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Preparation of Zirconium Guanidinate Complexes from the Direct Insertion of a Carbodiimine and Aminolysis Using a Guanidine. Comparison of the Reactions

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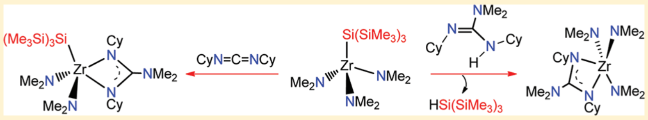
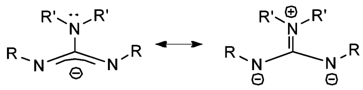
S *Supporting Information*

ABSTRACT: Direct insertion of 1 equiv of CyN=C=NCy (**1**; Cy = cyclohexyl) into the Zr–NMe$_2$ bonds in (Me$_2$N)$_3$Zr[N(SiMe$_3$)$_2$] (**2**) and (Me$_2$N)$_3$Zr[Si(SiMe$_3$)$_3$] (**3**) gave exclusively [CyNC(NMe$_2$)NCy]Zr(NMe$_2$)$_2$[N(SiMe$_3$)$_2$] (**5**) and [CyNC(NMe$_2$)NCy]Zr(NMe$_2$)$_2$[Si(SiMe$_3$)$_3$] (**6**), respectively. The reaction between **2** and guanidine CyNHC(NMe$_2$)=NCy (**9**) gave **5** and HNMe$_2$ through the preferred cleavage of a Zr–NMe$_2$ bond in **2**. The reaction between **3** and **9** led to the preferred cleavage of the Zr–Si(SiMe$_3$)$_3$ bond in **3**, yielding [CyNC(NMe$_2$)NCy]Zr(NMe$_2$)$_3$ (**7**) and HSi(SiMe$_3$)$_3$ and, upon cleavage of another Zr–NMe$_2$ bond, forming [CyNC(NMe$_2$)NCy]$_2$Zr(NMe$_2$)$_2$ (**8**). The aminolysis of Zr(NMe$_2$)$_4$ (**4**) by **9** first afforded **7** and then **8**. The structures of **5**, **6**, and **9** have been determined by X-ray diffraction.



Transition-metal guanidinate complexes have been actively studied in recent years for their unique chemistry and applications.[1−3] Complexes containing ancillary guanidinate ligands are catalysts or precatalysts for a variety of reactions.[3] In chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes, early-transition-metal amides such as **4** have been used as precursors to give metal-based materials.[4] The amide complexes are usually oxygen and moisture sensitive.[5,6] The introduction of ancillary ligands such as guanidinates ligands often makes the complexes more stable.[2] As shown in Scheme 1, bidentate anionic guanidinate ligands provide four electrons to the metal centers. Their zwitterionic resonance structures[7] also contribute to the stability of the complexes.

Scheme 1



We reported recently that in the reaction of Ta(NMe$_2$)$_4$[N(SiMe$_3$)$_2$] with **1**, the complex undergoes elimination of Me$_3$SiNMe$_2$ to give the imide "Ta(NMe$_2$)$_3$(=NSiMe$_3$)," observed as its dimer [Ta(NMe$_2$)$_3$(μ-NSiMe$_3$)]$_2$.[1t] **1** captures "Ta(NMe$_2$)$_3$(=NSiMe$_3$)" to give guanidinates Ta(NMe$_2$)$_{3-n}$(=NSiMe$_3$)[CyNC(NMe$_2$)NCy]$_n$ (n = 1, 2). We report here the preparation of guanidinates by insertion reactions between **1** and **2**,[8a] **3**,[8b] or **4**[8c,d] and compare the insertions with aminolysis of **2**, **3**, or **4** by **9** in order to understand the nature of the formation of the complexes containing silyl and amide ligands.

