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Structural and Chemical Features of Early Transition-Metal Compounds: Notable Differences between Corresponding Pairs of (*s*-*cis*-η^4-Conjugated diene)zirconocene and -hafnocene Complexes[†]

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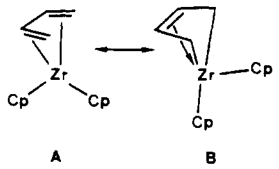
The crystal and molecular structures of (*s*-*cis*-2,3-dimethylbutadiene)hafnocene (**3b**), (1,2-bis(methylene)cyclohexane)zirconocene (**4a**), and (1,2-bis(methylene)cyclohexane)hafnocene (**4b**) have been determined from X-ray data. **3b** crystallizes in the orthorhombic space group *Pnma* with $a = 7.994$ (1) Å, $b = 11.741$ (1) Å, $c = 14.449$ (1) Å, $V = 1356.18$ Å^3, and $d_{calcd} = 1.914$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement of 82 parameters with 1403 unique observed reflections converged at $R = 0.030$. It is isostructural with the previously reported (*s*-*cis*-2,3-dimethylbutadiene)zirconocene complex (**3a**). **4a** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.506$ (1) Å, $b = 12.469$ (2) Å, $c = 12.803$ (1) Å, $\alpha = 104.77$ (1)°, $\beta = 103.083$ (7)°, $\gamma = 103.02$ (1)°, $V = 1506.77$ Å^3, and $d_{calcd} = 1.453$ g cm^{-3} for $Z = 4$. Refinement of 343 parameters based on 5184 reflections led to a final *R* of 0.033. **4b** crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.149$ (3) Å, $b = 8.600$ (1) Å, $c = 25.642$ (2) Å, $\beta = 101.732$ (9)°, $V = 3054.98$ Å^3, and $d_{calcd} = 1.813$ g cm^{-3} for $Z = 8$. Refinement of 343 parameters with 4778 reflections produced $R = 0.031$. In all three complexes the diene is η^4-bonded to the metallocene fragments with the metals in a ψ-tetrahedral coordination. The bonds of the diene termini to the metals are noticeably shorter than those of the internal C atoms of the dienes. The respective bond lengths (**3b**, 2.267 (5)–2.641 (5) Å; **4a**, 2.279 (2)–2635 (6) Å; **4b**, 2.255 (8)–2.72 (1) Å) are in a range typical for M–C σ and π bonds of the respective elements. Together with the other geometrical parameters of the diene–metallocene frameworks they allow the following generalizations: (a) (*s*-*cis*-η^4-diene)zirconocenes and -hafnocenes are best described as σ^2,π complexes, (b) the σ/π ratio in the metal–diene bonding is smaller for the zirconocene complexes than for their Hf analogues, (c) this ratio is smaller for **3b** than for **4b**, a trend which is similar in the previously reported (*s*-*cis*-η^4-2,3-dimethylbutadiene)zirconocene (**3a**) and **4a**, and (d), Zr–C bonds are slightly longer than their Hf counterparts. Differences in the chemical behavior of corresponding (*s*-*cis*-conjugated diene)zirconocene and -hafnocene complexes can be rationalized in view of their characteristic structural features.

Introduction

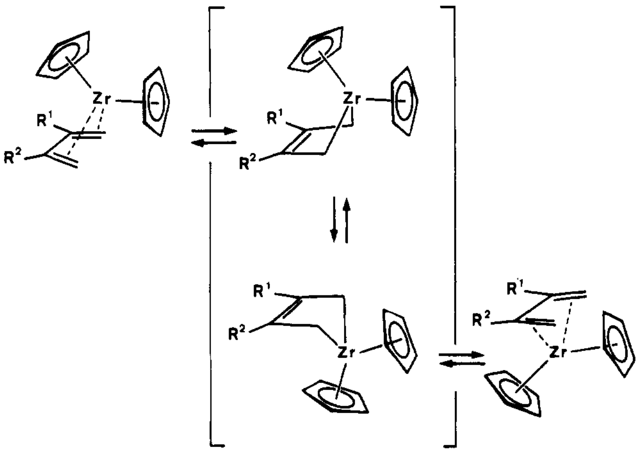
1,3-Butadiene complexes of early transition-metal fragments, especially zirconocene, have been shown to be distinctively different from those with late transition metals.[1-5] Not only that the unique bonding capabilities of the bent zirconocene fragment[6-8] led for the first time to the isolation and structural characterization of mononuclear complexes of *s*-*trans*-1,3-butadienes,[9-11] but also that marked differences with late transition-metal butadiene complexes could be inferred from reactivity patterns of the *s*-*cis*-η^4-1,3-butadiene complexes.[12] Structural results on a number of *s*-*cis*-η^4-2,3-substituted butadiene complexes of zirconocene (**1**, **3a**, **5**) obtained so far gave unequivocal proof of a σ^2,π mode of bonding (B) of the diene to the transition-metal fragment[9,13,14] (Scheme I).

Scheme I



This was evident from the highly asymmetric bonding of the butadiene, with the M–C bonds to the diene termini being shorter by up to 0.43 Å than those to the internal C atoms. The latter varied smoothly between 2.550 (5) and 2.714 (5) Å with different butadiene substituents thus approaching the limiting value of 2.855 (4) Å for the purely σ-bonded ligand in the zirconaindan **6a**.[14b] The different degree of σ vs. π bonding in (*s*-*cis*-η^4-butadiene)ZrCp$_2$ complexes followed also from their dynamic behavior and reactivity. Thus the rate of the automerization process depicted in Scheme II, as evident by dynamic NMR

Scheme II



[†] Dedicated to Professor Günther Wilke on the occasion of his 60th birthday

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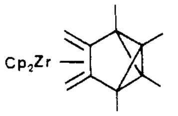
studies, could be directly correlated to the σ^2,π character as inferred from the structural studies. The fact that the lowest automerization barrier was found for the compounds with the longest Zr–C bonds to the internal butadiene atoms (i.e., the compounds with the largest σ vs. π ratio) pointed to a pronounced ground-state effect being responsible for the observed topomerization rates.[14a] Additional, although more indirect, proof could be obtained from reactivity patterns of *s-cis-* and *s-trans*-butadiene complexes of zirconocene.[12b,13] E.g., carbonyl insertion reactions into metal–carbon bonds, a typical reaction mode of (σ-alkyl) transition-metal complexes, were found to be increasingly favored with increasing σ character of the complexes.[13,14a]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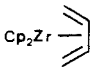
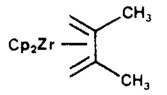
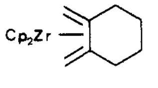
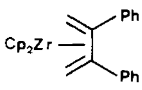
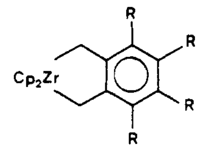

2a


3a


4a


5


6 R = H (a), CH_3 (b)

The close analogies between corresponding Zr and Hf compounds prompted us to extend these studies of structure and reactivity of the *s-cis*-butadiene complexes to those of hafnocene, where no structural data are available so far. We report here on the preparation and molecular structure of (*s-cis*-η^4-2,3-dimethylbutadiene)-$HfCp_2$ (**3b**) and (η^4-1,2-bis(methylene)cyclohexane)$HfCp_2$ (**4b**). The molecular structure of (η^4-1,2-bis(methylene)-cyclohexane)$ZrCp_2$ (**4a**) is included for comparison and to add further structural proof to the points discussed above. It was hoped that despite the expected gross overall similarities between organometallic compounds of Zr and Hf the subtle differences due to the much heavier Hf atom might give way for additional information about properties and reaction modes of this class of butadiene transition-metal complexes. Further impetus for this work came from the recent controversy about the assessment of the differences between Hf–C and Zr–C bond lengths.[15,16]

