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Notes

Structure of the 2-Lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane–*N*,*N*,*N′*,*N′*-Tetramethylethylenediamine Adduct

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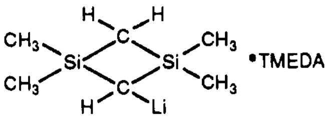
Summary: The solid-state structure of the title compound has been determined by X-ray diffraction. The lithium atom is tetracoordinate with short bonds to one carbon atom and two nitrogen atoms of the TMEDA ligand and a weaker (2.33-Å) intermolecular interaction with a hydrogen atom of a CH_3 group on the silicon atom of an adjacent molecule.

During the course of our work on polycarbosilanes,[1] we investigated the metalation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane by *t*-BuLi·TMEDA ($Me_2NCH_2CH_2NMe_2$ = TMEDA) and the reactivity of the resulting 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane–*N*,*N*,*N′*,*N′*-tetramethylethylenediamine reagent (1).[2] In an extension of this research, we have studied the NMR spectra of 2 and have determined the solid-state structure of the adduct by X-ray diffraction.



1

Results and Discussion

A solution of 1 was prepared by reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with a slight excess of *tert*-butyllithium in hexane in the presence of an excess of TMEDA. This solution was concentrated, a small amount of benzene was added, and the resulting solution was cooled to 3 °C. The white solid that crystallized was 2 on the basis of NMR data and the X-ray structural study.

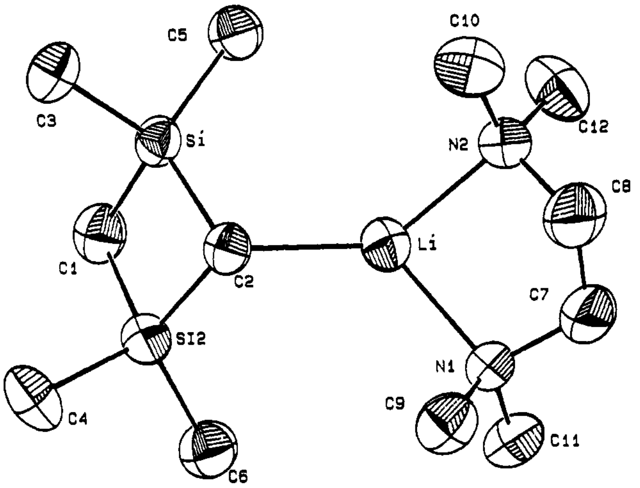


Figure 1. ORTEP diagram of 1, with hydrogen atoms excluded.

Table I. Intramolecular Distances (Å) Involving the Non-Hydrogen Atoms for 1

Si(1)–Si(2)	2.558 (3)	N(1)–C(9)	1.444 (7)
Si(1)–C(1)	1.876 (7)	N(1)–C(11)	1.464 (8)
Si(1)–C(2)	1.791 (6)	N(1)–Li	2.09 (1)
Si(1)–C(3)	1.876 (6)	N(2)–C(8)	1.455 (8)
Si(1)–C(5)	1.869 (6)	N(2)–C(10)	1.467 (8)
Si(2)–C(1)	1.852 (6)	N(2)–C(12)	1.451 (8)
Si(2)–C(2)	1.814 (6)	N(2)–Li	2.08 (1)
Si(2)–C(4)	1.874 (6)	C(2)–Li	2.10 (1)
Si(2)–C(6)	1.871 (8)	C(7)–C(8)	1.42 (1)
N(1)–C(7)	1.465 (8)	C(1)–C(2)	2.589 (8)

Table II. Selected Intermolecular Distances (Å) and Angles (deg) for 1[a]

	distance		angle
Li–H(4)*	2.327	H(4)*–Li–C(2)	116.0
Li–C(3)*	3.15 (1)	H(4)*–Li–N(1)	87.0
Li–Li**	5.76 (2)	H(4)*–Li–N(2)	102.1
		H(4)*–Li–C(3)*	12.5

[a] A single asterisk indicates atoms from the nearest next molecular unit in the polymeric structure. Two asterisks indicate the only Li found within 6.0 Å.

