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Reactions of Vinylzirconocene Complexes with a Zirconium Hydride. The Unexpected Formation of [μ-(β-η^1:α,β-η^2-Styryl)](μ-chloro)bis[bis(η^5-cyclopentadienyl)zirconium], a Binuclear (Olefin)zirconocene Complex

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(μ-Ethylene)bis(zirconocene chloride) (**1a**) is formed rapidly in nearly quantitative yield upon hydrozirconation of vinylzirconocene chloride, **5a**. In contrast, the slow reaction of (β-styryl)zirconocene chloride (**5d**) with oligomeric hydridozirconocene chloride (**4**) gives an equimolar mixture of Cp_2ZrCl_2 (**6**), $Cp_2ZrCl(CH_2CH_2Ph)$ (**7**), and the novel binuclear (olefin)zirconocene complex $Cp_2ZrCl(CH{=}CHPh)ZrCp_2$ (**8**). The latter crystallizes in space group $P2_1/n$ with cell constants a = 8.380 (4) Å, b = 22.256 (9) Å, c = 12.667 (6) Å, and β = 97.40 (3)°. The molecular structure of **8** is characterized by an almost planar bridging olefinic ligand. The Zr(1)–C(1) σ bond is short (2.196 (7) Å). Zr–C bond distances of 2.440 (7) and 2.462 (7) Å are found for the Zr(2)–(η^2-alkenyl) moiety. The chemistry of **8** is dominated by the reactive Zr–C σ bond. Carbon monoxide is rapidly inserted with preservation of a binuclear structure to form **14**. Reactions with protic reagents point to the formation of mononuclear (η^2-styrene)zirconocene as a reactive intermediate.

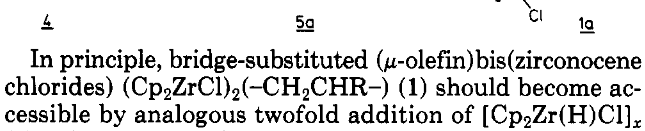
Binuclear early transition-metal complexes show fascinating unprecedented features.[1] Thus, (μ-ethylene)bis(zirconocene chloride) [$(Cp_2ZrCl)_2(-CH_2-CH_2-)$ (**1a**)][2] forms a Lewis acid adduct $(Cp_2ZrCl{\cdot}AlR_3)_2(-CH_2CH_2-)$ (**2**, R = ethyl) in which both zirconium atoms have been found bridging across the carbon–carbon bond of the ethylene unit.[3] This unique structure might serve as a model for the transition-state geometry of dyotropic rearrangements.[4]

It has recently been shown that for structurally related (μ-aldehyde)zirconocene complexes $(Cp_2ZrX)_2(\mu\text{-}CH_2O-)$ (**3**) such a degenerate rearrangement is an extremely facile process.[1e,4b,5] Therefore the synthesis of suitably substituted, yet unknown binuclear (μ-olefin)zirconocene complexes **1** is an appealing object in the search for further examples of organometallic substrates showing such dynamic features.

Unfortunately, compounds of type **1** possessing differently substituted bridging $-CH_2CHR-$ ligands[6] appear not to be available by the preparative method described for the parent compound **1a**.[2] In search for a novel synthetic access to organometallic substrates **1** we have discovered a new synthetic route that allows us to prepare appreciable quantities of the μ-ethylene complex **1a** quite easily (see below). However, our new procedure could not be extended to obtain substituted μ-olefin complexes **1**. Its application to differently substituted precursors of **1** led to the observation of a completely different reaction path that finally resulted in the unexpected formation of **8**, to our knowledge the first example of an (olefin)zirconocene complex.

Results

As an obvious alternative to the previously described organoaluminium route, we applied the hydrozirconation reaction[7] to the preparation of (μ-ethylene)bis(zirconocene chloride) (**1a**). Treatment of the oligomeric hydridozirconocene chloride (**4**)[8] with acetylene at 50 °C in benzene solution yielded the expected 1:1 reaction product **5a**. In the presence of an excess of **4** this substrate takes up a second equivalent of the hydrozirconation reagent to form (μ-ethylene)bis(zirconocene chloride), **1a**. After complete consumption of **4**, the binuclear zirconium complex **1a**, which is almost insoluble under the reaction conditions, could be recovered from the reaction medium by a simple filtration. **1a** can thus be obtained very easily quite pure in high yield.



In principle, bridge-substituted (μ-olefin)bis(zirconocene chlorides) $(Cp_2ZrCl)_2(-CH_2CHR-)$ (**1**) should become accessible by analogous twofold addition of $[Cp_2Zr(H)Cl]_x$ (**4**) to homologous, differently substituted acetylenes. We,

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[1] See, for example: (a) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218–220. Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1981**, *103*, 2650–2659. (b) Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Ibid.* **1980**, *102*, 2858–2860. LaCroce, S. J.; Cutler, A. R. *Ibid.* **1982**, *104*, 2312–2314. (c) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889–2894. Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447–2460. (d) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995–3002. Erker, G.; Rosenfeldt, F. *Tetrahedron* **1982**, *38*, 1285–1292; *J. Organomet. Chem.* **1982**, *224*, 29–42. $[Cp_2Zr(CH_2O)]_3$: Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353–3354. (e) Gell, K. I.; Williams, G. M.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1980**, 550–552. (f) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747–1748. Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. A.; Caulton, K. G. *Ibid.* **1981**, *103*, 209–210. Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Ibid.* **1981**, *103*, 5596–5598.

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[3] Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem.* **1976**, *88*, 688–689.

[4] (a) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33–65. Reetz, M. T. *Angew. Chem.* **1972**, *84*, 161–163. Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189–2194. Reetz, M. T.; Kliment, M.; Plachky, M.; Greif, N. *Chem. Ber.* **1976**, *109*, 2716–2742. Reetz, M. T. *Ibid.* **1977**, *110*, 954–978. (b) Erker, G.; Kropp, K. *Ibid.* **1982**, *115*, 2437–2446.

[5] Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269–270.

[6] Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373–378.

[7] (a) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 413–417. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem.* **1976**, *88*, 402–409.

[8] Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405–411.

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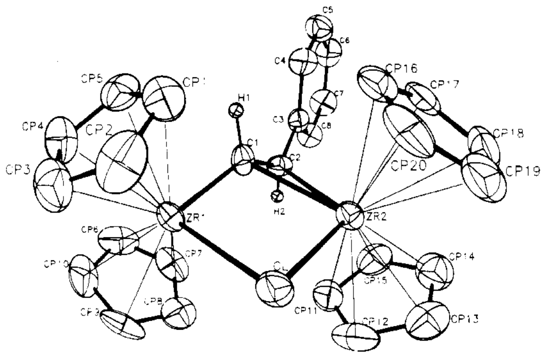
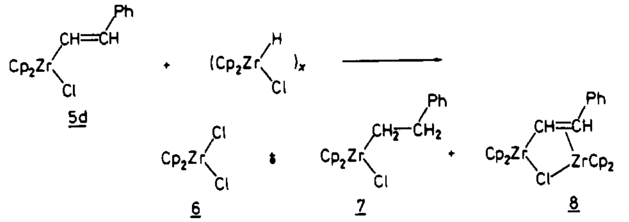


Figure 1. Molecular structure and atom numbering scheme for 8. The atoms are represented by their 50% probability ellipsoids for thermal motion.

therefore, performed hydrozirconation reactions with propyne (**b**), *tert*-butylacetylene (**c**), and phenylacetylene (**d**). Under reaction conditions that led directly to an almost quantitative yield of **1a**, only substituted vinylzirconocene chlorides **5b–d** could be obtained,[9] even if the reaction was carried out in the presence of a large excess of the hydrozirconation reagent.

