

## Highly Reactive Metal–Nitrogen Bond Induced C–H Bond Activation and Azametallacycle Formation

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Received November 27, 2009

Summary: A group 4 metal—nitrogen bond inserted into the carbon—nitrogen double bond of carbodiimides and  $\alpha$ -diimines to afford guanidinate and amido—imino ligand supported group 4 metal complexes, respectively. Metal—nitrogen mediated C—H bond activation  $\alpha$  to the nitrogen atom led to the formation of azametallacycle complexes.

Metal-nitrogen bonds of early- and lanthanide-metal complexes have been utilized as catalysts or stoichiometric reagents in a wide variety of organic syntheses to prepare a large number of nitrogen-containing organic molecules.<sup>1</sup> Some of these catalytic reactions involve the key step of inserting a metal-nitrogen bond into the unsaturated multiple bond of alkenes, alkynes, and allenes; the intramolecular hydroamination/cyclization reaction, developed by Marks et al., is one of the most well-established of these reactions (Scheme 1a).<sup>2</sup> On the other hand, insertion of the metal-nitrogen bond into polar unsaturated multiple bonds, such as C=N and C=O bonds, has been extensively explored

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as another key step in the syntheses of guanidines and transamidation (Scheme 1b).<sup>3</sup> Another catalytic transformation involving the metal–nitrogen bond, that is insertion of a C–H bond  $\alpha$  to the nitrogen into alkenes and alkynes, has attracted recent interest, and intermolecular hydroaminoalkylation reactions catalyzed by the homoleptic group 4 and 5 metal amide complexes were developed by Hartwig et al. and Doye et al., respectively (Scheme 1c,d).<sup>4,5</sup> As depicted in Scheme 1, these catalytic intermolecular hydroaminoalkylation reactions involve the elimination of amine from bis(amide)metal species **A** via the abstraction of an  $\alpha$  hydrogen atom to the nitrogen by the adjacent metal–nitrogen bond (intermediate **B**), leading to the formation of the three-membered azametallacycle **C** as a key species for further coupling with unsaturated organic substrates.

Thus, exploring the reaction pathway and further application of the insertion reaction of the C–H bond  $\alpha$  to the nitrogen into alkenes and alkynes via amine elimination is important, though such insertion into an azametallacycle generated via an alkane elimination from L<sub>n</sub>M(alkyl)-(amido) complexes has been utilized for the synthesis of nitrogen-containing organic compounds in a stoichiometric manner.<sup>6–8</sup> Recently, Schafer and co-workers reported the isolation of an azametallacycle species (**C** in Scheme 1) via an amine elimination reaction;<sup>4b,d</sup> however, the metallacyclic

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Scheme 1. Reaction Patterns of the Metal-Nitrogen Bond toward (a) Carbon-Carbon Multiple Bond, (b) Carbon-Heteroatom Multiple Bond, and (c, d) C-H Activation and Aminoalkylation Reactions



intermediates (**D** in Scheme 1), products of the reaction with unsaturated organic compounds, have not yet been isolated. In our effort to find a new C–H bond activation  $\alpha$  to the nitrogen by the metal–nitrogen bond during the course of the reaction of homoleptic tetrakis(amide) complexes of group 4 metals with conjugated diimine ligands, we found a fivemembered diazametallacyclopentane as the first example of an isolated metallacycle intermediate in the hydroaminoalkylation reaction. We also demonstrated that an  $\sigma^2, \pi$ -N,N'enediamido complex of zirconium was obtained by successive amination of the C=N bond and M–N mediated C–H bond activation of the  $\alpha$ -diimine ligand moiety.

Reaction of Ti(NMe<sub>2</sub>)<sub>4</sub> with an excess amount of diisopropylcarbodiimide (1a) at 90 °C for 48 h afforded the unprecedented titanium complex 2a in 33% yield, which was a product of the aliphatic C-H bond activation of the methyl group bound to the nitrogen atom, forming an azametallacyclopropane intermediate, followed by insertion into **1a** (eq 1). In the <sup>1</sup>H NMR spectrum of **2a**, ABq signals centered at  $\delta_{\rm H}$  4.23 and 4.53 ( $^2J_{\rm H-H}$  = 18.5 Hz) were observed as the methylene protons adjacent to the exo-imine moiety, consistent with a 2,5-diaza-3-exoimino-titanacyclopentane, whose structure was determined by X-ray crystallographic analysis (Figure 1).9 The titanium atom is surrounded by six nitrogen atoms to form a six-coordinated octahedral geometry, in which four of six nitrogen atoms coordinate to titanium as two guanidinate ligands. The notable structural feature of 2a is the five-membered metallacycle with an exocyclic imine moiety, as confirmed by the N8-C3 single bond and the N9-C3 double bond.



