

Titanium(III) Trisamidotriazacyclononane: Reactions with C₆₀ and Radicals

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The reaction of titanium trisamidotriazacyclononane, [Ti{N(Ph)SiMe₂}₃tacn] (**1**), with C₆₀ led to the synthesis of [Ti{N(Ph)SiMe₂}₃tacn]C₆₀ (**2**) in high yield. Treatment of **2** with PhCH₂Br led to the formation of [Ti{N(Ph)SiMe₂}₃tacn]Br and the radical PhCH₂C₆₀ (**3**). The reaction of CH₃I with **1** gives two products. One is [Ti{N(Ph)SiMe₂}₃tacn]I (**4**), which results from the oxidation of **1** by an I radical. The other product, **5**, resulting from a multistep reaction scheme that involves redox and nucleophilic reactions, presents an imido ligand formed by ligand rearrangement upon C–N bond cleavage. In solution, an exchange process that corresponds to a reversible 1,3-silyl shift between two Ti-bonded N atoms leads to isomers **5a** and **5b**. This equilibrium transforms an imido (TiNPh) into an amido ligand (Ti{NPh}SiMe₂CH₂Ph) with concomitant generation of an anionic moiety in the originally neutral triazacyclononane ring. In solution, either **5a** or **5b** displays additional fluxional processes that consist of its corresponding racemization processes.

Introduction

The tuning of electronic and stereochemical metal center properties provided by amido ligands, which combined or not with other donors allow kinetic and thermodynamic stabilization of diverse metal oxidation states and coordination geometries, is a well-established and widely explored strategy.^{1,2} In this context, we have been interested in group 3 and 4 trisamidotriazacyclononane (tacn) complexes^{3,4} and established that hexacoordinate Ti^{III} compounds are prone to oxidation to the corresponding Ti^{IV} cations by a variety of oxidants.⁵ Bearing in mind that C₆₀ reacts with suitable reducing species to form fulleride anions,⁶ we carried out the reaction of [Ti{N(Ph)SiMe₂}₃tacn] (**1**) with C₆₀. Different

types of interactions between [Ti{N(Ph)SiMe₂}₃tacn]⁺ and C₆₀[−] might a priori be speculative, namely, (i) an ion-pairing interaction between [Ti{N(Ph)SiMe₂}₃tacn]⁺ and C₆₀[−] or (ii) π–π-stacking or hydrogen-bonding interactions with the ligand's phenyl rings, which as a consequence of coordination to the Ti delineate a “pocket” that, in principle, would be suitable for interaction with the ball-shaped aromatic system.^{7–9}

The stereochemical protection created by the coordination of the six N atoms of trisamidotriazacyclononane ligands {N(Ph')SiMe₂}₃tacn (Ph' = C₆H₅ and 2-C₆H₄F) around the Ti prevents reactions at the metal coordination sphere.⁴ Thus, reactions of [Ti{N(Ph)SiMe₂}₃tacn]⁺ with nucleophiles proceed at the Si of one pending arm, leading to ligand rearrangement.¹⁰ We report now the reaction of **1** with a benzyl radical, which results in the observation of a reversible 1,3-silyl exchange between two N atoms. Related proton exchange between amine, amido, and imido ligands, the cleavage of N–Si bonds, and the activation of C–H bonds of silylamido moieties are well-documented reactions,^{11,12}

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but silyl exchange is an unusual reaction^{13,14} and, according to the authors knowledge, this is the first example of a reversible 1,3-silyl shift that interconverts amino, amido, and imido ligands. A reminiscent 1,3-silyl migration between two N atoms was reported to take place in alkaline-metal guanidinate derivatives.¹⁵

