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Base-Assisted Formation of Organozirconium Oxides with the [$Zr_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8$] Core Structure**

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Mathias Noltemeyer, and Hans-Georg Schmidt

Dedicated to Professor Dieter Sellmann
on the occasion of his 60th birthday

Zirconium oxides have long-been used as catalysts for the hydrogenation of carbon monoxide[1] and ethylene,[2] the highly selective isomerization of 1-butene and the formation of 1-butene from 2-butanol or 2-butanamine,[3] and the selective oxidation of hydroxy-containing organic compounds.[4] In general, complete hydrolysis of zirconium chlorides leading to zirconium oxides without an appreciable amount of chloride and hydroxide is difficult to achieve and only possible at very high temperatures. ZrO_2 is prepared by treating [$ZrOCl_2 \cdot 8H_2O$] at 1000 °C[5] or by calcining zirconium hydroxide in O_2 at 500 °C.[1g, 3a] Base-assisted hydrolysis of organozirconium chlorides results in the formation of organozirconium oxide complexes containing chloride or hydroxide ligands, such as [$(Cp_2ZrCl)_2(\mu\text{-}O)$],[6] [$\{(Cp^*ZrCl)(\mu\text{-}OH)\}_3(\mu_3\text{-}OH)(\mu_3\text{-}O)$]$\cdot$2THF,[7] [$\{(Cp^*ZrCl)(\mu\text{-}OH)\}_3(\mu_3\text{-}O)(\mu\text{-}Cl)$].[8] To the best of our knowledge so far no larger aggregate of an organozirconium oxide has been isolated or detected.

We are interested in studying the products formed by the reaction of early transition metal compounds in the liquid ammonia/toluene two-phase system. Recently we reported on the reaction of [L_2TiCl_2] ($L = p\text{-}MeC_6H_4C(NSiMe_3)_2$) with $NaNH_2$ in liquid ammonia and toluene[9] to yield [$(LTi)_6(\mu_3\text{-}N)_2(\mu_3\text{-}NH)_6$]$\cdot 6(C_7H_8)$, and on the formation of [$\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4$] from the reaction of [$(MeC_5H_4)_2ZrCl_2$] with K in liquid ammonia and toluene.[10] The imido-bridged dinuclear zirconium complex [$\{(\eta^3\text{-}L')Zr(\mu\text{-}NH)\}_2$] ($L' = (tBuNP)_2(tBuN)_2$) was obtained by treating [$L'ZrCl_2$] with KH in liquid ammonia and toluene.[11] These results prompted us to attempt the complete hydrolysis of metal chlorides, which is difficult to achieve under base-assisted conditions at low temperatures.

Herein we report on the reaction of [$(EtMe_4C_5)ZrCl_3$] (**1**) with H_2O (1:1.5 molar ratio) in toluene at room temperature with successive treatment by KH (1:3 molar ratio) in liquid ammonia and toluene at −78 °C. The strong basic reagent KH affords the complete removal of chloride and the formation of the organozirconium oxide **2** [Eq. (1)]. The influence of the solvent on the solid-state structure of **2** was demonstrated by recrystallization of **2** from mesitylene which gave cluster **3** [Eq. (2)].

$$\underset{\mathbf{1}}{6[(EtMe_4C_5)ZrCl_3]} + 9H_2O \xrightarrow[\text{toluene, }-78\,^{\circ}\text{C}]{\text{1. toluene, RT, 2 h; 2. 18KH, liq. NH}_3\text{,}} \underset{\mathbf{2}}{[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8} + 18KCl + 18H_2 \tag{1}$$

$$\underset{\mathbf{2}}{[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8} \xrightarrow[-\text{toluene}]{\text{mesitylene}} \underset{\mathbf{3}}{[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_9H_{12}} \tag{2}$$

A proposed mechanism for the formation of **2** is given in Equations (3)–(8) ($Cp' = EtMe_4C_5$; X = Cl, NH_2, or OH). The first step of the reaction involves the formation of the water adduct **4** [Eq. (3)]. The acidic nature of the hydrogen atoms of the coordinated H_2O results in hydrogen chloride elimination under formation of ammonium chloride in the presence of NH_3 [Eq. (4)]. We were unable to isolate **2** from the reaction of **1** with H_2O in liquid ammonia and toluene. Excess of ammonia does not result in a complete hydrolysis of **1**. Partial hydrolysis and ammonolysis have been also observed in the base-assisted hydrolysis of [Cp^*ZrCl_3][7, 8] and the ammonolysis of ZrX_4 (X = Cl, Br) in liquid NH_3.[12] In the presence of KH, NH_4Cl is converted to KCl and hydrogen [Eq. (5)]. On the other hand KH reacts with ammonia under formation of KNH_2 and hydrogen [Eq. (6)].[13] Moreover, we have shown that KNH_2 reacts with a compound containing a Zr−Cl bond to yield the amide [Eq. (7)].[10] Due to the Lewis acidity of the Zr^{IV} center, the OH group functions as an acid

