Characterization of $\beta$-B-Agostic Isomers in Zirconocene Amidoborane Complexes

Forster, Taryn; Tuononen, Heikki; Parvez, Masood; Roesler, Roland


All material supplied via JYX is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Characterization of β-B-Agostic Isomers in Zirconocene Amidoborane Complexes

Taryn D. Forster, Heikki M. Tuononen, Masood Parvez, and Roland Roesler*

Contribution from the Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4 Canada, and Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40014 Jyväskylä, Finland

roesler@ucalgary.ca

The agostic interaction is a thoroughly documented and well understood concept in organometallic chemistry, playing an essential role in transition metal catalysis. In spite of the ubiquity of complexes featuring agostic interactions, to our knowledge no stoereoisomers differing through the position of the C-H-M bond (agostic isomers) have been reported, although such species are believed to be responsible for determining the outcome of certain catalytic reactions, such as the stereochemistry in olefin polymerization. The pronounced hydridic nature of the B-H moiety renders the 3-center-2-electron B-H-M bonds considerably less elusive than the classical agostic interactions and numerous transition metal hydridoborate and related metal σ-borane complexes have been structurally characterized. Although the B-H-M and C-H-M interactions are based on closely related concepts, it has been stressed that the term “agostic interaction” should be restricted to hydrocarbon H-M and C-H-M interactions.

The reaction of Cp₂ZrCl₂ with two equivalents of NH₂-BH₃ in the presence of nBuLi produced cleanly the zirconocene hydride complexes 1 and 2 (Scheme 1). Reaction of Cp₂ZrCl₂ with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.

The reaction of Cp₂Zr(NH₂)BH₃ with ammonia borane as a hydrogen source, amidoborane alkali and earth alkali, were very recently reported, although attempts to prepare Cp₂Zr(NH₂)BH₃ however, attempts to prepare Cp₂Zr(NH₂)BH₃(4) with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.

The agostic interaction is a thoroughly documented and well understood concept in organometallic chemistry, playing an essential role in transition metal catalysis. In spite of the ubiquity of complexes featuring agostic interactions, to our knowledge no stoereoisomers differing through the position of the C-H-M bond (agostic isomers) have been reported, although such species are believed to be responsible for determining the outcome of certain catalytic reactions, such as the stereochemistry in olefin polymerization. The pronounced hydridic nature of the B-H moiety renders the 3-center-2-electron B-H-M bonds considerably less elusive than the classical agostic interactions and numerous transition metal hydridoborate and related metal σ-borane complexes have been structurally characterized. Although the B-H-M and C-H-M interactions are based on closely related concepts, it has been stressed that the term “agostic interaction” should be restricted to hydrocarbon H-M and C-H-M interactions.

The reaction of Cp₂ZrCl₂ with two equivalents of NH₂-BH₃ in the presence of nBuLi produced cleanly the zirconocene hydride complexes 1 and 2 (Scheme 1). Reaction of Cp₂ZrCl₂ with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.

The agostic interaction is a thoroughly documented and well understood concept in organometallic chemistry, playing an essential role in transition metal catalysis. In spite of the ubiquity of complexes featuring agostic interactions, to our knowledge no stoereoisomers differing through the position of the C-H-M bond (agostic isomers) have been reported, although such species are believed to be responsible for determining the outcome of certain catalytic reactions, such as the stereochemistry in olefin polymerization. The pronounced hydridic nature of the B-H moiety renders the 3-center-2-electron B-H-M bonds considerably less elusive than the classical agostic interactions and numerous transition metal hydridoborate and related metal σ-borane complexes have been structurally characterized. Although the B-H-M and C-H-M interactions are based on closely related concepts, it has been stressed that the term “agostic interaction” should be restricted to hydrocarbon H-M and C-H-M interactions.

The reaction of Cp₂ZrCl₂ with two equivalents of NH₂-BH₃ in the presence of nBuLi produced cleanly the zirconocene hydride complexes 1 and 2 (Scheme 1). Reaction of Cp₂ZrCl₂ with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.

The reaction of Cp₂ZrCl₂ with two equivalents of NH₂-BH₃ in the presence of nBuLi produced cleanly the zirconocene hydride complexes 1 and 2 (Scheme 1). Reaction of Cp₂ZrCl₂ with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.