An ORTEP representation of the 1:1 TMEDA adduct of 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane (1) is shown in Figure 1. On the basis of its Li–C and Li–N interactions, this organolithium compound is monomeric with an apparently tricoordinate lithium atom. Some known monomeric organolithium species contain tetracoordinate lithium: $(Me_3Si)_2CHLi·(Me_2NCH_2CH_2)_2NMe$;[3] $(Me_3Si)(Me_2P)CHLi·(Me_2NCH_2CH_2)_2NMe$;[4] $C_6H_5Li·(Me_2NCH_2CH_2)_2NMe$;[5] $(C_6H_5)_3CLi·Me_2NCH_2CH_2NMe_2$;[6] lithiofluorene·$2N(CH_2CH_2)_3CH$.[7] A few contain tricoordinate lithium atoms: $(C_6H_5)_2PCH_2Li·TMEDA$;[8] $(C_6H_5Me_2Si)_3CLi·THF$.[9] In the latter, in addition to the

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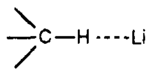
Table III. Intramolecular Bond Angles (deg) Involving the Non-Hydrogen Atoms for 1

	angle		angle
Si(2)–Si(1)–C(1)	46.3 (2)	C(7)–N(1)–C(11)	107.8 (5)
Si(2)–Si(1)–C(2)	45.2 (2)	C(7)–N(1)–Li	102.8 (5)
Si(2)–Si(1)–C(3)	117.5 (2)	C(9)–N(1)–C(11)	108.3 (5)
Si(2)–Si(1)–C(5)	139.8 (5)	C(9)–N(1)–Li	104.8 (4)
C(1)–Si(1)–C(2)	89.8 (3)	C(11)–N(1)–Li	120.6 (5)
C(1)–Si(1)–C(3)	110.7 (3)	C(8)–N(2)–C(10)	107.1 (6)
C(1)–Si(1)–C(5)	115.6 (3)	C(8)–N(2)–C(12)	112.9 (6)
C(2)–Si(1)–C(3)	119.8 (2)	C(8)–N(2)–Li	100.4 (5)
C(2)–Si(1)–C(5)	118.8 (3)	C(10)–N(2)–C(12)	108.0 (6)
C(3)–Si(1)–C(5)	102.3 (3)	C(10)–N(2)–Li	112.4 (5)
Si(1)–Si(2)–C(1)	47.1 (2)	C(12)–N(2)–Li	115.8 (5)
Si(1)–Si(2)–C(2)	44.4 (2)	Si(1)–C(1)–Si(2)	86.7 (3)
Si(1)–Si(2)–C(4)	115.3 (3)	Si(1)–C(2)–Si(2)	90.4 (3)
Si(1)–Si(2)–C(6)	139.4 (2)	Si(1)–C(2)–Li	109.4 (4)
C(1)–Si(2)–C(2)	89.9 (3)	Si(2)–C(2)–Li	115.4 (4)
C(1)–Si(2)–C(4)	109.9 (3)	N(1)–C(7)–C(8)	115.0 (6)
C(1)–Si(2)–C(6)	113.5 (3)	N(2)–C(8)–C(7)	115.7 (7)
C(2)–Si(2)–C(4)	117.8 (3)	N(1)–Li–N(2)	88.1 (4)
C(2)–Si(2)–C(6)	120.4 (3)	N(1)–Li–C(2)	123.2 (5)
C(4)–Si(2)–C(6)	104.7 (3)	N(2)–Li–C(2)	130.1 (6)
C(7)–N(1)–C(9)	112.5 (6)		

covalent C–Li and O–Li interactions, there also is a weaker, but still significant, interaction between the lithium atom and the ipso carbon atom of one of the phenyl groups.

