

X-Ray Crystal Structures and Quantum Chemical Calculations of Tetraphenyl-arsonium Tetraazidoaurate(III) and Azido(triphenylphosphine)Gold(I)

Wolfgang Beck*, Thomas M. Klapötke*, Peter Klüfers, Gernot Kramer and Claudia M. Rienäcker

München, Department Chemie, Ludwig-Maximilians-Universität

Received January 22nd, 2001.

Dedicated to Professor Kurt Dehnicke on the Occasion of his 70th Birthday

Abstract. The single crystal X-ray structure determinations are reported for $[\text{Ph}_4\text{As}][\text{Au}(\text{N}_3)_4]$ (**1**) and Ph_3PAuN_3 (**2**). Compound **1** is an ionic species with a “windmill” shaped anion. It crystallizes in the monoclinic space group $C2/c$, $a = 18.396(2)$, $b = 6.2492(4)$, $c = 23.555(2)$ Å; $\beta = 107.98(1)^\circ$, $Z = 4$, $R1_{(\text{all data})} = 0.0227$, $wR2 = 0.0374$. The lattice parameters of compound **2**, which crystallizes in the orthorhombic space group $P2_12_12_1$, are $a = 10.9252(1)$, $b = 11.5642(1)$, $c = 13.0993(1)$ Å; $Z = 4$, $R1_{(\text{all data})} = 0.0176$, $wR = 0.0334$.

The experimentally obtained X-ray data and vibrational frequencies of both compounds were compared with those calculated at B3LYP/LANL2DZ and B3LYP/SDD level of theory and for **1** also at the MP2/SDD level.

Keywords: Gold; Tetraphenylarsonium Tetraazidoaurate(III); Azido(triphenylphosphine)gold(I); Crystal structure; Quantum chemical calculations

Einkristallröntgenstrukturanalyse und ab Initio Rechnungen von Tetraphenylarsoniumtetraazidoaurat(III) und Azido(triphenylphosphin)gold(I)

Inhaltsübersicht. Die Einkristallröntgenstrukturanalysen von $[\text{Ph}_4\text{As}][\text{Au}(\text{N}_3)_4]$ (**1**) und Ph_3PAuN_3 (**2**) werden beschrieben. **1** ist eine ionische Verbindung mit einem „Windrad“-förmigen Anion. Sie kristallisiert in der monoklinen Raumgruppe $C2/c$, $a = 18.396(2)$, $b = 6.2492(4)$, $c = 23.555(2)$ Å; $\beta = 107.98(1)^\circ$, $Z = 4$, $R1_{(\text{alle Daten})} = 0.0227$, $wR2 = 0.0374$. Die Gitterparameter von Verbindung **2**, welche in der ortho-

rhombischen Raumgruppe $P2_12_12_1$ kristallisiert, sind $a = 10.9252(1)$, $b = 11.5642(1)$, $c = 13.0993(1)$ Å; $Z = 4$, $R1_{(\text{alle Daten})} = 0.0176$, $wR2 = 0.0334$. Die experimentell beobachteten Röntgendaten und die Schwingungsfrequenzen beider Verbindungen werden mit denen auf B3LYP/LANL2DZ- und B3LYP/SDD-Niveau und für **1** auch auf MP2/SDD-Niveau berechneten Daten verglichen.

Introduction

Gold azide species are difficult to prepare and often not available as pure compounds. All compounds are potentially explosive. To our knowledge, the two binary gold compounds AuN_3 and $\text{Au}(\text{N}_3)_3$ are hitherto unknown [1–4]. Stable are the anions $[\text{Au}(\text{N}_3)_2]^-$ [5–9] and $[\text{Au}(\text{N}_3)_4]^-$ [1, 5, 6, 10, 11]. For the first one counterions like $[\text{Ph}_4\text{As}]^+$ and $[\text{Bu}_4\text{N}]^+$ have been reported, and for the second one in addition to these two cations $[\text{Et}_4\text{N}]^+$ [10] and $[\text{Me}_3(\text{cetyl})\text{N}]^+$ [6] have also been described in the literature. The tendency of these

compounds to explode is very low. It is believed that the stability of the gold azide anions is so high, because of the “dilution” with the bulky cations. $[\text{Ph}_4\text{As}][\text{Au}(\text{N}_3)_4]$ is formed in aqueous solution from KAuCl_4 with an excess of sodium azide and the addition of tetraphenylarsoniumchloride [5, 11]. In an earlier X-ray structure determination it was found that **1** crystallizes in the tetragonal space group $P4/n$ with $Z = 2$ [12]. We found another polymorph caused by a different crystallization procedure.

