Two Successive Steps of Hypercoordination at Tin: The Gas-Phase and Solid-State Structures of (*N*,*N*-Dimethylaminoxy)trimethylstannane

Norbert W. Mitzel,*,† Udo Losehand,† and Alan Richardson‡

*Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4,
85747 Garching, Germany, and Department of Chemistry, Oregon State University,
Corvallis, Oregon 97331-4003*

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$Me_3SnONMe_2$ has been prepared from trimethyltin chloride and *O*-lithio-*N*,*N*-dimethylhydroxylamine and characterized by IR and NMR spectroscopy, mass spectrometry, and elemental analysis. Its gas-phase molecular structure has been determined by electron diffraction augmented by restraints taken from ab initio calculations at the MP2/DZ(P) level of theory. A secondary interaction (Sn···N, 2.731(14) Å) between the tin and nitrogen atoms has been detected and makes $Me_3SnONMe_2$ the first partially hypercoordinate tin compound studied in the gas phase. A solid-state structure of $Me_3SnONMe_2$ has been determined by X-ray diffraction of an in situ grown single crystal. In the crystal lattice the coordination sphere of tin is further enlarged by a weak intermolecular Sn···O contact (2.998(10) Å) and a 4+2 coordination geometry is achieved, which can be deduced from that of a distorted trigonal bipyramid with one of the axial substituents replaced by the two weak contacts. Important geometry parameter values are as follows (gas/solid): Sn−O 2.006(3)/2.063(6) Å, O−N 1.468(6)/1.440(9) Å, Sn−C(in plane) 2.148(4)/2.163(14) Å, Sn−C(out of plane) 2.146(3)/2.062(9) and 2.185(10) Å, Sn−O−N 102.5(8)/101.5(4)°, O−Sn−C(in plane) 99.6(10)/99.7(4)°, O−Sn−C(out of plane) 108.1(6)/119.6(4)° and 116.6(4)°.

Introduction

Indications for interactions between the atoms E and N in E−C−N linkages (E = Si, Ge, Sn; e.g., in $Me_3SnCH_2NMe_2$), also named the α-effect, were concluded, for example, from measurements of nitrogen basicities[1] and rationalized in terms of a “closed type” three-center bond caused by transitions of σ-electrons of the N atom participating in the N−C bond into the empty d-orbitals of the group 14 element.[2] Structurally documented examples for the existence of donor bonds between geminal p-block donor and acceptor elements include compounds with B−C−N,[3] Al−C═N,[4] and Al−N−N[5] linkages.

Recently we have established the occurrence of donor bonds for SiON[6] and SiNN[7] linkages. The most extreme case in our hands is $ClH_2SiONMe_2$,[8] which adopts a SiON angle of only 79.7(1)° in the crystal, but does not undergo even weak intermolecular interactions as detected in related systems such as ClH_2SiNMe_2.[9] Theoretical treatment of $ClH_2SiONMe_2$[8] and related systems showed that the Si···N attraction cannot be attributed solely to electrostatic interactions, and a better way to rationalize the experimental facts is negative hyperconjugation between the lone pair at nitrogen and the antibonding orbitals σ*(Si−Cl). It has also been found that the strength of the Si···N interaction is markedly dependent on the electronic nature of the substituent at silicon in anti position relative to the nitrogen atom.

Consequently we became interested in different acceptor centers, as elements such as tin with a higher acceptor ability than silicon should show more pronounced effects toward the donor center and hence lead to stronger β-donor interactions. The larger radius of tin, however, allows for accommodation of more atoms in its first coordination sphere, which opens up the possibility for further intermolecular contacts, as we report now for the simplest methylated SnON compound, $Me_3SnONMe_2$.

Results and Discussion

Synthesis. $Me_3SnONMe_2$ was prepared from lithiated *N*,*N*-dimethylhydroxylamine and trimethylchlorostannane in pentane and was isolated as colorless

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* Corresponding author. E-mail: N.Mitzel@lrz.tum.de.
† Technische Universität München.
‡ Oregon State University.

