then cooled to −80 °C. The clear upper layer was analyzed by GLC using heptane as internal standard. The initial rates were reproducible within ±10%. The volumetric measurements of evolved H_2 were carried out by using a described gasometric apparatus.[22]

Acknowledgment. We thank K. Moser and L. Nêmeth for help in processing the kinetic data.

Registry No. $Co_2(CO)_8$, 15226-74-1; $Et_3SiCo(CO)_4$, 14049-72-0; Et_3SiH, 617-86-7.

Thermally Induced Reaction of a Group 4 Bent Metallocene Unit with Elemental Sulfur and Selenium: The Formation of Four-Membered Metallacycles

Gerhard Erker,*[†] Thomas Mühlenbernd, Reinhard Benn, and Anna Rufińska

Max-Planck-Institut für Kohlenforschung, D 4330 Mülheim a.d. Ruhr 1, Germany

Gérard Tainturier* and Bernard Gautheron

Laboratoire de Synthèse et d'Electrosynthèse Organometalliques, Faculté des Sciences, 21100 Dijon, France

Received August 19, 1985

(Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium has been obtained by reacting $(\eta\text{-}C_5H_4CMe_3)_2ZrCl_2$ (**3**) with (butadiene)magnesium. The (diene)zirconium complex exists in two stable isomeric forms, (s-cis-η^4-butadiene)$Zr(C_5H_4CMe_3)_2$ (**5**) and (s-$trans$-η^4-butadiene)$Zr(C_5H_4CMe_3)_2$ (**7**). At room temperature the **5** ⇄ **7** equilibrium ratio is 95/5. UV irradiation of **5** at low temperature leads to almost pure **7**. The activation barrier of the thermally induced **7** → **5** rearrangement has been determined being $\Delta G^{\ddagger}_{-10\,^{\circ}\mathrm{C}} = 19.5 \pm 0.2$ kcal/mol. The **5** ⇄ **7** equilibrium mixture reacts with elemental selenium (ambient temperature, 6 days) to give the four-membered metallacycle $(Cp'_2ZrSe)_2$ (**2**). With stoichiometric amounts of sulfur a similar reaction of the (butadiene)$ZrCp'_2$ system is observed to give the analogous butadiene-free product $(Cp'_2ZrS)_2$ (**9**). With a tenfold excess of sulfur the reaction of the thermodynamic **5**/**7** mixture yields only a small amount of the four-membered metallacycle **9**. The six-membered metallacycle Cp'_2ZrS_5 (**8**) now is the major reaction product (**8**/**9** ≈ 10/1). **8** in turn is converted to **9** upon treatment with a stoichiometric amount of the (butadiene)metallocene mixture **5** ⇄ **7** at ambient temperature. The (butadiene)$Zr(\eta\text{-}C_5H_4CMe_3)_2$ system appears to be a reliable source for transferring the elusive group 4 bent metallocene unit for preparative purposes.

Deoligomerization of the stable forms of the chalcogen elements can be achieved in a number of ways. Substantial knowledge has been accumulated concerning the methodology and mechanisms of cleaving, e.g., sulfur to sulfur linkages starting from the S_8 molecule.[1] Many of the synthetic methods developed in sulfur chemistry have turned out to be suitable to prepare interesting selenium compounds as well.[2] Most notable among the published procedures are the reactions of the chalcogen rings and chains (or fragments derived thereof) with many transition-metal complexes to form new metallacyclic complexes of various ring sizes.[3] Examples of compounds containing "three"- to eight-membered rings containing sulfur have been reported.[4,5]

Frequently, late-transition-metal complexes are able to cleave the elemental chalcogens directly forming the stable metallacyclic deoligomerization products.[3] In addition, the same transition-metal–main-group element complexes can be obtained by stepwise reaction sequences. In this case, e.g., *cyclo*-S_8 is first transformed to an oligosulfide, S_n^{2-}, which is then treated with the corresponding transition-metal dihalide complex.[6]

Variations of this route have for a long time been the best way of preparing the structurally as well as chemically most interesting examples of metallacyclic oligosulfides and -selenides of many early transition metals.[5,6] In principle, early-transition-metal complexes should be able to directly cleave the chalcogen element–element linkage similar to the many reagents derived from the late transition metals. To us, the crucial point seems to be the availability of

---

[†] New address: Institut für Organische Chemie des Universtüt Würzburg, Am Hubland, D-8700 Würzburg, Germany.

(1) (a) Schmidt, M. *Angew. Chem.* **1973**, *85*, 474. (b) Meyer, B. *Chem. Rev.* **1964**, *64*, 429. (c) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149. (d) Parker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583. (e) Oae, S. "Organic Chemistry of Sulfur"; Plenum: New York, 1977.

(2) See, e.g.: Brintzinger, H.; Pfannstiel, K.; Vogel, H. *Z. Anorg. Allg. Chem.* **1948**, *256*, 75. Brandsma, L.; Wijers, H. E. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 68. Günther, W. H. H. *J. Org. Chem.* **1967**, *32*, 3929. Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.

(3) Schmidt, M.; Hoffmann, G. G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 451.

(4) Hofmann, K. A.; Höchtlen, F. *Chem. Ber.* **1903**, *36*, 3090. Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* **1969**, *8*, 779. Chatt, J.; Mingos, D. M. P. *J. Chem. Soc. A* **1970**, 1243 and literature cited in ref 3.