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and this favors the formation of a further Zr–O bond [Eq. (8)] rather than a Zr–N bond. Similar results were observed in the hydrolysis of $[Cp^*_2HfH(NH_2)]$[14] and $[(Cp^*Ti)_4(\mu_3\text{-}N)_4]$,[15] which led to $[Cp^*_2HfH(OH)]$ and $[(Cp^*Ti)_4(\mu\text{-}O)_6]$, respectively. Consequently, the addition of KH results in the complete hydrolysis of **1**. Certainly Equations (3)–(8) are

$$Cp'ZrCl_3 \xrightarrow{H_2O} Cp'ZrCl_3 \cdot OH_2\ (\mathbf{4}) \tag{3}$$

$$\mathbf{4} + NH_3 \longrightarrow Cp'ZrCl_2OH + NH_4Cl \tag{4}$$

$$NH_4Cl + KH \longrightarrow KCl + NH_3 + H_2 \tag{5}$$

$$NH_3 + KH \longrightarrow KNH_2 + H_2 \tag{6}$$

$$Cp'X_2ZrCl + KNH_2 \longrightarrow Cp'X_2ZrNH_2 + KCl \tag{7}$$

$$Cp'X_2ZrOH + H_2NZrCp'X_2 \longrightarrow Cp'X_2ZrOZrCp'X_2 + NH_3 \tag{8}$$

over simplified and other side reactions might occur. Evidently, the KH has two functions in this reaction, it completely converts the chloride to KCl and the resulting ZrOH and $ZrNH_2$ to ZrOZr species by an intermolecular ammonia elimination. It is well documented that the Zr–Cl, Zr–OH, and Zr–NH_2 compounds can be isolated when no KH is present in the reactions.[7, 8, 10] Finally, the two-phase system (ammonia/toluene) increases the solubility of the organic and inorganic components, so that the reaction preferentially occurs at the interface. Therefore we assume that the presence of KH and the in situ formation of $ZrNH_2$ as well as the liquid ammonia/toluene two-phase system are important for the formation of **2**.

Compounds **2** and **3** are colorless crystalline solids with unusual thermal stability. The melting points of **2** and **3** exceed 410 °C. Compounds **2** and **3** are very stable to H_2O and O_2. No reaction was observed on exposing the solution of **2** (**3**) to H_2O or air. The most intense peak in the EI mass spectrum of **2** appears at m/z 1437 $[M^+ - C_7H_8 - EtMe_4C_5]$, and the signal at 1586 (4%) is assigned to the $[M^+ - C_7H_8]$ fragment. The corresponding peaks of **3** appear at m/z 1437 (100%) $[M^+ - C_9H_{12} - EtMe_4C_5]$ and 1586 (12%) $[M^+ - C_9H_{12}]$.

Single crystals of **2**[16a] and **3**[16b] suitable for X-ray structural analysis were obtained from toluene and mesitylene, respectively, by keeping the reaction mixtures at 0 °C for one week. The molecular structure of **2** is shown in Figure 1. Each molecule of **2** (**3**) contains one molecule of toluene (mesitylene). Compound **2** crystallizes in the triclinic space group $P\bar{1}$, and **3** in the monoclinic space group $C2/c$. The molecular structure of **2** in the crystal consists of a perfect octahedron with $(EtMe_4C_5)Zr$ fragments arranged around an interstitial oxygen atom. The angles between adjacent zirconium atoms are either 60° or 90°. Eight of the faces of the octahedron are topped each by oxygen resulting in twelve four-membered Zr_2O_2 rings. The average O-Zr-O and Zr-O-Zr angles in the Zr_2O_2 rings are 81.34° and 94.65°, respectively. The coordination sphere of each zirconium atom is completed by the ligand $EtMe_4C_5$. The Zr–(μ_3-O) bond lengths (2.136(2)–2.169(2) Å, av 2.156 Å) are similar to those in $[\{(Cp^*ZrCl)(\mu\text{-}OH)\}_3(\mu_3\text{-}OH)(\mu_3\text{-}O)] \cdot 2\,THF$ (Zr–(μ_3-O) 2.134 Å)[7] and in $[\{(CpZr(\mu\text{-}OH))_3(\mu_3\text{-}O)(\mu\text{-}C_6H_5COO)_3\}^+]$ (Zr–(μ_3-O) 2.071(11) Å).[17]

