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Selective Incorporation of Primary Amines into a Trizirconium Imido System and Catalyic Cyclization of Aminoalkynes

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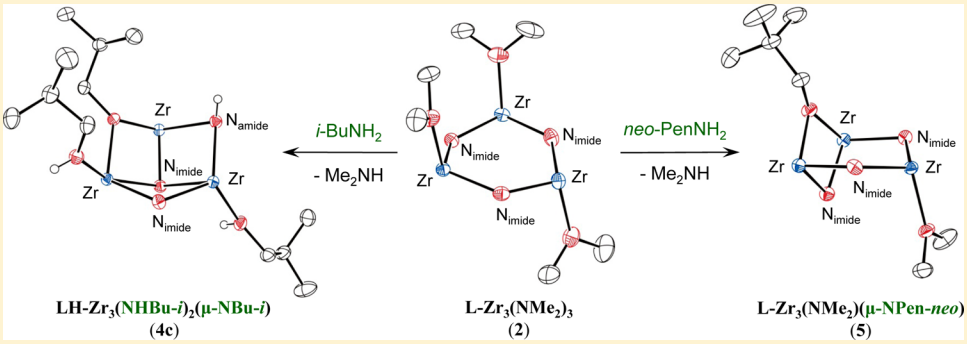
Supporting Information

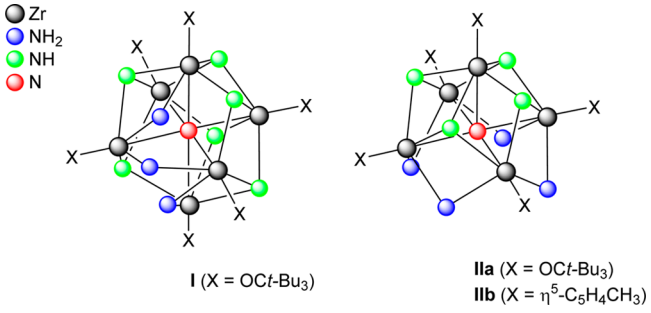


ABSTRACT: The trinuclear zirconium imido complex $[\{LZr(NMe_2)\}_3]$ (**2**, L = $C_5Me_4CH_2CH_2N$) was synthesized by amine elimination between $Zr(NMe_2)_4$ and *endo*-olefinic isomers of (tetramethylcyclopentadienyl)ethanamine (LH_3) (**1**). To study the fundamental reactivity of the trizirconium system, reactions of **2** with primary amines were examined. Selective incorporations of the primary amines were observed, depending on steric and electronic natures of the amine substrates. The amine-incorporated complexes $[(LZrNHR)(LHZrNHR)(LHZr)(\mu\text{-NHR})(\mu_3\text{-NR})]$ (**3**, R = Pr, Et), $[(LZrNHR)_2(LHZr)(\mu\text{-NR})]$ (**4**, R = Pr, *i*-Bu), $[(LZr)_2(LZrNMe_2)(\mu\text{-NR})]$ (**5**, R = *neo*-Pen), and $[(LZr)(LZrNHAr)(LH_2Zr)(\mu\text{-NAr})_2]$ (**6**, Ar = Ph, C_6H_4-4-Br, C_6H_4-4-OMe) were structurally characterized by NMR and XRD analysis and showed several coordination modes of the substrate nitrogen ligands: i.e., terminal amides, bridging amides, and bridging imides but not terminal imides. Thermolysis of a mixture of **3** and **4** led to C−H bond activation, giving rise to the zirconaaziridines $[\{LZr(\eta^2\text{-NCHR})\}(LZr)(LHZr)(\mu\text{-NHCH}_2R)]$ (**12**, R = Et, Me). Complex **2** proved to be a competent precatalyst in the hydroamination of the aminoalkynes $(H_2NCH_2CR^1{}_2CH_2C{\equiv}CR^2)$ (**13**, R^1 = H, R^2 = Bu, Ph, *t*-Bu; **14**, R^1 = Me, R^2 = Et, Ph). Stoichiometric or semicatalytic reactions of **2** and the aminoalkynes were studied to explore the reactivity of in situ formed Zr_3 species.

INTRODUCTION

Zirconium nitride (ZrN) thin films have many applications deriving from their unique properties such as hard protecting coatings,[1] diffusion barriers,[2] gate materials,[3] and Josephson junctions.[4] A variety of deposition techniques for ZrN thin films have been developed using certain zirconium precursors with NH_3, H_2/N_2, or the forming gas plasma.[5−7] Among the precursors $Zr(NMe_2)_4$ is the most representative, enabling mild and pinhole-free film growth. Thermal decomposition and deposition mechanism of such homoleptic zirconium amido precursors have been studied.[8] Zirconium polyamidoimidonitride structures may be formed as intermediates in the process, and the relevant molecular complexes containing amidoimidonitride substructures were reported previously.[9−12] Wolczanski studied ammonolysis of $XZr(CH_2Ph)_3$ (X = t-Bu_3CO) with NH_3 (1.0−1.75 equiv) and obtained hexa- and pentanuclear zirconium complexes, $(XZr)_6(\mu_6\text{-N})(\mu_3\text{-NH})_6(\mu\text{-NH}_2)_3$ (**I**) and $(XZr)_5(\mu_5\text{-N})(\mu_3\text{-NH})_4(\mu\text{-NH}_2)_4$ (**IIa**) (X = OCt-Bu_3, Chart 1).[9a] Further ammonolysis of **IIa** led to the formation of a polyamidonitrido complex. Independently, Roesky and co-workers reported reactions of zirconocene dichlorides with potassium in liquid ammonia, giving the pentanuclear zirconium complex **IIb** (X = η^5-$C_5H_4CH_3$, Chart 1) with loss of one cyclopentadienyl ligand.[10a,b] More recently, Xue and co-

Chart 1. Zirconium Polyamidoimidonitrido Complexes[9,10]



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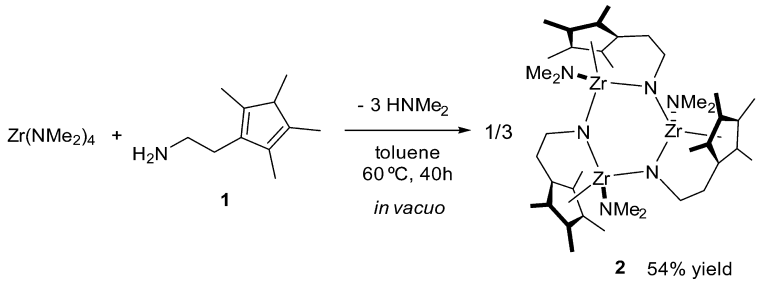
Scheme 1. Formation of Zr_3 Imido Complex 2



workers investigated the reaction between $M(NMe_2)_4$ (M = Zr, Hf) and dioxygen, resulting in the formation of the trinuclear oxo aminoxido complex $M_3(NMe_2)_6(\mu\text{-}NMe_2)_3(\mu_3\text{-}O)(\mu_3\text{-}ONMe_2)$ with liberation of Me_2NNMe_2.[12] The DFT study supports that insertion of dioxygen into M−N bonds and cleavage of one of the O−NMe_2 bonds lead to the formation of a key Zr_2 intermediate.

