collected, dried in vacuo, and recrystallized from chloroform–hexane to give 655 mg (0.5 mmol, 25%) of **36** as a yellow solid: mp 195–200 °C dec; IR (KBr) 3060, 2980, 2950, 2920, 2870, 1970 (br), 1900 (br), 1830 (br), 1630 (br), 1590, 1580, 1485, 1440, 1318, 1290, 1190, 1160, 1080 [very strong, $\nu_s(BF_4)^-$], 1000, 745, 690, 510, 415 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.20 (45 H, br s), 2.10 (1 H, br s), 1.75 (1 H, s), 0.85 (2 H, br s), 0.25 (3 H, br s), −0.55 (1 H, br d, J = 8 Hz); ^{13}C NMR ($CDCl_3$) 54.20, 53.32, 49.10, 27.71, 24.50 ppm (the 31 peak multiplet in the aromatic region has not been included in this listing); MS, m/e 981–982 [$Pt(PPh_3)_3^+$], 886–894 [$Pt(PPh_3)_2C_7H_8Br^{+\cdot}$], 715–725 [$Pt(PPh_3)_2^+$]. An analytical sample was prepared via recrystallization from chloroform–hexane; mp 210–213 °C dec. Anal. Calcd for $C_{61}H_{53}PtP_3BrBF_4\cdot 2CHCl_3$: C, 51.14; H, 3.75. Found: C, 50.87; H, 3.78.

Reaction of 2-Bromo-3-iodobicyclo[2.2.1]hept-2-ene with Tris(triphenylphosphine)platinum and Sodium Amalgam. A flask containing 1.61 g (1.4 mmol) of 2% sodium amalgam was purged with argon and charged with a solution of tris(triphenylphosphine)platinum (**5**) (500 mg, 0.5 mmol) in 10 mL of freshly distilled tetrahydrofuran. The mixture was placed under positive pressure of argon, and 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene (**8**) (210 mg, 0.7 mmol) in 2 mL of freshly distilled tetrahydrofuran was added. The mixture was stirred for 1.5 h at 25 °C and filtered under nitrogen pressure, and the filtrate was concentrated in vacuo. The residue was transferred to an inert-atmosphere drybox, and fractional crystallization with tetrahydrofuran–hexane was attempted. The crops of crystals were analyzed by NMR spectroscopy: first crop (30 mg), **12**; second crop (29 mg), **14**; third crop (135 mg), mixture of **13** and **14**; and fourth crop (239 mg), **12**. The combined modes of trapping of 2-bromo-3-iodobicyclo[2.2.1]hept-2-ene by platinum thus amounted to 433 mg (0.43 mmol) of adducts, or 86%, based on **5**.

Acknowledgment. We are indebted to the National Science Foundation for Grants CHE78-10231 and CHE81-14772 which supported this investigation and for Grant CHE77-28505 which aided in the purchase of an Enraf-Nonius X-ray diffractometer. We wish to thank Mr. M. McGuiggan and Professors L. Pignolet and D. Britton for assistance in the X-ray study.

Registry No. **11**, 87518-05-6; **12**, 87518-06-7; **13**, 87518-12-5; **14**, 87583-20-8; **15**, 87518-07-8; **16**, 87518-08-9; **17**, 87518-09-0; **18**, 87518-10-3; **19**, 87518-11-4; **31**, 87518-13-6; **32**, 87583-21-9; **33**, 18517-48-1; **35**, 87518-14-7; **36**, 87518-16-9; tris(triphenylphosphine)platinum, 13517-35-6; (ethylene)bis(triphenylphosphine)platinum, 12120-15-9; dibromobis(triphenylphosphine)platinum, 16242-58-3.

Supplementary Material Available: Tables of bond lengths and bond angles, atomic coordinates and thermal parameters, and structure factor amplitude (19 pages). Ordering information is given on any current masthead page.

Approaching the σ^2,π Structural Limit of s-cis η^4-Conjugated Diene Zirconocene Complexes

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(1,2,5,6-Tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane)zirconocene (**2a**), prepared by irradiation of diene **1a** and diphenylzirconocene, and (2,3-dimethylenebicyclo[2.2.1]heptane)zirconocene (**2b**), obtained by reduction of zirconocene dichloride with lithium in the presence of 2,3-dimethylenenorbornane (**1b**), both react with carbon monoxide under displacement of the conjugated diene forming zirconocene dicarbonyl. Envelope-shaped σ^2,π-type structures were found for the diene zirconocene units in X-ray diffraction studies of both complexes. **2a** crystallizes in space group $P\bar{1}$ (Z = 4) with cell constants a = 8.578 (2) Å, b = 14.466 (3) Å, c = 15.717 (1) Å, α = 75.00 (1)°, β = 88.566 (8)°, and γ = 89.12 (2)° (7110 observed reflections, R = 0.035). Compound **2b** crystallizes in space group $P\bar{1}$ (Z = 2) with cell constants a = 7.4540 (7) Å, b = 8.8377 (8) Å, c = 11.8934 (7) Å, α = 84.704 (5)°, β = 88.922 (5)°, and γ = 79.765 (7)° (3165 observed reflections, R = 0.021). Comparison of the molecular geometries of (diene)zirconocenes **2a**,**b**,**d**,**e** and the zirconaindan **3** reveals a continuously increasing metallacyclopentene character. In this series the reactivity of **2a** and **2b** toward carbon monoxide is markedly less influenced by ground-state effects as compared with that of **2d**, **2e**, and **3**.

