Complexes **4b** and **4c** exhibit identical "racemization" activation barriers as judged from the coalescence of the Cp resonances. For **4d**, $\Delta G^{\ddagger}_{ent}(350\ K) = 17.0 \pm 0.4$ kcal/mol has been obtained.

Complex **4e**, derived from coupling **3c** with a prochiral ketone, contains two chirality elements within the metallacyclic ring structure. Two diastereomers (85:15) are observed according to NMR spectroscopy at low temperature. Each of these exhibits a 1:1 pair of Cp resonances. The thermally induced topomerization process leaves the chirality center of **4e** unaffected. Pairwise exchange of Cp resonances is observed on increasing the temperature to give one averaged set of signals, still showing a pair of Cp singlets in the ^{1}H NMR spectrum. This observation shows beyond doubt that the metallacyclic ring system remains intact throughout the equilibration process. Carbon-carbon cleavage, which has been observed at higher temperatures,[15] is of no importance for the observed exchange

phenomena.

It is quite remarkable that the topomerization barriers of the nine-membered metallacycles **4** are rather close to the $\Delta G^{\ddagger}_{ent}$ value of *trans*-cyclononene. The rigidity introduced by the conjugatively interacting COZrOC moiety seems to compensate well for the much larger perimeter of the organometallic ring system.

Supplementary Material Available: Listings of atomic fractional coordinates, atomic thermal parameters, and interatomic distances and angles for **4c′** (9 pages); a listing of observed and calculated structure factors for **4c′** (24 pages). Ordering information is given on any current masthead page.

(14) Kessler, H. *Angew. Chem.* **1970**, *82*, 237; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

(15) At 70 °C complexes **4a** and **4b** cleanly loose 1 equiv of M(CO)₆ each to produce the seven-membered metallacyclic σ-allyl complex Cp₂ZrOC(CH₃)₂CH₂CH=CHCH₂ which had been independently prepared previously from (η⁴-s-trans-butadiene)ZrCp₂ and acetone: Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 494.

Hindered η-Cyclopentadienyl–Metal Rotation Caused by Lateral Interaction of Cp-Bonded Substituents at Chalcogen-Bridged Binuclear Bent Metallocene Complexes [(RCp)₂ZrX]₂

Gerhard Erker,*,† Rainer Nolte,† Gérard Tainturier,‡ and Arnold Rheingold§

Institut für Organische Chemie der Universität, Am Hubland, D-8700 Würzburg, FRG, Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Faculté des Sciences, 21100 Dijon, France, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received August 10, 1988

(η-Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium reacts with elemental tellurium to give [(Me₃CCp)₂Zr(μ-Te)]₂ (**6**). Upon controlled hydrolysis, one bridging tellurium is exchanged for oxygen to give the metallacyclic complex [(Me₃CCp)₂Zr]₂(μ-O)(μ-Te) (**7**). The analogous oxygen/selenium-bridged bimetallic zirconium complex [(Me₃CCp)₂Zr]₂(μ-O)(μ-Se) (**8**) is formed upon photolysis of the μ-oxo precursor (Me₃CCp)₂Zr(CH₃)OZr(CH₃)(CpCMe₃) in the presence of a suspension of elemental selenium. Complex **6** exhibits a nearly square-planar array of alternating zirconium and tellurium atoms. In contrast, the planar ZrTeZrO framework of **7** is characterized by very different bond angles at tellurium (average 72.1 (1)°) and oxygen (average 119.2 (2)°), bringing the zirconium atoms (average Zr···Zr = 3.390 (1) Å) more closely together than in **6** (Zr···Zr = 4.067 (1) Å). In the crystal each (Me₃CCp)₂Zr subunit is chiral, favoring a nearly C_2-symmetric conformation. The bulky *tert*-butyl groups are oriented trans to each other in the lateral sectors of the Cp-substituted bent metallocene unit. Combination of the two chiral (Me₃CCp)₂Zr moieties can give rise to the formation of two diastereomeric bis(metallocene) complexes. For the bis(tellurium)-bridged compound **6** an achiral C_{2h}-symmetric meso form is favored, while the oxygen, tellurium-bridged analogue **7** adopts a chiral nearly C_2-symmetric conformation in the solid state. Complex **7** crystallizes in the monoclinic space group Cc with cell constants $a = 18.231$ (5) Å, $b = 18.186$ (6) Å, $c = 22.563$ (6) Å, $\beta = 107.57$ (2)°, $V = 7132$ (3) Å³, $Z = 8$, and $R(F) = 4.08\%$. The [(Me₃CCp)₂Zr](μ-X)(μ-Y) complexes feature hindered (Me₃CCp)–metal rotation in solution. Activation barriers $\Delta G^{\ddagger}_{rot} \approx 9.6 \pm 0.4$ kcal/mol (for **7** at 206 K) and 11.0 ± 0.4 kcal/mol (for **8** at 222 K) have been estimated by dynamic ^{1}H NMR spectroscopy. Complexes **7** and **8** appear to be the first examples where hindered (RCp)–M rotation is induced by a lateral (RCp)···(RCp) interaction across a rigid metal complex framework.

Introduction

Rotational activation barriers in conformationally equilibrating systems have great informational value for estimating interactive forces between groups or substitu-ents brought into close proximity.[1] In alkanes the interaction of groups attached to adjacent carbon atoms

†Universität Würzburg.
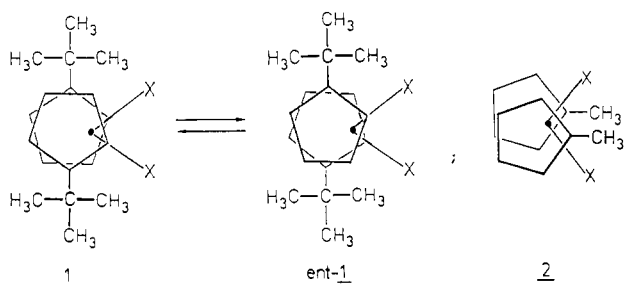‡Université de Dijon.
§Delaware University.

(1) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley: New York, 1965. Kagan, H. B. *Organische Stereochemie*; Thieme: Stuttgart, 1977. Dale, J. *Stereochemie und Konformationsanalyse*; Verlag Chemie: Weinheim, 1978. See also: Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.

across the connecting C–C bond frequently determines the rotational barrier. Similarly, the interaction of groups arranged *parallel* to each other can determine the rotational barriers in linear metallocene systems.[2] However, the interaction of substituents on coaxially arranged cyclic polyene ligands separated by the connecting metal center is usually very weak. Consequently, the Cp–M rotational barriers of simple linear metallocene systems, experimentally determined by various methods, are usually very low. For ferrocene typical values between 0.9 and 1.8 ± 0.3 kcal/mol have been reported.[3] The presence of bulky (e.g. *tert*-butyl) substituents is required to increase this barrier substantially.[4] Streitwieser has thus observed hindered rotation of ligands along the L–M–L vector for 1,1′,3,3′-tetra-*tert*-butylferrocene ($\Delta G^{\ddagger}_{rot}$ = 13.1 kcal/mol at −27.5 °C) or 1,1′,4,4′-tetra-*tert*-butyluranocene ($\Delta G^{\ddagger}_{rot}$ = 8.3 kcal/mol at −70 °C.[5]