The reaction of Cp₂ZrCl₂ with two equivalents of NH₂-BH₃ in the presence of nBuLi produced cleanly the zirconocene hydride complexes 1 and 2 (Scheme 1). Reaction of Cp₂ZrCl₂ with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.

The reaction of Cp₂ZrCl₂ with two equivalents of NH₂-BH₃ in the presence of nBuLi produced cleanly the zirconocene hydride complexes 1 and 2 (Scheme 1). Reaction of Cp₂ZrCl₂ with one equivalent of H₁-N-BH₃ and nBuLi yielded 3; however, attempts to prepare Cp₂Zr(Cl)NH₂-BH₃ (4) yielded only mixtures of 2 and unreacted Cp₂ZrCl₂. A plausible mechanism for the formation of 1 via the intermediate 3 would involve salt metathesis and formation of the sterically encumbered complex Cp₂Zr(NH₂BH₃), followed by spontaneous β-hydride elimination, which is common for metal ethyl derivatives. The steric strain provided by the bulky Cp₂ ligands in 4 could promote β-hydride elimination with formation of Cp₂Zr(HCl), which would undergo further salt metathesis to yield the sterically less encumbered complex 2. All complexes were isolated as colorless crystalline solids. The expected by-products of β-hydride elimination, cyclic borazine oligomers or open-chain polymers, were not identified.
distinct, sharp quartet resonances around -34, -31 and -23 ppm respectively, with $^{1}J_{BH} = 88 - 94$ Hz. This is comparable to the value of 92 Hz observed for ammonia borane, confirming that all three hydrogen atoms in each isomer are equivalent on NMR time scale.

![Figure 2. Simulated and experimental powder X-ray pattern of 1.](image)

Single crystal X-ray diffraction for samples of 1 revealed two coexisting polymorphs, 1bI and 1bII. Their metric parameters are very similar and only the former will be discussed. The crystal structures of 2b and 3a were also determined, however, the former suffered from significant disorder of the Cp ligands, preventing the location of the hydrogen atoms even at -150 °C, and will not be discussed. The molecular structure of 2b is nevertheless similar to the structure of 1b. The most important feature of all structures is the chelating NH$^-$BH$_3^-$ ligand, which binds to the metal through a Zr-N bond and a Zr-H-B bridge. The resulting planar Zr-N-B fragment is strikingly similar to the structure of the ZrCl fragment (Zr-Cl 2.137(2) Å, Zr-Cl 2.629(9) Å, vs. Zr-N 2.268(3) - 2.286(4) Å, Zr-N 1.523(5) - 1.539(7) Å, Zr-Cl 2.657(2) - 2.685(4) Å). The slight shortening of the B-N bond in ammonia borane, 1.597(3) Å, mirrors the shortening of the C=C bond in $\beta$-agostic ethylene complexes, which bind to the metal through $\eta$-agostic interaction. The NH$^-$BH$_3^-$ moiety around the BN bond in 1b is indeed situated trans to the nitrogen atom while the chloride in 3a is situated trans to the boron atom. The presence of pairs of resonances with solvent-dependent relative ratios in the NMR spectra of 1, 2 and 3 indicates that, for each compound, the two isomers coexist and are in equilibrium. The cross-peaks for the Cp protons in the EXSY NMR spectra of 1 and 3 in toluene-d$_4$ confirmed this supposition and the exchange rates were estimated at 0.27 s$^{-1}$ at 20 °C and 0.05 s$^{-1}$ at -20 °C for the former and 0.01 s$^{-1}$ at 20 °C for the latter. Powder X-ray diffraction showed that 1bI is the main constituent of 1 in the solid state, with no detectable amount of 1bII being present (Figure 2). No other major crystalline constituents were observed, and elemental analysis proved the purity of the sample.