1,2,5,6-Tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**1a**) is a remarkable molecule, whose special features[1] have led to a broad exploration of its organic chemistry.[2] However, only a few attempts to coordinate this diene to a transition-metal center have become known.[3] Structural properties of metal complexes of **1a** determined by X-ray diffraction methods, to our knowledge, have not been reported as yet.

We have recently prepared the bis(η-cyclopentadienyl)zirconium complex **2a** of the conjugated diene **1a**.[4] Among the known differently substituted (*s-cis-η^4*-conjugated diene)zirconocenes[5] (**2**, see Scheme I), **2a**

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(3) (a) $Fe(CO)_3$ complex: Elzinga, J.; Hogeveen, H. *Tetrahedron Lett.* **1976**, 2383; *J. Org. Chem.* **1980**, *45*, 3957. (b) Ring-opening rearrangement occurs upon treatment with $[Rh(CO)_2Cl]_2$: Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* **1976**, *98*, 6040.

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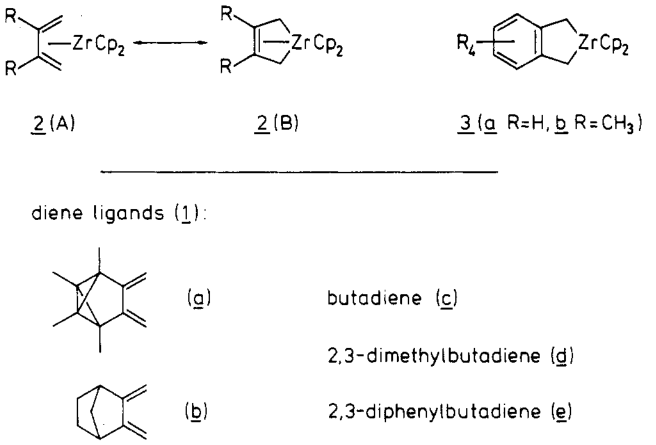
Scheme I



occupies an exceptional position with regard to its chemical behavior. Like **2c–e**, (η^4-1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane)zirconocene (**2a**) undergoes a thermally induced automerization—a rapid intramolecular migration of the bent metallocene unit from one "face" of the conjugated diene to the other—but exhibits a significantly higher activation barrier[6] [$\Delta G^{\ddagger}{}_{\mathrm{T}}$ (kcal/mol): **2a**, 14.3 (+11 °C); **2c**, 12.5 (−19.5 °C); 11.5 (−42 °C); **2e**, 8.0 (−112 °C); **3**, 6.5 (−140 °C)].

In this series of zirconocene complexes, **2a** shows the lowest carbonylation rate [k_{rel}(pseudo first order at 25 °C, 1 bar CO), **2a**/**2c**/**2d**/**2e**/**3** = 1/2.5/5/250/5000] and does not give a substituted cyclopentenone as do **2c–e** (after hydrolysis)[5b,6,7] but directly yields zirconocene dicarbonyl plus the free diene ligand **1a** upon treatment with CO.

The chemical differences between **2d** and **2e** predominantly reflect ground-state effects: from X-ray crystallographic studies[8] an in general rather high metallacyclopentene (i.e., σ-complex) character,[9] which differs in degree among individual members, is inferred for these complexes. However, from the existing data it was not clear whether this dominating influence of substituents on the ground-state properties of (diene)zirconocene complexes is equally important for **2a** or if other factors predominantly determine the chemistry of this zirconocene complex. We therefore wish to report here the results of an X-ray structure determination of **2a** and of $Cp_2Zr(\eta^4$-2,3-dimethylenebicyclo[2.2.1]heptane) (**2b**), two (diene)zirconocene complexes which show remarkable similarities concerning their structural features and chemical reactivities.

Experimental Section

(η^4-1,2,5,6-Tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane)zirconocene (**2a**) was prepared photochemically by irradiation of an equimolar mixture of **1a** and diphenylzirconocene in ether at −30 °C. (η^4-2,3-Dimethylenebicyclo[2.2.1]heptane)zirconocene (**2b**) was obtained from the reaction of zirconocene dichloride with Li metal (containing 2% Na) in ether in the presence of an excess of **1b**. Details of the workup and characterization of these complexes have been reported previously.[4,10]

Table I. Crystallographic Data for 2a and 2b

	2a	**2b**
formula	$C_{22}H_{26}Zr$	$C_{19}H_{22}Zr$
mol wt	381.7	341.6
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.578 (2)	7.4540 (7)
b, Å	14.466 (3)	8.8377 (8)
c, Å	15.717 (1)	11.8934 (7)
α, deg	75.00 (1)	84.704 (5)
β, deg	88.566 (8)	88.922 (5)
γ, deg	89.12 (2)	79.765 (7)
V, Å^3	1883.104	767.731
Z	4	2
D_{calcd}, g cm^{-3}	1.35	1.49
μ, cm^{-1}	5.71	6.98
T, °C	21	21
x-radiation	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69
scan	ω-2θ	ω-2θ
θ range, deg	1-27.44	1-27.44
reflectns measd	8518	3472
obsd reflectns ($I \geqslant 2\sigma(I)$)	7110	3165
no. of parameters refined	415	269
R	0.035	0.021
R_{w} ($w = 1/\sigma^2(F_{\mathrm{o}})$)	0.053	0.028

Crystals of **2a** suitable for X-ray analysis were obtained by crystallization from pentane/toluene (1:3) at −35 °C. **2b** was crystallized from toluene at that temperature.

