412.0466 52, $M_2L_3^+$ observed by LRMS[11] only—*m/e* 566 (<1% intensity)].

Synthesis of Bis(η^6-diphenylmethane)chromium(0) (VI). Chromium metal (0.496 g, 14.0 mmol) was evaporated into diphenylmethane (15.1 g, 89.9 mmol) by using a time-averaged 350 W at an average pressure of 9.3×10^{-6} torr during a period of 1.0 h. After transfer and workup, compound VI [mp 132–133 °C (lit.[12] 132–135 °C)] was collected by sublimation [140 °C (10^{-3} torr)]. Total yield was 2.15 g or 58.1%.

Synthesis of Bis(η^6-*trans*-stilbene)chromium(0) (VII). Chromium metal (0.388 g, 7.46 mmol) was evaporated into *trans*-stilbene (13.2 g, 73.3 mmol) by using a time-averaged 310 W at an average pressure of 9.9×10^{-6} torr during a period of 1.2 h. After transfer and workup, compound VII (mp 110–113 °C) was collected by sublimation [160 °C (10^{-3} torr)]. Total yield was 1.06 g or 34.5%. No oligomerization of *trans*-stilbene was observed during the metal atom reaction.

Additional characteristics of compounds VI and VII are presented in Table I.

Results and Discussion

Our synthetic route permits the direct synthesis of bis(η^6-arene)chromium(0) compounds that are difficult to prepare by other methods. The new route eliminates the need for (a) harsh reductive solution reactions, (b) highly volatile ligands, (c) reaction solvents which must be inert to chromium atoms and have low vapor pressure at the reaction temperature and in which the ligands and/or products must be relatively soluble, and (d) the need to monitor carefully the temperature of slush baths.

We found this solvent-free synthetic route to be more efficient than the conventional method when the same compounds were prepared by both techniques in our labortory.

Our technique has also proven valuable for the synthesis of compounds IV, V, VI, and VII that will be used as precursors in future polynuclear studies. The method shows promise as a route to the formation of metal π-complexes using ligands with a low volatility and/or solubility and hence not attainable using the conventional methods.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for their generous financial support of this work.

Registry No. I, 57820-98-1; II, 97102-75-5; III, 12156-66-0; IV, 12099-15-9; V, 72281-90-4; VI, 67775-54-6; VII, 97102-76-6; Cr, 7440-47-3; durene, 95-93-2; pentamethylbenzene, 700-12-9; hexamethylbenzene, 87-85-4; biphenyl, 92-52-4; diphenylmethane, 101-81-5; *trans*-stilbene, 103-30-0.

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[11] Low-resolution mass spectrometry performed using a Bell and Howell 21491 mass spectrometer with an ionization potential of 70 eV and a current of 7 μA.

[12] J. A. Gladysz, J. G. Fulcher, and A. B. Bocarsly, *Tetrahedron Lett.*, 20, 1725 (1978).

Theoretical and Experimental Evidence for a Thermally Induced η^4-Diene $\rightleftharpoons$ η^3-Allyl Ligand Interconversion in (*s*-*trans*-η^4-Conjugated diene)zirconocenes

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Photolysis of diphenylzirconocene (**5**) at low temperature (−50 °C) in the presence of the isomerically pure dienes (*Z,Z*)- and (*Z,E*)-2,4-hexadiene (**8a**) and (*Z,Z*)- and (*Z,E*)-1,4-diphenylbutadiene (**8b**), respectively, leads to the stereospecific formation of the corresponding (*s*-*trans*-η^4-conjugated diene)zirconocene complexes **1a**-*ZZ*, **1a**-*ZE*, **1b**-*ZZ*, and **1b**-*ZE*. Upon thermolysis, **1a**-*ZZ* ($\tau_{1/2} \approx 25$ min at −25 °C) first rearranges to give **1a**-*ZE* exclusively, which consecutively rearranges to a thermodynamic 60/40 mixture of **1a**-*EE*/**3a**-*EE* at higher temperature (+25 °C). Similarly, **1b**-*ZE* undergoes a thermally induced geometrical isomerization at +35 °C to form **1b**-*EE*/**3b**-*EE* (95/5). The same product mixture is obtained directly from **1b**-*ZZ* at +60 °C. The observed stepwise loss of the stereochemical information at the terminal carbon centers of the conjugated diene ligands of **1** indicates a rearrangement process proceeding through a π-allyl-type intermediate (**4**). This interpretation is supported by the result of an extended Hückel calculation: an approximate transition state (**10a′**) for a related isomerization process with an unsubstituted butadiene system can be reached by rotating this ligand around a $Zr-C_{term}$ bond (7°), lifting the exposed CH_2 group by 50°, and rotating it 90°. A barrier of 25 kcal/mol was computed. The orbitals of **10a** are in agreement with the formulation of an allyl complex. A low-lying LUMO predominantly localized at the exposed CH_2 moiety indicates carbenium ion character at this carbon. Terminal π-donor substituents at the butadiene ligand cause a drop of the rearrangement barrier to 12 kcal/mol, which can be explained by means of delocalization of carbenium p orbital character into filled wave functions of the π-donor residue. Stereochemistry and calculations have thus revealed a third general mechanistic pathway for an intramolecular diene transition-metal complex isomerization: rearrangement through π-allyl-type intermediates **4** can be of importance in addition to the established diene rotation and topomerization mechanisms.

