Heterometallic Cubes

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Addition of Terminal Alkynes to a Molecular Titanium–Zinc Nitride**

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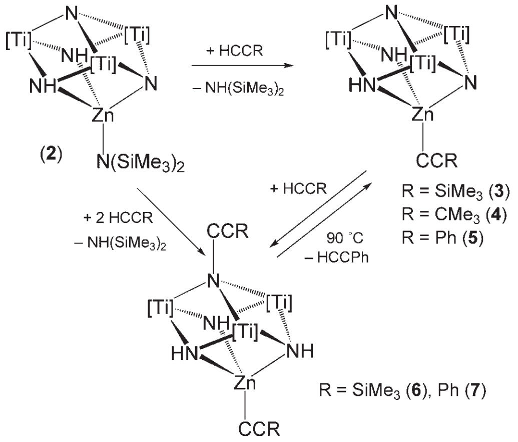
Dedicated to Professor Gerhard Erker on the occasion of his 60th birthday

Transition-metal nitrido complexes have been studied extensively in the past few decades.[1,2] While nitrido complexes of Group 6–8 metals usually bear the nitrido ligands as a terminal functionality, $\mathrm{M{\equiv}N}$,[3] the analogous derivatives of early transition metals exhibit polynuclear structures, with μ_n-nitrido ligands bridging two or more metal centers.[2,4,5] The reactivity of terminal nitrido ligands has received increasing attention because of their potential to show either nucleophilic or electrophilic character.[1,3,6] The net result of the latter is usually a two-electron reduction of the metal center and a reduced bond order between the metal and the nitrogen atom [Eq. (1)]. Recently a similar behavior has been proposed for the nucleophilic attack of a phosphine to a bridging dinitride species; in that case the reduction leads to a complex with a metal–metal bond.[7]

$$[\mathrm{M}^{n+}{\equiv}\mathrm{N}{:}] + {:}\mathrm{Nu} \rightarrow [\mathrm{M}^{(n-2)+}(\mathrm{NNu})] \quad (\mathrm{Nu} = \mathrm{PR}_3,\ \mathrm{S}_8,\ \mathrm{R}^-,\ \text{etc.}) \qquad (1)$$

Over the last few years we have been studying the reactivity of the trinuclear imido–nitrido titanium derivative $[\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})(\mu\text{-}\mathrm{NH})\}_3(\mu_3\text{-}\mathrm{N})]$[8] (**1**) towards metal complexes and have reported the coordination of **1** to these metals through the imido groups to give the cube-type adducts $[\mathbf{1}{\cdot}\mathrm{ML}_n]$.[9] The elimination of organic molecules and the formation of nitrido groups that bridge the metal centers occur if the N–H bonds of the organometallic ligand **1** are activated by metal–imido, metal–amido, or metal–alkyl linkages.[10] However, none of those processes involves the triply bridging apical nitrido ligand of **1**. Herein we present the first example of a reaction at this nitrido ligand, which leads to an alkynylimido ligand by C–N bond formation. We have studied this "apparent" nucleophilic attack of an acetylide at the apical nitrido ligand by density functional calculations and propose a plausible reaction mechanism.

Our synthetic route is outlined in Scheme 1. Treatment of the amido zinc derivative **2**[11] with one equivalent of terminal alkyne RCCH in toluene gives the expected zinc acetylides $[\{(\mathrm{RCC})\mathrm{Zn}\}(\mu_3\text{-}\mathrm{N})(\mu_3\text{-}\mathrm{NH})_2\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})\}_3(\mu_3\text{-}\mathrm{N})]$, with R = SiMe$_3$ (**3**), CMe$_3$ (**4**), or Ph (**5**), as brown or red solids in good yields (71–87 %). Because of the light sensitivity of **2** in solution, the reactions were performed in amber-stained glassware. Complexes **3** and **4** were obtained at room temperature, while **5** had to be prepared at 90 °C to obtain a pure sample. Reaction of **2** with two equivalents of Me$_3$SiCCH led to a complex which was shown by X-ray diffraction to be the zinc acetylide $[\{(\mathrm{RCC})\mathrm{Zn}\}(\mu_3\text{-}\mathrm{NH})_3\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})\}_3(\mu_3\text{-}\mathrm{NCCR})]$, with R = SiMe$_3$ (**6**). The analogous reaction with PhCCH gave the complex with R = Ph (**7**). Both **6** and **7** were obtained as black solids in good yields (81 and 91 %, respectively). In contrast, the reaction of **2** with more than two equivalents of *tert*-butylacetylene at a variety of temperatures only produced a mixture of **4** and the unreacted alkyne. [D$_6$]Benzene solutions of **6** are stable at different temperatures, whereas complex **7** decomposes partially at room temperature and completely at 90 °C to give **5** and PhCCH, as determined by NMR spectroscopy.[12]