Table I. Selected ^{13}C NMR Data of Cp_2M(*s-cis*-$H_2C{=}CRCR{=}CH_2$) Complexes **2–4**[a]

compd	R	Cp	C1	C2	ref
2a (Zr)	*b*	102.0	49.6 (144)	112.0[c]	9, 10, 13
2b (Hf)	*b*	102.2	45.0 (140)	114.5[d]	19
3a (Zr)	24.0[e]	103.1	55.4 (140)	119.9	9, 10
3b (Hf)	23.8[e]	103.3	51.7 (136)	121.1	*g*
4a (Zr)	22.8, 33.7[f]	103.3	53.4 (139)	122.7	10, 13
4b (Hf)	23.2, 34.4[f]	104.3	49.4 (132)	124.1	*g*

[a] In benzene-d_6 at ambient temperature, chemical shifts relative to Me_4Si, δ scale, coupling constants ($^1J_{CH}$, Hz) in parentheses. [b] R = H. [c] $^1J_{CH}$ = 165 Hz. [d] $^1J_{CH}$ = 156 Hz. [e] R = CH_3. [f] R = CH_2CH_2. [g] This work.

Table II. ^1H NMR Chemical Shifts[a] of Cp_2M(*s-cis*-$H_2C{=}CRCR{=}CH_2$) Complexes **2–4**

compd	R	Cp	$=CH_2$	ref
2a (Zr)	4.7[b]	5.20	1.28	9, 10, 13
2b (Hf)	5.0[b]	5.20	1.10	19
3a (Zr)	1.89[c]	5.42	1.26	9, 10
3b (Hf)	1.88[c]	5.33	0.91	*e*
4a (Zr)	2.2, 1.7[d]	5.52	1.05	10, 13
4b (Hf)	2.3, 1.6[d]	5.43	0.90	*e*

[a] Limiting high-temperature spectra; **2a** (94 °C), **3a** (60 °C) in toluene-d_8, **2b**, **3b**, **4b** in benzene-d_6 at ambient temperature, **4a** (+4 °C) in $CHFCl_2$, relative Me_4Si, δ scale. [b] R = H. [c] R = CH_3. [d] R = $-CH_2CH_2-$. [e] This work.

Structural investigations on systems containing Zr–C or Hf–C σ and π bonds were expected to yield additional valuable reference material on the bonds in question and to allow further insight into the factors determining the bonding mode exhibited in these complexes. Preliminary data on the compounds described here have already been mentioned in a recent review article.[17]

Experimental Section

Organometallic compounds were handled in an argon atmosphere using Schlenk-type glassware. Solvents were purified by the usual procedures and distilled under argon before use. NMR spectra were obtained with either a Varian NV 14 (^1H, 60 MHz, variable temperature) or a Bruker WP-250 FT (^1H, 250 MHz; ^{13}C, 62.9 MHz) spectrometer. Melting points were measured with a Büchi-Tottoli apparatus and are not corrected. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr.

(*s-cis*-2,3-Dimethylbutadiene)zirconocene (**3a**) and (1,2-bis-(methylene)cyclohexane)$ZrCp_2$ (**4a**) have been prepared by photolysis of diphenylzirconocene in the presence of the conjugated dienes. Details of the workup and characterization of these complexes have been reported previously.[10,13] The thermodynamic mixture of *s-cis-* and (*s-trans*-η^4-butadiene)zirconocene has been obtained by reacting Cp_2ZrCl_2 with "(butadiene)magnesium"[18,19] according to the literature procedure.[10] Recrystallization from a 90/10 mixture tetrahydrofuran/benzene (2-mL solution, saturated at ambient temperature, containing about 500 mg of the mixture of the (butadiene)zirconocene isomers) yielded pure (*s-cis*-butadiene)$ZrCp_2$ (**2a**).

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Table III. A Comparison of Automerization Barriers $\Delta G^{\ddagger}{}_{T_c}{}^{a}$ between (*s-cis*-Conjugated diene)zirconocenes and -hafnocenes and Selected Zirconocene Complexes

compd	diene ligand	a (Zr)	b (Hf)	ref
1	tetramethylbis(methylene)tricyclo[3.1.0.0^{2,6}]hexane	14.3 (+11)		13
2	butadiene	12.6 (−19.5)	8.1 (−108)^{b}	17
3	2,3-dimethylbutadiene	11.5 (−42)	8.3 (−105)^{b}	17
4	1,2-bis(methylene)cyclohexane	10.8 (−57)	7.6 (−121)^{b}	17
5	2,3-diphenylbutadiene	8.0 (−112)		13
6b	tetramethylzirconaindan	6.5 (−140)		13

[a] From Cp coalescence, $\Delta G^{\ddagger}{}_{T_c}$ ± 0.3 kcal/mol, coalescence temperature (T_c) given in parentheses. [b] This work.

Table IV. Summary of Crystal Data, Intensity Data Collection, and Structure Refinement for 3a,b and 4a,b

	3a	3b	4a	4b
formula	$C_{16}H_{20}Zr$	$C_{16}H_{20}Hf$	$C_{18}H_{22}Zr$	$C_{18}H_{22}Hf$
M_r	303.6	390.83	329.60	416.87
space group	*Pnma*	*Pnma*	$P\bar{1}$	$P2_1/n$
a, Å	8.008 (1)	7.994 (1)	10.506 (1)	14.149 (3)
b, Å	11.725 (1)	11.741 (1)	12.469 (2)	8.600 (1)
c, Å	14.452 (1)	14.449 (1)	12.803 (1)	25.642 (2)
α, deg	90	90	104.77 (1)	90
β, deg	90	90	103.08 (1)	101.73 (1)
γ, deg	90	90	103.02 (1)	90
V, Å^3	1356.8	1356.18	1506.77	3054.98
Z	4	4	4	8
d_{calcd}, g/cm^3	1.486	1.914	1.453	1.813
μ_{calcd}, cm^{-1}	7.73	76.00	7.02	67.54
F(000), e	624	752	680	1616
T, °C	21	21	21	21
cryst dimens (max), mm	0.18 × 0.5 × 0.36	0.07 × 0.28 × 0.22	0.14 × 0.15 × 0.54	0.28 × 0.24 × 0.17
radiation	MoKα	MoKα (λ = 0.710 69 Å)	MoKα	MoKα
scan mode	θ-2θ	θ-2θ	θ-2θ	θ-2θ
scan range (θ)	1.0–30.0	1.4–27.4	1.7–27.3	1.5–27.3
hkl range	+12,+17,+21	$+\underline{1}1,+1\underline{6},\underline{+}18$	$\pm 1\underline{4},\pm 17,+\underline{18}$	$\underline{\pm 1}9,+\underline{12},+\underline{3}4$
std refl	600, 0,10,0, 0,0,12	060, $00\bar{8}$, $\bar{6}00$	$00\bar{8}$, 600, $\overline{282}$	$\bar{2}51$, $8\bar{1}7$, 2,−1,12
refl measd	2266	1611	6835	7490
refl unique	2266	1611	6803	6880
$R_{int}{}^{a}$			0.02	0.02
refl obsd ($I \geqslant 2.0\sigma(I)$)	1614	1403	5184	4778
param varied	124	82	343	343
av shift/esd (last cycle)	0.01	0.001	0.1	0.45
R^{b}	0.030	0.030	0.033	0.031
$R_w{}^{c}$	0.044	0.040	0.042	0.036
$\Delta\rho$(max), e/Å^3		1.53	0.58	0.68