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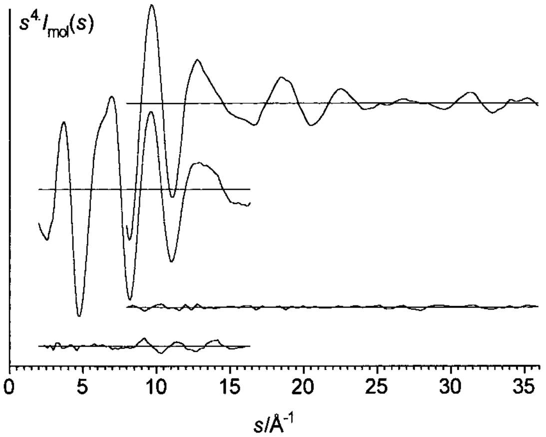

Figure 1. Molecular scattering intensity and final difference curves (vs model) as obtained by electron diffraction of gaseous $Me_3SnONMe_2$.

liquid by fractionation through a series of cold traps in vacuo. It was characterized by its IR and NMR spectra (^1H, ^{13}C, ^{15}N, ^{119}Sn). The ^{15}N NMR resonance at −252 ppm is shifted more than 40 ppm with respect to the simplest aminoxyosilane $H_3SiONMe_2$ (−210 ppm),[6] but there are no data for aminoxystannanes for a more direct comparison. The ^{119}Sn NMR resonance is split into a decet proving the identity of the $SnMe_3$ group.

Gas-Phase Structure Determination. The high volatility of $Me_3SnONMe_2$ allowed the determination of the molecular structure in the gas-phase by electron diffraction. The usual limitations in the refinement of gas-phase structures were overcome by augmenting the diffraction data by restraints derived from ab initio optimizations of the geometry (MP2/DZ(P)) in a combined and extended application of Bartell's method of predicate values[10] and Schäfer's MOCED method,[11] also called SARACEN.[13]

The molecular framework and atom-numbering scheme for $Me_3SnONMe_2$ are shown in Figure 3A. The mathematical model for the least-squares refinement was defined in C_s symmetry, with seven bond lengths: Sn−O, Sn−C7, Sn−C6, O−N, N−C, and two C−H distances for the methyl groups bound to tin and nitrogen. The differences between the C−H distances within these groups were fixed to the values obtained from ab initio calculations at the MP2/DZ(P) level of theory. Angle parameters were ∠O−Sn−C7, ∠O−Sn−C6, ∠Sn−O−N, ∠O−N−C, ∠C−N−C, and ∠C−Sn−C and the angles ∠Sn−C(7)−H, ∠Sn−C(6)−H, and ∠N−C−H as well as the torsion angles τCSnCH and τCNCH, whereby the differences in those parameters for the different hydrogen atoms were again fixed to calculated values. A total of 18 parameters were refined under the action of eight restraints defining the differences of parameters of similar nature or absolute values in the case of hydrogen-defining parameters. The parameter and restraint definitions are given in Table 2; the uncertainties are based on experience of the reliability of those calculations. A total of 24 amplitudes of vibration were refined concurrently, representing all amplitudes belonging to pairs of scatterers with a contribution of more than 5% of the scattering of the Sn−O pair. Most of these amplitudes were subject to restraints, either absolute or ratios between related amplitudes, with the values taken from a force field computed at the SCF/DZ(P) level of theory and transformed into amplitudes by means of

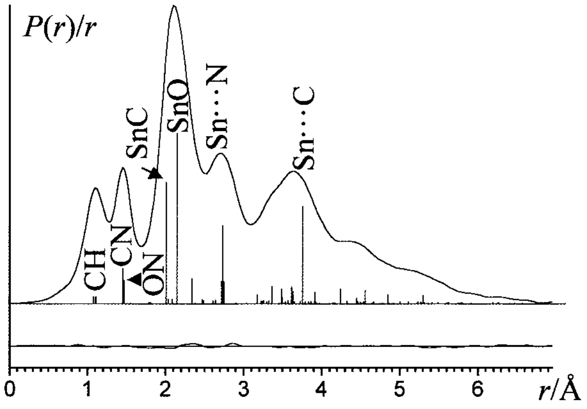

Figure 2. Radial distribution and difference curve for the electron diffraction refinement.

