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The search for dimethylzirconocene. Crystal structures of dimethylzirconocene, dimethylhafnocene, chloromethylzirconocene, and (.mu.-oxo)bis(methylzirconocene)

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other along the $(a + c)/2$ direction. A diagram of the unit cell is available.[17]

The structure is consistent with that of $Mg(SiMe_3)_2$·DME in which the Si–C distance is 2.630 (2) Å and Si–Mg–Si angle is 125.2 (1)°. The smaller Si–Mg–Si angle in the present result (115°) may be explained by VSEPR theory on the basis that the weaker base, TMEDA, will form less polar Mg–N bonds than the Mg–O bonds in the DME adduct. Alternatively the methyl groups on TMEDA may cause interference with those on the trimethylsilyl group forcing the smaller angle separation between these units.

Further, the N–Mg bond distances and angles are similar to those observed for organomagnesium compounds. Comparison with the three complexes $MgMe_2$·TMEDA,[22] $MgPh_2$·TMEDA,[23] and η^5-C_5H_5MgBr·$(Et_2N(CH_2)_2NEt_2)$,[24] which have average N–Mg distances of 2.24, 2.20, and 2.26 Å and N–Mg–N angles of 81.5, 82.5, and 82.5, respectively, are clearly within the range of those observed in the present system.

As in the $Mg(SiMe_3)_2$·DME adduct and in $[Al(SiMe_3)_3]_2$·TMEDA, the Me_3Si groups may be tilted inward toward the Si–Mg–Si bisector; however, the effect is offset by twisting about the Si–Mg bonds and is obscured by poorly determined Si–C bond lengths and C–Si–C angles.

The inconsistency in Si–C bond lengths is partly due to thermal averaging effects on the carbon atom positions. Attempts to correct Si–C bond lengths (Å) based on the "riding model" are as follows: Si_1–C_{11}, 1.96 (1); Si_1–C_{21}, 1.94 (1); Si_1–C_{31}, 1.92 (2); Si_2–C_{12}, 1.99 (2); Si_2–C_{22}, 2.03 (2); Si_2–C_{32}, 1.99 (20). The corrections are somewhat large, but they have the effect of bringing the bond lengths on Si(1) and Si(2) into closer agreement.

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Supplementary Material Available: Tables containing deviations from the mean plane, anisotropic thermal parameters for the non-hydrogen atoms, observed and calculated structure factors, and a packing diagram for I and tables containing anisotropic thermal parameters, observed and calculated structure factors, and a packing diagram also for II (22 pages). Ordering information is given on any current masthead page.

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The Search for Dimethylzirconocene. Crystal Structures of Dimethylzirconocene, Dimethylhafnocene, Chloromethylzirconocene, and (μ-Oxo)bis(methylzirconocene)

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The crystal structures of $(\eta^5$-$C_5H_5)_2Zr(CH_3)_2$, $(\eta^5$-$C_5H_5)_2Hf(CH_3)_2$, $(\eta^5$-$C_5H_5)_2Zr(Cl)(CH_3)$, and $[(\eta^5$-$C_5H_5)_2Zr(CH_3)]_2O$ have been determined from X-ray data measured by counter methods. Dimethylzirconocene crystallizes in the monoclinic space group $P2_1/n$ with unit-cell parameters a = 6.953 (3) Å, b = 11.902 (5) Å, c = 13.839 (5) Å, β = 91.95 (3)°, and Z = 4 for D_{calcd} = 1.45 g cm^{-3}. Full-matrix least-squares refinement has led to a final R factor of 0.029 based on 1672 independent observed reflections. Dimethylhafnocene is isostructural with a = 6.965 (4) Å, b = 11.854 (5) Å, c = 13.786 (6) Å, β = 92.02 (3)°, and D_{calcd} = 1.98 g cm^{-3}. Refinement on 1662 reflections produced R = 0.041. Chloromethylzirconocene exhibits crystallographically disordered chloro and methyl ligands and is isostructural with the dimethyl derivatives. The cell constants are a = 6.810 (8) Å, b = 11.821 (9) Å, c = 13.818 (9) Å, β = 92.30 (4)°, and D_{calcd} = 1.62 g cm^{-3}. A final R value of 0.043 resulted from the refinement on the basis of 1709 observed reflections. (μ-Oxo)bis(methylzirconocene) crystallizes in the trigonal space group $P3_221$ with a = 8.017 (3) Å, c = 28.376 (6) Å, and D_{calcd} = 1.54 g cm^{-3}. Refinement on 1358 reflections led to R = 0.026. The most important results concern the metal–carbon σ bond lengths in the $(\eta^5$-$C_5H_5)_2M(CH_3)_2$ compounds. For M = Zr the two independent determinations are 2.273 (5) and 2.280 (5) Å, while for M = Hf the distances are 2.233 (12) and 2.240 (12) Å. The average for the latter, 2.24 Å, is much shorter than the 2.35 Å value previously reported for $(\eta^5$-$C_5H_5)_2Hf(CH_3)_2$. In addition, the longer Zr–C(σ) is the reverse of that found for $(\eta^5$-$C_9H_7)_2M(CH_3)_2$, M = Zr and Hf. The answer to these apparent discrepancies is found in a consideration of the role of the disordered chloromethylzirconocene structure.

