

Facile Generation of Bimetallic Titanium Alkoxides with Silacycloalkyl- or Silacycloalkenyldiamide Ligands: Oxo-Insertion Involving Dimerization or Rearrangement

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Summary: The reaction between the spiro-siladiazatitanacyclobutane complexes (cyclo)Si(NBu^t)₂TiMe₂ (**1**) and (cyclo)Si(NBu^t)₂TiMeCl (**3a**) and dioxygen proceeds by insertion of an oxygen molecule into a Ti–C bond of **1** and **3a**, yielding methoxy-bridged titanium dimer [(cyclo)Si(NBu^t)₂Ti(μ-O)Me]₂ (**2**) or [(cyclo)Si(NBu^t)₂Ti(μ-O)Cl]₂ (**4a**), respectively. In contrast, the reaction of the titanium(IV) dichloride complex (cyclo)Si(NBu^t)₂TiCl₂ (**5a**) with O₂ gives hydrazido complex [(NBu^tNBu^t)-(cyclo)SiO]₂TiCl₂ (**6a**) as a result of facile formation of the Si–O–Ti bonds upon autoxidation.

Bidentate diamide ligands with silyl substituents¹ are of considerable interest as ligands in the coordination chemistry of main group elements² and transition metals.³ Such a complex is also attractive as an “open” chelating diamide ligand for the synthesis of olefin polymerization precatalysts.⁴ As an extension of our ongoing investigations of the chemical behavior of the metal complexes based on these diamide ligand systems,⁵ we have prepared the spiro-siladiazatitanacyclobutane complexes (cyclo)Si(NBu^t)₂TiMe₂ (**1**), in which amide groups are linked by a silacycloalkane or -alkene bridge. Thus, we report here the preparation of **1** containing rather bulky substituents on the silylene bridge which would kinetically stabilize the four-membered spiro-siladiazatitanacycle sufficiently to allow detailed investigation of the chemical behavior and the structures of this system. Despite the recent interest in the insertion of dioxygen into main group^{6,7} as well as transition metal alkyls,⁸ the reaction of O₂ with an “M–R” bond(s) of the group 4 metal amide complexes has not been reported. The greater stability of **1** has prompted us to investigate the formation of the titanium

alkoxide compound. Here we describe the generation of the novel [(cyclo)Si(NBu^t)₂Ti(μ-O)Me]₂ (**2**) by the preferential O₂ insertion reaction of a Ti–Me bond. The outcome of X-ray structural studies has provided an opportunity to evaluate the effect of the interannular bridge on the molecular geometry of these modified siladiazatitanacyclobutane complexes.

The most interesting property of **1** is its reaction with oxygen and transformation to **2**. Compound **2** was initially isolated in the synthesis of **1** as a minor orange product.⁵ No sources of methanol were available in the original synthesis of **1**; therefore, we postulate that the methoxy group was produced by the reaction of the methyl ligand with a trace amount of oxygen present in the reaction medium; thus **1** may be the direct precursor to **2**. In fact, we have found that reactions of **1** with O₂ always proceed in nearly quantitative yields as determined by ¹H NMR spectroscopy.⁹ These high yields are presumably due to the inertness of the formed dimeric titanium(IV) products, such as **2**, toward further oxidation by O₂. Thus, on a practical scale, as reaction 1 reveals, a variety of **2** derivatives can now be conveniently prepared by adding O₂ to a precooled (–78 °C) toluene solution of **1**, warming the reaction mixture to