(5) (a) Muller, E. G.; Peterson, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91. Epstein, E. F.; Bernal, I.; Köpf, H. *Ibid.* **1971**, *26*, 229. Abel, E. W.; Booth, M.; Orrell, K. G. *Ibid.* **1978**, *160*, 75. Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem.* **1968**, *80*, 660. Roesky, H. W.; Zamankhan, H.; Bats, J. W.; Fuess, H. *Ibid.* **1980**, *92*, 122. Bolinger, C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223. Bolinger, C. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1981**, *103*, 5620. (b) Köpf, H. *Angew. Chem.* **1969**, *81*, 332. Köpf, H.; Kahl, W.; Wirl, A. *Ibid.* **1970**, *82*, 814. Davis, B. R.; Bernal, I.; Köpf, H. *Ibid.* **1971**, *83*, 1018. Köpf, H.; Wirl, A.; Kahl, W. *Ibid.* **1971**, *83*, 146. Coucouvanis, D.; Swenson, D.; Stremple, P.; Baenziger, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 3392. Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *Ibid.* **1981**, *103*, 1218. Maheu, L. J.; Pignolet, L. H. *Ibid.* **1980**, *102*, 6346.

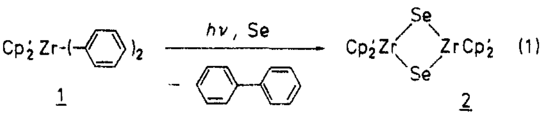
(6) (a) Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* **1968**, *101*, 272. (b) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. (c) Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2329. Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204. (d) Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, W. *Angew. Chem.* **1982**, *94*, 375. Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823. (e) Muller, E. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91. Rauchfuss, T. B., unpublished results, cited in: Draganjac, M.; Rauchfuss, T. B. *Angew. Chem.* **1985**, *97*, 745. See also: Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1974**, 2433.

0276-7333/86/2305-1023$01.50/0

sufficiently reactive early-transition-metal complex fragments to attack the intact chalcogen elemental linkage.

There is evidence that this problem can be overcome for the elusive group 4 bent metallocene complexes.[6e] The Dijon group has recently demonstrated that the Cp$_2$M unit, photochemically generated from stable diarylmetallocene complexes 1,[7] indeed reacts with elemental selenium to give 2.[8]

The disadvantages of carrying out a preparative photoreaction prompted us to search for a thermally induced analogue of the transformation outlined in (1). Monomeric group 4 metallocene complexes containing easily replaceable neutral ligands are obvious candidates as precursors in this reaction. Of the many possibilities,[9] we have investigated in some detail the potential of (conjugated diene)zirconocene complexes as a source for generating Cp$_2$M[10] as a transferable reactive species in a thermally induced reaction. This has led to some success. The thermal reaction of the previously unknown (butadiene)bis(*tert*-butylcyclopentadienyl)zirconium system with elemental sulfur or selenium proceeded in the expected manner with extrusion of the conjugated diene ligand and formation of zirconium–chalcogen-containing metallacycles as described below.

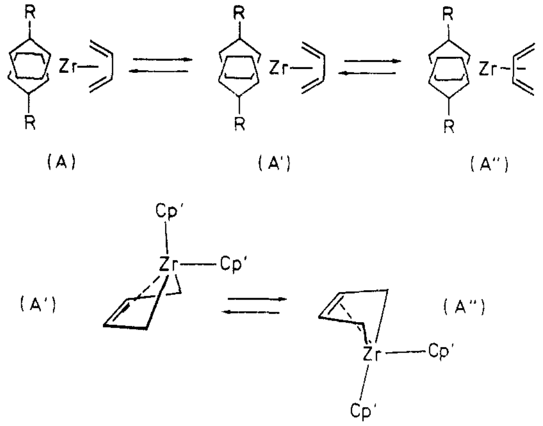


1 2

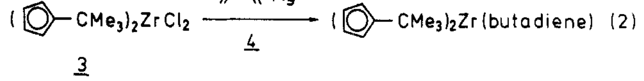
Cp' = η-C$_5$H$_4$-CMe$_3$

The (η-C$_5$H$_4$CMe$_3$)$_2$Zr(butadiene) System. Conjugated diene group 4 metallocene complexes can be prepared by a variety of synthetic methods.[11] The resulting systems are unique in several ways: for many examples the existence of two stable (η^4-diene)MCp$_2$ isomers has been demonstrated experimentally.[12] The (*s-cis*-η^4-diene)metallocene form exhibits a substantial metallacyclopentene character.[13] It often equilibrates with the (*s-trans*-η^4-diene)MCp$_2$ isomer.[14] The unprecedented ability of the group 4 bent metallocene unit[10] to form stable complexes where both double bonds of an s-transoid conformer of the conjugated diene ligand are coordinated to the same transition-metal center has only recently been paralleled by another mononuclear transition-metal fragment.[15]

Scheme I



We have obtained the (butadiene)bis(*tert*-butyl-cyclopentadienyl)zirconium system in good yield from the reaction of (η-C$_5$H$_4$CMe$_3$)$_2$ZrCl$_2$ with the oligomeric butadiene dianion equivalent "butadiene–magnesium".[16] After recrystallization from hexane the pure (*s-cis*-η^4-butadiene)ZrCp'$_2$ isomer (5) was obtained in crystalline form. A thorough structural analysis and an investigation of its dynamic properties in solution revealed the following characteristics of this (*s-cis*-conjugated diene)metallocene complex.[17] In the solid, the Zr(butadiene) framework adopts an envelope-shaped conformation. This early transition-metal diene complex exhibits substantial metal alkyl character. Bond distances of the metal to the terminal diene carbon atoms are short. They are clearly in the range expected for a zirconium to carbon σ-interaction.[18] In contrast, a π-interaction is indicated to be present between the metal center and the internal diene carbon atoms.[19] According to the X-ray crystal structure analysis, 5 is best being described as an example of a metallacyclic σ^2,π-type metallacyclopentene complex.[12,13]



In the crystal the substituted cyclopentadienyl ligands are oriented relative to each other to give a chiral geometry.[17] The most stable conformer in the crystal is characterized by a staggered orientation of the Cp units within

---

[7] Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

[8] (a) Pouly, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1982**, *232*, C65. (b) For a similar reaction see: Samuel, E.; Gianotti, C. *Ibid.* **1976**, *113*, C17.