Both zirconocene complexes crystallize in the triclinic space group $P\bar{1}$. Exact cell constants were obtained from a least-squares fit to the diffraction angles of 75 accurately centered reflections ($\theta \geq 13°$). Reflections [$I \geq 2\sigma(I)$] remaining after Lorentz and polarization corrections and averaging were used in the refinement. The structure of **2a** was solved by direct methods (SHELX-76) while the heavy-atom method (SHELX-76) was employed for **2b**. The positions of 44 hydrogen atoms of **2a** were taken directly from difference Fourier syntheses, and the positions of the remaining eight H atoms were calculated (C–H = 0.95 Å). All hydrogens could be located for **2b**. Anisotropic least-squares refinement was performed for zirconium and carbon atoms. For **2a** positions of Zr and the C atoms of the $C_{12}H_{16}$ ligand as well as the two Cp systems were refined in separate blocks for both independent molecules, and hydrogen atoms were kept fixed. Isotropic full-matrix refinement of all H atoms was performed for **2b**. Crystal data and additional information concerning the structure determinations are given in Table I.

Carbonylation of 2a and 2b. A solution of 2.66 g (6.9 mmol) of **2a** in 60 mL of benzene was stirred in a carbon monoxide atmosphere (90 bar) for 6 h at ambient temperature. The dark solution was then filtered from a small amount of an unidentified precipitate and concentrated in vacuo (10^{-4} torr, 60 °C). From the distillate 260 mg (25%) of **1a** was isolated by trap to trap distillation. The organometallic residue was extracted with 100 mL of pentane. A 1.6-g (82%) sample of zirconocene dicarbonyl[11] was recovered from the resulting black solution upon cooling. In a similar experiment 980 mg (65%) of zirconocene dicarbonyl was isolated from the reaction of 1.85 g (5.4 mmol) of **2b** with carbon monoxide.

NMR Experiments. A solution of **2a** in benzene-d_6 (~10%) was exposed to a CO atmosphere (90 bar) for 24 h. ^{1}H NMR analysis revealed that during this period the starting material had been completely consumed. Zirconocene dicarbonyl[11] and **1a**[10] in about equimolar amounts were the only detectable reaction products. In an analogous carbonylation experiment $Cp_2Zr(CO)_2$

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Table II. Selected Bond Lengths (Å) and Angles (deg) for 2a (Both Independent Molecules and Mean Values)

molecule 1		molecule 2		average
Zr1-C1	2.311 (3)	Zr2-C21	2.312 (3)	2.311 (1)
Zr1-C2	2.546 (3)	Zr2-C22	2.538 (3)	2.542 (6)
Zr1-C3	2.557 (3)	Zr2-C23	2.559 (3)	2.558 (1)
Zr1-C4	2.321 (3)	Zr2-C24	2.325 (3)	2.323 (3)
C1-C2	1.443 (4)	C21-C22	1.444 (5)	1.444 (1)
C2-C3	1.395 (4)	C22-C23	1.401 (4)	1.398 (4)
C3-C4	1.451 (4)	C23-C24	1.443 (4)	1.447 (6)
C2-C5	1.524 (4)	C22-C25	1.530 (4)	1.527 (4)
C5-C6	1.535 (5)	C25-C26	1.531 (5)	1.533 (3)
C5-C8	1.519 (4)	C25-C28	1.513 (5)	1.516 (4)
C6-C8	1.456 (5)	C26-C28	1.461 (5)	1.459 (4)
C6-C7	1.532 (5)	C26-C27	1.524 (5)	1.528 (6)
C8-C7	1.517 (5)	C28-C27	1.518 (5)	1.518 (1)
C7-C3	1.511 (5)	C27-C23	1.524 (4)	1.518 (9)
Zr-C(Cp)	2.545 (4)		2.544 (4)	2.545
Zr1-C1-C2	81.9 (2)	Zr2-C21-C22	81.5 (2)	81.7 (3)
Zr1-C4-C3	81.9 (2)	Zr2-C24-C23	81.9 (2)	81.9 (2)
C1-C2-C3	130.2 (3)	C21-C22-C23	130.1 (3)	130.2 (1)
C2-C3-C4	129.3 (3)	C22-C23-C24	128.9 (3)	129.1 (3)
C1-C2-C5	124.7 (3)	C21-C22-C25	125.7 (3)	125.2 (7)
C3-C2-C5	104.4 (3)	C23-C22-C25	103.6 (3)	104.0 (6)
C3-C3-C7	104.8 (3)	C22-C23-C27	104.7 (2)	104.8 (1)
C4-C3-C7	125.3 (3)	C24-C23-C27	125.8 (3)	125.6 (4)
C2-C5-C6	107.0 (3)	C22-C25-C26	107.8 (3)	107.4 (6)
C2-C5-C8	110.5 (3)	C22-C25-C28	111.3 (3)	110.9 (6)
C6-C5-C8	57.0 (2)	C26-C25-C28	57.4 (2)	57.2 (3)
C5-C6-C8	61.0 (2)	C25-C26-C28	60.7 (2)	60.9 (2)
C6-C8-C7	62.0 (2)	C26-C28-C27	61.5 (2)	61.8 (4)
C6-C7-C8	57.0 (2)	C26-C27-C28	57.4 (2)	57.2 (3)
C7-C6-C8	61.0 (2)	C27-C26-C28	61.1 (2)	61.1 (1)
C8-C7-C3	110.8 (3)	C28-C27-C23	110.6 (3)	110.7 (1)
C6-C7-C3	107.6 (3)	C26-C27-C23	107.9 (3)	107.8 (2)
D1-Zr1-D2	126.5 (1)	D3-Zr2-D4	125.9 (1)	126.2 (4)