Introduction

For several years our group has been interested in compounds of zirconium and hafnium that contain metal–carbon σ bonds. In the course of sorting out electronic and steric factors that affect the M–C(σ) bond length, we have had the occasion to carry out X-ray structural determinations on a wide range of compounds: $Cp_2M(CO)_2$ (M = Zr,[1] Hf,[2] Cp = $(\eta^5$-$C_5H_5)$), $Cp_2M[C_4(C_6H_5)_4]$ (M = Ti,[3] Zr,[4] Hf[3]), $Cp_2M[CH(C_6H_5)_2]_2$ (M = Zr, Hf),[5] $Cp_3Zr(\eta^1$-$C_5H_5)$,[6] $Cp_2Hf(\eta^1$-$C_5H_5)_2$,[7] $Cp_2Zr(C_6H_5)[CH\{Si(CH_3)_3\}_2]$,[8]

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$Cp_2Zr[(CH_2)_2C_6H_4\text{-}o]$,[9] $Cp_2Zr[CH_2Si(CH_3)_3]_2$,[10] $Cp_2Zr[CH_2C(CH_3)_3]_2$,[10] $[\eta^5\text{-}C_5H_4C(CH_3)_3]_2Zr(Cl)[CH\{Si(CH_3)_3\}_2]$,[11] $[\eta^5\text{-}C_5H_4Si(CH_3)_3]_2Zr(Cl)[CH\{Si(CH_3)_3\}_2]$,[11] and $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$ (M = Zr, Hf).[12] These studies have revealed several subtle differences between zirconium and hafnium, one of the most important of which concerns the M–C(sp^3) bond lengths. In $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$, the Zr–C bond distance is 2.255 (6) Å, while the Hf–C length is 2.332 (11) Å.[12]

Interest in dimethylzirconocene was high for two reasons. First, Fronczek et al.[13] had noted a significant asymmetry in the Hf–C(σ) bond lengths in dimethylhafnocene. The shorter one, 2.318 (8) Å, agreed closely with the value reported in $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$, but the second, 2.382 (7) Å, was 6σ larger. Since no ready explanation could be found for this inequivalence, we sought a comparison with the title compounds.

In the investigation of the reactions of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with salts such as $K[Al_2(CH_3)_6N_3]$, a compound was isolated that proved to be isostructural with $Cp_2Hf(CH_3)_2$. Subsequent X-ray work revealed that the compound was in fact $Cp_2Zr(Cl)(CH_3)$. In the latter, the chloro and methyl ligands are crystallographically disordered. This finding afforded a possible explanation for the reported Hf–C(σ) lengths in dimethylhafnocene: a percentage of $Cp_2Hf(Cl)(CH_3)$ cocrystallized with $Cp_2Hf(CH_3)_2$. In order to test this hypothesis, it was necessary to prepare the dimethyl derivative with no possible contamination from the chloro methyl. Since the synthesis and crystallization were *exceedingly* difficult to perform in the standard manner, i.e., reaction of Cp_2MCl_2 with methylating agents, we chose the Cp_2MI_2 route. Reported herein are the pertinent details for the structures mentioned above, together with those of (μ-oxo)bis(methylzirconocene) which was encountered along the way.

Experimental Section

All manipulations were performed in an inert atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) and dimethoxyethane (DME) were predried over sodium and freshly distilled from potassium/benzophenone before use. Pentane was dried over sodium and distilled from potassium before use. Dichlorozirconocene and hafnium tetrachloride were obtained from Alfa Inorganics and used without further purification.

Preparation of Dimethylzirconocene. Cp_2ZrCl_2 (1.00 g, 3.4 mmol) was dissolved in ca. 60 mL of dry acetone. Potassium iodide (1.13 g, 6.8 mmol) was then added. The solution was stirred for 45 min during which time the color changes from clear to light orange. The mixture was filtered and the solvent removed in vacuo. The pale orange Cp_2ZrI_2 was dissolved in 50 mL of THF. The solution was cooled to −78 °C, and 4.5 mL of methyllithium (6.8 mmol, 1.5 M in hexane) was added. The mixture was warmed to room temperature at which point the solvent was removed in vacuo. The residue was extracted three times with 50-mL portions of pentane. The pentane extracts were combined and filtered. The pentane was removed and the resulting residue sublimed. Dimethylzirconocene was obtained as large clear crystals (270 mg, 32%).

Preparation of Dimethylhafnocene. Hafnium tetrachloride (1.28 g, 4 mmol) was placed in ca. 80 mL of DME. Cyclopentadienylthallium (2.15 g, 8 mmol) was added and the mixture stirred for 15 h. It was then filtered and stripped of solvent in vacuo. Dry, degassed acetone (ca. 60 mL) was added to the residue followed by solid KI (1.33 g, 8 mmol). This mixture was stirred for 45 min. The resulting solution was filtered and the acetone removed in vacuo. The residue was dissolved in ca. 50 mL of THF and cooled to −78 °C. Methyllithium (5.3 mL, 1.5 M in hexane) was added and the mixture warmed to room temperature. After filtration, the solvent was removed. The residue was extracted three times with 50-mL portions of pentane. The extracts were combined and filtered. The pentane was removed and the residue sublimed. Dimethylhafnocene was obtained as large, clear, air-sensitive crystals (280 mg, 21%).