[9] (a) Cp$_2$M(N$_2$) complexes: Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. Manriquez, J. M.; Bercaw, J. E. *Ibid.* **1974**, *96*, 6229. Bercaw, J. E. *Ibid.* **1974**, *96*, 5087. (b) Cp$_2$M(CO)$_2$: Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *101*, C24. Sikora, D. J.; Rausch, M. D. *Ibid.* **1984**, *276*, 21 and references cited therein. Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1976**, 230. Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. (c) Cp$_2$M(CO)(PR$_3$): Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1984**, *276*, 21 and references cited therein. (d) Cp$_2$M(PR$_3$)$_2$: Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 982. Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem.* **1985**, *97*, 425 and references cited therein. Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244. (e) Cp$_2$M(olefin): Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

[10] Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729 and references cited therein.

[11] (a) Photochemical preparation: Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311. (b) Cp$_2$MCl$_2$ + butadiene dianion equivalent: Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388. Dorf, U.; Engel, K.; Erker, G. *Ibid.* **1983**, *2*, 462. (c) By coupling of vinyl ligands: Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945. Czisch, P.; Erker, G. *J. Organomet. Chem.* **1983**, *253*, C9. Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1984**, *268*, C7.

[12] Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

[13] Erker, G.; Krüger, C.; Engel, K.; Müller, G. *Organometallics* **1984**, *3*, 128. Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Ibid.* **1985**, *4*, 215.

[14] Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300.

[15] Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

[16] Ramsden, H. E. US Patent 3 388 179, 1968. Yasuda, H.; Fujita, K.; Ohnuma, Y.; Tani, H. *J. Organomet. Chem.* **1976**, *113*, 201. Wreford, S. S.; Whitney, J. F. *Inorg. Chem.* **1981**, *20*, 3918.

[17] The X-ray crystal structure analysis and the NMR investigation on **5** have been published previously as a communication. For details see: Erker, G.; Mühlenbernd, T.; Benn, R.; Rufińska, A.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 336.

[18] $\bar{d}$(Zr–CH$_2$(butadiene)) = 2.334 (7) Å for **5**;[17] for a comparison see: Hrncir, D. C.; Vann Bynum, R.; Atwood, J. L.; Hunter, W. E.; Penttila, R. A. *Organometallics* **1983**, *2*, 750 and references cited therein.

[19] $\bar{d}$(Zr–CH(butadiene)) = 2.525 (10) Å for **5**;[17] for a comparison see: Erker, G.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555 and references 12 and 13.

Table I. A Comparison of Selected NMR Data[a] of the Butadiene Ligands in (*s-cis*- or *s-trans*-$CH_2{=}CHCH{=}CH_2$)$M(CpR)_2$ Complexes (M = Zr, Hf; R = H, CMe_3)

	^1H NMR[b]			^{13}C NMR[b,c]		
compd	H1s	H1a	H2	C1	C2	lit.
s-cis isomers						
5′, Zr, CpH	3.15	−0.70	4.85	49.0 (138, 144)	112.0 (144)	12, 13
5, Zr, $CpCMe_3$	3.38	−0.72	4.95	50.8 (130, 153)	112.3 (157)	this work
	3.15	−0.39	4.68	49.6 (131, 155)	112.2 (156)	
5a′, Hf, CpH	3.36	−0.65	5.04	45.0 (140)	114.5 (156)	12, 22
5a, Hf, $CpCMe_3$	3.14	−0.87	5.20	46.4 (140)	114.7 (152)	this work
	2.92	−0.54	4.95	45.7 (139)	114.2 (152)	
s-trans isomers						
7′, Zr, CpH	3.20	1.20	2.90	59.0 (149, 159)	96.0 (152)	11a, 12, 14
7, Zr, $CpCMe_3$	3.17	1.56	2.91	61.1 (147, 157)	97.1 (147)	this work
7a′, Hf, CpH	3.13	1.13	2.83	57.8 (142, 148)	92.8 (147)	12, 22
7a, Hf, $CpCMe_3$	3.09	1.52	2.94	80.1 (144, 155)	94.4 (148)	this work

[a] Low-temperature (see Experimental Section) limiting spectra in toluene-d_8, chemical shift relative to internal Me_4Si, δ scale. [b] H1 denotes a hydrogen atom at the terminal carbon C1 of the conjugated diene ligand; relative position to H2 is indicated as s (syn) and a (anti). [c] Coupling constants $^1J_{CH}$ (Hz) are given in parentheses.

Table II. (*s-trans*-Diene)- → (*s-cis*-Diene)metallocene Isomerization Barriers and Equilibrium Ratio of (η^4-Butadiene)$M(CpR)_2$ Complexes (M = Zr, Hf; R = H, CMe_3)

compd	M	R	$\Delta G^\ddagger$(s-trans → s-cis), kcal/mol (*T*, °C)[a]	equil. ratio[b] (*T*, °C) (s-cis/s-trans)	lit.
5′, **7′**	Zr	H	22.7 (+10.5)	55/45 (25)	11a, 12, 14
5, **7**	Zr	CMe_3	19.5 (−10)	95/5 (37)	this work
5a′, **7a′**	Hf	H	24.7 (+60)	>99/1 (60)	11b, 12, 22
5a, **7a**	Hf	CMe_3	21.4 (+10)	>99/1 (37)	this work

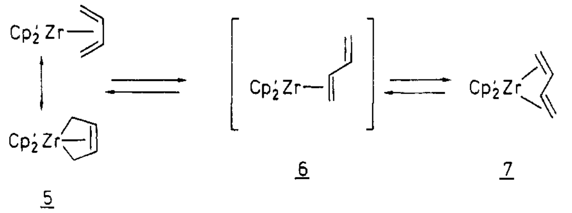
[a] ±0.3 kcal/mol. [b] In toluene-d_8.

the bent metallocene unit. The bulky *tert*-butyl substituents adopt trans positions to one another. They are positioned in the lateral sectors of the bent metallocene fragment.[20]

