An Octanuclear Gold(I) Cube with Amidinate Ligands Containing Two Hyper-coordinate Ylide Carbon Atoms

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Z. Naturforsch. **2009**, *64b,* 1487 – 1490; received October 16, 2009

This report is dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday anniversary. His scientific leadership has been instrumental to the exceptional development of gold chemistry over the past forty years. This chemistry has been enjoyed by the senior author of this paper who is grateful to Schmidbaur for the many years of friendship and scientific comradery received.

Disparate properties of gold(I) converge to produce the first known cube assembly of eight Au(I) atoms connected by four *N*-bridging amidinate ligands on the sides of the cube, capped above and below by hyper-coordinate carbon atoms from a phosphorous ylide. There are no phosphines coordinated to the Au(I) atoms. The cluster is formulated as $[Au_8\{CH(\mathbf{N}C_8H_9)_2\}_4\{(\eta^5\text{-}\mathbf{C})P(C_6H_5)_2(CH_3)\}_2]$. It displays a strong green luminescence under UV light. The novel product was generated in an attempt to produce luminescent species of gold(I) with mixed C- and N-coordination, an arrangement not abundant in the literature. The formation and structure of this cluster is reported.

Key words: Hyper-coordinate Carbon, Cuboidal Octagold(I) Cluster, Phosphine-free Gold(I)

Introduction

Clusters of gold(I) with mixed Au–N and Au–C connectivities are rare [1]. A prominent reason lies in the electron rich “soft acid” characteristics of Au(I) and the “hard base” attributes of a *N*-donor. Therefore compounds where gold(I) connects nitrogen only donors have been relatively little studied until recently [2]. In contrast, much early chemistry of gold(I) contained Au–C bonds which are stable, due to the similar Pauling electronegativities (gold 2.54, carbon 2.55) [3]. The high electronegativity of gold compared to other coinage metals results from direct relativistic effects, due to the large nuclear charge in gold. Concomitantly the atomic ionization potential is large at *ca.* 2 eV.

Hyper-coordination at carbon atoms bonded to gold(I) is known at the methyl group of trimethylsulfoxide, $[Me_3S{=}O]ClO_4$, to form a tetranuclear gold complex $[(AuPPh_3)_4\{\eta^5\text{-}\mathbf{C}\text{-}S({=}O)Me_2\}]^+$ [4]. The methyl group is deprotonated stepwise with $[Au(acac)PPh_3]$ in acetone at r. t. Hyper-coordinate carbon atoms also can be produced using carbon atom deliverers containing structures with naked carbon or methyne. The boryl species $C[B(OMe)_2]_4$ releases carbon to R_3PAuCl in presence of CsF, producing pentanuclear and hexanuclear gold complexes $[\mathbf{C}(AuPR_3)_5]^+$ and $[\mathbf{C}(AuPR_3)_6]^{2+}$ [5]. Lower gold nuclearity is possible by using boryl species $CH_2[B(OMe)_2]_2$ or $MeC[B(OMe)_2]_3$ which results in the formation of the tetranuclear gold complex $[Me\mathbf{C}(AuPR_3)_4]^+$ [6]. Auration of $[(R_3Si)_2CH(AuPPh_3)]$ using the assisting base, the oxonium salt $[O(AuPPh_3)_3]BF_4$, generates the trinuclear gold cation $[(R_3Si)_2\mathbf{C}(AuPPh_3)_3]^+$ [7]. The hyper-coordinated methyne cation $[H\mathbf{C}(Au(PPh_3)_4]^+$ is synthesized from the reaction of the oxonium salt $[O(AuPPh_3)_3]BF_4$ with silyldiazomethane Me_3SiCHN_2 by the loss of N_2 and desilylation [8]. Prior to this work, all of these clusters containing hyper-coordinate carbon atoms also had a phosphine coordinated to the gold atom.

Experimental Section

Synthesis

Reactions were carried out under nitrogen using Schlenk techniques. The THF, ether, hexane, and toluene solvents

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were obtained from a solvent system under argon using glass syringes. THF was kept over dry sieves under argon.

