Zirconocene–Carborane Complex

Synthesis, Structure, and Bonding of a Zirconocene–1,2-Dehydro-*o*-carborane Complex**

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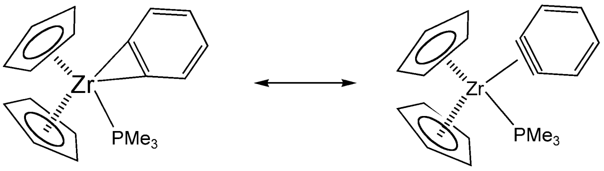
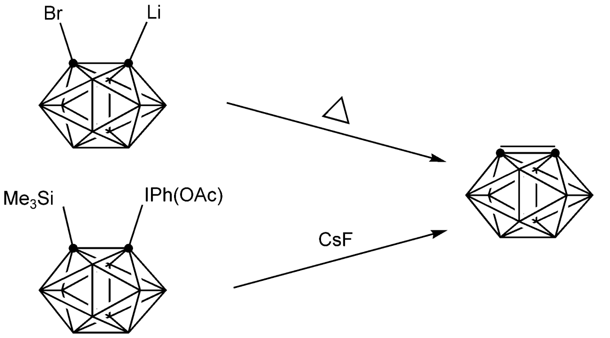
1,2-Dehydrobenzene (benzyne) has found many applications in organic synthesis, mechanistic studies, and the synthesis of functional materials since it was reported as an active intermediate in the 1950s.[1–4] The chemistry of its transition-metal complexes has been extensively studied.[5,6] The first zirconocene–benzyne complex stabilized by PMe_3 was structurally characterized in 1986 (Scheme 1).[7] In sharp contrast, 1,2-dehydro-*o*-carborane, a three-dimensional relative of benzyne, was suggested as a reactive intermediate for the first time in 1990 by heating a lithium salt of *o*-bromocarborane.[8] It was recently reported that 1,2-dehydro-*o*-carborane was also generated from phenyl(*o*-trimethylsilyl carboranyl)iodonium acetate in the presence of CsF (Scheme 2).[9] Reactivity studies showed benzyne and 1,2-dehydro-*o*-carborane to be quite similar in reactions with dienes.[8–10] In view of the rich chemistry of metal–benzyne complexes,[5,6] we are interested in the virtually undeveloped chemistry of metal 1,2-dehydro-*o*-carborane complexes. We report here the synthesis, single-crystal X-ray structure, and bonding of the first zirconocene–1,2-dehydro-*o*-carborane complex $[[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})][Li(thf)_4]]$ (**1**).

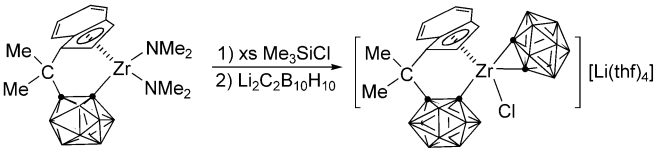


Scheme 1. The first structurally characterized zirconocene–benzyne complex.[7]



Scheme 2. Reported synthesis of 1,2-dehydro-*o*-carborane.[8,9]

Treatment of $[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}Zr(NMe_2)_2]$ with excess Me_3SiCl in toluene, presumably giving $[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl_2]$,[11] was followed by treatment with 1 equiv of $Li_2C_2B_{10}H_{10}$ to afford **1** as light-brown crystals in 60% yield (Scheme 3). Complex **1** is soluble in polar organic solvents such as THF, pyridine, and dimethoxyethane (DME), and is insoluble in toluene and hexane. It is extremely air- and moisture-sensitive but remains stable for months at room temperature under an inert atmosphere. Traces of air immediately convert the colored **1** to a white powder.



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Scheme 3. Synthesis of **1**.

