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Titanium Complexes Incorporating 1,1-Bis(*tert*-butylamido)-1-silacycloalkane Ligands: Generation of Alkyl Derivatives and Reactivity toward Molecular Oxygen

Sung-Joon Kim, Dong-Woong Choi, Young-Joo Lee, Byung-Hoon Chae,
Jaejung Ko,* and Sang Ook Kang*,†

*Department of Chemistry, Korea University, 208 Seochang,
Chochiwon, Chung-nam 339-700, Korea*

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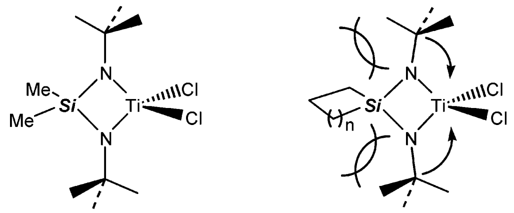
A series of methoxy-bridged diamidotitanium dimers have been synthesized and fully characterized. Treatment of the Grignard reagent MeMgBr with (cycl)Si(NBu^t)$_2$TiCl$_2$ (**2**; cycl = C_nH_{2n}, $n = 3-5$) in 2:1 or 1:1 stoichiometry yielded four-coordinate dimethyltitanium (cycl)Si(NBu^t)$_2$TiMe$_2$ (**3**) and monomethyltitanium $(CH_2)_3Si(NBu^t)_2TiMeCl$ (**5**) complexes, respectively. Subsequent reaction of these complexes with dioxygen proceeds by insertion of an oxygen molecule into the Ti−C bond of **3** and **5**, generating the respective methoxy-bridged titanium dimers [(cycl)Si(NBu^t)$_2$Ti(μ-OMe)Me]$_2$ (**4**) and [(cycl)Si(NBu^t)$_2$Ti(μ-OMe)Cl]$_2$ (**6**). In contrast, the reaction of the titanium(IV) dichloride complex $(CH_2)_3Si(NBu^t)_2TiCl_2$ (**2a**) with O_2 gives the hydrazido species $[\{(NBu^tNBu^t)(CH_2)_3SiO\}TiCl_2]_2$ (**7a**) as a result of facile Si−O−Ti bond formation upon autoxidation. To our knowledge, these complexes are the first examples of methoxy-bridged diamidotitanium(IV) dimers. Reaction of **2** with 2 equiv of $PhCH_2MgBr$ yielded the corresponding dibenzyl (Bn_2) derivatives of titanium (cycl)Si(NBu^t)$_2$TiBn$_2$ (**9**). When these dibenzyl complexes were used as precursors for the conversion of monomeric to dimeric alkoxy-bridged species, oxo insertion did not occur, presumably because formation of the alkoxy-bridged dimer was hampered by the presence of bulky dibenzyl units.

Introduction

Bidentate diamido ligands with a silene bridge[1] are of considerable interest as ligands in the coordination chemistry of main-group elements[2] and transition metals.[3] We have recently demonstrated that bidentate diamidotitanium(IV) complexes of the type (cycl)Si(NBu^t)$_2$TiCl$_2$, in which the bridging silene is cyclic, display variable steric protection toward the metal center, depending on the size of the ring. A diamido ligand with a cyclic silene bridge provides greater steric protection upon chelation to Ti than the corresponding acyclic silene-bridged diamides (**A**), as shown in Chart 1.

Chart 1. Steric Protection Derived from the Cyclic Silene Ligand Backbone



A

2

Steric interaction derived from the cyclic silene backbone is therefore likely to have a significant effect on the chemical reactivity of the metal center. As an extension of our ongoing investigations into the chemical behavior of these cyclic silene-bridged diamidometal complexes,[4] we now report on the dimethyltitanium complexes and their reactivity toward oxygen.[5] Despite the interest in the insertion of dioxygen into main-group[6,7] as well as transition-metal[8] alkyls, the reaction of O_2 with "M−R" bonds of the group 4 metal amido complexes has not been reported until now. In an earlier communication,[5] we outlined the preliminary results of our study of (cycl)Si(NBu^t)$_2$TiMe$_2$ (**2**) with O_2, which highlighted the preferential insertion of an oxygen atom into the titanium−carbon bond. Here, we report the full

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[†] Tel: +82-1-860-1334. Fax: +82-41-867-5396. E-mail: sangok@korea.ac.kr.

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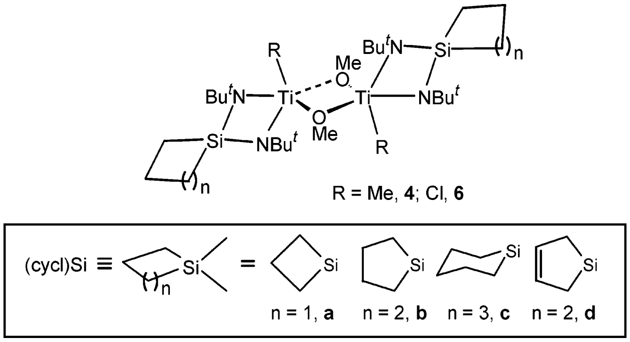
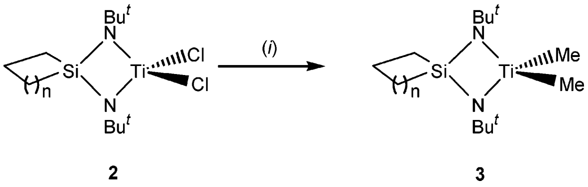
Chart 2. Methoxy-Bridged Dimeric Titanium Species 4 and 6



Scheme 1. Preparation of the Dimethyldiamido Complexes (cycl)Si(NBu^t)$_2$TiMe$_2$ (3)[a]



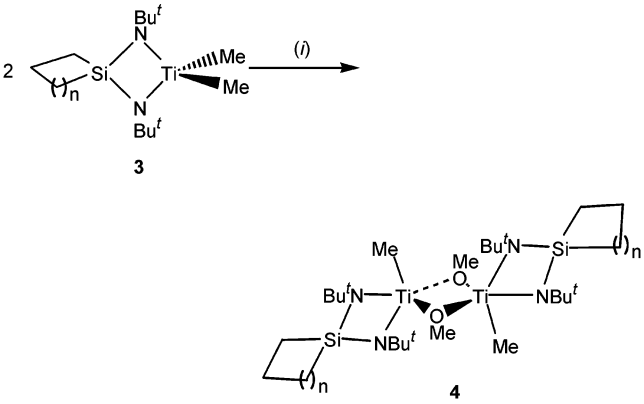
[a] Conditions: (i) 2 MeMgBr, Et$_2$O, −78 °C.

synthetic and structural details of the novel methoxy-bridged dimeric titanium complex [(cycl)Si(NBu^t)$_2$Ti(μ-OMe)R]$_2$ (R = Me (**4**), Cl (**6**)) and extend this chemistry to the related titanium chloride and benzyl derivatives. The outcome of X-ray crystallographic studies has provided an opportunity to evaluate the effect of the interannular bridge on the molecular geometry of these modified siladiazatitanacyclobutane complexes, as shown in Chart 2.

Results and Discussion

Reactions of the Dimethyldiamido Complexes (cycl)Si(NBu^t)$_2$TiMe$_2$ (3) with O$_2$. Dimethyltitanium complexes were prepared according to the literature methods, as shown in Scheme 1. Basically, methylation of a diethyl ether solution of **2** (1.0 mmol) with MeMgBr (2.4 mmol) at −78 °C for 2 h afforded high yields of **3** (66−86%) as red solids.

Scheme 2. Formation of the Series of Methoxy-Bridged Dimeric Titanium Complexes 4[a]



[a] Conditions: (i) O$_2$, toluene, −78 °C.

Attempted recrystallization of **3** from toluene, however, yielded yellow crystals of the methoxy-bridged dimer [(cycl)Si(NBu^t)$_2$Ti(μ-OMe)Me]$_2$ (**4**), rather than the desired dimethyl complex, as confirmed by X-ray analysis. Compound **4** was initially isolated in the synthesis of **3** as a minor yellow product. However, since no methoxy source was evident in the original synthesis, we postulate that this group was produced by the reaction of the methyl ligand with trace amounts of oxygen present in the reaction medium. We subsequently found that reactions of **3** with O$_2$ always proceed in near-quantitative yields, as determined by ^{1}H NMR spectroscopy. These high yields are presumably due to the inertness of the formed dimeric titanium(IV) products (e.g., **4**) toward further oxidation by O$_2$. Thus, as Scheme 2 reveals, a variety of **4** derivatives can be conveniently prepared by adding O$_2$ to a precooled (−78 °C) toluene solution of **3** and warming the reaction mixture to 25 °C. Recrystallization from toluene (−10 °C) affords the corresponding complex **4** in good yield.