For the interconversion of (butadiene)zirconocene isomers substantial experimental evidence has accumulated for a qualitative description of the energy profile as depicted in Figure 1.[2] The geometrical isomerization **1** $\rightleftharpoons$

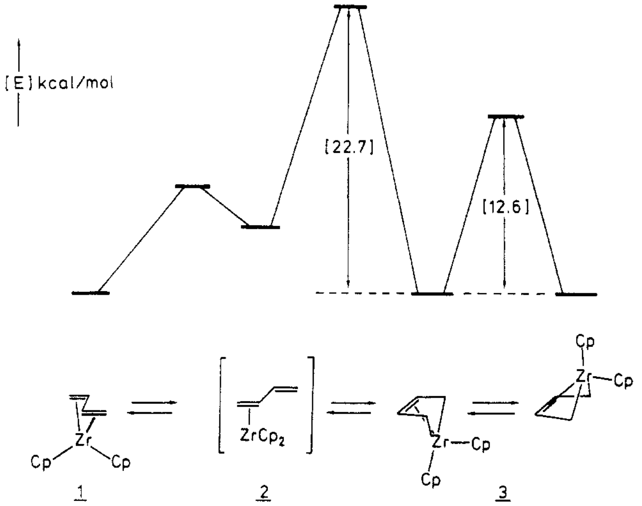
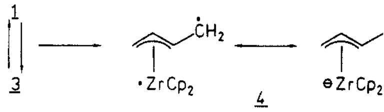


Figure 1. A qualitative description of the (butadiene)zirconocene energy surface.

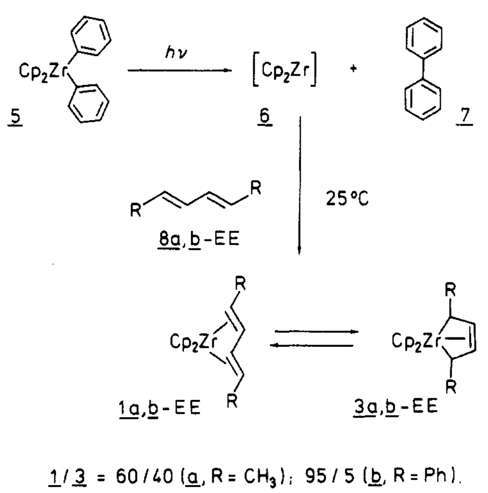
Scheme I



3 proceeds through a (η^2-butadiene)ZrCp$_2$ intermediate (2)[3] which rapidly equilibrates with the unique (*s-trans*-η^4-butadiene)ZrCp$_2$ (1),[4] whereas a rather substantial activation energy barrier separates 2 from 3. The (probably concerted) topomerization of the σ^2,π-type structured (*s-cis*-butadiene)zirconocene 3 is a rapidly proceeding competing reaction pathway (Figure 1).[5,6]

From an experimental as well as theoretical point of view it is still an open question if other types of intermediates represent additional chemically important local minima on the (diene)metallocene surface.[7] Of primary interest in this regard is the possible interconversion of the directly observable (η^4-butadiene)ZrCp$_2$ isomers 1 and 3 with π-allyl-type metallocene complexes 4.[8-10] Species 4 (Scheme I), where only one metal–carbon linkage of the (η^4-diene)metallocene moiety has been opened, might represent a "resting stage" of the 1 ⇌ 2 ⇌ 3 interconversion. It is also conceivable that complexes of this type are not involved in the (*s-cis*-diene)metallocene/(*s-trans*-diene)metallocene isomerization process at all but serve as important intermediates in separated independent reaction pathways starting from (η^4-conjugated diene)zirconocene (and η^4-conjugated diene)hafnocene systems.

Scheme II



Intermediates 2 and 4 are characterized by their different diene C(internal)–C(terminal) bond order.[11] In 2, the intact, uncoordinated carbon–carbon π-bond preserves the stereochemical integrity of conjugated diene ligands, suitably substituted at the diene termini, whereas a rather facile bond rotation is expected to result from a substantially reduced π-interaction of the C1–C2 linkage of 4. Therefore, obtaining evidence for the possible role of 4 in (diene)MCp$_2$ chemistry obviously represents a stereochemical problem. The availability of 4 should manifest itself by a loss of a stereochemical information at the diene termini of 1 or 3, observed in competition with the presently known reaction modes.[3-6]

We have experimentally examined the stereochemical behavior of (1,4-disubstituted *s-trans*-η^4-conjugated diene)zirconocenes using the complete set of *E,E*, *E,Z*, and *Z,Z* isomers of 2,4-hexadiene and 1,4-diphenylbutadiene. A theoretical investigation has confirmed the possibility of rapidly forming 4 from 1 in a thermally induced reaction.

Experimental Studies

Several rather different synthetic methods have been used previously for the preparation of (conjugated diene)zirconocene complexes.[3-6] Most important among these are procedures during the course of which the elusive monomeric Cp$_2$Zr unit 6 is generated from different precursors in the presence of the diene ligand. These syntheses have in common that a reactive (η^2-conjugated diene)ZrCp$_2$ intermediate (e.g., 2) is formed first.[3a,4a] Therefore, under kinetic control (*s-trans*-η^4-diene)metallocenes 1 are the observed principal reaction products, in accordance with the general energy profile of the diene metallocene system (see Figure 1).

