Journal of Organometallic Chemistry, 356 (1988) 31–38
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Substitution effects in trifluoromethylsilanes: crystal and molecular structure of CF_3SiPh_3

H. Beckers, D.J. Brauer, H. Bürger and C.J. Wilke
Anorganische Chemie, Fachbereich 9, Universität-Gesamthochschule, D-5600 Wuppertal (F.R.G.)

(Received April 29th, 1988)

Abstract

The crystal structure of CF_3SiPh_3 was determined from 2030 observed X-ray data and refined to a conventional R value of 0.046. The compound crystallizes in the monoclinic space group $C2/c$ with a 15.707(4), b 11.549(4), c 20.009(7) Å, β 112.91(2)°, $Z = 8$ and D_c 1.305 g/cm^3. The molecular geometry deviates only slightly from the expected C_3 symmetry, with the CF_3 group nearly staggered with respect to the propeller-like arrangement of the phenyl groups. A torsional barrier for the CF_3 group about the Si–CF_3 bond of 1.9(1) kcal/mol was derived from an analysis of thermal parameters of the CF_3SiC_3 fragment. The thermally corrected Si–CF_3 (1.933(4) Å) and mean C–F (1.370(3) Å) bonds are longer than those in other known CF_3SiX_3 (X = H, F) structures, and reasons for these differences are discussed.

Introduction

Trifluoromethylsilanes have been known for some time [1], but the first structural characterizations of such compounds have been carried out only recently [2,3]. The major feature of the results of these gas phase electron diffraction studies concerns the length of the Si–C bonds. In CF_3SiH_3 [2], this bond is 0.059(2) Å longer than that of CH_3SiH_3 [4], and that in CF_3SiF_3 is longer by 0.082(2) Å [3] than that in CH_3SiF_3[5].

That Si–CF_3 bonds are longer than Si–CH_3 bonds is consistent with the general trend for bonding of CF_3 and CH_3 groups to electropositive elements [6]. Owing to the electronegativity of the fluorine atoms, the partial charge on the carbon atom of a CF_3 group will be large and positive, and this results in different polarities along Si–CF_3 and Si–CH_3 linkages. The polar contributions are repulsive along the Si–CF_3 bond and attractive along the Si–CH_3 bond, ($Si^{\delta+}$–$C^{\delta+}F_3$, $Si^{\delta+}$–$C^{\delta-}H_3$) and this difference is the basis of an explanation for the relatively long Si–C distances in trifluoromethylsilane derivatives [3].

0022-328X/88/$03.50

A modification of the polar model was proposed in order to accommodate the above-mentioned Si–CF_3 bond lengths. In CF_3SiF_3, the distance (r_g 1.910(2) Å [3]) is shorter than that in CF_3SiH_3 (r_g 1.925(1) Å [2]), although polar repulsions along the Si–C bond must be stronger in CF_3SiF_3 than in CF_3SiH_3. This apparent contradiction was explained by suggesting that fluorination reduces the covalent radius of the silicon atom more than the additional polar repulsions stretch the Si–C bond [3]. While indirect support for variations in the silicon covalent radius was derived from molecular orbital calculations [3], the necessity for such changes must be questioned since the difference in the Si–CF_3 distances are in accord with VSEPRT [7] and isovalent hybridization theory [8].

A recent determination of the r_0 structure of CF_3SiH_3 by microwave spectroscopy [9] has not resolved the problem. The structure so derived for the CF_3Si fragment appears to differ slightly (e.g. Si–C 1.900(7) Å) from that found by electron diffraction, but due to correlation effects in the microwave study the differences were not considered to be significant [9].

In order to explore further the effects of substitution in trifluoromethylsilanes, we have examined the crystal structure of CF_3SiPh_3 [10], the first such derivative to be characterized in the solid state, and the results are presented below.

Experimental

Crystals of CF_3SiPh_3, which was prepared as described previously [10], were grown by sublimation in vacuum at 40 °C. A specimen with the dimensions 0.155 × 0.205 × 0.330 mm was attached to a glass fiber and used for the X-ray study. Examination of Weissenberg photographs indicated that the crystal is monoclinic, and the systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l(h) = 2n + 1$) are those of the space groups Cc and $C2/c$, the latter being confirmed by the refinement.