Synthesis of the ylide ligand, $[(CH_2)(CH_3)(Ph)_2P]$

Since the iodide at the phosphonium precursor interferes with gold(I), it was exchanged using $AgNO_3$ in acetone. $[(CH_3)_2(Ph)_2P]I$, (0.171 g, 0.5 mmol) and $AgNO_3$ (0.085 g, 0.5 mmol) were stirred under N_2 in distilled acetone for 2 h. After the AgI settles the colorless liquid was filtered through a Celite bed. The solution was brought to dryness under vacuum, giving white crystals of $[(CH_3)_2(Ph)_2P]NO_3$. Yield 98 %. The phosphonium nitrate (0.138 g, 0.5 mmol) and KH (0.05 g from a 25 % slurry in mineral oil) were weighed in a long Schlenk flask inside the glove box, and capped with a ground glass connection with tip. This flask, covered from the light, was cooled down to −40 °C over a dry ice bath, to add 10 mL of dry THF by canula through the glass connection. After stirring for 6 h a yellow solution of $[(CH_2)(CH_3)(Ph)_2P]$ had formed. The flask with the ylide was kept at −40 °C. Yield 98 %. – ^{1}H NMR ([D$_3$]chloroform): δ = 2.043 – 2.00 (d, CH_2), 1.76 – 1.72 (d, CH_3).

Reaction of dinuclear gold(I) amidinate and ylide ligand

The cold ylide solution (0.25 mmol) in toluene was cannuled into a Schlenk flask with the dinuclear gold(I) amidinate (0.080, 0.25 mmol) in the dark. The yellow suspension was stirred for 2 h in a dry ice bath. A white residue was formed, and the solution was clear yellow. The solution was cannulated to another flask and brought to dryness under vacuum. The yellow residue was rinsed with hexane and extracted with 4 mL of ether, then with 2 mL of toluene. The toluene extract is pale yellow and produced a small amount of $[Au_2(\text{amidinate})(\text{ylide})_2]NO_3$ crystals (20 %). The intense yellow ether extract was layered with hexane in a long Schlenk flask and covered from the light. At r. t. small crystals grew within a week. Yield 60 %. – ^{1}H NMR (300 MHz, [D$_6$]benzene): δ = 2.39 (C*H*$_3$-amidinate, 48 H), 2.15 (d, C*H*$_3$-ylide, 6H), 7.41 (N(C*H*)N), 6.43, 7.01 (*Ph*-amidinate), 6.77, 6.97 and 7.01 (*Ph*-ylide). – ^{13}C NMR (300 MHz, [D$_6$]benzene): δ = 20.3 (*C*H$_3$-amidinate), 123.0 (*C*H$_3$-ylide), 162.0, 150.0, 129.0, 128 (*o*-, *m*-, *p*-, *i*-Ph amidinate), 133.0, 129.4, 129.1, 128.9 (*Ph*-ylide), 162.1 (N*C*N). The hypercoordinated carbon atom was not detected.

Table 1. Crystallographic data for the cluster compound $[Au_8\{CH(NC_8H_9)_2\}_4\{(\eta^5\text{-}C)P(C_6H_5)_2(CH_3)\}_2]$.

Chemical formula	$Au_8P_2N_8C_{96}H_{102}$
M_r	3005.53
Crystal system	monoclinic
Space group	$C2/c$
a, Å	69.97(3)
b, Å	14.911(7)
c, Å	27.672(12)
β, deg	111.248(7)
Cell volume, Å^3	26910(21)
Z	12
d_{calcd}, g cm^{-3}	2.23
μ, mm^{-1}	13.1
λ, Å	0.71073
T, K	213(2)
2θ range, deg	3.74 – 50.7
Reflexions collected	108167
Reflexions unique	24489
Refined parameters	1567
$R1^a$ / $wR2^b$ $[I \geq 2\sigma(I)]$	0.0842 / 0.2404
GoF $(F^2)^c$	1.062
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	7.693 / −2.233

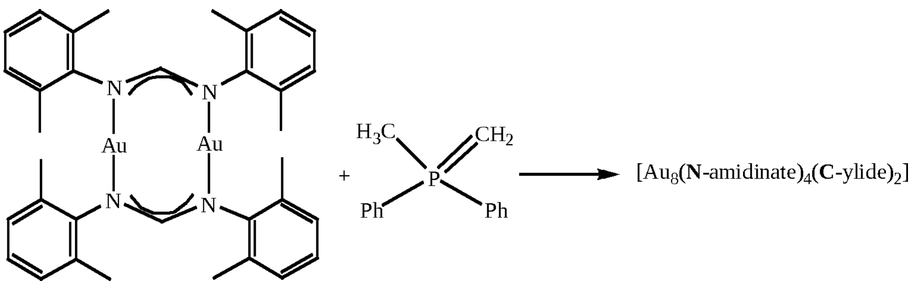
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, where $P = (\text{Max}(F_o{}^2,0) + 2F_c{}^2)/3$ and a and b are constants adjusted by the program; [c] GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Table 2. Selected bond lengths (Å) and angles (deg) of the octagold cluster.