Scheme 1. Synthesis of the alkynyl complexes **3**–**7**. [Ti] = Ti(η^5-C$_5$Me$_5$).

Complexes **3**–**7** are stable to ambient light and were characterized by spectroscopic and analytical techniques, as well as by an X-ray crystal structure determination in the case of **6**. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3**–**5** show signals for

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the η^5-C_5Me_5 ligands in a 2:1 ratio, one broad resonance for the equivalent NH groups, and the expected resonance signals for the alkynyl ligand. The NMR spectroscopic data are consistent with a C_s symmetry in solution and a tetrahedral geometry around the zinc center, as determined previously for the analogous cube-type complexes $[(RZn)(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti(\eta^5\text{-}C_5Me_5)\}_3(\mu_3\text{-N})]$ (R = $N(SiMe_3)_2$, $C_5H_4SiMe_3$).[11] The acetylide groups in complexes **3**–**5** are characterized by one weak absorption for the $\nu_{C\equiv C}$ vibration in the range 2162–2072 cm^{-1} in their IR spectra and two resonance signals for the C≡C fragment in the $^{13}C\{^1H\}$ NMR spectra.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** and **7** reveal equivalent η^5-C_5Me_5 and NH ligands and are consistent with a C_{3v} symmetry in solution. The presence of two different RC≡C groups in complexes **6** and **7** was confirmed by the existence of two $\nu_{C\equiv C}$ vibrations in their IR spectra and four resonance signals for the C≡C fragments in their $^{13}C\{^1H\}$ NMR spectra. The molecular structure of **6** contains a cubic Ti_3ZnN_4 core (Figure 1)[13] with the zinc atom bound to the three imido groups and one alkynyl carbon atom in a distorted tetrahedral geometry. The bond lengths and angles in the Zn−C≡CSiMe$_3$ fragment are in the normal range for other alkynyl zinc complexes.[14] The alkynylimido group is linear at C6 (178.9(5)°) and C7 (178.5(4)°) and has a C6−C7 bond length of 1.205(5) Å, all of which are typical for alkynes. The C_{sp}−Si bond length of 1.816(4) Å is similar to those in trimethylsilylalkynes,[14b,15] while the C6−N1 bond length of 1.356(5) Å is close to that of 1.344(3) Å in the aminoalkyne $C_{12}H_8N{-}C{\equiv}C{-}C{\equiv}C{-}NC_{12}H_8$.[16]

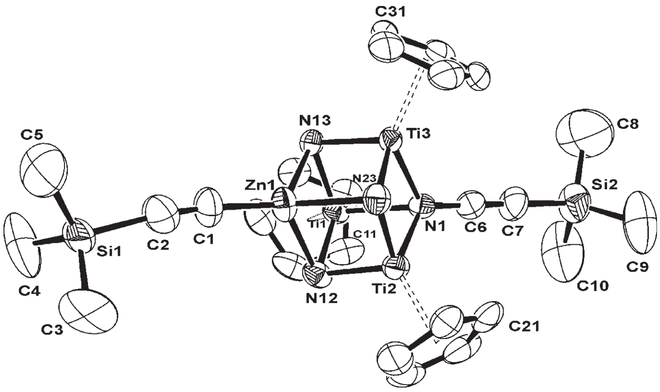


Figure 1. Structure of complex **6** (thermal ellipsoids are set at 50% probability). Hydrogen atoms and the methyl groups of the η^5-C_5Me_5 ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1-N 2.140(3), Zn1-C1 1.915(4), C1-C2 1.175(6), Ti-N1 2.074(3), N1-C6 1.356(5), C6-C7 1.205(5), C7-Si2 1.816(4), Ti-N 1.952(3), Ti-Ti 2.795(1), Ti···Zn 2.805(1); N-Zn1-N 87.9(1), N-Zn1-C1 126.6(2), Zn1-C1-C2 174.5(5), C1-C2-Si1 168.0(5), Ti-N1-Ti 84.8(1), Ti-N1-C6 128.9(3), N1-C6-C7 178.9(5), C6-C7-Si2 178.5(4).