Nevertheless, the substituted vinylzirconocene halides **5b–d** are not completely inert toward the zirconocene hydride **4**. Prolonged treatment (18 h) of the isolated vinyl complexes **5b–d** with equimolar amounts of $[Cp_2Zr(H)Cl]_x$ finally resulted in the disappearance of the starting materials. The hydridozirconium chloride is not consumed via formation of binuclear μ-olefin complexes **1**. A new mixture of organometallic products is formed instead.

Under such reaction conditions the interaction of $Cp_2Zr(-CH{=}CHPh)Cl$ (**5d**) and hydridozirconocene chloride (**4**) forms three products in equimolar ratio: zirconocene dichloride (**6**), (β-phenylethyl)zirconocene chloride (**7**), and the binuclear zirconocene complex **8**. The latter can formally be regarded as a 1:1 adduct of the elusive monomeric bent metallocene bis(η-cyclopentadienyl)zirconium(II) (**9**)[10] and the starting material **5d**. After recrystallization from toluene, large burgundy-red crystals of **8** were obtained which allowed a complete structure determination of this reaction product by X-ray diffraction methods.



The molecular structure and atom numbering scheme for 8 are shown in Figure 1. Several features of the novel bonding arrangement deserve discussion. First, the olefin defined by C(1), C(2), C(3), H(1), H(2), and Zr(1) is planar to 0.14 Å. From another viewpoint, C(1), C(2), H(1), and H(2) are planar to 0.09 Å, with C(3) and Zr(1) both 0.15 Å below the plane. This is most clearly shown in Figure 2. The Zr(1)–C(1) σ bond length, 2.196 (7) Å, is very short. The $Zr-C(sp^3)$ distance in $Cp_2Zr(Me)_2$, 2.277 (4) Å, may be taken as the standard.[11] A correction of 0.03 Å for the difference in $C(sp^2)$ vs. $C(sp^3)$ radii would lead to an expected 2.25 Å for the $Zr-C(sp^2)$ bond. For comparison purposes, the Zr–C(sp) length in $Cp_2Zr(CO)_2$, 2.187 (4) Å,[12] is not significantly different from that found in 8.

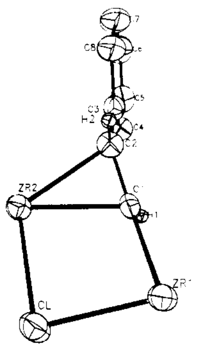


Figure 2. View of the olefinic portion of 8 normal to the Zr(2)–C(1)–C(2) plane.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 8

Bond Distances

Zr(1)-Zr(2)	3.498 (1)	Zr(1)-Cl	2.539 (2)
Zr(1)-C(1)	2.196 (7)	Zr(1)-Cp(1)	2.536 (8)
Zr(1)-Cp(2)	2.548 (9)	Zr(1)-Cp(3)	2.550 (9)
Zr(1)-Cp(4)	2.516 (9)	Zr(1)-Cp(5)	2.528 (8)
Zr(1)-Cp(6)	2.515 (8)	Zr(1)-Cp(7)	2.534 (8)
Zr(1)-Cp(8)	2.535 (8)	Zr(1)-Cp(9)	2.523 (8)
Zr(1)-Cp(10)	2.523 (8)	Zr(1)-Cent(1	2.239
Zr(1)-Cent(2	2.232	Zr(1)-Ave(1)	2.54 (1)
Zr(1)-Ave(2)	2.526 (7)	Zr(2)-Cl	2.629 (2)
Zr(2)-C(1)	2.462 (7)	Zr(2)-C(2)	2.440 (7)
Zr(2)-Cp(11)	2.564 (8)	Zr(2)-Cp(12)	2.581 (9)
Zr(2)-Cp(13)	2.539 (9)	Zr(2)-Cp(14)	2.530 (9)
Zr(2)-Cp(15)	2.535 (9)	Zr(2)-Cp(16)	2.561 (8)
Zr(2)-Cp(17)	2.517 (7)	Zr(2)-Cp(18)	2.504 (7)
Zr(2)-Cp(19)	2.510 (8)	Zr(2)-Cp(20)	2.550 (8)
Zr(2)-Cent(3	2.256	Zr(2)-Cent(4	2.232
Zr(2)-Ave(3)	2.55 (2)	Zr(2)-Ave(4)	2.53 (2)
C(1)-C(2)	1.42 (1)	C(1)-H(1)	1.064
		C(2)-H(2)	0.872

Bond Angles

Cl-Zr(1)-C(1)	92.1 (2)	Cl-Zr(2)-C(1)	84.2 (2)
Cl-Zr(2)-C(2)	114.1 (2)	C(1)-Zr(2)-C(2)	33.7 (2)
Zr(1)-Cl-Zr(2)	85.1 (6)	Zr(1)-C(1)-Zr(2)	97.2 (3)
Zr(1)-C(1)-C(2)	143.5 (6)	Zr(2)-C(1)-C(2)	72.3 (4)
Zr(1)-C(1)-H(1)	104.5 (2)	Zr(2)-C(1)-H(1)	119.0 (2)
C(2)-C(1)-H(1)	111.2 (4)	Zr(2)-C(2)-C(1)	74.0 (4)
Zr(2)-C(2)-C(3)	124.8 (5)	C(1)-C(2)-C(3)	126.1 (7)
Zr(2)-C(2)-H(2)	93.8 (2)	C(1)-C(2)-H(2)	119.2 (4)
C(3)-C(2)-H(2)	109.9 (4)		

The second zirconium atom, Zr(2), appears to be coordinated directly into the π cloud of C(1)–C(2). The torsion angle for C(1)–C(2)–C(3)–Zr(2) is 95°.[13,14] No appropriate comparisons exist for the $Zr-C(\eta^2)$ bonds, but the two values of 2.440 (7) and 2.462 (7) Å[15] demonstrate uniform coordination of Zr(2) to both C(1) and C(2). The C(1)–C(2)

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[9] Yoshifuji, M.; Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1977**, *15*, 1303–1306.

[10] (a) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1–50. (b) Brintzinger, H. H.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *94*, 1105–1107. (c) Lauher, J. W.; Hoffmann, R. *Ibid.* **1976**, *98*, 1729–1742.

[11] Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics*, submitted for publication.

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[13] With almost 3.5 Å the Zr-Zr distance in 8 is clearly too large for a direct metal-metal interaction. Imoto, H.; Corbett, J. D.; Cisar, A. *Inorg. Chem.* **1981**, *20*, 145–151. Guthrie, D. H.; Corbett, J. D. *Ibid.* **1982**, *21*, 3290–3295.

