_1/n$, with four formula units in the unit cell. The structure is built from independent *di*cations, two tetrafluoroborate anions, and one solvent molecule. The configuration of the dication is shown in Figure 2. It appears that the fourth $[Ph_3PAu]^+$ unit has been attached to the cation

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2**$\cdot C_4H_8O$[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2	atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
Au1	0.93280 (2)	0.14273 (1)	0.18814 (1)	0.022	C215	1.2635 (8)	0.3400 (5)	0.3206 (4)	0.058
Au2	1.02415 (2)	0.26761 (1)	0.17907 (1)	0.024	C216	1.2115 (7)	0.3321 (4)	0.2731 (4)	0.046
Au3	0.81694 (2)	0.29220 (1)	0.12147 (1)	0.020	C221	1.1928 (6)	0.3711 (4)	0.1458 (3)	0.028
Au4	0.72120 (2)	0.16364 (1)	0.12655 (1)	0.022	C222	1.2860 (6)	0.3993 (4)	0.1487 (3)	0.035
P1	1.0081 (2)	0.04769 (9)	0.20551 (8)	0.025	C223	1.2926 (7)	0.4572 (4)	0.1242 (3)	0.038
P2	1.1834 (2)	0.2967 (1)	0.17670 (8)	0.027	C224	1.2068 (7)	0.4846 (4)	0.0980 (3)	0.044
P3	0.7579 (2)	0.36664 (9)	0.06480 (7)	0.023	C225	1.1138 (7)	0.4580 (4)	0.0962 (3)	0.045
P4	0.7264 (2)	0.13149 (9)	0.05101 (7)	0.025	C226	1.1069 (6)	0.4006 (4)	0.1195 (3)	0.039
B1	0.6772 (9)	0.2298 (5)	0.4333 (4)	0.045	C231	1.2051 (5)	0.2390 (4)	0.1466 (3)	0.026
F11	0.6745 (5)	0.2027 (3)	0.4776 (2)	0.070	C232	1.2803 (6)	0.1825 (4)	0.1707 (3)	0.037
F12	0.7522 (4)	0.2023 (3)	0.4142 (2)	0.063	C233	1.3306 (7)	0.1373 (4)	0.1486 (4)	0.048
F13	0.5854 (4)	0.2181 (3)	0.4019 (2)	0.073	C234	1.3472 (7)	0.1491 (5)	0.1025 (4)	0.048
F14	0.6958 (6)	0.2926 (3)	0.4400 (3)	0.086	C235	1.3136 (7)	0.2039 (5)	0.0782 (4)	0.050
B2	0.5246 (4)	0.0258 (3)	0.8067 (2)	0.175	C236	1.2649 (6)	0.2486 (4)	0.1005 (3)	0.037
F21	0.6242 (5)	0.0249 (4)	0.8321 (3)	0.166	C311	0.6211 (6)	0.3747 (4)	0.0527 (3)	0.028
F22	0.5020 (7)	−0.0301 (3)	0.7819 (3)	0.202	C312	0.5683 (6)	0.3462 (4)	0.0852 (3)	0.034
F23	0.5105 (7)	0.0750 (4)	0.7740 (3)	0.223	C313	0.4629 (6)	0.3522 (5)	0.0784 (4)	0.043
F24	0.4618 (6)	0.0334 (5)	0.8386 (3)	0.255	C314	0.4084 (6)	0.3850 (5)	0.0386 (4)	0.045
N1	0.8772 (4)	0.2361 (3)	0.1816 (2)	0.022	C315	0.4600 (7)	0.4135 (5)	0.0061 (4)	0.046
N2	0.6918 (4)	0.1800 (3)	0.1965 (2)	0.022	C316	0.5641 (6)	0.4087 (4)	0.0134 (3)	0.036
C1	0.8373 (5)	0.2521 (3)	0.2238 (3)	0.022	C321	0.7930 (6)	0.3574 (4)	0.0065 (3)	0.025
C3	0.8819 (6)	0.2966 (4)	0.2565 (3)	0.031	C322	0.7274 (6)	0.3301 (4)	−0.0337 (3)	0.034
C3	0.8448 (6)	0.3107 (4)	0.2990 (3)	0.033	C323	0.7617 (7)	0.3191 (4)	−0.0766 (3)	0.041
C4	0.7638 (6)	0.2791 (4)	0.3084 (3)	0.030	C324	0.8583 (7)	0.3345 (4)	−0.0794 (3)	0.042
