

The Elusive Structures of Pentakis[(triphenylphosphine)gold]ammonium(2+) Bis[tetrafluoroborate(1-)][‡]

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{Pentakis[(triphenylphosphine)gold(I)]ammonium(2+)} bis[(tetrafluoroborate)(1-)] was prepared from {tetrakis[(triphenylphosphine)gold(I)]ammonium(1+)} [tetrafluoroborate(1-)] and [(triphenylphosphine)gold(I)] tetrafluoroborate in hexamethyl phosphoric triamide and tetrahydrofuran at 20 °C in 53% yield and crystallized from dichloromethane as the new solvate {[Ph₃P)Au]₅N}₃[BF₄]₆[CH₂Cl₂]₄. The crystal structure of this product has been determined by single-crystal X-ray methods [monoclinic, *P*2₁/*n*, *a* = 34.200(3), *b* = 15.285(1), *c* = 53.127(3) Å, β = 107.262(2)°, *V* = 26521(3) Å³, *Z* = 12, at 153 K]. The lattice contains three independent trinuclear dications that have no crystallographically imposed symmetry and are mutually similar in their molecular structure. The geometry of the [Au₅N] core with pentacoordinate nitrogen atoms is intermediate between trigonal-bipyramidal and square pyramidal with severe distortions to minimize the Au–Au distances along some of the edges of the polyhedra. The three structures are thus different from that found previously in the tetrahydrofuran solvate {[Ph₃P)Au]₅N}(BF₄)₂(C₄H₈O)₂, where the geometry of the same trinuclear dication is closer to the trigonal-bipyramidal reference model. The new results are discussed in the light of the structures of tetra(gold)ammonium cations in salts of the type {[Ph₃P)Au]₄N}⁺X⁻ and of related tetra-, penta-, and hexacoordinate poly(gold)phosphonium, -arsonium, -sulfonium, and -selenonium cations.

Introduction

The discovery of hypercoordination of carbon by gold atoms in exceedingly stable homoleptic complexes^{1,2} has prompted systematic investigations of the analogous boron and nitrogen compounds.³ However, whereas for carbon a fair number of other carbon-centered gold clusters could be added to the original prototypes,^{4–12} the search for boron¹³ and nitrogen compounds was less fruitful.

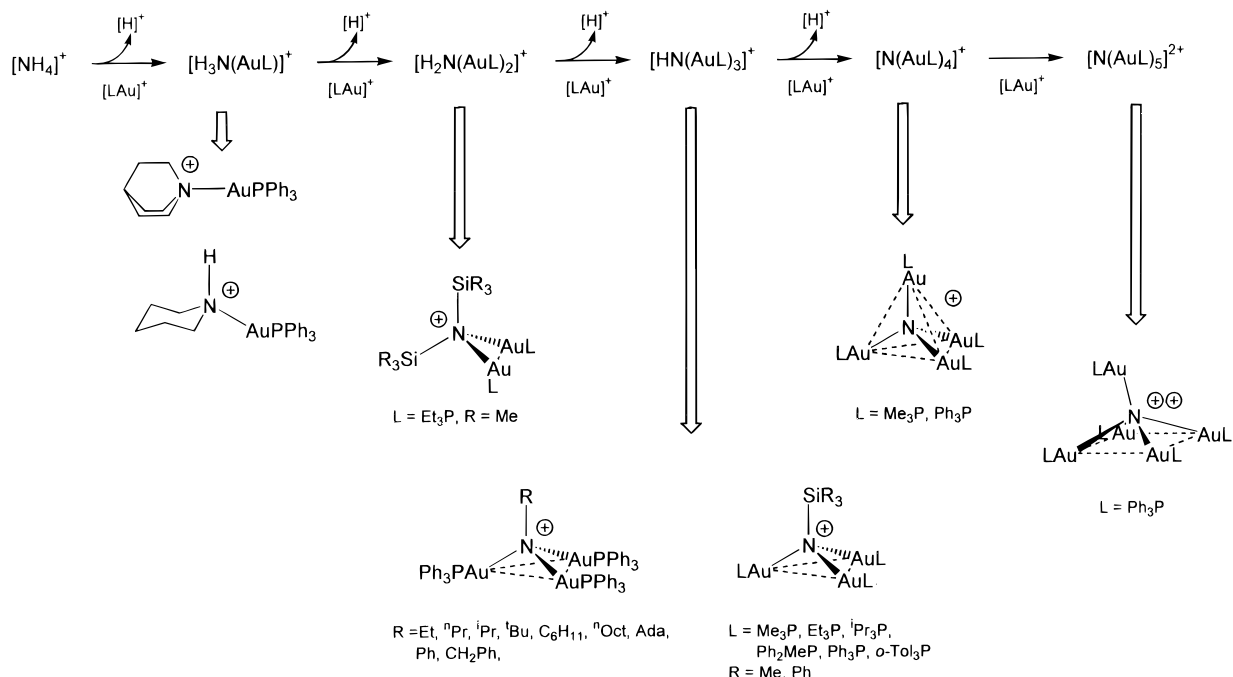
Tetracoordination of nitrogen by gold atoms in ammonium cations [(LAu)₄N]⁺ is well established,^{14–21} and recent work

has resulted also in the isolation of compounds with a lower degree of auration, including various alkyl-, aryl-, and silylammonium species^{22–39} (Scheme 1) and partially or fully aurred

[‡] Dedicated to Professor Martin A. Bennett on the occasion of his 65th birthday.

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Scheme 1. Partially and Fully Aurated Ammonium Cations and a Selection of Pertinent Examples

phosphine imines,^{40,41} hydrazines,^{42–44} and hydroxylamines.⁴⁵ Monoaurated ammonium cations also have been detected which show that stepwise substitution of the protons in the ammonium cation NH_4^+ by $[(\text{L})\text{Au}]^+$ cations is possible,^{21,46,47} thus corroborating the isolobal principle^{3,48} which predicts structure and bonding analogies between H^+ and $[(\text{L})\text{Au}]^+$.

