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Intramolecular Thermolytic C–H Activation Processes. Solid-State Structural Characterization of a Mononuclear η^6-$Me_4C_5CH_2$ Zirconium Complex and a Mechanistic Study of Its Formation from $(Me_5C_5)_2Zr(C_6H_5)_2$

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The complex $Cp'_2Zr(C_6H_5)_2$ (1, $Cp' = \eta^5$-Me_5C_5) undergoes unimolecular thermolysis in solution ($\Delta H^{\ddagger} = 22.5$ (3) kcal/mol, $\Delta S^{\ddagger} = -11.8$ (3) eu) to yield the ring-metalated complex $Cp'Zr(C_6H_5)(Me_4C_5CH_2)$ (2) and benzene. Complex 2 crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 13.550$ (2) Å, $b = 9.651$ (2) Å, $c = 17.613$ (3) Å, and $\beta = 94.94$ (1)° at 0 °C. Least-squares refinement led to a value for the conventional R index (on F) of 0.043 for 2594 reflections having $2\theta_{MoK\alpha} < 55°$ and $I > 3\sigma(I)$. The molecular structure of 2 consists of η^5-Cp′ and η^6-$Me_4C_5CH_2$ ligands in a distorted "bent sandwich" Cp'_2ZrX_2 configuration (∠ring centroid–Zr–ring centroid = 143.6 (3)°) with the X groups being an unexceptional phenyl ligand (Zr–C = 2.285 (5) Å) and a metalated cyclopentadienyl methyl group (Zr–C = 2.388 (7) Å). The latter carbon atom is displaced 0.88 Å (37°) from the C_5 mean plane in the direction of the zirconium atom and is bonded to the C_5 ring at a C–C distance of 1.468 (9) Å. The zirconium atom is displaced slightly from the center of the methyl-metalated C_5 ring toward the metalated carbon atom. It appears that the η^6 ligand has little fulvene character and that a metalated σ,η^5-Cp′ bonding description is more appropriate. Labeling and kinetic studies with $Cp'_2Zr(C_6D_5)_2$ show that thermolysis occurs via rate-limiting phenyl ortho hydrogen atom abstraction ($k_H/k_D = 6.5$ (10) at 70 °C) to yield a benzene/ortho phenylene intermediate which can be trapped with ethylene. Benzene elimination is followed by hydrogen atom abstraction from a Cp′ ligand to yield 2.

The pathways by which group 4 and f-element hydrocarbyl molecules undergo thermolysis have been the subject of considerable recent interest.[1] Much of this interest derives from the perception that differences in oxidation state energetics and bond disruption enthalpy patterns vis-à-vis middle and late transition metals may give rise to distinctive mechanistic pathways. Several major classes of C–H bond scission processes have been identified for group 4 and f-element hydrocarbyl thermolyses.[2] All involve C–H functionalization at an appended or exogenous hydrocarbon fragment by a departing hydrocarbyl ligand. Examples of functionalization at a *σ-bound* hydrocarbyl ligand include α-,[1a,3] β-,[1a,4–6] γ-,[1a,7] and ϵ-hydrogen[1a] elimination processes. Mechanistically, several cases are reasonably well-understood; however, only one system has been characterized thermodynamically.[8] Examples of *π-bound* cyclopentadienyl C–H functionalizations involve both C_5H_5[1,9] and Me_5C_5 (Cp′)[4a,b,7a,b,10,11] systems. Despite the importance of the latter ligand in contemporary organometallic chemistry and the widespread occurrence of C–H activating processes involving Cp′, mechanistic data are relatively sparse. Furthermore, there is little information on the molecular structures of mononuclear ring-metalated species and, in contrast to later transition metals (vide infra), issues such as the importance of a "fulvene-like" π-bonded (presumably planar)[3a,9a] vs. a ring-metalated σ,η^5 description (I vs. II) remain incompletely resolved.

During the synthesis of Cp'_2ZrPh_2 (1) for thermochemical studies, we discovered that thermolysis cleanly yielded

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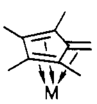

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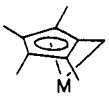

II

a crystallizable $Zr(\eta^6\text{-}Me_4C_5CH_2)$ complex. In the present contribution, we report the molecular structure of $Cp'Zr(Ph)(\eta^6\text{-}Me_4C_5CH_2)$ (**2**), the first structural characterization of such a Cp′-derived species by single-crystal diffraction techniques.[12] Furthermore, the formation of **2** as a relatively unreactive end product and certain features of the molecular structure of **2** raised kinetic/mechanistic questions about the pathway from **1** to **2**, which we likewise address.

Experimental Section

General Methods. All procedures were performed in air-free Schlenk-type glassware on a dual manifold Schlenk line or on a high vacuum (10^{-5} torr) system or in a nitrogen-filled Vacuum Atmospheres glovebox as described elsewhere.[7b,11,13] ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-270 (FT, 270 MHz ^1H; 63.7 MHz ^{13}C) spectrometer. Chemical shifts were referenced to the internal solvent resonance and are reported relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer with Nujol mulls sandwiched between salt (KBr, NaCl) plates in an O-ring sealed, air-tight holder. GC/MS studies were performed on a Hewlett-Packard 5985 instrument and interfaced data system with 15-eV electron-impact ionization.

Elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Syntheses. Cp'_2ZrPh_2 (1). Compound **1** was synthesized via a modification of the literature procedure.[2c] To a solution of 2.70 g (6.24 mmol) of Cp'_2ZrCl_2[14] in 50 mL of diethyl ether was added 10 mL of 2.0 M LiPh in cyclohexane under Ar flush at −78 °C. The yellow solution was allowed to come to room temperature with stirring. After 4 h, the diethyl ether was removed in vacuo and 50 mL of pentane condensed into the reaction vessel. The resulting solution was then filtered, and the white precipitate on the frit was washed by condensing ca. 10 mL of pentane back onto the frit twice. The dark orange filtrate was next concentrated and cooled to −78 °C. Filtration yielded 2.40 g of analytically pure pale yellow crystals (74.5% yield). Recrystallization from pentane, however, yielded 1.62 g of colorless crystals (50.3% yield).

^1H NMR (C_6D_6): δ 7.56 (d, 4 H), 7.28 (m, 4 H), 7.11 (t, 2 H), 1.56 (s, 30 H).

^{13}C NMR (C_6D_6): δ 193.47 (s, 2 C_6H_5), 136.86 (d, J_{CH} = 154.0 Hz, 2 C_6H_5), 133.97 (d, J_{CH} = 152.1 Hz, 2 C_6H_5), 126.89 (d, J_{CH} = 155.8 Hz, 2 C_6H_5), 125.76 (d, J_{CH} = 155.8 Hz, 2 C_6H_5), 124.54 (d, J_{CH} = 157.6, 2 C_6H_5), 120.41 (s, 10 $C_5(CH_3)_5$), 12.21 (q, J_{CH} = 126.5 Hz, 10 $C_5(CH_3)_5$).

IR (Nujol mull, cm^{-1}): 3050 (m), 3034 (sh), 2722 (w), 1568 (m), 1558 (sh), 1488 (sh), 1432 (sh), 1412 (m), 1236 (m), 1170 (w), 1154 (w), 1065 (sh), 1052 (m), 1023 (m), 995 (w), 726 (s), 708 (s), 593 (sh).

Anal. Calcd for $C_{32}H_{40}Zr$: C, 74.50; H, 7.81. Found: C, 74.58; H, 7.88.

$Cp'_2Zr(C_6D_5)_2$ (1-d). Compound **1-d** was prepared in the same manner as compound **1** except that a solution of LiC_6D_5 in diethyl ether[15] was used in place of the LiPh solution.

$Cp'ZrPh(C_5Me_4CH_2)$ (2). Compound **2** was prepared by heating 1.50 g (2.91 mmol) of **1** in ca. 25 mL of toluene at 100 °C for 6 h. The toluene was next evaporated from the dark red solution and ca. 15 mL of pentane condensed into the reaction vessel. The solution was stirred, warmed to dissolve all of **2**, and then slowly cooled to −78 °C. The resulting orange-red crystals were collected by cold filtration and dried in vacuo to yield 1.15 g of **2** (90% yield).

