J. Am. Chem. Soc. 1990, 112, 9635-9637 9635

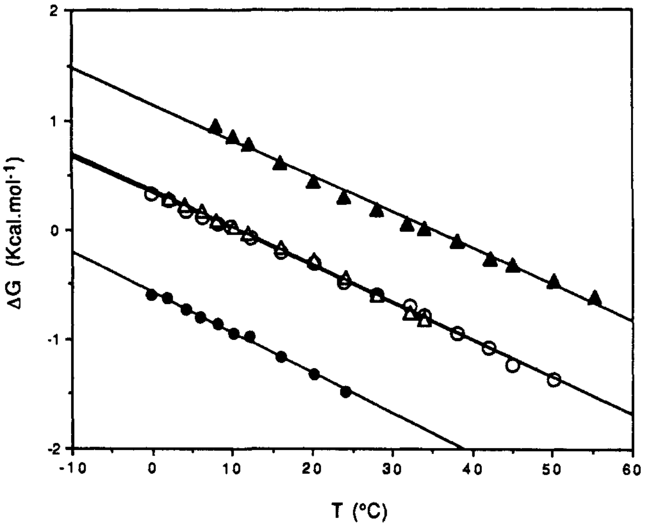


Figure 3. Plot of ΔG vs temperature for the unfolding of free and ruthenium-complexed peptides **1** and **2** [(5.0–6.3) × 10^{-6} M, in 20 mM MES, pH 6.0]: (●) peptide **2**; (○) Ru(III)–peptide **2**; (△) peptide **1**; (▲) Ru(III)–peptide **1**.

Restriction of the conformational mobility of peptides **1** and **2** by the formation of an exchange-inert macrocyclic Ru(III) complex affords remarkably stable α-helical metallopeptides (Figure 2). The analysis of CD spectra[16] of Ru(III)-complexed peptides **1** and **2** at 21 °C in water indicates 80% ($[\theta]_{222} = -28\,000$ deg·cm^2·dmol^{-1}) and 50% ($[\theta]_{222} = -17\,300$ deg·cm^2·dmol^{-1}) α-helicity, respectively.[17] In contrast, the free peptide **1** under similar conditions is 45% helical ($[\theta]_{222} = -16\,000$ deg·cm^2·dmol^{-1}) while uncomplexed peptide **2** exhibits the CD spectrum of a random coil structure.[16] In order to assess differences in helix stability between the metal-ion-complexed and uncomplexed forms of peptides **1** and **2**, the conformational stability of each peptide in the presence and absence of transition-metal ions was determined from heat denaturation studies.[18] The analysis of the thermal denaturation curves afforded linear ΔG vs T and van't Hoff plots (Figure 3). The data suggest that the formation of the exchange-inert Ru(III) complex contributes up to 1 kcal·mol^{-1} toward the stability of the α-helical conformation and dramatically increases the melting temperature of both peptides by about 25 °C. Complexed peptides **1** and **2** exhibit melting temperatures of 35 and 9.5 °C, respectively, while the corresponding free peptides have T_m values of 11 and −15.5 °C.

The above study unequivocally establishes that exchange-inert metal complexes can be effectively exploited in designing highly stable α-helical metallopeptides. The availability of a simple methodology for the formation of stable α-helical peptides can have considerable utility in the de novo design of biologically active peptides.

Acknowledgment. We thank Dr. Gary Siuzdak for mass spectroscopic analysis, C. Choi and V. Malendrez for their valuable technical assistance, and colleagues K. C. Nicolaou, R. Lerner, D. Hilvert, and D. Rideout for helpful discussions.

---

(16) (a) Woody, R. W. In *The Peptides*; Udenfriend, S., Meienhofer, J., Eds.; Academic Press Inc.: New York, 1985; Vol. 7, p 15. (b) Greenfield, N.; Fasman, G. D. *Biochemistry* **1969**, *8*, 4108. (c) Johnson, W. C., Jr. *Annu. Rev. Biophys. Chem.* **1988**, *17*, 145.