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(2) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.*, in press.

(3) (a) Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462. (b) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1982**, *94*, 915, 916. Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Ibid.* **1983**, *95*, 506. Erker, G.; Dorf, U. *Ibid.* **1983**, *95*, 800.

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(6) (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388. (b) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191. (c) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3735.

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(9) Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem.* **1984**, *96*, 445. Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Chem. Ber.* **1985**, *118*, 1383. Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Angew. Chem.* **1984**, *96*, 621. Berg, K.; Erker, G. *J. Organomet. Chem.* **1984**, *270*, C53.

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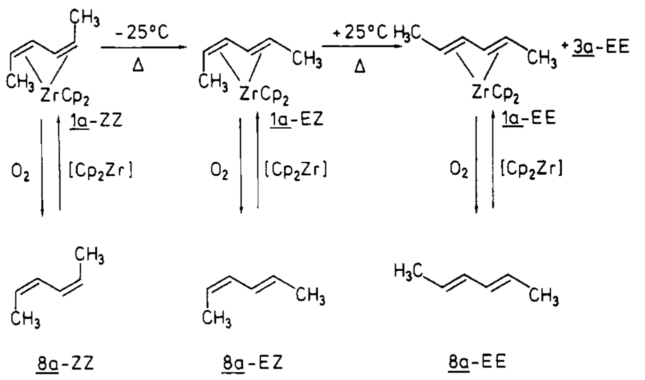
(11) Lehmkuhl, H.; Danowski, F.; Benn, R.; Rufinska, A.; Schroth, G.; Mynott, R. *J. Organomet. Chem.* **1983**, *254*, C11.

Scheme III



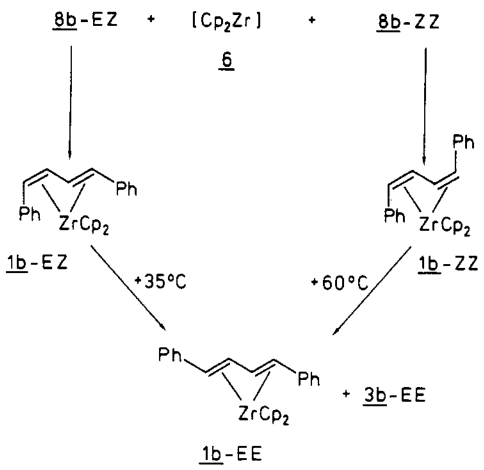
For the present investigation we have used diphenylzirconocene (**5**)[12] as the Cp_2Zr precursor. Photolysis of **5** results in the formation of biphenyl (**7**).[13] Bis(η-cyclopentadienyl)zirconium(II) (**6**), generated via the photochemically induced reductive elimination process, is effectively trapped to form (conjugated diene)zirconocene complexes.[3-5] At room temperature, in the presence of *E,E*-configurated 2,4-hexadiene, a thermodynamic mixture of (*s-cis*-(*E,E*)-2,4-hexadiene)- and (*s-trans*-(*E,E*)-2,4-hexadiene)zirconocene (**1a**-*E,E*/**3a**-*E,E* = 60/40) is formed in good yield (Scheme II).

The substituted (diene)zirconocene isomers can easily be identified and distinguished from each other by ^1H NMR. The (*s-trans*-diene)metallocene isomer **1a**-*EE* (C_2 symmetry) shows only one Cp singlet at rather high field[14] (δ 4.95 in benzene-d_6 solution) in addition to H_{anti} (δ 1.68) and H_{meso} (2.67) multiplets and a methyl doublet at δ 2.05, whereas the envelope-shaped **3a**-*EE* exhibits two distinctly different Cp resonances (δ 5.39 and 4.91, δ 4.50 (H_{meso}) δ −0.49 (H_{anti}), δ 2.10 (CH_3)). Similarly, a 95/5 mixture of **1b**-*EE* (^1H NMR δ 4.80 (Cp), 3.84 (H_{meso}), 3.17 (H_{anti})) and **3b**-*EE* (δ 5.28, 4.68 (Cp)) is formed upon irradiation of diphenylzirconocene in the presence of (*E,E*)-1,4-diphenylbutadiene at ambient temperature.

Irradiation of **5** with *E,E*-configurated dienes **8a** and **8b** at −65 °C proceeds analogously. In both cases the thermodynamic **1**/**3** mixture is obtained even at low temperature. Irradiation of diphenylzirconocene with equimolar amounts of *Z,Z*- and *Z,E*-configurated conjugated dienes **1a** and **1b** in toluene below −50 °C takes a somewhat different course. In each case a single (*s-trans*-η^4-diene)zirconocene complex is obtained. The reaction is stereospecific.