Alternatively, solid **1** was heated in a sublimer to ca. 125 °C under 1 atm of Ar, whereupon it thermolyzed to give **2** and benzene. The sublimer was then opened to vacuum and **2** sublimed onto a water-cooled cold finger (ca. 70% yield). Compound **2** sublimes at 90–100 °C (10^{-5} torr).

^1H NMR (C_6D_6): δ 6.99–7.18 (m, 4 H), 6.00 (d, 1 H, $^3J_{H-H}$ = 6.6 Hz), 2.24 (d, 1 H, $^3J_{H-H}$ = 6.6 Hz), 2.07 (d, 1 H, $^2J_{H-H}$ = 6.6 Hz), 1.75 (s, 3 H), 1.68 (s, 15 H), 1.63 (s, 3 H), 1.48 (s, 3 H), 0.99 (s, 3 H).

^{13}C NMR (C_6D_6): δ 194.28 (s, 1 C_6H_5), 134.16 (ddd, $^1J_{CH}$ = 155.8 Hz, 1 C_6H_5), 129.46 (s, 1 $C_5(CH_3)_4(CH_2)$), 126.89 (dd, $^1J_{CH}$ = 155.8 Hz, 1 C_6H_5), 125.86 (dd, $^1J_{CH}$ = 155.8 Hz, 1 C_6H_5), 125.70 (s, 1 $C_5(CH_3)_4(CH_2)$), 125.16 (ddd, $^1J_{CH}$ = 157.6 Hz, 1 C_6H_5), 123.03 (ddd, $^1J_{CH}$ = 148.5 Hz, 1 C_6H_5), 121.62 (s, 1 $C_5(CH_3)_4(CH_2)$), 119.35 (s, 1 $C_5(CH_3)_4(CH_2)$), 118.06 (s, 5 $C_5(CH_3)_5$), 117.76 (s, 1 $C_5(CH_3)_4(CH_2)$), 63.53 (t, J_{CH} = 144.8 Hz, $C_5(CH_3)_4(CH_2)$), 13.38 (q, J_{CH} = 126.5 Hz, 1 $C_5(CH_3)_4(CH_2)$, 11.92 (q, 1 $C_5(CH_3)_4(CH_2)$, 11.46 (q, J_{CH} = 126.5 Hz, 5 $C_5(CH_3)_5$), 10.48 (q, J_{CH} = 126.5 Hz, 2 $C_5(CH_3)_4(CH_2)$).

IR (Nujol mull, cm^{-1}): 3048 (sh), 3015 (sh), 2713 (w), 1485 (w), 1415 (sh), 1353 (sh), 1240 (w), 1170 (w), 1154 (w), 1075 (w), 1060 (w), 1050 (w), 1025 (m), 995 (w), 840 (s), 809 (w), 750 (sh), 725 (s), 710 (s), 612 (sh).

Anal. Calcd for $C_{26}H_{34}Zr$: C, 71.33; H, 7.83; mol wt, 437.8. Found: C, 71.28; H, 7.93; mol wt, 391 (cryoscopic in benzene).

Mechanistic Studies. Kinetic Measurements. The rates of thermolysis of **1** and **1-d** were measured by monitoring the decrease in integrated ^1H NMR peak intensity of Cp′ ring methyl groups of **1** or **1-d** relative to the total integrated intensity of ring methyl groups. Since the reaction proceeds quantitatively, this gives the percentage of **1** or **1-d** remaining. FT NMR spectra for temperatures 75 through 104 °C were recorded automatically at preset time intervals by using the JEOL FX 270 STACK-INIWT routine. Each spectrum consisted of eight scans with 5-s pulse delays. Reaction temperatures as given by the JEOL computer-controlled variable-temperature unit were checked by the peak separation in ethylene glycol and also by another thermocouple placed in an NMR tube containing the solvent. The reactions for temperatures 50–60 °C were carried out in a constant temperature bath. To record a spectrum, the NMR tube was removed from the bath and placed in dry ice–acetone to stop the reaction. The spectrum was then quickly recorded at room temperature, the NMR tube was returned to the constant temperature bath, and all times were recorded. A typical kinetic experiment involved ca. 40 mg of **1** dissolved in 0.3 mL of solvent (toluene-d_8, C_6D_6, or C_6D_{12}) sealed in an NMR tube under 1–2 atm of N_2. Reactions were followed for greater than 3 half-lives.

Kinetic, Arrhenius, and Eyring plots were fit by linear least-squares techniques. Confidence limits were established from standard deviations in the slopes and in the y intercepts of the lines, by equating them to $tS/(N)^{1/2}$, where t = critical value at the 95% confidence level, S = standard deviation calculated by using the inverse variance matrix technique, and N = number of data points.[16]

Mass Spectral Analysis of Thermolysis Products. Separate samples of **1** and **1-d** were thermolyzed in C_6D_{12}. The benzene released in the thermolysis and the solvent were collected via trap-to-trap distillation. The benzene and C_6D_{12} were then separated by GC using a 5% FFAP or 3% Carbowax column, and the benzene was analyzed by MS. In separate experiments, the LiC_6D_5 used to prepare **1-d** was reacted with D_2O and with H_2O. The benzene released in both cases was analyzed by MS to provide C_6D_6 and C_6D_5H reference spectra.

Crossover Experiment. A solution of 20 mg each of **1** and **1-d** in 0.4 mL of C_6D_{12} was heated in a sealed NMR tube at 80–90

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[12] (a) Reported in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; paper INOR 251. (b) The molecular structure of an η^6-$Me_4C_5CH_2$ hafnium complex was reported at this same meeting: Bulls, A. R.; Bercaw, J. E., paper INOR 131.

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[14] Prepared as in: Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078–3083, except that LiCp′ was synthesized in pentane and isolated as a solid. Cp'_2ZrCl_2 was synthesized in refluxing toluene rather than DME.

[15] LiC_6D_5 was prepared from C_6D_5Br (Aldrich) and Li sand in refluxing diethyl ether. After 1 h the solution was filtered and a small amount titrated with HCl solution to determine the concentration.

[16] Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. In *Experiments in Physical Chemistry*, 3rd ed.; McGraw-Hill: New York, 1974; pp 27–58.

Table I. Crystallographic Details for $Cp'Zr(Ph)(Me_4C_5CH_2)$ (2)

space group	$P2_1/c$
a, Å	13.550 (2)
b, Å	9.651 (2)
c, Å	17.613 (3)
β, deg	94.94 (1)
V, Å^3	2294.7 (1.2)
Z	4
D_{calcd}, g cm^{-3}	1.267
X-radiation	Mo K_α, graphite monochromator
μ, cm^{-1}	4.77
T, °C	0
scan mode	$\omega/2\theta$
scan range, deg	0.70
θ range, deg	2–27.5
unique data	5264
unique data with $I > 3\sigma(I)$	2594
final no. of variables	244
$R(F)$	0.043
$R_w(F)$	0.057
GOF	1.44

°C for >2 weeks. The tube was then opened by scoring with a file and the solution poured into a Schlenk-type flask. The volatile products were trap-to-trap distilled on the vacuum line and analyzed by GC/MS as described above.

Thermolysis in the Presence of Diphenylacetylene and Ethylene. A solution of 40 mg (0.078 mmol) of 1 and 21 mg (0.12 mmol, 0.30 M) of diphenylacetylene in 0.4 mL of toluene-d_8 was heated at 80 °C until thermolysis was complete. The product was analyzed by ^1H NMR spectroscopy. A similar experiment was also carried out with 1 under an ethylene atmosphere (ca. 2 atm, 0.09 M by integration).

X-ray Structural Analysis of $Cp'Zr(Ph)(C_5Me_4CH_2)$ (2).[17] Large red-orange plates of 2 were grown by slowly cooling a saturated solution of 2 in pentane from 20 to −20 °C over 7 h and then leaving it at −20 °C for an additional 3 h. Compound 2 crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 13.550$ (2) Å, $b = 9.651$ (2) Å, $c = 17.613$ (3) Å, $\beta = 94.94$ (1)°, and $Z = 4$ at ca. 273 K. Data in a quadrant of reciprocal space (5264 unique reflections having $2\theta \leq 55°$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation and a graphite monochromator. No correction was made for absorption (crystal size 0.27 × 0.23 × 0.17 mm; $\mu = 4.77$ cm^{-1}); there was no evidence of decomposition or extinction. The position of the Zr atom was determined from the Patterson function; all but one of the C atoms were then located by using DIRDIF.[18] Hydrogen atoms were located from difference Fourier syntheses and were included as fixed contributions after idealization [r(C–H) = 1.00 Å; $B = 1.3B_{eq}$ for the attached C atom]. The structure was refined (Enraf-Nonius Structure Determination Package;[19] neutral-atom scattering factors;[20] full-matrix least squares) to agreement factors R and R_w on F_o of 0.043 and 0.057, respectively, for 244 variables and the 2594 observations having $F_o^2 \geq 3\sigma(F_o^2)$. The error in an observation of unit weight is 1.44. The largest feature of the final difference map has height 1.04 e Å^{-3} and is associated with the Zr atom; all other peaks and troughs have heights or depths <0.49 e Å^{-3}. Experimental details are given in Table I.