(17) Ruthenium(III)–peptide complexes are monomeric in solution as inferred from the absence of any concentration dependency in the CD spectra in the measured range of 0.5–300 μM. The ruthenium complex does not make a significant contribution to the CD spectrum as judged by comparing the $[\theta]_{222}$ of heat and guanidine hydrochloride denatured ruthenium–peptide complexes to the $[\theta]_{222}$ of uncomplexed peptides under similar conditions. Peptide concentrations were determined by quantitative amino acid analysis (average of three runs) using norleucine as internal standard. All reported CD data have an uncertainty of ±2–5%. For 100% helix, $[\theta]_{222} = -35\,000$ and is based on several CD measurements for both peptides in various THF/H_2O mixtures at −10 to 20 °C. For 0% helix, an average value of $[\theta]_{222} = -5000$ was determined from thermal denaturation curves in the range of 80–90 °C. Also see ref 6, and see: (a) Lyu, P. C.; Marky, L. A.; Kallenbach, N. R. *J. Am. Chem. Soc.* **1989**, *111*, 2733. (b) Shoemaker, K. R.; Kim, P. S.; York, E. J.; Stewart, J. M.; Baldwin, R. L. *Nature* **1987**, *326*, 563.

(18) (a) Pace, N. C.; Shirley, B. A.; Thomson, J. A. In *Protein Structure*; Creighton, T. E., Ed.; IRL Press: Oxford, 1989; p 311. (b) Merutka, G.; Stellwagen, E. *Biochemistry* **1990**, *29*, 894.

Enantioselective Catalysis of the Triplex Diels–Alder Reaction: Addition of *trans*-β-Methylstyrene to 1,3-Cyclohexadiene Photosensitized with (−)-1,1′-Bis(2,4-dicyanonaphthalene)

Ji-In Kim and Gary B. Schuster*

Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

Received August 22, 1990
Revised Manuscript Received October 11, 1990

The discovery of enantioselective photochemical sensitization reactions has been pursued with modest success since 1965 when Hammond and Cole reported that triplet energy transfer from an optically active amide gives a 7.7% enantiomeric excess (ee) of *trans*-1,2-diphenylcyclopropanes.[1] Similarly, Takamuku and co-workers observe modest enrichments from isomerization of *trans*-cyclooctenes sensitized by optically active esters.[2] Inoue and co-workers described an unusual temperature dependence for this reaction.[3] The differential recognition of excited molecules bound to chiral surfaces by optically active quenchers was recently reported by Avnir and co-workers.[4] Despite a massive effort to develop chiral Lewis acids that will induce optical activity in cycloadducts formed by the Diels–Alder reaction,[5] only Vondenhof and Mattay have considered a photochemical route to this goal.[6] They describe use of an optically active sensitizer in a radical cation Diels–Alder reaction, but do not report an enantiomeric excess in the cycloadducts that result.

We recently described the [4 + 2] cycloaddition of electron-rich dienes to electron-rich dienophiles in nonpolar solvents catalyzed by irradiation of electron-deficient arene sensitizers.[7] This process

---

(1) Hammond, G. S.; Cole, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 3256.

(2) Inoue, Y.; Kunitomi, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1978**, 1024. Goto, S.; Takamuku, S.; Sakurai, H.; Inoue, Y.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1678.

(3) Inoue, Y.; Yokoyama, T.; Yamasaki, N.; Tai, A. *J. Am. Chem. Soc.* **1989**, *111*, 6480. Inoue, Y.; Yokoyama, T.; Yamasaki, N.; Tai, A. *Nature* **1989**, *341*, 225.

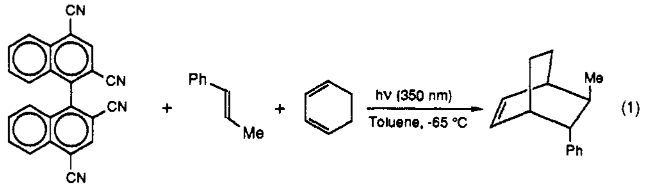
(4) Avnir, D.; Wellner, E.; Ottolenghi, M. *J. Am. Chem. Soc.* **1989**, *111*, 2001.