Results and Discussion

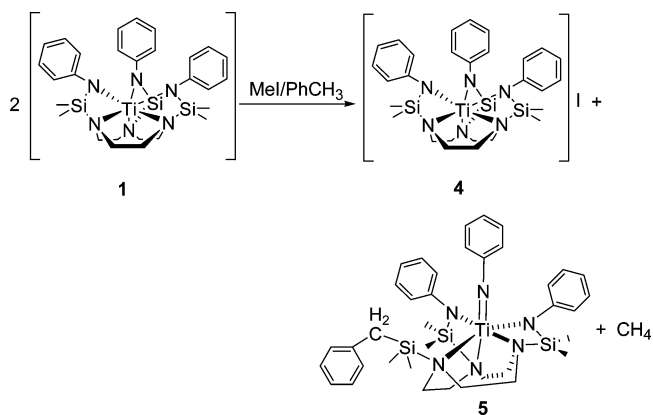
1 is readily oxidized to the corresponding Ti^{IV} cation with a series of oxidizing reagents, and a $E_{1/2}$ value of -1.71 V vs ferrocene/ferricinium was obtained by cyclic voltammetry measurement for the redox pair Ti^{IV}/Ti^{III}.⁵ Reactions of **1** with suitable oxidants allowed us to prepare [Ti{N(Ph)SiMe₂}₃tacn]X (X = Cl, I, PF₆, BPh₄, and SCN; Ph = C₆H₅ and 2-C₆H₄F).⁴ Treatment of **1** with 1 equiv of C₆₀ in toluene led to the formation of [Ti{N(Ph)SiMe₂}₃tacn]C₆₀ (**2**), which precipitates out of solution during the course of the reaction in 87% yield. This result is consistent with C₆₀ redox behavior, which is dictated by the low energy of the triply degenerated t_{1u} and t_{1g} lowest unoccupied molecular orbitals. Redox reactions between reduced transition-metal compounds and C₆₀ have been previously reported and shown to depend not exclusively on adequate redox potentials but also on the solubility of the resulting products in the reaction medium and the stability of the resulting cations, which ultimately may depend on solvent coordination.^{16–18} The ¹H NMR spectrum of **2** confirms the oxidation of Ti through observation of the aromatic resonances due to the ligand's phenylamido (δ 7.02–6.90, H_m and H_p; 6.27, H_o) and macrocycle methylenic proton resonances (δ 3.95–3.76, H_{syn}; 3.76–3.57, H_{anti}) (see the Supporting Information, Figure S1). The identification of C₆₀[−] is obtained from the ¹³C NMR spectrum, which displays a broad resonance at δ 189.0 with a 2.5 ppm line at half-height (see the Supporting Information, Figure S2). The downfield shift of ca. 45 ppm observed for C₆₀[−] relative to C₆₀ (δ = 143 ppm) is characteristic of the radical monoanion and has been ascribed to its $S = 1/2$ spin ground state.¹⁹ An interesting aspect that may be deduced from the macrocyclic NMR resonances is the ion-pairing association between C₆₀[−] and [Ti{N(Ph)SiMe₂}₃tacn]⁺. It was previously shown by us that ion pairing in [Ti{N(Ph)SiMe₂}₃tacn]X complexes (X = Cl, I, PF₆, and BPh₄) results in the upfield shift of macrocyclic H_{anti} resonances and that strong anion–cation associations are responsible for the ¹H NMR pattern $\delta H_{syn} > \delta H_{anti}$.¹⁰ The ¹H NMR spectrum of **2** follows this trend, suggesting thus that C₆₀[−] is located close to the macrocyclic H_{anti} protons, which are shielded by the

anion ring current. The broadening observed for the methylenic and Si(CH₃)₂ proton resonances is likely due to paramagnetic relaxation caused by the anion closeness. The location of the anion at the macrocycle side is also consistent with the sharp resonances observed for the phenyl protons that are not modified by the paramagnetism of the anion. Ion-pair association between the fulleride monoanion and tetrabutylammonium cations has been claimed to justify the presence of a broad signal in the electron paramagnetic resonance (EPR) spectrum of C₆₀ samples at room temperature, whereas the sharp signal also observed was attributed to the free anion.²⁰ Although this argument was later forsaken and EPR spectra of C₆₀^{•−} fullerides have been subjected to extensive discussion,^{18–21} noncovalent interactions involving C₆₀ have been characterized by X-ray diffraction and by spectroscopic methods,^{7,22,23} and so its occurrence in fulleride solutions might be anticipated considering the additional electrostatic component offered by charged species.