The ${}^1H$ NMR spectrum showed six multiplets for the aromatic protons in the region $\delta = 8.2$–6.5 ppm and two singlets at $\delta = 1.98$ and 1.76 ppm corresponding to two diastereotopic methyl groups of the bridging CMe_2 unit, and supported the ratio of four THF molecules per hybrid ligand. In addition to those peaks assignable to the indenyl, CMe_2, and THF groups observed in the ${}^{13}C$ NMR spectrum, there were four resonances in the region $\delta = 106$–94 ppm corresponding to the two carboranyl moieties. The ${}^{11}B$ NMR spectrum exhibited a 1:2:5:1:1 splitting pattern, which differs significantly from that of its parent complex.[11]

The molecular structure of **1** has been confirmed by single-crystal X-ray analysis (Figure 1).[12] It has an ionic structure consisting of well-separated, alternating layers of discrete cations $[Li(thf)_4]^+$ and zirconocene anions $[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\eta^3\text{-}C_2B_{10}H_{10})]^-$. In the anion, the Zr center is η^5-bound to the five-membered ring of the indenyl group, η^3-bound to a 1,2-dehydro-*o*-carborane moiety, and σ-bound to a cage carbon atom and a terminal chlorine atom in a distorted-tetrahedral geometry. The average Zr−C(C_5 ring) bond lengths of 2.515(5) Å, Zr−Cl bond length of 2.403(2) Å, and Zr-C2 bond length of 2.359(5) Å are close to the corresponding values found in $[\{\eta^5:\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2^-$.[11]

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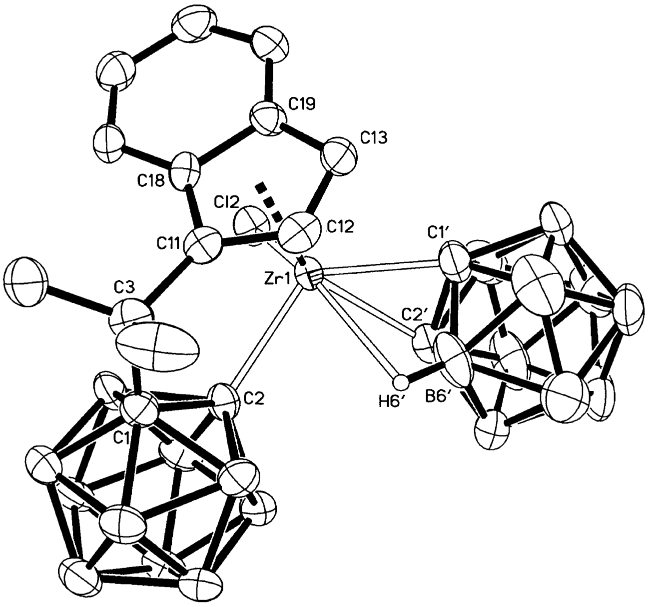
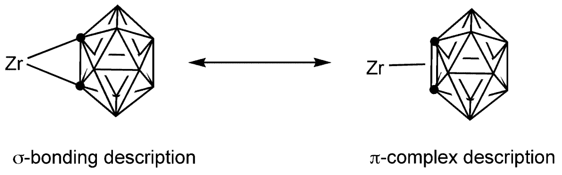


Figure 1. Molecular structure of the [{η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$}ZrCl-($\eta^3$-$C_2B_{10}H_{10}$)]$^-$ ion in **1**. Selected bond lengths [Å]: Zr1-C2 2.359(5), Zr1-C1′ 2.229(7), Zr1-C2′ 2.422(7), Zr1-Cl2 2.403(2), Zr1-B6′ 2.552(10), Zr1-C(C_5 ring; av) 2.515(5), C1-C2 1.711(7), C1′-C2′ 1.616(10).

The unique structural feature found in **1** displays a novel metal–1,2-dehydro-*o*-carborane bonding mode. The metal center is directly bonded to the two adjacent cage carbon atoms which do not have terminal hydrogen atoms (Zr–C: 2.229(7) and 2.422(7) Å). In addition, the metal center also interacts with the cage through an "agostic-like" Zr-H–B bond (Zr–B: 2.552(10) Å; Zr–H: 2.38 Å). Thus, the description Zr-η^3-(*o*-$C_2B_{10}H_{10}$) can be used to exemplify this novel bonding mode. In view of these structural parameters, we can formally consider that there are two Zr–C single bonds and one "agostic-like" Zr-H-B bond between the Zr center and the η^3-(*o*-$C_2B_{10}H_{10}$) ligand. With such a bonding description, the dianionic [η^3-(*o*-$C_2B_{10}H_{10}$)]$^{2-}$ ligand formally donates three pairs of electrons to the metal center and is isolobal with Cp^-. Therefore, one can conveniently correlate the zirconium complex ion with complexes having a general formula of d^0 Cp_2MX_2. Alternatively, one can describe the bonding interaction between the metal center and the two carbon atoms of the η^3-(*o*-$C_2B_{10}H_{10}$) ligand in terms of the metal–1,2-dehydro-*o*-carborane form shown in Scheme 4. This alternative description explains the shorter C–C bond length (1.616(10) Å) of the η^3-(*o*-$C_2B_{10}H_{10}$) ligand in comparison with that (1.711(7) Å) found in the σ-bonded carborane unit.



