The Controversy over the Thermal Stability of Bis(cyclopentadienyl)zirconium(III) Halides. Synthesis of Cp'_2ZrX ($Cp' = Cp, C_5H_4Me$; $X = Cl, Br, I$) via Photolysis of $Cp'_2Zr(i\text{-}Bu)X$. The X-ray Structures of $[(C_5H_4Me)_2Zr(\mu\text{-}I)]_2$ and $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}I)]_2$

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Low-temperature photolysis (−20 °C) of $Cp'_2Zr(R)X$ [Cp' = Cp (**1**), C_5H_4Me (**2**); X = I (**a**), Br (**b**), Cl (**c**); R = *i*-Bu] in toluene or ether led to the formation of the corresponding $[Cp'_2ZrX]_2$ derivatives. Isolation in crystalline form was possible for $[Cp'_2ZrI]_2$ [Cp' = Cp (**3a**), C_5H_4Me (**4a**)]. Crystal data for **4a** are as follows: monoclinic, $P2_1/n$, $a = 7.572$ (1) Å, $b = 11.074$ (2) Å, $c = 14.410$ (3) Å, $\beta = 92.11$ (1)°, $V = 1207.5$ (4) Å^3, $Z = 2$, $R = 0.037$, $R_w = 0.030$. Complexes **3** and **4** are thermally and chemically labile because of the high tendency to disproportionate to Cp'_2ZrX_2 and low-valent species. The thermal stability decreases following the order I > Br > Cl. In the case of different alkyl substituents (R = *n*-Bu, Et), the photolysis of **1a** led to the formation of a mixture of $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}I)]_2$ (**6**) and **3a**. Crystal data for **6** are as follows: monoclinic, $P2_1/n$, $a = 8.772$ (1) Å, $b = 15.899$ (1) Å, $c = 13.805$ (1) Å, $\beta = 95.44$ (1)°, $V = 1916.7$ (5) Å^3, $Z = 4$, $R = 0.029$, $R_w = 0.029$.

Introduction

In contrast to the rich chemistry of the well-established bis(cyclopentadienyl)titanium(III) complexes,[1] the trivalent zirconium analogues Cp_2ZrX remain surprisingly elusive. The magnetic properties, the spectroscopic data, and the chemical reactivity reported to date are in general far from being understood. The almost complete absence of structural characterizations of Zr(III) derivatives has probably been the reason for the amount of confusion and contradiction present in the chemical literature.[2] For example, different colors[3] and different magnetic properties[3,4] have been reported for complexes "Cp_2ZrCl" obtained from different reaction pathways. Even the presence of a Zr–Zr strong single bond in dinuclear Zr(III) species is controversial. Its existence, supported by the short intermetallic contact found in the dinuclear $[ZrCl_3(PR_3)_2]_2$,[5a,b] is a postulate commonly accepted in order to explain the observed diamagnetism,[5c,d] and it has even been claimed in the absence of bridging ligands.[6] However, the crystallographic characterization of three dinuclear and diamagnetic bis(cyclopentadienyl)zirconium(III) derivatives suggested that such a Zr–Zr bond does not occur in these cases.[7,8] Finally, the recent characterization of $[Cp_2ZrI]_2$ suggested that the failure to characterize bis(cyclopentadienyl)zirconium(III) species might be ascribed to a high thermal instability toward disproportionation.[8]

$$\mathrm{Zr(III)} \rightarrow \mathrm{Zr(II)} + \mathrm{Zr(IV)}$$

In this paper we report the synthesis of $[Cp'_2ZrX]_2$ (Cp' = Cp, C_5H_4Me; X = I, Br, Cl) via low-temperature photolysis of $Cp'_2Zr(i\text{-}Bu)X$ together with a crystallographic characterization and a study of their stabilities.

Experimental Section

All operations were performed under dry nitrogen with the use of standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB200). Cp'_2ZrX_2 (X = Cl, Br, I) have been prepared according to published methods.[9] Solvents were purified and dried according to standard procedures. *t*-BuLi solutions in pentane (Aldrich) were titrated before use. Solvents used for nuclear magnetic resonance (benzene-d_6, toluene-d_8, THF-d_8) were vacuum transferred from Na–K alloy. ^1H and ^{13}C NMR spectra were recorded on Varian VXR300 and Bruker WH 90 spectrometers. Chemical shifts are reported in units of δ, referenced to tetramethylsilane and calculated from the position of the solvent

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absorption. Photolysis experiments have been carried out in a photochemical reactor, equipped with a cooled jacket quartz cold finger, using a 125-W high pressure Hg lamp. NMR tube photolyses have been carried out in a quartz NMR tube. Elemental analyses were carried out at the Chemistry Department of the University of Groningen. Gas volumetric measurements have been carried out by using a Töpler pump.