and **1b**[10] were the only observed products starting from **2b**.

Results and Discussion

The crystal structure of **2a** shows the presence of two crystallographically independent molecules per unit cell. Their molecular geometries are equal within three standard deviations. Averaged bond lengths and angles are given in Table II. The structural features of the bicyclobutane unit remain almost unchanged upon complexation of **1a**. In **2a** typical bond lengths and angles are found as expected for a bicyclo[1.1.0]butane unit in a tricyclo[3.1.0.0^{2,6}]hexane framework.[12] All four carbon atoms of the conjugated diene skeleton are clearly within bonding distance to the zirconium center of the bent metallocene (angle Cp_{centr}–Zr–Cp_{centr} = 126.7°). The framework of the diene ligand (plane C1, C2, C3, C4) is planar, the deviation of these carbon atoms from their best plane being within three standard deviations. The C–C bond lengths differ considerably from those of a free conjugated diene.[13] The extent of the influence of the metal on the diene carbon–carbon bond distances found here is far in excess of the C–C bond length compensation effect usually observed for diene transition-metal compounds.[14] This marks the most remarkable structural feature of **2a**.

Compared to a free conjugated diene values of 1.444 (1) Å for C1–C2, 1.398 (4) Å for C2–C3, and 1.447 (6) Å for C3–C4 denote an inverted (long–short–long) sequence of carbon–carbon bond distances for the coordinated cisoid-fixed diene ligand.

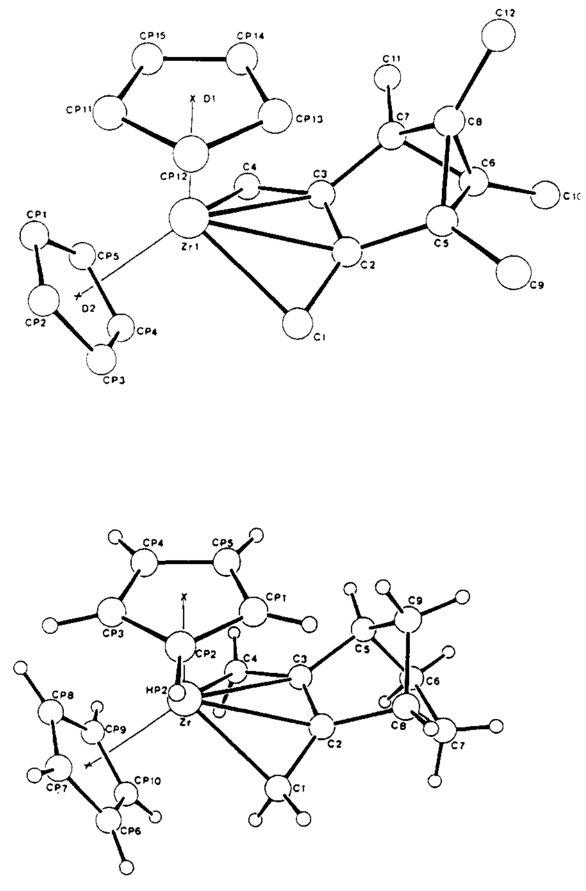

Figure 1. ORTEP representation of $Cp_2Zr(C_{12}H_{16})$ (**2a**) (above) and $Cp_2Zr(C_9H_{12})$ (**2b**) (below).

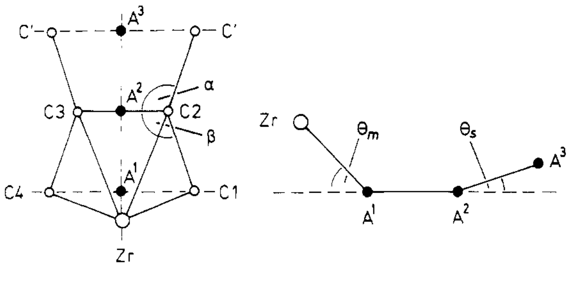

Figure 2. Definitions of some structural features of (diene)zirconocene complexes **2** selected for comparison in Table IV.

