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Synthesis, Characterization, and X-ray Structure Determination of $[Au_{18}(P)_2(PPh)_4(PHPh)(dppm)_6]Cl_3$[#]

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The reaction of $[(AuCl)_2dppm]$ (dppm $=$ $Ph_2PCH_2PPh_2$) with $PhP(SiMe_3)_2$ and $P(SiMe_3)_3$ leads to the formation of the gold cluster compound $[Au_{18}(P)_2(PPh)_4(PHPh)(dppm)_6]Cl_3$ (**1**). The crystal structure investigation shows a central Au_7P_2 unit formed by two P centered gold tetrahedra sharing the central gold corner. This central unit is surrounded by a 10-membered Au_5P_5 ring which, together with the remaining six gold atoms, builds two Au_4P rectangular and two Au_3P trigonal pyramids. The different structure motifs are connected by the phosphine ligands. The compound has been characterized using microanalysis, IR spectroscopy, ESI-MS, and ^{31}P NMR techniques. Luminescence measurements have also been carried out.

Introduction

During the past years, much effort has been dedicated to the study of gold(I) complexes and clusters due to their potential photophysical and photochemical properties.[1−5] While a number of gold cluster complexes with selenium or tellurium bridges have already been published, some of them showing very promising properties,[2,6] only few examples of gold(I) cluster complexes containing phosphorus or arsenic bridges have been reported. Most of the compounds containing phosphorus bridges are small molecules which present different structure motifs like tetrahedron, $[(o\text{-Tol})P(AuPPh_3)_3][BF_4]$,[7] centered tetrahedron, $[(AuPtBu_3)_4P][O(BPhO)_2BPh_2]$,[8] square pyramid, $[(o\text{-Tol})P(AuPPh_3)_4][BF_4]_2$,[9] $[P(AuPPh_3)_5][BF_4]_2$,[10] $[(Ph_3PAu)_4As]BF_4$,[11] octahedron $[P(AuL)_6][BF_4]_3$ (L $=$ *t*Bu, *i*Pr, Ph),[12] or a puckered ladder $[Au_8(AuCl)_2\{\mu_3\text{-}P(tBu)\}_2\{\mu\text{-}P(tBu){=}C(NMe_2)_2\}_6]Cl_4$.[13] The

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[#] Dedicated to Prof. J. Strähle on the occasion of his 70th birthday.

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existence of gold phosphorus rings of different sizes like [Au(PR_2)]$_6$ (R = *c*-C_6H_{11}, *t*Bu), [Au(PR_2)]$_4$ (R = 2,4,6-$Me_3C_6H_2$), or [Au(PR_2)]$_3$ (R = 2,4,6-(*i*Pr)$_3C_6H_2$) has also been described.[14] Recently, we reported on the larger [Au_{12}(PPh)$_2$(P_2Ph_2)$_2$(dppm)$_4Cl_2$]Cl_2, which consists of two inverted opposite Au_6P_3 chains.[15]

Continuing our investigations on gold cluster complexes containing phosphorus bridges, we report here the synthesis, characterization via microanalysis, IR spectroscopy, ESI mass spectrometry, and ^{31}P NMR spectroscopy, as well as the crystal structure determination of [Au_{18}(P)$_2$(PPh)$_4$(PHPh)(dppm)$_6$]Cl_3 (**1**).

Experimental Section

Materials and General Methods. All experiments were carried out under a dry nitrogen atmosphere. CH_2Cl_2 was dried over P_2O_5, THF over sodium benzophenone, and *n*-pentane over $LiAlH_4$. P($SiMe_3$)$_3$[16] and P(Ph)($SiMe_3$)$_2$[17] were prepared according to standard procedures.

Mass spectrometric probes were taken on a 7 T FT-ICR mass spectrometer (Bruker Apex II) equipped with an electrospray ion source (Analytica). ^{31}P NMR spectra were recorded on Bruker AV400 and Bruker AMX-300 spectrometers with 85% H_3PO_4 as the external standard. IR spectra were obtained as KBr pellets on a FT-IR spectrometer SPECTRUM GX from Perkin-Elmer. Photoluminescence measurements were performed on a SPEX Fluorolog-3 spectrometer equipped with a closed-cycle optical cryostat (Leybold) operating at 20−293 K. A R5509 near-infrared photomultiplier (Hamamatsu) was used as photodetector.

