ORGANOMETALLICS

Volume 24, Number 13, June 20, 2005

# Communications

## A New Synthetic Route to High-Valent Half-Sandwich Group 4 Metallacarborane Alkyls. Synthesis and Structural Characterization of $[\eta^1:\eta^6\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Hf(CH_2SiMe_3)_2$

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*Received April 15, 2005*

*Summary: A half-sandwich group 4 metallacarborane alkyl was prepared and structurally characterized for the first time via an alkane elimination reaction of Hf-*$(CH_2SiMe_3)_4$ *with the zwitterionic salt* $Me_2NHCH_2CH_2C_2B_{10}H_{12}$*. This method avoids using the strong reducing agents* [*nido*-$R_2C_2B_{10}H_{10}$]$M_2$ *(M = group 1 metal) as starting materials, which allows the synthesis of high-valent group 4 metallacarboranes of the* $C_2B_{10}$ *system.*

Group 4 metallacarboranes of the $C_2B_4$ and $C_2B_9$ systems have been extensively investigated.[1] A series of full- and half-sandwich complexes have been prepared and structurally characterized, in which group 4 metals are usually $\eta^5$ bound to the open $C_2B_3$ pentagonal bonding face.[2,3] In sharp contrast, the chemistry of group 4 metallacarboranes of the $C_2B_{10}$ system is highly limited due to the strong reducing power of *nido*-$R_2C_2B_{10}H_{10}^{2-}$ dianions, which can readily reduce M(IV) to M(II).[4,5] It is clear that the high-valent group 4 metallacarboranes involving an $\eta^6$-carboranyl ligand cannot be prepared by conventional salt metathesis methods. The recently developed redox methodology for the synthesis of $[\eta^5:\eta^6:\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10}CH_2NMe)]Zr(NC_5H_5)$ is not applicable to prepare half-sandwich group 4 metallacarboranes bearing an $\eta^6$-carboranyl ligand.[6] Therefore, a new methodology is definitely desirable.

On the other hand, it has been documented that the alkane elimination reaction of $C_2B_9H_{13}$ with $Cp^*M(CH_3)_3$ ($Cp^* = C_5Me_5$) is a very effective method for the preparation of mixed-sandwich group 4 metallacarbo-

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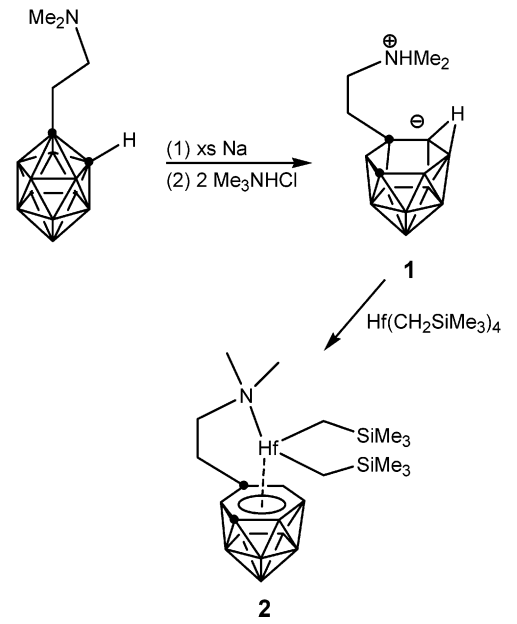
10.1021/om050290y CCC: $30.25 © 2005 American Chemical Society
Publication on Web 05/26/2005

rane alkyl complexes.[3a] We wondered if such an alkane elimination methodology could be applied to the $C_2B_{10}$ ligand system. Although the neutral acids of $R_2C_2B_{10}H_{12}$ are unknown, their deprotonated forms $R_2C_2B_{10}H_{11}^-$ have been well characterized.[7,8] It is anticipated that only the kinetic isomers of $R_2C_2B_{10}H_{11}^-$ containing a bridging hydrogen atom are capable of reacting with neutral metal alkyls. In view of the coordination ability and Lewis basicity of the appended amine in the $Me_2NCH_2C_2B_9H_{10}^{2-}$ ligand,[3k,l] 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$[9] was chosen as the starting material. We report in this communication the synthesis and structural characterization of the first half-sandwich group 4 metallacarborane alkyl complex.

**Scheme 1**



Treatment of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ with excess finely cut Na metal in THF gave, after removal of Na by filtration, $[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Na_2(THF)_x$, followed by reaction with 2 equiv of $Me_3NHCl$ in THF at −30 °C to afford the kinetic product 1-$Me_2NHCH_2$-$CH_2$-1,3-$C_2B_{10}H_{12}$ (**1**) in 92% yield.[10] The $^1H$ and $^{13}C$ NMR spectra supported the presence of the $Me_2NHCH_2$-$CH_2$ group. Its $^{11}B$ NMR spectrum exhibited a 1:1:1:2:1:1:1:1:1 splitting pattern, which changed to a 2:1:1:2:2:2 pattern after heating at 80 °C for 5 h. This result suggested that **1** is the kinetic product.[7,8] Compound **1** is a zwitterionic salt containing two acidic protons, one from the appended $CH_2CH_2NHMe_2$ unit and the other from the open six-membered $C_2B_4$ face. Treatment of **1** with 1 equiv of $Hf(CH_2SiMe_3)_4$[11] in toluene at room temperature gave, after recrystallization from toluene, $[\eta^1{:}\eta^6\text{-}(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Hf(CH_2SiMe_3)_2$ (**2**) in 30% isolated yield (Scheme 1).[12] It is noteworthy that the corresponding zirconium analogue was not isolable, due to low thermal stability. Complex **2** was extremely air- and moisture-sensitive but was stable for days under an inert atmosphere in the solid state.

