Inorg. Chem. **2009**, *48*, 3073−3079

Inorganic Chemistry
Article

Synthesis and Characterization of Siloxy, Aminoxy, and Oxo Complexes from the Reaction of a Tantalum Amide Silyl Complex with Oxygen

He Qiu,[†] Shu-Jian Chen,[†] Chang-Sheng Wang,[‡,§] Yun-Dong Wu,[‡] Ilia A. Guzei,[‖] Xue-Tai Chen,[⊥] and Zi-Ling Xue*[,†]

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China, Department of Chemistry, Liaoning Normal University, Dalian 116029, China, Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706-1396, and State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Received December 13, 2008

$(Me_2N)_4Ta{-}SiBu^tPh_2$ (**1**) reacts with O_2 to give $(Me_2N)_4Ta(OSiBu^tPh_2)$ (**2**), $(Me_2N)_3Ta(ONMe_2)(OSiBu^tPh_2)$ (**3**), and the unusual μ-oxo amino $(Me_2N)_2(Ph_2Bu^tSiO)_2(\mu,\eta^2\text{-}Me_2NCH_2NMe)_2Ta_2(\mu\text{-}O)_2$ (**4**) containing two bridging chelating (aminomethyl)amides -$N(Me)CH_2NMe_2$. The dimer **4** was characterized by X-ray crystallography. **2** also reacts with O_2 to give both **3** and **4**. Reaction pathways in the formation of these complexes are discussed. In reactions of O_2 with d^0 **1** and **2**, oxidation of the ligands is the prevailing pathway.

Introduction

Reactions of O_2 with transition-metal complexes have been widely studied in fundamental biological processes and the design of oxidation catalysts. Most studies of these reactions involve d^n complexes.[1−3] The presence of the valence d electrons in the metal centers often leads to the oxidation of the metals by O_2, and this oxidation is believed to be a driving force of the reactions. There are fewer studies of the reactions of d^0 complexes with O_2. In these complexes, d^0 metal atoms at their highest oxidation states are unlikely to be oxidized.[4−14] In the reactions of O_2 with d^0 alkyl complexes, oxygen insertion into M−R bonds has been reported.[4−6] A similar insertion into a M−Si bond was observed in the reaction of $Cp_2Zr(SiMe_3)Cl$ with O_2.[7]

Reactions of d^0 transition-metal complexes with O_2 have recently become one of the most important processes in the preparation of metal oxide thin films as microelectronic gate insulator materials.[14−16] In the next generation of very large scale integrated (VLSI) transistor devices, the thickness of the gate insulator material needs to be less than 20 Å, and thin films of metal oxides with large dielectric constants are needed. Much research has been conducted to prepare oxides of early transition metals such tantalum, zirconium, and hafnium.[14−18]

We have recently investigated reactions of O_2 with d^0 amides $M(NMe_2)_4$ ($M = Zr, Hf$)[19] and $Ta(NMe_2)_5$[20] to provide an understanding of the reactions involving diradical O_2 and the pathway in the formation of metal oxides. Reactions of $M(NMe_2)_4$ ($M = Zr, Hf$) with O_2 are fast, yielding oxo aminoxo complexes $M_3(NMe_2)_6(\mu\text{-}NMe_2)_3(\mu_3\text{-}O)(\mu_3\text{-}ONMe_2)$ (Scheme 1) and $Me_2N\text{-}NMe_2$.[19] Reaction of $Ta(NMe_2)_5$ with O_2 is also fast, giving two aminoxy complexes $(Me_2N)_nTa(\eta^2\text{-}ONMe_2)_{5-n}$ ($n = 4, 3$), as well as $(Me_2N)_4Ta_2[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\mu\text{-}O)_2$ and $(Me_2N)_6Ta_3[\eta^2\text{-}N(Me)CH_2NMe_2]_2(\eta^2\text{-}ONMe_2)(\mu\text{-}O)_3$ containing novel chelating (aminomethyl)amide -$N(Me)CH_2NMe_2$ ligands (Scheme

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* To whom correspondence should be addressed. E-mail: xue@utk.edu.
[†] The University of Tennessee.
[‡] The Hong Kong University of Science and Technology.
[§] Liaoning Normal University.
[‖] The University of Wisconsin.
[⊥] Nanjing University.