Results and Discussion

Synthesis and Preliminary Characterization. Compound 1 can be straightforwardly prepared by the reaction of Cp'_2ZrCl_2 with LiPh in diethyl ether. Recrystallization from pentane affords 1 as colorless crystals which are stable at room temperature under inert atmosphere for months. However, solutions of 1 slowly become dark red at room temperature. This process is accelerated at higher temperatures and quantitatively yields red-orange complex 2 and benzene. Both ^1H and ^{13}C NMR spectra of 2, supplemented by appropriate homonuclear and off-resonance decoupling experiments (see Experimental Section), show one η^5-Cp′ ligand, one C_6H_5 ligand lacking C_{2v} symmetry (and having an ortho hydrogen signal at rather high field, δ 6.00), and another Cp′-derived ligand having four magnetically nonequivalent CH_3 groups and two magnetically nonequivalent, coupled ($J_{geminal} = 6.6$ Hz) methylene protons. Combined with elemental analysis and molecular weight data, this information strongly implicates an η^6-$Me_4C_5CH_2$ structure such as 2a or 2b for 2. Further comments on NMR spectral parameters follow the discussions of the solid-state structure.

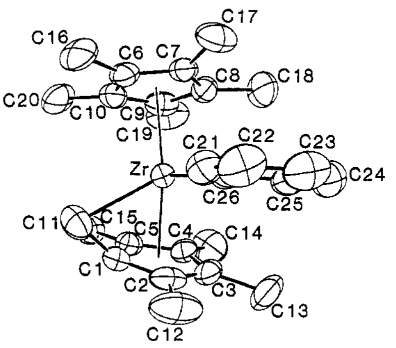
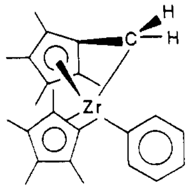
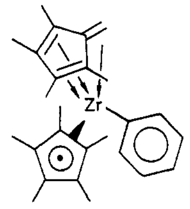


Figure 1. Perspective ORTEP drawing of the molecular structure of $[\eta^5\text{-}(CH_3)_5C_5]Zr(C_6H_5)[\eta^6\text{-}(CH_3)_4C_5CH_2]$ (2). The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement, and the hydrogen atoms have been omitted for the sake of clarity.



2a



2b

Molecular Structure of $[\eta^5\text{-}(CH_3)_5C_5]Zr(C_6H_5)[\eta^6\text{-}(CH_3)_4C_5CH_2]$ (2). The structural analysis reveals that crystals of 2 are composed of discrete, mononuclear $Cp'Zr(Ph)(\eta^6\text{-}Me_4C_5CH_2)$ molecules as shown in Figures 1 and 2. The atom-labeling scheme is given in Figure 1. Final atomic coordinates and anisotropic displacement parameters for non-hydrogen atoms of 2 are given in Tables II and III,[17] respectively, while bond lengths and angles involving non-hydrogen atoms of 2 are given in Tables IV and V, respectively.

As can be seen in Figures 1 and 2, the molecular structure of 2 is derived from a Cp_2MX_2, Cp'_2MX_2 "bent-sandwich" geometry,[1,21] with metalation of one Cp′ methyl group. The ligation of the nonfunctionalized Cp′ ligand is unexceptional. As can be seen in Table VI, the present Zr–ring centroid distance of 2.237 Å compares favorably with those of other relevant $Zr^{IV}Cp'$ complexes (as well as $Zr^{IV}Cp$ complexes).[22-36] The average Zr–C(Cp′)

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

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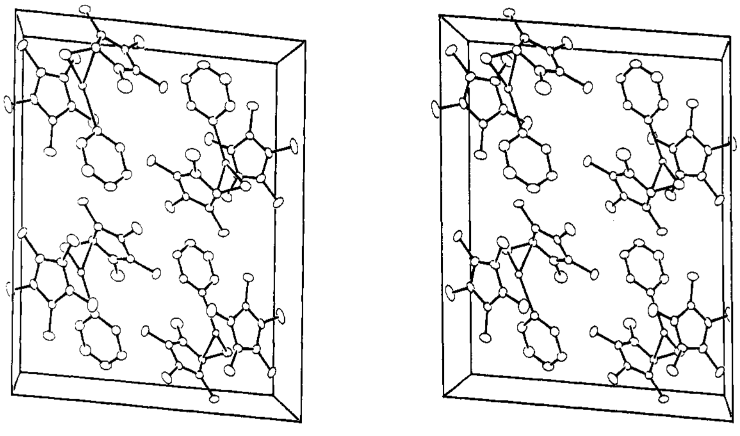

Figure 2. Stereoview of the unit cell of $[\eta^5\text{-}(CH_3)_5C_5]Zr(C_6H_5)[\eta^6\text{-}(CH_3)_4C_5CH_2]$ (**2**).

Table II. Positional Parameters and Equivalent *B* Values for Atoms of Cp′Zr(Ph)(MeC_5CH_2) (2)[a]

atom	x	y	z	B_{eq}, Å^2
Zr	0.23294 (4)	0.45809 (7)	0.32625 (3)	2.726 (7)
C(1)	0.2759 (5)	0.6213 (7)	0.4169 (4)	3.7 (1)
C(2)	0.3544 (5)	0.6352 (8)	0.3686 (4)	4.5 (1)
C(3)	0.4150 (4)	0.5182 (9)	0.3773 (4)	4.4 (2)
C(4)	0.3789 (4)	0.4292 (7)	0.4319 (3)	3.5 (1)
C(5)	0.2939 (5)	0.4938 (7)	0.4579 (3)	3.4 (1)
C(6)	0.0634 (4)	0.3639 (8)	0.2813 (4)	3.9 (1)
C(7)	0.1298 (4)	0.3040 (7)	0.2337 (3)	3.3 (1)
C(8)	0.1939 (5)	0.2149 (7)	0.2792 (4)	3.5 (1)
C(9)	0.1654 (5)	0.2181 (8)	0.3540 (4)	4.0 (1)
C(10)	0.0856 (5)	0.3111 (8)	0.3559 (4)	4.4 (1)
C(11)	0.1738 (6)	0.6570 (9)	0.3891 (4)	4.9 (2)
C(12)	0.3728 (8)	0.761 (1)	0.3206 (6)	7.6 (2)
C(13)	0.5112 (5)	0.497 (1)	0.3419 (5)	7.8 (3)
C(14)	0.4317 (6)	0.303 (1)	0.4649 (5)	6.3 (2)
C(15)	0.2371 (5)	0.446 (1)	0.5237 (3)	5.2 (2)
C(16)	−0.0229 (5)	0.460 (1)	0.2573 (6)	7.3 (2)
C(17)	0.1208 (6)	0.312 (1)	0.1478 (4)	5.6 (2)
C(18)	0.2740 (6)	0.1264 (9)	0.2497 (6)	6.2 (2)
C(19)	0.2036 (7)	0.119 (1)	0.4162 (5)	6.4 (2)
C(20)	0.0210 (5)	0.333 (1)	0.4213 (5)	7.4 (2)
C(21)	0.2854 (4)	0.5182 (8)	0.2108 (4)	3.8 (1)
C(22)	0.2310 (6)	0.623 (1)	0.1703 (5)	5.1 (2)
C(23)	0.2525 (7)	0.670 (1)	0.1002 (5)	6.2 (2)
C(24)	0.3294 (7)	0.614 (1)	0.0660 (4)	6.4 (2)
C(25)	0.3862 (6)	0.512 (1)	0.1029 (4)	5.4 (2)
C(26)	0.3636 (5)	0.465 (1)	0.1733 (4)	4.4 (1)