(5) (a) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986; Vol. 4, p 261. (b) *Nachr. Chem., Tech. Lab.* **1987**, *35*, 836. (c) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. (d) Yamamoto, H.; Maruoka, K.; Furata, K.; Ikeda, N.; Mori, A. In *Stereochemistry of Organic and Bioorganic Transformations*; Bartmann, W., Sharpless, K. B., Eds.; VCH Publishers: Weinheim, 1987; p 13. (e) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310. (f) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238. (g) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109. (h) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436. (i) Furuta, K.; Miwa, Y.; Iwanaga, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 6254. (j) Paquette, L. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter (k) Iwasawa, N.; Sugimori, J.; Kawase, Y.; Narasaka, K. *Chem. Lett.* **1989**, 1947. (l) Cossu, S.; Delogu, G.; De Lucchi, O.; Fabbri, D.; Licini, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 766. (m) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340. (n) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493. (o) Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545.

(6) Vondenhof, M.; Mattay, J. *Tetrahedron Lett.* **1990**, *31*, 985.

(7) (a) Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870. (b) Calhoun, G. C.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 911. (c) Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 8021. (d) Akulbut, N.; Schuster, G. B. *Tetrahedron Lett.* **1988**, *29*, 5125. (e) Hartsough, D.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 3. (f) Akbulut, N.; Hartsough, D.; Kim, J.-I.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 2549.

was designated the triplex Diels–Alder reaction since it was shown to occur by formation of a ternary complex of the singlet excited sensitizer with the diene and dienophile. According to our mechanistic proposal, the triplex is formed by reaction of an exciplex composed of the sensitizer and dienophile (detected by emission in some cases) with the diene. It is generally recognized that formation of an exciplex requires intimate contact between its component parts.[8] Also, the stabilization energy of an exciplex (compared with the locally excited state) and its lifetime are often found to be strongly dependent on both electronic and steric properties of its components. On this basis we reasoned that diastereomeric exciplexes formed from a chiral sensitizer and a prochiral dienophile might have different properties that would provide a basis for enantioselective product formation in the triplex Diels–Alder reaction. Herein we report that irradiation of (–)-1,1′-bis(2,4-dicyanonaphthalene) [(–)BDCN] in toluene solution containing *trans*-β-methylstyrene (tBMS) and 1,3-cyclohexadiene (CHD) gives enantioselective formation of *endo–trans*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-ene (**1**), as shown in eq 1. To the best of our knowledge, this is the first report of an enantioselective photochemical cycloaddition reaction.[9]

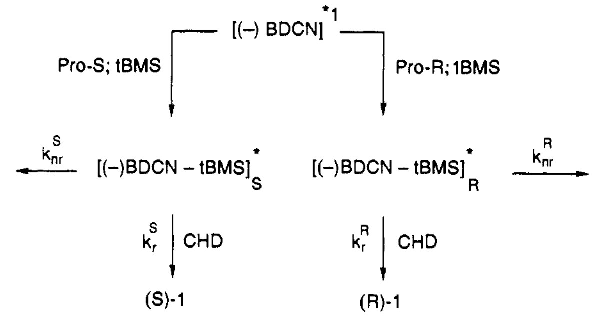


(–)BDCN tBMS CHD 1 (15 ± 3% ee)

Irradiation of (±)BDCN (5 × 10^{-4} M) in an air-saturated toluene solution containing tBMS (0.13 M) and CHD (0.12 M) at room temperature in a Rayonet photoreactor equipped with 350-nm lamps gives (±)-**1** as well as dimers of CHD and the [2 + 2] cycloadducts of CHD and tBMS (bicyclo[4.2.0]octenes). The distribution of cycloaddition products is similar to that obtained when 1,4-dicyanonaphthalene is the sensitizer.[7e,f] By analogy with previous work,[7] this finding signals the operation of both the triplex path and a conventional triplet sensitization route for formation of cycloadducts. The enantiomers of cycloadduct **1** were resolved by capillary gas chromatography on a column coated with chiral 3-(trifluoroacetyl)-2,6-dimethoxy-β-cyclodextrin.[10] When the formation of **1** is sensitized with racemic BDCN, the two enantiomers of **1** are formed in equal amounts.