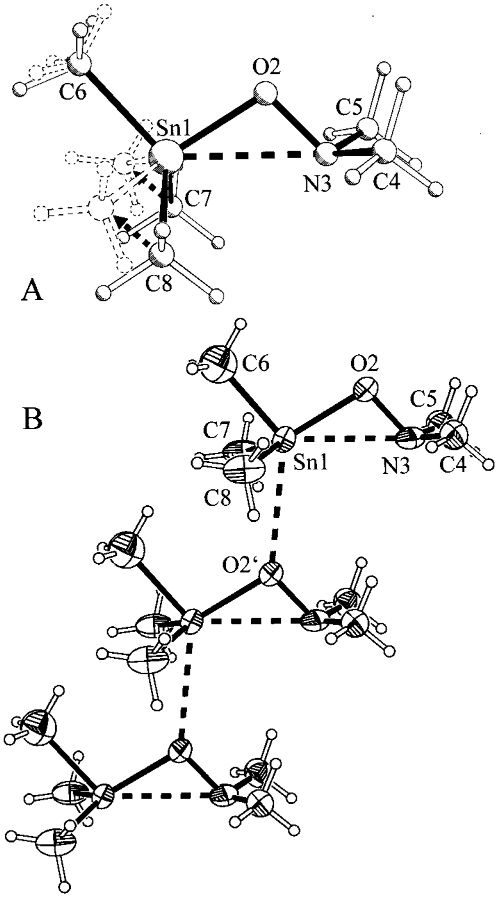

Figure 3. (A) Molecular structure of $Me_3SnONMe_2$ in the gas phase as determined by electron diffraction. The arrows show the deformation occurring upon incorporation of a free molecule into the crystal, as indicated by a superposition of one molecule from the solid state (dashed part). (B) Aggregation of $Me_3SnONMe_2$ in the crystal as determined by low-temperature X-ray crystallography.

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Table 1. Selected Geometrical Parameter Values [Å/deg] for $Me_3SnONMe_2$

	GED gas-phase	ab initio MP2/DZ(P)	XRD solid-state
Sn−O	2.006(3)	1.983	2.063(6)
Sn−C6	2.148(4)	2.140	2.163(14)
Sn−C(7/8)	2.146(3)	2.138	2.062(9)/2.185(10)
Sn···N	2.731(14)	2.661	2.745(9)
O−N	1.468(6)	1.480	1.440(9)
N−C(4/5)	1.452(4)	1.464	1.423(12)/1.436(11)
N−O−Sn	102.5(8)	99.4	101.5(4)
O−Sn−C6	99.6(10)	103.2	99.7(4)
O−Sn−C(7/8)	108.1(6)	108.7	119.6(4)/116.6(4)
O−N−C	106.5(8)	104.9	106.6(6)/107.2(6)

Table 2. Independent Parameters and Restraints for the GED Refinement of $Me_3SnONMe_2$

no.	parameter	value	restraint
*p*1	Sn−O	2.006(3)	
*p*2	Sn−C7	2.146(3)	
*p*3	Sn−C6	2.148(4)	$p3 - p2 = 0.002(5)$
*p*4	O−N	1.468(6)	
*p*5	N−C	1.452(4)	$p5 - p4 = -0.016(10)$
*p*6	C−H(N)	1.103(4)	
*p*7	C−H(Sn)	1.106(3)	$p7 - p6 = 0.004(5)$
*p*8	∠OSnC(7)	108.1(6)	
*p*9	∠OSnC(6)	99.6(10)	
*p*10	∠Sn−O−N	102.5(8)	
*p*11	∠O−N−C	106.5(8)	
*p*12	∠C−N−C	107.3(18)	
*p*13	∠C−Sn−C	109.3(10)	
*p*14	∠SnCH(7)	111.2(8)	$p14 = 112.0(10)$
*p*15	∠SnCH(6)	109.4(12)	$p15 - p14 = -1.4(10)$
*p*16	∠NCH	108.4(9)	$p16 = 108.8(10)$
*p*17	τCSnCH	176.4(49)	$p17 = 176.9(50)$
*p*18	τCNCH	−176.7(38)	$p18 = -177.3(50)$