Azido(triphenylphosphine)gold(I) is very often used in photolysis chemistry as a precursor for interesting gold clusters [13]. It is formed by reaction of the chloro or bromo complex with sodium azide [14, 15]. Other methods have been reported, where $\text{Ph}_3\text{PAuNO}_3$ is reacted with NaN_3 in a methanol/acetone mixture [16] or the acetato complex Ph_3AuOAc is reacted with HN_3 [17].

Experimental

Samples of $[\text{Ph}_4\text{As}][\text{Au}(\text{N}_3)_4]$ [5, 11] and Ph_3PAuN_3 [14] were prepared ca. 35 years ago by literature methods and stored in a dry and dark room. The recrystallizations were

* Prof. Dr. W. Beck, Prof. Dr. T. M. Klapötke
Department Chemie
Ludwig-Maximilians-Universität
Butenandtstr. 5–13 (Haus D)
D-81377 München
Phone: (WB)++49-89-21 80-74 64,
(TMK)++49-89-21 80-74 91
Fax: (WB)++49-89-21 80-78 66,
(TMK)++49-89-21 80-74 92
e-mail: wbe@cup.uni-muenchen.de,
tmk@cup.uni-muenchen.de

carried out in dried dichloromethane which contained traces of pentane. The recrystallization vessels were kept at 5 °C over a period of 3 weeks. The obtained single crystals were embedded in oil and mounted with Lithelen. The X-ray data of **1** were collected on a *Stoe IPDS* diffractometer using Mo- $K\alpha$ radiation (0.71069 Å). The X-ray data of **2** were collected on a *Nonius Kappa-CCD* diffractometer with a FR591 rotating anode using Mo- $K\alpha$ radiation (0.71069 Å). The structures were solved by direct methods (SHELXS97 [18]) and were refined by means of full-matrix least squares procedures based on F^2 using SHELXL97 [19], weights w were applied according to $w^{-1} = \alpha^2(F_o^2) + (\chi P)^2 + \gamma P$. Hydrogen atoms were confined to chemically reasonable positions. Table 1 shows the crystal data and summary of data collection for compounds **1** and **2**.

Further information is available from the Cambridge Crystallographic Data Centre under the deposition numbers CCDC 152952 for [Ph₄As][Au(N₃)₄] and CCDC 153002 for Ph₃PAuN₃.

The ¹⁴N NMR spectrum was recorded using a GSX400 MHz multinuclear instrument. Chemical shifts are

Table 1 Crystal Data and Summary of Data Collection for Compounds **1** and **2**

Compound	[Ph ₄ As][Au(N ₃) ₄] (1)	Ph ₃ PAuN ₃ (2)
Chemical formula	C ₂₄ H ₂₀ AsAuN ₁₂	C ₁₈ H ₁₅ AuN ₃ P
Molecular weight	748.41	501.27
<i>T</i> /K	200(2)	200(2)
Crystal system, space group	monoclinic, <i>C</i> 2/ <i>c</i>	orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	18.396(2)	10.9252(1)
<i>b</i> /Å	6.2492(4)	11.5642(1)
<i>c</i> /Å	23.555(2)	13.0993(1)
β /°	107.98(1)	90.00
Volume/Å ³	2575.6(3)	1654.98(2)
<i>Z</i>	4	4
Density (calc.)/g · cm ⁻³	1.930	2.012
Absorption coefficient/mm ⁻¹	7.027	8.987
<i>F</i> (000)	1440	952
Crystal color	red	colorless
Crystal size/mm	0.3 × 0.11 × 0.02	0.14 × 0.08 × 0.06
Scan type	image-plate area detection	CCD area detection
2 θ range for data collection/°	3.64 to 51.60	7.04 to 46.52
Index ranges (maximum)	-22 ≤ <i>h</i> ≤ 22 -7 ≤ <i>k</i> ≤ 7 -28 ≤ <i>l</i> ≤ 28	-12 ≤ <i>h</i> ≤ 12 -12 ≤ <i>k</i> ≤ 12 -14 ≤ <i>l</i> ≤ 14
Reflections collected	9489	24310
Independent reflections	2463	2368
<i>R</i> _{int}	0.0339	0.0515
Observed reflections	2130	2254
Max. and min. transmission factors	0.8336 and 0.2706	0.6099 and 0.4312
Structure solution	direct methods	direct methods
<i>x</i> (weighting scheme)	0.021300	0.0
<i>y</i> (weighting scheme)	0.0	2.830900
Data/parameters	2463/174	2368/208
Final <i>R</i> indices (<i>F</i> > 4 σ (<i>F</i>))	<i>R</i> 1 = 0.0162, <i>wR</i> 2 = 0.0366	<i>R</i> 1 = 0.0160, <i>wR</i> 2 = 0.0329
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0227, <i>wR</i> 2 = 0.0374	<i>R</i> 1 = 0.0176, <i>wR</i> 2 = 0.0334
Goodness of Fit	0.955	1.088
Largest Δ / σ	0.001	0.001
Largest difference peak/e Å ⁻³	0.442	0.307
Largest difference hole/e Å ⁻³	-0.714	-0.392

