Gold(I) Thiolates as Metalloligands for the Synthesis of the First Zirconocene−Gold Complexes

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Dedicated to Professor Dr. Peter Welzel on the occasion of his 65th birthday

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The reactions of the mercaptocarboxylic acids $HOOC(CH_2)_nSH$ (n = 1, 2) with $H[AuCl_4]$ followed by treatment with PMe_2Ph led to the (phosphane)gold thiolates $[Au\{S(CH_2)_nCOOH\}(PMe_2Ph)]$ [n = 1, (**1**) 2 (**2**)], which can act as metalloligands towards complex fragments of a second metal. Compounds **1** and **2** react with $[Cp°_2ZrMe_2]$ (Cp° = C_5EtMe_4) to give the trinuclear Zr/Au complexes $[Cp°_2Zr\{\kappa^1O\text{-}OOC(CH_2)_nSAu(PMe_2Ph)\}\{\kappa^2O,O'\text{-}OOC(CH_2)_nSAu(PMe_2Ph)\}]$ [n = 1 (**3**), n = 2 (**4**)]. Complexes **1**–**4** were characterized by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy. The crystal structure of **4** shows mono- and bidentate coordination of two metalloligands to one zirconocene fragment. In solution at room temperature **3** and **4** are dynamic, and the carboxylato groups alternate between the mono- and bidentate bonding modes. Complex **4** shows catalytic activity in the oxidation of PPh_3 with O_2.

Introduction

Research in early/late heterobimetallics (ELHBs) has grown in the last few years and has been the subject of numerous reports.[1−4] The reasons for the interest include their relevance to bioinorganic bimetallic systems and their potential in homogeneous catalysis. The pairing of two electronically different metals in a single compound may lead to cooperative interactions between them, such as those observed in heterogeneous catalysis, and there is also the possibility for stereo- or regioselective catalysis. Heterogeneous catalysts in which late transition metals are dispersed on a Lewis acid (TiO_2 or Al_2O_3) support often show increased catalytic activity.[5−9] Such strong metal−support interactions (SMSI) are not well understood but have been attributed to the electronic communication between the metals and cooperative activation of substrates by the different metal centers.[10,11]

For the synthesis of related homogeneous systems we have used an early transition metal complex of a bifunctional ligand as a so-called metalloligand for a late transition metal. For example we reported on the synthesis of a monomeric (mercaptoacetato)zirconocene complex that acted as metalloligand to form heterobimetallic Zr/Ni and Zr/Pd complexes.[12] Furthermore, we described the synthesis of macrocyclic, dimeric zirconocene complexes as metalloligands by using thioglycolates as bridging ligands, and the formation of a tetranuclear Zr/Mo complex.[13] In the present study, we prepared Au^I-based metalloligands. Thus, we describe the synthesis of phosphanylgold thiolates from mercaptoacetic and mercaptopropionic acid and their reactions with $[Cp°_2ZrMe_2]$ to give trinuclear Zr/Au complexes. The formation of linearly coordinated thiolato complexes is a well-known property of Au^I that is also important for our purposes, since an attempt to prepare a related bis(phosphane)nickel thiolate as a metalloligand led only to formation of the energetically stable chelate complex.[14]

Results and Discussion

Gold(I) Thiolates $[Au\{S(CH_2)_nCOOH\}]$ (n = 1, 2)

Gold(I) thiolates are well known.[15] Their preparation usually starts from gold(III), in the form of sodium tetrachloroaurate(III) or the corresponding acid, which then requires a reduction step. Bishop et al.[16] described the synthesis of $[Au(SCH_2COOH)]$ using ethyl 2-hydroxyethyl sulfide as reducing agent. We found that $HSCH_2COOH$ and $HS(CH_2)_2COOH$ also function as reductants to give nearly quantitative yields of the thiolates $[Au(SCH_2COOH)]$ and $[Au(SCH_2CH_2COOH)]$.

(Phosphane)gold(I) Thiolates $[Au\{S(CH_2)_nCOOH\}(PMe_2Ph)]$ [n = 1 (1), n = 2 (2)]

Bishop et al.[16] also reported the synthesis of $[Au(SCH_2COOH)(PPh_3)]$, which is only sparingly soluble in ethanol.

