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Structure of the Unreactive Hindered Cyclopentadienylzirconium Compound $[C_5H_2(SiMe_3)_3]_2ZrCl_2$

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Summary: The title compound crystallizes from hexane in space group $Pna2_1$ with cell parameters a = 42.700(3) Å, b = 17.484(2) Å, c = 10.946(1) Å, Z = 8, R = 0.046, and R_w = 0.053. In the crystal, monomeric units are observed with the tris(trimethylsilyl)cyclopentadienyl rings staggered due to steric congestion at the metal, to form a Cp(centroid)–Zr–Cp(centroid) angle of 135.4(2)° and relatively short Zr–Cl bond lengths of 2.420(3) and 2.438(3) Å (133.7(2)°, 2.415(3) Å, and 2.421(3) Å, respectively, in a second independent molecule). Following chemical reduction of 1 with sodium amalgam (Na/Hg), there is ESR evidence for Zr(III) species (g = 1.936 in toluene; g = 1965 in THF, as the ligand adduct), whereas electrochemical reduction was not observed by cyclic voltammetry up to 40 V/s. No reaction occurs between 1 and $LiAlH(OCMe_3)$, $LiAlH_4$, $NaAlH_2(OCH_2CH_2OCH_3)_2$, LiMe, and $LiBH_4$, probably due to the steric effect of the hindered tris(trimethylsilyl)cyclopentadienyl rings.

Introduction

Recent studies in our group have been directed toward the synthesis and structural characterization of metallocene derivatives of zirconium hydrides.[1] In our continuing efforts to study zirconium hydride complexes by changing the nature of the substituents attached to the cyclopentadienyl ligand,[2] the recently reported complex $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ (1)[3] was believed to be a suitable starting material for zirconium hydride chemistry. The complex 1 was synthesized according to the literature procedure[3] and its chemistry examined.

Results and Discussion

Experimental Studies. Complex 1 failed to react with $LiAlH(OCMe_3)$, $LiAlH_4$, $NaAlH_2(OCH_2CH_2OCH_3)_2$, or $LiBH_4$ in THF, diethyl ether, or toluene or with LiMe in diethyl ether to give, as is usually the case, the corresponding hydride or methyl complex.[1a,c,4] For the complete series of titanium complexes $[C_5H_x(SiMe_3)_{5-x}][C_5H_y(SiMe_3)_{5-y}]_2TiCl_2$ (x = 2, 3; y = 3–5) studied by Winter and co-workers,[5b] the effects of increasing steric bulk were apparent in their reactivity and the lack of reaction between $[C_5H_2(SiMe_3)_3][C_5H_3(SiMe_3)_2]TiCl_2$ and LiMe was already pointed out: the five bulky trimethylsilyl ligands protect the chlorine atoms from substitution. Nevertheless, in our studies, all these reactions afford, after classical workup, the crystalline complex 1 in hexane. Winter and co-workers failed in their attempts to obtain crystals of 1. Our success in the formation of 1 in its crystalline form is probably due to a further purification of the starting material 1 by these chemical reactions, purification which could not be easily effected with a highly soluble product.[5] Attempts to activate the cyclopentadienyl ligand of 1 via trimethylsilyl chloride elimination, whether by thermolysis in toluene-d_8 in a sealed ^1H NMR tube at 80 °C or by heating at 120 °C under high vacuum, left complex 1 unchanged.

