Molecular Structure of a Monomeric, Base-Free Metal(I) Amide, $TlN[Si(CH_3)_3]_2$, by Gas Electron Diffraction and by Density Functional Theory and ab Initio MP2 Calculations

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Thallium bis(trimethylsilyl)amide is a monomer in the gas phase. The molecular symmetry is C_2, the Tl−N bond length is 214.8(12) pm by gas electron diffraction as compared to about 258 pm in the crystalline dimer (Klinkhammer, K. W.; Henkel, S. *J. Organomet. Chem.* **1994**, *480*, 167). Structure optimization by DFT or ab initio (MP2) calculations with the ECP basis set on the Tl atom fails to reproduce the experimental Tl−N bond distance unless the 5s,5p,5d electrons on the metal are described explicitly and the atomic basis set includes both polarization and diffuse functions.

Introduction

All known base-free amides of monovalent metals, $M(I)NR_2$, appear to form oligomers or polymers in the solid state.[1] Thus investigations of bis(trimethylsilyl)amides by single-crystal X-ray diffraction have shown that $LiN(SiMe_3)_2$, Me = CH_3, forms cyclic trimers,[2] $NaN(SiMe_3)_2$ infinite polymers,[3] $KN(SiMe_3)_2$ and $RbN(SiMe_3)_2$ cyclic dimers,[4,5] and $CuN(SiMe_3)_2$ and $AgN(SiMe_3)_2$ cyclic tetramers.[6,7] Cyclic dimers have also been found in the crystalline dioxane solvates $MN(SiMe_3)_2 \cdot 0.5(C_4H_8O_2)$, M = Rb or Cs.[8]

An investigation of $LiN(SiMe_3)_2$ by gas electron diffraction (GED) has shown that the gas consists of cyclic dimers.[9] $NaN(SiMe_3)_2$ is reported to be distillable at 170 °C and 2 Torr.[10] In an effort to determine the structure of a base-free, monomeric amide we have attempted to record GED data with inlet systems made of metal or ceramic materials but found that the compound suffered extensive, perhaps complete, decomposition.[11]

Klinkhammer and Henkel have recently reported the synthesis of $TlN(SiMe_3)_2$ which was found to be dimeric in the crystalline state.[12] The compound may be sublimed without decomposition, and is monomeric in the gas phase (by MS) and in benzene solution (by freezing point depression).[12] We decided, therefore, to determine the structure of the monomer by GED and density functional theory (DFT) calculations. This represents, to the best of our knowledge, the first structure determination of a monomeric, base-free metal(I) amide.

Experimental Section

Quantum Chemical Calculations. All calculations were carried out with the program system GAUSSIAN94.[13] The structure of $TlN(SiMe_3)_2$ was first optimized under C_2 symmetry by DFT calculations using the BPW91 density functional. For Si and Tl we used the Lan2DZ effective core potential (ECP) basis;[14] For Tl only the three valence shell electrons were treated explicitly while the remaining 78 electrons were assigned to the core (78e-ECP). For Si the basis describes the 3s and 3p electrons while 10 electrons are assigned to the core. Standard DZ basis sets were used for N, C, and H.[15] Optimal structure parameters are listed in Table 1 under the heading DFT(BPW91)(78e-ECP). The molecular force field was calculated and transferred to the program ASYM40[16] for computation of root-mean-square vibrational amplitudes of all atom pairs at the temperature of the gas electron diffraction experiment.

The optimal structure parameters obtained by the DFT(BPW91)-(78e-ECP) calculations are in poor agreement with those obtained by GED. In particular the calculated Tl−N bond distance is about 16 pm longer than the experimental. We decided therefore to repeat structure optimization at higher computational levels and with larger basis sets.