(–)BDCN was prepared in 70 ± 5% enantiomers excess. 1,1′-Bis(2-naphthoic acid) was resolved with quinine and converted to the diester with diazomethane.[11] The diester was brominated and converted to dimethyl 1,1′-bis(4-cyano-2-naphthoate) with CuCN. Treatment of the dinitrile-substituted diester with trimethylaluminum and ammonium chloride in benzene[12] followed by addition of P_2O_5 gives (–)BDCN in 64% yield. The optical purity of (–)BDCN was determined by complexation[13] with (+)-Yb(hfbc)$_3$ and Ag(fod) in $CDCl_3$ and integration of the NMR absorbances assigned to the 8 and 8′ naphthalene ring protons at δ 7.10 and 7.17 (d, J = 7.2 Hz) in the diastereomeric complexes. A toluene solution of partially resolved BDCN gives $[\alpha]_D = -18.0°$.

Scheme I. Possible Mechanism for Chirality Transfer



Irradiation of enriched (–)BDCN (5 × 10^{-4} M) in toluene containing tBMS (0.02 M) and CHD (0.15 M) at –65 °C gives bicyclooctenes **1** with 15 ± 3% ee.[14] As a check of the analytical procedures, we showed that irradiation of (+)BDCN under similar conditions gives comparable enrichment of the other enantiomer of **1**. Significantly, irradiation of (–)BDCN in an acetonitrile solution containing tBMS and CHD at –30 °C gives a low yield of cycloadducts **1** with no enantiomeric excess (1 ± 1%). The ee observed in the triplex Diels–Alder reaction in toluene solution is strongly temperature dependent. At room temperature this value is 1 ± 1%; at –5 °C, it is 9 ± 2%.

In an effort to probe the mechanism for transfer of chirality from the sensitizer to the cycloadduct, we examined the photophysical properties of BDCN. The fluorescence of BDCN (λ_{max} = 400 nm; τ_s = 6 ± 1 ns) in toluene solution is irreversibly quenched by tBMS at approximately the diffusion-limited rate (1.0 × 10^{10} M^{-1} s^{-1}). This reaction leads to formation of exciplexes detected by their emission at ca. 470 nm. No exciplex emission is detected from acetonitrile solutions of BDCN and tBMS. Exciplex formation is an expected result since BDCN is electron deficient [E_{redn} = –1.52 V (reversible, CH_3CN) vs SCE] and tBMS is an electron-rich quencher.

Diastereomeric BDCN–tBMS exciplexes that may differ in lifetime and stabilization energy can be formed in this reaction. At room temperature we observe a single-exponential decay of the exciplex emission with a lifetime of 26 ± 1 ns. At 0 °C, where different lifetimes for the two diastereomeric exciplexes might be detected, we are unable to distinguish with certainty between a single-exponential decay with a lifetime of 34 ns and a biexponential decay of the exciplex emission with components of 32 and 36 ns. Significantly, at room temperature the exciplex emission is quenched by CHD with a rate constant of 4.0 × 10^9 M^{-1} s^{-1}. This observation confirms formation of a ternary complex (triplex), but of course does not prove that it is on the reaction path leading to cycloadducts **1**. These findings support the reaction mechanism shown in Scheme I.

According to the proposed mechanism, generation of an ee in cycloadducts **1** arises from selective capture of diastereomeric exciplexes [(–)BDCN–tBMS]$_S$ and [(–)BDCN–tBMS]$_R$ by CHD. The precise structures of the exciplexes are unknown. However, we expect that they differ only in the facial orientation of the tBMS with respect to BDCN. To account for our findings, we must conclude that these two exciplexes differ in their lifetime due to a dependence of the nonreactive rate constants for decay (k^S_{nr}, k^R_{nr}) on structure, or in the rate constants for reaction of the diastereomeric exiplexes with CHD (k^S_r, k^R_r). Experiments are underway that are designed to probe these details of the reaction mechanism and to develop more effective chiral sensitizers

---

[8] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; Chapter 7.