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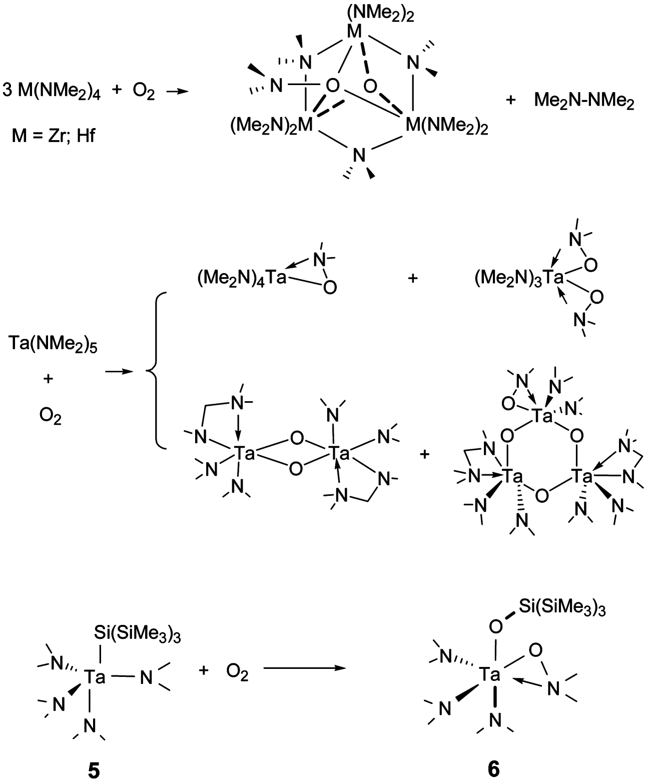
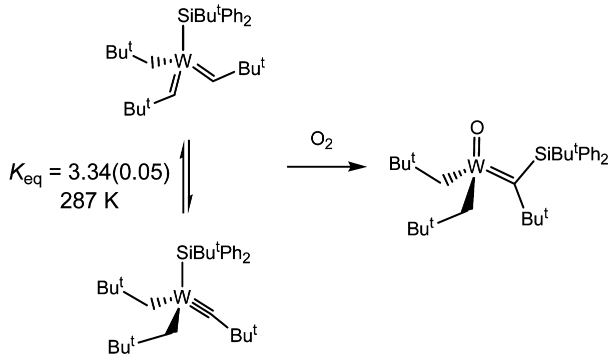
10.1021/ic802380u CCC: $40.75

Scheme 1. Reactions of $M(NMe_2)_n$ ($n = 4$, M = Zr, Hf; $n = 5$, M = Ta) and **5** with O_2[19−21]



1).[20] These studies followed our earlier work in the investigation of the reactions of silyl complexes with O_2.[21−25]

Scheme 2. Reactions of O_2 with an Equilibrium Mixture of d^0 Tungsten Silyl Alkylidyne and Silyl Bis-alkylidene Complexes[22,24k]



Silyl amide $(Me_2N)_4Ta{-}Si(SiMe_3)_3$ (**5**) reacts with O_2 to give O_2-stable $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)[OSi(SiMe_3)_3]$ (**6**, Scheme 1).[21] Oxygen insertion into the Ta−Si and one Ta−N bond occurs in the reaction. We have also found that the reaction of O_2 with a mixture of d^0 tungsten silyl alkylidyne and its bis-alkylidene tautomer gives $(Bu^tCH_2)_2W({=}O)[{=}CBu^t(SiBu^tPh_2)]$ where the silyl ligand has migrated to the alkylidyne ligand (Scheme 2).[22]

In the current studies, $(Me_2N)_4Ta{-}SiBu^tPh_2$ (**1**), an analogue of **5**, was treated with O_2. This reaction gives **2**, **3**, and the oxo amide **4** containing two chelating $\text{-}N(Me)CH_2NMe_2$ ligands (Scheme 3). **2** and **3** were also prepared from the reactions of $(Me_2N)_4TaCl$ (**7**) with $LiOSiBu^tPh_2$ (**8**) and $(Me_2N)_3TaCl_2$ (**9**) with **8** and $LiONMe_2$, respectively. The reaction between **2** and O_2 gives **3** and **4** as well. Possible reaction pathways giving **2**−**4** are discussed.

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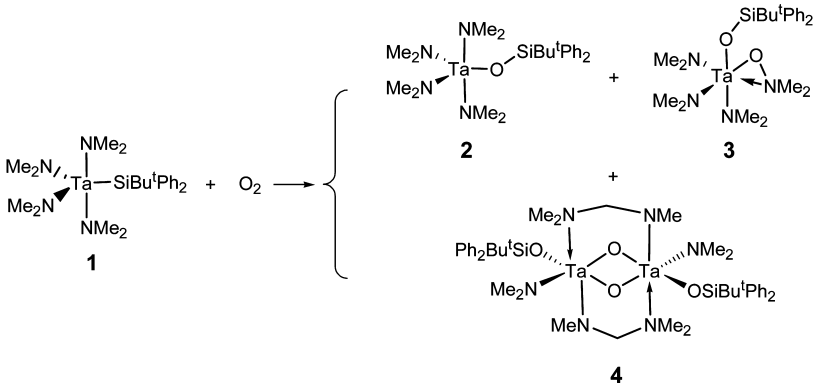
Scheme 3. Formation of **2**−**4** from the Reaction of **1** with O_2



Results and Discussion

Preparation of 2, 3, and 4 from the Reaction of 1 with O_2. d^0 amide silyl **1** was prepared earlier from the reaction of $(Me_2N)_4TaCl$ (**7**) with 1 equiv of $Li(THF)_2SiBu^tPh_2$ (**10**).[21] After **1** was extracted from the reaction mixture, it was directly used in the reaction with 1.5 equiv of O_2. The deep brown solution of **1** slowly turned to light yellow at −60 °C. A white precipitate was observed. After removal of the volatiles, extraction of the residue by CH_2Cl_2 followed by cooling gave colorless crystals of **4·CH₂Cl₂** (4% yield). The residue was also extracted by toluene to give crystals of **4·toluene** upon cooling which were used for elemental analysis. When the reaction mixture was analyzed by ^1H NMR, it was mostly **2**, **3**, and $HSiBu^tPh_2$. The presence of **4** was not clear. The solubility of **4** in non-polar solvents is low. The solubilities of both **2** and **3** are high. In fact, **2** is apparently a liquid at 23 °C, as discussed below.