There is considerable evidence from a detailed NMR study[17] that a conformation of the same symmetry properties is representing the most stable local minimum on the (η-$C_5H_4CMe_3$)$_2$Zr (butadiene) energy surface in solution. The observation of eight different Cp methine resonances in addition to four chemically differentiated diene carbon atoms by NMR at very low temperature was taken as an indication for a substantially hindered Cp′–metal rotation[21] in addition to a slow M(diene) topomerization[12] on the NMR time scale. Increasing the NMR observation temperature resulted in a stepwise symmetrization of the NMR spectra. First, the activation barrier for Cp rotation (A ⇄ A′, see Scheme I; $\Delta G^\ddagger_{-40\,°C} = 9.8 \pm 0.2$ kcal/mol) was overcome. At still higher temperature, additional topomerization (A′ ⇄ A″; $\Delta G^\ddagger_{-8\,°C} = 13.5 \pm 0.2$ kcal/mol) taking place rapidly on the NMR time scale resulted in the observation of apparent C_{2v} molecular symmetry of the (*s-cis*-butadiene)metallocene complex **5** in the high-temperature limiting NMR spectra.[17]

We were able to identify a second isomer on the Cp'_2Zr(butadiene) surface. Irradiation of the isolated (*s-cis*-η^4-butadiene)Zr(η-$C_5H_4CMe_3$)$_2$ (**5**) at −40 °C in toluene rapidly resulted in the almost quantitative formation of its photoisomer **7**. The newly formed compound exhibited NMR spectra consistent with a C_2 molecular symmetry. The NMR appearance of the butadiene ligand is substantially different from the *s-cis*-diene moiety in **5**. By close inspection (see Table I) of the NMR spectra and comparison with typical examples **7** has been identified as the (*s-trans*-η^4-butadiene)ZrCp'_2 isomer.

Scheme II



At room temperature the less stable **7** rapidly isomerizes to the thermodynamically favored (*s-cis*-diene)metallocene **5**. Similar to other (*s-trans*-η^4-conjugated diene)- to (*s-cis*-η^4-conjugated diene)metallocene isomerizations (Table II), we propose an unsaturated (η^2-butadiene)ZrCp'_2 complex, **6**, to function as a reactive intermediate in the **7** → **5** isomerization pathway. An energy surface similar to the one that has been qualitatively established for the isomerization of the parent (*s-trans*-η^4-butadiene)- ⇄ (*s-cis*-η^4-butadiene)Zr(η-C_5H_5)$_2$ system[12,22,23] can readily account for the observations here made for the analogous ($C_5H_4CMe_3$)$_2$Zr system: rapid equilibration of the intermediate **6** with the *s-trans*-diene complex **7** contrasted by a substantial activation barrier for the rearrangement to the (*s-cis*-butadiene)ZrCp'_2 isomer (**5**). Consequently, **6** is forced to stabilize itself by rearrangement to **7**, if formed from **5** by irradiation at sufficiently low temperature.

Knowing the spectroscopic data of **7** and its thermal stability enabled us to identify the (*s-trans*-η^4-butadi-

---

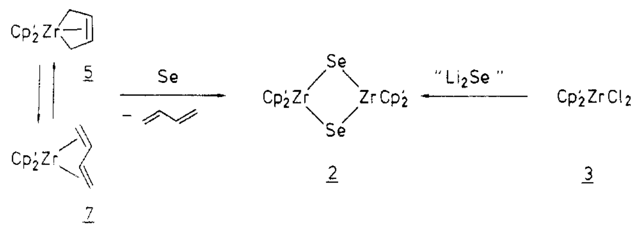
[20] An analogous preferred conformation was found for (η-$C_5H_4CMe_3$)$_2TiCl_2$: Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149.

[21] (η-Cp)M rotational barriers are usually very low, e.g., between 1 and 2 kcal/mol for the ferrocene molecule: Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39 (loc. cit.). See also: Gilson, D. F. R.; Gomez, G. *J. Organomet. Chem.* **1982**, *240*, 41. Some notable exceptions are given in: Luke, W. D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3241. Hofmann, W.; Buchner, W.; Werner, H. *Angew. Chem.* **1977**, *89*, 836. Davidson, J. L. *J. Chem. Soc.* **1980**, 113.

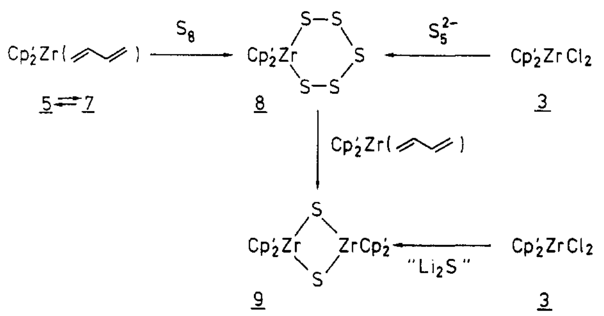
[22] Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L. *Angew. Chem.* **1982**, *94*, 915.

[23] Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506. Erker, G.; Dorf, U. *Ibid.* **1983**, *95*, 800. Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Peterson, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. Erker, G.; Engel, K.; Korek, U.; Czisch, P.; Berke, H.; Caubère, P.; Vanderesse, R. *Organometallics* **1985**, *4*, 1531.