However, bending the Cp–M–Cp angle from 180° to about 130°[6] results in a large barrier for substituents passing each other at the narrow side of the Cp_2M wedge. From various X-ray crystallographic studies it is known that Cp-bonded *tert*-alkyl substituents in bent metallocene complexes $(RCp)_2MX_2$ (M = Ti, Zr, Hf) prefer to be arranged trans, oriented in lateral positions at the bent metallocene framework.[7] In contrast to the $(H_3CCp)_2MX_2$ complexes (2),[8] the $(Me_3CCp)_2MX_2$ compounds (1) exhibit chiral ground-state geometries.[9]

Therefore, hindered Cp–M rotation would be easily detectable by monitoring the pairwise coalescence of diastereotopic cyclopentadienyl C–H resonances in the dynamic ^1H or ^{13}C spectra for the 1 ⇌ ent-1 rearrangement. Unfortunately, the mutual interaction between the Cp-bound *tert*-butyl groups in front of the bent metallocene system as well as their interference with most metal-bound ligands, X (halogen, alkyl, aryl), oriented in the CpMCp bisecting plane is too small to allow hindered (RCp)–M rotation in simple bis(η-*tert*-butylcyclopentadienyl)titanium(IV), -zirconium(IV), or -hafnium(IV) complexes to be observed experimentally by dynamic NMR in solution.

This situation is changed when spacious ligands are coordinated to the $(RCp)_2M$ unit. A considerable steric interaction between, e.g., the substituents at C(2), C(3) of a conjugated diene ligand and the Cp-bonded *tert*-butyl groups is built up in front of the bent metallocene upon rotation around the (RCp)–M vector. This leads to typical rotational activation barriers of about 10 kcal/mol observed by dynamic NMR spectroscopy for the pairwise interconversion of enantiomeric [e.g. 3 ⇌ ent-3; $\Delta G^{\ddagger}_{rot}$ (−80 °C) = 9.8 kcal/mol] or diastereomeric complexes [e.g. 4 ⇌ 5; $\Delta G^{\ddagger}_{rot}$ (−100 °C) = 8.6 kcal/mol].[10,11]

Hindered (RCp)–M rotation can potentially be observed by bringing together two chiral Cp-substituted bent metallocene units. Thus, connecting two (η-*tert*-butylcyclopentadienyl)metal moieties by sufficiently rigid bridging ligands brings the cyclopentadienyl groups at adjacent metal centers in close opposition at the "open" side of the bent metallocene wedges. The ensuing Cp-*tBu*/CpH interactions between laterally adjacent cyclopentadienyl systems across the bridging ligands can thus induce a substantial activation barrier for the (RCp)–M rotation of each individual bent metallocene moiety. This is observed when bis(η-*tert*-butylcyclopentadienyl)zirconium units are doubly bridged by chalcogen ligands. We have prepared several binuclear $(η-t-BuCp)_4Zr_2(μ-X)(μ-Y)$ complexes; their syntheses, structures, and dynamic behavior which shows hindered (RCp)–M rotation will be described below.

Syntheses. The *tert*-butylcyclopentadienyl ligand was prepared via the fulvene route.[12] The 6,6-dimethylfulvene

(2) Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39; *Pure Appl. Chem.* **1970**, *23*, 413. Westman, L.; Rinehart, K. L., Jr. *Acta Chem. Scand.* **1962**, *16*, 1199.

(3) Haaland, A.; Nilsson, J. E. *Acta Chem. Scand.* **1968**, *22*, 2653. Haaland, A.; Bohn, R. *J. Organomet. Chem.* **1966**, *5*, 470. Haaland, A. *Fortschr. Chem. Forsch.* **1975**, *53*, 1. Holm, C. H.; Ibers, J. A. *J. Chem. Phys.* **1969**, *30*, 885. Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Yavari, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2027, loc. cit. Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 98. Makova, M. K.; Leonova, E. V.; Karimov, Y. S.; Kochetkova, N. S. *J. Organomet. Chem.* **1973**, *55*, 185. Gilson, D. F. R. *Can. J. Chem.* **1983**, *61*, 737. Shaver, A.; Eisenberg, A.; Yamada, K.; Clark, A. J. F.; Farrokyzad, S. *Inorg. Chem.* **1983**, *22*, 4154.

(4) Hofmann, W.; Buchner, W.; Werner, H. *Angew. Chem.* **1977**, *89*, 836; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 795. Davidson, J. L. *J. Chem. Soc., Chem. Commun.* **1980**, 113.

(5) Luke, W. D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3241. See also: Moore, R. M., Jr.; Streitwieser, A., Jr.; Wang, H.-K. *Organometallics* **1986**, *5*, 1418.
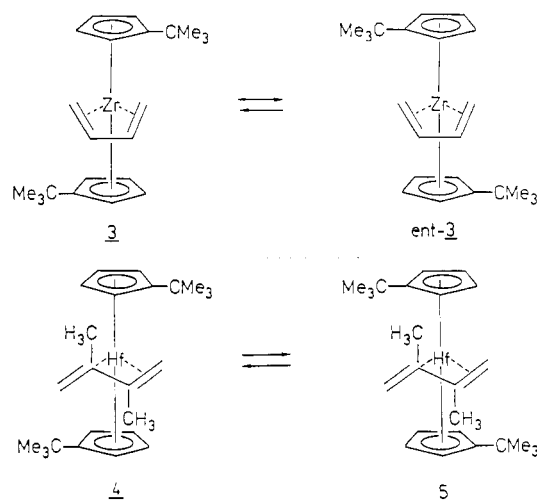
(6) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic Press: New York, 1974; p 122. Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986 and references cited therein.

(7) Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149. Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A.; *Ibid.* **1986**, *303*, 213. Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2347. Stahl, K.-P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984**, *277*, 113. Lappert, M. F.; *J. Chem. Soc., Dalton Trans.* **1987**, 1463.

(8) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. Dusausoy, J.; Protas, J.; Renaut, P.; Gautheron, B.; Tainturier, G. *J. Organomet. Chem.* **1978**, *157*, 167. Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C.; *Angew. Chem.* **1986**, *98*, 456; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463. Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4.

(9) This is, of course, not limited to *t*-BuCp-substituted systems. By X-ray diffraction we have recently found an analogous chiral ground-state bent metallocene conformation to be favored for (1-methylcyclohexyl-$C_5H_4)_2ZrCl_2$: Erker, G.; Nolte, R.; Krüger, C.; Schlund, R.; Benn, R.; Grondey, H.; Mynott, R. *J. Organomet. Chem.*, in press.

(10) Erker, G.; Mühlenbernd, T.; Rufinska, A.; Benn, R. *Chem. Ber.* **1987**, *120*, 507.