Synthesis of [(AuCl)$_2$dppm]. A solution of [Au(thiodiglycol)-Cl][18] (0.26 g Au, 1.30 mmol) in MeOH (5 mL) was added to a solution of dppm (1 g, 2.60 mmol) (dppm = $Ph_2PCH_2PPh_2$) in CH_2Cl_2 (10 mL). The final mixture was stirred for 3 h. The solvents were removed in vacuo, and water (50 mL) was added. The white precipitate was filtered off, washed with water and Et_2O, and dried in vacuo. Yield: 80% (1.76 g).

Synthesis of [Au_{18}(P)$_2$(PPh)$_4$(PHPh)(dppm)$_6$]Cl_3 (**1**). To a solution of [(AuCl)$_2$dppm] (90 mg, 0.106 mmol) in CH_2Cl_2 (10 mL) was added a solution of P($SiMe_3$)$_3$ (0.0077 mL, 0.027 mmol) and P(Ph)($SiMe_3$)$_2$ (0.021 mL, 0.080 mmol) in CH_2Cl_2 (2 mL). The final dark brown solution was layered with THF, and after a few days black crystals of **1** were isolated. Yield: 15 mg, 85% (in relation to the P(Ph)(H)($SiMe_3$)). Anal. Calcd for $C_{180}H_{158}P_{19}Au_{18}Cl_3$: C, 32.95; H, 2.43. Found: C, 33.1; H, 2.46. The IR-spectrum consists of bands at 3048 (s), 2353 (s), 1482 (s), 1436 (vs), 1100 (vs) and 999 (s) cm^{-1}. ^{31}P{^{1}H} NMR (161.97 MHz, DMSO-d_6, 295 K, multiplets only partially resolved, positions tentatively assigned): δ 38−30 (12 P, m, P5−P10), 1.6 (1P, q, ~165 Hz, P3), −1.8 (1P, q, ~181 Hz, P3), −29.7 (1P, br, P2), −32.8 (1P, t, $^2J_{PAuP}$ = 181 Hz, P1), −36.8 (1P, m, ~145 Hz, P2), −78.1 (2P, m, ~152 Hz, P4). Only one signal changed in ^{31}P NMR: δ = −32.8 ppm (td, $^1J_{HP1}$ = 317 Hz). No better resolution at 213, 208, or 203 K (in CD_2Cl_2) or 323, 353, or 373 K (in DMSO-d_6).

Table 1. Crystallographic Data and Structure Refinement Details for **1**

empirical formula	$C_{183}H_{164}Au_{18}Cl_9P_{19}$
fw	6816.02
cryst syst	orthorhombic
space group	$C222_1$
T (K)	150(2)
a (pm)	2243.8(5)
b (pm)	2489.5(5)
c (pm)	3901.9(8)
Z	4
V ($\times 10^6$ pm^3)	21796(8)
D_{calcd} (g/cm^3)	2.077
$2\theta_{max}$ range (deg)	2.44−49.7
reflns collected	56038
independent reflns	18839
R_{int}	0.0572
reflns with $F_0 > 4\sigma(F_0)$	18122
refined params	584
R1	0.0534
wR2 (all data)	0.1491
largest difference peak (e Å^{-3})	2.398 and −1.028
GOF	1.027
Flack parameter	0.49(1)
$\lvert E^2 - 1\rvert$	0.744

