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The X-ray crystal structures of the mononuclear silyllithium species $Li(THF)_3SiPh_3$ and $Li(THF)_3Si(SiMe_3)_3$ *

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Abstract

The organosilyllithium tetrahydrofuranate complexes $Li(THF)_3SiPh_3$ (**1**) and $Li(THF)_3Si(SiMe_3)_2$ (**2**) were crystallized and structurally characterized by X-ray crystallography. Both compounds possess monomeric structures with relatively long (*ca.* 2.67 Å) Li–Si bonds. In addition, the lithium-bound silicons have distorted tetrahedral geometries with low C–Si–C and Si–Si–Si angles of 101.3° (av.) (**1**) and 102.6° (av.) (**2**). Compound **1**, which has not been reported as an isolated species, has been characterized by ^1H, ^7Li, ^{29}Si NMR and IR spectroscopy. These studies indicate that the Li–Si bond remains intact in THF solution at −80°C.

1. Introduction

Structural studies of silyllithium species have received very little attention in comparison to their alkyl or aryllithium analogues. Currently, the experimentally determined structures of only a few such compounds are known. These are of the hexamer $(LiSiMe_3)_6$ (**3**) [1], the adducts $(LiSiMe_3)_2 \cdot (TMEDA)_3$ (**4**) [2] and $LiSi(SiMe_3)_3 \cdot 1.5$ DME (**5**) [3] (TMEDA = tetramethylenediamine, DME = 1,2-dimethoxyethane) and the compound $[\{Li(THF)_3\}_2Si_4Ph_8]$ (**6**) [4] in which THF solvated lithiums are terminally bonded to each end of an $(SiPh_2)_4$ chain. Owing to the uniqueness of the latter species, the non-solvated nature of **3**, and the presence of chelating ligands in the structures of **4** and **5**, it was felt that their molecular structures might not prove to be typical of simple lithium silyls in donor solvents where these reagents are often employed. The main object of the work reported here was to prepare crystalline samples of some simple solvated lithium silyls and to determine their structures by X-ray crystallography.

2. Experimental details

All operations were performed under an N_2 atmosphere. Solvents were distilled from conventional drying agents and degassed twice prior to use. ^1H, ^7Li, ^{29}Si NMR spectra were recorded on a General Electric QE-300 spectrometer operating near 300 (^1H), 116.59 (^7Li) or 59.6 (^{29}Si) MHz. IR spectra were recorded on a Perkin-Elmer Model 1430 instrument.

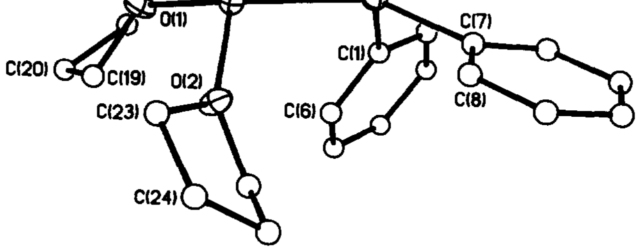

Fig. 1. Computer generated drawing of **1**. H atoms are omitted for clarity.

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* Dedicated to Professor Mike Lappert on the occasion of his 65th birthday; a true scholar and pioneer of organometallic chemistry.

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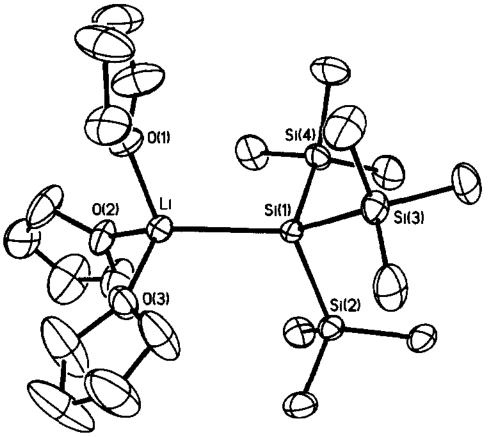

Fig. 2. Computer generated thermal ellipsoidal drawing of **2**. H atoms are omitted for clarity.