<sup>1a</sup> When a mixture of  $Ti(NMe_2)_4$  and **1a** in toluene was heated to 50 °C, the mono(guanidinate)titanium complex (<sup>i</sup>PrNC(NMe\_2)N<sup>i</sup>Pr)Ti(NMe\_2)<sub>3</sub> (**3a**) was isolated as a yellow oil in 94% yield. In the <sup>1</sup>H NMR spectrum of **3a**, resonances corresponding to the NMe<sub>2</sub> group were observed in a



Figure 1. Molecular structure of complex 2a. Selected bond distances (Å) and angles (deg): Ti-N1 = 2.080(6), Ti-N2 = 2.185(6), Ti-N4 = 2.158(6), Ti-N5 = 2.131(6), Ti-N7 = 1.916(6), Ti-N8 = 2.013(6), N8-C3 = 1.374(8), N9-C3 = 1.281(8); N1-Ti-N2 = 62.5(2), N4-Ti-N5 = 62.6(2), N7-Ti-N8 = 79.7(2).

Scheme 2. Proposed Mechanism for the Formation of 2a



3:1 ratio, indicating that one NMe<sub>2</sub> group migrated into the C=N bond of **1a**. When a mixture of **1a** and **3a** was heated at 70 °C, the signals assignable to **2a** gradually increased in the <sup>1</sup>H NMR spectrum of the mixture. Thus, the formation of **2a** could be rationalized as shown in Scheme 2. In the first stage, successive amination toward 2 equiv of diisopropylcarbodimide by Ti(NMe<sub>2</sub>)<sub>4</sub> resulted in the formation of a bis(guanidinate)titanium complex. Due to the strong electron-donating nature of the alkyl-substituted guanidinate ligand, <sup>10</sup> there was an increase in the basicity of the dimethylamido group bound to the titanium. Following C-H bond activation  $\alpha$  to the nitrogen atom of the dimethylamino group via a four-membered transition state, three-membered titanaaziridine was formed, and subsequent insertion of diisopropylcarbodiimide gave **2a**.

In sharp contrast, treatment of  $Ti(NMe_2)_4$  with dicyclohexylcarbodiimide (1b) in toluene at 90 °C afforded mono-(dicyclohexylguanidinate) complex 3b, presumably due to the bulky cyclohexyl substituents of the complex preventing the second insertion of 1b (Scheme 3). In this complexation, an amido transfer from titanium to one of the two C=N

<sup>(9)</sup> Crystal data for **2a**: C<sub>27</sub>H<sub>59</sub>N<sub>9</sub>Ti, FW 557.70, monoclinic, space group  $P2_1/c$ , a = 30.991(5) Å, b = 10.561(5) Å, c = 21.320(5) Å,  $\beta = 109.550(5)^{\circ}$ , V = 6576(4) Å<sup>3</sup>, T = 120 K, Z = 8,  $D_{calcd} = 1.127$  g cm<sup>-3</sup>,  $2\theta_{max} = 55^{\circ}$ ,  $\mu = 0.290$  mm<sup>-1</sup>, R1 and wR2 = 0.0906 and 0.2325 ( $I > 2\sigma(I)$ ), GOF = 0.989.

<sup>(10)</sup> We previously reported a benzyl transfer from metal to  $\alpha$ -diimine ligands: (a) Tsurugi, H.; Ohnishi, R.; Kaneko, H.; Panda, T. K.; Mashima, K. *Organometallics* **2009**, *28*, 680. (b) Mashima, K.; Ohnishi, R.; Yamagata, T.; Tsurugi, H. *Chem. Lett.* **2007**, *36*, 1420.

Scheme 3. Reactions of M(NMe<sub>2</sub>)<sub>4</sub> with Dicyclohexylcarbodiimide



bonds of carbodiimides proceeded in the same manner as previously reported by Arnold et al. for the reaction of carbodiimides with Cl<sub>2</sub>Ti(NMe<sub>2</sub>)<sub>2</sub>.<sup>3a</sup> The mono(guanidinate) complex 3b was too stable, even when heated in a toluene solution at 90 °C in the presence of excess 1a,b. These findings suggest that the coordination of two guanidine ligands to the titanium atom might be key to activating the aliphatic C-H bond of NMe2. In contrast to the reaction of 1b with Ti(NMe<sub>2</sub>)<sub>4</sub>, we found that Zr(NMe<sub>2</sub>)<sub>4</sub> and Hf(NMe<sub>2</sub>)<sub>4</sub> reacted with 1b at 90 °C to give bis(guanidinate) complexes 4b and 5b,<sup>8</sup> respectively, without any mono(guanidinate) and C-H bond-activated products (Scheme 2). Unlike the titanium case, both complexes were stable even with prolonged heating at 90 °C for 48 h. Further reactions of 4b or 5b with carbodiimides leading to the zirconium and hafnium analogues of 2a were not observed but decomposed under xylene reflux conditions, suggesting that the bis(guanidinate) complexes of zirconium and hafnium did not have adequate basicity or bulkiness.