Intra- and intermolecular bond distances and angles in 1 are given in Tables I–III. The methyl group hydrogen atoms shown in Figure 2 were placed in calculated positions with an average C–H distance of 0.96 Å. In addition to the Li–C interaction of 2.10 (1) Å and the two Li–N interactions of 2.09 (1) and 2.08 (1) Å, there is a weaker, but still significant, interaction of the lithium atom with a hydrogen atom of a methyl group on a silicon atom in an adjacent molecule (Li–H(4)* = 2.33 Å; Figure 2). This Li–H bonding is continuous throughout the crystal. Thus, the lithium atoms in 1 may be regarded as tetracoordinate, and hence 1 may be considered to be polymeric. In 1, with the assumed position of the bridging H atom, the C(3)*–H(4)*–Li angle is 142° and the C(3)*–Li distance is 3.15 (1) Å. The Li–H interaction can be viewed as bridging, 2, as found in dilithiomethane[10] or as semibridging, 3, as found in cyclohexyllithium.[11] Noteworthy is the similarity of the intermolecular Li···H distance in 1 with those observed in dimeric, unsolvated $[(Me_3Si)(Me_2P)CHLi]_2$ (Li···H = 2.33 (3), 2.30 (3), 2.46 (3) Å),[4] for which Li···H–C interactions also were discussed. Intermolecular Li···H–C interactions of similar magnitude, 2.36 Å, which serve to give the lithium atoms a coordination number of 4, also occur in the methyllithium tetramer.[12]



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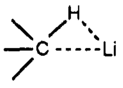

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The intramolecular C–Li bond distance in 1 of 2.10 (1) Å is comparable to those found in $(Me_3Si)_2CHLi\cdot(Me_2NCH_2CH_2)_2NMe$ (2.13 (5) Å),[3] $(PhMe_2Si)_3CLi\cdot THF$ (2.12 (2) Å),[9] $(Me_3Si)(Me_2P)CHLi\cdot(Me_2NCH_2CH_2)_2NMe$ (2.207 (5) Å),[4] $(Me_2PCH_2Li\cdot TMEDA)_2$ (2.14 (5) Å),[13] $(PhSCH_2Li\cdot TMEDA)_2$ (2.131 (4) Å),[14] and 2-lithio-2-methyl-1,3-dithiane·TMEDA (2.18 (6) Å).[15] These distances are rather short, and on that basis one might consider them to involve a covalent, at most polarized Li–C bond. However, we note the discussion of Amstutz, Laube, Schweizer, Seebach, and Dunitz[14] in which it is concluded that X-ray results, even those involving electron density difference maps, cannot distinguish between covalent and ionic Li–C interactions.

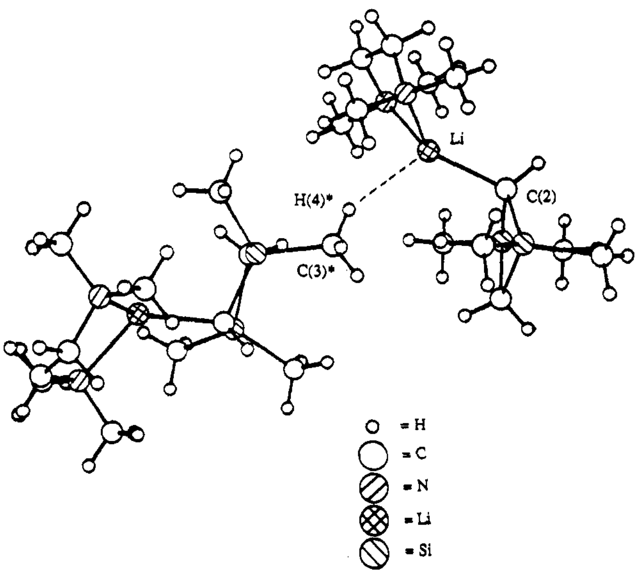
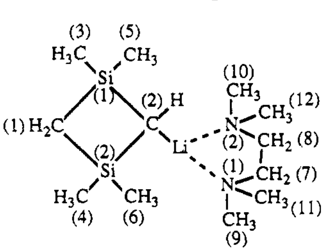


Figure 2. PLUTO diagram of 1 showing Li–H(4)* bonding.