Both $LiSiPh_3$ (**1**) [5] and $LiSi(SiMe_3)_3$ (**2**) [6] were generated in THF solutions according to literature procedures. However, only **2** has been previously isolated as a crystalline species [7]. Crystals for X-ray crystallography were grown by adding hexane concentrated THF solutions of **1** or **2** until incipient crystallization. Slow cooling over 24 h ion a −20°C freezer afforded suitably sized crystals for X-ray crystallography. The species **1** was obtained in 63% yield; m.p. dec. > 95°C. ^{7}Li NMR (C_7D_8): s, −1, J (^{7}Li–^{29}Si) = 45 Hz. ^{29}Si NMR (C_7D_8): q, 9.28, J (^{29}Si–^{7}Li) = 45 Hz. ^{1}H NMR (C_7D_8):m, 1.31 (12H, THF); m, 3.46 (12H, THF); m, 7.13 (6H, Ph); m, 7.26, (6H, Ph); m, 7.76, (3H, Ph). IR (Nujol): 1948m, 1877m, 1812m, 1572m, 1426m, 1295w, 1258w, 1182w, 1106sh, 1070w, 1041w, 992w, 955–978br, m, 802s, 730br, 694s, 521s cm^{-1}.

2.1. X-Ray crystallographic studies

All data were collected with a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 low temperature device using graphite monochromated Mo Kα (λ = 0.71069 Å) radiation. Calculations were car-

TABLE 1. Crystal data and summary of data collection and refinement

	$Li(THF)_3SiPh_3$ (**1**)	$Li(THF)_3Si(SiMe_3)_3$ (**2**)
Formula	$C_{30}H_{39}LiO_3Si$	$C_{21}H_{51}LiO_3Si_4$
FW	482.67	470.92
Crystal system	Orthorhombic	Monoclinic
Space group	*Fdd*2	$P2_1/c$
Conditions	hkl, $h+k=2n$, $k+l=2n$; $0kl$, $k+l=4n$; $h0l$, $l+h=4n$	$0k0$, $k=2n$; $h0l$, $l=2n$
Crystal dimensions (mm)	0.20 × 0.37 × 0.62	0.38 × 0.68 × 0.73
Crystal color and habit	Colorless plates	Colorless parallelepipeds
a (Å)	23.362(15)	9.956(3)
b (Å)	24.723(16)	19.913(9)
c (Å)	19.371(14)	16.194(5)
β (°)	-	93.09(2)
V (Å^3)	11,188(14)	3206(2)
Z	16	4
T (K)	130	213
d_{calc} (g cm^{-3})	1.15	0.98
Linear abs.coefficient (cm^{-1})	1.1	2.0
Range of abs.correction factors	0.96–0.98	0.88–0.94
Scan speed (° min^{-1})	15	15
Scan width (°)	1.0	1.0
ω offset for background (°)	1.0	1.0
2θ range (°)	1–45	0–48
No. reflections collected	3945	5426
No. of unique data	2936	5044
R (merge)	0.020	0.008
No. of data used in refinement	2225 ($I > 3\sigma(I)$)	1985 ($I > 3\sigma(I)$)
No. of variables	165	262
data/variable ratio	13.5:1	7.6:1
$R(F)$	0.053	0.071
$R_w(F)$	0.053	0.086
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$	$w^{-1} = \sigma^2(F)$
Largest Δ/σ	0.014	0.003
Largest feature on final Difference map (e Å^{-3})	0.50	0.36

TABLE 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for $Li(THF)_3SiPh_3$ (**1**) and $Li(THF)_3Si(SiMe_3)_3$ (**2**)