The initial attempts to accomplish hypercoordination of nitrogen by gold atoms were immediately successful and led to the isolation of the dication $\{[(\text{Ph}_3\text{P})\text{Au}]_5\text{N}\}^{2+}$ as its tetrafluoroborate salt.^{3,49} The dicationic nature was confirmed by mass spectrometry. Monoclinic crystals of the salt with two tetrahydrofuran molecules (space group $P2_1/n$, $Z = 4$) contained dications with an NAu_5 core of low symmetry, which can be described as a distorted trigonal-bipyramid (tbp). Temperature-dependent NMR spectra indicated a fluxional structure in solution, but ^{197}Au Mössbauer spectra of solvent-free polycrys-

talline samples at 4 K showed two doublet signals in the intensity ratio 3:2 suggesting also a tbp structure. The new compound was thus a unique case of nitrogen pentacoordination in molecular chemistry.^{3,49}

These findings attracted considerable interest regarding the bonding in this cluster. Quantum-chemical studies on various levels of sophistication were carried out on the fully hydrogenated model $\{[(\text{H}_3\text{P})\text{Au}]_5\text{N}\}^{2+}$, which confirmed a stable diamagnetic configuration for the tbp structure.^{50–52}

However, preparative work with ligands other than triphenylphosphine (Ph_3P) met with limited success. With trimethylphosphine (Me_3P) only an adduct of the expected dication with two molecules of $(\text{Me}_3\text{P})\text{AuCl}$ could be isolated.⁵³ Nevertheless, the core of this complex does again feature the tbp coordination of nitrogen: $\{[(\text{Me}_3\text{P})\text{Au}]_5\text{N}\}[(\text{Me}_3\text{P})\text{AuCl}]_2(\text{BF}_4)_2$. No pentanuclear compounds were obtained with other phosphines,⁵⁴ and the results of efforts to extend the coordination number of nitrogen beyond 5 are not definitive.²⁰

In the course of all the auration studies of ammonia performed in this laboratory with the $[(\text{Ph}_3\text{P})\text{Au}]^+$ system, a second crystalline modification of the tetrafluoroborate salt was obtained (from dichloromethane). It showed analytical and spectroscopic data very similar to those of the tetrahydrofuran (THF) solvate (above), but the unit cell of the crystals was so large that for several years the crystal structure could not be solved in a satisfactory way.⁵⁴

Recent improvements in the data collection and computing facilities now made it possible to reach a reliable solution of this pending challenge. The result is important because it is only the second crystallographic confirmation of a novel type of

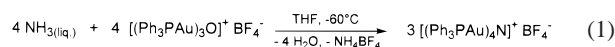
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structure. It adds to the value of the new data that the crystals turned out to contain no less than three crystallographically independent pentanuclear dications, none of which has an enforced element of symmetry. The structure of the bis-(tetrahydrofuran) solvate previously published only as a short note⁴⁹ is also reconsidered in the present discussion.

Preparation and Characteristics of the Compounds

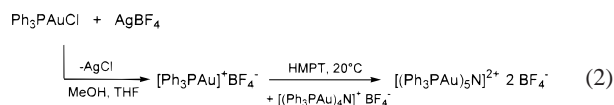
The synthesis of the title compound starts from ammonia, which is fully aminated and quaternized by reaction with tris-[(triphenylphosphine)gold]oxonium tetrafluoroborate in tetrahydrofuran at $-60\text{ }^{\circ}\text{C}$ (eq 1).^{15,19,21,49} After 3 h a colorless



crystalline product (72% yield) is obtained which decomposes at $200\text{ }^{\circ}\text{C}$. The composition has been confirmed in several laboratories by elemental analysis,^{15,19,21} and the results of mass spectrometric and NMR and IR spectroscopic studies are in agreement with the proposed structure (Experimental Section). It is noteworthy that the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum shows a 1:1:1 triplet with a $^{31}\text{P}-^{14}\text{N}$ coupling (26 Hz) probably owing to the high symmetry of the cation at the nitrogen nucleus.^{21,49} This multiplicity is absent in the spectrum of the corresponding fluoride,¹⁹ where the small anion appears to lower the symmetry of the cation in solvated ion pairs.

The crystal structures of three salts $\{[(\text{Ph}_3\text{P})\text{Au}]_4\text{N}\}^+ \text{X}^-$, with $\text{X} = \text{F}, \text{BF}_4$, and PF_6 , have been determined.^{16,19,20,39} The cation of the fluoride is distorted along one of the 3-fold axes of the tetrahedron bringing three gold atoms closer together, whereas the fourth one is in a unique apical position.¹⁹ The cations of the tetrafluoroborate¹⁶ and hexafluorophosphate²⁰ are similar, but with different distortions of the Au_4N core away from the ideal tetrahedron. The $\text{Au}-\text{N}-\text{Au}$ angles are in the large range $94.3-120.7^{\circ}$. Only the {tetrakis[tri(*n*-butyl)phosphine]gold}-ammonium cation with its 12 very bulky alkyl groups has a more regular tetrahedral structure but is still far from the ideal configuration.³⁴ These phenomena will be discussed below in a general context.

Treatment of $\{[(\text{Ph}_3\text{P})\text{Au}]_4\text{N}\}^+ \text{BF}_4^-$ with freshly prepared $[(\text{Ph}_3\text{P})\text{Au}]^+ \text{BF}_4^-$ [from $(\text{Ph}_3\text{P})\text{AuCl}$ and AgBF_4] in hexamethyl phosphoric triamide (HMPT) gives a colorless precipitate of the pentanuclear salt.⁴⁹ Precipitation is complete after addition of tetrahydrofuran to the mother liquor. The product can be recrystallized from tetrahydrofuran/dichloromethane or from dichloromethane to give the corresponding solvates in 61 and 53% yield, respectively (eq 2).



After drying in a vacuum the products are free of solvent and show correct elemental analysis data. Mass spectrometry and IR and NMR spectroscopic data suggest the presence of dications with a homoleptic coordination of the central nitrogen atom (Experimental Section). The $\{^1\text{H}\}^{31}\text{P}$ NMR spectra give sharp singlet resonances largely independent of temperature ($+30$ to $-50\text{ }^{\circ}\text{C}$). There is no discernible fine structure from $^{31}\text{P}-^{14}\text{N}$ coupling, probably owing to reduced symmetry (nonzero field gradients) at the nitrogen nucleus in a trigonal-pyramidal or square-planar environment compared with a tetrahedron (above).