reported with respect to CH₃NO₂. The Raman spectra of [Ph₄As][Au(N₃)₄] and Ph₃PAuN₃ were obtained on powders contained in glass capillary tubes with a Perkin Elmer 2000 NIR spectrometer. The IR spectra were taken on a Nujol mull between KBr plates on a Nicolet 520 FT IR spectrometer.

[Ph₄As][Au(N₃)₄] (**1**)

IR ν in cm⁻¹: 2027 s ($\nu_{\text{as}}\text{N}_3^-$), 1250 s ($\nu_s\text{N}_3^-$), 1159 m, 1082 m, 1020 m, 997 m, 917 w, 735 s, 683 s, 575 w (N_3^-), 477 m, 461 m, 427 s ($\nu_{\text{Au-N}}$), 352 m, 300 w and 220 m.

Raman (20 mW) ν in cm⁻¹: 3066(10), 2049(22, $\nu_{\text{as}}\text{N}_3^-$), 1578(9), 1440(2), 1261 (3, $\nu_s\text{N}_3^-$), 1187(4), 1162(3), 1083(3), 1023(6), 1001(17), 676(9), 614(2), 414 (100, $\nu_{\text{Au-N}}$), 402(32), 273(4), 236(8), 208(22), 188(9), 172(10) and 120(28).

¹⁴N NMR (28.9 MHz, DMSO-*d*₆) [ppm]: -133 (N2), -178 (N3), -283 (N1).

Ph₃PAuN₃ (**2**)

IR ν in cm⁻¹: 2050 s ($\nu_{\text{as}}\text{N}_3^-$), 1477 m, 1432 m, 1326 w, 1175 m ($\nu_s\text{N}_3^-$), 1157 w, 1099 s, 1024 m, 997 m, 747 s, 742 s, 710 s, 691 s, 545 vs (N_3^-), 502 vs, 437 w ($\nu_{\text{Au-N}}$) and 397 w.

Raman (20 mW) ν in cm⁻¹: 2058 (26, $\nu_{\text{as}}\text{N}_3^-$), 1586(93), 1573(48), 1437(35), 1330(34), 1296(33), 1185 (32, $\nu_s\text{N}_3^-$), 1162(31), 1102(54), 1081(27), 1027(50), 999(99), 713(21), 693(27), 617(17) 398(23), 329(23), 255(32), 233(29), 208(35), 184(40), 164(38) and 103(100).

¹⁴N NMR (28.9 MHz, DMSO-*d*₆) [ppm]: -133 (N2), -183 (N3), -311 (N1).

Discussion

Crystal structure determination

Compound **1** crystallizes in the monoclinic space group *C*2/*c* with *Z* = 4. The gold atom has a planar-square coordination by four nitrogen atoms. The Au–N1 distances are in the range 2.031(2)–2.033(2) Å, the values for the bond distances of N1–N2 lie in the expected range of 1.204(3)–1.220(4) Å and are longer than the ones for N2–N3 with 1.133(4)–1.138(4) Å. The Au–N1–N2 angles are 115.1(2)–116.9(2)°. The azide moieties are slightly bent with angles of 174.4(3)–175.8(3)° for N1–N2–N3.

