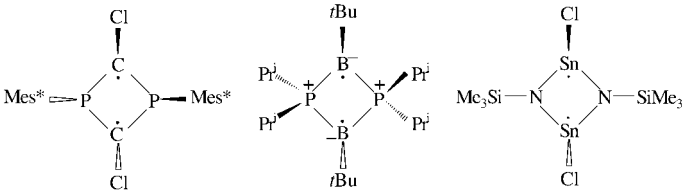
Main-Group Chemistry

A 1,3-Diaza-2,4-distannacyclobutanediide: Synthesis, Structure, and Bonding**

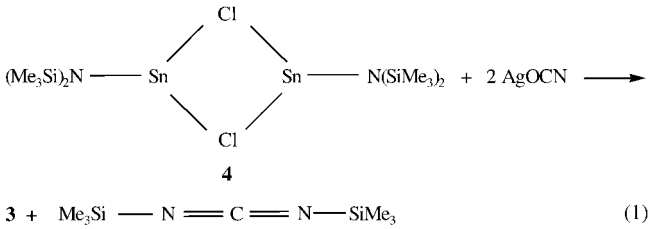
Hazel Cox, Peter B. Hitchcock, Michael F. Lappert,* and Luc J.-M. Pierssens*

There is much current interest in four-membered ring compounds containing heteroatoms that are isoelectronic with a cyclobuta-1,3-dienediide; the first thermally robust parent compound $\{[C(SiMe_3)]_4\}^{2-}$ was only reported in 2000.[1] Homocyclic "aromatic" inorganic compounds include $[E_4]^{2+}$ (E = S, Se, Te),[2] $(\{B(NMe_2)[B(NMe_2)_2]\}_2)^{2-}$,[3] $\{[Al(Cl)(NH_3)]_4\}^{2-}$,[4] and $[Ga_4\{C_6H_3(C_6H_2iPr_3\text{-}2',4',6')\text{-}2,6\}_2\text{-}1,3]^{2-}$.[5] Particular attention has focused on analogues with alternating heteroatoms that have a biradicaloid electronic structure and a feature of interest is the relative stability of the triplet and singlet states; an early example was the labile $[SN]_2$,[6a] a 6π-electron aromatic molecule.[6b] A trigger was the discovery by Niecke et al. of the modestly robust, diamagnetic 1,3-diphosphacyclobutane-2,4-diyl **1**,[7] which was followed by the related compounds $[C(Cl)P(TMP)]_2$,[8a] $[C(H)P(Mes^*)C(SiMe_3)P(Mes^*)]$,[8b] $[C(Cl)P(Mes^*)C(SiMe_3)P(Mes^*)]$,[8b] $[C(SiMe_3)P(Mes^*)C(AlMe_3)P(Mes^*)]^-$,[8c] $[C(Mes^*)P(Me)C(Mes^*)P(tBu)]$,[8d] $[C(SiMe_3)P(Mes^*)]_2$,[8e] and $\{[C(SiMe_3)P]_2\}^{2-}$.[8e] The Group 13/15 isoelectronic system was initially represented by the planar ring compound **2** of Bertrand et al.;[9] puckered ring analogues $[B^-(R)P^+R'_2]_2$ (R, R′ = Dur, *i*Pr; *t*Bu, Ph; Dur, Et; Ph, Ph) were subsequently described.[10a,b] The bonding in compounds of the type **1** and **2** has already been discussed.[11a,b]

Herein we report on the 1,3-diaza-2,4-distanna-cyclobutadienediide **3**. It is unprecedented on two counts: 1) previously reported three-coordinate tin compounds were ionic, free radical, or cluster [as in, for example, $SnCl_3^-$, $[Sn\{Si(Me)tBu_2\}_3]$ (radical or cation),[12a] $[Sn\{N(SiMe_3)_2\}_3]$,[12b] $[(SnR_2)_3Sn_2]$,[12c] $[(SnR_2)_3(SnR)_2Sn_2]$ (R = $C_6H_3Et_2$-2,6)],[12d] or one of the bonds was dative [as in **4**[12e] or $[\{Sn(CH(SiMe_3)_2)_2\}_2]$,[12f]]; 2) it is the first alternating heteroatom analogue of a cyclobuta-1,3-dienediide featuring a 5p-block element.