The ^{13}C NMR spectra show second-order splitting (filled-in triplets) indicative of strong PAuP' coupling. This finding is evidence that there is no significant autodissociation of (Ph_3P) or $[(\text{Ph}_3\text{P})\text{Au}]$ groups from the central nitrogen atom in solution.

Crystal Structures of the Dichloromethane and Tetrahydrofuran Solvates of Pentakis[(triphenylphosphine)gold]-ammonium(2+) bis[tetrafluoro-borate(1-)]. Crystals of $\{[(\text{Ph}_3\text{P})\text{Au}]_5\text{N}\}_3(\text{BF}_4)_6(\text{CH}_2\text{Cl}_2)_4$ (obtained by slow cooling of solutions of the title compound in dichloromethane) are monoclinic, space group $P2_1/n$. The huge unit cell with a volume of $26521(3)\text{ }^{\circ}\text{A}^3$ [$a = 34.200(3)$, $b = 15.285(1)$, $c = 53.127(3)\text{ }^{\circ}\text{A}$, $\beta = 107.262(2)^{\circ}$, at 150 K] contains $Z = 12$ formula units. From a data set of 44 193 reflections the structure was solved and refined for 3097 parameters with no restraints to conventional R-factors $R_1 = 0.0565$, $wR_2 = 0.1382$ [$I \geq 2\sigma(I)$] and $R_1 = 0.0687$, $wR_2 = 0.1457$ (all data, full matrix-block least squares on F^2).

The asymmetric unit of the lattice contains four dichloromethane molecules, six tetrafluoroborate anions, and three pentanuclear dications. There are no sub-van der Waals contacts between these components, so all groups can be considered separately. The anions and the solvent molecules show no structural anomalies.

The structure of the three dications is shown in Figure 1a-c. The molecular geometries are not identical, but very similar, as also illustrated by the selection of bond lengths and angles presented in Table 1. The nitrogen atoms (N1-N3) clearly are pentacoordinated by five gold atoms with $\text{N}-\text{Au}$ distances in the narrow range between 2.067 and $2.143\text{ }^{\circ}\text{A}$ (average of 15 independent distances, $2.092\text{ }^{\circ}\text{A}$). The coordination geometry at the gold atoms is close to linear with angles $\text{N}-\text{Au}-\text{P}$ spreading from $171.6(2)$ to $178.3(2)^{\circ}$ (average of 15 data, 175.5°) with standard $\text{Au}-\text{P}$ distances (average, $2.245\text{ }^{\circ}\text{A}$).

The configuration of the NAu_5 cores is clearly irregular and far from the two standard polyhedra for pentacoordination, the trigonal bipyramid (tbp), and the square pyramid (sqp). These two standard reference structures are related by interconversion pathways of which the Berry pseudorotation is the most used (Figure 2).

To classify the three dications according to these standard geometries, the following approaches can be followed.

a. The Trigonal Bipyramidal Model. To find the principal axis of an idealized trigonal bipyramid the largest $\text{Au}-\text{N}-\text{Au}$ angle is chosen for each dication. These axes

$\text{Au}2-\text{N}1-\text{Au}4$	$168.2(4)^{\circ}$
$\text{Au}7-\text{N}2-\text{Au}9$	$161.9(3)^{\circ}$
$\text{Au}12-\text{N}3-\text{Au}14$	$172.8(3)^{\circ}$

are clearly distorted with bendings at nitrogen of up to 18.1° away from the 180° linearity. Two of the five gold atoms are thus defined as apical atoms Au_{ap} , and the remaining gold atoms as the three equatorial atoms Au_{eq} in the tbp. The sums of angles $\text{Au}_{\text{eq}}-\text{N}-\text{Au}_{\text{eq}}$ are almost exactly 360° , indicating coplanarity with the nitrogen atoms: 359.0° for N1, 359.1° for N2, and 359.4° for N3. However, the three angle components of these 360° differ very strongly and have the following individual data:

$\text{Au}1-\text{N}1-\text{Au}3$	$105.6(3)^{\circ}$	$\text{Au}6-\text{N}2-\text{Au}8$	$107.2(3)^{\circ}$	$\text{Au}11-\text{N}3-\text{Au}13$	$103.7(3)^{\circ}$
$\text{Au}1-\text{N}1-\text{Au}5$	$111.3(3)^{\circ}$	$\text{Au}6-\text{N}2-\text{Au}10$	$110.6(3)^{\circ}$	$\text{Au}11-\text{N}3-\text{Au}15$	$113.4(3)^{\circ}$
$\text{Au}3-\text{N}1-\text{Au}5$	$142.1(4)^{\circ}$	$\text{Au}8-\text{N}2-\text{Au}10$	$141.3(3)^{\circ}$	$\text{Au}13-\text{N}3-\text{Au}15$	$142.3(3)^{\circ}$
Σ	359.0°		359.1°		359.4°

It is immediately obvious that one of the three angles is particularly large, and the other two are smaller, but mutually different. This means that the trigonal symmetry of the tbp

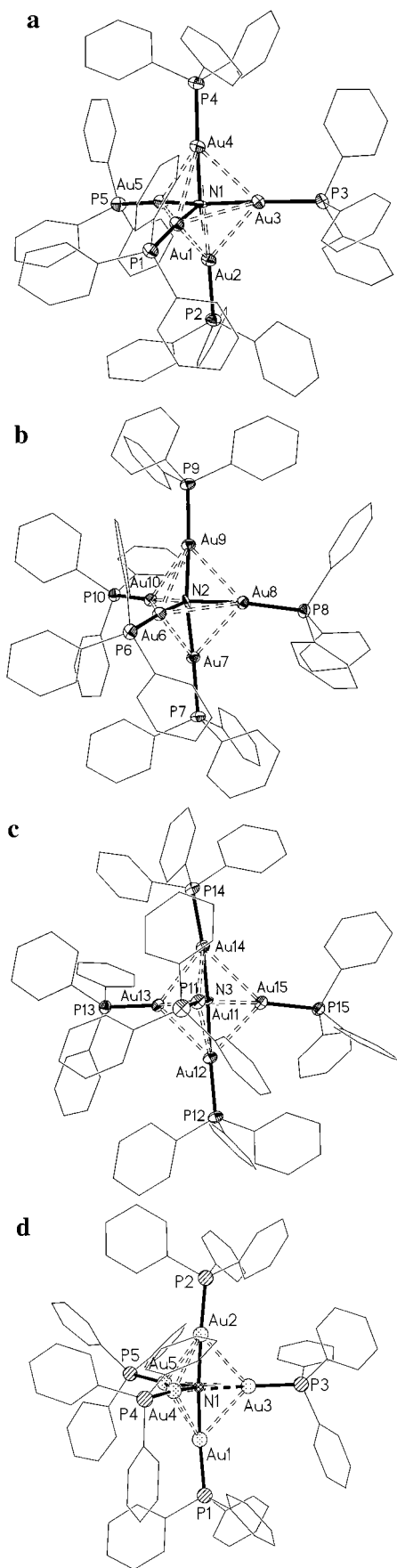


Figure 1. The structures of the three crystallographically independent dications in the dichloromethane solvate (a–c) and the structure of the dication in the tetrahydrofuran solvate (d) in the trigonal bipyramidal description.

