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Synthesis and Structural Characterization of Tantalum(IV) Amido Compounds

Seigi Suh and David M. Hoffman*

Department of Chemistry, University of Houston, Houston, Texas 77204

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Tantalum(IV) amido complexes have been synthesized from Ta(V) precursors. $Ta(N(SiMe_3)_2)_2Cl_3$ reacts with Na/Hg to give $Ta(N(SiMe_3)_2)_2Cl_2$, and $Ta(NEt_2)_2Cl_3$ reacts with $LiNPh_2$ and Na/Hg to yield $Ta(NPh_2)_2(NEt_2)_2$. $Ta(N(SiMe_3)_2)_2Ph_2$ is prepared by reacting $Ta(N(SiMe_3)_2)_2Cl_2$ with LiPh. Attempts to prepare other organometallic derivatives failed to yield clean products. X-ray crystallographic studies show that $Ta(N(SiMe_3)_2)_2Cl_2$, $Ta(N(SiMe_3)_2)_2Ph_2$, and $Ta(NPh_2)_2(NEt_2)_2$ have distorted tetrahedral geometries.

We are interested in reduced Ta amido complexes as possible precursors to tantalum nitride thin films.[1,2] Although numerous well characterized Ta(V) amido complexes are known,[3−12] to our knowledge only two reduced tantalum amido complexes have been reported, $Ta(NMe\text{-}n\text{-}Bu)_4$ and the dimer $[Ta(\mu\text{-}H)_2(cb)(PMe_2Ph)_2(H)]_2$ (cb = carbazole anion).[5,13] Herein, we report the syntheses and structural characterizations of three new monomeric tantalum(IV) amido complexes, $Ta(N(SiMe_3)_2)_2Cl_2$, $Ta(N(SiMe_3)_2)_2Ph_2$ and $Ta(NPh_2)_2(NEt_2)_2$.[14]

Experimental Section

General Techniques. All manipulations were carried out in a nitrogen-filled drybox or by using standard Schlenk techniques. $TaCl_5$ was purchased from Strem Chemicals and PhLi (1.8 M in cyclohexane−ether) from Aldrich Chemicals. Both chemicals were used as received. $LiN(SiMe_3)_2$ was purchased from Aldrich Chemicals and recrystallized from hexanes before use. Solvents were purified by using standard techniques and stored in the drybox over 4 Å molecular sieves until they were needed. $Ta(N(SiMe_3)_2)_2Cl_3$ and $[Ta(NEt_2)_2Cl_3]_2$ were prepared according to the literature methods.[7,8] NMR spectra were recorded on a GE 300-MHz spectrometer and referenced to the residual protons in the solvent. Infrared spectra were recorded on a Mattson Instruments FT-IR spectrometer. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

$Ta(N(SiMe_3)_2)_2Cl_2$. Na/Hg (0.2% Na in Hg, 0.015 g of Na, 0.65 mmol) was added to a pale yellow solution of $Ta(N(SiMe_3)_2)_2Cl_3$ (0.30 g, 0.49 mmol) in hexanes (7 mL). The reaction mixture turned deep purple within 2 h. After being stirred for a total of 4.5 h, the reaction mixture was filtered through Celite, and the solid on the frit was washed with hexanes (3 × 5 mL). The filtrate and washings were combined and then concentrated to ca. 1 mL in vacuo. Cooling the solution at −35 °C overnight afforded the product as dark crystals (yield 0.18 g, 64%). Anal. Calcd for $TaCl_2Si_4N_2H_{36}C_{12}$: C, 25.17; H, 6.34; N, 4.89. Found: C, 25.24; H, 6.33; N, 4.77. ^1H NMR (C_6D_6): δ 7.5 (br). $\mu = 0.96\ \mu_B$ (Evans' method).[15,16] IR (Nujol, CsI, cm^{-1}): 1299 w, 1257 m (sh), 1245 s, 1165 w, 1139 w, 888 s, 847 s, 789 m, 667 w, 642 w, 619 w, 400 w, 387 w, 337 m, 308 w.