For hexadiene zirconocenes **1a**-*ZZ* and **1a**-*ZE* the conservation of the diene stereochemistry upon complex formation was confirmed by chemical degradation. Treatment of a sample of (*s-trans*-η^4-(*Z,Z*)-2,4-hexadiene)zirconocene (^1H NMR (toluene-d_8, −65 °C) δ 4.68 (Cp), 3.85 (H_{syn}), 2.92 (H_{meso}), 1.29 (CH_3)) with dry oxygen gas at −65 °C yields (*Z,Z*)-2,4-hexadiene as the predominant isomer (≥95%) of the C_6H_{10} fraction. Similarly, only **1a**-*ZE* is formed upon irradiation of Cp_2ZrPh_2 and (*Z,E*)-2,4-hexadiene at −65 °C. Oxidative cleavage at low temperature[15] leads back to **8**-*ZE* (Scheme III)

Scheme IV



Retention of the diene ligand stereochemistry upon formation of *Z,Z*- and *Z,E*-configurated (*s-trans*-η^4-1,4-diphenylbutadiene)$ZrCp_2$ complexes is inferred from a direct comparison of the ^1H NMR spectra of the three geometrical **1b** isomers. At low conversions (~20%) irradiation of **5** at −50 °C in the presence of (*Z,Z*)-1,4-diphenylbutadiene yields ≥95% isomerically pure **1b**-*ZZ* (^1H NMR (toluene-d_8, −50 °C) δ 4.81 (Cp), 5.16 (H_{meso}), 4.05 (H_{syn})). Unfortunately, stereochemical information is being lost in part upon prolonged irradiation times due to substantial *Z*/*E* isomerization of the uncomplexed conjugated dienes.[16] For this reason, stereospecific formation (≥95%) of (*s-trans*-η^4-(*Z,E*)-1,4-diphenylbutadiene)zirconocene (**1b**-*ZE*) (^1H NMR δ 5.01, 4.51, (Cp), 5.08 (2 H_{meso}), 3.20 (H_{anti}), 2.75 (H_{syn})) from **6** and **8b**-*EZ* at −50 °C can be demonstrated only at a similarly low conversion rate.

In the absence of light, moisture, and oxygen (*s-trans*-η^4-(*Z,Z*-2,4-hexadiene)zirconocene appears to be a completely stable molecule at −65 °C. However, at higher temperature it becomes apparent that **1a**-*ZZ* is a thermally rather labile zirconium complex. A stepwise loss of the stereochemistry at the diene termini can be monitored by ^1H NMR spectroscopy upon warming of a toluene solution of this *Z,Z*-configurated (*s-trans*-η^4-diene)zirconocene complex. The reaction sequence starts at −25 °C. At this temperature **1a**-*ZZ* in a clean reaction undergoes a thermally induced rearrangement ($\tau_{1/2} \approx$ 25 min) to yield **1a**-*ZE*. The ^1H NMR spectrum (in toluene-d_8 at −25 °C) of the product exhibits two Cp singlets separated by 1.2 Hz centered around δ 4.75, a complex pattern for the methine hydrogen atoms (multiplet at δ 3.78, 3.23, 2.30, and 1.62) and two distinctly different methyl resonances (δ 2.08 (syn-CH_3), 1.18 (anti-CH_3)). **1a**-*ZE* had been prepared (from Cp_2Zr (**6**) and (*Z,E*)-2,4-hexadiene, see above) and characterized independently.

1a-*ZE* itself is thermally labile. At room temperature it slowly rearranges ($\tau_{1/2} \approx$ 30 min at +25 °C in toluene solution) to give the thermodynamic (*s-cis*-η^4-(*E,E*)-2,4-hexadiene)zirconocene/(*s-trans*-η^4-(*E,E*)-2,4-hexadiene)zirconocene mixture (**1a**-*EE*/**3a**-*EE* = 60/40 (see Scheme III).[3a]

(*s-trans*-η^4-(*Z,E*)-1,4-Diphenylbutadiene)zirconocene (**1b**-*ZE*) exhibits an analogous behavior. A thermally induced rearrangement takes place above room temperature ($\tau_{1/2} \approx$ 20 min at +35 °C) to give a 5/95 mixture of **3b**-*EE*

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(12) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

(13) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) See also: Erker, G.; Engel, K.; Vogel, P. *Angew. Chem.* **1982**, *94*, 791. Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555.

(14) This seems to be a general observation for Cp_2Zr(II) vs. Cp_2Zr(IV) complexes; see, e.g.: Thomas, J. L.; Brown, K. T. *J. Organomet. Chem.* **1976**, *111*, 297. Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812.

(15) Engel, K. Dissertation, Ruhr-Universität Bochum, 1983.

(16) Misumi, S.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 399. Schlosser, M.; Christmann, K. F. *Liebigs Ann. Chem.* **1967**, *708*, 1. Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540. Bestmann, H. J.; Stransky, W.; Vostrowsky, O. *Ibid.* **1976**, *109*, 1694.

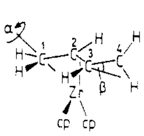
and **1b**-*EE*.[3a] In contrast, **1b**-*ZZ* takes a somewhat exceptional position among the members of these series of isomeric (1,4-disubstituted butadiene)zirconocene complexes. Photochemically synthesized (*s-trans*-η^4-(*Z*,*Z*)-1,4-diphenylbutadiene)$ZrCp_2$ is of substantially higher thermal stability than the **1b**-*ZE* isomer. This obviously prevents **1b**-*ZE* from being detected as an intermediate in the thermally induced sequential geometrical isomerization starting from **1b**-*ZZ*. Therefore, it is not surprising that the rearrangement of (*s-trans*-η^4-(*Z*,*Z*)-1,4-diphenylbutadiene)zirconocene at elevated temperatures (~95% conversion after 75 min at 60 °C) yields the thermodynamic **1b**-*EE*/**3b**-*EE* mixture as the only observed reaction products (Scheme IV).

