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Communications

Chemoselective Deprotonations of a Cationic Zirconium Primary Amido Complex to Either a Neutral Zirconium Terminal Imido or a Noninterconverting Tautomer

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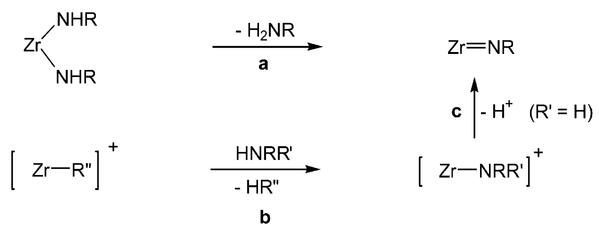
Summary: Chemoselective deprotonation of {Cp*Zr(NH^{t}Bu)[N(^{i}Pr)C(Me)N(^{i}Pr)]}[B(C$_6$F$_5$)$_4$] (**2a**) *cleanly provides either the neutral enolamide,* Cp*Zr(NH^{t}Bu)[N(^{i}Pr)C(CH$_2$)N(^{i}Pr)] (**5**), *or the terminal imido,* Cp*Zr(N^{t}Bu)[N(^{i}Pr)C(CH$_3$)N(^{i}Pr)] (**6**). *These two tautomers do not interconvert, and no evidence was obtained for deprotonation of* **2a** *in the presence of an excess of the primary amine* ^{t}BuNH$_2$.

Inter- and intramolecular metal-catalyzed hydroaminations of carbon−carbon multiple bonds (i.e., alkenes, alkynes, and allenes) represent highly desirable synthetic organic transformations.[1] In this regard, Bergman and Doye pioneered the use of zirconium and titaninum bis(amido) complexes as catalysts for the intermolecular hydroamination of alkynes and allenes with primary amines.[2,3] For these transformations, support now exists for a mechanism in which the bis(amido) metal complex undergoes α-elimination of a primary amine to generate a highly reactive transient metal terminal imido species according to path **a** in Scheme 1. Unfortunately, in contrast to their reactivity with alkynes, such group 4 metal imido complexes do not appear to readily engage in [2+2] cycloadditions with alkenes,[4] and therefore, the development of well-defined group 4 metal catalysts for the more thermodynamically difficult intermolecular hydroamination of alkenes with primary amines remains a major challenge. Recently, Scott and co-workers[5] introduced a successful strategy for the intramolecular hydroamination cyclization of aminoalkenes that is reasonably proposed to proceed via alkene insertion into the Zr−N bond of a cationic metal amido species that is initially generated in situ through aminolysis of a zirconium alkyl cation precursor according to path **b** in Scheme 1. The inactivity of ω-aminoalkenes containing primary amine groups (i.e., R′ = H in Scheme 1) to undergo similar hydroaminations was tentatively rationalized as possibly being due to facile deprotonation of the corresponding cationic zirconium primary amido complex to generate a neutral zirconium imido species according to path **c** in Scheme 1, which, as previously stated, would then be unreactive toward alkenes. Herein, we experimentally probe this deprotonation hypothesis further using relevant, well-characterized model complexes in order to better understand the relative importance of this possible deactivation process that could represent a significant barrier to the development of successful cationic group 4 metal amido catalysts for the hydroamination of alkenes with primary amines.

Scheme 1



Our interest in hydroamination stems from previous studies establishing that cationic methyl monocyclopentadienylzirconium acetamidinate complexes of the general formula {Cp*Zr(X)[N(R^1)C(Me)N(R^2)]}[B(C$_6$F$_5$)$_4$] (Cp* = η^5-C$_5$Me$_5$, R^1 and R^2 = alkyl, X = Me) (**1**) can function as highly active initiators for the living Ziegler−Natta polymerization of α-olefins.[6] Thus, we became intrigued with the question of whether the corresponding coordinatively unsaturated cationic zirconium primary amido complexes **2** (X = NHR′ in **1**) could serve in the capacity of catalysts for the hydroamination of alkenes by primary amines. To systematically explore this concept, we desired a synthesis that could generate these coordinatively unsaturated, highly electron deficient, cationic metal complexes in the absence of any strong σ-donors, such as amines.