[14] A similar structural situation is found in a binuclear zirconocene naphthyl hydride: Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933–6937.

[15] These Zr–C bond distances may be compared with those found in (*s-trans*-η^4-conjugated diene)$ZrCp_2$ complexes: (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344–6346. (b) Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300–3310. (c) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191–192.

Table II. A Comparison of Selected ^{1}H [^{13}C] NMR Data between Substituted Vinylzirconocene Complexes $Cp_2ZrX(-CH_a{=}CH_bR)$ (5) and $Cp_2ZrX(-CH_a{=}CH_bR)ZrCp_2$ (8, 12)[a]

	R	X	Cp		CH_a	CH_b
5b	CH_3	Cl	6.20		6.87 (17.8)	5.80
5d	Ph	Cl	6.31		7.76 (18.8)	6.70
			[113.0		177.7 (122)	140.5 (153)]
8	Ph	Cl	5.65	5.29	7.70 (18.2)	4.56
			5.39	4.88		
			[106.7	105.9	170.3 (108)	84.9 (145)]
			[106.3	104.9]		
12	Ph	Ph	5.50	5.03	7.87 (18.0)	6.87
			5.10	4.97		

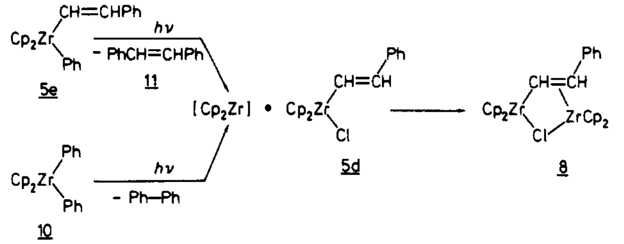
[a] 5 in $CDCl_3$ and 8 and 12 in C_6D_6 solvent; chemical shifts are relative to Me_4Si on the δ scale; coupling constants ($^3J_{HH}$, $^1J_{CH}$) are given in parentheses (Hz). ^{13}C NMR data given in brackets.

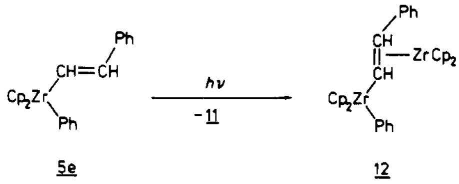
bond distance, 1.42 (1) Å, shows a considerable lengthening over the expected double-bond value because of the interaction with Zr(2).

The Zr-Cl bonds, 2.538 (2) and 2.629 (2) Å, are very long because of the fact that the halide functions as a bridge. Accurate determination of normal Zr–Cl (terminal) lengths are available: 2.441 (10) Å in $(CH_2)_3(C_5H_4)_2ZrCl_2$,[16a] 2.447 (1) Å in $(C_5H_4SiMe_3)_2Zr(Cl)[CH(SiMe_3)_2]$,[16b] 2.452 (2) Å in $(C_5H_4CMe_3)_2Zr(Cl)[CH(SiMe_3)_2]$, and 2.472 (4) Å in $[Li(DME)_2][(\eta^5\text{-}C_5Me_5)Zr(\eta^1\text{-}NC_4H_4)(Cl)]_2(\mu\text{-}O)(\mu\text{-}Cl)$.[16c] In the latter, the symmetrical chloride bridge reveals a Zr–Cl of 2.665 (4) Å. The average Zr–Cp(η^5) lengths, 2.53 (1) Å for Zr(1) and 2.54 (2) Å for Zr(2), are well within the expected range.[11]

A very characteristic appearance of the NMR spectra results from the specific way the β-styryl ligand connects two chemically nonequivalent prochiral zirconocene units to form the binuclear structure 8. Four sharp singlets representing five hydrogens of a η-cyclopentadienyl ligand each can be observed in the ^{1}H NMR spectrum (Table II). The bridging organic ligand shows phenyl hydrogens at δ 7.35, 7.20, and 7.00 and an AX pattern of two methine protons (δ 7.70, 4.56 ($^3J_{HH}$ = 18.2 Hz)). An even more pronounced chemical shift difference can be observed for the carbon atoms of the bridging –CH=CHPh ligand. In the gated-decoupled ^{13}C NMR spectrum features at δ 84.9 ($^1J_{CH}$ = 145 Hz) and 170.3 ($^1J_{CH}$ = 108 Hz)[17] become attributed to the "olefinic" carbons. The very low value of the C–H coupling constant of the low-field resonance points to a sterically crowded situation at the β-carbon atom.[18] In addition, signals resulting from the phenyl substituent (δ 150.6, 123.4, 122.8) and four clearly separated Cp resonances are observed (Table II).

The identification of 8 as a component of even quite complex reaction mixtures is greatly facilitated by this characteristic appearance of the NMR spectra. It was, therefore, not difficult to detect the formation of the obviously thermodynamically favorable substrate 8 from alternative starting materials under quite different reaction conditions. Formally, 8 should be accessible by coordination of Cp_2Zr (9)[10] to the styryl and the chloro ligands of **5d**. Indeed, this product is formed in high yield upon photolysis of diphenylzirconocene (**10**) (to form **9** plus biphenyl[13a,b,19]) in the presence of **5d** as a "trapping agent". Irradiation of mixtures of **5d** with another likely zirconocene-precursor, the phenyl(β-styryl)zirconocene complex (**5e**), produced an even greater quantity of the adduct **8**. In addition a quantitative yield of the organic reaction product *trans*-stilbene (**11**) was obtained. Only half the expected amount (0.5 equiv) of **11** is formed, however, if **5e** is photolyzed in benzene solution at ambient temperature without further admixtures. As a second component under these conditions the new binuclear zirconocene complex **12** is obtained. Unfortunately, crystals of this product suitable for characterization by X-ray diffraction could not be obtained. However, from chemical degradation experiments (see Experimental Section) and spectroscopic features (Table II), it becomes obvious that **12** is structurally closely related to the [μ-(η^1:η^2-styryl)](μ-chloro)bis(zirconocene) (**8**). From these observations a description of **12** as a [μ-(β-η^1:α,β-η^2-styryl)](phenylzirconocene)zirconocene complex is suggested.[20]





At ambient conditions **8** rapidly takes up 1 equiv of carbon monoxide with formation of **14**. Dihydrocinnamaldehyde is formed upon hydrolysis. Treatment with bromine (2 equiv) followed by workup with aqueous alkali yields *trans*-cinnamic acid. The cyclic enolate **14** exhibits features at *m/e* 606 (M^+) and 578 (M^+ – CO) in the mass spectrum showing the isotopic distribution typical of a complex possessing two zirconium and a chlorine atom per molecular unit. **14** displays four sharp Cp resonances in the ^{1}H (benzene-d_6, δ 5.91, 5.84, 5.80, and 5.34) as well as the ^{13}C NMR spectrum (benzene-d_6, δ 111.7, 110.3, 109.5, and 108.9). A benzylic CH group gives rise to resonances (^{1}H NMR δ 2.80 (d, $^3J_{HH}$ = 5 Hz); ^{13}C NMR δ 63.6 ($^1J_{CH}$ = 131 Hz)) quite different from the ones found for **8** (see Table II for a comparison). Signals of the olefinic CH moiety in **14** were obscured by either the signals of the phenyl substituent or the intense Cp resonances. A singlet due to the quaternary "enolate carbon atom", derived from added carbon monoxide, could be located at δ 195 in the "gated-decoupled" ^{13}C NMR spectrum of **14**. The for-

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(16) (a) Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880–2885. (b) Lappert, M. F.; Riley, P. I.; Yarrow, P. I. W.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Dalton Trans.* **1981**, 814–821. (c) Atwood, J. L.; Bynum, R. V.; Rogers, R. D. *J. Crystallogr. Spectrosc. Res.*, submitted for publication.