X-ray-quality crystals of the colorless, diamagnetic (4–298 K) compound **3** were isolated in modest yield from the reaction according to Equation (1); monitoring the reaction



(1)

by ^{119}Sn NMR spectroscopy showed that **3** was the major tin-containing product. It is assumed that Ag and CO_2 had been eliminated.

The above reaction was unexpected in the light of our prior observations on Sn(X)X′/AgY systems. Thus, we had

[*] Dr. H. Cox,[+] Dr. P. B. Hitchcock, Prof. M. F. Lappert, Dr. L. J.-M. Pierssens
Department of Chemistry, School of Life Sciences
University of Sussex, Brighton, BN1 9QJ (UK)
Fax: (+44) 1273 677196
E-mail: h.cox@sussex.ac.uk
m.f.lappert@sussex.ac.uk

[+] Computational studies.

[**] This work was supported by the European Commission (category 20 TMR fellowship for L.J.-M.P.) and EPSRC (Advanced research fellowship for H.C.; Time on the UK computational facilities, Columbus, at RAL for HC). We thank Dr. B. Mahieu (Mössbauer) and Drs. J. Keates and G. A. Lawless (CP-MAS-NMR) for spectral data.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200460039

found: 1) metathetical exchange with (a) **4** + AgOTf, to yield $[\{Sn[N(SiMe_3)_2](\mu\text{-}OTf)\}_2]$ ($OTf = OS(O)_2CF_3$),[13a] (b) SnX_2 + 2 AgOCN, to give $[\{Ag(\mu\text{-}X)\}_4]$ [$X = N(SiMe_3)_2$ or TMP];[13b] 2) oxidative addition to the SnX_2 by AgY to afford $[Sn\{CH(SiMe_3)_2\}_2Y_2]$ (Y = I or NCO) or $[Sn\{2,6\text{-}(NMe_2)_2C_6H_3\}_2Y_2]$ (Y = NCO or NCS);[13c] or (iii) adduct formation between $[Sn\{CH(SiMe_3)_2\}_2]$ + AgY → $[Ag(CN)\{Sn(CH(SiMe_3)_2)_2\}_2]_\infty$ or $[\{Ag(SCN)[Sn(CH(SiMe_3)_2)_2]_2(thf)\}_2]$.[13c] We attribute the driving force of the reaction of **4** with AgOCN to be the oxophilicity of silicon. A common intermediate in each of the above reactions is suggested to be a 1:1 X(X′)Sn→AgY adduct. For X = $N(SiMe_3)_2$, X′ = Cl, and Y = OCN, this leads to a redox reaction, yielding $Me_3SiN{=}C{=}NSiMe_3$ and $[Sn\{N(SiMe_3)\}Cl]$ (which dimerises→**3**) + Ag + Me_3SiOCN. The latter is believed to be transformed into bis(trimethylsilyl) carbodiimide + CO_2, possibly under the catalytic influence of silver. We note that the same carbodiimide has been obtained from $NaN(SiMe_3)_2$ and CO_2 and that Me_3SiOCN was suggested to have been an intermediate.[14]

The NMR spectra of **3** were recorded at 298 K both in solution ($PhMe/C_6D_6$: ^1H, ^{13}C, ^{29}Si, ^{119}Sn) and in the solid state by cross- polarization magic-angle spinning (CPMAS) spectroscopies (^{13}C, ^{29}Si, ^{119}Sn). The ^{119}Sn NMR chemical shift showed that the structure of **3** in $PhMe/C_6D_6$ was temperature-invariant in the range 298 ($\delta = -83$ ppm) to 183 K ($\delta = -104$ ppm). The ^{119}Sn chemical shift at 298 K was solvent-dependent: $\delta = -87$ (C_6D_6), −83 ($PhMe\text{-}C_6D_6$), −102 (CD_2Cl_2), −140 (thf/C_6D_6), −285 ppm ($HMPA/PhMe/C_6D_6$; HMPA is hexamethylphosphoramide). The CPMAS NMR chemical shifts (δ) were observed at lower frequencies than equivalent solution shifts ($PhMe/C_6D_6$; shown in parentheses): δ ^{13}C, −9 (2.62); ^{29}Si, −28 (22.0); ^{119}Sn, −17 (−84). Evidently the "solvent" donates to the Sn centers, consistent with ligating strengths decreasing in the sequence HMPA > thf > CD_2Cl_2 > PhMe > C_6H_6.

