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Determination of the Stabilization Energy of Planar-Tetracoordinate Carbon in Dynamic Dinuclear (μ-Hydrocarbyl)bis(zirconocene) Cation Complexes and Detection of an Organometallic Memory Effect in Their Formation

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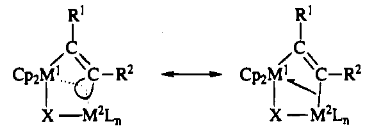
Abstract: Bis(propynyl)zirconocene (**7a**) reacts with $[Cp_2ZrCH_3(THF)]^+[BPh_4]^-$ (**8a**) to yield the $[(\mu\text{-propynyl})(\mu\text{-}\eta^1{:}\eta^2\text{-MeCCMe})(Cp_2Zr)_2]$ cation complex **5b** that contains a planar-tetracoordinate carbon atom. Complex **5b** was characterized by X-ray diffraction. The planar-tetracoordinate carbon center (C2) of **5b** exhibits four strong bonds to its nearest in plane neighbors, i.e. to two carbon and two zirconium centers. In solution, complex **5b** is dynamic. The C_s symmetric planar-tetracoordinate carbon compound **5b** undergoes a thermally induced automerization reaction [$\Delta G^\ddagger$ (250 K) = 11.8 ± 0.5 kcal mol^{-1}] that proceeds through a C_{2v}-symmetric geometry (**6b**) that has the characteristics of a transition state according to a theoretical analysis of the $\mathbf{5} \rightleftharpoons \mathbf{6} \rightleftharpoons \mathbf{5'}$ rearrangement process. This means that the extra stabilization energy of planar-tetracoordinate carbon relative to ordinary planar-tricoordinate carbon in the "semi-fenestrane" environment of the complexes **5** amounts to ca. 10−12 kcal mol^{-1}. The $\mathbf{5} \rightleftharpoons \mathbf{5'}$ equilibrium is strongly influenced by substituents at the $\mu\text{-}\eta^1{:}\eta^2\text{-RCCCH}_3$ ligand and by electronically active Cp substitution. In addition, a strong memory effect is operative in the formation of **5**. It can be observed by using suitably substituted pairs of isomeric complexes **5**. Thus, the reaction between $[Cp_2ZrCD_3(THF)]^+$ (**8d**) and $(MeCp)_2Zr(-C{\equiv}C-CH_3)_2$ (**7e**) gives only complex **5h**, which exhibits the CH_3 group at the planar-tetracoordinate carbon center C2, whereas the reaction of the complementary reagent combination $[(MeCp)_2ZrCD_3(THF)]^+$ (**8e**)/$Cp_2Zr(-C{\equiv}C-CH_3)_2$ (**7a**)] in this double-labeling experiment exclusively leads to the same type of product (**5i**) that has the CD_3 group bonded to C2. This and other examples of this organometallic memory effect indicate that dimetallic intermediates are involved in the formation of the unusually structured stable planar-tetracoordinate carbon compounds **5**.

Introduction

We have recently described a systematic way to prepare stable and easily isolable compounds that contain planar-tetracoordinate carbon.[1] This unusual carbon coordination geometry is in most cases very unfavorable, and therefore, stabilizing it requires a special electronic situation.[2] In the cases disclosed by us[3] and others,[4,5] this thermodynamic stabilization is achieved by the combined action of two metal centers.[6] Formally, in these compounds, a σ-electron pair of an alkenyl anion is shared between the two metals which results in a stabilized three-center−two-electron bonding situation in the carbon σ plane.[7]



Many examples of complexes of this general type have been prepared that contain a planar-tetracoordinate carbon stabilized by a combination of a group 4 metallocene [M^1] and a main group metal [M^2], namely aluminum, gallium, or boron.[1,3,4] In all these cases the structural alternative, a 1,2-dimetalated olefin

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(1) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. *J. Am. Chem. Soc.* **1990**, *112*, 9620.

(2) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181. Collins, J. B.; Dill, J. C.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419 and references cited therein. Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1981**, 260. Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. *Tetrahedron* **1981**, *37*, 921. Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 5818. Frenking, G. *Chem. Phys. Lett.* **1984**, *111*, 529. Glukhovtsev, M. N.; Simkin, B. Ya.; Minkin, V. I. *J. Org. Chem. USSR* **1990**, *26*, 1933. Schleyer, P. v. R.; Seeger, R.; Boldyrev, A. I. *J. Chem. Soc., Chem. Commun.* **1991**, 1536. Boldyrev, A. I.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1991**, *113*, 9045. Glukhovtsev, M. N.; Simkin, B. Y.; Minkin, V. I. *J. Org. Chem. USSR* **1991**, *27*, 1. Glukhovtsev, M. N.; Simkin, B. Y.; Minkin, V. I.; Kirienkova, T. V. *Dokl. Akad. Nauk SSSR* **1991**, *319*, 364. *Chem. Abstr.* **1992**, *116*, 83726d. Gordon, M. S.; Schmidt, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 7486. Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. *J. Am. Chem. Soc.* **1994**, *116*, 8259.

(3) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. *Organometallics* **1991**, *10*, 3791. Albrecht, M.; Erker, G.; Nolte, M.; Krüger, C. *J. Organomet. Chem.* **1992**, *427*, C21. Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. *Chem. Ber.* **1992**, *125*, 1953. Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F. *Organometallics* **1992**, *11*, 3517. Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. *J. Am. Chem. Soc.* **1992**, *114*, 8531.

(4) Binger, P.; Sandmeyer, F.; Krüger, C.; Kuhnigk, J.; Goddard, R.; Erker, G. *Angew. Chem.* **1994**, *106*, 213. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 197. Binger, P.; Sandmeyer, F.; Krüger, C.; Erker, G. *Tetrahedron* **1995**, *51*, 4277.

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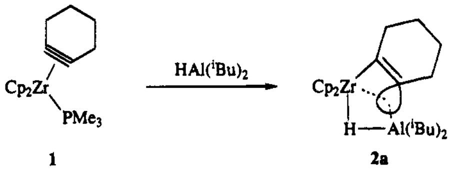
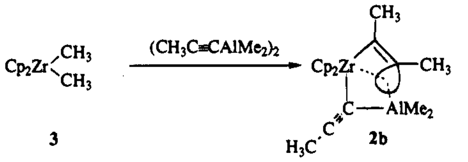
with ordinary three-coordinate sp^2 carbon, is much higher in energy (~30–50 kcal mol^{-1} calculated[7]).[8]

Many syntheses of the planar-tetracoordinate carbon complexes **2** utilize (η^2-alkyne)metallocenes and related systems[9] as precursors. However, there are also major synthetic pathways to these complexes that employ carbon–carbon coupling reactions to construct the bridging hydrocarbyl ligand during the synthesis. Equations 1 and 2 provide very typical examples.

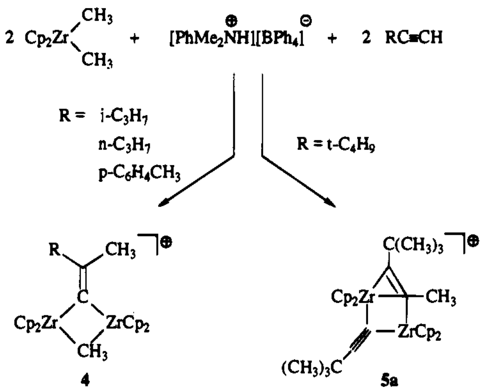


(1)



(2)

A. Horton and G. Orpen first described an analogous cationic dinuclear zirconium complex containing a planar-tetracoordinate carbon. Unfortunately their synthesis only allowed for a very specific substitution pattern at the central core of this interesting complex.[10]



We devised another synthetic entry that allowed a broad range of substituents to be introduced. We used this to prepare the cationic system **5b** that was suited for determining the extra stabilization energy of planar-tetracoordinate carbon in such complexes on a sound experimental basis.[11] From the activation barrier of the automerization reaction—as determined by dynamic NMR spectroscopy—and a theoretical evaluation (see below), the energy gain introduced by forming the planar tetracoordination could be accurately obtained for the first time.

In view of the reaction depicted in eq 1, one might speculate that the formation of the related cationic planar-tetracoordinated bis(zirconocene) complexes could possibly also envoke a simple (η^2-alkyne)metallocene intermediate.[12] However, there were many reactions of σ-alkynyl group 4 metallocenes known that preferred to take routes via dimetallic intermediates, clearly showing a tendency of avoiding the involvement of possible mononuclear (η^2-alkyne)metallocene intermediates.[13] Therefore, we experimentally investigated the preferred reaction course taken in the synthesis of the planar-tetracoordinate bis(zirconocene) complexes as depicted in Scheme 1. We have devised a variety of suitable experiments to answer this question and distinguish between potential alternatives. The results are described in this article.

Results and Discussion

Synthesis and Dynamic Behavior. Complex **5b** was prepared by the reaction of bis(propynyl)zirconocene[13] with the methylzirconocene–tetrahydrofuran cation, employed as the

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(5) Seidel, W.; Kreisel, G.; Mennenga, H. *Z. Chem.* **1976**, *16*, 492; Cotton, F. A.; Millar, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7886. Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802. Dietrich, H.; Mahdi, W.; Storck, W. *J. Organomet. Chem.* **1988**, *349*, 1. Buchwald, S. L.; Lucas, E. A.; Davis, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397. Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Folting, K.; Ellis, P. D.; Huggins, B. A. *Angew. Chem.* **1989**, *101*, 1547; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1523. Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. *Organometallics* **1991**, *10*, 3722. Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. v. R. *Organometallics* **1992**, *11*, 2623. Chi, Y.; Cheng, P.-S.; Wu, H.-L.; Kwang, D.-K.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Chem. Commun.* **1994**, 1839. See also: Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 978. Layh, M.; Uhl, W. *Polyhedron* **1990**, *9*, 277. Cotton, F. A.; Shang, M. Y. *J. Am. Chem. Soc.* **1990**, *112*, 1584. Uhl, W.; Layh, M.; Massa, W. *Chem. Ber.* **1991**, *124*, 1511. Dufour, N.; Schier, A.; Schmidbaur, H. *Organometallics* **1993**, *12*, 2408.