[a] The equivalent displacement parameter is defined as $^4/_3\mathrm{Tr}(\beta\cdot G)$, where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

Table IV. Bond Lengths (Å) in Cp′Zr(Ph)($Me_4C_5CH_2$) (2)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist
Zr	C(1)	2.282 (5)	C(3)	C(13)	1.505 (8)
Zr	C(2)	2.444 (6)	C(4)	C(5)	1.421 (7)
Zr	C(3)	2.617 (6)	C(4)	C(14)	1.503 (9)
Zr	C(4)	2.610 (5)	C(5)	C(15)	1.517 (8)
Zr	C(5)	2.418 (6)	C(6)	C(7)	1.407 (8)
Zr	C(6)	2.533 (5)	C(6)	C(10)	1.417 (9)
Zr	C(7)	2.536 (6)	C(6)	C(16)	1.523 (9)
Zr	C(8)	2.529 (5)	C(7)	C(8)	1.420 (8)
Zr	C(9)	2.553 (6)	C(7)	C(17)	1.510 (8)
Zr	C(10)	2.541 (6)	C(8)	C(9)	1.403 (8)
Zr	C(11)	2.388 (7)	C(8)	C(18)	1.508 (8)
Zr	C(21)	2.285 (5)	C(9)	C(10)	1.408 (9)
Zr	Cg	2.165	C(9)	C(19)	1.509 (9)
Zr	Cg′	2.237	C(10)	C(20)	1.521 (8)
C(1)	C(2)	1.423 (8)	C(21)	C(22)	1.408 (10)
C(1)	C(5)	1.437 (9)	C(21)	C(26)	1.393 (8)
C(1)	C(11)	1.468 (9)	C(22)	C(23)	1.370 (10)
C(2)	C(3)	1.398 (10)	C(23)	C(24)	1.358 (12)
C(2)	C(12)	1.512 (10)	C(24)	C(25)	1.382 (12)
C(3)	C(4)	1.408 (8)	C(25)	C(26)	1.377 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Cg and Cg′ are the centroids of the rings composed of atoms C(1) to C(5) and of atoms C(6) to C(10), respectively.

distance of 2.538 (6, 7, 15, 5)[37] Å in **2** also compares favorably with literature $Zr^{IV}Cp'$ and $Zr^{IV}Cp$ data where available (Table VI). As noted before,[24b] such metal–ring distances appear surprisingly to be slightly *longer* than analogous $Zr^{II}Cp'$ and $Zr^{II}Cp$ parameters (Table VI). This has been attributed to population in the d^2 system of molecular orbitals with metal–ring bonding character.[34b] The internal C–C distances of the η^5-Cp′ ligand in **2** (C–C = 1.411 (9, 6, 9, 5) Å (average); C–C(methyl) = 1.514 (9, 6, 8, 5) Å (average)) are essentially identical with those reported for numerous group 4 and f-element η^5-Cp′ complexes.[1,7a,b,35,36] The phenyl group coordination in **2** is also unexceptional, with Zr–C(21) = 2.285 (5) Å, comparable to other Zr(IV)–C(sp^2) distances or Zr(IV)–C(sp^3) distances corrected for differences in carbon covalent radius[38a] except

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(37) The first number in parentheses following an averaged value of a bond length or angle is the estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

Table V. Selected Bond Angles (deg) in $Cp'Zr(Ph)(Me_4C_5CH_2)$ (2)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(1)	Zr	C(11)	36.6 (2)	C(4)	C(5)	C(15)	126.5 (6)
C(1)	Zr	C(21)	111.5 (2)	C(7)	C(6)	C(10)	108.1 (5)
C(1)	Zr	Cg	31.8	C(7)	C(6)	C(16)	126.8 (7)
C(1)	Zr	Cg′	141.6	C(10)	C(6)	C(16)	125.0 (7)
C(11)	Zr	C(21)	110.5 (2)	C(6)	C(7)	C(8)	107.7 (5)
C(11)	Zr	Cg	68.3	C(6)	C(7)	C(17)	125.1 (5)
C(11)	Zr	Cg′	118.0	C(8)	C(7)	C(17)	126.3 (6)
C(21)	Zr	Cg	105.5	C(7)	C(8)	C(9)	108.2 (5)
C(21)	Zr	Cg′	104.8	C(7)	C(8)	C(18)	124.8 (6)
C(2)	C(1)	C(5)	106.2 (5)	C(9)	C(8)	C(18)	126.8 (7)
C(2)	C(1)	C(11)	120.6 (6)	C(8)	C(9)	C(10)	108.1 (5)
C(5)	C(1)	C(11)	118.8 (5)	C(8)	C(9)	C(19)	124.2 (7)
C(1)	C(2)	C(3)	108.7 (6)	C(10)	C(9)	C(19)	126.9 (6)
C(1)	C(2)	C(12)	125.3 (7)	C(6)	C(10)	C(9)	108.0 (5)
C(3)	C(2)	C(12)	125.9 (7)	C(6)	C(10)	C(20)	124.2 (6)
C(2)	C(3)	C(4)	109.4 (5)	C(9)	C(10)	C(20)	126.9 (7)
C(2)	C(3)	C(13)	125.8 (7)	C(22)	C(21)	C(26)	114.1 (5)
C(4)	C(3)	C(13)	124.4 (7)	C(21)	C(22)	C(23)	123.5 (7)
C(3)	C(4)	C(5)	107.0 (6)	C(22)	C(23)	C(24)	119.9 (8)
C(3)	C(4)	C(14)	125.2 (6)	C(23)	C(24)	C(25)	119.4 (7)
C(5)	C(4)	C(14)	127.0 (6)	C(24)	C(25)	C(26)	120.0 (7)
C(1)	C(5)	C(4)	108.7 (5)	C(21)	C(26)	C(25)	123.0 (7)
C(1)	C(5)	C(15)	124.7 (6)				
Cg	Zr	Cg′	143.6				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Cg and Cg′ are the centroids of the rings composed of atoms C(1) to C(5) and of atoms C(6) to C(10), respectively.

Table VI. Comparison of Structural Parameters in Compounds Related to $Cp'Zr(Ph)(C_5Me_4CH_2)$ (2)

compd	Zr–C(σ), Å	Zr–C(ring)(av), Å	Zr–Cg, Å	Cg–Zr–Cg, deg	X–Zr–X, deg	ref
$Cp'Zr(Ph)(\eta^6\text{-}Me_4C_5CH_2)$ (2)	2.388 (7) (C11)	2.538 (6)	2.237	143.6 (3)	10.5 (2)	this work
	2.285 (5) (C21)					
Cp_2ZrMe_2	2.273 (5)	2.525 (12)	2.23	132.5	95.6 (12)	22
	2.280 (5)					
$Cp_2Zr(Ph)[CH(SiMe_3)_2]$	2.324 (7) (Ph)	2.542[a]		126.9	104.4	23
	2.329 (6)					
$Cp_2Zr[CH_2C(CH_3)_3]_2$	2.294 (8)	2.51 (2)	2.25	128.3	89.9 (4)	24
$Cp_2Zr[CH_2Si(CH_3)_3]_2$	2.278 (4)	2.53 (3)	2.24	129.9	97.8 (1)	24
	2.281 (4)	2.52 (2)	2.23			
$Cp_2Zr(CHPh_2)_2$	2.379 (6)	2.513 (15)	2.22	128.2	95.5 (4)	25
	2.396 (6)					
$Cp_2Zr(CH_2PPh_2)_2$	2.284 (8)				100.2 (3)	26
	2.340 (9)					
$Cp_2Zr[\eta^4\text{-}CH_2C(CH_3)C(CH_3)CH_2]$	2.300 (3)	2.560 (5)		123.9		27
$Cp_2ZrC(H){=}C(Ph)C(Ph){=}CH$	2.293 (2)	2.545 (2)		125.4		28
	2.285 (2)					
$Cp'_2Zr(py)(C,O\text{-}\eta^2\text{-}H_2C{=}CO)$	2.181 (2)		2.278[a]	138.8		29
$Cp'_2ZrOCH{=}C[Zr(I)Cp_2]O$	2.268 (10)		2.220[a] (Cp)	128.9	100.1 (3)	30
			2.254 (Cp′)	136.9	76.9 (3)[b]	
$Cp_2(PMe_3)Zr{=}CHOZr(I)Cp'_2$			2.22[a] (Cp)	135.4	95.0 (2)	30
			2.282[a] (Cp′)	134.0	95.8 (1)	
$Cp_2W{=}CHOZr(H)Cp'_2$		2.50–2.58	2.24[a] (3)	138.3 (4)		31
$Cp_3Zr(\eta^1\text{-}Cp)$	2.447 (6)	2.58 (3)		117[a]		32
$(C_9H_7)_2ZrMe_2$	2.251 (6)	2.548		120.8 (5)	96.9 (3)	33
$Cp'_2Zr(CO)_2$	2.145 (9)	2.498 (9)	2.20	147.4	86.3 (5)	34a
$Cp_2Zr(CO)_2$	2.187 (4)	2.48 (2)	2.184	143.4	89.2 (2)	34b
$(Cp'_2ZrN_2)_2N_2$		2.54 (3)	2.232 (3)	141.3 (3)	87.1 (8)	35
$(Cp'Ti)_2[\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)](\mu\text{-}O)_2$		2.420 (6)[a]	2.150[a] (Cp′)	140.6		36
	2.178 (6)	2.416 (5)	2.100			