Table 2 Selected bond lengths/Å and angles/° for [Ph₄As][Au(N₃)₄], as determined by X-ray diffraction

Au(1)–N(12)	2.031(2)	As(1)–C(12)	1.915(3)
Au(1)–N(11)	2.033(2)	As(1)–C(11)	1.918(2)
N(12)–N(22)	1.204(3)	N(11)–N(21)	1.220(4)
N(22)–N(32)	1.138(4)	N(21)–N(31)	1.133(4)
N(22)–N(12)–Au(1)	115.1(2)	N(21)–N(11)–Au(1)	116.9(2)
N(32)–N(22)–N(12)	175.8(3)	N(31)–N(21)–N(11)	174.4(3)
C(12)–As(1)–C(12B)	112.1(2)	C(12)–As(1)–C(11)	108.6(1)
C(12B)–As(1)–C(11)	108.2(1)	C(11)–As(1)–C(11B)	111.1(2)
N(12)–Au(1)–N(11)	89.6(1)		

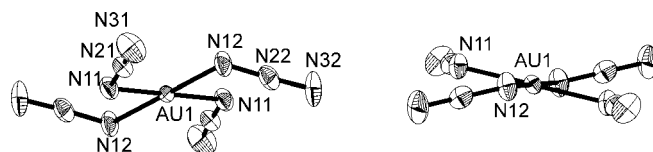


Fig. 1 ORTEP views of the anion of **1**, [Au(N₃)₄]⁻ (50% thermal ellipsoids).