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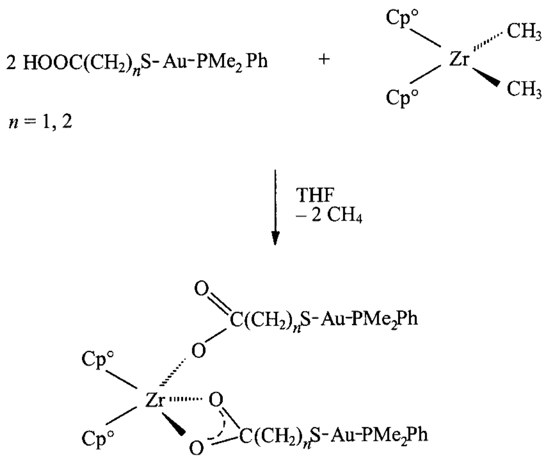
To increase the solubility in common solvents, which is important for the introduction of the second metal in subsequent reactions, we used PMe_2Ph instead of PPh_3. $[Au(SCH_2COOH)(PMe_2Ph)]$ (**1**) and $[Au(SCH_2CH_2COOH)(PMe_2Ph)]$ (**2**) were obtained by treating the gold(I) thiolates $[Au(SCH_2COOH)]$ and $[Au(SCH_2CH_2COOH)]$ with 1 equiv. of PMe_2Ph in ethanol at room temperature; **1** was obtained as a pale yellow solid, but **2** was only obtained as a yellow oil. Both complexes are soluble in THF and were characterized by ^1H, ^{31}P, ^{13}C NMR and IR spectra. In the ^1H NMR spectra the protons of the carboxyl groups were observed as very broad signals in a range of δ = 10−12 ppm owing to exchange processes. The IR spectrum of **1** shows two strong bands at 1690 and 1303 cm^{-1} for the C=O and C−O stretching vibrations of the COOH group.

Trinuclear Gold(I)−Zirconocene Complexes $[Cp°_2Zr\{\kappa^1O\text{-}OOC(CH_2)_nSAu(PMe_2Ph)\}\{\kappa^2O,O'\text{-}OOC(CH_2)_n\text{-}SAu(PMe_2Ph)\}]$ [n = 1 (3), n = 2 (4)]

The trinuclear Zr/Au complexes **3** and **4** were obtained by reaction of the metalloligands **1** and **2** with $[Cp°_2ZrMe_2]$ in a molar ratio of 2:1 (Scheme 1). Both complexes were obtained as pale yellow solids, and X-ray quality crystals of **4** were grown from a concentrated solution in THF at room temperature.



Scheme 1

Structural Studies on 4

An ORTEP plot of **4** is shown in Figure 1. The trinuclear complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules of the complex and three THF molecules in the unit cell. One of the THF molecules is disordered and lies on the inversion center. The zirconium atom is coordinated by two η^5-cyclopentadienyl rings, as well as one monodentate and one bidentate carboxylato group, so that the Zr atom has 18 valence electrons. This bonding mode was also observed in related zirconocene bis(carboxylates)[17−19] and in a zirconocene mercaptoacetate[12] and the Zr−O bond lengths and O−Zr−O bond angles are similar to these complexes. Both Au atoms are almost linearly coordinated by one P and one S donor [S1−Au1−P1 174.63(6), S2−Au2−P2 176.83(6)°]. The Au−S and Au−P bond lengths are similar to those in related Au^I complexes, e.g., $[Au(SCH_2COOH)(PPh_3)]$, $[Au(SCMe_2COOH)(PPh_3)]$[16] and $[Au(SPh)(PPh_3)]$.[20] The Au1−Au2 distance of 3.2992(4) Å suggests intramolecular gold−gold interaction. Intermolecular Au−Au contacts are very common and are also found for other gold(I) complexes with sulfur-containing ligands; the distances observed range from 2.9 to 3.5 Å[21] and are attributed to relativistic effects in the valence orbitals of gold atoms,[22] e.g., $[Au(SPh)(PPh_3)]$ [Au−Au 3.1355(3) Å].[20] To facilitate this interaction the S−Au−P fragments in **4** have an almost perpendicular arrangement [torsion angles: P1−Au1−Au2−P2 116.5(3), S1−Au1−Au2−S2 118.9(3)°; see Figure 2]. This arrangement is similar to that in $[Au(SPh)(PPh_3)]$, in which torsion angles of 96.1 and 110.8° were observed.[20] Depending on the structural properties of the ligands, in other complexes the "head-to-head" or "head-to-tail" arrangements were found.