(11) Erker, G.; Mühlenbernd, T.; Benn, R.; Rufinska, A.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 336; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 321.

starting material was obtained from acetone and cyclopentadienyl anion by a variation of the original Thiele method,[13] employing sodium methoxide as a base. Addition of etheral methyllithium yielded *tert*-butylcyclopentadienyl lithium, which was isolated as an off-white solid and then reacted with $ZrCl_4$ in toluene/tetrahydrofuran (2:1) solvent to give bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride.[14]

From this starting material we have prepared the binuclear chalcogen-bridged complexes [($Me_3CCp)_2Zr(\mu$-Te)]$_2$ (6), [($Me_3CCp)_2Zr]_2(\mu$-O)(μ-Te) (7), and [($Me_3CCp)_2Zr]_2(\mu$-O)(μ-Se) (8) by using two different synthetic approaches. Complex 8, [($Me_3CCp)_2Zr]_2(\mu$-O)(μ-Se), was obtained by a sequential construction of the central four-membered Zr_2OSe core of atoms, introducing one chalcogen atom at a time.[15] Reaction of ($Me_3CCp)_2ZrCl_2$ with 2 equiv of methyllithium in ether yielded ($Me_3CCp)_2Zr(CH_3)_2$ (9). Subsequent treatment with water (stoichiometric, 0.5 molar equiv) produced the oxygen-bridged synthetic intermediate ($Me_3CCp)_2Zr(CH_3)(\mu$-O)$Zr(CH_3)(Me_3CCp)_2$ (10). Irradiation of the binuclear complex 10 in toluene in the presence of finely suspended elemental selenium furnished the product [($Me_3CCp)_2Zr]_2(\mu$-O)(μ-Se) (8) in good yield.

A different synthetic approach was used for the preparation of the tellurium-containing complexes [($Me_3CCp)_2ZrTe]_2$ (6) and [($Me_3CpZr]_2(\mu$-O)(μ-Te) (7). Treatment of bis(η-*tert*-butylcyclopentadienyl)zirconium dichloride with the oligomeric butadiene magnesium reagent [(–CH_2CH=$CHCH_2$–)Mg]$_x$ produced (butadiene)$Zr(CpCMe_3)_2$.[10,16]

An equilibrating mixture of the (*s-cis*-η^4-butadiene)- and (*s-trans*-η^4-butadiene)$Zr(CpCMe_3)_2$ isomers (11) was treated with tellurium powder for prolonged times in toluene solvent. The butadiene ligand was liberated from the bis(η-*tert*-butylcyclopentadienyl)zirconium complex and 1 equiv of tellurium taken up per ($Me_3CCp)_2Zr^{II}$ unit to give the binuclear doubly tellurium-bridged complex 6.[17]
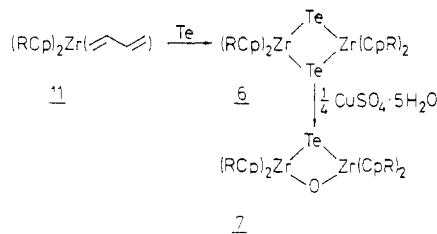
(12) Nesmeyanov, A. M.; Materikova, R. B.; Brainina, E. M.; Kochetkova, N. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1969, 1220. Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* 1978, *148*, 35. Tainturier, G.; Gautheron, B.; Renaut, P.; Etievant, P. *C. R. Acad. Sci., Ser. C* 1975, *281*, 951. See also: Ziegler, K.; Schäfer, W. *Liebigs Ann. Chem.* 1934, *511*, 101. Little, W. F.; Koestler, R. C. *J. Org. Chem.* 1961, *26*, 3245. Knox, G. R.; Pauson, P. L. *J. Chem. Soc.* 1961, 4610. Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* 1967, *8*, 277. Schore, N. E.; LaBelle, B. E. *J. Org. Chem.* 1981, *46*, 2306.

(13) Thiele, B. *Ber. Dtsch. Chem. Ges.* 1900, *33*, 666. Thiele, B.; Ballhorn, H. *Liebigs Ann. Chem.* 1906, *348*, 1. Freiesleben, W. *Angew. Chem.* 1963, *75*, 576; *Angew. Chem., Int. Ed. Engl.* 1963, *2*, 396.

(14) Tainturier, G.; Gautheron, B.; Renaut, P.; Etieviant, P. *C. R. Acad. Sci., Ser. C* 1975, *281*, 1035.

(15) Tainturier, G.; Gautheron, B.; Fahim, M. *J. Organomet. Chem.* 1985, *290*, C4. See also: Granger, P.; Gautheron, B.; Tainturier, G.; Pouly, S. *Org. Magn. Reson.* 1984, *22*, 701. Gautheron, B.; Tainturier, G.; Pouly, S. *J. Organomet. Chem.* 1984, *268*, C56. Gautheron, B.; Tainturier, G.; Meunier, P. *Ibid.* 1981, *209*, C49.

(16) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* 1980, *102*, 6344. Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* 1982, *115*, 3300. Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* 1982, *115*, 3311. Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* 1982, *1*, 388. Dorf, U.; Engel, K.; Erker, G. *Organometallics* 1983, *2*, 462. Erker, G.; Engel, K.; Krüger, C.; Müller, G. *Organometallics* 1984, *3*, 128. Reviews: Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* 1985, *24*, 1. Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* 1985, *18*, 120. Yasuda, H.; Nakamura, A. *Angew. Chem.* 1987, *99*, 745; *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 723.

Carefully controlled hydrolysis of [($Me_3CCp)_2Zr(\mu$-Te)]$_2$ (6) using the crystal water of 0.25 molar equiv of $CuSO_4\cdot5H_2O$ resulted in a clean substitution of one bridging tellurium atom in 6 for oxygen. Recrystallization from toluene provided crystals for a structure determination of the mixed-chalcogen-bridged complex [($Me_3CCp)_2Zr]_2(\mu$-O)(μ-Te) (7).

Structures of the Chalcogen-Bridged Binuclear Zirconocene Complexes.

The crystal structure of [($Me_3CCp)_2Zr(\mu$-Te)]$_2$ (6), recently described in a short communication,[18] is characterized by an almost exactly square-planar Zr_2Te_2 core. The zirconium–tellurium distances average 2.855 (1) Å, the Te,Zr,Te angle is 89.14 (1)°, and the Zr,Te,Zr angle is 90.86 (1)°. Both diagonal element–element separations are clearly beyond bonding distance. The Te···Te separation is 4.006 (1) Å; the Zr···Zr distance is 4.067 (1) Å.[19]

In contrast, [($Me_3CCp)_2Zr]_2(\mu$-O)(μ-Te) (7) exhibits a considerably distorted arrangement of zirconium and chalcogen atoms in the central plane. The Zr,Te,Zr angle has decreased to 72.1 (1)° (av). The zirconium–tellurium distances, 2.880 (1) Å (av), are elongated. Even the Te,Zr,O angles 84.4 (3)° (av) are noticably smaller in 7 than the Te,Zr,Te angles in 6. This distortion allows the Zr,O,Zr angle in 7 to open up to 119.2 (2)° (av). Although this angle is still far from 180° the Zr–O distance 1.967 (7) Å (av) indicates substantial Zr–O bond strengthening by μ-oxygen ligand-to-metal back-donation. The observed short Zr–O distances of 7 are in the range typical for linear or nearly linear open-chain (μ-oxo)metallocene complexes like ($Cp_2ZrCl)_2$O (Zr–O (Å) and Zr,O,Zr (deg): 1.94 (1), 1.95 (1) Å; 168.9°),[20] {$Cp_2Zr[OC(Ph)Mo(CO)_5]$}$_2$O (1.958 (1) Å; 180°),[21] [$Cp_2Zr(SPh)]_2$O (1.968 (3), 1.964 (3) Å; 165.8°),[22] or [$Cp_2Zr(CH_3)]_2$O (1.948 (1) Å; 174.1°).[23] For the distorted hexagonally shaped [$Cp_2ZrO]_3$ (12) (Zr,O,Zr = 142.5 (2)°), a similarly shortened Zr–O distance is observed (1.959 (3) Å).[24] Similar values have been found for the metallacycle $Cp_2ZrOC(Ph)_2CH_2CH$=$CHCH_2$ (Zr–O = 1.946 (4) Å; Zr,O,C = 150.5 (4)°; C,Zr,O = 91.9 (2)°).[25] Distinctly different M–O distances are found when the zirconium to oxygen π-interaction is suppressed by employing the oxygen lone pair for either conjugation as in 16 (e.g. L_nM = Cr(CO)$_5$: d(Zr–O) = 2.188 (3) Å; Zr,O,C

(17) See, for a comparison: Erker, G.; Mühlenbernd, T.; Benn, R.; Rufinska, A.; Tainturier, G.; Gautheron, B. *Organometallics* 1986, *5*, 1023.