Atom	*x*	*y*	*z*	*U* [a]
Compound 1				
Si	2591(1)	47(1)	1906	23(1)
Li	2564(4)	−39(4)	531(5)	27(3)
O(1)	1992(1)	442(1)	90(2)	31(1)
O(2)	3299(1)	154(1)	88(2)	31(1)
O(3)	2308(1)	−777(1)	261(2)	31(1)
C(1)	2410(2)	741(2)	2317(3)	23(1)
C(2)	2187(2)	804(2)	2982(3)	28(1)
C(3)	2073(2)	1314(2)	3262(3)	34(2)
C(4)	2178(2)	1772(2)	2864(3)	36(1)
C(5)	2393(2)	1723(2)	2218(3)	38(2)
C(6)	2509(2)	1216(2)	1938(3)	29(1)
C(7)	3312(2)	−126(2)	2359(3)	22(1)
C(8)	3770(2)	−300(2)	1957(3)	29(1)
C(9)	4303(2)	−425(2)	2257(3)	35(2)
C(10)	4380(2)	−384(2)	2951(3)	31(1)
C(11)	3929(2)	−213(2)	3367(4)	36(2)
C(12)	3405(2)	−83(2)	3063(3)	28(1)
C(13)	2066(2)	−416(2)	2391(3)	25(1)
C(14)	1468(2)	−338(2)	2314(3)	30(1)
C(15)	1070(3)	−693(2)	2591(4)	39(2)
C(16)	1246(2)	−1149(3)	2951(3)	42(2)
C(17)	1820(2)	−1237(3)	3036(3)	36(2)
C(18)	2225(2)	−887(2)	2771(3)	28(1)
C(19)	2158(3)	909(2)	−298(4)	40(2)
C(20)	1660(2)	1296(2)	−277(3)	40(2)
C(21)	1388(2)	1161(2)	410(3)	41(2)
C(22)	1461(2)	560(2)	449(3)	34(1)
C(23)	3526(2)	−41(3)	−567(4)	40(1)
C(24)	4169(2)	46(3)	−530(4)	47(2)
C(25)	4266(3)	363(3)	128(4)	59(2)
C(26)	3680(2)	572(2)	317(4)	36(1)
C(27)	1919(2)	−851(2)	−312(3)	33(1)
C(28)	1766(2)	−1443(2)	−325(3)	37(2)
C(29)	2107(3)	−1149(2)	784(3)	36(2)
C(30)	1910(2)	−1647(2)	399(3)	32(1)
Compound 2				
Si(1)	2291(2)	845(1)	2731(1)	50(1)
Si(2)	4530(2)	1135(1)	3038(1)	66(1)
Si(3)	1189(3)	1293(1)	3838(2)	78(1)
Si(4)	1702(3)	1583(1)	1650(1)	75(1)
O(1)	−107(6)	−641(3)	2135(4)	85(2)
O(2)	2549(6)	−786(3)	1336(4)	96(3)
O(3)	2417(7)	−1092(3)	3154(4)	95(3)
Li	1781(13)	−436(7)	2343(8)	65(5)
C(1)	5347(8)	489(5)	3750(6)	95(4)
C(2)	4905(9)	1974(5)	3531(6)	97(4)
C(3)	5525(9)	1135(5)	2078(6)	104(4)
C(4)	1948(12)	994(5)	4863(5)	125(5)
C(5)	1119(12)	2239(5)	3944(6)	120(5)
C(6)	−610(10)	1008(7)	3800(7)	148(6)
C(7)	2532(11)	2422(5)	1657(6)	120(5)
C(8)	−155(11)	1778(6)	1577(7)	142(6)
C(9)	2045(13)	1187(5)	634(5)	127(5)
C(10)	−904(13)	−300(8)	1530(7)	160(7)
C(11)	−2289(13)	−474(10)	1619(10)	170(9)
C(12)	−2337(13)	−815(8)	2367(11)	189(9)
C(13)	−946(13)	−936(6)	2673(8)	145(7)
C(14)	2009(13)	−1233(8)	731(9)	178(8)
C(15)	3058(18)	−1420(8)	230(8)	169(8)
C(16)	4157(18)	−1014(10)	451(11)	213(11)
C(17)	3853(13)	−625(7)	1114(9)	143(6)
C(18)	3142(22)	−1681(8)	3039(11)	233(12)
C(19)	3584(19)	−1942(10)	3809(11)	245(12)
C(20)	2992(23)	−1574(10)	4363(10)	249(13)
C(21)	2466(17)	−993(6)	3997(7)	164(8)