polyhedron is destroyed by an opening of one of the three equatorial angles at the expense of the two others, while at the same time one of the apical gold atoms is shifted away from the principal (3-fold) axis toward this equatorial opening. That only one of the apical gold atoms is responsible for the bending of the principal axis is recognized from the values of the $\text{Au}_{\text{ap}}-\text{N}-\text{Au}_{\text{eq}}$ angles, which are close to 90° for the lower pyramids, but very different from 90° for the upper pyramids of each bipyramid (Figure 1a–c, Table 1).

The angles and their distortions are responsible for a wide range of intramolecular gold–gold contacts. The wide equatorial angles of about 141° are associated with the longest $\text{Au}_{\text{eq}}-\text{Au}_{\text{eq}}$ separations of almost 4 Å: Au_3-Au_5 3.926(1), $\text{Au}_8-\text{Au}_{10}$ 3.947(1), $\text{Au}_{13}-\text{Au}_{15}$ 3.928(1) Å, whereas the other $\text{Au}_{\text{eq}}-\text{Au}_{\text{eq}}$ distances have values between 3.256(1) and 3.464(1) Å and are thus approaching the range where weak auriphilic bonding can be assumed.³ The circumference of the triangle of equatorial gold atoms in all cases is ca. 10.6 Å (average of the three dications). For three 120° angles ($\text{Au}_{\text{eq}}-\text{N}-\text{Au}_{\text{eq}}$) three long $\text{Au}_{\text{eq}}-\text{Au}_{\text{eq}}$ separations of 3.558 Å are calculated which would have to be considered as nonattractive.

All three $\text{Au}_{\text{ap}}-\text{Au}_{\text{eq}}$ contacts in the lower pyramids and two in each upper pyramid are well below 3.0 Å, where strong auriphilic bonding can be diagnosed.³ Only one $\text{Au}_{\text{ap}}-\text{Au}_{\text{eq}}$ distance in each of the upper pyramids is longer than 3.0 Å [Au_1-Au_4 3.2218(5), Au_6-Au_9 3.3545(5), $\text{Au}_{11}-\text{Au}_{14}$ 3.0804(5) Å] and will thus contribute less to the cluster stability.

The result of the tbp approximation can be summarized as follows. In a regular tbp structure there would be six short $\text{Au}_{\text{ap}}-\text{Au}_{\text{eq}}$ (ca. 2.95 Å) and three long $\text{Au}_{\text{eq}}-\text{Au}_{\text{eq}}$ contacts (ca. 3.56 Å) as determined by $\text{Au}-\text{N}-\text{Au}$ angles of 90° and 120° , respectively, and by $\text{Au}-\text{N}$ distances of ca. 2.09 Å. The mutually consistent distortions in all three independent dications lead to five short (<3.0 Å), two medium-sized (3.0–3.4 Å), and one very long $\text{Au}-\text{Au}$ (3.9 Å) edge, which in total appear to lower the overall cluster energy.

b. The Square Pyramidal Model. Inspection of the molecular geometries in Figure 1 shows that for a description of the structure an alternative approach is at least equally justified. If the gold atoms Au_1 , Au_6 , and Au_{11} are chosen as the apexes of square pyramids (Au_{ap}), three distorted squares are defined as the bases of these polyhedra (Figure 3). Deviations (in Å) of these sets of four basal gold atoms (Au_{b}) from their common “best plane” are not very large, as shown by the following data:

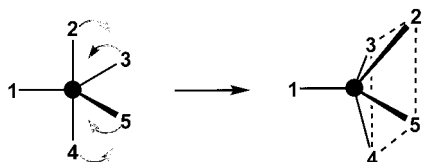
Au_2 0.2311	Au_3 -0.2270	Au_4 0.2227	Au_5 -0.2269
Au_7 -0.1810	Au_8 0.1796	Au_9 -0.1785	Au_{10} 0.1799
Au_{12} -0.2809	Au_{13} 0.2835	Au_{14} -0.2684	Au_{15} 0.2658

Alternating around the base, the gold atoms are about equally displaced above and below the plane in each dication. This is in excellent agreement with an intermediate case of the Berry pseudorotation model, where starting from the tbp structure the four future base atoms have not fully reached their common square plane (Figure 2).

In all three cases the apical atom (Au_1 , Au_6 , Au_{11}) is bent away from its principal (4-fold) axis toward one of the base gold atoms giving one exceptionally small angle $\text{Au}_{\text{ap}}-\text{N}-\text{Au}_{\text{b}}$. This bending leads to one short $\text{Au}_{\text{ap}}-\text{Au}_{\text{b}}$ contact in each pyramid, which together with the four short $\text{Au}_{\text{b}}-\text{Au}_{\text{b}}$ contacts yields a total of five $\text{Au}-\text{Au}$ distances smaller than 3.0 Å which of course correspond to the five short distances also defined in the tbp model. Of the remaining $\text{Au}_{\text{ap}}-\text{Au}_{\text{b}}$ contacts two are medium-sized and one (opposite to the short one) is very long.

