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Synthesis, structure, and reactivity of mixed-sandwich zirconacarborane methyl complex (η^5-C_5Me_5)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]ZrMe

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ABSTRACT

A neutral mixed-sandwich zirconacarborane methyl complex (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**1**) (Cp* = C_5Me_5) was prepared via methane elimination reaction of 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ with (η^5-Cp*)$ZrMe_3$. It underwent intramolecular C–H activation at 70 °C to afford [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]Zr(η^5-Cp*) (**2**) and eliminate CH_4. This complex reacted with internal alkynes to give the Zr–C σ bond mono-insertion products, in which both electronic and steric factors played a role in controlling the regioselectivity of the insertion process. In the case of terminal alkynes, both insertion and acid-base reaction products were obtained, dependent upon the substituents. On the other hand, complex **1** reacted with alkyl nitriles at room temperature to give the mono-insertion zirconacarborane imide complexes, whereas high temperature was required to promote the insertion reaction with aryl nitrile, generating a different type of insertion product, zirconacarborane amide. All new complexes were characterized by NMR spectroscopy and elemental analyses. Most of them were further confirmed by single-crystal X-ray analyses.

1. Introduction

Ligands impose a dominant control over both chemical and physical properties of the resultant metal complexes. It is documented that incorporation of a dicarbollide fragment into the ligand framework provides new metal/charge combinations, which has an impact on the properties of metal complexes [1]. For example, replacement of an uninegative $C_5R_5^-$ in 14e$^-$ group 4 metallocene alkyl cations of the general type $(C_5R_5)_2M(R)^+$ by a dinegative isolobal $C_2B_9H_{11}^{2-}$ ligand leads to the formation of a class of neutral mixed-sandwich group 4 metallacarborane alkyls $(C_5Me_5)(C_2B_9H_{11})M(R)$ that exhibit rich insertion, olefin polymerization, and C–H bond activation chemistry [2], similar to those of cationic species $(C_5R_5)_2M(R)^+$ [3]. To improve the kinetic and thermal stability of such reactive neutral metallacarborane alkyls like $(C_5Me_5)(C_2B_9H_{11})ZrMe$ [2], we have introduced Me_2C/H_2C linkage to prepare carbon-bridged hybrid ligands $[Me_2C(C_5H_4)(C_2B_9H_{10})]^{3-}$, $[Me_2C(C_9H_6)(C_2B_9H_{10})]^{3-}$ and $[H_2C(C_5Me_5)(C_2B_9H_{10})]^{3-}$, resulting in the formation of ansa-metallocene dialkyl anionic complexes rather than the expected neutral metallocene alkyls [4]. This can be ascribed to the more open “bite angles” [4,5] of the resultant ansa-metallocenes in comparison with the corresponding unbridged ones [2], facilitating the binding of additional alkyl ligand. An alternative way to address the stability issue is to incorporate a functional sidearm to the dicarbollyl ligand in the hope that coordination of the heteroatom from the sidearm could occupy one binding site, enhancing the stability [6]. With this in mind, reaction of Cp”$ZrMe_3$ (Cp” = 1,3-$(Me_3Si)_2C_5H_3$) with the zwitterionic salt 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ gives a mixed-sandwich zirconacarborane [η^1:σ:η^5-{$MeN(CH_2)CH_2CH_2$}$C_2B_9H_{10}$]ZrCp”, rather than the expected zirconacarborane methyl complex (Cp”)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]ZrMe [7]. In order to make a close comparison to the known complex $(C_5Me_5)(C_2B_9H_{11})ZrMe$ [2a], so as to learn the factors dominating the thermal stability and reactivity of such type of complexes, we have synthesized (C_5Me_5)[η^1:η^5-($Me_2NCH_2CH_2$)

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$C_2B_9H_{10}$]ZrMe and studied its reactivity patterns toward various kinds of alkynes and nitriles. These results are reported in this article.