C5	0.7133 (6)	0.2335 (4)	0.2745 (3)	0.027	C325	0.9238 (7)	0.3619 (4)	−0.0397 (3)	0.042
C6	0.6294 (6)	0.1985 (4)	0.2836 (3)	0.032	C326	0.8902 (6)	0.3728 (4)	0.0032 (3)	0.037
C7	0.5809 (6)	0.1572 (4)	0.2506 (3)	0.035	C331	0.8086 (5)	0.4439 (3)	0.0864 (3)	0.022
C8	0.6133 (6)	0.1497 (4)	0.2059 (3)	0.034	C332	0.7980 (6)	0.4955 (4)	0.0546 (3)	0.036
C9	0.7471 (5)	0.2222 (3)	0.2310 (3)	0.022	C333	0.8344 (6)	0.5541 (4)	0.0715 (4)	0.037
C111	0.9355 (6)	−0.0051 (4)	0.2353 (3)	0.026	C334	0.8804 (6)	0.5624 (4)	0.1201 (4)	0.039
C112	0.9787 (6)	−0.0591 (4)	0.2587 (4)	0.042	C421	0.6288 (6)	0.1661 (4)	0.0028 (3)	0.029
C113	0.9201 (8)	−0.1015 (5)	0.2794 (4)	0.054	C336	0.5867 (6)	0.4534 (4)	0.1352 (3)	0.031
C114	0.8191 (7)	−0.0895 (5)	0.2770 (4)	0.048	C411	0.8470 (6)	0.1490 (4)	0.0364 (3)	0.026
C115	0.7744 (7)	−0.0375 (5)	0.2520 (4)	0.052	C412	0.8593 (7)	0.1894 (4)	−0.0002 (4)	0.042
C116	0.8331 (7)	0.0047 (4)	0.2317 (4)	0.046	C413	0.9550 (7)	0.2044 (4)	−0.0077 (4)	0.047
C121	1.1346 (6)	0.0587 (4)	0.2446 (3)	0.028	C414	1.0397 (7)	0.1814 (4)	0.0222 (3)	0.040
C122	1.2100 (6)	0.0120 (4)	0.2498 (3)	0.036	C415	1.0308 (7)	0.1412 (5)	0.0595 (3)	0.048
C123	1.3069 (7)	0.0240 (5)	0.2786 (3)	0.042	C416	0.9342 (7)	0.1249 (5)	0.0665 (3)	0.038
C124	1.3285 (7)	0.0825 (5)	0.3008 (3)	0.045	C421	0.6288 (6)	0.1661 (4)	0.0028 (3)	0.029
C125	1.2550 (7)	0.1286 (5)	0.2958 (3)	0.045	C422	0.5606 (6)	0.2095 (4)	0.0147 (3)	0.032
C126	1.1585 (6)	0.1168 (4)	0.2683 (3)	0.038	C423	0.4867 (6)	0.2368 (4)	−0.0222 (3)	0.040
C131	1.0294 (6)	0.0028 (4)	0.1531 (3)	0.029	C424	0.4797 (7)	0.2202 (4)	−0.0707 (3)	0.042
C132	0.9561 (6)	−0.0387 (4)	0.1295 (3)	0.038	C425	0.5489 (7)	0.1764 (5)	−0.0820 (3)	0.044
C133	0.9718 (8)	−0.0688 (5)	0.0871 (4)	0.050	C426	0.6222 (7)	0.1494 (4)	−0.0462 (3)	0.039
C134	1.0573 (9)	−0.0571 (5)	0.0700 (4)	0.055	C431	0.7082 (6)	0.0470 (4)	0.0452 (3)	0.029
C135	1.1306 (9)	−0.0168 (5)	0.0945 (4)	0.060	C432	0.7522 (7)	0.0115 (4)	0.0142 (3)	0.042
C136	1.1183 (7)	0.0131 (4)	0.1368 (3)	0.043	C433	0.7326 (8)	−0.0525 (5)	0.0093 (4)	0.049
C211	1.2591 (6)	0.3070 (4)	0.2385 (3)	0.029	C434	0.6705 (9)	−0.0820 (5)	0.0346 (4)	0.056
C212	1.3610 (6)	0.2910 (4)	0.2524 (3)	0.038	C435	0.629 (1)	−0.0472 (5)	0.0656 (5)	0.066
C213	1.4130 (7)	0.2991 (5)	0.3004 (4)	0.051	C436	0.6467 (8)	0.0178 (4)	0.0714 (4)	0.051
C214	1.3640 (9)	0.3231 (5)	0.3340 (4)	0.054	O	0.94570	0.13930	0.33010	0.057
					C(no. 1)	0.91540	0.02980	0.37720	0.022
					C(no. 2)	1.00120	0.05030	0.39040	0.058
					C(no. 3)	0.85850	0.09320	0.34940	0.085
					C(no. 4)	1.02520	0.11240	0.37070	0.160