To begin, protonolysis of the η^2-styrene zirconium complex **3**[7] with 2 equiv of ^{t}BuNH$_2$ cleanly provided a high yield of the bisamido species **4** according to Scheme 2.[8] As the zirconacyclopropane ring of **3** has been shown to undergo ring-opening protonolysis with terminal acetylenes,[7] the coproduct of this reaction is presumed to be ethylbenzene. Interestingly, all

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[1] For recent reviews, see: (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686. (b) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935−946. (c) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391.

[2] See for instance: (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708−1719. (b) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753−2763.

[3] Doye, S. *Synlett* **2004**, 1653−1672, and references therein.

[4] A few reports of the reversible [2+2] cycloaddition of ethene and norbornene to group 4 and 5 imido complexes have appeared, see: (a) de With, J.; Horton, A. D. *Organometallics* **1993**, *12*, 1493−1496. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723. (c) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179−2180.

[5] Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N. O.; Scott, P. *J. Chem. Soc., Chem. Commun.* **2004**, 894−895.

[6] (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959. (b) Kissounko, D. A.; Zhang, Y.; Harney, M. B.; Sita, L. R. *Adv. Synth. Catal.* **2005**, *347*, 426−432, and references therein.

[7] Kissounko, D. A.; Epshteyn, A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **2006**, *25*, 531−535.

[8] Details are provided in the Supporting Information.

10.1021/om051007y CCC: $33.50

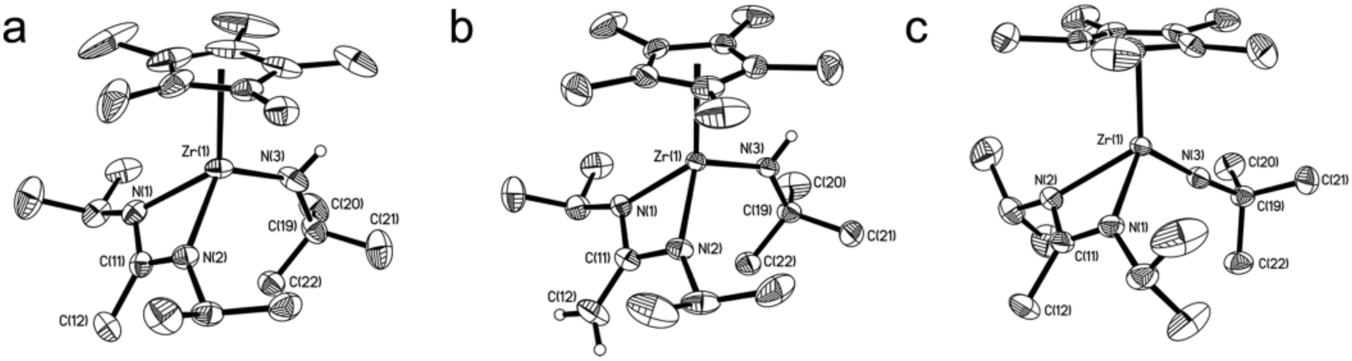
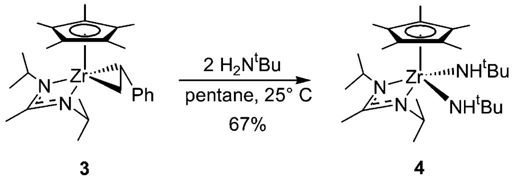
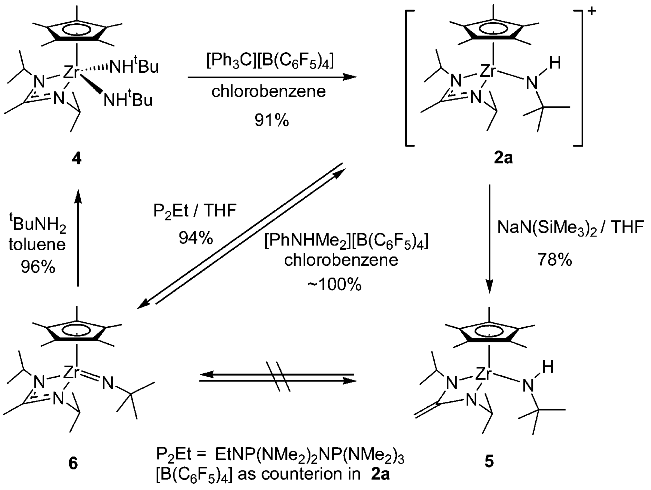