The ^{119}Sn-Mössbauer spectra of **3** and **4** were measured.[15] The values of the isomer shift were similar: 3.21 (**3**), 3.28 (**4**) $mm\,s^{-1}$, but those for the quadrupole splitting deviated significantly: 1.76 (**3**), 3.10 (**4**) $mm\,s^{-1}$; this result indicates that **3** and **4** have similar s-electron density at the Sn nucleus, but that their bonding differs.

The molecular structure of **3** shows it to be a monomer (Figure 1 a),[16] with long-range $(Sn\cdots Cl'')_2$ (3.29 Å) contacts (Figure 1 b) to a neighboring molecule.

The monomer has a planar centro-symmetric four-membered $\{(SnN)_2\}$ ring, with *trans*-silicon atoms only 6° out of this plane; the *trans*-chlorine ligands are disposed orthogonally. The Sn–Sn′ separation of 3.398 Å shows that there is no transannular bonding (see the data reported in reference [17] in which the Sn–Sn distance is 2.810 Å in α-tin). The endocyclic bond angles in **3**, as well as the mean Sn–N bond length, are similar to those in the tin(II) complex $[\{Sn^I(\mu\text{-}N{=}PPh_3)\}_2]$ (**5**): 78.3(1) and 101.7° at Sn and N, respectively, and 2.163(4) Å.[18] The Sn–Cl bond length in **3** is significantly shorter than that in the hypothetical chloro-analogue of **5** (about 2.60 Å, which is based on the ionic radii of Cl^- and I^-; l(Sn–I) in **5**, 2.9085(5) Å[18]). The Si–N, Sn–N, and Sn–Cl bond lengths in **3** may be compared with those in **4** (which has a planar $\{(SnCl)_2\}$ ring) of 1.729(3), 2.069(3), and 2.598(1) Å, respectively.[12c]

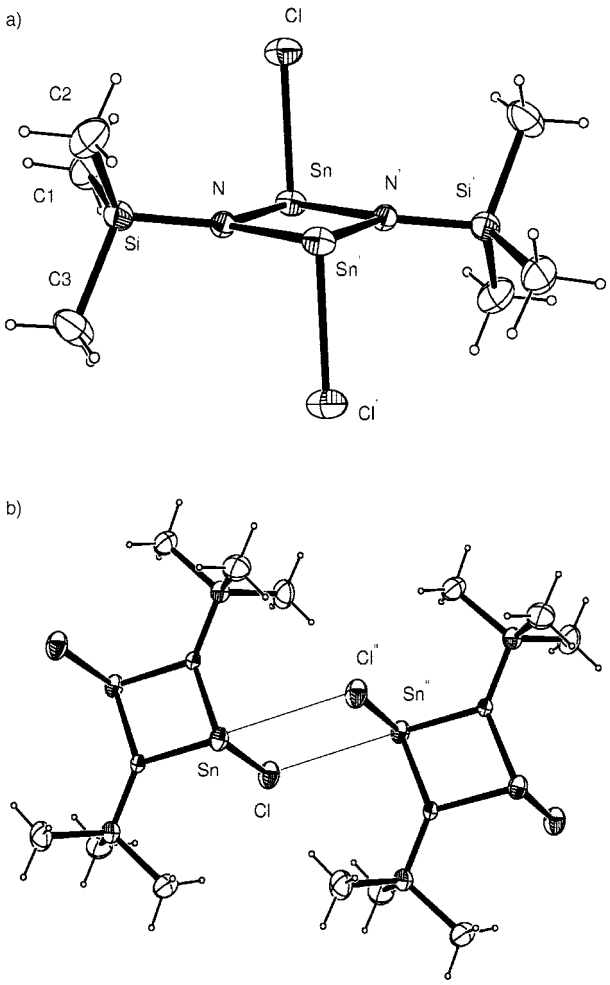
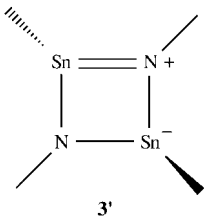