(6) For other approaches, see: (a) Georgian, V.; Saltzman, M. *Tetrahedron Lett.* **1972**, *42*, 4315. Hoeve, W. T.; Wynberg, H. *J. Org. Chem.* **1980**, *45*, 2925; 2930. Keese, R. *Nachr. Chem. Tech. Lab.* **1982**, 30, 844. Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. Krohn, K. *Nachr. Chem. Tech. Lab* **1987**, *35*, 264. Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399. Keese, R. *Angew. Chem.* **1992**, *104*, 307; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 344. (b) McGrath, M. P.; Radom, L.; Schaefer, H. F. III. *J. Org. Chem.* **1992**, *57*, 4847. McGrath, M. P.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 3320. Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L. *Angew. Chem.* **1994**, *106*, 1722; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1667. (c) Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem.* **1989**, *101*, 1313; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1321 and references cited therein. Wong, M. W.; Radom, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 1155. See for a comparison: Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S.; Burkhart, M.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 3187. (d) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1993**, *115*, 4527. Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 5961.

(7) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. *Angew. Chem.* **1993**, *105*, 753; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 754.

(8) Erker, G. *Comments Inorg. Chem.* **1992**, *13*, 111; Erker, G. *Nachr. Chem. Tech. Lab.* **1992**, *40*, 1099. Albrecht, M.; Erker, G.; Krüger, C. *Synlett* **1993**, 441.

(9) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. Buchwald, S. L. Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. Takahashi, T.; Swanson, D. R.; Negishi, E.-I. *Chem. Lett.* **1987**, 623. Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035.

(10) Horton, A. D.; Orpen, A. G. *Angew. Chem.* **1992**, *104*, 912; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 876.

(11) Preliminary communication: Erker, G.; Röttger, D. *Angew. Chem.* **1993**, *105*, 1691; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1623.

(12) For stable analogues, see: Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **1993**, *105*, 1228; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193. See also: Warner, B. P.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5471 and references cited therein.

(13) See, for example: Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem.* **1986**, *98*, 456; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463. Kumar, P. N. V. P.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125. Müller, J.; Tschampel, M.; Pickardt, J. *J. Organomet. Chem.* **1988**, *355*, 513. Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5. Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7. Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1992**, *439*, C36. Lang, H.; Imhof, W. *Chem. Ber.* **1992**, *125*, 1307. Berenguer, J. R.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1993**, *12*, 6. Erker, G.; Albrecht, M.; Krüger, C.; Nolte, M.; Werner, S. *Organometallics* **1993**, *12*, 4979 and references cited therein; Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem.* **1994**, *106*, 1678; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605. Temme, B.; Erker, G.; Fröhlich, R.; Grehl, M. *Angew. Chem.* **1994**, *106*, 1570; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1480.

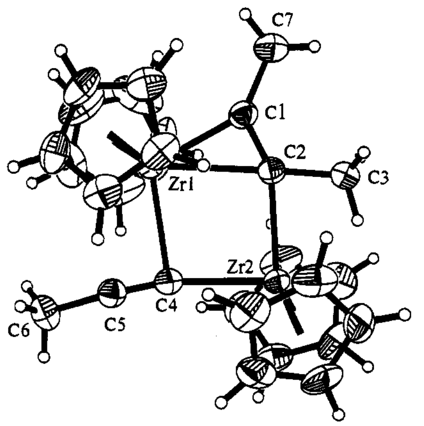

Figure 1. View of the molecular structure of **5b**.

Scheme 1

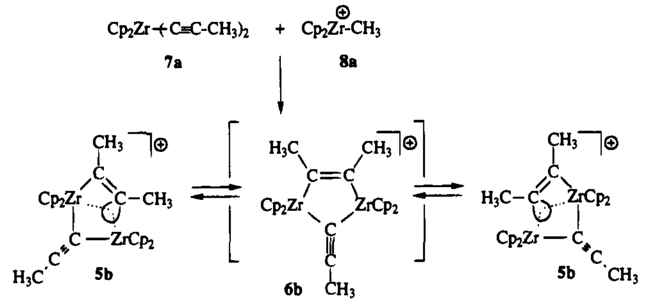

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **5b**

Zr1−C1	2.182(5)	C1−Zr1−C2	31.3(2)
Zr1−C2	2.508(4)	C1−Zr1−C4	110.5(2)
Zr1−C4	2.472(4)	C2−Zr1−C4	79.3(1)
Zr1−C(Cp)	2.524	C2−Zr2−C4	87.7(2)
Zr2−C2	2.324(5)	Zr1−C1−C2	88.3(3)
Zr2−C4	2.262(4)	Zr1−C1−C7	142.3(4)
Zr2−C(Cp)	2.511	C2−C1−C7	129.4(5)
C1−C2	1.305(6)	Zr1−C2−C1	60.4(3)
C1−C7	1.491(7)	Zr1−C2−C3	176.7(3)
C2−C3	1.543(6)	Zr1−C2−Zr2	95.2(2)
C4−C5	1.209(6)	Zr2−C2−C3	83.6(3)
C5−C6	1.461(7)	C1−C2−C3	121.0(4)
		Zr1−C4−Zr2	97.8(2)
		Zr1−C4−C5	93.3(3)
		Zr2−C4−C5	168.9(4)
		C4−C5−C6	175.2(5)

tetraphenylborate salt **8a**,[14] in bromobenzene at ambient temperature. Recrystallization from dichloromethane/pentane gave the crystalline complex **5b** in 85% yield.

Single crystals of **5b** that contained 1.5 equiv of CH_2Cl_2 were used for the X-ray crystal structure analysis. Complex **5b** shows a planar central core of atoms. The zirconium centers are bridged by a μ-(η^1-propynyl) ligand [*d* Zr1−C4 2.472(4), Zr2−C4 2.262(4), Zr1−C5 2.814(5), C4−C5 1.209(6) Å, angles Zr1−C4−Zr2 97.8(2)°, Zr1−C4−C5 93.3(3)°, Zr2−C4−C5 168.9(4)°] and by an unsymmetrically bridging μ-(η^1,η^2-CH_3CCCH_3) ligand. Carbon atom C2 is planar tetracoordinate. It binds strongly to the two adjacent carbon centers [*d* C2−C1 1.305(6), C2−C3 1.543(6) Å] and the zirconium atoms [*d* C2−Zr1 2.508(4), C2−Zr2 2.324(5) Å]. The pertinent bond angles at C2 are 95.2(2) (Zr1−C2−Zr2), 60.4(3) (Zr1−C2−C1), 121.0(4) (C1−C2−C3), and 83.6(3)° (C3−C2−Zr2). The C1−C2 distance is within the typical C=C double-bond range. It is noteworthy that the C1−Zr distance is very short, as is also found in the related Zr/Al, Zr/Ga, or Zr/B complexes (**2**, see above).[1−4] In the crystal, there is evidence for an agostic Zr···H···C interaction between Zr2 and the methyl substituent at the planar-tetracoordinate carbon atom (the calculated distance between Zr2 and the closest H at C3 is 2.293 Å). A similar structural feature was also observed with the related μ-(η^1,η^2-Me_3CCCCH_3)-bridged dizirconium cation **5a** described by Horton and Orpen.[10]

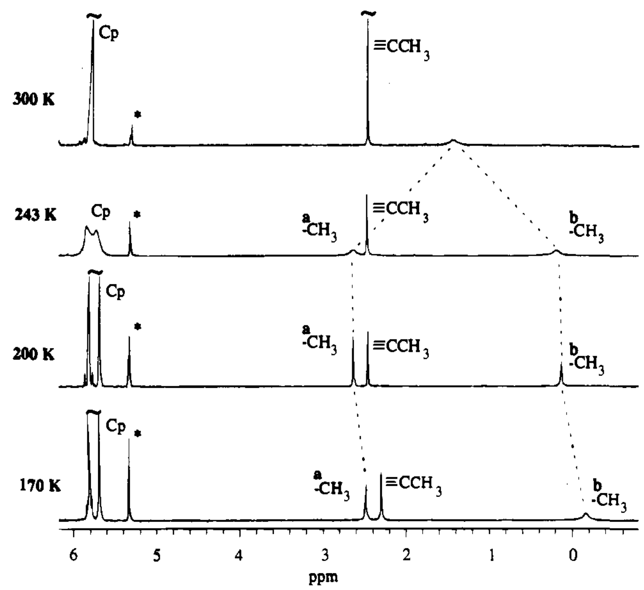

Figure 2. Dynamic ^1H NMR spectra of **5b** (in dichloromethane-d_2, 200 MHz).