In spite of these structural studies of the multinuclear zirconium complexes as the products, the reaction chemistry of the nitrogen-rich systems has not been studied in detail and may attract renewed attention to the chemistry of acid−base complexes. We envisage that the coordination environment created by a multimetallic motif could render multiple substrate incorporation and/or multisite activation of a single substrate, whereby bridging nitrogen ligands could serve as proton acceptors toward protic substrates, with cooperation of the Zr centers as Lewis acidic coordination sites. Accordingly, it is a highly challenging task to identify reactive nitrogen-bridged multizirconium systems under stoichiometric and catalytic reaction conditions. Herein we report the synthesis and structure of Zr_3 imido complexes and reactions with primary amines.

RESULTS AND DISCUSSION

Synthesis and Structure of Zr_3 Imido Complex 2. Chelating cyclopentadienyl-amide ligands have been recognized as excellent ancillary ligands for group 4 metal complexes in many catalytic reactions and polymerizations.[13−17] In contrast to the dianionic ligand class, chelating cyclopentadienyl-imide systems are far less prevalent. The synthesis and structure of dinuclear niobium and titanium complexes bearing a cyclopentadienyl-propylimide ligand were previously reported by Green and Mountford.[18] We decided to exploit the known (2,3,4,5-tetramethylcyclopenta-1,4-dienyl)-1-ethanamine (**1**) as a supporting ligand and initially attempted metalation of **1** with $Zr(NMe_2)_4$. After several examinations, we found that the Zr_3 imido complex **2** could be obtained from the *endo*-diene isomers of **1** (including the *exo* isomer <5%) in a moderate yield (Scheme 1).[19] There are two possible stereoisomers for complex **2**: up−up−up and up−up−down orientations for the three NMe_2 groups over the six-membered Zr_3N_3 ring. Solution- and solid-state structural characterizations revealed specific formation of the C_1-symmetric up−up−down structure (Figure 1). In the Zr_3 core containing three supporting imides, the mean distance of the *Cp*,*N*-nonchelating Zr−N bonds (2.093 Å) is comparable to that of the *Cp*,*N*-chelating bonds (2.042 Å). This may imply robustness of the μ-imido linkages. In fact, the Zr_3 core displayed inertness toward some Lewis bases: e.g., THF and 4-(dimethylamino)pyridine.[20]

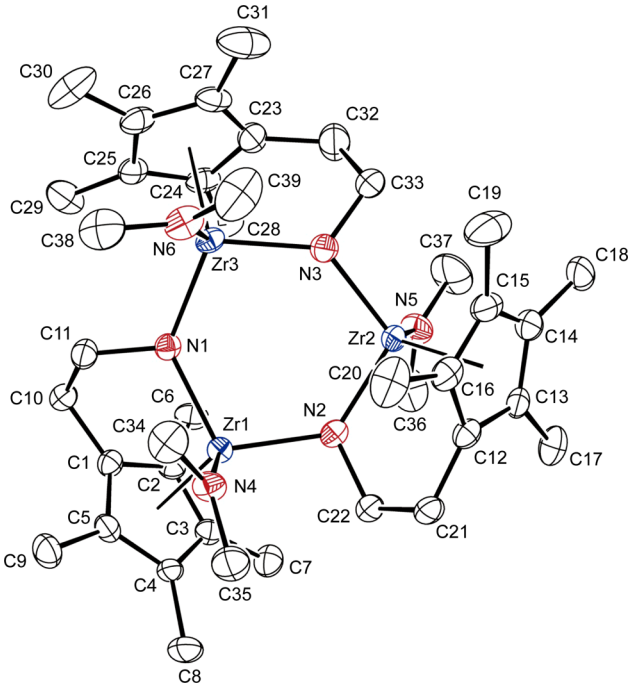


Figure 1. Crystal structure of **2** (ellipsoids set at 40% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr(1)−N(1) 2.064(5), Zr(2)−N(2) 2.022(7), Zr(3)−N(3) 2.039(7), Zr(1)−N(2) 2.093(7), Zr(2)−N(3) 2.102(7), Zr(3)−N(1) 2.083(5), Zr(1)−N(4) 2.080(5), Zr(2)−N(5) 2.079(7), Zr(3)−N(6) 2.073(6), Zr(1)−Zr(2) 3.713, Zr(2)−Zr(3) 3.782, Zr(3)−Zr(1) 3.759; N(1)−Zr(1)−N(2) 108.(2), N(2)−Zr(2)−N(3) 109.5(2), N(3)−Zr(3)−N(1) 106.6(2).

Amine Incorporations. To find out the fundamental reactivity of **2** toward nitrogen-containing substrates, reactions of **2** with several primary amines were examined, and the results are summarized in Scheme 2. An NMR-scale reaction of **2** with ca. 9 equiv of *n*-$PrNH_2$ was performed in C_6D_6 at 25 °C. Four equivalents of *n*-$PrNH_2$ was smoothly consumed, and a new complex $\mathbf{3a}_{kinetic}$ was initially observed. After 16 h, instead of the initially observed structure ($\mathbf{3a}_{kinetic}$), a more thermodynamically stable structure (**3a**) emerged in the NMR spectrum (92% NMR yield), still containing 5 equiv of free *n*-$PrNH_2$ (Figure S2 in the Supporting Information). The structure of **3a** was determined by NMR and XRD analysis, as shown in Scheme 2 (Figure S4 in the Supporting Information). Interestingly, use of decreased amounts of *n*-$PrNH_2$ or exposure of **3a** to reduced pressure gave a mixture of the two complexes **3a** and **4a**. In practice, the ratio **3a**/**4a** varied by addition or removal of *n*-$PrNH_2$. The structure of metastable **4a** was determined by ^{1}H NMR and preliminary XRD analysis (Figure S5 in the