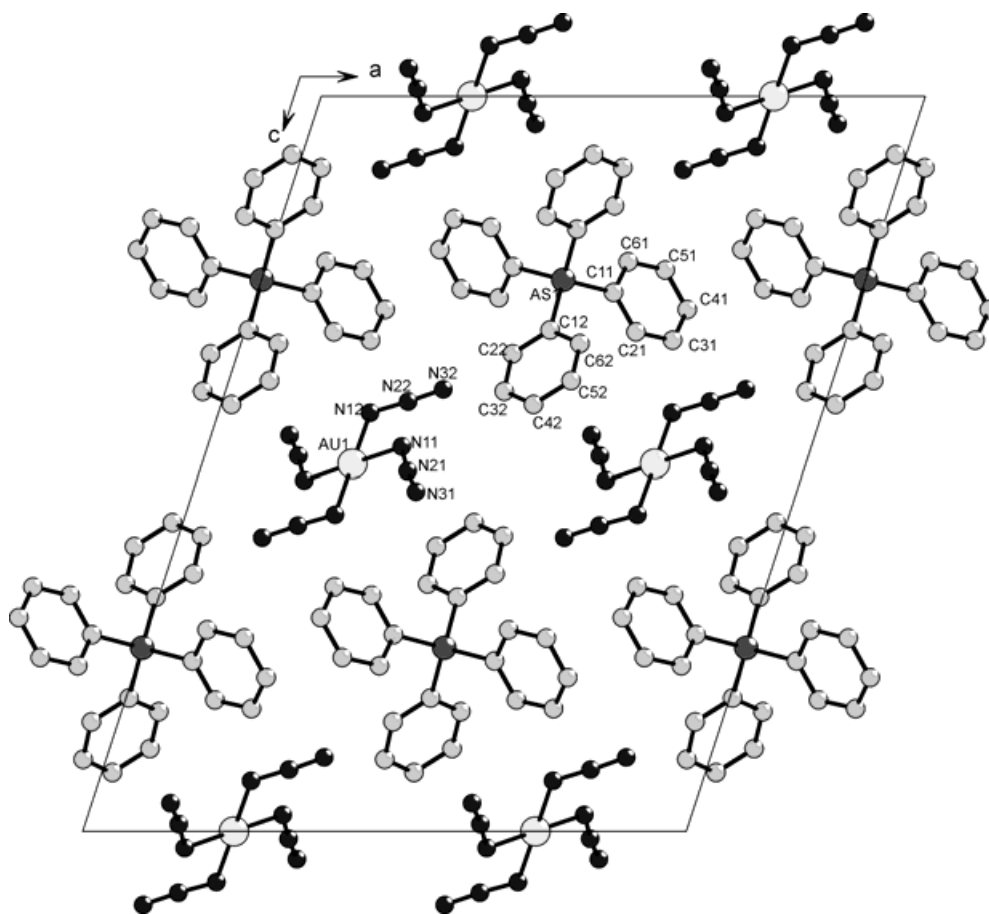


Fig. 2 Projection of the unit cell of $[\text{Ph}_4\text{As}][\text{Au}(\text{N}_3)_4]$ along the *b* axis.

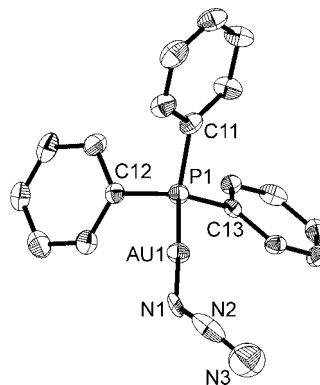
Similar values are found for azides which are covalently bonded to a metal atom or an organic substituent, where N1-N2-N3 angles of ca. 170° have been reported [20, 21]. Table 2 shows some selected bond lengths and angles of $[\text{Ph}_4\text{As}][\text{Au}(\text{N}_3)_4]$. The structure of $[\text{Au}(\text{N}_3)_4]^-$ is shown in Figure 1. In Figure 2 the unit cell is presented.

Azido(triphenylphosphine)gold(I) (**2**) crystallizes as colorless prisms in the orthorhombic crystal system in the space group $P2_12_12_1$. The crystal consists of discrete Ph_3PAuN_3 molecules separated by normal van der Waals distances. No gold-gold interactions are visible. The Au-N distance is 2.100 Å, which lies in the same dimension as do the Pd-N distances in the compounds $[\text{Pd}(\text{NH}_3)_4][\text{Pd}(\text{N}_3)_4]$, $\text{Pd}(\text{pyridine})_2(\text{N}_3)_2$ and $\text{Pd}(\text{chinoline})_2(\text{N}_3)$ with values between 2.037 to 2.056 Å [22]. Also the Pt-N distances in the compounds $[\text{Ph}_4\text{As}]_2[\text{Pt}(\text{N}_3)_4]$, $[\text{Ph}_4\text{As}]_2[\text{Pt}(\text{N}_3)_6]$ and $[\text{n-Bu}_4\text{N}]_2[\text{Pt}(\text{N}_3)_4\text{X}_2]$ with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ [23,24] lie in the range 1.97–2.122 Å. Of special interest are the distances within the azide moiety. The N1–N2 length refined to 0.995(7) Å, which is shorter than the value for N2–N3 with 1.294(8) Å. This is astonishing, because the relation should be the other way round [25]. This phenomenon was also found in the above-men-

tioned and some other [26] platinum-azide compounds. In the current crystallographic work, attempts are made to correct the diffraction data for untypically high valence-electron contributions and effects that are caused by the close proximity of heavy and light atoms. Additionally, we addressed ourselves to factors that affect the thermal parameters, in particular disorder phenomena. Current experimental work thus focussed on X-ray investigations at different temperatures. No elemental analysis was performed due to the fact that we had previously experienced severe problems due to explosion of Au azide species in the apparatus. Since the same structural anomaly was also observed for the “chloride free” Pt azide compounds discussed above where no Cl^-/N_3^- exchange was detected we also saw a Cl^-/N_3^- exchange very unlikely and refrained from doing a combustion analysis. The N1–N2–N3 angle is $171.8(6)^\circ$, which is smaller as with the mentioned palladium or platinum azide compounds with values of $174.2\text{--}178.3^\circ$. The N1–Au–P moiety is almost linear with an angle of $176.9(1)^\circ$. The distance of Au–P (2.2370(9) Å) is shorter than the sum of the covalent radii with 2.44 Å. Table 3 shows some selected bond lengths and angles of Ph_3PAuN_3 . The structure of **2** is shown in Figure 3.