Satisfactory elemental analyses and ^{1}H and ^{13}C NMR spectral data for **4** are consistent with the presence of methoxy-bridged ligands (see the Experimental Section). An additional factor that leads to the high-field shift in the Ti-bound methyl proton resonance of **4a**−**d** may be the electron-donating character of the OMe ligand. The ^{1}H and ^{13}C NMR spectral data for **4** also reveal that the replacement of a cyclic alkyl or an alkenyl group on the central silicon atom has little effect on the methyl and methoxy chemical shifts.

Suitable crystals of **4**, grown from cooled toluene solutions (−10 °C), were found to crystallize isostructurally as molecular solids without the unusual intermolecular contacts, as determined by X-ray crystallography. The crystal data for complexes **4** are summarized in Table 1, while the refinement details are discussed in the Experimental Section. Selected bond distances and bond angles are listed in Tables 2 and 3, respectively, and the molecular geometries and atom-labeling schemes are shown in Figures 1−4. The structural analyses of **4** reveal a molecular core in which the metal center occupies a distorted-square-pyramidal environment defined by the two nitrogen atoms of the silyldiamido ligand, with the methyl and bridging methoxy ligands completing the coordination sphere. The O atom of one (cycl)Si(NBu^t)$_2$Ti(OMe)Me unit coordinates to Ti of the other unit, and both Ti atoms are pentacoordinated. Thus, the geometry about each titanium atom can be described as distorted square pyramidal, in which

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Table 1. X-ray Crystallographic Data and Processing Parameters for Compounds 4a–d, 6a, and 7a

	4a	**4b**	**4c**	**4d**	**6a**	**7a**
formula	$C_{26}H_{60}N_4O_2$-Si_2Ti_2	$C_{28}H_{64}N_4O_2$-Si_2Ti_2	$C_{30}H_{68}N_4O_2$-Si_2Ti_2	$C_{28}H_{60}N_4O_2$-Si_2Ti_2	$C_{24}H_{54}N_4O_2$-$Si_2Cl_2Ti_2$	$C_{22}H_{48}N_4O_2$-$Si_2Cl_4Ti_2$
fw	612.69	640.82	668.86	636.78	653.59	694.42
cryst class	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	2	2	2	2	2	4
cell constants						
a, Å	8.9319(5)	9.0485(6)	8.991(1)	8.6178(8)	9.040(1)	9.3229(9)
b, Å	10.0666(5)	10.4505(7)	10.4085(7)	9.0100(6)	13.9374(7)	13.1281(7)
c, Å	10.5719(7)	10.5315(6)	10.9796(5)	12.120(1)	14.3703(6)	13.8955(5)
α, deg	90.046(5)	87.845(6)	83.523(5)	93.400(7)	80.857(4)	
β, deg	113.521(4)	66.313(5)	81.554(6)	98.586(9)	80.421(8)	95.917(5)
γ, deg	94.306(5)	82.331(6)	67.081(7)	102.250(7)	83.290(8)	
V, Å^3	868.63(9)	903.7(1)	934.4(1)	905.3(1)	1755.0(3)	1691.6(2)
μ, mm^{-1}	0.555	0.536	0.521	0.535	0.701	0.884
cryst size, mm	0.4 × 0.5 × 0.5	0.3 × 0.4 × 0.4	0.35 × 0.35 × 0.4	0.3 × 0.3 × 0.35	0.4 × 0.4 × 0.5	0.25 × 0.3 × 0.3
d_{calcd}, g/cm^3	1.171	1.178	1.189	1.168	1.237	1.363
$F(000)$	332	348	364	344	696	728
θ range, deg	2.03–25.98	1.97–25.97	1.88–25.97	1.71–24.97	1.45–25.97	2.14–25.97
h, k, l collected	+11, ±12, ±13	+11, ±12, ±13	+11, ±12, ±13	+10, ±11, ±14	+11, ±17, ±17	+11, +16, ±17
no. of rflns measd	3652	3760	3907	3410	4964	3558
no. of unique rflns	3384	3523	3658	3176	4788	3312
no. of rflns with $I > 2\sigma(I)$	2349	2528	2948	2363	3218	2182
no. of params	171	180	189	182	339	169
R1[a] ($I > 2\sigma(I)$)	0.0458	0.0813	0.0367	0.0437	0.1254	0.0415
wR2[b] (all data)	0.1274	0.2610	0.1037	0.1243	0.3935	0.1410
GOF	1.051	1.023	1.050	0.996	1.083	0.876

[a] $R1 = \sum||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

Table 2. Selected Interatomic Distances (Å) for Compounds 4a–d, 6a, and 7a

Compound **4a**									
Ti(1)–N(2)	1.878(2)	Ti(1)–N(1)	1.907(2)	Ti(1)–O(1)	2.058(2)	Ti(1)–O(1)*	2.031(2)	Si(1)–N(1)	1.740(3)
Si(1)–N(2)	1.737(3)	Ti(1)–C(12)	2.126(4)						
Compound **4b**									
Ti(1)–N(2)	1.913(4)	Ti(1)–N(1)	1.883(4)	Ti(1)–O(1)	2.065(3)	Ti(1)–O(1)*	2.029(3)	Si(1)–N(1)	1.731(5)
Si(1)–N(2)	1.748(4)	Ti(1)–C(13)	2.148(6)						
Compound **4c**									
Ti(1)–N(2)	1.905(2)	Ti(1)–N(1)	1.877(2)	Ti(1)–O(1)	2.033(2)	Ti(1)–O(1)*	2.063(2)	Si(1)–N(1)	1.758(2)
Si(1)–N(2)	1.750(2)	Ti(1)–C(14)	2.183(2)						
Compound **4d**									
Ti(1)–N(2)	1.871(2)	Ti(1)–N(1)	1.898(2)	Ti(1)–O(1)	2.039(2)	Ti(1)–O(1)*	2.048(2)	Si(1)–N(1)	1.736(2)
Si(1)–N(2)	1.753(3)	Ti(1)–C(14)	2.148(4)						
Compound **6a**									
Ti(1)–N(2)	1.875(7)	Ti(1)–N(1)	1.869(9)	Ti(1)–O(1)	2.029(8)	Ti(1)–O(1)*	2.050(8)	Si(1)–N(1)	1.756(8)
Si(1)–N(2)	1.75(1)	Ti(1)–Cl(1)	2.498(3)						
Compound **7a**									
Ti(1)–N(2)	1.834(3)	Ti(1)–O(1)*	1.932(2)	Ti(1)–O(1)	2.153(2)	Ti(1)–N(1)	2.233(3)	Ti(1)–Cl(2)	2.291(1)
Ti(1)–Cl(1)	2.298(1)	Ti(1)–Si(1)	2.936(1)	Si(1)–N(1)	1.795(3)	N(1)–N(2)	1.437(4)	Si(1)–O(1)	1.635(2)

the C(1) atom and the remaining four atoms (N(1), N(2), O(1), O(1*)) are in axial and basal positions, respectively. Overall, the four structures (**4a–d**) exist as dimers in the solid state, where the two molecular units comprising the dimer are each constrained by the crystallographic center of inversion. Thus, in all of the compounds **4** studied, the (cycl)Si(NBu^t)$_2$Ti core forms a nearly planar siladiazatitanacyclobutane metallacyclic ring (torsional angles of N–Ti–N–Si ~1.02(8)–4.0(1)°). The cyclic silyldiamido ligand chelates the titanium center in a near-symmetrical conformation to form a planar siladiazatitanacyclobutane ring with a bite angle (N–Ti–N) of 82.6–83.5°. The Ti–N bond lengths (1.87–1.91 Å) are comparable to those found in other titanium amido complexes (1.88–1.94 Å),[9] indicating a significant N→Ti π-donation to the bonding. Consequently, each nitrogen atom occupies an sp^2-hybridized environment, as indicated by the sum of the angles around the nitrogens. The distances between the bridging alkoxides and the titanium center, Ti(1)–O(1) and Ti(1)–O(1*), fall within the range expected for a Ti_2O_2 core, 2.03–2.04 and 2.05–2.07 Å, respectively,[10] while the Ti(1)–C(1) distance of 2.13–2.18 Å is typical. The Ti_2O_2 core is undoubtedly coplanar due to its symmetry, with the

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Table 3. Selected Interatomic Angles (deg) for Compounds 4a−d, 6a, and 7a