[a] *U* is the equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor for all the non-hydrogen atoms of compound **2** and the Si, Li and O atoms of compound **1**.

ried out on Data General Eclipse and Micro VAX computers using versions of SHELXTL. The atomic form factors including anomalous dispersion were from ref. 8.

Colorless plates of **1** and colorless parallelepipeds of **2** were obtained as described above. To prevent possible reaction with air or loss of solvent, the crystals were stored in the mother liquor prior to use. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and immediately placed in the low temperature nitrogen stream as described in ref. 9. Crystals of **2** shattered below *ca.* −70°C. The data were collected at −60°C to prevent this occurrence. However, the refinement yielded unusually large thermal parameters with no significant residual electron density, indicating nearness to a phase transition at this temperature. The crystal structures of **1** and **2** were solved by direct methods and refined by full-matrix least squares refinement. In **1** only the silicon, lithium and the three oxygen atoms were refined anisotropically; in **2** all non-hydrogen atoms were refined in this way. Hydrogen atoms were included in the refinement at calculated positions using a riding model with C–H = 0.96 Å and $U_H = 1.2\ U_C$. A summary of experimental details is provided in Table 1 with additional details given below. Atom coordinates are listed in Table 2 and selected bond distances and angles in Table 3. Complete bond distances, angles, anisotropic thermal parameters, hydrogen atom coordinates and structure factor tables are provided in the supplementary material (available from the authors).

2.2. *Description of structures*

2.2.1. $Li(THF)_3SiPh_3$ (*1*)

The asymmetric unit contains a mononuclear structure (Fig. 1) with no crystallographic symmetry. Both the lithium and silicon centers are four-coordinate with distorted tetrahedral geometries. The Li–Si distance is

TABLE 3. Selected bond distances (Å) and angles (°) for $Li(THF)_3SiPh_3$(**1**) and $Li(THF)_3Si(SiMe_3)_3$ (**2**)

Compound 1			
Si–Li	2.672(9)	Li–O(1)	1.983(9)
Si–C(1)	1.940(5)	Li–O(2)	1.976(9)
Si–C(7)	1.947(5)	Li–O(3	1.991(10)
Si–C(13)	1.923(5)		
Li–Si–C(1)	118.3(3)	Si–Li–O(1)	113.5(4)
Li–Si–C(7)	116.9(2)	Si–Li–O(2)	113.2(4)
C(1)–Si–C(7)	101.4(2)	O(1)–Li–O(2)	104.7(4)
Li–Si–C(13)	115.2(3)	Si–Li–O(3)	109.9(4)
C(1)–Si–C(13)	100.8(2)	O(1)–Li–O(3)	103.5(4)
C(7)–Si–C(13)	101.6(2)	O(2)–Li–O(3)	111.6(4)
Compound 2			
Si(1)–Si(2)	2.330(4)	Si(3)–C(6)	1.877(11)
Si(1)–Si(3)	2.328(4)	Si(4)–C(7)	1.865(10)
Si(1)–Si(4)	2.336(4)	Si(4)–C(8)	1.887(11)
Si(1)–Li	2.669(13)	Si(4)–C(7)	1.865(10)
Si(2)–C(1)	1.882(9)	Si(4)–C(9)	1.873(9)
Si(2)–C(2)	1.880(9)	O(1)–Li	1.935(14)
Si(2)–C(3)	1.889(10)	O(2)–Li	1.965(14)
Si(3)–C(4)	1.883(9)	O(3)–Li	1.935(14)
Si(3)–C(5)	1.895(10)		
Si(2)–Si(1)–Si(3)	103.1(1)	Si(1)–Si(3)–C(6)	110.4(4)
Si(2)–Si(1)–Si(4)	101.7(1)	C(4)–Si(3)–C(6)	105.6(5)
Si(3)–Si(1)–Si(4)	103.1(1)	C(5)–Si(3)–C(6)	105.3(5)
Si(2)–Si(1)–Li	117.0(3)	Si(1)–Si(4)–C(7)	117.8(3)
Si(3)–Si(1)–Li	117.1(3)	Si(1)–Si(4)–C(8)	112.5(4)
Si(4)–Si(1)–Li	112.8(3)	C(7)–Si(4)–C(8)	104.3(5)
Si(1)–Si(2)–C(1)	109.7(3)	Si(1)–Si(4)–C(9)	110.1(3)
Si(1)–Si(2)–C(2)	118.4(3)	C(7)–Si(4)–C(9)	106.3(5)
C(1)–Si(2)–C(2)	106.1(4)	C(8)–Si(4)–C(9)	104.8(5)
Si(1)–Si(2)–C(3)	111.3(3)	Si(1)–Li–O(1)	114.4(6)
C(1)–Si(2)–C(3)	106.1(4)	Si(1)–Li–O(2)	117.2(6)
C(2)–Si(2)–C(3)	104.4(4)	Si(1)–Li–O(3)	115.7(6)
Si(1)–Si(3)–C(4)	112.0(4)	O(1)–Li–O(3)	104.8(7)
Si(1)–Si(3)–C(5)	118.2(4)	O(2)–Li–O(3)	101.3(6)
C(4)–Si(3)–C(5)	104.4(5)	O(1)–Li–O(2)	101.5(6)

