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Cyclopentadienyl−Hydrazido Titanium Complexes: Tuning of Coordination Modes of Hydrazido Ligands to the Titanium Center

Sung Cheol Yoon,[†] Byoung-Jae Bae,[†] Il-Hwan Suh,[‡] and Joon T. Park*[,†]

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea, and Department of Physics, Chungnam National University, Taejon 305-701, Korea

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Summary: Cyclopentadienyl−hydrazido titanium complexes $[(\eta^5\text{-}C_5Me_4)SiMe_2(NNMe_2)]TiR_2$ *(R =* NMe_2 *(**2**), Cl (**3**), Me (**5**)) and* $[(\eta^5\text{-}C_5Me_4)SiMe_2(NNMe_2AlMe_3)]TiMe_2$ *(**4**) have been prepared and characterized. Single-crystal X-ray diffraction studies reveal that complexes **2**−**5** contain* η^1*-hydrazido (**2** and **4**) and* η^2*-hydrazido (**3** and **5**) groups depending on the electronic nature of the titanium center. The reaction of **2** with* H_2O *produces a tetrameric organotitanoxane* $[(\eta^5\text{-}C_5Me_4)(SiMe_2NHNMe_2)Ti]_4O_6$ *(**6**) with an adamantane-like cage structure.*

Cyclopentadienyl−amido titanium complexes containing an amido ligand linked to a cyclopentadienyl group have recently attracted considerable attention as olefin polymerization catalysts with remarkable activity for copolymerization of ethylene with α-olefins.[1] The sterically open nature of the catalyst center is considered to facilitate incorporation of various α-olefins into growing polymer chains. As an extension of structural variations in cyclopentadienyl−amido titanium complexes, the hydrazido moiety has been employed as a donor group instead of the amido ligand. The strong donor nature of the hydrazido moiety stabilizes the catalytically active cationic species compared to the amido ligand, which may result in interesting polymerization characteristics. Two η^2-hydrazido complexes, $(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NHNMe_2)TiCl_2$ and $(\eta^5\text{-}C_5H_5)(\eta^2\text{-}NPhNH_2)TiCl_2$, are the only known hydrazido titanium complexes before this work.[2] Herein we report synthesis, characterization, and reactivity of cyclopentadienyl−hydrazido titanium complexes, which involves tuning of coordination modes of the hydrazido ligands in these complexes as shown in Scheme 1.

An *N*,*N*-dimethyl hydrazido ligand, $(C_5Me_4H)SiMe_2(NHNMe_2)$ (**1**),[3] was prepared by the reaction of $LiNHNMe_2$ with $(C_5Me_4H)SiMe_2Cl$[1f] as a greenish liquid in 54% yield. Neat reaction of **1** with $Ti(NMe_2)_4$ at 130 °C afforded an η^1-hydrazido bis(dimethylamido) complex, $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ (**2**),[4] as a red solid via amine elimination[5] in 42% yield. Treatment of **2** with excess Me_3SiCl in dichloromethane gave an η^2-hydrazido dichloro compound **3**[6] as an orange solid in 63% yield. The methyl proton resonances on the hydrazido moiety of **2** and **3** appear at 2.49 and 2.95 ppm, respectively. This downfield shift (0.46 ppm) for **3** supports the structural characterization that the hydrazido moiety in **3** is η^2-coordinated to the titanium metal center. Synthesis of a dimethyl derivative **5** was attempted from the reaction of **3** with 2 equiv of trimethylaluminum, but the reaction was sluggish. However, when an excess amount (ca. 5 equiv) of trimethylaluminum was used, a trimethylaluminum adduct of **5** was isolated in 43% yield as air-sensitive brownish yellow crystals. The trimethylaluminum molecule is coordinated to the hydrazido nitrogen with dimethyl groups to yield the η^1-hydrazido complex $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2AlMe_3)]TiMe_2$ (**4**),[7] in which the methyl proton resonance is shifted further downfield to 3.29 ppm due to the Lewis acid coordination. Upon treatment of **4** with triethylamine at −78 °C in toluene, the trimethylaluminum molecule could be eliminated to produce the dimethyl complex $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiMe_2$ (**5**)[8] as a green solid in 77% yield. The ^1H NMR spectrum of **5** exhibits a single resonance at 3.00 ppm for the methyl groups of the hydrazido moiety, which suggests the η^2-hydrazido ligand in **5**.