Figure 1. Structure of **3** (H atoms not shown; a) the monomer ; b) showing close Sn···Cl contacts to a neighboring molecule. Selected interatomic distances [Å] and angles [°]: Sn-N 2.120(3), Sn-N′ 2.179(3), Sn-Cl 2.470(2), Si-N 1.666(3), Si-Cl 1.859(5), Sn···Cl″ 3.29, Sn···Sn′ 3.398(1), N-Sn-N′ 75.57(14), N-Sn-Cl 88.71(10), N′-Sn-Cl 91.53(11), Si-N-Sn′ 130.2(2), Sn-N-Sn′ 104.43(14), Sn′-Sn-Cl 90.1

Electronic structure calculations were performed to answer the following questions posed by the experimental results: 1) what is the bonding in **3**, 2) what are the relative energies of the singlet and triplet states, and 3) what is the explanation for the discrepancies between the solid-state and solution NMR spectroscopic data?

The bonding: Geometry optimizations on **3** were performed,[19,20] and in no case was a Sn–Sn′ bond implicated and hence no buckling of the geometry was found. Each N atom and each Sn atom is three-coordinate leaving each N atom to donate two electrons to the ring and each Sn atom one electron. Thus the most appropriate description of **3** is as a pseudo six-π-electron four-center system.

The valence bond structure shown in **3′** (this is one of four resonance structures) is consistent with the calculated molecular orbitals in which three of the four π molecular orbitals, two almost nonbonding orbitals, and a bonding orbital, are



3'

filled and the antibonding orbital is empty.[2] These four orbitals arising from the four ring atoms consist of combinations of p orbitals on the N atoms (++ and +−) and combinations of sp^3 hybrids on the Sn atoms (again ++ and +−). Of these four orbitals, three are filled: the ++ combination of the tin atoms and both N-centred orbitals. This is in basic agreement with the schematic representation of the π orbitals of a delocalized π complex given by Niecke, et al. for **1**.[7]

Table 1 shows the percentage contribution of N and Sn atoms to the frontier orbitals. As the Sn atom is less electronegative than the N atom, the bonding orbitals have greater N character whilst the antibonding orbitals have greater Sn character.[21]

Table 1: Percentage contribution of nitrogen and tin atoms to the frontier orbitals.

Orbital	Energy [eV]	Atom	s	p_x	p_y	p_z
Lumo	−5.037	Sn	30.36	3.23	10.94	6.56
		N		5.30	16.90	11.40
Homo	−6.201	Sn				
		N		72.22		
Homo-1	−6.343	Sn	34.87	10.59	6.16	4.19
		N	1.80	1.48	1.97	4.62
Homo-2	−6.817	Sn		4.40		
		N		39.22	2.83	

The electronic and geometric structure: Initially, a single-point energy calculation was performed on the X-ray crystal structure (C_i symmetry). However, although SCF convergence was obtained, the filling of the orbitals was non-aufbau: the Sn-centred orbitals, although lower in energy than the lone pair on the nitrogen atoms (−5.81 and −5.67 eV, respectively), were not filled. It was possible to force the electrons into the Sn-centred orbital but this resulted in a destabilization of the Sn orbital and a destabilization of the molecule as a whole. Thus, a full geometry optimization of structure **3** was performed; the results are shown in Table 2, from which it is evident that the singlet state is favored by over 57 kJ mol^{-1} regardless of whether scalar relativistic effects are included or not.* This is in accord with the study by Schoeller, et al.[22] on substituted derivatives of 2,4-diphosphacyclobutane-diyl-1,3, which showed that σ-donating substituents at the phosphorus atom tend to increase the singlet–triplet energy separation.