The linkages between the metal and the diene termini are short. At 2.311 (1) Å (Zr–C1) and 2.323 (3) Å (Zr–C4) they are within a range typical for Cp_2Zr–C σ bonds.[15] Distances between zirconium and the internal diene carbon atoms C2/C3 are substantially longer. Observed values of 2.542 (6) Å for Zr–C2 and 2.558 (1) Å for Zr–C3 are equal within three standard deviations to the Zr–C(Cp) distances and indicate a Cp_2Zr–olefin π-type interaction.[16] Obvi-

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[16] No appropiate comparisons exist for Zr–C bond lengths of a true $Cp_2Zr(\eta^2$-olefin) moiety. These Zr–C bond distances may, however, be compared with those found in (*s-trans*-η^4-diene)zirconocenes[4,5]a (Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191) or the π bond (Zr–C1 = 2.440 Å, Zr–C2 = 2.462 Å) of $Cp_2Zr(\mu$-Cl)(CH=CHPh)-$ZrCp_2$ (Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E., *Organometallics* **1983**, *2*, 1555).

Table III. X-ray Structure Determination of 2a: Atomic Positional Parameters ($\times 10^4$)

atom	x	y	z	atom	x	y	z
			Molecule 1				
Zr1	6784 (1)	−925 (1)	13 130 (1)	H01A	4466	120	14 098
C1	5469 (3)	180 (2)	13 717 (2)	H01B	6275	278	14 114
C2	5450 (3)	708 (1)	12 802 (1)	H04A	8830	515	12 577
C3	6577 (3)	774 (1)	12 135 (1)	H04B	8648	437	11 525
C4	8105 (3)	324 (2)	12 172 (2)	H09A	2589	1661	13 242
C5	4011 (3)	1193 (2)	12 326 (2)	H09B	1913	703	12 945
C6	4591 (4)	1997 (2)	11 546 (2)	H09C	1701	1594	12 348
C7	5773 (4)	1299 (2)	11 302 (2)	H10A	4825	3482	11 574
C8	4032 (3)	1116 (2)	11 381 (2)	H10B	4250	3278	10 613
C9	2498 (4)	1301 (2)	12 793 (2)	H10C	3176	3100	11 413
C10	4279 (5)	3050 (2)	11 224 (2)	H11A	6873	941	10 250
C11	6618 (5)	1560 (2)	10 428 (2)	H11B	6085	1886	9 937
C12	2846 (5)	900 (3)	10 770 (2)	H11C	7568	1931	10 405
Cp1	8808 (4)	−2192 (2)	13 797 (2)	H12A	2903	1275	10 159
Cp2	7663 (4)	−2216 (2)	14 459 (2)	H12B	2790	293	10 779
Cp3	7765 (5)	−1369 (3)	14 710 (2)	H12C	1875	1104	10 950
Cp4	8945 (4)	−811 (2)	14 206 (2)	HP01	9005	−2743	13 467
Cp5	9596 (4)	−1320 (2)	13 626 (2)	HP02	6918	−2728	14 768
Cp11	5671 (5)	−2445 (2)	12 916 (3)	HP03	6988	−1140	15 190
Cp12	4394 (4)	−1906 (2)	13 111 (2)	HP04	9337	−144	14 147
Cp13	4221 (3)	−1109 (2)	12 411 (2)	HP05	10266	−948	13 070
Cp14	5387 (4)	−1146 (2)	11 775 (2)	HP11	6013	−3059	13 313
Cp15	6276 (4)	−1963 (3)	12 097 (2)	HP12	3778	−2093	13 679
				HP13	3280	−650	12 406
				HP14	5488	−549	11 210
				HP15	7225	−2192	11 806
atom	x	y	z	atom	x	y	z
			Molecule 2				
Zr2	2362 (1)	5975 (1)	6800 (1)	H21A	2386	4693	5869
C21	1349 (3)	4863 (2)	6145 (2)	H21B	502	4909	5695
C22	1006 (3)	4377 (1)	7053 (2)	H24A	3674	4720	8503
C23	1883 (3)	4303 (1)	7808 (1)	H24B	4254	4535	7521
C24	3376 (3)	4716 (2)	7886 (2)	H29A	−2540	3539	7215
C25	−560 (3)	3938 (2)	7419 (2)	H29B	−1495	3646	6308
C26	−243 (3)	3141 (2)	6252 (2)	H29C	−2221	4478	6491
C27	801 (3)	3819 (2)	8571 (2)	H30A	−1871	2074	8435
C28	−890 (3)	4053 (2)	8336 (2)	H30B	−798	1920	9137
C29	−1868 (4)	3885 (3)	6803 (3)	H30C	96	1738	8299
C30	−688 (4)	2118 (2)	8550 (2)	H31A	2541	3252	9550
C31	1324 (5)	3582 (2)	9502 (2)	H31B	1483	4090	9681
C32	−2315 (4)	4338 (3)	8801 (3)	H31C	732	3159	9904
Cp21	4589 (4)	7160 (2)	6313 (2)	H32A	−3093	4106	8505
Cp22	3689 (5)	7224 (2)	5561 (2)	H32B	−2517	5149	8747
Cp23	3852 (4)	6360 (2)	5322 (2)	H32C	−2218	4089	9339
Cp24	4849 (3)	5771 (2)	5912 (2)	HP21	4674	7705	6559
Cp25	5315 (3)	6262 (2)	6521 (2)	HP22	3110	7877	5202
Cp31	1216 (5)	7552 (2)	6921 (3)	HP23	3479	6334	4737
Cp32	72 (5)	7101 (3)	6555 (3)	HP24	5211	5062	5876
Cp33	−413 (4)	6297 (3)	7200 (3)	HP25	5828	5941	7240
Cp34	432 (4)	6258 (2)	7959 (2)	HP31	1804	8147	6601
Cp35	1434 (4)	7030 (2)	7770 (2)	HP32	−263	7333	5914
				HP33	−1239	5822	7191
				HP34	327	5752	8552
				HP35	2250	7089	8316

ously the (diene)ZrCp_2 unit in **2a** exhibits considerable σ-complex character. To a first approximation, **2a** can be described as a metallacyclic σ^2,π complex (Scheme I, resonance form B). The Zr, C1–C4 framework of **2a** is envelope shaped. The rather small angle of fold $\theta_m = 56.6°$ (see Figure 2) is not much different from the expected value for a true bis(η-cyclopentadienyl)zirconacyclopent-3-ene (as compared with $\theta_m = 53.1°$ for **3**,[17] certainly a good model for such a metallacycle).