$Ta(N(SiMe_3)_2)_2Ph_2$. $Ta(N(SiMe_3)_2)_2Cl_2$ in hexanes (22 mL) was generated in situ from $Ta(N(SiMe_3)_2)_2Cl_3$ (0.30 g, 0.49 mmol) and Na/Hg as described above. PhLi (1.2 mmol) was added dropwise to the purple solution. The reaction mixture turned green and then reddish purple. After the reaction mixture was stirred for 30 min, it was stripped in vacuo. The reddish purple residue was extracted with hexanes (3 × 5 mL), and the extracts were filtered through Celite. The filtrate was concentrated to 4 mL in vacuo and then cooled at −35 °C overnight. Dark red crystals formed, which were isolated by decanting the mother liquor (yield 0.21 g, 65%). Anal. Calcd for $TaSi_4N_2H_{46}C_{24}$: C, 43.94; H, 7.06; N, 4.27. Found: C, 44.39; H, 7.09; N, 4.06. ^1H NMR (C_6D_6): δ 5.6 (br). IR (Nujol, NaCl, cm^{-1}): 1562 w, 1416 w, 1267 m, 1252 s, 858 s, 845 s, 789 m, 719 m, 691 m, 669 m.

$Ta(NEt_2)_2(NPh_2)_2$. $LiNPh_2$ (0.24 g, 1.39 mmol) was added slowly to an orange solution of $[Ta(NEt_2)_2Cl_3]_2$ (0.30 g, 0.35 mmol) in ether (10 mL). An exothermic reaction occurred, and a yellow suspension appeared. After 10 min of stirring, Na/Hg (0.2% Na in Hg, 0.024 g Na, 1.04 mmol) was added. The reaction mixture turned green and finally deep purple in about 3 h. After an additional 3 h of stirring, the mixture was stripped in vacuo. The dark residue was extracted with hexanes (3 × 10 mL), and the extracts were filtered. The deep purple filtrate was reduced in volume to 3 mL under vacuum and then cooled at −35 °C overnight to give the product as dark purple blocks (yield 0.30 g, 64%). A satisfactory H analysis was not obtained. Anal. Calcd for $C_{32}H_{40}N_4Ta$: C, 58.09; H, 6.09; N, 8.47. Found: C, 58.41; H, 5.30; N, 8.20. ^1H NMR (C_6D_6): δ 11.01 (br), 9.09 (br), 1.22 (br). IR (Nujol, CsI, cm^{-1}): 1595 w, 1201 s (br), 1149 s (br), 962 s, 903 s, 831 w, 657 m, 596 s, 546 m.

X-ray Crystallography. Crystal data are presented in Table 1 and final atomic coordinates in Table 2.

Crystal colors and morphologies are as follows: $Ta(N(SiMe_3)_2)_2Cl_2$, nearly black thick slabs; $Ta(N(SiMe_3)_2)_2Ph_2$, ruby red flat plates; and $Ta(NPh_2)_2(NEt_2)_2$, dark purple blocks. The crystals were manipulated under mineral oil before being rapidly transferred to the cold nitrogen stream for data collection on a Nicolet R3m/V diffractometer. Data collection was carried out for $Ta(N(SiMe_3)_2)_2Cl_2$ using the $\theta-2\theta$ scan technique and for $Ta(N(SiMe_3)_2)_2Ph_2$ and $Ta(NPh_2)_2(NEt_2)_2$ using the ω scan method. Two standard reflections were monitored after every 2 h or every 100 data collected. The data for $Ta(N(SiMe_3)_2)_2Ph_2$ showed a linear decay of 30% over the course of the experiment, which was corrected for by applying a normalization factor as a function

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Table 1. Crystal Data

	$Ta(N(SiMe_3)_2)_2Cl_2$	$Ta(N(SiMe_3)_2)_2Ph_2$	$Ta(NPh_2)_2(NEt_2)_2$
empirical formula	$C_{12}H_{36}N_2Si_4Cl_2Ta$	$C_{24}H_{46}N_2Si_4Ta$	$C_{32}H_{40}N_4Ta$
fw	572.71	656.03	661.71
crystal dimens, mm	0.50 × 0.40 × 0.35	0.45 × 0.45 × 0.15	0.50 × 0.40 × 0.25
space group	*Pbcn* (orthorhombic)	$P2_1/c$ (monoclinic)	$P\bar{1}$ (triclinic)
a, Å	15.240(6)	13.375(3)	8.600(2)
b, Å	12.613(5)	11.838(2)	10.558(4)
c, Å	12.985(6)	19.830(3)	16.821(6)
α, deg			88.82(3)
β, deg		90.55(1)	90.12(2)
γ, deg			105.60(2)
temp, °C	−60	−50	−75
Z	4	4	2
V, Å^3	2496	3140	1471
D_{calcd}, g/cm^3	1.52	1.39	1.49
μ, cm^{-1}	47.6	36.2	37.2
R, R_w[a]	0.037, 0.029	0.031, 0.029	0.024, 0.026

