

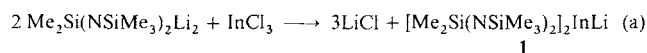
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[9] The physical and chemical properties of **1** described by Schnöckel et al. are slightly different from those found by us.
[10] A single-crystal X-ray structure analysis at -120°C confirms the existence of **1**. Crystal data: $C_{40}H_{60}Al_4$, $M_r = 648.85$, triclinic, space group $P\bar{1}$, $a = 10.759(4)$, $b = 10.913(3)$, $c = 18.027(5)\text{Å}$, $\alpha = 82.94$, $\beta = 81.82$, $\gamma = 66.88$, $V = 2116.6(12)\text{Å}^3$, $Z = 2$.
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A Molecular Heterometal Amide with High Molecular Dynamics: Does the Lithium Atom Orbit?*

By Michael Veith,* Michael Zimmer, and Stefan Müller-Becker

Dedicated to Professor Ulrich Wannagat on the occasion of his 70th birthday

Whilst the motion of lithium atoms in solids, such as, for example, in solid Li_3N , has been thoroughly investigated and is generally accepted,^[1] many indications, but little concrete evidence for such a motion in molecules exists, in spite of much effort (see e.g. ref. [2]). Here we report on our studies of the heterometal amide $[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2]_2\text{InLi}$ (**1**), an example of a class of molecular complexes that has still not been investigated in detail.^[3] Compound **1** can easily be prepared according to Equation (a).



According to the X-ray crystal structure analysis,^[4] (Fig. 1) the trivalent indium and the monovalent lithium atom in **1** are bound close together in a tricycle of four-membered rings ($\text{In} \cdots \text{Li} = 2.748(9)\text{Å}$). The ^1H , ^{13}C , ^{15}N , and ^{29}Si NMR spectra of **1** at room temperature in toluene (see Experimental Procedure) are not consistent with the molecular structure represented in Figure 1. Thus, only one reso-

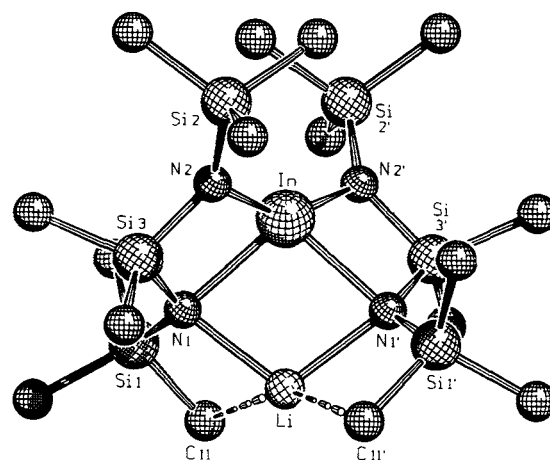


Fig. 1. Molecular structure of **1**. Some important distances [Å] and angles [°]: $\text{N1}-\text{In}$ 2.223(3), $\text{N2}-\text{In}$ 2.055(3), $\text{N1}-\text{Li}$ 2.064(6), $\text{N1}-\text{Si1}$ 1.720(3), $\text{N1}-\text{Si3}$ 1.737(3), $\text{N2}-\text{Si2}$ 1.714(3), $\text{N2}-\text{Si3}$ 1.717(3), $\text{Li} \cdots \text{C11}$ 2.635(7); $\text{N1}-\text{In}-\text{N1}'$ 95.2(1), $\text{N2}-\text{In}-\text{N2}'$ 148.4(1), $\text{N1}-\text{In}-\text{N2}$ 76.2(1), $\text{N1}-\text{In}-\text{N2}'$ 127.3(1), $\text{N1}-\text{Li}-\text{N1}'$ 105.4(3).

nance signal is found for both the dimethylsilylene and trimethylsilyl groups in the ^{13}C NMR spectrum, whereas a double set of signals would be expected because of the low C_2 symmetry of the molecule (the twofold axis passes through the two metal atoms).