At room temperature complex **5b** shows a very simple ^1H NMR spectrum (in dichloromethane-d_2) exhibiting a single Cp resonance at δ 5.85, a methyl singlet at δ 1.25 (6H), and a μ-C≡C−C*H*$_3$ resonance at δ 2.34 (see Figure 2). The latter does not change very much with temperature, whereas the former two signals each split into two resonances as the degenerate rearrangement process of **5b** becomes frozen on the ^1H NMR time scale. At 200 MHz, the coalescence temperature of the Cp signals is at 244 K and that of the μ-(η^1,η^2-CH_3CCCH_3) resonances is at 266 K. At 235 K, a low-temperature limiting spectrum is observed showing two Cp resonances at δ 5.87 and 5.72, two CH_3 signals at 2.50 and −0.12 (methyl at the planar-tetracoordinate carbon center), and a methyl singlet at δ 2.31 (μ-C≡C−C*H*$_3$). Similarly there are two Cp signals in the ^{13}C NMR spectrum of **5b** at low temperature (200 K, 90.6 MHz, δ 109.8, 108.2) and methyl resonances at δ 28.9 (1-CH_3), 10.0 (C≡C−*C*H$_3$), and −25.6 (CH_3 at the planar-tetracoordinate carbon). As expected, there are four quarternary carbon resonances observed at the low temperature. The C1 resonance is at very high δ values (δ 210.4) as is typically observed for this class of compounds. The remaining three quarternary C resonances appear at δ 127.7, 124.3, and 110.3. The former is likely to be due to the planar-tetracoordinate carbon atom C2. In the solid state the automerization of **5b** is still slow on the ^{13}C NMR time scale at 300 K. In the ^{13}C CP/MAS NMR spectrum of **5b** we have observed separate Cp signals at 110.8 and 109.2 as well as methyl resonances at δ 27.7, 7.1, and −22.9. From the temperature-dependent dynamic ^1H NMR spectra (Cp and CH_3 resonances), an activation barrier of $\Delta G^{\ddagger}$ (250 K) ≈ 11.8 ± 0.5 kcal mol^{-1} was derived[15] for the degenerate rearrangement of complex **5b**, using the DNMR5 program package.[15b]

Molecular Orbital Investigations

Calculations. To obtain some insight into the degenerate rearrangement and to investigate the electronic features of **5b**,

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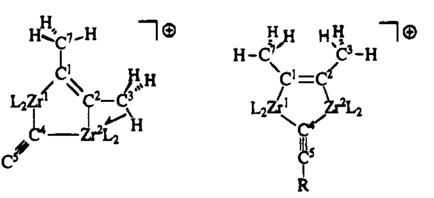
(14) Jordan, R. F. *Adv. Organomet. Chem.* **1991,** *32,* 325 and references cited therein. See also: Röttger, D.; Erker, G.; Grehl, M.; Fröhlich, R. *Organometallics* **1994,** *13,* 3897.

Scheme 2



L	R		
Cp	CH_3	**5b**	**6b**
Cp	H	**5b′** (C_s)	**6b′** (C_{2v})
Cl	H	**5m** (C_s)	**6m** (C_{2v})

we have carried out *ab initio* and extended-Hückel (EH) calculations on the model compounds **5m** and **6m** as well as on the parent molecules **5b′** and **6b′**.

In the model compounds **5m** and **6m**, we have replaced the Cp ligands with chlorine atoms. It was shown in other studies that such substitution reduces the computer time but does not affect the essential features of the investigated systems.[7,16] In order to take advantage of the C_{2v} symmetry of the intermediates **6m,b** in all complexes under study, we have also replaced the propynyl bridge ligand with an ethynyl group. The geometries of **5m**, and **6m,b′** were gradient optimized at the *ab initio* restricted Hartree–Fock (RHF) level. In order to check the stationarity of the structures and to obtain vibrational frequencies, the optimized geometries were used for analytical calculations of the Hessian matrices. For a better estimation of the relative energy, restricted second-order Møller–Plesset perturbation (RMP2) calculations were carried out on **5m** and **6m** with geometries optimized at the RHF level (RMP2//RHF). The *ab initio* calculations reported here were carried out with the Gaussian 92 program[17] using Cartesian Gaussian basis sets. For zirconium and chlorine, effective core potentials of Hay and Wadt were used to replace the core electrons.[18] The valence orbitals of Zr and Cl were described by (5s, 5p, 4d) and (3s, 3p) basis sets, respectively, and contracted to a valence double-ζ basis.[18] Respective basis sets of (10s, 5p) and (4s) were used for carbon and hydrogen and contracted to split valence.[19] For the EH calculations on **5b′**, we have used the bond lengths and bond angles obtained by the X-ray investigation, and in the case of **6b′**, they were taken from the *ab initio* optimized structure. The EH calculations were carried out with standard parameters for all atoms.[20]

Electronic Structures of 5b′ and 6b′. In Figure 3 we show a simplified interaction diagram obtained from EH calculations on **6b′**. The frontier orbitals of the $ZrCp_2$ dimer can be easily constructed as bonding and antibonding combinations of the well-known valence MOs of the d⁰ bent metallocene.[21] Due to the ability of the Zr d valence shell to give nonzero overlap even at very large distances,[22] all 10 resulting combinations with dominant metal character are characterized by an important mixing and splitting of the metallocene levels. For the sake of clarity we show on the right of Figure 3 only the five lowest combinations which are able to interact with the frontier MOs of both bridging ligands. The resulting $1a_1$, $1b_1$, $2a_1$, and $2b_1$ MOs of **6b′** are strongly stabilized with respect to the MOs of the molecular fragments. In spite of the relatively low energy of the valence MOs of the zirconocene dimer, all resulting orbitals of **6b′** have predominant ligand character. Similar to the dinuclear zirconium complex $(C_5H_5)_2Zr[(\mu\text{-}CH_3)(\mu\text{-}C_6H(OCH_3)_2]Zr(C_5H_5)_2$ (**9**), the bonding in **6b′** is achieved through the donation from the valence MOs localized on the bridging ligands to the acceptor levels of the formally d⁰ zirconocene dimer and occurs in the dimetallacyclus plane.[23] Interaction between π orbitals plays essentially no role. We notice that the HOMO of **6b′** (not displayed in Figure 3) is mainly localized on the π system of the 2-butene dianion moiety. In Figure 4a we show the MO plots of the bonding levels of **6b′**. The MOs $2b_1$ and $2a_1$ describe the two Zr(1)–C(1) and Zr(2)–C(2) σ-bonds. The MOs $1b_1$ and $1a_1$ describe the bonding between

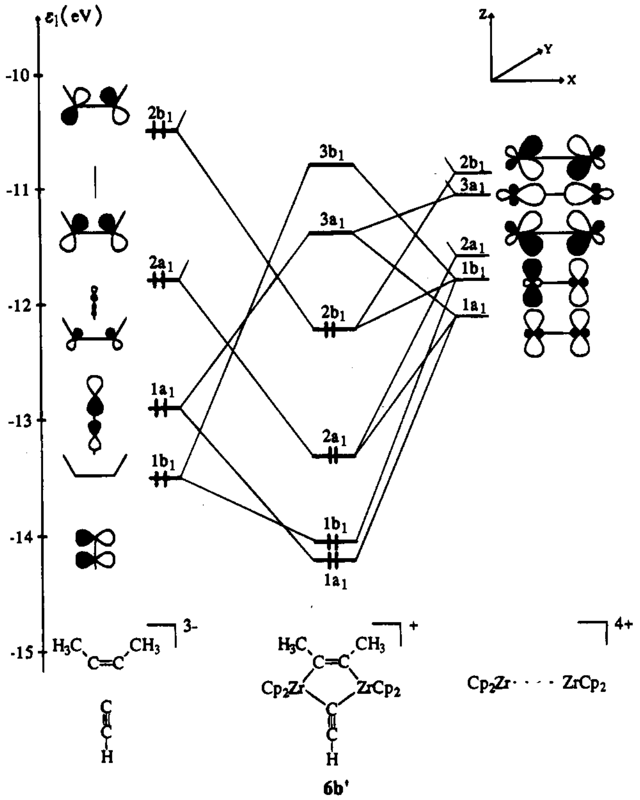


Figure 3. Orbital interaction diagram between $[CH_3{-}C{=}C{-}CH_3]^{2-}$, $[HC{\equiv}C]^-$, at left and $[Cp_2Zr{-}ZrCp_2]^{4+}$ at right to yield the frontier orbitals of $[(Cp_2Zr)(\mu\text{-}CCH)(\mu\text{-}H_3CCCCH_3)(Cp_2Zr)]^+$ (**6b′**) in the center.

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(15) (a) Green, M. L. H.; Wong, L.-L.; Seela, A. *Organometallics* **1992**, *11*, 2660 and references cited therein. (b) Stephenson, D. S.; Binsch, G. DNMR5: A Computer Program for Iterative Analysis of Exchange-Broadened NMR spectra. *QCPE* **1978**, *10*, 365. Binsch, G. *Dyn. Nucl. Magn. Reson. Spectrosc.* **1975**, 45. Binsch, G.; Kessler, H. *Angew. Chem.* **1980**, *92*, 445; *Angew. Chem., Int. Ed. Engl.* **1992**, *11*, 2660 and references cited therein.

(16) Koga, N.; Morokuma, K. *Chem. Rev.* **1991**, *91*, 823 and references cited therein. Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 2359. Castonguay, L. A. Rappé, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 5832.

(17) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision A*; Gaussian, Inc.: Pittsburgh, PA, 1993.

(18) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283, 284–298, 299–310.

(19) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Plenum: New York, 1976.

(20) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240. Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(21) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. In *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(22) Rohmer, M.-M.; Bénard, M. *Organometallics* **1991**, *10*, 157. Bénard, M.; Rohmer, M.-M. *J. Am. Chem. Soc.* **1992**, *114*, 4785. De Kock, R. L.; Peterson, M. A.; Reynolds, L. E. L.; Chen, L.-H.; Baerends, E. J.; Vernooijs, P. *Organometallics* **1993**, *12*, 2794.

(23) Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. *J. Am. Chem. Soc.* **1994**, *116*, 8259.

