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A stable aquo-complex of lithiated di-tert-butylfluorosilanol. Synthesis and crystal structure *

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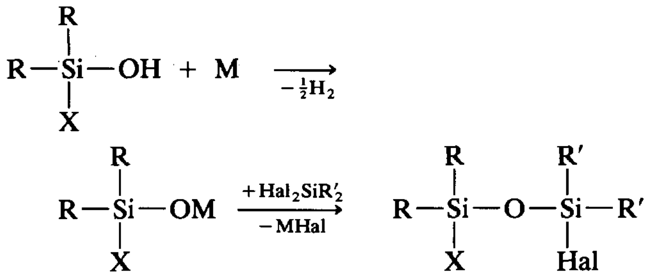
Abstract

It was possible by crystallizing the lithiated derivative of di-tert-butylfluorosilanol to isolate a stable aquo-complex of this tetrameric compound as the first hydrolysis product. An X-ray diffraction study has revealed the existence of $\{[R_2Si(F)OLi]_3 \cdot [R_2Si(OH)OLi] \cdot THF \cdot H_2O\}$ ($R = CMe_3$; THF = tetrahydrofuran). The mechanism of hydrolysis from $[R_2Si(F)OLi]_4$ to this aquo-complex is discussed.

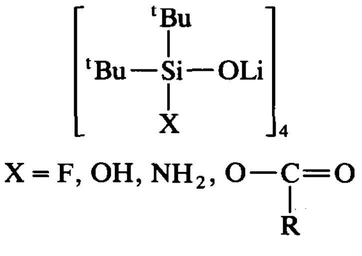
1. Introduction

An important method of preparing acyclic and cyclic siloxanes bearing functional groups involves metallation of functionalized silanols followed by treatment with appropriate silicon halides. This approach allows stepwise building up of functionalized siloxane units of almost any size [1].

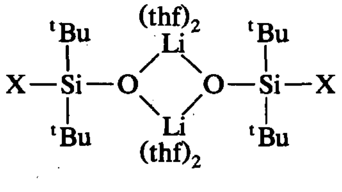


$M = Li, Na, K; X = OH, F, Cl, Br, NH_2; Hal = F, Cl$

Alkali-metal derivatives of stable functionalized silanols have a key position in siloxane synthesis. Thus, a detailed structural analysis of those metallated compounds is important for assisting understanding of the mechanisms of their reactions. Of the known monometallated compounds, most information is available for the mono-lithiated derivatives of di-tert-butylsilanols bearing various functional groups X [2–4], and for these there is a relationship between the nature of these functional groups and the structural type of the oligomer formed. The $(Li\text{-}O_4)$-cubane unit is found in all structures of mono-lithiated silanols crystallized from a donor solvent such as THF (tetrahydrofuran) and bearing a second functional group X containing fluorine, oxygen or nitrogen. In contrast, in the case where X is Cl a dimer is formed, containing a central four-membered $(Li\text{-}O)_2$ ring system [5]. Each lithium atom is further coordinated by donor solvents (*e.g.* THF).



$X = F, OH, NH_2, O{-}\underset{R}{\underset{|}{C}}{=}O$



X = Cl

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* Dedicated to Prof. Dr. Dr. h.c. Mikhail Grigoryevich Voronkov on the occasion of his 70th birthday.

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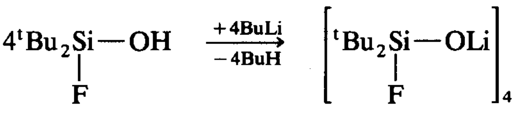
The structural type formed is determined by the basicity of the silicon-bound oxygen relative to that of the donor solvents used (*e.g.* THF). If the basicity of the silicon-bound oxygen is increased by (p–p)π or (p–d)π back-donation from the functional group (recognizable from ^{29}Si NMR data) or if no donor solvent is involved, a cubane structure is formed. Lithiated derivatives of functionalized silanols are sensitive to hydrolysis, but up to now only the final products of hydrolysis, usually silanols and lithium hydroxide, have been identified.