2.672(9) Å and the average Si–C bond length is 1.937(9) Å. The distortion in angles surrounding silicon and lithium may be gauged from the average values 101.3(3) and 116.8(11)° for C–Si–C and Li–Si–C and 106.6(10) and 112.2(15) for O–Li–O and O–Li–S angles.

2.2.2. $Li(THF)_3Si(SiMe_3)_3$ (2)

The asymmetric unit of **2** comprises a single molecule (Fig. 2) with no imposed symmetry. There is distorted tetrahedral coordination at both lithium and silicon. The Li–Si bond length is 2.669(13) Å and the average Si–Si distance is 2.331(3) Å. For the central silicon atom the average Si–Si–Si and Si–Si–Li bond angles are 102.6(6) and 115.6(19)°. The asymmetry in the angles surrounding lithium is apparent from the average O–Li–O and O–Li–Si values of 102.5(15) and 115.8(10)°.

3. Discussion

The species $LiSiPh_3$ [5] and $LiSi(SiMe_3)_3$ [6,7] were generated in solution by literature procedures. Crystallization from THF/hexane mixtures resulted in crystals that had the stoichiometry given by the formulae of **1** and **2**. The compound **2** has already been obtained as a crystalline material [7] and spectroscopically characterized, whereas **2**, to our knowledge, has not been previously reported as an isolated species.

Both **1** and **2** possess very similar structures. The Li–Si bond lengths are essentially identical and the amount of pyramidicity defined by sum of the angles (Σ°) at the SiC_3 (Σ°Si = 303.8°) and $SiSi_3$ (Σ°Si = 307.9°) moieties is very similar. These two characteristics, together with the monomeric nature of **1** and **2** are the most noteworthy aspects of the structures.