In addition, the reactions of  $M(NMe_2)_4$  (M = Ti, Zr, Hf) with  $\alpha$ -diimines, as a one-carbon extension analogous to the carbodiimides, were perfomed. Treatment of 2,6-diisopropylphenyl-1,4-diaza-1,3-butadienes (1c) with  $M(NMe_2)_4$ (M = Zr, Hf) in a 1:1 ratio at 90 °C selectively produced the corresponding (amido-imino) $M(NMe_2)_3$  complexes **6c** and **7c**, which were products of an amido transfer from the metal to one of the two C=N bonds of 1c (eq 2).<sup>11</sup> Complexes **6d** and **7d** were also obtained when  $M(NMe_2)_4$  species were treated with 2,6-dimethylphenyl-1,4-diaza-1,3-butadiene (1d) under similar conditions. The reaction of Ti(NMe\_2)\_4 with  $\alpha$ -diimine ligands did not proceed, however, presumably due to the small ionic radius of the titanium atom preventing the approach of  $\alpha$ -diimines.



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Figure 2. Molecular structure of complex 6d. Selected bond distances (Å): Zr-N1 = 2.3952(13), Zr-N2 = 2.1210(14), Zr-N3 = 2.0958(14), Zr-N4 = 2.0742(15), Zr-N5 = 2.0641(16), N1-C1 = 1.314(2), C1-C2 = 1.508(2), N2-C2 = 1.446(2), N6-C1 = 1.344(2).

The solid-state structures of complexes **6d** and **7d** were determined by X-ray analyses. The molecular structure of **6d** is shown in Figure 2,<sup>12</sup> (see the Supporting Information for the structure of **7d**). Due to the similar ionic radii of zirconium and hafnium, compounds **6d** and **7d** are isostructural with respect to each other. In the coordination sphere, the central metal is coordinated by two nitrogen atoms (one imino and one amido), N1 and N2, of the modified  $\alpha$ -diimine ligand and three metal-bound amido nitrogen atoms: N3–N5. Dissymmetric ligation is revealed by the bond distance of Zr–N(imino) (2.3952(13) Å) being significantly longer than that of Zr–N(amido) (2.1210(14) Å) along with the shorter bond distance of N2–C2(amido) (1.446(2) Å).

A further insertion reaction of the C=N bond into the metal-nitrogen bond or a C-H bond activation  $\alpha$  to the nitrogen atom did not take place for tris(amide) complexes 6 and 7. Protonation of one of the three M-N bonds by phenol derivatives resulted in activation of the C-H bond adjacent to the nitrogen atom. Treatment of 6c with 2,6-di-tertbutylphenol in toluene at 90 °C afforded 8c in 79% yield as yellow crystals (eq 3). In the <sup>1</sup>H NMR spectrum of 8c, a singlet resonance with one proton intensity was observed at  $\delta$  5.07, while two singlet signals observed with six proton intensity were assignable to the NMe<sub>2</sub> group. The disappearance of the signal corresponding to the imine carbon was also confirmed by the <sup>13</sup>C NMR spectrum. The solid-state structure (Figure 3)<sup>13</sup> clarified that **8c** has a pentacoordinated zirconium center with aryloxide and supine-DAD ligands where the distances of Zr1-C1 and Zr1-C2 are short enough to interact with the olefinic carbon to the metal center, which is also confirmed by the folding angle of the ligand ( $\theta = 123.54^{\circ}$ ).<sup>14</sup>

<sup>(12)</sup> Crystal data for **6d**:  $C_{26}H_{44}N_6Zr$ , FW 531.89, orthorhombic, space group *Pna2*<sub>1</sub>, a = 13.737(5) Å, b = 14.285(5) Å, c = 14.705(5) Å, V = 2885.6(18) Å<sup>3</sup>, T = 120(2) K, Z = 4,  $D_{calcd} = 1.224$  g cm<sup>-3</sup>,  $2\theta_{max} = 61^{\circ}$ ,  $\mu = 0.404$  mm<sup>-1</sup>, R1 and wR2 = 0.0186 and 0.0472 (all), GOF = 1.010.