σ-bonding description

π-complex description

Scheme 4. Possible bonding interactions in **1**.

The results of molecular orbital calculations[13] at the B3LYP level of theory based on the experimental geometry of the complex suggest that a resonance hybrid of the two bonding descriptions discussed above most accurately describes the Zr-η^3-(*o*-$C_2B_{10}H_{10}$) bonding situation for the complex anion. Figure 2 shows the contour plots of the lowest unoccupied (LUMO) and the highest occupied (HOMO) molecular orbitals derived from the B3LYP calculations. The LUMO is an unoccupied metal d orbital mixed with orbitals from the η^5-indenyl ligand, which represents a feature commonly found for a d^0 Cp_2MX_2 complex.[14] Meanwhile, the HOMO, despite containing the metal–carbon σ-bonding interactions, can also be viewed as having the character of metal(d)-to-π^* back-donation commonly used in describing metal–olefin or metal–acetylene bonds.[15] It is not too surprising that the two bonding descriptions discussed above are both responsible for the Zr-η^3-(*o*-$C_2B_{10}H_{10}$) interactions in view of the molecular structure of [$Cp_2Zr(\eta^2$-benzyne)(PMe_3)][7] and the fact that the Lewis structures of metallacyclopropane (or metallacyclopropene) and metal–π complex forms are normally invoked to describe the bonding in metal–olefin or metal–acetylene complexes.[15]

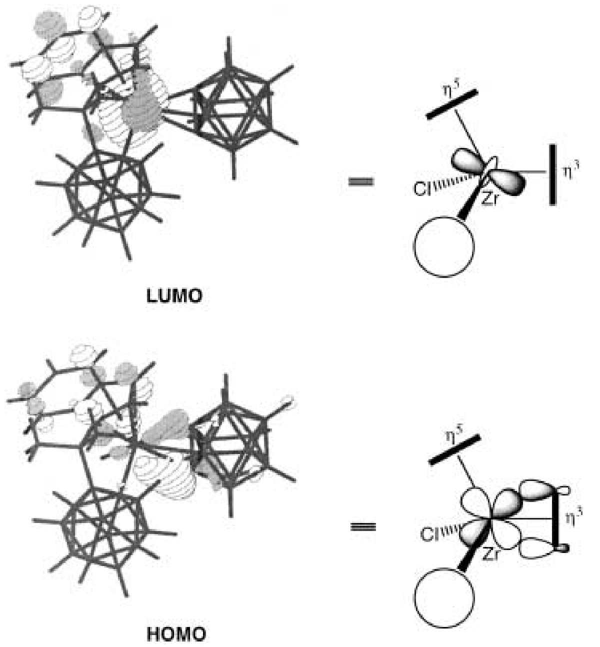


Figure 2. Contour plots of the lowest unoccupied and the highest occupied molecular orbitals calculated for the [{η^5:σ-$Me_2C(C_9H_6)(C_2B_{10}H_{10})$}ZrCl($\eta^3$-$C_2B_{10}H_{10}$)]$^-$ complex ion.

In summary, the first example of zirconocene–1,2-dehydro-*o*-carborane complex has been prepared and structurally characterized, which also exhibits a brand new bonding mode for carboranes. Molecular-orbital calculations suggest that the bonding interactions between Zr and 1,2-dehydro-*o*-carborane are best described as a resonance hybrid of both the Zr–C σ and Zr–C π bonding forms shown in Scheme 4. The reactivity patterns of **1** are under investigation.