[a] $R_{av} = \Sigma(I - \langle I \rangle)/\Sigma I$. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

(*s-cis*-Butadiene)hafnocene (2b). A 6.2-g (28-mmol) sample of "(butadiene)magnesium" and 9.7 g (25.5 mmol) of hafnocene dichloride were mixed in a dry Schlenk tube. Toluene (150 mL) was added slowly at −78 °C. The reaction mixture was allowed to warm up to room temperature and stirred at 25 °C for an additional 1 h. The mixture was filtered. The solvent was removed in vacuo to give 7.8 g (84%) of crude (*s-trans*-η^4-butadiene)hafnocene. The orange solid was recrystallized from toluene, then redissolved in 150 mL of toluene, and heated to 90 °C for 1 h. Removal of the solvent in vacuo at ambient temperature yielded pure (*s-cis*-butadiene) hafnocene **2b**. The product has been described and characterized previously.[19]

(*s-cis*-2,3-Dimethylbutadiene)hafnocene (3b). A 5.0-g (13.2-mmol) sample of hafnocene dichloride was mixed with 1.6 g (230 mmol) of lithium powder (containing 2% sodium). A mixture of 100 mL of toluene and 30 mL of tetrahydrofuran was slowly added at −78 °C. Excess 2,3-dimethylbutadiene (5 mL, ~50 mmol) was added. The mixture was stirred for several hours at −78 °C. The red solution was filtered at −40 °C, then warmed up to room temperature, and stripped. The residue was dissolved in 200 mL of benzene and filtered at room temperature. The solvent was removed in vacuo to yield 3.5 g (70%) of **3b** as a dark red powder. Recrystallization from toluene at −30 °C yielded a nicely crystalline material: mp 162–164 °C; NMR spectra, see Tables I and II. Anal. Calcd for $C_{16}H_{20}Hf$ (390.8): C, 49.17; H, 5.12. Found: C, 49.16; H, 5.14.

(1,2-Bis(methylene)cyclohexane)hafnocene (4b). **4b** was prepared from 3.0 g (7.9 mmol) of hafnocene dichloride, 0.6 g (86 mmol) of Li (2% Na) powder, and 2.5 mL (~18.5 mmol) of 1,2-bis(methylene)cyclohexane[20] in a mixture of 60 mL of toluene/10 mL of tetrahydrofuran as described above for **3b**. One obtained 2 g (60%) of **4b** as an orange solid, recrystallized from hexane; mp 171 °C. Subsequent recrystallization from pentane gave crystals suitable for an X-ray analysis. Anal. Calcd for $C_{18}H_{22}Hf$ (416.9): C, 51.86; H, 5.28. Found: C, 52.30; H, 5.19.

X-ray Structure Determination. (*s-cis*-η^4-2,3-Dimethylbutadiene)hafnocene (3b). A suitable single crystal of **3b** was grown from toluene and sealed under an atmosphere of argon in a glass capillary. The space group was assigned to be *Pnma* from systematic absences in the data set. Pertinent crystal data as well as a summary of intensity data collection and structure refinement are given in Table IV. The crystal quality was checked by ω scans of several strong, low-angle reflections. The orientation matrix for the intensity data collection was obtained from the setting angles of 25 centered reflections. After data collection, accurate cell dimensions and their esd's were obtained by a least-squares fit to the Bragg angles of 75 strong reflections (10.5° ≤ θ ≤ 24.5°) centered on an Enraf-Nonius CAD-4 automated four-circle diffractometer. Intensity data were collected by using graphite-monochromated Mo Kα radiation and θ–2θ scans. A variable scan/variable speed technique was used. The final scan speed (3.5–10° min^{-1}) was determined by the standard deviation to an intensity ratio of a preliminary 10° min^{-1} scan. The ω scan width was given by (0.8 + 0.347 tan θ)° and the horizontal detector aperture by (3.0 + 0.5 tan θ) mm. Moving crystal–moving counter

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Table V. Final Atomic Fractional Coordinates for (*s-cis*-2,3-Dimethylbutadiene)hafnocene (3b) ($\times 10^4$)

atom	*x*	*y*	*z*
Hf	1835 (1)	2500	5175 (1)
C1	3118 (6)	3716 (5)	1223 (1)
C2	2159 (7)	3087 (5)	3445 (4)
C3	1531 (8)	3775 (6)	2715 (5)
Cp1	−917 (9)	2500	1251 (6)
Cp2	−932 (7)	3473 (6)	1830 (1)
Cp3	−1021 (6)	3097 (6)	5763 (5)
Cp4	2345 (8)	3073 (7)	6831 (4)
Cp5	3758 (8)	3472 (7)	6343 (5)
Cp6	1607 (10)	2500	6062 (7)
H1A	1107	3590	1161
H1B	2981	1648	4102
H3A	876	3179	2275
H3B	2381	4277	2303
H3C	636	4330	3047
HCp1	−794	2500	3513
HCp2	−1035	1303	4515
HCp3	−1078	3662	6351
HCp4	1310	3505	7161
HCp5	1082	4363	6283
HCp6	5730	2500	5714

Table VI. Final Atomic Fractional Coordinates for (1,2-Bis(methylene)cyclohexane)zirconocene (4a) ($\times 10^4$)

atom	*x*	*y*	*z*
Zr1	626 (1)	2669 (1)	521 (1)
Zr2	5669 (1)	7591 (1)	4191 (1)
C1	−118 (1)	1324 (3)	1328 (3)
C2	−1238 (3)	1857 (3)	1424 (3)
C3	−1025 (1)	3041 (3)	1736 (3)
C4	318 (4)	3889 (3)	2041 (3)
C5	−2686 (1)	1015 (4)	1049 (4)
C6	−3728 (6)	1568 (6)	1337 (7)
C7	−3594 (6)	2685 (6)	1418 (7)
C8	−2230 (4)	3533 (4)	1691 (4)
C11	7329 (3)	8694 (3)	5852 (3)
C12	8175 (3)	7966 (3)	5497 (3)
C13	7671 (3)	6778 (3)	4977 (3)
C14	6232 (3)	6107 (3)	4717 (3)
C15	9635 (3)	8621 (3)	5615 (3)
C16	10480 (4)	7918 (5)	5182 (6)
C17	10068 (5)	6747 (5)	4941 (7)
C18	8570 (4)	6104 (3)	4520 (4)
Cp1	−1721 (4)	2331 (4)	−851 (3)
Cp2	−1233 (4)	1437 (3)	−1324 (3)
Cp3	−110 (4)	1916 (4)	−1644 (3)
Cp4	110 (4)	3095 (4)	−1350 (4)
Cp5	−865 (5)	3369 (4)	−835 (3)
Cp6	2746 (4)	1995 (4)	960 (4)
Cp7	2787 (4)	2398 (4)	47 (3)
Cp8	3010 (4)	3594 (4)	414 (4)
Cp9	3111 (4)	3944 (3)	1569 (3)
Cp10	2954 (3)	2963 (4)	1904 (3)
Cp11	7276 (4)	7775 (5)	2981 (3)
Cp12	6809 (5)	8744 (4)	3098 (3)
Cp13	5414 (4)	8355 (4)	2508 (3)
Cp14	5028 (4)	7154 (4)	2043 (3)
Cp15	6168 (5)	6774 (4)	2346 (3)
Cp16	1220 (1)	8462 (4)	5319 (5)
Cp17	3594 (5)	8308 (5)	4174 (6)
Cp18	3076 (4)	7131 (4)	3609 (4)
Cp19	3365 (3)	6546 (3)	4367 (3)
Cp20	1068 (4)	7363 (4)	5423 (3)