Scheme III



Scheme IV



ene)zirconocene complex as the minor component of the $5 \rightleftarrows 7$ equilibrium. At 25 °C the **5**/**7** equilibrium ratio was determined to be 95/5. The activation barrier of the thermal rearrangement of (*s-trans*-η^4-butadiene)Zr($C_5H_4CMe_3$)$_2$ (**7**) to the s-cis isomer **5** was measured to be $\Delta G^{\ddagger}{}_{-10^\circ C} = 19.5 + 0.2$ kcal/mol. Qualitatively analogous behavior was observed for the (butadiene)Hf(η-$C_5H_4CMe_3$)$_2$ isomers **5a** and **7a**.[24]

Reaction of the (Butadiene)Zr(η-$C_5H_4CMe_3$)$_2$ Equilibrium System (5 ⇌ 7) with Elemental Selenium and Sulfur. The (η^4-butadiene)ZrCp'$_2$ equilibrium system $5 \rightleftarrows 7$ reacts at room temperature slowly with elemental selenium. Typical reaction conditions are as follows. A sample of the 95/5 mixture of the zirconium complexes **5** and **7** are vigorously stirred with a twofold molar excess of gray selenium in toluene at ambient temperature. The progress of the reaction was checked by ^{1}H NMR. After 6–7 days practically no organometallic starting material could be detected in the reaction mixture. The product-containing solution was separated from the remaining selenium powder. After usual workup and recrystallization from toluene/heptane we isolated a single organometallic reaction product in about 45% yield. The bright green crystalline product proved to be identical in every respect with the four-membered metallacyclic (Cp'$_2$ZrSe)$_2$ (**2**), which had previously been prepared by an independent route starting from ($C_5H_4CMe_3$)$_2$ZrCl$_2$ (**3**) and Li$_2$Se (see Scheme III).[25]

The reaction of the $5 \rightleftarrows 7$ equilibrium mixture with elemental sulfur proceeded somewhat differently. First of all, the (butadiene)ZrCp'$_2$ system reacted much faster with sulfur than with selenium. However, this is probably not due to an intrinsic reactivity difference but is controlled by the necessarily different reaction conditions applied: while the reaction with the insoluble Se powder proceeds in a heterogeneous system, the reaction between **5**, **7**, and sulfur occurs homogeneously in toluene. In a typical experiment the reaction of an equimolar mixture of (butadiene)ZrCp'$_2$ and sulfur in the aromatic solvent was complete after 2 days at ambient temperature. Workup and recrystallization of the obtained material gave a somewhat low but reproducable yield of 25–35% of the four-membered metallacyclic complex (Cp'$_2$ZrS)$_2$ (**9**).[6d] Again the identity of the product was unequivocally established by a comparison with authentic material (Scheme IV).[25c]

For any mechanistic investigation it would have been important to know the relative reactivity of the single (butadiene)ZrCp'$_2$ isomers **5** and **7** toward the sulfur reagent.[23] Unfortunately the "geometrical" $5 \rightleftarrows 7$ isomerization seems to be by far faster than any reaction leading to sulfur-containing products. The obvious experiment to be carried out to possibly change this situation, i.e., increasing the rate of the bimolecular reaction vs. the unimolecular isomerization by adding a large excess of the trapping reagent, did not turn out to be suitable to produce the wanted effect but led to another interesting unexpected observation.

The reaction of the $5 \rightleftarrows 7$ equilibrium mixture with a tenfold molar excess of sulfur in toluene was much faster than the equimolar reaction, as expected. However, the reaction under these conditions led to a different product mixture. At room temperature, the reaction is almost complete after 5 h. It resulted in the formation of the four-membered metallacycle **9** only as a minor component. The major reaction product now is the six-membered metallacyclic zirconium pentasulfide **8**. The ratio of **8**/**9** under the applied reaction conditions appeared to be almost independent of the reaction time. The two metallacyclic products were formed in about a ratio of **8**/**9** = 10:1. The newly formed reaction product **8** was not isolated from the reaction mixture as such. However, its identity was clearly confirmed by an independent synthesis by "classical" means, i.e., by reaction of a pentasulfide dianion with **3** (see Scheme IV).[5]

We were able to demonstrate that the zirconium pentasulfide **8** may indeed serve as a starting material for the formation of the bimetallic four-membered metallacycle **9**. Reaction of a sample of the independently synthesized **8** with a stoichiometric amount of the "metallocene source" (butadiene)Zr($C_5H_4CMe_3$)$_2$ ($5 \rightleftarrows 7$) at room temperature in toluene solution (24 h) resulted in the formation of **9** in high yield (ca. 60% isolated yield of practically pure material before recrystallization).

Conclusion

It has recently been demonstrated that chalcogen elements can easily undergo insertion reactions into zirconium to carbon σ-bonds. The clean conversion of dimethylzirconocene **10** with selenium to give Cp$_2$Zr(SeCH$_3$)$_2$ (**11**) is a typical example.[26] On the other hand, zirconocene olefin π-complexes also seem to be able to react with, e.g., elemental selenium. Thermally generated (η^2-aryne)-ZrCp$_2$,[7,27] as an example, takes up 2 equiv of the chalcogen element to yield **13** (see Scheme V).[28] In view of these established reaction pathways it is rather surprising that

---

(24) As usual, the activation barrier for topomerization is much lower for the hafnium compound **5a**, as compared to its zirconium analogue **5**. Therefore, the two dynamic processes taking place, i.e., Cp–M rotation and (diene)metallocene topomerization could not clearly be distinguished by the NMR experiment at low temperature for this (*s-cis*-butadiene)-hafnocene complex (an averaged $\Delta G^{\ddagger} \approx 9.5 + 1$ kcal/mol was estimated from the dynamic NMR spectra).