X-ray Crystallography. Crystals were removed from the reaction flask under a stream of N_2 gas and immediately covered with a layer of perfluoropolyether oil (Riedel-de Haën). A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream. The data were collected with a STOE IPDS II diffractometer using Mo Kα (λ = 0.71073 Å) radiation. Structure solution and refinement against F^2 were carried out using SHELXS and SHELXL software.[19] All carbon atoms could be located during the refinement process. During the following refinement cycles the phenyl rings were refined as rigid groups. Hydrogen atoms were calculated on idealized positions. The crystal and refinement data are summarized in Table 1, and selected distances and angles are shown in Figure 1. Molecular drawings were prepared with Diamond 3.1d.[20] Crystallographic data (atom coordinates, thermal parameters, and full tables of bond lengths and angles) have been deposited with the Cambridge Crystallographic Data Center, No. CCDC 625276. Copies of this information can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-(1223) 336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Results and Discussion

With the aim of building larger cluster compounds, two different phosphorus ligands, P($SiMe_3$)$_3$ and P(Ph)($SiMe_3$)$_2$, have been used. The use of a small amount of the P^{3-} ligand should help to build the core of the cluster, while the P(Ph)$^{2-}$ ligands should lead to the formation of additional bridges, containing organic rests, between the gold atoms. The use of more than one silylated compound in the preparation of a cluster is a known synthesis strategy used, for example,

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for the preparation of selenium-bridged copper clusters.[21] Nevertheless, this strategy was never used to prepare gold−selenium cluster compounds, since all our attempts to synthesize gold clusters containing Se(R)$^-$ (R = organic group) ligands were not successful and led to the formation of gold cluster containing only naked Se^{2-} ligands, with the consequent cleavage of the Se−C bond.[22]

In the case we report here, we used an empirical approach to determine the best procedure to achieve a well reproducible synthesis of **1**; different molar ratios and solvents were tested to explore the reaction of the gold phosphine complex with the two different silylated phosphorus compounds. (Only a molar ratio of Au:P^{3-}:P(Ph)$^{2-}$ = 4:1:3 in CH$_2$Cl$_2$, after layering the solution with THF, led to the crystallization of compound **1**.)

Compound **1** crystallizes in the orthorhombic space group $C222_1$ with four molecules per unit cell. Three molecules of CH$_2$Cl$_2$ per formula unit have been found as lattice bound solvent in the crystal. The X-ray analysis of **1** revealed some problems due to the disorder of the phosphorus atom (on positions P1 or P1′) of the P(Ph)(H)$^-$ group. In the solid state, there exists a crystallographic 2-fold axis running through the atoms Au1, Au6. This symmetry is broken by the above mentioned P1 and its phenyl group and hydrogen atom, which were all refined with occupancy of 0.5 assuming that the P(Ph)(H)$^-$ are statistically disordered on one of the two possible positions. All phenyl groups had to be refined restrained; hydrogen atoms were calculated on idealized positions. The Flack parameter of 0.49 indicates that the crystal used for X-ray analysis was a twin. Though we tried several other crystals of different sizes, we could not find one consisting of only a single domain. An additional symmetry check was carried out using the program PLATON,[23] which confirmed the space group $C222_1$.

Compound **1** shows a quite complicated structure with three different types of edge-sharing polyhedra. The central part (Au$_7$P$_2$) is formed by two phosphorus centered gold tetrahedra (Figure 1, red polyhedra) sharing one corner (Au1), which occupies the central position of the molecule. This central gold atom is surrounded by a 10-membered P$_5$Au$_5$ ring (in Figure 1 represented by thick blue bonds), the gold and phosphorus atoms of which are involved in the formation of two Au$_3$P trigonal pyramids (Figure 1, yellow polyhedra) and two Au$_4$P rectangular pyramids (Figure 1, blue polyhedra), together with other six gold atoms. All these polyhedra are connected by the phosphine ligands, building the structure's core. Although all of these structure motifs are separately known, this is, to the best of our knowledge, the first time they are all present in a single molecule. The shortest Au−Au distances are found between the central atom and one of the gold atoms in the P$_5$Au$_5$ ring, 286.5(2) pm (Au1−Au6) and 290.8(1) pm (Au6−Au10), which are building one of the edges of the rectangular pyramids. All gold atoms show a slightly distorted linear coordination with angles ranging from 153.9(2)° to 174.1(2)°. Four different types of coordination modes for the phosphorus atoms in the phosphorus ligands, phosphido- and phosphinido-, are present in this structure. Two P^{3-} ligands (P2 and P2′) occupy the central positions in the centered tetrahedra of the Au$_7$P$_2$ unit. In this slightly distorted tetrahedral coordination environment, the Au−P−Au angles range from 88.4(2)° to 120.1(2)°. The phosphorus atoms of two of the four P(Ph)$^{2-}$ ligands (P3 and P3′) act as μ_3-bridges between gold atoms forming two Au$_3$P trigonal pyramids, with the gold atoms at the base and phosphorus atoms at the apex of the pyramid. Here the Au−P−Au angles range from 97.9(2)° to 115.5(2)°. The phosphorus atoms of the other two P(Ph)$^{2-}$ ligands (P4 and P4′) are bonded to four gold and one carbon atom and act as μ_4-bridges between the gold atoms. In this case,