Compound **4a**							
O(1)−Ti(1)−O(1*)	72.61(9)	Ti(1)−O(1)−Ti(1*)	107.39(9)	N(2)−Ti(1)−N(1)	82.9(1)	C(4)−N(1)−Si(1)	128.3(2)
C(4)−N(1)−Ti(1)	139.2(2)	Si(1)−N(1)−Ti(1)	91.8(1)	C(8)−N(2)−Si(1)	130.6(2)	C(8)−N(2)−Ti(1)	135.6(2)
Si(1)−N(2)−Ti(1)	92.9(1)	N(1)−Ti(1)−C(12)	94.3(1)	N(2)−Ti(1)−C(12)	111.2(2)	O(1)−Ti(1)−C(12)	86.7(1)
O(1*)−Ti(1)−C(12)	135.1(2)						
Compound **4b**							
O(1)−Ti(1)−O(1*)	72.4(1)	Ti(1)−O(1)−Ti(1*)	107.6(1)	N(2)−Ti(1)−N(1)	82.6(2)	C(5)−N(1)−Si(1)	131.3(4)
C(5)−N(1)−Ti(1)	134.6(4)	Si(1)−N(1)−Ti(1)	93.4(2)	C(9)−N(2)−Si(1)	129.2(4)	C(9)−N(2)−Ti(1)	138.4(3)
Si(1)−N(2)−Ti(1)	91.9(2)	N(1)−Ti(1)−C(13)	111.7(2)	N(2)−Ti(1)−C(13)	93.4(2)	O(1)−Ti(1)−C(13)	86.7(2)
O(1*)−Ti(1)−C(13)	134.6(2)						
Compound **4c**							
O(1)−Ti(1)−O(1*)	71.80(6)	Ti(1)−O(1)−Ti(1*)	108.20(6)	N(2)−Ti(1)−N(1)	83.29(7)	C(6)−N(1)−Si(1)	129.7(2)
C(6)−N(1)−Ti(1)	135.7(1)	Si(1)−N(1)−Ti(1)	92.95(8)	C(10)−N(2)−Si(1)	130.0(2)	C(10)−N(2)−Ti(1)	136.9(2)
Si(1)−N(2)−Ti(1)	92.25(8)	N(1)−Ti(1)−C(14)	111.68(9)	N(2)−Ti(1)−C(14)	93.96(8)	O(1)−Ti(1)−C(14)	133.88(8)
O(1*)−Ti(1)−C(14)	86.68(8)						
Compound **4d**							
O(1)−Ti(1)−O(1*)	71.90(9)	Ti(1)−O(1)−Ti(1*)	108.10(9)	N(2)−Ti(1)−N(1)	83.5(1)	C(5)−N(1)−Si(1)	128.5(2)
C(5)−N(1)−Ti(1)	138.9(2)	Si(1)−N(1)−Ti(1)	92.1(1)	C(9)−N(2)−Si(1)	129.3(2)	C(9)−N(2)−Ti(1)	137.7(2)
Si(1)−N(2)−Ti(1)	92.5(1)	N(1)−Ti(1)−C(14)	93.5(1)	N(2)−Ti(1)−C(14)	108.3(2)	O(1)−Ti(1)−C(14)	138.6(1)
O(1*)−Ti(1)−C(14)	87.0(1)						
Compound **6a**							
O(1)−Ti(1)−O(1*)	71.8(5)	Ti(1)−O(1)−Ti(1*)	108.2(5)	N(2)−Ti(1)−N(1)	84.1(4)	C(4)−N(1)−Si(1)	126.7(8)
C(4)−N(1)−Ti(1)	140.7(8)	Si(1)−N(1)−Ti(1)	92.4(4)	N(2)−Ti(1)−Cl(1)	110.0(3)	O(1)−Ti(1)−Cl(1)	142.4(2)
Si(1)−N(2)−Ti(1)	92.3(4)	N(1)−Ti(1)−Cl(1)	93.5(3)	O(1*)−Ti(1)−Cl(1)	88.3(3)		
Compound **7a**							
Si(1)−O(1)− Ti(1*)	148.5(2)	Si(1)−O(1)−Ti(1)	100.7(1)	Ti(1*)−O(1)−Ti(1)	106.8(1)	O(1)−Si(1)−N(1)	94.8(1)
Si(1)−N(1)−Ti(1)	93.0(1)	O(1)−Ti(1)−N(1)	70.3(1)	O(1*)−Ti(1)−O(1)	73.2(1)	N(2)−Ti(1)−N(1)	39.9(1)
O(1*)−Ti(1)−N(1)	136.8(1)						

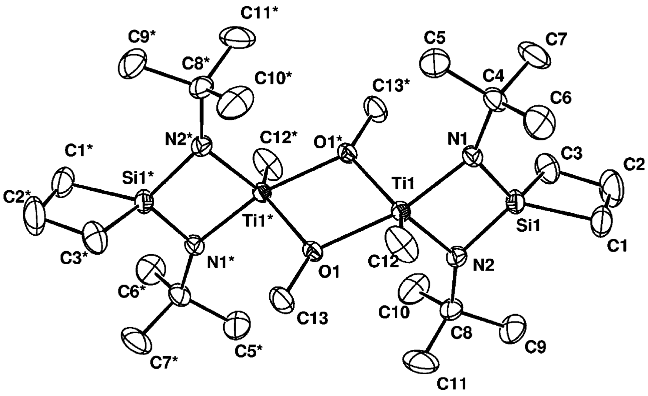


Figure 1. Molecular structure of **4a** with thermal ellipsoids drawn at the 30% level.

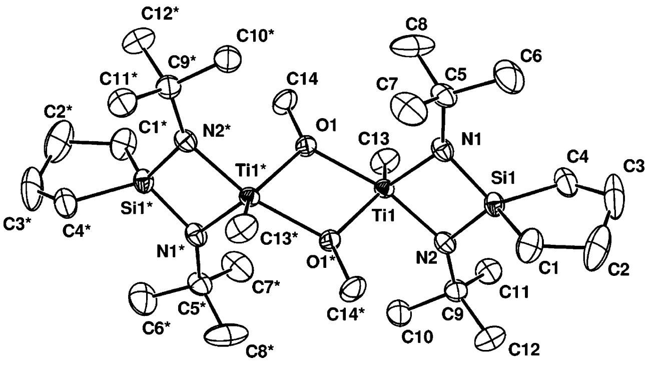


Figure 2. Molecular structure of **4b** with thermal ellipsoids drawn at the 30% level.

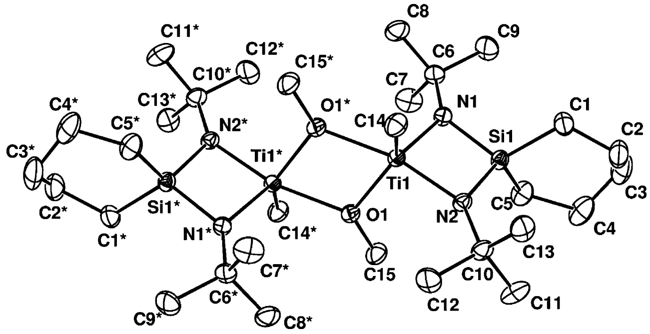


Figure 3. Molecular structure of **4c** with thermal ellipsoids drawn at the 30% level.

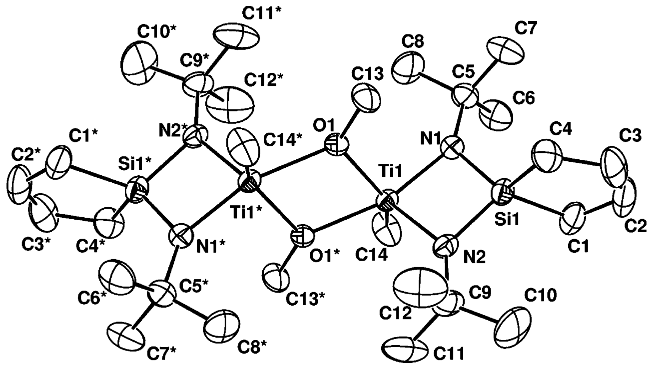
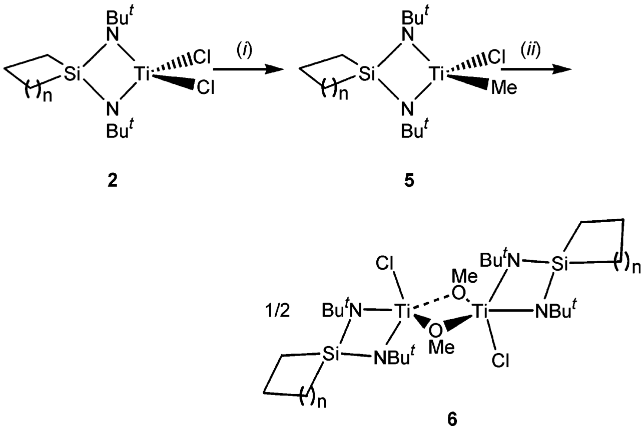


Figure 4. Molecular structure of **4d** with thermal ellipsoids drawn at the 30% level.

interatomic angles being O(1)−Ti(1)−O(1*) = 71.8−72.6° and Ti(1)−O(1)−Ti(1*) = 107.4−108.2°.