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Table 1. Interatomic Distances (r_{a}), Root Mean Square Vibrational Amplitudes (l), Valence and Torsional Angles of TlN(SiMe$_3$)$_3$ Obtained by Gas Electron Diffraction (GED) and by DFT or MP2 Calculations[a]

	GED[b]		DFT(BPW91)	MP2
	r_{a}	l	(78e-ECP) r_{e}	(60e-ECP) r_{e}
		Bond Distances		
Tl−N	216.4(13)	[7.0]	232.7	222.4
Si−N	171.8(5)	[5.1]	177.4	175.1
Si−C	187.3(3)	[5.7]	191.9[c]	190.8[c]
C−H	109.7(4)	[7.8]	110.5[c]	109.8[c]
		Nonbonded Distances		
Tl···Si	330.6(7)	[11.6]	349.3	338.7
Tl···C	443(2)	22(3)	468.1	458.2
Tl···C	493(1)	22(3)	501.1	488.8
Tl···C	355(3)	[23.2]	343.8	339.1
N···C	303(2)	[9.6]	299.6	298.5
N···C	306(1)	[10.5]	307.7	304.6
N···C	308(2)	[10.2]	309.0	306.0
Si···Si	308(1)	[7.9]	318.5	313.9
Si···C	415(2)	15(5)[d]	410.3	404.1
Si···C	377(3)	17(5)[d]	386.2	381.3
Si···C	465(2)	[10.3]	471.9	468.3
Si···H	249.0(4)	8.8(7)	253.7[c]	252.4[c]
C···C	290(1)	10(2)	309.1[c]	306.9[c]
		Valence Angles		
∠TlNSi	116.3(5)		116.1	116.4
∠SiNSi	127.4(9)		127.7	127.3
∠CSiC	101.6(10)		107.3[c]	107.3[c]
∠NSiC	114.9(10)		108.1	108.9
∠NSiC	116.7(10)		112.9	112.8
∠NSiC	118.0(10)		113.6	113.6
∠SiCH	[111.2]		111.2[c]	111.6[c]
		Torsional Angle		
ϕ(TlNSiC)	23(2)		13.2	24.8
		Tilt Angle		
τ(SiMe$_3$)[e]	1.8(11)		–	–
R factor [f]	0.036			

[a] Interatomic distances and vibrational amplitudes in pm, angles in degrees. Estimated standard deviations in parentheses in units of the last digit. [b] Nonrefined parameters in square brackets were fixed at the DFT(BPW91)(78e-ECP) values. [c] Mean value. [d] These amplitudes were refined with constant difference. [e] See text for definition. [f] $R = \sqrt{[\sum w(I_{\mathrm{obs}} - I_{\mathrm{calc}})^2/\sum wI_{\mathrm{obs}}^2]}$.

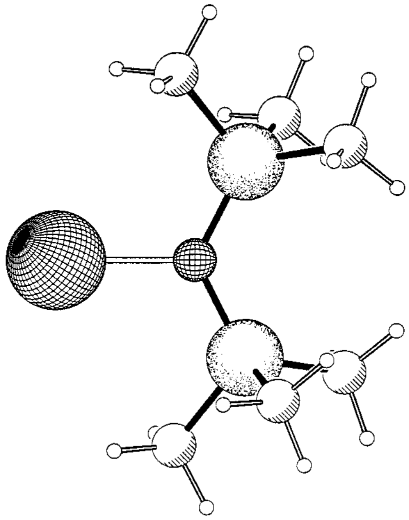

Figure 1. Molecular model of TlN(SiMe$_3$)$_2$, symmetry C_2.

DFT calculations with the B3LYP functional and the 78e-ECP basis did not lead to significant changes, in particular the Tl−N bond distance decreased by less than 2 pm. Schwerdtfeger and co-workers[17] have shown that calculations with a similar, large core ECP, basis set for indium failed to yield satisfactory results for InCl. Calculations were therefore continued at the DFT(B3LYP) level with much larger basis sets: For Tl we used a recently published quasi-relativistic pseudopotential[18] which mimics the inner 60e core, while the 5s, 5p, 5d, 6s, and 6p electrons were described by a (7s, 6p, 4d) basis.[19] The basis set on N was of DZ+P quality with added diffuse functions (aug-cc-pVDZ[13]), the valence shell of Si was described at the DZ+P level, and C and H at the standard 6-31G* level. These calculations yielded a Tl−N bond distance of 229.2 pm, still about 13 pm longer than the experimental value.

At this point we switched to ab initio methods. MP2 optimization with the basis sets described in the preceding paragraph yielded the structure parameters listed in Table 1 under the heading MP2-(60e-ECP).