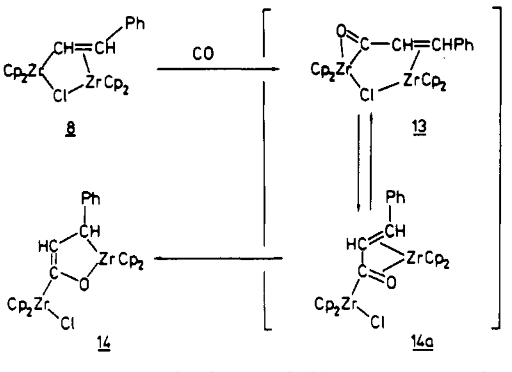
(17) See for a comparison: (a) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387–393. (b) Schmidt, J. R.; Duggan, D. M. *Ibid.* **1981**, *20*, 318–323. (c) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613. (d) Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1–C2.

(18) A similar ^{13}C NMR effect is frequently observed; see the following series for example: $PhCH_3$ (δ 21 (J_{CH} = 126 Hz)), Ph_2CH_2 (δ 36 (J_{CH} = 126 Hz)), Ph_3CH (δ 61 (J_{CH} = 107 Hz)): Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience, New York, 1972.

(19) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189–202.

(20) The obtained spectroscopic data do not give any indication that the zirconium–σ-aryl moiety present in 12 might be functioning as a second bridging ligand. Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1979**, 127–128; *J. Chem. Soc., Dalton Trans.* **1981**, 1938–1943.

mation of the cyclic enolate 14 can be understood as being the consequence of a simple stabilizing intramolecular rearrangement process[21,22] of the expected primary CO insertion product 13.[23]



Treatment of 8 with electrophilic reagents such as hydrochloric acid, bromine, or methanol results in the cleavage of the zirconium to carbon σ bond. However, at the same time in all cases observed, the olefin–zirconocene π bond to the bridging β-styryl ligand takes part in the reaction, even in case of the limited addition of less than 1 molar equiv of the protic reagent or halogen.

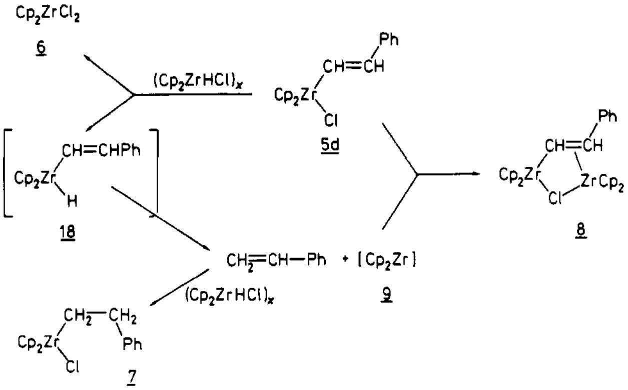
Hydrolysis of 8 with aqueous HCl yields zirconocene dichloride and ethylbenzene. We could not detect any styrene under these reaction conditions. An equimolar mixture of zirconocene dihalide and 1,1,2-tribromo-2-phenylethane results from degradation of 8 with an excess of bromine. A different organic product is obtained upon careful addition of only 2 equiv of molecular halogen in benzene solution: after the usual workup procedure β-bromostyrene is isolated in almost quantitative yield.

Treatment of 8 with an excess of methanol results in the formation of the expected ethylbenzene. With 2 equiv of this reagent, however, the liberation of free organic substances does not take place. The formation of a mixture of three organometallic components is observed instead: methoxyzirconocene chloride (15), methoxy(2-phenylethyl)zirconocene (16), and methoxy(1-phenylethyl)zirconocene (17). These products are formed in a molar ratio of 15:16:17 = 2:1:1.

Discussion

Alkenylzirconocene halides 5 can principally react with hydridozirconocene complexes in two ways. The first, addition of the zirconium hydride to the olefinic bond of the substrate obviously takes place in the reaction of 4 with ethenylzirconocene chloride (**5a**). However, it appears that the relative rate of this reaction can become drastically reduced by substituents on the olefin moiety. Slowing down the rate of the addition reaction opens up the possibility of forming products via an alternative reaction mode for the Zr–H functionality, hydride for halide exchange with substrates 5.[1c,24]

Starting from (β-styryl)zirconocene chloride (**5d**), such mutual ligand transfer would yield zirconocene dichloride (**6**), a principal reaction product actually obtained, and hydrido (β-styryl)zirconocene (**18**). It is not at all surprising that the latter could not be directly observed in the reaction mixture since quite similar alkylhydridozirconocene complexes are known to be rather reactive thermally. Alkane formation takes place quite readily under similar reaction conditions.[25] Reductive elimination of styrene (which consecutively is consumed by hydridozirconocene chloride (**4**) present in the reaction medium to form (2-phenylethyl)zirconocene chloride (**7**)) from **18** formally yields zirconocene (**9**). Combination of this metallocene and the starting material **5d** would provide an attractive way of stabilizing the coordinatively highly unsaturated species **9** under formation of the binuclear chloride-bridged (olefin)zirconocene complex **8**.



This description is supported by our observation that 8 is readily formed upon photolysis of quite different zirconocene precursors **10** and **5e** in the presence of **5d**. Although the formation of 9 in these reactions has not been demonstrated unequivocally as yet by direct experimental evidence, the photochemical formation of **9**, followed by the stabilization of this species by subsequent coordination to **5d**, remains an attractive mechanistic possibility.

Two different types of monoolefin complexes have been suggested to function as key intermediates in reactions of zirconocene complexes. While coordinatively saturated 18-electron bis(η-cyclopentadienyl)zirconium(IV) compounds have been proposed as intermediates in stoichiometric processes such as the hydrozirconation reaction,[7] highly unsaturated, very reactive 16-electron (olefin)bis(η-cyclopentadienyl)zirconium(II) complexes (**19**) may play a vital role in catalytic conversions such as olefin isomerizations, transfer hydrogenation reactions, and the oligomerization of alkenes.[10a,26]

To our knowledge, the binuclear (μ-styryl)zirconocene complex 8 represents the first example of a both thermodynamically and kinetically stable (olefin)zirconocene complex[27] that could be isolated and whose structural features have been established by X-ray diffraction. It may well turn out that structural and spectroscopic characteristics obtained from 8 will provide an experimentally sound basis for the development of a deeper understanding of the properties of coordinatively saturated (olefin)zirconocene complexes. Moreover, it appears that the observed chemical behavior of 8 might even offer an experimental access to obtain some information about the reactivity of an example of an intermediate (olefin)bis(η-cyclopentadienyl)zirconium(II) complex, (η^2-styrene)zirconocene (**19b**).

