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Imido–Gold Clusters: Synthesis and Magnetic Resonance Spectroscopy of "Gilded" Diamines

Andreas Grohmann and Hubert Schmidbaur*

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

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Aliphatic and aromatic diamines $H_2N–X–NH_2$ (X = $–CH_2CH_2–$, 1,4-C_6H_4, 1,3-C_6H_4, 1,2-C_6H_4) were reacted in THF with 2 equiv of tris[(triphenylphosphine)gold(I)]oxygen(1+) tetrafluoroborate, $[O(AuL)_3]^+BF_4^-$, to yield bis(imido) cluster compounds of the type $[(LAu)_3N–X–N(AuL)_3]^{2+}(BF_4^-)_2$ (L = PPh_3). The compounds were obtained as crystalline solids in high yields and were characterized by IR and NMR spectroscopy as well as mass spectrometry and elemental analysis. In the series of isomeric phenylene compounds, the increasing proximity of the two triaurioammonio substituents (para, meta, ortho) results in characteristic changes in ^1H and ^{31}P NMR spectroscopic features whose diagnostic value is assessed in relation to similar species. Further auration to give hypercoordinated species could not be accomplished.

Introduction

The chemistry of small, heteroatom-centered gold clusters has undergone a rapid development in recent years.[1] Systematic investigations were prompted by the recognition that, both in solid-state aggregates and in discrete molecules, many compounds of monovalent gold display intra- and intermolecular bonding interactions between the linearly two-coordinate metal atoms.[2] This phenomenon was expected to become more conspicuous with an increasing number of gold(I) atoms at a given center in the molecular entity.

In a series of experiments, compounds of the types $[RC(AuL)_3]$,[3] $[RN(AuL)_3]^+$,[4–6] and $[RP(AuL)_3]^+$ [7] could be synthesized (L = tertiary phosphine). These compounds have standard tetrahedral geometry but (in particular for carbon and nitrogen as the central atoms E) have angles Au–E–Au of less than 109°, suggesting significant Au···Au attraction. The homoleptic cation $[N(AuL)_4]^+$ described[8] in the literature also has a tetrahedral structure but displays marked nonrigidity. Various ways of distortion, depending on the counterion present in the lattice, have been observed.[9] This implies that there is no perfect solution for Au···Au bonding along all edges of an NAu_4 tetrahedron, with all Au–N–Au angles at 109°.

The related arsenic-centered cation $[As(AuL)_4]^+$,[9] however, was found to have a square pyramidal structure of approximate C_{4v} symmetry, with an arsenic atom capping a square of gold atoms. In the case of a suitably large central atom such as arsenic, attractive Au···Au interactions obviously induce a rearrangement, leading to the violation of one of the central tenets of structural chemistry, the rule of *van't Hoff* and *LeBel*, which requires arsonium ions to be tetrahedral.[10] The structure of the $P(AuL)_4^+$ cation is still unknown but expected to be also square pyramidal.

Similarly, Au···Au interactions have to be invoked to rationalize the facile synthesis of *hypercoordinated* heteroatom-centered gold clusters, such as $[RC(AuL)_4]^+$ [11] and $[RP(AuL)_4]^{2+}$ [12] as well as the homoleptic species $[C(AuL)_5]^+$,[13] $[C(AuL)_6]^{2+}$,[14] $[N(AuL)_5]^{2+}$,[15] and $[P(AuL)_5]^{2+}$,[7] which are obtained by further auration of the tetracoordinate precursors. It should be noted that one of these was predicted on the basis of MO calculations[16] and also obtained serendipitously but not recognized as $[C(AuL)_6]^{2+}$.[17] Recent theoretical work has shown the importance of relativistic effects for the description of such systems.[18]

Whereas triaurated phosphonium cations $[RP(AuL)_3]^+$ were found to be easily aurated further to give phosphonium dications $[RP(AuL)_4]^{2+}$, in a way similar to the generation of $[N(AuL)_5]^{2+}$ from $[N(AuL)_4]^+$, the synthesis of the corresponding hypercoordinated organo*ammonium* ions $[RN(AuL)_4]^{2+}$ could not be achieved. The auration of *two* separate amino groups in the same molecule proved feasiable, however, giving dications in which the charges are separated in space. The results obtained in the course of these studies are the subject of the present paper. Further, some spectroscopic data for the compounds $[PhN(AuPPh_3)_3]^+BF_4^-$ and $[C_6H_{11}N(AuPPh_3)_3]^+BF_4^-$ are appended for comparison (cf. ref 6).