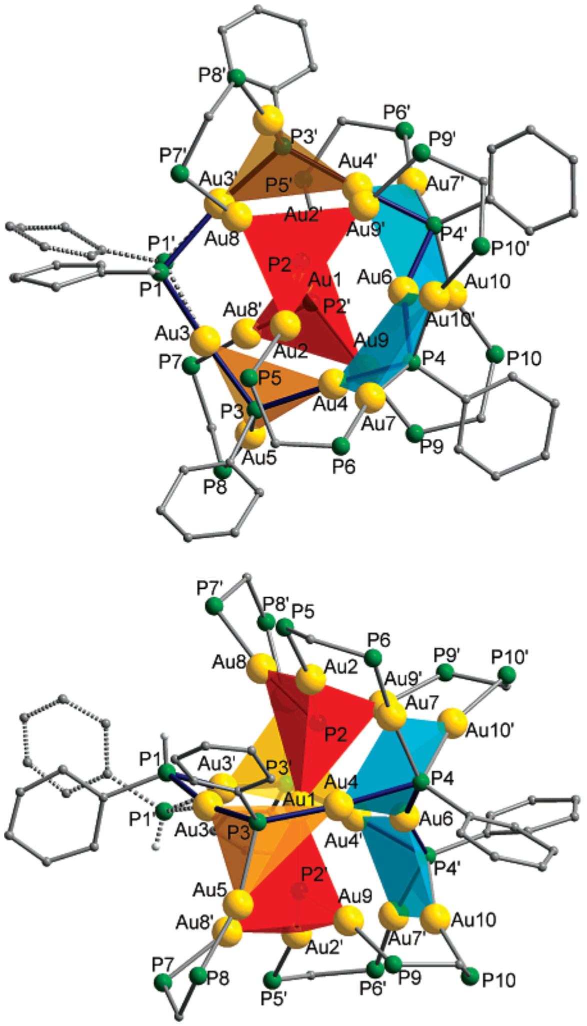

Figure 1. Molecular structure of the cation in **1** showing the different coordination polyhedra. Phenyl rings of the dppm ligands are omitted for clarity. Selected bond lengths (pm) and angles (deg): Au(1)−Au(6) 286.5(2), Au(1)−Au(3) 296.8(1), Au(1)−Au(4) 301.0(1), Au(4)−Au(7) 293.4(1), Au(5)−Au(8′) 297.2(1), Au(6)−Au(10) 290.8(1), Au(1)−P(2) 230.6(4), Au(2)−P(2) 229.8(5), Au(3)−P(1) 225(1), Au(3′)−P(1) 249(1), Au(3)−P(3) 229.5(5), Au(4)−P(3) 231.4(5), Au(4)−P(4) 236.6(4), Au(6)−P(4) 233.2(5), Au(8)−P(2) 233.4(4), Au(9)−P(2′) 231.2(4); Au(3)−P(1)−Au(3′) 103.2(4), Au(1)−P(2)−Au(2) 115.6(2), Au(1)−P(2)−Au(9′) 113.8(2), Au(1)−P(2)−Au(8) 120.1(2), Au(3)−P(3)−Au(4) 108.2(2), Au(4)−P(3)−Au(5) 115.5(2), Au(3)−P(3)−Au(5) 97.9(2), Au(4)−P(4)−Au(6) 83.8(2), Au(7)−P(4)−Au(10′) 87.6(2), Au(4)−P(4)−Au(7) 77.2(1).