EXPERIMENTAL SECTION

Manipulations were performed under dry N$_2$. Solvents were purified by distillation from K/benzophenone ketyl.[9]

Formation of 5 by Insertion. Hexanes were added to a mixture of **2** (1.191 g, 3.102 mmol) and **1** (0.640 g, 3.102 mmol). After it was stirred for 15 h, the solution was filtered, and cooling at −32 °C overnight gave colorless crystals of **5** (1.556 g, 2.636 mmol, 85% yield). ^{1}H NMR (benzene-d_6, 399.79 MHz, 23 °C): δ 3.20–3.10 (br, 2H, C*H*), 3.09 (s, 12H, N*Me*$_2$), 2.40 (s, 6H, CN*Me*$_2$), 1.85–1.15 (m, 20H, C*H*$_2$), 0.43 (s, 18H, Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 100.53 MHz, 23 °C): δ 172.89 (*C*NMe$_2$), 57.04 (*C*H), 45.10 (N*Me*$_2$), 40.06 (CN*Me*$_2$), 35.48, 26.79, 26.28 (*C*H$_2$), 5.49 (Si*Me*$_3$). Anal. Calcd for $C_{25}H_{58}N_6Si_2Zr$: C, 50.88; H, 9.91; N, 14.24. Found: C, 50.77; H, 9.91; N, 14.16.

Formation of 6 by Insertion. To **3** (1.130 g, 2.400 mmol) in hexanes was added **1** (0.495 g, 2.400 mmol) in hexanes. After it was stirred for 18 h, the yellow solution was filtered, and crystallization at −20 °C gave pale yellow crystals of **6** (1.021 g, 1.507 mmol, 63% yield). ^{1}H NMR (benzene-d_6, 399.79 MHz, 23 °C): δ 3.20–3.10 (br, 2H, C*H*), 2.97 (s, 12H, N*Me*$_2$), 2.34 (s, 6H, CN*Me*$_2$), 1.80–1.10 (m, 20H, C*H*$_2$), 0.51 (s, 27H, Si*Me*$_3$). ^{13}C NMR (benzene-d_6, 100.54 MHz, 23 °C): δ 172.18 (*C*NMe$_2$), 57.80 (*C*H), 40.69 (CN*Me*$_2$), 40.47 (N*Me*$_2$), 35.26, 26.44, 26.01 (*C*H$_2$), 6.07 (Si*Me*$_3$). Anal. Calcd for $C_{28}H_{67}N_5Si_4Zr$: C, 49.64; H, 9.97; N, 10.34. Found: C, 49.76; H, 10.10; N, 10.17.

Formation of a Mixture of 7 and 8 by Insertion. In an NMR tube, **4** (0.0269 g, 0.100 mmol) and **1** (0.0206 g, 0.100 mmol) were dissolved in benzene-d_6. After 10 min, **7** and **8** in a molar ratio of ca. 0.6:1 were found along with a white precipitate of **7**.[10] ^{1}H NMR of **7** (toluene-d_8, 400.25 MHz, 23 °C): δ 3.13 (s, 18H, N*Me*$_2$), 3.16–3.08 (br, 2H, C*H*), 2.48 (s, 6H, CN*Me*$_2$), 1.79–1.21 (m, 20H, C*H*$_2$). ^{13}C

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NMR (toluene-d_8, 100.65 MHz, 23 °C): δ 172.05 ($CNMe_2$), 56.64 (CH), 43.43 (NMe_2), 39.83 ($CNMe_2$), 35.34, 26.82, 26.60 (CH_2). Anal. Calcd for $C_{21}H_{46}N_6Zr$: C, 53.23; H, 9.78; N, 17.74. Found: C, 53.17; H, 9.66; N, 17.42. NMR data of **8** at 35 and 23 °C are given in ref 1e and the Supporting Information, respectively.