The formation of the observed products from the degradation of 8 with electrophiles can be understood by as-

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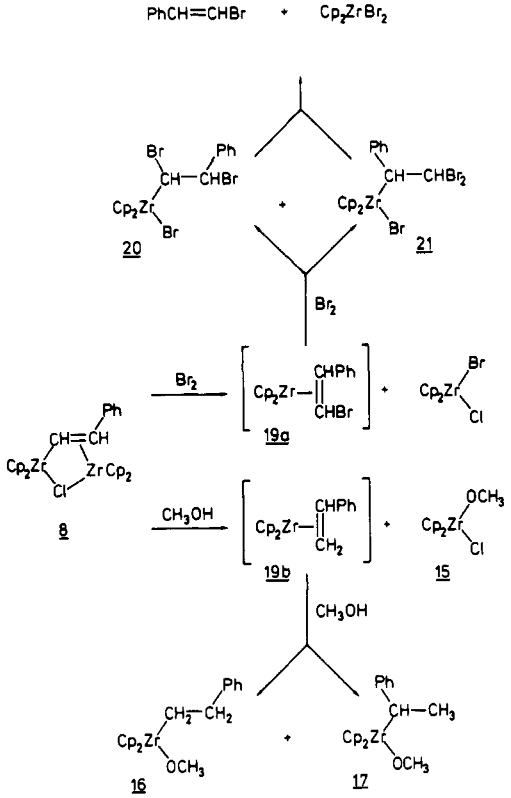
(26) Dorf, U.; Engel, K.; Erker, G. *Angew. Chem.* **1982**, *94*, 916–919.

(27) For an example of an isolable bis(olefin)zirconocene see: Erker, G.; Engel, K.; Vogel, P. *Angew. Chem.* **1982**, *94*, 791–792.

suming the usual cleavage of the zirconium–carbon σ bond followed by a rapid addition of the electrophile to the resulting intermediate (η^2-olefin)zirconocene complex **19** Such a consecutive reaction with an excess of protic reagents should produce ethylbenzene, the sole organic product observed besides a high yield of zirconocene dichloride (**6**) upon treatment of **8** with excess hydrochloric acid.

In the course of the reaction of **8** with bromine, further halogen addition to the intermediate (η^2-β-bromostyrene)zirconocene (**19a**) could yield two different products (1,2-dibromo-2-phenylethyl)zirconocene bromide (**20**) or (2,2-dibromo-1-phenylethyl)zirconocene bromide (**21**), both of which are unstable with regard to formation of the actually observed final products β-bromostyrene and zirconocene dibromide.

Such a description of the mechanistic course of the cleavage of **8** by electrophilic reagents is strongly supported by the formation of the zirconocene complexes **16** and **17** together with methoxyzirconocene chloride (**15**) as the only products in the reaction of **8** with 2 equiv of methanol. The fact that the isomeric products **16** and **17** resulting from methanol addition to the suggested intermediate (η^2-styrene)zirconocene (**19b**) are formed in almost equal amounts indicates that **19b** might be regarded as being an example of a very reactive, quite unselective (olefin)-zirconocene complex.



Experimental Section

Organometallic compounds were handled in an argon atmosphere by using Schlenk type glassware. Solvents were distilled under argon from P_4O_{10} (Sicapent, Merck) or lithium aluminum hydride (ether, tetrahydrofuran). Cp_2ZrCl_2,[28] $[Cp_2Zr(H)Cl]_x$ (**4**),[8] and substituted acetylenes[29] were prepared according to literature procedures. NMR spectra were obtained with either a Varian T 60 (^{1}H, 60 MHz) or Bruker WP-250 FT (^{1}H, 250 MHz; ^{13}C, 62.9 MHz) spectrometer. IR spectra were recorded with a Perkin-Elmer 325 spectrophotometer. Mass spectra were obtained on a CH 5 MAT Varian mass spectrometer (70 eV); MS features given refer to most abundant isotopes (e.g., ^{90}Zr, 51.5%). Melting points were measured with a Büchi-Tottoli apparatus and are not corrected. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr.

Vinylzirconocene Chloride (5a). At ambient temperature, acetylene was bubbled through a well-stirred suspension of 10.0 g (38.7 mmol) of **4** in 400 mL of benzene for 3 h at a rate of ~50 mL/min. The resulting dark red solution was filtered and the solvent evaporated in vacuo to yield 9.4 g (85.5%) of **5a** as a microcrystalline red solid: mp 97–98 °C; ^{1}H NMR (C_6D_6) δ 5.65, 5.95, 7.20 (ABX, J_{AX} = 20 Hz, J_{BX} = 15 Hz, J_{AB} = 3.5 Hz, 3 H), 5.80 (s, 10 H, Cp); ^{13}C NMR (C_6D_6) δ 186.4 (d, J_{CH} = 126 Hz, ZrCH=), 113.0 (d, Cp), 127.1 (t, J_{CH} = 153 Hz, =CH$_2$). Anal. Calcd for $C_{12}H_{13}ZrCl$ (283.79): C, 50.75; H, 4.62. Found: C, 50.82; H, 4.60.

(μ-Ethylene)bis(zirconocene chloride) (1a). (a) To a red solution of 5.5 g (19.4 mmol) of vinylzirconocene chloride (**5a**) in 400 mL of benzene was added 4.5 g (17.4 mmol) of hydridozirconocene chloride (**4**) in several portions with stirring. After 3 h at room temperature, 7.9 g (75.3%) of the addition product **1a**, which is poorly soluble in benzene, was filtered, washed repeatedly with benzene and then with pentane, and dried in vacuo. Anal. Calcd for $C_{22}H_{24}Zr_2Cl_2$ (541.55): C, 48.75; H, 4.47. Found: C, 48.73; H, 4.50.

(b) **1a** can also be obtained directly from $[Cp_2Zr(H)Cl]_x$ (**4**) in a one-flask synthesis. At room temperature, acetylene was introduced into a suspension of 3.1 g (12.0 mmol) of **4** in benzene (60 mL) for 10 min at a rate of 50 mL/min. Then the Schlenk tube was sealed with a glass stopper and the reaction mixture heated to 50 °C for 1 h. After the mixture was cooled to room temperature, the resulting suspension was filtered. The precipitate was washed twice with benzene and then dried in vacuo to yield 2.3 g (71%) of practically pure **1a**: mp 180 °C; ^{1}H NMR (C_6D_6) δ 6.02 (s, 20 H, Cp), 1.5–0.6 (br m, 4 H, CH$_2$); IR (KBr) ν (cm^{-1}) 3100, 1435, 1010, 800 (Cp);[30] MS, *m/e* 510 ($M^+ - C_2H_4$). Hydrolysis (10% aqueous NH_4Cl) of **1a** produces Cp_2ZrCl_2 and ethane. Degradation with bromine: a suspension of ~0.5 g of **1a** in benzene was titrated with Br_2. After removal of the solvent in vacuo pentane was added. The precipitated zirconium complexes were filtered. 1,2-Dibromoethane was obtained as the only organic reaction product after evaporation of the pentane in vacuo.

