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Unprecedented Gold–Tellurolate Clusters $[Au_8(\mu\text{-TeR})_8(PR'_3)_4]$

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The reaction of $[AuCl(PR'_3)]$ with KTeR, prepared from RTeTeR and K-selectride, gives the gold–tellurolate clusters $[Au_8(\mu\text{-TeR})_8(PR'_3)_4]$ (R = Ph, Tol; PR'_3 = PPh_3, PPh_2py) in high yield. This result contrasts with the one obtained from the reaction with thiolates or selenolates, from which mononuclear complexes are synthesized. The structures of these species have been determined and consist on three layers of gold and tellurium atoms in the ratio Au_3Te_2:Au_2Te_4:Au_3Te_2. There are short gold···gold interactions ranging from 2.9463(7) to 3.31132(7) Å, and the clusters are composed of di- and tri-coordinated gold centers. The result is unprecedented in gold–chalcogenolate chemistry from which mononuclear species are expected and represents one of the few examples of gold–tellurolate derivatives. These species show an interesting luminescent behavior in the solid state (at 77 K) and in solution (both at 298 and 77 K).

Introduction

Tellurium ligands have, until recently, been neglected in transition-metal chemistry compared with the corresponding sulfur and to a lesser extent selenium derivatives. Gold complexes with tellurium ligands are very scarce, in the Cambridge Data Base only 23 entries are found, which is in contrast with the fact that Au–Te bonds are present in nature as the gold–telluride minerals calaverite and krennerite (both $AuTe_2$), the thermally metastable mineral montbrayite, Au_2Te_3, and the gold–silver sylvanita and petzite, $(Au,Ag)Te_2$. Most of the gold–tellurium derivatives structurally characterized are polytellurides as, for example, $[KAu_9Te_7]^{4-}$,[1] $[Au_2Te_4]^{2-}$,[2,3] $[AuTe_7]^{3-}$,[4,5] $[Au_3Te_4]^{3-}$,[6] $[Au_4Te_4]^{4-}$,[1] $[Au_2Te_{12}]^{4-}$,[7] $[Au_2SeTe_4]^{2-}$,[3] $[AuSn_2Te_6]^{3-}$,[8] $[Ag_2AuSn_2Te_9]^{4-}$,[9] or the triply telluride-bridging compounds $[Te(AuPPh_3)_3]BF_4$[10] or $[Te(GaCl_3)\{Au_2(\mu\text{-PP})\}]$ (PP = 1,6-bis(diphenylphosphino)hexane).[11] However, gold complexes with tellurollate ligands are very poorly represented in contrast with the rich chemistry of gold thiolates, which have a great importance in fields such as medicine, optical devices, and nanomaterials. As far as we are aware, only a few gold–tellurolate complexes such as $[Au\{TeC(SiMe_3)_3\}(PPh_3)]$ and $[Au\{TeC(SiMe_3)_3\}]_4$ described by Arnold et al.[12] or $[Au_2(\mu\text{-TeC}_6H_2\text{-}2,4,6\text{-Ph}_3)(PPh_3)_2]^+$ and $[Au_2I_4(\mu\text{-TeC}_6H_2\text{-}2,4,6\text{-Ph}_3)_2]$ described by Strahle et al.[13] or the recently reported $NMe_4[Au(TeCF_3)_2]$[14] have been prepared and structurally characterized. They have been mostly prepared with sterically hindered substituents in the tellurollate moiety, and their structures are the classical ones obtained for thiolate or selenolate ligands. In contrast, the chemistry of the group 11 congeners (copper, silver) with tellurium has been

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considerably developed by the work of Fenske et al., and several Cu−TeR or Ag−TeR clusters have been prepared; these complexes must be regarded as clusters of different sizes with the TeR moieties found in terminal (μ-Te), bridging (μ_2-Te), and/or capping (μ_3-Te) bonding modes.[15] The lack of gold−tellurolate complexes prompts us to search for new derivatives to compare them with the corresponding thiolate or selenolate complexes. Here, we report on the high-yield synthesis of gold−tellurollate clusters of the form $[Au_8(\mu\text{-TeR})_8(PR'_3)_4]$ (TeR = TePh, TeTol), (PR'_3 = PPh_3, PPh_2py), which are obtained by the reaction of $[AuCl(PR'_3)]$ and KTeR at room temperature (see eq 1); the reactivity does not follow the pattern observed for thiolate or even selenolate complexes for which the linear $[Au(SR)(PR'_3)]$ or $[Au(SeR)(PR'_3)]$ are obtained. Furthermore, these gold−tellurium complexes are not only novel because they are very poorly represented but also because of their special structural features.