Synthesis of [$Cp'_2Zr(i\text{-}Bu)X$] (1a–c and 2a–c). In a standard procedure, a suspension of $(C_5H_4Me)_2ZrCl_2$ (3.8 g, 11.9 mmol) in toluene (150 mL) was reacted with a solution of *t*-BuLi (7 mL, 1.7 N) in pentane at −40 °C. The mixture was allowed to warm to room temperature under vigorous stirring. After filtration, the NMR spectrum of the resulting solution revealed the quantitative formation of $(C_5H_4Me)_2Zr(i\text{-}Bu)Cl$. The solvent was evaporated in vacuo and the residue redissolved in ether. Analytically pure $(C_5H_4Me)_2Zr(i\text{-}Bu)Cl$ was obtained upon addition of pentane: yield 1.4 g, 4.1 mmol, 35%. Anal. Calcd for $C_{16}H_{25}ZrCl$ (Found): C, 55.89 (55.78), H, 7.28 (7.32); Zr, 26.49 (26.51); Cl, 10.33 (10.31).

Synthesis of [Cp_2ZrI]$_2$ (3a). Cp_2ZrI_2 (4.50 g 9.57 mmol) was suspended in 150 mL of toluene. After being cooled to −40 °C, a solution of *t*-BuLi in pentane (5.7 mL, 1.7 N) was added. The deep orange slurry was filtered and the toluene removed in vacuo at room temperature. The resulting red solid was suspended in ether and refluxed for 2 h. Analytically pure, deep red, poorly soluble [$CpZrI$]$_2$ was obtained in 25% yield (0.8 g). Large and well-formed emerald green crystals suitable for X-ray diffraction were obtained upon standing the toluene solution at room temperature for 3 days. Anal. Calcd for $C_{10}H_{10}ZrI$ (Found): C, 35.50 (35.48); H, 2.96 (2.91); Zr, 26.92 (26.88); I, 37.57 (37.60).

Identification of the gas mixture: Cp_2ZrI_2 (0.150 g) in 10 mL of toluene was treated with 0.19 mL of *t*-BuLi (1.7 N). The flask was irradiated overnight at −20 °C. The gas was pumped off with a Toepler pump yielding 1 equiv of gas/Zr consisting of 52% $i\text{-}C_4H_{10}$ and 48% $i\text{-}C_4H_8$ (GC). No traces of hydrogen were detected.

Synthesis of [$(C_5H_4Me)_2ZrI$]$_2$ (4a). A solution of $(C_5H_4Me)_2ZrI_2$ (8.12 g, 16.1 mmol) in 200 mL of toluene was cooled to −40 °C. After addition of a solution of *t*-BuLi in pentane (10 mL, 1.7 N), the resulting slurry was allowed to reach room temperature under vigorous stirring. The LiI was filtered out and the solvent evaporated in vacuo. Addition of ether (200 mL) yielded a deep red solution that was irradiated at −20 °C. The progress of the reaction was monitored by NMR. After 15 h the resonances of the $(MeCp)_2Zr(i\text{-}Bu)I$ had disappeared and a microcrystalline solid was present at the bottom of the flask. Isolation of this solid yielded [$(MeCp)_2ZrI$] (1.3 g, 21%). A second crop of crystals was obtained after concentration and precipitation with pentane (0.7 g). Yield: 2 g (32%). Crystals suitable for X-ray analysis were obtained upon recrystallization from ether. Anal. Calcd for $C_{12}H_{14}ZrI$ (Found): C, 38.29 (38.25); H, 3.72 (3.69); Zr, 24.20 (24.19); I, 33.77 (33.63).

Preparation of [Cp'_2ZrBr]$_2$ [Cp′ = Cp (3b), C_5H_4Me (4b)]. In a standard procedure, a toluene solution (150 mL) of $Cp'_2Zr(i\text{-}Bu)Br$ (6.5 mmol) was irradiated at −20 °C. The reaction progress was monitored by NMR. After the solution was warmed to room temperature and worked up, the NMR spectrum of the crude solid showed the presence of [Cp'_2ZrBr]$_2$ contaminated by significant amounts of Cp'_2ZrBr_2 (~15%). Any attempt to purify the product was unsuccessful and increased the amounts of contamination.