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* To whom correspondence should be addressed. E-mail: jtpark@sorak.kaist.ac.kr. Fax: +82-42-869-2810.

[†] Korea Advanced Institute of Science and Technology.

[‡] Chungnam National University.

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(3) Compound **1**: ^1H NMR ($CDCl_3$, 25 °C) δ 2.44 (s, 1H, SiC*H*), 2.37 (s, 6H, NN*Me*$_2$), 1.94, 1.78 (s, 12H, C_5*Me*$_4$), −0.06 (s, 6H, Si*Me*$_2$).

(4) Compound **2**: A neat mixture of **1** (0.73 g, 3.1 mmol) and $Ti(NMe_2)_4$ (0.70 g, 3.1 mmol) in a 250 mL Schlenk flask was heated at 130 °C for 4 h. The reaction mixture was cooled to room temperature and evacuated in vacuo to remove volatiles. Recrystallization of the orange residue in pentane at −20 °C afforded **2** (0.48 g, 42%) as red crystals: ^1H NMR ($CDCl_3$, 25 °C) δ 2.99 (s, 12H, TiN*Me*$_2$), 2.49 (s, 6H, NN*Me*$_2$), 2.11, 2.02 (s, 12H, C_5*Me*$_4$), 0.49 (s, 6H, Si*Me*$_2$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 127.6, 124.9, 103.1 (*C*$_5$Me$_4$), 51.1 (NN*Me*$_2$), 48.6 (TiN*Me*$_2$), 14.0, 11.7 (C_5*Me*$_4$), 4.6 (Si*Me*$_2$). Anal. Calcd for $C_{17}H_{36}N_4SiTi$: C, 54.82; H, 9.74; N, 15.04. Found: C, 54.51; H, 9.34; N, 14.64.

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(6) Compound **3**: A dichloromethane (10 mL) solution of Me_3SiCl (0.36 g, 3.4 mmol) was slowly added to a dichloromethane (30 mL) solution of **2** (0.50 g, 1.3 mmol). The reaction mixture was stirred at room temperature for 5 h, and the solvent was removed in vacuo. The orange residue was washed with ether (3 × 10 mL) and extracted with toluene. Evaporation of the solvent and recrystallization in toluene at −20 °C yielded **3** (0.30 g, 63%) as orange crystals: ^1H NMR ($CDCl_3$, 25 °C) δ 2.95 (s, 6H, NN*Me*$_2$), 2.20, 1.92 (s, 12H, C_5*Me*$_4$), 0.66 (s, 6H, Si*Me*$_2$); ^{13}C NMR ($CDCl_3$, 25 °C) δ 136.4, 133.1, 96.5 (*C*$_5$Me$_4$), 50.0 (NN*Me*$_2$), 15.5, 12.2 (C_5*Me*$_4$), 4.2 (Si*Me*$_2$). Anal. Calcd for $C_{13}H_{24}Cl_2N_2SiTi$: C, 43.96; H, 6.81; N, 7.89. Found: C, 43.62; H, 6.40; N, 7.86.