Table VII. Final Atomic Fractional Coordinates for (1,2-Bis(methylene)cyclohexane)hafnocene (4b) ($\times 10^4$)

atom	*x*	*y*	*z*
Hf1	1392 (1)	5888 (1)	6612 (1)
Hf2	3165 (1)	8128 (1)	3776 (1)
C1	1534 (5)	8449 (8)	6438 (3)
C2	2545 (5)	8203 (8)	6395 (2)
C3	3148 (5)	7184 (8)	6714 (3)
C4	2852 (5)	6337 (9)	7140 (3)
C5	2846 (6)	9056 (10)	5934 (3)
C6	3921 (7)	9068 (12)	5978 (4)
C7	4344 (6)	7503 (12)	6093 (4)
C8	4124 (5)	6812 (10)	6601 (3)
C11	2079 (5)	7531 (9)	4282 (3)
C12	2013 (5)	9166 (9)	4446 (3)
C13	2814 (5)	10103 (9)	4547 (2)
C14	3775 (5)	9506 (9)	4503 (3)
C15	1025 (5)	9813 (12)	4456 (3)
C16	1022 (6)	11396 (13)	4732 (4)
C17	1713 (7)	12487 (11)	4551 (4)
C18	2727 (5)	11815 (9)	4666 (3)
Cp1	2193 (7)	4765 (19)	5904 (6)
Cp2	1310 (10)	5419 (12)	5628 (4)
Cp3	602 (6)	4554 (14)	5755 (4)
Cp4	983 (10)	3430 (13)	6078 (5)
Cp5	1954 (12)	3528 (15)	6194 (5)
Cp6	−57 (6)	6877 (11)	6950 (4)
Cp7	−245 (5)	5358 (12)	6801 (3)
Cp8	407 (7)	4404 (11)	7144 (4)
Cp9	984 (6)	5357 (11)	7515 (4)
Cp10	698 (6)	6888 (11)	7402 (3)
Cp11	2381 (13)	10525 (13)	3335 (4)
Cp12	1782 (7)	9409 (17)	3158 (5)
Cp13	2183 (14)	8499 (13)	2864 (5)
Cp14	3052 (13)	8985 (24)	2825 (5)
Cp15	3200 (10)	10330 (21)	3152 (7)
Cp16	3448 (8)	5216 (12)	3777 (5)
Cp17	3749 (9)	5806 (14)	3354 (4)
Cp18	4551 (8)	6744 (13)	3533 (5)
Cp19	4728 (6)	6712 (12)	4077 (5)
Cp20	4049 (10)	5774 (13)	4226 (4)

background scans were made by scanning a quarter of the peak width before the start and also after the end of each peak scan. The time spent measuring the backgrounds was half that taken to measure the peak. Three monitor reflections served as a check on the centering and stability of the crystal and diffractometer system. They were repeated every 4000 s for the intensity check and every 250 reflections for the centering check. A Zr filter was inserted in front of the detector if the peak count was greater than 50 000 counts s^{-1}. The intensity of a reflection and its standard deviation were calculated as $I = k[\mathrm{PI} - 2(\mathrm{BGL} + \mathrm{BGR})]$ and $\sigma(I) = k(\mathrm{PI} + 4(\mathrm{BGL} + \mathrm{BGR}))^{1/2}$ where PI is the peak intensity, BGL and BGR are the left and the right background intensities, and k is a constant that depends on the scanning speed. Intensities were corrected for check reflection fluctuation, Lorentz and polarization effects, and absorption. For the latter a numerical integration using a Gaussian grid was employed. Its validity was checked by using the same correction for several reflections measured at various ψ values. The calculated transmission factors varied from 0.195 to 0.573. Reflections with $I \geq 2\,\sigma(I)$ were assumed "observed". Each observed reflection was assigned a standard deviation $\sigma(F_o) = [\sigma^2(I)_{\mathrm{counting}} + (KI)^2]^{1/2}/2F$ ($K = 0.02$). "Unobserved" reflections were not used in all subsequent calculations.

The atomic positions of all non-hydrogen atoms, taken from the isostructural Zr analogue (*s-cis*-2,3-dimethylbutadiene)zirconocene **3a**,[9,13] served as a starting point in the full-matrix least-squares refinement. Since difference Fourier syntheses did not reveal reasonable H atom positions, these were introduced at idealized geometrical positions (C–H = 0.95 Å) and kept constant in further refinements cycles ($U = 0.05$). All other atoms were allowed anisotropic thermal motion. The function minimized was $\sum w(|F_o| - |F_c|)$ with $w = 1/\sigma^2(F_o)$. A final difference map was qualitatively featureless. The maxima were located near the Hf atom with much smaller values elsewhere. No attempt to refine the structure in the acentric space group $Pna2_1$ was undertaken because the derived structural parameters are chemically reasonable. Neutral, isolated atom scattering factors for all nonhydrogen atoms were those of Cromer and Waber.[21] Scattering factors of the H atoms based on a bonded spherical atom model were those of Stewart, Davidson, and Simpson.[22] Anomalous

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(21) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(22) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for 3a,b and 4a,b[a]

	2,3-dimethylbutadiene		1,2-bis(methylene)cyclohexane	
	3a (Zr)	**3b** (Hf)	**4a** (Zr)[b]	**4b** (Hf)[b]
M-C1	2.300 (3)	2.267 (5)	2.279 (4)	2.264 (7)
			2.282 (4)	2.263 (8)
M-C4	*c*	*c*	2.281 (4)	2.262 (7)
			2.275 (3)	2.230 (7)
M-C2	2.597 (3)	2.641 (5)	2.631 (4)	2.703 (7)
			2.646 (3)	2.747 (7)
M-C3	*c*	*c*	2.619 (4)	2.688 (7)
			2.643 (3)	2.727 (7)
C1-C2	1.451 (4)	1.472 (8)	1.462 (5)	1.47 (1)
			1.469 (5)	1.48 (1)
C3-C4	*c*	*c*	1.459 (5)	1.45 (1)
			1.469 (5)	1.48 (1)
C2-C3	*d*	*d*	1.378 (6)	1.37 (1)
			1.379 (5)	1.37 (1)
C2-C2*	1.398 (4)	1.378 (8)		
C2-C5	*d*	*d*	1.530 (6)	1.52 (1)
			1.521 (5)	1.51 (1)
C3-C8	*d*	*d*	1.523 (6)	1.50 (1)
			1.517 (5)	1.51 (1)
C2-C3	1.511 (5)	1.522 (9)		
C5-C6			1.485 (7)	1.502 (13)
			1.481 (6)	1.536 (15)
C7-C8			1.482 (8)	1.521 (13)
			1.497 (7)	1.520 (12)
C6-C7			1.34 (1)	1.479 (14)
			1.357 (9)	1.495 (14)
M-CP (range)	2.547 (3)-2.580 (4)	2.523 (6)-2.572 (8)	2.527 (5)-2.573 (4)	2.480 (12)-2.572 (8)
M-CP (av)[e]	2.560 (5)	2.547 (7)	2.553 (3)	2.515 (5)
M-C1-C2	84.4 (2)	87.2 (3)	86.5 (2)	90.1 (4)
			86.9 (2)	92.1 (5)
M-C4-C3	*c*	*c*	85.9 (2)	90.2 (4)
			87.0 (2)	92.4 (4)
C1-C2-C3	*d*	*d*	123.3 (3)	122.9 (6)
			123.5 (3)	121.0 (6)
C2-C3-C4	*d*	*d*	123.4 (3)	122.1 (6)
			123.6 (3)	121.3 (7)
C1-C2-C2*	122.7 (3)	121.7 (5)		
C3-C2-C5	*d*	*d*	120.6 (3)	122.1 (6)
			120.6 (3)	120.9 (7)
C2-C3-C8	*d*	*d*	120.5 (4)	120.4 (7)
			120.4 (3)	120.7 (6)
C2*-C2-C3	121.8 (3)	122.1 (5)		
α^f	123.9	124.3	125.7	125.2
			125.8	125.4
β^g	112.8	116.5	117.8	123.4
			119.8	124.8
γ^g	172.9	171.1	174.7	174.1
			173.1	175.1