Synthesis of [$\eta^5{:}\eta^5\text{-}C_{10}H_8$][$CpZr(\mu\text{-}I)$]$_2$ (6). The preparation is a modification of the procedure reported by Schwartz.[27a] [$(\eta^1{:}\eta^5\text{-}C_5H_4)CpZrP(CH_3)_3$]$_2$ (2.05 g, 3.4 mmol) was reacted in toluene (50 mL) at −80 °C with stoichiometric amounts of iodine (0.88 g, 3.4 mmol). The mixture turned deep purple, and a large amount of deep red microcrystalline solid precipitated. After slowly being warmed to room temperature, the mixture was refluxed and toluene/PMe_3 was distilled out by using a 20-cm Vigreux column. Neat toluene (20 mL) was added dropwise to the reaction mixture during the distillation to keep the volume constant. When all the solid disappeared, the resulting purple solution was concentrated. Large size crystals of 6 separated upon cooling at −30 °C (1.33 g, 1.91 mmol, 65% yield). Anal. Calcd for $C_{20}H_{18}Zr_2I_2$ (Found): C, 34.58 (34.57); H, 2.59 (2.57); Zr, 26.22 (26.20); I, 36.60 (36.58). ^1H NMR (300 MHz, benzene-d_6, 25 °C): δ 5.61 (s, 10 H, Cp), 4.58 (pseudo-t, 4 H, fulvalene), 4.18 (pseudo-t, 4 H, fulvalene). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C): δ 101.0 (d, $J_{C\text{-}H}$ = 175.0 Hz, fulvalene), 100.2 (d, $J_{C\text{-}H}$ = 172.7 Hz, Cp), 97.7 (s, fulvalene), 97.5 (d, $J_{C\text{-}H}$ = 170.4 Hz, fulvalene).

Table I. Crystal Data and Details on the Structure Determinations for 4a and 6

	4a	6
formula	$C_{24}H_{28}I_2Zr_2$	$C_{20}H_{18}I_2Zr_2$
mol wt	752.73	694.61
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
Z	2	4
$F(000)$	716	1296
a, Å	7.572 (1)	8.772 (1)
b, Å	11.074 (2)	15.899 (1)
c, Å	14.410 (3)	13.805 (3)
β, deg	92.11 (1)	95.44 (1)
V, Å^3	1207.5 (4)	1916.7 (5)
μ(Mo Kα), cm^{-1}	33.9	42.6
D_{calc}, g cm^{-3}	2.070	2.407
cryst size	0.13 × 0.13 × 0.25	0.17 × 0.20 × 0.30
radiatn	Mo Kα, λ = 0.71073	Mo Kα, λ = 0.71073
θ(min,max), deg	1.4, 30.0	1.28, 27.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.60 + 0.35 \tan\theta$	$\Delta\omega = 1.05 + 0.35 \tan\theta$
data set	H, 0 to 10; *k*, −15 to 0; *l*, −20 to 20	*h*, −11 to +11; *k*, −1 to 20; *l*, 0 to 17
total data, unique data	4261, 3517	4823, 4166
obsd data [$I > 2.5\sigma(I)$]	2453	3471
R, R_ω, S	0.037, 0.030, 1.61	0.029, 0.029, 2.119
weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
N_{ref}, N_{par}	2453, 129	3471, 290
max and av shift/error	0.10, 0.01	0.014, 0.0011
min and max resd dens, e Å^{-3}	−0.76, 1.25	−1.07, 0.53

Attempted Isolation of Cp'_2ZrCl [Cp′ = Cp (3c), C_5H_4Me (4c)]. In a standard experiment a toluene solution of $(C_5H_4Me)_2Zr(i\text{-}Bu)Cl$ was irradiated in a quartz NMR tube at −20 °C. The simultanesous formation of [$(C_5H_4Me)_2ZrCl$]$_2$ and [$(C_5H_4Me)_2ZrCl_2$] was monitored by NMR during the photolysis. The resonances of the product disappeared within 1 h when the NMR tube was allowed to stand at room temperature.

Structure Determination and Refinement of 4a. X-ray data were collected at 295 K on an Enraf-Nonius CAD4F diffractometer for an emerald-green crystal sealed in a Lindemann glass capillary. Unit-cell parameters were obtained from SET4 setting angles[10] for 25 reflections in the range 16–21°. The space group was derived from the observed systematic absences and checked for the presence of higher metrical symmetry.[11] Two references reflections showed a small decay of 1% during data collection (63.3 h of X-ray exposure time). The 360° ψ scan for the close to the axial $1\bar{2}\bar{1}$ reflection showed an intensity variation of 13% about the mean value. The data set was corrected for Lp and absorption (DIFABS;[12] corrections ranging from 0.90 to 1.14). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance in the reference reflections:[13] $\sigma^2(I) = \sigma^2_{CS}(I) + (0.01I)^2$. The structure was solved with Patterson and Fourier techniques (SHELXS-86)[14] and refined on F by full-matrix least squares using a MicroVAX-II computer with the SHELX-76 program package.[15] The final refinement converged to $R_F = 0.037$ ($R_w = 0.030$). Hydrogen atoms