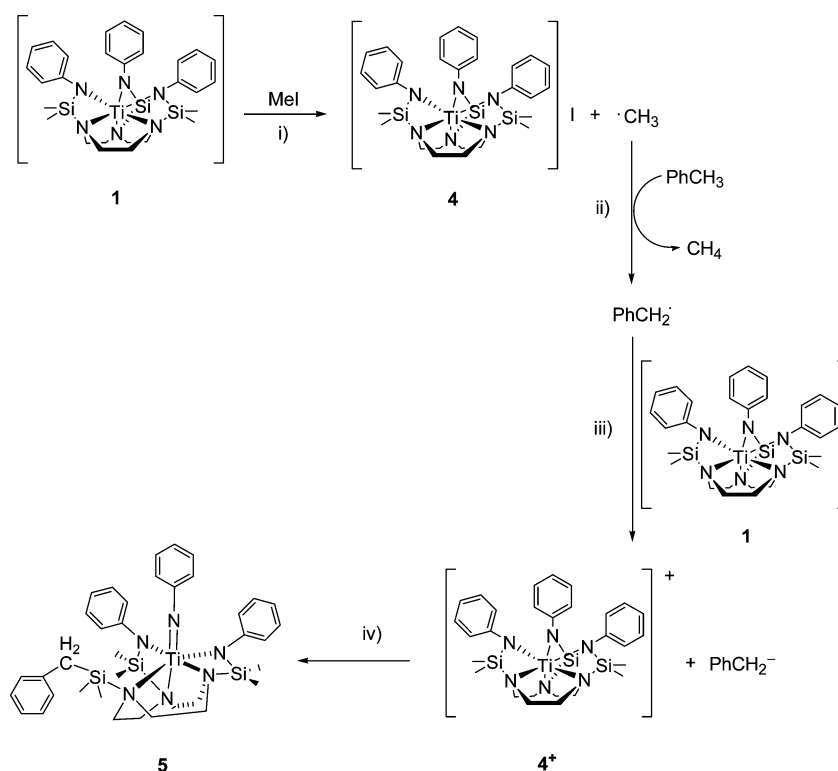
The EPR spectrum of **2**, recorded in tetrahydrofuran (THF) at 295 K, shows a very broad absorption with $g = 1.999$ and $\Delta H = 84$ G and a sharp minor absorption at $g = 1.9996$ with 1.58 G line width. The identification of these signals was very controversial until it was clarified by Reed et al. that the broad band corresponds to C₆₀[−] whereas the sharp absorption is due to C₁₂₀O[−], which may arise from reaction with traces of O as a common impurity of C₆₀ samples.^{24,25} In the case of **2**, the contamination with C₁₂₀O[−] is not detected in the elemental analysis, which instead of a higher C content than that calculated for **2** presents an experimental value slightly lower, which reflects the high instability of the complex in air.

The reaction of **2** with PhCH₂Br, carried out in THF, led to the formation of C₆₀CH₂Ph (**3**) and [Ti{N(Ph)SiMe₂}₃tacn]Br, which was extracted in acetonitrile and identified by NMR.⁴ High-resolution mass spectrometry (MS) of **3** shows a peak at m/z 811.05559, corresponding to the radical anion [C₆₀CH₂Ph]^{•−}. Polybenzyl C₆₀ derivatives (PhCH₂)_nC₆₀ have been reported to form by the addition of benzyl radicals to C₆₀.²⁶ In our case, the product stoichiometry is readily controlled because, instead of radical reactions, [C₆₀CH₂Ph][−] forms from the electrophilic addition of the benzyl cation to the fulleride monoanion.

The reaction of **1** with MeI in toluene led to the formation of [Ti{N(Ph)SiMe₂}₃tacn]I (**4**) and [Ti(NPh)-1,4-{N(Ph)SiMe₂}₂-7-SiMe₂CH₂Phtacn] (**5**; eq 1).



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Scheme 1^a

^a (i) Redox reaction between **1** and MeI and leading to **4** and a methyl radical. (ii) Radical reaction between the methyl radical and toluene, leading to CH₄ and a benzyl radical. (iii) Redox reaction between **1** and PhCH₂•, leading to **4** and a benzyl anion. (iv) Nucleophilic attack of the benzyl anion to the Si of a pending arm.