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Table I. Starting Compounds and Products of Reaction 1

X	diamine $X(NH_2)_2$	diammonium salt $\{X[N(AuL)_3]_2\}^{2+}(BF_4^-)_2$
$-CH_2CH_2-$	**1a**	**3a**
1,4-C_6H_4	**1b**	**3b**
1,3-C_6H_4	**1c**	**3c**
1,2-C_6H_4	**1d**	**3d**

Experimental Section

Starting Materials and Physical Methods. All diamines were commercial products of reagent grade, used as supplied. The oxonium salt $[O(AuPPh_3)_3]^+BF_4^-$ was prepared by the published method.[19] NMR spectra were recorded on a Jeol-GX 400 spectrometer. Elemental analyses were performed in the microanalytical laboratory of this Institute.

Syntheses of Compounds. All experiments were carried out in an atmosphere of purified nitrogen, employing standard Schlenk techniques. The solvents were dried, saturated with nitrogen, and distilled before use.

$\{1,2\text{-}C_2H_4[N(AuPPh_3)_3]_2\}^{2+}(BF_4^-)_2$ (3a), $\{1,4\text{-}C_6H_4[N(AuPPh_3)_3]_2\}^{2+}(BF_4^-)_2$ (3b), $\{1,3\text{-}C_6H_4[N(AuPPh_3)_3]_2\}^{2+}(BF_4^-)_2$ (3c), and $\{1,2\text{-}C_6H_4[N(AuPPh_3)_3]_2\}^{2+}(BF_4^-)_2$ (3d). Typically, a suspension of the oxonium salt **2** (0.56 g, 0.38 mmol) in THF (20 mL) was added to a solution of the diamine (**1a**, 0.012 g; **1b–d**, 0.022 g, 0.20 mmol) in THF (20 mL), and the reaction mixture was stirred for 2–5 h at room temperature. The resulting suspension (**3a,b,d**) or solution (**3c**) was then evaporated to dryness, the residue dissolved in methylene chloride, the solution filtered over cellulose to remove impurities of colloidal gold, and the compounds reprecipitated by addition of pentane. Yield: **3a**, 0.44 g, 73%; **3b**, 0.50 g, 88%; **3c**, 0.56 g, 98%; **3d**, 0.58 g, 100%. Anal. Calcd for $C_{110}H_{94}B_2Au_6F_8N_2P_6$ (**3a**): C, 44.26; H, 3.17; N, 0.94; P, 6.23. Found: C, 43.53; H, 3.60; N, 0.92; P, 5.97. Calcd for isomers $C_{114}H_{94}B_2Au_6F_8N_2P_6$ (**3b–d**): C, 45.14; H, 3.12; N, 0.92; P, 6.13. Found for **3b**: C, 45.01; H, 3.08; N, 0.99; P, 6.68. Found for **3c**: C, 45.03; H, 3.14; N, 0.89; P, 6.27. Found for **3d**: C, 44.76; H, 3.27; N, 0.86; P, 6.26.

Results

Diamines **1** chosen for this study were ethylenediamine and the three isomeric phenylenediamines (Table I). In each case, both amino groups were found to become triply aurated on reaction with a stoichiometric amount of tris[(triphenylphosphine)gold(I)]oxygen(1+) tetrafluoroborate (**2**). After evaporation of THF, the products **3** were obtained as yellowish brown or greenish yellow solids in high yield (eq 1). The compounds are insensitive

$$\underset{\mathbf{1}}{H_2N{-}X{-}NH_2} + 2\underset{\mathbf{2}}{\{[(Ph_3PAu)_3O]^+BF_4^-\}} \xrightarrow[-2H_2O]{THF} \underset{\mathbf{3}}{[(Ph_3PAu)_3N{-}X{-}N(AuPPh_3)_3]^{2+}(BF_4^-)_2} \qquad (1)$$

to air and moisture and dissolve readily in polar solvents. They were characterized by means of $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR, IR, and (where applicable) mass spectrometry and elemental analysis. Infrared spectra from samples on KBr (4000–400 cm^{-1}) show the characteristic "fingerprint" bands of triphenylphosphine and tetrafluoroborate units. The IR absorption characteristics of symmetrically disubstituted benzenes could not be observed, which may be due to the large substituent masses and high symmetry (where applicable). Attempts to grow single crystals of complexes **3a–d** suitable for an X-ray study have so far been unsuccessful. The compounds tend to separate from solution as oils, which turn into polycrystalline solids upon drying in vacuo.