Complex **2** was fully characterized by $^1H$, $^{13}C$, and $^{11}B$ NMR spectroscopy and elemental analyses.[12] Its molecular structure was further confirmed by single-crystal X-ray diffraction studies.[13] The Hf atom is $\eta^6$ bound to the open $C_2B_4$ bonding face of a *nido*-carboranyl ligand, $\sigma$ bound to two $CH_2SiMe_3$ units, and coordinated to the nitrogen atom of the side arm in a three-legged piano-stool geometry, as shown in Figure 1. The Hf−cage atom distances range from 2.489(4) to 2.732(5) Å with an average value of 2.602(5) Å, indicating a highly asymmetrical $\eta^6$ bonding. Such a slip distortion may result from the intramolecular coordination of the functional side arm. As expected, this measured value is much longer than the average Hf−cage atom distances observed in the $C_2B_9$ system due to the larger bonding

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(10) To a THF (25 mL) solution of 1-$Me_2NCH_2CH_2$-1,2-$C_2B_{10}H_{11}$ (215 mg, 1.0 mmol) was added finely cut Na metal (230 mg, 10.00 mmol), and the mixture was stirred at room temperature for 3 days. After removal of excess Na and addition of $Me_3NHCl$ (191 mg, 2.0 mmol) at −30 °C, the reaction mixture was then stirred for 1 h at room temperature. The precipitate was filtered off and washed with THF (5 mL × 3). The THF solutions were then combined and concentrated under vacuum to give **1** as a white solid (200 mg, 92%). $^1H$ NMR (acetone-$d_6$): $\delta$ 3.62 (m, 2H, $CH_2CH_2NH(CH_3)_2$), 3.16 (s, 6H, $CH_2CH_2NH(CH_3)_2$), 2.82 (m, 2H, $CH_2CH_2NH(CH_3)_2$). $^{13}C$ NMR (acetone-$d_6$): $\delta$ 67.7 ($CH_2CH_2NH(CH_3)_2$), 60.6 ($CH_2CH_2NH(CH_3)_2$), 40.2 ($CH_2CH_2NH(CH_3)_2$), cage carbons were not observed. $^{11}B$ NMR (acetone-$d_6$): $\delta$ 17.6 (1B), 13.6 (1B), 7.8 (1B), −4.3 (2B), −9.1 (1B), −16.4 (1B), −18.9 (1B), −21.6 (1B), −31.6 (1B). IR (KBr, cm$^{-1}$): $\nu_{BH}$ 2524 (vs). Anal. Calcd for $C_6H_{23}B_{10}N$: C, 33.16; H, 10.67; N, 6.44. Found: C, 32.86; H, 10.39; N, 6.41.

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(12) To a toluene (15 mL) suspension of **1** (217 mg, 1.0 mmol) was slowly added a toluene (10 mL) solution of $Hf(CH_2SiMe_3)_4$ (527 mg, 1.0 mmol) with stirring at room temperature, and the reaction mixture was stirred overnight. The precipitate was filtered off and washed with toluene (5 mL × 2). The toluene solutions were then combined and concentrated under vacuum to about 10 mL, from which **2** was isolated as colorless crystals after this solution stood at room temperature overnight (170 mg, 30%). Mp: 53 °C dec. $^1H$ NMR (benzene-$d_6$): $\delta$ 2.65 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.33 (m, 2H, $CH_2CH_2N(CH_3)_2$), 2.15 (s, 6H, $CH_2CH_2N(CH_3)_2$), 1.79 (d, $J$ = 12.0 Hz, 2H, $CH_2Si(CH_3)_3$), 0.91 (d, $J$ = 12.0 Hz, 2H, $CH_2Si(CH_3)_3$), 0.48 (s, 18H, $CH_2Si(CH_3)_3$). $^{13}C$ NMR (benzene-$d_6$): $\delta$ 68.9 ($CH_2CH_2N(CH_3)_2$), 41.8 ($CH_2CH_2N(CH_3)_2$), 32.0 ($CH_2CH_2N(CH_3)_2$), 14.4 ($CH_2Si(CH_3)_3$), 3.1 ($CH_2Si(CH_3)_3$). $^{11}B$ NMR (benzene-$d_6$): $\delta$ 7.9 (1B), 3.5 (1B), 0.4 (2B), −3.2 (2B), −5.4 (3B), −21.3 (1B). IR (KBr, cm$^{-1}$): $\nu_{BH}$ 2529. Anal. Calcd for $C_{14}H_{43}B_{10}HfNSi_2$: C, 29.59; H, 7.63; N, 2.46. Found: C, 29.23; H, 7.22; N, 2.55.