Au(1)–Au(2)	2.856(2)	Au(1)–Au(4)	2.921(2)
Au(1)–Au(5)	2.987(2)	Au(2)–Au(3)	2.820(2)
Au(2)–Au(6)	2.941(2)	Au(3)–Au(4)	2.905(2)
Au(3)–Au(7)	2.934(2)	Au(4)–Au(8)	2.923(2)
Au(1)–C(1)	2.18(3)	Au(2)–C(1)	2.16(3)
Au(3)–C(1)	2.16(3)	Au(4)–C(1)	2.12(3)
Au(1)–N(1)	2.21(2)	Au(2)–N(3)	2.16(2)
Au(3)–N(5)	2.20(2)	Au(4)–N(7)	2.13(2)
Au(2)–Au(1)–Au(4)	86.7	Au(2)–Au(1)–Au(5)	75.7
Au(4)–Au(1)–Au(5)	102.5	Au(3)–Au(2)–Au(1)	93.9
Au(3)–Au(2)–Au(6)	101.3	Au(1)–Au(2)–Au(6)	103.6
Au(2)–Au(3)–Au(4)	87.7	Au(2)–Au(3)–Au(7)	78.1
Au(4)–Au(3)–Au(7)	82.7	Au(3)–Au(4)–Au(1)	90.8
Au(3)–Au(4)–Au(8)	95.8	Au(1)–Au(4)–Au(8)	73.3

X-Ray diffraction data collection

Colorless block-shaped crystals of the Au_8 cluster were obtained after three days upon layering 3 mL of the solution of the compound in ether with 15 mL of hexanes. A crystal measuring 0.35 × 0.24 × 0.08 mm^3 was coated with Parathone oil and mounted on a nylon cryoloop affixed to a goniometer head. The diffraction data were collected using a Bruker D8 three-circle diffractometer with APEX II detector equipped with an LT-2 low-temperature apparatus operating at 213 K [9]. A full multi-run data set was obtained by collecting 2000 frames using omega scans of 0.3 deg per frame with 20 s per frame. Cell parameters were determined and refined using APEX II software on all observed reflections [9]. This compound was uniquely identified as belonging to the monoclinic space group $C2/c$ by its systematic absences. Data reduction was performed using APEX II software, which corrects for LP and decay [9], while absorption corrections were applied by using the program SADABS [10].



Scheme 1. Synthesis of the Au_8 cluster.

The structure was initially determined using the program XPREP from the SHELXTL [11] software package. The positions of the gold atoms were found *via* Direct Methods using the program SHELXTL [11]. Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were then added in idealized positions and included in the structure factor calculations and were refined as a riding model. Additional details of data collection and refinement for this compound are provided in Table 1. All non-hydrogen atoms were refined with anisotropic displacement parameters. Selected bond lengths and angles are listed in Table 2.

CCDC 752745 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis

The synthesis relies on the affinity between gold and carbon. Thermodynamically, the interaction of the ylide with the dinuclear gold amidinate promotes formation of mixed Au–C, Au–N connectivities depending on the ratio of the ylide ligand to the dinuclear gold amidinate complex (Scheme 1). For the ylide ligand, starting with the phosphonium iodide, the iodide anion was exchanged by nitrate using $AgNO_3$. The resulting $[(CH_3)_2P(Ph)_2]NO_3$ is deprotonated with KH in THF to form a yellow solution of the neutral ylide $[(CH_2)(CH_3)P(Ph)_2]$.