Table 1. A Comprehensive List of the Relevant Bond Lengths and Angles in All Four Independent Dications (from Both Solvates)

	$\{[(\text{Ph}_3\text{P})\text{Au}]_5\text{N}\}_3(\text{BF}_4)_6(\text{CH}_2\text{Cl}_2)_4$			
	cluster 1	cluster 2	cluster 3	$\{[(\text{Ph}_3\text{P})\text{Au}]_5\text{N}\}(\text{BF}_4)_2(\text{THF})_2$
Au–N [Å]	Au1: 2.067(6) Au2: 2.143(7) Au3: 2.083(7) Au4: 2.086(7) Au5: 2.086(7)	Au6: 2.077(6) Au7: 2.135(7) Au8: 2.097(7) Au9: 2.078(7) Au10: 2.086(7)	Au11: 2.067(6) Au12: 2.141(6) Au13: 2.073(7) Au14: 2.079(6) Au15: 2.078(6)	Au1: 2.116(6) Au2: 2.116(6) Au3: 2.051(7) Au4: 2.081(6) Au5: 2.066(7)
Au–P [Å]	Au1: 2.255(2) Au2: 2.239(3) Au3: 2.246(3) Au4: 2.246(3) Au5: 2.240(3)	Au6: 2.262(2) Au7: 2.236(2) Au8: 2.247(2) Au9: 2.241(2) Au10: 2.251(2)	Au11: 2.246(2) Au12: 2.239(2) Au13: 2.241(2) Au14: 2.242(2) Au15: 2.249(2)	Au1: 2.248(3) Au2: 2.244(3) Au3: 2.244(3) Au4: 2.248(3) Au5: 2.242(3)
Au...Au [Å]	1–2: 2.9607(5) 1–3: 3.3062(5) 1–4: 3.2218(5) 1–5: 3.4310(5) 2–3: 2.8854(5) 3–5: 3.9260(6) 2–5: 2.8731(6) 3–4: 2.9266(6) 4–5: 2.9405(5)	6–7: 2.9903(6) 6–8: 3.3598(5) 6–9: 3.3545(5) 6–10: 3.4230(6) 7–8: 2.8253(6) 7–10: 2.9335(5) 8–9: 2.9563(5) 8–10: 3.9470(6) 9–10: 2.8421(6)	11–12: 2.9774(5) 11–13: 3.2564(5) 11–14: 3.0804(5) 11–15: 3.4640(6) 12–13: 2.9218(5) 12–15: 2.8723(6) 13–14: 2.8580(6) 13–15: 3.9280(6) 14–15: 3.0742(5)	1–3: 2.933(1) 1–4: 2.910(1) 1–5: 3.074(1) 2–3: 2.885(1) 2–4: 2.984(1) 2–5: 2.965(1) 3–4: 3.729(1) 3–5: 3.590(1) 4–5: 3.388(1)
N–Au–P [°]	1: 176.9(2) 2: 171.6(2) 3: 178.3(2) 4: 177.8(2) 5: 174.7(2)	6: 176.3(2) 7: 174.7(2) 8: 173.7(2) 9: 177.0(2) 10: 176.7(2)	11: 173.1(2) 12: 176.0(2) 13: 176.6(2) 14: 174.7(2) 15: 174.7(2)	1: 174.3(2) 2: 176.8(2) 3: 177.8(2) 4: 176.5(2) 5: 174.6(2)
Au–N–Au [°]	1 2: 89.3(2) 1 3: 105.6(3) 1 4: 102.4(3) 1 5: 111.3(3) 2 3: 86.1(3) 2 4: 168.2(4) 2 5: 86.0(2) 3 4: 89.7(2) 3 5: 142.1(4) 4 5: 90.6(3)	6 7: 90.5(2) 6 8: 107.2(3) 6 9: 107.7(3) 6 10: 110.6(3) 7 8: 83.8(2) 7 9: 161.9(3) 7 10: 88.0(3) 8 9: 90.2(3) 8 10: 141.3(3) 9 10: 86.1(2)	11 12: 90.0(2) 11 13: 103.7(3) 11 14: 96.0(2) 11 15: 113.4(3) 12 13: 87.8(3) 12 14: 172.8(3) 12 15: 85.8(2) 13 14: 87.0(2) 13 15: 142.3(3) 14 15: 95.4(3)	1 2: 174.9(4) 1 3: 89.5(4) 1 4: 87.8(4) 1 5: 94.6(4) 2 3: 87.7(4) 2 4: 90.8(4) 2 5: 90.4(4) 3 4: 129.0(3) 3 5: 121.4(3) 4 5: 109.6(3)

**Figure 2.** Berry pseudorotation pathway for the interconversion of the trigonal bipyramid (tbp) and the square pyramid (spp).

(Note that a square pyramid has only eight edges compared with nine edges for a trigonal bipyramid.)

It thus appears that the tbp and spp models are complementary descriptions of the complicated structures of the new clusters in the *dichloromethane solvate*.

Crystals of $\{[(\text{Ph}_3\text{P})\text{Au}]_5\text{N}\}(\text{BF}_4)_2(\text{C}_4\text{H}_8\text{O})_2$ are monoclinic (space group $P2_1/n$, $Z = 4$). The asymmetric unit contains two tetrafluoroborate anions, two tetrahydrofuran molecules, and one pentanuclear dication, which has no crystallographically imposed symmetry (Figure 1d).⁴⁹

For this dication, the geometry of the Au_5N core is closer to the model of a trigonal bipyramid, because the distortions are much smaller than in the three dications of the dichloromethane solvate (above). The main axis has an angle $\text{Au}_{\text{ap}}\text{–N–Au}_{\text{ap}}$ of $174.9(4)^\circ$, and the angles between the equatorial gold atoms $\text{Au}_{\text{eq}}\text{–N–Au}_{\text{eq}}$ are $109.6(3)$, $121.4(3)$, and $129.0(3)^\circ$. The sum of these three angles is exactly 360° placing the nitrogen atom in the equatorial plane (Figure 1d). The deviations from 120° are thus less than 10° for $\text{Au}_{\text{eq}}\text{–N–Au}_{\text{eq}}$, and the deviation from 180° is only 5° for $\text{Au}_{\text{ap}}\text{–N–Au}_{\text{ap}}$, compared with almost 20° for both angles in the dichloromethane solvate. Referring to the

Berry pseudorotation pathway, the dication in the *tetrahydrofuran solvate* is not far from the tbp configuration, and a description as a distorted square pyramid is thus impractical. Notwithstanding, the differences are only gradual and not fundamental. Small intramolecular motions are enough to interconvert the geometries and to shift them closer to the tbp or spp model, respectively.