Extended Hückel Calculations

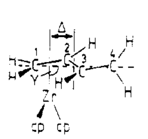
MO analyses on a relatively qualitative level often provide very useful tools to distinguish between or to support specific reaction paths. In order to elucidate the intermediacy of a π-allyl-type complex **4** in the isomerization processes of **1a** and **1b**, we have carried out EHT calculations[17] on (*trans*-butadiene)zirconocene model systems **1**. Exploratory calculations showed that a *trans*-butadiene ligand can be rotated around a $Zr-CH_2$ bond axis or linearly shifted in the mirror plane between the Cp rings of a Cp_2Zr fragment on relatively shallow potential energy curves. This indicated that such motions have considerable probability of being inherent in low barrier molecular rearrangements.

In the search for an approximate transition state for the transformation **9** a full optimization of all degrees of freedom was not carried out, nor would we expect it to lead to a good reaction path from the extended Hückel method. Approaching a simplified but satisfactory model for the transition state for **9**, we started from a butadiene ligand with one terminal methylene group rotated at 90° and a Cp_2Zr fragment underneath the central C–C bond. From the exploratory calculations it seemed reasonable to restrict the optimization procedures to two alternative reaction paths as demonstrated in **10a** and **10b**. In either case two crucial geometrical parameters were fitted: for **10a** the angle of rotation, α, of the butadiene ligand around the $Zr-C_1$ bond and the liftoff angle of C_4, β; for **10b** the displacement, Δ, of the Cp_2Zr moiety from the butadiene center in the plane of the terminal C's and Zr and the hinging angle, γ, of the butadiene ligand. In both cases the structural parameters were taken from an X-ray structure determination.[6b]

9



10a



10b

10b with Δ = 0.65 Å and γ = 70° (**10b'**) was found to be a local minimum and lay 73 kcal/mol above the total energy calculated for **1** in the geometry from the X-ray analysis,[6b] while **10a'** (α = 7° and β = 50° in **10a**) was computed to only cause a 25 kcal/mol barrier of process **9**. C_3 lies only in **10a'** in the mirror plane between the two Cp rings, and its orbitals find satisfactory interaction with the linearly arranged "valence orbitals" of the Cp_2Zr fragment.

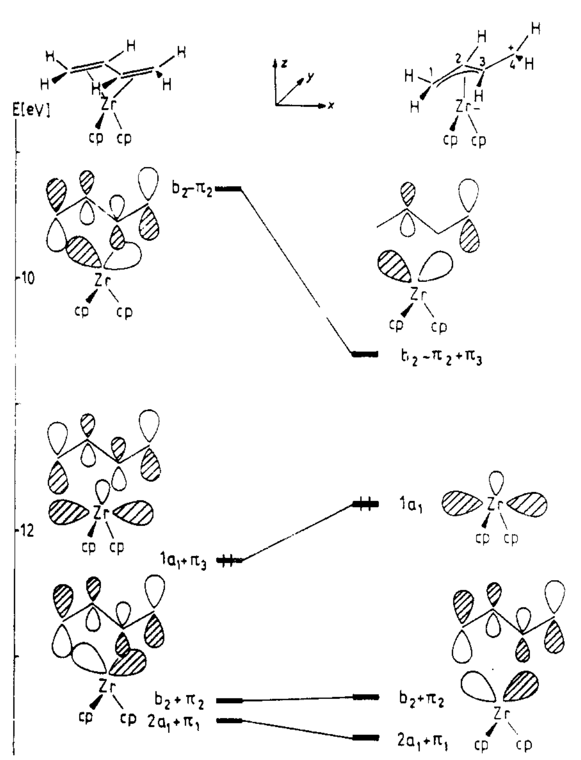
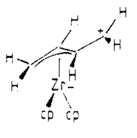


Figure 2. Evolution of selected orbitals (HOMO/LUMO region) along the **1** → **11** transformation.

From these results it seemed obvious that **10a'** was a better model for the transition state of **9**. This value of 25 kcal/mol is, however, still too high if compared to the experimental data of **1a** and **1b**. This may reflect an insufficient optimization procedure, but it could also reveal the general problem that theoretical calculations deal with isolated gas-phase molecules. Thus, computed potential energy differences can only be compared with solution chemistry in the cases of series of related compounds[18] for which the interaction with their environment is of the same magnitude. **1** represents a relatively unpolar complex, and a molecular structure such as **10a'** with a resonance formulation, **4**, should exhibit a high degree of carbenium ion character at the exposed methylene group (as we shall see later). **10a'** should, therefore, experience much greater stabilization by the interaction with solvent molecules.

Of great importance for the understanding of the conversion **1** → **10a'** are the concomitant orbital transformations. The **1** → **10a'** process was separated into two stages, the *trans*-butadiene rotation together with the C_4 lifting leading to **11** and the subsequent CH_2 group rotation; the former will be discussed first. The orbitals of the starting



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[17] Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; 3489; **1962**, *37*, 2878. Hoffmann, R. *Ibid.* **1963**, *39*, 1397. Structural parameters: idealized geometry of ref 6b. Atomic parameters: C, O, H, standard; Zr, 5s, H_{ii} = −10.1 eV and ζ = 1.817, 5p, H_{ii} = −6.89 eV and ζ = 1.505, and 4d, H_{ii} = −12.1 eV and ζ_1 = 3.835; C_1, 0.621 05, ζ_2 1.505, C_2 0.579 63, double-ζ expansion.