Preparation of 9. **1** (8.212 g, 0.0398 mmol) in Et_2O was added to freshly prepared $LiNMe_2$ (2.030 g, 0.0398 mmol) suspended in Et_2O with stirring. After 4 h, degassed H_2O (0.72 mL, 0.040 mmol) was slowly added by a syringe to the solution at 0 °C. Stirring at 23 °C for 16 h gave a colorless solution. Et_2O was removed in vacuo to give an oily residue that was extracted by hexanes. The extract was dried by anhydrous Na_2SO_4, and hexanes were removed by distillation in a Kugelrohr apparatus at 85 °C and 6 Torr. Cooling the resulting liquid to 23 °C gave a few colorless crystals. A white solid formed at −20 °C overnight. The solid−liquid mixture was pumped at 23 °C for 6 h to give more crystals. The total weight of the solid and crystals was 8.110 g (0.0391 mmol, 98% yield). ^1H NMR ($CDCl_3$, 400.25 MHz, 23 °C): δ 2.94−2.89 (m, 1H, CH), 2.82−2.77 (m, 1H, CH), 2.63 (s, 6H, $CNMe_2$), 1.84−0.93 (m, 21H, N-H, CH_2). ^{13}C NMR ($CDCl_3$, 100.65 MHz, 23 °C): δ 155.60 ($CNMe_2$), 56.58, 53.18 (CH), 39.08 ($CNMe_2$), 35.39, 34.48, 25.76, 25.60, 25.43, 25.34 (CH_2). NMR data of **9** in benzene-d_6 are given in the Supporting Information.

Formation of 5 by Aminolysis. In an NMR tube, **2** (15.3 mg, 0.0398 mmol), **9** (10.0 mg, 0.0398 mmol), and $SiMePh_3$ (NMR standard) were dissolved in toluene-d_8. In 10 min, **5** was obtained in ca. 100% yield.

Formation of 7 from 3 by Aminolysis. In an NMR tube, **3** (18.8 mg, 0.0398 mmol), **9** (10.0 mg, 0.0398 mmol), and $SiMePh_3$ (NMR standard) were dissolved in toluene-d_8. In 20 min, **7** was obtained in ca. 100% yield.

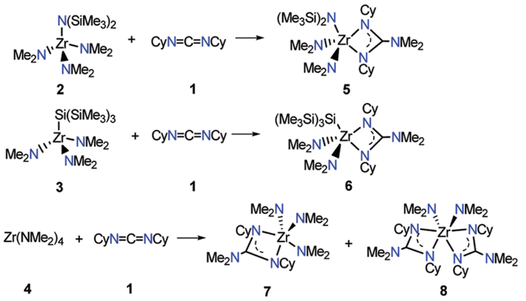
Formation of 7 from 4 by Aminolysis. *NMR Tube.* **9** (10.0 mg, 0.0398 mmol) was added to a solution of **4** (12.9 mg, 0.0482 mmol) and $SiMePh_3$ (NMR standard) in toluene-d_8. The formation of **7** was complete in 5 min (yield of ca. 100% based on **9**).[9]

Schlenk Flask. **9** (0.999 g, 3.973 mmol) in Et_2O was added dropwise to **4** (1.063 g, 3.973 mmol) in Et_2O. After the mixture was stirred for 5 h, volatiles were removed in vacuo to give an off-white solid of **7** (1.603 g, 3.383 mmol, 85.1% yield).

■ RESULTS AND DISCUSSION

Formation of 5−7 from Insertion Reactions. **5**−**7** were prepared by the insertion of **1** into the Zr−NMe_2 bonds in **2**−**4**, respectively (Scheme 2). In fact, the reaction of 1 equiv of **1** with **4** gave a mixture of **7** and **8** with unreacted **4**. Another 1 equiv of **1** inserts into another Zr−NMe_2 bond in **7** to give **8**. **8** was reported by Lappert and co-workers through a di-insertion reaction between **1** and **4**.[10] It is interesting to note that only 1 equiv of **1** inserts into a Zr−NMe_2 bond in **2** and **3** to form **5** and **6**, respectively. There is *no* insertion into the Zr−$N(SiMe_3)_2$ bond in **2** or the Zr−$Si(SiMe_3)_3$ bond in **3**, although the $\{CyNC[N(SiMe_3)_2]NCy\}^-$ ligand is known[1p,q,2a,11] and insertion into M−$N(SiMe_3)_2$ bonds has been reported.[11f,h] In other words, insertion into the Zr−NMe_2 bonds in **2** and **3** is exclusive. The bulkiness of the $N(SiMe_3)_2$ and $Si(SiMe_3)_3$ ligands perhaps makes the insertion into their bonds with the Zr atom difficult. **5**−**7** are thermally stable at 23 °C.

