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Reaction of $[\sigma{:}\eta^5\text{-}(C_9H_6)C_2B_9H_{10}]Zr(NMe_2)(DME)$ with Guanidines: Metallacarborane-Mediated C−N Bond Cleavage and 1,5-Sigmatropic Rearrangement

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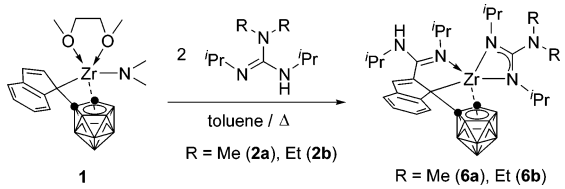
Guanidine derivatives, as electronically and sterically flexible ligands, have received increasing attention. They are capable of exhibiting a variety of coordination modes and a range of donor properties leading to compatibility with a wide range of metal ions from all parts of the periodic table.[1,2] The inert nature of guanidinates as suitable spectator ligands supporting organometallic fragments is well demonstrated in various types of reactions of $[\eta^2\text{-}(^i\text{PrN})_2C(NR_2)]ZrCl_2$.[2d] In view of these, we would like to incorporate guanidinates into metallacarboranes[3] to study the effects of metal/charge combinations on the reactivity of group 4 metal complexes. From the reaction of **1** with 2 equiv of guanidines, we isolated unprecedented zirconacarboranes **6**.[4] This result shows clearly that C−N bond-breaking and C−C bond-forming reactions are involved in the process, and the Zr−indenyl σ-bond remains surprisingly in the product. This communication describes the mechanism by which they are formed.

Treatment of **1** with 2 equiv of guanidines ^{i}PrNHC(NR$_2$)=N^{i}Pr (R = Me (**2a**), Et (**2b**)) in refluxing toluene gave $[\eta^1{:}\sigma{:}\eta^5\text{-}\{2\text{-}[C{=}N^i\text{-}Pr(NH^iPr)]C_9H_5\}C_2B_9H_{10}]Zr[\eta^2\text{-}(^i\text{PrN})_2C(NR_2)]$ (R = Me (**6a**), Et (**6b**)) in 30−47% isolated yields (Scheme 1).[4] The molecular structures of both **6a**,**b** were confirmed by single-crystal X-ray analyses. The key structural data indicate that the interactions between the Zr atom and the indenyl−dicarbollyl unit in **6a**,**b** are very similar to those observed in **1**.[4]

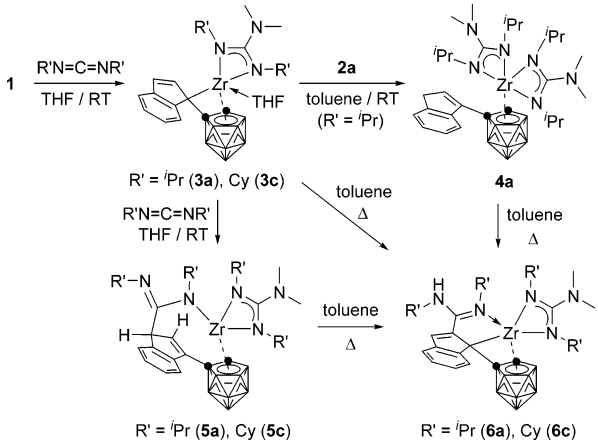
The ^{1}H NMR spectra showed that the molar ratio of R$_2$N/^{i}Pr = 1/4 in **6** rather than the expected 1/2, suggesting that one of R$_2$N groups was dissociated from the guanidinate unit during the reaction. The NMR experiments indicated the formation of both Me$_2$NH and Et$_2$NH in the reaction mixture of **1** with **2b**, which was further confirmed by GC/MS. This result may suggest that (1) 1 equiv of **2b** reacts with **1** via amine exchange to give Me$_2$NH and the guanidinate ligand which is η^2-bound to the Zr atom,[5] and (2) the second equivalent of **2b** undergoes presumably a C−NEt$_2$ bond cleavage, generating Et$_2$NH and the amidine. To gain some insight into these reactions, a stepwise reaction of **1** with carbodiimides R′N=C=NR′ was performed.

An equimolar reaction of **1** with R′N=C=NR′ in THF at room temperature afforded monoinsertion products $[\sigma{:}\eta^5\text{-}(C_9H_6)C_2B_9H_{10}]\text{-}Zr[\eta^2\text{-}(R'N)_2C(NMe_2)](THF)$ (R′ = ^{i}Pr (**3a**), Cy (cyclohexyl; **3c**)) in 71−74% isolated yields (Scheme 2).[4] They were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopic techniques and elemental analyses. The proton chemical shift of the Me$_2$N group was shifted from 3.11 ppm in **1** to 2.64 ppm in **3a** and 2.70 ppm in **3c**, respectively. A characteristic *C*N$_3$ resonance at 174.4 ppm in **3a** and 174.0 ppm in **3c** was observed in their ^{13}C NMR spectra. The spectroscopic features of the indenyl group are very similar in both **1** and **3**. These data suggested that R′N=C=NR′ inserted into the Zr−N bond to form a guanidinate unit. The bonding interactions between the indenyl and Zr atom remained intact, which probably

Scheme 1. Reaction of **1** with Guanidines



Scheme 2. Transformations among Complexes **1**−**6**



indicates that the indenyl group may be η^3-bound to the Zr atom in the solution.[6]

Treatment of **3a**,**c** with 1 equiv of R′N=C=NR′ in THF at room temperature generated another type of insertion products $[\sigma{:}\eta^5\text{-}\{3\text{-}[C(=NR')\text{-}NR']\text{-}1\text{-}C_9H_6\}C_2B_9H_{10}]Zr[\eta^2\text{-}(R'N)_2C(NMe_2)]$ (R′ = ^{i}Pr (**5a**), Cy (**5c**)) in >90% isolated yields (Scheme 2).[4] Both structures were confirmed by single-crystal X-ray analyses.[4] It is very clear that the R′N=C=NR′ inserted into the 3-position, rather than 1-position, of the indenyl ring. This result supported the argument of an η^3-bonding mode between the indenyl and Zr atom in the solution of **3a**,**c**.