Figure 1. Molecular structures (30% thermal ellipsoids) of compounds (a) **2a**, (b) **5**, and (c) **6**. The $[B(C_6F_5)_4]$ counterion of **2a** and all hydrogen atoms, except for some selected crystallographically located ones for **2a** and **5**, have been omitted for the sake of clarity.

Scheme 2



Scheme 3



attempts to prepare **4** through protonolysis of $Cp^*ZrMe_2[N(^iPr)C(Me)N(^iPr)]$ under identical conditions failed to provide the desired product in acceptable yield and purity. Next, as Scheme 3 reveals, direct amide abstraction of **4** using the borate $[Ph_3C][B(C_6F_5)_4]$ provided the desired cationic zirconium amido **2a** ($R^1 = R^2 = {}^iPr$) in high yield. Although similar methide ($^-CH_3$) abstraction using this borate is commonly performed to prepare zirconium alkyl cations from neutral dimethyl precursors,[6,9] to the best that we can determine, this is the first example of analogous amide abstraction chemistry, and it may represent a general route to a variety of other cationic metal amido species.

Analytically pure **2a** was obtained through recrystallization from pentane, and single crystals were subjected to X-ray analysis.[8] Figure 1a presents the molecular structure of **2a**, and of particular interest are the Zr(1)−N(3) bond length of 2.021(5) Å involving the exocyclic amido group, which is shorter than the Zr−N bond lengths involving the amidinate fragment [cf. Zr(1)−N(1) and Zr(1)−N(2) of 2.1516(17) and 2.1549(18) Å, respectively], and the nearly trigonal coplanar geometry of the N(3) atom. Given the electrophilic nature of the d^0 metal center, it is reasonable to conclude that these geometric features might be associated with partial multiple-bond character between zirconium and nitrogen. Finally, no insertion of ethene, propene, or higher α-olefins into the Zr−N bond of **2a** has been observed under a variety of conditions.

With compound **2a** in hand, efforts to form a zirconium imido complex through deprotonation yielded quite unexpected results. Thus, as Scheme 3 presents, the sterically hindered base $NaN(SiMe_3)_2$ provided only the "enolamido" complex **5** through selective deprotonation of the amidinate ligand.[8,10] Compound **5** was isolated in analytically pure form through recrystallization, and Figure 1b provides the molecular structure of this complex as determined by X-ray crystallography.[8] Of particular note is that the Zr(1)−N(3) bond length of 2.0533(16) Å is only slightly contracted relative to the Zr(1)−N(1) and Zr(1)−N(2) bond lengths of 2.0596(15) and 2.0631(15) Å, respectively. Importantly, both the short C(11)−C(12) bond length of 1.351(3) Å and the trigonal coplanarity of C(12) support the depicted enolamido structure [cf. the C(11)−C(12) bond length of 1.498(3) Å in **2a**]. There are also no short distances observed in the solid state between the fluorines of the borate anion and the cationic metal center. Finally, in the ^1H NMR (400 MHz, benzene-d_6, 25 °C) spectrum of **5**, a distinct singlet resonance for the two methylene protons of the enolamido structure is observed at 3.39 ppm.

