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

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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-Cl-1-(C_4H_8O)-2,2′,3,3′-$(SiMe_3)_4$-5,4′,5′-$Li(C_4H_8O)_2$-[1,1′-*commo*-$Zr(C_2B_4H_4)_2$] (I) as represented in a thermal ellipsoid diagram in Figure 1.[5]

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

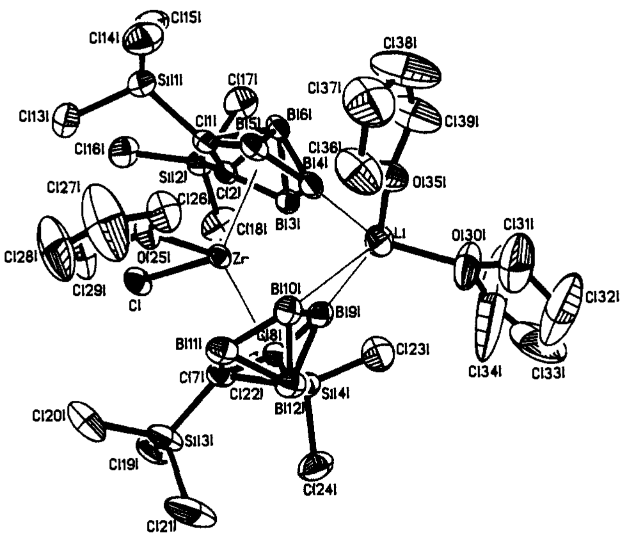

Figure 1. Perspective view of I with thermal ellipsoids drawn at the 40% probability level and showing the atom numbering scheme. The hydrogen atoms are omitted for clarity. Pertinent distances (Å) and angles (deg) include Zr–C(1), 2.587 (6); Zr–C(2), 2.583 (5); Zr–B(3), 2.534 (6); Zr–B(4), 2.538 (6); 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

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(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-Cl-1-(C_4H_8O)-2,2′,3,3′-$(SiMe_3)_4$-5,4′,5′-$Li(C_4H_8O)_2$-[1,1′-*commo*-$Zr(C_2B_4H_4)_2$] (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, α = 93.27 (2)°, β = 90.35 (2)°, γ = 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).

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between Zr and Li atoms is rather too long to have any significant interactions between them. The eclipsed conformation of the C_{cage}–$SiMe_3$ groups of the opposing ligands in I could be due to the presence of a $Li^+(THF)_2$ moiety.

In addition to the X-ray analysis, compound I was also characterized by ^1H, ^{11}B, and ^{13}C NMR and IR spectroscopy.[8] Although the ^1H and ^{13}C NMR spectra indicated the presence of two nonequivalent $SiMe_3$ groups and two nonequivalent THF molecules, the proton-coupled ^{11}B NMR spectrum of I showed broad, ill-defined resonances at 33.16, 25.48, and −16.32 ppm, whose relative areas indicate a 1:2:1 distribution of basal and apical BH groups, respectively. This indicates that I could be either a closo or a commo complex, thus inferring that the ^{11}B NMR spectroscopy is not an effective tool to elucidate the structure of I. The presence of the coordinated THF and the heterocarborane complex was also confirmed by the IR spectrum of I.[8]

The bright yellow color of I may be due to the presence of a $[Li(THF)_2]^+$ moiety. The bent structure of the complex could be rationalized on the basis of the location of the THF molecule and the Cl atom on the *commo*-Zr metal. Similar bent-sandwich geometries have been recently reported for anionic carborane complexes, $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ and [3,3′-$(THF)_2$-*commo*-3,3′-$Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^-$.[9,10] It is important to note that the coordination of a Lewis base to the apical heteroatom of the main group results in slip distortion of the heterocarborane cage, invariably toward the boron atoms above the C_2B_3 face.[11] However, the bond distances in I indicate that the *commo*-Zr metal is symmetrically bonded to the carborane cages, and hence, the bonding of a THF molecule to the zirconium metal in the complex has very little effect on the cage geometries unlike the cases of main-group metallacarboranes. In any case, compound I represents the first Zr^{IV} sandwich carborane complex ever to be reported.

The presence of a chlorine atom on zirconium metal suggests that I could be converted to a neutral alkyl derivative of the type $R\text{-}Zr[\eta^5\text{-}(SiMe_3)_2C_2B_4H_4]_2Li(THF)_2$ since its most exciting prospects lie in the potential for developing better catalysts than those based on the mixture of zirconocene alkyl derivative and methylaluminoxane in the Ziegler–Natta olefin polymerization systems. Such a neutral, isoelectronic, carborane-based analogue obviates the severe problems of devising an innocent, noncoordinating counteranion which have plagued the zirconocene system.[1] Our efforts in such an endeavor are currently in progress.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-8800328), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Dr Siriwardane thanks the State of Louisiana (Grant No. NSF-LaSER (1990)-RFAP-07) and the Louisiana Tech University for a faculty development and summer research stipend to conduct research at Southern Methodist University.