The alkynylimido ligand in **6** is bound to the three titanium atoms with Ti−N bond lengths (average 2.074(3) Å) that are larger than those of the μ_3-N nitrido groups in **1** (average 1.91 Å),[8a] $[\{Ti(\eta^5\text{-}C_5Me_5)\}_4(\mu_3\text{-N})_4]$ (average 1.939 Å),[17] and other cube-type derivatives of **1**.[9–11] These Ti−N bond lengths lie between those found in the cube-type titanium(III) complex $[\{Ti(\eta^5\text{-}C_5H_5)\}_4(\mu_3\text{-NSnMe}_3)_4]$ (average 2.021 Å)[18] and those for the μ_3-NPMe$_3$ ligands in the titanium(IV) compound $[Ti_3Cl_8(NPMe_3)_3]^+Cl^-$ (2.101(4) and 2.136(5) Å).[19]

To the best of our knowledge, complex **6** is the first alkynylimido complex to be characterized by X-ray crystallography, therefore we decided to perform density functional theory (DFT) calculations[20] on compounds **3** and **6** to try to understand the electronic structure and formation of these unprecedented alkynylimido clusters. The pentamethylcyclopentadienyl ligands were modeled by cyclopentadienyl groups in all calculations. The computed geometry for complex **6** is in good agreement with the crystallographic data (see the Supporting Information) and its formation from the monoalkynyl derivative **3** is calculated to be exothermic by 75 kJ mol^{-1}. Analysis of the frontier orbitals of **3** and **6** reveals that the titanium centers in **3** remain totally oxidized, as in previously studied hetero-[9] and homotitanocubanes,[5,21] but the formation of **6** is accompanied by a two-electron reduction of the Ti_3 core. The highest occupied molecular orbital (HOMO) in **6** may be described as a bonding combination of titanium d orbitals (86%) with other smaller contributions (see the Supporting Information for details). Thus, the oxidation state of the titanium atoms of complex **6** should not be regarded as +4, but somewhere between +3 and +4.

We also evaluated the effect of the R group on the relative stability of complexes $[(RZn)(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-N})]$ (**A**) and $[(RZn)(\mu_3\text{-NH})_3\{Ti(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-NR})]$ (**B**) (see the Supporting Information). The calculations show that the formation of the titanium-reduced compound **B** is favored for alkynyl groups, whereas for methyl, cyclopentadienyl, and amido groups the process is endothermic and the reaction energies follow the order $CCSiMe_3 > CCPh > CCCMe_3 > Me > C_5H_5 > NH_2$. We also noted a relationship between the exothermicity of the process and the negative charge supported by the NR moiety in compound **B**. These results suggest that compound **B** is stabilized by electron-withdrawing R groups, which are able to release charge density from the reduced complex to the NR ligand.

We used the simplest alkyne substrate HCCH and the model complex $[\{(HCC)Zn\}(\mu_3\text{-N})(\mu_3\text{-NH})_2\{Ti(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-N})]$ (**A^{H}**) to analyze the possible sequence leading to the formation of the dialkynyl complexes. Initially, we considered a process involving protonation of the basal nitrido ligand and subsequent nucleophilic attack of the RCC^- fragment to the protonated complex. As expected for processes involving charge separation, in vacuo calculations suggest a very high energy requirement for the protonation of **A^{H}** (ca. 500 kJ mol^{-1}). Although the incorporation of solvent effects through a continuum model (COSMO) reduces the energetic cost significantly, we need highly polar solvents to obtain an energy barrier that is accessible at room temperature. Since the reactions were carried out in toluene and the energy required in this solvent is according to our calculations still 278 kJ mol^{-1}, this mechanism is not likely to be operative in these systems.