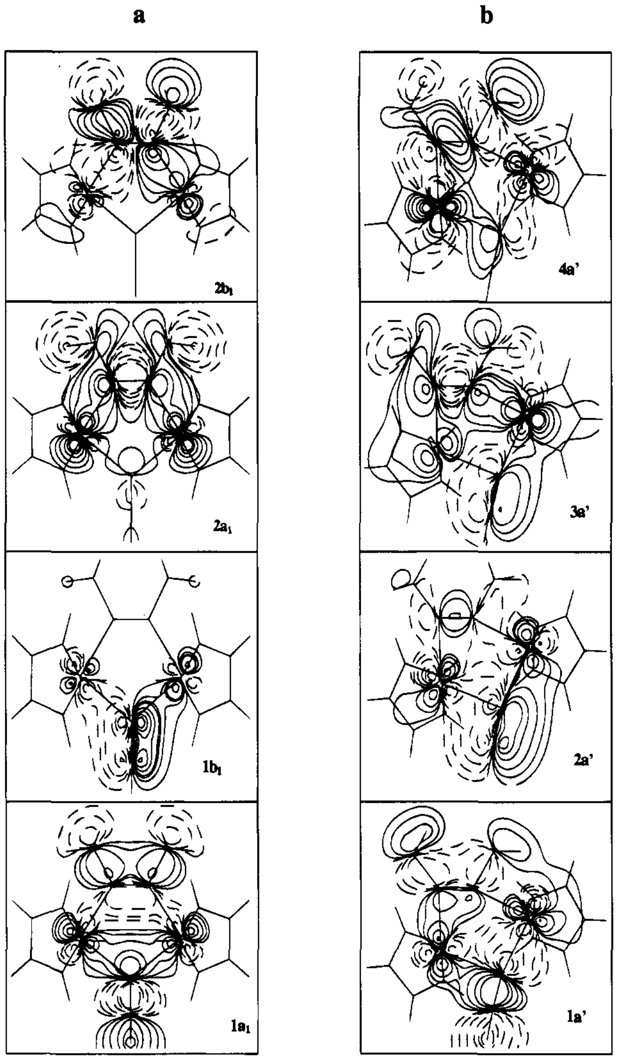
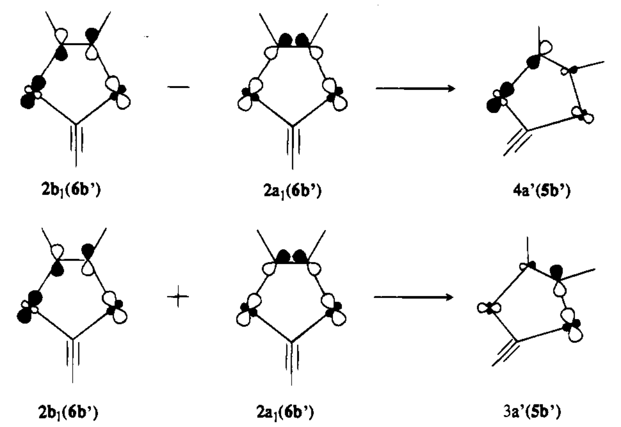


Figure 4. (a) Contour plots of the $2b_1$, $1b_1$, $2a_1$, and $1a_1$ MOs of **6b′**. (b) Contour plots of 1a′, 2a′, 3a′, and 4a′ of **5b′**. The values of the contour lines are ± 0.01, 0.02, 0.04, 0.08, 0.12, and 0.15.

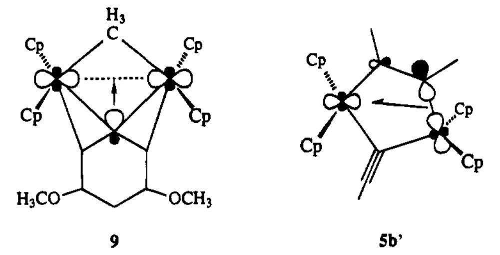
the ethynyl bridge ligand and the zirconocene dimer. Although eight electrons are stabilized on the $1a_1$, $1b_1$, $2a_1$, and $2b_1$ MOs of **6b′**, the electronic structure of **6b′** does not correspond to a stable situation. We notice that in **6b′** none of its bonding MOs shows "an extra" stablization due to an agostic interaction. One can suppose that the geometry perturbation introduced in **6b′** can lead to a more stable structure. This is indeed the case. In going from **6b′** to **5b′** the four occupied MOs are stabilized by 0.1 eV each, leading to a stabilization by 4.6 eV for **5b′** with respect to **6b′**. The corresponding MO plots are shown in Figure 4b. The lowering in symmetry from C_{2v} (**6b′**) to C_s (**5b′**) introduces an orbital mixing, as is schematically shown below for the $2b_1$ and $2a_1$ MOs.

The four-center−two-electron interactions, describing the Zr−C σ bonds in the $2b_1$ and $2a_1$ MOs of **6b′** are replaced by a more efficient two-center−two-electron like interaction in the 4a′ and 3a′ MOs of **5b′**. The same is valid for the bonding between the ethynyl bridge and the zirconocene dimer. The plot of the 3a′ MO of **5b′** (Figure 4b) shows that **5b′** receives an additionally stabilization due to two agostic interactions. The first one concerns the bonding interactions between the Zr(2) center and the C(3)−H σ bond, the second one between the Zr(1) center and the C(2)−Zr(2) σ bond. Both agostic interactions contribute to "an extra" stabilization of **5b′** with respect to **6b′**. Although the bonding interactions between the bridging ligands and zirconocene dimer have the same character in complexes **9** and **5b′**, the reasons for the planar-tetracoordinate geometry of the carbon atoms are different. In **9**, this "unusually" geometry is achieved through donor−acceptor interactions between the lone pair of the dimethoxyphenyl ligand and the empty Zr−Zr σ orbital, while in **5b′**, it is due to the agostic interaction between the Zr(1) center and the C(2)−Zr(2) σ bond.

Scheme 3



Scheme 4



9 **5b'**

Molecular Orbital Picture of the Degenerate Rearrangement of 5b. The *ab initio* optimized structures of the model compounds **5m** and **6m** are shown in Figure 5. The geometry optimizations were carried out under C_s and C_{2v} symmetry constraints for **5m** and **6m**, respectively. The calculated structural parameters of the model compound **5m** reproduce well the essential features of the experimental structure **5b**. Small differences between the calculated and experimental bond lengths and angles are due to the introduced structural approximations for **5m**. With exception of the Zr−C bond lengths, all calculated bond lengths agree within 0.06 Å with the experimental values. The optimized Zr−C bond lengths of **5m** are by 0.1 Å shorter than those of **5b**. This difference can be traced back to the replacement of the Cp ligands by chlorine atoms. We notice, that the optimized Zr−C bond length of **6b′** (2.256 Å) is elongated with respect to those of **6m** (2.132 Å) by 0.124 Å.

At the RMP2//RHF level the model compound **5m** is by 14.2 kcal/mol more stable than **6m**. This value can be compared to the experimental activation barrier of 11.8 kcal/mol obtained in NMR experiments for the thermally induced degenerate rearrangement of complex **5b**. No imaginary frequency has been found for **5m**, and consequently, **5m** represents a true minimum on the energy surface. The calculated harmonic frequencies for **5m** of 2118 and 1674 cm^{-1} agree well with the experimental values of 2070 and 1580 cm^{-1} obtained for the C≡C and C=C stretches in **5b**, respectively.[11] One imaginary b_2 mode (i165 cm^{-1}) was found for **6m**, which suggest that **6m** is a transition state on the potential energy surface of the degenerate rearrangement **5m** → **6m** → **5m**!

The elongated C(3)−H_a bond length of 1.099 Å as well as the short Zr(2)−H_a distance at 2.354 Å (experimental value, 2.293 Å) confirm the qualitative consideration from the previous

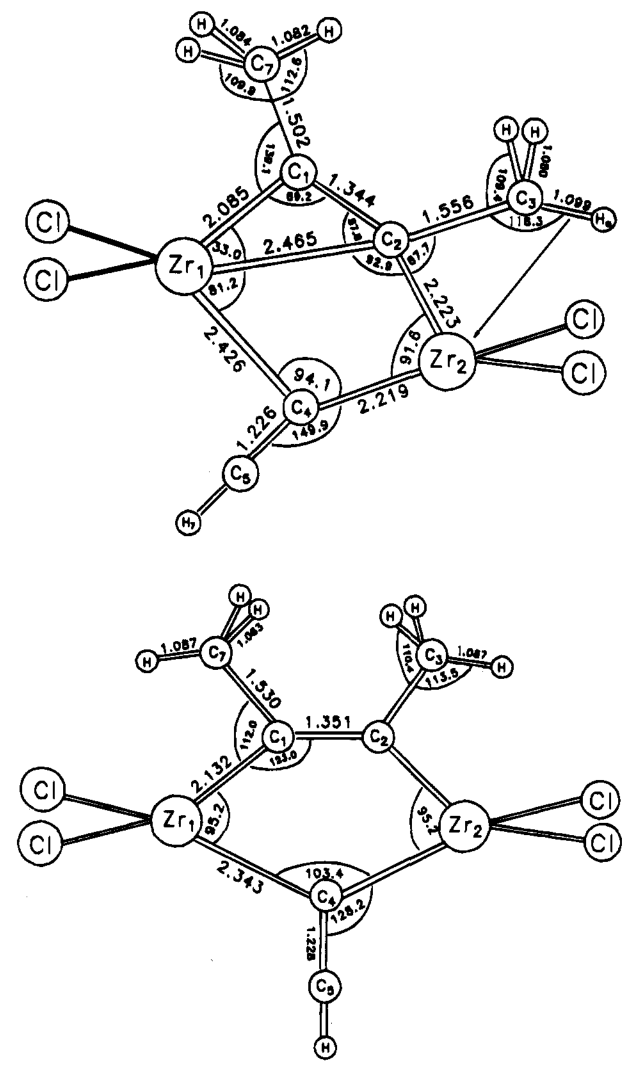
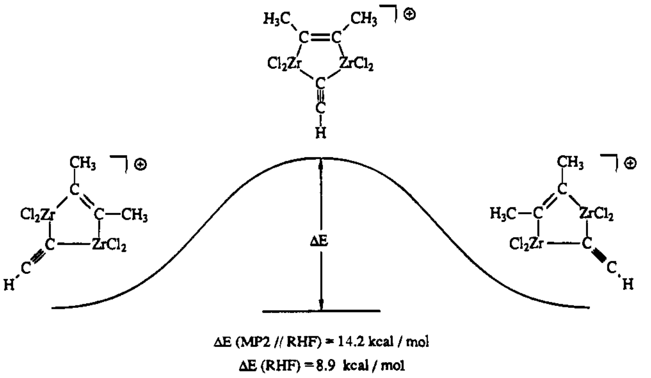


Figure 5. Calculated geometrical parameters for **5m** (top) and **6m** (bottom).