[a] See footnote *a* of Table II.

of compound **1** not only by utilizing the donor capacity of the quinoline nitrogen atom (N2) but also by establishing short contacts to two gold atoms of one edge of the former Au_3 triangle. This triangle (Figure 1) has thereby been enlarged to give a distorted rhombus with almost equidistant Au···Au contacts (Figure 2).

While the distance between the ammonium nitrogen atom N1 and the newly added gold atom Au4 [2.773 (6) Å] is too long to be considered a bonding contact, the distance between the quinoline nitrogen atom N2 and Au4 [2.115 (6) Å] is indicating a normal donor/acceptor bond. This interpretation is supported by the quasi-linearity of N2–Au4–P4 [168.1 (2)°]. Deviations from linearity are also small for the other three N1–Au–P triples (Table V), resembling the situation in **1**.

The Au···Au distances of the gold rhombus fall in two pairs, with the outer edges of the ammonium-capped gold triangle slightly shorter [Au1–Au2 = 2.945 (1), Au2–Au3 = 2.940 (1) Å] and the distances to the quinoline-supported gold atom slightly longer [Au2–Au4 = 3.015 (1), Au3–Au4 = 3.023 (1) Å]. There can be no doubt that these distances represent significant gold–gold interactions.[12]

In the solid state the (triphenylphosphine)gold units in the dication of **2** are clearly structurally inequivalent, at least in the ratio 1:2:1. The NMR equivalence of the phosphine ligands observed for solutions of the compound in polar solvents (CD_2Cl_2) must therefore be ascribed to a dynamic phenomenon. For the site exchange we favor a model where the $[Ph_3PAu]^+$ units, and not only the Ph_3P ligands, are subject to a scrambling on the NMR time scale. The most likely mechanism is a dissociation of the pyridine donor from Au4, followed by a shift of the ammonium nitrogen to a different triplet of gold atoms and finally a coordination of the pyridine donor to the remaining gold atom.

The dimensions of the triphenylphosphine ligands and of the quinolinyl group show no anomalies.