Table 3. Selected Distances, Amplitudes, and Amplitude Restraints for the GED Refinement of $Me_3SnONMe_2$

no.	atom pair	distance	amplitude	restraint
*d*1	Sn1−O2	2.006(3)	0.053(4)	
*d*2	Sn1−C6	2.148(4)	0.059(4)	$u2/u1 = 1.18(12)$
*d*3	Sn1−C7	2.146(3)	0.057(3)	$u3/u2 = 1.00(10)$
*d*4	O2−N3	1.468(6)	0.052(3)	
*d*5	N3−C4	1.452(4)	0.055(3)	$u5/u4 = 1.03(10)$
*d*6	C4−H9	1.103(4)	0.085(2)	
*d*7	Sn1···N3	2.73(14)	0.121(13)	0.101(20)
*d*8	O2···C6	3.175(23)	0.125(23)	0.132(26)
*d*9	O2···C7	3.363(14)	0.116(13)	0.121(24)
*d*10	O2···C4	2.340(13)	0.073(7)	0.065(13)
*d*11	C6···C7	3.631(17)	0.118(16)	0.136(27)
*d*12	C7···C8	3.501(22)	0.137(26)	0.135(27)
*d*13	C4···C5	2.338(28)	0.071(12)	0.066(13)
*d*14	Sn1···C4	3.754(13)	0.165(8)	0.141(28)
*d*15	N3···C6	4.451(19)	0.108(16)	0.117(23)
*d*16	N3···C7	3.488(24)	0.227(46)	0.237(47)
*d*17	C6···C4	5.297(23)	0.220(28)	0.199(40)
*d*18	C7···C4	4.848(23)	0.236(35)	0.255(51)
*d*19	C7···C5	3.913(32)	0.317(58)	0.316(63)
*d*20	Sn1···H15	2.724(17)	0.153(13)	0.124(25)
*d*21	N3···H9	2.082(13)	0.110(19)	0.101(20)
*d*22	Sn1···H9	3.614(31)	0.248(48)	0.248(50)
*d*23	Sn1···H10	4.556(21)	0.198(32)	0.188(38)
*d*24	Sn1···H11	4.240(38)	0.177(28)	0.181(36)

the program ASYM40.[13] These amplitudes and restraints are given in Table 3. The quality of the refinement can be assessed from the residuals in the molecular scattering curves (Figure 1) and the radial distribution curve (Figure 2). The final *R* factors were 0.088 for the long camera distance and 0.058 for the short camera distance data.

In the vapor the tin atom of $Me_3SnONMe_2$ is partially hypercoordinate, as is indicated by the pronounced deviation of its coordination geometry from an ideal tetrahedral surrounding (Table 1, Figure 3). The O−Sn−C angles of 99.6(10)° (in-plane angle) and 108.1(6)° (out-of-plane angle) reflect the sterical requirement of the approaching nitrogen donor center at a 2.731(14) Å distance to the tin atom. Such a deformation of the tin coordination is absent in triorganotinoxides, e.g., $[(PhCH_2)_3Sn]_2O$,[14] due to the inability of the tin center to form such interactions with geminal donor atoms. The Sn−O−N angle is 102.5(8)°, which is significantly compressed with respect to the related tin alkoxides (or distannoxanes),[15] which generally have Sn−O−C angles much greater than the tetrahedral angle. In the isopropoxytin fragment Me_2CHOSn, which is isoelectronic to the Me_2NOSn unit, the Sn−O−C angles are in the range of 128° (e.g., range of ∠Sn−O−C angles in *i*PrSn(O*i*Pr)$_3$ 126.6(5)−129.5(3)°).[16]

A small Sn−O−N angle similar to that in $Me_3SnONMe_2$ was found in the closely related compound cyclohexanonoximatotrimethylstannane (102.7°),[17] but here the tin atom adopts a typical trigonal bipyramidal coordination $OC_3Sn\cdots O$ due to an intermolecular Sn···O contact. There are no gas-phase structures of acyclic tin alkoxides,[18] which limits the possibility for further comparison.

The geometry predicted by ab initio calculations (MP2/DZ(P)) in general is in satisfying agreement with that refined on the electron scattering intensities (see Table 1 for comparison). Due to the different nature of the geometries (r_a for the experimental results, r_e for the calculated geometry), differences in interatomic distances have to be expected. Differences in angles are telling more about the suitability of the theoretical method applied. The Sn−O−N angle is predicted more than 3° smaller than found experimentally. This overestimation of the strength of the β-donor interaction has been observed for various Si−O−N systems before[19] and seems to indicate the use of a too small basis set. Similar deviations occur in the O−Sn−C angles, with the O−Sn−C(6) angle predicted 3.6° larger than determined experimentally. However, if three standard deviations are taken into consideration, the significant deviations in angles are all less than 1°, showing the calculations to be of sufficient quality although not perfectly reproducing the experimental facts.