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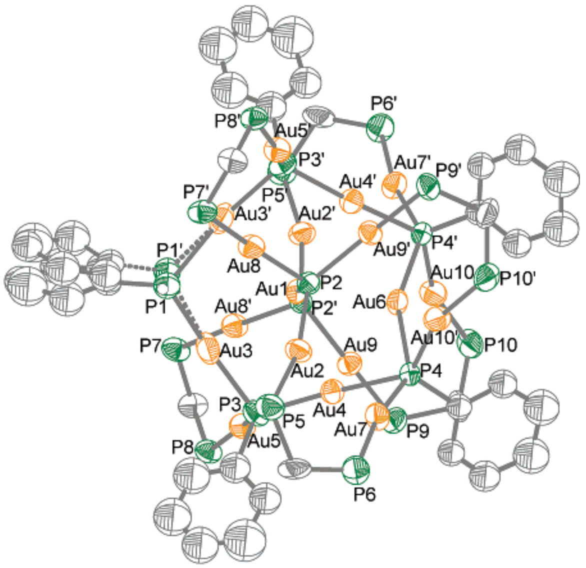

Figure 2. ORTEP view for the cation in **1**. Thermal ellipsoids are shown at the 30% probability level.

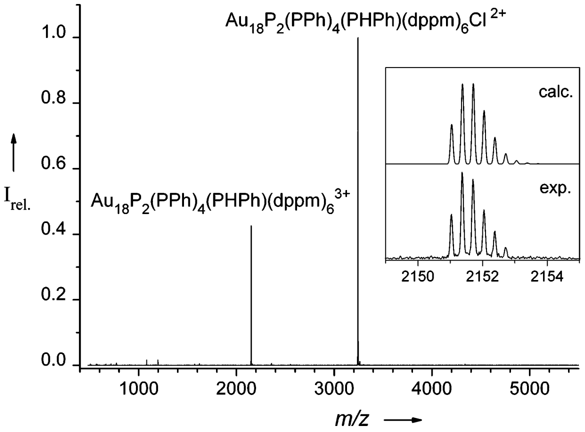

Figure 3. Positive-ion ESI mass spectrum of **1**. The inset shows an enlarged view of the triply charged cluster-ion peak contrasted to its calculated isotope pattern.

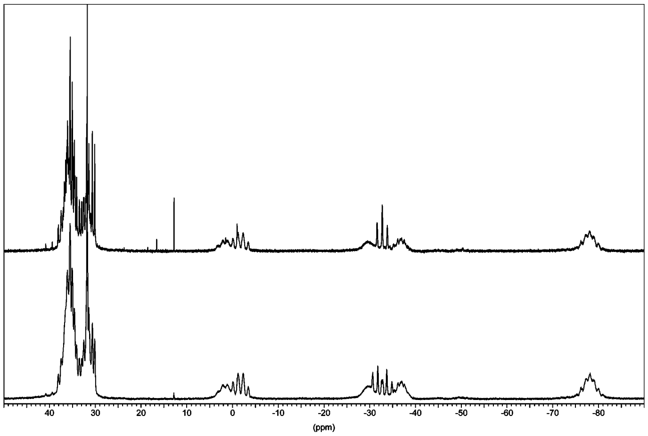

Figure 4. Top: $^{31}P\{^1H\}$ NMR spectrum of **1**. Bottom: ^{31}P NMR spectrum of **1**.