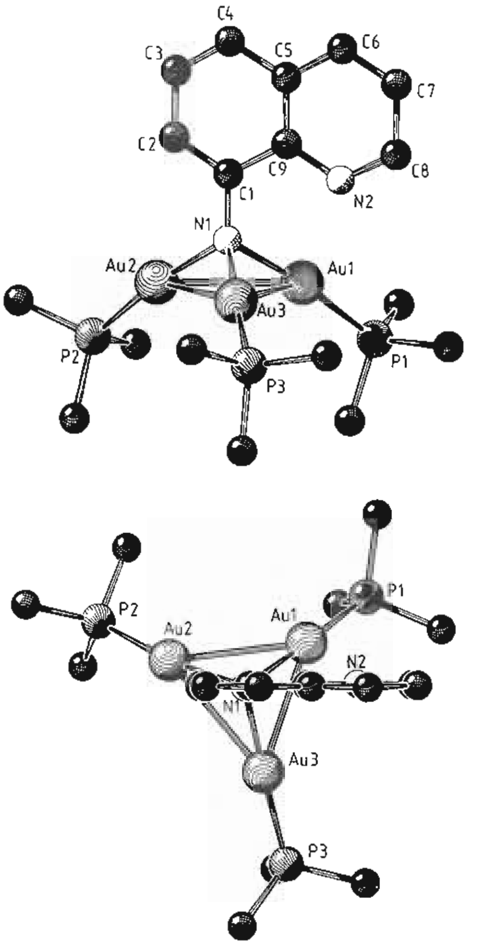

Figure 1. Structure of the cation in compound **1**, with atomic numbering: (a, top) Side projection; (b, bottom) projection perpendicular to the plane of the gold atoms. (SCHAKAL was used, with phenyl rings of the triphenylphosphine ligands omitted for clarity, except for the ipso carbon atoms.)

Table IV. Selected Bond Distances (Å) and Angles (deg) of Compound **1**[a]

	Distances		
Au1–P1	2.233 (1)	N1–C1	1.427 (5)
Au2–P2	2.237 (1)	Au1···N2	2.805 (4)
Au3–P3	2.242 (1)	Au1···Au2	3.081 (1)
Au1–N1	2.071 (3)	Au1···Au3	2.998 (1)
Au2–N1	2.040 (3)	Au2···Au3	3.207 (1)
Au3–N1	2.059 (3)		
	Angles		
N1–Au1–P1	173.1 (1)	Au1–N1–Au2	97.1 (1)
N1–Au2–P2	169.7 (1)	Au1–N1–Au3	93.1 (1)
N1–Au3–P3	177.9 (1)	Au2–N1–Au3	102.9 (1)
C1–N1–Au1	120.3 (3)	N1–C1–C2	121.8 (4)
C1–N1–Au2	123.9 (3)	N1–C1–C9	119.5 (4)
C1–N1–Au3	114.0 (2)		

[a] For atomic numbering, see Figure 1a.