[a] Esd's in units of last significant figure are given in parentheses. See Figures 1-3 for atom numbering scheme used. [b] The values for both crystallographically equivalent molecules are given. The numbering scheme used for molecule II is obtained by adding 10 to the equivalent figures of molecule I. [c] This value is redundant due to the crystallographically imposed mirror symmetry of the molecule. The equivalent value is given directly above. [d] The corresponding values for 3a and 3b are given below. [e] Standard deviations for the averaged values are taken as the larger of $[\Sigma^n_{i=1}(p_i - \bar{p})^2/n(n-1)]^{1/2}$ and $(\Sigma^n_{i=1}\sigma_i^2)^{1/2}/n$, where p_i and σ_i are the individual observations and their esd's, respectively. [f] Angle between normals to planes of Cp rings. [g] See Scheme III for definition of these angles.

scattering factors for the heavy atom were taken from ref 23. All computer programs used are summarized in ref 24. Table V contains the final atomic coordinates; important bond lengths and angles are collected in Table VIII. The final values of the thermal parameters are given in the supplementary material.

(η^4-1,2-Bis(methylene)cyclohexane)zirconocene (4a). Single crystals of **4a** were obtained by crystallization from toluene. According to diffractometer data it crystallizes triclinic. No higher symmetry was indicated by reduced cell calculations.[24] Pertinent crystal data as well as a summary of intensity data collection and structure refinement are given in Table IV. Data collection and refinement procedures followed closely those described for **3b**. Intensity data were not corrected for absorption, in this case. The reflections used for determination of accurate cell dimensions were in a range 10.3° ≤ θ ≤ 26.8°. The position of the two independent heavy atoms could be deduced from a Patterson map. All other non-hydrogen atoms followed from difference Fourier syntheses. A total of 26 out of the 44 H atoms could be located in difference maps; all others were calculated (d(C–H) = 0.95 Å). In the least-squares refinement they were treated as fixed atom contributions (U = 0.05); all other atoms were refined anisotropically.

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(23) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(24) In addition to several locally written programs, local VAX-780 versions of other programs used were: TRACER by Lawton and Jacobson for reduced cell calculations, DATAP by Coppens, Leiserowiz, and Rabinovich for data reduction and analytical absorption correction, DIFABS by Walker and Stuart for empirical absorption correction, Sheldrick's SHELX-76 for Fourier calculations and initial least squares, GFMLS, a highly modified version of ORFLSD, by Hirshfeld, Coppens, Leiserowiz, and Rabinovich for full-matrix least squares with blocking option, Davis' DAESD for bond distances and angle calculations, XANADU by Roberts and Sheldrick for geometrical calculations and best plane and torsion angle calculations, and Johnson's ORTEP for the molecular drawings.

Attempts were made to resolve the disorder of C6/C7 and C16/C17 indicated by the relatively large values of $U(2,2)$ and $U(3,3)$. Difference maps phased with isotropic C6/C7 and C16/C17 and with half occupancy of these did not reveal reasonable alternatives that could be refined separately. Table VI contains the final atomic coordinates; important bond lengths and angles are collected in Table VIII. The final values of the thermal parameters are given in the supplementary material.

(η^4-1,2-Bis(methylene)cyclohexane)hafnocene (4b). Single crystals of **4b** were grown from pentane. The space group $P2_1/n$ was uniquely determined from the systematic absences. A summary of crystal data, intensity data collection, and structure refinement is given in Table IV. Data collection and refinement procedures followed closely those described for **3b**. The reflections used for refinement of accurate cell dimensions were in the range $7.6° \leq \theta \leq 22.0°$. The positions of the two independent Hf atoms in the unit cell were obtained by a novel Patterson search and interpretation routine (SHELX 84).[25] Subsequent difference Fourier maps revealed the positions of the other non-hydrogen atoms. Since the irregular crystal shape did not permit an analytical absorption correction, an empirical absorption correction was undertaken using the program DIFABS.[26] After convergence of the isotropic refinement of all non-hydrogen atoms with the nonmerged data set (141 redundant reflections included), the F_o and F_c values of 4846 observed reflections were taken together with the atomic positions of all non-hydrogen atoms to evaluate the transmission factors. A minimum correction of 0.795 and a maximum correction of 1.207 was employed for 4875 observed reflections. Thereupon the relative residual dropped from 0.081 for the uncorrected data set to 0.050. Equivalent reflections were merged to give a unique data set of 4778 observed reflections that were used for further refinement. The H atom positions at the diene termini as well as 16 of the methylene hydrogens could be located in difference maps. All others were calculated at idealized positions. H atom positions were kept constant during refinement (U = 0.05); all other atoms were refined anisotropically. Table VII contains the final atomic coordinates; selected bond lengths and angles are summarized in Table VIII. The final values of the thermal parameters are given in the supplementary material.

NMR Spectra and Dynamic Features of (*s-cis*-Conjugated diene)metallocene Complexes 2–4 in Solution

(*s-cis*-Diene)zirconocene and -hafnocene complexes 2–4 exhibit dynamic behavior in solution as revealed by NMR spectroscopy. Corresponding (diene)hafnocene and -zirconocene complexes show very similar spectroscopic features. For given pairs of compounds 2–4 Cp resonances (^{1}H/^{13}C) are almost identical for hafnium and zirconium. For each complex a rather substantial chemical shift difference is noticed between hydrogen atoms at internal and terminal diene centers (Table II). An analogous trend is observed in the ^{13}C NMR spectra (Table I).[17,27] This effect is in line with a rather substantial σ-complex character of conjugated diene group 4 metallocenes.[9,13] For the hafnium complexes a slightly higher metal alkyl character, as compared to that of their Zr analogues, is inferred from the NMR data given in Tables I and II, following this interpretation.[19] This is expressed by a shift of the ^{1}H and ^{13}C resonances of the diene ($=CH_2$) units to lower δ values. Consistently, for all three pairs of (diene)metallocene complexes the C2 ^{13}C resonance is shifted to slightly higher δ values on going from Zr to Hf ($\Delta\delta$ = 2.5 (**2a** − **2b**), 1.2 (**3a** − **3b**), and 1.4 ppm (**4a** − **4b**); see Table I). The appearance of the NMR spectra of the (*s-cis*-diene)metallocene complexes 2–4 changes drastically with temperature. E.g., the ^{1}H NMR spectrum of **4a** would be in accord with a structure of C_{2v} symmetry for (1,2-bis(methylene)cyclohexane)zirconocene in solution at ambient temperature.[28] However, broadening of all four separated groups of signals (Cp, $-CH_2CH_2$, $=CH_2$) is observed with decreasing temperature. After separate coalescences a complex pattern of the $(CH_2)_4$ unit of the organic six-membered ring system is obtained. A large chemical shift difference is observed for syn and anti diene ($=CH_2$) hydrogens (**4a**, δ 2.75 and −0.78 ($^2J_{HH}$ = 10.5 Hz) at −110 °C in $CHFCl_2$) as well as the protons of the Cp rings (δ 5.69 and 5.35).