Rather than suggesting that there is complete oxygenation of the two Ti−Me bonds in **3**, we propose that, in the initial stages, oxo insertion only occurs in one of the Ti−Me bonds. In this way, the monoalkoxytitanium formed behaves like a stepping stone to realizing pentacoordination in the second monoalkoxytitanium center. Wolczanski reported similar behavior in the (tritox)$_2$MMe$_2$ (M = Ti, Zr, Hf) complex, where oxidation of one of the methyl functionalities results in the formation of (tritox)MMe$_{3-n}$(OMe)$_n$ (n = 1−3).[8b,c] The bulky tri-*tert*-butylmethoxy ((Me$_3$C)$_3$CO$^-$, tritox) ancillary ligand, with a cone angle of 125°, no doubt contributes to the overall stability of the resultant metal alkoxides.

Scheme 3. Formation of Methoxy-Bridged Dimeric Species 6 Derived from the Monomethyl Derivative 5[a]



[a] Conditions: (i) MeMgBr, Et_2O, −78 °C; (ii) O_2, toluene, −78 °C.

Reactions of the Monomethyl Diamido Complexes (cycl)Si(NBu^t)$_2$Ti(Me)Cl (5) with O_2. Monomethylation of a diethyl ether solution of **2** (1.0 mmol) with MeMgBr (1.0 mmol) at −78 °C afforded high yields of **5** (68−80%) as red solids (Scheme 3). Efficient purification procedures and corresponding X-ray structural information were crucial in this case, since complicated and usually uninformative NMR data are obtained for chloride complexes. Thus, crystallization of the crude product obtained from the reaction of **2** with 1 equiv of MeMgBr in Et_2O was attempted under different conditions. The monochloride complexes **5** are, however, extremely soluble even in pentane, and their isolation, handling, and characterization are very arduous. Thus, crystallization of the crude product was attempted under different conditions. The low-temperature (−40 to −45 °C) crystallization from a pentane solution proved more successful, leading reproducibly to the series of monochloride complexes **5**. The composition of **5** was confirmed by elemental analysis, and the ^1H NMR spectrum is consistent with a species displaying pseudo-C_s symmetry. Characteristic ^1H and ^{13}C NMR resonances associated with the Ti−Me groups were observed around 0.2 and 34.0 ppm, respectively. The silacycloalkyl groups exhibit unresolved multiplets between 0.6 and 1.9 ppm, while the chemically equivalent *tert*-butyl protons produce a singlet around 1.5 ppm.

We found that treatment of the series of monomethyl diamido complexes **5** with O_2 provides the corresponding methoxy complex **6**, as indicated by the replacement of the methyl signal in the ^1H NMR with one due to a methoxy group at 4.1 ppm. Complex **6** was isolated as a yellow powder in 67−76% yield, where the elemental analyses and $^1H/^{13}C$ NMR spectra are consistent with the uptake of 0.5 equiv of O_2 per (cycl)Si(^{t}BuN)$_2$ unit. The solid-state structure of **6a**, determined by X-ray crystallography (Figure 5), confirms it to be isostructural with its methoxy methyl analogue **4**. Essentially, **6a** contains two equivalent titanium centers and two cyclic silene-bridged diamide ligands. The structure also reveals the existence of two intramolecular Ti−O coordination bonds and a Ti- - -Ti nucleus bridged by two oxygen atoms. The Ti−Cl and Ti−O bond lengths are longer than those previously reported for [$TiCl_4\{C_2O_4(CH_2CH_2Ph)_2\}$],[11] [$TiCl_4\{C_4H_7O(CO_2Et)\}_2$],[12,13] *cis*-[$TiCl_2(\eta^2$-maltolato)$_2$],[14] and [$Ti_2(\mu$-O)$Cl_2(\eta^2$-guaiacolato)$_4$].[14] The two equivalent titanium centers adopt distorted-square-pyramidal environments in which the methoxy group oxygens bridge the two metals, while the two terminal chlorides reside above and below the Ti_2O_2 core, respectively. For comparison, the analogous methoxy methyl derivatives **4** are dimeric, showing the insensitivity of these oxo-insertion reactions to small changes in the central ligand.

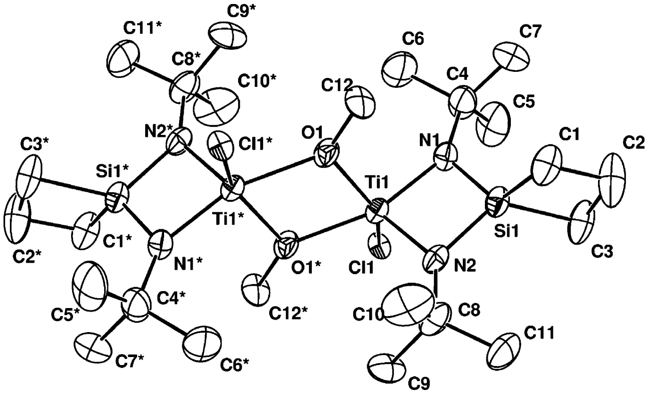
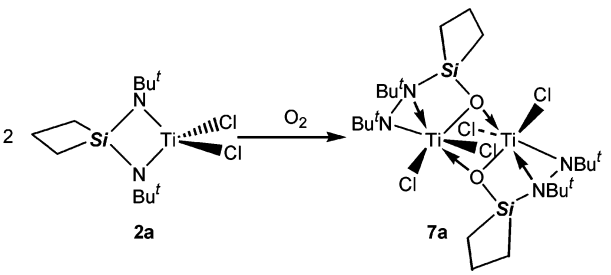


Figure 5. Molecular structure of **6a** with thermal ellipsoids drawn at the 30% level.

Reactions of the Dichloro Complexes (cycl)Si(NBu^t)$_2TiCl_2$ (2) with O_2. Given the π-donor properties of chloride ligands, it was expected that the dichlorides of **2** would exhibit distinct structural and chemical reactivity differences compared to the corresponding dimethyl diamide complex **3**. As anticipated, our results indicate that the dichlorides failed to react with molecular oxygen under the same experimental conditions as found in the dimethyl diamide complex **3**. The increased complex stability of **2** can be ascribed to the involvement of the chloride ligands in metal binding, due to the strong electron π-donor properties of chloride atoms. Indeed, at low temperature (−78 °C) with prolonged reaction time (ca. 3 h), the reaction between **2** and O_2 yielded only intractable products, while at room temperature, **2** decomposed rapidly to yield as yet unidentifiable species. In the case of **2a** (eq 1), only trace amounts of oxo-insertion products were observed.



(1)

Crystals of **2a** suitable for X-ray diffraction were obtained from a toluene solution in the presence of

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[11] Sobota, P.; Utko, J.; Szafert, S.; Szczegot, K. *J. Chem. Soc., Dalton Trans.* **1997**, 679.

[12] Sovota, P.; Szafert, S.; Utko, J.; Lis, T. *J. Organomet. Chem.* **1992**, *423*, 195.

[13] Sobota, P.; Wróblewska, M.; Szafert, S.; Glowiak, T. *J. Organomet. Chem.* **1994**, *481*, 57.

[14] Sobota, P.; Przybylak, K.; Utko, J.; Jerzykiewicz, L. B.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Szczegot, K. *Chem. Eur. J.* **2001**, *7*, 951.

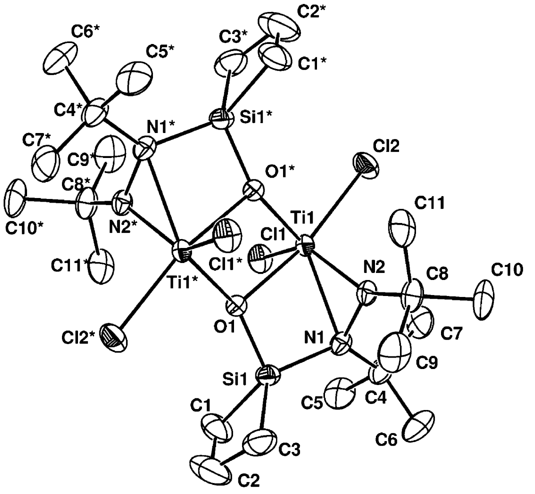
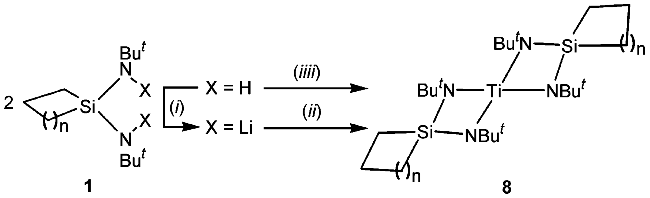


Figure 6. Molecular structure of **7a** with thermal ellipsoids drawn at the 30% level.