[9] There are several examples of diastereoselective photochemical cycloaddition reactions: (a) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 1742. (b) Koch, H.; Runsink, J.; Scharf, H.-D. *Tetrahedron Lett.* **1983**, *24*, 3217. (c) Lange, G. L.; Lee, M. *Tetrahedron Lett.* **1985**, *26*, 6163. (d) Mortezaei, R.; Henin, F.; Muzart, J.; Pete, J.-P. *Tetrahedron Lett.* **1985**, *26*, 6079. (e) Okada, K.; Samizo, F.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1044. (f) Herzog, H.; Koch, H.; Scharf, H.-D.; Runsink, J. *Tetrahedron* **1986**, *42*, 3547. (g) Okada, K.; Samizo, F.; Oda, M. *Tetrahedron Lett.* **1987**, *28*, 3819. (h) Runsink, J.; Koch, H.; Nehrings, A.; Scharf, H.-D.; Nowack, E.; Hahn, T. *J. Chem. Soc., Perkin Trans. 2* **1988**, 49. (j) Buschmann, H.; Scharf, H.-D.; Hoffmann, N.; Plath, M. W.; Runsink, J. *J. Am. Chem. Soc.* **1989**, *111*, 5367. (j) Pelzer, R.; Scharf, H.-D.; Buschmann, H.; Runsink, J. *Chem. Ber.* **1989**, *122*, 1187. (k) Chung, W.-S.; Turro, N. J.; Mertes, J.; Mattay, J. *J. Org. Chem.* **1989**, *54*, 4881. (l) Flemming, I.; Sarkar, A. K.; Doyle, M. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2023. (m) Hoffmann, N.; Scharf, H.-D.; Runsink, J. *Tetrahedron Lett.* **1989**, *30*, 2637.

[10] Schurig, V.; Nowotny, H.-D.; Schmalzing, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 736.

[11] Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242.

[12] Weinreb, S. M.; Levin, J. I.; Turos, E. *Synth. Commun.* **1982**, *12*, 989.

[13] Offermann, W.; Mannschreck, A. *Tetrahedron Lett.* **1981**, *22*, 3227.

[14] The reported ee is calculated on the basis of the measured optical purity of the sensitizer.

for the triplex Diels–Alder reaction.

Acknowledgment. This work was supported by a grant from the National Science Foundation, for which we are grateful. We thank Professor Volker Schurig of the University of Tubingen, West Germany, for his advice and assistance in the separation of the enantiomers of **1** by gas chromatography and Ms. Ingrid Wölfle and Mr. David Hartsough of this department for assistance with these experiments.

Synthesis and X-ray Crystal Structure of the First Bent, Zwitterionic Bis(η^5-C_2B_4-carborane)zirconium Sandwich Complex

Upali Siriwardane,[†] Hongming Zhang,[‡] and
Narayan S. Hosmane[*,‡]

Departments of Chemistry, Louisiana Tech University
Ruston, Louisiana 71272
Southern Methodist University, Dallas, Texas 75275
Received August 17, 1990

There has been a rapidly increasing interest in the chemistry of organozirconocene, particularly in the development of effective catalysts for alkene polymerization, hydrogenation, isomerization, or metathesis.[1] However, the analogous zirconacarborane chemistry has not been investigated. Even though zirconium compounds of any kind in the C_2B_4 carborane system are not yet known, the synthesis of an anionic zirconium sandwich compound of the type $[Et_4N]_2[4,4'\text{-}Zr(1,6\text{-}Me_2\text{-}1,6\text{-}C_2B_{10}H_{10})_2]$ has been reported.[2] In this compound, the *commo*-zirconium[3] atom is present in a formal oxidation state of 2+ and hence represents a 14 interstitial electron system. Nevertheless, the X-ray crystal structure of this compound to confirm its molecular geometry has not been reported to date. We report herein the synthesis, characterization, and crystal structure of the first bent, zwitterionic zirconium sandwich complex which could be envisioned as a potential precursor for the neutral, alkyl-substituted zirconium compounds of the C_2B_4 carborane system.