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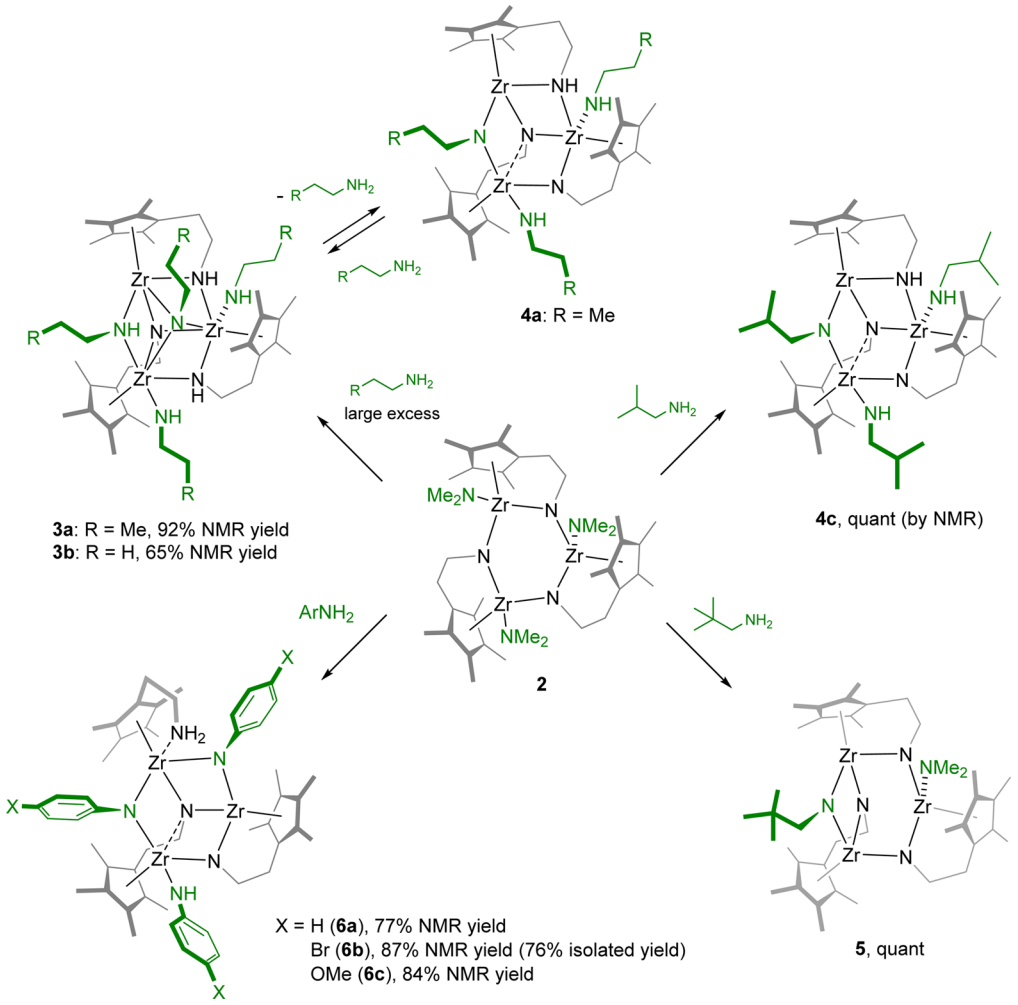
Scheme 2. Reactivty of 2 toward Primary Amines



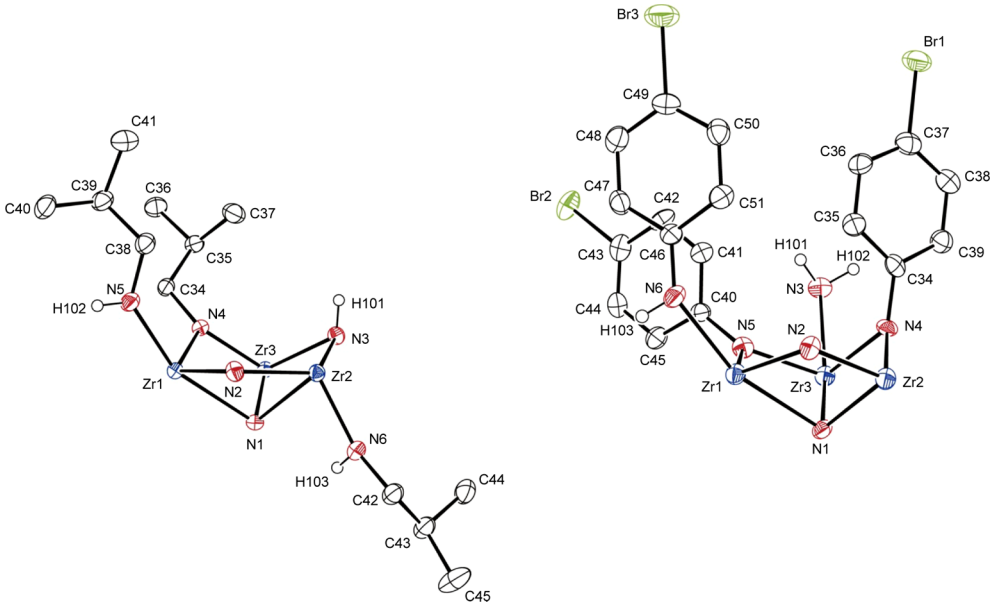


Figure 2. Crystal structures of **4c** (left) and **6b** (right). Thermal ellipsoids are set at 40% probability, and carbon atoms of the supporting ligands and hydrogen atoms except NH protons are omitted for clarity.

Supporting Information). Similar behavior was observed by NMR analysis when **2** was treated with a THF solution of $EtNH_2$, affording **3b** via $\mathbf{3b}_{kinetic}$. Treatment of **2** with an excess amount of *i*-$BuNH_2$ under similar conditions gave **4c**

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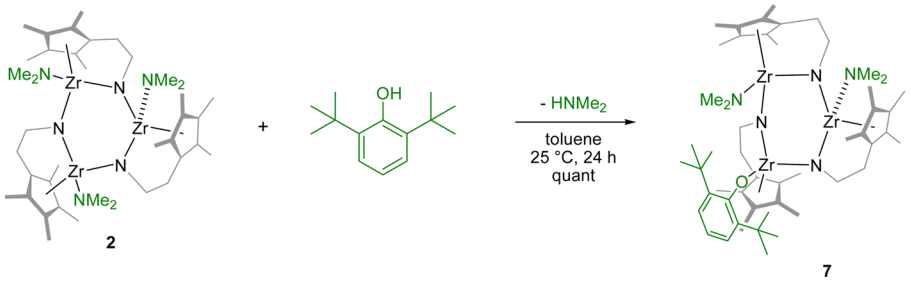
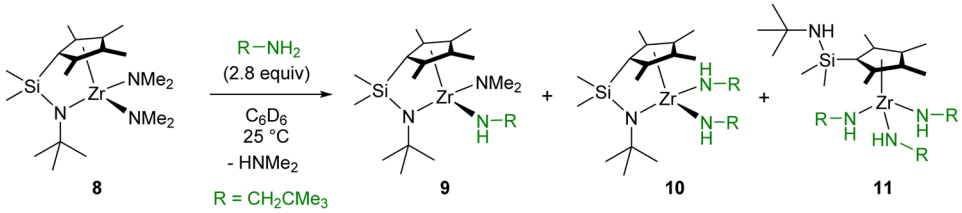
Scheme 3. Formation of Monoaryloxide 7



Scheme 4. Reaction of 8 with *neo*-PenNH$_2$



time	distribution (%)* **8** : **9** : **10** : **11**
20 min	30 : 27 : 25 : 10
5 h	1 : 31 : 42 : 13
28 h	1 : 31 : 42 : 13

* based on the internal standard

selectively, which was characterized by NMR and XRD analysis to be a three-amine-incorporated complex (Figure 2, left). The crystal structures of **4a,c** have common structural features; one of the supporting imide ligands is slipped to the Zr_3 face, and the three substrate nitrogen ligands coordinate to Zr centers in the up−up−down orientation as one μ-imide and two terminal amides, respectively. The solid-state structures of **4** are quite consistent with the solution structures as assigned by NMR analysis.