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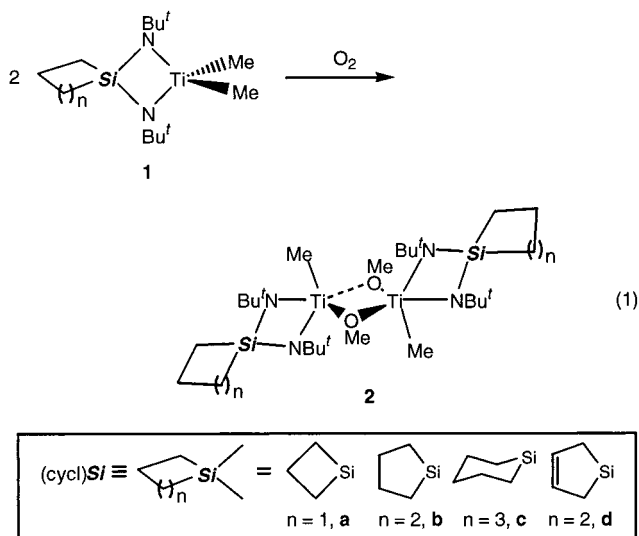
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25 °C, and then isolating the product by recrystallization at -10 °C. The molecular structure of **2a** is shown in Figure 1.¹⁰ The complex **2a** exists as a dimer connected through two methoxy bridges in the solid state, and the two molecular units comprising the dimer are each constrained by the crystallographic center of inversion. The distances between bridging alkoxides and titanium, Ti(1)–O(1) and Ti(1)–O(1*), are 2.030(2) and 2.058(2) Å, respectively, within the normal range for a Ti₂O₂ core.¹¹ The Ti(1)–C(1) distance is not exceptional, having a value of 2.126(4) Å. The Ti₂O₂ core is undoubtedly coplanar due to its symmetry, with the interatomic angles being O(1)–Ti(1)–O(1*) = 72.6(1)° and Ti(1)–O(1)–Ti(1*) = 107.4(1)°. The geometry about each titanium atom can be described as distorted square pyramidal, in which the C(1) atom and the remaining four atoms (N(1), N(2), O(1), O(1*)) are in axial and basal positions, respectively. The Ti–N bond lengths (1.893 Å (average)) are relatively short, indicating significant N→Ti π -donation character to the bonding. Consequently, each nitrogen atom is in an sp²-hybridized environment, as indicated by the sum of the angles around the nitrogens. Complete bis-oxygenation of the Ti–Me bonds has not occurred in **2**, but rather **1** has undergone a single oxo-insertion and has oxygen atoms inserted into one Ti–Me bond. In this way, the monoalkoxytitanium produced is perfect for provision of additional coordination to the other titanium center of the monoalkoxytitanium intermediate, raising each such center to a coordination number of five. Similar

(9) **2**: A solution containing **1a** (0.290 g, 1.0 mmol) in toluene, generated in situ, was stirred under O₂ (1 atm) for 1 h; conversion into **2a**, as monitored by ¹H NMR spectroscopy, was quantitative. The solution was filtered, volatiles were removed, and the resulting solid was recrystallized from toluene at -10 °C to give 0.251 g of yellow crystals (0.41 mmol, 82% yield). ¹H NMR: δ –0.008 (s, 6H, TiMe), 1.444 (s, 36H, NBu^t), 1.987 (m, 8H, SiCH₂), 1.994 (m, 4H, CH₂CH₂), 3.748 (s, 6H, TiOMe). ¹³C{¹H} NMR: δ 12.730 (SiCH₂), 26.770 (CH₂CH₂), 33.201 (TiMe), 34.041 (NCMe₃), 60.751 (NCMe₃), 63.013 (TiOMe). Anal. Found for C₂₆H₆₀N₄O₂Si₂Ti₂: C, 50.83; H, 9.69; N, 9.04. Calcd: C, 50.97; H, 9.87; N, 9.14. **2b**, **2c**, and **2d** were synthesized analogously to **2a**.

(10) Crystal structure analysis: diffractometer: CAD-4. **2a**: Triclinic, *P*1, *a* = 8.9319(5) Å, *b* = 10.0666(5) Å, *c* = 10.5719(7) Å, α = 90.046(5)°, β = 113.521(4)°, γ = 94.306(5)°. *V* = 868.63(9) Å³, *Z* = 2, 3384 observed reflections, 171 parameters. *R*₁ = 0.0376, *wR*₂ = 0.0931 (*I* > 2 σ); *R*₁ = 0.0940, *wR*₂ = 0.1280 (all data). **6a**: Monoclinic, *P*2₁/*n*, *a* = 9.3229(9), *b* = 13.1281(7), *c* = 13.8955(5) Å, β = 95.917(5)°, *V* = 1691.6(2) Å³, *Z* = 4, 3312 observed reflections, 169 parameters. *R*₁ = 0.0415, *wR*₂ = 0.1138 (*I* > 2 σ); *R*₁ = 0.0944, *wR*₂ = 0.1410 (all data).

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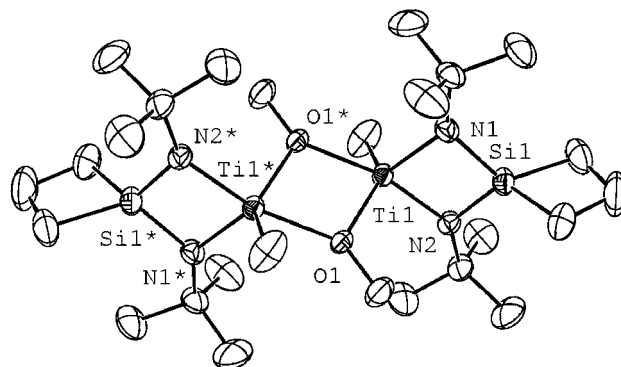