<sup>(13)</sup> Crystal data for **8c**:  $C_{44}H_{68}N_4OZr$ , FW 760.24, triclinic, space group  $P\overline{1}$ , a = 11.073(5) Å, b = 19.721(5) Å, c = 20.299(5) Å,  $\alpha = 96.394(5)^\circ$ ,  $\beta = 92.780(5)^\circ$ ,  $\gamma = 94.972(5)^\circ$ , V = 4381(3) Å<sup>3</sup>, T = 120(2)K, Z = 4,  $D_{calcd} = 1.153$  g cm<sup>-3</sup>,  $2\theta_{max} = 61^\circ$ ,  $\mu = 0.286$  mm<sup>-1</sup>, R1 and wR2 = 0.0820 and 0.2047 (all), GOF = 1.074.

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Figure 3. Molecular structure of complex 8c. Selected bond distances (Å) and angles (deg): Zr1-O1 = 1.997(2), Zr1-N1 = 2.045(2), Zr1-N2 = 2.091(2), Zr1-N3 = 2.062(3), Zr1-C1 = 2.470(3), Zr1-C2 = 2.525(3), N1-C1 = 1.413(3), N2-C2 = 1.394(4), C1-C2 = 1.384(4), N4-C2 = 1.416(3); C29-O1-Zr1 = 171.85(19).

The bond distances of N1-C1, C1-C2, and N2-C2 indicate a long-short-long bonding sequence, revealing a dianionic  $\sigma^2$ , $\pi$ -enediamido canonical form. The very large C29-O1-Zr1 angle is consistent with the presence of a  $p\pi$ -d $\pi$ interaction between the phenolic oxygen atom and the zirconium atom.



The plausible mechanism for Scheme 4 is, at the first stage, selective protonation of  $Zr-NMe_2$  by 2,6-diisopropylphenol to give **8c'** and then a C(sp<sup>3</sup>)-H bond activation  $\alpha$  to the nitrogen atom of the amido-imino ligand accompanied by transformation of the amido-imino moiety, proceeding to the  $\sigma^2$ -enediamido ligand (Scheme 4). Differential reactivity of **6c** and **8c'** toward activation of the C-H bond might be due to differences in the electron-donating nature of Zr-N(amido) and Zr-O(aryloxide), depending on the increased basicity of the dimethylamino group bound to the zirconium, which is caused by increases in the electron-donating 2,6-diisopropylphenoxy ligand, as in the formation of **2a** from bis(guanidinate)Ti(NMe\_2)<sub>2</sub>.

After mixing of a sterically less hindered zirconium derivative, **6d**, and 4-*tert*-butylphenol, and subsequent addition

Scheme 4. Proposed Mechanism for the Formation of 8c



of **1b** to the reaction mixture, a new aryloxide zirconium complex having DAD and guanidinate ligands was isolated (eq 4). Because the insertion reaction of carbodiimides into the metal-nitrogen bond of **6d** did not proceed, the complex **9d** was formed via the formation of  $(4-{}^{T}BuC_{6}H_{4}O)$ -Zr(DAD<sup>NMe2</sup>)(NMe<sub>2</sub>) and successive amination of **1b** by Zr-NMe<sub>2</sub> (see the Supporting Information for the structure of **9d**). In contrast to the coordinates to the zirconium atom as the *prone* mode whose electronic contribution to the metal center is weaker than that of the supine mode due to coordination of the electron-donating guanidinate moiety.



In summary, we have demonstrated that activation of the C–H bond  $\alpha$  to the nitrogen, leading to azametallacyclopropane, and successive insertion into diisopropylcarbodiimide afforded a five-membered diazametallacyclopentane, which is a key intermediate for the aminoalkylation reaction. To enhance the reactivity of the M–N bond toward C–H bond activation, increasing the electron density of the metal center is crucial.

Acknowledgment. We acknowledge a JSPS Fellowship to T.K.P. and K.P. H.T. acknowledges financial support by a Grant-in-Aid for Young Scientists(B) and The Sumitomo Foundation. K.M. acknowledges financial support by a Grant-in-Aid for Scientific Research(A).

Supporting Information Available: Text, tables, figures, and CIF files giving experimental details for the syntheses of all compounds and crystallographic data for 2a, 3a, 4b, 6d, 7d, 8c, and 9d. This material is available free of charge via the Internet at http://pubs.acs.org.