(18) Erker, G.; Mühlenbernd, T.; Nolte, R.; Petersen, J. L.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* 1986, *314*, C21.

(19) Cherin, P.; Unger, P. *Acta Crystallogr.* 1967, *23*, 670. Burns, R. C.; Gillespie, R. J.; Luk, W. C.; Slim, D. R. *Inorg. Chem.* 1979, *18*, 3086. Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* 1985, *107*, 3843. Di Vaira, M.; Perruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* 1986, 374.

(20) Clarke, J. F.; Drew, M. B. *Acta Crystallogr.* 1974, *B30*, 2267.

(21) Erker, G.; Dorf, U.; Krüger, C.; Tsay, Y.-H. *Organometallics* 1987, *6*, 680.

(22) Petersen, J. L. *J. Organomet. Chem.* 1979, *166*, 179.

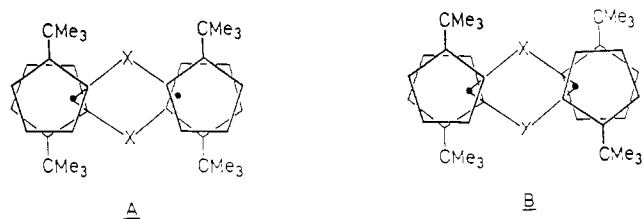(23) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics* 1983, *2*, 750.

(24) Fachinetti, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1979, *101*, 1767.

(25) Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* 1983, *95*, 506; *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 494; *Angew. Chem. Suppl.* 1983, 675.

= 136.1 (3)°)[26] or **17** (e.g. $L_nM = W(CO)_5$: $d(Zr–O) = 2.16$ (2), 2.15 (1) Å)[27] or the formation of dimeric structures like **13** (Zr–O = 2.164 (2), 2.165 (2) Å),[28] **14** (2.111 (2), 2.296 (2) Å),[29] or **15** (2.190 (3), 2.234 (7) Å).[30] By this comparison, $[(Me_3CCp)_2Zr]_2(\mu\text{-O})(\mu\text{-Te})$ (**7**) appears to be the (μ-oxo)metallocene complex with by far the smallest Zr,O,Zr angle exhibiting strong metal to oxygen π-conjugative interaction. This effect brings the zirconium atoms in **7** much closer together (average Zr···Zr = 3.390 (1) Å) than in the bis(tellurium) analogue **6**.[18]

Zr···Zr	4.067(1)		(av)	3.390(1)	Zr···Zr
Te···Te	4.006(1)		(av)	3.324(6)	Te···O
Zr – Te	2.855(1)		(av)	2.880(1)	Zr – Te
			(av)	1.967(7)	Zr – O
Te,Zr,Te	89.14(1)		(av)	84.4(3)	Te,Zr,O
Zr,Te,Zr	90.86(1)		(av)	72.1	Zr,Te,Zr
			(av)	119.2(2)	Zr,O,Zr

Figure 1. A comparison of selected structural features between the four-membered metallacyclic cores of $[(Me_3CCp)_2Zr(\mu\text{-Te})]_2$ (**6**) and $[(Me_3CCp)_2Zr]_2(\mu\text{-O})(\mu\text{-Te})$ (**7**).

The different bonding features of the metal/chalcogen framework reflect in different preferred conformational arrangements for the RCp ligands at the early-transition-metal centers of the complexes $[(Me_3CCp)_2Zr(\mu\text{-Te})]_2$ (**6**) and $[(Me_3CCp)_2Zr]_2(\mu\text{-O})(\mu\text{-Te})$ (**7**). Each complex comprises two bent metallocene subunits, $(Me_3CCp)_2Zr$, having chiral ground-state conformations. For each of these units in the crystal, (RCp)–M rotamers are found which exhibit bulky t-BuCp substituents oriented trans to each other in the lateral sectors of the bent metallocene unit (θ ($tert$-butyl, Cp centroid, Cp centroid, $tert$-butyl) $\approx$ 180°, similar to the arrangement found in $(Me_3CCp)_2Zr(s\text{-}cis\text{-}\eta^4\text{-buta-}$ diene) (**3**), $(Me_3CCp)_2ZrCl_2$ (**1**, X = Cl), or $(Me_3CCp)_2TiCl_2$[7]).[31] Incorporation of two of these chiral rotameric (RCp)$_2$M subunits into a four-membered metallacyclic framework as found in **6** or **7** may result in the formation of two diastereomeric conformers. According to their idealized symmetry properties these may be described as meso or racemic forms A or B, respectively.

Figure 2. Molecular structure of **7**. One of two crystallographically independent, but chemically similar, molecules is shown. The $tert$-butyl groups are shown with atoms of arbitrary radii for clarity. Thermal ellipsoids are drawn with 40% probability limits.

According to the results of the X-ray crystal structure analysis, $[(Me_3CCp)_2Zr(\mu\text{-Te})]_2$ (**6**) adopts the achiral meso form A (X = Te) in the solid state.[18] In **7** the direct op-

position of $tert$-butyl substituents at adjacent Cp rings across the double chalcogen bridge is avoided. In the crystal, complex **7** favors a chiral, near to C_2-symmetric, conformation which can be regarded as an example of the chiral form B (X = O, Y = Te).