When the reaction was conducted with less than 1 equiv of O_2, it was not possible to obtain **4** through crystallization. An excess of O_2 (1.5 equiv) is important for the preparation of **4**. **4** was also prepared from the reaction of **2** with O_2, as discussed below.

The reaction of **1** with about 0.9 equiv of O_2 was monitored by NMR. ^1H and ^{13}C NMR spectra of the mixture after 20 min showed it was a mixture of **2** (34% yield), **3** (5% yield), and unreacted **1** (16%). It is not clear if **4** was produced from this reaction involving excess **1**.

Characterization and Crystal Structure of 4. The ^1H NMR spectrum of **4** at 23 °C is consistent with the structural assignment. There is an inversion center in **4**. The two H atoms in the $-CH_2-$ group are diastereotopic, and the bridging η^2-$MeNCH_aH_bNMe_2$ ligand thus gives three methyl peaks and two doublets for H_a and H_b, respectively. These two doublets were found at 5.49 and 4.87 ppm in the ^1H NMR spectrum ($^2J_{H-H} = 9.8$ Hz, Supporting Information). The two methyl groups in $-NMe_2$ in the $-MeNCH_aH_bNMe_cMe_d$ ligand are inequivalent, thus giving three methyl resonances at 3.36 ($\mathit{Me}NCH_aH_bNMe_cMe_d$), 2.88 ($MeNCH_aH_bN\mathit{Me}_cMe_d$) and 2.78 ppm ($MeNCH_aH_bNMe_c\mathit{Me}_d$) in a 1:1:1 ratio for the ligand. The $Ta-NMe_2$ amide ligand apparently does not undergo a free rotation around the Ta−N bond. Thus, the two methyl groups in $Ta-NMe_2$ are not chemically equivalent, and they were observed at 3.75 (s, 6H, $Ta-N\mathit{Me}_eMe_f$) and 3.62 (s, 6H, $Ta-NMe_e\mathit{Me}_f$) ppm. A peak at 1.35 ppm was assigned to the butyl group of the siloxy Ph_2Bu^tSiO-ligand.

Crystals of **4** were obtained from both CH_2Cl_2 and toluene solutions. They were found to contain solvent molecules. **4·CH₂Cl₂** was characterized by single crystal X-ray diffraction. Molecular drawing, crystallographic data, selected bond distances and angles of **4·CH₂Cl₂** are given in Figure 1 and Tables 1 and 2, respectively. The dimeric **4** contains two bridging oxo ligands. Each Ta center is coordinated by six ligands in a pseudo octahedral geometry. The $-OSiBu^tPh_2$ and $-NMe_2$ ligands and the two bridging oxo atoms are in equatorial positions. The chelating $-MeNCH_2NMe_2$ ligands are in axial positions, where the -NMe- unit is bound to a Ta atom with a regular σ bond, and the NMe_2 group in the ligand forms a dative N→Ta bond through the lone pair electrons on the N atom. The Ta(1)−N(1) and Ta(1)−N(2) σ bond distances of 2.034(4)−2.016(3) Å are similar to those of $Ta-NMe_2$ bonds in **1** [1.979(10)−2.029(10) Å] and $(Me_2N)_3TaCl(SiBu^tPh_2)$ [1.926(11)-1.989(11) Å].[21] The dative Ta(1)−N(4) bond length of 2.509(3) Å is significantly

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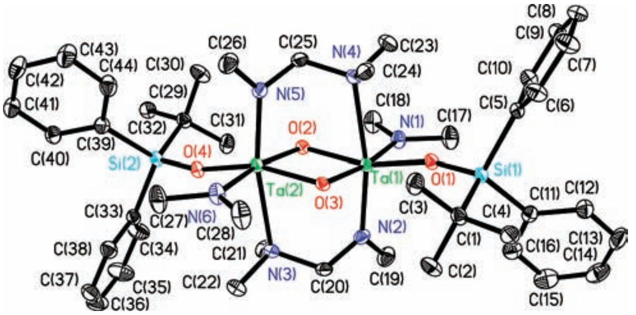


Figure 1. Molecular Structure of **4** in **4·CH$_2$Cl$_2$** Showing 30% Probability Thermal Ellipsoids.

Table 1. Crystal Data and Structure Refinement for **4·CH$_2$Cl$_2$**

empirical formula (fw)	$C_{46}H_{76}C_{l4}N_6O_4Si_2Ta_2$ (1337.01)
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 10.965(3)$ Å, $\alpha = 82.008(4)°$ $b = 14.209(3)$ Å, $\beta = 75.331(3)°$ $c = 18.356(4)$ Å, $\gamma = 89.577(3)°$
volume	2738.6(11) Å^3
Z	2
density (calculated)	1.621 Mg/m^3
absorption coefficient	4.276 mm^{-1}
F(000)	1336
crystal size	0.38 × 0.27 × 0.10 mm^3
theta range for data collection	1.16 to 26.38°
index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-22 \le l \le 22$
reflections collected	26802
independent reflections	10983 [*R*(int) = 0.0297]
completeness to theta = 25.00°	99.5%
absorption correction	semiempirical from equivalents
max. and min. transmission	0.6744 and 0.2933
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	10983/0/593
goodness-of-fit on F^2	0.969
final *R* indices [$I > 2\sigma(I)$]^a	R1 = 0.0280, wR2 = 0.0649
R indices (all data)^a	R1 = 0.0434, wR2 = 0.0723
largest diff. peak and hole	1.639 and −0.671 e Å^{-3}