As has recently been discussed by us in detail,[13,14a,17] this NMR behavior is caused by a degenerate molecular rearrangement process, rapid on the NMR time scale, in the course of which the bent metallocene unit migrates from one face of the diene ligand to the other. This reorganization process proceeds through five-membered metallacyclic structures (see Scheme II).[29,30] The activation barrier of this automerization reaction can easily be calculated from the chemical shift difference of the Cp resonance as observed in the limiting low-temperature NMR spectra and the coalescence temperature T_c(Cp). For the example of the (diene)zirconocene complex **4a** a Gibbs activation energy of $\Delta G^{\ddagger}_{-57°C}$ = 10.8 ± 0.3 kcal/mol has been obtained accordingly. We have demonstrated that the magnitude of the automerization barrier is very much dependent on substituents on the conjugated diene moiety as well as on structural details of the *s-cis*-diene group 4 metallocene complexes.[13,17] Qualitatively, the numerical value of $\Delta G^{\ddagger}_{T_c}$ (autom) for a given (diene)ZrCp$_2$ complex is an indication for its position on the continuum of ground-state structures between the limiting extremes of a purely σ-bonded metallacyclopentene and a metallacyclic σ^2,π-type structure possible for a (*s-cis*-conjugated diene)zirconocene.[31] The hafnium complexes **2b**–**4b** exhibit analogous spectroscopic features. There is only a marked difference as to the numerical value of the automerization activation energy (Table III). For the hafnium complexes **2b**–**4b** $\Delta G^{\ddagger}_{T_c}$(autom) is substantially lower (up to $\Delta(\Delta G^{\ddagger})$ = 4.5 kcal/mol for **2b** vs. **2a**) as compared to their zirconium analogues. However, the Gibbs activation energies for the degenerate rearrangement of **2b**–**4b** are still clearly within the typical range expected for this reaction type (Scheme II).

From these solution data it is obvious that the Hf systems **2b**–**4b** and their Zr analogues at least qualitatively behave rather similarly, as expected.[19] The observed substantial rate differences probably originate from the same principal effect that has been found to be responsible for the wide range of $\Delta G^{\ddagger}_{T_c}$ values in differently substituted (*s-cis*-conjugated diene)ZrCp$_2$ complexes;[13,17] i.e., the hafnium complexes **2b**–**4b** exhibit a higher degree of σ-complex character in the ground state than their Zr counterparts. This interpretation for the observed differences in chemical behavior between these (diene)ZrCp$_2$

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(25) Sheldrick, G. M., University of Göttingen, to be submitted for publication.

(26) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(27) Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71.

(28) See for a comparison: Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, *1839*. Wilke, G.; Gausing, W., unpublished results. Gausing, W. Dissertation, Bochum, 1979.

(29) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. Wilke, G. *Fundamental Res. Homogeneous Catal.* **1979**, *3*, 1. Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834.

(30) For different rearrangement modes of conjugated diene transition-metal compounds see: Kruczynski, L.; Takats, J. *J. Am. Chem. Soc.* **1974**, *96*, 932; *Inorg. Chem.* **1976**, *15*, 3140. Kreiter, C. G.; Stüber, S.; Wackerle, L. *J. Organomet. Chem.* **1974**, *66*, C49. Busch, M. A.; Clark, R. J. *Inorg. Chem.* **1975**, *14*, 226. Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Organomet. Chem.* **1979**, *168*, C25. Kotzian, M.; Kreiter, C. G.; Özkar, S. *Ibid.* **1982**, *229*, 29.

(31) For a recent calculation see: Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*, 145.

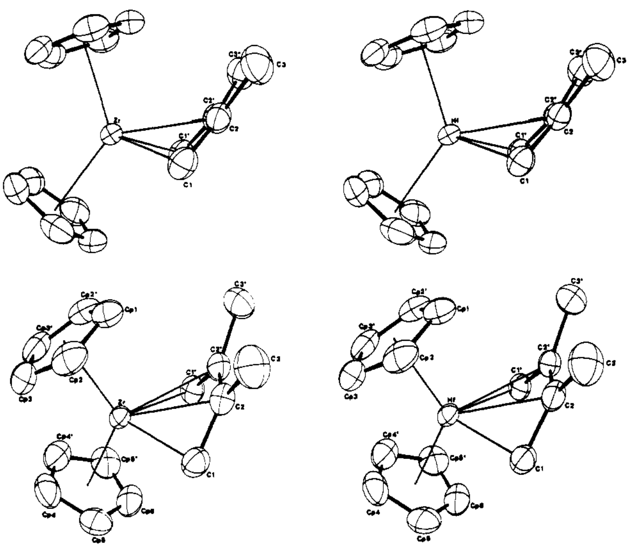
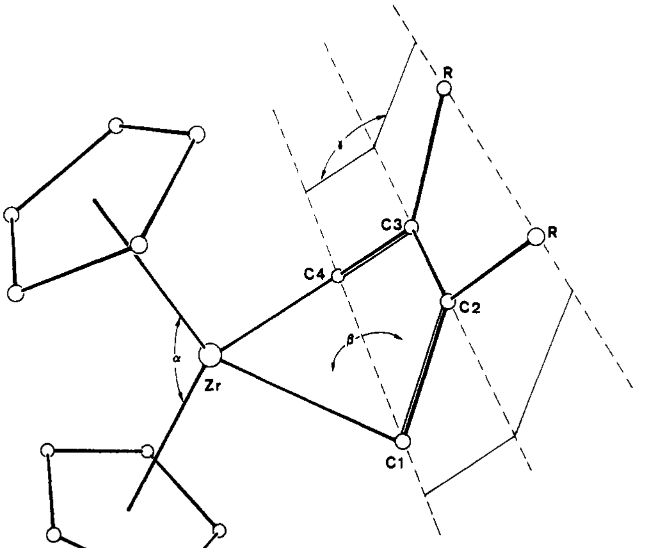


Figure 1. Perspective views of **3b** and its Zr analogue **3a**[9,13] in two different orientations, showing the close similarities between both compounds. Thermal ellipsoids (ORTEP) are at the 50% probability level.

Scheme III



and (diene)HfCp$_2$ complexes in solution finds its confirmation in the results of a comparative X-ray structural analysis of the zirconium and hafnium complexes **3a**,[9,13] **3b**, and **4a,b** which are described below.

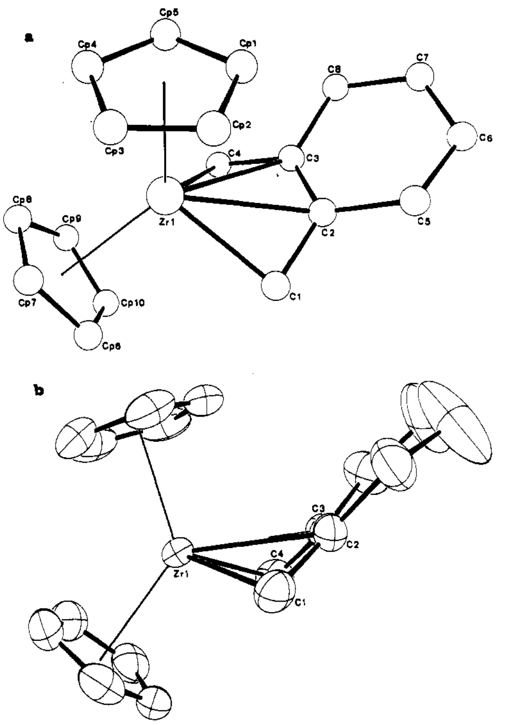


Figure 2. Perspective views of one of the crystallographically independent molecules of **4a** in two different orientations with numbering scheme used.