The numerical value of the angle of fold θ_m (though frequently used) turns out to be rather unsuited for a realistic evaluation of the extent of the σ-complex character in comparison to other (diene)zirconocene complexes.[6] As shown in Table IV, for **2a** C–C–C angles α and β at C2/C3 (see Figure 2) are substantially different from the ones found for Cp_2Zr complexes of open-chain conjugated dienes (**2d**,**e**). The incorporation of carbon atoms C2/C3 of the diene ligand into a five-membered ring system, forced into a rigid strongly folded envelope geometry by the tricyclic structure of **1a**, results in a strong compression of α, at the same time increasing the value of β considerably. **2a** very effectively evades this steric constraint by flattening the Cp_2Zr–diene envelope, i.e., reducing the angle of the fold θ_m.

The geometric situation at the internal carbon atoms of the diene skeleton should, however, influence the zirconium to carbon bond distances much less. Therefore, a comparison of Zr–C2/C3 bond lengths of differently substituted (diene)zirconocene complexes, together with the Zr–C1–C4 distances, is likely to serve as a reasonably sensitive qualitative measure for detecting differences in

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[17] Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1980**, 476.

Table IV. Comparison of Characteristic Structural Parameters of (Diene)zirconocene Complexes **2a,b,d,e** and Zirconaindan **3**[a, b]

	C1-C2[c] C3-C4	C2-C3	Zr-C1/C4[c]	Zr-C2/C3[c]	θ_m	θ_s	α[c]	β[c]
2a[d]	1.446	1.398	2.317	2.550	56.6	8.9	104.4	129.7
2b	1.454	1.391	2.318	2.578	57.7	1.6	106.1	128.5
2d	1.451	1.398	2.300	2.597	68.0	7.1	121.8	122.7
2e	1.473	1.392	2.289	2.714	60.7	4.7	122.8	121.2
3	1.47	1.42	2.30	2.86	53.1	5.6	118.0	119.4

[a] **2a,b**, this work; **2d,e**, ref 6; **3**, ref 7. [b] Bond lengths in Å, angles in deg; see Figure 2 for definitions. [c] Averaged values. [d] Mean values from two crystallographically independent molecules.

Table V. Selected Bond Lengths (Å) and Angles (deg) for **2b**

	Bond Lengths		
Zr-C1	2.307 (2)	Zr-C4	2.329 (2)
Zr-C2	2.569 (2)	Zr-C3	2.578 (2)
C1-C2	1.456 (2)	C3-C4	1.451 (2)
C2-C3	1.391 (2)	C3-C5	1.535 (2)
C2-C8	1.532 (2)	C8-C9	1.539 (3)
C5-C9	1.534 (3)	C8-C7	1.559 (3)
C5-C6	1.561 (3)	Zr-C(Cp)	2.561 (2)
C6-C7	1.562 (3)		
	Bond Angles		
Zr-C1-C2	82.8 (1)	Zr-C4-C3	82.5 (1)
C1-C2-C3	128.4 (2)	C2-C3-C4	128.7 (2)
C1-C2-C8	125.3 (1)	C4-C3-C5	125.3 (2)
C3-C2-C8	106.2 (1)	C2-C3-C5	106.0 (1)
C2-C8-C7	104.4 (1)	C3-C5-C6	103.8 (1)
C2-C8-C9	103.4 (1)	C3-C5-C9	103.3 (1)
C9-C5-C6	100.4 (2)	C9-C8-C7	99.7 (2)
C5-C6-C7	102.6 (2)	C8-C7-C6	102.6 (2)
C5-C9-C8	93.6 (2)	D1-Zr-D2	123.3

metallocyclopentene character. In the series **2a**, **2d**, **2e**, and **3** an experimentally significant equalization of bond distances Zr–C1/C4 vs. Zr–C2/C3 can for the first time be observed in the structure of **2a**. However, the order of magnitude of this effect (~0.02 Å for Zr–C1/C4 and ~0.05 Å for Zr–C2/C3, see Table IV) is rather small, probably not large enough to account by itself for the chemical differences observed for these zirconocene complexes. In other words, on going from **3** over **2e** to **2d** a significant gradual decrease in metallacyclopentene character is observed by X-ray crystallography (Table IV). Basically, these pronounced ground-state differences appear to exercise a direct influence only on the reaction rates[6] (here of automerization and carbonylation) of these compounds. In contrast, a drastic change of chemical reaction type is observed going from **2d** to **2a** (the carbonylation of **2a** and **2d** proceeds at rather similar rates but yields completely different types of products, see Scheme II) though the relevant structural parameters of the Cp_2Zr–diene units are much less different for these two complexes.