Discussion

The present results confirm the existence of pentaaurated ammonium dications $[(\text{LAu})_5\text{N}]^{2+}$ with triphenylphosphine ligands L in a second crystal environment. Supported also by the findings for a Me_3PAuCl adduct of the corresponding trimethylphosphine complex,⁵³ this type of compound can now be considered well established.^{3,21,49} There is also convincing support from theoretical calculations which describe the model dications with H_3P ligands as stable, diamagnetic species.^{3,50–52}

The remaining problem to be addressed in this context is why these dications $[(\text{LAu})_5\text{N}]^{2+}$, and in fact even the tetranuclear, quasi-tetrahedral precursors^{16,19,20} of the type $[(\text{LAu})_4\text{N}]^+$, are so strongly distorted. The following observations and arguments need to be considered.

Even very minor changes in the crystalline environment (dichloromethane vs tetrahydrofuran solvate) cause major distortions in different directions and to a different extent. This indicates that the energy differences between the various structural forms of the polyhedron are very small. This is in agreement with the fluctuational behavior of the dications in solution, which suggest a largely contourless energy profile of

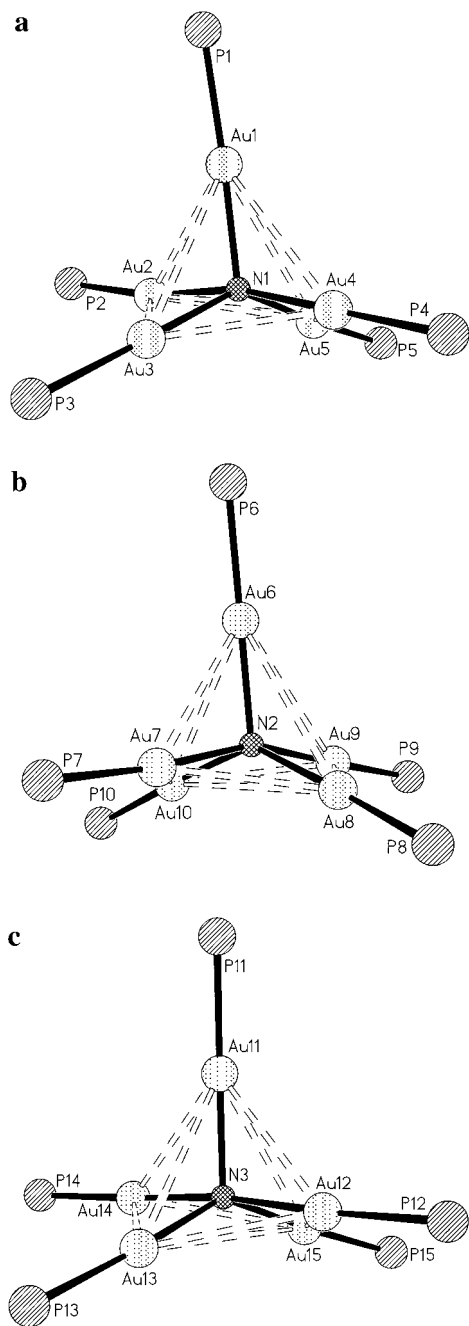


Figure 3. Square pyramidal description of the structures of the three dications in the dichloromethane solvate.

pseudorotation.⁴⁹ In other words, there is little to lose or to gain in energy as the gold atoms are moved away, within limits, from their *tbp* or *sqp* symmetry positions.

A purely electrostatic description of bonding of the core unit does not appear to be justified, because repulsions between the gold atoms should lead to forms in which the gold atoms are separated from each other as much as possible. On the contrary, the gold atoms appear to move together in whatever form this is possible in a given environment. Partial dissociation into $[(\text{LAu})_4\text{N}]^+$ and $[\text{LAu}]^+$ cations, which would separate the two charges, is also unlikely because all Au–N distances are within a narrow range regardless if apical or equatorial/basal gold atoms are involved. Dissociation is also ruled out for the solution by the NMR data of the clusters.

Some of the Au–Au contacts observed in the new clusters are among the shortest encountered in the structural chemistry

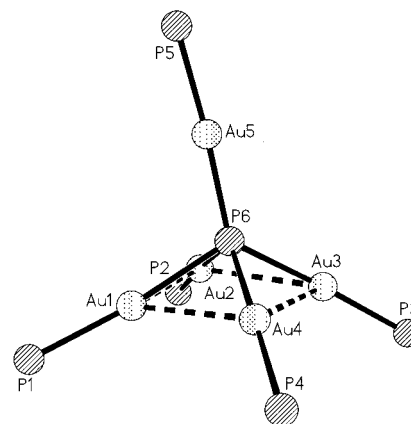


Figure 4. The molecular structure of the phosphonium analogue of the title ammonium dication.⁵⁷

of polynuclear gold compounds [e.g. Au7–Au8 2.8253(6) Å is much shorter than the interatomic distance in metallic gold: 2.898 Å]. All structures suggest that the gold atoms are drawn closely together as permitted by the steric bulk of the ligands and the loss of intermetallic contacts in other parts of the cluster. It also appears that the regular *tbp* or *sqp* geometries are *not* ideal for the Au/N system. This also applies to the tetrahedral $[\text{Au}_4\text{N}]^+$ cation, which is distorted in different ways depending on the nature of the counterion in the lattice.^{16,19,20,38} The atomic radii of gold^{55,56} and nitrogen lead to edges for the tetrahedra, trigonal bipyramids, and square pyramids which are too large for efficient metal–metal interactions. It may be surprising then that hexacoordination in $[(\text{LAu})_6\text{N}]^{3+}$ cannot be achieved,^{20,49} but electrostatic arguments may be valid in this context.