Compound **5** was found to be surprisingly quite stable in solution, resisting tautomerization to a zirconium terminal imido up to temperatures of at least 100 °C. It was eventually discovered, however, that among a wide range of bases (e.g., *n*-butyllithium, triethylamine, DBU, and $LiSiPh_3$[10]—all of which provide a complex mixture of products) commercially available $EtNP(NMe_2)_2NP(NMe_2)_3$ (abbreviated as P_2Et)[3,11] was exceptional in selectively deprotonating **2a** to provide a high isolated yield of the desired imido complex **6** as shown in Scheme 3.[8] Compound **6** was again isolated as single crystals, and X-ray analysis was used to determine the molecular structure shown in Figure 1c. Relative to both **2a** and **5**, compound **6** possesses a significantly shorter Zr(1)−N(3) bond of 1.839(2) Å, which is similar in magnitude to other known zirconium imido complexes and which supports the depicted multiple-bond character [cf. Zr(1)−N(1) and Zr(1)−N(2): 2.232 (2) Å].[7,12,13] The Zr(1)−N(3)−C(19) bond angle is also nearly collinear at 175.52(18)°.

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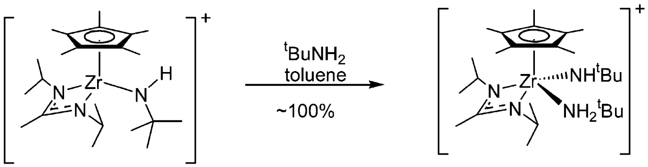
Scheme 4



2a **7**

[B(C$_6$F$_5$)$_4$] as counterion

A preliminary survey of the stability and reactivity of **6** revealed that neither alkenes nor alkynes engage in formal [2+2] cycloadditions, and no C−H additions of alkanes across the Zr═N bond occur as previously observed for other zirconium imido species.[14] Addition of 1 equiv of ^{t}BuNH$_2$ to a toluene solution of **6** quantitatively provided the bisamido **4**, and protonation using 1 equiv of [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] in chlorobenzene cleanly regenerated **2a** (Scheme 3). Finally, at elevated temperatures up to 100 °C, **6** again does not tautomerize to **5** in solution as determined by NMR spectroscopy.

With the ability to spectroscopically establish formation of **3**−**5** by NMR, final attention was turned to determining whether a stoichiometric or an excess amount of a primary amine could deprotonate **2a**. With 1 equiv of ^{t}BuNH$_2$, only complexation occurred to provide the amine adduct **7** shown in Scheme 4, which was isolated in crystalline form.[8] Interestingly, a 2D ^{1}H EXSY NMR spectrum established that, at 25 °C, the solution structure of **7** is static with no evidence for either proton or group exchange occurring between the two chemically distinct exocyclic nitrogen-containing substituents on the NMR time frame. Compound **7** also proved to be thermally stable in toluene solutions up to at least 100 °C. Finally, in the presence of excess ^{t}BuNH$_2$ (10 equiv), solutions of **2a** in chlorobenzene once again yielded only **7**, even at elevated temperatures, and with no evidence for deprotonation.

Since pK_a's of cationic zirconium primary amido species can reasonably be expected to vary according to overall formal electron count of the complex, it remains to be seen whether model complexes for the more electron-deficient intermediates (vis-à-vis **2a**) that are involved in Scott's catalytic process are more susceptible to deprotonation by primary amines. In the present case of catalysts based on **2**, this process might not pose as big of a threat to their success as simple irreversible coordination of these primary amines to potential olefin binding sites of the highly electrophilic metal center. Fortunately, steric tuning of the ligand environment about the metal may serve to help ameliorate the situation with respect to the latter deactivation process. Further hydroamination studies with several structural derivatives of **2** are now in progress.

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Supporting Information Available: Experimental details, including crystallographic analyses of **2a**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Compound **6** is structurally analogous to monocyclopentadienyltitanium imido amidinate complexes prepared by Mountford and co-workers, see: (a) Guiducci, A. E.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2001**, 1392−1394. (b) Boyd, C. L.; Clot, E.; Guiducci, A. E.; Mountford, P. *Organometallics* **2005**, *24*, 2347−2367.

(13) See for instance: (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723. (b) Ong, T. G.; Wood, D.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **2002**, *21*, 1−3.

(14) See, for instance: (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731−8733. (b) Hoyt, H. M.; Michael, F. E.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 1018−1019.