trace amounts of O_2 at −10 °C. X-ray crystallography shows that, rather than being a simple oxo-containing compound, **7a** is in fact a dimer of the formulation $[\{(NBu^tNBu^t)(CH_2)_3SiO\}TiCl_2]_2$ (Figure 6), which exhibits an extensive structural rearrangement compared to the starting material. The structure of **7a** is essentially a ladderlike arrangement composed of a Ti_2O_2 core with edge-fused rings on either side. The coordination sphere around each titanium center comprises a side-on-bound hydrazido residue and two terminal chlorides, giving rise to six-coordinate metal centers. The molecular dimensions of the hydrazido complex **7a** are almost identical with those found in $CpTiCl_2(NR^1NR^2R^3)$ (R^1, R^2, R^3 = Me;[15] R^1, R^2 = Me, R^3 = $SiMe_3$;[15] R^1 = Ph, R^2, R^3 = H;[16] R^1 = H, R^2, R^3 = Me[16]). Consequently, the Ti−N(2) separation (1.834(3) Å) infers considerable Ti−N double bonding, in which the N−N separation is on the same order as that found in hydrazine itself,[17] and the Ti−N(1) bond distance of 2.233(3) Å is typical of that found in N→Ti dative bonding. The surprise in the synthesis of **7a** is the dual specificity of oxo insertion. We previously surmised that the oxophilicities of both Ti and Si atoms were possibly the driving forces for both the rearrangement observed in the formation of **7a** and the side-on hydrazide bonding.[5] Although it is expected that oxo insertion causes a significant structural change, structural evidence for this type of rearrangement has not previously been observed in organotitanium amide complexes. The dimeric structure of **7a** suggests that this reaction proceeds with cleavage of a Si−N bond and is accompanied by the formation of Si−O and N−N bonds. This alternate reaction pathway is probably a consequence of the weaker Ti−N(amido) bonds that arise when the σ-donating methyl ligands of **3a** are replaced by a pair of π-donating chloride ligands in **2a**, thus making the Ti−N(amido) bonds of **2a** more reactive. Although the precise mechanism by which **6a** is formed is not understood, the observations noted above suggest either that the oxo insertion is templated or that the conversion of **2a** to **7a** requires that the process of ladder formation and oxo insertion occur concurrently. Our data allow us to speculate on the importance of π-donor properties of chloride ligands, and they point out that oxo insertion in the diamide complexes is modulated by a subtle balance between binding features of the metal and the ligands.

Scheme 4. Preparation of the Spirobis(siladiazatitanacyclobutane) Complexes 8[a]



[a] Conditions: (i) Bu^nLi, Et_2O, −78 °C; (ii) $TiCl_4$, Et_2O, −78 °C; (iii) $Ti(NMe_2)_4$, toluene, 110 °C.

Preparation of the Spirobis(siladiazatitanacyclobutane) Complexes $[(cycl)Si(NBu^t)_2]_2Ti$ (8). A key question that arises from the results shown above is whether this oxo insertion can be extended to nonalkylated titanium complexes. To address this, we first utilized the spirobis(siladiazatitanacyclobutane) **8** and found that these complexes remained intact following reaction with O_2. Complexes **8** were prepared as shown in Scheme 4.

Thus, reaction of a diethyl ether solution of the dilithiated complex **1** (2.0 mmol) with $TiCl_4$ (1.0 mmol) at −78 °C for 2 h afforded high yields of **8** (74−81%) as red solids. Alternatively, the reaction of $Ti(NMe_2)_4$ with 2 equiv of $(cycl)Si(HNBu^t)_2$ (**1**) in toluene (Scheme 4), followed by recrystallization of the crude residue from a pentane solution, produced red microcrystalline crystals **8** in 38−43% yields. From elemental analysis and ^1H and ^{13}C NMR spectroscopy, complex **8** was deemed to be a titanium bis(diamido) complex with a spiro backbone. Attempts to establish an unequivocal structural characterization of **8c** by X-ray crystallography, however, proved difficult due to poorly diffracting crystals. Consequently, these results are provided as Supporting Information only. Nevertheless, the crystallographic data were sufficient to establish that the silacyclohexyl diamide moieties $\mathbf{1c}^{2-}$ bind the metal centers through the amide N atoms, forming two four-membered chelate rings, resulting in tetrahedral coordination around titanium center. In addition, the increased kinetic stability of **8** is most likely a consequence of the constraints imposed by the cyclic silyl backbone of the spiro ring. The structural characterization of the related spiro titanium complex $[(Me_2)Si(NBu^t)_2]_2Ti$, derived from the acyclic silene-bridged diamido ligand, has previously been reported.[3b,d,f] However, as far as we are aware, compound **8** is the first example of a cyclic silene-bridged diamido spirotitanium(IV) complex.

Synthesis and Reactivity of the Dibenzyl Ti(IV) Complexes $(cycl)Si(NBu^t)_2Ti(Bn)_2$ (9). The benzyl derivatives $(cycl)Si(NBu^t)_2Ti(Bn)_2$ (**9**), prepared from the reaction between **2** and 2 equiv of $PhCH_2MgBr$, were isolated as thick brownish red oils (Scheme 5). All attempts to purify these complexes via recrystallization were precluded by their reluctance to crystallize from toluene solution. The resulting products are thought to contain small amounts of impurities, as suggested by

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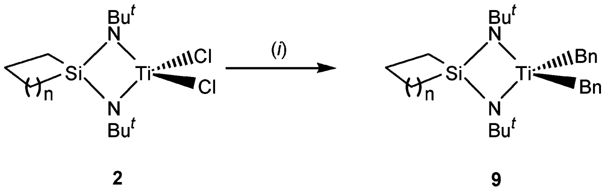
(15) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Walker, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, 2389.

(16) Latham, I. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 385.

(17) Yamaguchi, A.; Ichishima, I.; Shimanouchi, T.; Mizushima, S.-I. *J. Chem. Phys.* **1959**, *31*, 843.

Scheme 5. Preparation of the Dibenzyl Ti(IV) Complexes 9[a]



[a] Conditions: (i) 2 $PhCH_2MgBr$, Et_2O, −78 °C.

their color; however, NMR spectroscopy failed to yield evidence to corroborate this.

Alternatively, the Ti dibenzyl complexes **9** were obtained by reacting the diamido ligand (cycl)Si$(HNBu^t)_2$ (**1**) with $Ti(Bn)_4$ (Bn = CH_2Ph) in toluene. The same crystallization approach found in monochloride complexes **5** was applied to the isolation of **9**. Thus, the resulting complexes were isolated from a cold pentane solution (−40 to −45 °C) as red crystalline air- and moisture-sensitive solids in good yield (81−89%). The ^1H and ^{13}C NMR spectra of **9** are consistent with pseudo-C_{2v}-symmetric structures and symmetrical bidentate coordination of the diamido ligand. The benzylic protons in **9** give rise to two doublets in the ^1H NMR spectra at around 2.2 and 2.1 ppm ($^2J_{HH}$ = ~10 Hz), respectively, while in the ^{13}C NMR spectrum the TiCH_2Ph carbon appears at around 69 ppm. These NMR shifts are consistent with η^1 coordination of the benzyl group and fall within the expected ranges reported for similar Ti benzyl complexes.[18]

The reaction between **9** and dioxygen (in benzene-d_6) failed to proceed after 3 h at room temperature. Indeed, heating the reaction mixture at 80 °C resulted in decomposition of the starting materials, with no evidence to suggest the formation of the desired benzyloxy-bridged dimeric complexes. Since ^1H and ^{13}C NMR spectral data confirm the existence of a TiC_2 core within complex **9**, one might expect oxo insertion to occur between the Ti−CH_2Ph bonds, in accordance with the analogous dimethyl complexes. Surprisingly, we were unable to find any indication of oxo insertion, which draws us to the conclusion that this reaction is probably hampered by the bulkiness of the benzyl group. It would appear that the steric congestion imposed by the bulky benzyl substituents in **9** is responsible for preventing the oxo-insertion process in a manner that has been observed in the related dimethyl complexes **4**. These benzyl ligands, instead, impart a high degree of stability to the titanium dibenzyldiamido complexes.

In summary, a series of dimethyl- and monomethyltitanium complexes (**3**, **5**) have been shown to react with molecular oxygen to yield methoxy-bridged dimeric complexes (**4**, **6**), which have been structurally characterized by X-ray crystallography. Complexes **4** and **6** contain bulky cyclic substituents on the silylene bridge, which kinetically stabilize the four-membered spirosiladiazatitanacycle sufficiently to allow detailed investigations of their chemical behavior and structures. Of particular interest are the methoxy-bridged dimeric complexes, which reveal an increased stability in their coordination geometry, ranging from square pyramidal to near octahedral. This outcome is likely due to the relative steric interaction experienced by the Si−(cycl) and N−*Bu*^{t} groups. It can be concluded that the diamido ligand comprising the sterically demanding silacycloalkyl group chelates the titanium center with greater steric protection than in the planar silacyclobutyl case (**A**), leading to the formation of stable methoxy-bridged titanium dimers.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. Diethyl ether, toluene, hexane, and pentane were distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with CaH_2. Benzene-d_6 was distilled under nitrogen from sodium and stored in a Schlenk storage flask until needed. $CDCl_3$ was predried under CaH_2 and vacuum-transferred. *n*-BuLi (1.6 M in hexanes), MeMgBr, and $TiCl_4$ were used as received from Aldrich. (cycl)Si$(^tBuN)_2$-$TiMe_2$ (**3**)[4] and $Ti(CH_2Ph)_4$[19] were obtained by literature methods. All ^1H (300.1 MHz, measured in $CDCl_3$) and ^{13}C (75.4 MHz, measured in $CDCl_3$) NMR spectra were recorded on a Varian Mercury-300BB spectrometer unless otherwise stated. ^1H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. Elemental analyses were performed with a Carlo Erba Instruments CHNS−O EA1108 analyzer.