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma(F)]^{-2}$.

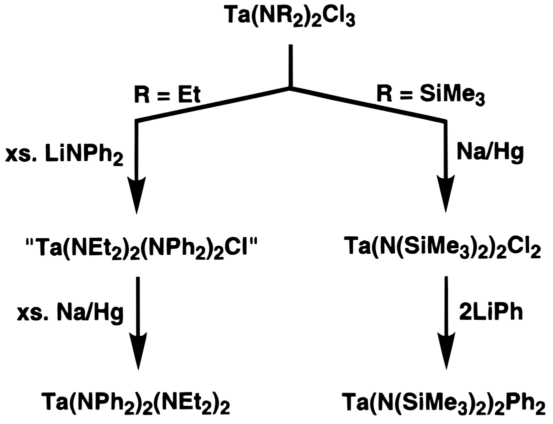
Table 2. Atomic Coordinates ($\times 10^4$) for the Significant Atoms in $Ta(N(SiMe_3)_2)_2Cl_2$, $Ta(N(SiMe_3)_2)_2Ph_2$, and $Ta(NPh_2)_2(NEt_2)_2$

atom	*x*	*y*	*z*
	$Ta(N(SiMe_3)_2)_2Cl_2$		
Ta	203(1)	1913(1)	2628(1)
Cl(1)	-630(4)	434(4)	2179(4)
Cl(2)	1441(4)	950(5)	3179(4)
Si(1)	826(1)	2240(2)	244(2)
Si(2)	1433(1)	3688(2)	2016(2)
N	709(3)	2696(4)	1529(4)
	$Ta(N(SiMe_3)_2)_2Ph_2$		
Ta	7304(1)	3136(1)	6122(1)
Si(1)	8227(2)	530(2)	6078(1)
Si(2)	9513(2)	2470(2)	6595(1)
Si(3)	6846(2)	5806(2)	6552(1)
Si(4)	6692(2)	3901(2)	7587(1)
N(1)	8348(4)	1970(5)	6291(3)
N(2)	6979(4)	4363(5)	6762(3)
C(13)	7661(6)	3700(6)	5130(3)
C(19)	5858(5)	2534(6)	5793(3)
	$Ta(NPh_2)_2(NEt_2)_2$		
Ta	5099(1)	4974(1)	2523(1)
N(1)	4177(3)	6474(3)	2367(2)
N(2)	3206(3)	3443(3)	2657(2)
N(3)	6427(3)	5018(3)	3523(2)
N(4)	6449(3)	4960(3)	1542(2)
C(1)	3497(5)	6635(5)	1570(2)
C(3)	3826(5)	7326(5)	2966(2)
C(5)	2406(5)	3223(5)	3431(2)
C(7)	2338(5)	2620(5)	2021(3)
C(9)	6745(4)	4022(4)	4024(2)
C(15)	7274(4)	6349(4)	3713(2)
C(21)	7398(4)	5999(4)	1046(2)
C(27)	6448(4)	3638(4)	1352(2)

of X-ray exposure time. Data for the other two compounds did not show significant decay. During data reduction, Lorentz and polarization corrections were applied, as well as a semiempirical absorption correction based on ψ scans of 10 reflections having χ angles between 70 and 90°.