Scheme 2. Preparation of 5−8 through Insertion



The ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** are consistent with its structure.[12] Both NMe_2 (3.09 ppm) and $N(SiMe_3)_2$ (0.43 ppm) resonances are shifted downfield from those of **2** (2.90 and 0.30 ppm).[8a] In the $^{13}C\{^1H\}$ NMR spectrum, a peak at 172.89 ppm is assigned to the central C atom in the $CyNC(NMe_2)NCy$ ligand. The $^{13}C\{^1H\}$-APT NMR spectrum shows the −CH− atom in the Cy ring at 57.04 ppm.

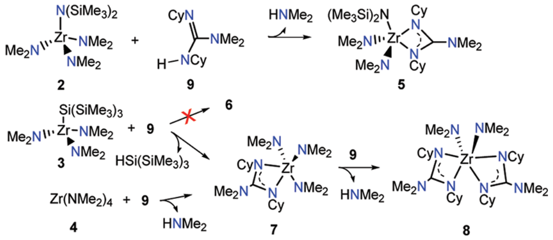
In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **6**, the resonances of both NMe_2 and $Si(SiMe_3)_2$ are shifted downfield from those of **3** (to 2.97 from 2.40 ppm for NMe_2; to 0.51 from 0.39 ppm for $Si(SiMe_3)_2$).[8b] The central C atom in the $CyNC(NMe_2)NCy$ ligand was observed at 172.18 ppm. The 57.80 ppm peak is assigned to the −CH− atom in the Cy rings, as confirmed by a $^{13}C\{^1H\}$-APT NMR spectrum.

NMR spectra of **7** are typical of amide guanidinates. In comparison to $Zr(NMe_2)_2$ (**4**), its NMe_2 peaks are less shifted than those of the guanidinate **8**.[9]

Synthesis of Guanidine CyNH-C(NMe₂)=NCy (9) and Its Aminolysis Reactions Forming 5, 7, and 8. Guanidines have been usually prepared by the reaction of an amine with an electrophilic guanylating reagent[13] and by catalytic hydroamination of carbodiimides[3j,k,14] and transamination.[3k,15] In the current work, **9** was prepared through the reaction of H_2O with $Li[CyNC(NMe_2){=}NCy]$ which had been made by the reaction of **1** with $LiNMe_2$, using a modified procedure.[16] In Et_2O, crystals of **9** were obtained in 98% yield. Another major difference is that **9** was reported to be a liquid,[16] and we obtained it in the pure crystalline state, allowing it to be characterized by single-crystal diffraction discussed below. We did not observe the reported N−H peak at 7.40 ppm in our ^1H NMR spectrum.[9] The N−H peak may overlap with multiplets of the Cy groups. The crystals of **9** are sensitive to moisture, probably because of the hydrophilicity of its N−H bond. When the crystals were exposed to the air, they became a liquid.

In the aminolysis between **2** and **9**, a NMe_2 ligand in **2** captures a proton in **9** to give $HNMe_2$ and **5** in nearly 100% yield (Scheme 3). The aminolysis gives the same product (**5**) as that from the insertion of **1** into **2**. However, the $N(SiMe_3)_2$ ligand in **2** did not undergo aminolysis, indicating that it is more inert (and perhaps less basic) than the NMe_2 ligands in **2**. Unexpectedly, the aminolysis of **3** by **9** gives **7**, wherein the $Si(SiMe_3)_3$ ligand in **3** is removed by a proton in **9**. In comparison, the insertion reaction of **3** with **1** gives **6**, in which the $Si(SiMe_3)_3$ ligand is retained. The current work suggests that the ligands here may have the following relative strength as bases: $[N(SiMe_3)_2]^- < [CyNC(NMe_2){=}NCy]^- < NMe_2^- < Si(SiMe_3)_3^-$.