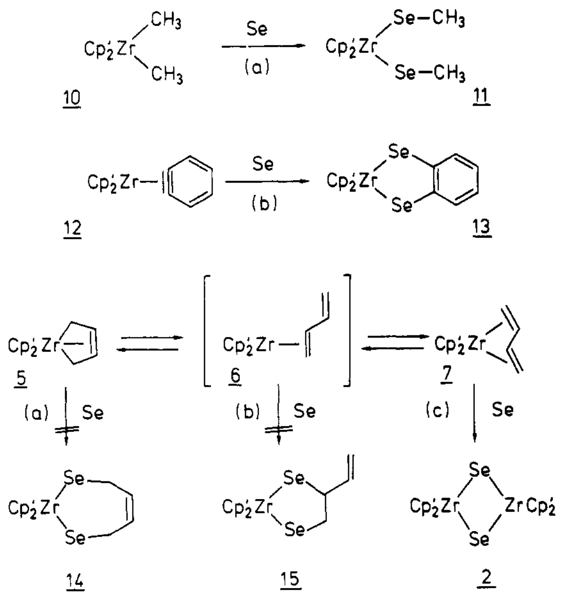
(25) (a) Gautheron, B.; Tainturier, G.; Pouly, S. *J. Organomet. Chem.* **1984**, *268*, C56. (b) Granger, P.; Gautheron, B.; Tainturier, G.; Pouly, S. *Org. Magn. Reson.* **1984**, *22*, 701. (c) Tainturier, G.; Gautheron, B.; Fahim, M. *J. Organomet. Chem.* **1985**, *290*, C4.

(26) Gautheron, B.; Tainturier, G.; Meunier, Ph. *J. Organomet. Chem.* **1981**, *209*, C49.

(27) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572. Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310.

(28) Gautheron, B.; Tainturier, G.; Pouly, S.; Thēobald, F.; Vivier, H.; Laarif, A. *Organometallics* **1984**, *3*, 1495.

Scheme V



we have not obtained any evidence for the occurrence of analogous reaction sequences upon treatment of the (butadiene)Zr(η-C_5H_4-CMe_3)$_2$ system with selenium or sulfur.

It is well-known that the σ^2,π-type structured (*s-cis*-diene)zirconocene complexes undergo many typical metal alkyl complex reactions.[12] So an insertion type reaction leading to, e.g., **14** would not at all have been surprising. On the other hand, it is quite clear by analogy with the parent (butadiene)zirconocene system that a reactive (η^2-butadiene)Zr(η-$C_5H_4CMe_3$)$_2$ intermediate, **6**, should be existing in equilibria with **7** and **5**. An expected typical reaction analogous to (b) (Scheme V) of such a (monoolefin)metallocene complex leading to **15** has not been observed.

Instead we observe as the only important reaction type a complete extrusion of the conjugated diene ligand to give the adduct of the chalcogen element with the elusive bent metallocene unit. Although the kinetics of the observed reactions preclude gaining a more specific knowledge of the mechanistic pathways taken in the reaction of the **5** ⇄ **7** system with elemental chalcogens to give **2** (or **8** and **9**, respectively), we have to conclude that the (butadiene)metallocene system has turned out to be a very reliable source for (at least in a formal sense) the thermal generation of the (η-$C_5H_4CMe_3$)$_2$Zr bent metallocene unit for preparative purposes.[29] Its reactions with elemental sulfur and selenium is in a way similar to the well-known chemistry of many reactive late-transition-metal complexes with the chalcogens.[3]

Moreover, the resulting four-membered metallacyclic systems **2** and **9** have the potential of becoming useful synthetic building blocks themselves. If the S_8/**8**/**9** ratio observed in our experiment described above turns out to be the equilibrium situation at room temperature, compounds like **9** or **2**, respectively, should serve as valuable reagents for introducing a single specific chalcogen atom into a given chalcogen chain.

Experimental Section

Reactions with organometallic materials were carried out under argon by using standard Schlenk techniques. Solvents were dried and freshly distilled from $LiAlH_4$ or P_4O_{10} under argon before use. Deuterated solvents were treated with sodium/potassium alloy or P_4O_{10}, distilled immediately, and stored under argon. NMR spectra were recorded on a Bruker WP 80 or JEOL FX 100 (^1H), Bruker WM 300 (^{13}C, 75.5 MHz) and Bruker WH 400 (^1H and ^{13}C, 100.6 MHz) spectrometer. Chemical shifts are given relative to Me_4Si (δ scale). Mass spectra were recorded on a Finnegan 311 A mass spectrometer at 70 eV; *m/e* values given correspond to most abundant isotopes. Microanalyses were performed by Dornis & Kolbe Mikroanalytisches Laboratorium, Mülheim/Ruhr. According to literature procedures we prepared bis(η-*tert*-butylcyclopentadienyl)zirconium and -hafnium dichloride[30] (from (*tert*-butylcyclopentadienyl)lithium—obtained via treatment of dimethylfulvene with methyllithium—and $ZrCl_4$) and the (butadiene)magnesium reagent.[11b,16] Sulfur and selenium were purified by sublimation.

Preparation of (η^4-Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium. (a) The **5** ⇄ **7** equilibrium mixture was obtained in the following way: a mixture of 10.1 g (25 mmol) of bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride (**3**) and 5.9 g (26.5 mmol) of (2-butene-1,4-diyl)magnesium–bis(tetrahydrofuran) ("butadiene–magnesium", **4**) was cooled to −78 °C. At this temperature 80 mL of cold diethyl ether were rapidly added. During 6 h the well-stirred reaction mixture was allowed to warm to room temperature. The solvent was removed in vacuo, and the orange-red residue was dissolved in 100 mL of pentane. After removal of excess "butadiene–magnesium" and the formed magnesium chloride by filtration, the red solution was evaporated to give 8.9 g (23 mmol, 92%) of the **5** ⇄ **7** mixture.