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Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters with Their Esd's in Parentheses for 4a

atom	x	y	z	U(eq),[a] Å^2
I	0.23632 (4)	0.10491 (3)	0.05951 (2)	0.0364 (1)
Zr	−0.00438 (6)	−0.08978 (4)	0.10607 (3)	0.0288 (1)
C(1)	−0.0562 (8)	−0.0358 (5)	0.2739 (3)	0.042 (2)
C(2)	−0.1932 (8)	−0.1129 (5)	0.2436 (4)	0.051 (2)
C(3)	−0.2958 (8)	−0.0548 (6)	0.1740 (4)	0.053 (2)
C(4)	−0.2238 (8)	0.0589 (5)	0.1599 (4)	0.046 (2)
C(5)	−0.0763 (7)	0.0711 (4)	0.2226 (3)	0.040 (2)
C(6)	0.074 (1)	−0.0535 (6)	0.3541 (4)	0.077 (3)
C(7)	0.0212 (8)	−0.3157 (4)	0.0943 (4)	0.043 (2)
C(8)	0.1304 (7)	−0.2711 (4)	0.0245 (4)	0.044 (2)
C(9)	0.2731 (7)	−0.2078 (5)	0.0654 (4)	0.047 (2)
C(10)	0.2521 (8)	−0.2106 (5)	0.1628 (4)	0.052 (2)
C(11)	0.1008 (8)	−0.2778 (4)	0.1794 (4)	0.045 (2)
C(12)	−0.1360 (9)	−0.3962 (5)	0.0806 (4)	0.067 (3)

[a] $U(\mathrm{eq}) = {}^1/_3\sum_{ij}U_{ij}{}^*a_ia_j\mathbf{a}_i{\cdot}\mathbf{a}_j$.

were introduced at calculated positions (C–H = 0.98 Å) and refined with fixed geometry. The refined parameter set included a scale factor, the coordinates of the non-hydrogen atoms, their anisotropic thermal parameters, and two separate isotropic thermal motion parameters for the H atoms. Scattering factors were taken from ref 16 and corrected for anomalous dispersion.[17] The calculations of geometrical data and the preparation of the thermal motion ellipsoid plot were performed with the program PLATON of the EUCLID package.[18] Crystal data and numerical details on the structure determination are given in Table I; positional parameters for the non-hydrogen atoms are listed in Table II.

Table III. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms with Their Esd's in Parentheses for 6

	x	y	z	U_{eq},[a] Å^2
I(1)	0.24002 (3)	0.23767 (2)	0.28021 (3)	0.0348 (1)
I(2)	−0.07964 (3)	0.10625 (2)	0.32865 (2)	0.0333 (1)
Zr(1)	−0.08686 (5)	0.19589 (3)	0.27688 (3)	0.0256 (1)
Zr(2)	0.21284 (5)	0.05642 (3)	0.25600 (3)	0.0228 (1)
C(1)	−0.0793 (6)	0.2183 (4)	0.4575 (4)	0.049 (1)
C(2)	−0.0464 (6)	0.2963 (4)	0.4206 (4)	0.054 (2)
C(3)	−0.1742 (8)	0.3242 (4)	0.3632 (5)	0.059 (3)
C(4)	−0.2869 (6)	0.2626 (4)	0.3680 (4)	0.057 (2)
C(5)	−0.2304 (6)	0.1978 (4)	0.4255 (4)	0.046 (1)
C(6)	0.4075 (6)	0.0727 (4)	0.4059 (4)	0.043 (1)
C(7)	0.3000 (6)	0.0153 (4)	0.4304 (4)	0.045 (1)
C(8)	0.3071 (6)	−0.0561 (4)	0.3714 (4)	0.047 (1)
C(9)	0.4217 (6)	−0.0413 (4)	0.3102 (4)	0.047 (1)
C(10)	0.4803 (6)	0.0384 (4)	0.3293 (4)	0.048 (1)
C(11)	−0.0646 (6)	0.1475 (3)	0.1090 (3)	0.034 (1)
C(12)	−0.0588 (6)	0.2379 (3)	0.1066 (4)	0.039 (1)
C(13)	−0.2001 (6)	0.2689 (4)	0.1274 (4)	0.045 (1)
C(14)	−0.2966 (6)	0.2022 (4)	0.1428 (4)	0.047 (1)
C(15)	−0.2172 (6)	0.1270 (4)	0.1309 (4)	0.041 (1)
C(16)	0.0628 (6)	0.0884 (3)	0.1005 (3)	0.033 (1)
C(17)	0.0578 (6)	−0.0002 (3)	0.1120 (3)	0.035 (1)
C(18)	0.2057 (7)	−0.0316 (3)	0.1068 (4)	0.043 (1)
C(19)	0.3024 (6)	0.0353 (4)	0.0909 (4)	0.044 (1)
C(20)	0.2160 (6)	0.1093 (3)	0.0871 (3)	0.038 (1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_jU_{ij}{}^*a_ia_j\mathbf{a}_i{\cdot}\mathbf{a}_j$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 4a and 6[a]