We also evaluated the likelihood of a concerted 1,2-RH-addition pathway, in which the alkyne C−H bond activation by the basal nitrido ligand is accompanied by formation of an alkynyl titanium species, as it is already known that the imido titanium(IV) complex [(η^5-C$_5$Me$_5$)$_2$Ti=NPh] activates the alkynyl C–H bond of phenyl- and trimethylsilylacetylene to give the corresponding anilido–alkynyl complexes.[22]

Figure 2 summarizes the results of the theoretical analysis of the proposed reaction mechanism. We located two alkynyl titanium intermediates, **Ca** and **Cb**, which result from the approach of the alkyne to two different faces of the cubic Ti$_3$ZnN$_4$ core. A molecular orbital analysis of these complexes revealed that the Ti$_3$ fragment is totally oxidized. The alkynyl ligand in **Ca** is *trans* to the apical nitrido ligand, whereas in **Cb** it is *cis* (Scheme 2). Both alkynyl complexes are quite stable; their energies relative to the reactants are −17 and −11 kJ mol^{-1}, respectively.

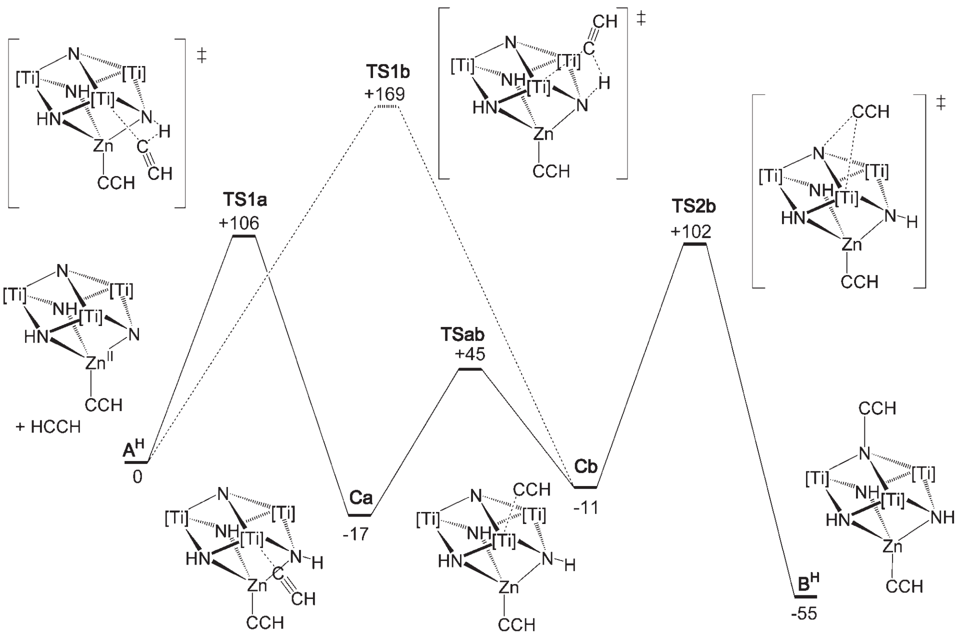
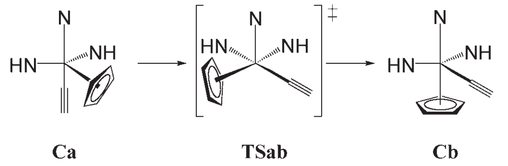


Figure 2. Potential energy profile [kJ mol^{-1}] for the formation of alkynylimido clusters. [Ti] = Ti(η^5-C$_5$H$_5$).



Scheme 2. Interconversion between alkynyl intermediates **Ca** and **Cb** via transition state **TSab** by ligand rearrangement.