2. Results and discussion

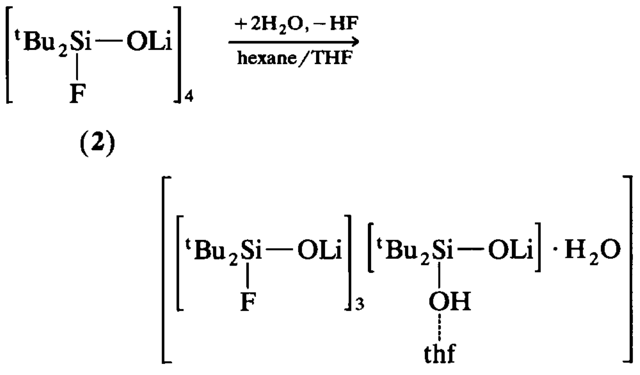
Preparation of the aquo-complex of the lithiated derivative of di-tert-butylfluorosilane began by treatment of the fluorosilanol with n-butyllithium in n-hexane [6].



$$4\,{}^{t}Bu_2\underset{F}{\underset{|}{Si}}-OH \xrightarrow[-4BuH]{+4BuLi} \left[{}^{t}Bu_2\underset{F}{\underset{|}{Si}}-OLi\right]_4$$

(1) (2)

Recrystallization from a mixture of n-hexane and THF, gave crystals suitable for an X-ray structural study. These crystals were identified as the stable aquo-complex of the tetrameric compound **2** formed by what can be regarded as the first step of complete hydrolysis.



$$\left[{}^{t}Bu_2\underset{F}{\underset{|}{Si}}-OLi\right]_4 \xrightarrow[\text{hexane/THF}]{+2H_2O,\,-HF}$$

(2)

$$\left[\left[{}^{t}Bu_2\underset{F}{\underset{|}{Si}}-OLi\right]_3\left[{}^{t}Bu_2\underset{\underset{\text{thf}}{\underset{\vdots}{OH}}}{\underset{|}{Si}}-OLi\right]\cdot H_2O\right]$$

(3)

The X-ray crystal structural study of **3** (Fig. 1) revealed the presence of a (Li–O)$_4$-cubane unit composed of three molecules of the lithiated derivative of di-tert-butylfluorosilanol and one molecule of the mono-lithiated derivative of di-tert-butylsilanediol, the latter being formed by the hydrolysis of a molecule of lithiated di-tert-butylfluorosilanol. Two of the lithium atoms are four-coordinate and the other two three-coordinate. Three coordination of each alkali-metal atom is achieved by bonding to the silicon-bound oxygen atoms of the (Li–O)$_4$-cubane unit. One of the two four-coordinate lithium atoms, Li(1), is also bonded to the oxygen atom O(1), which is not involved in the cubane-cage structure but belongs to the non-lithiated hydroxyl group of the di-tert-butylsilanediol unit. As shown for a pyridine-*N*-oxide adduct [7], the hydrogen atom H(1) of the same hydoxyl group forms an OH ··· O bond with a THF molecule. A second lithium atom becomes four-coordinate by interaction with the oxygen atom O(6) of a water molecule. The hydrogen atoms in the water molecule are disordered between three sites about the Li(4)–O(6) bond. H(61) and H(63) form equivalent intramolecular hydrogen bonds to the nearest fluorine atoms F(2) and F(4) (Fig. 2), and the intermolecular hydrogen bond H(62) ··· F(4a) is slightly longer (287 pm compared to a mean of 222 pm). This presence of the water molecule has not changed the

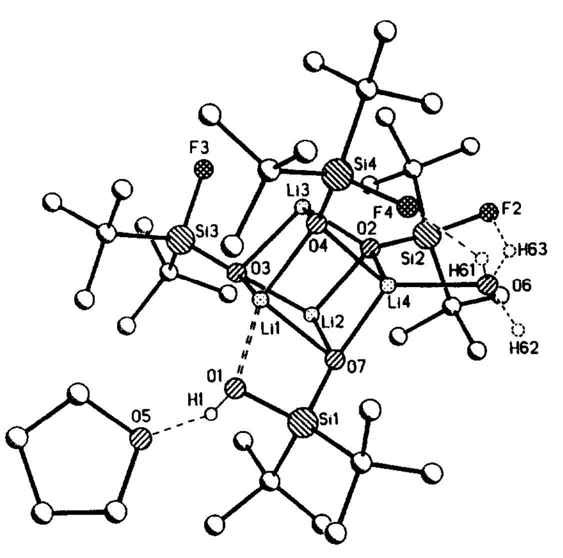


Fig. 1. The crystal structure of 3.