Preparation of Chloromethylzirconocene. $Cp_2Zr(Cl)(CH_3)$ was first obtained during the workup of the reaction of Cp_2ZrCl_2 with $K[Al_2Me_6N_3]$. The sample used for the reported X-ray diffraction study was prepared from $[Cp_2ZrCl]_2O$ by the method of Wailes et al.[14] (μ-Oxo)bis(chlorozirconocene) was synthesized as reported by Reid et al.[15]

Preparation of (μ-Oxo)bis(methylzirconocene). Dimethylzirconocene (500 mg, 2 mmol) was dissolved in 30 mL of benzene. The solution was stirred open to the air for 16 h. At the end of this time, the solvent was removed in vacuo and the residue sublimed. (μ-Oxo)bis(methylzirconocene) was obtained as clear crystals (50 mg, 10%).

X-ray Data Collection, Structure Determination, and Refinement for $Cp_2Zr(CH_3)_2$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined as $P2_1/n$ from the systematic absences in $0k0$ for $k = 2n + 1$ and in $h0l$ for $h + l = 2n + 1$.

Data were collected on a Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[16] A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption (the transmission factors varied from 0.86 to 0.92).

Calculations were carried out with the SHELX system of computer programs.[17] Neutral atom scattering factors for Zr and C were taken from Cromer and Waber,[18] and the scattering for zirconium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[19] Scattering factors for H were from ref 20.

The position of the zirconium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the zirconium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.080$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.08 Å from the bonded carbon atom and were not refined. The methyl hydrogen atoms were located with the aid of a difference Fourier map. Refinement of the non-hydrogen atoms with anisotropic temperature factors and of the positional parameters of the hydrogen atoms led to final values of $R = 0.029$

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement[a]

	$Cp_2Zr(Cl)(CH_3)$	$Cp_2Zr(CH_3)_2$	$Cp_2Hf(CH_3)_2$	$[Cp_2Zr(CH_3)]_2O$
mol wt	271.9	251.5	338.8	488.9
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P3_121$
cell constants				
a, Å	6.810 (8)	6.953 (3)	6.965 (4)	8.017 (3)
b, Å	11.821 (9)	11.902 (5)	11.854 (5)	
c, Å	13.818 (9)	13.839 (5)	13.786 (6)	28.376 (6)
β, deg	92.30 (4)	91.95 (3)	92.02 (3)	
cell vol, $Å^3$	1111.5	1144.5	1137.5	1579.6
molecules/unit cell	4	4	4	3
ρ(calcd), g cm^{-3}	1.62	1.45	1.98	1.54
μ(calcd), cm^{-1}	11.61	8.89	96.16	9.76
radiation	Mo Kα ($\bar{\lambda}$ = 0.710 73 Å)	Mo Kα	Mo Kα	Mo Kα
max cryst dimens, mm	0.52 × 0.24 × 0.26	0.60 × 0.52 × 0.44	0.62 × 0.38 × 0.34	0.50 × 0.28 × 0.30
scan width, deg	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ
std reflctns	200, 040, 004	200, 080, 0010	200, 040, 004	200, 020
decay of stds	±3%	±2%	±2%	±2%
reflctns measd	2341	2459	2421	2823
2θ range, deg	1-50	1-50	1-50	1-50
obsd reflctns	1709	1672	1662	1358
no. of parameters varied	137	118	118	114
largest parameter shift/esd	0.20	0.03	0.01	0.01
GOF	1.69	1.04	1.05	1.16
R	0.043	0.029	0.041	0.025
R_w	0.054	0.034	0.041	0.029

[a] The unit-cell parameters in $P2_1/n$ may be transformed to those in $P2_1/c$: a = 6.965 (4) Å, b = 11.854 (5), c = 15.664 (6) Å, and β = 118.42 (4)°. They agree with those from ref 13 for $Cp_2Hf(CH_3)_2$ to within two esd's.

Table II. Final Fractional Coordinates for Dimethylzirconocene

atom	x/a	y/b	z/c
Zr	0.05748 (5)	0.29132 (3)	−0.13946 (3)
C(1)	0.3002 (7)	0.2877 (5)	−0.0022 (3)
C(2)	0.3478 (7)	0.1969 (5)	−0.0612 (4)
C(3)	0.1987 (9)	0.1178 (4)	−0.0568 (4)
C(4)	0.0599 (8)	0.1597 (5)	0.0049 (4)
C(5)	0.1253 (8)	0.2639 (5)	0.0396 (3)
C(6)	0.3145 (8)	0.3516 (6)	−0.2511 (4)
C(7)	0.159 (1)	0.3216 (5)	−0.3119 (4)
C(8)	0.0124 (8)	0.3974 (6)	−0.2990 (4)
C(9)	0.0753 (9)	0.4749 (5)	−0.2314 (4)
C(10)	0.2608 (9)	0.4464 (5)	−0.2005 (4)
C(11)	−0.1871 (8)	0.3905 (5)	−0.0745 (5)
C(12)	−0.1345 (9)	0.1584 (5)	−0.2108 (5)
H(1)	0.3846	0.3648	0.0095[a]
H(2)	0.4778	0.1889	−0.1032
H(3)	0.1914	0.0375	−0.0951
H(4)	−0.0743	0.1184	0.0228
H(5)	0.0518	0.3170	0.0908
H(6)	0.4529	0.3077	−0.2447
H(7)	0.1529	0.2507	−0.3627
H(8)	−0.1297	0.3949	−0.3350
H(9)	−0.0092	0.5467	−0.2058
H(10)	0.3511	0.4903	−0.1467
H(11)	−0.265 (8)	0.347 (5)	−0.034 (4)
H(12)	−0.171 (8)	0.443 (5)	−0.044 (4)
H(13)	−0.280 (8)	0.423 (5)	−0.123 (4)
H(14)	−0.243 (8)	0.187 (5)	−0.244 (4)
H(15)	−0.093 (8)	0.101 (5)	−0.256 (4)
H(16)	−0.226 (8)	0.111 (5)	−0.161 (4)