Refinement of $Ta(N(SiMe_3)_2)_2Ph_2$ and $Ta(NPh_2)_2(NEt_2)_2$. In each case, interpretation of the Patterson map revealed the position of the Ta atom. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement followed. The hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for the methyl or ethyl hydrogens and a separate variable for the phenyl hydrogens. Final difference maps showed maximum peaks of about 1.25 ($Ta(N(SiMe_3)_2)_2Ph_2$) and 1.5 ($Ta(NPh_2)_2(NEt_2)_2$) e/Å^3 located near Ta. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Scheme 1



Refinement of $Ta(N(SiMe_3)_2)_2Cl_2$. The structure was solved by using the SHELXTL direct methods program, which revealed most the the atoms in the asymmetric unit, consisting of one-half molecule situated about a 2-fold axis. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which the hydrogen atoms attached to carbon were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor for all of them. The core of the molecule, consisting of Ta and Cl atoms, is disordered 50:50 over two sites related by the 2-fold axis. Thus, the Ta and Cl atoms were refined with occupancy factors of 50%. The final difference map showed a maximum peak of about 0.5 e/Å^3.

Results and Discussion

Synthesis. We initially attempted to synthesize low-valent Ta amido complexes by reducing preformed di*alkyl*amido Ta(V) complexes but this approach did not result in isolable compounds. In one reaction involving the reduction of $[Ta(NEt_2)_2Cl_3]_2$,[7] however, we isolated the dinuclear imido complex $[Ta(\mu\text{-}Cl)Cl(NEt_2)(THF)]_2(\mu\text{-}NEt)$ resulting from diethylamide ligand breakdown.[17] On the basis of this result, we decided to use complexes having amido ligands with more robust nitrogen-to-substituent bonds, such as $N(SiMe_3)_2$ and NPh_2. Scheme 1 summarizes our synthetic results obtained by this approach.

$Ta(N(SiMe_3)_2)_2Cl_2$ and $Ta(NPh_2)_2(NEt_2)_2$ were both prepared by reducing Ta(V) compounds with Na/Hg. The precursor to $Ta(N(SiMe_3)_2)_2Cl_2$ is the known complex $Ta(N(SiMe_3)_2)_2Cl_3$,[8,9] and the proposed precursor to $Ta(NPh_2)_2(NEt_2)_2$ is $Ta(NEt_2)_2$-

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[17] Suh, S.; Hoffman, D. M. Unpublished results.

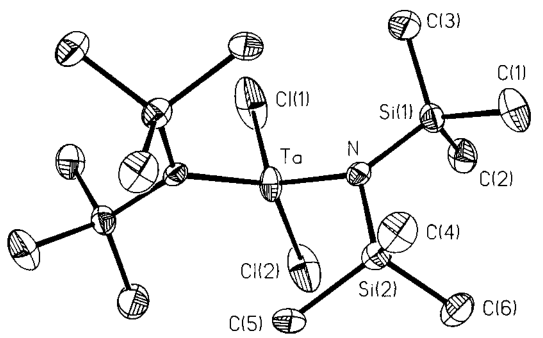

Figure 1. View of $Ta(N(SiMe_3)_2)_2Cl_2$ showing the atom-numbering scheme (30% probability ellipsoids).

$(NPh_2)_2Cl$, which is generated in situ by reacting Wigley's complex[7] $[Ta(NEt_2)_2Cl_3]_2$ with $LiNPh_2$.

$Ta(N(SiMe_3)_2)_2Cl_2$ is extremely air sensitive and soluble in hexanes, but it decomposes slowly in ether. The crystalline product is usually contaminated with minute amounts (<5%) of $Ta(N(SiMe_3)_2)_2Cl_3$ even though an excess of Na/Hg is used in the synthesis. Attempts to prevent the contamination by using longer reaction times resulted in lower yields and unidentified oily materials. Attempts to prepare $Ta(N(SiMe_3)_2)_2Cl_2$ from $LiN(SiMe_3)_2$ and $TaCl_4(py)_n$ or $TaCl_4(PMe_2Ph)_2$ were not successful.

$Ta(NPh_2)_2(NEt_2)_2$ is very air sensitive, and it is soluble and stable in both hexane and ether. As a solid, it decomposes over a period of weeks when stored in a glovebox freezer at −35 °C. It is not clear whether the decomposition is due to thermal instability or its extreme air sensitivity.