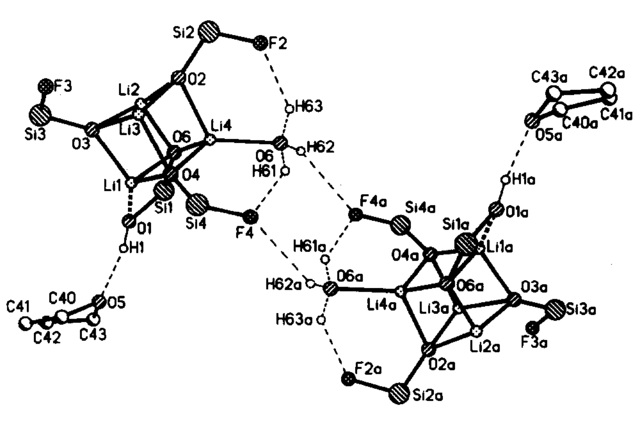
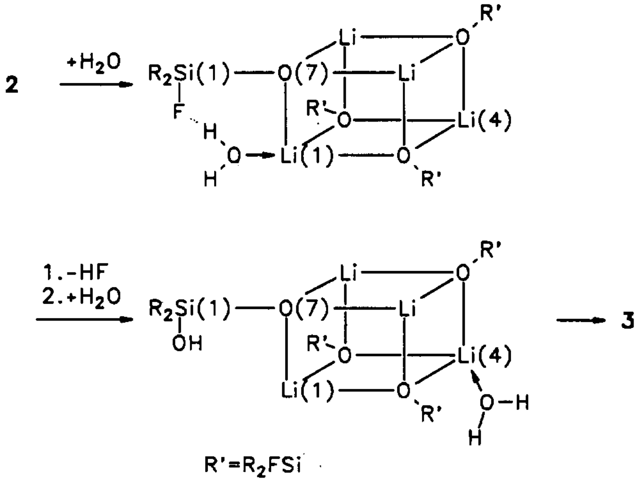


Fig. 2. Two crystallographically-related cubes of 3 showing the inter- and intra-molecular H ··· F hydrogen bridge network.



structural type of the cubane, and so **3** can be described as a stable aquo-complex [8,9].

With one of the four fluorine atoms the one silanolate unit of the tetrameric aggregate **3** substituted by one hydroxyl group, **3** must be regarded as the product of the first of four possible steps in the hydrolysis of **2**. Some reasonable assertions about the conformation of the non-hydrolized lithiated fluorosilanol can thus be made. Firstly, in view of the low degree of hydrolysis (25%), and in the light of the structures of other monolithiated functionalized silanols [2–5], the presence of a $(Li-O)_4$ cubane structure can be postulated for compound **2**. This assumption is further supported by mass spectroscopic data, which reveal that the tetramer **2** is present in the gaseous state. Secondly, because there are no Li–F bonds in the unhydrolized part of **3** [*e.g* Li(3), F(3)], such Lewis acid to base interactions are not likely for **2** even though they were found for the monolithiated diol [5] or aminosilanol [2]. The reason for this difference lies in the nature of the Si–F bond, which is shorter than Si–O and Si–N bonds and correspondingly strong. The isolation and characterization of **3** allows understanding of the mechanism of the hydrolysis process.

As would be expected, the oxygen atom O(1) of the first water molecule attacks a lithium atom [Li(1)] of the cubane. Next, an H–F bridge is formed between one hydrogen atom of that H_2O molecule and the fluorine atom bound to silicon Si(1). The Si–F bonds in functionalized lithiated silanols can be seen as elongated (and therefore weakened), as revealed by a comparison between Si–F distances in metallated species (av. Si–F distance = 163.1 pm) and non-metallated species (157.1 pm. [10]). Because of this it becomes possible for the fluorine atom bound to Si(1) to be substituted by the remaining hydroxyl group [O(1), H(1)] of the H_2O molecule in an S_N2 process. The water molecule [O(6), H(61–63)] found by the X-ray structural study is then the second such molecule that attacks the aggregate. Formation of three partial hydrogen bonds by the two disordered (between three sites) hydrogen atoms of this water molecule, with three different fluorine atoms (two intramolecular and one intermolecular H bonds), initates the second step of hydrolysis. Compound **3** can be viewed as a frozen frame in a multi-step hydrolysis process. The final product of this hydrolysis, hydrogen-bonded dimers of di-tert-butylsilanediol linked by further hydrogen bondings into ladder chains, has already been identified [11].