2. Results and discussion

2.1. Synthesis and structure of 1 and 2

Alkane elimination is a general method for the clean formation of zirconacarborane alkyl complexes [8]. Treatment of (η^5-Cp*)$ZrMe_3$ (Cp* = C_5Me_5) with 1 equiv of zwitterionic dicarbollide salt 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ in THF at room temperature afforded a mixed-sandwich zirconacarborane methyl complex (η^5-Cp*)[η^1:η^5-($Me_2NCH_2CH_2$)$C_2B_9H_{10}$]Zr(Me) (**1**) in 91% isolated yield (Scheme 1). Complex **1** was very stable at room temperature. However, upon heating a toluene solution of **1** at 70 °C overnight, [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp*) (**2**) was formed quantitatively via the rupture of a C–H bond at one of the *N*-methyl groups (Scheme 1). Such intramolecular C–H activation has been observed in methylzirconocenes [8a,b,9] and group 4 metallacarborane alkyls [2b,2g,10].

Both complexes **1** and **2** were fully characterized by various spectroscopic techniques and elemental analyses. In addition to the resonances corresponding to the protons of Cp* and sidearm, the ^{1}H NMR spectrum of **1** showed a broad singlet at 4.23 ppm assignable to the cage C*H* and one singlet at 0.54 ppm attributable to the Zr–CH_3 protons. On the other hand, one broad singlet at 2.95 ppm attributable to the cage C*H* and two doublets at 2.10 and 1.51 ppm with J = 9.0 Hz assignable to the Zr–CH_2 unit were observed in the ^{1}H NMR spectrum of **2**. Their ^{11}B NMR spectra showed a 1:1:1:1:1:1:1:1:1 pattern.

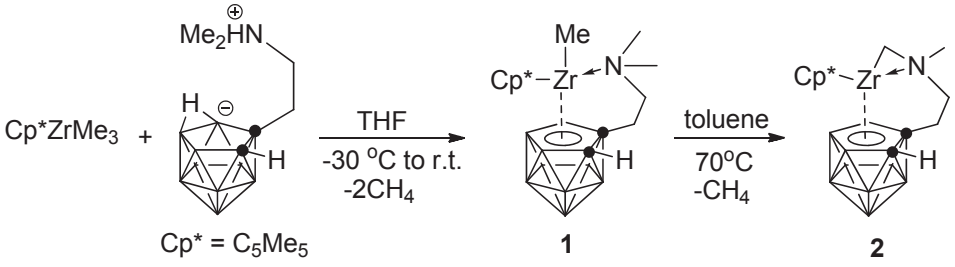
The molecular structures of **1** and **2** were further confirmed by single-crystal X-ray analyses. Their key structural parameters are compiled in Table 1. The Zr atom in **1** and **2** is η^5-bound to both cyclopentadienyl ring and dicarbollyl ligand, σ-bound to one carbon atom (from a methyl unit in **1** and a methylene group in **2**, respectively) and coordinated to the N atom in a three-legged piano stool geometry (Figs. 1 and 2). The average Zr–C_5 ring distances of 2.565(3) Å in 1 and 2.543(3) Å in **2** are comparable to that of 2.533(6)/2.535(7) Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2) [2a] and 2.538(9) Å in (Cp*)[Me_2C(Cp)($C_2B_{10}H_{10}$)]ZrCl [11], but are longer than that of 2.505(4) Å in (Cp*)($C_2B_9H_{11}$)Zr[C(Me)=CMe_2] [2a], and 2.509(5) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') [7]. The average Zr-cage atom distance of 2.582(3) Å in **1** is longer than that of 2.534(3) Å in **2**, 2.522(5) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') [7], 2.535(7)/2.533(8) Å in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2) [2a], and 2.544(6) Å in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(CH_2SiMe_3)(THF) [10]. The Zr–Me distance of 2.300(3) Å in **1** is similar to that of 2.282(3)/2.270(2) Å in Cp*Zr(2,4-^{t}Bu_2-6-(OCH_2CH_2N=CH)–C_6H_2O)Me_2 [12], and 2.282(2) Å in (Cp'')(Cp*)ZrH(Me) [13], but is longer than that of 2.245(2)/2.236(2) Å in Cp*Zr(CH_3)$_2$($CB_{11}H_{12}$) [14], and 2.260(3) Å [Zr–C(N)] in **2**. The Cent(C_5 ring)-Zr-Cent(C_2B_3) angles of 135.7° in **1** and 138.3° in **2** compare with that of 134.9° in [(Cp*)($C_2B_9H_{11}$)Zr]$_2$(μ-CH_2) [2a] and 140.0° in [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') [7]. These measured values are significantly larger than those observed in the corresponding *ansa*-metallocenes, such as [η^5:η^5-Me_2C(C_5Me_4)($C_2B_9H_{10}$)]Zr($NHC_6H_3Pr^i_2$)(THF) (119.2°) [4a], [η^5:η^5-Me_2C(C_9H_6)($C_2B_9H_{10}$)]Zr(NMe_2)($NHMe_2$) (115.9°) [4b] and [η^5:η^5-Me_2C(C_5Me_4)($C_2B_9H_{10}$)]Zr[σ:σ-CH_2(NMe_2)-*o*-C_6H_4] (120.2°) [4c].