1-Propenylzirconocene Chloride (5b). A suspension of 5.1 g (20.0 mmol) of hydridozirconocene chloride (**4**) in benzene (50 mL) containing 0.8 g (20.0 mmol) of propyne was stirred for 30 min at 50 °C. The resulting mixture was filtered. After evaporation of the benzene solvent in vacuo, **5b** was obtained as an extremely air- and moisture-sensitive orange-red oil: ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 10 H, Cp), 6.87, 5.80, 1.67 (AMX$_3$ system); IR (CS_2) ν (cm^{-1}) 3100, 1425, 1013, 800 (Cp), 988 (*trans*-alkene).

(3,3-Dimethyl-1-butenyl)zirconocene Chloride (5c). As described above, **5c** was obtained from the reaction of 5.1 g (20.0 mmol) of **4** with 1.64 g (20 mmol) of *tert*-butylacetylene: ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 10 H, Cp), 6.67 and 5.73 (AB system, J_{AB} = 18.4 Hz, 2 H, olefin), 0.90 (s, 9 H, CH$_3$); IR (CCl_4) ν (cm^{-1}) 3100, 1440, 1015 (Cp), 990 (trans-alkene). Anal. Calcd for $C_{16}H_{21}ZrCl$ (340.01): C, 56.52; H, 6.23. Found: C, 56.47; H, 6.20. Hydrolysis (NH_4Cl) of **5c** yields Cp_2ZrCl_2 and *tert*-butylethylene.

(β-Styryl)zirconocene Chloride (5d). Analogously, **5d** was obtained as an orange-red oil from the reaction of 5.1 g (20 mmol) of **4** with 2.04 g (20 mmol) of phenylacetylene: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 5 H, Ph), 6.31 (s, 10 H, Cp), 7.76 and 6.70 (AB system, J_{AB} = 18.8 Hz, 2 H, olefin); ^{13}C NMR ($CDCl_3$) δ 177.7 (d, $^1J_{CH}$ = 122 Hz, ZrCH), 140.5 (d, $^1J_{CH}$ = 153 Hz, PhCH), 139.0 (s), 128.4 (d), 126.6 (d), 125.8 (d, aromatic C), 113.0 (d, $^1J_{CH}$ = 179 Hz, Cp); IR (CS_2) ν (cm^{-1}) 3100, 1435, 1017, 810 (Cp), 989 (*trans*-alkene). Anal. Calcd for $C_{18}H_{17}ZrCl$ (360.00): C, 60.00; H, 4.76. Found: C, 60.09; H, 4.74. Hydrolysis (NH_4Cl) of **5d** yields Cp_2ZrCl_2 and styrene; degradation with a stoichiometric amount of bromine results in the formation of β-bromostyrene.

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Table III. Crystal Data for 8

compd	$C_{28}H_{27}ClZr_2$	radiation	Mo Kα
mol wt	616.89	max cryst dimens, mm	0.35 × 0.40 × 0.50
space group	$P2_1/n$	scan width, deg	0.8 + 0.2 tan θ
cell constants		std reflctns	800, 0120
a, Å	8.380 (4)	decay of stds	2%
b, Å	22.256 (9)	reflctns measd	3332
c, Å	12.667 (6)	2θ range	1-44
β, deg	97.40 (3)	obsd reflctns	2581
cell vol, Å^3	2342.8	no. of parameters varied	280
molecules/unit cell	4	GOF	2.81
ρ(calcd) g cm^{-3}	1.75	R	0.042
μ(calcd), cm^{-1}	11.14	R_w	0.050

Phenyl(β-styryl)zirconocene (5e). To a solution of 1.1 g (3.0 mmol) of β-styrylzirconocene chloride (**5d**) in 60 mL of toluene/ether (1:1) at -78 °C was added a solution of 3 mmol of phenyllithium in 30 mL of ether. With stirring, the reaction mixture was allowed to warm to room temperature. Solvents were removed in vacuo. Benzene (30 mL) was added to the residue. After filtration and removal of the benzene in vacuo, **5e** was obtained as a brown oil: ^{1}H NMR ($CDCl_3$) δ 7.8–7.0 (m, 10 H, aromatic), 8.07 and 6.90 (AB system, J_{AB} = 19 Hz, 2 H, olefin), 6.27 (s, 10 H, Cp). Hydrolysis (aqueous HCl) yields benzene, styrene, and zirconocene dichloride.

Attempted Hydrozirconation of 1-Propenylzirconocene Chloride (5b). Since no reaction between **4** and **5b** had been detected after 48 h at ambient temperature, a suspension of 1.1 g (3.7 mmol) of 1-propenylzirconocene chloride (**5b**) and 0.9 g (3.5 mmol) of hydridozirconocene chloride (**4**) in 20 mL of toluene was heated for 18 h to 50 °C. The resulting brown suspension was filtered to yield 0.9 g of an unidentified solid. The remaining clear brown solution contained Cp_2ZrCl_2 (~35%) and *n*-propylzirconocene chloride (~45%, as judged from the ^{1}H NMR) along with several unidentified organometallic products.

Reaction of (3,3-Dimethyl-1-butenyl)zirconocene Chloride (5c) with 4. The reaction of **5c** with **4** was performed analogously as described above for **5b**. Similar workup yielded a rather complicated mixture of organometallic reaction products which was not further analyzed.

(β-Phenylethyl)zirconocene Chloride (7). Styrene (0.3 mL, 2.6 mmol) was added to a suspension of 0.66 g (2.57 mmol) of hydridozirconocene chloride (**4**) and the mixture stirred for 30 min at room temperature. Filtration from a small amount of precipitate and subsequent removal of solvent in vacuo yields **7** as a yellow oil: ^{1}H NMR (C_6D_6) δ 7.13 (s, 5 H, Ph), 5.77 (s, 10 H, Cp), 2.83 (m, 2 H, $PhCH_2$), 1.40 (m, 2 H, $ZrCH_2$). Hydrolysis (NH_4Cl) of **7** yields zirconocene dichloride plus ethylbenzene.