The usefulness of $Ta(N(SiMe_3)_2)_2Cl_2$ as a starting material for other Ta(IV) amido compounds was examined. Thus, the organometallic complex $Ta(N(SiMe_3)_2)_2Ph_2$ was isolated as dark ruby red plates from the reaction of the dichloride with LiPh. Clean products could not be obtained from similar reactions of $Ta(N(SiMe_3)_2)_2Cl_2$ with LiMe, $LiCH_2SiMe_3$, $LiCH_2CMe_3$, $PhCH_2MgCl$, $ZnMe_2$, $ZnEt_2$, or $LiN(SiMe_3)_2$. The reactions with $LiCH_2SiMe_3$ and $LiCH_2CMe_3$, which resulted in difficult-to-purify paramagnetic purple oils, were the most promising of the failed attempts.

Proton NMR spectra for $Ta(N(SiMe_3)_2)_2Cl_2$, $Ta(N(SiMe_3)_2)_2Ph_2$, and $Ta(NPh_2)_2(NEt_2)_2$ have shifted, broad resonances consistent with paramagnetic compounds. $Ta(N(SiMe_3)_2)_2Cl_2$ gives a room-temperature magnetic moment of 0.96 μ_B by the Evans NMR method,[15,16] which is consistent with the low moments observed for Nb(IV) amido complexes (0.8−1.03 μ_B).[18,19]

X-ray Crystallographic Studies. X-ray crystallographic studies of $Ta(N(SiMe_3)_2)_2Cl_2$ (Figure 1), $Ta(N(SiMe_3)_2)_2Ph_2$ (Figure 2), and $Ta(NPh_2)_2(NEt_2)_2$ (Figure 3) were carried out to definitively identify the compounds. In the structure of $Ta(N(SiMe_3)_2)_2Cl_2$, the $TaCl_2$ unit is disordered 50:50 over two sites related by a 2-fold axis. Only one $TaCl_2$ orientation of the disordered pair is shown in Figure 1. As a consequence of the disorder, there are two crystallographically distinct Ta−N distances.

All three compounds have distorted tetrahedral geometries that probably result from steric crowding. The cores of each compound have virtual C_2 symmetry rather than the C_{2v} symmetry expected for an idealized tetrahedral geometry (taking into account the different amide ligands in $Ta(NPh_2)_2(NEt_2)_2$). The deviation is emphasized by the interplanar angles $TaN_2/TaCl_2$, TaN_2/TaC_2, and Ta[N(1)N(2)]/Ta[N(3)N(4)] which deviate from 90° by 17, 9.5, and 6.8°, respectively.

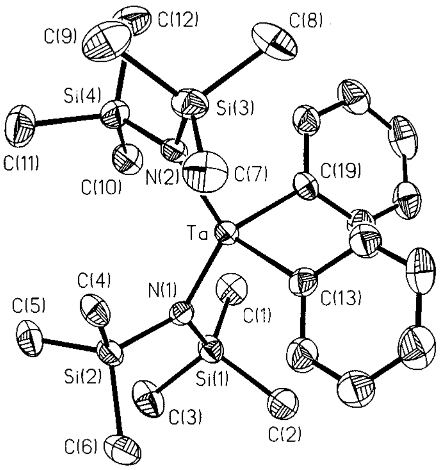

Figure 2. View of $Ta(N(SiMe_3)_2)_2Ph_2$ showing the atom-numbering scheme (40% probability ellipsoids).

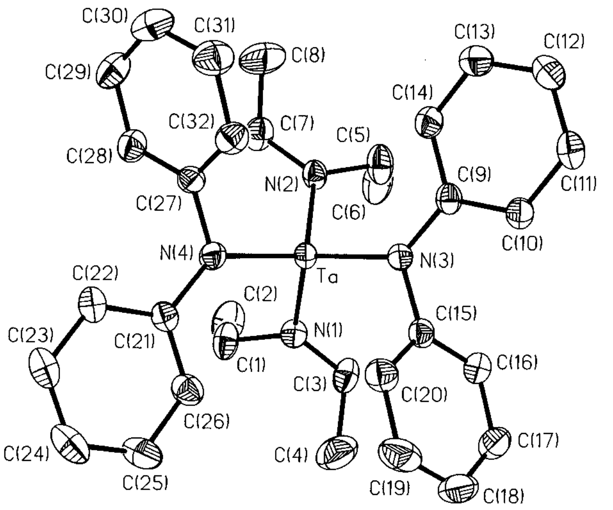

Figure 3. View of $Ta(NPh_2)_2(NEt_2)_2$ showing the atom-numbering scheme (40% probability ellipsoids).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ta(N(SiMe_3)_2)_2Cl_2$