Complexes **5a**,**c** were quantitatively converted to $[\eta^1{:}\sigma{:}\eta^5\text{-}\{2\text{-}[C{=}NR'(NHR')]C_9H_5\}C_2B_9H_{10}]Zr[\eta^2\text{-}(R'N)_2C(NMe_2)]$ (R = ^{i}Pr (**6a**), Cy (**6c**)) upon refluxing in toluene.[4] This can be rationalized by 1,5-sigmatropic rearrangement (vide infra).[7] The molecular structure of **6c** is very similar to that of **6a**,**b** as confirmed by single-crystal X-ray analyses.[4]

Reaction of **3a** with 1 equiv of **2a** in toluene at room temperature gave proton exchange product $[\eta^5\text{-}(C_9H_7)C_2B_9H_{10}]Zr[\eta^2\text{-}(^i\text{PrN})_2C\text{-}(NMe_2)]_2$ (**4a**) in 79% isolated yield.[4,8] Its molecular structure shows that the Zr atom has no bonding interactions with the neutral indenyl ring. Complex **4a** was converted to **6a** upon refluxing in toluene, from which **6a** was isolated in 62% yield[4] and Me$_2$NH was detected by GC/MS. Complex **6a** was also isolated in 31% yield[4] from the

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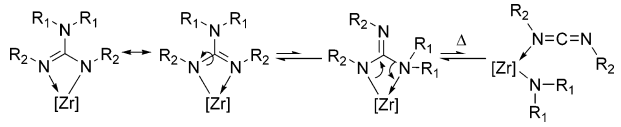
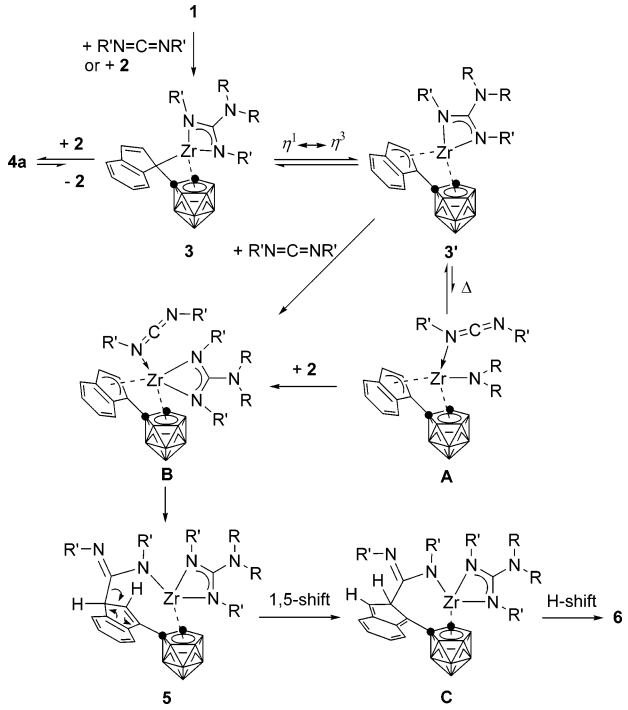
Scheme 3. Proposed Pathway for C−N Bond Cleavage



Scheme 4. Proposed Mechanism for the Formation of **6**



refluxing toluene solution of **3a**. The formation of Me_2NH was confirmed by GC/MS. These transformations are outlined in Scheme 2.

A mechanism for the C−N bond cleavage of a guanidinate unit is proposed in Scheme 3. This process may be driven by heat and can be viewed as a deinsertion of a carbodiimide from the guanidinate ligand.[9] This proposal is evident from the following carbodiimide exchange experiments. Treatment of **3c** with 8 equiv of ^{i}PrN═C═N^{i}Pr in refluxing toluene afforded **6a** in 18% isolated yield. On the other hand, under the same reaction conditions, reaction of **4a** with 6 equiv of CyN═C═NCy generated **6c** in 12% isolated yield.

On the basis of the aforementioned experimental results, a proposed mechanism for the formation of complexes **6** is illustrated in Scheme 4. Reaction of **1** with carbodiimides or guanidines **2** yields **3** which is able to react reversibly with another equivalent of **2** to generate **4**. Heating of **3**/**3′** results in the cleavage of the C−N bond and in situ generation of carbodiimide and amido, leading to the formation of intermediate **A**. Interaction of **A** with **2** or of **3′** with carbodiimide produces **B** which gives **5** via an insertion reaction. 1,5-Sigmatropic rearrangement[7] over the indenyl ring in **5** affords **C**, which undergoes an intramolecular proton-transfer reaction to generate the final products **6**.

In conclusion, although it is well-established that insertion of carbodiimides into amides is a very useful method for the preparation of guanidines,[2m−o,10] this work provides experimental evidence for the corresponding reverse reaction. In other words, guanidinates are not inert ligands in certain cases that can undergo C−N bond cleavage to form carbodiimides and amido units.

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Supporting Information Available: Detailed experimental procedures, full characterization data, and X-ray data for **1**, **4a**, **5a**·C_7H_8, **5c**·C_7H_8, **6a**, **6b**, and **6c**·THF in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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