		4a	
Zr–I	2.9172 (8)	Zr–I–Zr	77.47 (2)
Zr′–I	2.9150 (8)	I–Zr–I′	102.53 (2)
Zr–cp[b]	2.209 (2)	cp′–Zr–cp	130.13 (9)
Zr···Zr	3.649 (1)		
I···I′	4.549 (1)		
		6	
Zr(1)–I(1)	2.9394 (8)	Zr(1)–I(1)–Zr(2)	72.85 (2)
Zr(1)–I(2)	2.9434 (9)	Zr(1)–I(2)–Zr(2)	72.72 (2)
Zr(2)–I(1)	2.9082 (9)	I(1)–Zr(1)–I(2)	102.53 (2)
Zr(2)–I(2)	2.9128 (8)	I(1)–Zr(2)–I(2)	104.06 (2)
C(11)–C(16)	1.473 (7)	cp(1)–Zr(1)–cp(3)	133.72 (2)
Zr(1)–cp(1)	2.222 (1)	cp(2)–Zr(2)–cp(4)	134.82 (2)
Zr(2)–cp(2)	2.222 (1)	C(15)–C(11)–C(16)–C(17)	0.3 (7)
Zr(1)–cp(3)	2.170 (1)	I(1)–Zr(1)–Zr(2)–I(2)	153.93 (2)
Zr(2)–cp(4)	2.174 (1)		
Zr(1)···Zr(2)	3.472 (1)		

[a] Primed atoms are related by symmetry operation $-x$, $-y$, $-z$. [b] cp = Cp centroid.

Structure Determination and Refinement of 6. A suitable polyfacial crystal was sealed in a thin-walled Lindemann glass capillary and mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a MicroVAX 2000 computer. Lattice parameters and their standard deviation were determined from the setting angles of 22 reflections in the range 20.04° < θ < 21.65° in four alternate settings.[10] Reduced cell calculations did not indicate any higher lattice symmetry.[19] Space group $P2_1/n$ was determined from the systematic extinctions: $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$. The intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied. Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the three reference reflections: $\sigma^2(I) = \sigma^2_{\mathrm{CS}}(I) + (0.016I)^2$.[13] A total of 3471 reflections satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS-86).[14] Refinement using anisotropic thermal parameters followed by difference Fourier synthesis allowed us to locate all the hydrogen atoms. Weights were introduced in the final refinement cycles. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged at $R_F = 0.029$ ($R_w = 0.029$). The quantity minimized by the least-squares procedure was $Q = \sum_h [w(|F_o| - |F_c|)^2]$. A final difference Fourier map did not show any significant residual feature. Crystal data and experimental details of the structure determination are given in Table I. Fractional atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table III. Molecular geometry data are reported in Table IV. Tables of hydrogen atoms positions and thermal parameters, comprehensive lists of bond distances and angles, and tables of (F_o), (F_c), and $\sigma(F)$ are given as supplementary material for this paper. Scattering factors[16] were corrected for anomalous dispersion corrections.[17] The calculations and the preparation of the thermal ellipsoids plot were carried out on the CDC-Cyber 170/760 computer of the University of Groningen using the program XTAL,[20] the EUCLID package (calculation of geometric data),[18] and an extended version of the program PLUTO (preparation of illustrations).[22]

Results and Discussion

Low-temperature reactions (−40 °C) of Cp'_2ZrX_2 (Cp′ = Cp, C_5H_4Me; X = I, Br, Cl) with t-BuLi in toluene lead to the formation of $Cp'_2Zr(i\text{-Bu})X$ almost exclusively (eq 1). The isomerization of the t-Bu alkyl group into the less crowded i-Bu is probably enforced by steric factors. We

$$Cp'_2ZrX_2 + t\text{-BuLi} \rightarrow Cp'_2Zr(i\text{-Bu})X \qquad (1)$$

$$Cp' = Cp\ (\mathbf{1}),\ C_5H_4Me\ (\mathbf{2});\ X = I\ (\mathbf{a}),\ Br\ (\mathbf{b}),\ Cl\ (\mathbf{c})$$