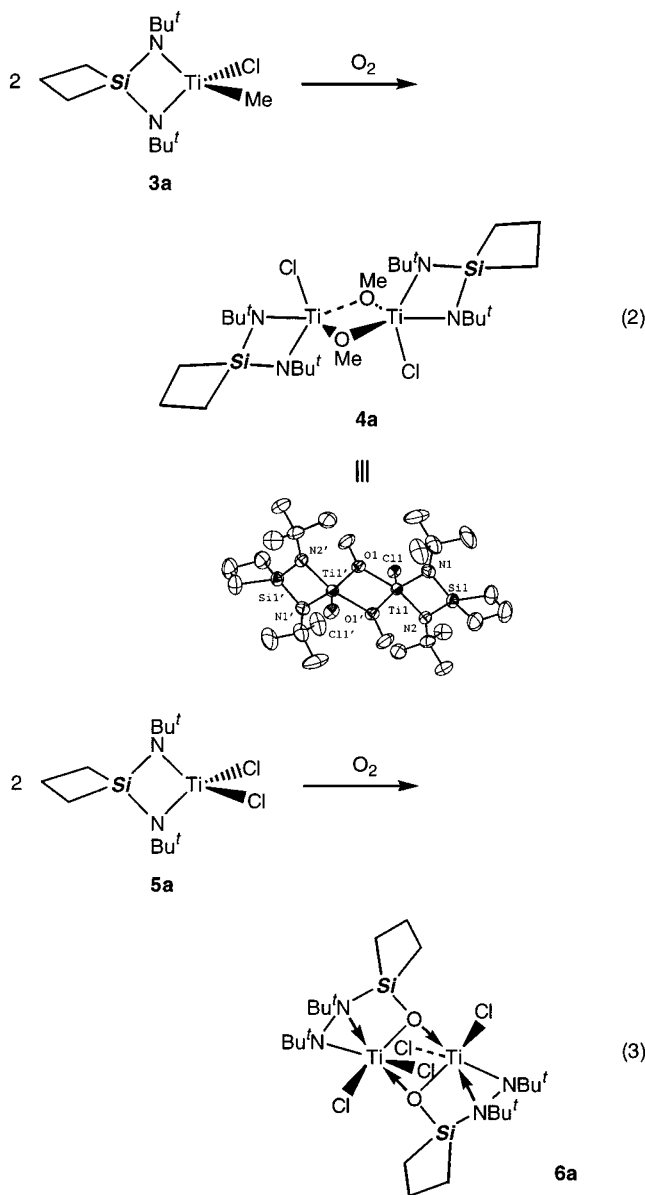
Figure 1. Molecular structure of **2a** with atom labeling. Ellipsoids are shown at 30% probability levels, the unlabeled atoms are carbon atoms, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti(1)–N(2) 1.879(3), Ti(1)–N(1) 1.906(3), Ti(1)–O(1) 2.030(2), Ti(1)–O(1*) 2.058(2), Ti(1)–C(12) 2.126(4), Ti(1)–Ti(1*) 3.295(1), Si(1)–N(2) 1.737(3), Si(1)–N(1) 1.740(3), O(1)–Ti(1)–O(1*) 72.6(1), Ti(1)–O(1)–Ti(1*) 107.4(1), N(2)–Ti(1)–N(1) 82.9(1), C(4)–N(1)–Si(1) 128.4(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) 92.8(1), N(2)–Si(1)–N(1) 92.2(1).

oxidation of the methyl functionality into the methoxy group has been observed in Wolczanski's work^{8b,c} on the transformation of (tritox)₂MMe₂ (M = Ti, Zr, Hf) to (tritox)₂MMe_{3–*n*}(OMe)_{*n*} (*n* = 1, 2, 3). The bulky alkoxy ancillary ligand with a cone angle of 125°, tri-*tert*-butylmethoxide ((Me₃C)₃CO[–], tritox), no doubt contributes to the overall stability of the resultant metal alkoxides.

Further, noting that the reaction of **1** with O₂ was extremely rapid even at -78 °C, we prepared the less electrophilic Ti(IV) reagent, (cyclo)Si(NBu^t)₂Ti(Me)Cl (**3a**), and have now found by ¹H NMR that the reaction of this compound with O₂ proceeded smoothly at 25 °C to provide the desired methoxy-bridged titanium dimer, [(cyclo)Si(NBu^t)₂Ti(*μ*-OMe)Cl]₂ (**4a**), as the sole product. Elemental analyses and ¹H/¹³C NMR spectra of **4a** are consistent with the retention of the 1:1 ratio of (cyclo)Si(NBu^t)₂:OMe ligands and the uptake of 0.5 equiv of O₂ per (cyclo)Si(NBu^t)₂ unit. The solid-state structure of **4a** has been determined by X-ray crystallography and is shown to be isostructural with the methyl analogue **2** (reaction 2).

A key question that we wished to answer next was whether this oxo-insertion could be extended to the reaction of nonalkylated titanium complexes. To prove this, we first utilized the known titanium(IV) dichloride (cyclo)Si(NBu^t)₂TiCl₂⁵ and gratifyingly found that a 28% isolated yield of **6a** could be obtained at room temperature by reacting a toluene solution of **5a** with O₂.