3. Experimental details

3.1. Lithiated fluorosilanol 2 and aquo-complex 3

Di-tert-butylfluorosilanol (0.03 mol) was treated with 0.03 mol of $^nC_4H_9Li$ (23% in n-hexane) in 150 ml n-hexane. The resulting white precititation **2** was brought into solution by addition of THF. The mixture was stirred in an open flask with exposure to atmospheric moisture for 8 h, and the flask then resealed. After 2 days −12°C the first small crystals appeared. After several recrystallizations crystals of **3** suitable for X-ray structure analysis were isolated in a 10% yield. Lithium-[di-tert-butylfluorosilanolate] **2**: $[C_8H_{18}FliOSi]_4$ (737.02), yield 1.4 g (25%) MS: $m/e = 337$ (20)[M − 7C(CH$_3$)$_3$], 280(2) [M − CH$_3$)$_3$].

Crystal data of 3 (see Tables 1 and 2): $C_{36}H_{83}Li_4O_7F_3Si_4$, M = 825.14, Triclinic, space group $P\bar{1}$, $a = 12.89$ (3), $b = 12.86$ (3), $c = 17.48$ (3) Å, $\alpha = 80.91$ (10), $\beta = 85.24$ (10), $\gamma = 60.72$ (10)°, $U = 2495$ Å^3, $Z = 2$, $D_c = 1.098$ mg m^{-3}, $F(000) = 900$, $\lambda = 0.71073$ Å, $T = 153$ K, μ(Mo Kα) = 0.168 mm^{-1}. Data were collected on a Siemens-Stoe AED using a rapidly-cooled oil-coated crystal of dimensions 0.6 × 0.4 × 0.4 mm by the $2\theta/\omega$ method ($8° \leq 2\theta \leq 48°$). Of a total of 7794 collected reflections, 7794 were unique and 6268 were observed with ($F > 4\sigma(F)$. The structure was solved by direct methods (SHELXS-92) and refined by full matrix least-squares on F^2 with all data to R_1 and wR_2 values of 0.050 and 0.127, respectively (SHELXL-92), and goodness of fit on F^2 of 1.043; largest diff. peak and hole 481 and −328 e mm^{-3}. The hydrogen atoms H1, H61, H62 and H63 were refined with restraints with site occupation factors of 0.66 for H61, H62, and H63. All other hydrogen atoms are placed in calculated positions and refined using a riding model with fixed U values. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of **3**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Li1	1564(4)	687(4)	7221(3)	28(2)
Li2	2551(4)	1838(4)	7577(3)	29(2)
Li3	424(4)	2932(4)	7251(3)	31(2)