Table IV. ^1H and ^{13}C NMR Spectral Data for 1



NMR	2	1	3-6	9-12	7,8
^1H	−0.76 (t) J = 2.2 Hz	0.37 (d) J = 2.7 Hz	0.53 (s)	1.78 (s)	1.64 (s)
$^{13}C^a$	10.04 (dm) ^1J = 128.8 Hz ^3J = 4.3 Hz	5.20 (td) ^1J = 126.9 Hz ^3J = 14.3 Hz	9.36 (q) J = 116.3 Hz	44.93 (qd) ^1J = 133.8 Hz ^2J = 5.6 Hz	56.03 (td) ^1J = 132.5 Hz ^2J = 6.0 Hz

[a] At room temperature the $SiCH_3$ groups (C(3)–C(6)) of the ring silicon atoms give a single resonance at 9.36 ppm. Upon cooling to −32 °C (in toluene-d_8), this resonance broadened only slightly, indicating the equivalence of the CH_3 groups on the NMR time scale. The methine carbon (C(2)) signal remained sharp upon cooling, and no ^{13}C–Li coupling was observed.

Aspects of the NMR spectra of 1 may, in principle, be rationalized in terms of the presence of a covalent C–Li bond in which the electron density of the carbon atom is affected by the adjacent silicon atoms. NMR data for 1 are given in Table IV. In the ^1H NMR spectrum of 1 the methine proton signal is a hyperfine triplet that is shifted upfield relative to the methylene proton signal. The triplet pattern results from long-range coupling to the methylene

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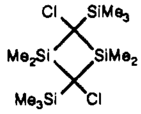
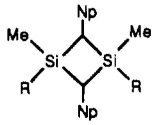
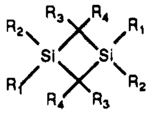
Table V. Structurally Characterized 1,3-Disilacyclobutanes

	molecule	Si_{ring}–C_{ring} av length (Å)	Si_{ring}–C_{ring}–Si_{ring} av angle (deg)	C_{ring}–Si_{ring}–C_{ring} av angle (deg)	θ (deg)	method (ref)
2		1.888 (2)	86.8 (3)	90.6 (3)	25 (2)	gas-phase electron diffraction (19)
3		1.895		89 (1)	14 (3)	gas-phase electron diffraction (20)
4		1.918 (5)	87.2 (2)	91.4 (5)	17.8	single-crystal X-ray (21)
5[a]		1.902 (2)	87.38 (9)	89.62 (9)	18.7	single-crystal X-ray (22)
6[b]		1.962	84.5	95.4	2.4–5.9	single-crystal X-ray (23)

[a] R = $Fe(CO)_2Cp$. [b] A: R_1 = Me; R_2 = $OSiMe_3$; R_3 = Ad; R_4 = $SiMe_2{}^tBu$. B: R_1 = R_2 = Me; R_3 = Ad; R_4 = $SiMe^tBu(OSiMe_3)$. C: R_1 = R_2 = Me; R_3 = Ad; R_4 = $SiMePh(OSiMe_3)$ isomers.

group protons. The methylene proton signal is a hyperfine doublet due to this coupling. Such long-range proton spin–spin coupling is well-known for small, strained ring systems, and the coupling constants can be as large as 7 Hz.[16] The $SiCH_3$ proton resonances appear as a singlet. The NCH_2 and $N(CH_3)_2$ proton signals are singlets. The integrated intensities of the $SiCH_3$ and NCH_3 proton signals are in agreement with the formulation of 1 as indicated.