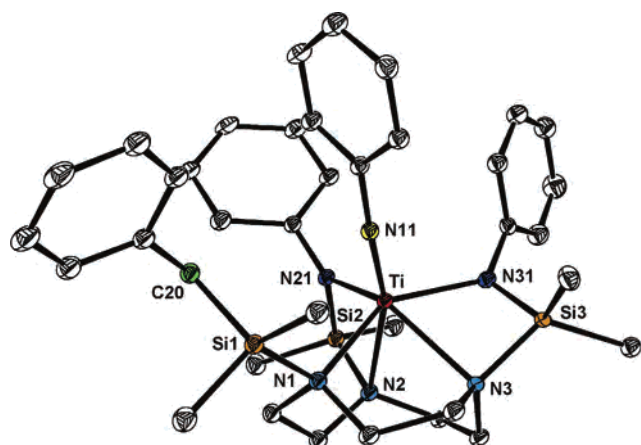


Figure 1. ORTEP view of **5a** along the equatorial plane, showing the octahedral coordination of Ti.

Complex **4** is the oxidation product of **1** by an I radical formed by homolytic cleavage of MeI. The formation of **5** occurs upon attack of a PhCH₂[−] anion at the silicon of one SiMe₂ group. The formation of the benzyl anion is most probably the result of the redox reaction between **1** and a benzyl radical formed in situ by the reaction of the methyl radical and the solvent toluene (Scheme 1).

The nucleophilic attack at Si, followed by the cleavage of one N–Si bond and the formation of an imido ligand, was

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Table 1. Selected Bond Lengths [Å] Angles [deg] for **5a**

Ti1–N11	1.7527(19)	Ti1–N2	2.4421(18)
Ti1–N21	1.9889(18)	N21–C21	1.414(3)
Ti1–N31	2.0638(18)	N11–C11	1.375(3)
Ti1–N1	2.3536(18)	N31–C31	1.406(3)
Ti1–N3	2.4141(18)		
Angles between Planes			
N11–Ti1–N2	164.29(8)	N21–Ti1–N1	109.03(7)
N1–Ti1–N3	73.62(6)	N31–Ti1–N1	141.88(7)
N21–Ti1–N3	141.11(7)	N21–Ti1–N31	101.69(7)
N31–Ti1–N3	68.30(7)	C11–N11–Ti1	166.93(17)
Torsion Angles			
N1–Si1–C20–C41	−173.00(14)	N2–Si2–N21–C21	−172.13(17)
N3–Si3–N31–C31	−176.36(19)		

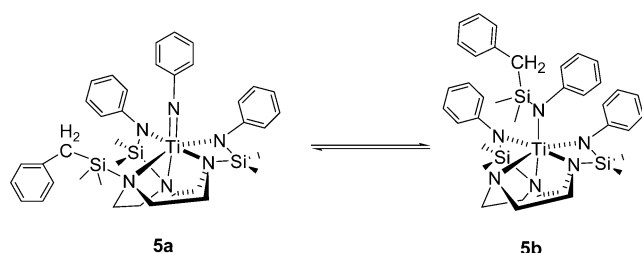
previously observed for the reaction of LiNMe₂ with **4** and may be reasoned based on the positive charge lying at the Si, as was inferred from the solid-state and solution structures of [Ti{N(Ph)SiMe₂}₃tacn]X (X = I and BPh₄).^{4,10}

The molecular structure of **5a** is depicted in Figure 1, and selected bond lengths and angles are listed in Table 1.

Ti coordination geometry may be described as a very distorted octahedral with an equatorial plane defined by