Crystal Structure Determination. We were successful in growing a single crystal of liquid $Me_3SnONMe_2$ by in situ methods, which allows a comparison of the gas-phase and solid-state geometries and thus to identify phase-related changes. Upon incorporation of the $Me_3SnONMe_2$ molecules into the monoclinic

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crystal lattice, the coordination geometry at tin changes substantially due to the formation of an additional intermolecular Sn···O contact of 2.998(10) Å length (Figure 3B). A trigonal pyramid is made up of the atoms of the SnC_3O unit and is further weakly coordinated: intramolecularly to the nitrogen center and intermolecularly to the oxygen atom of a neighboring molecule. It is possible to describe this type of 4+2 coordination as a trigonal bipyramid, with one axial substituent replaced by two weak contacts. As the involvement of a β-donor center is uncommon and most of the sterically nonovercrowded triorganooxostannanes are aggregated in chains with the two oxygen atoms occupying the axial positions of a trigonal bipyramid, this coordination mode of tin in $Me_3SnONMe_2$ is unprecedented. It is also noteworthy that the primarily coordinate oxygen atom occupies an equatorial position of the trigonal pyramid, rather than an axial, as is commonly found in trimethylstannyl halides[20] and other SnC_3O_2 units. Only for compounds with chelating ligands have oxygen atoms been found in axial positions in the trigonal SnC_3O_2 bipyramids. Note that similar findings of axial site occupancy by the least electronegative ligands in trigonal bipyramidally coordinated compounds were recently reported also for tetraoxyphosphoranes[21] and pentacoordinate spirophosphoranes.[22]

Interestingly only two O−Sn−C angles are widened by slightly more than 8° as compared to the gas-phase structure to accommodate the additional Sn···O contact. The third angle O(2)−Sn(1)−C(6) is almost unchanged as is the Sn(1)−O(2)−N(3) angle; that is, the strength of the β-donor attraction between tin and nitrogen atoms is not altered by the change of the coordination geometry at the tin atom. This bears witness to the importance of even weak intermolecular contacts between donor centers and metal atoms for the structural chemistry of organometallic compounds.

Conclusion

The present ab initio, GED and X-ray diffraction study on $Me_3SnONMe_2$ provides insight into the stepwise hypercoordination at tin, first through an intramolecular β-donor interaction with the nitrogen center, then through an intermolecular Sn···O contact to give a total coordination number of six, but in a new type of coordination geometry. In this case two weak donor−acceptor interactions can act in combination in a way that resembles the action of one single donor ligand in five-coordinate tin compounds, which is not comparable to the established way of coordination sphere enlargement in tin chemistry. The large structural distortion of the $SnMe_3$ group upon formation of the weak Sn···O contact shows how limited our structural information is, if only a single phase is studied, and how carefully such results have to be interpreted. Only a combination of gas-phase and solid-state structural methods allows us to draw a more complete picture of hypercoordination.

Table 4. Correlation Matrix Elements (× 100) with Absolute Values Greater than 50 for the Least-Squares Refinement of the Gas-Phase Structure of $Me_3SnONMe_2$

	*p*4	*p*10	*p*11	*p*14	*u*7	*u*10
*p*5	−85					
*p*11		−52	100			
*p*12		54	−80			
*p*14		−63	50	100		
*p*15		−58		57		
*p*18		−59				
*u*13						−58
*u*20					−86	

Experimental Section

General Considerations. The experiments were carried out using a standard Schlenk line or a vacuum line with greaseless high-vacuum PTFE stopcocks, which is directly attached to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). All NMR spectra were recorded at 21 °C on a JEOL JNM-LA400 spectrometer in sealed tubes with C_6D_6 as a solvent directly condensed onto the sample from K/Na alloy.