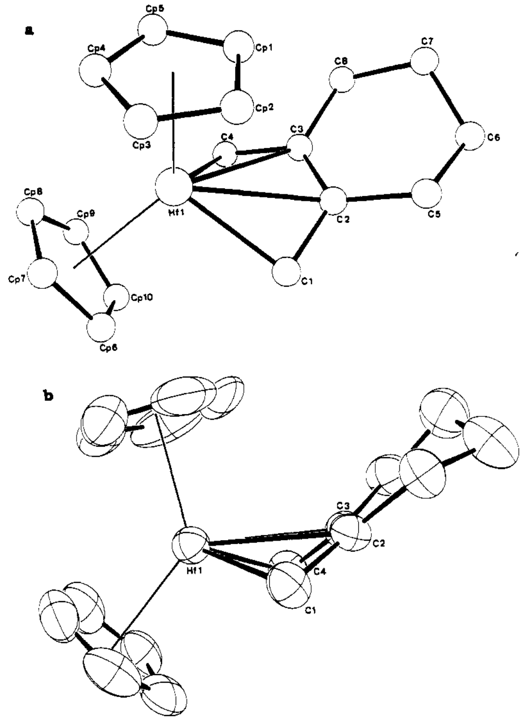


Figure 3. Perspective views of one of the crystallographically independent moelcules of **4b** with numbering scheme used.

Description of the Structures. (*s-cis*-η^4-2,3-Dimethylbutadiene)HfCp$_2$ (3b). The molecular structure of **3b** resembles closely its analogous Zr compound **3a**[9,13] with which it is isostructural. As Figure 1 shows, the similarities even extend to the thermal behavior of most atoms. The metal atom again is pseudotetrahedrally coordinated by two cyclopentadienyl rings and the double bonds of the cisoid fixed conjugated diene ligand. The C1, C2, C1*, C2* moiety of the ligand containing the double bonds remains essentially planar upon coordination to the bent hafnocene fragment. Its bond lengths show a long–short–long sequence with values of d(C1–C2)/(C1*–C2*) = 1.472 (8) Å and d(C2–C2*) = 1.378 (8) Å. These compare to the 1.451 (4) and 1.398 (4) Å found in the Zr analogue **3a**[9,13] but are drastically different from the short–long–short sequence found in free uncomplexed 2,3-dimethylbutadiene.[32] The symmetrical bonding of the diene to the metal with respect to equal M–C bond lengths of the diene termini C1/C1* as well as of the internal C atoms C2/C2*, respectively, is imposed crystallographically upon the molecules. A crystallographic mirror plane bisects the diene atoms plane and contains the normals to the Cp rings[33] as indicated in Figure 1 and Scheme II. There exist

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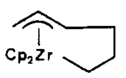
[32] d(C=C) = 1.349 (6) Å and d(C—C) = 1.504 (5) Å as determined by electron diffraction: Aten, C. F.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1968**, *90*, 2463.

pronounced differences between the M–C1/C1* and M–C2/C2* bond lengths, however. The latter amount to 2.641 (5) Å and thus are longer by 0.37 Å over those to the diene termini (2.267 (5) Å). In **3a** values of 2.597 (3) and 2.300 (3) Å were found.[9,13] The M–C bond lengths to the Cp rings range between 2.523 (6) and 2.572 (8) Å (average 2.547 (7) Å).[34] Some significance for the variation in length can be inferred from the fact that Cp1 which comes closest to the butadiene methyl groups has the longest distance to Hf whereas Cp4 on the opposite side has a noticeably shorter bond to Hf. The same trend was observed for **3a** where they ranged between 2.547 (3) and 2.580 (4) Å (average 2.560 (5) Å). Another noteworthy difference lies in the M–C1–C2 angle which was found to be 87.2 (3)° in **3b** whereas in **3a** this parameter was found to be 84.4 (2)°.[9,13] All other geometrical parameters are directly comparable between both compounds and are listed in Table VIII.

(η^4-1,2-Bis(methylene)cyclohexane)MCp$_2$ (M = Zr (4a), Hf (4b)). In contrast to many other pairs of analogous Zr and Hf compounds[35,36] **4a** and **4b** are not isomorphous. For **4a** the triclinic space group $P\bar{1}$ was found, whereas **4b** crystallizes in monoclinic space group $P2_1/n$. Both compounds crystallize with two crystallographically independent molecules per asymmetric unit. All attempts failed to find a higher symmetric space group for **4a** despite the fact that both compounds showed close resemblances in their molecular geometries. Again the coordination geometry around the metal atoms in **4a** and **4b** resembles closely the one previously found for **3b** and a series of other (*s-cis*-butadiene)ZrCp$_2$ complexes.[9,13,14a] The already familiar feature of unequal bond lengths to the diene termini and to the internal C atoms of the butadiene ligand is manifested for **4a** by average values of 2.279 (2) Å (M–C1/C4) and 2.635 (6) Å (M–C2/C3), whereas in **4b** those bond lengths amount to 2.255 (8) and 2.72 (1) Å. The distances to the Cp ring atoms are slightly shorter for the Hf compound **4b** (average 2.515 (5) Å) in contrast to the average of 2.553 (3) Å found in **4a**. As in the case of **3a** and **3b** the angle M–C1–C2 (M–C4–C3) is larger for the Hf compound (91.2 (6)° vs. 86.6 (2)°). Besides these rather small, though for the scope of the present discussion highly significant, differences in the molecular geometry of **4a** and **4b** there exist noteworthy differences with respect to the conformation of the 1,2-bis(methylene)cyclohexane ligands and the vibrational behavior of the Cp ligands. The symmetry of the immediate coordination geometries around the metal centers in both complexes comes close to *m* (C_s) as in all other *s-cis*-1,3-butadiene complexes of zirconocene and hafnocene examined so far. Due to the two different possible conformations of the 1,2-bis(methylene)cyclohexane ligands in **4a** and **4b** the two crystallographically independent molecules of **4a** are enantiomers whereas in **4b** equal conformers are found. Furthermore, in **4a** relatively high thermal parameters of C6 and C7 (C16/C17) imply a slight conformational disorder of these atoms which is estimated to be at most 20%. In **4b** the thermal parameters of these atoms are normal, however. On the other hand, higher thermal parameters of the Cp ring atoms in **4b** indicate a slight rotational disorder of these ligands, a fact which was not observed in **4a**. We presume that these conformational and rotational labilities of the ligand in **4a** and **4b** are responsible for their different crystallization behavior. The fact that both compounds crystallize with two crystallographically independent molecules in the asymmetric unit is most probably related to the same conformational lability of compounds **4a** and **4b** and might thus give additional proof for it to be reason for the heteromorphism of **4a** and **4b**.