Gas Electron Diffraction. The sample of TlN(SiMe$_3$)$_2$ was synthesized as described elsewhere.[12] GED data were recorded on the Balzers KDG2 unit at the University of Oslo[20] with a metal (brass and steel) inlet system at 80 ± 5 °C. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Structure refinements were based on data from six plates for each distance. The plates were scanned on an Agfa Arcus II scanner and the data processed as described elsewhere.[21]

Atomic scattering factors were taken from ref 22. Backgrounds were drawn as least-squares adjusted polynomials to the difference between the total experimental and the calculated molecular intensities. Structure refinements were carried out with the program KCED25 written by G. Gundersen, S. Samdal, T. G. Strand, and H. M. Seip.

The structure refinements were based on a molecular model of C_2 symmetry as indicated by the DFT calculations. See Figure 1. The SiMe$_3$ groups were assumed to have C_{3v} symmetry with methyl groups in staggered orientations. The C_3 axes were assumed to lie in the plane defined by the TlNSi$_2$ fragment and a *tilt* angle defined as the angle between the symmetry axes of the SiMe$_3$ groups and the Si−N bonds and counted as positive when the tilt served to increase the distance between methyl groups in different SiMe$_3$ fragments. The model is then characterized by nine independent parameters, e.g. the Tl−N, Si−N, Si−C, and C−H bond distances, the valence angles ∠SiNSi, ∠CSiC, and ∠SiCH, the tilt angle τ(SiMe$_3$), and the torsional angle ϕ(TlNSiC). Attempts to refine the ∠SiCH valence angle were, however, unsuccessful, this angle and nonrefined rms vibrational amplitudes were fixed at the calculated values as indicated in Table 1; the remaining eight independent structure parameters were refined along with five rms vibrational amplitudes. The estimated standard deviations of the ∠CSiC angle was increased from 0.2 to 1.0° and the ∠NSiC angles were increased from 0.2 to 0.4 to 1.0° to include uncertainty introduced by the imposition of local symmetry. Other estimated standard deviations calculated by the program were multiplied by a factor of 3 to include added uncertainty due to data correlation and nonrefined amplitudes, and expanded to included an estimated scale uncertainty of 0.1%.

Results and Discussion

Least-squares refinement of the molecular model shown in Figure 1 and further described in the preceding section to the gas electron diffraction data yielded the structure parameters listed in Table 1. Calculated and observed intensity and radial distribution curves are compared in Figures 2 and 3. We consider the agreement satisfactory.

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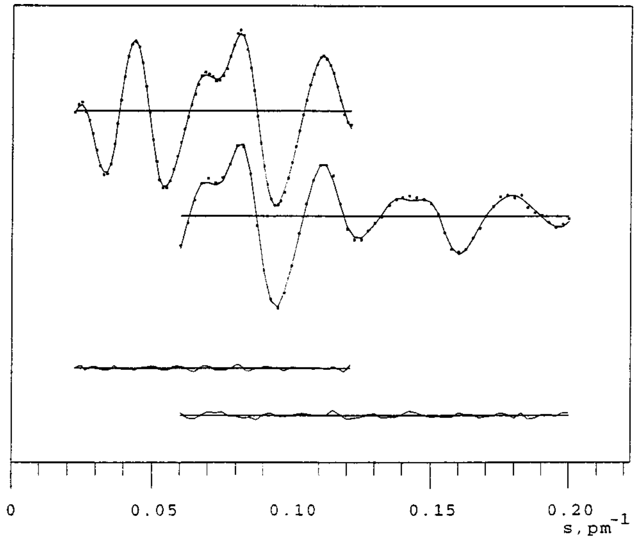

Figure 2. Experimental (dots) and calculated (lines) modified molecular intensity curves of $TlN(SiMe_3)_2$. Below: difference curves.