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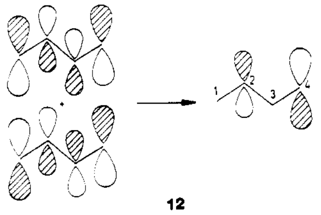
molecule 1 have been analyzed earlier.[7] There are two dominant interactions between the "valence orbitals" of a Cp_2Zr fragment ($2a_1 + b_2 + 1a_1$)[19] and the π-set of a butadiene system: $1a_1 + \pi_3$ and $b_2 + \pi_2$ (see Figure 2).

The product of the 1 to 11 transformation can be identified by its orbital features as a Cp_2Zr allyl-type complex. When the rotational process of the butadiene ligand in 1 starts, overlap between $1a_1$ and π_3 diminishes and at later stages of that motion it almost disappears. The $1a_1$ Cp_2Zr orbital does not find a proper partner for interaction from the butadiene π-set anymore. The remaining π_3 character, set free, is now allowed to be mixed into the LUMO composed of $b_2-\pi_2$, because the symmetry of the system has been lowered. As shown in 12, a nonbonded allylic type π-function results within the organic framework. This orbital, localized considerably more on C_4 than on C_2, represents a low-lying LUMO and reminds one of a carbenium ion situation. In fact the atomic charges developed along the $1 \rightarrow 11$ process reflect this feature: C_2 and especially C_4 show increasing positive values, while the zirconium center accumulates the corresponding negative charge predominantly because of the newly formed $1a_1$ "lone pair", which can no longer be back-donated into empty ligand orbitals. This MO picture of a charge separation in 11 justifies the polar resonance description **4**. The binding of the butadiene system to the Zr center is almost exclusively accomplished by the $b_2 + \pi_2$ interaction (Figure 2), which appears slightly polarized by an admixture of π_3 character. The $1a_1 + \pi_3 \rightarrow 1a_1$ orbital conversion (see Figure 2) is responsible for the greater part of the energy barrier of the $1 \rightarrow 11$ process.

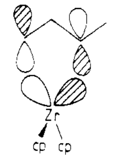


12

The lifting of C_4 is a decisive geometric distortion in process **9**. It accounts for almost no energetic change. A weakening of the $Zr-C_4$ bond ($Zr-C_4$ overlap population drops from 0.25 to 0.01) is compensated by hybridizing C_3 orbitals toward a stronger contact to the Zr center and by releasing strain of the nonplanar arrangement of the butadiene system in 1.

The slipping of olefin ligands in transition-metal complexes along the olefinic C–C axis is electronically very similar to the discussed $1 \rightarrow 11$ butadiene reaction.[20] An olefin shift proceeds under formation of charge-separated "incipient" carbenium ions,[21] important intermediates in catalytic reactions.

The methylene group rotation at C_4 (reaction 11 → **10a′**) is sterically and electronically supported by the $1 \rightarrow 11$ conversion and costs 18 kcal/mol. Especially the lifting of C_4 provides a long C_4-Zr distance of 3.46 Å. This helps to avoid steric contacts of the rotating CH_2 residue and reduces bonding of C_4 to the Zr center. The energetic barrier originates from the loss of π-interaction in the butadiene moiety. For the major part it is expressed in an energetic increase of the $b_2 + \pi_2$ orbital (Figure 2), which converts to a $b_2 + n\pi$ function (**13**) in **10a′**.



13

Further theoretical investigations were directed toward the influence of certain terminal trans butadiene substituents. The simulation of the conversion of **1a**-*EE* to **1a**-*ZE* (Scheme III) with an analogous transition state as **10a′** shows only a slightly lower barrier than the process 1 → **10a′**. Instead, modeling the reaction **1b**-*EE* to **1b**-*EZ* by having terminal OH groups on the butadiene system and by again assuming a transition-state geometry like **10a′** leads to a computed activation energy of 12 kcal/mol, significantly lower than the values for the rearrangements of **1a** or **1**. This drop in the activation barrier originates from a lower $C_{int}-C_{term}$ barrier of rotation in π-donor derivatized butadienes. It can be explained by means of the stabilizing influence of these substituents on the zwitterionic structure of the organic moiety in **10a′**. Comparable to the stability situation of a methylium vs. a benzylium ion empty orbital character on C_4 is delocalized into filled combinations of the π-donor substituent. A stabilization of the corresponding occupied wave functions results.

The observed differences in the activation barrier between the rearrangements of **1a**-*ZZ* and **1a**-*ZE* or **1b**-*EZ* and **1b**-*ZZ*, respectively, must be rationalized on steric grounds. Electronically, all these processes of different isomers are not distinguishable.