Therefore, NMR spectroscopy played the key role in the elucidation of the structures (Table II). Proton, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra confirm the equivalence of the triphenylphosphine groups in all cases.

In the ^1H-NMR spectrum of **3a**, the methylene protons give rise to a singlet broadened by ^{31}P coupling. There is no discernible fine structure, but the ratio of integrals of aliphatic and aromatic protons is correct (4:90). There are two separate multiplets in the aromatic region with an intensity ratio of 3:2, which are assigned to *o*-/*p*- and *m*-H atoms of the phenyl rings, respectively. The chemical shift of the methylene protons in uncomplexed ethylenediamine is $\delta = 2.60$ ppm; auration of both amino functions thus shifts the resonance by $\Delta\delta = +2.2$ ppm. In the related ethylammonium salt[6] $[EtN(AuPPh_3)_3]^+BF_4^-$ (**4**), the corresponding value for the methylene protons is $\Delta\delta = +1.5$ ppm. Similarly, the ^{13}C resonance of the methylene groups is deshielded by $\Delta\delta = +27$ ppm upon auration, as compared to the uncomplexed ligand.

In the spectroscopic characterization of compounds **3b–d**, particular attention was paid to the effects of the decreasing distance between the $[(LAu)_3N]^+$ substituents.

The ^1H-NMR spectrum of **3b** has a well-resolved singlet signal in the aromatic region which is assigned to the phenylene protons. The phenyl protons in PPh_3 show a pattern similar to that in **3a**.

The $^{13}C\{^1H\}$ NMR spectrum of **3b** shows some interesting details in comparison to that of the related anilinium salt $[PhN(AuPPh_3)_3]^+BF_4^-$ (**4**): In **4**, the resonance of C1 is shifted by $\Delta\delta \approx +10$ ppm and that of C4 by $\Delta\delta \approx +5$ ppm as compared to the parent compound aniline. In **3b**, the resonance of C1/4 is shifted by $\Delta\delta \approx +15$ ppm as compared to the parent compound 1,4-phenylenediamine. Further, in **3b** the resonance assigned to C2/3/5/6 appears as a quartet, just as in **4** where the signal assigned to C2/6 has the same multiplicity. Although there are examples of observed $^4J(PC)$ couplings in the literature, compounds **3b** and **4** are unusual in that the coupling occurs over two heteroatoms.

The dication in **3b** is detected directly by means of field desorption mass spectrometry. The base peak at $m/e = 1429.4$ corresponds to half the mass of the parent ion. It is accompanied only by a peak at $m/e = 970.0$ (20%, $[M - 2Ph_3PAu]^{2+}$).

The spectral assignments for **3c** follow from what has been said. In the proton NMR spectrum two triplets in the aromatic region can be assigned to H2 and H5 of the phenylene unit, respectively. The *J* values are similar to those typically encountered in aromatic systems for $^4J(HH)$ and $^3J(HH)$ coupling. The resonances of H4 and H6 are obscured by the phenyl signals (PPh_3), which show the usual pattern (intensity ratio 3:2). In the ^{13}C-NMR spectrum, no unusual multiplicities can be observed.

Again, the field desorption mass spectrum provides direct evidence for the existence of the dication ($m/e = 1430.2$, 3%). The base peak is at $m/e = 1155.8$ and indicates the presence of the hypercoordinated ammonium dication $[N(AuPPh_3)_5]^{2+}$.[15] Perhaps, internal reaction of the substituents is facilitated by their increased proximity in **3c** as compared to **3b**. Another signal at $m/e = 1103.7$ (44%) can be assigned to the species $[Ph_2P(AuPPh_3)_2]^+$.