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Table V. NMR Data (in δ)

		1a[a]	2a[a]	3a[b]	4a[a]	1b[a]	2b[a]	3b[c]	4b[c]	1c[a]	2c[a]	3c[c]	4c[c]
		^1H Data											
Cp	CH	5.83 s	6.15 m	5.04 s	4.92 m	5.82 s	6.05 m	5.06 s	4.98 m	5.80 s	6.00 m	5.16 s	4.96 m
	CH		5.79 m		4.74 m		5.75 m		4.73 m		5.72 m		4.80 m
	CH		5.70 m				5.54 m				5.48 m		
	CH		5.36 m				5.35 m				5.32 m		
	CH_3		2.05 s		1.71 s		2.08 s		1.74 s		2.06 s		1.76 s
i-Bu	CH_3	0.92 d	0.93 d			0.96 d	0.99 d			0.99 d	1.02 d		
	CH_2	0.46 d	0.51 d			0.81 d	0.83 d			0.97 d	0.96 d		
	CH	0.94 m	1.05 m			0.93 m	1.05 m			0.93 m	1.06 m		
		^{13}C Data											
Cp	C_{CH}	110.9	115.2	102.0	105.0	111.4	115.5			111.4	115.3		
	C_{CH}		112.4		98.9		111.2				110.6		
	C_{CH}		110.4				110.5				110.1		
	C_{CH}		106.2				106.5				106.7		
	C_{CH_3}		15.4		15.4		14.8				14.3		
i-Bu	C_{CH_3}	26.8	26.9			26.8	26.9			26.9	26.9		
	C_{CH_2}	76.4	74.2			70.2	67.9			66.5	64.6		
	C_{CH}	33.0	32.8			32.7	32.4			32.5	32.2		

[a] Benzene-d_6. [b] THF-d_8. [c] Toluene-d_8.

believe that a β-elimination/reinsertion mechanism, analogous to that reported for the olefin isomerization promoted by zirconium hydrides,[22,23] is operating in the present case. The ^1H and ^{13}C NMR spectra of the crude reaction mixtures showed the same patterns in all cases (Table V). The cleanest spectra have been recorded in the cases of **1c** and **2c**. Due to their high stability they are virtually the only reaction products isolated in analytically pure form. In fact, in the case of $Cp_2Zr(i\text{-Bu})I$ (**1a**) a decomposition reaction proceeds spontaneously in toluene at room temperature (3 days) with formation of $[Cp_2ZrI]_2$ (**3a**) as poorly soluble emerald green crystals (eq 2).[24] The reaction can be considerably accelerated by

$$2Cp'_2Zr(i\text{-Bu})I \xrightarrow{h\nu} [Cp'_2ZrI]_2 + \text{isobutene} + \text{isobutane} \quad (2)$$

$$Cp' = Cp\ (\mathbf{3}),\ C_5H_4Me\ (\mathbf{4})$$

photolysis at -20 °C or thermolysis at 40 °C (in the case of **1a** only). In the case of the methyl-substituted derivative $(C_5H_4Me)_2Zr(i\text{-Bu})I$ (**2a**), the reaction requires a 15-h photolysis in ether at -20 °C for the complete transformation. Isolation in crystalline form was possible upon concentration and cooling the resulting ether solution to -30 °C.

The dimeric structure of the diamagnetic $[(C_5H_4Me)_2ZrI]_2$ has been clarified by an X-ray diffraction analysis. The unit cell contains two discrete units with the usual bent Cp_2Zr moieties linked by two bridging iodine atoms (Figure 1). The orientation of the methyl groups in the Cp rings is similar to that observed for $[(C_5H_4Me)_2TiBr]_2$[25] and is close to a trans configuration on each zirconium atom. The value of the intermetallic distance [Zr⋯Zr = 3.649 (1) Å] compares well with those found in $[Cp_2Zr(\mu\text{-PMe}_2)]_2$ and $[(Cp_2Zr)_2(\mu\text{-Cl})(\mu\text{-PMe}_2)]$.[7] Although the quite large value excludes the presence of a Zr–Zr bond, it is still significantly shorter than those observed in the case of the paramagnetic Ti analogues.[25] Selected bond distances and angles are given in Table IV.