Conclusions

Irradiation of diphenylzirconocene (**5**) in the presence of the geometrical 1,4-disubstituted butadiene isomers **8a**-*EE*, -*EZ*, and -*ZZ* and **8b**-*EE*, -*EZ*, and -*ZZ* at low temperature results in the stereospecific formation of (*s-trans*-η^4-conjugated diene)zirconocene complexes **1a**,**b**. This observation clearly rules out that a π-allyl-type intermediate (**4**) might be involved in the formation of **1** from (η^2-diene)metallocene **2**. However, the (*s-trans*-η^4-diene)zirconocene complexes **1a** and **1b** subsequently undergo a thermally induced rearrangement process which leads to a specific loss of the stereochemical information at the terminal carbon centers of the conjugated diene ligands. The clearly observed sequential *Z*/*E* isomerization indicates that this process is fundamentally different from the topomerization of the (*s-cis*-diene)metallocene systems, which is characterized by a simultaneous inversion of the stereochemistry at both diene termini.[2,5] The stepwise geometrical isomerization process is observed for methyl- as well as phenyl-substituted butadiene ligands of **1**; this argues against a specific β-hydrogen elimination/readdition pathway as a general interpretation of this behavior.[22] In view of the result of our theoretical investigation, **4** is an attractive intermediate for the observed rearrangement process. According to this calculation, "slipping" of the diene ligand in front of the bent metallocene unit should be rather sensitive to steric hindrance. This could be the simple explanation for the unusual stereochemical stability of the (*s-trans*-η^4-(*Z*,*Z*)-1,4-diphenylbutadiene)zirconocene isomer (**1b**-*ZZ*).

Using diene stereochemistry as a tool in the (butadiene)$ZrCp_2$ system has revealed a third general mechanistic

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pathway for an intramolecular diene transition-metal complex isomerization. Rearrangement through π-allyl-type intermediates **4** can be of importance in addition to the established diene rotation and topomerization (i.e., ring inversion) mechanisms.[2-6,8,23]

Experimental Section

General Remarks. Organometallic materials were prepared and handled in an argon atmosphere using Schlenk-type glassware. ^{1}H NMR spectra were recorded by using a Bruker WP 250 FT, a Bruker WP 80 FT, and a Varian NV 14 (60 MHz, variable temperature) spectrometer; IR spectra were recorded by using a Perkin-Elmer IR spectrometer 325; gas chromatograms were recorded by using a Varian aerograph P 90. A Phillips HPK 125 UV lamp in a water-cooled Pyrex immersion well equipped with a vacuum jacket was used for the irradiation experiments. Diphenyl-zirconocene (**5**) was prepared according to a literature procedure.[12,13] Thermodynamic mixtures of **1a**-*EE*/**3a**-*EE* and **1b**-*EE*/**3b**-*EE* were isolated and completely characterized by NMR, IR, MS, and elemental analyses as was previously described in full detail.[4b] The results of an X-ray structure analysis were reported for **1b**-*EE*.[6b] Conjugated diene ligands **8a,b** were obtained as follows.

Isomerically pure 2,4-hexadienes were obtained by gas chromatographic separation from a C_6H_{10} equilibrium mixture on Carbowax 20 M on Chromosorb P (5 m, T_s = 55 °C, 12 mL of He/min): 6 min (1,3-hexadiene), 7.5 min (*E,E*)-2,4-hexadiene), 8 min ((*E,Z*)-2,4-hexadiene), 9 min ((*Z,Z*)-2,4-hexadiene). The isomeric hexadienes were identified by a comparison of their IR spectra with literature data.[24]

(*E,Z*)-1,4-Diphenylbutadiene was prepared by two different variants of the Wittig reaction between benzaldehyde and the ylide derived from *trans*-cinnamyltriphenylphosphonium chloride (**9**).[16]

(a) A mixture of 40 g (0.26 mol) of *trans*-cinnamyl chloride and 82 g (0.31 mol) of triphenylphosphine in 500 mL of xylene was refluxed overnight. The colorless crystals of *trans*-cinnamyltriphenylphosphonium chloride (**9**) obtained after a hot filtration (60 °C) of the reaction mixture were washed twice with benzene and then pentane. Residual organic solvent was evaporated in vacuo (70 °C, 10 h): yield of **9**, 94 g (87%); mp 225–226 °C.

A solution of lithium ethanolate (from 0.15 g lithium metal, i.e., 21.6 mmol of $LiOC_2H_5$) in absolute ethanol was added dropwise to a suspension of 6.9 g (16 mmol) of **9** in 40 mL of ethanol containing 1.7 mL (13 mmol) of benzaldehyde. The mixture was stirred in the dark for 15 h at ambient temperature and then hydrolyzed (70 mL of water). The resulting precipitate was filtered to yield 1.5 g (56%) of (*E,E*)-1,4-diphenylbutadiene (recrystallized from cyclohexane). The filtrate was extracted with pentane. Chromatography of the concentrated pentane extracts on silica gel (Merck) produced the desired (*E,Z*)-1,4-diphenylbutadiene contaminated with substantial amounts of lower boiling hydrocarbons among which β-methylstyrene was positively identified by ^{1}H NMR. After evaporation of these byproducts in vacuo (30 h, 10^{-3} torr, ambient temperature) **8b**-*EZ* (0.5 g, 18%) was obtained reasonably pure (~95%, as judged by ^{1}H NMR).