Scheme 3. Preparation of 5, 7, and 8 through Aminolysis



It is interesting that the insertion reaction between **4** and 1 equiv of **1** unavoidably gives a mixture of **7** and **8**. However, the aminolysis of **4** by 1 equiv of **9** yields only **7** (and $HNMe_2$). The reaction of another 1 equiv of **9** with **7** gives **8**. Thus, the aminolysis here demonstrates an advantage over the insertion: it gives a pure product rather than a mixture.

X-ray Structures of 5, 6, and 9. The Zr center in **5** (Figure 1) is a distorted square pyramid (SP) with an axial N(6) atom, as indicated by the Addison τ value of 0.06. The τ parameter[17] has been used to describe the degree of distortion of pentacoordinated structures ($\tau = 0$ for a perfect SP; $\tau = 1$ for a perfect trigonal bipyramid (TBP)). The N(2)−C(7)−N(1) angle of 113.05(18)° for the guanidinate ligand is significantly smaller than 127.09(10)° in the free guanidine **9** discussed below. This angle is, however, similar to those in other guanidinate ligands, such as 113.00(16)° in **6**. The small angle in the guanidinate ligand is a result of a rigid four-membered ring, making room for other large angles around the metal atom. The bond lengths of Zr(1)−N(1) (2.2530(19) Å) and Zr(1)−N(2) (2.3176(19) Å) are larger than the other three Zr−N bond lengths (2.0456(19)−2.143(2) Å), reflecting the fact that there is a significant contribution of a dative bond between the guanidinate ligand and the metal atom. The bulky ligand $N(SiMe_3)_2$ and less d−p π bonding between this ligand and the Zr atom may lead to the Zr(1)−N(4) bond (2.143(2) Å) being longer than the two $Zr-NMe_2$ bonds (2.0664(19), 2.0456(19) Å).

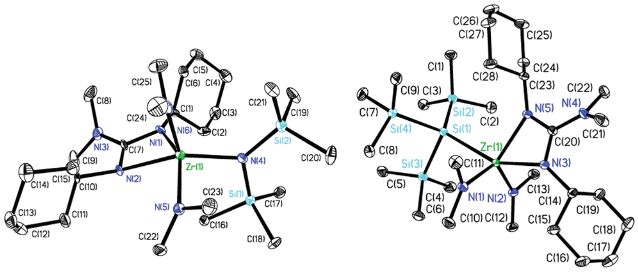


Figure 1. Structures of **5** (left) and **6** (right). Selected bond lengths (Å) and angles (°) are as follows. **5**: Zr(1)−N(1) = 2.2530(19), Zr(1)−N(2) = 2.3176(19), Zr(1)−N(4) = 2.143(2), Zr(1)−N(5) = 2.0664(19), Zr(1)−N(6) = 2.0456(19), C(7)−N(1) = 1.346(3), C(7)−N(2) = 1.338(3), C(7)−N(3) = 1.384(3); N(1)−Zr(1)−N(2) = 58.63(6), N(4)−Zr(1)−N(1) = 97.45(7), N(4)−Zr(1)−N(2) = 141.36(7), N(5)−Zr(1)−N(1) = 145.19(7), N(5)−Zr(1)−N(2) = 91.69(7), N(5)−Zr(1)−N(4) = 96.16(7), N(6)−Zr(1)−N(1) = 100.11(8), N(6)−Zr(1)−N(2) = 102.40(7), N(6)−Zr(1)−N(4) = 112.09(7), N(6)−Zr(1)−N(5) = 104.14(8). **6**: Zr(1)−N(1) = 2.025(2), Zr(1)−N(2) = 2.0147(19), Zr(1)−N(3) = 2.2610(19), Zr(1)−N(5) = 2.269(2), Zr(1)−Si(1) = 2.9240(19), N(3)−C(20) = 1.337(3), N(4)−C(20) = 1.388(2), N(5)−C(20) = 1.348(3); N(1)−Zr(1)−Si(1) = 96.12(7), N(2)−Zr(1)−N(1) = 115.24(7), N(1)−Zr(1)−N(3) = 93.80(8), N(1)−Zr(1)−N(5) = 124.16(7), N(2)−Zr(1)−N(3) = 98.02(7), N(2)−Zr(1)−N(5) = 116.26(8), N(2)−Zr(1)−Si(1) = 97.10(6), N(3)−Zr(1)−N(5) = 59.23(6), N(3)−Zr(1)−Si(1) = 156.30(5), N(5)−Zr(1)−Si(1) = 97.61(5).