Scheme 5



section concerning agostic interactions. We notice that theoretical investigations on stabilizing interactions in zirconocene complexes showed that in complexes stabilized through an agostic interaction the C$-$H$_a$ bond lengths are elongated up to 1.14 Å and the Zr$-$H$_a$ distances range from 2.2 to 2.5 Å, while in complexes without agostic interactions, no elongation of the C$-$H bonds was observed and the corresponding Zr$-$H distances are greater than 2.8 Å.[24] In order to further explore the nature of the agostic interactions, we have carried out single-point *ab initio* calculations on **5b′**. The canonical MOs of the RHF wave function of **5b′** and **6b′** have been transformed into a set of natural bond orbitals (NBOs) according to the Weinhold NBO localization procedure.[25] This treatment allows the quantification of the particular interactions taking place between NBOs with high (donor) and low (acceptor) occupancy. According to second-order perturbation theory the stabilization energy ΔE_{ij} associated with donor NBO$_{(i)}$$-$acceptor NBO$_{(j)}$ interactions is expressed as

Table 2. Results of NBO Analyses for the Donor$-$Acceptor ($i \rightarrow j$) Interactions in the Dimetallacyclic Rings of **6b′** and **5b′**

	n_i			n_j		ΔE_{ij} (kcal/mol)	
NBO(i)	**6b′**	**5b′**	NBO(j)	**6b′**	**5b′**	**6b′**	**5b′**
σ-C1$-$C2	1.979	1.976	d$_\sigma$: Zr1	0.106	0.358	1.7	4.8
			d$_\sigma$: Zr2	0.106	0.135	1.7	1.6
σ-Zr2$-$C2	1.953	1.745	d$_\sigma$: Zr1	0.407	0.419	2.7	61.4
σ-C3$-$Ha	1.994	1.952	d$_\sigma$: Zr2	0.407	0.419	0.7	11.0
σ-Zr2$-$C4	1.786	1.917	d$_\sigma$: Zr1	0.407	0.419	77.7	27.4
π-C1$-$C2	1.893	1.888	d$_\pi$: Zr1	0.320	0.436	11.2	21.3
			d$_\pi$: Zr2	0.320	0.334	11.2	11.1

$$\Delta E_{ij} = n_i \frac{F_{ij}^{\,2}}{\epsilon_i - \epsilon_j} \qquad (1)$$

where n_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements, and F_{ij} is the off-diagonal element of the NBO Fock matrix. Table 2 summarizes the results for the most important donor$-$acceptor interactions of **5b′** and **6b′**.

In **5b′** the occupation numbers n_i for the Zr(2)$-$C(2) and C(3)$-$H$_a$ σ-NBOs are smaller than in **6b′** and the corresponding ΔE_{ij} values increase from 2.7 and 0.7 kcal/mol (**6b′**) to 61.4 and 11.0 kcal/mol in **5b′**, respectively. Both above features are indicative of a strong agostic interaction between the Zr(2)$-$C(2) σ bond and the d$_\sigma$ acceptor levels of the Zr(1) center as well as to a smaller extend between the C(3)$-$H$_a$ σ bond and the d$_\sigma$ acceptor levels of the Zr(2) center (see Table 2). A contribution of the C(1)$-$C(2) π bond to the stabilization of **5b′** is observed. The corresponding ΔE_{ij} value increases from 11.2 kcal/mol (**6b′**) to 21.3 kcal/mol (**5b′**) and points to a partially double bond character for the Zr(1)$-$C(1) bond in **5b′**. This result is in accord with the relative short Zr(1)$-$C(1) distance (experimental 2.186 Å) observed in **5b**.

Regiochemistry and Memory Effects

The question arises as to how such cationic hydrocarbyl-bridged bis(zirconocene) complexes, that contain a planar-tetracoordinate carbon atom, are formed. In view of the syntheses of the related neutral Zr/Al-containing systems according to eq 1 (see above), one might assume that a reactive mononuclear (η^2-alkyne)zirconocene intermediate could also be formed in the cationic series, which is subsequently trapped in a bimolecular reaction by a suitably substituted zirconocene cation.

The validity of this straightforward and least complicated mechanistic description can easily be tested experimentally by using suitably labeled precursors. Let us assume that bis(σ-phenylacetylide)zirconocene (**7b**) is reacted with the methylzirconocene cation and that this reaction is initiated by a σ-alkynyl ligand abstraction (see Scheme 6). This could lead to methyl(phenylacetylide)zirconocene (**7c**) that may serve as a precursor

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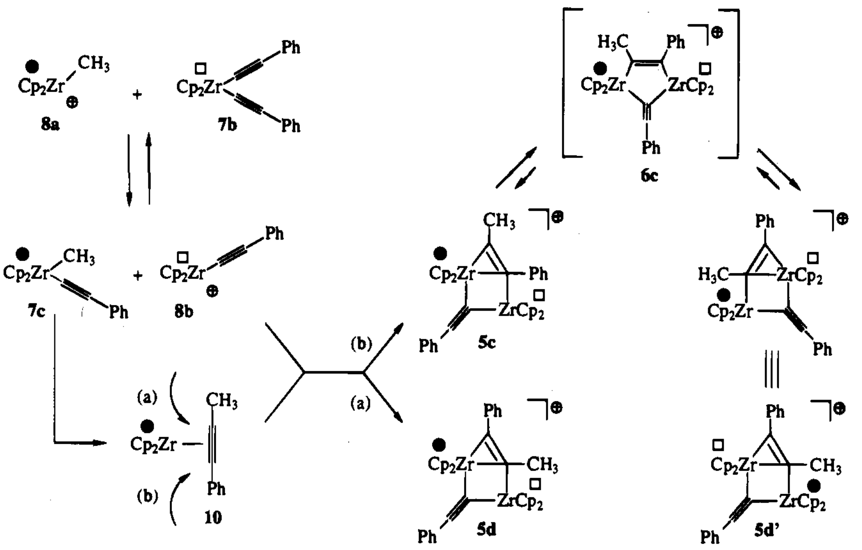
(24) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.-Q.; Erker, G. *Organometallics* **1993**, *12*, 3828.

(25) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. Reed, A. E.; Curtis, L. A.; Weinhold, F. *J. Chem. Rev.* **1988**, *88*, 899.

Scheme 6

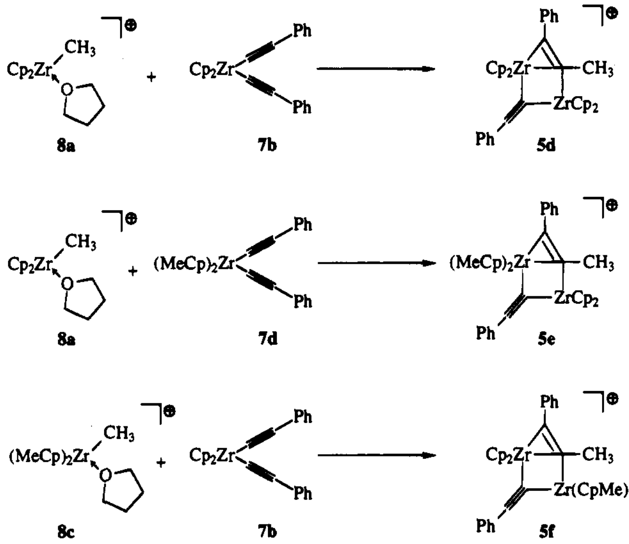


for the formation of the alleged (η^2-CH_3—C≡C—Ph)$ZrCp_2$ intermediate (**10**). If this is really formed in this reaction, it would likely be attacked by the cogenerated $Cp_2Zr(-C{\equiv}C-Ph)^+$ cation (**8b**) to give two regioisomeric products. Attack of the cationic reagent from the methyl-substituted side (pathway a in Scheme 6) would leave the methyl substituent at the planar-tetracoordinate carbon center, whereas attack from the phenyl-substituted side (b) would lead to the immediate formation of the regioisomer with a phenyl-substituted planar-tetracoordinate carbon.

Unfortunately, this simple situation is complicated by the expected rapid intramolecular rearrangement of such cationic bis(zirconocene) planar-tetracoordinate carbon complexes that leads to an exchange between the carbon centers C1 and C2 in the μ-(η^1;η^2-R^1CCR^2) bridge (see above). In this case this would lead to a rapid interconversion of the two regioisomers. However, the inherent mechanistic information about the regiochemical characteristics of this reaction can easily be retained by a double-labeling experiment (as is depicted in Scheme 6) using an additional set of markers attached to the Cp ligands. For an experimental evaluation of the general course taken in such syntheses of cationic bis(zirconocene) planar-tetracoordinate carbon compounds, one consequently needs to know the preferred regiochemical outcome and, in addition, the fate of a dependent second regiochemical label that is introduced by a suitably Cp-substituted metallocene fragment. Both parts of this regiochemical analysis were carried out during the course of our study.