(13) Crystal data for **2** ($C_{14}H_{43}B_{10}HfNSi_2$; fw, 568.3): monoclinic, space group $P2_1/n$, $a$ = 9.686(1) Å, $b$ = 17.468(1) Å, $c$ = 16.423(1) Å, $\beta$ = 103.43(1)°, $V$ = 2702.7(3) Å$^3$, $T$ = 293 K, $Z$ = 4, $d_{calcd}$ = 1.397 g/cm$^3$, R1 = 0.037 ($I > 2\sigma(I)$), wR2($F^2$) = 0.087.

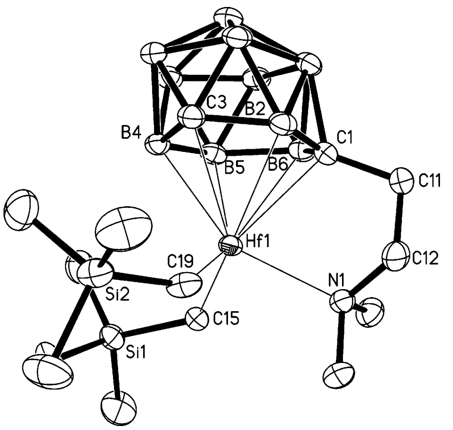

**Figure 1.** Molecular structure of $[\eta^1:\eta^6\text{-}(Me_2NCH_2CH_2)\text{-}C_2B_{10}H_{11}]Hf(CH_2SiMe_3)_2$ (**2**). Selected bond distances (Å) and angles (deg): Hf(1)−C(1) = 2.489(4), Hf(1)−B(2) = 2.705(5), Hf(1)−C(3) = 2.674(4), Hf(1)−B(4) = 2.418(5), Hf(1)−B(5) = 2.593(5), Hf(1)−B(6) = 2.732(5), Hf(1)−N(1) = 2.340(4), Hf(1)−C(15) = 2.173(4), Hf(1)−C(19) = 2.163(5); Si(1)−C(15)−Hf(1) = 130.7(2), Si(2)−C(19)−Hf(1) = 141.7(3), C(15)−Hf(1)−N(1) = 92.8(1), C(19)−Hf(1)−N(1) = 95.7(2), C(15)−Hf(1)−C(19) 105.2(2).

face: for example, 2.505(5) Å in $[Cp^*(C_2B_9H_{11})HfMe]_n$[3e] and 2.516(10) Å in $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5:\eta^1\text{-}C_2B_9H_{10})\text{-}Hf(Cp^*)(H)$,[3f] but is close to the average Zr−cage atom distance of 2.623(5) Å found in $[\eta^5:\eta^6:\sigma\text{-}Me_2Si(C_9H_6)\text{-}(C_2B_{10}H_{10}CH_2NMe)]Zr(NC_5H_5)$[6] if the difference, 0.02 Å, between Shannon's ionic radii[14] of Zr(IV) and Hf(IV) is taken into account. The Hf−C $\sigma$ bond distances of 2.173(4) and 2.163(5) Å with an average value of 2.168(5) Å compare to the average Hf−C distances of 2.261(12) Å in $(C_{23}H_{28}N_4\text{-}4,5)Hf(CH_2SiMe_3)_2$,[15a] 2.331(16) Å in $(C_{20}H_{22}N_4\text{-}3,3)Hf(CH_2SiMe_3)_2$,[15a] 2.316(8) Å in $Cp_2Hf(CH_2\text{-}CMe_2)(PMe_3)$,[15b] and 2.255(1) Å in $Cp_2Hf(CH_2CH_2CPh{=}CPh)$.[15c]

In summary, the alkane elimination reaction of $Hf(CH_2SiMe_3)_4$ with the zwitterionic salt $1\text{-}Me_2NHCH_2\text{-}CH_2\text{-}1,3\text{-}C_2B_{10}H_{12}$ (**1**) resulted in the isolation and structural characterization of the first example of half-sandwich group 4 metallacarborane alkyls of the $C_2B_{10}$ system. The advantages of using **1** as a reagent are as follows: (1) to avoid redox reactions, facilitating the formation of high-valent group 4 metallacarboranes, (2) to stabilize the resultant metal alkyl complexes via the intramolecular coordination, and (3) to provide the second acidic proton. This is also a new route to high-valent group 4 metallacarboranes.

**Acknowledgment.** The work described in this article was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. CUHK4254/01P), Direct Grant (Project No. 2060274), and State Key Laboratory of Elemento-Organic Chemistry, Nankai University (Project No. 0314).

**Supporting Information Available:** Tables of crystallographic data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complex **2** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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