During the course of our study of the reactivity of C_2B_4 carborane dianions toward early-transition-metal halides, the $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt was reacted with $ZrCl_4$ in a molar ratio of 2:1 in dry benzene (C_6H_6) to produce in high yield a previously unknown zirconacarborane complex (I).[4] This compound was isolated from a solution mixture of *n*-hexane (90%) and THF (10%) as a yellow, air-sensitive, crystalline solid as shown in eq 1. Since the molecular geometry of this species could not be determined unambiguously from its solution spectra alone, an X-ray analysis of I was undertaken to show this to be a novel zirconacarborane sandwich complex $1\text{-}Cl\text{-}1\text{-}(C_4H_8O)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,4',5'\text{-}Li(C_4H_8O)_2\text{-}[1,1'\text{-}\mathit{commo}\text{-}Zr(C_2B_4H_4)_2]$ (I) as represented in a thermal ellipsoid diagram in Figure 1.[5]

$$2Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-} + ZrCl_4 \xrightarrow[\text{(ii) hexane/THF}]{\text{(i) } C_6H_6 \text{ at } 0\ {}^\circ\text{C}} 2NaCl + LiCl + 1\text{-}Cl\text{-}1\text{-}(C_4H_8O)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,4',5'\text{-}Li(C_4H_8O)_2\text{-}[1,1'\text{-}\mathit{commo}\text{-}Zr(C_2B_4H_4)_2] \qquad (1)$$

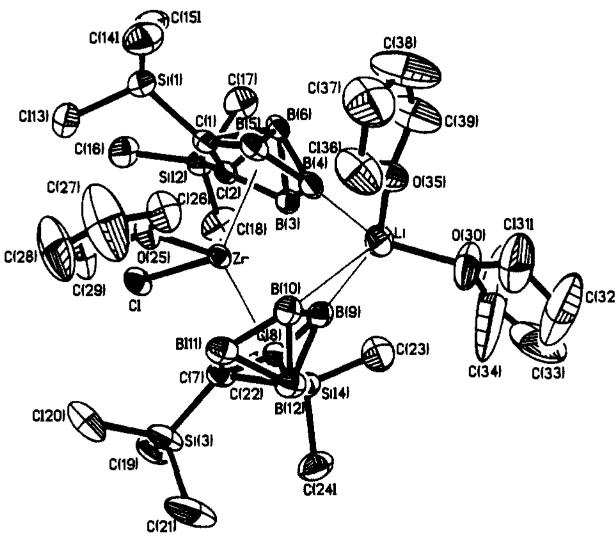


Figure 1. Perspective view of I with thermal ellipsoids drawn at the 40% probability level and showing the atom numbering scheme. The hydrogen atoms are omitted for clarity. Pertinent distances (Å) and angles (deg) include Zr–C(1), 2.587 (6); Zr–C(2), 2.583 (5); Zr–B(3), 2.534 (6); Zr–B(4), 2.538 (6); Zr–B(5), 2.557 (6); Zr–C(7), 2.567 (6); Zr–C(8), 2.553 (5); Zr–B(9), 2.542 (6); Zr–B(10), 2.556 (6); Zr–B(11), 2.563 (7); Zr–O(25), 2.296 (3); Zr–Cl, 2.461 (1); Zr–(C_2B_3 centroid 1), 2.175; Zr–(C_2B_3 centroid 2), 2.173; Li–B(4), 2.606 (11); Li–B(9), 2.494 (9); Li–B(10), 2.413 (10); Li–O(30), 1.935 (10); and Li–O(35), 1.916 (9); (centroid 1)–Zr–O(25), 105.1, (centroid 2)–Zr–O(25), 104.9; (centroid 1)–Zr–Cl, 108.1; (centroid 2)–Zr–Cl, 110.1; (centroid 1)–Zr–(centroid 2), 130.4.