Due to the relative *cis* disposition of the alkynyl and the apical nitrido ligand in **Cb**, it is reasonable to suppose that the alkynyl ligand can migrate to yield the alkynylimido product. However, the computed energy barrier for the formation of **Cb** (169 kJ mol^{-1} for transition state **TS1b**) seems to be too high for this reaction to occur at room temperature. Interestingly, the computed energy barrier for the formation of **Ca** is significantly lower (106 kJ mol^{-1} for transition state **TS1a**). Moreover, this latter value is similar to previous experimentally and theoretically determined barriers for C–H bond activation by imido titanium complexes.[23] Thus, the reaction most probably proceeds via intermediate **Ca**, which undergoes an intramolecular rearrangement of the alkynyl and cyclopentadienyl ligands that are not involved in the cube skeleton to form **Cb** (Scheme 2). The computed energy for this rearrangement is a modest 62 kJ mol^{-1} (see Figure 2). Once **Cb** has formed, the alkynyl ligand migrates to the neighboring apical nitrido ligand and the Ti$_3$ core simultaneously undergoes a two-electron reduction to form the more stable alkynylimido complex **B^H**. The estimated migration energy barrier is of the same order of magnitude as the C–H bond activation to give **Ca** (see the Supporting Information for details).

In summary, reaction of the alkynyl titanium–zinc cube-type complexes **3** and **5** with terminal alkynes leads to the formation of μ_3-NCCR ligands in the final derivatives **6** and **7**. Density functional calculations suggest that this reaction proceeds by a concerted 1,2-addition to form an alkynyl titanium complex followed by a rearrangement of the alkynyl and η^5-C$_5$Me$_5$ ligands on this titanium atom, and, finally, migration of the alkynyl group to the apical nitrido ligand to afford the alkynylimido complex with reduction of the Ti$_3$ system.

Experimental Section

Synthesis of **3**–**5**: Complex **2** and the terminal alkyne (1:1), and toluene (25 mL) were placed in a 100-mL amber-stained ampoule fitted with a Teflon stopcock (see the Supporting Information for quantities and details). The reaction mixture was then stirred at 25 °C (**3** and **4**) or 90 °C (**5**) for 2 days. After filtration, the volatile components were removed under reduced pressure to afford complexes **3** (orange solid, 87 %), **4** (red solid, 78 %), or **5** (brown solid, 71 %).

3: IR (KBr): $\tilde{\nu}$ = 3366 (m) (NH), 2072 (w) cm^{-1} (C≡C); ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 10.35 (br s, 2H; NH), 2.01 (s, 30H; C$_5$Me$_5$), 1.84 (s, 15H; C$_5$Me$_5$), 0.22 ppm (s, 9H; SiMe$_3$); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 124.2, 114.4 (*C*CSiMe$_3$), 119.4, 118.4 (*C*$_5$Me$_5$), 11.8, 11.6 (C$_5$*Me*$_5$), 1.0 ppm (SiMe$_3$); MS (70 eV): *m*/*z* (%) 770 (1) [*M*]$^+$; elemental analysis (%) calcd. for C$_{35}$H$_{56}$N$_4$SiTi$_3$Zn: C 54.60, H 7.34, N 7.28; found: C 54.84, H 7.60, N 6.99.

4: IR (KBr): $\tilde{\nu}$ = 3367 (m) (NH), 2123 (w) cm^{-1} (C≡C); ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): δ = 10.41 (br s, 2H; NH), 2.03 (s, 30H; C$_5$Me$_5$), 1.86 (s, 15H; C$_5$Me$_5$), 1.30 ppm (s, 9H; CMe$_3$);

^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta = 119.2$, 118.2 (C_5Me$_5$), 116.5, 86.2 (CCCMe$_3$), 32.4 (CMe_3), 28.7 (CMe$_3$), 11.8, 11.7 ppm (C$_5$$Me_5$); MS (70 eV): m/z (%) 754 (31) [M]$^+$; elemental analysis (%) calcd. for $C_{36}H_{56}N_4Ti_3Zn$: C 57.36, H 7.49, N 7.43; found: C 57.36, H 7.58, N 7.06.

5: IR (KBr): $\tilde{\nu} = 3360$ (w) (NH), 2162 (w) cm^{-1} (C≡C); ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta = 10.42$ (br s, 2 H; NH), 7.60 (m, 2 H; o-Ph), 7.04–6.86 (m, 3 H; m- and p-Ph), 2.05 (s, 30 H; C$_5$Me$_5$), 1.86 ppm (s, 15 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta = 132.2$, 128.5, 128.2, 126.6 (C$_6$H$_5$), 119.5, 118.5 (C_5Me$_5$), 107.9, 102.8 (CCPh), 11.8, 11.7 ppm (C$_5$$Me_5$); MS (70 eV): m/z (%) 774 (1) [M]$^+$; elemental analysis (%) calcd. for $C_{38}H_{52}N_4Ti_3Zn$: C 58.98, H 6.77, N 7.24; found: C 58.73, H 7.07, N 6.49.