[a] Hydrogen atoms placed in calculated positions 1.08 Å from the bonded cyclopentadienyl carbon atom.

and R_w = 0.034. A final difference Fourier showed no feature greater than 0.3 e/$Å^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or (sin θ)/λ was noted. The final values of the thermal parameters are given in the supplementary material.[21] Table II contains the final fractional coordinates.

X-ray Data Collection, Structure Determination, and Refinement for $Cp_2Hf(CH_3)_2$. Data collection procedures were identical with those of dimethylzirconocene except for the absorption correction. An empirical method similar to that of Churchill[22] was employed. The observed transmission factors varied from 0.19 to 0.52.

Table III. Final Fractional Coordinates for Dimethylhafnocene

atom	x/a	y/b	z/c
Hf	0.05749 (7)	0.29122 (5)	−0.13951 (4)
C(1)	0.300 (2)	0.289 (1)	−0.002 (1)
C(2)	0.344 (2)	0.194 (2)	−0.062 (1)
C(3)	0.196 (2)	0.117 (1)	−0.058 (1)
C(4)	0.059 (2)	0.160 (1)	0.003 (1)
C(5)	0.125 (2)	0.263 (1)	0.0372 (9)
C(6)	0.311 (2)	0.355 (2)	−0.248 (1)
C(7)	0.156 (2)	0.320 (1)	−0.3122 (9)
C(8)	0.010 (2)	0.397 (2)	−0.298 (1)
C(9)	0.074 (2)	0.474 (1)	−0.231 (1)
C(10)	0.252 (2)	0.450 (1)	−0.201 (1)
C(11)	−0.178 (2)	0.391 (1)	−0.0737 (9)
C(12)	−0.134 (2)	0.162 (1)	−0.210 (1)
H(1)	0.3819	0.3665	0.0094
H(2)	0.4785	0.1901	−0.1010
H(3)	0.1887	0.0418	−0.1009
H(4)	−0.0722	0.1190	0.0230
H(5)	0.0536	0.3185	0.0892
H(6)	0.4456	0.3069	−0.2473
H(7)	0.1471	0.2488	−0.3599
H(8)	−0.1270	0.3967	−0.3367
H(9)	−0.0082	0.5463	−0.2077
H(10)	0.3482	0.4884	−0.1459
H(11)	−0.1804	0.4619	−0.0264
H(12)	−0.2594	0.3322	−0.0358
H(13)	−0.2667	0.4177	−0.1316
H(14)	−0.2400	0.1907	−0.2500
H(15)	−0.1946	0.1130	−0.1586
H(16)	−0.0584	0.1106	−0.2526

Tha atomic positions from dimethylzirconocene were used as the starting point for the least-squares refinement. The only departure from the method described above was that a weighting scheme based on $\sigma(I)$ was used and the methyl hydrogen atoms were not refined. The final features of the refinement are listed in Table I, and the positional and thermal parameters are given

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[21] See paragraph at the end of paper regarding supplementary material.

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Table IV. Final Fractional Coordinates for Chloromethylzirconocene

atom	*x/a*	*y/b*	*z/c*
Zr	0.06188 (8)	0.20663 (6)	−0.13597 (4)
C(1)	0.314 (1)	0.2128 (8)	−0.0005 (6)
C(2)	0.134 (1)	0.2370 (8)	0.0419 (5)
C(3)	0.065 (1)	0.3413 (8)	0.0062 (6)
C(4)	0.201 (1)	0.3827 (7)	−0.0578 (6)
C(5)	0.356 (1)	0.3047 (9)	−0.0609 (6)
C(6)	0.167 (1)	0.1799 (8)	−0.3069 (6)
C(7)	0.327 (1)	0.1513 (9)	−0.2467 (6)
C(8)	0.280 (1)	0.0553 (9)	−0.1960 (6)
C(9)	0.091 (1)	0.0223 (8)	−0.2252 (7)
C(10)	0.023 (1)	0.1000 (9)	−0.2942 (6)
Cl(1)	−0.2105 (4)	0.0994 (3)	−0.0639 (3)
Me(2)	−0.144 (2)	0.344 (1)	−0.2115 (9)
Cl(2)	−0.1602 (6)	0.3467 (4)	−0.2173 (4)
Me(1)	−0.191 (2)	0.100 (1)	−0.067 (1)
H(1)	0.4029	0.1362	0.0117
H(2)	0.0633	0.1838	0.0954
H(3)	−0.0726	0.3811	0.0252
H(4)	0.1899	0.4621	−0.0989
H(5)	0.4884	0.3110	−0.1035
H(6)	0.1569	0.2548	−0.3560
H(7)	0.4672	0.1981	−0.2409
H(8)	0.3760	0.0110	−0.1413
H(9)	0.0074	−0.0516	−0.1982
H(10)	−0.1202	0.0983	−0.3331