[μ-(β-η^1:α,β-η^2-Styryl)](μ-chloro)bis(zirconocene) (8). To a suspension of 5.0 g (13.9 mmol) of styrylzirconocene chloride (**5d**) in 100 mL of benzene was added 4.0 g (15.6 mmol) of hydridozirconocene chloride **4**, and the mixture was stirred for 18 h. The resulting red-brown suspension was filtered, yielding 2.8 g (34%) of **8** as a red amorphous solid. After repeated recrystallization from toluene (90 to -25 °C), large burgundy-red crystals of **8**; mp 215–216 °C, are obtained: ^{1}H NMR (C_6D_6) δ 7.70, 4.56 (AB, J_{AB} = 18.6 Hz, 2 H, ZrCH=CHPh), 7.40–6.95 (m, 5 H, Ph), 5.65, 5.39, 5.29, 4.88 (s, 5 H each, Cp); ^{13}C NMR (C_6D_6) δ 170.3 (d, $^1J_{CH}$ = 108 Hz, ZrCH=), 150.6 (s), 123.4 (d), 122.8 (d, Ph), 106.7, 106.3, 105.9, 104.9 (d each, Cp), 84.9 (d, $^1J_{CH}$ = 145 Hz, =CHPh); IR (C_6D_6) ν (cm^{-1}) 3100, 1437, 1010 (Cp); MS, *m/e* 578 (M^+), 547, 493, 463, 426, 255 (Cp_2ZrCl^+, 100%), 220 (Cp_2Zr^+). Anal. Calcd for $C_{28}H_{27}ClZr_2$ (616.89): C, 57.84; H, 4.68. Found: C, 57.69; H, 4.59.

X-ray Data Collection, Structure Determination, and Refinement for 8. Crystals suitable for an X-ray structure determination were obtained by a slow isothermal diffusion of pentane into a saturated solution of **8** in toluene at ambient temperature. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 15 reflections ($2\theta > 40°$) accurately centered on the diffractometer are given in Table III. The space group was uniquely determined as $P2_1/n$ from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. The method has been previously described.[31] A summary of the data collection parameters is given in Table III. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Calculations were carried out with the SHELX system of computer programs.[32] Neutral atom scattering factors for Zr, Cl, and C were taken from Cromer and Waber,[33] and the scattering for zirconium was corrected for real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.[34] Scattering factors for H were from ref 35.

The position of the zirconium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the zirconium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.096$. The hydrogen atoms of the phenyl and cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atom and were allowed to ride on the appropriate carbon atom. The two hydrogen atoms on the olefinic unit were located with the aid of a difference Fourier map and were not refined. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.042 and R_w = 0.050. A final difference Fourier showed no feature greater than 0.3 e/Å^3. The weighting scheme was based on unit weights; no systematic variation of $(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.[36]

Reactions of 8 with Electrophilic Reagents. Treatment of **8** with a stoichiometric amount of bromine (1 equiv of Br_2/Zr) (as described above for **5d**) results in the formation of β-bromostyrene; degradation with excess aqueous HCl yields zirconocene dichloride and ethylbenzene.

A solution of 0.7 g (1.2 mmol) of **8** in 20 mL benzene was treated with methanol until no remaining starting material was found by ^{1}H NMR. A 0.8-mL (2.4-mmol) sample of CH_3OH was consumed. From an aliquot (5 mL) of the resulting solution, the solvent was evaporated in vacuo. The residue consists of a mixture of three components as judged by ^{1}H NMR (C_6D_6): methoxyzirconocene chloride (**15**) (two parts), δ 5.97 (s, 10 H, Cp), 3.67 (s, 3 H, OCH_3); methoxy(2-phenylethyl)zirconocene (**16**) (one part), δ 7.2 (m, Ph), 5.77 (s, 10 H, Cp), 3.67 (s, 3 H, OCH_3), 3.0 (br m, 2 H, $PhCH_2$), 1.2 (br m, 2 H, $ZrCH_2$); methoxy(1-phenylethyl)zirconocene (**17**) (one part), δ 7.2 (m, Ph), 6.05 and 5.47 (s, 5 H each, Cp), 3.53 (s, 3 H, OCH_3), 3.0 (m, 1 H, PhCH), 1.62 (d, 3 H, CH_3).

Treatment of the reaction mixture with aqueous HCl results in the formation of zirconocene dichloride, ethylbenzene, and methanol.

The remaining 15 mL of the reaction mixture were treated with bromine. Solvent was removed in vacuo, and organic products were extracted with pentane. After removal of the solvent, one obtains a 1:1 mixture of 1-bromo-2-phenylethane and 1-bromo-1-phenylethane (identified by comparison with authentic material).

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

Table IV. X-ray Structure Determination of 8: Positional Parameters

atom	*x/a*	*y/b*	*z/c*	*U*(eqv), Å^2
Zr(1)	0.52676 (8)	0.89685 (3)	0.71564 (6)	0.029
Zr(2)	0.37581 (8)	0.83087 (3)	0.47254 (6)	0.030
Cl	0.3859 (2)	0.94184 (9)	0.5443 (2)	0.038
C(1)	0.4771 (9)	0.8048 (3)	0.6580 (6)	0.031
C(2)	0.5288 (8)	0.7593 (3)	0.5915 (6)	0.031
C(3)	0.4923 (9)	0.6943 (3)	0.5969 (6)	0.031
C(4)	0.3672 (9)	0.6696 (4)	0.6462 (6)	0.041
C(5)	0.342 (1)	0.6084 (4)	0.6479 (7)	0.047
C(6)	0.441 (1)	0.5696 (4)	0.6021 (7)	0.050
C(7)	0.567 (1)	0.5921 (4)	0.5546 (7)	0.049
C(8)	0.591 (1)	0.6537 (4)	0.5521 (6)	0.041
Cp(1)	0.260 (1)	0.8879 (4)	0.7885 (7)	0.049
Cp(2)	0.293 (1)	0.9496 (5)	0.7873 (7)	0.062
Cp(3)	0.428 (1)	0.9609 (5)	0.8612 (8)	0.062
Cp(4)	0.480 (1)	0.9062 (4)	0.9072 (7)	0.051
Cp(5)	0.376 (1)	0.8608 (4)	0.8642 (7)	0.050
Cp(6)	0.8151 (9)	0.8772 (5)	0.7898 (9)	0.061
Cp(7)	0.8075 (9)	0.8681 (5)	0.6802 (9)	0.056
Cp(8)	0.775 (1)	0.9208 (5)	0.6283 (8)	0.055
Cp(9)	0.764 (1)	0.9653 (4)	0.7033 (9)	0.059
Cp(10)	0.789 (1)	0.9398 (5)	0.8041 (8)	0.064
Cp(11)	0.648 (1)	0.8351 (5)	0.4004 (7)	0.056
Cp(12)	0.562 (1)	0.8870 (4)	0.3583 (8)	0.065
Cp(13)	0.428 (1)	0.8676 (5)	0.2904 (8)	0.061
Cp(14)	0.432 (1)	0.8065 (5)	0.2857 (7)	0.060
Cp(15)	0.563 (1)	0.7851 (5)	0.3527 (7)	0.057
Cp(16)	0.1243 (9)	0.7967 (5)	0.5514 (7)	0.051
Cp(17)	0.1490 (9)	0.7566 (4)	0.4706 (7)	0.045
Cp(18)	0.124 (1)	0.7868 (4)	0.3743 (7)	0.050
Cp(19)	0.088 (1)	0.8473 (4)	0.3946 (9)	0.057
Cp(20)	0.0873 (9)	0.8521 (5)	0.5057 (9)	0.056
Hc(1)	0.3953 (9)	0.7874 (3)	0.7080 (6)	iso
Hc(2)	0.6173 (8)	0.7645 (3)	0.5632 (6)	iso
H(21)	0.2950 (9)	0.6970 (4)	0.6808 (6)	iso
H(22)	0.250 (1)	0.5920 (4)	0.6828 (7)	iso
H(23)	0.421 (1)	0.5253 (4)	0.6035 (7)	iso
H(24)	0.640 (1)	0.5639 (4)	0.5228 (7)	iso
H(25)	0.682 (1)	0.6698 (4)	0.5173 (6)	iso
H(1)	0.169 (1)	0.8672 (4)	0.7440 (7)	iso
H(2)	0.230 (1)	0.9801 (5)	0.7414 (7)	iso
H(3)	0.479 (1)	1.0010 (5)	0.8766 (8)	iso
H(4)	0.574 (1)	0.9007 (4)	0.9632 (7)	iso
H(5)	0.384 (1)	0.8171 (4)	0.8825 (7)	iso
H(6)	0.8350 (9)	0.8461 (5)	0.8469 (9)	iso
H(7)	0.8242 (9)	0.8285 (5)	0.6458 (9)	iso
H(8)	0.761 (1)	0.9264 (5)	0.5493 (8)	iso
H(9)	0.741 (1)	1.0088 (4)	0.6876 (9)	iso
H(10)	0.788 (1)	0.9612 (5)	0.8734 (8)	iso
H(11)	0.748 (1)	0.8342 (5)	0.4529 (7)	iso
H(12)	0.593 (1)	0.9297 (4)	0.3744 (8)	iso
H(13)	0.343 (1)	0.8941 (5)	0.2521 (8)	iso
H(14)	0.351 (1)	0.7809 (5)	0.2411 (7)	iso
H(15)	0.594 (1)	0.7419 (5)	0.3647 (7)	iso
H(16)	0.1317 (9)	0.7870 (5)	0.6289 (7)	iso
H(17)	0.1795 (9)	0.7133 (4)	0.4805 (7)	iso
H(18)	0.132 (1)	0.7691 (4)	0.3026 (7)	iso
H(19)	0.067 (1)	0.8806 (4)	0.3416 (9)	iso
H(20)	0.0633 (9)	0.8893 (5)	0.5449 (9)	iso