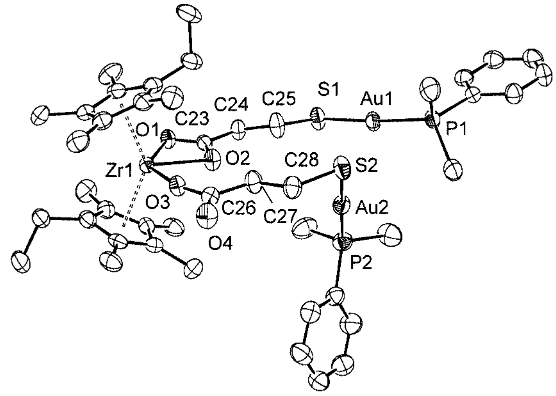


Figure 1. ORTEP plot of **4** (50% probability thermal ellipsoids are shown; hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: Zr1−O1 2.352(4), Zr1−O2 2.213(4), Zr1−O3 2.067(4), Au1−S1 2.302(2), Au1−P1 2.265(2), Au2−S2 2.306(2), Au2−P2 2.268(2), O1−C23 1.260(7), O2−C23 1.279(6), O3−C26 1.291(7), O4−C26 1.226(7); O1−Zr1−O2 56.5(1), O2−Zr1−O3 78.9(1), S1−Au1−P1 174.63(6), S2−Au2−P2 176.83(6), O1−C23−O2 117.0(5), O3−C26−O4 123.2(6)

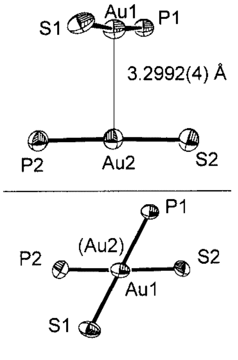


Figure 2. Front and top view of the S−Au−P fragments in **4**

Spectroscopic Studies on 3 and 4

The IR spectra of **3** and **4** exhibit two strong bands for the C=O and C−O stretching vibrations of the monodentate ligand, and two strong bands for the asymmetric and symmetric vibrations of the bidentate ligand. Compared to the free carboxyl group in **1**, the C=O and C−O vibration bands in the heterobimetallic complexes are shifted to lower wavenumbers owing to coordination to the Lewis acidic zirconium atoms.

In the NMR spectra of **3** and **4** the CH_2 groups of the two metalloligands next to the carboxylate groups were observed as one signal for both complexes. On the basis of the molecular structure of **4** in the solid state, we would expect at least two signals for these CH_2 groups owing to the different bonding mode of the ligands. Therefore the NMR spectroscopic data suggest a rapid dynamic process in which the carboxylato groups alternate between mono- and bidentate bonding. Such dynamics are well known and were observed for most zirconocene bis(carboxylates)[17−19] and in a zirconocene mercaptoacetate[12] and dimeric zirconocene thioglycolates.[13] Low-temperature NMR experiments on **3** and **4** down to −70 °C failed to freeze out this dynamic process, and we only observed slight broadening of the signals.

Preliminary catalytic investigations in oxidation reactions were performed with **4**. We used the model system O_2/PPh_3, and the ratio PPh_3/PPh_3O was determined by ^{31}P NMR spectroscopy. Complex **4** catalyzes the oxidation of PPh_3 in a molar ratio of 1:10 without apparent decomposition (only the PMe_2Ph ligands are partly oxidized) over 1.5 h at 50 °C. On the basis of earlier investigations on the catalytic properties of a similar zirconocene mercaptoacetato complex,[12] we assume that the catalytic activity of **4** is due to the Lewis acidic Zr atom, which is coordinatively unsaturated in solution. Investigations on possible interactions between the two metals in these complexes are in progress.