The spectra of **3d** are similar to those of **3b** and **3c**; however, one novel aspect deserves particular attention. The resonances of the phenyl protons in the $AuPPh_3$ units are now resolved into three distinct sets. Assignment is possible on the basis of both fine structure and intensity. This is in contrast to the corresponding spectra obtained for **3a–c** and is indicative of the proximity of the positive charges in **3d**. The homoleptic ammonium dication $[N(AuPPh_3)_5]^{2+}$ has a similar proton NMR spectrum, and this charge dependence may thus be expected to be a general phenomenon. The phenylene protons give rise to a symmetrical multiplet which has the features expected for an AA′BB′ spin system.

Finally, the concentration of positive charges in **3d** is also reflected in the ^{31}P chemical shift (26.9 ppm), which is a value

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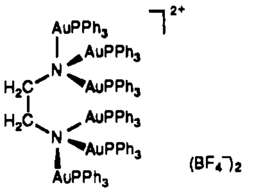
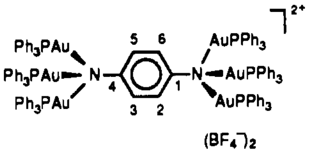
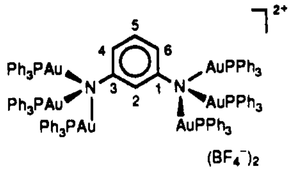
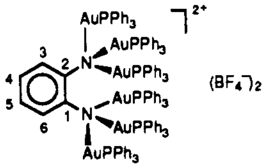
Table II. Proton, ^{31}P, and ^{13}C Chemical Shifts of Diammonium Salts **3a–d** (CD_2Cl_2 Solutions at 20 °C)[a] with ^{13}C-NMR Data for the Aurated Monoammonium Salts[6] $[PhN(AuPPh_3)_3]^+BF_4^-$ (**4**) and $[C_6H_{11}N(AuPPh_3)_3]^+BF_4^-$ (**5**) Listed for Comparison[c]

compd	type	chem shift (δ)
 **3a**	^{1}H	4.83, m, 4 H; 7.11–7.16, m, 36 H; 7.33–7.39, m, 54 H
	^{31}P[b]	28.7, s
	^{13}C[b]	C1, 71.2, s; C_{ipso}, 129.7, d, ^1J(CP) = 58.0; C_{ortho}, 134.3, d, ^2J(CP) = 13.7; C_{meta}, 129.6, d, ^3J(CP) = 11.4; C_{para}, 132.2, s; free diamine C1, 44.3
 **3b**	^{1}H	7.24–7.28, m, 36 H; 7.31, s, 4 H; 7.39–7.47, m, 54 H
	^{31}P[b]	28.9, s
	^{13}C[b]	C1/4, 153.3, s; C2/3/5/6, 124.4, quart, ^4J(CP) = 2.5; C_{ipso}, 129.3, d, ^1J(CP) = 61.0; C_{ortho}, 134.2, d, ^2J(CP) = 13.0; C_{meta}, 129.6, d, ^3J(CP) = 9.9; C_{para}, 132.3, d, ^4J(CP) = 2.5; free diamine C1/4, 138.8, and C2/3/5/6, 116.9
 **3c**	^{1}H	H5, 6.97, t, ^3J(HH) = 7.94; 7.14–7.19, m; 7.33–7.42, m; H2, 7.87, t, ^4J(HH) = 2.14; H4/6 obscured by phenyl protons
	^{31}P[b]	28.7, s
	^{13}C[b]	C1/3, 159.7, s; C2, 121.5, s; C4/6, 118.7, s; C5, 128.1, s; C_{ipso}, 129.2, d, ^1J(CP) = 59.7; C_{ortho}, 134.2, d, ^2J(CP) = 13.7; C_{meta}, 129.7, d, ^3J(CP) = 11.7; C_{para}, 132.4, s; free diamine C1/3, 147.9, C2, 102.2, C4/6, 106.2, and C5, 130.4
 **3d**	^{1}H	6.93–6.98, m, 36 H (meta); 7.14–7.22, m, 36 H (ortho); 7.27–7.30, m, 18 H; 8.44–8.48, AA′BB′, *N* = 16.48, 4 H
	^{31}P[b]	26.9, s
	^{13}C[b]	C1/2, 153.6, s; C3/6, 130.2, s; C4/5, 121.5, s; C_{ipso}, 129.2, d, ^1J(CP) = 59.5; C_{ortho}, 134.1, d, ^2J(CP) = 13.7; C_{meta}, 129.6, d, ^3J(CP) = 11.4; C_{para}, 132.3, s; free diamine C1/2, 135.0, C3/6, 117.0, and C4/5, 120.5
$[PhN(AuPPh_3)_3]^+BF_4^-$ (**4**)	^{13}C[b]	C1, 159.7, s; C2/6, 124.9, quart, ^4J(PC) = 2.3; C3/5, 128.6, s; C4, 121.7, s; C_{ipso}, 129.3, d, ^1J(CP) = 60.6; C_{ortho}, 134.3, d, ^2J(CP) = 13.7; C_{meta}, 129.7, d, ^3J(CP) = 11.7; C_{para}, 132.4, d, ^4J(CP) = 2.4; free aniline C1, 148.7, C2/6, 114.4, C3/5, 129.1, and C4, 116.3
$[C_6H_{11}N(AuPPh_3)_3]^+BF_4^-$ (**5**)	^{13}C[b]	C1, 67.9, s; C2/6, 48.8, s; C3/5, 26.3, s; C4, 25.6, s; C_{ipso}, 130.1, d, ^1J(CP) = 58.2; C_{ortho}, 134.4, d, ^2J(CP) = 13.2; C_{meta}, 129.6, d, ^3J(CP) = 11.7; C_{para}, 132.2, s (br); free $C_6H_{11}NH_2$ (–NH_2 eq) C1, 51.2, C2/6, 37.5, C3/5, 25.8, and C4, 26.1