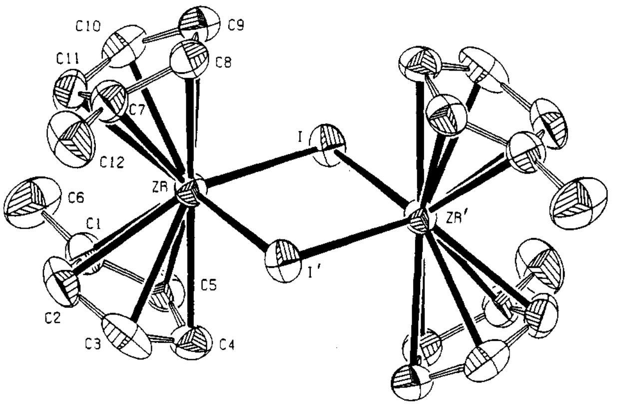

Figure 1. ORTEP plot for **4a** drawn at the 50% probability level showing the labeling scheme.

The nature of the R substituent in Cp_2ZrRI significantly affects the result of the reductive elimination reaction (eq 2). For example, in the case of other smaller alkyl substituents (R = Et, *n*-Bu) a mixture of $[\eta^5{:}\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-I})]_2$ (**6**) and **3a** (ca. 1:4 and 2:1, respectively) is obtained. Reduction to Zr(III) has been found also in the case of CPh_3, **3a** and **6** being, however, only minor products of an intractable mixture in this case. Cp_2ZrRI did not show any significant decomposition with other alkyl substituents (R = CH_3, CH_2Ph), upon prolonged thermolysis or photolysis in the usual manner.[26] These results suggest that some peculiarity of the *i*-Bu radical might be the origin of the selective formation of complexes **3** and **4**. It is remarkable in this respect that the stoichiometric amount of gas recovered from this reaction with the Toepler pump showed only the quantitative formation of the disproportionation products isobutene/isobutane in a 1:1 ratio (eq 2). Conversely, the formation of significant amounts of the fulvalene derivative **6** in the decomposition of Cp_2ZrRX (R = Et, *n*-Bu) indicates a preference of the *ethyl* and *n-butyl* radicals for abstracting hydrogen from the cyclopentadienyl rings presumably with the formation of complexes containing $\eta^1{:}\eta^5$-bonded cyclopentadienyl rings (eq 3). The involvement of intermediates containing $\eta^1{:}\eta^5$-cyclopentadienyl rings (**5**) during the formation of fulvalene-containing complexes has been widely demonstrated by Schwartz in the controlled oxidation of Zr(II).[27]

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(24) Crystals of the Zr(III) species appear to be shiny green. When ground under inert atmosphere, the solid is actually deep red. Toluene and THF solution are also red.

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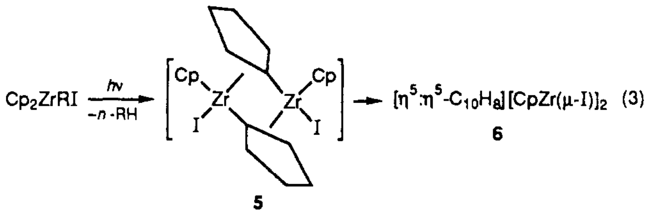
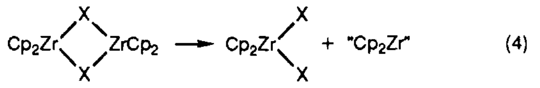


R = Et, *n*-Bu

Analytically pure **6** was prepared in crystalline form by using a modification of a published procedure.[27a] The spectroscopic and analytical data are consistent with the solid-state structure as solved by X-ray analysis. The crystal is composed of discrete molecules of $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}I)]_2$ (Figure 2) containing two Zr atoms bonded to two bridging iodines and η^5-bonded to the cyclopentadienyl ring and the bridging fulvalene ligand. All the bond distances and angles are normal and compare quite well with those observed in $[\eta^5:\eta^5\text{-}C_{10}H_8][CpZr(\mu\text{-}Cl)]_2$.[28] The most striking difference is provided by the values of the bond distances and angles of the Zr_2I_2 core. As a result of the increased steric congestion, the Zr–Zr separation is increased to 3.472 (1) Å. This value, which excludes the presence of Zr–Zr single bond in this diamagnetic derivative, is still shorter than that found in complex **4a**. This is probably caused by the rigidity of bridging fulvalene ligand which constrains the two metal centers. Selected bond distances and angles are given in Table IV.