The Li–Si bond lengths (*ca.* 2.67 Å) in **1** and **2** are marginally shorter than the bond distance (2.69 Å) predicted by the sum of the covalent radii of lithium (1.52 Å) and silicon (1.17 Å) [10]. They are significantly longer than the 2.542 Å calculated for non-solvated $LiSiH_3$ [11]. The Li–Si distances are, however, very similar to the average Li–Si bond length (2.68 Å) observed in $(LiSiMe_3)_6$ [1] in which the lithium bridges $-SiMe_3$ groups. In addition, they are only slightly shorter than the Li–Si bonds (2.69(1) and 2.70(1) Å) observed in **4** [2]. A comparison of the structures of **2** and **5**, both of which contain the $-Si(SiMe_3)_3$ moiety, show that the Li–Si distance in **5** (2.630(5) Å) is a little shorter than that seen in **2**. The observation of relatively long Li–Si bonds in all the compounds **1**–**6** is, in some respects surprising since heteronuclear bonds are normally found to be shorter than the sum of the radii of the bonding atoms. This contraction has often been attributed to an ionic contribution to bond strength [12]. In the case of the Li–Si derivatives, however, the ionic contribution to the bond is probably reduced significantly since the electronegativity of silicon is relatively low and the SiR_3^- anion is rather large. Furthermore, the geometry of the $[SiR_3]^-$ (R = Ph or $SiMe_3$) moiety indicates that the silicon orbital that interacts with lithium has an increased s-orbital component. The less directionalized character of this orbital may thus contribute to the longer Li–Si distances observed.

The structure of **1** may be compared with those of the closely related carbon derivative $Li(Et_2O)_2CPh_3$ (**7**) [13] and the tin and lead derivatives Li(PMDETA) MPh_3 (M = Sn (**8**) [14]; Pb (**9**) [15], PMDETA = pentamethyldiethylenetriamine). In **7**, the coordination at the central carbon is essentially planar, in contrast to the pyramidal coordination of silicon in the $[SiPh_3]^-$ moiety in **1**. The large difference between the geometry of 7 and the silicon, tin or lead species may be viewed as a consequence of the much greater inversion barrier in the case of the heavier elements. It is notable, however, that the Li–C distances in 7 are also somewhat long (> 2.306(14) Å); this is most probably a consequence of some delocalization of the negative charge onto the phenyl rings which results in interactions between the Li^+ ion and three (instead of one) of the $[CPh_3]^-$ carbons. Thus, the higher effective coordination of the Li^+ ion combined with some negative charge delocalization leads to the longer Li–C distances observed. The fairly short C–Ph distances observed in 7 are consistent with the delocalization. These short C–Ph bonds may be contrasted with the long Si–Ph distances in **1** which average 1.937(9) Å. This distance is much longer than that normally seen between silicon the carbon of Ph substituents (*ca.* 1.85 Å) [16]. The lengthening may be a consequence of the increased negative charge density in silicon which reduces the ionic contribution to the Si–C bond strength. The hybridization of the Si–C bond may also play a role. In spite of the length of the Li—Si interaction, ^{7}Li and ^{29}Si NMR studies at *ca.* −80°C indicate that the Li–Si bond remains intact in solution at least at low temperature. The ^{29}Si NMR spectrum displays a quartet pattern centered at 9.28 ppm with a J (^{29}Si–^{7}Li) coupling of 45 Hz which is comparable to that measured for **6** [4]. Similarly, the ^{7}Li pattern consists of a broad peak which displays two satellite peaks owing to coupling to the ^{29}Si nucleus. The coupling constant is identical to that observed in the ^{29}Si spectrum.

The monomeric formulation of both **1** and **2** in the crystal phase also merits comment. The observed unassociated structures are not characteristic of many of the more familiar lithium derivatives of alkyls, aryls, amides or alkoxides [17]. In these species, monomers are seen only for very hindered or delocalized molecules or where strong chelating agents are used to complex the Li^+ ion. Recent results for a variety of lithium derivatives of several heavier main group moieties (*e.g.* $Li(THF)_3P(H)Mes$ [18], $Li(dioxane)_3AsPh_2$ [19], $Li(py)S\text{-}2\text{-}Me\text{-}C_6H_4$ [20]) have suggested that monomeric character is much easier to achieve for the heavier element compounds. A further illustration of this phenomenon is seen in a comparison of the structures of $[Li(THF)O(2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2)]_2$ [21] and $Li(THF)_3S(2,4,6\text{-}^tBu_3C_6H_2)$ [22] where a monomer is seen only in the case of the thiolate derivative. The structures observed for **1** and **2** are thus in harmony with these findings and it appears that the major reason for the difference in structural patterns is the relative weakness of the lithium interaction with the heavier main group element. It seems that the interaction of the lithium ion with neutral donors such as ethers is competitive with the interaction with groups such as $-SR^-$, $-AsR_2^-$ or $-SiR_3^-$. In other words, solvation by donors like Et_2O or THF is apparently preferred to increasing the number of weak interactions to the main group elements as a result of association. Currently, the number of structures of lithium derivatives of the heavier main group elements is relatively small. It remains to be seen if this tendency toward monomeric structures in the heavier derivatives is observed in a wider range of compounds.