[a] The average was calculated from two values given in the reference. [b] Chelating ligand.

in cases which appear to be crowded (Table VI). The unsymmetrical orientation of the phenyl ligand with respect to the magnetically anisotropic Cp′ and η^6-$Me_4C_5CH_2$ ligands plausibly explains the nonequivalence of the phenyl ring edges and the unusual chemical shift of one ortho hydrogen atom. Thus, the phenyl ring is tipped slightly away from C(11) so that one β atom, C(22), is closest to C(7) (3.586 Å)[38b] of the Cp′ ring and to the methyl carbon atoms, C(17) (3.355 Å) and C(12) (3.407 Å), while the other β-carbon atom, C(26), is closest to the methyl groups C(13) (3.449 Å) and C(17) (3.599 Å) and is greater than 3.6 Å from any other carbon atom. This environment also explains the very large barrier to rotation of the phenyl ring (vide infra).

Perhaps the most unusual feature of the molecular structure of 2 is the coordination of the $Me_4C_5CH_2$ ligand. Atom C(11) (Figure 1) is displaced 0.925 (8) Å or 39° from the mean plane of atoms C(2)–C(5) and 0.885 (8) Å or 37° from the C(1)–C(5) mean plane. The Zr–C(11) distance

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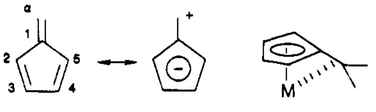
[38] (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224. (b) The van der Waals radius of a methyl group is 2.0 Å and that of a carbon atom, 1.7 Å (ref 38a, p 260).

of 2.388 (7) Å is long but not unprecedented for a Zr–C(sp^3) bond (Table VI). The Zr–C(1) distance of 2.282 (5) Å is shorter than Zr–C(11) and also shorter than Zr–C(Cp′) (2.538 (6, 7, 15, 5) Å (average)). Atom C(1) is displaced 0.041 (7) Å from the C(2)–C(5) mean plane in the direction of the Zr ion. Also, Zr–C(2) (2.444 (6) Å) and Zr–C(5) (2.418 (6) Å) are significantly shorter than the average Zr–C(Cp′), while Zr–C(3) (2.617 (6) Å) and Zr–C(4) (2.610 (5) Å) are significantly longer. The net result is a slipping of the Zr ion toward the C(11), C(1), C(2), C(5) portion of the ring. Within the C(1)–C(5) ring, the C–C distances do not differ significantly (3σ) from each other nor from those in the Cp′ ligand. The C(1)–C(11) distance of 1.468 (9) Å is shorter than the average C–C(methyl) distance by 0.044 (9) Å. The displacements of methyl groups out of the Cp′ and η^6-C_5 ring planes are in the range 0.043–0.253 (9) Å—not exceptional for a Cp′ complex.[1,7a,b,35,36]

The disposition of ligands in the coordination sphere of **2** is unusual for a Cp'_2MX_2 complex. The present ring centroid–Zr–ring centroid angle of 143.6 (3)° is significantly larger than values in the 134–139° range commonly observed for Cp'_2Zr^{IV} complexes (Table VI). However, it is smaller than the value of 147.4° in $Cp'_2Zr(CO)_2$.[34a] The C(11)–Zr–C(21) angle of 110.5 (2)° in **2** is larger than X–M–X values of 88–110° commonly found for d^0 Cp_2MX_2 compounds[21] and ca. 95° commonly found for the limited number of d^0 Cp'_2ZrX_2 compounds for which data are available and which have two nonchelating, σ-bonding ligands. Analogous angles for d^2 Cp_2Zr^{II} and Cp'_2Zr^{II} complexes are in the 86–89° range (Table VI).

The question[3a,36] of whether the Zr(η^6-$Me_4C_5CH_2$) interaction in **2** is best described as a formally Zr(II) fulvene complex (idealized as I and **2b**) or as a ring-metalated formally Zr(IV) σ,η^5 complex (idealized as II) must, from a structural perspective, be qualified in several ways. Before it can be asked whether a Zr complex adheres to a diene/olefin bonding picture (I), it must be asked whether other "fulvene complexes" do (are there credible model compounds?). Secondly, the degree to which existing Zr "diene complexes" adhere to structure I must also be scrutinized.

A substantial data base of "fulvene complex" structure determinations now exists; many were undertaken with reference to bonding questions in α-metallocenyl carbenium ions.[39,40] An important bonding consideration is that resonance-stabilized zwiterionic canonical forms make an important contribution to the structure of free fulvenes (III, IV).[41–43] Representative group 6 and group 7 struc-



III IV V

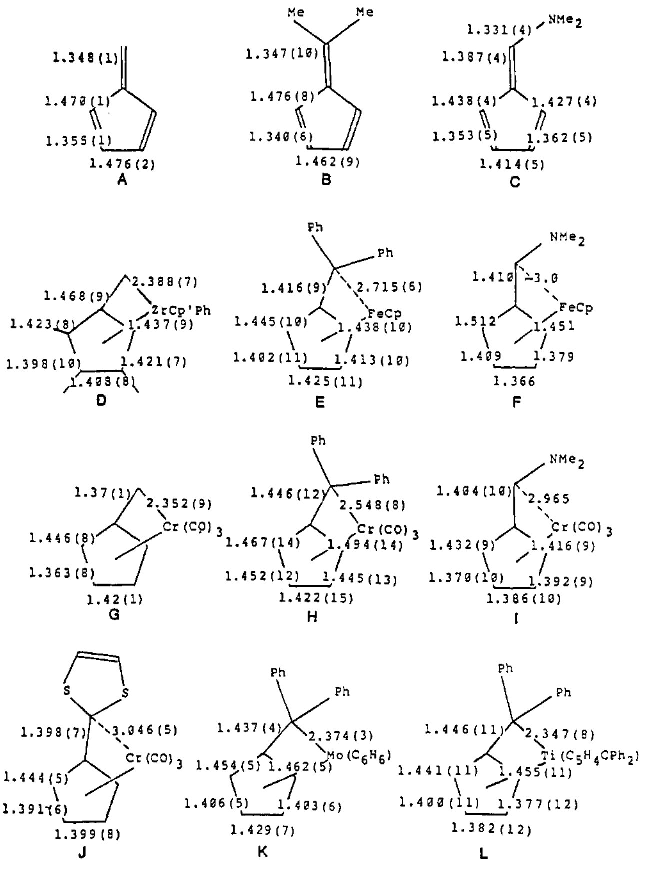


Figure 3. Carbon–carbon and metal–carbon bond distances for fulvenes and transition-metal fulvene complexes. Standard deviations are indicated where available. Given below are references and the angle, θ, by which the C(1)–C(α) vector is bent from the C_5 plane (90° = parallel to the ring normal): A, ref 41a; B, ref 42a; C, ref 43; D, this work, θ = 37°; E, ref 44a, θ = 20.7°; F, ref 39d, $\theta \approx$ 0°; G, ref 45, θ = 35°; H, ref 46, θ = 28.9°; I, ref 47, θ = 10°; J, ref 45b, θ = 6°; K, ref 40e, θ = 38°; L, ref 40e, θ = 36, 37°.