The ^{13}C NMR spectrum shows the methine (CLi) carbon atom resonance at 10.04 ppm and that of the methylene carbon atom at 5.02 ppm. This small difference in chemical shifts suggests that the carbon atom bonded to lithium carries only a fractional negative charge. The C–H spin–spin coupling constant for the carbon atom to which the lithium is bonded merits comment. A decrease in J_{C-H} on going from the parent hydrocarbon (e.g., RCH_3) to the organolithium (RCH_2Li) has been taken to indicate an increase in negative charge on the carbon atom.[17] In the ^{13}C NMR spectrum of 1, J_{C-H} for the carbon atom bonded to Li, 128.8 Hz, actually is slightly greater than J_{C-H} for the methylene carbon atoms of the parent hydrocarbon, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 123.1 Hz. Thus, both the chemical shift data and the J_{C-H} values indicate that the methine carbon atom of 1 does not contain an excess of negative charge. This, however, is not necessarily evidence in support of a covalent C–Li bond since in this case it is likely that some of the negative charge originally generated at the methine carbon atom is drained away by interaction with the two silicon atoms ($d\pi$–$p\pi$ interaction or, more likely, by polarization). Enhancement of CH acidity by adjacent organosilicon groups that facilitates preparation of silyl-substituted alkyllithiums by CH deprotonation is a well-known phenomenon that has been explained in terms of such stabilization of alkyllithiums by adjacent silicon groups.[18] In agreement with the participation of the silicon atoms in the stabilization of 1 is the ^{29}Si NMR resonance of 1 observed at −10.10 ppm, an upfield shift from δ_{Si} 2.53 ppm for the parent disilacyclobutane. Such a shift would be expected if some of the negative charge is absorbed by the Me_2Si groups of 1. In this connection, it is noteworthy that the endocyclic Si–C(methine) bond distances, C(2)–Si(1) = 1.791 (6) and C(2)–Si(2) = 1.814 (6) Å, are significantly shorter than those of the Si–C(methylene) bonds, C(1)–Si(1) = 1.876 (7) and C(1)–Si(2) = 1.852 (6) Å. Similarly short Si–CLi bonds have been observed in $(Me_3Si)_2CHLi\cdot(Me_2NCH_2CH_2)_2NMe$ (1.78 (3) and 1.79 (3) Å)[3] and $(PhMe_2Si)_3CLi\cdot THF$ (1.786 (2) and 1.819 (12) Å).[9] Such short Si–C distances result from the Si–CLi interactions mentioned above.

The internal angles of the disilacyclobutane ring of 1 all are approximately 90° (Table III), and the ring is puckered by 19.03° from planarity. This value for the ring torsion angles falls well within the values of these angles in other structurally characterized 1,3-disilacyclobutanes (Table V).[19-23] The Si–CH_3 bond distances in 1 are normal (approximately 1.87 Å), but the Si–CH_2 bond distances are short compared with the endocyclic Si–C distances in other known 1,3-disilacyclobutanes (Table V). (Inspection of the Si–C bond distances in Table V shows that the steric crowding resulting from the presence of sterically demanding substituents on the ring carbon atoms results in considerable elongation of the endocyclic Si–C bonds.)

Experimental Section

All reactions were performed under an argon atmosphere with standard Schlenk techniques. Solvents were distilled under nitrogen from the appropriate drying agents. *tert*-Butyllithium was purchased from Aldrich and titrated for RLi content by the Gilman double-titration method. Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and distilled from calcium

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Table VI. Experimental Details