Upon addition of *neo*-PenNH$_2$ to complex **2**, only two Me_2N ligands were liberated, affording the μ-neopentylimido complex **5**, in which three μ-imide supporting ligands remained intact (Figure S6 in the Supporting Information). The rest of the Me_2N group in **5** could not be replaced with *neo*-PenNH$_2$ even at 90 °C. Reaction of **2** with the much bulkier *t*-BuNH$_2$ did not occur even under more forcing conditions (3 days at 90 °C), resulting in recovery of **2**. In the above reactions of **2** with the primary amines more than two Me_2N ligands are eliminated, and we attempted to verify the most reactive Me_2N group in complex **2**. 2,6-Di-*tert*-butylphenol was employed as a bulky protic reagent for this purpose, and monoaryloxide **7** was formed from **2** and the phenol as the sole product in high yield (Scheme 3). XRD analysis of **7** unambiguously clarified the regiochemistry (Figure S7 in the Supporting Information). The reactivity difference between the two adjacent NMe_2 groups and the significant deviation of the N angles of *neo*-PenNZr$_2$ moiety in **5** (Zr(1)−N(4)−Zr(3) = 95.08(14)°, C(34)−N(4)−Zr(1) = 94.2(3)°, C(34)−N(4)−Zr(3) = 156.1(3)°) can be ascribed to the steric effect of the peralkylated cyclopentadienyl ligand.[21]

The reaction of **2** with excess amounts of unsubstituted aniline, 4-bromoaniline, or *p*-anisidine at 25 °C led to the formation of a Zr_3 complex (**6a−c**), incorporating three molecules of aniline (Scheme 2), whereas no reaction was observed with the sterically demanding 2,4,6-trimethylaniline under identical conditions. ^{1}H NMR spectra of **6a−c** are quite similar to each other with respect to resonance patterns for the ethylene-chain protons of the supporting ligands. Complex **6b** was characterized crystallographically. As shown in Figure 2, the structure of **6b**, in contrast to **4a,c**, reveals that three bromoanilines lie on the same side of the Zr_3 plane (up−up−up orientation) and two of three bromoanilines coordinate as μ-imido ligands and the third bromoaniline coordinates as a terminal amide. Complex **6b** has a quite long Zr−$N_{supporting}$ distance (Zr(3)−N(3) = 2.463(7) Å), assigned as a terminal amine ligand on the basis of these NMR and XRD results.[22]

In addition, ^{1}H NMR spectra of **6** recorded at 298 K showed restricted rotation of one of the two μ-N−$C_{aromatic}$ bonds, nonequivalent $NH_{2,support}$ (**6a**, δ 2.00 and 0.78 ppm; **6b**, δ 1.73 and 0.52 ppm; **6c**, δ 2.02 and 0.89 ppm), and screened resonances for one of three sets of the ethylene-chain protons (**6a**, δ 1.75−1.30 ppm; **6b**, δ 1.70−1.20 ppm; **6c**, δ 1.75−1.44 ppm). A variable-temperature ^{1}H NMR study of **6b** was carried out. The spectra in the aromatic region are shown in Figure S3 in the Supporting Information. Two signals for the *m*-Ar-H of the μ-NAr group, restricted at ambient temperature (δ 7.47 and 7.31 ppm), coalesced at 333 K (marked with solid circles). When the temperature was lowered to 233 K, two doublet signals for the other μ-NAr′ group decoalesced into four broad signals (open squares) while the terminal NH−$C_{Ar''}$ bond was rotating even at 193 K (solid triangles). A NOESY spectrum recorded at 273 K showed correlation between signals for *o*-Ar-H and *o*-Ar″-H (δ 6.82−6.40 ppm), indicating that the NAr ligand is located at a position cis to the NHAr″ ligand. These observations suggest that the three aniline ligands in **6** are located in significantly different environments over the temperature range and do not undergo site exchange on the Zr_3 system.

In the case of a related mononuclear bis(amido) complex, $Me_2Si(C_5Me_4)(Nt\text{-}Bu)Zr(NMe_2)_2$ (**8**), reaction with *neo*-

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$PenNH_2$ (excess) in a sealed NMR tube resulted in an equilibrium mixture containing mono-, bis-, and tris(neopentylamido) complexes **9**–**11** and $HNMe_2$ (Scheme 4).[23]

In this context, the selective reactions of **2** with the amines are noteworthy. We deem that the number of amines incorporated into the Zr_3 core may be dependent upon two factors: (i) NH acidity of the amines (pK_a: anilines (3.9–5.3 in H_2O) vs aliphatic amines (10.2–10.7 in H_2O))[24] and (ii) the size of alkyl groups on the N atom (*t*-Bu ≫ *neo*-Pen ≫ *i*-Bu > *n*-Pr). Complex **4c** was treated with 6 equiv of 4-bromoaniline in C_6D_6, and the reaction was monitored by ^1H NMR analysis. After the reaction mixture was heated at 60 °C for 2 h, relatively clean formation of **6b** was observed with liberation of *i*-$BuNH_2$. This observation accounts for the order of the NH acidity: namely, the pK_a dependence. The origin of the latter size selectivity of **2** toward amines, in particular aliphatic amines, may be addressed in part by comparison of effective volumes (V_{eff}) of the actor NMe_2 ligands in the crystal structure of **2** because of the consistency between the solution- and solid-state structures. According to the definition by Ohashi and coworkers,[25,26] V_{eff} values of the NMe_2 groups in **2** and known mononuclear zirconium bis(amido) complexes bearing a permethylated cyclopentadienyl ligand, $[Me_2Si(C_5Me_4)(E)Zr(NMe_2)_2]$ (E = N-*t*-Bu,[27a] NCHMePh,[27b] NC_6H_4-4-CH=CH_2,[27c] N(2-Py),[27d] $C_2B_{10}H_2$[27e]) and $[(C_5Me_5)$(salicyloxazoline)$Zr(NMe_2)_2]$ (salicyloxazoline = OC_6H_2-2,4-*t*-Bu_2-6-(4,4-Me_2-4,5-dihydrooxazol-2-yl), OC_6H_2-2,4-*t*-Bu_2-6-(4-*t*-Bu-4,5-dihydrooxazol-2-yl))[28] were approximated by the SV-Cavity (Figure 3, Figure S8 in the Supporting Information,