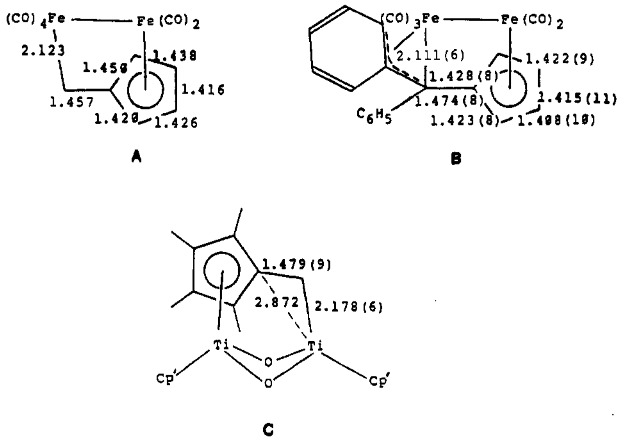


Figure 4. Carbon–carbon and metal–carbon bond distances for binuclear transition-metal fulvene complexes. Standard deviations are indicated where available. Given below are references and the angle, θ, by which the C(1)–C(α) vector is bent from the C5 plane: A, ref 49; B, ref 50; C, ref 37, θ = 8.7°.

tural results and a highly C(α)-functionalized Ti result are shown in Figure 3[40e,44–48] along with those for several free

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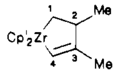
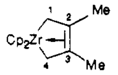
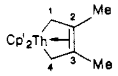
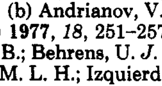
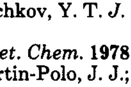
Table VII. Chemical Shifts and Coupling Constants for Specified Groups in Some Fulvene Molecules, Fulvene Complexes, and Zirconium Complexes

compd	atom	$\delta(^1H)$	$^2J_{HH}$	$\delta(^{13}C)$	$^1J_{CH}$	ref
		2.07				this work
$Cp'Zr(Ph)(Me_4C_5CH_2)$ (2)	C(α)	2.24	6.59	63.53	144.8	
Cp'_2ZrMe_2	C(Me)	−0.62		36.2		57
	C(1)	−0.17				
		1.35		57.7	119	58
	C(2)	2.51		41.6	127	
	C(3)			151.3		
	C(4)	5.49		184.3	128	
	C(1), C(4)			55.5	140	59
	C(2), C(3)			120		
$C_5H_4CH_2$	C(α)	5.85		123.4	160	60
$C_5H_4CMe_2$	C(α)			149.3		45b
$Cp'Ti(Me)(Me_4C_5CH_2)$	C(α)		4.0	73.9	150	3a
$(Cp'Ti)_2[\mu\text{-}(\eta^1{:}\eta^5\text{-}Me_4C_5CH_2)](\mu\text{-}O)_2$	C(α)			50.4		37
$CpTi[Me_3C_5(CH_2)_2]$	C(α)	0.90	4.4	67.64	160	1c
$[CpFe(C_5H_4CH_2)]^+$	C(α)	5.95		86.8	165	61, 62, 63
$[CpFe(C_5H_4CHPh)]^+$	C(α)	8.09		121.5	160	61, 63
$[CpFe(C_5H_4CMe_2)]^+$	C(α)			158.6		62
$(CO)_3Cr(C_5H_4CH_2)$	C(α)	3.97		73.7		45
$(CO)_3Cr(C_5H_4CMe_2)$	C(α)			121.2		45b
$(CO)_3Cr(C_5H_4CPh_2)$	C(α)			128.1		45b
	C(1), C(4)	1.15		77.8	133	64
$Ti(C_5H_4CPh_2)_2$	C(α)			132.1		40e

ligands. Related binuclear structures are shown in Figure 4.[36,49,50] The bonding can be understood in terms of hybrid IV, in which the metal–C(α) interaction is enhanced by donation from metal d orbitals into the empty ligand π^* orbital localized principally on C(α) (V). Structure I becomes less important as the donation increases. Bending of the C(1)–C(α) vector from the C_5 plane by angles as large as 35° is common. Furthermore, π-donor substituents on C(α) decrease this angle and increase the M–C(α) bond length, as expected. Bond alternation in the "diene" fragment of most structures in Figure 3 is not statistically significant nor are there clear-cut patterns. It is noteworthy that some of the strongest evidence for bond alternation is in (η^6-$C_5H_4CH_2$)$Cr(CO)_3$ (Figure 3G), in which substituents that might stabilize structure IV are absent. As a point of reference, [C(1)–C(2), C(3)–C(4)]–[C(2)–C(3)] averages 0.021 (2) Å in 13 precise (diene)$Fe(CO)_3$ structures (VI).[51,52] It can also be seen in Figure 3 that intra-ring distances C(1)–C(2) and C(1)–C(5) are probably slightly longer than C(2)–C(3), C(3)–C(4), and C(4)–C(5). The C(1)–C(α) distances generally fall in the 1.37–1.42-Å range but appear to be perturbed by bulky phenyl substituents. These results indicate that rigorous planarity of the fulvene ligand and extensive bond alternation in the diene portion of the fulvene ligand, as implied literally by I, are not observed in typical mononuclear fulvene complexes.


VI


VII

An extensive data base of Cp_2Zr(diene) structures also exists.[27,28,53,54] For reasons that are both electronic and steric in origin, these are best described as σ^2,π-metallacyclopentenes (VII).[53a,55] These structures exhibit more pronounced bond alternation than the aforementioned (diene)$Fe(CO)_3$ complexes, i.e., [C(1)–C(2), C(3)–C(4)]–[C(2)–C(3)] ≈ 0.05 Å, and have shorter contacts to the outer than to the inner diene carbon atoms, i.e., [Zr–C(2), Zr–C(3)]–[Zr–C(1), Zr–C(4)] = 0.23–0.46 Å, vs. a corresponding value of −0.08 (11) Å for VI.[51] The closest approach to η^4 coordination is found in (dmpe)Hf(η^4-butadiene)$_2$.[56] For the four independent butadiene ligands, [C(1)–C(2), C(3)–C(4)]–[C(2)–C(3)] = 0.054 (7) Å and [Hf–C(2), Hf–C(3)–[Hf–C(1), Hf–C(4)] = 0.035 (6) Å. Shortening of the central C–C bond and shorter metal–C(terminal) bond distances still prevail. Clearly, there are no examples where zirconium is bound to a diene fragment in the classical manner of structures I and VI.

It can thus be seen that no mononuclear transition-metal complex conforms closely to structure I, and there is no reason to believe that electropositive Zr(II) is more likely to than any other transition metal. We can, however,

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Table VIII. First-Order Rate Constants for the Thermolysis of Cp'_2ZrPh_2 (1) and $Cp'_2Zr(C_6D_5)_2$ (1-d)[a]

temp, °C	solv	rate constants ($s^{-1} \times 10^4$) 1	1-d
50	toluene-d_8	0.112 (11)	0.0159 (10)
60	toluene-d_8	0.35 (3)	
60	C_6D_{12}	0.35 (3)	0.036 (3)
65	C_6D_6	0.51 (3)	
75	toluene-d_8	1.58 (13)	
80	toluene-d_8		0.33 (2)
82	toluene-d_8	2.67 (12)	
90	toluene-d_8	5.6 (6)	1.56 (8)
104	toluene-d_8	21.2 (12)	

[a] k_H/k_D = 13.5 (20) at 25 °C and 6.5 (10) at 70 °C.

inquire whether 2 may have more or less I character than middle transition-metal "fulvene complexes". As is already evident, arguments based upon C_5 ring alternation, η^6 ring planarity, or Zr(II)/Zr(IV) characteristics (Cp′–Zr distance, ring centroid–Zr–ring centroid angle, C11–Zr–C21 angle) are not without ambiguity. However, while C(α) in I may have significant sp^2 character, the hybridization in II should closely correspond to sp^3. The 1.468 (9)-Å C(1)–C(11) bond length in 2 approaches a C(sp^2)–C(sp^3) distance (1.514 (9) Å for C(Cp′)–C(CH_3)) and, with the possible exception of the highly C(α)-functionalized Ti complex in Figure 3L, appears to be significantly longer than the corresponding distances in other mononuclear fulvene complexes. Interestingly, it is comparable to that in binuclear complexes (Figure 4) where description I seems less appropriate. We suggest that 2 has less π "fulvene complex" character than the middle transition-metal complexes of Figure 3.