NMR Spectra and Dynamic Features of the Chalcogen-Bridged Zirconocene Complexes in Solution. The binuclear complex $[(Me_3CCp)_2Zr(\mu\text{-Te})]_2$ (**6**) exhibits C_{2h}-molecular symmetry in the solid state. The presence of an analogous static molecular structure in solution would reveal itself by signals due to four different methine CH groups of the η-$Me_3CC_5H_4$ rings, in addition to a single set of $tert$-butyl resonances. However, the NMR spectra of **6** are much simpler. At ambient temperature one observes only two RCp C–H resonances in each ^1H (toluene-d_8, δ 6.79, 6.64) and ^{13}C NMR spectra (δ 114.0, 111.6). This indicates an apparent higher overall symmetry of complex **6** in solution than in the crystalline state. This is likely to be caused by the dynamic process of rapid (η-

(26) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649.
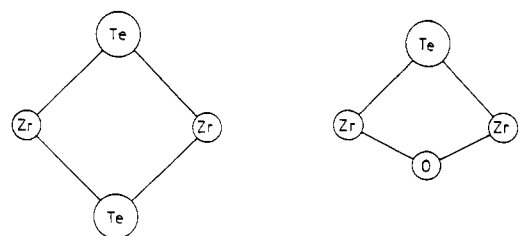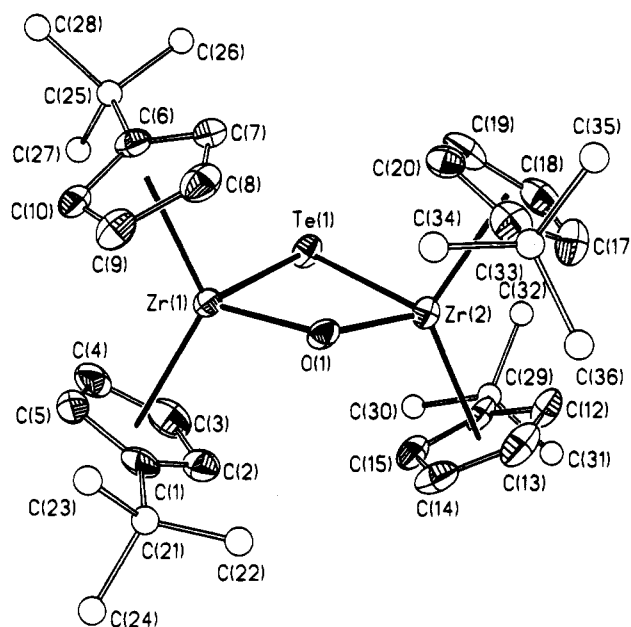
(27) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 584.

(28) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462.

(29) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668.

(30) Takaya, H.; Yamakawa, M.; Mashima, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1283.

(31) In the carbene complex **16a** (R = Me$_3$C; ML$_n$ = W(CO)$_5$), the bulky $tert$-butyl groups are pushed even more to the narrow side of the bent metallocene unit ($\theta \approx 123°$). This probably occurs to avoid unfavorable interaction between the Cp substituents and the substituted η^3-allyl ligand. Erker, G.; Lecht, R.; Sosna, F.; Uhl, S.; Tsay, Y.-H.; Krüger, C.; Grondey, H.; Benn, R. *Chem. Ber.* **1988**, *121*, 1069.
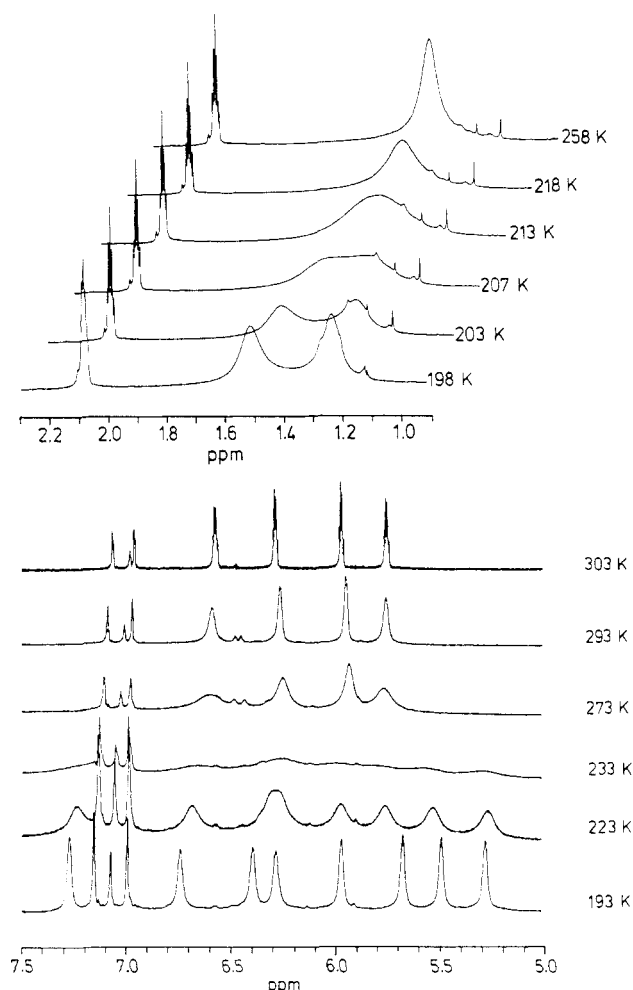
Figure 3. Different regions of the dynamic ^{1}H NMR spectra of $[(Me_3CCp)_2Zr]_2(\mu\text{-}O)(\mu\text{-}Te)$ (7) (*tert*-butyl region, top) and $[(Me_3CCp)_2Zr]_2(\mu\text{-}O)(\mu\text{-}Se)$ (8) (RCp region, bottom).

Me$_3$CCp)–M rotation. Indeed, the ^{13}C and ^{1}H Cp–methine resonances broaden considerably with decreasing temperature and almost merge with the base line at 173 K, while the Me$_3$C resonances retain their ordinary half-width. However, we were unable to obtain limiting low-temperature NMR spectra of **6** at 9.4 T.

Fortunately, the experimental situation is more favorable with complexes $[(Me_3CCp)_2Zr]_2(\mu\text{-}O)(\mu\text{-}Te)$ (7) and $[(Me_3CCp)_2Zr]_2(\mu\text{-}O)(\mu\text{-}Se)$ (8). NMR spectra indicating an apparent C_{2v}-symmetric molecular structure are observed for the tellurium complex **7** at high temperature [^{1}H (toluene-d_8, 200 MHz, ambient temperature) δ 6.83, 6.31, 5.79, 5.61 (RC$_5H_4$), 1.30 (Me$_3$C); ^{13}C (100 MHz, 323 K) δ 111.9, 111.5, 111.1, 109.2, (RC(CH)$_4$), 32.4 (CH$_3$)$_3$C), 32.9 (Me$_3C$)]. Decreasing the monitoring temperature rapidly results in splitting of the *tert*-butyl signals as well as the η-cyclopentadienyl resonances to give doubled sets of NMR lines. The low-temperature limiting spectra of **7** (eight RCp CH resonances, two different *tert*-butyl groups) are in accord with an overall C_2-molecular symmetry as observed in the solid state. From the ^{1}H NMR Me$_3$C coalescence at 206 K (see Figure 3, top) an activation energy for hindered (RCp)–M rotation of $\Delta G^{\ddagger}{}_{\text{rot}}$ (206 K) $\approx$ 9.6 $\pm$ 0.4 kcal/mol was estimated.

Similar dynamic NMR spectra were obtained from the binuclear selenium-bridged complex $[(Me_3CCp)_2Zr]_2(\mu\text{-}O)(\mu\text{-}Se)$ (8). Again, only one set of Me$_3$CC$_5H_4$ resonances was observed at high temperature, splitting into two sets of *t*-BuCp signals of equal intensity, lowering the temperature. Four RCp CH multiplets at high temperature

coalesce giving rise to eight different groups of methine resonances at low temperature (see Figure 3, bottom). From the dynamic NMR spectra (99.6 MHz, Δv = 29 Hz for CMe$_3$ at –80 C) a (RCp)–M rotational barrier of $\Delta G^{\ddagger}{}_{\text{rot}}$ (222 K) $\approx$ 11.0 $\pm$ 0.4 kcal/mol was estimated, which is markedly higher than that observed for the analogous tellurium-containing complex **7**.