Table 3 Selected bond lengths/Å and angles/° for Ph₃PAuN₃, as determined by X-ray diffraction

Au(1)–N(1)	2.100(4)	P(1)–C(13)	1.811(6)
Au(1)–P(1)	2.2370(9)	P(1)–C(11)	1.822(4)
N(1)–N(2)	0.995(7)	P(1)–C(12)	1.813(6)
N(2)–N(3)	1.294(8)		
N(1)–Au(1)–P(1)	176.9(1)	C(12)–P(1)–Au(1)	114.6(2)
N(1)–N(2)–N(3)	171.8(6)	C(13)–P(1)–C(11)	105.6(3)
N(2)–N(1)–Au(1)	120.4(4)	C(13)–P(1)–C(12)	104.8(2)
C(13)–P(1)–Au(1)	113.5(2)	C(12)–P(1)–C(11)	107.4(3)
C(11)–P(1)–Au(1)	110.4(1)		

**Fig. 3** ORTEP view of Ph₃PAuN₃ (50% probability, H atoms are omitted for clarity).

Computational methods and results

All computations were performed using the program package Gaussian 98 [27].

For gold, two slightly different sets of pseudopotentials and basis sets were used. First, the Los Alamos ECP plus a double zeta valence basis set [28–30]

(denoted as LANL2DZ) for gold and Dunning/Huzinaga's full double zeta basis set for the first and second row elements (H, C, N) [31]. Secondly, the

Table 4 Comparison between computational and experimental results for [Au(N₃)₄][−]

	B3LYP/LANL2DZ	B3LYP/SDD	MP2/SDD	exptl. [5, 12, 46] and this work
Symmetry	C _{4h}	C _{4h}	C _{4h}	
−E/a. u.	792.155502	792.492071	789.340616	
NIMAG	0	0	0	
zpe/kcal mol ^{−1}	29.5	29.6	29.6	
d(Au–N1)/Å	2.095	2.082	2.094	2.03(1) 2.033(2)
d(N1–N2)/Å	1.247	1.248	1.284	1.22(3) 1.220(4)
d(N2–N3)/Å	1.183	1.182	1.212	1.15(3) 1.133(4)
∠(Au–N1–N2)/°	119.7	120.5	117.5	116(1) 116.9(2)
∠(N1–N2–N3)/°	175.1	174.5	171.7	172(2) 174.4(3)
ν/cm ^{−1} (Int.) ^a	180(8)	184(9/0)	178(7)	172(10) (Ra)
ν/cm ^{−1} (Int.) ^a	190(0)	193(0/40)	170(0)	188(9) (Ra)
ν/cm ^{−1} (Int.) ^a	219(50)	220(52/0)	193(60)	236 m (IR) 220 w (IR)
ν/cm ^{−1} (Int.) ^a	329(0)	348(0/34)	356(0)	236(8) (Ra) 403 (Ra) 352 m (IR)
ν/cm ^{−1} (Int.) ^a	353(0)	363(0/244)	359(0)	402(32) (Ra) 413(100) (Ra) 414 (100) (Ra)
ν/cm ^{−1} (Int.) ^a	388(88)	398(96/0)	405(108)	423 m (IR) 427 s (IR)
ν/cm ^{−1} (Int.) ^a	523(0)	517(0/9)	428(0)	573 s (IR)
ν/cm ^{−1} (Int.) ^a	524(11)	519(13/0)	431(1)	575 w (IR)
ν/cm ^{−1} (Int.) ^a	623(0)	624(0/51)	432(0)	614(2) (Ra)
ν/cm ^{−1} (Int.) ^a	625(0)	626(0/17)	628(0)	
ν/cm ^{−1} (Int.) ^a	646(18)	645(22/0)	639(66)	683 s (IR) 676(9) (Ra)
ν/cm ^{−1} (Int.) ^a	1258(354)	1256(394/0)	1142(550)	1250 m (IR), 1259 (Ra) 1250 s (IR) 1261(3) (Ra)
ν/cm ^{−1} (Int.) ^a	1260(0)	1259(0/8)	1147(0)	
ν/cm ^{−1} (Int.) ^a	1999(2844)	2005(2908/9)	2220(4463)	2033 vvs (IR) 2027 s (IR)
ν/cm ^{−1} (Int.) ^a	2005(0)	2010(0/328)	2241(0)	
ν/cm ^{−1} (Int.) ^a	2008(0)	2015(0/933)	2250(0)	2054 (Ra) 2049(22) (Ra)

^a only frequencies above 180 cm^{−1} are listed; frequencies are unscaled; IR intensities in parentheses in km mol^{−1}, Raman intensities in Å⁴ amu^{−1} (IR/Raman).

multielectron adjusted quasirelativistic Stuttgart/Dresden effective core potential (denoted as SDD) plus a (8s7p6d)/[6s5p3d] valence basis set for Au [32–34] and Dunning/Huzinaga's valence double zeta basis set for the first and second row elements (H, C, N) [31].