Synthesis of **6** and **7**: Complex **2** and the terminal alkyne (1:2), and toluene (25 mL) were placed in a 100-mL amber-stained Schlenk flask. The reaction mixture was then stirred at 70 °C (**6**) or 25 °C (**7**) for 20 h to give a dark solution. After filtration, the volatile components were removed under reduced pressure to afford **6** (81 %) or **7** (91 %) as black solids.

6: IR (KBr): $\tilde{\nu} = 3364$ (w), 3341 (w) (NH), 2205 (w), 2084 (s) cm^{-1} (C≡C); ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta = 10.09$ (br s, 3 H; NH), 1.95 (s, 45 H; C$_5$Me$_5$), 0.29 (s, 9 H; SiMe$_3$), 0.17 ppm (s, 9 H; SiMe$_3$); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta =$ 125.2, 115.4, 113.5, 85.8 (CCSiMe$_3$), 117.5 (C_5Me$_5$), 11.1 (C$_5$$Me_5$), 1.2, 1.0 ppm (SiMe$_3$); MS (70 eV): m/z (%) 868 (1) [M]$^+$, 771 (3) [$M-$CCSiMe$_3$]$^+$; elemental analysis (%) calcd. for $C_{40}H_{66}N_4Si_2Ti_3Zn$: C 55.34, H 7.66, N 6.45; found: C 55.84, H 7.92, N 5.95.

7: IR (KBr): $\tilde{\nu} = 3361$ (w), 3336 (w) (NH), 2162 (s), 2056 (w) cm^{-1} (C≡C); ^{1}H NMR (300 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta = 10.22$ (br s, 3 H; NH), 7.56–7.44 (m, 4 H; o-Ph), 7.04–6.98 (m, 6 H; m- and p-Ph), 2.00 ppm (s, 45 H; C$_5$Me$_5$); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 20 °C, TMS): $\delta = 132.1$, 129.5, 129.3, 128.8, 127.9, 126.6, 125.6 (C$_6$H$_5$), 117.7 (C_5Me$_5$), 107.2, 104.6, 103.8, 89.8 (CCPh), 11.5 ppm (C$_5$$Me_5$); one C$_6H_5$ resonance signal was not found, possibly due to coincidence with the solvent signals; MS (70 eV): m/z (%) 775 (4) [$M-$CCPh]$^+$; elemental analysis (%) calcd. for $C_{46}H_{58}N_4Ti_3Zn$: C 63.07, H 6.67, N 6.40; found: C 63.16, H 7.16, N 5.95.

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[12] Curiously, attempts to synthesize **5** at temperatures lower than 90 °C gave mixtures of **2**, **5**, and **7**.

[13] X-ray data for $C_{46}H_{80}N_4Si_2Ti_3Zn$ (**6**·C_6H_{14}): $0.49 \times 0.45 \times 0.38$ mm^3, monoclinic, $C2/c$, $a = 35.683(7)$, $b = 13.885(1)$, $c = 22.538(2)$ Å, $\beta = 110.93(1)°$, $V = 10430(2)$ Å^3, $\rho_{\rm calcd} = 1.216$ Mg m^{-3}, 95294 measured reflections, 11933 independent, $R1 = 0.058$, $wR2 = 0.162$ (for 7227 reflections with $F > 4\sigma(F)$), largest difference peak/hole: 0.89/−0.438 e Å^{-3}. CCDC-627182 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[20] DFT calculations were carried out with the ADF program by using a triple-ζ-quality basis set augmented with one set of polarization functions (TZP) for all the atoms. The $1s^22s^22p^6$ core electrons of Ti, Zn, and Si, and the $1s^2$ electrons of C and N, were treated by a frozen-core approximation. Scalar relativistic effects were taken into account using the zero-order regular approximation (ZORA). See the Supporting Information for further details.

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