A. Crystal Data	
empirical formula	$C_{12}H_{31}LiN_2Si_2$
formula weight	266.50
crystal color, habit	colorless, needle
crystal dimensions	0.100 × 0.100 × 0.300 mm
crystal system	monoclinic
no. of reflections used for unit cell determination (2θ range)	25 (12–15°)
ω scan peak width at half-height	0.19
lattice parameters	a = 9.408 (6) Å b = 16.63 (1) Å c = 11.849 (7) Å β = 108.51 (4)° V = 1757 (4) Å^3
space group	$P2_1/n$ (No. 14)
Z	4
D_{calc}	1.007 g/cm^3
F_{000}	592
μ(Mo Kα)	1.81 cm^{-1}
B. Intensity Measurements	
diffractometer	Rigaku AFC6R
radiation	Mo Kα (λ = 0.71069 Å)
temperature	−72 ± 1 °C
takeoff angle	2.8°
detector aperture	6.0 mm horizontal 6.0 mm vertical
crystal to detector distance	31.0 cm
scan type	ω–2θ
scan rate	8.0°/min (in ω) (8 rescans)
scan width	(0.84 + 0.35 tan θ)°
$2\theta_{max}$	50.4°
no. of reflections measured	total 2895 unique 2678 (R_{int} = .053)
corrections	Lorentz–polarization absorption (transmissn factors 0.51–1.48) decay (−48.00% decline)
C. Structure Solution and Refinement	
structure solution	direct methods
refinement	full-matrix least squares
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p factor	0.03
anomalous dispersion	all non-hydrogen atoms
no. observations ($I > 3.00\sigma(I)$)	1204
no. of variables	154
reflection/parameter ratio	7.82
residuals: R; R_w	0.054; 0.063
goodness of fit indicator	1.97
max shift/error in final cycle	0.00
max peak in final diff map	0.30 e$^-$/Å^3
min peak in final diff map	−0.27 e$^-$/Å^3

Table VII. Positional Parameters and B(eq) Values (Å^2) for Compound 1

atom	x	y	z	B(eq)
Si(1)	0.5359 (2)	0.2309 (1)	0.4592 (1)	4.10 (7)
Si(2)	0.7750 (2)	0.1676 (1)	0.4400 (1)	4.71 (8)
N(1)	0.8201 (6)	0.0164 (3)	0.7579 (4)	4.7 (2)
N(2)	0.5441 (6)	0.0834 (3)	0.7776 (4)	5.1 (3)
C(1)	0.7141 (8)	0.2731 (3)	0.4445 (5)	5.2 (3)
C(2)	0.6223 (7)	0.1339 (3)	0.4908 (4)	4.0 (2)
C(3)	0.3757 (8)	0.2470 (3)	0.3187 (5)	5.3 (3)
C(4)	0.7679 (9)	0.1407 (4)	0.2847 (6)	6.6 (4)
C(5)	0.4665 (7)	0.2801 (4)	0.5735 (5)	5.1 (3)
C(6)	0.9742 (8)	0.1494 (4)	0.5326 (6)	6.1 (3)
C(7)	0.751 (1)	−0.0114 (5)	0.8458 (7)	7.8 (4)
C(8)	0.594 (1)	0.0019 (5)	0.8144 (7)	8.3 (5)
C(9)	0.8078 (8)	−0.0420 (4)	0.6651 (6)	6.1 (3)
C(10)	0.385 (1)	0.0785 (4)	0.7070 (7)	6.9 (4)
C(11)	0.9794 (8)	0.0307 (4)	0.8202 (5)	5.7 (3)
C(12)	0.5577 (9)	0.1367 (5)	0.8774 (6)	7.2 (4)
Li	0.680 (1)	0.1107 (6)	0.6738 (8)	5.0 (5)
H(1)	0.6994	0.3051	0.3740	6.3
H(2)	0.7700	0.3051	0.5114	6.3
H(3)	0.5596	0.0922	0.4393	5.0
H(4)	0.3560	0.3030	0.2978	6.9
H(5)	0.3977	0.2232	0.2481	6.9
H(6)	0.2844	0.2227	0.3188	6.9
H(7)	0.6683	0.1466	0.2292	8.5
H(8)	0.8344	0.1725	0.2574	8.5
H(9)	0.7957	0.0845	0.2799	8.5
H(10)	0.5405	0.2781	0.6524	6.5
H(11)	0.4482	0.3381	0.5569	6.5
H(12)	0.3764	0.2580	0.5782	6.5
H(13)	1.0047	0.0940	0.5284	7.4
H(14)	1.0440	0.1818	0.5056	7.4
H(15)	0.9929	0.1619	0.6147	7.4
H(16)	0.7725	−0.0647	0.8650	9.2
H(17)	0.7915	0.0215	0.9177	9.2
H(18)	0.5585	−0.0153	0.8778	9.2
H(19)	0.5476	−0.0358	0.7476	9.2
H(20)	0.7082	−0.0538	0.6217	7.4
H(21)	0.8575	−0.0219	0.6094	7.4
H(22)	0.8593	−0.0917	0.6967	7.4
H(23)	0.3460	0.1304	0.6810	8.6
H(24)	0.3703	0.0445	0.6394	8.6
H(25)	0.3292	0.0562	0.7552	8.6
H(26)	1.0288	−0.0191	0.8511	6.8
H(27)	1.0259	0.0510	0.7639	6.8
H(28)	0.9932	0.0677	0.8820	6.8
H(29)	0.6629	0.1422	0.9243	8.9
H(30)	0.5236	0.1898	0.8482	8.9
H(31)	0.5041	0.1178	0.9253	8.9