Electrochemical and Chemical Reduction of 1. An electrochemical study by cyclic voltammetry in tetrahydrofuran (THF) with tetrabutylammonium tetrafluoroborate as supporting electrolyte, in the presence or absence of Cp_2Fe as reference, at 0.1, 2.0, and 40 V/s does not yield reduction or oxidation waves in the range −3.0 to +1.0 V (only the ferrocenium couple Cp_2Fe/Cp_2Fe^+ is observed). Complex 1 reacts very slowly in THF or toluene with Na/Hg at room temperature to give a light yellow solution. In constrast, red and blue solutions were observed in the reduction of $[C_5H_3(SiMe_3)_2]ZrCl_2$ in THF and toluene, respectively.[6] When the reduction is carried out in C_6D_6, ^1H NMR spectroscopy reveals the presence of unreacted 1, after 1 day of stirring. The light yellow toluene solution was characterized by ESR spectroscopy: there was a large signal at g = 1.936 with a line width of 20 G ($^{91}a(Zr)$ = 56 G) and a less intense signal at g = 1.965 with a narrower line width of 6–7 G. Incomplete chemical reduction of 1 was assumed with paramagnetic moment measurements by Evans' method[7] (1.2 μB is obtained), and no attempts were made to isolate the reduced Zr(III) species. In THF, the low-field resonance increased in intensity (Figure 1a). A similar trend has already been observed in the literature,[6,8] suggesting that the lower field signal arises from the complex with a donor ligand such as THF. The toluene glass of 1 at 103 K yields the spectrum displayed in Figure 1b. The room-temperature signal splits

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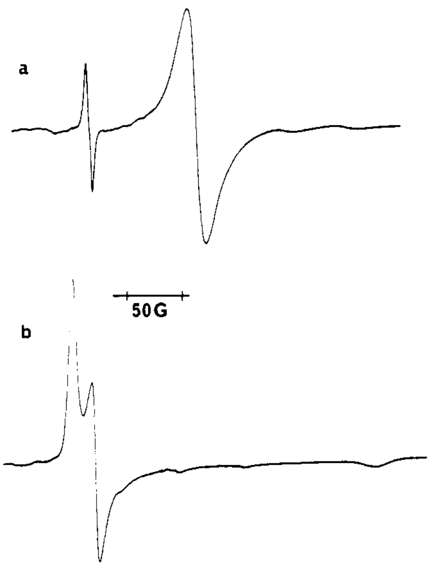

Figure 1. ESR spectra for the Na/Hg chemical reduction of 1: (a) at room temperature in THF; (b) frozen solution (103 K) in toluene.

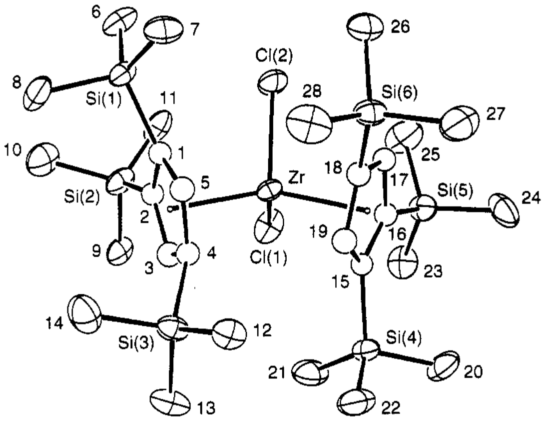

Figure 2. ORTEP view of compound 1, molecule A, with atom-labeling scheme. C atoms are only numbered, and H atoms are omitted for clarity.

into g_1 = 1.994, g_2 = 1.982, and g_3 = 1.850 components (g_{average} = 1.942), which are somewhat lower than values for related Zr(III) species already reported[8] but have some analogies with the signals for $[C_5H_3(SiMe_3)_2]HfCl_2$.[9]