Table V. Final Fractional Coordinates for (μ-Oxo)bis(methylzirconocene)

atom	*x/a*	*y/b*	*z/c*
Zr	0.23783 (8)	0.13438 (7)	0.06369 (2)
C(1)	0.2004 (7)	0.2004 (7)	0.0000
C(1)	0.067 (1)	−0.2240 (9)	0.0837 (3)
C(2)	0.248 (1)	−0.145 (1)	0.1028 (3)
C(3)	0.380 (1)	−0.084 (1)	0.0663 (4)
C(4)	0.278 (1)	−0.126 (1)	0.0242 (3)
C(5)	0.087 (1)	−0.2096 (9)	0.0353 (3)
C(6)	0.409 (2)	0.492 (1)	0.0786 (5)
C(7)	0.546 (1)	0.448 (2)	0.0667 (3)
C(8)	0.561 (1)	0.341 (1)	0.1029 (5)
C(9)	0.427 (2)	0.315 (1)	0.1360 (3)
C(10)	0.337 (1)	0.408 (2)	0.1215 (4)
C(11)	−0.053 (1)	0.073 (2)	0.0922 (3)
H(1)	−0.0659	−0.2871	0.1031
H(2)	0.2832	−0.1315	0.1398
H(3)	0.5346	−0.0174	0.0697
H(4)	0.3377	−0.0978	−0.0108
H(5)	−0.0296	−0.2558	0.0104
H(6)	0.3672	0.5776	0.0583
H(7)	0.6280	0.4867	0.0344
H(8)	0.6609	0.2896	0.1051
H(9)	0.3976	0.2348	0.1683
H(10)	0.2240	0.4158	0.1400
H(11)	−0.02 (1)	0.21 (1)	0.094 (3)
H(12)	−0.155 (9)	−0.03 (1)	0.074 (2)
H(13)	−0.07 (1)	0.04 (1)	0.124 (2)

in the supplementary material.[21] Table III contains the final fractional coordinates.

X-ray Data Collection, Structure Solution, and Refinement for $Cp_2Zr(Cl)(CH_3)$. Data collection procedures were identical with those of dimethylzirconocene.

It was apparent that $Cp_2Zr(Cl)(CH_3)$ and $Cp_2Zr(CH_3)_2$ were isostructural. As a starting point the zirconium and cyclopentadienyl carbon atoms were positioned and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions. A difference Fourier map phased on these atoms revealed two large peaks of relative size 400 and 330, 2.46 Å from the metal. Refinement of the model as though it were Cp_2ZrCl_2 (isotropic temperature factors for chlorine) produced $R = 0.078$. The B values for the two "chlorine" atoms were 7.35 and 9.06 Å^2. Conversion to anisotropic thermal parameters for the chlorine atoms and further refinement led to $R = 0.061$. The two Zr–"Cl" bond lengths were 2.45 and 2.47 Å. Calculation of difference Fourier maps with and without the chlorine contribution failed to reveal any feature indicative of the presence of the disordered carbon atoms of the methyl groups.

Next the model was treated as through the compound was $Cp_2Zr(CH_3)_2$. Refinement of the zirconium atom and the ring carbon atoms with anisotropic thermal parameters, and the "methyl carbon" atoms with isotropic temperature factors led to $R = 0.110$. The B value for one of the two "methyl carbon" atoms was 0.80 Å^2, while that for the second was not positive definite (less than zero and therefore not representative of reality).

It was assumed at this point that the compound was $Cp_2Zr(Cl)(CH_3)$. (This was borne out by an elemental analysis of the bulk sample.) The model of choice consisted of 50% chlorine and 50% carbon atoms near each of the original "chlorine" positions. (Both atoms were placed along the bond vector, the chlorine 2.44 Å and the carbon 2.30 Å from the zirconium atom, although their positions could not be resolved on a difference Fourier map.) Refinement was carried out such that the two atoms separated by ca. 0.15 Å were never varied in the same cycle. The methyl carbon and chlorine atom occupancy factors were also constrained such that the sum of the two "neighbor atoms" was 100%. The process converged at chlorine occupancy factors of 43 and 57%. The R value was 0.043. The parameters in Tables I and IV are based on this treatment.

X-ray Data Collection, Structure Solution, and Refinement for $[Cp_2ZrMe]_2O$. Data collection procedures were similar to those for dimethylzirconocene. Structure solution was accomplished with the use of direct methods techniques.[17] The final refinement produced the parameters given in Tables I and V.[21] Refinement in space group $P3_121$ produced $R = 0.025$ and $R_w = 0.029$ compared to $R = 0.026$ and $R_w = 0.030$ in $P3_221$ (the enantiomorph of $P3_121$). We therefore concluded that $P3_121$ is the correct choice.