Li4	1146(4)	1529(4)	8560(2)	28(2)
Si1	3443.9(6)	−944.0(6)	8050.4(4)	23.6(3)
Si2	1147.6(6)	3976.2(6)	8608.8(4)	24.5(4)
Si3	1708.9(7)	2602.3(7)	5774.1(4)	30.6(4)
Si4	−1175.2(6)	1704.2(6)	7917.3(4)	25.2(4)
O(1)	2776(2)	−1031(2)	7298.8(10)	29.2(9)
H(1)	2900(39)	−1847(27)	7165(26)	95(14)
F(2)	283.8(14)	3982.4(14)	9341.6(9)	33.9(9)
F(3)	506(2)	3908(2)	5795(2)	83.6(12)
F(4)	−1102.9(14)	1086.0(14)	8813.7(9)	36.1(8)
O(7)	2647.1(14)	445(2)	8150.7(10)	25.1(9)
O(2)	1226.8(15)	3052(2)	8066.8(10)	25.6(9)
O(3)	1844(2)	1941(2)	6636.5(10)	32.4(11)
O(4)	51.7(14)	1685(2)	7685.0(10)	25.1(9)
O(6)	599(2)	1429(2)	9703.3(14)	52.9(14)
H(61)	−152(29)	1311(42)	9714(28)	48(8)
H(62)	1211(35)	803(36)	10125(23)	48(8)
H(63)	293(42)	2269(27)	9888(27)	48(8)
C(2)	3326(2)	−1958(3)	8932(2)	31.7(14)
C(3)	3563(3)	−1597(3)	9671(2)	45(2)
C(4)	4156(3)	−3304(3)	8909(2)	47(2)
C(5)	2040(3)	−1745(3)	8974(2)	44(2)
C(6)	5027(2)	−1336(2)	7722(2)	29.6(13)
C(7)	5824(3)	−1546(3)	8391(2)	44.0(15)
C(8)	4961(3)	−271(3)	7147(2)	44(2)
C(9)	5594(3)	−2450(3)	7296(2)	44(2)
C(10)	365(2)	5598(2)	8128(2)	31(2)
C(11)	−61(4)	6486(3)	8722(2)	60(3)
C(12)	−731(3)	5811(3)	7711(2)	53(2)
C(13)	1151(3)	5886(3)	7529(2)	63(2)
C(14)	2646(3)	3408(3)	9070(2)	35(2)
C(15)	3631(3)	3148(4)	8448(2)	56(2)
C(16)	2949(3)	2214(3)	9584(2)	44(2)
C(17)	2641(4)	4281(3)	9577(2)	59(2)
C(18)	2936(3)	2990(3)	5459(2)	45(2)
C(19)	3382(4)	3200(4)	6176(2)	62(2)
C(20)	2481(4)	4117(4)	4849(3)	77(2)
C(21)	4030(3)	1963(4)	5114(2)	67(2)
C(22)	1389(4)	1811(3)	5088(2)	54(3)
C(23)	2366(5)	495(4)	5130(2)	83(5)
C(24)	196(4)	1860(5)	5355(3)	82(4)
C(25)	1240(5)	2421(5)	4240(2)	82(4)
C(26)	−1512(3)	740(3)	7374(2)	37(2)
C(27)	−2297(4)	296(4)	7866(3)	62(2)
C(28)	−327(3)	−370(3)	7206(2)	53(2)
C(29)	−2132(3)	1402(3)	6596(2)	51(2)
C(30)	−2416(2)	3310(2)	7929(2)	29.6(13)
C(31)	−3644(2)	3412(3)	8093(2)	41.4(14)
C(32)	−2457(3)	4091(3)	7155(2)	38.6(15)
C(33)	−2144(3)	3808(3)	8585(2)	39.2(15)
O(5)	2952(2)	−2954(2)	6715.4(14)	52.7(14)
C(40)	2373(3)	−2639(4)	5992(2)	57(2)
C(41)	3313(5)	−3248(6)	5413(3)	100(4)
C(42)	4385(4)	−4176(4)	5885(3)	77(3)
C(43)	3969(3)	−4109(3)	6700(2)	52(2)