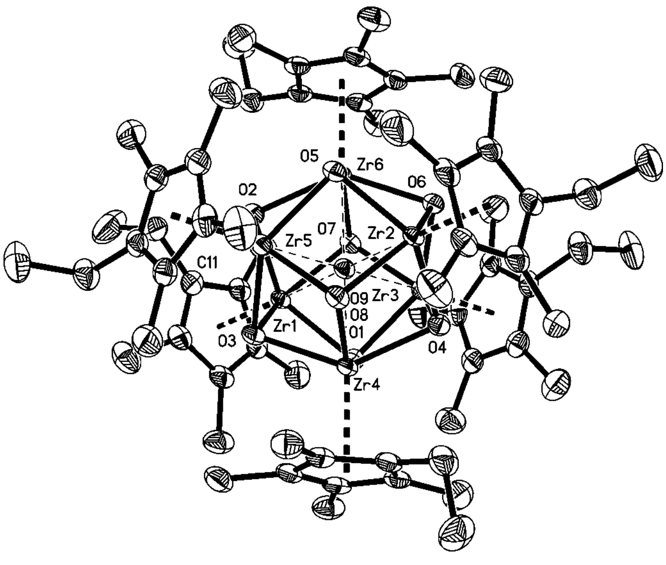

Figure 1. Molecular structure of **2** in the crystal. The hydrogen atoms and the toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1-O1 2.136(2), Zr1-O2 2.169(2), Zr1-O3 2.142(2), Zr1-O7 2.165(2), Zr1-O9 2.241(2), Zr2-O9 2.245(2), Zr1-Zr4 3.1542(9), Zr1-Zr5 3.1657(11); O1-Zr1-O3 82.19(9), O1-Zr1-O7 81.42(9), O2-Zr1-O3 81.37(9), O2-Zr1-O7 80.53(9), Zr1-O1-Zr3 94.87(9), Zr1-O1-Zr4 94.48(9), Zr3-O1-Zr4 94.32(9), Zr4-Zr1-Zr5 60.25(2), Zr1-Zr4-Zr2 90.53(2), Zr1-O9-Zr4 89.70(8), Zr1-O9-Zr2 179.52(11).

Whereas the Zr–(μ_6-O) bond lengths (2.231(2)–2.247(2) Å, av 2.241 Å) are distinctively longer. Moreover the Zr–(μ_3-O) and Zr–(μ_6-O) bond lengths are longer than the Zr–(μ-O) bond lengths in $[(Cp_2ZrCl)_2(\mu\text{-}O)]$ (1.945(3) Å),[6] $[(Cp_2ZrMe)_2(\mu\text{-}O)]$ (1.948(1) Å),[18] and $[\{Cp_2Zr(\mu\text{-}O)\}_3]$ (1.959(3) Å).[19] The Zr⋯Zr distances (3.1542(9)–3.1709(11) Å, av 3.1635 Å) are comparable to those in $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$ ($Zr_a \cdots Zr_b$ 3.1433(10) Å, $Zr_b \cdots Zr_b$ 3.1566(8) Å; Zr_a and Zr_b represent the apical and the four basal zirconium atoms of the square-pyramidal cluster, respectively).[10] Furthermore the Zr⋯Zr distances are also similar to those exhibited by the zirconium halide clusters $[KZr_6Cl_{15}C]$ (3.225 Å),[20] $[CsZr_6I_{14}C]$ (3.283 Å),[21] $[Zr_6Cl_{12} \cdot K_2ZrCl_6]$ (3.201 Å),[22] and $[Zr_6Cl_{14}B]$ (3.257 Å).[23] The molecular structure of **3** in the crystal is more symmetric than that of **2** due to the more symmetric mesitylene in **3**. But the core structure of **3** is nearly the same as that of **2**. The bond lengths of Zr–(μ_3-O) (2.145(2)–2.175(2) Å, av 2.163 Å) and Zr–(μ_6-O) (2.2407(4)–2.2481(4) Å, av 2.2432 Å), and the Zr⋯Zr distances (3.1664(7)–3.1728(7) Å, av 3.1687 Å), as well as the average O-Zr-O (81.35°) and Zr-O-Zr (94.61°) angles in the four-membered Zr_2O_2 rings of **3** are almost the same as those found in **2**.