Experimental Section

1: A solution of $\mathrm{Me_3SiCl}$ (217 mg, 2.0 mmol) in dry toluene (10 mL) was added dropwise to a solution of $[\{\eta^5{:}\sigma\text{-}\mathrm{Me_2C(C_9H_6)(C_2B_{10}H_{10})}\}\mathrm{Zr(NMe_2)_2}]$[11] (240 mg, 0.5 mmol) in toluene (20 mL) and was stirred at room temperature overnight. After removal of the solvent and excess $\mathrm{Me_3SiCl}$, the resulting yellow solid was washed with *n*-hexane and redissolved in THF (20 mL). To the resulting clear yellow solution was added $\mathrm{Li_2C_2B_{10}H_{10}}$ (freshly prepared from *o*-carborane (72 mg, 0.5 mmol) and 2 equiv of *n*BuLi in toluene/$\mathrm{Et_2O}$) at −78 °C with stirring. The reaction mixture was then warmed to room temperature and stirred overnight. After removal of the precipitate, the clear brown solution was concentrated to about 10 mL and cooled to −30 °C to give **1** as light-brown crystals (260 mg, 60 %). ^{1}H NMR (300 MHz, [D$_5$]pyridine): $\delta = 8.18$ (d, $J = 8.4$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.40 (m, 1H), 7.13 (m, 1H), 6.89 (d, $J = 3.6$ Hz, 1H), 6.52 (d, $J = 3.6$ Hz, 1H; $\mathrm{C_9}\mathit{H}_6$), 3.63 (m, 16H), 1.61 (m, 16H; THF), 1.98 (s, 3H), 1.76 ppm (s, 3H; $(\mathrm{C}\mathit{H}_3)_2\mathrm{C}$); ^{13}C NMR (75 MHz, [D$_5$]pyridine): $\delta = 136.09$, 127.99, 126.55, 125.92, 125.67, 125.10, 124.77, 124.35, 115.86 ($\mathit{C}_9\mathrm{H}_6$), 106.89, 106.84, 98.42, 94.52 ($\mathit{C}_2\mathrm{B_{10}H_{10}}$), 67.17, 25.14 ($\mathrm{O}\mathit{C}_4\mathrm{H}_8$), 44.32, 34.25, 32.75 ppm ($(\mathit{C}\mathrm{H}_3)_2\mathit{C}$); ^{11}B NMR (128 MHz, [D$_5$]pyridine): $\delta = -0.9$ (2), −2.8 (4), −6.7 (10), −9.3 (2), −13.4 ppm (2); IR (KBr): $\tilde{\nu} = 3064$ (w), 2979 (s), 2883 (s), 2557 (vs), 1614 (w), 1453 (m), 1386 (w), 1257 (W), 1184 (w), 1090 (m), 1042 (s), 888 (m), 818 (m), 746 (m), 677 cm^{-1} (w); elemental analysis calcd (%) for $\mathrm{C_{32}H_{64}B_{20}ClLiO_4Zr}$: C 44.55, H 7.48; found: C 44.35, H 7.30.

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Keywords: agostic interactions · carboranes · coordination modes · metallacycles · metallocenes

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[12] Crystal data for **1**: $\mathrm{C_{32}H_{64}B_{20}ClLiO_4Zr}$, $M_r = 862.6$, monoclinic, space group $P2_1/c$, $a = 11.329(2)$, $b = 17.691(4)$, $c = 24.394(5)$ Å, $\beta = 102.67(1)°$, $V = 4770(2)$ Å^3, $T = 298$ K, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.201$ g cm^{-3}, $2\theta_{\max} = 52°$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, absorption corrections applied by using SADABS,[16] relative transmission factors in the range 0.872–1.000. A total of 27 668 reflections were collected and led to 9347 unique reflections, 9347 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.0599$, wR_2 $(F^2) = 0.1377$. This structure was solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL/PC package of crystallographic software.[17] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were geometrically fixed using the riding model. CCDC-210368 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] In the B3LYP calculations, effective core potentials with a Lanl2DZ basis set were used for Zr and Cl. For B, C, and H atoms, the 6-31G basis set was employed. Polarization functions were also added for Cl ($\zeta_d = 0.514$).

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