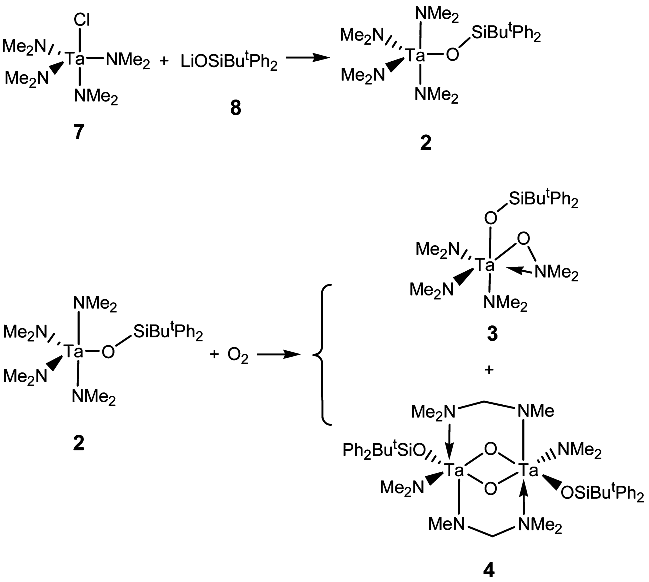
^{a} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) in **4·CH$_2$Cl$_2$**

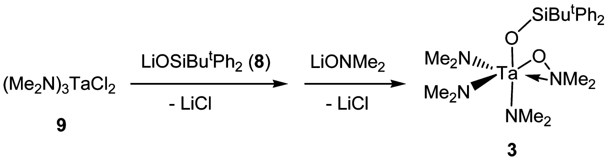
Ta(1)−O(2)	1.927(3)	Ta(1)−N(4)	2.509(3)
Ta(1)−O(1)	1.964(3)	N(2)−C(20)	1.453(5)
Ta(1)−N(2)	2.016(3)	Si(1)−O(1)	1.623(3)
Ta(1)−N(4)	2.509(3)	N(3)−C(20)	1.504(5)
Ta(1)−N(1)	2.034(4)	N(2)−C(19)	1.474(5)
N(3)−C(21)	1.482(5)	N(3)−C(22)	1.466(6)
Si(1)−C(1)	1.895(4)		
O(2)−Ta(1)−O(1)	160.98(11)	O(1)−Ta(1)−N(4)	83.04(11)
O(2)−Ta(1)−O(3)	80.90(11)	O(3)−Ta(1)−N(4)	81.73(11)
O(1)−Ta(1)−O(3)	95.06(11)	N(2)−Ta(1)−N(4)	166.63(13)
O(1)−Ta(1)−N(2)	102.81(12)	N(1)−Ta(1)−N(4)	92.80(13)
O(3)−Ta(1)−N(2)	85.75(13)	O(2)−Ta(1)−Ta(2)	41.03(8)
O(2)−Ta(1)−N(1)	90.24(13)	O(1)−Ta(1)−Ta(2)	132.30(8)
O(3)−Ta(1)−N(1)	170.38(12)	N(2)−Ta(1)−Ta(2)	90.59(10)
N(2)−Ta(1)−N(1)	98.93(15)	N(1)−Ta(1)−Ta(2)	131.17(10)
O(2)−Ta(1)−N(4)	77.99(11)	N(2)−C(20)−N(3)	113.3(3)
Si(1)−O(1)−Ta(1)	162.59(17)	Ta(1)−O(2)−Ta(2)	99.19(12)
O(2)−Ta(1)−O(3)	80.90(11)		

larger than the Ta−N dative bonds in **6** [2.254(9) Å][21] and [TaCl(μ-Cl)(NBu^t)(NHBu^t)(NH$_2$Bu^t)]$_2$ [2.23(3) Å].[26] It is not clear why the dative Ta(1)−N(4) bond is longer than other reported N→Ta bonds. The Ta−O bonds lengths [1.927(3)−1.964(3) Å] are close to those in other Ta complexes: Ta(CH$_2$SiMe$_3$)(O$_2$CNMe$_2$)$_4$ [1.932(5)−2.132(5) Å],[27a] [(Me$_2$N)$_2$(Me$_2$NH)TaCl$_2$]$_2$O [1.917(6)−1.928(6) Å][27b] and (Me$_2$N)$_3$Ta(η^2-ONMe$_2$)[OSi(SiMe$_3$)$_3$] [1.991(8) Å].[21] The Ta(1)−O(2)−Ta(2) angle of 99.19(12)° in the Ta(1)−O(2)−Ta(2)−O(3) four-member ring is much larger than the O(2)−Ta(1)−O(3) bond angle of 80.90(11)°.