It is interesting to compare the coordination environment of Zr in **2** and **3** with that in monoclinic ZrO_2 (Figure 2).[24] Compounds **2** and **3** can be regarded as deriva-

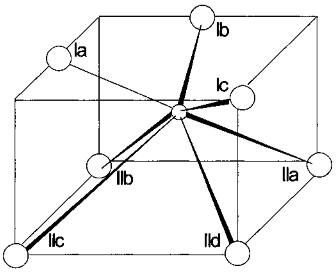

Figure 2. Monoclinic ZrO_2. Small circle = zirconium atom; large circles = oxygen atoms.

tives of ZrO_2. One $EtMe_4C_5$ ligand is sterically equivalent to three O_I positions, while the interstitial O coordinates to zirconium from the center of the plane formed by the four O_{II} atoms by enlarging the O_{II}-Zr-O_{II} angles (av 74.1° in ZrO_2). The Zr−(μ_3-O) bond lengths in **2** and **3** are between the Zr−O_I (2.07 Å) and Zr−O_{II} (2.21 Å) bond lengths, while the Zr−(μ_6-O) bond lengths are comparable to those of Zr−O_{II}.

In summary we describe a new method for the preparation of organozirconium oxides by hydrolysis of an organozirconium chloride at low temperatures. Using this method, we have obtained the organozirconium oxides **2** and **3**. In comparison to the traditional preparation of ZrO_2 from $ZrCl_4$ at 1000 °C the new route yields crystalline products below room temperature. The core structures of **2** and **3** can be regarded as a dimer of the previously reported $[\{(Cp^*ZrCl)(\mu\text{-}OH)\}_3(\mu_3\text{-}OH)(\mu_3\text{-}O)]\cdot 2\,THF$ cluster[7] (without containing six HCl, four THF, and one H_2O molecules). We assume that the formation of **2** proceeds via zirconium hydroxide and amide intermediates. KH and the two-phase system (NH_3/toluene) are important for the formation of **2**. The more symmetric coordinated mesitylene leads to the more symmetric molecule of **3**, but has evidently no influence on the core structure. Further studies using this new method for the preparation of Ti−O, Hf−O, Al−O, and rare-earth systems are in progress.

Experimental Section

2: H_2O (0.08 g, 4.5 mmol) was added to the solution of **1** (1.04 g, 3.0 mmol) in toluene (80 mL) at room temperature. The solution turned light yellow and was stirred for 2 h at this temperature. KH (0.37 g, 9.2 mmol) was added to the solution, and then ammonia (50 mL) was condensed onto the resulting suspension at −78 °C with stirring. The mixture was stirred for 1 h at this temperature. Then the excess of ammonia was allowed to evaporate from the reaction mixture over a period of 4 h. During this time the mixture slowly warmed to room temperature. The resulting solution was filtered and the remaining yellowish brown precipitate was extracted with warm toluene (50 °C, 2 × 20 mL). The combined light yellow solution was concentrated (to 15 mL) in vacuo and kept at 0 °C for one week. Colorless crystals of **2** (0.10 g) were obtained. After concentration (to 5 mL) of the filtrate, the solution was kept at −20 °C for one week. An additional crop of **2** (0.11 g) was obtained. Total yield 0.21 g (25 %); m.p. > 410 °C; IR (Nujol): $\tilde{\nu} = 1580$, 1309, 1261, 1097, 1050, 1023, 779, 727, 659, 562, 506, 454 cm^{-1}; ^1H NMR (200 MHz, C_6D_6, 60 °C): $\delta = 2.74$ (q, $^3J = 7.5$ Hz, 12 H; CH_2Me), 2.23, 2.17 (s, 72 H; C_5Me_4), 1.08 (t, $^3J = 7.5$ Hz, 18 H; CH_2Me); EI-MS: *m/z* (%): 1586 (4) $[M^+ - C_7H_8]$, 1437 (100) $[M^+ - C_7H_8 - EtMe_4C_5]$; elemental analysis (%) calcd for $C_{73}H_{110}O_9Zr_6$ (1679.0): C 52.2, H 6.6; found: C 52.7, H 6.7.