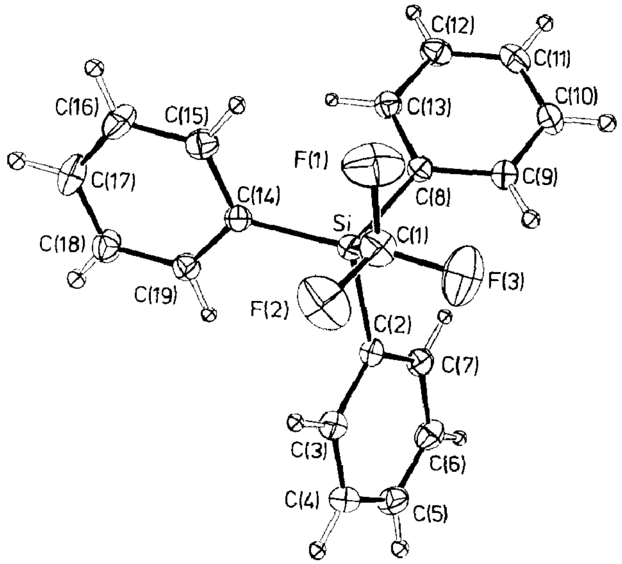


Fig. 1. A perspective drawing of CF_3SiPh_3 with 20% probability thermal ellipsoids for all non-hydrogen atoms.

Table 1

Positional and equivalent isotropic [a] temperature factors for the non-hydrogen atoms of CF_3SiPh_3

Atom	x	y	z	U
Si	0.37843(4)	0.24787(6)	0.43071(4)	0.0463(3)
F(1)	0.5303(2)	0.1601(2)	0.4121(1)	0.128(1)
F(2)	0.4331(1)	0.2308(2)	0.3157(1)	0.120(1)
F(3)	0.5183(2)	0.3402(2)	0.3985(1)	0.127(1)
C(1)	0.4681(2)	0.2444(3)	0.3872(2)	0.070(1)
C(2)	0.3069(2)	0.3794(2)	0.3949(1)	0.049(1)
C(3)	0.2612(2)	0.3966(2)	0.3202(1)	0.059(1)
C(4)	0.2042(2)	0.4908(3)	0.2931(2)	0.069(1)
C(5)	0.1913(2)	0.5688(3)	0.3397(2)	0.072(1)
C(6)	0.2357(2)	0.5551(3)	0.4132(2)	0.067(1)
C(7)	0.2930(2)	0.4607(2)	0.4406(1)	0.054(1)
C(8)	0.4464(1)	0.2537(2)	0.5303(1)	0.0480(9)
C(9)	0.5080(2)	0.3436(2)	0.5621(2)	0.061(1)
C(10)	0.5578(2)	0.3471(3)	0.6359(2)	0.069(1)
C(11)	0.5478(2)	0.2613(3)	0.6795(2)	0.068(1)
C(12)	0.4882(2)	0.1719(3)	0.6497(1)	0.065(1)
C(13)	0.4376(2)	0.1677(2)	0.5759(1)	0.051(1)
C(14)	0.3095(2)	0.1129(2)	0.4027(1)	0.046(1)
C(15)	0.3506(2)	0.0041(2)	0.4146(2)	0.063(1)
C(16)	0.2996(2)	−0.0952(3)	0.3961(2)	0.075(2)
C(17)	0.2046(2)	−0.0890(3)	0.3638(2)	0.077(2)
C(18)	0.1616(2)	0.0170(3)	0.3508(2)	0.069(1)
C(19)	0.2131(2)	0.1163(2)	0.3703(1)	0.054(1)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j \bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$.

Further measurements were made with a Siemens AED 1 diffractometer employing Zr filtered Mo-K_α radiation (λ 0.71073 Å). The cell constants determined at 23°C from the Bragg angles ($10.0° < \theta < 14.6°$) of 36 centered reflections are a 15.707(4), b 11.549(4), c 20.009(7) Å and β 112.91(2)° which imply D_c 1.305 g/cm^3 for $Z = 8$. Intensity data (hkl, $\bar{h}kl$, $2° \leq \theta \leq 25°$) were collected by the θ–2θ step scan technique ($\Delta\theta$ 0.02°, 0.61 s/step). Depending on θ, the number of steps per reflection varied between 48 and 56 with the counts occurring in the middle two-thirds of the scan range being assigned to the peak. A reflection was subjected to a second scan and the results were accumulated if the initial intensity fell between $2\sigma(I)$ and $25\sigma(I)$. The intensities of three hourly-monitored standards fell 9% during data collection. A total of 3356 reflections were measured and corrected for the fluctuations of the standards. These data were reduced to 2946 unique reflections; of these, only the 2030 with $|F_o| \geq 4\sigma(F_o|)$ were used in the refinement. No correction was made for absorption (μ(Mo-K_α) 1.6 cm^{-1}).