Full geometry optimisations and frequency calculations were performed at the electron correlated MP2 and the B3LYP density functional level of theory [35–43] (for definition see also [44]).

For the experimentally well-characterized anion $[\text{Au}(\text{N}_3)_4]^-$ the agreement between computed and observed structural and vibrational data was found to be good at all levels of theory applied with the B3LYP/SDD method giving the best results. This finding is in nice accord with an earlier study on AuF_3 and Au_2F_6 which showed the B3LYP methods in combination with a SDD core potential to be well suited to compute Au(III) ground state structures and energies [45]. Consequently, all calculations for possible new gold azide complexes should be performed at this level of theory (B3LYP/SDD). A comparison between computational and experimental results for $[\text{Au}(\text{N}_3)_4]^-$ are shown in Table 4. The calculated Au–N1, N1–N2 and N2–N3 distances are slightly longer than the experimental obtained ones, which could be explained by crystal packing effects. The angles are almost identical.

In Table 5 a comparison between computational and experimental results for Ph_3PAuN_3 is shown. In contrast to the single crystal X-ray structure determination where the values for the N1–N2 and N2–N3 distances are not in the expected range, the calculated ones agree with the expectation, which means that the N1–N2 length is larger than the one for N2–N3. Both used methods, B3LYP/LANL2DZ and B3LYP/SDD, give similar results. With the exception of the P–Au–N1 angle of 164.1° respectively 176.4° all other theoretical computed distances and angles are almost identical. In conclusion, the agreement between the observed and computed data is good, with the exception of the N–N distances.

Table 5 Comparison between computational and experimental results for Ph_3PAuN_3

	B3LYP/LANL2DZ	B3LYP/SDD	X-ray data
–E/a.u.	1000.986935	1336.1493667	
NIMAG	0	0	
zpc/kcal mol ^{–1}	181.4	181.4	
d(Au–N1)/Å	2.037	2.031	2.100(4)
d(P–Au)/Å	2.384	2.370	2.2370(9)
d(N1–N2)/Å	1.245	1.244	0.995(7)
d(N2–N3)/Å	1.184	1.184	1.294(8)
∠(P–Au–N1)/°	164.1	176.4	176.9(1)
∠(Au–N1–N2)/°	127.1	128.3	120.4(4)
∠(N1–N2–N3)/°	173.8	173.5	171.8(6)

Acknowledgements: The authors gratefully acknowledge the University of Munich and the Fond der Chemischen Industrie for financial support.