(b) To get crystalline **5**, the mixture was dissolved in 50 mL of hexane and stored overnight at −50 °C. This led to the isolation of 8.5 g (22 mmol, 88%) of the orange, crystalline (*s-cis*-η^4-butadiene)Zr($C_5H_4CMe_3$)$_2$ complex (**5**): mp 93 °C; *m/z* 386 (M^+), 332 (M^+ − butadiene), 317, 302. IR (KBr) ν 3040, 2960, 1515, 1470, 1360, 920, 975 cm^{-1}; ^1H NMR (−90 °C, toluene-d_8; for signals of the diene ligand see Table I) δ 5.46, 5.58, 5.72, 3.84, 4.75, 5.28, 4.42, 4.50 (Cp'), 1.07, 1.29 (*t*-Bu); ^1H NMR (+35 °C, benzene-d_6) δ 4.94, 5.37 (Cp'), 1.15 (*t*-Bu); ^{13}C NMR (−85 °C, toluene-d_8; coupling constants $^1J_{CH}$ (Hz) are given in parentheses; for signals of the diene ligand see Table I) δ 104.5 (167), 96.5 (168), 109.8 (171), 99.9 (167), 132.8 (...), 125.9 (...), 99.5 (168), 106.1 (166), 91.3 (170), 105.1 (171) (Cp'); 32.5 (...), 32.2 (125), 31.5 (...), 31.9 (126) (*t*-Bu); ^{13}C NMR (+37 °C, toluene-d_8) δ 101.3, 102.5, 129.3 (Cp'), 32.3 ($C(CH_3)_3$ and $C(CH_3)_3$). Anal. Calcd for $C_{22}H_{32}Zr$ (387.7): C, 68.15; H, 8.32. Found: C, 68.19; H, 8.08.

(c) Preparation of the (*s-trans*-η^4-Butadiene)Zr($C_5H_4CMe_3$)$_2$ Isomer (7). A solution of 0.25 g of the (*s-cis*-η^4-butadiene)ZrCp'$_2$ isomer **5** in 3.5 mL of toluene-d_8 was irradiated at −40 °C for 30 min (Philips HPK 125 W, Pyrex filter). From the ^1H NMR spectrum of the resulting dark red solution the **5**/**7** ratio was determined to be < 10/90. **7**: ^1H NMR (−90 °C, toluene-d_8; for signals of the diene ligand see Table I) δ 4.24, 4.29, 4.85, 5.00 (Cp'), 1.26 (*t*-Bu); ^{13}C NMR (−30 °C, toluene-d_8; coupling constants $^1J_{CH}$ (Hz) are given in parentheses; for signals of the diene ligand see Table I) δ 102.7 (168), 98.1 (167), 97.9 (170), 97.7 (170) (Cp'), quarternary Cp'C hidden by solvent, 31.2, 32.4 (125) (*t*-Bu).

(d) The thermally induced rearrangement of **7** to **5** was studied in an ^1H NMR experiment. A solution of **7** in toluene-d_8 was prepared as described above. **7** was allowed to equilibrate with the (*s-cis*-butadiene)ZrCp'$_2$ isomer (**5**) at −10 °C. The reaction was followed by integration of the signals of the diene CH_2 hydrogen atoms. For the numerical value of the isomerization activation barrier see Table II.

Preparation of (η^4-Butadiene)bis(η-*tert*-butylcyclopentadienyl)hafnium. (a) The **5a** ⇄ **7a** equilibrium mixture was obtained analogously to the zirconium compounds **5** and **7**. (Butadiene)HfCp'$_2$ was isolated in 86% yield as yellow crystals: mp 96.5 °C; *m/z* 476 (M^+), 422 (M^+ − butadiene); IR ν(KBr) 3020, 2950, 1520, 1480, 1460, 1355, 950 cm^{-1}; ^1H NMR (−95 °C, toluene-d_8; for signals of the diene ligand see Table I) δ 5.23, 5.44, 5.78, 4.06, 4.62, 5.28, 4.48, 4.72 (Cp'), 1.12, 1.30 (*t*-Bu); ^1H NMR (+27 °C, toluene-d_8) δ 5.34, 4.95 (Cp'), 1.15 (*t*-Bu); ^{13}C NMR (−85 °C, toluene-d_8; coupling constants $^1J_{CH}$ (Hz) are given in par-

---

[29] This is in a way comparable to the reaction of the (butadiene)-$ZrCp_2$ system (**5'** ⇄ **7'**) with alkynes: Erker, G.; Skibbe, V. *J. Organomet. Chem.* **1983**, *241*, 15.

[30] Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 35 (loc. cit.).

entheses; for signals of the diene ligand see Table I) δ 102.7 (165), 95.2 (168), 111.7 (168), 100.4 (166), 133.1 (...), 99.7 (168), 106.6 (168), 90.5 (170), 104.1 (170) (Cp′), one quarternary Cp′*C* hidden by solvent signals, 32.6 (...), 31.8 (126) "double" intensity, 31.6 (...) (*t*-Bu); ^{13}C NMR (+37 °C, toluene-d_8) δ 102.0 (169), 101.6 (171), 131.1 (...) (Cp′), 32.1 (125), 32.5 (...) (*t*-Bu). Anal. Calcd for $C_{22}H_{32}Hf$ (475.0): C, 55.63; H, 6.79. Found: C, 56.19; H, 7.23.

(b) Preparation of the (*s-trans*-η⁴-Butadiene)Hf($C_5H_4CMe_3$)$_2$ Isomer (7a). In analogy to the zirconium compound an toluene-d_8 solution of **5a** was irradiated at −40 °C for 30 min (Philips HPK 125 W, Pyrex filter). The **5a**/**7a** ratio was determined to be 25/75: ^{1}H NMR (−80 °C, toluene-d_8; for signals of the diene ligand see Table I) δ 4.30, 4.33, 4.67, 4.94 (Cp′), 1.27 (*t*-Bu); ^{13}C NMR (−60 °C, toluene-d_8; coupling constants $^1J_{CH}$ (Hz) are given in parentheses; for signals of the diene ligand see Table I) δ 102.9 (168), 97.2 (170), 96.8 (169), "double" intensity (Cp′), the position of the quarternary Cp′*C* not determined, 32.3 (...), 32.2 (125) (*t*-Bu).