The structure was solved by direct methods and refined by full-matrix least-squares techniques. The function minimized was $\Sigma w\, \Delta^2$, where $w = 1/(\sigma^2(|F_o|) + 0.0002|F_o|^2)$ and $\Delta = ||F_o| - |F_c||$. Dispersion-corrected relativistic Hartree-Fock scattering factors were used for all atoms except H(SDS) [11]. Non-hydrogen atoms were varied anisotropically. Hydrogen atoms, all of which were evident in a difference Fourier synthesis, were placed in idealized positions (C–H 0.95 Å), were allowed to ride on the corresponding carbon atom, and were assigned isotropic temperature factors. Refinement of the 223 parameters converged (max. $|\Delta|/\sigma =$

Table 2

Selected bond distances (Å) in CF_3SiPh_3

Si-C(1)	1.923(3)	C(3)-C(4)	1.378(4)	C(11)-C(12)	1.365(4)
Si-C(2)	1.859(3)	C(4)-C(5)	1.368(4)	C(12)-C(13)	1.379(4)
Si-C(8)	1.860(3)	C(5)-C(6)	1.370(4)	C(14)-C(15)	1.390(3)
Si-C(14)	1.855(3)	C(6)-C(7)	1.383(4)	C(14)-C(19)	1.397(3)
C(1)-F(1)	1.331(4)	C(8)-C(9)	1.393(3)	C(15)-C(16)	1.365(4)
C(1)-F(2)	1.328(4)	C(8)-C(13)	1.390(3)	C(16)-C(17)	1.378(4)
C(1)-F(3)	1.326(4)	C(9)-C(10)	1.376(4)	C(17)-C(18)	1.372(4)
C(2)-C(3)	1.398(3)	C(10)-C(11)	1.369(4)	C(18)-C(19)	1.371(4)
C(2)-C(7)	1.386(4)				

0.04) with $R = \Sigma \Delta/\Sigma|F_o| = 0.046$, $wR = [\Sigma w \Delta^2/\Sigma w|F_o|^2]^{1/2} = 0.054$ and $S = [\Sigma w \Delta^2/(2030 - 223)]^{1/2} = 1.95$. Densities in the final difference Fourier range between 0.30 and -0.17 e/Å^2 and thus confirm the structure. Coordinates of the non-hydrogen atoms are listed in Table 1, and the labelling is defined in Fig. 1, hydrogen atoms being numbered according to the carbon atoms to which they are attached. Programs include SHELX-76 [12], THMA [13], ORTEP-2 [14] and several local routines [15*].

Description of the crystal structure

In the solid state, the symmetry of CF_3SiPh_3 is approximately C_3. This symmetry is apparent in Fig. 1, and suggested by the bond distances and angles, which are listed in Tables 2 and 3, respectively. The $SiPh_3$ fragment has adopted the customary propeller-like arrangement of the phenyl groups. This arrangement leads to two groups of C(1)-Si-C-C torsion angles (Table 4), averaging 56.6 and $-125.0°$ respectively. The spread of the torsion angles in each group is significant, and presumably arises from packing effects. Packing forces are probably also responsible for the pivoting of two phenyl groups towards the C_3 axis, the compression displacing the Si atom by 0.100(1) and 0.049(1) Å from the plane of the phenyl groups of C(2) and C(14), respectively. However, intermolecular contacts are not unusual, the shortest, H(5)...H(17) (x, $1+y$, z), being calculated as 2.25 Å after extension of the C-H bonds to 1.096 Å.

The F-C(1)-Si-C torsion angles in Table 4 show that the CF_3 group is rotated by 4.9(5)° about the C(1)-Si bond away from the staggered position. This rotation lengthens the three short F...H(*o*-phenyl) contacts, which average 2.69(4) Å after extension of the C-H bonds to 1.096 Å. For comparison, the sum of the Van der Waals radii for hydrogen and fluorine is 2.67 Å [16]; thus no additional structural effects due to steric interactions between the CF_3 and $SiPh_3$ portions of the molecule are to be expected.

Examination of the shapes of the thermal ellipsoids in Fig. 1 suggests that the CF_3 group is undergoing torsional oscillation about the C(1)-Si bond. A quantitative estimate of this torsional motion was determined by analyzing the thermal parameters of the CF_3SiC_3 fragment by the TLS rigid-body-motion formalism [17]

---

* Reference number with asterisk indicates a note in the list of references.