In **6** (Figure 1), the Zr center is better described as a distorted TBP, as indicated by the Addison τ value of 0.54.[17] N(1)−Zr(1)−Si(1) (96.12(7)°), N(2)−Zr(1)−Si(1) (97.10(6)°), and N(5)−Zr(1)−Si(1) (97.61(5)°) as well as N(1)−Zr(1)−N(3) (93.80(8)°) and N(2)−Zr(1)−N(3) (98.02(7)°) angles are close to 90° expected between an axial and equatorial ligands. As in **5**, the two $Zr-NMe_2$ bonds (2.0147(19)−2.025(2) Å) are shorter than the Zr−N bonds in the guanidinate ligand (2.2610(19)−2.269(2) Å) as a result of a dative bond in the latter.

The crystal structure of **9** (Figure 2) reveals that the NMe_2 and one Cy group [C(1)] are *trans* to each other with respect to the N=C imine bond. In comparison, they are *cis* to each other in the guanidinate ligands in **5** and **6**. The lone pair electrons on N(1) is *trans* to the N(3)(Cy)−H group (and point away from the N(3)−H bond). The average distance between N(1) and the H atom (on the N(3) atom) of 2.53(4) Å and the N(1)−H- - -N(3) angle of 71(3)° suggest there is little hydrogen-bonding interaction between N(1) and the H atom.[18]

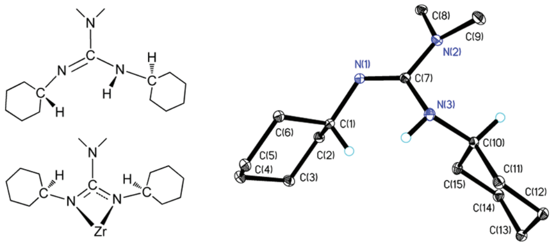


Figure 2. *trans* structure in **9** (left) and its crystal structure (right). Selected bond lengths (Å) and angles (°): C(1)−N(1) = 1.4615(14), C(7)−N(1) = 1.2850(15), C(7)−N(2) = 1.3799(14), C(7)−N(3) = 1.3997(15); N(1)−C(7)−N(2) = 120.17(10), N(1)−C(7)−N(3) = 127.09(10), N(2)−C(7)−N(3) = 112.73(10).

The current work shows that, in complexes with NMe_2, $N(SiMe_3)_2$, and $Si(SiMe_3)_3$ ligands, carbodiimide **1** inserts exclusively into the $Zr-NMe_2$ bonds. In the reactions of guanidine $CyNHC(NMe_2)=NCy$ (**9**) with the complexes, the silyl ligand is preferentially removed as $HSi(SiMe_3)_3$ by the proton in **9**, followed by the removal of the NMe_2 ligand as $HNMe_2$. The $N(SiMe_3)_2$ ligand seems to be most inert of the three studied in the current work. The results suggest the aforementioned relative strength of the ligands as bases.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, and CIF files giving additional experimental procedures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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