Experimental Section

General Details: All operations except the synthesis of the gold thiolates were carried out under dry nitrogen using standard Schlenk techniques. The reagents and solvents were purified by standard procedures. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded with an AVANCE DRX 400 spectrometer. The IR spectra were recorded with an FT-IR spectrometer Perkin−Elmer System 2000 in the range 400−4000 cm^{-1}. $[Cp°_2ZrMe_2]$[23] was prepared by a literature procedure. Mercaptoacetic and mercaptopropionic acid were purchased from Fluka. $H[AuCl_4]$ was donated by Degussa.

$[Au\{S(CH_2)_nCOOH\}]$ (*n* = 1, 2): An aqueous solution of $H[AuCl_4]$ was treated with an aqueous solution of a mercaptocarboxylic acid ($HOOCCH_2SH$, $HOOCCH_2CH_2SH$) in a molar ratio of 1:3. Both gold thiolates were obtained as pale yellow solids in nearly quantitative yields and were characterized by elemental analyses.

$[Au(SCH_2COOH)(PMe_2Ph)]$ (1): 0.31 mL (2.2 mmol) of PMe_2Ph was added to a suspension of 0.64 g (2.2 mmol) of $[Au(SCH_2COOH)]$ in 20 mL of ethanol. After about 30 min, the yellow solution became clear. Complete removal of the solvent gave a yellow oil, which was dissolved in 10 mL of THF. At −20 °C, **1** was obtained as a nearly colorless precipitate. Yield: 0.70 g (73%); m.p. 134−136 °C. ^1H NMR ($CDCl_3$, 25 °C, 400 MHz): δ = 1.81 [d, $^2J_{H,P}$ = 9.7 Hz, 6 H, $P(CH_3)_2Ph$], 3.68 (s, 2 H, SCH_2COOH), 7.49 (br. m, 3 H, $PMe_2C_6H_5$), 7.51 (m, 2 H, $PMe_2C_6H_5$) ppm, OH signal not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 16.3 [d, $^1J_{C,P}$ = 35.9 Hz, $P(CH_3)_2Ph$], 32.1 (s, SCH_2COOH), 130.0 (d, $^3J_{C,P}$ = 11.3 Hz, *m*-C of PC_6H_5), 132.3 (br. s, *p*-C of PC_6H_5), 132.5 (s, *o*-C of PC_6H_5), 132.6 (d, $^1J_{C,P}$ = 57.3 Hz, *ipso*-C of PC_6H_5), 176.5 (s, SCH_2COOH) ppm. Signals for THF are observed in the ^1H and ^{13}C NMR spectrum. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 162 MHz): δ = 11.2 (s, PMe_2Ph). IR (KBr pellet): $\tilde{\nu}$ = 1690 (C=O), 1303 (C−O) cm^{-1}. $C_{10}H_{14}AuO_2PS \cdot 1/4THF$ (444.25): calcd. C 29.7, H 3.6, S 7.2; found C 29.1, H 4.3, S 6.9.