Results and Discussion

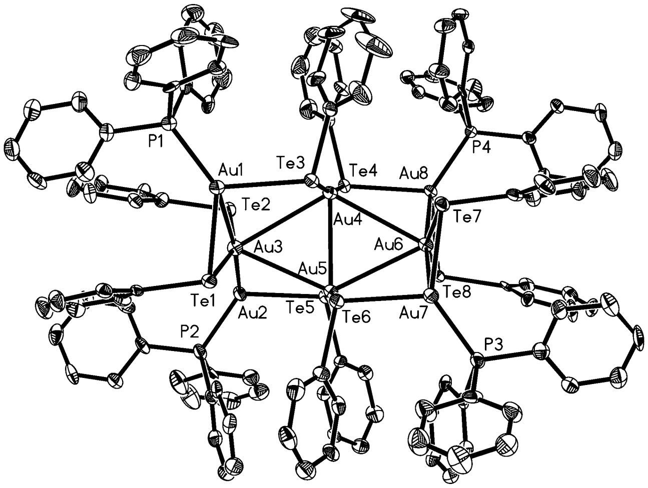


Figure 1. Structure of **1** showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

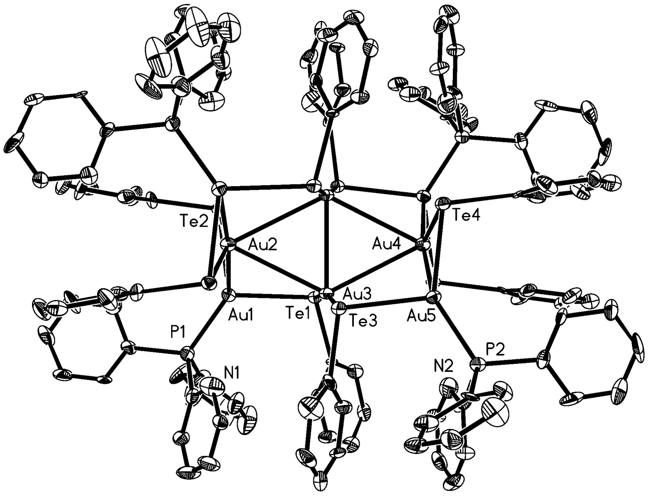
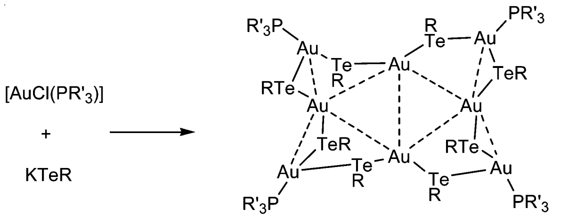


Figure 2. Structure of **2** showing the atom numbering scheme. Displacement parameter ellipsoids represent 30% probability surfaces. Hydrogen atoms are omitted for clarity.



(1)

R = Ph; PR'3 = PPh3 (**1**), PPh2py (**2**)
R = Tol; PR'3 = PPh3 (**3**), PPh2py (**4**)

