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Arsenic-Functionalized Zirconocene Mono- and Bis(arsenido) Complexes. Syntheses and Crystal Structures of $[Cp_2Zr\{As(SiMe_3)_2\}_2]$ and $[Cp'_2Zr\{As(SiMe_3)_2\}(Cl)]$ ($Cp = C_5H_5$, $Cp' = C_5H_4Me$)

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Summary: The arsenic-functionalized zirconocene arsenido complexes $[Cp'_2Zr\{As(SiMe_3)_2\}(Cl)]$ *(1;* $Cp' = C_5H_4Me$*) and* $[Cp_2Zr\{As(SiMe_3)_2\}_2]$ *(2;* $Cp = C_5H_5$*) are obtained by the reaction of* $[Cp'_2ZrCl_2]$ *or* $[Cp_2ZrCl_2]$ *with* $Li(THF)_2As(SiMe_3)_2$*. 1 and 2 were characterized by spectroscopy (IR, NMR, mass spectrum) and by X-ray structure determinations. In 2 there are two distinctly different* $As(SiMe_3)_2$ *groups and Zr—As bond lengths (Zr—As1 = 2.799(2) Å, Zr—As2 = 2.616(2) Å), indicating the presence of a Zr—As1 single bond and a Zr—As2 double bond.*

Whereas complexes with terminal phosphido ligands are well-known for most transition metals, the number of compounds containing a terminal arsenido ligand is much smaller,[1] and only a few examples are known with bridging μ_2-AsR_2 ligands.[2] This could be due to the fact that arsenic compounds are far more sensitive and toxic than their phosphorus analogues.

For some time we have been interested in the synthesis and chemistry of $PSiMe_3$-functionalized zirconocene phosphido complexes,[3] which have proved to be versatile starting materials for the synthesis of novel P-functionalized ligands[4] that are unobtainable by other routes. To extend this chemistry to $AsSiMe_3$-functionalized zirconocene arsenido complexes, we prepared the zirconocene mono(arsenido) complex $[Cp'_2Zr\{As(SiMe_3)_2\}(Cl)]$[5] (**1**; $Cp' = C_5H_4Me$) and the bis(arsenido) compound $[Cp_2Zr\{As(SiMe_3)_2\}_2]$[6] (**2**; $Cp = C_5H_5$) from $[Cp'_2ZrCl_2]$ or $[Cp_2ZrCl_2]$ and $Li(THF)_2As(SiMe_3)_2$.[7] Like the analogous zirconocene phosphido complexes, these compounds are intensely colored (**1** is bright red and **2** brown-red). **1** and **2** are extremely sensitive toward air and moisture. At ambient temperature, **2** slowly decomposes in solution or in the solid state even under an atmosphere of nitrogen.

X-ray crystal structure determinations of **1** and **2** were carried out.[8] In **2**, the Zr atom shows a distorted-tetrahedral environment and is coordinated by two Cp and two $As(SiMe_3)_2$ ligands (Figure 1).[9] The As1—Zr—As2 bond angle (95.00(7)°) is comparable to that found in the zirconocene bis(phosphido) complex $[Cp'_2Zr\{P(SiMe_3)_2\}_2]$ (**3**; 96.95(7)°).[3b] While **3** shows two nearly equivalent Zr—P bond lengths and a trigonal-planar environment for both phosphido groups, the Zr—As bond lengths in **2** differ significantly (Zr—As1 = 2.799(2) Å, Zr—As2 = 2.616(2) Å, Δ = 0.18 Å). The As atom (As1) which participates in the longer Zr—As bond shows a pyramidal geometry (sum of angles 329.2°), while As2, which exhibits the shorter Zr—As bond length, is coordinated in a trigonal-planar fashion (sum of angles 359.6°; the atoms Zr, As2, Si3, and Si4 are