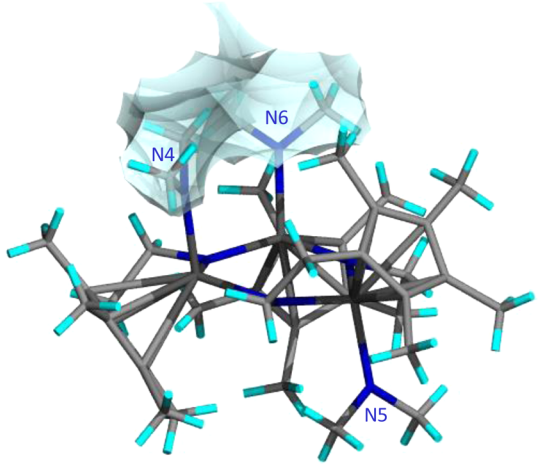
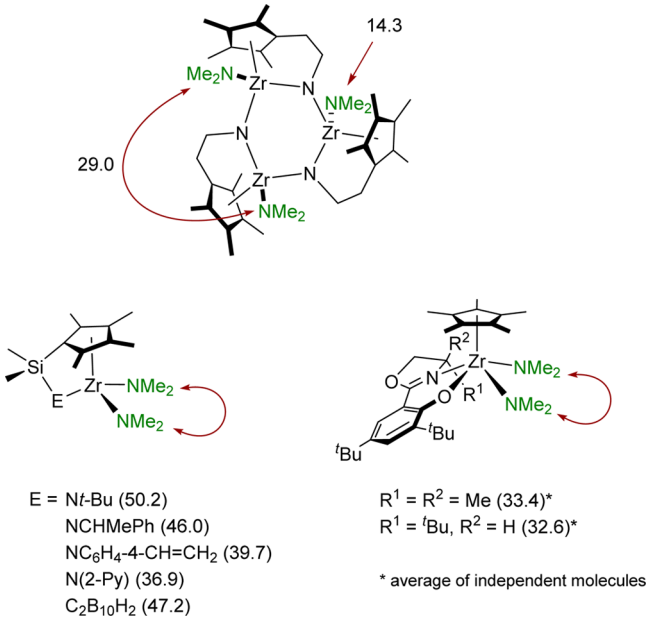


Figure 3. Representation of V_{eff} for two adjacent NMe_2 groups in **2**.

and Chart 2). These data indicate that the V_{eff} value in complex **2** is significantly small among the relevant chelating cyclopentadienyl-amido complexes, even smaller than that for a salicyloxazoline system with a four-legged piano-stool geometry. Therefore, the space available for incoming substrates in the Zr_3 system seems to be significantly limited by the three up–up–down peralkylated cyclopentadienyl-imide ligands in **2**.

Thermolysis of 3 and 4. The above equilibrium between **3** and **4** led us to study further elimination of the amines under thermolytic conditions. A C_6D_6 solution of a mixture of **3a** and **4a** (57:43) was heated at 100 °C for 1 h, and then a mixture of the new complexes **12a** and **12a′** was obtained with free *n*-$PrNH_2$ and complexes **3a** and **4a** (**3a**:**4a**:**12a**:**12a′** = 24:19:44:13). After the solution stood at 25 °C for 9 h, the

Chart 2. V_{eff} (Å^3) for NMe_2 Group(s) Estimated from X-ray Structures of 2 and Reported Half-Zirconocene Bis(amides)[27,28]



ratio of four complexes slightly changed to **3a**:**4a**:**12a**:**12a′** = 38:13:38:11 with a decreased amount of free *n*-$PrNH_2$. Repeated thermolysis/evaporation resulted in nearly complete consumption of **3a** and **4a**, leaving complexes **12a** and **12a′**. The uniform ratio of **12a** and **12a′** (~3.3:1) observed by ^1H NMR spectra and SST experiments (Figure S9 in the Supporting Information) showed that **12a** and **12a′** are in equilibrium in solution. Although the minor product **12a′** could not be characterized clearly, COSY, HSQC, and HMBC experiments of the mixture suggested that the major product **12a** contained not only μ-NHPr-*n* ligand (NH protons: δ 0.44 ppm) but also one zirconaaziridine substructure ((κ_N:η^2-NCH-Et): $\delta(^{13}C/^1H)$ 91.2/(2.15–2.09) ppm).[29] Likewise, the corresponding $EtNH_2$-derived complexes **12b** and **12b′** were formed by thermolysis of **3b**. We have not been able to obtain crystal structures of **12** or **12′** and tentatively propose the most plausible structure for **12a** by a ROESY experiment (Figure S10 in the Supporting Information). Formation of multinuclear group 4 metalaaziridines was reported by Schafer and coworkers;[30,31] a dinuclear titanaaziridine was isolated and characterized by crystallography. In addition, generation of the related dinuclear zirconaaziridines from primary amines in intramolecular hydroaminoalkylation is proposed. Accordingly, we summarize the proposed equilibrium of the Zr_3 complexes with such *n*-alkylamines in Scheme 5.

Catalytic Cyclization of Aminoalkynes. Hydroamination has been intensely studied for the last several decades using a variety of metal complexes.[32] In particular, intramolecular hydroamination is of synthetic importance, because it provides an atom-economical route for the synthesis of nitrogen-containing heterocycles. It would be an appropriate test catalytic reaction using complex **2** as a potential precatalyst. We undertook NMR-scale cyclization of five aminoalkynes (**13** and **14**) in C_6D_6 (Table 1). In the cyclization of **13a** and **13b** heating at 90 °C was required to complete the reaction, and the corresponding cyclic imines **15a** and **15b** were produced in excellent yields (entries 1 and 2). Substrate **13c** with a *t*-Bu

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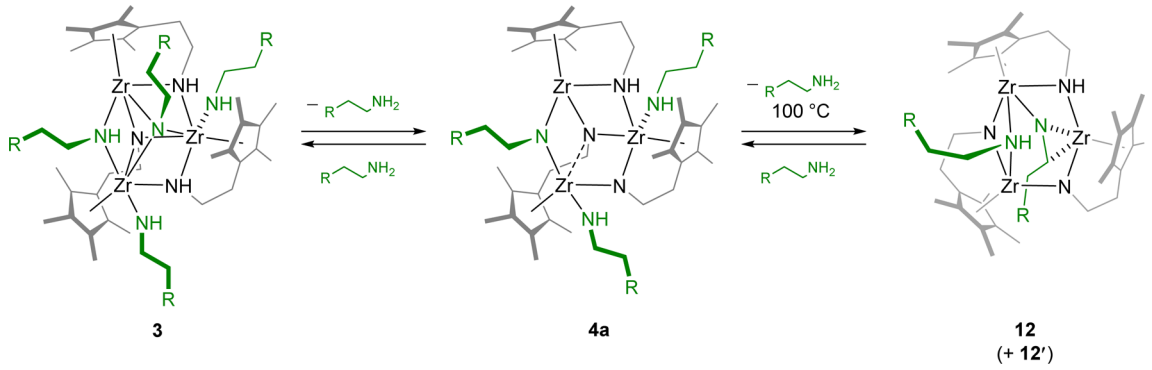
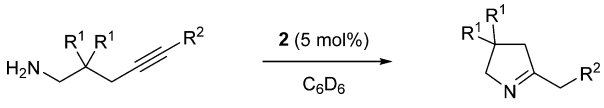
Scheme 5. Proposed Equilibrium between Zr_3 Species and *n*-Alkylamines[a]



[a]R = H, Me, etc. The most plausible structure is given for **12**.