Treatment of $Cp_2ZrCH_3(THF)^+(BPh_4)^-$ (**8a**) with 1 mol equiv of bis(phenylethynyl)zirconocene (**7b**) in tetrahydrofuran at ambient temperature gives a single dimetallic addition product (**5d**) that was isolated in 41% yield. As expected, the ^{13}C NMR spectrum of complex **5d** exhibits the signals of six quarternary carbon atoms (at δ 217.2 (C1), 151.5, 135.6, 130.2, 121.6, and 120.7). The methyl group is bonded to the planar-tetracoordinate carbon atom C2, as is evident from the typical ^{13}C NMR chemical shift at δ −18.2 (^1H NMR resonance at δ 0.12). The $^1H/^{13}C$ NMR spectra of **5d** do not change much with temperature. There is no dynamic behavior observed. We thus conclude that only one of the two possible regioisomeric complexes is observed for this system under conditions of thermodynamic control, namely that exhibiting the phenyl substituent at carbon atom C1 and the methyl substituent at the planar-tetracoordinate carbon center C2.

Scheme 7



We next treated the $Cp_2ZrCH_3(THF)^+(BPh_4)^-$ salt (**8a**) with bis(phenylethynyl)bis(methylcyclopentadienyl)zirconium (**7d**). Again, a single dimetallic reaction product was obtained (**5e**, 71% isolated) that showed static NMR spectra over the temperature range from 190 K to ambient temperature. The methyl group at the bridging hydrocarbyl ligand shows a ^{13}C NMR resonance at δ −13.6 ($^1J_{CH}$ = 130 Hz) which is typical for a CH_3 substituent at the planar-tetracoordinate carbon center C2. The resonance of the carbon center C1, bearing the phenyl substituent, appears at δ 219.7. The Cp_2Zr moiety is bonded to the CH_3C end of the μ-η^1:η^2-$PhCCCH_3$ bridging ligand. This is evident from the results of an ^1H NMR NOE experiment [irradiation at the Cp_2Zr resonance gives a response at the ^1H NMR CH_3 signal at δ 0.23 and vice versa (~5%)] and from a comparison with an isomer that was characterized by X-ray diffraction (see below).[26]

The necessary complementary experiment was carried out by reacting $[(MeC_5H_4)_2ZrCH_3(THF)]^+(BPh_4)^-$ (**8c**) with $Cp_2Zr(C{\equiv}C-Ph)_2$ (**7b**) in bromobenzene at room temperature (3 h). Again, a single organometallic reaction product was obtained (69% isolated) that showed temperature-invariant NMR

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[26] In addition the regiochemistry of **5e** was confirmed independently by an X-ray crystal structure analysis. Because of its rather high *R* value of 12.7%, details of this structure will not be discussed.

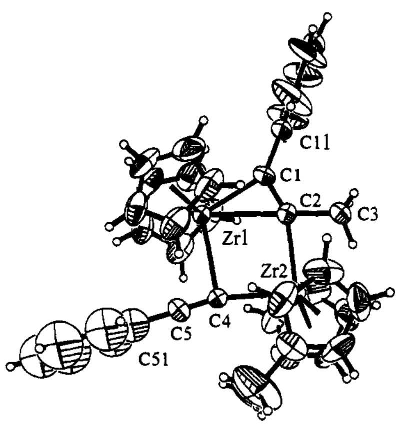


Figure 6. Molecular geometry of **5f**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **5f**

Zr1−C1	2.186(10)	C1−Zr1−C2	31.3(4)
Zr1−C2	2.491(10)	C1−Zr1−C4	111.9(4)
Zr1−C4	2.502(9)	C2−Zr1−C4	80.6(3)
Zr1−C(Cp)	2.521	C2−Zr2−C4	88.3(3)
Zr2−C2	2.352(10)	Zr1−C1−C2	87.4(7)
Zr2−C4	2.284(9)	Zr1−C1−C11	143.1(8)
Zr2−C(Cp)	2.509	C2−C1−C11	129.5(10)
C1−C2	1.296(15)	Zr1−C2−C1	61.3(6)
C1−C11	1.487(14)	Zr1−C2−C3	179.1(7)
C2−C3	1.563(14)	Zr1−C2−Zr2	94.8(4)
C4−C5	1.179(12)	Zr2−C2−C3	84.2(6)
C5−C51	1.42	C1−C2−C3	119.7(9)
		Zr1−C4−Zr2	96.3(3)
		Zr1−C4−C5	96.5(6)
		Zr2−C4−C5	167.2(8)
		C4−C5−C5	178.8(6)

spectra. This product (**5f**) is different from the one obtained in the complementary experiment described above. The regioisomer **5f** again has the CH_3 substituent bonded to the planar-tetracoordinate carbon atom (^{13}C NMR resonance at δ −16.6; ^1H NMR signal at δ 0.09) and the phenyl group located at the position C1. Only this time the $(MeC_5H_4)_2Zr$ group is bonded to the CH_3C end of the bridging PhCCMe ligand [irradiation at the various MeC_5H_4 ^1H NMR resonances leads to a NOE response at the signal of the C2-bonded CH_3 group].

This regiochemical assignment was confirmed by an X-ray crystal structure analysis of complex **5f** (see Figure 6). The cation **5f** exhibits a plane of symmetry in the crystal. It shows a planar arrangement of the core of atoms of the dimetallic cation. Carbon atom C2 is planar tetracoordinate with pertinent bond lengths and angles of 1.296(15) Å (C1−C2), 1.563(14) Å (C2−C3), 2.491(10) Å (C2−Zr1), 2.352(10) Å (C2−Zr2), 119.7(9)° (C1−C2−C3), 61.3(6)° (C1−C2−Zr1), 94.8(4)° (Zr1−C2−Zr2), and 84.2(6)° (C3−C2−Zr2). The phenyl group at C1 is arranged almost perpendicularly to the central plane. The planar-tetracoordinate carbon atom (C2) bears the CH_3 substituent. The $(MeC_5H_4)_2Zr$ group is attached to the CH_3C end of the CH_3CCPh bridging ligand.

This characteristic regiochemical outcome of the methylzirconocene cation plus bis(alkynyl)zirconocene addition and coupling reaction seems to be generally observed. It is not dependent on the presence of the phenyl substituent but is analogously observed with simple alkyl substituents as well. This was shown by carrying out a set of experiments involving double labeling using the $(MeC_5H_4)_2Zr/Cp_2Zr$ metallocene pair in connection with a CD_3/CH_3 pair of alkyl substituents.

$Cp_2ZrCH_3(THF)^+(BPh_4)^-$ (**8a**) was treated with $(MeC_5H_4)_2Zr(C{\equiv}CCH_3)_2$ (**7e**) at room temperature in bromobenzene (24 h) to yield **5g** (88% isolated). Complex **5g** exhibits static and almost temperature independent NMR spectra throughout the temperature range between 190 K and room temperature. It consists of a single regioisomer exhibiting ^1H NMR resonances (213 K, CD_2Cl_2) of the methyl groups at the central framework at δ 2.52 (1-CH_3), 2.35 (CC-CH_3), and −0.10 (2-CH_3) [^{13}C NMR δ −22.8 (2-CH_3)] (see Figure 7). The Cp_2Zr moiety is probably η^2-coordinated to the MeCCMe ligand (the 1-CH_3/Cp_2Zr pair shows a strong ^1H NMR NOE effect). It appears that the $(MeC_5H_4)_2Zr$ group favors η^1-coordination to this bridging ligand at the planar-tetracoordinate carbon atom.

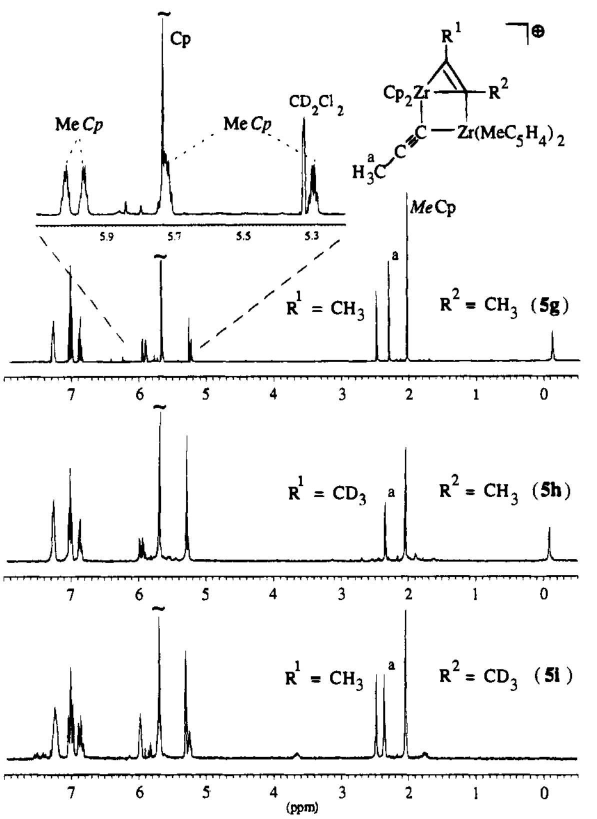


Figure 7. ^1H NMR spectra of the complexes **5g**−**i** showing the pronounced memory effect during their formation from suitably labeled pairs of $(RCp)_2ZrMe^+$ and $(RCp)_2Zr(C{\equiv}CMe)_2$ reagents.