hydride before use. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was prepared according to the method of Kriner.[24]

Proton NMR spectra were obtained in C_6D_6 solution with a Varian XL-300 NMR spectrometer with C_6D_6/C_6H_6 as a reference at 7.15 ppm downfield from tetramethylsilane. ^{13}C NMR spectra, both proton coupled and decoupled, were obtained in C_6D_6 on a Varian XL-300 NMR spectrometer operating at 75.4 MHz. ^{29}Si NMR spectra were obtained in C_6D_6 on a Varian XL-300 NMR spectrometer operating at 59.59 MHz with tetramethylsilane (0.00 ppm) as the external standard.

Preparation of 1. A 50-mL flask was charged with 3.198 g (0.022 mol) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 5.2 mL (0.034 mol) of TMEDA, and 5 mL of hexane (all operations under an inert atmosphere). To this solution was added by syringe 16.2 mL of 1.5 M *tert*-butyllithium (0.024 mol) in pentane. The mixture was stirred at room temperature for 25 min. Subsequently, the volume was reduced to about 5 mL by distillation of volatiles at room temperature and 0.05 Torr into a liquid nitrogen cooled trap. Freshly distilled benzene (3 mL) was added to the residue, and the resulting clear, slightly yellow solution was kept at 3 °C for 4 h. White crystals formed. The supernatant solution was removed by cannula, and the crystals were washed twice with 10-mL portions of cold hexane. Subsequently, they were dried in vacuo.

X-ray Crystallographic Study of 1. Data Collection. A colorless needle crystal of 1, $C_{12}H_{31}N_2LiSi_2$, having approximate dimensions of 0.100 × 0.100 × 0.300 mm was mounted on a glass fiber under a stream of nitrogen. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and 12-kW rotating-anode generators.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of two carefully centered reflections in the range $13.08 < 2\theta < 13.40°$, corresponded to a monoclinic cell with the dimensions given in Table VI. Based on the systematic absences of $h01$ ($h + 1 \neq 2n$) and $0k0$ ($k \neq 2n$), the space group was determined to be $P2_1/n$ (No. 14).

Structure Solution and Refinement. The structure was solved by direct methods.[25] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions ($\langle$C–H$\rangle$ = 0.96 Å; B(H) = 1.2B(C)). The final cycle of

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full-matrix least-squares refinement was based on 1204 observed reflections ($I > 3.00\sigma(I)$) and 154 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c|| / \sum|F_o| = 0.054$ and $R_w = [(\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)]^{1/2} = 0.063$. The standard deviation of an observation of unit weight was 1.97. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.30 and −0.27 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[26] Anomalous dispersion effects were included in F_c;[27] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[28] All calculations were performed with use of the TEXSAN[29] crystallographic software package of Molecular Structure Corp.

Table VII is a listing of the positional parameters and the *B*(eq) values for the atoms.