Scheme 4. Direct Preparation of **2** and Its Reaction with O$_2$



Scheme 5. Preparation of **3** from the Reaction of **9** with **8** and LiONMe$_2$

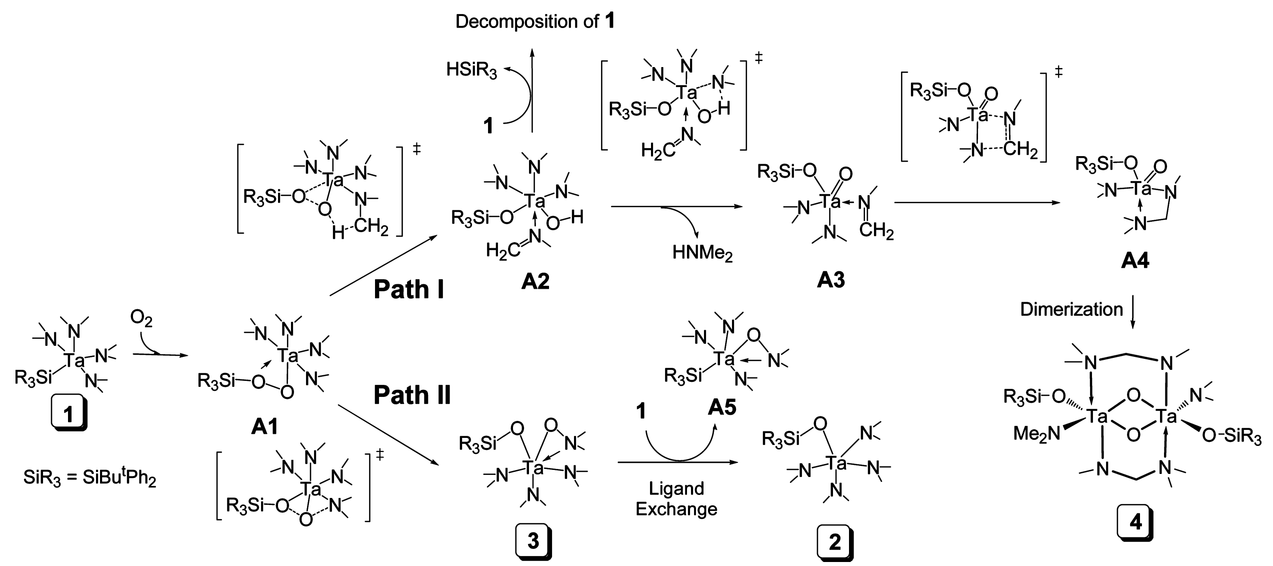


4 was found to be thermally unstable in solution at 23 °C, but stable in the solid state. Decomposition of **4** gave Me$_2$NCH$_2$NMe$_2$ and an unknown Ta species. The formation of Me$_2$NCH$_2$NMe$_2$ was confirmed by ^{1}H and ^{13}C NMR.[28] Me$_2$NCH$_2$NMe$_2$ is perhaps a product of a methyl exchange between MeHNCH$_2$NMe$_2$ and HNMe$_2$ that may have yielded H$_2$NMe as well.[28]

The chelating ligand -N(Me)CH$_2$NMe$_2$ forms one σ bond and one dative bond with a Ta atom. Such chelating ligand is rare. In the reaction of MCl$_5$ (M = Nb, Ta) with LiNMe$_2$, M(NMe$_2$)$_4$(η^2-MeNCH$_2$NMe$_2$) (M = Nb, Ta) containing this chelating ligand was isolated as a minor product.[28] In the reaction of d^0 Ta(NMe$_2$)$_5$ with O$_2$ (Scheme 1), this ligand was observed in two products (Me$_2$N)$_4$Ta$_2$[μ,η^2-N(Me)-CH$_2$NMe$_2$]$_2$(μ-O)$_2$ and (Me$_2$N)$_6$Ta$_3$[η^2-N(Me)CH$_2$NMe$_2$]$_2$(η^2-ONMe$_2$)(μ-O)$_3$.[20] Mechanistic considerations of the formation of the chelating -N(Me)CH$_2$NMe$_2$ ligand in **4** are discussed below.

Preparation of 2 from 7 and 8 and Its Characterization.[22b] **2** was also prepared by the reaction in Scheme 4 and characterized to confirm its formation in the reaction of **1** with O$_2$ and study its reactivities. This substitution reaction between **7** and **8** was found to be relatively slow, and requires overnight stirring at 23 °C to give an oil of **2** in 77% yield. When **2** was pure, it was a

Scheme 6. Proposed Pathways in the Reaction of **1** with O_2



liquid at 23 °C with a high solubility in non-polar solutions such as pentane and benzene.

The NMR spectra of **2** are consistent with the structural assignment. The ^1H NMR spectrum of **2** shows only one resonance for the four -NMe_2 ligands at 3.17 ppm and one signal for the Bu^t group of the siloxy ligand at 1.21 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows a single amide resonance at 46.0 ppm and the Bu^t resonances at 27.9 (CMe_3) and 20.0 (CMe_3) ppm. These observations suggest that amide ligands in **2** undergo a fast exchange.[21]

Once **2** is formed in the reaction of **1** with O_2, does it react with O_2 further to give **3** and **4**?