TABLE 2. Selected bond lengths (Å) and angles (°) of **3**

Li1-O(4)	1.930(8)	Li1-O(3)	1.940(9)
Li1-O(1)	1.975(9)	Li1-O(7)	2.117(9)
Li2-O(7)	1.861(8)	Li2-O(3)	1.901(9)
Li2-O(2)	1.912(8)	Li3-O(2)	1.897(8)
Li3-O(4)	1.920(9)	Li3-O(3)	1.988(9)
Li4-O(7)	1.909(8)	Li4-O(2)	2.059(9)
Li4-O(6)	2.069(9)	Li4-O(4)	2.087(9)
Si1-O(7)	1.597(6)	Si1-O(1)	1.676(7)
Si2-O(2)	1.594(6)	Si2-F(2)	1.625(6)
Si3-O(3)	1.587(6)	Si3-F(3)	1.640(6)
Si4-O(4)	1.589(6)	Si4-F(4)	1.629(6)
O(1)-H(1)	1.043(23)	H(1) ··· O(5)	1.702(26)
O(6)-H(61)	1.048(24)	O(6)-H(62)	1.049(24)
O(6)-H(63)	1.048(24)	H(61) ··· F(4)	2.208(39)
H(62) ··· F(4A)	2.868(41)	H(63) ··· F(2)	2.253(40)
O(4)-Li1-O(3)	99.02(30)	O(4)-Li1-O(1)	138.45(29)
O(3)-Li1-O(1)	122.04(29)	O(4)-Li1-O(7)	97.13(29)
O(3)-Li1-O(7)	93.04(29)	O(1)-Li1-O(7)	76.23(26)
O(7)-Li2-O(3)	103.06(31)	O(7)-Li2-O(2)	101.13(30)
O(3)-Li2-O(2)	100.62(30)	O(2)-Li3-O(4)	103.42(31)
O(2)-Li3-O(3)	98.10(29)	O(4)-Li3-O(3)	97.68(30)
O(7)-Li4-O(2)	94.43(29)	O(7)-Li4-O(6)	125.94(30)
O(2)-Li4-O(6)	118.42(29)	O(7)-Li4-O(4)	98.80(29)
O(2)-Li4-O(4)	92.53(28)	O(6)-Li4-O(4)	119.39(29)
O(7)-Si1-O(1)	101.12(23)	O(2)-Si2-F(2)	108.77(22)
O(3)-Si3-F(3)	104.52(25)	O(4)-Si4-F(4)	108.87(22)
Si1-O(1)-Li1	92.71(26)	Si1-O(1)-H(1)	122.58(247)
Li1-O(1)-H(1)	140.55(245)	Si1-O(7)-Li2	132.08(23)
Si1-O(7)-Li4	140.80(22)	Li2-O(7)-Li4	83.97(29)
Si1-O(7)-Li1	89.94(26)	Li2-O(7)-Li1	79.15(28)
Li4-O(7)-Li1	81.75(28)	Si2-O(2)-Li3	142.00(22)
Si2-O(2)-Li2	131.57(23)	Li3-O(2)-Li2	80.48(29)
Si2-O(2)-Li4	119.33(24)	Li3-O(2)-Li4	82.10(29)
Li2-O(2)-Li4	78.77(28)	Si3-O(3)-Li2	138.14(23)
Si3-O(3)-Li1	138.55(22)	Li2-O(3)-Li1	82.87(29)
Si3-O(3)-Li3	109.13(26)	Li2-O(3)-Li3	78.44(28)
Li1-O(3)-Li3	80.03(29)	Si4-O(4)-Li3	132.13(23)
Si4-O(4)-Li1	139.81(22)	Li3-O(4)-Li1	81.99(29)
Si4-O(4)-Li4	118.90(24)	Li3-O(4)-Li4	80.81(28)
Li1-O(4)-Li4	82.05(28)	Li4-O(6)-H(61)	107.22(268)
Li4-O(6)-H(62)	119.43(265)	H(61)-O(6)-H(62)	110.36(376)
Li4-O(6)-H(63)	108.44(271)	H(61)-O(6)-H(63)	105.21(377)
H(62)-O(6)-H(63)	105.29(381)		

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References

1 O. Graalmann, U. Klingebbiel, W. Clegg, M. Haase and G. M. Sheldrick, *Chem. Ber., 117* (1984) 2988.
2 O. Graalmann, U. Klingebiel, W. Clegg, M. Haase and G. M.

Sheldrick, *Angew. Chem., 96* (1984) 904; *Angew. Chem., Int. Ed. Engl., 23* (1984) 891.
3 K. Dippel, N. K. Keweloh, P. G. Jones, U. Klingebiel and D. Schmidt-Bäse, *Z. Naturforsch., Teil B., 42* (1987) 1253.
4 D. Schmidt-Bäse and U. Klingebiel, *Chem. Ber., 122* (1989) 815.
5 D. Schmidt-Bäse and U. Klingebiel, *Chem. Ber., 123* (1990) 499.
6 U. Klingebiel, *Angew. Chem., 93* (1981) 696; *Angew. Chem., Int. Ed. Engl., 20* (1981) 678.
7 W. Clegg, G. M. Sheldrick, U. Klingebiel, D. Bentmann, G. Henkel and B. Krebs, *Acta Crystallogr., Sect. C, 40* (1984) 819.
8 D. Barr, P. R. Raithby, P. v. R. Schleyer, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.,* (1990) 643.
9 P. R. Raithby, D. Reed, R. Snaith and D. S. Wright, *Angew. Chem., 103* (1991) 1040.
10 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and A. K. Saxena, *J. Organomet. Chem., 287* (1985) 157.
11 N. H. Buttrus, C. Eaborn, P. B. Hitchcock and A. K. Saxena, *J. Organomet. Chem., 284* (1985) 291.