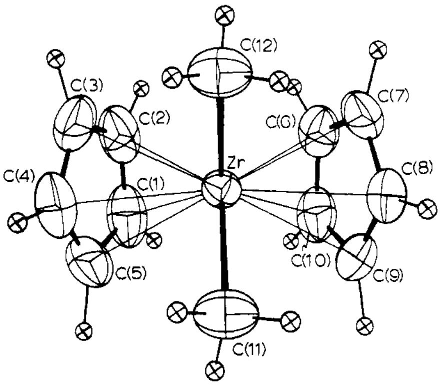

Figure 1. Molecular structure and atom numbering scheme for $Cp_2Zr(CH_3)_2$. The atoms are represented by their 50% probability ellipsoids for thermal motion.

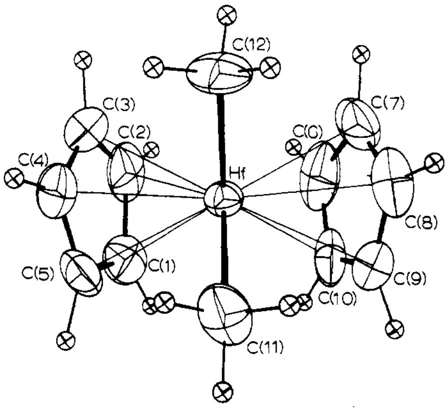

Figure 2. Molecular structure of $Cp_2Hf(CH_3)_2$. The cell packing is the same as that given in ref 13.

Description of the Structures

$Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$. The molecular structure and atom numbering scheme of dicyclo-

Table VI. Bond Lengths (Å) and Angles (deg)

	$Cp_2Zr(CH_3)_2$	$Cp_2Hf(CH_3)_2$	$[Cp_2Zr(CH_3)]_2O$	$Cp_2Zr(Cl)(CH_3)$
M-C(1)	2.498 (4)	2.491 (12)	2.553 (6)	2.490 (8)
M-C(2)	2.523 (5)	2.509 (13)	2.538 (7)	2.513 (7)
M-C(3)	2.542 (5)	2.528 (15)	2.527 (7)	2.528 (9)
M-C(4)	2.538 (5)	2.502 (14)	2.526 (7)	2.513 (9)
M-C(5)	2.528 (5)	2.487 (12)	2.526 (6)	2.504 (8)
M-C(6)	2.507 (5)	2.479 (12)	2.516 (8)	2.516 (9)
M-C(7)	2.537 (5)	2.524 (12)	2.495 (8)	2.500 (9)
M-C(8)	2.554 (5)	2.534 (14)	2.529 (8)	2.489 (10)
M-C(9)	2.533 (5)	2.512 (15)	2.534 (7)	2.515 (9)
M-C(10)	2.490 (5)	2.485 (14)	2.527 (8)	2.528 (10)
M-C(av)	2.52 (1)	2.50 (2)	2.53 (2)	2.51 (1)
M-C(11)	2.280 (5)	2.240 (12)	2.276 (9)	
M-C(12)	2.273 (5)	2.233 (12)	1.948 (1)[a]	
M-Cent(1)[b]	2.23	2.20	2.24	2.21
M-Cent(2)	2.23	2.22	2.24	2.24
Cent(1)-M-Cent(2)	132.5	133.0	128.5	
Cent(1)-M-C(11)	105.5	105.2	103.2	
Cent(1)-M-C(12)	105.4	105.5	108.8[a]	
Cent(2)-M-C(11)	105.5	104.9	105.3	
Cent(2)-M-C(12)	106.3	106.4	109.5[a]	
C(11)-M-C(12)	95.6 (12)	95.8 (5)	96.3 (2)[a]	

[a] C(12) is O(1) for the $[Cp_2Zr(CH_3)]_2O$ structure. [b] Cent(1) is the centroid of the cyclopentadienyl ring defined by C(1) → C(5).

pentadienyldimethylzirconium(IV) is presented as Figure 1, while that of its hafnium analogue is given in Figure 2. The Zr–C(σ) bond lengths, 2.273 (5) and 2.280 (5) Å (Table VI), compare well with the 2.284 (4) Å average in $Cp_2Zr[CH_2Si(CH_3)_3]_2$[10] but are appreciably longer than the 2.251 (6)-Å value found with $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$.[12] The reason for the shorter length is not obvious but may be related to the average Zr–C(η^5) distances: 2.525 (12) Å in $Cp_2Zr(CH_3)_2$ vs. 2.55 (3) Å in $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$.[12] In $Cp_2Zr(CH_3)_2$ both the average and the range, 2.490 (5)–2.554 (5) Å, of the Zr–C(η^5) lengths are in reasonable agreement with those determined for $Cp_2Zr[CH_2Si(CH_3)_3]_2$,[10] 2.495 (4)–2.516 (5) Å, 2.507 (8)-Å average, and for $(CH_2)_3(\eta^5\text{-}C_5H_4)_2ZrCl_2$, 2.477 (7)–2.516 (7) Å, 2.494 (4) Å average.[23]