$[Au(SCH_2CH_2COOH)(PMe_2Ph)]$ (2): 0.21 mL (1.4 mmol) of PMe_2Ph was added to a suspension of 0.44 g (1.4 mmol) of $[Au(SCH_2CH_2COOH)]$ in 20 mL of ethanol. After about 30 min, the yellow solution became clear. Complete removal of the solvent gave a yellow oil which was dissolved in 20 mL of THF. However, in contrast to **1**, complex **2** could only be isolated as an oil. Yield: 0.45 g (85%). ^1H NMR ($CDCl_3$, 25 °C, 400 MHz): δ = 1.75 [d, $^2J_{H,P}$ = 8.8 Hz, 6 H, $P(CH_3)_2Ph$], 2.70 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, SCH_2CH_2COOH), 3.07 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, SCH_2CH_2COOH), 7.44 (br. s, 3 H, $PMe_2C_6H_5$), 7.62 (m, 2 H, $PMe_2C_6H_5$) ppm, OH signal not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 16.4 [d, $^1J_{C,P}$ = 32.8 Hz, $P(CH_3)_2Ph$], 23.4 (s, SCH_2CH_2COOH), 42.0 (s, SCH_2CH_2COOH), 129.7 (d, $^3J_{C,P}$ = 10.8 Hz, *m*-C of PC_6H_5), 131.9 (d, $^4J_{C,P}$ = 1.8 Hz, *p*-C of PC_6H_5), 132.2 (d, $^2J_{C,P}$ = 13.5 Hz, *o*-C of PC_6H_5), 133.8 (d, $^1J_{C,P}$ = 51.3 Hz, *ipso*-C of PC_6H_5), 177.2 (s, SCH_2COOH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 162 MHz): δ = 7.2 (s, PMe_2Ph) ppm.

$[Cp°_2Zr\{\kappa^1O\text{-}OOCCH_2SAu(PMe_2Ph)\}\{\kappa^2O,O'\text{-}OOCCH_2SAu(PMe_2Ph)\}]$ (3): A solution of 0.08 g (0.2 mmol) of $[Cp°_2ZrMe_2]$ in 5 mL of THF was added to a solution of 0.17 g (0.4 mmol) of **1** in 5 mL of THF. The reaction mixture was stirred overnight at room temperature. Concentration of the solution to about half of its volume and addition of 10 mL of petroleum ether gave a pale yellow precipitate of **3** at −20 °C. Yield: 0.21 g (85%); m.p. 163−169 °C. ^1H NMR ($CDCl_3$, 25 °C, 400 MHz): δ = 0.84 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, $C_5Me_4CH_2CH_3$), 1.82 [d, $^2J_{H,P}$ = 10.0 Hz, 12 H, $P(CH_3)_2Ph$], 1.88 [s, 12 H, $C_5Et(CH_3)_4$], 1.90 [s, 12 H, $C_5Et(CH_3)_4$], 2.38 (q, $^3J_{H,H}$ = 7.6 Hz, 4 H, $C_5Me_4CH_2CH_3$), 3.74 (s, 4 H, SCH_2COO), 7.46 (br. m, 6 H, $PMe_2C_6H_5$), 7.77 (m, 4 H, $PMe_2C_6H_5$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 11.7, 11.9 [s, $C_5Et(CH_3)_4$], 15.0 (s, $C_5Me_4CH_2CH_3$), 16.6 [d, $^1J_{C,P}$ = 35.1 Hz, $P(CH_3)_2Ph$], 19.7 (s, $C_5Me_4CH_2CH_3$), 32.9 (s, SCH_2COO), 121.4, 122.2, 127.1 (s, C_5EtMe_4), 129.7 (d, $^3J_{C,P}$ = 11.1 Hz, *m*-C of PC_6H_5), 132.0 (s, *p*-C of PC_6H_5), 132.5 (d, $^2J_{C,P}$ = 13.1 Hz, *o*-C of PC_6H_5), 133.6 (d, $^1J_{C,P}$ = 55.3 Hz, *ipso*-C of PC_6H_5), 183.1 (s, SCH_2COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 162 MHz): δ = 10.7 (s, PMe_2Ph) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1635 (C=O), 1523, 1323 (O−C−O), 1191 (C−O) cm^{-1}. $C_{42}H_{60}Au_2O_4P_2S_2Zr$ (1240.15): calcd. C 40.6, H 4.8, S 5.1; found C 38.2, H 4.9, S 4.2.