Surprisingly, however, the optimized geometry differed substantially from the X-ray crystal structure. Selected geometric parameters are compared in the Supporting Information. The Sn–N and N′–Sn bond lengths are reasonably reproduced, within an error of 5%, although this is poor for current density functional methods. However, the Sn′-Sn-Cl bond angle is hugely inaccurate (119.4°) and this, along with the shortening of the Sn–Sn′ bond (3.06 Å), could be responsible for the deviations in the Sn-N-Sn′ and N-Sn-N′ angles (96.1° and 83.9°, respectively). It is pertinent to note that these optimized bond angles are comparable with the bond angles in the isoelectronic $\{C_2P_2\}$ system: P-C-P = 92.2° and C-P-C = 87.8°.[7]

Table 2: Calculated singlet–triplet energy difference (relativistic and nonrelativistic)

	Non-relativistic	Relativistic
Singlet (S) [eV]	−158.832	−158.097
Triplet (T) [eV]	−158.041	−157.505
Δ(T-S) [eV]	0.791	0.592
Δ(T-S) [kJ mol^{-1}]	76.3	57.1

To investigate these substantial differences, a series of single-point energies was performed on the experimental geometry with the Sn′-Sn-Cl bond angle varied at 10° intervals in the range 90° to 130°. A smooth continuous curve was produced with a minimum at 120°, from which a floppy Sn′-Sn-Cl bending mode was estimated. Two alternative methods (the semiempirical method PM3 and the hybrid functional B3LYP with a Gaussian effective core potential[20]) also predicted a Sn′-Sn-Cl bond angle of 120 ± 4°.

However, the X-ray crystal structure revealed close intermolecular Sn···Cl″ contacts (Figure 1b), which may be the cause of the constraint of the Sn′-Sn-Cl bond angle in the X-ray crystal structure.

It was noted by Janssen that out-of-plane distortions factor considerably in the stability of these electron-rich four-membered rings in the free molecule.[23] Thus, an extensive ab initio study was performed to establish whether inorganic six-π-electron four-membered rings (with and without substituents), are more stable than corresponding organic rings. It was concluded that the concept of resonance stabilization, in general, does not fully account for the geometric preferences of six-π-electron four-membered rings that contain atoms from the second-row of the periodic table. Other effects, including σ-bond strengths and especially energy-lowering out-of-plane distortions, are at least of equal importance. Zandwijk, et al.[24] had also shown that low-frequency out-of-plane vibrational modes of substituents on the ring are of major significance for the stability of these electron-rich, six-π-electron, four-membered rings.

NMR chemical-shift calculations: Calculations of the chemical shifts of both the geometry-optimized structure and the X-ray crystal structure were performed. It was proposed that if the electronic-structure calculations were correct and the true relaxed geometry would be that predicted by theory, then this structure would be the most probable in solution in an inert solvent. Thus, the constrained (X-ray) crystal structure would produce different chemical shifts to those of the latter. To test this proposition, NMR chemical shifts were calculated for both the X-ray crystal structure

* Note that all further discussion will refer to the ADF scalar relativistic singlet geometry.

(single-point energy calculations SPE) and the possible solution (monomeric) structure (optimized geometry).

The calculated relative chemical shifts are compared with the experimental data in Table 3. In each case, the total isotropic shielding constant for each atom in the molecule was calculated and the average was compared to that of the corresponding shift of $SiMe_4$ (for C, H, and Si) and to that of $SnMe_4$ (for Sn) to compare with the experimental relative shifts.