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(5) Synthesis of $[Cp'_2Zr\{As(SiMe_3)_2\}(Cl)]$ (**1**): A solution of $Li(THF)_2As(SiMe_3)_2$ (5.00 g, 13.40 mmol) in 30 mL of toluene was added to a slurry of $[Cp'_2ZrCl_2]$ (4.31 g, 13.40 mmol) in 20 mL of toluene at room temperature. After it was stirred for 1 h, the dark red solution was reduced to ca. 20 mL and filtered through Celite; the remaining solid (LiCl) was washed with 20 mL of hexane. Cooling the filtrate to −30 °C gave vivid red crystals of **1**: yield 4.25 g (62.7%); mp 158 °C; ^1H NMR (C_6D_6) δ several multiplets for C_5H_4Me at 6.44 (m, 2), 6.55 (m, 2), 5.40 (m, 2), and 5.25 (m, 2), 2.06 (s, 6, C_5H_4Me), 0.52 (s, 18, $SiMe_3$); IR (Nujol, cm^{-1}) 3107 w, 1667 w, br, 1493 m, sh, 1413 m, sh, 1245 st, 1152 w, 1116 w, 1074 m, 1033 st, 933 st, 837 st, br 734 st, br, 616 st, 453 m, 309 st, br, 262 st, br. Mass spectrum (EI, 70 eV; *m/e* (relative intensity)) 504 (M^+, 1.9), 442 ($As_2(SiMe_3)_4$, 0.5), 431 ($M^+ - SiMe_3$, 0.4), 357 ($M^+ - 2\ SiMe_3$, 3.6), 294 ($As(SiMe_3)_3$, 16.6), 283 ($M^+ - As(SiMe_3)_2$, 21.7) 266 ($As_2Si_2Me_4$, 3.1), 206 ($AsSi_2Me_5$, 19.4), 73 ($SiMe_3$, 100). The thermal instability of this compound has precluded elemental analysis.

(6) Synthesis of $[Cp_2Zr\{As(SiMe_3)_2\}_2]$ (**2**): A solution of $Li(THF)_2As(SiMe_3)_2$ (3.14 g, 8.44 mmol) in 10 mL of toluene was added to a slurry of $[Cp_2ZrCl_2]$ (1.23 g, 4.21 mmol) in 25 mL of toluene at −60 °C. The mixture was warmed to room temperature overnight, and LiCl was removed from the solution by filtration. Volatiles were removed from the filtrate in vacuo, and the tarry residue was dissolved in 8 mL of hexane. When the temperature is lowered to −30 °C, **2** is obtained as brownish red crystals: yield 1.69 g (60.7%); mp 107−109 °C; ^1H NMR (C_6D_6) δ 6.05 (s, 10, C_5H_5), 0.53 (s, 36, $SiMe_3$); IR (Nujol, cm^{-1}) 2074 w, 1399 m, 1305 w, 1248 vst, 1014 st, 987 vst, 959 vst, 930 vst, 878 vst, 841 vst, 793 vst, 754 vst, 689 st, 524 m, br, 409 m, br, 335 m, br; Mass spectrum (EI, 70 eV; *m/e* (relative intensity)) 662 (M^+, 0.5), 592 ($As_4(SiMe_3)_4$, 1.6), 519 ($As_4(SiMe_3)_3$, 1.5), 513 ($M^+ - As(SiMe_3)$, 0.7), 442 ($As_2(SiMe_3)_4$, 10.4), 294 ($As(SiMe_3)_3$, 13.2), 266 ($As_2Si_2Me_4$, 9.1), 206 ($AsSi_2Me_5$, 18.2), 73 ($SiMe_3$, 100). The thermal instability of this compound has precluded elemental analysis.