Table 1. Catalytic Cyclization of 13 and 14[a]



13, **14** **15**, **16**

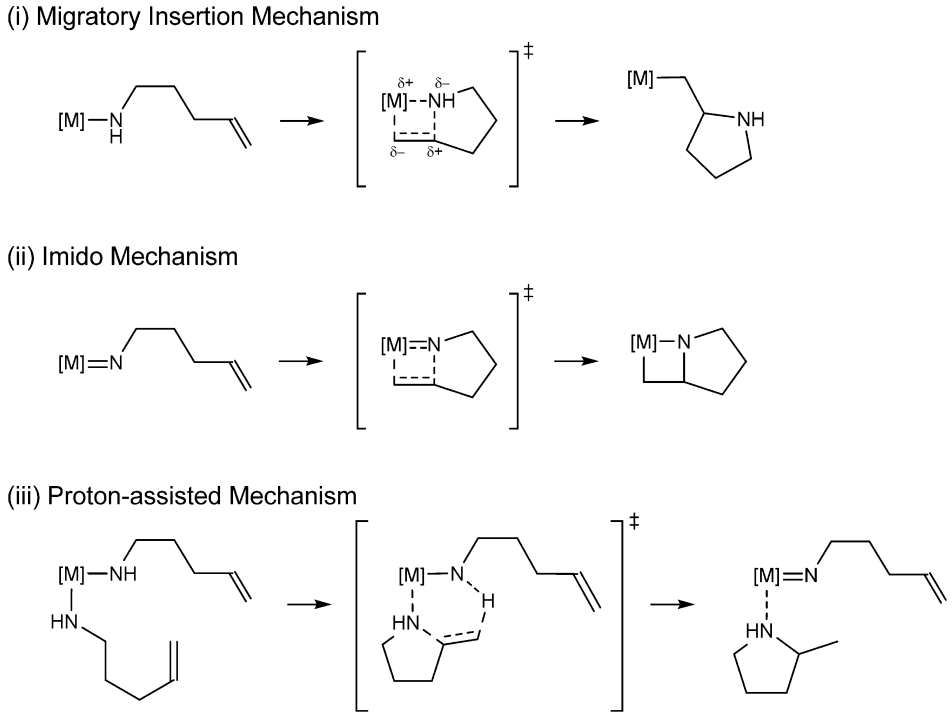
entry	substrate	R^1, R^2	conditions (°C, h)	product	yield (%)[b]
1	**13a**	H, Bu	90, 6	**15a**	>95
2	**13b**	H, Ph	90, 6	**15b**	>95
3	**13c**	H, *t*-Bu	110, 120	**15c**	81
4	**14a**	Me, Et	40, 3	**16a**	>95
5	**14b**	Me, Ph	40, 2	**16b**	>95

[a]The reaction was carried out in a J. Young NMR tube and monitored by ^{1}H NMR analysis using an internal standard: **2** (2.5–4.7 μmol), **13** or **14** (20 equiv), C_6D_6 solvent (0.45 mL). [b]NMR yield determined on the basis of $(Me_3Si)_2CH_2$ as the internal standard.

group on the alkyne carbon atom needed higher temperature and longer reaction time (entry 3). On the other hand, substrates **14** with *gem*-dimethyl substitution β to nitrogen cyclized under much milder conditions than for **13** (entries 4 and 5).

Group 4 terminal and bridged imido complexes have been well characterized,[21b,33] and the terminal imide structure is recognized as the reactive species in catalytic hydroaminations: in particular, alkyne and allene hydroaminations.[34] On the other hand, mechanisms for alkene hydroaminations by group 4 metal catalysts, more investigated than alkyne hydroaminations, are currently argued to have three major mechanisms: (i) a migratory insertion into the metal–nitrogen bond,[15b,35] (ii) an imido mechanism via $[2\pi + 2\pi]$ cycloaddition,[36] and (iii) a proton-assisted mechanism via a six-centered, concerted transition state for C–N and C–H bond formation (Scheme 6).[37] According to Scheme 2, primary amines are incorporated into the Zr_3 core as bridging imides, amides, and terminal amides, whereas no terminal imido structure is observed in the

Scheme 6. Three Simplified Mechanisms for Aminoalkene Cyclizations (e.g., M = Zr, Ti)[15b,35–37]



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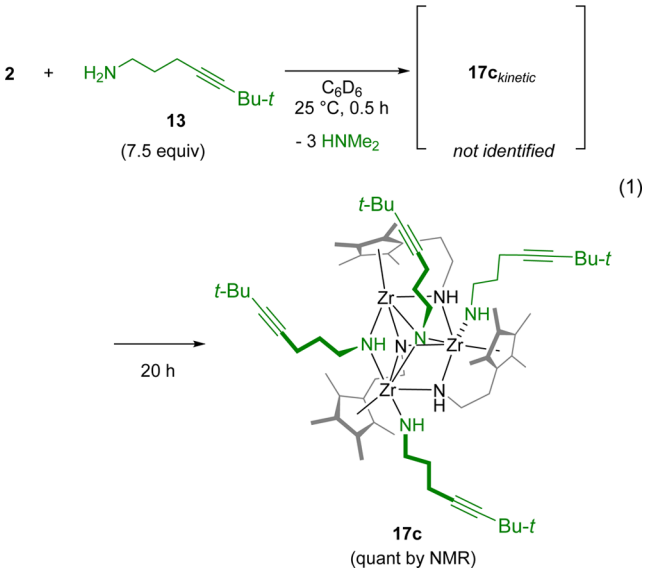
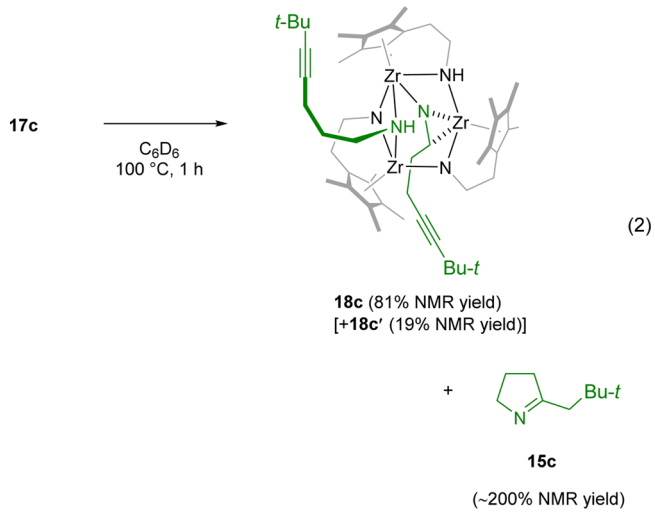
system. Therefore, a mechanism for the hydroamination using complex **2** might be incompatible with the well-recongnized imido mechanism for many group 4 metal systems. Accordingly, stoichiometric or semicatalytic cyclizations were examined to explore the reaction behaviors of Zr_3-based species.