The reaction of $[AuCl(PR'_3)]$ with KTeR, prepared from RTeTeR and K-selectride, $KB[CH(CH_3)C_2H_5]_3H$, leads to the formation of complexes $[Au_8(\mu\text{-TePh})_8(PR'_3)_4]$ (PR'_3 = PPh_3 (**1**), PPh_2py (**2**)) and $[Au_8(\mu\text{-TeTol})_8(PR'_3)_4]$ (PR'_3 = PPh_3 (**3**), PPh_2py (**4**)), which are isolated in high yield (≥70%) as orange solids (see eq 1). For these compounds, the $^{31}P\{^1H\}$ NMR spectra exhibit only one singlet, suggesting the equivalence of the phosphorus atoms in solution. The spectra have also been carried out at low temperature, and again only one singlet is observed for all the complexes. The formation of these clusters is in contrast to the corresponding thiolate or selenolate chemistry, for which the mononuclear $[Au(ER)(PR'_3)]$ species are obtained in the same conditions. However, the reaction of silver or copper chlorides with $RTe(SiMe_3)$ in the presence of phosphines, at low temperature, gives several clusters of different nuclearities, depending on the reaction conditions; they contain both RTe^- and Te^{2-} ligands as a result of the facile cleavage of the Te−C bond.[16] None of these silver or copper species corresponds to the stoichiometry obtained for the gold derivatives described in this work, and no cleavage of the Te−C bond has been observed for the gold complexes. Furthermore, only one species is detected for the gold compounds, even when the phosphine changes from PPh_3 to PPh_2py or the substituent in the tellurollate changes from Ph to Tol. The ^1H NMR spectra are in agreement with their formulation; the spectrum of **1** shows only phenylic protons, whereas the spectrum of **2** presents the resonances due to pyridine groups. Similarly, the ^1H NMR spectra of **3** and **4** show, in addition to the resonances for the phosphine ligands, one singlet at around 2 ppm arising from the methyl protons of the tolyl group. The crystal structures of **1** and **2** have been determined by X-ray diffraction (Figures 1 and 2). Selected bond lengths and angles are collected in Tables 1 and 2. In **1**, the gold atoms are disposed in such a manner that they form three layers of gold atoms and tellurium ligands, in a ratio Au_3Te_2:Au_2Te_4:Au_3Te_2. The Au···Au interactions are in the range 2.9462(7)−3.3133(7) Å, with the shortest interaction corresponding to the two gold atoms of the Au_3Te_2 layers. In the outside layers, the three gold atoms have different coordination geometries. If the Au···Au interactions are not taken into account, the central metal atoms are bonded to

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Table 1. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **1**

Au(1)−P(1)	2.298(3)	Au(4)−Au(6)	3.3018(7)
Au(1)−Te(1)	2.7111(9)	Au(5)−Te(6)	2.5745(10)
Au(1)−Te(3)	2.7369(9)	Au(5)−Te(5)	2.5863(10)
Au(1)−Au(3)	2.9689(7)	Au(5)−Au(6)	3.2064(7)
Au(2)−P(2)	2.289(3)	Au(6)−Te(7)	2.6092(8)
Au(2)−Te(2)	2.6952(9)	Au(6)−Te(8)	2.6116(8)
Au(2)−Te(5)	2.7063(9)	Au(6)−Au(8)	2.9462(7)
Au(2)−Au(3)	2.9990(7)	Au(6)−Au(7)	2.9831(7)
Au(3)−Te(1)	2.5982(9)	Au(7)−P(3)	2.288(3)
Au(3)−Te(2)	2.5994(9)	Au(7)−Te(7)	2.6785(9)
Au(3)−Au(5)	3.1899(7)	Au(7)−Te(6)	2.7157(9)
Au(3)−Au(4)	3.3133(7)	Au(8)−P(4)	2.291(3)
Au(4)−Te(4)	2.5862(10)	Au(8)−Te(8)	2.6991(8)
Au(4)−Te(3)	2.5877(9)	Au(8)−Te(4)	2.7358(9)
Au(4)−Au(5)	2.9942(7)		
P(1)−Au(1)−Te(1)	138.32(7)	Te(7)−Au(7)−Te(6)	100.49(3)
P(1)−Au(1)−Te(3)	122.64(7)	P(4)−Au(8)−Te(8)	140.31(7)
Te(1)−Au(1)−Te(3)	98.81(3)	P(4)−Au(8)−Te(4)	120.79(7)
P(2)−Au(2)−Te(2)	138.93(8)	Te(8)−Au(8)−Te(4)	98.84(2)
P(2)−Au(2)−Te(5)	121.13(8)	Au(3)−Te(1)−Au(1)	67.96(2)
Te(2)−Au(2)−Te(5)	99.62(3)	Au(3)−Te(2)−Au(2)	68.98(2)
Te(1)−Au(3)−Te(2)	158.75(3)	Au(4)−Te(3)−Au(1)	98.29(3)
Te(4)−Au(4)−Te(3)	167.19(3)	Au(4)−Te(4)−Au(8)	100.90(3)
Te(6)−Au(5)−Te(5)	169.85(3)	Au(5)−Te(5)−Au(2)	89.06(3)
Te(7)−Au(6)−Te(8)	160.07(3)	Au(5)−Te(6)−Au(7)	96.11(3)
P(3)−Au(7)−Te(7)	137.40(7)	Au(6)−Te(7)−Au(7)	68.67(2)
P(3)−Au(7)−Te(6)	122.09(7)	Au(6)−Te(8)−Au(8)	67.37(2)