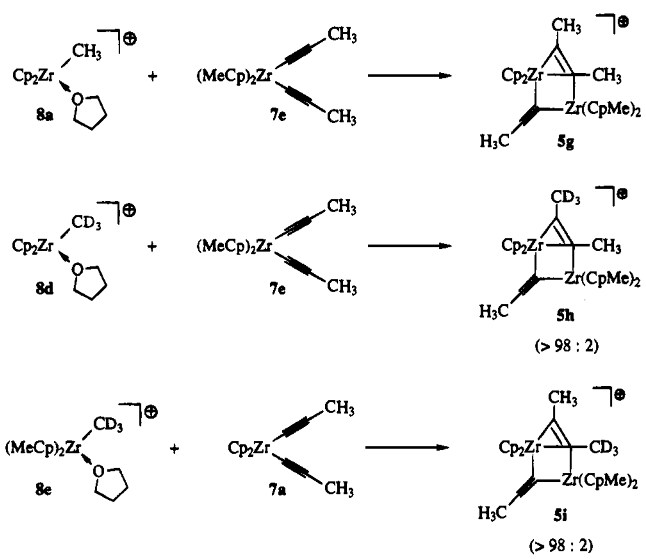
We then treated $Cp_2Zr(CD_3)(THF)^+(BPh_4)^-$ (**8d**) with $(MeC_5H_4)_2Zr(C{\equiv}C{-}CH_3)_2$ (**7e**) and obtained a single regioisomeric product (**5h**). From its spectral characteristics (see Figure 7) we assume that the $(MeC_5H_4)_2Zr$ moiety has retained its "southeast" position (i.e., η^1-bonded to the planar-tetracoordinate carbon center C2). Comparison with the analogous protio complex **5g** has revealed that the CH_3 group is attached to the planar-tetracoordinate carbon whereas the CD_3 group has ended up being bonded at carbon atom C1.

The complementary experiment was carried out by reacting the $[(MeC_5H_4)_2ZrCD_3(THF)]^+$ cation [as the $(BPh_4)^-$ salt (**8e**)] with the unlabeled $Cp_2Zr(C{\equiv}C{-}CH_3)_2$ reagent **7a**. This cleanly and exclusively gave the regioisomer **5i** (80% isolated), where the CH_3/CD_3 groups are attached in the opposite sense at the μ-η^1:η^2-RCCR ligand, i.e. the CH_3 group being bonded to C1 and the CD_3 substituent to the planar-tetracoordinate carbon center C2 (see Figure 7).

Conclusions

Usually strong electrophiles add to C=C double bonds by attaching themselves to the π system. Complexes **5** can be thought of formally to arise from adding the Cp_2ZrR^+ electrophile in the olefinic σ plane. By this unusual coordination the zirconocene electrophile is allowed to share the electrons of

Scheme 8



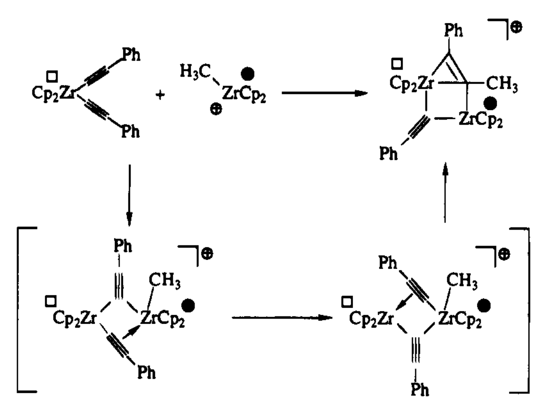
the adjacent Zr−C(sp^2) σ bond and form some distorted three-center−two-electron bond including two zirconium centers and a carbon atom that has become planar tetracoordinate. In this way all prerequisites are met that one would expect to be found in a stable planar-tetracoordinate carbon derivative, only that its isomeric alternative is a planar-tricoordinate carbon compound and not tetrahedral-tetracoordinate C.

Our study has revealed that planar-tetracoordinate carbon is by ca. 10−12 kcal mol^{-1} more stable than the ordinary three-coordinate sp^2-hybridized carbon inside the framework of the complexes **5**. This we deduce from the outcome of the dynamic NMR experiment described above and the result of the quantum mechanical calculation that has indicated that the C_{2v}-symmetric intermediate structure **6** is probably a transition state on the hypersurface of the thermally induced automerization reaction of complexes **5**.[7] We think that the rigid "half-fenestrane" framework of **5** helps to make these planar-tetracoordinate carbon centers so stable, but much of the extraordinary thermodynamic stabilization undoubtedly arises from the special electronic features encountered here where a second very strong electron acceptor is used to interact favorably with a vinyl anion that has already received some stabilization by bonding interaction with the first metal center.

Our study has also revealed a pronounced substituent dependence of planar-tetracoordinate carbon. Under equilibrium conditions the phenyl substituent always ends up at carbon center C1 having the methyl substituent attached to the planar-tetracoordinate carbon center (C2) in complexes **5**. One might agree that this pronounced substituent preference is due to steric reasons, the room in the plane of the planar-tetracoordinate carbon is more congested than at the adjacent planar-tricoordinate center, but this could also be due to electronic effects. The latter is probably true for the high preference of the more electron-donating $(MeC_5H_4)_2Zr$ unit to favor η^1-coordination to the planar-tetracoordinate carbon center over the weaker electron-donating $(C_5H_5)_2Zr$ metallocene moiety.

Finally the outcome of the double-labeling experiments carried out in this study has revealed that a free (η^2-alkyne)-metallocene intermediate is not involved in the formation of the dinuclear planar-tetracoordinate carbon compounds **5** from the reaction of bis(alkynyl)zirconocenes and methylzirconocenyl cations. This reaction exhibits a *memory effect* that is not compatible with any pathway involving dissociation of mononuclear species after some ligand transfer step. It turns out that the methyl group and the metallocene moiety originating from the methylzirconocenyl cation reagent have a high tendency to stay close together and to end up in adjacent positions in the final product. Therefore, it is likely that the carbon−carbon coupling reaction forming the bridging $RCCCH_3$ ligand is taking place at a dinuclear intermediate, maybe as it is schematically depicted in Scheme 9. We assume that the alkynyl plus methyl coupling at the "right" zirconocene center is taking place metal induced with the help of the other Cp_2Zr−C≡C−R group.

Scheme 9



Experimental Section

All reactions were carried out in an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The NMR spectra were obtained on a Bruker AC 200 P, ARX 300, or AM 360 NMR spectrometer. IR spectra were recorded on a Nicolet 5 DXC FT-IR spectrometer. Melting points were determined by DSC (DuPont 2910 DSC, STA Instruments). The bis(alkynyl)zirconocene complexes **7a,b,d,e** were prepared according to literature procedures.[13] Methylzirconocene cations **8** were employed as their stable THF adducts with tetraphenylborate anion; the respective reagents **8a,c,d,e** were synthesized analogously to published procedures.[14]

Preparation of 5b. A suspension of 100 mg (0.33 mmol) of bis(propynyl)zirconocene (**7a**) and 200 mg (0.32 mmol) of $[Cp_2ZrCH_3(THF)]^+[BPh_4]^-$ (**8a**) in 25 mL of bromobenzene was stirred for 5 h at room temperature. The product formed as a precipitate that was collected by filtration and recrystallized from dichloromethane/pentane to give 230 mg (85%) of **5b**, containing 0.5 equiv of CH_2Cl_2, mp 155 °C (dec). ^{1}H NMR (THF-d_8, 300 K): δ 5.90 (s, 20 H, Cp), 2.30 (s, 3 H, C≡C−CH_3), 1.25 (broad, 6 H, 1-CH_3 and 2-CH_3); BPh_4^-: 3 multiplets at δ 7.40−7.30 (m, 8H), 6.94−6.86 (m, 8H), 6.79−6.71 (m, 4H). ^{1}H NMR (dichloromethane-d_2, 185 K, 360 MHz): δ 5.82 (s, 10H, Cp), 5.69 (s, 10H, Cp), 2.47 (s, 3H, 1-CH_3), 2.29 (s, 3H, C≡C−CH_3), −0.18 (s, 3H, 2-CH_3). ^{13}C NMR (dichloromethane-d_2, 200 K, 90.6 MHz): δ 210.4 (C1), 127.7, 124.3, 110.3 (C2 and −C≡C−), 109.8 ($^1J_{CH}$ = 168 Hz, Cp), 108.2 ($^1J_{CH}$ = 166 Hz, Cp), 28.9 ($^1J_{CH}$ = 127 Hz, 1-CH_3), 10.0 ($^1J_{CH}$ = 133 Hz, −C≡C−CH_3), −25.6 ($^1J_{CH}$ = 130 Hz, 2-CH_3); BPh_4^-: 163.4 ($^1J_{CB}$ = 50 Hz), 135.3 ($^1J_{CH}$ = 153 Hz), 125.7 ($^1J_{CH}$ = 154 Hz), 121.6 ($^1J_{CH}$ = 157 Hz). ^{13}C NMR (CPMAS, 4100 s^{-1}, 300 K): δ 214.7 (C1), 110.8 (Cp), 109.2 (Cp), 27.7 (1-CH_3), 7.1 (−C≡C−CH_3), −22.9 (2-CH_3); BPh_4^-: 136.5, 126.3, 122.4, remaining signals not located. IR (KBr): $\tilde{\nu}$ = 2070 cm^{-1} (C≡C), 1580. Anal. Calcd for $C_{51}H_{49}BZr_2 \cdot 0.5\ CH_2Cl_2$ (897.7): C, 68.91; H, 5.61. Found: C, 68.23; H, 5.69. Single crystals of **5b** (× 1.5CH_2Cl_2) were obtained by crystallization from CH_2Cl_2/pentane at −20 °C. X-ray crystal structure analysis: crystal size 0.4 × 0.25 × 0.1 mm, M_r = 982.5 g mol^{-1}, monoclinic space group *C*2/*c*, cell constants a = 34.573(7) Å, b = 13.608(3) Å, c = 23.342(5) Å, β = 124.11(3)°, V = 9092(3) Å^3, Z = 8, ρ_{calcd} = 1.436 g cm^{-3}, Enraf Nonius Mach 3 diffractometer, λ = 0.710 73 Å, T = −50 °C, $[(\sin\theta)/\lambda]_{max}$ = 0.62 Å^{-1}, μ = 6.7 cm^{-1}, no absorption correction, 10 342 reflections collected, $(+h,+k,\pm l)$, 9217 independent and 6668 observed reflections, 523 refined parameters, full-matrix least-squares refinement on F^2, hydrogen atoms calculated and kept fixed in the final refinement, goodness of fit on F^2 1.041, final fourier difference 1.64 (−1.06) e Å^{-3}, R = 0.050, $R_w{}^2$ = 0.138.