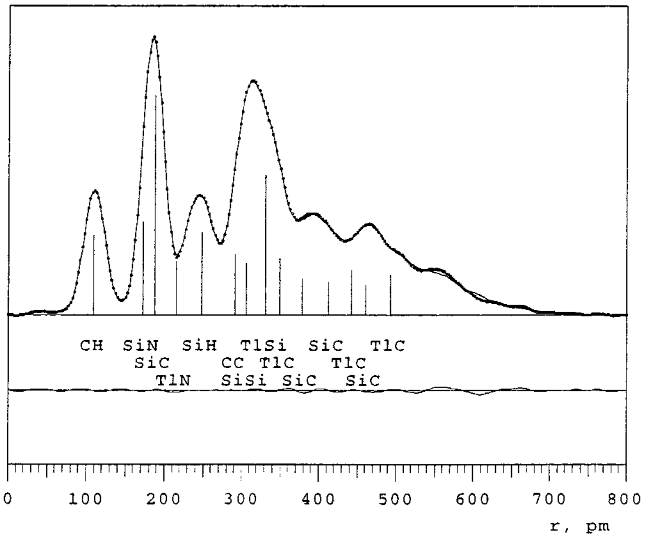

Figure 3. Experimental (dots) and calculated (lines) radial distribution curves of $TlN(SiMe_3)_2$. Below: difference curves. Artificial damping constant, $k = 25$ pm^2.

The most interesting aspect of the structure is probably the Tl^{I}–N bond distance which is some 7 pm longer than in the corresponding Tl(III) trisamide, $Tl[N(SiMe_3)_2]_3$, 209 pm.[23] A similar difference has been found between metal to chlorine bond distances in the gaseous, monomeric mono- and trichlorides of the less heavy group 13 metals Al, Ga, and In.[24] Even larger differences have been observed between the Tl^{I}–C distances in $[TlC(SiMe_3)_3]_4$ (237 pm)[25] or $TlC_6H_3(C_6H_2{}^{i}Pr_3)_2$ (234 pm)[26] and the Tl–C distances in Tl(III) organyls; mean value 215 pm.[27] These bond energy differences may be rationalized as hybridization effects;[24] Population analysis shows that the lone pair on Tl resides in a strongly relativistically contracted 6s orbital leaving only p-orbitals for bonding to N. Tl–N bonding in the trisamide is presumably effected through sp^2 hybrid orbitals on the metal atom.

The Tl–N bond distance in the crystalline dimer $Tl_2[\mu\text{-}N(SiMe_3)_2]_2$ is 258.1(7) pm,[12] more than 40 pm longer than in the gaseous monomer, by far exceeding the expectation from the increase of bond order. This may be due to steric congestion in the dimer and to significant N→Tl π-bonding in the monomer: such bonding is precluded by symmetry in the dimer.

The structure parameters of the ligand, i.e., the Si–N and Si–C bond distances and the SiNSi and CSiC valence angles fall in the rather wide range spanned by the corresponding parameters in the gaseous amides $Mg[N(SiMe_3)_2]_2$,[28] $Cd[N(SiMe_3)_2]_2$,[29] $Hg[N(SiMe_3)_2]_2$,[30] $Sn[N(SiMe_3)_2]_2$,[31] or $Pb[N(SiMe_3)_2]_2$.[32]

Structure optimization of $TlN(SiMe_3)_2$ at the DFT(BPW91)-(78e-ECP) level indicated that the C_2 model represented a minimum on the potential energy surface. The optimal Tl–N bond distance was 232.7 pm, about 16 pm longer than the experimental value. Structure optimization at the MP2(60e-ECP) level led to a Tl–N bond distance of 222.4 pm, about 6 pm longer than the experimental. At this level the calculated Si–N and Si–C bond distances were about 3 and 4 pm longer than their experimental counterparts, respectively (see Table 1). The experimental valence angles at the N atom are satisfactorily reproduced, but the calculated CSiC valence angles are about 6° larger than the experimental (and the NSiC valence angles consequently too small). Inclusion of spin–orbit coupling is expected to lead to a shortening of the Tl–N bond by 1 or 2 pm.[33] Like the difference between calculated and experimental structure parameters of the ligand, the small remaining difference between calculated and experimental Tl–N bond distances may be due to inadequate basis sets for all atoms: To test this hypothesis we fixed the ligand at the experimental geometry, added f-type polarization functions[33] to the basis sets of Tl and N, and did a potential scan for the Tl–N bond distance. The equilibrium distance was now found to be 217 pm, in good agreement with the experimental value.

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Supporting Information Available: The basis sets used for the final geometry optimization at the MP2 level and for the final potential energy scan of the Tl–N distance. This material is available free of charge via the Internet at http://pubs.acs.org.

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