two tellurolate ligands with angles of Te(1)−Au(3)−Te(2) 158.75(3) and Te(7)−Au(6)−Te(8) 160.07(3)°), whereas the gold atoms in the corners are three-coordinated by a phosphine and two tellurolate ligands with Te−Au−Te angles ranging from 98.81(3) to 100.49(3)° and P−Au−Te angles from 121.13(8) to 140.31(7)°. The gold atoms in the middle layer are also bonded to two tellurolate ligands, with Te−Au−Te angles of 169.85(3) and 167.19(3)°. The Au−Te distances are longer for the three-coordinated gold centers (range from 2.6785(9) to 2.7369(9) Å) than for the linear Te−Au−Te gold centers (range from 2.5745(10) to 2.6116(8) Å). The latters are similar to those found in the other tellurolate gold complexes reported. The Au−P bond lengths lie in the range of 2.288(3) to 2.298(3) Å and are slightly shorter than those reported for other trigonal-planar gold derivatives, for example $[Au(PPh_3)_3]^+$ (2.343(2)−2.409(2) Å).[17] The structure of **2** has also been established by X-ray diffraction, and the molecule is shown in Figure 2; it displays two-fold symmetry, with atoms Au2 and Au4 lying on the special positions 0, *y*, 0.75. The overall bonding scheme and other structural features are very similar to those in **1**.

1−**4** are luminescent in solution, both at 298 and 77 K and in the solid state at 77 K (Table 3). In the solid state, at 77 K, the complexes exhibit a broad band in the 650 region. In some cases, the emission consists in a band and a shoulder. For **3**, it is possible to identify two components; upon excitation at $\lambda < 450$ nm, the maximum is observed at 620 nm, whereas upon excitation at higher wavelengths, the emission displays a maximum at 655 nm. The excitation spectrum corresponding to the band at 655 nm displays a shoulder from 450 to 550 nm, which is not observed for that corresponding to the band at 620 nm.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **2**[a]

Au(1)−P(1)	2.291(5)	Au(3)−Au(3)#1	2.9514(15)
Au(1)−Te(1)	2.7126(16)	Au(3)−Au(4)	3.2496(13)
Au(1)−Te(2)	2.7211(14)	Au(4)−Te(4)	2.6045(14)
Au(1)−Au(2)	2.9097(9)	Au(4)−Au(5)#1	2.9216(8)
Au(2)−Te(2)	2.6071(13)	Au(5)−P(2)	2.297(5)
Au(2)−Au(3)	3.3007(13)	Au(5)−Te(4)	2.7080(14)
Au(3)−Te(3)	2.584(2)	Au(5)−Te(3)	2.7257(16)
Au(3)−Te(1)	2.587(2)		
P(1)−Au(1)−Te(1)	123.15(14)	P(2)−Au(5)−Te(3)	116.11(14)
P(1)−Au(1)−Te(2)	138.24(14)	Te(4)−Au(5)−Te(3)	102.76(4)
Te(1)−Au(1)−Te(2)	98.19(5)	Au(3)−Te(1)−Au(1)	95.22(6)
Te(2)−Au(2)−Te(2)#1	161.41(8)	Au(2)−Te(2)−Au(1)	66.16(3)
Te(3)−Au(3)−Te(1)	167.87(5)	Au(3)−Te(3)−Au(5)	96.22(6)
P(2)−Au(5)−Te(4)	140.74(14)	Au(4)−Te(4)−Au(5)	66.69(4)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z + 3/2$.