[a] In ppm from $SiMe_4$ and external 85% aqueous H_3PO_4, respectively; *J* and *N* (distance between outermost lines in a high-order multiplet) in Hz. [b] ^{1}H-Decoupled. [c] ^{13}C chemical shift values for uncomplexed diamines and amines from the literature.[20]

significantly smaller than in the case of either **3b** or **3c**, approaching that in $[N(AuPPh_3)_5]^{2+}(BF_4^-)_2$ (25.3 ppm).[15] Mass spectrometric analysis of **3d** (by field desorption or fast atom bombardment) gives a peak at *m/e* = 2399.0 (3%) for the heaviest fragment, which is identified as $[M - Ph_3PAu]^+$. There is now no direct evidence for the parent ion, which appears to be too labile under the given conditions. The spectrum is dominated by signals at *m/e* = 459.1 (100%, $[Ph_3PAu]^+$) and *m/e* = 721.1 (55%, $[(Ph_3P)_2Au]^+$), which indicates that extensive fragmentation is taking place.

Discussion

Whereas phosphonium cations of the type $RP(AuL)_3^+$ can be aurated further to give dications of the type $RP(AuL)_4^{2+}$, all attempts to add further $[Ph_3PAu]^+$ units to the previously described[5,6] triaurioammonium salts $RN(AuL)_3^+$ have met with no success. Since the new compounds reported in this work possess *two* triaurioammonio substituents within the same molecule, there was reason to assume that the presence of gold aggregates in close proximity might be able to assist the addition of further gold(I) units in a synergistic manner, in particular in the case of the ortho-disubstituted compound **3d**. However, treatment of compounds **3a–d** with $[Ph_3PAu]^+BF_4^-$ or $[(Ph_3PAu)_3O]^+BF_4^-$ did not lead to further auration, and the starting compounds were recovered unchanged in each case. At a small nitrogen atom carrying one or two organic substituents, the formation of hypercoordinate compounds may be topologically unfavorable. Studies to clarify this point by changing the basic structural situation are in progress.

In the present study it has been shown that "polyauration of polyamines" is a straightforward process leading readily to polygold species of high stability. It should be pointed out that this possibility of introducing centers of high electron density into polyamines in a selective way may be of high diagnostic value, e.g. in the investigation of certain biomolecules by electron microscopy. Gold clusters in particular have been employed successfully for this purpose.[21]

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