Conclusions

This study shows that considerable hindrance in η-cyclopentadienyl–metal rotation can be induced by bringing Cp rings bearing a bulky *tert*-alkyl substituent into close lateral contact. The examples presented here clearly show that for creating easily observable Cp rotational barriers, the metal centers to which the substituted η-cyclopentadienyl rings are attached have to be brought rather closely together. Thus, the ca. 4-Å Zr···Zr separation in the (RCp)$_4$Zr$_2$Te$_2$ complex **6** is still too large to allow for a substantially increased interaction of substituents at the Cp's. Therefore, complex **6** is not characterized by an unexceptionally large $\Delta G^{\ddagger}{}_{\text{rot}}$ value. Exchanging one bridging tellurium center for oxygen brings the RCp-bearing metal centers much closer together (Zr···Zr $\approx$ 3.4 Å in **7**). This leads to a considerably increased lateral RCp/RCp interaction, which is now easily monitored by dynamic NMR spectroscopy. The rotational barrier is further increased when the early-transition-metal centers are brought closer together by varying a bridging atom. Consequently, the observed barrier for (RCp)–M rotation is slightly higher for the selenium/oxygen-bridged complex **8** than for the tellurium/oxygen-bridged analogue.

It has to be assumed that the observed rotational barrier in these conformationally equilibrating binuclear metallocene systems originates primarily from unfavorable nonbonded interaction between *tert*-butyl and hydrogen substituents at adjacent η-RCp rings above the center of the four-membered Zr$_2(\mu\text{-}X)(\mu\text{-}Y)$ core. This appears to be an ideally constructed system to allow for experimental studies of close contacts (which may be repulsive or attractive in nature) between organic substituents. The described systems have the advantage that their formation does not appear to be affected very much by introducing large and bulky substituents. In the ground-state structure these are conveniently "parked" far away from one another in sideways oriented positions at each bent metallocene subunit. The change from a C_{2h}- to C_2-symmetric structure in the solid state upon going from **6** to **7** demonstrates the ability of the Cp$_4$Zr$_2(\mu\text{-}X)(\mu\text{-}Y)$ systems to respond favorably to increased steric hindrance in the ground-state conformation.

A comparison of (RCp)–M rotational activation barriers of differently substituted (RCp)$_4$M$_2(\mu\text{-}X)(\mu\text{-}Y)$ complexes should provide readily accessible information of interaction between many organic substituents, a variety of which can be attached to Cp-ring systems quite easily by convenient literature procedures.[32] Therefore, we are confident that the systems presented here, and other similarly structured metallocene complexes, represent a new advantageous approach for studying steric effects in organic chemistry favorably supplementing the various existing "classical" methods.[33]

(32) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1. Dormond, A.; Tirouflet, J.; le Moigne, F. *Ibid.* **1974**, *69*, C7. Kohl, F. X. Jutzi, P. *Ibid.* **1983**, *243*, 119.

(33) Hünig, S.; Schmitt, M. *Tetrahedron Lett.* **1987**, *28*, 4521. Ermer, O.; Boedecker, C. D.; Prent, H. *Angew. Chem.* **1984**, *96*, 57; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 55. Ermer, O.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1983**, 53. Ermer, O.; Mason, S. A.; Anet, F. A. L.; Miura, S. S. *J. Am. Chem. Soc.* **1985**, *107*, 2330 and references cited therein.

Table I. Crystallographic Data for 7

(a) Crystal Parameters

formula	$C_{36}H_{52}OTeZr_2$	V, Å³	7132 (3)
mol wt	810.82	Z	8
cryst system	monoclinic	cryst size, mm	0.31 × 0.31 × 0.34
		cryst color	deep purple
space group	Cc	μ(Mo Kα), cm⁻¹	7.36
a, Å	18.231 (5)	D(calcd), g cm⁻³	1.510
b, Å	18.186 (6)	temp, K	294
c, Å	22.563 (6)		
β, deg	107.57 (2)		

(b) Data Collection

diffractometer	Nicolet R3m/µ	rflns colltd	6672
radiatn	Mo Kα	indpdt rflns	6290
λ, Å	0.710 73	R(int), %	2.97
2θ limits, deg	$4 \le 2\theta \le 50$	obsd rflns	5247
scan method	ω	$(5\sigma(F_o))$	
octants colltd	$\pm h,k,l$		

(c) Refinement

$R(F)$, %	4.08	Δ/σ (final)	0.082
$R(wF)$, %	5.23	$\Delta(\rho)$, e Å⁻³	1.66
GOF	1.197	N_o/N_v	7.3

a Unit-cell parameters obtained from the least-squares fit of 25 reflections ($21° \le 2\theta \le 30°$).

Experimental Section

Organometallic compounds were handled in an argon atmosphere by using Schlenk-type glassware. Solvents were purified and dried by the usual procedures and distilled under argon before use. NMR spectra were obtained with Bruker AC 200 and WM 400 and Jeol FX-100 FT spectrometers. Melting points were measured with a Büchi-Tottoli apparatus and are not corrected. Elemental analyses were performed by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim, a. d. Ruhr, or by Service Central de microanalyses du CNRS. A Finnigan 311A and 3300 mass spectrometer and a Nicolet 7199 FT-IR spectrometer were used.

Synthesis of (Me₃CCp)₂Zr(μ-Te)₂Zr(CpCMe₃)₂ (6). Elemental tellurium powder (0.48 g, 3.76 mmol) was stirred for 24 h at room temperature in dry toluene. The (η⁴-butadiene)Zr-(CpCMe₃)₂ complex (1.19 g, 3.07 mmol) was added and the mixture stirred for another 48 h. The red mixture was heated to 70 °C for 30 h and then filtered at room temperature to give 0.71 g (50%) of deep violet crystals: mp 328 °C; ¹H NMR (toluene-d_8, ambient temperature) δ 6.79, 6.64 (m, 8 H each, Cp), 1.15 (s, *t*-Bu); ¹³C NMR (toluene-d_8, ambient temperature) δ 141.0 (ipso-C, Cp); 114.0, 111.6 (CH, Cp); 33.0 (CMe_3), 32.2 (C(CH₃)₃); MS (70 eV), m/z (relative intensity) 924 (100, M⁺), 462 [20, (Me₃CCp)₂ZrTe⁺], 332 [41, (Me₃CCp)₂Zr⁺]; IR (KBr) 2955, 1478, 1456, 1358, 1155, 790 cm⁻¹. Anal. Calcd for $C_{36}H_{52}Te_2Zr_2$ (922.5): C, 46.87; H, 5.68. Found: C, 47.34; H, 5.89.