the two rectangular pyramids share one gold corner with the phosphorus atoms again occupying the apex position. The angles Au−P−Au considering adjacent corners of the pyramid range from 76.9(2)° to 87.6(2)°. Both rectangular pyramids share one gold corner with each other and a neighboring one with one of the trigonal pyramids, building a kind of pyramid chain around the central Au_7P_2 unit. Finally, the $P(Ph)(H)^-$ ligand (P1) acts as a μ_2-bridge between two gold atoms. The presence of the $P(Ph)(H)^-$ ligand could be attributed to some traces of $P(Ph)(H)(SiMe_3)$ mixed with the $P(Ph)(SiMe_3)_2$ used as starting material (ca. 3% $P(Ph)(H)(SiMe_3)$). The angles around P1 show a slightly distorted tetrahedral coordination: C1−P1−Au3 112(1)°, C1−P1−Au3′ 117(2)°, and Au3−P1−Au3′ 103.2(4)°. All P−Au distances are within the expected range except for the Au3′−P1 (249(1) pm). All gold atoms, except for the central one and the ones belonging to the Au_5P_5 ring, are bound to the phosphine ligands bridging the different polyhedra to form the Au−P core of the structure.

In order to determine the exact elemental composition of **1,** we also carried out a mass spectrometric study using electrospray ionization (ESI) as the method of choice employing a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Figure 3 displays a positive-ion FT-ICR mass spectrum obtained upon spraying a solution of **1** in dichloromethane. There are two major peaks detected that can be identified as a doubly and a triply charged species with elemental composition as given in Figure 3. Note that the mass accuracy between experimental and assigned *m*/*z* values (e.g., 2151.365 vs 2151.379, see inset of Figure 3) is better than 7 ppm. This accuracy was helpful to unequivocally determine the nature of the phosphine ligands. The peaks observed can be thought of as ions being formed from **1** upon losing three and two Cl^- counterions, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of **1** could not be fully assigned due to the unusually broad, scarcely resolved, and overlapping lines (Figure 4). Nevertheless, an integration (12:2:3:2) shows the distribution of the P atoms to the positions in the skeleton of **1**. The signal group between 38 and 30 ppm contains the 12 atoms P5−P10, namely, the six dppm ligands which appear in the same chemical shift range as in the related cluster $[Au_{12}(PPh)_2(P_2Ph_2)_2(dppm)_4Cl_2]Cl_2$.[15] There is a further division (8:4) in this range, the origin of which is not clear. By comparison of spectra recorded on spectrometers with different basis frequencies, the multiplets of the remaining seven P atoms in the core of **1** can be easily identified. In a ^{31}P NMR spectrum with proton couplings only one signal changes significantly. The triplet at −32.8 ppm ($^2J_{PAuP}$ = 181 Hz) appears as a doublet of triplets ($^1J_{HP1}$ = 317 Hz) and can definitely be assigned to P1. Without the unit P1HPh, the remaining framework of **1** would possess C_2 symmetry instead of C_1 in the complete compound **1**. The influence of the symmetry breaking unit P1HPh is stronger on P2 than on P3 and is weakest on P4. So, both atoms P2 should be assigned to signals at −29.7 and −36.8 ppm because the difference in their chemical shifts is larger than that for P3 with signals at 1.6 and −1.8 ppm. Additionally, the apparent coupling constant in both P3 multiplets is nearly the same as that in the P3 triplet (181 Hz). Then, both atoms P4 must be assigned to the quintet-like multiplet at −78.1 ppm. If no long-range couplings were present, each signal of the 12 atoms P5−P10 should appear as a doublet of doublets. However, only one multiplet with

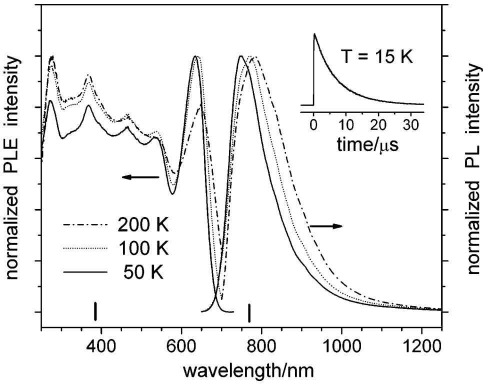

Figure 5. Normalized PLE and PL spectra of Nujol mulls of crystals of **1**. The emission and excitation wavelengths for the PLE and PL spectra, respectively, are indicated by short vertical lines. The insert shows PL decay at $T = 15$ K (excited by N_2-laser pulses at 337 nm and recorded at 750 nm).