As a dominating ground-state effect cannot be inferred from the existing X-ray data the different ability to substituents at diene-C2/C3 to stabilize involved intermediates (and the tranisition states leading to them) might account for the differing chemical behavior of **2a** and **2d**. Due to the considerable strain energy of the developing benzvalene system[18] the 18-electron zirconium(IV) intermediate **4a** is likely to be so unfavorable as compared with **4c** that otherwise unobserved reaction paths (here: ligand displacement) can effectively compete with the C–C bond-forming CO insertion reaction[19] (Scheme II).

Scheme II

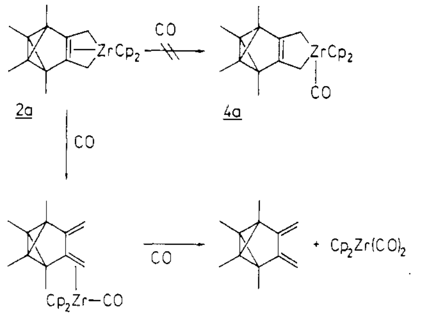

Table VI. X-ray Structure Determination of **2b**: Atomic Positional Parameters (×10⁴)

atom	*x*	*y*	*z*
Zr	1190 (1)	1588 (1)	2427 (1)
C1	3180 (2)	700 (2)	3901 (1)
C2	3433 (2)	−721 (2)	3344 (1)
C3	2134 (2)	−1361 (2)	2817 (1)
C4	198 (2)	−774 (2)	2680 (2)
C5	3166 (3)	−2841 (2)	2361 (2)
C6	3647 (3)	−3969 (2)	3445 (2)
C7	5135 (3)	−3257 (2)	4014 (2)
C8	5259 (2)	−1795 (2)	3197 (2)
C9	5046 (3)	−2443 (2)	2059 (2)
Cp1	3973 (3)	1336 (2)	1104 (2)
Cp2	3416 (3)	3919 (2)	1206 (2)
Cp3	1703 (3)	3389 (3)	693 (2)
Cp4	1186 (3)	2080 (3)	290 (2)
Cp5	2584 (3)	808 (3)	541 (2)
Cp6	−45 (3)	3478 (2)	3900 (2)
Cp7	−375 (3)	4293 (2)	2838 (2)
Cp8	−1677 (3)	3650 (3)	2276 (2)
Cp9	−2152 (3)	2434 (3)	3008 (2)
Cp10	−1143 (3)	2328 (2)	4003 (2)
H5	2503 (31)	−3199 (26)	1788 (19)
H8	6323 (30)	−1340 (24)	3305 (17)
H11	2253 (33)	819 (26)	4499 (19)
H12	4304 (32)	983 (26)	4122 (19)
H41	−546 (34)	−555 (28)	3377 (21)
H42	−448 (33)	−1367 (27)	2189 (20)
H61	2525 (31)	−4041 (25)	3954 (18)
H62	4155 (33)	−5022 (28)	3243 (20)
H71	4845 (32)	−3070 (26)	4833 (20)
H72	6254 (34)	−3969 (28)	4064 (20)
H91	6002 (29)	−3388 (24)	1917 (18)
H92	5051 (33)	−1669 (29)	1402 (20)
HP1	5068 (35)	747 (29)	1374 (21)
HP2	4081 (35)	3591 (29)	1583 (21)
HP3	918 (38)	4443 (32)	653 (22)
HP4	102 (40)	2089 (32)	−93 (24)
HP5	2596 (36)	−153 (30)	344 (22)
HP6	839 (35)	3685 (28)	4446 (22)
HP7	199 (40)	5111 (33)	2621 (24)
HP8	−2230 (36)	3960 (30)	1526 (22)
HP9	−2983 (37)	1763 (31)	2831 (22)
HP10	−1168 (31)	1593 (27)	4668 (20)

This interpretation finds support in the structural and chemical properties of (2,3-dimethylenenorbornane)-zirconocene (**2b**). There is a striking similarity in the

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[18] Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connon, H. A. *Tetrahedron Lett.* **1976**, 4133. Baird, N. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1969**, *91*, 352.

[19] (a) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (b) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45.

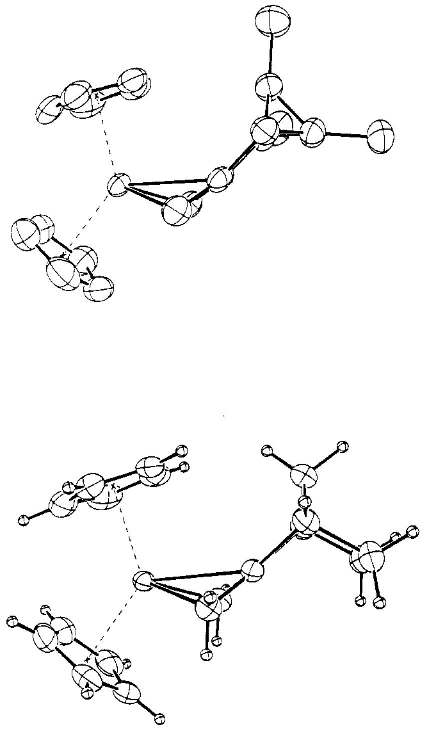

Figure 3. Side views of the molecular structures of **2a** (above) and **2b** (below) (for **2a** C9 has been omitted for clarity).