Synthesis of (Me₃CCp)₂Zr(μ-O)(μ-Te)Zr(CpCMe₃)₂ (7). Copper sulfate (CuSO₄·5H₂O; 0.11 g, 0.48 mmol) was added to a solution of 1.65 g (1.8 mmol) of 6 in 50 mL of toluene and stirred for 40 h at room temperature. A black precipitate of tellurium is formed. Filtration gave a dark green solution, from which green crystals of 7 (0.88 g, 60%) were obtained at –30 °C: mp 274 °C; ¹H NMR (toluene-d_8; 200 MHz, ambient temperature): δ 6.83, 6.31, 5.79, 5.61 (m, 4 H each, Cp), 1.30 (s, *t*-Bu); ¹H NMR (400 MHz, 198 K) δ 7.73, 6.88, 6.27, 6.08 (twofold intensity), 5.62, 5.33, 5.04 (Cp), 1.51, 1.23 (*t*-Bu); ¹³C NMR (100 MHz, 323 K) δ 139.3 (ipso-C, Cp), 111.9, 111.5, 111.1, 109.2 (CH, Cp), 32.9 (CMe_3), 32.4 (C(CH₃)₃); ¹³C NMR (193 K) δ 139.8 (ipso-C, Cp, second ipso-C not localized), 118.6, 113 (three overlapping signals), 109.4, 108.6,

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	y	z	U^a		x	y	z	U^a
Te(1)	8337	3807.2 (3)	310	36.6 (2)	C(33)	8971 (9)	1004 (7)	−1031 (6)	65 (5)
Te(2)	1876.3 (4)	2279.5 (4)	248.3 (4)	44.5 (2)	C(34)	9374 (11)	718 (8)	−382 (7)	92 (8)
Zr(1)	8787.7 (6)	2526.2 (5)	1084.3 (6)	29.1 (3)	C(35)	9522 (14)	882 (11)	−1426 (9)	139 (12)
Zr(2)	7954.4 (6)	2532.6 (5)	−477.5 (4)	30.9 (3)	C(36)	8225 (12)	558 (9)	−1282 (12)	147 (13)
Zr(3)	3445.5 (6)	2206.1 (5)	1042.6 (6)	35.7 (3)	C(41)	4128 (7)	2977 (7)	2004 (6)	55 (5)
Zr(4)	2870.5 (6)	2330.9 (5)	−529.9 (6)	35.5 (3)	C(42)	3343 (7)	3099 (7)	1861 (6)	55 (5)
O(1)	8382 (4)	1986 (3)	293 (4)	34 (2)	C(43)	3102 (7)	3473 (7)	1321 (7)	62 (5)
O(2)	3708 (4)	2266 (4)	255 (3)	42 (3)	C(44)	3742 (7)	3613 (6)	1109 (6)	51 (4)
C(1)	7972 (6)	1735 (5)	1637 (5)	43 (4)	C(45)	4388 (8)	3282 (8)	1525 (6)	62 (5)
C(2)	7465 (7)	2234 (7)	1222 (5)	50 (4)	C(46)	3256 (7)	798 (5)	1025 (6)	54 (5)
C(3)	7640 (8)	2967 (7)	1447 (7)	59 (5)	C(47)	4034 (8)	971 (7)	1120 (7)	61 (5)
C(4)	8298 (8)	2909 (7)	1979 (6)	57 (5)	C(48)	4318 (7)	1274 (7)	1708 (7)	63 (5)
C(5)	8486 (7)	2155 (7)	2095 (5)	47 (4)	C(49)	3703 (7)	1303 (6)	1964 (5)	49 (4)
C(6)	10183 (5)	3125 (6)	1531 (5)	39 (4)	C(50)	3042 (7)	1002 (6)	1552 (5)	44 (4)
C(7)	10156 (6)	2729 (7)	978 (5)	47 (4)	C(51)	2451 (7)	3245 (7)	−1454 (5)	50 (5)
C(8)	10054 (6)	1990 (7)	1062 (6)	49 (4)	C(52)	3248 (7)	3243 (7)	−1198 (6)	58 (5)
C(9)	9984 (6)	1883 (6)	1655 (5)	44 (4)	C(53)	3400 (8)	3600 (7)	−610 (7)	61 (5)
C(10)	10078 (6)	2579 (7)	1952 (5)	46 (4)	C(54)	2707 (7)	3744 (6)	−505 (6)	52 (5)
C(11)	6505 (5)	3051 (6)	−917 (5)	39 (4)	C(55)	2111 (7)	3544 (7)	−1033 (6)	51 (5)
C(12)	6628 (6)	2545 (5)	−1347 (5)	44 (4)	C(56)	2861 (7)	1559 (7)	−1474 (5)	55 (5)
C(13)	6779 (7)	1854 (7)	−1059 (6)	56 (5)	C(57)	2150 (7)	1466 (7)	−1378 (6)	58 (5)
C(14)	6721 (6)	1911 (6)	−462 (6)	51 (4)	C(58)	2276 (7)	1068 (7)	−819 (7)	62 (5)
C(15)	6594 (6)	2674 (7)	−356 (6)	46 (4)	C(59)	3053 (7)	924 (6)	−580 (6)	54 (5)
C(16)	8812 (7)	1823 (7)	−1014 (5)	51 (4)	C(60)	3445 (6)	1226 (6)	−986 (5)	42 (4)
C(17)	8250 (7)	2221 (7)	−1488 (5)	54 (5)	C(61)	5216 (8)	3389 (10)	1520 (7)	81 (6)
C(18)	8387 (7)	2982 (7)	−1374 (6)	55 (5)	C(62)	5232 (10)	3557 (15)	861 (10)	163 (13)
C(19)	9038 (8)	3032 (6)	−834 (6)	56 (5)	C(63)	5526 (12)	4009 (13)	1976 (11)	144 (12)
C(20)	9304 (6)	2338 (6)	−630 (5)	40 (4)	C(64)	5693 (10)	2720 (13)	1766 (12)	163 (13)
C(21)	7906 (7)	888 (6)	1606 (6)	54 (5)	C(65)	2321 (8)	816 (8)	1718 (6)	65 (5)
C(22)	7592 (19)	590 (9)	987 (9)	165 (15)	C(66)	1993 (7)	1477 (8)	1947 (6)	65 (5)
C(23)	8629 (12)	521 (10)	1931 (13)	158 (13)	C(67)	1683 (9)	486 (9)	1155 (6)	83 (6)
C(24)	7394 (15)	690 (13)	2013 (12)	149 (14)	C(68)	2538 (9)	223 (9)	2238 (8)	88 (7)
C(25)	10429 (7)	3889 (7)	1696 (6)	56 (5)	C(69)	1253 (8)	3753 (7)	−1211 (6)	63 (5)
C(26)	10499 (8)	4352 (8)	1144 (7)	74 (6)	C(70)	749 (8)	3114 (9)	−1416 (7)	72 (6)
C(27)	9894 (8)	4303 (7)	1993 (6)	63 (5)	C(71)	1116 (9)	4337 (9)	−1716 (8)	94 (7)
C(28)	11252 (8)	3846 (9)	2166 (8)	93 (7)	C(72)	1102 (9)	4097 (9)	−617 (7)	86 (7)
C(29)	6210 (6)	3843 (6)	−1075 (6)	52 (4)	C(73)	4307 (7)	1105 (7)	−969 (6)	55 (5)
C(30)	6160 (8)	4248 (7)	−499 (6)	68 (5)	C(74)	4622 (8)	1795 (8)	−1180 (7)	79 (7)
C(31)	5413 (8)	3762 (9)	−1558 (7)	78 (6)	C(75)	4779 (8)	901 (10)	−302 (6)	90 (7)
C(32)	6709 (8)	4260 (7)	−1393 (7)	69 (6)	C(76)	4289 (8)	480 (8)	−1409 (7)	78 (7)

a Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances and Angles for 7

molecule A		molecule B	
(a) Bond Distances (Å)			
Zr(1)–Te(1)	2.879 (1)	Zr(3)–Te(2)	2.884 (1)
Zr(2)–Te(1)	2.875 (1)	Zr(4)–Te(2)	2.881 (2)
Zr(1)–O(1)	1.975 (7)	Zr(3)–O(2)	1.978 (8)
Zr(2)–O(1)	1.949 (7)	Zr(4)–O(2)	1.961 (6)
Zr(1)–CNT(1)^a	2.290 (9)	Zr(3)–CNT(5)	2.274 (9)
Zr(1)–CNT(2)	2.269 (9)	Zr(3)–CNT(6)	2.268 (9)
Zr(2)–CNT(3)	2.287 (10)	Zr(4)–CNT(7)	2.265 (9)
Zr(2)–CNT(4)	2.261 (9)	Zr(4)–CNT(8)	2.282 (10)
(b) Bond Angles (deg)			
Zr(1)–Te(1)–Zr(2)	72.2 (1)	Zr(3)–Te(2)–Zr(4)	72.0 (1)
Zr(2)–O(1)–Zr(2)	119.5 (3)	Zr(3)–O(2)–Zr(4)	118.8 (2)
CNT(1)–Zr(1)–CNT(2)	125.9 (3)	CNT(5)–Zr(3)–CNT(6)	125.7 (3)
CNT(3)–Zr(2)–CNT(4)	125.9 (3)	CNT(7)–Zr(4)–CNT(8)	126.1 (3)
Te(1)–Zr(1)–O(1)	83.9 (2)	Te(2)–Zr(3)–O(2)	84.4 (2)
Te(1)–Zr(2)–O(1)	84.4 (2)	Te(2)–Zr(4)–O(2)	84.8 (3)
CNT(1)–Zr(1)–Te(2)	108.6 (3)	CNT(5)–Zr(3)–Te(2)	108.5 (3)
CNT(1)–Zr(1)–O(1)	110.2 (4)	CNT(5)–Zr(3)–O(2)	109.5 (5)
CNT(2)–Zr(1)–Te(1)	109.3 (2)	CNT(6)–Zr(3)–Te(2)	109.0 (3)
CNT(2)–Zr(1)–O(1)	110.9 (4)	CNT(6)–Zr(3)–O(2)	112.0 (4)
CNT(3)–Zr(2)–Te(1)	109.1 (3)	CNT(7)–Zr(4)–Te(2)	108.0 (3)
CNT(3)–Zr(2)–O(1)	110.6 (4)	CNT(6)–Zr(7)–O(2)	109.8 (4)
CNT(4)–Zr(2)–Te(1)	108.6 (3)	CNT(8)–Zr(4)–Te(2)	108.2 (3)
CNT(4)–Zr(2)–O(1)	110.4 (5)	CNT(8)–Zr(4)–Te(2)	112.0 (4)

^{a} CNT = centroid of Cp ring.

104.5, 103.7 (CH, Cp), 32.8, 32.5 (CMe$_3$), 32.3, 31.9 (C(CH$_3$)$_3$). Anal. Calcd for C$_{36}$H$_{52}$OTeZr$_2$ (810.85): C, 53.33; H, 6.46. Found: C, 53.58; H, 6.48.

Crystallographic Structural Determination for Complex 7. Crystals of **7** suitable for single-crystal X-ray studies were obtained by crystallization at –30 °C from toluene. Crystallographic data are collected in Table I. Preliminary photographic evidence and diffraction data revealed $2/m$ Laue symmetry and either of the monoclinic space groups Cc or $C2/c$. Statistics based on E values suggested the former, but, given that $Z = 8$, the initial solution and refinement was carried out in $C2/c$. This resulted in unusual excursions in thermal parameters and the development of chemically unreasonable bond distances particularly evident in the cyclopentadienyl rings. Conversion to a model containing two chemically similar independent molecules in Cc provided relief from these problems. All further refinement was confined to this noncentrosymmetric model. No correction for absorption was required (μ(Mo Kα) = 7.4 cm^{-1}; uniform crystal dimensions; T_{max}/T_{min} = 1.06).

The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were treated as idealized, updated isotropic contributions (d(CH) = 0.96 Å). All computations used the SHELXTL program library (G. W. Sheldrick, Nicolet XRD, Madison, WI). Table II contains the atomic coordinates and Table III selected bond distances and angles.

Synthesis of (Me$_3$CCp)$_2$Zr(CH$_3$)(μ-O)Zr(CH$_3$)(CpCMe$_3$)$_2$ (10). A solution of 1.18 g (3.25 mmol) of (Me$_3$CCp)$_2$ZrMe$_2$ (9) in 45 mL of heptane was sonicated for 0.5 h with 0.030 g (1.66 mmol) of water in 1 mL of THF. The resulting mixture was evaporated to dryness and the residue recrystallized from hot hexane giving 0.90 g (1.26 mmol, 77%) of colorless crystals: mp 141 °C; ^{1}H NMR (benzene-d_6, ambient temperature) δ 6.10, 5.98, 5.86, 5.77 (m, 4 H each, Cp), 1.26 (s, t-Bu), 0.49 (s, 6 H, Me). Anal.

Calcd for C$_{38}$H$_{58}$OZr$_2$ (713.32): C, 63.98; H, 8.19; Zr, 25.58. Found: C, 63.65; H, 8.12, Zr, 25.92.

Synthesis of (Me$_3$CCp)$_2$Zr(μ-O)(μ-Se)Zr(CpCMe$_3$)$_2$ (8). A stirred mixture of 10 (0.93 g, 1.30 mmol) in 85 mL of toluene and gray selenium powder (0.13 g, 1.66 mmol) was irradiated (medium-pressure Hg lamp) at room temperature for 7 days. The remaining selenium powder was removed by filtration and the orange solution evaporated to dryness. Recrystallization of the solid residue afforded 0.59 g (0.77 mmol, 59%) of orange crystals: mp >260 °C; ^{1}H NMR (toluene-d_8, 400 MHz, ambient temperature) δ 6.57, 6.29, 5.97, 5.75 (m, 4 H each, Cp), 1.28 (s, t-Bu); ^{1}H NMR (400 MHz, 203 K) δ 7.28, 6.73, 6.37, 6.28, 5.97, 5.70, 5.50, 5.27 (Cp), 1.49, 1.23 (t-Bu); ^{13}C NMR (50 MHz, ambient temperature) δ 139.1 (ipso-C, Cp), 112.5, 111.4, 111.0, 109.3 (CH, Cp), 32.8 (CMe$_3$), 32.2 (C(CH$_3$)$_3$; ^{13}C NMR (100 MHz, 203 K) δ 139.7, 136.9 (ipso-C, Cp), 119.1, 113.3, 112.4, 112.0, 109.9, 109.1, 104.7, 104.4 (CH, Cp), 32.8, 32.4 (CMe$_3$), 32.0, 31.8 (C(CH$_3$)$_3$). Anal. Calcd for C$_{36}$H$_{52}$OSeZr$_2$ (762.21): C, 56.73; H, 6.88; Se, 10.36; Zr, 23.93. Found: C, 55.59; H, 6.86; Se, 12.4; Zr, 23.41.