this structure can be clearly identified in the range from 38 to 30 ppm, the coupling constants ($^2J_{PAuP} = 205$ Hz, $^2J_{PCH2P} = 82$ Hz) lie exactly in the range known from $[Au_{12}(PPh)_2(P_2Ph_2)_2(dppm)_4Cl_2]Cl_2$.[15] So, probably not only overlapping signals but also long-range couplings $J_{PAuPAuP}$ contribute to the complex multiplets. Such coupling constants may assume considerable values provided the related atoms are situated more or less in one plane which is the case in **1**. No better resolution could be achieved by recording spectra at various temperatures (solvent CD_2Cl_2: 213, 208, or 203 K; DMSO-*d*$_6$: 323, 353, or 373 K), just some minor temperature shift was observed. A comparison with the cation of $[Au\{P(AuPPh_3)_4\}_2]^{3+}[BF_4]^-$ supports the assignment of the P atoms in **1**. The chemical shifts for P atoms in comparable units are in the same range, related coupling constants are of similar size, and even a comparable small temperature shift was reported.[24] Whereas the dynamic process in $[Au\{P(AuPPh_3)_4\}_2]^{3+}$ could be frozen by cooling the solution to 203 K, this was not possible with **1** or the line width in the spectra of **1** could not be reduced by heating the sample.

The IR spectrum of **1** shows bands at 3048 and 1482 cm^{-1} corresponding to the aliphatic and aromatic C−H vibrations, respectively. At 1100.6 and 999 cm^{-1} the bands corresponding to the aromatic and aliphatic C−C bonds, respectively, can also be observed. At 1436 cm^{-1} the spectrum shows the vibrations due to the P−Ph bonds, and those to the P−H bond at 2353 cm^{-1}.[25]

In the solid state (polycrystalline), **1** shows a near-infrared photoluminescence (PL) with a maximum at ~780 nm (Figure 5). The PL intensity is relatively low at ambient temperature but increases ~20-fold by decreasing the temperature below ~50 K. The increase of the PL intensity is accompanied by increase of the PL lifetime: from ~40/200 ns (biexponential curve fit) at ambient temperature to 3.5/8 μs at $T = 15$ K. The emission peak becomes sharper and shifts to 750 nm at low temperatures. The luminescence excitation (PLE) spectrum of **1** is well structured and indicates several optical transitions at 296, 367, 466, 536, and 635 nm corresponding to the energies of 4.49, 3.38, 2.66, 2.31, and 1.95 eV, respectively (Figure 5). The low-energy transition peak becomes more pronounced and sharper by decreasing the temperature; otherwise the PLE spectrum shows no significant temperature dependence. The PLE intensity is relatively regularly spread over the whole visible spectral range up to the absorption edge at ~700 nm, which is in agreement with a dark, almost black color of the crystals. In this case, the spectrum shows a difference compared to the other gold cluster complexes studied by us;[6b,26] the Stokes shift between the low-energy absorption transition at 635 nm and the emission peak at 750 nm (at $T = 50$ K) is relatively small. Therefore, we could assign these features to the same optically allowed low-energy excited state (or a group of excited states close in energy). The relatively moderate PL intensity may be explained by nonradiative relaxation channels in **1** effectively competing with the emission channel. This is supported by the PL increase at low temperatures. Similar, but very weak and broad PL emission with a maximum at about 780 nm was detected from a dichloromethane solution of **1** (not shown).[27]

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Supporting Information Available: X-ray crystallographic data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Crystals of **1** were dispersed in Nujol and layered between two quartz plates. A solution of **1** in dichloromethane was measured in a standard cuvette at ambient temperature. Emission spectra are corrected for the wavelength-dependent response of the spectrometer and the detector. Time-resolved luminescence was recorded using a N_2 laser (337 nm, ≤4 ns) for pulse excitation.