![Figure 3. Variable temperature $^1$H($^1$B) NMR spectra of 1 in toluene-d$_4$, showing the area featuring the resonances corresponding to the protons in the NH$^-$BH$_3^-$ ligand.](image)

A variable-temperature boron-decoupled $^1$H NMR study of 1 in toluene-d$_4$ allowed for a more precise assignment of the resonances corresponding to the hydrogen atoms attached to boron (Figure 3). At 60 °C, these hydrogen atoms are equivalent on the NMR time scale and generate a sharper resonance at 0.01 ppm (1b) and a broader one at -0.38 ppm (1a). The resonance at 0.01 ppm broadens upon cooling and shifts slightly downward, reaching 0.31 ppm at -80 °C. The broader resonance at -0.38 ppm coalesces around 0 °C and splits upon further cooling into two signals in a 2 : 1 ratio at 1.17 and -2.88 ppm (at -80 °C), corresponding to the terminal (BH$_2$) and bridging (BH-Zr) hydrogen atoms, respectively, in 1a. This behavior indicates a noticeably lower free enthalpy of activation with respect to the rotation of the BH$_3$ moiety around the BN bond in 1b than in 1a, where $\Delta G^{\ddagger}_{273}$ was estimated using NMR data to be 48 kJ·mol$^{-1}$. A lower free enthalpy of activation would be expected in 1b, where...
the BH3 moiety experiences less steric strain from the Cp groups when compared to 1a, in which the tilted Cp groups sandwich the BH3 moiety more tightly. A computational study confirmed this supposition, estimating the enthalpy of activation with respect to the rotation of the BH3 moiety around the BN bond at 46 kJ mol⁻¹ in 1a and 19 kJ mol⁻¹ in 1b, allowing for the correlation between the solid-state structures and the NMR signals. Between -80 and -90 °C, NMR reveals that 1b starts to crystallize out of the toluene solution, in good agreement with the results of the solid state structural studies.

The low-temperature ¹H NMR spectra of 1a,b featured broad signals corresponding to the BH protons, preventing the determination of the ¹JBH coupling constant. Similarly, the ¹JHH coupling was not resolved in the low-temperature ¹H NMR spectra. COSY NMR was used for the assignment of the peaks in the ¹H NMR spectra of 1a,b. Cross-peaks were observed between the resonances assigned to the terminal zirconium hydride and those corresponding to the terminal BH3 protons, as well as to those corresponding to the bridging BH and temperature-averaged BH3 protons in both isomers. The scalar coupling confirmed that the β-B-agarstic interaction is preserved in solution in both 1a and 1b.

An open-chain isomer would be expected to be considerably higher in energy and its relative concentration would be expected to be strongly temperature dependent. A computational analysis showed the structurally characterized derivatives 1b and 2b to be, in vacuum, energetically on par with their isomers 1a and 2a, respectively, with the energy differences between them being less than the expected accuracy of the employed method. Under the same conditions, the crystallized isomer 3a was ca. 25 kJ mol⁻¹ more stable than 3b. In all cases, the energy minima were very shallow because of the low energy barrier for the rotation of the Cp²Cp² groups and, more importantly, the improbable open-chain isomers featuring monodentate amidoborane ligands were not found to constitute stable minima on the potential energy surface.

In conclusion, we report herein the first structural characterization of transition metal amidoborane complexes. All complexes feature chelating NH=BH⁻ ligands binding through a Zr-N bond and a classical Zr-H-B bridge and their structural and spectroscopic properties mirror the properties of their isoelectronic β-agarstic ethyl analogs. The relative position of the amidoborane ligand with respect to the chloride or hydride ligand on zirconium gives rise to stereoisomers that have not been characterized in the chemistry of less robust β-agarstic derivatives. The parallel between the more stable β-B-agarstic amidoborane complexes and their isoelectronic β-agarstic ethyl analogs should allow for a better understanding of both systems. In addition, the structure and dynamic of the derivatives characterized herein is relevant to the thriving field of catalytic hydrogen generation from ammonia borane.

Acknowledgement. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, the Academy of Finland and the Alberta Science and Research Investments Program. We thank Dr. Venkataraman Thangadurai for support with powder X-diffraction experiments, Dr. Farideh Jalilehvand for the Raman measurements and Dr. Tom Ziegler for helpful discussions. TDJ thanks the NSERC for a CGS-D scholarship.

Supporting Information Available: Experimental details and complete spectroscopic data for 1–3, crystallographic details including CIF files for 1b, 1bII, and 3a, powder X-ray diffraction data for 1, and computational details for 1–4. This material is available free of charge via the internet at http://pubs.acs.org.