If a toluene solution of **1** is cooled, ^1H , ^{13}C , and ^{29}Si NMR spectra are obtained at lower temperature (as an ex-

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ample ^{13}C NMR spectra are reproduced in Fig. 2) with twice (or one and a half times) the number of signals as expected from the crystal structure. An activation energy of 44.3 kJ mol^{-1} can be determined from analysis of the coalescence temperature and the signal splitting derived from heteronuclear NMR spectra.^[5] The signal of the trimethylsilyl groups shifted to high field shows unusual behavior: With decreasing temperature a selective broadening is found, a phenomenon that can be explained by a rotation barrier about the Si–N bond, which is also found for trimethylsilyl groups of other molecules.^[6] On examination of the solid-state molecular structure (Fig. 1), it becomes apparent that the reason for the rotational barrier of this one trimethylsilyl group is due to lithium methyl contacts (dotted lines); at the same time, this finding allows the assignment of the resonance signals.

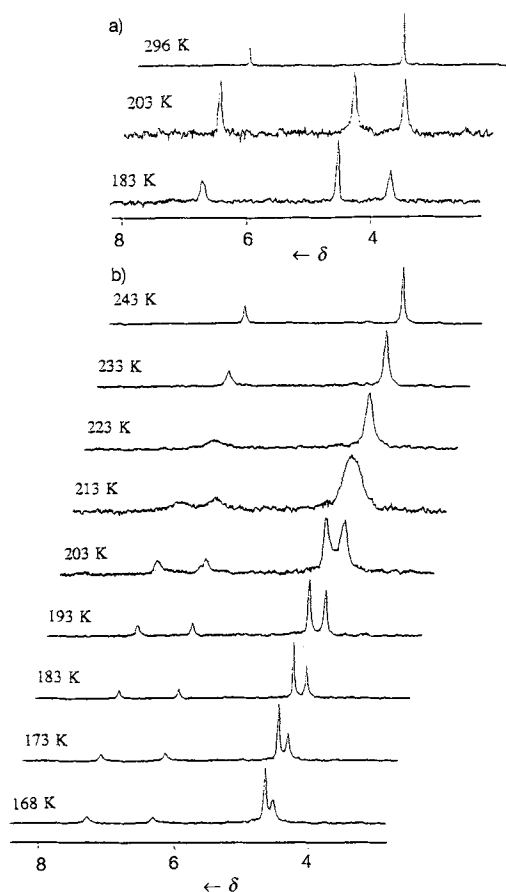


Fig. 2. ^{13}C NMR spectra (50.3 MHz) of **1** a) in hexane at three temperatures and b) in toluene between 243 and 168 K.

Temperature-dependent measurements of the spin-lattice relaxation T_1 of the ^7Li isotope give the expected curve shape on plotting the graph with a minimum at 203 K. Analysis of the Arrhenius plot gives a value of 13.8 kJ mol^{-1} for the high-temperature end; this value is typical for methyl and trimethylsilyl rotations about threefold axes.^[7] It implies several coupled migrations in the molecule and suggests that the lithium atom is involved in these.

The series of temperature-dependent ^{13}C NMR spectra shown in Figure 2 were also repeated for significantly higher and lower concentrations of **1** in toluene (about five- and tenfold), without any observable changes occurring in the

comparable spectra. We conclude from this that an intermolecular process is unlikely to be the reason for the observed spectra at room temperature. Clearly all findings are consistent with a higher “average” point symmetry of the molecule at room temperature. Instead of the $C_2(2)$ symmetry in the crystal lattice, in which the molecules are exclusively bound by van der Waals contacts, $D_{2d}(42m)$ symmetry must be ascribed to the whole molecular unit in solution. The increase in symmetry is clearly determined by dynamic phenomena in which lithium, as the lightest of the atoms (if one neglects the covalently bonded hydrogen atoms), plays a special role.