Complexes **3a** and **4a** are indefinitely stable in solid state and for several days in solution (toluene) at room temperature. However, complete decomposition is observed when toluene solutions are treated at 90 °C for 9–10 h. The compounds are even less stable in coordinating solvents such as THF or pyridine. Significant decomposition was observed within 6 days at room temperature in THF and within 1 day in pyridine. Full decomposition was observed in both cases in 1 h at 60 °C. The reaction mixture recovered from the thermal decomposition showed Cp_2ZrI_2 as the only clearly identifiable complex. This suggests the disproportionation reaction shown in eq 4.



X = Cl, Br, I

Substitution of iodine for bromine in complexes **3** and **4** decreases their stability significantly. Decomposition occurs at room temperature in toluene within 8 h for both **3b** and **4b**, and also in this case decomposition is considerably accelerated by the presence of coordinating solvents like ether or THF. Disproportionation can also be achieved under irradiation at -20 °C. Furthermore, the higher stability of the isobutyl precursors **1b** and **2b** also requires longer photolysis times. For these reasons, unavoidable contamination of $[Cp'_2ZrBr]_2$ by Cp'_2ZrBr_2 prevents the isolation of **3b** and **4b** in analytically pure form. Even mild thermolysis at 40 °C in toluene (successful in the case of **3a**) failed in the case of **3b**.

The thermal instability of $[Cp'_2ZrCl]_2$ is more striking by far. It is formed only when **1c** and **2c** are photolyzed at -20 °C in toluene-d_8 in a quartz NMR tube. In both cases disproportionation to Cp'_2ZrCl_2 was observed during the low-temperature photolysis and was complete within 1 h when the tube was allowed to stand at room temperature. However, the near identity of the ^{1}H NMR spectra of **3c** and **4c** with those for **3a,b** and **4a,b** identifies this elusive species as $[Cp'_2ZrCl]_2$ without doubt (Table V). Photolysis of **1c** and **2c** in a coordinating solvent such as THF-d_8 showed the formation of disproportionation products evclusively; $[Cp'_2ZrCl]_2$ could not be observed even when the irradiation was carried out at -50 °C.

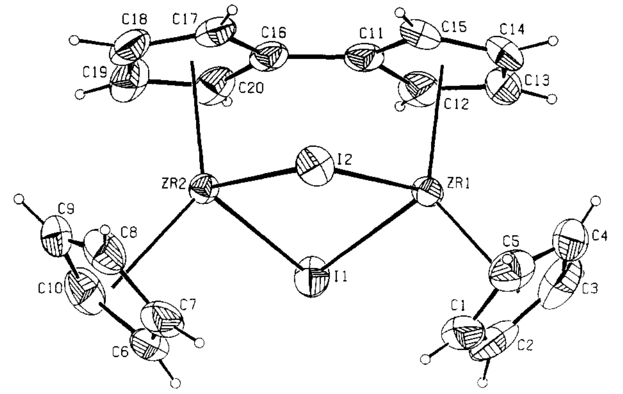


Figure 2. ORTEP plot for **6** drawn at the 50% probability level showing the labeling scheme.

The high thermal instability of $[Cp_2ZrCl]_2$ contrasts sharply with previous claims.[3] Paramagnetic and monomeric Cp_2ZrX complexes prepared via photolysis or electrolysis have been characterized on the basis of the ESR spectra.[26b,29] There is some disagreement about the ability of these species to interact with phosphines.[26b,29] We found that in contrast to CO and butadiene, which accelerate the disproportionation reaction (eq 5), phosphines do not react.

$$[Cp_2ZrI]_2 + L \rightarrow Cp_2ZrI_2 + Cp_2ZrL_2 \qquad (5)$$

$$L = CO, \text{butadiene}$$

The tendency to disproportionate also dominates the chemistry of these species. Attempts to replace iodine with alkyl groups (CH_3, $CH_2C_6H_5$) in **3a** and **4a** led to the formation of large amounts of Cp'_2ZrR_2 as the only identifiable product.

In summary these results show that (a) bis(cyclopentadienyl)zirconium(III) halides really do exist and can be synthesized in preparative scale and in crystalline form depending on the nature of the halide, (b) the thermal instability of these species toward disproportionation (Cl > Br > I) partly explains the contradictions in the literature, and (c) the existence of the Zr–Zr bond, which has been postulated in order to explain the diamagnetism of Zr(III) dinuclear species, deserves a careful reevaluation.

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Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, hydrogen atom positional parameters, and bond distances and angles for **4a** and **6** and tables of final fractional coordinates and torsion angles for **6** (22 pages); listings of structure factors (40 pages). Ordering information is given on any current masthead page.

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