The reaction of **2** with O_2 gives **3** and **4** (Scheme 4). Not surprisingly no detectable amount of $HSiBu^tPh_2$ was in the reaction mixture. The yield of **3** (77%) is higher than that in the reaction of **1** with O_2. The yields of **4** in the two reactions are, however, similar. Attempts to isolate **3** from the reaction mixture were unsuccessful. Recrystallization yielded **4** as crystals. This is perhaps not surprising, as **3** was found to have high solubility in most organic solvents.

Preparation of 3 from 8, 9, and $LiONMe_2$ and Its Characterization. Reaction of $(Me_2N)_3TaCl_2$ (**9**) with **8** and $LiONMe_2$ also led to the formation of **3** (Scheme 5) which was purified for spectroscopic characterization and elemental analysis.

^1H and $^{13}C\{^1H\}$ NMR spectra of **3** suggest that the structure of **3** is similar to that of **6**.[21] Three resonances were observed in the ^1H NMR spectrum of **3**. The -NMe_2 resonance (3.28 ppm) and -$ONMe_2$ signal (2.36 ppm) are only slightly upfield-shifted from those in **6**. In the $^{13}C\{^1H\}$ NMR spectrum of **3**, the -NMe_2 and -$ONMe_2$ resonances at 47.1 and 49.6 ppm are close to those in $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)[OSi(SiMe_3)_3]$ (**6**). Both ^1H and ^{13}C resonances of the methyl groups in the -$OSiBu^tPh_2$ ligand in **3** are close to those in **2**.

Unlike **6**, **3** is not stable to O_2, and the reaction gives unknown species. One interpretation is that the -$OSiBu^tPh_2$ ligand in **3** is not as bulky as the -$OSi(SiMe_3)_3$ ligand in **6** and is thus not effective in protecting the metal center in **3** from O_2 attack.

Mechanistic Considerations of the Reaction between 1 and O_2. Our recent density-functional theory (DFT) studies of the reaction between $Ta(NMe_2)_5$ and O_2 show that O_2 inserts into a Ta−NMe_2 bond, forming $(Me_2N)_4$-Ta−O−O−NMe_2.[20] The α-O atom in this species either abstracts a hydride from a neighboring -$N(CH_3)_2$ ligand, yielding $(Me_2N)_2Ta(ONMe_2)(OH)(MeN{=}CH_2)$, or inserts into another Ta−NMe_2 bond to give $(Me_2N)_3Ta(O\text{-}NMe_2)_2$.[20] The imine ligand $MeN{=}CH_2$ in $(Me_2N)_2Ta(ONMe_2)$-$(OH)(MeN{=}CH_2)$ then inserts into a Ta−NMe_2 bond to give the chelating -$N(Me)CH_2NMe_2$ ligand that is also observed in **4** in the current studies. DFT calculations reveal exchanges between Ta−NMe_2 and Ta−$ONMe_2$ ligands, and such an exchange was observed in the following reaction: $Ta(NMe_2)_5 + (Me_2N)_3Ta(O\text{-}NMe_2)_2 \rightleftharpoons 2(Me_2N)_4TaO\text{-}NMe_2$.[20] $(Me_2N)_4Ta(SiBu^tPh_2)$ (**1**) and $(Me_2N)_4Ta{-}Si(SiMe_3)_3$ (**5**) are similar to $Ta(NMe_2)_5$ except that the former contain an anionic silyl ligand. The reactions of **1**, **5**,[21] and $Cp_2Zr(SiMe_3)Cl$[7] with O_2 yield products with O insertion into M−Si bonds. Given that silicon is known to be oxophilic, it is reasonable to assume that the initial step in the reaction of **1** with O_2 involves O_2 insertion into the Ta−Si bond, forming Ta peroxide species $(Me_2N)_4Ta(O{-}O{-}SiBu^tPh_2)$ (**A1**) in Scheme 6. **A1** then undergoes reactions as shown in the two pathways in Scheme 6. In Path I, the α-O atom in **A1** abstracts a hydride from a neighboring -$N(CH_3)_2$ ligand to give **A2** containing an OH and an imine $MeN{=}CH_2$ ligand. Two reactions subsequently occur: elimi-

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nation of $HNMe_2$ from **A2**, yielding **A3**, and an imine insertion into a $Ta-NMe_2$ bond to give **A4** containing the -N(Me)CH_2NMe_2 ligand. Dimerization of **A4** yields **4** containing two oxo and two -N(Me)CH_2NMe_2 bridging ligands (Figure 1). If the hydroxyl ligand in **A2** reacts with **1**, it may lead to the formation of $HSiBu^tPh_2$ (or $HNMe_2$) and decomposition of **1**.

In a parallel pathway in Scheme 6 (Path II), the α-O atom in Ta peroxide **A1** may insert into another $Ta-NMe_2$ bond, yielding **3**. An exchange between the aminoxide $Ta-O-NMe_2$ in **3** and the amide $Ta-NMe_2$ in **1** gives **2**. This exchange is similar to the exchange $Ta(NMe_2)_5$ + $(Me_2N)_3Ta(O\text{-}NMe_2)_2$ $\rightleftharpoons$ $2(Me_2N)_4TaO\text{-}NMe_2$ observed earlier.[20]

It is perhaps not surprising that reactions of both **1** and **2** with O_2 give **3** and **4** containing O-NMe_2 and chelating -N(Me)CH_2NMe_2 ligands, given that **2** contains four amide ligands.[20] Pathways similar to those in Scheme 6 could be postulated for the reaction of **2** with O_2.