Analogous results were obtained if 8 was treated with less than the stoichiometric amount of methanol: **15**, **16**, and **17** were found besides unreacted starting material.

Carbonylation of 8. A solution of 2.8 g (4.8 mmol) of 8 in 75 mL of benzene was stirred for 1 h at room temperature in a CO atmosphere. During this period 125 mL (5.6 mmol) of carbon monoxide was consumed. After removal of the solvent in vacuo, a brown-black, amorphous residue was obtained that contains ~90% of the cyclic zirconium enolate **14**: ^{1}H NMR (C_6D_6) δ 7.60–6.80 (m, Ph), 5.91, 5.84, 5.80, 5.34 (s, 5 H each, Cp), 2.80 (d, J = 5 Hz, 1 H, PhCH); ^{13}C NMR (C_6D_6) δ 195.0 (s, ZrOC=), 149.1 (s), 123.8 (d), 122.1 (d, Ph), 111.7, 110.3, 109.5, 108.9 (d, Cp), 63.6 (d, $^1J_{CH}$ = 131 Hz, PhCH); IR (C_6D_6) ν (cm^{-1}) 3100, 1435, 1012 (Cp); MS, *m/e* 606 (M$^+$), 578 (M$^+$ − CO), 551, 509, 463.

Dihydrocinnamaldehyde was formed upon hydrolysis of **14**. For a further characterization, a solution of 1.0 g (1.6 mmol) of the zirconium enolate **14** in 10 mL of benzene was treated with bromine (ca. 5% excess). A 20-mL sample of 40% NaOH was added, and the mixture was stirred for 20 min at ambient temperature. The aqueous phase was separated and acidified with 50% aqueous sulfuric acid. The resulting mixture was extracted with ether. After the mixture was dried over magnesium sulfate, the solvent was evaporated in vacuo to yield *trans*-cinnamic acid (70%).

Photolysis of Diphenylzirconocene (10) in the Presence of (β-Styryl)zirconocene Chloride (5d). A solution of 0.3 g (0.8 mmol) of **5d** and 0.6 g (1.6 mmol) of diphenylzirconocene in 0.5 mL of benzene-d_6 was sealed in a Pyrex NMR tube. The solution was irradiated for 16 h (Philips HPK 125, 20 °C). As judged by ^{1}H NMR, the photolysis has led to the formation of 8 as the main product (ca. 80%) plus some zirconocene dichloride (ca. 10%) and several unidentified minor components (ca. 10% total) besides some unchanged residual diphenylzirconocene.

Photolysis of Phenyl(β-styryl)zirconocene (5e) in the Presence of (β-Styryl)zirconocene Chloride (5d). As described above, a solution of **5e** and **5d** (molar ratio 1.2:1) was irradiated for 17 h at 20 °c (sealed NMR tube, Philips HPK 125, Pyrex filter). By ^{1}H NMR 8 was identified as being the major component (>80%) of the organometallic product mixture. *trans*-Stilbene was identified as the organic product.

Photolysis of Phenyl(β-styryl)zirconocene (5e). A solution of 6.0 g (15 mmol) of **5e** in 150 mL of benzene was irradiated for 4.5 h (Philips HPK 125, Pyrex filter, room temperature). Evaporation of the solvent yields a product mixture consisting mainly (≥90%) of *trans*-stilbene and **12**. The organic component can be removed with great loss of organometallic material by successive washing with pentane/benzene (1:1) to yield 0.4 g of >95% pure **12**: ^{1}H NMR (C_6D_6) δ 7.87 (d, $^3J_{HH}$ = 18 Hz, 1 H, ZrCH=), 7.5–7.0 (m, 10 H, aromatic), 6.87 (d, $^3J_{HH}$ = 18 Hz, =CHPh), 5.50, 5.10, 5.03, 4.97 (s, 5 H each, Cp).

Benzene, ethylbenzene, and zirconocene dichloride have been identified as products of hydrolysis (aqueous HCl). For a further characterization, a solution of **12** in benzene was treated with bromine dropwise as long as it was spontaneously decolorized. Bromobenzene and β-bromostyrene were identified by comparison with authentic material (^{1}H NMR and GC analysis).

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Registry No. **1a**, 56026-70-1; 4, 86953-31-3; **5a**, 81894-89-5; **5b**, 86954-91-8; **5c**, 63817-18-5; **5d**, 81939-33-5; **5e**, 86954-92-9; 7, 86954-93-0; 8, 86954-94-1; **10**, 51177-89-0; **12**, 86968-51-6; **14**, 86968-52-7; **15**, 11087-26-6; **16**, 86954-95-2; **17**, 86954-96-3; HC≡CH, 74-86-2; CH_2DbdCH—Ph, 100-42-5; propyne, 74-99-7; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3; *n*-propylzirconocene chloride, 69124-52-3; dihydrocinnamaldehyde, 104-53-0.

Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.