Table 3: Comparison of calculated and experimental chemical shifts

	Average isotropic chemical shifts (ppm)			
		Experimental	Calculated	
	Solid	Solution/C_6D_6/298 K	Expt. geom.	Opt. Geom.
^{13}C	−9	2.62	−3.1	10.8
^{1}H		0.09	−5.6	0.5
^{29}Si	−28	22	−176.1	10.7
^{119}Sn	−17	−84	641.2	740.6

A negative shift indicates that there is more shielding, and a positive number indicates that there is less shielding, in the specified molecule than in the reference molecule. Thus, as expected, there is more shielding in the solid (as evinced by the SPE calculation) than in the solution (to be compared with the optimized geometry). With the exception of Sn, in each case the relative shift follows the trend of the experimental data, and in the case of ^{13}C the shifts are within 8 ppm of the experimental values. This favorable comparison gives credence to the assumption that the relaxed (geometry optimized) structure is indeed the "free" structure that appears in solution, and that in the solid state, intermolecular forces play an important role in fixing the Cl atoms in optimum positions for the interaction with neighboring Sn atoms.

In summary, we have presented the synthesis of the first 1,3-diaza-2,4-distanna-cyclobutanediide [$\overline{N(SiMe_3)\text{-}Sn(Cl)N'(Si'Me_3)Sn'Cl'}$] (**3**) by the unusual reaction between $[Sn\{N(SiMe_3)_2\}(\mu\text{-}Cl)]_2$ and AgOCN. Compound **3** was shown to be diamagnetic in the crystal and in solution. Crystalline **3** has a planar four-membered $\{(SnN)_2\}$ ring with the *trans*-chlorine ligands orthogonal to this plane. There are long range $(Sn\cdots Cl)_2$ contacts between neighboring molecules. The CPMAS NMR ^{13}C, ^{29}Si, and ^{119}Sn chemical shifts were observed at lower frequency than those recorded in PhMe/C_6D_6; and the ^{119}Sn signal was particularly sensitive to solvent, the frequency decreasing in the sequence PhMe/C_6D_6 < CD_2Cl_2 < thf/C_6D_6 ≪ HMPA/PhMe/C_6D_6, attributed to an interaction from the "solvent" donor to the tin atom, probably at the limit disrupting the virtual dimer in the crystal. The computational studies show that the singlet ground state is substantially favored over the triplet. The optimized geometry showed considerable disparity between the calculated and the experimentally determined Sn′-Sn-Cl angle, which is attributed to the constrained geometry of the monomer (Figure 1 a) and does not take into account the intermolecular contacts with the neighboring molecule (Figure 1 b). Calculated ^{13}C- and ^{29}Si-NMR chemical-shift differences as between the solid-state and the PhMe/C_6D_6 solution qualitatively reproduce the experimental observations. Note added in proof: the compound $[\{Ge(R)N(SiMe_3)\}_2]$ [R = $C_6H_3(2,6\text{-}i\text{Pr}_2\text{-}C_6H_3)C_6H_3$] was recently described.[25]

Experimental Section

All manipulations were carried out under vacuum or argon by using Schlenk techniques.

Silver cyanate (2.47 g, 16.5 mmol) was added to a stirring solution of $[Sn\{N(SiMe_3)_2\}(\mu\text{-}Cl)]_2$ (5.18 g, 8.2 mmol) in diethyl ether (150 mL) at room temperature. The brown, cloudy reaction mixture was stirred in darkness for about 16 h. A brown–grey precipitate was removed by filtration and the filtrate concentrated under vacuum. A second filtration and storage of the filtrate at −5 °C yielded a beige solid, which was extracted with refluxing toluene (50 mL). The colorless extract yielded colorless microcrystals of **3** (0.96 g, 24 %), mp 53–56 °C (decomp), which on recrystallization from benzene gave large colorless plates of X-ray quality.

NMR (PhMe + C_6D_6, 303 K): ^{1}H, $\delta = 0.09$ ppm; $^{13}C\{^{1}H\}$, $\delta = 2.62$ ppm; $^{29}Si\{^{1}H\}$, $\delta = 22.0$ ppm; $^{119}Sn\{^{1}H\}$, $\delta = -84$ ppm. CPMAS-NMR: ^{13}C, $\delta = -9$ ppm; ^{29}Si, $\delta = -28$ ppm, ^{119}Sn, $\delta = -17$ ppm. ^{119}Sn Mossbauer (90 K): IS, 3.21 mm s^{-1}; QS, 1.76 mm s^{-1}.