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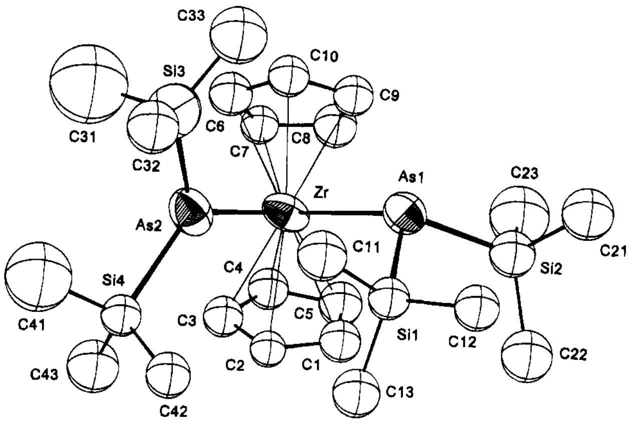


Figure 1. Molecular structure of $[Cp_2Zr\{As(SiMe_3)_2\}_2]$ (**2**) (ORTEP plot). Only one molecular arrangement of the disordered $SiMe_3$ and Cp ligands is shown. Selected bond lengths (Å) and angles (deg) are given for this set of atoms:[9] Zr—As1 = 2.799(2), Zr—As2 = 2.616(2), As1—Si1 = 2.426(5), As1—Si2 = 2.410(8), As2—Si3 = 2.359(5), As2—Si4 = 2.432(6); As1—Zr—As2 = 95.00(7), Zr—As1—Si1 = 111.5(2), Zr—As1—Si2 = 119.0(2), Si1—As1—Si2 = 98.7(3), Zr—As2—Si3 = 122.7(1), Zr—As2—Si4 = 125.9(2), Si3—As2—Si4 = 111.0(2). No hydrogen atoms were included.

coplanar). Therefore, we assume the presence of a Zr—As single bond (Zr—As1) and a Zr—As double bond (Zr—As2) in this compound (isomer B or C). Although **3** shows two equivalent Zr—P bond lengths, there are structurally characterized hafnocene and zirconocene bis(phosphido) complexes with a bonding situation similar to that in **2**. Thus, $[Cp_2Hf\{P(SiMe_3)_2\}_2]$ and $[Cp_2Hf(PEt_2)_2]$ both exhibit unequal Hf—P bond lengths ($P(SiMe_3)_2$, Hf—P = 2.553(1), 2.654(1) Å;[10] PEt_2, Hf—P = 2.488(1), 2.682(1) Å[11]), and the P atom involved in the shorter Hf—P bond has a trigonal-planar environment (sum of angles 360°). Also, two different bond lengths (Zr—P = 2.560(4), 2.647(6) Å[12]) are present in the zirconocene *o*-phenylenebis(phosphido) complex $[Cp_2Zr\{1,2\text{-}(PPh)_2C_6H_4\}]$.

The mono(arsenido) complex **1** (Figure 2) has a Zr—As bond length (2.7469(7) Å) and bond angles around As (sum of bond angles 328.8°) which are closer to those of the Zr—As1 environment in **2**, suggesting the presence of a Zr—As single bond.

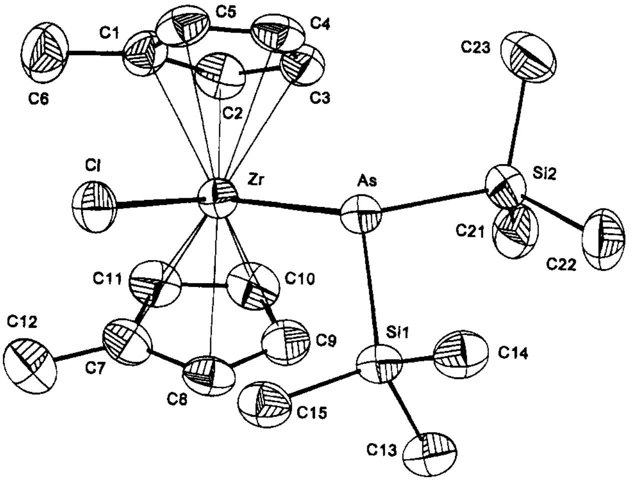
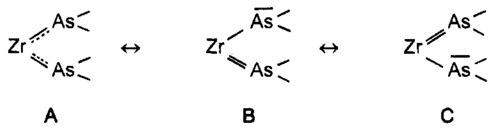