NMR Data for 2. Structure/Bonding Implications. Structurally diagnostic NMR parameters for 2 are compared to those of various model complexes in Table VII.[1c,36,46,57-64] From the standpoint of the I ↔ II description, the parameters $\delta(^{13}C(\alpha))$ (in a closely related series) and $^1J_{^{13}C(\alpha)-H}$ should be structurally most informative. Upon complexation, olefinic carbon atoms generally exhibit a substantial upfield chemical shift but little change in $^1J_{^{13}C-H}$.[64,65] The fulvene complexes of chromium and iron conform to this trend (Table VII). In addition, a linear relationship exists in the $(C_5H_4CR_2)Cr(CO)_3$ series between the Cr–C(α) distance and the upfield displacement of $\delta(^{13}C(\alpha))$.[45b] In comparison, $\delta(^{13}C(\alpha))$ for 2 occurs at higher field and falls in the region of σ-bonded Zr–C(sp^3)–C data, in agreement with the Zr–C(11) and C(1)–C(11) metrical parameters. In addition, the magnitude of $^1J_{^{13}C(\alpha)-H}$ is below the values for later transition-metal fulvene complexes, suggesting greater C(α) sp^3 character. Indeed, both $\delta(^{13}C(\alpha))$ and $^1J_{^{13}C(\alpha)-H}$ are rather close to parameters for σ^2,π-butenediyl Cp'_2Zr(butadiene) complexes.[53-55]

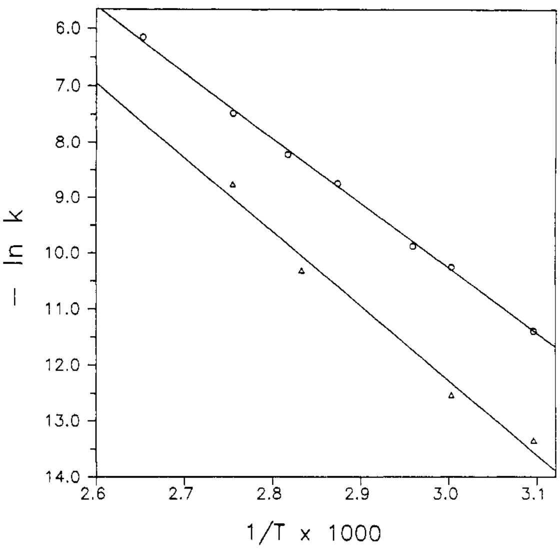

Figure 5. Arrhenius plots for the thermolysis processes 1 → 2 (circles) and 1-d → 2-d (triangles).

Thermolytic Pathway from 1 to 2. Kinetics and Mechanism. As monitored by ^1H NMR, compound 1 undergoes thermolysis to yield 2 quantitatively (eq 1).

$$\underset{1}{Cp'_2Zr(C_6H_5)_2} \xrightarrow[\Delta]{} \underset{2}{Cp'Zr(C_6H_5)(\eta^6\text{-}Me_4C_5CH_2)} + C_6H_6 \qquad (1)$$

The 1 → 2 conversion is first order in 1 over greater than 3 half-lives and identical in C_6D_6, C_6D_{12}, and toluene-d_8 (Table VIII). Kinetic studies as a function of temperature (Figure 5) yield the activation parameters: E_a = 23.1 (3) kcal mol^{-1}, log A = 10.7 (2), $\Delta H^\ddagger$ = 22.5 (3) kcal mol^{-1}, and $\Delta S^\ddagger$ = −11.8 (3) eu. The derived $\Delta S^\ddagger$ suggests some loss of rotational degrees of freedom on approaching the transition state (not without precedent[7b,8b]). These data are compared to data for similar group 4 and organoactinide reactions in Table IX. At 70 °C, the rate of 1 → 2 is more rapid than the thermolysis of Cp_2MR_2 group 4 diaryls but considerably slower than that of Cp_2UPh_2.

In regard to the pathway of hydrogen atom transfer, thermolysis of $Cp'_2Zr(C_6D_5)_2$ (1-d) in cyclohexane yields only $Cp'Zr(C_6D_4H)(C_5Me_4CH_2)$ (2-d, by ^1H NMR) and C_6D_6 (≥99% d_6 by GC/MS). The single phenyl proton of 2-d is distributed over both magnetically nonequivalent ortho positions. Likewise, thermolysis of $Cp'_2Zr(C_6H_5)_2$ in toluene-d_8, C_6D_6, or C_6D_{12} yields only $Cp'Zr(C_6H_5)(C_5Me_4CH_2)$ (by ^1H NMR) and benzene (≥99% C_6H_6 by GC/MS). Comparison of kinetic data for 1 and 1-d reveals a substantial kinetic isotope effect, k_H/k_D = 13.5 (20) at 25 °C and 6.5 (10) at 70 °C. Hence, aryl rather than Cp′ methyl C–H bond scission is rate-limiting. The magnitude of k_H/k_D, which suggests a symmetrical transition state with possible tunneling contributions,[67] is not unprecedented for metal-centered C–H activation.[7b] Temperature dependence of the kinetic isotope effect yields the parameters $[\Delta E_a]_H^D$ = 3.4 (7) and A_H/A_D = 0.050 (8). While these values tend toward the far end of the range generally observed for hydrogen atom transfer reactions, they are not unprecedented and also suggest a symmetrical transition state with possible tunneling.[67]

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Table IX. Activation Parameters and Rate Constants (at 70 °C) for the Thermolysis of Cp'_2ZrPh_2 (1) and Related Compounds

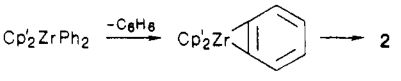
compd	E_a, kcal/mol	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	$\Delta G^\ddagger_{25°C}$, kcal/mol	$10^4 k_{70°C}$, s^{-1}	ref
Cp'_2ZrPh_2 (1)	23.1 (3)[a]	22.5 (3)[a]	−11.8 (3)[a]	26.0 (4)[a]	0.92	this work
$Cp'_2Zr(C_6D_5)_2$ (**1-d**)	26.5 (4)[a]	25.8 (4)[a]	−5.8 (15)[a]	27.5 (8)[a]		this work
Cp_2ZrPh_2					0.30	2f
Cp_2Zr(*p*-tolyl)$_2$					0.28	2f
Cp_2Zr(*o*-tolyl)$_2$					0.42	2f
Cp_2TiPh_2	22	20.9[b]	1.0[b]	20.6[b]	0.62[b]	5c
$Cp_2Ti(Ph)Cl$	29	27.7[b]	4.0[b]	26.5[b]	1.15[b]	66
Cp'_2UPh_2					≳17	6
Cp'_2TiMe_2	28.36	27.6 (3)	−2.9 (7)	28.4	0.14[b]	3a
$Cp'_2Th[CH_2Si(CD_3)_3]_2$[c]		25.4 (13)	−14 (4)	29.6		7b
$Cp'_2Th[CH_2Si(CD_3)_3]_2$[d]		28.5 (11)	−3 (3)	29.4		7b

[a] Numbers in parentheses are confidence limits established as described in Experimental Section. [b] Calculated by using data given in the reference and the Eyring equation. [c] Thermolysis to $Cp'_2\overline{ThCH_2Si(CD_3)_2C}D_2$ via γ-H abstraction. [d] Thermolyses to $Cp'(C_5Me_4CH_2D)\text{-}\overline{ThCH_2Si(CD_3)_2C}D_2$ via ring H abstraction.

Verification that arene formation is intramolecular is provided by a crossover experiment involving a mixture of 1 and **1-d** (eq 2). Arene products that would be formed

$$Cp'_2Zr(C_6H_5)_2 + Cp'_2Zr(C_6D_5)_2 \rightarrow \mathbf{2} + C_6H_6 + \mathbf{2\text{-}d} + C_6D_6 + <1.5\%\ C_6D_5H + <2.5\%\ C_6H_5D \quad (2)$$

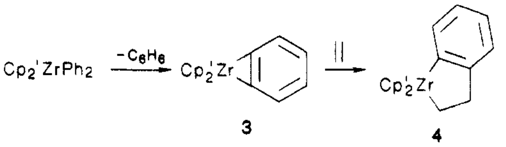
by an intermolecular abstraction reaction are present in only small quantities. The mechanistic data thus strongly implicate a benzyne/*o*-phenylene complex[5,6] as the initial thermolysis product of 1 (eq 3). Formation of 3 would then be followed by or occur in concert with ring methyl C–H transfer.