$[Cp°_2Zr\{\kappa^1O\text{-}OOC(CH_2)_2SAu(PMe_2Ph)\}\{\kappa^2O,O'\text{-}OOC(CH_2)_2SAu(PMe_2Ph)\}]$ (4): A solution of 0.16 g (0.39 mmol) of $[Cp°_2ZrMe_2]$ in 10 mL of THF was added to a solution of 0.35 g (0.79 mmol) of **2** in 10 mL of THF. The reaction mixture was stirred overnight at room temperature. Concentration of the solution to about half of its volume gave a pale yellow precipitate of **4** at −20 °C. Suitable crystals for a structure analysis were obtained from a saturated THF solution at room temperature. Yield: 0.38 g (77%); m.p. 95−98 °C. ^1H NMR ($CDCl_3$, 25 °C, 400 MHz): δ =

Table 1. Crystal data and data collection parameters for **4**

Empirical formula	$C_{44}H_{64}Au_2O_4P_2S_2Zr{\cdot}1.5THF$
Mr	1376.32
T [K]	223(2)
λ [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a [Å]	11.2310(14)
b [Å]	15.5919(19)
c [Å]	15.895(2)
α [°]	89.650(2)
β [°]	73.971(2)
γ [°]	86.307(2)
V [Å^3]	2669.5(6)
Z	2
Density (calcd.) [Mg/m^3]	1.712
Absorption coefficient [mm^{-1}]	5.855
F(000)	1360
Θ range [°]	1.31−28.71
Reflections collected	27960
Independent reflections [$R_{(int)} = 0.0597$]	12413
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	12413/8/562
GOF on F^2	0.976
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0411$, $wR_2 = 0.1026$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.1213$
Largest difference peak/hole [e·Å^{-3}]	1.989/−1.876

0.82 (t, $^3J_{H,H} = 7.6$ Hz, 6 H, $C_5Me_4CH_2CH_3$), 1.82−1.79 [overlapping signals, 36 H, $P(CH_3)_2Ph$ and $C_5Et(CH_3)_4$], 2.26 (q, $^3J_{H,H} = 7.6$ Hz, 4 H, $C_5Me_4CH_2CH_3$), 2.71 (t, $^3J_{H,H} = 8.8$ Hz, 4 H, SCH_2CH_2COO), 3.29 (t, $^3J_{H,H} = 8.8$ Hz, 4 H, SCH_2CH_2COO), 7.46 (m, 6 H, $PMe_2C_6H_5$), 7.75−7.69 (m, 4 H, $PMe_2C_6H_5$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 11.5, 11.7 (s, $C_5Et(CH_3)_4$], 14.9 (s, $C_5Me_4CH_2CH_3$), 16.4 (d, $^1J_{C,P} = 34.8$ Hz, $P(CH_3)_2Ph$), 19.6 (s, $C_5Me_4CH_2CH_3$), 25.0 (s, SCH_2CH_2COO), 46.7 (s, SCH_2CH_2COO), 121.3, 122.0, 127.1 (s, C_5EtMe_4), 129.8 (d, $^3J_{C,P} = 11.0$ Hz, *m*-C of PC_6H_5), 132.1 (d, $^4J_{C,P} = 2.3$ Hz, *p*-C of PC_6H_5), 132.4 (d, $^2J_{C,P} = 13.2$ Hz, *o*-C of PC_6H_5), 133.5 (d, $^1J_{C,P} = 54.4$ Hz, *ipso*-C of PC_6H_5), 181.4 (s, SCH_2CH_2COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 162 MHz): δ = 11.6 (s, PMe_2Ph) ppm. IR (KBr pellet): ṽ = 1644 (C=O), 1538, 1353 (O−C−O), 1186 (C−O) cm^{-1}. $C_{44}H_{64}Au_2O_4P_2S_2Zr{\cdot}1.5THF$ (1376.32): calcd. C 43.6, H 5.6, S 4.6; found C 44.1, H 5.1, S 4.2.

Data Collection and Structural Refinement of 4: The X-ray diffraction data[24] were measured with a Siemens diffractometer of the type SMART CCD (Mo-K_α = 0.71073 Å). All observed reflections were used for refinement (SAINT) of the unit cell parameters. Empirical absorption correction with SADABS.[24] The structures was solved by direct methods (SHELXTL PLUS).[24] Zr, Au, P, S, O, and C atoms were refined anisotropically; H atoms were refined isotropically in calculated positions. Table 1 lists crystallographic details. CCDC-177457 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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