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Scheme 2



atoms N1, N3, N21, and N31 [maximum deviation of $-0.318(1)$ Å for atom N3] and N11 and N2 occupying the apical positions, even though the angle N11–Ti1–N2, which is the widest angle between trans positions [$164.29(8)^\circ$], deviates appreciably from linearity. The metal is coordinated to six N atoms in a chiral environment, with Ti–N distances that range from $1.7527(19)$ Å for Ti1–N11 to $2.4421(18)$ Å for Ti1–N2. The shortest metal–N bond length and the corresponding Ti1–N11–C11 angle [$166.93(17)^\circ$] are consistent with values reported for titanium imido ligands.^{27–30} Reflecting the trans effect created by the imido ligand, the longest metal–N distance (Ti1–N2) is observed for the tacn amine positioned trans to the imido ligand. The two four-membered metallocycles Ti–N_{amine}–Si–N_{amido} define two almost perpendicular planes with a dihedral angle of $75.75(5)^\circ$ between them. The metal–N distances and the sum of angles around N21 and N31 in **5** are, in general, comparable with the values reported for related Ti–N bonds in complexes with polyfunctional N ligands.³¹ As expected, because of the presence of an imido ligand and the fact that **4** is a neutral complex, the Ti–N_{tacn} and Ti–N_{amido} bond lengths in **5** are slightly longer than those in [Ti{N(Ph)SiMe₂}₃tacn]X (X = I and BPh₄).⁴

In solution, **5** exhibits a fluxional behavior that is represented in Scheme 2 and corresponds to the intramolecular exchange of SiMe₂(CH₂Ph) between N1 (**5a**) and N11 (**5b**). The equilibrium ratio between the two isomers was determined by NMR as **5a**:**5b** = 2:3 at 23 °C, thus meaning that the crystals of **5a** isolated reflect the lower solubility of this isomer.

The ¹³C NMR spectrum of **5** shows two sets of three resonances for the SiMe₂ groups, one set of two resonances for the CH₂ benzyl, and two sets of three resonances for the triazacyclononane C atoms. In the aromatic region, there are two sets of three resonances due to quaternary C atoms (two benzyl and four NPh groups) and two sets of nine resonances due to the CH aromatic C atoms. In each group of two sets, the major resonances correspond to **5b** and the minor carbons to **5a**, in a ratio close to 3:2. The NMR data described are thus indicative of C_s symmetry for both **5a** and **5b**, which does not correspond to the solid-state structure of **5a**,

Scheme 3

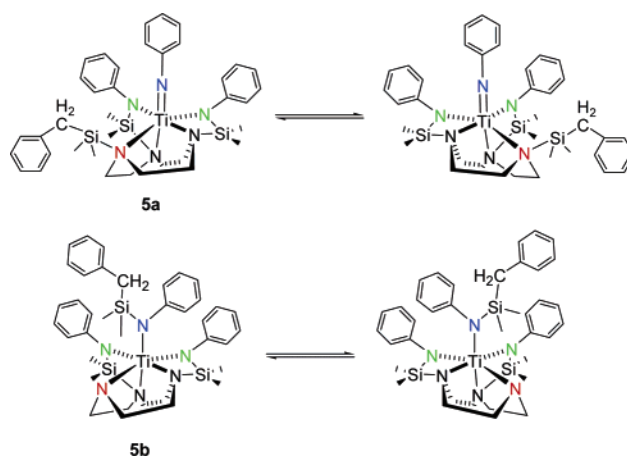
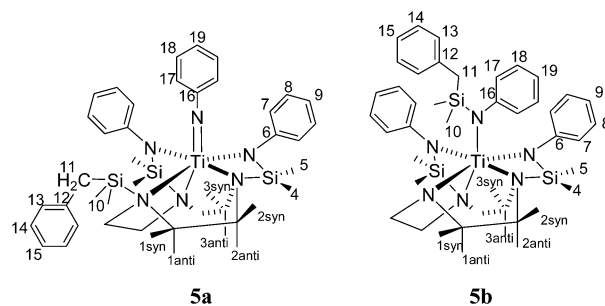


Chart 1



implying that, together with the equilibrium represented in Scheme 2, either **5a** or **5b** participates in fluxional processes, which result in its racemization (Scheme 3). The exchanges create average symmetry planes that contain N1 (in red) and N11 (in blue) and bisect the N21–Ti–N31 angles (in green) in a way that may be visualized as a pendulum displacement of the Ti–N1 bonds.