Figure 2. Molecular structure of $[Cp'_2Zr\{As(SiMe_3)_2\}(Cl)]$ (**1**) (ORTEP plot). Selected bond lengths (Å) and angles (deg): Zr—As = 2.7469(7), Zr—Cl = 2.445(1), As—Si1 = 2.342(2), As—Si2 = 2.345(2); As—Zr—Cl = 95.46(4), Zr—As—Si1 = 114.61(4), Zr—As—Si2 = 111.48(4), Si1—As—Si2 = 102.72(5). Hydrogen atoms are omitted for clarity.

In solution there is no indication of B or C; only one resonance is observed for the $SiMe_3$ protons in the ^1H NMR spectrum even at low temperature (−80 °C), indicating the presence of two equivalent $As(SiMe_3)_2$ groups (A). Therefore, we believe that in solution an equilibrium between B and C exists, which is fast on the NMR time scale.



The only other reported zirconocene arsenido complex is $[Cp_2Zr(AsPh_2)_2]$, which has been characterized spectroscopically.[13] In the mass spectrum, this complex exhibits signals for polyarsenides $(AsPh_2)_n$ (n = 2−4) only, while for **1**[5] and **2**[6] the parent ion peak (*m/e* 504 (**1**) and 662 (**2**)) and fragmentation products thereof are observed, as well as signals for polyarsenides.

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Supplementary Material Available: Tables of crystal data and details of intensity collection, positional parameters, anisotropic thermal parameters, and bond lengths and angles for **1** and **2** and figures giving additional views of **2** (26 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for $[Cp'_2Zr\{As(SiMe_3)_2\}(Cl)]$ (**1**): Crystals of **1**, $C_{18}H_{32}AsClSi_2Zr$, M_r = 506.21, were grown from toluene/hexane at room temperature and are of space group $P2_1/c$ (No. 14) with a = 11.545(2) Å, b = 17.294(3) Å, c = 13.071(2) Å, β = 115.96(1)°, V = 2346.4 Å^3, Z = 4, d_{calc} = 1.433 g cm^{-3}, and μ(Mo Kα) = 20.82 cm^{-1}. Data (λ(Mo Kα) = 0.710 69 Å) were collected with a STOE IPDS diffractometer (imaging plate diffractometer system) at 213 K. The structure was solved by direct methods (SHELXS-86)[14] and subsequent difference Fourier syntheses and refined by least-squares techniques (SHELXL-93).[15] Final $R1$ = 0.0491, w$R2$ = 0.1309 (for reflections with $I > 2\sigma(I)$); $R1$ = 0.0585, w$R2$ = 0.1440 (all data). Crystal data for $[Cp_2Zr\{As(SiMe_3)_2\}_2]$ (**2**): Crystals of **2**, $C_{22}H_{46}As_2Si_4Zr$, M_r = 664.01, were grown from hexane at room temperature and are of space group Cc (No. 9) with a = 13.356(7) Å, b = 17.767(12) Å, c = 14.948(10) Å, β = 113.04(5)°, V = 3264 Å^3, Z = 4, d_{calc} = 1.351 g cm^{-3}, and μ(Mo Kα) = 25.04 cm^{-1}. Data in the range $4° \leq 2\theta \leq 54°$ (λ(Mo Kα) = 0.710 69 Å, Wyckoff ω-scans) were collected at 203 K. The structure was solved by direct methods (SHELXS-86)[14] and subsequent difference Fourier syntheses and refined by least-squares techniques (SHELXL-93).[15] Final $R1$ = 0.0472, w$R2$ = 0.1348 (for reflections with $I > 2\sigma(I)$]; $R1$ = 0.0555, w$R2$ = 0.1436 (all data).

(9) Due to disorder of the $SiMe_3$ groups and Cp ligands, all bond distances and bond angles involving these ligands are discussed here for one molecular arrangement only (atoms indicated with "A" in the supplementary material). For details of the disordered model, refer to the supplementary material.

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