Table 3. Emission Maxima (λ in nm) for **1**−**4**

compound	solid state 298 K	solution 298 K	solution 77 K
1	645 (sh), 660	450	645 (br)
2	630 (sh), 660	500	560, 700
3	620, 665	420	580, 660 (sh)
4	650 (br)	440	555, 655 (sh)

The spectra in frozen solution resemble those commented above, but the difference in energy between the two emissions (or the maximum of the shoulder and the maximum of the principal band) is higher, as they appear at about 550 and 660 nm, respectively (except for **1**, which displays a broad band at about 650 nm).

Metal-to-ligand charge-transfer transitions (MLCT $Cu_2 \rightarrow ER^-$) have been assigned as the origin of the observed luminescence at high energy (about 430 nm) in the solid state for the copper complexes $[Cu_2(\mu\text{-dppm})_2(\mu\text{-ER})]BF_4$[18] (ER = SePh, TePh; TeC_6H_4-4-Me, SeC_6H_4-4-Cl), and the emission observed in the these complexes in solution at lower energies (about 630 nm) is assigned as mixed metal-centered ds-ps with some MLCT (copper → chalcogenide/phosphine) character. Probably, the observation of two bands in **1**−**4** indicates a complicated origin of the emissions with both metal-centered and MLCT transitions involved. Because of the complex nature of these bands, it is difficult to analyze the influence of the methyl substituent of the phenyl ring in the maximum of emission when comparing **1** with **3** and **2** with **4** (which could help in a more-detailed assignation), as it is difficult to assign clearly such a maxima. The solution behavior at room temperature is different from that commented above. Except for **1**, a band at about 450 nm is observed; in addition, another structured band appears. The band at 450 nm could be related to those at higher energies observed in the solid state at 77 K or in frozen solution. As the solutions quickly decompose (tellurium precipitation is observed) at room temperature, a correct interpretation of the nature of the bands in solution is complicated.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a PerkinElmer 883 spectrophotometer using

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Table 4. Details of Data Collection and Structure Refinement for **1** and **2**

compound	**1**·5CH_2Cl_2	**2**·5$CHCl_3$
chemical formula	$C_{125}H_{100}Au_8Cl_{10}P_4Te_8$	$C_{121}H_{101}Au_8Cl_{15}N_4P_4Te_8$
crystal habit	orange prism	orange prism
cryst size (mm^3)	0.30 × 0.24 × 0.10	0.20 × 0.16 × 0.16
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a (Å)	16.600(2)	25.903(2)
b (Å)	19.456(3)	24.6724(19)
c (Å)	21.226(3)	24.9786(18)
α (deg)	81.776(2)	90
β (deg)	72.255(2)	117.430(2)
γ (deg)	86.996(2)	90
U (Å^3)	6461.5(15)	14168.8(19)
Z	2	4
D_{calcd} (g cm^{-3})	2.404	2.280
M	4676.96	4863.22
F(000)	4256	8872
T (°C)	−173	−173
$2\theta_{max}$ (deg)	50	50
μ(Mo−$K\alpha$) (mm^{-1})	11.118	10.237
transmission	0.2262, 0.4027	0.2340, 0.3318
no. of reflns measured	49 971	38 703
no. of unique reflns	22 704	12 470
R_{int}	0.0492	0.0985
R^a ($F > 4\sigma(F)$)	0.0465	0.0804
WR2^b(F^2, all refl.)	0.1076	0.170
no. of reflns used	22 704	12 470
no. of params	1404	740
no. of restraints	244	42
S^c	1.060	1.114
max. $\Delta\rho$ (eÅ^{-3})	2.77	2.42

Nujol mulls between polyethylene sheets. Carbon, hydrogen, and nitrogen analyses were carried out with a PerkinElmer 2400 microanalyzer. NMR spectra were recorded on a Bruker ARX 400 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^{1}H, external) and 85% H_3PO_4 (^{31}P, external). Steady-state photoluminescence spectra were recorded with a Jobin-Yvon Horiba fluorolog FL-3−11 spectrometer using band pathways of 5 nm for excitation and 3 nm for emission. Degassed dichloromethane was used to prepare the solutions (5×10^{-4} M).

Starting Materials. The starting materials, [AuCl(PPh_3)][19] and [AuCl(PPh_2py)],[20] were prepared according to published procedures. All of the other reagents were commercially available.