It is not clear why the current reaction of **1** with O_2 gives three products **2**−**4** and the reaction of another silyl complex **5** with O_2 yields only **6** (Scheme 1).[21] The $-Si(SiMe_3)_3$ ligand is known to be bulkier than the $-SiBu^tPh_2$ ligand.[23a,b,24a,b,d,f,g,j,p,r] It would not be surprising if steric bulkiness in the peroxo intermediate $(Me_2N)_4Ta[\text{-}O\text{-}OSi(SiMe_3)_3]$ (similar to **A1** in Scheme 6) prevents the α-O atom from reaching a *β*-H atom of an amide ligand in $(Me_2N)_4Ta[\text{-}O\text{-}OSi(SiMe_3)_3]$, making Path I in Scheme 6 unfavorable for the $-Si(SiMe_3)_3$ analogue. Steric bulkiness in **6** may also prevent it from undergoing a ligand exchange with unreacted **5**. In other words, kinetic barriers may have limited the reactivities of bulkier **5** and **6**.

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere with the use of either a dry box or standard Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl. Benzene-d_6 and toluene-d_8 were dried over activated molecular sieves and stored under N_2. $TaCl_5$ (Strem) was freshly sublimed. O_2 (National Welders Supply Co.) was dried by P_2O_5 before use. **7**,[27a] **8**,[22a] **9**,[27b] and **10**[29] were prepared by the literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 or AMX-400 spectrometer and referenced to solvent (residual protons in ^1H spectra). Elemental analyses were performed by Complete Analysis Laboratories Inc., Parsippany, NJ.

The addition of O_2 was conducted by the following procedure. The volume of an empty NMR tube or Schlenk flask (100−500 mL) was measured. After a fixed volume of solvent (benzene-d_6 or pentane) and reactants were added, the solution was frozen by liquid nitrogen, and the headspace was evacuated for 10 min on a gas manifold system. The bottom of the NMR tube or flask containing the solution was then kept at −60 °C, while the top was kept at 23 °C. O_2 was then introduced till the system reached a preset pressure (100−760 torr). The ideal gas law $PV = nRT$ (T = 296 K) was used to calculated the amount of O_2 in the NMR tube or Schlenk flask. The vapor pressures of benzene-d_6 or pentane at −60 °C were ignored in the calculation. The solution was then slowly warmed to 23 °C with stirring.

Reaction of 1 with O_2 in an NMR Tube. **7** (0.041 g, 0.110 mmol) and **10** (0.047 g, 0.120 mmol) were mixed in a Young NMR tube (benzene-d_6, 0.6 mL) to yield **1**. Bibenzyl (0.018 g, 0.100 mmol) was used as an internal standard. O_2 (0.10 mmol) was added as described above, and the solution shaken for 10 min at 23 °C. The brown solution gradually turned into light yellow during this period. ^1H and ^{13}C NMR spectra of the mixture after 20 min of the reaction showed that it was a mixture of **2** (34% yield), **3** (5% yield) and unreacted **1** (16%).

Reaction of 1 with O_2 to Give 2−4. **10** (1.622 g, 4.160 mmol) in Et_2O (20 mL) at −30 °C was added dropwise to **7** (1.502 g, 3.830 mmol) in Et_2O (30 mL) at −30 °C. The mixture was warmed with stirring to 23 °C in 2 h. The volatiles were removed. Pentane (20 mL) was added, and the solution was then filtered. After filtration, O_2 (5.520 mmol) was added. The yellow solution was stirred overnight at 23 °C. A white precipitate was observed in the mixture. All volatiles were removed in vacuo to leave a yellow oil containing a white solid. This mixture was then dissolved in CH_2Cl_2, and the solution was cooled to −30 °C to grow colorless crystals of **4** (0.092 g, 0.078 mmol, 4%). ^1H NMR (benzene-d_6, 399.87 MHz, 23 °C) δ 8.00−6.80 (m, C_6H_5), 5.49 (d, 2H, $MeNCH_aH_b\text{-}NMe_2$, $^2J_{H-H}$ = 9.8 Hz), 4.87 (d, 2H, $MeNCH_aH_bNMe_2$), 3.75 (s, 6H, NMe_eMe_f), 3.62 (s, 6H, NMe_eMe_f), 3.36 (s, 6H, $MeNCH_2NMe_2$) 2.88 (s, 6H, $MeNCH_2NMe_cMe_d$), 2.78 (s, 6H, $MeNCH_2NMe_cMe_d$) 1.35 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.57 MHz, 7 °C) δ 115−135 (C_6H_5), 87.6 ($MeNCH_2NMe_2$), 48.7 (NMe_eMe_f), 48.6 (NMe_eMe_f), 46.8 ($MeNCH_2NMe_cMe_d$), 46.6 ($MeNCH_2NMe_cMe_d$), 38.8 ($MeNCH_2NMe_2$), 27.5 (CMe_3), 22.7 (CMe_3). In obtaining crystals of high purity for elemental analysis, toluene was also used to grow the colorless crystals. Anal. Calcd for $C_{51}H_{80}N_6O_4Si_2Ta_2$ (**4·toluene**): C, 48.64; H, 6.40. Found: C, 48.56; H, 6.29. A ^1H NMR spectrum of the mixture in benzene-d_6 showed that it was mostly **2**, **3**, and $HSiBu^tPh_2$ (19% yield). The presence of **4** was not clear in the spectrum.