2.2. Reaction with symmetrical alkynes

It is documented that [Cp*($C_2B_9H_{11}$)$ZrCH_3$]$_n$ can catalyze ethylene polymerization in the absence of any co-catalyst [2a,b]. However, zirconacarborane complexes **1** and **2** showed no reactivity toward alkenes even under harsh reaction conditions, due probably to the intramolecular coordination of N atom from sidearm, leading to decreased Lewis acidity of the Zr center. Complex **1** did not react with alkynes at room temperature. On the other hand, **2** reacted readily with 1 equiv of EtC≡CEt in THF at room temperature to afford the alkyne insertion product **3a** in 92% isolated yield. This result indicates that a strained three-membered zirconacycle can promote the insertion of alkyne into the Zr–C bond. Subsequently, treatment of **1** with 1 equiv of symmetrical internal alkynes RC≡CR in refluxing THF gave, after recrystallization from THF, the mono-insertion products (η^5-Cp*)[η^1:σ:η^5-{MeN[CH_2(R)C=C(R)]CH_2CH_2}$C_2B_9H_{10}$]Zr (R = Et, **3a**; ^{n}Pr, **3b**; ^{n}Bu, **3c**) in 82–86% isolated yields (Scheme 2). It is suggested that all reactions proceed via an intermediate **2**. The resultant complexes **3** did not show any reactivity towards another equivalent of alkynes, probably owing to the stronger Zr–C(sp^2) bond and less ring-strain of the insertion products.

Complexes **3a-c** were characterized by various spectroscopic techniques and elemental analyses. The main features of their NMR spectra were two doublets at ~3.6 and ~2.8 ppm attributable to the methylene protons of NCH_2C(sp^2) in the ^{1}H NMR spectra and two characteristic vinyl carbon resonances at ~196 and ~137 ppm in the ^{13}C NMR spectra.

The molecular structures of **3a**–**c** were further confirmed by single-crystal X-ray analyses, in which the Zr atom is η^5-bound to both Cp* ring and dicarbollyl ligand, σ-bound to sp^2-C atom of the vinyl unit and coordinated to the N atom from the sidearm in a three-legged piano stool geometry as shown in Figs. 3–5, respectively. Their key structural parameters are compiled in Table 1 for comparison. The Zr–C_5 ring, Zr-cage atom distances as well as the Cent(C_5)–Zr-Cent(C_2B_3) angles in **3a-c** are close to those observed in **1** and **2**. The Zr–C(sp^2) distances of 2.285(5) Å in **3a**, 2.286(3) Å in **3b** and 2.295(5) Å in **3c** fall in the range 2.27–2.34 Å found for the Zr–C(sp^2) bond distances in (η^5-Cp'')[η^1:σ:η^5-{MeN[CH_2(R)C=C(R)]CH_2CH_2}$C_2B_9H_{10}$]Zr [7].



Scheme 1. Synthesis of mixed-sandwich zirconacarborane alkyls.