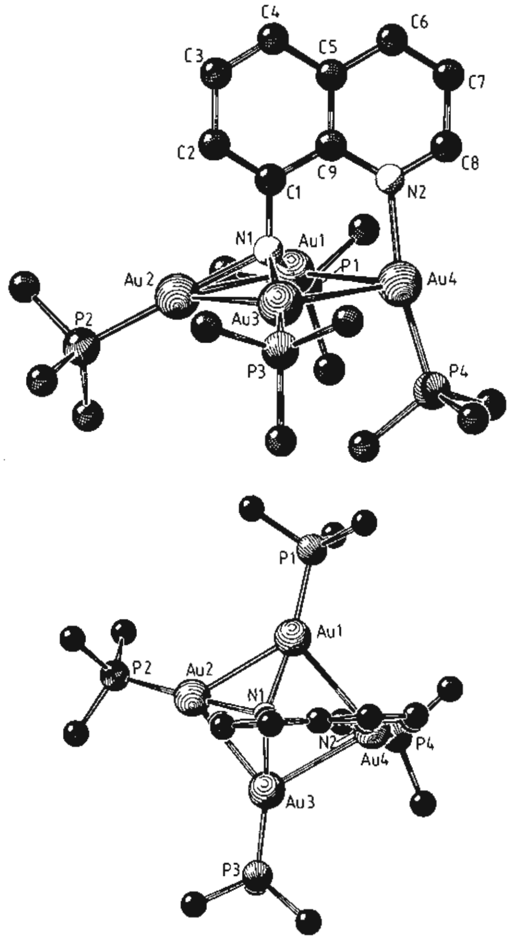

Figure 2. Structure of the dication in compound **2**·C_4H_8O, with atomic numbering: (a, top) Side projection; (b, bottom) projection perpendicular to the plane of the gold atoms. (SCHAKAL was used, with phenyl rings of the triphenylphosphine ligands omitted for clarity, except for the ipso carbon atoms.)

Table V. Selected Bond Distances (Å) and Angles (deg) of Compound **2**[a]

	Distances		
Au1–P1	2.253 (2)	Au3–N1	2.074 (6)
Au2–P2	2.242 (2)	Au4–N2	2.115 (6)
Au3–P3	2.252 (2)	N1–C1	1.442 (9)
Au4–P4	2.240 (2)	Au1···Au2	2.945 (1)
Au1–N1	2.103 (6)	Au1···Au4	3.015 (1)
Au2–N1	2.101 (5)	Au2···Au3	2.940 (1)
		Au3···Au4	3.023 (1)
	Angles		
N1–Au1–P1	171.4 (2)	Au1–N1–Au2	88.9 (2)
N1–Au2–P2	177.4 (2)	Au1–N1–Au3	132.4 (3)
N1–Au3–P3	170.5 (2)	Au2–N1–Au3	89.5 (2)
N2–Au4–P4	168.1 (2)	Au1–N1–Au4	75.0 (2)
C1–N1–Au1	109.8 (4)	Au2–N1–Au4	139.2 (3)
C1–N1–Au2	118.5 (4)	Au3–N1–Au4	75.6 (2)
C1–N1–Au3	112.5 (4)	N1–C1–C2	121.8 (7)
C1–N1–Au4	102.3 (4)	N1–C1–C9	119.8 (6)

[a] For atomic numbering, see Figure 2a.

Discussion

The results of this study have demonstrated that a nitrogen-capped triangle of gold atoms in triply aurated primary ammonium cations $RN[AuL]_3^+$ can be enlarged to give a rhomboid gold quadrangle if auxiliary donor capacity is provided in the substituent R of the primary amine. In contrast to the situation with the analogous phosphonium cations $RP[AuL]_3^+$, tetraauration of the ammonium nitrogen center is not possible in the absence of such a donor center, owing to the small radius of the nitrogen atom as compared to phosphorus. While in the hypercoordinate dications $RP[AuL]_4^{2+}$ a square of gold atoms is η^4-capped by the phosphorus atom to give a regular PAu_4 square pyramid, in the tetraaurated quinolinylammonium dication (**2**) the rhombus of gold atoms is supported by the η^1/η^3-coordinated aminoquinolinyl substituent (Figure 2). In the triply aurated precursor (**1**), it is only the ammonium nitrogen atom which functions as the η^3-donor for the triangle of gold atoms, and the quinolinyl nitrogen atom is not yet engaged in complexation (Figure 1).

All of the multiaurated nitrogen compounds are characterized by a surprising ease of formation and a high thermal and chemical stability. This clustering phenomenon of formally (d^{10}) closed-shell cations $[AuL]^+$ is unexpected in classical bonding concepts and must be ascribed to Au$\cdots$Au interactions on the basis of metal orbital energies modified by relativistic effects.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft (Leibniz-Programm), by the Fonds der Chemischen Industrie, and—through the donation of chemicals—by Hoechst AG, Degussa AG, and Heraeus GmbH. Mr. J. Riede is thanked for carefully compiling the X-ray data sets, and Professor F. H. Kreissl for mass spectra.

Supplementary Material Available: Tables of atomic coordinates, anisotropic temperature factors, and bond lengths and angles and ORTEP drawings (27 pages). Ordering information is given on any current masthead page.