After exclusion of an intermolecular process only an intramolecular and a dissociative mechanism remain. We consider the formation of an ion pair of the type $\text{Li}^+ \{[\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{In}]^-\}$ in solution, which would involve an anion with D_{2d} symmetry, to be unlikely in toluene due to the large amount of energy required to break the Li–N bond and to the relatively low expected solvation energy. Furthermore, analogous ^1H and ^{13}C NMR spectra with few signals are obtained when **1** is dissolved in nonpolar hexane (Fig. 2 a). Here too, a splitting of the Me_3Si signal is observed at lower temperatures. Thus, identical activation energies (44.3 kJ mol^{-1}) to those in toluene are determined. In contrast to the spectra in toluene (dipole moment: 0.36 D), in hexane the signal for the dimethylsilyl group does not split up to the freezing point of the solvent. The molecule must therefore retain a residual mobility in nonpolar solvents, which is suppressed in polar toluene, because the static molecule itself is strongly dipolar.

We believe that the observed spectra can best be explained by an intramolecular dynamic process. In this context, two processes can be discussed: One possibility is an essentially oscillating motion of the lithium atom in an orbit around the center of the molecule, which can be described as an indium-centered N_4 -bisphenoid (Fig. 3). A conceivable alternative

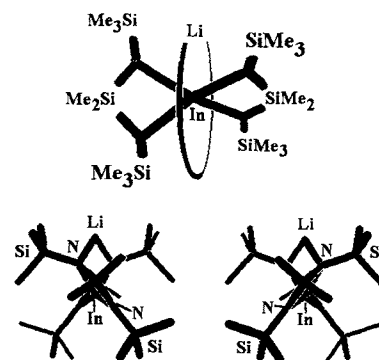


Fig. 3. Top: An intramolecular model for the “lithium migration”. Bottom: The two structures of **1** found in the crystal (view orthogonal to the upper drawing). Their interconversion could explain the “residual mobility” of **1** in hexane.

would be that the $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2$ ligands move disrotatory around a pseudo Si3–Si3' axis (see Fig. 1); thus, the two metal atoms remain in their positions. Molecular dynamic model calculations^[8] and the consideration of group vibrations show, however, that both processes are basically the same and that only a different reference point has been chosen. Moreover, this model explains the nature of the above-mentioned residual mobility in hexane below 220 K. In this

case the lithium atom is now only in contact with two nitrogen atoms at which inversions take place. In the extreme case this leads to the two molecules represented in the lower half of Figure 3. These are enantiomers and both crystallize together (in the crystal structure they are connected by inversion centers).

Solid-state NMR spectra were also obtained for **1**. The central line of the Magic Angle Spinning (MAS) ^7Li NMR spectrum (77.7 MHz) of **1** at room temperature consists of two components: a broad resonance signal showing the typical quadrupolar splitting obtained in MAS experiments for quadrupolar nuclei^[9] (586 Hz), as well as a quasi-superimposed relatively sharp resonance with a half-width of about 120 Hz. If a second spectrum of the same sample is recorded at 116.5 MHz, the peak separation of the outer peaks is reduced, which is consistent with a quadrupolar effect. The sharp resonance signal at 296 K combines about 8% of the total intensity including the side bands and should be due to "readily mobile" lithium atoms.^[10] Whether the signal is due to a partial "lithium dynamic" as a result of lattice vibrations in **1** or whether it is caused by a small amount of some impurity still needs to be clarified by further investigations.