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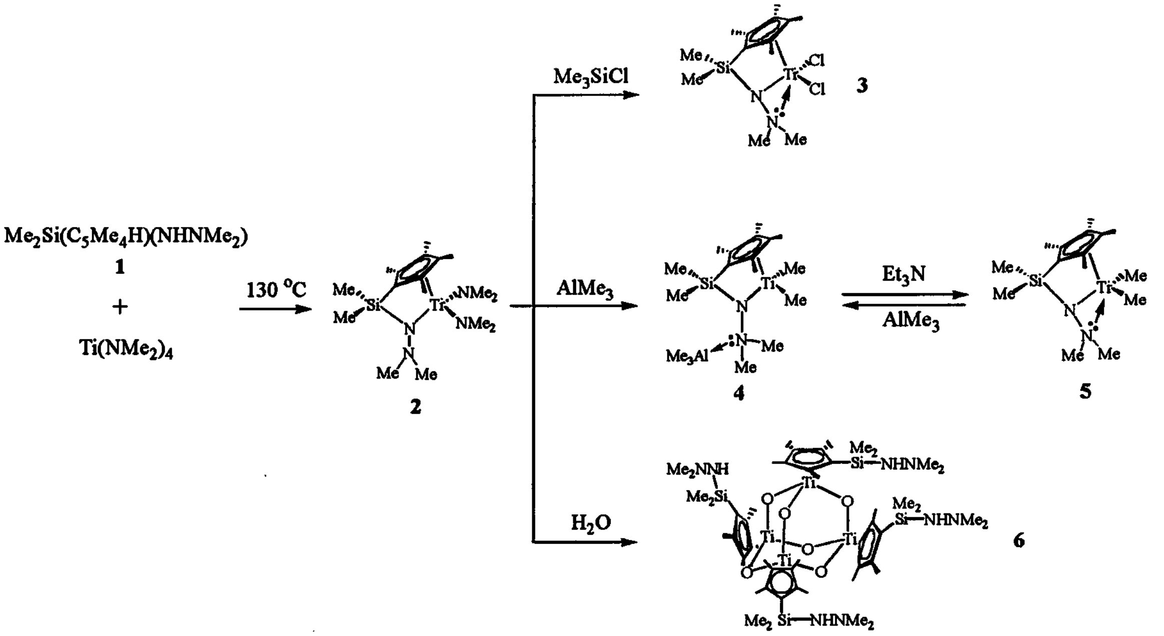
Scheme 1



The X-ray crystal structures of **2**−**5** have been determined to examine the structural details of the hydrazido moieties. The overall molecular geometry and the atomic labeling scheme of **2** and **3** are illustrated in Figures 1 and 2, respectively. The structure[9] of **2** exhibits a distorted tetrahedral geometry consisting of a bifunctional tetramethylcyclopentadienyl−hydrazido ligand and two terminal dimethylamido groups. General structural features of **2** are similar to those previously reported for $[(C_5H_4)SiMe_2(N\text{-}^tBu)]Ti(NMe_2)_2$ and $[(C_5Me_4)SiMe_2(N\text{-}^tBu)]Zr(NMe_2)_2$.[11] Complex **2** has a pseudo C_s symmetry with the mirror plane including the Ti, Si, and N1 atoms, and bisecting the $Me_2N-Ti-NMe_2$ angle and the Cp ring. The short Ti−N3 and Ti−N4 bond distances (1.927(8) and 1.912(8) Å) and the planar geometry of the N3 and N4 nitrogen atoms indicate sp^2 hybridization of the two nitrogen atoms with the out-of-plane lone pairs giving an $N(p\pi) \rightarrow M(d\pi)$ interaction. The electron-rich nature of the titanium center due to the d−p-π interaction appears to cause the hydrazido moiety to be η^1-bonded to the titanium metal. The Ti−N1 bond length (1.977(7) Å) is similar to that (1.972(4) Å) of $[(C_5H_4)SiMe_2(N\text{-}^tBu)]Ti(NMe_2)_2$, but longer than that for amido CGC complexes such as $[(C_5Me_4)SiMe_2(N\text{-}^tBu)]TiCl_2$ (1.907(4) Å),[11] $[(C_5H_4)SiMe_2(N\text{-}^tBu)]TiCl_2$ (1.901(3) Å),[11] and $[(C_5H_4)SiMe_2(N\text{-}^iPr)]TiCl_2$ (1.878(2) Å).[12] This observed difference in the Ti−N1 bond lengths is probably a consequence of a decrease in the relative degree of $N \rightleftharpoons Ti$ π-overlap for complexes with terminal amido ligands. The molecular structure[13] of **3** is similar