Suitable crystals for X-ray diffraction analysis were obtained from a toluene solution of compound **5a** in the presence of traces of O₂ at -20 °C. X-ray crystallography shows that, rather than being a simple oxo-containing compound, **6a** is, in fact, a dimer of the formulation [(NBu^tNBu^t)(cyclo)SiO}TiCl₂]₂ (Figure 2) with extensive rearrangement. The structure of **6a** shows a dimeric feature that contains a ladder composed of three edge-fused rings with a Ti₂O₂ core. Supplementary to this core, the two hydrazido residues are bound side-on with



four chlorides, giving rise to six-coordinate metal centers. The molecular dimensions of the hydrazido complex **6a** are almost identical to those found in $\text{CpTiCl}_2(\text{NR}^1\text{NR}^2\text{R}^3)$ ($\text{R}^1, \text{R}^2, \text{R}^3 = \text{Me}$;¹² $\text{R}^1, \text{R}^2 = \text{Me}, \text{R}^3 = \text{SiMe}_3$;¹² $\text{R}^1 = \text{Ph}, \text{R}^2, \text{R}^3 = \text{H}$;¹³ $\text{R}^1 = \text{H}, \text{R}^2, \text{R}^3 = \text{Me}$ ¹³). Thus, the Ti–N(2) separation (1.834 (3) Å) is consistent with considerable Ti–N double bonding, the N–N separation is on the order of that in hydrazine itself,¹⁴ and the Ti–N(1) bond distance of 2.233(3) Å is typical of that found in N→Ti dative bonding. We had surmised that the oxophilicity of both Ti and Si atoms could have been the driving force both for the rearrangement observed in the formation of **6a** and for the side-on

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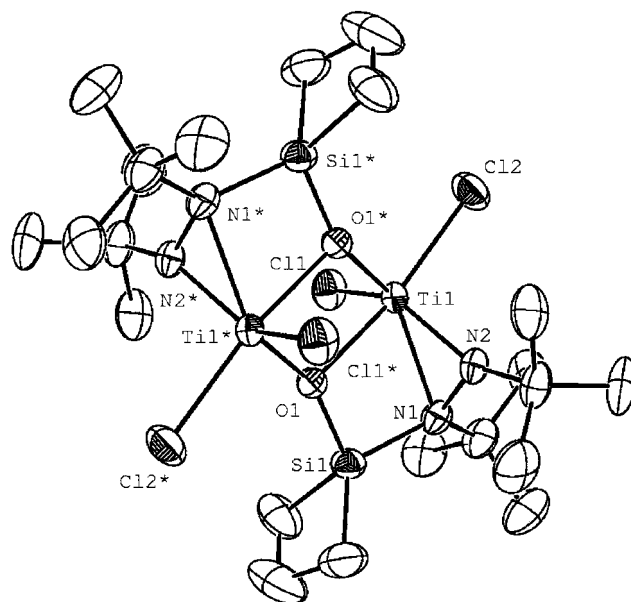


Figure 2. Molecular structure of **6a** with atom labeling. Ellipsoids are shown at 30% probability levels, the unlabeled atoms are carbon atoms, and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ti(1)–N(2) 1.834(3), Ti(1)–O(1*) 1.932(2), Ti(1)–O(1) 2.153(2), Ti(1)–N(1) 2.233(3), Ti(1)–Cl(2) 2.291(1), Ti(1)–Cl(1) 2.298(1), Si(1)–O(1) 1.635(2), Si(1)–N(1) 1.795(3), N(1)–N(2) 1.437(4), O(1*)–Ti(1)–O(1) 73.2(1), Ti(1*)–O(1)–Ti(1) 106.8(1), N(2)–Ti(1)–N(1) 39.88(12), O(1)–Ti(1)–N(1) 70.3(1).

hydrazide bonding. Although it is not unexpected that the oxo-insertion causes a significant structural change because the resulting siloxy group has a strong tendency to become a bridging ligand, structural evidence for this type of rearrangement, especially that induced by oxidation with oxygen, has not been observed in organotitanium amide complexes.

The complex can be obtained repeatedly, albeit so far in low yields, from exposure of a preformed solution of **5a** to O_2 . Although the precise mechanism by which **6a** is formed is not yet understood, the observations noted above suggest that either oxo-insertion is templated or the conversion of **5a** to **6a** requires that the processes of ladder formation and oxo-insertion occur concurrently. Attempts to determine the precise structural nature of **6a**, and thus to better understand the reasons for the preferential oxo-insertion, are ongoing.

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Supporting Information Available: Spectroscopic data and crystallographic data (excluding structure factors) for the structures (**2a**, **4a**, and **6a**) reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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