The crystal structure reveals that the zirconium atom adopts an essentially η^5-bonding posture with respect to each of the C_2B_3 faces with the metal to cage distances ranging from 2.534 to 2.587 Å, which are slightly longer than the Zr–η^5-carbon distance of 2.49 Å in $ZrCl_2(\eta^5\text{-}C_5H_5)_2$.[6,7] However, the ($C_2B_3$ centroid 1)–Zr–(C_2B_3 centroid 2) angle is slightly enlarged to 130.4° when compared to 126° found in the structure of $ZrCl_2(\eta^5\text{-}C_5H_5)_2$. As shown in Figure 1, the coordination geometry of I could be viewed as a distorted tetrahedron with average ring centroid–Zr–O(THF) and ring centroid–Zr–Cl angles of 105° and 109°, respectively. Although the Zr–Cl distance of 2.461 (1) Å, the Cl–Zr–OC_4H_8 angle of 90.5 (1)°, and the bent geometry of I resemble those of a zirconocene derivative, the most important difference to be noted is that of charge; each carborane ligand bears a 2– charge while the cyclopentadienide ligands are monoanions. Since the zirconium is bonded to a chlorine atom as well as the carborane cages, for charge compensation an additional $Li^+(THF)_2$ moiety is bound to the unique boron in one cage and to the unique boron and one other boron in the second cage of I with distance of about 2.606 (11), 2.413 (10), and 2.494 (9) Å, respectively. In a formal sense I is a "zwitterion" consisting of an anionic $\{Zr(Cl)(THF)[\eta^5\text{-}(SiMe_3)_2C_2B_4H_4]_2\}^-$ sandwich compound that is complexed with an exo-polyhedral $[Li(THF)_2]^+$ cation. The distance of 3.865 Å

---

[*] Author to whom correspondence should be addressed.

[†] On summer research leave from Louisiana Tech University, Ruston, LA.

[‡] Southern Methodist University.

(1) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(2) Salentine, C. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 426.

(3) The prefix "commo" represents the common vertex for two C_2B_3 pentagonal faces in polyhedral metal sandwich complexes; see: Hosmane, N. S. In Carborane. *1990 McGraw-Hill Yearbook of Science & Technology*; McGraw-Hill: New York, 1989; p 50.

(4) A 4.5-mmol sample of $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt (Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600. Barreto, R. D.; Hosmane, N. S. *Inorg. Synth.*, in press.) was allowed to react with 2.25 mmol of anhydrous $ZrCl_4$ (0.524 g) in dry benzene (25 mL) at 0 °C for 2 h, during which time the color of the solution turned to yellow. At this point, the heterogeneous product mixture was filtered through a frit in vacuo, and the residue was washed repeatedly with a solvent mixture of hexane (90%) and THF (10%), to collect a clear yellow-orange filtrate. After slow removal of the solvents from the filtrate in vacuo, a yellow, air-sensitive crystalline solid, identified as $1\text{-}Cl\text{-}1\text{-}(C_4H_8O)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,4',5'\text{-}Li(C_4H_8O)_2\text{-}[1,1'\text{-}\mathit{commo}\text{-}Zr(C_2B_4H_4)_2]$ (I), was obtained in 68% yield (1.20 g, 1.53 mmol; reasonably soluble in polar and slightly soluble in nonpolar organic solvents; decomposes above 160 °C forming a brown residue).

(5) A room temperature data set was collected on a yellow rectangular crystal (mounted in a 0.7-mm glass capillary in a drybox) of triclinic space group $P\bar{1}$ with the following unit cell parameters: $a = 11.428$ (3) Å, $b = 12.140$ (3) Å, $c = 17.685$ (4) Å, $\alpha = 93.27$ (2)°, $\beta = 90.35$ (2)°, $\gamma = 114.91$ (2)°, $V = 2220.4$ (8) Å^3, and $Z = 2$. Full-matrix least-squares refinements of I converged at $R = 0.044$, and $wR = 0.057$ for 4842 observed [$I > 3.0\,\sigma(I)$] reflections. The structure was solved by the heavy-atom methods in SHELXTL-PLUS (Sheldrick, G. M. *Structure Determination Software Programs*; Nicolet Instrument Corp., USA: 1988).

(6) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290.

(7) Ronova, I. A.; Alekseev, N. V. *Zh. Strukt. Khim.* **1977**, *18*, 212.

0002-7863/90/1512-9637$02.50/0