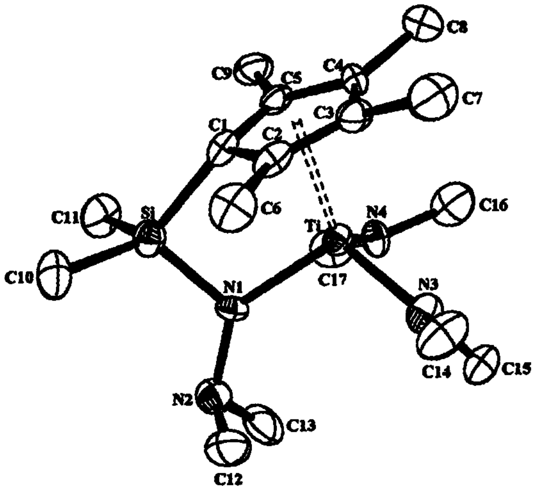


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NNMe_2)]Ti(NMe_2)_2$ (**2**-A). Selected interatomic distances (Å) and angles (deg): Ti−N1 = 1.977(7), Ti−N3 = 1.927(8), Ti−N4 = 1.912(8), Ti−Cp′(Cen) = 2.098, N1−N2 = 1.449(1); N1−Ti−Cp′(Cen) = 103.85.

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(7) Compound **4**: To a toluene (30 mL) solution of **2** (1.01 g, 2.7 mmol) was added a pentane (10 mL) solution of $AlMe_3$ (0.98 g, 13.6 mmol) at −50 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. The solvent was removed in vacuo, and the residue was extracted with pentane (3 × 10 mL). Evaporation of the solvent and recrystallization in pentane at −20 °C gave **4** (0.45 g, 43%) as green crystals: ^1H NMR ($CDCl_3$, 25 °C) δ 3.29 (s, 6H, NN*Me*2), 2.18, 1.98 (s, 12H, C_5Me_4), 0.60 (s, 6H, Si*Me*2), 0.40 (s, br, 6H, Ti*Me*2), −0.84 (s, 9H, Al*Me*3); ^{13}C NMR ($CDCl_3$, 25 °C) δ 135.7, 131.5, 101.1 (C_5Me_4), 55.8 (NN*Me*2), 52.8 (Ti*Me*2), 15.2, 12.4 (C_5Me_4), 6.01 (Si*Me*2), −7.4 (Al*Me*3).

(8) Compound **5**: A toluene (10 mL) solution of Et_3N (0.28 g, 2.7 mmol) was added dropwise to a toluene (30 mL) solution of **4** (1.00 g, 2.6 mmol) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. The solvent was evaporated in vacuo, and the yellow residue was extracted with pentane (3 × 10 mL). Evaporation of the solvent and recrystallization in pentane at −20 °C afforded **5** (0.63 g, 77%) as yellow crystals: ^1H NMR ($CDCl_3$, 25 °C) δ 3.00 (s, 6H, NN*Me*2), 2.17, 1.72 (s, 12H, C_5Me_4), 0.43 (s, 6H, Si*Me*2), −0.39 (s, 6H, Ti*Me*2); ^{13}C NMR ($CDCl_3$, 25 °C) δ 129.4, 125.5, 91.4 (C_5Me_4), 52.2 (NN*Me*2), 41.2 (Ti*Me*2), 14.5, 11.7 (C_5Me_4), 5.1 (Si*Me*2). Anal. Calcd for $C_{15}H_{30}N_2SiTi$: C, 57.31; H, 9.62; N, 8.91. Found: C, 57.26; H, 9.37; N, 8.87.

(9) Crystal data for **2**: $C_{17}H_{36}N_4SiTi$; M_r = 372.49; triclinic; space group $P\bar{1}$; a = 9.171(6) Å, b = 15.428(2) Å, c = 16.488(2) Å; α = 70.75(1)°, β = 76.35(2)°, γ = 89.21(2)°; V = 2135.0(1) Å^3; Z = 4; μ(Mo Kα) = 0.462 mm^{-1}. Diffraction data were collected using a CAD4 diffractometer. The structure was solved by SHELXS-86[10a] and refined by SHELXL-93.[10b] The final discrepancy indices were R = 0.069, R_w = 0.132, and GOF = 1.073 for 415 parameters refined against 4161 reflections that had $I > 2\sigma(I)$. There are two equivalent molecules (**2**-A and **2**-B) in the crystallographic asymmetric unit.