Preparation of Dimeric Methoxy-Bridged Monomethyltitanium Complexes 4. A representative procedure is as follows: in a solution of **3a** (0.29 g, 1.0 mmol) in 20 mL of toluene, precooled to −78 °C, was bubbled 1 atm of predried O_2 for 1 h. The resultant yellow mixture was warmed to 25 °C and stirred for 2 h. ^1H NMR spectroscopy demonstrated that **4a** was formed quantitatively after 5 min at room temperature. The mixture was concentrated to ca. 5 mL and placed at −10 °C, giving a yellow precipitate of **4a** which was filtered and dried in vacuo. Suitable crystals for X-ray diffraction analysis were obtained from a saturated toluene solution at −10 °C. Yield: 82% (0.25 g, 0.41 mmol). ^1H NMR: δ 3.75 (s, 6H, TiO*Me*), 1.99 (m, 4H, CH_2CH_2), 1.99 (m, 8H, SiCH_2), 1.44 (s, 36H, ^{t}BuN), −0.01 (s, 6H, Ti*Me*). $^{13}C\{^1H\}$ NMR: δ 63.01 (TiO*Me*), 60.75 (N*C*Me$_3$), 34.04 (NC*Me*$_3$), 33.20 (Ti*Me*), 26.77 (CH_2CH_2), 12.73 (SiCH_2). Anal. Calcd for $C_{26}H_{60}N_4O_2Si_2Ti_2$: C, 50.97; H, 9.87; N, 9.14. Found: C, 50.83; H, 9.69; N, 9.04.

4b. A procedure analogous to the preparation of **4a** was used, but starting from **3b** (0.30 g, 1.0 mmol) in toluene. Thus, **4b** was crystallized from toluene at −10 °C. Yield: 0.28 g (0.44 mmol, 87%). ^1H NMR: δ 3.76 (s, 6H, TiO*Me*), 1.83 (m, 8H, CH_2CH_2), 1.40 (s, 36H, ^{t}BuN), 0.90 (m, 8H, SiCH_2), −0.03 (s, 6H, Ti*Me*). $^{13}C\{^1H\}$ NMR: δ 62.52 (TiO*Me*), 60.47 (N*C*Me$_3$), 34.20 (NC*Me*$_3$), 33.74 (Ti*Me*), 25.83 (CH_2CH_2), 12.95 (SiCH_2). Anal. Calcd for $C_{28}H_{64}N_4O_2Si_2Ti_2$: C, 52.48; H, 10.07; N, 8.74. Found: C, 52.33; H, 9.98; N, 8.60.

4c. A procedure analogous to the preparation of **4a** was used, but starting from **3c** (0.32 g, 1.0 mmol) in toluene. Thus, **4c** was crystallized from toluene at −10 °C. Yield: 0.27 g (0.41 mmol, 81%). ^1H NMR: δ 4.07 (s, 6H, TiO*Me*), 1.96 (m, 8H, CH_2CH_2), 1.61 (m, 4H, CH_2CH_2), 1.18 (s, 36H, ^{t}BuN), 0.60 (m, 8H, SiCH_2), 0.07 (s, 6H, Ti*Me*). $^{13}C\{^1H\}$ NMR: δ 66.43 (TiO*Me*), 65.36 (N*C*Me$_3$), 33.98 (NC*Me*$_3$), 33.27 (Ti*Me*), 30.62 (CH_2CH_2), 25.49 (CH_2CH_2), 17.71 (SiCH_2). Anal. Calcd for $C_{30}H_{68}N_4O_2Si_2Ti_2$: C, 53.87; H, 10.25; N, 8.38. Found: C, 53.72; H, 10.12; N, 8.26.

4d. A procedure analogous to the preparation of **4a** was used, but starting from **3d** (0.30 g, 1.0 mmol) in toluene. Thus,

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(18) (a) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2001**, *20*, 1365. (b) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836.

(19) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

4d was crystallized from toluene at −10 °C. Yield: 0.25 g (0.39 mmol, 77%). ^{1}H NMR: δ 5.88 (s, 4H, C═C*H*), 3.82 (s, 6H, TiO*Me*), 1.44 (s, 8H, SiC*H*$_2$), 1.22 (s, 36H, ^{t}BuN), 0.07 (s, 6H, Ti*Me*). ^{13}C{^{1}H} NMR: δ 56.10 (TiO*Me*), 49.36 (N*C*Me$_3$), 33.70 (NC*Me*$_3$), 32.72 (Ti*Me*), 25.83 (CH$_2$*C*H$_2$), 19.95 (Si*C*H$_2$). Anal. Calcd for $C_{28}H_{60}N_4O_2Si_2Ti_2$: C, 52.82; H, 9.50; N, 8.80. Found: C, 52.70; H, 9.39; N, 8.69.

Preparation of the Monomethyl Spirosiladiazatitanacyclobutane Complex (cycl)Si(^{t}BuN)$_2$TiMeCl (5). A representative procedure is as follows: to a solution of **2a** (1.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added MeMgBr (3.0 M in ether, 0.40 mL, 1.2 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting red solution was dried under vacuum to afford a red solid. The solid was extracted with pentane, and the filtrate was concentrated and cooled to −40 to −45 °C. Red solid **5a** was isolated by filtration, washing with cold pentane, and drying in vacuo. Yield: 0.21 g (0.68 mmol, 68%). ^{1}H NMR: δ 1.96 (m, 2H, CH$_2$C*H*$_2$), 1.65 (s, 18H, ^{t}BuN), 1.29 (m, 4H, SiC*H*$_2$), 0.26 (s, 6H, Ti*Me*). ^{13}C{^{1}H} NMR: δ 69.93 (N*C*Me$_3$), 36.79 (NC*Me*$_3$), 36.72 (Ti*Me*), 24.44 (CH$_2$*C*H$_2$), 13.12 (Si*C*H$_2$). Anal. Calcd for $C_{12}H_{27}N_2ClSiTi$: C, 46.38; H, 8.76; N, 9.01. Found: C, 46.58; H, 8.93; N, 9.22.

5b. A procedure analogous to the preparation of **5a** was used, but starting from **2b** (0.35 g, 1.0 mmol) in toluene. Thus, **5b** was crystallized from pentane at −40 to −45 °C. Yield: 0.23 g (0.71 mmol, 71%). ^{1}H NMR: δ 1.80 (m, 4H, CH$_2$C*H*$_2$), 1.53 (s, 18H, ^{t}*Bu*N), 0.87 (m, 4H, SiC*H*$_2$), 0.21 (s, 3H, Ti*Me*). ^{13}C{^{1}H} NMR: δ 69.95 (N*C*Me$_3$), 36.90 (NC*Me*$_3$), 36.83 (Ti*Me*), 25.89 (CH$_2$*C*H$_2$), 13.17 (Si*C*H$_2$). Anal. Calcd for $C_{13}H_{29}N_2SiClTi$: C, 48.13; H, 9.02; N, 8.64. Found: C, 47.97; H, 8.99; N, 8.67.

5c. A procedure analogous to the preparation of **5a** was used, but starting from **2c** (0.36 g, 1.0 mmol) in toluene. Thus, **5c** was crystallized from pentane at −40 to −45 °C. Yield: 0.27 g (0.80 mmol, 80%). ^{1}H NMR: δ 1.79 (m, 4H, CH$_2$C*H*$_2$), 1.54 (m, 2H, CH$_2$CH$_2$C*H*$_2$), 1.49 (s, 18H, ^{t}*Bu*N), 0.57 (m, 4H, SiC*H*$_2$), 0.27 (s, 3H, Ti*Me*). ^{13}C{^{1}H} NMR: δ 70.01 (N*C*Me$_3$), 36.99 (NC*Me*$_3$), 36.93 (Ti*Me*), 30.91 (CH$_2$*C*H$_2$), 25.93 (CH$_2$CH$_2$*C*H$_2$), 17.79 (Si*C*H$_2$). Anal. Calcd for $C_{14}H_{31}N_2SiClTi$: C, 49.68; H, 9.24; N, 8.28. Found: C, 49.87; H, 9.27; N, 8.25.