Supplementary Material Available: Tables of positional and thermal parameters, bond distances, bond angles, and torsion angles for compound I (8 pages); listing of observed and calculated structure factors for compound I (18 pages). Ordering information is given on any current masthead page.

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(8) Spectroscopic data for I: ^1H NMR (C_6D_6, relative to external Me_4Si) δ 3.82 (s, 4 H, THF), 3.6 [br, ill-defined peak, 6 H, basal H_t, $^1J(^1H\text{–}^{11}B)$ = unresolved], 3.35 (s, 8 H, THF), 2.6 [br, ill-defined peak, 2 H, apical H_t, $^1J(^1H\text{–}^{11}B)$ = unresolved], 1.15 (s, 4 H, THF), 1.09 (s, 8 H, THF), 0.30 (s, 18 H, $SiMe_3$), 0.21 (s, 18 H, $SiMe_3$); ^{11}B NMR (C_6D_6, relative to external $BF_3{\cdot}OEt_2$) δ 33.16 [br, ill-defined peak, 1 B, basal BH, $^1J(^{11}B\text{–}^1H)$ = unresolved], 25.48 [br, ill-defined peak, 2 B, basal BH, $^1J(^{11}B\text{–}^1H)$ = unresolved], −16.32 [br, ill-defined peak, 1 B, apical BH, $^1J(^{11}B\text{–}^1H)$ = unresolved]; ^{13}C NMR (relative to external Me_4Si) δ 123.92 [s (br), cage carbons (SiCB)], 123.42 [s (br), cage carbons (SiCB)], 76.43 [t, 2 C, Zr–THF, $^1J(^{13}C\text{–}^1H)$ = 150 Hz], 68.63 [t, 4 C, Li–THF, $^1J(^{13}C\text{–}^1H)$ = 148 Hz], 33.24 [t, 2 C, Zr–THF, $^1J(^{13}C\text{–}^1H)$ = 127 Hz], 25.49 [t, 4 C, Li–THF, $^1J(^{13}C\text{–}^1H)$ = 134 Hz], 3.65 [q, $SiMe_3$, $^1J(^{13}C\text{–}^1H)$ = 119.8 Hz], 3.25 [q, $SiMe_3$, $^1J(^{13}C\text{–}^1H)$ = 118.81 Hz]; IR (cm^{-1}; C_6D_6 vs C_6D_6) 2954 (vs), 2896 (vs) [ν(C–H)], 2543 (vvs), 2496 (vs, sh), 2449 (m, sh) [ν(B–H)], 1443 (w), 1402 (w, br) [$\delta(CH)_{asym}$], 1355 (w, br), 1337 (w), 1249 (vs) [$\delta(CH)_{sym}$], 1179 (m, s), 1126 (w, br), 1067 (w, sh), 1044 (m), 1002 (m, br), 914 (w, sh), 844 (vvs, br) [ρ(CH)], 761 (s, s), 703 (w, br), 632 (m, s) [ν(Zr–Cl)], 602 (w, sh), 532 (w, br), 479 (w, br).

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New Nuclear Magnetic Resonance Technique for Determining Long-Range Heteronuclear ^1H–^{15}N Correlations in Proteins

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Received May 30, 1990

An exciting advance in the last few years has been the demonstration that complete structures of proteins in solution can be deduced from high-resolution NMR data. The use of inverse detection heteronuclear ^1H–^{15}N NMR techniques in conjunction with ^{15}N labeling has proved invaluable for such studies.[1-4] Experiments that reveal not only intraresidue correlations but also interresidue ones[5-9] between $C_\alpha H(i)$ and $^{15}N(i+1)$ are particularly useful since they aid sequential assignment.[10-15] In addition, the heteronuclear scalar coupling giving rise to a correlation between $C_\alpha H(i)$ and $^{15}N(i+1)$ is very sensitive to the backbone torsion angle, ψ, and is consequently a source of structural information;[11,12] for example, $J \simeq 6$ Hz for α-helical regions and $J < 1.5$ Hz in β-sheets. The HMBC (^1H-detected *h*eteronuclear *m*ultiple *b*ond correlation) experiment[5-9] has been successfully used to obtain this information, Figure 1A. There are however disadvantages to this experiment; for example, the data cannot be recorded in the pure absorption mode. Consequently spectra are usually displayed in mixed-mode absorption in F_1 and absolute-value mode in F_2. This hinders the recovery of the heteronuclear coupling constant.[9] Correlation peaks exhibit a homonuclear ^1H multiplet in F_1 that reduces the signal-to-noise ratio and increases the possibility of peak overlap. In this communication we propose a new technique that has a number of advantages over the HMBC experiment.

The alternative multiple bond pulse sequence described here (Figure 1B) allows data to be acquired in the pure absorption mode; all correlations that occur in the spectrum are singlets in F_1 and multiplets antiphase with respect to the active heteronuclear coupling in F_2. Consequently the heteronuclear coupling constant

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