N,*N*′-Bis(trimethylsilyl)carbodiimide, bp 158–162 °C; MS (70 eV, EI): *m*/*z* (%): 180 (10) [M^+], 171 (100) [M−Me]$^+$; IR: $\tilde{\nu}_{max} = 2190$ cm^{-1}, was isolated among the volatile products.

Received: March 18, 2004 [Z460039]

Keywords: density functional calculations · heterocycles · radicals · tin

[1] a) A. Sekiguchi, T. Matsuo, H. Watanabe, *J. Am. Chem. Soc.* **2000**, *122*, 5652; b) T. Matsuo, A. Sekiguchi, *Bull. Chem. Soc. Jpn.* 2004, 77, 211.
[2] See R.J Gillespie, *Chem. Soc. Rev.* **1979**, *8*, 315.
[3] W. Mesbah, C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2003**, *115*, 1758; *Angew. Chem. Int. Ed.* **2003**, *42*, 1717.
[4] a) X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, L. S. Wang, *Science* **2001**, *291*, 859; b) A. E. Kuznetsov, A. I. Boldyrev, *Inorg. Chem.* **2002**, *41*, 3596.
[5] B. Twamley, P. P. Power, *Angew. Chem.* **2000**, *112*, 3648; *Angew. Chem. Int. Ed.* **2000**, *39*, 3500.
[6] a) C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, A. J. Heger, *J. Am. Chem. Soc.* **1975**, *97*, 6358; b) Y. Jung, T. Heine, P. v. R. Schleyer, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 3132.
[7] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schoeller, *Angew. Chem.* **1995**, *107*, 640; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 555.
[8] a) O. Schmidt, A. Fuchs, D. Gudat, M. Nieger, W. Hoffbauer, E. Niecke, W. W. Schoeller, *Angew. Chem.* **1998**, *110*, 995; *Angew. Chem. Int. Ed.* **1998**, *37*, 949; b) E. Niecke, A. Fuchs, M. Nieger, *Angew. Chem.* **1999**, *111*, 3213; *Angew. Chem. Int. Ed.* **1999**, *38*, 3028; c) E. Niecke, A. Fuchs, M. Nieger, O. Schmidt, W. W. Schoeller, *Angew. Chem.* **1999**, *111*, 3216; *Angew. Chem. Int. Ed.* **1999**, *38*, 3031; d) H. Sugiyama, S. Ito, M. Yoshifuji, *Angew. Chem.* **2003**, *115*, 3932; *Angew. Chem. Int. Ed*, **2003**, *42*, 3802; e) M. Sebastian, M. Nieger, D. Szieberth, L. Nyulászi, E. Niecke, *Angew. Chem.* **2004**, *116*, 647; *Angew. Chem. Int. Ed*, **2004**, *43*, 637.
[9] D. Scheschkewitz, H. Amii, H. Gornitzka, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880.
[10] a) W. W. Schoeller, A. Rozhenko, D. Bourissou, G. Bertrand, *Chem. Eur. J.* **2003**, *9*, 3611; b) D. Scheschkewitz, H. Amii, H.

Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem.* **2004**, *116*, 595; *Angew. Chem. Int. Ed.* **2004**, *43*, 585.

[11] a) R. A. J. Janssen, *J. Phys. Chem.* **1993**, *97*, 555b) H. Grützmacher, F. Breher, *Angew. Chem.* **2002**, *114*, 4178; *Angew. Chem. Int. Ed.* **2002**, *41*, 4006.

[12] a) A. Sekiguchi, T. Fukawa, V. Ya. Lee, M. Nakamoto, *J. Am. Chem. Soc.* **2003**, *125*, 9250; b) A. Hudson, M. F. Lappert, P. W. Lednor, *J. Chem. Soc. Dalton Trans.* **1976**, 2369; c) L. R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* **1989**, *111*, 6454; d) L. R. Sita, I. Kinoshita, *J. Am. Chem. Soc.* **1992**, *114*, 7024; e) R. W. Chorley, P. B. Hitchcock, B. S. Jolly, M. F. Lappert, G. A. Lawless, *J. Chem. Soc. Chem. Commun.* **1991**, 1302; f) P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1976**, 2268.