5d. A procedure analogous to the preparation of **5a** was used, but starting from **2d** (0.30 g, 1.0 mmol) in toluene. Thus, **5d** was crystallized from pentane at −40 to −45 °C. Yield: 0.25 g (0.77 mmol, 77%). ^{1}H NMR: δ 5.37 (s, 2H, C═C*H*), 1.52 (s, 18H, ^{t}*Bu*N), 1.40 (m, 4H, SiC*H*$_2$), 0.29 (s, 3H, Ti*Me*). ^{13}C{^{1}H} NMR: δ 130.62 (C═*C*H), 69.92 (N*C*Me$_3$), 36.98 (NC*Me*$_3$), 36.95 (Ti*Me*), 19.98 (Si*C*H$_2$). Anal. Calcd for $C_{13}H_{27}N_2SiClTi$: C, 48.43; H, 8.45; N, 8.69. Found: C, 48.25; H, 8.42; N, 8.66.

Preparation of Dimeric Methoxy-Bridged Monomethyltitanium Complexes 6. A representative procedure is as follows: a stirred solution of methyltitanium chloride **5a** (0.31 g, 1.0 mmol) in 20 mL of toluene at −78 °C was treated with predried O$_2$ (1 atm) by bubbling the gas through it for 1 h. The resultant yellow mixture was warmed to 25 °C and stirred for 2 h. The formation of **6a** was demonstrated by ^{1}H NMR spectroscopy. Removal of the volatiles provided the final crude product. Extraction of the residue with toluene (20 mL), followed by concentration of the extract to approximately half its volume and cooling to −10 °C, resulted in crystallization of pure **6a** (0.24 g, 0.36 mmol, 72% yield). Suitable crystals for X-ray diffraction analysis were obtained from a saturated toluene solution at −10 °C. ^{1}H NMR: δ 4.10 (s, 6H, TiO*Me*), 2.12 (m, 4H, CH$_2$C*H*$_2$), 2.06 (m, 8H, SiC*H*$_2$), 1.48 (s, 36H, ^{t}*Bu*N). ^{13}C{^{1}H} NMR: δ 68.30 (TiO*Me*), 64.27 (N*C*Me$_3$), 32.88 (NC*Me*$_3$), 26.78 (CH$_2$*C*H$_2$), 13.22 (Si*C*H$_2$). Anal. Calcd for $C_{24}H_{54}N_4O_2Si_2Cl_2Ti_2$: C, 44.16; H, 8.34; N, 8.59. Found: C, 44.02; H, 8.37; N, 8.62.

6b. A procedure analogous to the preparation of **6a** was used, but starting from **5b** (0.32 g, 1.0 mmol) in toluene. Thus, **6b** was crystallized from toluene at −10 °C. Yield: 0.23 g (0.34 mmol, 67%). ^{1}H NMR: δ 4.14 (s, 6H, TiO*Me*), 1.84 (m, 8H, CH$_2$C*H*$_2$), 1.41 (s, 36H, ^{t}*Bu*N), 1.01 (m, 8H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: δ 62.69 (TiO*Me*), 60.59 (N*C*Me$_3$), 34.29 (NC*Me*$_3$), 25.95 (CH$_2$*C*H$_2$), 12.98 (Si*C*H$_2$). Anal. Calcd for $C_{26}H_{58}N_4O_2Si_2Cl_2Ti_2$: C, 45.87; H, 8.59; N, 8.23. Found: C, 46.03; H, 8.62; N, 8.25.

6c. A procedure analogous to the preparation of **6a** was used, but starting from **5c** (0.34 g, 1.0 mmol) in toluene. Thus, **6c** was crystallized from toluene at −10 °C. Yield: 0.25 g (0.35 mmol, 70%). ^{1}H NMR: δ 4.18 (s, 6H, TiO*Me*), 1.98 (m, 8H, CH$_2$C*H*$_2$), 1.65 (m, 4H, CH$_2$CH$_2$C*H*$_2$), 1.21 (s, 36H, ^{t}*Bu*N), 0.64 (m, 8H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: δ 66.54 (TiO*Me*), 65.39 (N*C*Me$_3$), 33.97 (NC*Me*$_3$), 30.74 (CH$_2$*C*H$_2$), 25.62 (CH$_2$CH$_2$*C*H$_2$), 17.83 (Si*C*H$_2$). Anal. Calcd for $C_{26}H_{62}N_4O_2Si_2Cl_2Ti_2$: C, 47.44; H, 8.82; N, 7.91. Found: C, 47.30; H, 8.85; N, 7.94.

6d. A procedure analogous to the preparation of **6a** was used, but starting from **5d** (0.32 g, 1.0 mmol) in toluene. Thus, **6d** was crystallized from toluene at −10 °C. Yield: 0.26 g (0.38 mmol, 76%). ^{1}H NMR: δ 5.59 (s, 4H, C═C*H*), 3.89 (s, 6H, TiO*Me*), 1.47 (m, 8H, SiC*H*$_2$), 1.24 (s, 36H, ^{t}*Bu*N). ^{13}C{^{1}H} NMR: δ 130.70 (C═*C*H), 57.32 (TiO*Me*), 49.81 (N*C*Me$_3$), 33.78 (NC*Me*$_3$), 19.94 (Si*C*H$_2$). Anal. Calcd for $C_{26}H_{54}N_4O_2Si_2Cl_2Ti_2$: C, 46.14; H, 8.05; N, 8.28. Found: C, 46.30; H, 8.03; N, 8.30.

Preparation of the Dimeric Silacyclobutyloxo-Bridged Titanium Complex 7a. A stirred solution of **2a** (0.33 g, 1.0 mmol) in 20 mL of toluene at −78 °C was treated with predried O$_2$ (1 atm) by bubbling the gas through it for 3 h. The reaction of **2a** proceeded similarly, with the exception that the reaction required ca. 3 h to go to completion and was accompanied by decomposition. The solvent was removed in vacuo and the resulting solid crystallized from toluene to give 0.035 g (0.05 mmol) of yellow microcrystals (10% yield). Suitable crystals for X-ray diffraction analysis were obtained from a toluene solution of compound **7a** in the presence of traces of O$_2$ at −10 °C. ^{1}H NMR: δ 2.14 (m, 4H, CH$_2$C*H*$_2$), 1.65 (s, 18H, *Bu*^{t}N), 1.54 (s, 18H, ^{t}*Bu*N), 1.27 (m, 4H, SiC*H*$_2$), 0.99 (m, 4H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: δ 71.78 (N*C*Me$_3$), 66.57 (N*C*Me$_3$), 33.42 (NC*Me*$_3$), 28.74 (NC*Me*$_3$), 26.98 (CH$_2$*C*H$_2$), 14.84 (Si*C*H$_2$), 12.95 (Si*C*H$_2$). Anal. Calcd for $C_{22}H_{48}N_4O_2Si_2Cl_4Ti_2$: C, 38.05; H, 6.97; N, 8.07. Found: C, 37.90; H, 6.88; N, 7.95.

Preparation of the Spirobis(siladiazatitanacyclobutane) Complexes [(cycl)Si(^{t}BuN)$_2$]$_2$Ti (8). A representative procedure is as follows: to a solution of **1a** (2.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added 2.6 mL of *n*-BuLi (1.6 M in hexanes). The reaction mixture was warmed to room temperature and stirred for 2 h, whereupon it was transferred, via cannula, to a suspension of 0.5 equiv of titanium tetrachloride in 20 mL of Et$_2$O that was cooled to −78 °C. The resultant red mixture was warmed to room temperature and stirred for 2 h. Removal of the volatiles provided the final crude product, which was further crystallized from pentane at −45 °C to provide pure [(CH$_2$)$_3$Si(NBu^t)$_2$]$_2$Ti (**8a**) as a red solid. Yield: 0.35 g (0.74 mmol, 74%). ^{1}H NMR: δ 1.92 (m, 4H, CH$_2$C*H*$_2$), 1.48 (s, 36H, *Bu*^{t}N), 1.21 (m, 8H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: δ 66.59 (N*C*Me$_3$), 33.72 (NC*Me*$_3$), 26.47 (CH$_2$*C*H$_2$), 12.50 (SiCH$_2$). Anal. Calcd for $C_{22}H_{48}N_4Si_2Ti$: C, 55.90; H, 10.24; N, 11.86. Found: C, 55.73; H, 10.28; N, 11.83.

8b. Red crystals (0.38 g, 0.76 mmol, 76%) were obtained by recrystallization (−40 to −45 °C, pentane). ^{1}H NMR: δ 1.78 (m, 8H, CH$_2$C*H*$_2$), 1.51 (s, 36H, *Bu*^{t}N), 0.77 (m, 8H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: δ 66.03 (N*C*Me$_3$), 32.59 (NC*Me*$_3$), 25.07 (CH$_2$*C*H$_2$), 12.37 (Si*C*H$_2$). Anal. Calcd for $C_{24}H_{52}N_4Si_2Ti$: C, 57.56; H, 10.47; N, 11.20. Found: C, 57.35; H, 10.44; N, 12.24.