Four molecules of **13** were readily incorporated into the Zr_3 complex at ambient temperature. In fact, ^{1}H NMR spectra for the catalytic cyclizations of these substrates in C_6D_6 recorded before heating (0.5 h at 25 °C) showed characteristic signals at low field for parts of ethylene protons of the supporting ligands of $\mathbf{17}_{kinetic}$ ($\mathbf{17a}_{kinetic}$, δ 4.77−4.68 (2H, m), 4.47 (1H, dd), 4.00−3.91 (1H, m) ppm; $\mathbf{17b}_{kinetic}$, δ 4.78−4.70 (2H, m), 4.47 (1H, dd), 4.00−3.90 (1H, m) ppm; $\mathbf{17c}_{kinetic}$, δ 4.74−4.65 (2H, m), 4.35 (1H, dd), 3.96−3.88 (1H, m) ppm), signal patterns which are quite similar to those of $\mathbf{3}_{kinetic}$ (Figure S11 in the Supporting Information). For spectral simplicity, substrate **13c** was chosen for the stoichiometric study in this work. After a mixture of complex **2** and **13c** (1:7.5) in C_6D_6 stood at 25 °C for 20 h, analogously to the formation of **3**, the majority of the initially observed $\mathbf{17c}_{kinetic}$ was replaced by the more thermodynamically stable form **17c** (eq 1 and Figures S12 and S13 in the Supporting Information), which we were not able to isolate but whose ^{13}C NMR spectrum clearly showed that **17c** contained 4 mol equiv of **13c**. After it was heated in C_6D_6 at 100 °C for 1 h, **17c** disappeared, resulting in the formation of the new complexes **18c** and **18c′** (4.3:1) together with the organic product **15c** (eq 2). The major product, **18c**, was detected throughout the above NMR-scale catalytic reaction. Although isolation of **18c** was not successful, NMR analysis showed that **18c** was an analogue of **12** incorporating two amine substrates, on the basis of the presence of a bridging N_{sub}-H proton (δ 0.37 ppm) and a bridging N'_{sub}-CH (κ_N:η^2-$N'CHCH_2CH_2C{\equiv}CBu$-*t*: $\delta(^{13}C/^1H)$ 87.9/(2.32−2.22) ppm) (Figure S14 and the Supporting Information). An attempted NMR-scale thermolytic cyclization of **18c** and **18c′** (C_6D_6 solvent at 100 °C) resulted in no ligand cyclization. Therefore, we currently surmise that zirconaaziridines **18** and **18′** are resting states and incorporate more amine substrates for the catalytic reaction.



Next, stoichiometric reactions of **2** with substrates **14** were examined. For **14** the subsequent catalytic cyclizations proceeded at 25 °C significantly faster than the initial stoichiometric amine incorporations, resulting in low conversion of **2** and catalytic formation of **16**. Owing to the lack of information under these conditions, semicatalytic reactions of **14** using 15 mol % of **2** were undertaken, and the metal-based products were monitored by ^{1}H NMR spectroscopy. The NMR spectra for the reaction of **14b** (C_6D_6 solvent, 25 °C) are shown in Figure 4. The ^{1}H NMR spectrum at the initial stage (e.g., t = 30 min) indicated the presence of almost a single new species, **19b**, on the basis of 1 set of 12 singlet signals for 3 C_5Me_4 ligands (δ 2.26−1.92 ppm). Because **19b** disappeared at the end of the semicatalytic reaction, the structure was determined only by comparison of the ^{1}H NMR spectrum with those of **5** to be a mono-μ-imido complex (Figure S15 in the Supporting Information) (characteristic resonances: NMe_2 group, δ 2.80 ppm (solid circles in Figure 4); three $CH_2N_{support}$ moieties, δ 5.07 (2H, m), 4.93 (1H, dd), 4.78 (2H, m), and 4.47 ppm (1H, dd)). After thorough consumption of substrate **14b** ($t \approx 2$ h), complex **19b** was replaced by another new species, **20b**, which has two NMe_2 groups (δ 2.89 and 2.74 ppm (1:1); open squares in Figure 4) (Scheme 7).



Complex **20b** could not be isolated, and the structure was tentatively determined by COSY, ROESY, HSQC, and HMBC spectroscopic experiments to be a tris(amide) with a 2-benzylidene-pyrrolidide ligand (characteristic signals for benzylidene C=*CH*Ph moiety: $\delta(^1H)$ 5.25 ppm and $\delta(^{13}C)$ 95.5 ppm (Supporting Information and Figure S16)). Active metal complexes were also observed in the semicatalytic reaction of **14a**. However, the NMR spectra became complicated at the end of the reaction; therefore, no other species were identified. The two possible intermediates $\mathbf{Int}_a$ and $\mathbf{Int}_b$ between **19b** and **20b** are proposed in Chart 3. $\mathbf{Int}_a$ is directly associated with a migratory insertive mechanism of the catalytic reaction, whereas $\mathbf{Int}_b$ is a requisite intermediate for a concerted proton-assisted cyclization, directly leading to **20b**. Although further studies are required to prove their existence and to determine the mechanism of the catalytic reaction, formation of the Me_2NH adduct **20b** indicates significant reactivity of the bridging imide moiety in **19b**.

CONCLUSIONS

We have synthesized and structurally characterized the trinuclear zirconium complex **2** with three cyclopentadienyl-imide ligands. The multimetallic motif allowed us to observe