3: Crystals of **2** (0.05 g) were dissolved in warm mesitylene (80 °C; 8 mL). The resulting colorless solution was kept at 0 °C for one week. A quantitative yield of colorless crystals of **3** was obtained; m.p. > 410 °C; EI-MS: *m/z* (%): 1586 (12) $[M^+ - C_9H_{12}]$, 1437 (100) $[M^+ - C_9H_{12} - EtMe_4C_5]$.

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[16] a) Crystal data for **2**: $C_{73}H_{110}O_9Zr_6$ (including one toluene molecule), $M_r = 1678.93$, triclinic, space group $P\bar{1}$, $a = 12.959(3)$, $b = 14.341(4)$, $c = 19.189(5)$ Å, $\alpha = 82.85(3)$, $\beta = 84.562(17)$, $\gamma = 83.767(13)$°, $V = 3505.7(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.591$ Mg m^{-3}, $F(000) = 1720$, $\lambda = 0.71073$ Å, $T = 200(2)$ K, $\mu(Mo_{K\alpha}) = 0.914$ mm^{-1}. Data for the structure were collected on a Stoe-Siemens-AED2 four-circle diffractometer. Intensity measurement was performed at 200(2) K on a rapidly cooled crystal with the dimensions $1.0 \times 0.6 \times 0.4$ mm^3 in an oil drop[25] in the range $7.04 \leq 2\theta \leq 50.10$°. Of the 15669 measured reflections, 12318 were independent ($R_{int} = 0.0787$). The structure was solved by direct methods (SHELXS-90)[26] and refined with all data by full-matrix least-squares on F^2.[27] The hydrogen atoms of C−H bonds were added in idealized positions. $R1 = 0.0408$ for $I > 2\sigma(I)$, $wR2 = 0.1187$ for all data. The final difference Fourier synthesis gave a min./max. residual electron density $-1.173/+0.891$ e Å^{-3}. b) Crystal data for **3**: $C_{75}H_{114}O_9Zr_6$ (including one mesitylene molecule), $M_r = 1706.98$, monoclinic, space group $C2/c$, $a = 22.641(5)$, $b = 13.0808(11)$, $c = 24.550(6)$ Å, $\beta = 93.196(12)$°, $V = 7259(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.562$ Mg m^{-3}, $F(000) = 3504$, $\lambda = 0.71073$ Å, $T = 200(2)$ K, $\mu(Mo_{K\alpha}) = 0.884$ mm^{-1}. Data for the structure were collected on a Stoe-Siemens-AED2 four-circle diffractometer. Intensity measurement was performed at 200(2) K on a rapidly cooled crystal in an oil drop[25] with the dimensions $0.6 \times 0.6 \times 0.4$ mm^3 in the range $7.06 \leq 2\theta \leq 50.04$°. Of the 7944 measured reflections, 6365 were independent ($R_{int} = 0.0330$). The structure was solved by direct methods (SHELXS-90)[26] and refined with all data by full-matrix least-squares on F^2.[27] The hydrogen atoms of C−H bonds were added in idealized positions. $R1 = 0.0307$ for $I > 2\sigma(I)$, $wR2 = 0.0683$ for all data. The final difference Fourier synthesis gave a min./max. residual electron density $-0.476/+0.756$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155721 (**2**) and CCDC-155720 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Luminescent Gold Ring That Flips Like Cyclohexane[**]

John H. K. Yip[*] and Janardhana Prabhavathy

Coordination-directed self-assembly of metal centers and multidentate ligands has successfully created many discrete inorganic molecules with intricate supramolecular architectures.[1] Among these compounds are metallacycles[2] which are not only aesthetically pleasing but potentially functional as catalysts, sensors, and in molecular electronics.[3] The modular character of the compounds allows their physical properties to be tailored readily and previous studies of metallacycles focused mainly on their photoluminescence and electrochemistry.[2b,c, 3, 4] On the other hand, our understanding of the fluxionality of metallacycles is still relatively limited. Given the rich fluxionality of organic rings and cyclophanes,[5] it is surprising that analogous behavior is not widely observed in their inorganic counterparts. This paucity could be a result of the rigidity of many metallacycles. Outstanding examples of metallacycle fluxionality are the PtS_5 ring inversion in $[NH_4]_2[Pt(S_5)_3]$ and the cyclooctane-like inversion of the eight-membered ring $[Pt_2Me_4(\mu\text{-}Me_2PCH_2Me_2)_2]$ reported by Riddell et al.[6a] and Puddephatt and co-workers,[6b] respectively. Herein we report the synthesis of 9,10-bis(diphenylphosphino)anthracene (PAnP), a ligand designed to form emissive cyclophanes with low-valent metal centers. Subsequent treatment of PAnP with Au^I ions produced a fluorescent trinuclear gold ring that has structure and fluxionality reminiscent of cyclohexane.