Preparation of [Au_8(μ-TePh)$_8$(PR'_3)$_4$] (PR'_3 = PPh_3 (1), PPh_2py (2)). A mixture of Ph_2Te_2 (0.102 g, 0.25 mmol) and KB[$CH(CH_3)C_2H_5$]$_3$H (K-selectride) 1 M (0.5 mL, 0.5 mmol) in 20 mL of anhydrous THF was stirred for 4 h at room temperature, under argon. The resulting orange solution was treated dropwise with a solution of [AuCl(PPh_3)] (0.247 g, 0.5 mmol) or [AuCl(PPh_2py)] (0.248 g, 0.5 mmol) in 10 mL of anhydrous THF. After stirring for an additional 1 h, the solvent was removed in a vacuum and the remaining solid was treated with methylene dichloride and then filtered over celite. The filtrate was evaporated under reduced pressure to ca. 2 mL and the addition of *n*-hexane gave orange solids of **1** or **2**. The solid was separated by filtration, washed with *n*-hexane, and dried in a vacuum. **1**: Yield: 69%. Analytical data, Found: C, 33.54; H, 2.23. Calcd for $C_{120}H_{100}Au_8P_4Te_8$: C, 33.81; H, 2.36. ^{31}P{^{1}H} NMR, room-temperature $CDCl_3$, δ: 36.2 (s, br, 4P); −60 °C, δ = 35.2 (s, 4P). **2**: Yield 72%. Analytical data, Found: C, 32.48; H, 2.06; N, 1.25. Calcd for $C_{116}H_{96}Au_8N_4P_4Te_8$: C, 32.66; H, 2.27; N, 1.31. ^{31}P{^{1}H} NMR, room-temperature $CDCl_3$, δ: 30.0 (s, br, 4P); −60 °C, δ = 29.3 (s, 4 P).

Preparation of [Au_8(μ-TeTol)$_8$(PR'_3)$_4$] (PR'_3 = PPh_3 (3), PPh_2py (4)). A mixture of Tol_2Te_2 (0.109 g, 0.25 mmol) and KB[$CH(CH_3)C_2H_5$]$_3$H (K-selectride) 1 M (0.5 mL, 0.5 mmol) in 20 mL of anhydrous THF was stirred for 4 h at room temperature, under argon. The resulting orange solution was treated dropwise with a solution of [AuCl(PPh_3)] (0.247 g, 0. 5 mmol) or [AuCl(PPh_2py)] (0.248 g, 0.5 mmol) in 10 mL anhydrous THF. After stirring for an additional 1 h, the solvent was removed in a vacuum and the remaining solid was treated with methylene dichloride and then filtered over celite. The filtrate was evaporated under reduced pressure to ca. 2 mL, and the addition of *n*-hexane gave orange solids of **3** or **4**. The solid was separated by filtration, washed with *n*-hexane, and dried in a vacuum. **3**: Yield: 71%. Analytical data, Found: C, 33.14; H, 2.67. Calcd for $C_{128}H_{116}Au_8P_4Te_8$: C, 33.43; H, 2.82. ^{31}P{^{1}H} NMR, room temperature, $CDCl_3$ δ: 36.5 (s, br, 4P); −95 °C, CD_2Cl_2, δ = 39.2 (s, 4P). **4**: Yield 70%. Analytical data, Found: C, 34.01; H, 2.58; N, 1.28. Calcd for $C_{124}H_{112}Au_8N_4P_4Te_8$: C, 34.15; H, 2.73; N, 1.35. ^{31}P{^{1}H} NMR, room temperature, $CDCl_3$ δ: 31.4 (s, br, 4P); $CDCl_3$, −60 °C, δ = 30.25 (s, 4P).

Crystal Structure Determinations. Data were recorded on a Bruker Smart Apex CCD diffractometer. The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer. Data were collected using monochromated Mo Kα radiation (λ = 0.71073) in ω scans. An absorption correction with the program *SADABS*[21] based on multiple scans was used. The structures were solved by direct methods and refined on F^2 using the program *SHELXL-97*.[22] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Special refinement details for **2**: The complex crystallizes as chloroform solvate; two molecules have been perfectly defined, and the other residual electron density was interpreted as another molecule of disordered chloroform and refined as half-occupied atoms. Further crystal data are given in Table 4.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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