Crystal structure

Crystals as thin rectangular colorless plates grew in ether layered with hexane in the dark. The X-ray crystallography experiment shows units with a cuboidal arrangement of the type $[Au_8\{CH(\mathbf{N}C_8H_9)_2\}_4\{(\eta^5\text{-}\mathbf{C})P(C_6H_5)_2(CH_3)\}_2]$ in the monoclinic space group $C2/c$ with $Z = 12$, *i. e.*, the asymmetric unit comprises

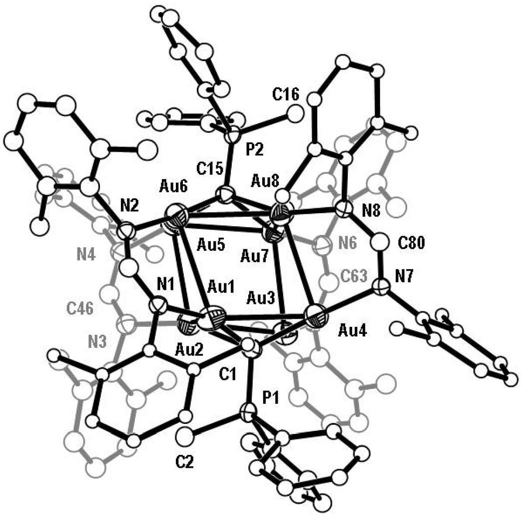


Fig. 1. Structure of one of the two crystallographically independent $[Au_8\{CH(NC_8H_9)_2\}_4\{(\eta^5\text{-}C)P(C_6H_5)_2(CH_3)\}_2]$ clusters in the solid state. The displacement ellipsoids are drawn at the 50 % probability level.

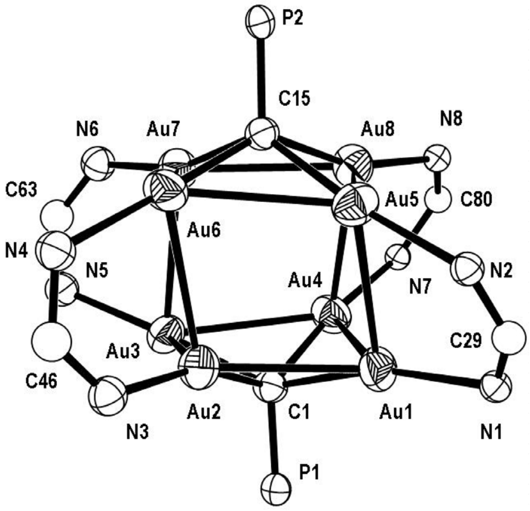


Fig. 2. Connectivity of gold atoms arranged in a cube with nitrogen and carbon donor ligands.

one and a half molecules. The eight gold atoms in the cube are connected along the sides through four amidinate ligands, with Au $\cdots$ Au distances slightly shorter at the upper and lower faces, 2.850 and 2.854 Å, than along the amidinate sides, 2.946 Å (av.) (Fig. 1). Although there are two crystallographically unique octanuclear structures in the unit cell, with one cluster sitting on the 2-fold axis, and the other having no crystallographic symmetry, there are no significant differences between these two clusters. Hence the cluster without crystallographic symmetry pictured in Fig. 1 is not significantly different from the cluster on the 2-fold axis in which the two hyper-coordinate C atoms (and P atoms) are structurally equivalent.

Striking features are the hyper-coordinate carbon atoms on the opposite faces of the distorted Au_8-cube, connecting simultaneously five atoms: four gold and one phosphorous atom. This is the first structure with a hyper-coordinate P-ylide carbon atom bonded to four gold atoms and an *N*-donor ligand. The C–Au–N units are nearly linear, with an average angle of 165.7°, which is achieved mainly by the approach of the deprotonated ylide carbon atom to the plane of the four gold atoms at a distance of 0.755 Å, such that the Au–C–Au angles are on average 80.7°. This angle reflects the strength of the aurophilic interactions as has been pointed out for other structures with hyper-coordinated carbon atoms on gold [4]. The Au–hyper-C bond lengths are $\sim$2.161 Å which is similar to the bond lengths found in the cluster $[(AuPPh_3)_4\{\eta^5\text{-}\mathbf{C}\text{-S(=O)Me}_2\}]^+$ (2.131 – 2.198 Å) [4].

The Au $\cdots$ Au distances around the hyper-coordinated carbon atom are slightly longer in this cube cluster than in the pyramidal sulfur cluster (2.799 – 2.818 Å) which thus has the hyper-coordinated carbon atom placed a little farther into the basal plane (0.861 Å) (Fig. 2) [4]. The Au_8 cluster is neutral, which is in contrast with other gold structures with hyper-coordinated carbon atom structures having an ancillary triphenylphosphine ligand. They all are positively charged species, and are less rigid than the reported cluster which may help to account for its strong luminescence.

Acknowledgement

The support of the Robert A. Welch Foundation of Houston, Texas, is acknowledged.

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