The Hf–C(σ) bond lengths, 2.233 (12) and 2.240 (12) Å, are surprisingly short. If one disregard the previously reported values for $Cp_2Hf(CH_3)_2$, there are only two Hf–C(sp^3) bond lengths available for comparison: 2.332 (12) Å in $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$[12] and 2.295 (14) Å in $[Cp_2Hf(CH_3)]_2O$.[13] (It should be noted that the Zr–C(σ) length in $[Cp_2Zr(CH_3)]_2O$, 2.276 (9) Å, is slightly *shorter* than that found in $Cp_2Zr(CH_3)_2$.) Thus, on the basis of the structures of $[Cp_2Hf(CH_3)]_2O$ in $(\eta^5\text{-}C_9H_7)_2HfMe_2$, the length for $Cp_2Hf(CH_3)_2$ is ca. 0.1 Å less than expected. On the other hand, the Hf–C(sp^2) distance in $Cp_2Hf[C_4(C_6H_5)_4]$,[3] 2.20 (2) Å, compares well with the 2.24 (2) Å average for $Cp_2Hf(CH_3)_2$, after a correction of 0.03 Å for the radious of C(sp^3) vs. C(sp^2). Although the relative inaccuracy of the determination of the Hf–C lengths makes a detailed comparison difficult, these results show the need for further structural work in this area. They also raise the spectre of doubt on the purity of the $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$ used in the structural study, since a small percentage of $(\eta^5\text{-}C_9H_7)_2Hf(Cl)(CH_3)$ would have the effect of elongating the observed Hf–"C(sp^3)" bond.

The Hf–C(η^5) lengths range from 2.479 (12) to 2.534 (14) Å and average 2.50 (1) Å. These compare with average values of 2.513 (5) Å in $[Cp_2Hf(CH_3)]_2O$[13] and 2.482 (4) Å in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2HfCl_2$.[24]

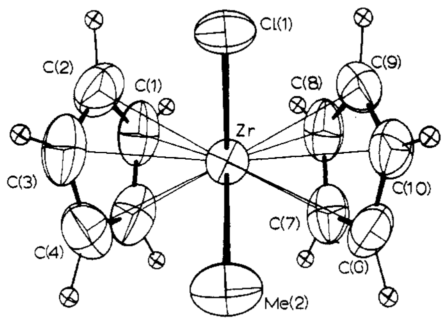

Figure 3. Molecular structure of $Cp_2Zr(Cl)(CH_3)$.

The similarity among $Cp_2Zr(CH_3)_2$, $Cp_2Hf(CH_3)_2$, $(CH_2)_3(\eta^5\text{-}C_5H_4)_2ZrCl_2$, and $(CH_2)_3(\eta^5\text{-}C_5H_4)_2HfCl_2$ is underscored by the values of the ligand(σ)–metal–ligand(σ) angles, 95.6 (2), 95.8 (5), 96.92 (7), and 95.87 (8)°, respectively.[25] The centroid–metal–centroid angles in $Cp_2Zr(CH_3)_2$, 132.5°, and in $Cp_2Hf(CH_3)_2$, 133.0°, are close to those found in related compounds.[5,10,26]

$Cp_2Zr(Cl)(CH_3)$. The molecular structure and atom numbering scheme for the "average" molecule is given in Figure 3. Because of the disorder of chloro and methyl ligands, a detailed comparison of bond lengths and angles cannot be made. However, one feature concerning the Zr–ligand(σ) bond should be mentioned. The Zr–Cl lengths in $Cp_2Zr(Cl)(CH_3)$, 2.476 (9) and 2.476 (9) Å, are longer than those found in more accurate determinations: 2.441 (10) Å in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2ZrCl_2$,[24] 2.435 (4) Å in $[\eta^5\text{-}C_5H_4C(CH_3)_3]_2Zr(Cl)[CH\{Si(CH_3)_3\}_2]$,[11] and 2.435 (4) in $[\eta^5\text{-}C_5H_4Si(CH_3)_3]_2Zr(Cl)[CH\{Si(CH_3)_3\}_2]$.[11] Likewise, the Zr–C(σ) distances, 2.35 (1) and 2.36 (2) Å, are larger than normal, but in view of the associated crystallographic problems no chemical significance should be inferred.

It is interesting to note a related point concerning "$Cp_2Hf(CH_3)_2$". If one accepts as normal values Hf–Cl = 2.42 Å[24] and Hf–C(sp^3) = 2.24 Å, the weighted average[27] for a disordered structure is 2.37 Å. This is near the mean

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[23] Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *J. Organomet. Chem.* **1974**, *80*, 79.

[24] Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880.

[25] The M–C(η^5) lengths are slightly shorter in the dichloro derivatives due to the influence of the electron-withdrawing chlorine ligands.

[26] Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290.

[27] The weighted average is calculated as [(17/23)(2.42) + (6/23)(2.24)] Å = 2.37 Å.