(3)

3

In the presence of excess ethylene, thermolysis of 1 does not yield 2, but rather a zirconaindan (4), as judged by the characteristic NMR spectral parameters.[5a,68] At both 60°

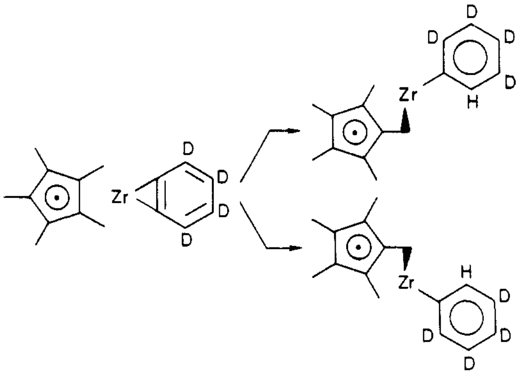


(4)

3 4

and 90°, the thermolysis of 1 in the presence of ethylene obeys good first-order kinetics with derived rate constants indistinguishable from those in the absence of ethylene (Table VIII). These results indicate that 4 does not arise from the direct reaction of 1 + ethylene but rather and plausibly, intermediate 3 is being intercepted after rate-limiting H transfer.[69a] Interestingly and unlike Cp'_2UPh_2[6] and group 4 Cp_2MPh_2 complexes,[5] 3 could not be trapped with diphenylacetylene under the same conditions (possibly for steric reasons), and careful NMR analysis gives no evidence for arene metathesis[6] during any of the kinetic runs.[69b] These results additionally imply that 2 is energetically "downhill" from 3 (and 1).

The isotopic labeling experiments for **1-d** → **2-d** also convey potential information on the regiochemistry of the 1 → 2 transformation. Concerted, regiospecific delivery of the Cp′ methyl hydrogen atom from either Cp′ ring as shown for the foreground ring in eq 5 should yield a single



(5)

pair of single pair of enantiomorphous isotopomers, identifiable via nonequivalence of the phenyl ortho positions in the NMR (a single ortho resonance would be observed).[70] Experimentally, however, it is found that two ortho product signals of equal intensity are observed in **2-d** during all stages of the thermolysis. A kinetic analysis shows that these signals grow in at rates which are experimentally indistinguishable and also indistinguishable from the rate of disappearance of **1-d**. One explanation is that hydrogen atom transfer does occur as portrayed in eq 5 but that rotation of the phenyl group about the Zr–C(22) bond or oscillation of the η^6-$Me_4C_5CH_2$ ligand about the ring centroid–Zr axis scrambles the two ortho hydrogen positions subsequent to formation of 2. Efforts to establish lower limits to the barriers of these processes via dynamic NMR studies of 2 (phenyl rotation identifiable by permutation of phenyl ortho protons; η^6 ring oscillation identifiable by simultaneous permutation of phenyl ortho and ring methylene protons) revealed negligible broadening of the signals in question up to 130 °C (toluene-d_8) at 270 MHz. Hence, we estimate that $\Delta G^\ddagger$[71] must be ≳24 kcal

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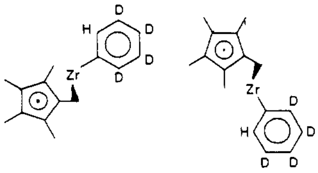
[68] (a) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45–60. (b) ^{1}H NMR (C_6D_6): δ 0.92 (t, 2 H, *J* = 7.6 Hz), 1.70 (s, 30 H), 3.19 (t, 2 H, *J* = 7.6 Hz), 6.54 (dd, 1 H, *J* = 6.6, 2.0 Hz), 6.95 (dd, 1 H, *J* = 7.3, 2.0 Hz), 7.03–7.07 (m, 2 H).

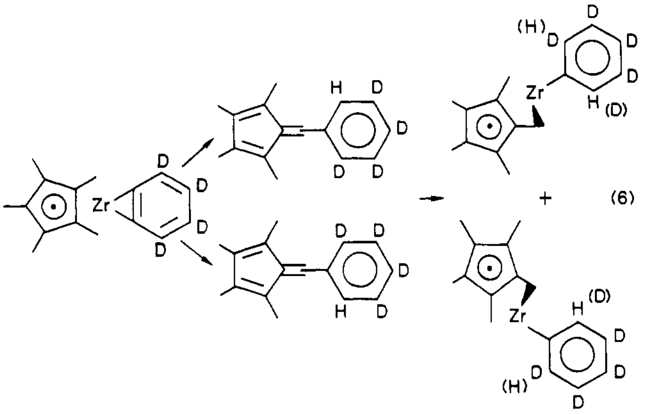
[69] (a) Interestingly, we find that 2 also reacts with ethylene to yield 4. Since direct 2 + ethylene → 4 conversion seems highly unlikely, we infer that 2 is in equilibrium with 3. Further discussion awaits kinetic and thermochemical studies. (b) This does not exclude the possibility of arene metathesis at higher temperatures or longer reaction times.

[70] As drawn, eq 5 portrays a 1:1 metathesis of Zr-C bonds in the plane bisecting the ring centroid–Zr–ring centroid angle. It is conceivable but less plausible that hydrogen atom transfer could yield the isotopomers with the opposite phenyl H/CH_2 relationship, i.e.

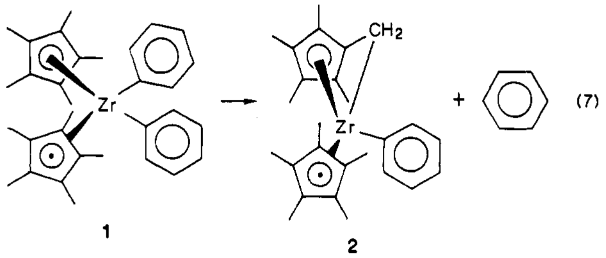


[71] (a) Binsch, G. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; Chapter 3. (b) Küspert, R. *J. Magn. Reson.* **1982**, *47*, 91–102 and references therein.

mol^{-1} for these processes. This barrier is comparable to that for the thermolysis of **1-d** (Table IX) so that phenyl ortho hydrogen atom scrambling could occur at rates comparable to, but not appreciably more rapid than, the formation of **2-d**. That the ^{1}H intensity in **2-d** is only distributed between the ortho positions upon thermolysis argues that the reverse of eq 5 coupled with phenyl rotation and/or η^6 ring oscillation is not important under the present thermolysis conditions. An alternative to eq 5 would be hydrogen atom transfer involving a symmetrical *o*-phenylene and fulvene intermediate (e.g., eq 6). This process would also give the observed label distribution.



Additional Comments. While the pathway from 1 to 2 is now relatively clear, the actual driving force for this reaction (and many analogous intramolecular C–H activating processes) is not. As shown below, the enthalpy of this transformation (eq 7) can be expressed in terms of the disruption enthalpies of bonds being made and broken. While the difference $D(RCH_2–H) - D(Ph–H)$ can be reasonably estimated as ca. −20 kcal mol^{-1} [72] and is likely a major contributor to ΔH_{rxn}, the presumably strained character of **2**[73] and what is likely crowding in 1 render the relevant Zr–C disruption enthalpies rather interesting. We are presently measuring zirconium–ligand bond disruption enthalpies in this and related systems; results will be reported in due course.



$$\Delta H_{rxn} = D(Zr\text{-}Ph) + D(RCH_2\text{-}H) - D(Ph\text{-}H) - D(Zr\ CH_2R)$$
$$R = Me_4C_5$$

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Registry No. 1, 79847-76-0; **1-d**, 105472-44-4; **2**, 105501-02-8; $Cp_2'ZrCl_2$, 54039-38-2; D_2, 7782-39-0.

Supplementary Material Available: Tables of anisotropic displacement parameters (*U* values) for non-H atoms (Table III) and positional parameters and isotropic displacement parameters (*B* values) for the fixed H atoms for compound 2 (2 pages); a table of structure factors for compound 2 (30 pages). Ordering information is given on any current masthead page.

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(72) Golden, D. M.; McMillen, D. F. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(73) We find the Zr–CH_2 linkage to be far more reactive toward H_2O and H_2 (to yield $Cp'_2Zr(OH)Ph$ and $Cp'_2Zr(H)Ph$, respectively) than the Zr–Ph linkage (Schock, L. E.; Marks, T. J., unpublished results).