	Bond Distances		
Ta−Cl(1)	2.330(6)	Ta−Cl(2)	2.356(6)
Ta−N	1.899(5)	Ta−N′	2.027(5)
	Bond Angles		
Cl(1)−Ta−Cl(2)	95.7(2)	Cl(1)−Ta−N	116.7(2)
Cl(2)−Ta−N	99.8(2)	Cl(1)−Ta−N′	98.7(2)
Cl(2)−Ta−N′	129.5(2)	N−Ta−N′	115.5(3)
Ta−N−Si(1)	125.3(3)	Ta−N−Si(2)	110.5(3)
Si(1)−N−Si(2)	120.0(3)		

The N−Ta−N angle is about 8° larger in $Ta(N(SiMe_3)_2)_2Ph_2$ than in $Ta(N(SiMe_3)_2)_2Cl_2$. The N−Ta−N angle in $Ta(N(SiMe_3)_2)_2Ph_2$ is larger perhaps because the Ph ligands can get closer (C(13)−Ta−C(19) = 92°) to each other than the Cl groups (Cl−Ta−Cl = 96°). The N−Ta−N angles in $Ta(NPh_2)_2(NEt_2)_2$ range from 104 to 115°.

The ispo carbon atoms in the Ph ligands of $Ta(N(SiMe_3)_2)_2Ph_2$ have compressed C−C−C angles averaging 114° (cf. the average $C-C_{ipso}-C$ angle is 119° for the NPh_2 ligands of $Ta(NPh_2)_2(NEt_2)_2$), and the Ta−C−C angles differ significantly (≈120° vs 126°). All of the amido ligands in the complexes are essentially planar, and the Si−N−Si and C−N−C angles do not vary much from ligand to ligand. For each individual

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Table 4. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{Ta(N(SiMe_3)_2)_2Ph_2}$

Bond Distances			
Ta−N(1)	1.989(5)	Ta−N(2)	1.981(6)
Ta−C(13)	2.135(7)	Ta−C(19)	2.156(7)
Bond Angles			
N(1)−Ta−N(2)	124.0(2)	N(1)−Ta−C(13)	102.1(2)
N(2)−Ta−C(13)	114.5(2)	N(1)−Ta−C(19)	116.6(2)
N(2)−Ta−C(19)	103.5(2)	C(13)−Ta−C(19)	91.9(3)
Ta−N(1)−Si(1)	124.6(3)	Ta−N(1)−Si(2)	116.1(3)
Si(1)−N(1)−Si(2)	118.9(3)	Ta−N(2)−Si(3)	125.4(3)
Ta−N(2)−Si(4)	114.6(3)	Si(3)−N(2)−Si(4)	119.7(3)
Ta−C(13)−C(14)	126.2(5)	Ta−C(13)−C(18)	120.3(5)
Ta−C(19)−C(20)	126.1(5)	Ta−C(19)−C(24)	119.3(5)
C(14)−C(13)−C(18)	113.6(7)	C(20)−C(19)−C(24)	114.6(7)

Table 5. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$

Bond Distances			
Ta−N(1)	1.965(4)	Ta−N(2)	1.971(3)
Ta−N(3)	2.025(3)	Ta−N(4)	2.022(3)
Bond Angles			
N(l)−Ta−N(2)	104.4(1)	N(l)−Ta−N(3)	115.1(1)
N(2)−Ta−N(3)	105.8(1)	N(l)−Ta−N(4)	105.5(1)
N(2)−Ta−N(4)	115.1(1)	N(3)−Ta−N(4)	110.9(1)
Ta−N(l)−C(l)	116.9(3)	Ta−N(l)−C(3)	127.9(3)
Ta−N(2)−C(5)	118.0(2)	Ta−N(2)−C(7)	126.1(2)
Ta−N(3)−C(9)	133.1(2)	Ta−N(3)−C(15)	110.9(2)
Ta−N(4)−C(27)	110.8(2)	Ta−N(4)−C(21)	132.0(3)
C(1)−N(1)−C(3)	114.3(4)	C(5)−N(2)−C(7)	115.0(3)
C(9)−N(3)−C(15)	115.9(3)	C(21)−N(4)−C(27)	117.2(3)