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Supplementary Material Available: Tables of *U* values, intramolecular distances involving the hydrogen atoms, and torsion or conformation angles (5 pages); listings of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Bis((2,6-diisopropylphenyl)imido) Complexes of Molybdenum(VI)

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Summary: The molybdenum(VI) complex $(Ar'N)_2MoCl_2 \cdot THF$ (Ar′ = 2,6-diisopropylphenyl) was prepared by reaction of MoO_2Cl_2 with Ar′NCO at 70 °C in THF. The preparations of the derivatives $Mo(NAr')_2Np_2$, $Mo(NAr')_2Mes_2$, $Mo(NAr')_2MesBr$, $Mo(NAr')_2(NEt_2)Cl$, and $Mo(NAr')_2(NEt_2)_2$ from $Mo(NAr')_2Cl_2 \cdot THF$ are described. In addition, the complex $Mo(NAr')_2(NHAr')_2$ has been synthesized and characterized crystallographically. Crystal data: $MoC_{48}H_{70}N_4$, M_r = 799.06, monoclinic, $P2_1/n$, a = 9.874 (3) Å, b = 24.004 (8) Å, c = 19.220 (7) Å, β = 93.34 (2) Å, V = 4547 Å^3, Z = 4, ρ_{calc} = 1.167 g cm^{-3}, λ = 1.5418 Å, μ = 26.35 cm^{-1}, T = −100 °C, R = 4.22% for 4426 unique observed [$I \geq 3\sigma(I)$] reflections, R_w = 7.65%.

The organoimido ligand $=NR^{2-}$ exerts a stabilizing influence on high oxidation states similar to that of the oxo ligand O^{2-} but additionally can provide, by modification of the R groups, variations in electronic and steric effects. For example, complexes involving imido groups have found use as designed electrophilic catalysts for olefin metathesis[1,2] and for C–H activation.[3] Also, interesting protonation–deprotonation reactions of tungsten and molybdenum imido complexes have recently been reported.[4,5] We have been interested in generating coordinatively unsaturated molybdenum(VI) complexes of the (2,6-diisopropylphenyl)imido ligand (Ar′) for further investigations in the area of hydrocarbon activation. Although molybdenum complexes of this ligand exist, they have been prepared by rather tedious routes.[1] In this paper, we describe the convenient preparation of the $(Ar'N)_2MoCl_2 \cdot THF$ complex, which serves as an important starting material for this chemistry. The synthesis of some alkyl (aryl) and amido derivatives are presented along with an X-ray structure of one such derivative.

Results and Discussion

The complex $Mo(NAr')_2Cl_2 \cdot THF$ (1) was prepared under an inert atmosphere by reacting freshly sublimed MoO_2Cl_2 with 2 equiv of Ar′NCO in THF at 70 °C according to a method previously reported.[2] The reaction was complete after 3 days. Following evaporation of the solvent, 1 was recovered as a dark red powder in excellent yield. $Mo(NAr')_2Cl_2 \cdot THF$, which is very soluble in nonpolar organic solvents, was recrystallized from pentane to give analytically pure material. The product is very sensitive to air and moisture both in solution and in the solid state.

Alkylation of 1 using neopentyllithium in diethyl ether yielded the orange air-sensitive $Mo(NAr')_2Np_2$ (2), which was recrystallized from pentane. If 1 equiv of LiNp was used, only the starting material 1 and the dineopentyl complex 2 (in a 1:1 ratio) were observed by ^1H NMR spectroscopy. Comparison of the ^1H NMR spectra of $Mo(NAr')_2Np_2$ (2) and $Mo(NBu^t)_2Np_2$[2] prepared previously shows that the stronger electron-withdrawing arylimido ligand leads to a significant downfield shift of the neopentyl α-hydrogens from 1.89 to 2.35 ppm.

The compound $Mo(NAr')_2Cl_2 \cdot THF$ (1) was allowed to react with 2 equiv of mesitylmagnesium bromide (MesMgBr) in THF. After 12 h, the monosubstituted product $Mo(NAr')_2MesX$ (4) (X = Br) comprised ca. 75% of the reaction products as determined by ^1H NMR spectroscopy. The analytical results and mass spectrum

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