The phosphorus analogue of the title ammonium dication was recently prepared and structurally characterized.⁵⁷ It has a clear-cut square pyramidal structure, in which the gold atoms of the base are drawn very closely together (Figure 4). Owing to the large radius of the central phosphorus atom the apical gold atom is too far away from the basal gold atoms to reach contact within an acceptable bending range. This dication is known⁵⁸ to accept a sixth $[\text{LAu}]^+$ unit to give a hexacoordinate trication $[(\text{LAu})_6\text{P}]^{3+}$. Pentacoordination at phosphorus is also met in polycations with unconventional stoichiometries: $\{[(\text{Ph}_3\text{P})\text{Au}]_4\text{P}[\text{Au}(\text{PPh}_3)_2]\}^{2+}$, where one of the five gold atoms bears an extra Ph_3P ligand,⁵⁹ and $[\text{Au}\{\text{P}[\text{Au}(\text{PPh}_3)_4]\}_2]^{3+}$ with a gold atom bridging the apices of two pyramids.⁶⁰

Tetra(gold)phosphonium salts with cations $[(\text{LAu})_4\text{P}]^+$ are only stable with large phosphine ligands L. The crystal structure of a tetraphenyltriboroxolate salt and with $\text{L} = \text{tBu}_3\text{P}$ was determined and the cation shown to have a regular tetrahedral structure,⁶¹ no doubt owing to the bulkiness of the phosphine which rules out any close approach of the gold atoms. Auration of primary phosphines $\text{R}-\text{PH}_2$ gives (di-)cations with tetra- and pentacoordinate phosphorus atoms: $\{\text{R}-\text{P}[\text{Au}(\text{PR}_3)_3]\}^+$ and $\{\text{R}-\text{P}[\text{Au}(\text{PR}_3)_4]\}^{2+}$ with tetrahedral and square pyramidal

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structures, respectively.^{62–65} The latter can be classified as alkylated cations $\{P[Au(PR_3)_4]^+\}$. Their $[PAu_4]$ pyramids feature small Au–P–Au angles and consequently tightly bonded gold atoms with Au–Au contacts much shorter than 3.0 Å.

Finally, these $[PAu_4]$ units also resemble very closely the square pyramidal $[AsAu_4]$ groups found in arsonium salts¹⁹ $\{[(Ph_3P)Au]_4As\}^+ X^-$ and in the isoelectronic $[SAu_4]$ and $[SeAu_4]$ groups present in sulfonium/selenonium(2+) salts $\{E[Au(PPh_3)_4]X_2 (E = S, Se)\}$.^{66,67}

Hypercoordination is not restricted to cations in gold chemistry. The general issue of ‘onium’ chemistry has just been summarized by Olah et al.^{68,69} and many parallels are immediately obvious. Another related area is easily recognized in the chemistry of polylithium compounds and their proton analogues as developed both in theory and in experiment by v. Schleyer and by Schwarz and in other laboratories.^{70–72}

Conclusion

The detailed discussion of the existing information on hypercoordinate compounds of nitrogen, phosphorus, and arsenic has shown that there are many parallels for the elusive structural chemistry of hypercoordinate ammonium dications. Fluxional structures in solution and variable, highly distorted structures in the crystals should be taken, and expected, as the rule rather than as the exception.

The systems exhibit a preference for polyhedra with as many short gold–gold contacts as possible along the edges of the polyhedra. Although the small nitrogen¹⁹ and oxygen⁷³ atoms in the center of a tetrahedron of four gold atoms still provide sufficiently short edges allowing for a set of appreciable metal–metal contacts, the larger phosphorus, arsenic, sulfur, and selenium atoms require a complete reorganization to produce square pyramids with all four gold atoms at short-edged bases.

The small nitrogen atom in the environment of five gold atoms can adopt virtually any polyhedral geometry between square pyramidal and trigonal bipyramidal, with a certain preference already for the former, but with almost random distortions. For the larger phosphorus atom there is a clear decision in favor of the square pyramid, and the prediction can be made that the dication $[S(AuL)_5]^{2+}$ will also have this structure rather than the suggested trigonal bipyramid.⁶⁶ All existing polyaurated compounds with pentacoordinate phosphorus atoms^{58–65} are derivatives of the square pyramidal $[P(AuL)_4]^+$ units. If ever a free cation of this type can be

detected with small ligands L, it will almost certainly be square pyramidal.^{3,74}

This prediction is ventured against all classical rules or paradigms regarding the symmetrical distribution of an electron octet in space, and the LeBel and van't Hoff principle of tetrahedral tetracoordination at carbon and isoelectronic species. Note, however, that we have every reason to believe that even tetra(auro)methanes $[C(AuL)_4]$ with small groups L will be square pyramidal.^{3,74} The protonated form $[HC(AuL)_4]^+$ has already been isolated and structurally characterized,^{11,12} and recent high-level quantum-chemical calculations have shown that square pyramidal $[C(AuL)_4]$ molecules are stable. However, their basicity is extremely high⁷⁵ and makes them super bases and super nucleophiles, which are difficult to recover unchanged from virtually any medium.

Experimental Section

All experiments were conducted routinely under an atmosphere of dry purified nitrogen. Standard equipment was used throughout. Starting materials were prepared following (modified) reported procedures: $(Ph_3P)AuCl$,⁷⁶ $\{[(Ph_3P)Au]_3O\}^+ BF_4^-$,⁷⁷ $[(Ph_3P)Au]^+ BF_4^-$,⁴⁹ $\{[(Ph_3P)Au]_4N\}^+ BF_4^-$.^{15,19,21}

Tetrakis(triphenylphosphine)gold(I)ammonium(1+) tetrafluoroborate(1–). Liquid ammonia (3 mL) is condensed into a cold trap and dissolved in tetrahydrofuran (10 mL) at $-60^\circ C$ and treated with a slurry of tris(triphenylphosphine)gold(oxonium) tetrafluoroborate (3.0 g, 2.03 mmol) in 40 mL of tetrahydrofuran. The yellow slurry is stirred for 4 h at $-60^\circ C$ and filtered. The product is washed four times with 5 mL of cold tetrahydrofuran ($0^\circ C$) and dried in a vacuum (yield, 2.1 g, 72%), decomposition temperature $200^\circ C$. NMR (CD_2Cl_2 , $25^\circ C$): $^1P\{^1H\}$ 29.5, t, $J(^1P^{14}N)$ 26 Hz. 1H 7.31–7.40, m, 24 H, C-3; 7.45–7.61, m, 36 H, C-2,4. $^{13}C\{^1H\}$ 130.9, d, $J(PC)$ 56.2 Hz, C-1; 134.5, d, $J(PC)$ 13.2 Hz, C-2; 129.4, d, $J(PC)$ 11.4 Hz, C-3; 131.8, d, $J(PC)$ 2.0 Hz, C-4. MS (FD) m/e 1850.9 (100%, M^+), 1392.7 (30%, $M^+ - AuPPh_3$), 1155.3 (8%, $\{N[Au(PPh_3)]_5\}^{2+}$).