Discussion

As was found for a variety of other Cp$_2$Zr(*s-cis*-η^4-1,3-butadiene) complexes,[9,13,14a,17] the M–C bond lengths of the diene termini in **4a** fit well into the overall pattern of M–C bond lengths observed in a large number of zirconocene alkyls.[35-42] Bond lengths between 2.289 (4) Å in **5** and 2.329 (2) Å in (2.3-bis(methylene)norbornane)ZrCp$_2$ centered around the 2.300 (4) Å observed in the zirconaindan **6a**[14b,36] where pure σ bonding of the *o*-xylylene ligand can be presumed. These bond lengths are only slightly longer than the 2.251 (6) and 2.277 (4) Å found in bis(η^5-indenyl)dimethylzirconium[35] and dimethylzirconocene.[16] They are even shorter than those with bulky substituents as in Cp$_2$Zr(CHPh$_2$)$_2$ (2.39 (1) Å[37]) or in Cp$_2$ZrPh(CH(SiMe$_3$)$_2$) (2.329 (6) Å[38]). Also in cyclic systems such as **7** and **8** the Zr–C σ bonds are appreciably longer (**7**; 2.41 (1) Å;[43] **8**; 2.311 (7) Å[44]). The Zr–C bonds in **4a** are the shortest observed so far in this series of compounds and have to be regarded as essentially σ in nature as well. In the complexes examined so far the Zr–C2/C3 bonds (i.e., those to the internal C atoms of the butadiene moiety of the ligands) were found to be of crucial importance for an assessment of the varying degree of σ vs. π bonding of the butadiene ligands. We inferred from the trend of smoothly increasing Zr–C2/C3 bond lengths from 2.550 (5) Å in **1** toward the essentially nonbonding 2.855 (4) Å in **6a**[14b,36] that these bond lengths could be taken as a measure of the σ character of these diene complexes.[14] The 2.63 (1) Å value found in **4a** places the 1,2-bis(methylene)cyclohexane complex between the 2.714 (5) Å value of the 2,3-diphenylbutadiene complex **5**[13] and the 2.597 (3) Å value of the 2,3-dimethylbutadiene complex **3a**.[13] In other words, the conjugated diene ligand in **4a** should be more σ bonded to the metallocene fragment than that in **3a** but less so



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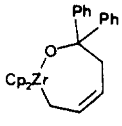

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[33] Actually, the normals to the Cp rings and the lines connecting the metals and the midpoints of the respective rings as indicated in the figure are different geometrical features that do not necessarily coincide depending whether the Cp ring is symmetrically bonded or not. In these cases, however, the slight differences in M–C(Cp) bond distances (Table VIII) as compared to the standard deviations only causes minor discrepancies as manifested by small angles between both lines.

[34] See Table VIII, footnote *e*, for definition of the standard deviations of averaged values.

[35] For examples see ref 15 and 16 or: Atwood, J. L.; Hunter, W. E.; Hrncir, D. C.; Samuel, E.; Alt, H.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 1757.

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[41] Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

[42] Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555.

[43] Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1982**, *94*, 916.

[44] Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506.

than that in **5** or **6a**. This compares well with the trend in the Zr–C1–C2/Zr–C4–C3 bond angles. Increasing values indicated greater σ character in the diene bonding. The 86.6 (3)° in **4a** again fits nicely between the 89.7 (4)° in **5** and the 84.4 (2)° in **3a**. This trend is paralleled by the topomerization rate of **4a**.

The molecular structures of **3b** and **4b** as the first structurally characterized (*s-cis*-η^4-butadiene)HfCp$_2$ complexes allow an extension of these findings to the analogous Hf compounds. Although very similar in their gross overall geometries there exist subtle differences within the metal diene frameworks among the Hf compounds **3b** and **4b** as well as in comparison with their Zr analogues **3a** and **4a**. In both pairs of compounds the M–C bonds to the diene termini are slightly shorter in the Hf complexes. This is supported by the M–η^5-Cp bond lengths that are slightly shorter for M = Hf, too. Since the Zr–C1/C4 bonds were shown to be independent of the varying σ vs. π character in the respective metal–diene bonds, these findings should allow reliable comparisons in an assessment of bond length differences between analogous Zr and Hf compounds. They substantiate recent observations on M–CH$_3$ bonds, where shorter bonds were found for M = Hf than for M = Zr.[16] As also implied by the atomic radii of Zr and Hf (1.45 Å vs. 1.44 Å[45]) these differences are only minor in **3b**/**3a** and **4b**/**4a**, however.

In sharp contrast to this, the Hf–C bonds to the internal C atoms C2/C3 are generally *longer* than their Zr counterparts. The above observed slight shortening of M–C bonds on going from Zr to Hf renders these findings especially important. It implies that the Hf complexes **3b** and **4b** show a distinctly greater σ/π ratio in their metal–diene bonds. It should be kept in mind, however, that C2/C3 are still in a range to be π bonded to the central Hf atoms. These observations are matched by other geometrical parameters of the metal–butadiene moieties. Especially the angles M–C1–C2/M–C4–C3 are consistently greater for the Hf compounds than for their Zr analogues, again implying more σ character for the Hf complexes. Although at the margin of significance, differences in the long–short–long bond length pattern in the butadiene moiety are also consistent with that. Whereas no systematic variation is observed in **4a** and **4b**, where the butadiene framework is part of a cyclic system, the internal C2–C2* bond in **3a** and **3b** is slightly shorter for Hf whereas the external C1–C2/C1*–C2* bonds are somewhat longer. This is what is expected if the butadiene double bonds are more σ bonded to the metal, thus giving the C2–C2* bond more π character. The difference in the short–long–short sequence in uncomplexed butadiene has already been pointed out. In "true" π complexes of butadiene, as exemplified by late transition-metal butadiene complexes these bonds are of approximately equal length.[46] Finally, one further aspect in the structures of **3** and **4** deserves comment. The substituent carbons at C2/C3 (C2/C2* in **3**) do not lie in the plane determined by the diene carbon atoms but their linkages with C2/C3 (C2/C2*) are markedly bent *toward* the metal center. Values of this "substituent angle" γ as defined in Scheme III are included in Table VIII. This effect probably arises from the antibonding interaction between the π orbitals at C1/C4 and C2/C3 on the diene face opposite to the metal. The observed substituent bending toward the metal clearly diminishes this repulsive interaction.[47]

These observations may be summarized as follows: Hf–C bonds are slightly shorter than their Zr counterparts; (*s-cis*-η^4-diene)hafnocene complexes show the same bonding characteristics as do their Zr analogues; the σ/π ratio in the diene bonding is slightly shifted toward a larger σ character in the case of Hf; the ligand dependency of this ratio is the same for the HfCp$_2$ complexes as for the respective ZrCp$_2$ compounds, as exemplified by the greater σ character of the 1,2-bis(methylene)cyclohexane complexes **4a** and **4b** over that of the corresponding 2,3-dimethylbutadiene complexes **3a** and **3b**.

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Registry No. 1, 84079-50-5; **2a**, 83780-95-4; **2b**, 83829-08-7; **3a**, 84142-90-5; **3b**, 93603-13-5; **4a**, 75361-78-3; **4b**, 93531-46-5; **5**, 93531-47-6; **6b**, 84601-75-2; Cp$_2$Hf(*s*-trans-H$_2$C=CH—CH=CH$_2$), 83780-94-3; Hafnocene dichloride, 12116-66-4.

Supplementary Material Available: Detailed information on the crystal structure determination of **3a**, **3b**, **4a**, and **4b**, including tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles, and lists of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

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(45) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; p 824.

(46) Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522. See also ref 17 for further references on this topic.

(47) Further discussion of this effect may be found in ref 14a and 17.