The assignment of the ¹H and ¹³C NMR resonances was achieved by COSY, NOESY, and HETCOR experiments (see the Supporting Information). The NOESY spectrum (Figure S6) shows the exchange peaks corresponding to the equilibrium represented in Scheme 2 and positive peaks due to the Overhauser effect. The differentiation between macrocyclic H_{syn} and H_{anti} resonances was based on the spatial interactions between H_{syn} and the dimethylsilyl protons (Figure S7). The most relevant NOE contacts of the methylsilyl groups allowed differentiation between the resonances of the methyls H5M and H5m, corresponding respectively to **5b** (Major) and **5a** (minor) isomers. The assignment of methyls H10M, H10m and H4M, H4m of each isomer was based on the assignment of all methylsilyl C atoms provided by the HETCOR spectra (Figure S10). In another region of the NOESY spectrum (Figure S8), we show that the higher intensity observed with the cross-peaks between H17M/H11M relative to that of H17m/H11m supports the structure proposed for major species **5b** (see Chart 1 for proton and carbon numbering).

The reactions described point out that trisamidotriazacyclononantitanium(III) is readily oxidized and that two main reactivity patterns are accessible, depending on the availability in the reaction medium of an anion suitable to stabilize

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the resulting Ti^{IV} complex. When the redox reaction leads to the formation of such an ion, $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]\text{X}$ complexes are the end products obtained. When the redox reaction leads to the formation of nucleophilic anions, $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]^+$ undergoes an attack at one Si pending arm that leads to the cleavage of one Si–NPh bond and the formation of a Ti–NPh moiety. In the present case, an intramolecular exchange of the newly formed $\text{SiMe}_2\text{CH}_2\text{Ph}$ moiety between the macrocyclic amine and the new imido groups is observed by NMR in solution. This process, which reversibly exchanges the functions amine/imido into amido/amido through 1,3-silyl migration between two N atoms, is rare and, according to our knowledge, has not been reported to take place in transition-metal compounds. A similar, although irreversible, silyl shift was recently reported to occur in an anionic imidotrisamidozirconium complex, and a mechanism, which assumes the nucleophilic attack of an imido ligand to the Si, passing through a five-coordinated Si atom, is proposed for the reaction.¹³ A similar process may drive the equilibrium between **5a** and **5b**. The required electronic density at the two N atoms involved in the exchange is available from the ligand's donor set that might potentially release a maximum of 20 electrons for bonding.

Experimental Section

General Procedures and Starting Materials. All reactions were conducted under a nitrogen atmosphere. Solvents were predried using 4-Å molecular sieves, refluxed over sodium benzophenone (diethyl ether, THF, and toluene) or calcium hydride (*n*-hexane) under an atmosphere of nitrogen, and distilled. Deuterated solvents were dried with molecular sieves and freeze–pump–thaw–degassed prior to use. Proton (300 MHz) and carbon (75.419 MHz) NMR spectra were recorded in a Varian Unity 300, at 298 K unless stated otherwise, referenced internally to residual protiosolvent (^1H) or solvent (^{13}C) resonances, and reported relative to tetramethylsilane (δ 0). An EPR spectrum was recorded in a THF solution (3×10^{-3} M) at 22 °C with a Bruker 300E spectrometer at X-band frequency ($\nu \approx 9.5$ GHz). A high-resolution mass spectrum was recorded on a FT/MS 2001 DT mass spectrometer interfaced to a pulsed Nd:YAG laser operating at the fundamental wavelength (1064 nm). Elemental analyses were obtained from Laboratório de Análises, IST, Lisbon, Portugal. $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]$ was prepared according to the described procedures.⁴

$[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]\text{C}_{60}$ (2). C_{60} (0.58 g, 0.89 mmol) in 100 mL of toluene was treated at -50 °C with a solution of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]$ (0.50 g, 0.89 mmol) in 15 mL of the same solvent. The solution was allowed to warm until room temperature and stirred for 44 h. The solvent was filtered off, and the precipitate was washed with toluene and with Et_2O until the solvents became colorless. **2** was obtained as a brown-dark solid extremely sensitive to air and moisture and was recrystallized from THF. Yield: 0.93 g, 87%.