X-ray Structure of $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ (1). Complex 1 crystallizes in the space group $Pna2_1$ with two independent molecules. An Ortep[10] drawing of one of the two molecules of complex 1 appears in Figure 2. Selected bond distances and angles are provided in Table 1. The sterically crowded complex 1 is monomeric in the solid state. The structures of the two independent units are rather similar, differing mainly in the relative staggered orientation of the $[C_5H_2(SiMe_3)_3]$ rings. The staggered ring configurations[11] are shown in Figure 3: the situation of the trimethylsilyl groups on opposite cyclopentadienyl rings minimizes steric interaction between these groups. The overall substituent positions are in fact approaching ideal symmetry within the molecule. There is no observed asymmetry in the exocyclic angles at the points of attachment of the silicon atoms. The Cp(centroid)–Zr distances are greater than those in Cp_2ZrCl_2[12] and $(C_5H_4SiMe_3)_2ZrCl_2$,[13] suggesting that steric interactions between $SiMe_3$ groups on opposite cyclopentadienyl rings elongate the Zr–Cp bonds. These steric repulsions also cause the large Cp(centroid)–Zr–Cp(centroid) angle in this complex. The chlorine atoms are symmetrically placed between the Cp rings in the plane containing the Cp ring centroid and zirconium atom (dihedral angles between Cl-Zr-Cl and Cp(1)-Zr-Cp(2) planes are 90.8(1) and 91.9(1)° for molecules A and B, respectively). The Zr–Cl bond lengths are the shortest among several isostructural Zr compounds.[6,12,13] It is noteworthy that two $SiMe_3$ substituents (Si(2) and Si(5)) project within the Cl–Zr–Cl angle and would favor an increase in this angle. The effect of introducing $SiMe_3$ groups on the cyclopentadienyl ring in the system $[C_5H_{5-x}(SiMe_3)_x]ZrCl_2$ (x = 1–3) is perceptible only on the Cp(centroid)–Zr–Cp(centroid) angle, larger by *ca.* 9° than in Cp_2ZrCl_2.[12] The umbrella effect of the three substituents on the cyclopentadienyl group,[5b] shielding the chlorine atoms, seems responsible for the lack of the reactivity of 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg)[a] with Esd's in Parentheses for $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ (1)

	molecule A	molecule B
Zr–Cp(1)	2.247(6)	2.232(7)
Zr–Cp(2)	2.244(6)	2.227(6)
Zr–Cl(1)	2.420(3)	2.415(3)
Zr–Cl(2)	2.438(3)	2.421(3)
C(1)–Si(1)	1.891(6)	1.893(7)
C(2)–Si(2)	1.901(7)	1.888(7)
C(4)–Si(3)	1.923(7)	1.901(7)
C(15)–Si(4)	1.895(6)	1.885(7)
C(16)–Si(5)	1.906(6)	1.908(6)
C(18)–Si(6)	1.907(6)	1.912(7)
Cp(1)–Zr–Cp(2)	135.4(2)	133.7(2)
Cp(1)–Zr–Cl(1)	104.0(1)	103.6(2)
Cp(1)–Zr–Cl(2)	105.8(2)	106.6(2)
Cp(2)–Zr–Cl(1)	104.7(2)	106.6(2)
Cp(2)–Zr–Cl(2)	104.1(1)	104.3(2)
Cl(1)–Zr–Cl(2)	96.2(1)	96.0(1)
C(2)–C(1)–Si(1)	131.7(5)	132.5(5)
C(5)–C(1)–Si(1)	116.4(4)	117.9(4)
C(1)–C(2)–Si(2)	131.2(5)	132.1(5)
C(3)–C(2)–Si(2)	120.4(4)	119.1(4)
C(3)–C(4)–Si(3)	121.3(4)	119.8(4)
C(5)–C(4)–Si(3)	121.3(4)	125.4(4)
C(16)–C(15)–Si(4)	127.1(4)	131.5(5)
C(19)–C(15)–Si(4)	123.8(4)	118.6(4)
C(15)–C(16)–Si(5)	135.3(4)	132.6(5)
C(17)–C(16)–Si(5)	116.3(4)	118.4(4)
C(17)–C(18)–Si(6)	119.4(4)	121.2(4)
C(19)–C(18)–Si(6)	129.9(4)	125.0(4)

[a] Cp(1) and Cp(2) are the centroids of the C_5H_2 rings C(1)–C(5) and C(15)–C(19) respectively.