Preparation of 2 from 7 and 8. A mixture of **7** (1.281 g, 3.260 mmol) and **8** (0.801 g, 3.05 mmol) was placed in a Schlenk flask at 0 °C. Cold Et_2O (30 mL) at 0 °C was added. The yellow solution was slowly warmed to 23 °C overnight with stirring. After volatiles were removed in vacuo, residue was extracted with pentane (2 × 20 mL) and filtered. Removing volatiles in the filtrate gave a yellow oil of **2** (1.438 g, 2.350 mmol, 77% yield). ^1H NMR (benzene-d_6, 300.09 MHz, 23 °C) δ 8.00−6.80 (m, C_6H_5), 3.17 (s, 24H, NMe_2), 1.22 (s, 9H, CMe_3). $^{13}C\{^1H\}$ NMR (benzene-d_6, 75.46 MHz, 23 °C) δ 135−127 (C_6H_5), 46.0 (NMe_2), 27.9 (CMe_3), 20.0 (CMe_3). Anal. Calcd for $C_{24}H_{43}N_4SiOTa$: C, 47.05; H, 7.07. Found: C, 47.02; H, 6.85.

Preparation of 3 from 8 and 9 or 2 and O_2. Method 1. **8** (0.322 g, 1.23 mmol) in tetrahydrofuran (THF, 15 mL) was added to **9** (0.472 g, 1.23 mmol) in THF (10 mL) at −78 °C with stirring. After the mixture was stirred for 22 h, $LiONMe_2$ (0.082 g, 1.2 mmol) was added at −18 °C. After additional stirring for 24 h, all volatiles were removed in vacuo. The residue was extracted with hexanes and filtrated. The volatiles in the filtrate were removed in vacuo to give light yellow powders of **3** (0.434 g, 0.690 mmol, 56% yield). ^1H NMR (benzene-d_6, 400.04 MHz) δ 8.00−7.00 (m, 4H, C_6H_5), 3.28 (s, 18H, NMe_2), 3.36 (s, 6H, $ONMe_2$) 1.25 (s, 9H, CMe_3). ^{13}C NMR (benzene-d_6, 100.59 MHz) δ 147.0−127.0 (C_6H_5), 49.4 ($ONMe_2$), 46.9 (NMe_2), 27.4 (CMe_3), 28.7 (CMe_3). Anal. Calcd for $C_{24}H_{43}N_4SiO_2Ta$: C, 45.85; H, 6.89. Found: C, 45.68; H, 6.79.

Method 2. A solution of **2** (1.038 g, 1.700 mmol) in pentane (30 mL) was added O_2 (1.020 mmol) as described above. The yellow solution was vigorously stirred overnight. A white precipitate was observed. Volatiles were then removed in vacuo to give a

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liquid. ^{1}H NMR of the liquid showed no detectable amount of $HSiBu^tPh_2$. Pentane (2 × 20 mL) was added to extract the liquid, and the solution was filtered. After removal of the volatiles, crude **3** was obtained as a yellow solid (0.825 g, 1.31 mmol, 77% yield). It should be noted that in a few times when **3** was prepared by this reaction, a white precipitate of **4** was obtained.

Preparation of 4 from 2 and O_2. A solution of **2** (1.369 g, 2.360 mmol) in pentane (30 mL) was added O_2 (2.51 mmol) as described above. The yellow solution was vigorously stirred overnight. A white precipitate was observed. Then all volatiles were removed in vacuo. The residue was extracted with pentane (2 × 20 mL) and filtered. Pentane in the filtrate was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (3 mL). Recrystallization at −30 °C yielded colorless crystals of **4·CH_2Cl_2** (0.074 g, 0.055 mmol, 5% yield).

Determination of the Structure of 4 by Single Crystal X-ray Diffraction. The data were collected on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and a graphite-monochromated Mo source (K_α radiation, 0.71073 Å) and fitted with an upgraded Nicolet LT-2 low temperature device. A suitable crystal was coated with paratone oil (Exxon) and mounted on a hairloop under a stream of nitrogen at −100(2) °C. The structure was solved by direct methods. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were treated as idealized contributions. Empirical absorption correction was performed with SADABS.[30a] In addition, the global refinements for the unit cells and data reductions were performed using the Saint program (version 6.02).[30a] All calculations were performed using SHELXTL (version 5.1) proprietary software package.[30b]

Acknowledgment is made to the U.S. National Science Foundation (CHE-0516928 to Z.X.), Research Grant Council of Hong Kong (HKUST6083/02M to Y.D.W.), National Basic Research Program of China (Nos. 2006CB806104 to X.T.C.), and Changjiang (Cheung Kong) Lecture Professorship (to Z.X.) for support of the research.

Supporting Information Available: ^{1}H NMR spectrum of **4** showing two doublets of the η^2-$MeNCH_aH_bNMe_2$ ligand; a table listing NMR resonances of **2**, **3**, and **6** in benzene-d_6; crystallographic data of **4·CH_2Cl_2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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