PAnP (see Scheme 1) was synthesized from the reaction of dilithioanthracene and PPh_2Cl. A similar monodentate ligand 9-diphenylphosphinoanthracene was first synthesized by Mingos and co-workers.[7] PAnP shows a singlet at $\delta = -21.9$ in the $^{31}P\{^1H\}$ NMR spectrum and its structure was confirmed by X-ray crystallography (see Supporting Information). Prolonged reflux of PAnP and Me_2SAuCl (1:1) in methanol produced a yellow solution from which a trinuclear Au^I complex $[Au_3(PAnP)_3][ClO_4]_3$ (**1**) was isolated. Single-crystal X-ray analysis shows that the cation of **1** is a ring comprising three bridging PAnP ligands and three gold atoms (Figure 1).[8] The three anthracenyl units are nearly perpendicular to the ring, the diameter of which, taken as the distance between P(1) and P(4), is 10.04 Å. One of the three ClO_4^- ions is in the center of the ring and three of its oxygen atoms (O(1), O(2), and O(4)) are directed towards, and are almost equidistant from, the central rings of the three PAnP anthracene units (3.083(3)–3.170(3) Å). Notably, the anthracenyl rings curve slightly from the center of the cavity, with a dihedral angle of 15.3° between the two lateral benzene rings. Similar ring distortion has been observed in 9,10-bis(trimethylsilyl)anthracene,[9] and possibly occurs in **1** to alleviate steric congestion between the peripheral protons of anthracenyl and Ph rings. The coordination geometry of the Au atoms is close to linear (169.54(1)–178.84(1)°) and the

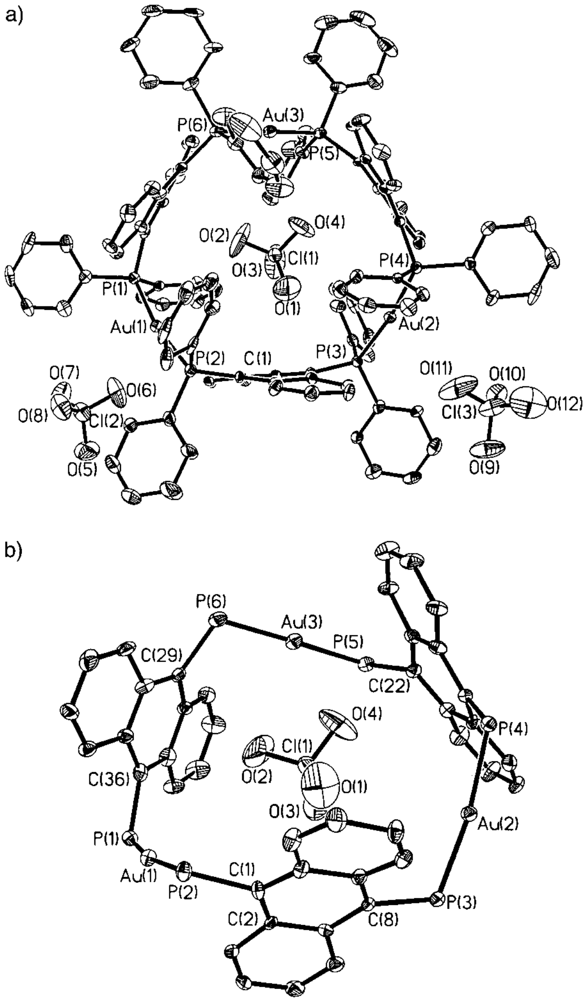

Figure 1. ORTEP drawing of $\mathbf{1}\cdot 0.5\,Et_2O$; a) top and b) side view. H atoms, ClO_4 ions, Ph rings, and Et_2O are omitted for clarity (thermal ellipsoids are set at the 50% probability level). Selected bond lengths [Å] and angles [°]: Au(1)-P(1) 2.294(3), Au(2)-P(3) 2.312(3), Au(3)-P(5) 2.309(3), P(2)-C(1) 1.850(9), Au(1)···Au(2) 8.123(3), Au(1)···Au(3) 7.892(3), Au(2)···Au(3) 7.742(3); P(1)-Au(1)-P(2) 169.54(1), P(3)-Au(2)-P(4) 171.91(9), P(5)-Au(3)-P(6) 178.84(1), Au(1)-P(2)-C(1) 109.6(3).

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