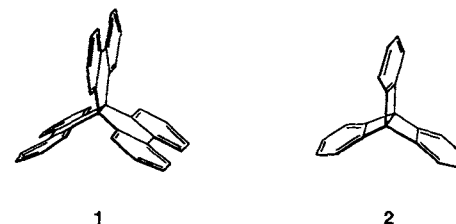
Experimental Procedure

Indium chloride (0.7 g, 3.2 mmol) in diethyl ether (5 mL) was added to two molar equivalents of $\text{Me}_2\text{Si}(\text{NSiMe}_3)_2\text{Li}_2$ [11] in *n*-hexane (25 mL) and stirred for 6 h at room temperature. The suspension was filtered and the solution concentrated; during this process crystals of the ether adduct of **1** formed. The ether was eliminated from the compound in the subsequent sublimation (70–80 °C bath temperature/ 10^{-3} Torr) and 1.37 g (73%) of **1** were obtained as colorless crystals (m.p. 142 °C). Correct analyses and mass spectra. Chemical shifts of **1** in solution (200 MHz [D_8]toluene, 296 K, TMS): ^1H NMR: $\delta = 0.18$ (s, 36H, SiMe_3), 0.33 (s, 12H, SiMe_2); ^{13}C NMR ([D_8]toluene): $\delta = 4.2$ (s, 12C, SiMe_3), 6.6 (s, 4C, SiMe_2); ^{13}C NMR (hexane): $\delta = 3.9$ (s, SiMe_3), 6.4 (s, SiMe_2); ^{29}Si NMR: $\delta = -0.55$ (s, SiMe_2), -5.80 (s, SiMe_3); ^{15}N NMR (CH_3NO_2 ext.): $\delta = -308.5$ (s, $b_{1,2} = 10$ Hz); ^7Li NMR (ext. standard: $\text{LiCl}/\text{D}_2\text{O}$): $\delta = 3.0$ (s, $b_{1,2} = 5.7$ Hz). Chemical shifts of **1** in the solid state (200 MHz, 296 K, sec. standard: adamantane, TMS = 0), ^{13}C NMR: $\delta = 5.8$ ($b_{1,2} = 85$ Hz), ^7Li NMR (ext. standard: LiCl): $\delta = 1.0$ [12].

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1

2

The hexacyclic hydrocarbon **7** is the key compound in the synthesis of the desired propellanes and can be prepared in one step from acenaphthylene and 1,8-diiodonaphthalene by a palladium-catalyzed annelation.^[5] Formation of the [3.3.3]propellane **3**, which contains a threefold symmetry axis, was achieved in a single step by way of a second palladium-catalyzed annelation, this time with monoiodonaphthalene **5** (Scheme 1).^[6] The use of 1,8-diiodonaphthalene in

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[4] Crystal data for **1**: monoclinic, space group $C2/c$, $a = 11.814(9)$, $b = 16.986(20)$, $c = 16.719(20)$ Å, $\beta = 104.63(9)^\circ$, $V = 3246$ Å³, $Z = 4$, $\mu = 9.14$ cm⁻¹. Siemens-AED2 diffractometer, ω - θ scan, 2109 reflections of which 81 with $F_0 < MK > 2\sigma_F$, $2\theta_{\text{max}} = 45^\circ$; measurement temperature: 293 K. Structure solution by Patterson methods, H atom positions idealized ($C-H = 1.08$ Å, $H-C-H = 109.5^\circ$); 153 parameters (all non-hydrogen atoms with anisotropic temperature factors), $R = 0.033$ ($R_w = 0.038$; weighting scheme: $w = 1.00/(\sigma^2 + 0.006384 F^2)$). Maximum and minimum residual electron density: 0.27 and -0.80 e Å⁻³. Programs used: SHELX 86 [13] and SCHAKAL [14]. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-57682, the names of the authors, and the journal citation.

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Palladium-Catalyzed Arylation of Tetrasubstituted Double Bonds: A Simple Synthesis of Annelated Propellanes**

By Gerald Dyker,* Jutta Körning, Peter G. Jones, and Peter Bubenitschek

As a result of their special topology propellanes have stimulated a multitude of syntheses and investigations into their chemical and physical properties.^[1] The benzoannellated [4.4.4]propellane **1**^[2] is of particular interest in this respect, as in this compound a hexaarylethane^[3] structure is stabilized by triple clamping. However, the increased ring strain caused by reducing the size of the propellane rings can cause destabilization of the central single bond to reoccur. The highly strained dehydrotriptycene **2**—a [2.2.2]propellane—represents an extreme example and so far all attempts at its synthesis have been unsuccessful.^[4] We report here on a rational entry to aryl-annellated [3.3.*n*]propellanes with $n = 2, 3$, and 4.

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