(c) The rearrangement of **7a** to **5a** was studied by an ^{1}H NMR experiment. For this purpose a solution of **7a** was prepared as described above. **7a** was allowed to equilibrate with **5a** at +10 °C. The reaction was followed by ^{1}H NMR. Integration of the *t*-Bu signal led to the activation barrier given in Table II.

1,1,3,3-Tetrakis(η-*tert*-butylcyclopentadienyl)-1,3-dizirconacyclotetraselenane (2). A solution of the (*s-cis*- and *s-trans*-η-butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium (**5**/**7**, 95/5) mixture (0.62 g, 1.6 mmol) in 15 mL of toluene was added to freshly sublimed selenium powder (0.27 g, 3.42 mmol), and the mixture was stirred in the dark at room temperature for 6 days. The excess selenium was removed by centrifugation and the mixture washed twice with 5 mL of toluene. The clear supernatant solution and the combined extracts were evaporated to dryness in vacuo. The product was first purified by washing with 5 mL of cold heptane, recrystallized from 16 mL of boiling heptane/toluene (5/3), and isolated as bright emerald green crystals: 0.33 g (50.0%); mp 290 °C; ^{1}H NMR (C_6D_6, 25 °C) δ 6.52 (m, 16 H, Cp), 1.28 (s, 36 H, *t*-Bu). The product has been described and characterized previously.[25]

Bis(η-*tert*-butylcyclopentadienyl)zirconacyclohexasulfane (8). A stirred suspension of 0.48 g (15.0 mmol) of freshly sublimed sulfur powder in 3 mL of tetrahydrofuran was treated with 6.0 mL of lithium triethylborohydride solution (1 mol/L, 6.0 mmol) in tetrahydrofuran, and the resulting solution was left for 20 min at room temperature. Then a solution of 1.21 g (3.0 mmol) of bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride in 20 mL of tetrahydrofuran was added and the resulting mixture stirred overnight. After evaporation of solvent in vacuo the product was extracted with 15 mL of dichloromethane/pentane solvent (v/v). The insoluble residue was filtered and washed with 2 mL of the same solvent, and the filtrates were slowly cooled to −20 °C to give an overall yield of 1.06 g (71.5%) of orange crystals: mp 162–163 °C; ^{1}H NMR (C_6D_6, 25 °C) δ 5.85 (t, 4 H, Cp), 5.68 (t, 4 H, Cp), 1.10 (s, 18 H, *t*-Bu); MS, *m/e* 492 (M^+), 428 ($M^+ - S_2$), 3.96 ($M^+ - S_3$), 372 ($M^+ - C_9H_{13}$). Anal. Calcd for $C_{18}H_{26}S_5Zr$ (493.95): C, 43.77; H, 5.30; S, 32.45; Zr, 18.47. Found: C, 43.84; H, 5.40; S, 31.61; Zr, 18.84.

Reaction of the (*s-cis*- and *s-trans*-Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium (5/7) Mixture with Elemental Sulfur. NMR Experiments. A solution of 0.07 g (0.18 mmol) of the **5**/**7** mixture in ≃0.6 mL of deuterated benzene was transferred into a NMR tube containing 0.064 g (2 mmol) of finely divided sulfur powder. The tube was sealed and shaken vigorously. ^{1}H NMR analysis revealed that the consumption of the starting (butadiene)zirconocene complex is almost quantitative after a period of 30 min, giving a rather complicated spectrum in which the signals of the two final products **8** and **9** could be identified (molar ratio of **8**/**9** growing from about 8/1 after 30 min to ca. 10/1 after 3 h. It could be noticed that considerable simplification of the spectrum occurred in the last period, indicating the further reaction of several unidentified transient species. In this experiment the reaction was shown to go almost to completion within a period of 5 h at 25 °C.

1,1,3,3-Tetrakis(η-*tert*-butylcyclopentadienyl)-1,3-dizirconacyclotetrasulfane. (a) From Sulfur. A solution of (*s-cis*- and *s-trans*-η-butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium mixture (**5**/**7**; 0.72 g, 1.86 mmol) in 10 mL of toluene was added to freshly sublimed sulfur (0.07 g, 2.19 mmol), and the solution was left at room temperature in the dark for 26 h. After evaporation in vacuo the residue was washed twice with 5 mL of cold pentane and the washings were discarded. The remaining product was then treated with 18 mL of boiling heptane, and the resulting hot mixture was filtered. Cooling (−20 °C) and workup of the mother liquors finally gave 0.23 g (34%) of deep blue-green crystals: mp >260 °C; ^{1}H NMR (C_6D_6, 25 °C) δ 6.42 (s, 16 H, Cp), 1.30 (s, 36 H, *t*-Bu). This compound has been prepared by another route as described previously.[25c]

(b) From ($C_5H_4CMe_3$)$_2$Zr(S_5) (8). A solution of 1.02 g (2.63 mmol) of the (*s-cis*- and *s-trans*-η-butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium (**5**/**7**, 95/5) mixture in 13 mL of toluene was added at 15 °C to a solution of bis(η-*tert*-butylcyclopentadienyl)zirconacyclohexasulfane (**8**; 0.32 g, 0.65 mmol) in 15 mL of toluene, and the resulting mixture was kept in the dark at room temperature for 40 h. After evaporation of solvent in vacuo, washing with two 20-mL portions of cold pentane, and drying, the reaction product was recrystallized as described above from 33 mL of boiling heptane to yield 0.49 g (41%) of **9**.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie (grant to G.E.) is gratefully acknowledged. G.T. thanks the MPG and the CNRS for generous support of his stay at Mülheim and Mrs. Geneviève Delmas for highly valuable technical assistance.

Registry No. **2**, 92066-60-9; **3**, 32876-92-9; **4**, 70809-00-6; **5**, 95464-95-2; **5a**, 95464-96-3; **7**, 100992-04-9; **7a**, 100992-05-0; **8**, 100909-19-1; **9**, 100581-47-3; Se, 7782-49-2; S, 7704-34-9.