Experimental Data

All manipulations were carried out under an inert atmosphere (argon) by conventional Schlenk tube techniques or using a drybox (Vacuum Atmospheres Dri-Lab) filled with argon. Liquids were transferred *via* syringe. All solvents were dried and distilled

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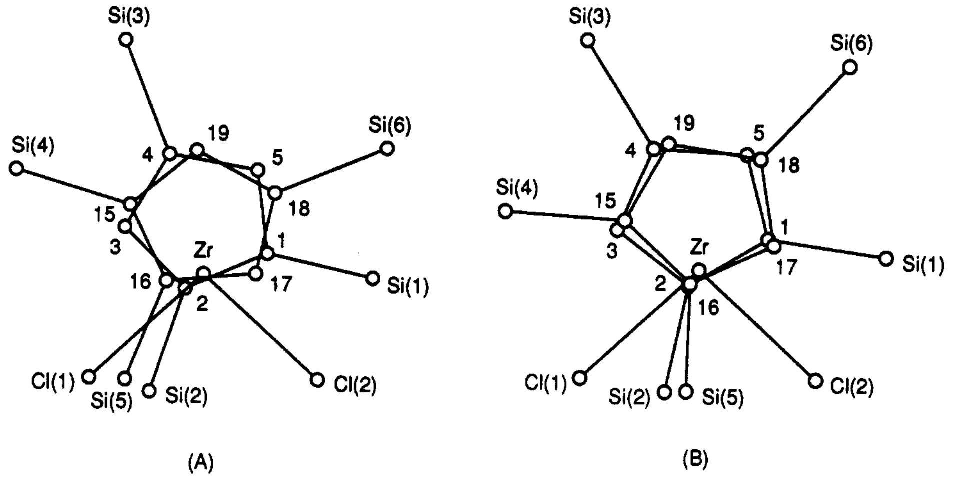

Figure 3. View perpendicular to the plane defined by Cl(1), Zr, and Cl(2) for molecules A and B of compound 1.

under argon and degassed before use. ^1H NMR spectra were recorded on Bruker WH 90 or WM 250 spectrometers. ESR spectra were recorded on a Bruker ER 200 T spectrometer. Elemental analyses were performed by the Service Central de Microanalyse du CNRS. The melting point was determined using a Setaram TG-DTA 92 thermoanalyzer allowing simultaneous measurement of TG and DTA signals, under helium carrier gas. A "homemade microcomputer-controlled instrument" with ohmic resistance compensation was used for cyclic voltammetry studies. A platinum auxiliary electrode and an SCE reference electrode were used in conjunction with a platinum-disk electrode as working electrode. NBu_4PF_6 was used as supporting electrolyte for cyclic voltammetry studies. It was melted under vacuum before use to ensure efficient dehydration. $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ was prepared by the published procedure.[3]

Reaction of 1 with $LiAlH(OCMe_3)$, $NaAlH_2(OCH_2CH_2OMe)$, $LiAlH_4$, $LiBH_4$, or LiMe. These reactions were effected in the same manner. The experimental procedure with $LiAlH(OCMe_3)$, as a representative example, was as follows. To a stirred solution of 1 (0.560 g, 0.77 mmol) in 20 mL of THF was added a slight excess of $LiAlH(OCMe_3)_3$ (0.235 g, 0.92 mmol) in THF. The mixture was stirred for 1 day at room temperature and evaporated to dryness. Hexane (100 mL) then was added and the solution filtered on Celite. The resulting solution was concentrated to 20 mL and left overnight at −30 °C to give colorless crystals suitable for X-ray analysis. Microcrystals of 1 were separated by filtration: mp 162 °C. ^1H NMR (toluene-d_8; δ (ppm)): 7.29 (s, $C_5H_2(SiMe_3)_3$); 0.69 (s, $2SiMe_3$); 0.57 (s, $SiMe_3$). Anal. Calcd for $C_{28}H_{58}Cl_2Si_6Zr$: C, 46.36; H, 8.06. Found: C, 46.30; H, 8.10.

Chemical Reduction of 1 with Na/Hg. In a typical procedure, 1 (100 mg, 0.138 mmol) in 2 mL of THF was treated with 1.1 equiv of Na/Hg. The solution was stirred for 1 day and placed in an ESR tube. The tube was sealed and the solution monitored by ESR. In another experiment, the reduction was carried out with Na/Hg in toluene-d_8 solvent and the resulting solution placed in a ^1H NMR tube. ^1H NMR and ESR spectra were monitored on the same sample.