^1H NMR (THF- d_8): δ 7.02–6.90 (m, 9H, H_m , H_p , NPh), 6.27 (d, 6H, H_o , NPh), 3.95–3.76 (m, 6H, H_{syn} , $\text{N}(\text{CH}_{\text{syn}}\text{H}_{\text{anti}})_2\text{N}$), 3.75–3.57 (m, 6H, H_{anti} , $\text{N}(\text{CH}_{\text{syn}}\text{H}_{\text{anti}})_2\text{N}$), 0.57 (s, 18H, SiCH_3), ^{13}C - $\{^1\text{H}\}$ NMR (THF- d_8): δ 189.0 (C_{60}^-), 152.8 (C_{ipso} , NPh), 129.6 (C_m , NPh), 124.3 (C_p , NPh), 123.9 (C_o , NPh), 55.8 ($\text{N}(\text{CH}_2)_2\text{N}$), 0.8 (SiCH_3). EPR (3×10^{-3} M, THF, 295 K): $g = 1.999$, $\Delta H = 84$ G. Elem anal. Calcd for $\text{C}_{90}\text{H}_{45}\text{N}_6\text{Si}_3\text{Ti}$: C, 80.52; H, 3.82; N, 6.26. Found: C, 78.05; H, 3.88; N, 6.29.

Table 2. Crystal Data and Structure Refinement for Compound **5**

empirical formula	$\text{C}_{37}\text{H}_{52}\text{N}_6\text{Si}_3\text{Ti}$
fw	713.02
T (K)	293(2)
wavelength (Å)	0.710 73
cryst syst, space group	monoclinic, <i>Cc</i>
unit cell dimens	
a (Å)	12.9820(2)
b (Å)	16.7928(3)
c (Å)	18.2427(4)
β (deg)	107.0130(10)
V (Å ³)	3802.94(12)
Z , calcd density (Mg/m ³)	4, 1.245
abs coeff (mm ⁻¹)	0.354
$F(000)$	1520
cryst size (mm)	$0.5 \times 0.5 \times 1$
θ range for data collection (deg)	3.28–27.48
reflns collected/unique	15 297/7567 [$R(\text{int}) = 0.0386$]
completeness to $\theta = 27.48$ (%)	98.7
refinement method	full-matrix least squares on F^2
data/restraints/param	7567/2/470
GOF on F^2	1.031
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0332$, $wR2 = 0.0742$
R indices (all data)	$R1 = 0.0380$, $wR2 = 0.0759$
absolute structure param	–0.038(16)
largest diff peak and hole (e Å ⁻³)	0.295 and –0.326

$\text{C}_{60}\text{CH}_2\text{Ph}$ (3). PhCH_2Br (0.10 mL, 0.84 mmol) was added to a solution of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}](\text{C}_{60})$ (0.75 g, 0.56 mmol) in THF, and the mixture was stirred for 18 h. The solvent was removed to dryness, and the residue was extracted with CH_3CN until the solution became colorless. The yellow CH_3CN solution was evaporated to dryness, and the residue was washed with hexane and dried, leading to 0.28 g of a yellow solid identified by NMR and IR as $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]\text{Br}$ (0.40 mmol, 72% yield). The CH_3CN insoluble fraction was extracted in THF, filtered, and cooled at -20 °C. **3** precipitated out of the solution as a brown solid in 52%. Yield: 0.24 g.

HRMS. Calcd for C_{67}H_7 (M^-): m/z 811.05532. Found: m/z 811.05559.

$[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]\text{I}$ (4) and $[\text{Ti}(\text{NPh})\text{-1,4-}\{\text{N}(\text{Ph})\text{SiMe}_2\}_2\text{-7-SiMe}_2\text{CH}_2\text{Phtacn}]$ (5). MeI (221 μL , 3.55 mmol) was added through a syringe to a solution of $[\text{Ti}\{\text{N}(\text{Ph})\text{SiMe}_2\}_3\text{tacn}]$ (4.41 g, 7.10 mmol) in toluene at -60 °C. The temperature was allowed to rise slowly to room temperature. The solution was stirred for 20 h while a yellow crystalline solid formed. The volatiles were removed to dryness, and the residue was extracted in hexane and filtered. The insoluble fraction, obtained in 42% yield (2.39 g), was dried under vacuum and identified as **4**.⁴ The hexane filtrate was evaporated to dryness, and the remaining solid was extracted, filtered, and precipitated out from diethyl ether at 4 °C. Yield: 25% (1.20 g).