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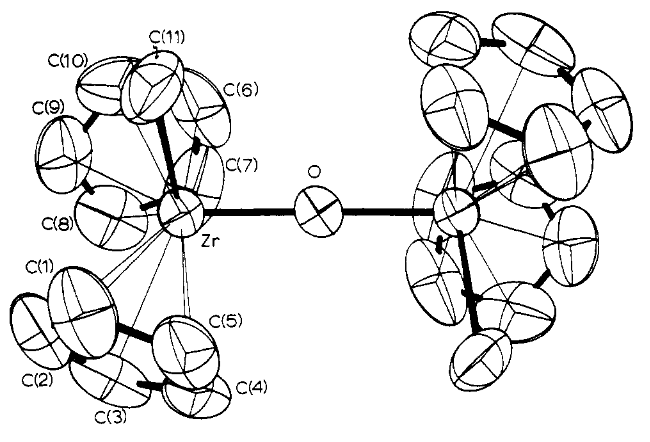

Figure 4. Molecular structure of $[Cp_2Zr(CH_3)]_2O$.

of the two reported Hf–"C(sp^3)" lengths, 2.35 Å.[13]

$[Cp_2Zr(CH_3)]_2O$. The only parameters not mentioned above concern the Zr–O linkage: the length, 1.948 (1) Å, is close to the 1.945 (3) Å value given in $[CpZrCl]_2O$,[28] and 1.966 (5) Å in $[Cp_2Zr(SC_6H_5)]_2O$.[29] The Zr–O–Zr bond angle, 174.1 (3)°, falls within the range for M–O–M (M = group 4b metal), 169–180°.[30] The molecular structure is shown in Figure 4.

Discussion

Two important points concerning the title compounds should be reiterated. First, the published structure of $Cp_2Hf(CH_3)_2$ is probably that of the disordered $Cp_2Hf(Cl)(CH_3)$ or a mixture of $Cp_2Hf(Cl)(CH_3)$ and $Cp_2Hf(CH_3)_2$. This is understandable since (a) the disordered $Cp_2Zr(Cl)(CH_3)$ is isostructural with $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$ and (b) it is very difficult to prepare pure $Cp_2M(CH_3)_2$ (M = Zr or Hf) from the reaction of Cp_2MCl_2 with 2 mol of methylating agents.

Second, the present study affords the most accurate value for M–C(sp^3) bond lengths (M = Zr or Hf) in (η^5-ligand)$_2$M[R(sp^3)]$_2$ compounds because (a) the values are internally consistent, (b) for R = CH_3 steric problems are minimized, (c) for (η^5-ligand) = Cp the electronic effects are well-understood, and (d) the values compare well between $Cp_2Zr(CH_3)_2$ and $Cp_2Hf(CH_3)_2$, as well as with M–C(sp^2) bond lengths.[3,4]

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. $(\eta^5-C_5H_5)_2Zr(CH_3)_2$, 12636-72-5; $(\eta^5-C_5H_5)_2Hf(CH_3)_2$, 37260-88-1; $(\eta^5-C_5H_5)_2Zr(Cl)(CH_3)$, 1291-45-8; $[(\eta^5-C_5H_5)_2Zr(CH_3)]_2O$, 79169-19-0.

Supplementary Material Available: A listing of structure factor amplitudes, thermal parameters, and additional bond lengths and angles for all four structures (44 pages). Ordering information is given on any current masthead page.

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Structural Study of W[η^5-C_5Me_4(*t*-Bu)](η^2-MeC≡CMe)Cl_2, a Paramagnetic Tungsten(III) Species with a Four-Electron Acetylene–Metal Bond

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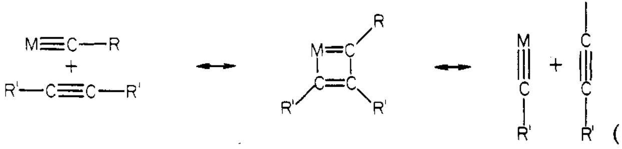
Received November 30, 1982

The complex W[η^5-C_5Me_4(*t*-Bu)](η^2-MeC≡CMe)Cl_2, prepared by Pedersen and Schrock from the reaction of excess 2-butyne with W(≡$CCMe_3$)(dme)Cl_3 (dme = 1,2-dimethoxyethane), crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (No. 14) with a = 8.411 (1) Å, b = 26.639 (5) Å, c = 8.971 (7) Å, and β = 114.32 (1)°. Diffraction data to 2θ = 50° (Mo Kα radiation) were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to R_F = 3.2% and R_{wF} = 3.0% for all 2244 independent data. The paramagnetic complex contains a "strongly bound", four-electron-donating, 2-butyne ligand, with W–C(alkyne) = 2.007 (7) and 2.021 (6) Å and with C–C = 1.312 (10) Å; these parameters are compared with those in various "strongly bound" diamagnetic complexes of tantalum(III) and tungsten(II).

Introduction

The four-coordinate tungsten(VI) complex[1] W(≡$CCMe_3$)($OCMe_3$)$_3$ has recently been shown[2] to be an efficacious catalyst for the metathesis of internal acetylenes. In an extension of the now accepted path for *olefin* metathesis, the acetylene metathesis is believed to proceed through a metallacyclobutadiene intermediate[3] (see eq 1).



(1)

In contrast to the catalytic behavior noted for W(≡$CCMe_3$)($OCMe_3$)$_3$, the related octahedral tungsten(VI) neopentylidyne complex W(≡$CCMe_3$)(dme)Cl_3 (dme = 1,2-dimethoxyethane) is *not* a useful metathesis catalyst.

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(1) We regard the alkylidyne ligand as formally a six-electron-donating trianion and the alkoxide ligand as a monoanion. This approach is consistent with the accepted concept of formal oxidation state, viz., that charge remaining on an atom when all shared (bonding) electrons are formally assigned to the more electronegative of the atoms involved in the bond.

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