ligand, however, the pairs of Ta−N−Si and Ta−N−C angles vary significantly. For example, the C−N−C angles in the $\mathrm{NPh_2}$ ligands of $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$ are 116 and 117°, but the Ta−N−C angles are 111 and 133° in one $\mathrm{NPh_2}$ ligand and 111 and 132° in the other. The angles in the $\mathrm{NEt_2}$ ligands of $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$ and in the amido ligands of the other complexes follow a similar pattern albeit with less dramatic differences in the Ta−N−R angles. Analogous angular distortions in amido ligands were reported previously for four-coordinate (bis(trimethylsilyl)amido)niobium complexes and in $\mathrm{[Ta(\mu\text{-}NSiMe_3)Cl(N(SiMe_3)_2)]_2}$.[14,18,19] The potential energy curve for variation of M−N−R in these complexes must be relatively shallow to allow for such large variations in the angles, with the final values being set by steric interactions and crystal packing.

In $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$ one Ta−N distance (1.899(5) Å) is shorter than the other (2.027(5) Å). The Ta−N distances for each amido ligand type in $\mathrm{Ta(N(SiMe_3)_2)_2Ph_2}$ and $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$ are the same within experimental error. None of the Ta−N distances are extraordinary; for example, in $\mathrm{Ta(N(SiMe_3)_2)_2Cl_3}$, $\mathrm{Ta(N\text{-}}t\mathrm{\text{-}Bu)(N(SiMe_3)_2)_2Cl}$, and $\mathrm{[Ta(\mu\text{-}X)X(NSiMe_3)(N(SiMe_3)_2)]_2}$ (X = Cl, Br, OMe), the Ta−N distances range from 1.928(7) to 2.023(14) Å,[8,10,11] and in $\mathrm{Ta(N\text{-}}t\mathrm{\text{-}Bu)(NMe_2)_3}$, $\mathrm{Ta(}t\mathrm{\text{-}Bu)(NMe_2)_4}$, and $\mathrm{Ta(}p\mathrm{\text{-}tolyl)Br(NMe_2)_3}$, they range from 1.94(2) to 2.09(2) Å.[12,20] The Ta−Cl and Ta−C distances in $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$ and $\mathrm{Ta(N(SiMe_3)_2)_2Ph_2}$ are within the range of distances reported for other Ta complexes.[8,10−12]

Conclusion

Reduction of tantalum(V) amido precursors gave $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$ and $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$. The chlorides in $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$ were substituted to yield $\mathrm{Ta(N(SiMe_3)_2)_2Ph_2}$. Attempts to synthesize other organometallic derivatives failed to give clean products. $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$, $\mathrm{Ta(N(SiMe_3)_2)_2Ph_2}$, and $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$ are paramagnetic in solution, and X-ray crystallographic studies show they are monomeric distorted tetrahedral complexes in the solid state.

We know of no other structurally characterized monomeric Ta(IV) amido complexes, but the three closely related niobium(IV) compounds $\mathrm{Nb(N(SiMe_3)_2)_2X_2}$, $\mathrm{Nb(N(SiMe_3)_2)_2ClPh}$, and $\mathrm{Nb(N(SiMe_3)_2)_2Ph_2}$ have been characterized.[18,19,21] Also, d^0 congeners are known, such as $\mathrm{M(N(SiMe_3)_2)_2Cl_2}$ (M = Zr, Hf).[22] Reactivity studies involving the new Ta(IV) complexes are in progress.

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Note Added in Proof. Ta(III) amido complexes were recently reported: Scoles, L.; Ruppa, K. B. P.; Gambarotta, S. *J. Am. Chem. Soc.* **1996**, *118*, 2529.

Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles, a figure showing the disorder in $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$, and packing diagrams for $\mathrm{Ta(N(SiMe_3)_2)_2Cl_2}$, $\mathrm{Ta(N(SiMe_3)_2)_2Ph_2}$, and $\mathrm{Ta(NPh_2)_2(NEt_2)_2}$ (21 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors can be obtained from the authors.

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