Preparation of 5d. Tetrahydrofuran (10 mL) was added to a mixture of **8a** (500 mg, 0.80 mmol) and 338 mg (0.80 mmol) of bis(phenylethynyl)zirconocene (**7b**) and the solution stirred for 2 h at ambient temperature. The product was precipitated with pentane, and the precipitate was collected by filtration, dissolved in dichloromethane, and precipitated again by adding toluene to give 320 mg (41%) of **5d**, mp 161 °C (dec). ^{1}H NMR (dichloromethane-d_2): δ 7.9−7.4 (m, 10H, Ph), 6.11 (s, 10H, Cp), 5.87 (s, 10H, Cp), 0.12 (s, 3H, CH$_3$) plus BPh$_4^-$ resonances. ^{13}C NMR (dichloromethane-d_2): δ 217.2 (C1), 151.5, 135.6, 130.2, 121.6, 120.7 (quart. C), 134.1, 133.3, 130.4, 129.6, 126.5, 123.4 (CH), 111.7 (Cp), 110.1 (Cp), −18.2 ($^1J_{CH}$ = 129 Hz, 2-CH$_3$); BPh$_4^-$: 164.4 ($^1J_{CB}$ = 49 Hz), 136.4, 126.0, 122.1. IR (KBr): $\tilde{\nu}$ = 2044 cm^{-1} (C≡C), 1579. Anal. Calcd for $C_{61}H_{53}BZr_2$ (979.3): C, 74.81; H, 5.45. Found: C, 74.78; H, 5.67.

Preparation of 5e. A suspension of 185 mg (0.30 mmol) of the salt **8a** and 134 mg (0.30 mmol) of bis(methylcyclopentadienyl)bis(phenylethynyl)zirconium (**7d**) in 15 mL of bromobenzene was stirred for 13 h at room temperature. The product was precipitated from the red solution by adding pentane, collected by filtration, washed with toluene and then with pentane, and dried in vacuo to yield 210 mg (71%) of **5e**, mp 146 °C (dec). ^{1}H NMR (dichloromethane-d_2): δ 7.85−7.40 (m, 10H, Ph), 6.07 (s, 10H, Cp), 5.91−5.65 (m, 8H, C_5H_4-Me), 1.94 (s, 6H, $C_5H_4CH_3$), 0.23 (s, 3H, 2-CH$_3$) plus BPh$_4^-$ resonances. ^{13}C NMR (dichloromethane-d_2): δ 219.7 (C1), 149.1, 142.5, 131.0, 120.4, 114.2, 112.9 (quart. C), 134.7, 133.5, 130.3, 129.4, 126.6, 124.4 (CH, phenyl), 113.4, 112.5, 110.4, 105.9 (CH of C_5H_4Me), 112.0 (Cp), 15.2 ($^1J_{CH}$ = 127 Hz, $C_5H_4CH_3$), −13.6 ($^1J_{CH}$ = 130 Hz, 2-CH$_3$); BPh$_4^-$: 164.4 ($^1J_{CB}$ = 49 Hz), 136.4, 126.0, 122.1. IR (KBr): $\tilde{\nu}$ = 2045 cm^{-1} (C≡C), 1579. Anal. Calcd for $C_{63}H_{57}BZr_2$ (1007.4): C, 75.11; H, 5.70. Found: C, 72.50; H, 5.72. The composition of complex **5e** was supported by X-ray analysis, see ref 26.

Preparation of 5f. A solution containing 285 mg (0.44 mmol) of the [(MeC$_5$H$_4$)$_2$ZrCH$_3$(THF)]$^+$[BPh$_4$]$^-$ salt **8c** and 200 mg (0.47 mmol) of bis(phenylethynyl)zirconocene (**7b**) in 25 mL of bromobenzene was stirred for 3 h at room temperature. The solution was cooled to 0 °C, and the yellow product was precipitated with pentane, collected by filtration, washed with pentane, and dried in vacuo to give 300 mg (69%) of **5f**, mp 160 °C (dec). ^{1}H NMR (dichloromethane-d_2): δ 7.9−7.1 (m, 10H, Ph), 6.29, 6.06, 5.91, 5.66 (m, each 2H, C_5H_4Me), 5.87 (s, 10H, Cp), 2.12 (s, 6H, $C_5H_4CH_3$), 0.09 (s, 3H, 2-CH$_3$) plus BPh$_4^-$ resonances. ^{13}C NMR (dichloromethane-d_2): δ 217.1 (C1), 152.1, 136.0, 129.8, 122.9, 122.8 120.9 (quart. C), 134.0, 133.2, 130.4, 129.6, 126.3, 123.2 (CH, phenyl), 115.6, 113.4, 111.0, 109.8 (CH of C_5H_4-Me), 110.1 (Cp), 15.7 ($^1J_{CH}$ = 129 Hz, $C_5H_4CH_3$), −16.6 ($^1J_{CH}$ = 130 Hz, 2-CH$_3$); BPh$_4^-$: 164.4 ($^1J_{CB}$ = 50 Hz), 136.3, 126.0, 122.1. IR (KBr): $\tilde{\nu}$ = 2045 cm^{-1} (C≡C), 1594. Anal. Calcd for $C_{63}H_{57}BZr_2$ (1007.4): C, 75.11; H, 5.70. Found: C, 72.23; H, 5.63. Single crystals were obtained from dichloromethane. X-ray crystal structure analysis of **5f**: crystal size 0.3 × 0.2 × 0.15 mm, M_r = 1007.3 g mol^{-1}, orthorhombic space group *Pnma*, cell constants a = 24.768(1) Å, b = 14.364(1) Å, c = 13.992(1) Å, V = 4977.9(5) Å^3, Z = 4, ρ_{calcd} = 1.344 g cm^{-3}, Enraf Nonius Mach 3 diffractometer, λ = 0.710 73 Å, T = −50 °C, [(sin θ)/λ]$_{max}$ = 0.62 Å^{-1}, μ = 4.6 cm^{-1}, 5255 reflections collected (−*h*,−*k*,+*l*), 5255 independent and 3011 observed reflections, 296 refined parameters, goodness of fit on F^2 1.032, final fourier difference 1.39 (−1.01) e Å^{-3}, R = 0.069, $R_w{}^2$ = 0.166; the phenyl group C51−C56 is disordered and was refined as a rigid group with isotropic temperature factors. Refinement in acentric space group *Pn*2$_1$*a* did not improve the disordered Ph group. Programs used: SHELX 86, SHELX 93, XP.

Preparation of 5g. A mixture of the cation **8a** (1.00 g, 1.59 mmol) and 600 mg (1.83 mmol) of bis(methylcyclopentadienyl)bis(propynyl)zirconium (**7e**) in 20 mL of bromobenzene was stirred for 24 h at ambient temperature. During this time the product had precipitated, it was collected by filtration, washed with toluene, and dried in vacuo to yield 1.23 g (88%) of **5g**, mp 153 °C (dec). ^{1}H NMR (dichloromethane-d_2, 213 K, 360 MHz): δ 6.02, 5.96, 5.72, 5.29 (m, each 2H, C_5H_4Me), 5.73 (s, 10H, Cp), 2.52 (s, 3H, 1-CH$_3$), 2.35 (s, 3H, −C≡C−CH$_3$), 2.07 (s, 6H, $C_5H_4CH_3$), −0.10 (s, 3H, 2-CH$_3$) plus BPh$_4^-$ signals. ^{13}C NMR (dichloromethane-d_2, 213 K, 90.6 MHz): δ 211.0 (C1), 127.3, 125.7, 120.4, 112.4 (quart. C), 115.1, 112.3, 109.8, 106.7 (CH of C_5H_4-Me), 108.2 (Cp), 29.0 ($^1J_{CH}$ = 127 Hz, 1-CH$_3$), 15.3 ($^1J_{CH}$ = 128 Hz, $C_5H_4CH_3$), 9.7 ($^1J_{CH}$ = 133 Hz, −C≡C−CH$_3$), −22.8 ($^1J_{CH}$ = 130 Hz, 2-CH$_3$); BPh$_4^-$: 163.4 ($^1J_{CB}$ = 50 Hz), 135.4, 125.6, 121.7. IR (KBr): $\tilde{\nu}$ = 2068 cm^{-1} (C≡C), 1580. Anal. Calcd for $C_{53}H_{53}BZr_2$ (883.3): C, 72.07; H, 6.05. Found: C, 71.95; H, 6.00.

Preparation of 5h. A mixture of the deuterated cation **8d** (1.00 g, 1.59 mmol) and the bis(propynyl)Zr(C$_5$H$_4$CH$_3$)$_2$ reagent **7e** (600 mg, 1.83 mmol) was stirred for 24 h at room temperature in 20 mL of bromobenzene. The solvent was removed in vacuo and the residue taken up in 100 mL of toluene. The solid product **5h** was collected by filtration, washed with 30 mL of toluene, and dried in vacuo to give 760 mg (54%) of **5h**.

Preparation of 5i. The salt [(MeC$_5$H$_4$)$_2$ZrCD$_3$(THF)]$^+$[BPh$_4$]$^-$ (**8e**) (1.45 g, 2.20 mmol) was stirred with 700 mg of **7a** for 4 h in 40 mL of bromobenzene. The product was collected by filtration, washed with toluene (20 mL), and dried in vacuo to give 1.55 g (80%) of **5i**.

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Supporting Information Available: Details of the X-ray crystal structure determinations of the complexes **5b,f** including listings of bond lengths and angles, positional parameters, and thermal parameters (21 pages); listings of the observed and calculated structure features (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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