Anal. Calcd for $C_{72}H_{60}Au_4BF_4NP_4$ (1937.86): C, 44.63; H, 3.12; N, 0.72; P, 6.39. Found: C, 44.11; H, 3.17; N, 0.72; P, 6.42.

Pentakis(triphenylphosphine)gold(I)ammonium(2+) bis(tetrafluoroborate(1–)). A solution of (triphenylphosphine)gold(I) chloride (1.1 g, 2.2 mmol) in tetrahydrofuran (40 mL) is treated with a solution of 0.46 g of silver tetrafluoroborate (2.3 mmol) in methanol (5 mL) for 30 min at $20^\circ C$. The precipitate of silver chloride is filtered off, and the filtrate is added to a solution of $\{[(Ph_3P)Au]_4N\}BF_4$ (2.13 g, 1.1 mmol) in hexamethyl phosphoric triamide (20 mL). The mixture is stirred for 20 min at $20^\circ C$ and tetrahydrofuran (40 mL) is added. The product is filtered and dried in a vacuum. For purification the first crop is redissolved in dichloromethane and precipitated with tetrahydrofuran (yield, 1.72 g, 61%). Decomposition temperature above $210^\circ C$. Single crystals are grown either by layering the dichloromethane solution with tetrahydrofuran or by careful crystallization from dichloromethane solution in a temperature gradient ($1^\circ h^{-1}$ from the whole setup, and $1.5^\circ cm^{-1}$ along the tube) (1.5 g, 53% yield). NMR (CD_2Cl_2 , $25^\circ C$): $^1P\{^1H\}$ 25.3, s. 1H 7.14–7.21, m, 30H, C-3; 7.31–7.39, m, 30H, C-2; 7.44–7.51, m, 15H, C-4. $^{13}C\{^1H\}$ 128.5, d, $J(PC)$ 61.6 Hz, C-1; 134.2, centered d, N = 13.7 Hz, C-1; 129.9, centered d, N = 12.2, C-3; 132.9, s, C-4. MS (FD) m/e 1155.2 (100%, M^{2+}), 722.4 (3%), $[(Ph_3P)_2AuH]^+$. ^{197}Au Mössbauer spectrum (4 K): IS(1) 2.81(1) mm/s, QS(1) 6.79(1) mm/s; QS(2) 3.32(1) mm/s; QS(2) 7.53(1) mm/s (for a figure see ref 49). After short drying in a vacuum one THF molecule remains, but is lost after prolonged vacuum treatment.

Anal. Calcd for $C_{94}H_{83}Au_5B_2F_8NOP_5$ (2556.00, including 1 C_4H_8O): C, 44.17; H, 3.27; N, 0.55; P, 6.06. Found: C, 44.31; H, 3.42; N, 0.54; P, 6.16.

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Anal. Calcd for $C_{90}H_{75}Au_5B_2F_8NP_5$ (2483.91, no THF): C, 43.52; H, 3.04; N, 0.56. Found: C, 43.47; H, 3.14; N, 0.54.

X-ray Structure Analysis. Suitable single crystals of $[N(AuPPh_3)_5][BF_4]_2 \cdot 2THF$ and $[N(AuPPh_3)_5][BF_4]_6 \cdot 4CH_2Cl_2$ were sealed in glass capillaries and used to measure precise cell constants and intensity data collection. The structures were solved by direct methods and refined by blocked-matrix least-squares calculations against F (THF) and F^2 (CH_2Cl_2), respectively. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions.

Data for $C_{90}H_{75}Au_5B_2F_8NP_5 \cdot 2C_4H_8O$. Data collection on an Enraf Nonius CAD4 diffractometer, graphite-monochromated Mo- $K\alpha$ radiation; $\lambda(Mo-K\alpha) = 0.71073 \text{ \AA}$, empirical absorption correction ($\mu(Mo-K\alpha) = 78.0 \text{ cm}^{-1}$, relative transmission: 0.58–1.00. $M_r = 2628.17$, colorless crystals, monoclinic, $a = 15.242(2)$, $b = 23.637(3)$, $c = 26.518(3) \text{ \AA}$, $\beta = 94.83(1)^\circ$, space group $P2_1/n$, $Z = 4$, $V = 9520.3(5) \text{ \AA}^3$, $\rho_{calc} = 1.833 \text{ g cm}^{-3}$, $F(000) = 5016$; $T = 23^\circ\text{C}$. 17 744 measured, 16 632 unique [$(\sin \theta/\lambda)_{max} = 0.60 \text{ \AA}^{-1}$; $R_{int} = 0.0262$], and 9.358 ‘observed’ reflections with $F_o \geq 4\sigma(F_o)$; 1090 refined parameters, $R(R_w) = 0.041$ (0.027), $w = 1/\sigma^2(F_o)$. Residual electron densities: $+0.90/-0.90$.

Data for $C_{90}H_{75}Au_5B_2F_8NP_5 \cdot 1.333CH_2Cl_2$. Data collection with an Enraf Nonius DIP2020 image plate (135 images of 1 degree each; crystal-to-plate distance, 75 mm; exposure time, 300 s per image),

graphite-monochromated Mo- $K\alpha$ radiation; $\lambda(Mo-K\alpha) = 0.71073 \text{ \AA}$. $M_r = 2597.05$, colorless crystals, monoclinic, $a = 34.200(3)$, $b = 15.285(1)$, $c = 53.127(3) \text{ \AA}$, $\beta = 107.262(2)^\circ$, space group $P2_1/n$, $Z = 12$, $V = 26521(3) \text{ \AA}^3$, $\rho_{calc} = 1.951 \text{ g cm}^{-3}$, $F(000) = 14 760$; $T = -123^\circ\text{C}$. 44 193 measured and unique reflections, 3097 refined parameters, $R(wR_2) = 0.0565$ (0.1382) [$I \geq 2\sigma(I)$]; the function minimized was: $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0914$, $b = 33.32$. Residual electron densities: $+2.05/-4.65$.

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Supporting Information Available: Tables of data collection and refinement parameters, atomic coordinates, and the thermal parameters including hydrogen, complete bond distances and angles, and anisotropic displacement parameters of the CH_2Cl_2 solvate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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