5a. ^1H NMR (C_6D_6): δ 7.23 (t, 4H, H_8), 7.20 (d, 4H, H_7), 7.13 (t, 2H, H_{14}), 6.97 (t, 3H, H_{18} , H_{15}), 6.90 (t, 2H, H_9), 6.67 (t, 3H, H_{19} , H_{13}), 6.60 (d, 2H, H_{17}), 3.25–3.16 (m, 2H, $H_{3\text{syn}}$), 3.04–2.94 (m, 2H, $H_{2\text{syn}}$), 2.90–2.80 (m, $H_{1\text{syn}}$), 2.56 (s, 2H, H_{11}), 2.28–2.15 (m, 2H, $H_{3\text{anti}}$), 2.20–2.100 (m, 2H, $H_{2\text{anti}}$), 2.15–2.05 (m, 2H, $H_{1\text{anti}}$), 0.31, 0.27 (s, H_4 , H_5 , SiMe_2), 0.29 (s, H_{10} , SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 160.6 (C_{16}), 156.2 (C_6), 138.8 (C_{12}), 129.3 (C_{13}), 128.5 (C_8 , C_{18}), 128.2 (C_{14}), 125.4 (C_7), 124.8 (C_{15}), 124.6 (C_{17}), 120.1 (C_9), 50.1 (C_1), 48.5 (C_3), 47.6 (C_2), 24.9 (C_{11}), 0.1, –0.2, –2.8 (SiMe_2). **5b.** ^1H NMR (C_6D_6): δ 7.22 (t, 2H, H_{18}), 7.11 (t, 4H, H_8), 7.07 (d, 2H, H_{13}), 6.96 (t, 1H, H_{15}), 6.94 (d, 4H, H_7), 6.84 (t, 2H, H_9), 6.70 (t, 2H, H_{14}), 6.53 (t, 1H, H_{19}), 6.39 (d, 2H, H_{17}), 4.50–4.35 (m, 2H, $H_{1\text{syn}}$), 3.38–3.25 (m, 2H, $H_{2\text{syn}}$), 2.90–2.80 (m, 4H, $H_{1\text{anti}}$, $H_{3\text{syn}}$), 2.55–2.42 (m, 2H, $H_{2\text{anti}}$), 2.40–2.30 (m, 2H, $H_{3\text{anti}}$), 2.33 (2H, H_{11}), 0.30, 0.20 (s, H_4 , H_5 , SiMe_2), 0.30 (s,

H₁₀, SiMe₂). ¹³C{¹H} NMR (C₆D₆): δ 154.8 (C₁₆), 154.1 (C₆), 142.1 (C₁₂), 129.0 (C₁₃), 128.3 (C₁₈), 128.2 (C₈), 127.6 (C₁₄), 126.0 (C₁₇), 124.0 (C₁₅), 122.9 (C₇), 122.0 (C₁₉), 120.5 (C₉), 59.5 (C₁), 50.2 (C₂), 49.8 (C₃), 29.5 (C₁₁), 1.3, 0.3, -0.1 (SiMe₂). Elem anal. Calcd for C₃₇H₅₂N₆Si₃Ti: C, 62.33; H, 7.35; N, 11.79. Found: C, 62.40; H, 7.07; N, 11.77.

X-ray Experimental Details. Data were collected at 120 K on a Nonius Kappa CCD using a Mo rotating anode using ω and θ scans. Cell refinement and data reduction were done using DENZO³² and COLLECT.³³ Absorption correction was done using multiple and symmetry-related data measurements via the program SORTAV.³⁴ Data collection and refinement details are presented in Table 2.

The structure was solved with SIR97³⁵ and refined using SHELXL³⁶ included in the WINGX program package, version 1.6403b.³⁷ Compounds crystallized in the noncentrosymmetric space group Cc. All non-H atoms were refined anisotropically, and all H

atoms were inserted in idealized positions, riding in the parent C atom. Figure 1 was drawn with ORTEP³⁸.

Data for complex **5a** was deposited in CCDC under the deposit number 278495 (can be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., tel +44 1223 336408, fax +44 1223 336033).

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Supporting Information Available: NMR spectra of **5** (¹H, ¹³C, NOESY, HETCOR, and COSY) and crystallographic data including complete information on bond lengths and angles, as well as torsion angles, and hydrogen bonds, also deposited as CCDC 278495. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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