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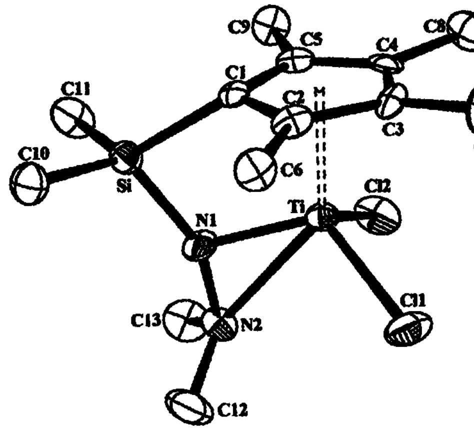

Figure 2. Molecular structure of $[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^2\text{-}NNMe_2)]TiCl_2$ (**3**-A). Selected interatomic distances (Å) and angles (deg): Ti−N1 = 1.857(1), Ti−N2 = 2.364(1), Ti−Cl1 = 2.303(4), Ti−Cl2 = 2.305(4), Ti−Cp′(Cen) = 2.060, N1−N2 = 1.405(1); N1−Ti−Cp′(Cen) = 101.12, N2−Ti−Cp′(Cen) = 137.54.

to that of **2** except that the hydrazido moiety is η^2-bound to the titanium metal (Figure 2). The Ti−N1 and Ti−N2 bond distances (1.857(1) and 2.364(1) Å) are comparable to those of known η^2-hydrazido titanium complexes, $(C_5H_5)(NHNMe_2)TiCl_2$ (1.83 and 2.22 Å) and $(C_5H_5)(NPhNH_2)TiCl_2$ (1.88 and 2.14 Å).[2] The hydrazide (−1) fragment can be best represented formally as a six-electron donor with a N1 $\rightleftharpoons$ Ti π-interaction and a N2 → Ti dative bond. Complex **3**, therefore, can be considered to be a 16-electron species. Structural characterization[14] of **4** and **5** reveals that **4** and **5** contain η^1- and η^2-hydrazido ligands, respectively, as depicted in Scheme 1.

As clearly seen by spectroscopic and structural characterization for hydrazido CGC complexes, **1**−**5**, the coordination mode of the hydrazido moiety can be tuned either by the electronic property of the two terminal ligands or by addition of Lewis acids or bases. Complex **2** with NMe_2 donor ligands contains an electron-rich titanium center, which consequently results in η^1-coordination of the hydrazido moiety. Complexes **3** and **5**, however, have η^2-hydrazido groups because of the relatively electron-poor titanium metal with electron-withdrawing Cl and Me ligands. Interestingly, reversible interconversion (**4** $\rightleftarrows$ **5**) between η^1- and η^2-hydrazido ligands has been observed upon addition of external NEt_3 and $AlMe_3$ reagents.

To understand water sensitivity of **2**, the reaction of **2** with H_2O was attempted to yield a tetrameric organotitanoxane $[(\eta^5\text{-}C_5Me_4)(SiMe_2NHNMe_2)Ti]_4O_6$ (**6**)[15] as green crystals in 52% yield. X-ray structural analysis[16] of **6** reveals an adamantane-like cage structure with a tetrahedral Ti_4O_6 core, which is similar to that previously reported for $[(\mu^5\text{-}C_5Me_5)Ti]_4O_6$[17] (Figure 3). The coordination geometry of each Ti atom is pseudo-tetrahedral with three sites being occupied by bridging oxygen atoms and the remaining site by a π-bonded η^5-tetramethyl cyclopentadienyl ligand with a hydrazidodimethylsilyl substituent. Compound **6** is likely to be formed by similar hydrolysis and condensation reaction proposed for the formation of $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$ from hydrolysis of $(\eta^5\text{-}C_5Me_5)TiCl_3$ under basic conditions.[17]