(*N*,*N*-Dimethylaminoxy)trimethylstannane. *n*-Butyllithium (0.96 g, 15 mmol, 1.6 M in hexane) was added dropwise to a solution of 1.0 mL of *N*,*N*-dimethylhydroxylamine (0.86 g, 15 mmol) in 20 mL of pentane at −30 °C. The mixture was stirred for 1 h at ambient temperature, and then the solvents were removed in vacuo. The remaining salt was suspended in 20 mL of diethyl ether, and a solution of freshly sublimed trimethylchlorostannane (3.0 g, 15 mmol) in 15 mL of diethyl ether was added dropwise. The mixture was stirred for 1 h. All volatile products were condensed into a trap (−196 °C), and (*N*,*N*-dimethylaminoxy)trimethylstannane (1.01 g, 4.5 mmol, 30%) was isolated as a colorless liquid (mp = −85 °C) by fractionation through a series of cooled traps (−20, −78, −196 °C) with the product retained in the trap held at −78 °C.

^{1}H NMR: $\delta = 0.23, 2.50$. ^{13}C NMR: $\delta = -5.0$ (q, $^1J_{CH} = 30$ Hz), 51.9 (qq, $^1J_{CH} = 133$ Hz, $^3J_{CNCH} = 6$ Hz). ^{15}N{^{1}H} NMR: $\delta = -252$. ^{119}Sn NMR: $\delta = 106$ (dec, $^2J_{SnH} = 77$ Hz). MS(Cl): $m/z = 223$ (M^+), 163 ($M^+ - ONMe_2$). Anal. Calcd $Me_3SnONMe_2$ (223.89 g/mol): C 26.82, H 6.75, N 6.23. Found: C 26.44, H 6.62, N 6.19. IR: ν/cm^{-1} 2990 s (ν CH), 2957 s (ν CH), 2865 s (ν CH), 1142 m, 810 s, 770 s, 539 s.

Electron Diffraction Experiment. Electron scattering intensity data for $Me_3SnONMe_2$ were recorded on Kodak Electron Image film using the Oregon State University diffraction apparatus. Temperatures: inlet nozzle 52 °C, sample 34−48 °C. Diffraction experiments on CO_2 were performed concurrently for the purpose of wavelength calibration. Two data sets from three and four exposures at camera distances of 746.37 and 300.79 mm were recorded with wavelength 0.048942 Å and data ranges $s_{min} = 2.0$ to $s_{max} = 16.4$ and $s_{min} = 8.0$ to $s_{max} = 36.0$. Refinement: trapezoidal weighting function: $s_1 = 4.0$, $s_2 = 14.0$ and $s_1 = 10.0$, $s_2 = 30.8$, scale factors 1.050(10) and 1.130(21). Standard programs catered for the data reduction and least-squares refinement,[23] with the scattering factors established by Fink and co-workers.[24] The refined molecular parameters, their definition and the applied restraints, a list with selected interatomic distances including vibrational amplitudes and applied restraints, and elements of the correlation matrix are given in Tables 2, 3, and 4.

Crystal Structure Determination for $Me_3SnONMe_2$. A single cylindrical crystal (0.9 mm length, 0.3 mm diameter)

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was grown in situ by slowly cooling the melt sealed in a capillary after generation of a suitable seed crystal: crystal system monoclinic, space group *Pn*, $Z = 2$, $a = 7.354(1)$ Å, $b = 4.545(1)$ Å, $c = 13.720(1)$ Å, $\alpha = 90°$, $\beta = 95.55(1)°$, $\gamma = 90°$, $V = 456.4(1)$ Å^3 at 163(2) K, cell from 96 reflections (θ-range 19–24°), $2\theta_{\max} = 54°$, ω-scan, 1290 independent reflections. Diffractometer: Enraf-Nonius CAD4, Mo Kα radiation, graphite monochromator, Solution: Patterson methods.[25] Refinement: SHELXL97.[26] No absorption correction applied. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters; hydrogen atoms were calculated in idealized positions and refined with a riding model. Weight $= 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.75P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$. A total of 73 parameters, $R_1 = 0.0358$ for 1283 reflections with $F_o > 4\sigma(F_o)$ and $wR_2 = 0.1201$ for all data.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out on an IBM SP2 parallel computer using the Gaussian 94 program.[27] Geometry optimizations were performed at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the 3-21G*,[28–30] DZ(P)[31] basis sets, while the larger basis set was used for calculations at the MP2 level of theory. Vibrational frequency calculations were performed from analytic first and second derivatives up to the SCF/DZ(P) level of theory.

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Supporting Information Available: Tables with crystal data, atomic coordinates, and a full set of bond lengths and angles for the crystal structure determination of $Me_3SnONMe_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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