8c. Red crystals (0.43 g, 0.81 mmol, 81%) were obtained by recrystallization (−40 to −45 °C, pentane). ^{1}H NMR: δ 1.66 (m, 8H, CH$_2$C*H*$_2$), 1.38 (m, 4H, CH$_2$CH$_2$C*H*$_2$), 1.19 (s, 36H, N*Bu*^{t}), 0.62 (m, 8H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: δ 64.84 (N*C*Me$_3$), 33.27 (NC*Me*$_3$), 29.30 (CH$_2$*C*H$_2$), 25.48 (CH$_2$CH$_2$*C*H$_2$), 17.65 (Si*C*H$_2$). Anal. Calcd for $C_{26}H_{56}N_4Si_2Ti$: C, 59.05; H, 10.68; N, 10.60. Found: C, 58.84; H, 10.72; N, 10.56.

8d: Red crystals (0.37 g, 0.74 mmol, 74%) were obtained by recrystallization (−40 to −45 °C, pentane). ^{1}H NMR: *δ* 5.09 (s, 4H, C═C*H*), 1.38 (m, 8H, SiC*H*$_2$), 1.49 (s, 36H, *Bu*^{t}N). ^{13}C{^{1}H} NMR: *δ* 130.59 (C═*C*H), 66.27 (N*C*Me$_3$), 33.12 (NC*Me*$_3$), 16.59 (Si*C*H$_2$). Anal. Calcd for $C_{24}H_{48}N_4Si_2Ti$: C, 58.03; H, 9.75; N, 11.29. Found: C, 58.20; H, 9.73; N, 11.25.

Preparation of 8 from Amine Elimination of Ti(NMe$_2$)$_4$ with Diamido Ligand 1. A representative procedure is as follows: complex **1a** (2.0 mmol) in toluene (10 mL) was added to Ti(NMe$_2$)$_4$ (0.41 g, 1.0 mmol) in toluene (10 mL) at room temperature. The reaction mixture was heated to reflux temperature and stirred for 12 h. The resulting red solution was dried under vacuum to afford a yellow solid. The solid was extracted with pentane, and the filtrate was concentrated and cooled to −40 to −45 °C. Red solid **8a** was isolated by filtration, washing with cold pentane, and drying in vacuo. **8a**: red powder; yield 0.17 g (0.36 mmol, 36%). **8b**: red powder; yield 0.21 g (0.42 mmol, 42%). **8c**: red powder; yield 0.23 g (0.43 mmol, 43%). **8d**: red powder; yield 0.19 g (0.38 mmol, 38%).

Preparation of the Dibenzyldiamido Ti(IV) Complexes (cycl)Si(NBu^t)$_2$Ti(C$_6$H$_5$CH$_2$)$_2$ (9). A representative procedure is as follows: to a solution of **2a** (1.0 mmol) in 20 mL of diethyl ether, precooled to −78 °C, was added $C_6H_5CH_2MgBr$ (3.0 M in ether, 0.80 mL, 2.4 mmol). The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting red solution was dried under vacuum to afford a red oil. The oil was extracted with pentane, and the filterate was concentrated and cooled to −40 to −45 °C. Red solid **9a** was isolated by filtration, washing with cold pentane, and drying in vacuo.

9a: red powder; yield 0.37 g (0.84 mmol, 84%). ^{1}H NMR: *δ* 7.31, 7.29, 7.23 (m, 10H, *Ph*), 2.23 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 10 Hz), 2.08 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 10 Hz), 1.89 (m, 2H, CH$_2$C*H*$_2$), 1.33 (s, 18H, *Bu*^{t}N), 1.11 (m, 4H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: *δ* 141.94, 128.85, 128.12 (*Ph*), 68.92 (Ti*C*H$_2$), 60.44 (N*C*Me$_3$), 34.15 (NC*Me*$_3$), 26.57 (CH$_2$*C*H$_2$), 13.43 (Si*C*H$_2$). Anal. Calcd for $C_{25}H_{38}N_2SiTi$: C, 67.84; H, 8.66; N, 6.33. Found: C, 68.09; H, 8.68; N, 6.31.

9b: red powder; yield 0.40 g (0.88 mmol, 88%). ^{1}H NMR: *δ* 7.38, 7.28, 7.20 (m, 10H, *Ph*), 2.25 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 11 Hz), 2.10 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 11 Hz), 1.77 (m, 4H, CH$_2$C*H*$_2$), 1.27 (s, 18H, *Bu*^{t}N), 0.77 (m, 4H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: *δ* 143.41, 129.08, 128.52 (*Ph*), 68.76 (Ti*C*H$_2$), 60.24 (N*C*Me$_3$), 35.50 (NC*Me*$_3$), 24.96 (CH$_2$*C*H$_2$), 13.07 (Si*C*H$_2$). Anal. Calcd for $C_{26}H_{40}N_2SiTi$: C, 68.38; H, 8.84; N, 6.14. Found: C, 68.61; H, 8.82; N, 6.12.

9c: red powder; yield 0.41 g (0.87 mmol, 87%). ^{1}H NMR: *δ* 7.28, 7.10, 6.84 (m, 10H, *Ph*), 2.23 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 10 Hz), 2.09 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 10 Hz), 1.89 (m, 4H, CH$_2$C*H*$_2$), 1.52 (m, 2H, CH$_2$CH$_2$C*H*$_2$), 1.37 (s, 18H, *Bu*^{t}N), 0.89 (m, 4H, SiC*H*$_2$). ^{13}C{^{1}H} NMR: *δ* 146.18, 128.02, 126.30 (*Ph*), 69.97 (Ti*C*H$_2$), 59.98 (N*C*Me$_3$), 33.81 (NC*Me*$_3$), 29.17 (CH$_2$*C*H$_2$), 26.04 (CH$_2$CH$_2$*C*H$_2$), 18.22 (Si*C*H$_2$). Anal. Calcd for $C_{27}H_{42}N_2SiTi$: C, 68.90; H, 9.00; N, 5.96. Found: C, 68.65; H, 8.97; N, 5.98.

9d: red powder; yield 0.37 g (0.81 mmol, 81%). ^{1}H NMR: *δ* 7.34, 7.27, 7.21 (m, 10H, *Ph*), 6.09 (s, 2H, C═C*H*), 2.25 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 11 Hz), 2.12 (d, 2H, TiC*H*$_2$, $^2J_{HH}$ = 11 Hz), 1.49 (m, 4H, SiC*H*$_2$), 1.26 (s, 18H, *Bu*^{t}N). ^{13}C{^{1}H} NMR: *δ* 141.95, 128.77, 128.10 (*Ph*), 132.33 (C═*C*H$_2$), 70.02 (Ti*C*H$_2$), 59.19 (N*C*Me$_3$), 35.34 (NC*Me*$_3$), 17.47 (Si*C*H$_2$). Anal. Calcd for $C_{26}H_{38}N_2SiTi$: C, 68.69; H, 8.43; N, 6.17. Found: C, 68.88; H, 8.46; N, 6.19.

Preparation of 9 from Toluene Elimination of Ti(CH$_2$C$_6$H$_5$)$_4$ with Diamido Ligand 1. A representative procedure is as follows: complex **1a** (1.0 mmol) in toluene (10 mL) was added to Ti(CH$_2$C$_6$H$_5$)$_4$ (0.23 mL, 1.0 mmol) in toluene (10 mL) at room temperature. The reaction mixture was heated to 40 °C and stirred for 12 h. The resulting red solution was dried under vacuum to afford a red solid. The solid was extracted with pentane, and the filtrate was concentrated and cooled to −40 to −45 °C. Red solid **9a** was isolated by filtration, washing with cold pentane, and drying in vacuo. **9a**: red powder; yield 0.39 g (0.88 mmol, 88%). **9b**: red powder; yield 0.34 g (0.74 mmol, 74%). **9c**: red powder; yield 0.42 g (0.89 mmol, 89%). **9d**: red powder; yield 0.37 g (0.81 mmol, 81%).

Crystal Structure Determination. Crystals of **4a**−**d**, **6a**, and **7a** were obtained from toluene, sealed in glass capillaries under argon, and mounted on the diffractometer. Data were collected and corrected for Lorentz and polarization effects. Each structure was solved by the application of direct methods using the SHELXS-96 program[20a] and least-squares refinement using SHELXL-97.[20b] After anisotropic refinement of all non-H atoms, several H atom positions could be located in difference Fourier maps. These were refined isotropically, while the remaining H atoms were calculated in idealized positions and included in the refinement with fixed atomic contributions. Further detailed information is listed in Table 1.

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Supporting Information Available: Tables of crystallographic data (excluding structure factors) for the structures **4a**−**d**, **6a**, and **7a** reported in this paper; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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