References

- [1] R. G. Clem, E. H. Huffman, *Anal. Chem.* **1965**, 37, 1155.
- [2] B. L. Evans, A. D. Yoffe, *Proc. Roy. Soc. [London] A* **1957**, 238, 568.
- [3] B. L. Evans, A. D. Yoffe, *Chem. Rev.* **1959**, 59, 515.
- [4] W. P. Fehlhammer, W. Beck, P. Pöllmann, *Chem. Ber.* **1969**, 102, 3903.
- [5] W. Beck, W. F. Fehlhammer, P. Pöllmann, E. Schuierer, K. Feldl, *Chem. Ber.* **1967**, 100, 2335.
- [6] A. Vogler, C. Quett, H. Kunkely, *Ber. Bunsenges. Phys. Chem.* **1988**, 92, 1486.
- [7] W. Beck, K. Schorpp, *Angew. Chem.* **1970**, 82, 701; *Angew. Chem. Int. Ed. Engl.* **1970**, 9, 735.
- [8] W. Beck, W. Becker, K. F. Chew, W. Derbyshire, N. Logan, D. M. Revitt, D. B. Sowerby, *J. Chem. Soc., Dalton Trans.* **1972**, 245.
- [9] H. D. Bartunik, W. Potzel, R. L. Mössbauer, G. Kaindl, *Z. Phys.* **1970**, 240, 1; F. Holsboer, W. Beck, *Z. Naturforsch.* **1972**, 27b, 884.
- [10] H.-H. Schmidtke, D. Garthoff, *J. Am. Chem. Soc.* **1967**, 89, 1317.
- [11] W. Beck, E. Schuierer, K. Feldl, *Angew. Chem.* **1966**, 78, 267; *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 249.
- [12] W. Beck, H. Nöth, *Chem. Ber.* **1984**, 117, 419.
- [13] J. Strähle, *J. Organomet. Chem.* **1995**, 488, 15.
- [14] W. Beck, W. P. Fehlhammer, P. Pöllman, H. Schächl, *Chem. Ber.* **1969**, 102, 1976.
- [15] R. F. Ziolo, J. A. Thich, Z. Dori, *Inorg. Chem.* **1972**, 11, 626.
- [16] G. Beuter, J. Strähle, *J. Organomet. Chem.* **1989**, 372, 67.
- [17] D. I. Nicols, A. S. Charleston, *J. Chem. Soc. A* **1969**, 2581.
- [18] G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, Universität Göttingen, **1997**.
- [19] G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.
- [20] U. Müller, *Struct. Bonding (Berlin)* **1973**, 14, 141.
- [21] Z. Dori, R. F. Ziolo, *Chem. Rev.* **1973**, 73, 247.
- [22] T. M. Klapötke, J. Knizek, H. Nöth, T. Schütt, *Eur. J. Inorg. Chem.* **1999**, 523; T. M. Klapötke, K. Polborn, T. Schütt, *Z. Anorg. Allg. Chem.* **2000**, 626, 1444.
- [23] B. Neumüller, F. Schmock, S. Schlecht, K. Dehnicke, *Z. Anorg. Allg. Chem.* **2000**, 626, 1792.
- [24] S. Schröder, W. Preetz, *Z. Anorg. Allg. Chem.* **2000**, 626, 1757.
- [25] T. M. Klapötke, A. Schulz, R. D. Harcourt, *Quantum Chemical Methods in Main-Group Chemistry*, Wiley, **1998**, chapter 12.2, p. 170.
- [26] S. Schlecht, N. Faza, W. Massa, S. Dapprich, G. Frenking, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, 624, 1011; M. Atam, U. Müller, *J. Organomet. Chem.* **1974**, 71, 435.
- [27] *Gaussian 98, Revision A.3*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery (Jr.), R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci,

- C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Peterson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA **1998**.
- [28] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.
- [29] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284.
- [30] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
- [31] T. H. Dunning, Jr., P. J. Hay, in *Modern Theoretical Chemistry*, H. F. Schaefer III (ed.), Vol. 3, Plenum, New York **1976**, p. 1.
- [32] P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* **1989**, *91*, 1762.
- [33] M. Dolg, H. Stoll, A. Savin, H. Preuss, *Theor. Chim. Acta* **1989**, *75*, 173.
- [34] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123.
- [35] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.
- [36] M. Head-Gordon, J. A. Pople, M. J. Frisch, *Chem. Phys. Lett.* **1988**, *153*, 503.
- [37] M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett.* **1990**, *166*, 275.
- [38] M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett.* **1990**, *166*, 281.
- [39] M. Head-Gordon, T. Head-Gordon, *Chem. Phys. Lett.* **1994**, *220*, 122.
- [40] S. Saebo, J. Almlof, *Chem. Phys. Lett.* **1989**, *154*, 83.
- [41] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [42] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [43] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200.
- [44] T. M. Klapötke, A. Schulz, R. D. Harcourt, *Quantum Chemical Methods in Main-Group Chemistry*, Wiley, **1998**, chapter 3, p. 64 and 69.
- [45] B. Reffy, M. Kolonitis, A. Schulz, T. M. Klapötke, M. Hargittai, *J. Am. Chem. Soc.* **2000**, *122*, 3127.
- [46] C.-J. Oetker, W. Beck, *Spectrochim. Acta* **1973**, *29 A*, 1075.