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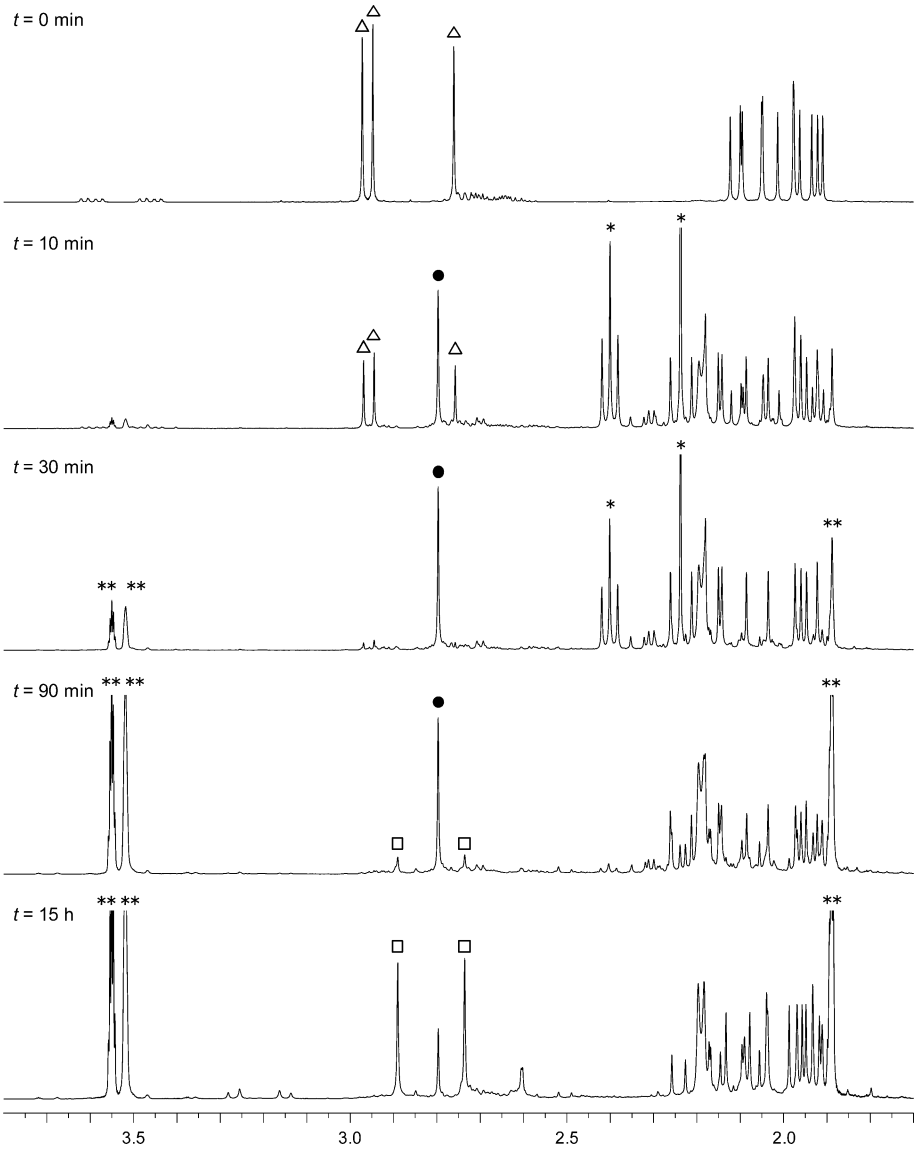
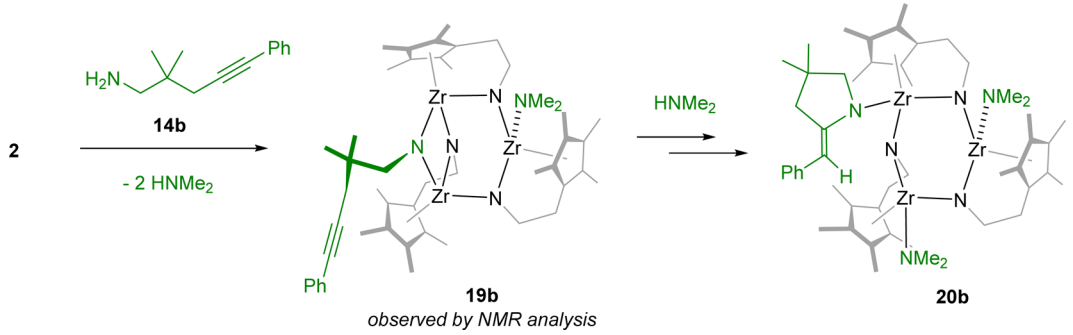


Figure 4. Partial ^{1}H NMR spectra for the semicatalytic reaction of **14b** using **2** (15 mol %) (25 °C in C_6D_6). $[\mathbf{14b}]_0$ = 0.075 M. Open triangles, solid circles, and open squares show Me_2N signals for complexes **2**, **19b**, and **20b**, respectively. The asterisk and double asterisk denote signals for substrate **14b** and product **15b**, respectively.

Scheme 7. Formation of Me_2NH Adduct 20b



selective incorporation of primary amines, depending upon their size and electronic nature. For instance, *n*-$PrNH_2$ as a relatively small substrate displayed several types of incorporation into the Zr_3 system (two to four amine molecule incorporation); in sharp contrast, only a single molecule of *neo*-$PenNH_2$ can be bound as a bridging imide ligand. The selective reactivity may be ascribed to both the flexibility and robustness of the supporting bridging imide ligands, which can adequately serve as proton acceptors toward incoming amine substrates and be converted to terminal amine, bridging amides, and μ-

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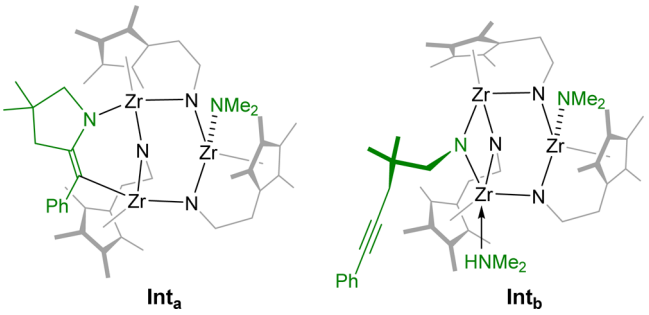
Chart 3. Possible Intermediates between 19b and 20b



Int_a Int_b

and μ_3-imides. For actor nitrogen ligands coordination modes of terminal and bridging amides and μ- and μ_3-imides were observed but not terminal imide. With this finding, we examined the cyclization of aminoalkynes using **2** to explore the mechanistic features. Two substrate classes, **13** and **14**, were examined and showed different coordination characteristics; multiply substrate incorporated complexes $\mathbf{17}_{kinetic}$, **17c**, and **18c** from complex **2** and **13** were observed under catalytic and stoichiometric conditions, respectively, while the latter β-dimethylated aminoalkynes **14** underwent formation of active mono-μ-imide intermediates **19**. In the semicatalytic reaction of **2** with **14b** the observed μ-imido intermediate **19b** was transformed into the Me_2NH adduct **20b** instead of a simple ligand cyclization product (i.e. $\mathbf{Int}_a$) at the end of the reaction. The present study clearly demonstrates that these bridging imides or amides are readily formed on the Zr_3 system and the observed **17c** and **19b** have sufficiently reactive substructures to undergo ligand cyclizations. The cyclization mechanism still remains elusive. Computational and further experimental studies on elucidation of the reaction mechanism and development of multimetallic effects of the Zr_3 system will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01311.

Experimental procedures and spectroscopic and crystallographic data of new compounds (PDF)

Accession Codes

CCDC 1551050−1551055 and 1551396 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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