(b) A suspension of 3.7 g (20 mmol) of the base (hexamethyldisilazanyl) sodium (prepared from equimolar amounts of hexamethyldisilazane and sodium amide in toluene) and 7.9 g (19 mmol) *trans*-cinnamyltriphenylphosphonium chloride (**9**) in 50 mL of hexane was refluxed for 30 h. The reaction mixture was cooled to −20 °C. Low-temperature filtration yielded a mixture of the ylide **10** and sodium chloride. **10** was extracted from the mixture with tetrahydrofuran. The solution was stripped. The residue was dissolved in a minimum amount of toluene and then added to 250 mL of pentane at −40 °C. After 12 h at −70 °C precipitated **10** was recovered by low-temperature filtration and washed with pentane; yield 5.4 g (71%).

A 1.2-g (11-mmol) sample of benzaldehyde was added to a suspension of 4.2 g (11 mmol) of **10** in 50 mL of ether at −40 °C. The mixture was stirred at −40 °C for 48 h and then filtered. Solvent was removed in vacuo. The resulting precipitate was extracted with pentane. The concentrated pentane extract was chromatographed on silica gel (Merck) to yield 1.0 g (44%) of pure (*E,Z*)-1,4-diphenylbutadiene.

(*Z*)-2-Bromostyrene was prepared as described by Cristol and Norris.[25]

(*Z,Z*)-1,4-Diphenylbutadiene (8b-*ZZ*) was obtained by coupling (*Z*)-2-bromostyrene by NiCRA-bpy (2, 2, 1, 2)[26] under nitrogen R (L'Air Liquide). *t*-AmOH (20 mmol, distilled from sodium) in 10 mL of THF (Badisch Anilin reagent grade, distilled from a benzophenone–sodium adduct and stored over sodium wire) was added dropwise to a suspension of NaH (40 mmol, Degussa, 55–60% in oil), $Ni(OAc)_2$ (10 mmol, Prolabo, dried in vacuo for 12 h at 120–125 °C) in refluxing THF (30 mL) containing 2,2′-bipyridine (bpy, 20 mmol, Fluka, used without further purification). After 2 h of stirring at 63 °C, the reagent temperature was cooled to 30 °C and (*Z*)-2-bromostyrene (10 mmol) in 10 mL of THF was then added. After 2 h of stirring at the same temperature the halide was consumed (GC analysis of small aliquot on 5-m column OV 101 at 120 °C). The flask was cooled to 0 °C, and EtOH/water mixture was carefully added. The mixture was then acidified and the organic phase extracted into diethyl ether and dried over $MgSO_4$. After removal of solvents under reduced pressure, the product was purified by chromatography on silica column (Woelm silica gel, 0.063–0.200 mm, petroleum ether/ether mixture as eluent). (*Z,Z*)-1,4-Diphenylbutadiene was isolated with 75% yield and identified by comparison of its spectroscopic properties (^{1}H NMR, IR, UV) with those reported in the literature.[27]

Photochemical Preparation of (*s-trans*-η^4-Conjugated diene)zirconocene Complexes. General Procedure. A sample of 50 mg (0.13 mmol) of diphenylzirconocene (**5**) was dissolved in 600 μL of toluene-d_8. One molar equivalent of the conjugated diene was added. The solution was transferred into a NMR tube (5-mm diameter) under argon and sealed. The reaction mixtures were irradiated for 90 min at −65 °C (2,4-hexadienes, product formation was almost quantitative) or 20 min at −50 °C (1,4-diphenylbutadienes, ca. 20% conversion; longer irradiation times led to a substantial *Z*/*E* isomerization of the starting materials **8b**-*ZZ* and **8b**-*ZE* even in the absence of **5**, respectively. ^{1}H NMR spectra were measured at low temperature and are described and discussed in the text. The thermal stability of complexes **1** was tested by directly monitoring ^{1}H NMR spectra of the irradiated solutions at different increasing temperatures. Each isomerization reaction was followed by ^{1}H NMR spectroscopy at a constant temperature as indicated in the text.

The (hexadiene)zirconocene complexes obtained directly by irradiation of **5** and the isomers **8a** as well as the rearrangement products **1a** were degradated by treatment with O_2. A slow stream of dry oxygen gas was introduced into the solutions of **1a** in toluene-d_8 at −78 °C for a period of 5 min. Then the sample was warmed to room temperature and filtered through a dry 0.3 × 3 cm silica gel column. From the resulting clear toluene solution the distribution of the 2,4-hexadiene isomers was directly determined by gas chromatography under the conditions given above for the separation of the conjugated dienes **8a**.

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Registry No. **1a**-*EE*, 84142-88-1; **1a**-*ZZ*, 97335-02-9; **1a**-*ZE*, 97277-45-7; **1b**-*EE*, 84142-89-2; **1b**-*ZZ*, 97335-03-0; **1b**-*ZE*, 97335-04-1; **3a**-*EE*, 97277-43-5; **3b**-*EE*, 97277-44-6; **5**, 51177-89-0; **8a**-*EE*, 5194-51-4; **8a**-*ZZ*, 6108-61-8; **8a**-*ZE*, 5194-50-3; **8b**-*EE*, 538-81-8; **8b**-*ZZ*, 5807-76-1; **8b**-*EZ*, 5808-05-9; **9**, 83780-93-2; **10**, 97277-42-4; *trans*-cinnamyl chloride, 17082-09-6; triphenylphosphine, 603-35-0; *trans*-cinnamyltriphenylphosphonium chloride, 69052-20-6; benzaldehyde, 100-52-7; (*Z*)-2-bromostyrene, 588-73-8.

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