essential structural features of the (diene)zirconocene units between **2b** and **2a** (see Table IV, Figures 1 and 3). Again rather long C1–C2 (1.456 (2) Å) and C3–C4 (1.451 (2) Å) bonds are opposed by a short C2–C3 (1.391 (2) Å) linkage in **2b**.[20] The metal forms σ bonds to the diene termini [2.307 (2) Å (Zr–C1), 2.329 (2) Å (Zr–C4)] and exhibits a substantial π interactions with the internal carbon atoms of the diene unit [2.569 (2) Å (Zr–C2), 2.578 (2) Å (Zr–C3)]. The σ bond system of the Cp_2Zr–diene part of the molecule is oriented in a rather flat envelope conformation (θ_m = 57.7°),[20] the metallocene unit being coordinated to the exo side of the ligand. The norbornane unit in **2b** does not show significant deviations from bonding parameters usually found for bicyclo[2.2.1]heptane derivatives.[20]

2b, like **2a**, exhibits a carbonylation reaction pattern completely different from the one typically observed for **2d** and **2e**. Indications for the formation of new carbon–carbon bonds are not found. Instead, with carbon monoxide **2b** appears to react exclusively with ligand displacement and formation of zirconocene dicarbonyl.

The X-ray structures of (*s-cis*-diene)zirconocene complexes obtained so far seem to set the limits of structural variations possible for this class of compounds. It appears that there is a continuous transition from a η^4-bonding situation toward a purely metallacyclic σ structure depending on the substituents on the diene moiety. However, the very special bonding situation of the bent metallocene unit[21] does not seem to allow an equally smooth approach of the opposed bonding situation extreme,[8] a true diene zirconocene π complex. From the molecular structures of **2a, 2b**, and **2d** it may be inferred that the limiting situation in this direction is marked by reaching a metallacyclic σ^2,π structure.

Finally, a special feature of the structure of **2a** deserves to be mentioned. Carbon atoms C5/C7 of the tricyclic "substituent", bound to the internal carbon centers of the diene ligand, are oriented markedly outside the plane determined by the diene carbon atoms. Relative to that plane linkages C2–C5 and C3–C7 are bent significantly *toward* the metal center (Figure 3). The angle of fold between planes C1,C2,C3,C4 and C5,C2,C3,C7 for this (diene)zirconocene complex amounts to θ_s = 8.9° (Figure 2). This effect, though sometimes being less pronounced, can be observed for other (diene)zirconocene complexes **2** as well[22,23] (Table IV).

We propose a similar explanation for this phenomenon as was developed to account for the observed bond bending at the meso carbon atom of η^3-allyl transition-metal complexes.[24,25]

Upon complexation of a conjugated diene to the d^2-configurated Cp_2Zr–bent metallocene unit a rehybridization of all the diene carbon atoms to diminish the antibonding interaction from participation of ψ_3 of the diene π system is especially favored because of the high σ character of the Zr–C1/C4 linkage. The resulting increased coefficients of the π-orbital lobes at C2/C3 on the diene face opposite to the metal, in turn, directly cause substituents on these carbon atoms to lean toward the metal center.

Surprisingly this effect appears to be almost nonexistent for **2b**. At present it is not clear if this is primarily due to a repulsive interaction between the metallocene and the syn-H9 of the norbornane unit or if this reflects a special feature of the bicyclic ligand system.

Acknowledgment. We thank Dr. R. Goddard for helping us to understand the origin of substituent bending at C2/C3 (θ_s). Financial aid from the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Supplementary Material Available: Tables of thermal parameters and lists of observed and calculated structure factor amplitudes for **2a** and **2b** (52 pages). Ordering information is given on any current masthead page.

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[20] The structural differences to, e.g., $Fe(CO)_3$ complexes of similar bicyclic conjugated diene ligands are noteworthy: Wenger, J.; Thuy, N. H.; Boschi, T.; Roulet, R.; Chollet, A.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *J. Organomet. Chem.* **1979**, *174*, 89. Barras, C.; Roulet, R.; Vieira, E.; Vogel, P.; Chapuis, G. *Helv. Chim. Acta* **1981**, *64*, 2328.

[21] Brintzinger, H. H.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 1105. Lauher, J. W.; Hoffmann, R. *Ibid.* **1976**, *98*, 1729. Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605; *J. Organomet. Chem.* **1980**, *188*, C1 and references cited.

[22] (a) (2,3-Dimethylbutadiene)zirconocene:[6] θ_s = 7.1°. (b) (2,3-Diphenylbutadiene)zirconocene:[6] θ_s = 4.7°.

[23] This effect can sometimes be observed for diene complexes of late transition metals, as well. See, for example, (*o*-quinodimethane)$Fe(CO)_3$, θ_s = 7.9° (Krüger, C.; Mühlenbernd, T., unpublished results), and [(2,3-dimethylbutadiene)$Co(CO)_2]_2$ θ_s = 4.0° (Stephens, F. S. *J. Chem. Soc. A* **1970**, 2745).

[24] Goddard, R. J.; Krüger, C., unpublished results.

[25] For early examples see: Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1966**, 26. Churchill, M. R.; O'Brien, T. A. *Ibid.* **1968**, 246.