X-ray Crystal Structure Determination of $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ (1). Crystal data and intensity collection parameters for 1 are summarized in Table 2. Diffraction experiments were performed at 20 °C on an Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation. A least-squares fit of 25 reflections (10.3° < θ < 14.0°) was used to obtain the final lattice parameters and the orientation matrix. The observed extinctions were consistent with space groups *Pnam* and *Pna*2$_1$. A first data shell was collected up to 24° with l, $-12 \rightarrow 0$. As resolution unambiguously showed noncentrosymmetric space group *Pna*2$_1$ with two independent molecules, a second data shell with $l > 0$ was collected up to 21°. During data collection, intensity data of three reflections were monitored every 2 h. Their intensities showed a linear decay of 13%. The data were reduced in the usual way with the MolEN package[14] and corrected for decay. An empirical absorption correction[15] was applied on the basis of ψ scans.

Table 2. Summary of Crystal Data and Intensity Collection Parameters for $[C_5H_2(SiMe_3)_3]_2ZrCl_2$ (1)

Crystal Data

chem formula: $C_{28}H_{58}Si_6Cl_2Zr$
fw: 725.4
cryst habit: light yellow parallelepiped
cryst dimens: 0.40 × 0.25 × 0.125 mm
crystal syst: orthorhombic
space group: *Pna*2$_1$ (No. 33)
a = 42.700(3) Å
b = 17.484(2) Å
c = 10.946(1) Å
V = 8172(2) Å^3
Z = 8
$F(000)$ = 3072
D_{calc} = 1.179 g cm^{-3}
μ(Mo Kα) = 5.8 cm^{-1}

Measurement of Intensity Data

diffractometer: CAD-4 κ geom
T = 20 ± 1 °C
Mo Kα radiation (λ = 0.710 73 Å) graphite-monochromated
scan mode: ω–2θ
2θ range: 3–48° (h, 0–48; k, 0–19; l, −12 to 0)
2θ range: 3–42° (h, 0–43; k, 0–17; l, 1–11)
scan range: $(0.70 + 0.35 \tan\theta)$°
scan speed: 0.97–8.24 °/min
no. of rflns collected: 10 848
empirical abs cor T_{min}–T_{max} = 0.966–0.999
observn criterion: $I > 3\sigma(I)$
No. of used rflns: 7439
$R(F_o)$ = 0.046
R_w = 0.053

Atomic scattering factors (f', f'') were taken from literature.[16] Heavy atom positions were determined by a Patterson map, using the SHELXS-86 program.[17] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out with the SHELX-76 program[18] by using full-matrix least-squares techniques minimizing the function $\sum w(\|F_o\| - |F_c\|)^2$. Methyl carbon atoms of three $SiMe_3$ groups of molecule B were found disordered and were refined in a 55:45

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ratio. This disorder observed on molecule B (and not on molecule A) confirmed the noncentrosymmetric space group $Pna2_1$. All non-H atoms were refined anisotropically. All H atoms bonded to nondisordered atoms were observed on a difference-Fourier map and introduced in calculations in constrained geometry (C–H = 0.97 Å) with two general isotropic temperature factors (0.05 Å^2 for cyclopentadienyl and 0.10 Å^2 for methyl groups). Disordered H atoms were not calculated. Calculation of both enantiomers ($R_w(1) = 0.053$, $R_w(2) = 0.058$) and comparison of Bijvoet pairs allowed us to determine the absolute configuration. The final refinement cycle converged to $R = 0.046$ and $R_w = 0.053$ with a maximum shift/esd of 0.020 on the final cycle with 7439 observations and 521 variable parameters. There are no correlations between parameters of molecules A and B. A fit of $S = 1.36$ for the data using the weighting scheme $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$ was obtained. The maximum residual peak was near a disordered C atom at 0.56 e/Å^3.

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Supplementary Material Available: Tables of all atomic coordinates, thermal parameters, bond distances, bond angles, and least-squares-planes equations and deviations therefrom for 1 (11 pages). Ordering information is given on any current masthead page.

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