[13] a) P. B. Hitchcock, M. F. Lappert, G. A. Lawless, D. M. de Lima, L. J.-M. Pierssens, *J. Organomet. Chem.* **2000**, *601*, 142; b) P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *Chem. Commun.* **1996**, 1189; c) P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *Organometallics* **1998**, *17*, 2686.

[14] a) U. Wannagat, J. Pump, H. Bürger, *Monatsh. Chem.* **1963**, *94*, 1013; b) U. Wannagat, H. Kuckertz, C. Krüger, J. Pump, *Z. Anorg. Allg. Chem.* **1964**, *333*, 54.

[15] B. Mahieu, L. J.-M. Pierssens, unpublished work.

[16] X-ray analysis data for **3**: $C_6H_{18}Cl_2N_2Si_2Sn_2$: $a = 6.791(6)$, $b = 6.872(3)$, $c = 9.414(4)$ Å, $\alpha = 84.62(3)$, $\beta = 85.28(5)$, $\gamma = 65.58(6)°$, $Z = 1$, $M_r = 482.7$; triclinic, space group $P\bar{1}$ (No.2), $V = 397.8(4)$ Å^3, $\mu(Mo_{K\alpha}) = 3.60$ mm^{-1}, $T = 173(2)$ K, 2325 independent reflections [$R(\text{int}) = 0.008$], reflections with $I > 2\sigma(I)$ 2155. The structure was solved by direct methods and refined to F^2 anisotropically, the H atoms were included in a riding mode. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.039$, $wR_2 = 0.104$; R indices (all data): $R_1 = 0.043$, $wR_2 = 0.108$. CCDC-233571 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[17] J. Thuoliss, A. R. Davey, *Nature* **1954**, *174*, 1011.

[18] S. Chitsaz, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1670.

[19] Calculations were performed by using Slater-type orbitals with the BP86 functional as implemented in ADF2000.02 (E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41). The numerical integration procedure applied for the calculations is that of G. te Velde and E. J. Baerends (*J. Comput. Phys.* **1992**, *99*, 84). A triple-ξ Slater-Type-Orbital (STO) basis set with a polarization function was used for describing the valence electrons of Sn (4d 5s 5p), N (2s 2p), Cl (3s 3p) and Si (3s, 3p). A double-ξ STO basis set was used for C (2s 2p) and H, augmented by an extra polarization function. Electrons in lower shells were treated with the frozen core approximation. Energies of **3** were calculated by using the local density approximation (LDA) (S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200). The non-local exchange of A. D. Becke (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 2398) and the non-local correlation correction of J. P. Perdew (J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822) and the scalar relativistic correction (T. Ziegler, V. Tschinke, E. J. Baerends, J. G. Snijders, W. J. Ravenek, *J. Phys. Chem.* **1989**, *93*, 3050) were applied to the LDA density. NMR chemical shifts were calculated by using the implementation by G. Schreckenbach, T. Ziegler, *J. Phys. Chem.* **1995**, *99*, 606.

[20] For confirmation, calculations were carried out by using the Gaussian 98 program. (Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.). The geometries were optimized by using the B3LYP functional and the effective core potential LANL2DZ.

[21] A. J. Bridgman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc. Dalton Trans.* **2001**, 2095.

[22] W. W. Schoeller, C. Begemann, E. Niecke, D. Gudat, *J. Phys. Chem. A* **2001**, *105*, 10731.

[23] R. A. J. Janssen, *J. Phys. Chem.* **1993**, *97*, 6384.

[24] G. van Zandwijk, R. A. J. Janssen, H. M. Buck, *J. Am. Chem. Soc.* **1990**, *112*, 4155.

[25] C. Cui, M. Brynda, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2004**, *126*, 6510.