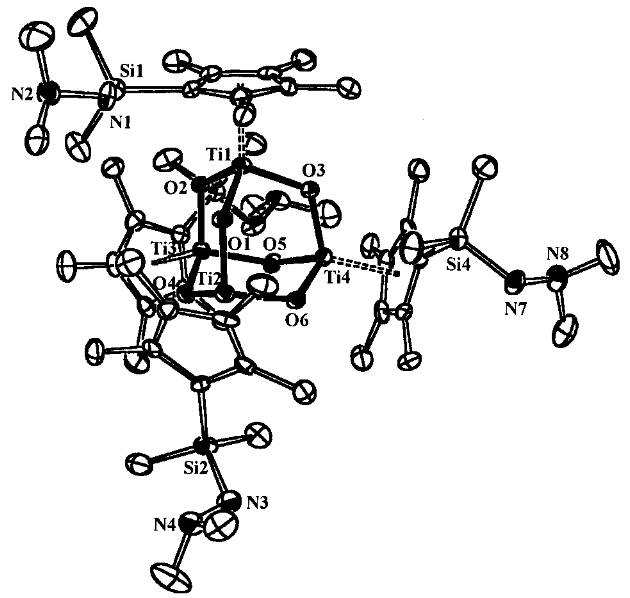

Figure 3. Molecular structure of **6**. Selected interatomic distances (Å) and angles (deg): Ti−O1 = 1.824(5), Ti−O2 = 1.834(5), Ti−O3 = 1.852(5), Ti−Cp′(Cen) (av) = 2.078, N7−N8 = 1.406(9); Cp′(Cen)−Ti−O (av)= 116.6, O−Ti−O (av) = 101.4, Ti−O−Ti (av) = 124.0.

In conclusion, we have prepared various cyclopentadienyl−hydrazido titanium complexes, **2**−**5**, which involve η^1- and η^2-bound hydrazido moieties depending on the electronic nature of the titanium metal and, to our knowledge, are the first examples of η^1- and η^2-hydrazido ligand interconversion. Further studies on reactivity and α-olefin polymerization characteristics of **2**−**5** are being investigated.

Acknowledgment. We are grateful to SK corporation for financial support of this work.

Supporting Information Available: Figures of molecular geometry for **4**, **5**, and **6** and tables of crystal data, atomic coordinates, thermal parameters, bond distances, and angles for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for **3**: $C_{13}H_{24}Cl_2N_2SiTi$; $M_r = 355.22$; orthorhombic; space group $Pbc2_1$; $a = 7.717(1)$ Å, $b = 16.735(2)$ Å, $c = 26.731(3)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 3452.2(9)$ Å^3; $Z = 8$; μ(Mo Kα) = 0.862 mm^{-1}. Diffraction data were collected and treated as described for **2**. The final discrepancy indices were $R = 0.049$, $R_w = 0.109$, and GOF = 1.054 for 343 parameters refined against 2474 reflections that had $I > 2\sigma(I)$. There are two equivalent molecules (**3**-A and **3**-B) in the crystallographic asymmetric unit.

(14) Details of structural characterization of **4** and **5** are described in the Supporting Information and will be reported in a full paper.

(15) Compound **6**: Deoxygenated water (24 μL, 1.34 mmol) was added to a toluene (50 mL) solution of **2** (0.50 g, 1.3 mmol) at room temperature. The reaction mixture was stirred for 5 h and turned to a yellow solution. The solution was evaporated in vacuo, and the yellow residue was extracted with pentane (3 × 10 mL). Evaporation of the solvent and recrystallization in pentane at −20 °C yielded **6** (0.22 g, 52%) as green crystals: ^{1}H NMR ($CDCl_3$, 25 °C) δ 2.42 (s, 24H, N*Me*$_2$), 2.22, 1.99 (s, 48 H, C_5*Me*$_4$), 2.11 (s, 4H, N*H*), 0.42 (s, 24H, Si*Me*$_2$). Anal. Calcd for $C_{52}H_{100}O_6N_8Si_4Ti_4$: C, 50.48; H, 8.15; N, 9.06. Found: C, 50.11; H, 7.98; N, 8.81.

(16) Crystal data for **6**: $C_{52}H_{100}O_6N_8Si_4Ti_4$; $M_r = 1237.36$; triclinic; space group $P\bar{1}$; $a = 12.321(5)$ Å, $b = 15.958(2)$ Å, $c = 19.194(3)$ Å; $\alpha = 79.64(1)$ °, $\beta = 71.47(2)°$, $\gamma = 67.27(2)°$; $V = 3293.4(2)$ Å^3; $Z = 2$; μ(Mo Kα) = 0.589 mm^{-1}. Diffraction data were collected and treated as described for **2**. The final discrepancy indices were $R = 0.063$, $R_w = 0.115$, and GOF = 1.078 for 667 parameters refined against 7338 reflections that had $I > 2\sigma(I)$.

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