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References

1 T.F. Schaaf, W. Butler, M.D. Glick and J.P. Oliver, *J. Am. Chem. Soc.*, *96* (1974) 7593, W.H. Ilsley, T.F. Schaaf, M.D. Glick and J.P. Oliver, *J. Am. Chem. Soc.*, *102* (1980) 3769.

2 B. Tecle, W.H. Ilsley and J.P. Oliver, *Organometallics*, *1* (1982) 875.

3 G. Becker, H.-M. Hartmann, A. Münch and H. Riffel, *Z. Anorg. Allg. Chem.*, *580* (1985) 29.

4 G. Becker, H.-M. Hartmann, E. Hengge and F. Schrank, *Z. Anorg. Allg. Chem.*, *572* (1989) 63.

5 H. Gilman and G.D. Lichtenwalter, *J. Am. Chem. Soc.*, *80* (1958) 608.

6 H. Gilman and C.L. Smith, *J. Organomet. Chem.*, *9* (1967) 67.

7 G. Gutekunst and A.G. Brook, *J. Organomet. Chem.*, *225* (1982) 1.

8 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, Vol. IV.

9 This method is described in: H. Hope, in *ACS Symposium Series 357*, American Chemical Society, Washington, DC, 1987, Chapter 10.

10 J.E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, 1983, p. 258; N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 86 and 382.

11 B.T. Luke, J.A. Pople, M.-B. Krogh-Jespersen, Y. Apeloig, J. Chandrasekhar and P.v.R. Schleyer, *J. Am. Chem. Soc.*, *108* (1986) 260.

12 V. Schomaker and D.P. Stevenson, *J. Am. Chem. Soc.*, *63* (1941) 57.

13 R.A. Bartlett, H.V.R. Dias and P.P. Power, *J. Organomet. Chem.*, *341* (1988) 1.

14 D. Reed, D. Stalke and D.S. Wright, *Angew. Chem., Int. Ed. Engl.*, *30* (1991) 1459.

15 D.R. Armstrong, M.G. Davidson, D. Moncrieff, D. Stalke and D.S. Wright, *J. Chem. Soc., Chem. Commun.*, (1992) 1413.

16 E. Lukevics, O. Pudova and R. Sturkovich, *Molecular Structure of Organosilicon Compounds*, Ellis-Horwood, Chichester, UK, 1989, Ch. 1.

17 W.N. Setzer and P.v.R. Schleyer, *Adv. Organomet. Chem., 24* (1985) 353.

18 R.A. Bartlett, M.M. Olmstead, P.P. Power and G.A. Sigel, *Inorg. Chem., 26* (1987) 1941.

19 R.A. Bartlett, H.V.R. Dias, H. Hope, B.D. Murray, M.M. Olmstead and P.P. Power, *J. Am. Chem. Soc., 108* (1986) 6921.

20 A.J. Banister, W. Clegg and W.R. Gill, *J. Chem. Soc., Chem. Commun.*, (1987) 850.

21 B. Cetinkaya, I. Gumrükcü, M.F. Lappert, J.L. Atwood and R. Shakin, *J. Am. Chem. Soc., 102* (1980) 2086.

22 G.A. Sigel and P.P. Power, *Inorg. Chem., 26* (1987) 2819.