Table 3

Selected bond angles (°) in CF_3SiPh_3

C(1)–Si–C(2)	106.4(1)	C(5)–C(6)–C(7)	119.9(3)
C(1)–Si–C(8)	105.6(1)	C(2)–C(7)–C(6)	121.1(3)
C(1)–Si–C(14)	106.8(1)	Si–C(8)–C(9)	121.6(2)
C(2)–Si–C(8)	113.1(1)	Si–C(8)–C(13)	121.0(2)
C(2)–Si–C(14)	112.1(1)	C(9)–C(8)–C(13)	117.4(2)
C(8)–Si–C(14)	112.2(1)	C(8)–C(9)–C(10)	121.1(3)
Si–C(1)–F(1)	114.0(2)	C(9)–C(10)–C(11)	120.2(3)
Si–C(1)–F(2)	114.9(2)	C(10)–C(11)–C(12)	120.0(3)
Si–C(1)–F(3)	113.4(2)	C(11)–C(12)–C(13)	120.3(3)
F(1)–C(1)–F(2)	104.6(3)	C(8)–C(13)–C(12)	121.0(3)
F(1)–C(1)–F(3)	104.2(3)	Si–C(14)–C(15)	122.0(2)
F(2)–C(1)–F(3)	104.6(3)	Si–C(14)–C(19)	121.1(2)
Si–C(2)–C(3)	120.7(2)	C(15)–C(14)–C(19)	116.9(2)
Si–C(2)–C(7)	121.8(2)	C(14)–C(15)–C(16)	121.9(3)
C(3)–C(2)–C(7)	117.5(2)	C(15)–C(16)–C(17)	119.8(3)
C(2)–C(3)–C(4)	121.2(3)	C(16)–C(17)–C(18)	119.9(3)
C(3)–C(4)–C(5)	119.8(3)	C(17)–C(18)–C(19)	120.0(3)
C(4)–C(5)–C(6)	120.5(3)	C(14)–C(19)–C(18)	121.5(3)

as modified for internal motion by Dunitz and White [18]. This 21 parameter model fits the 48 U_{ij}'s fairly well $R = [\Sigma(U^{o}_{ij} - U^{c}_{ij})^2/\Sigma U^{o2}_{ij}]^{1/2} = 0.058$. The root-mean-square amplitude of torsion about the C(1)–Si bond is 14.9(5)°, which corresponds to a barrier of 1.9(1) kcal/mol if a threefold, cosine potential function is assumed. Compared to those of isolated molecules, higher barriers are usually found in the solid state [19]; therefore, the fact that the barrier found here is higher than the gas phase values for CF_3SiF_3 (1.2(2) and 1.4(1) kcal/mol by electron diffraction [2] and microwave spectroscopy [20], respectively) and CF_3SiH_3 (1.15(6) kcal/mol [9]) is not necessarily a consequence of substitution.

Interatomic distances in the F_3CSiC_3 fragment were corrected for torsional and librational shortening. The reliability of these corrections is demonstrated by their effect on the mean F...F separation, which is known to be fairly constant in CF_3 groups [21]. For CF_3SiPh_3 the average F...F contact is increased from 2.100 (3) to 2.177(5) Å, the latter being insignificantly longer than the values reported for CF_3SiH_3 (2.163 [2] and 2.164 Å [9]) and CF_3SiF_3 (2.166 Å [3]). Uncorrected values are used in this paper unless otherwise specified.

While the structure of CH_3SiPh_3 has not been reported, an estimate of the fluorination effect on the Si–C bonds in CF_3SiPh_3 may be conjectured from

Table 4

Selected torsion angles (°) in CF_3SiPh_3

C(1)–Si–C(2)–C(3)	55.8(3)	C(1)–Si–C(2)–C(7)	−127.4(3)
C(1)–Si–C(8)–C(9)	59.2(3)	C(1)–Si–C(8)–C(13)	−120.6(3)
C(1)–Si–C(14)–C(15)	54.8(3)	C(1)–Si–C(14)–C(19)	−127.1(3)
F(1)–C(1)–Si–C(8)	54.2(3)	F(1)–C(1)–Si–C(14)	−65.5(3)
F(2)–C(1)–Si–C(14)	55.2(3)	F(2)–C(1)–Si–C(2)	−64.7(3)
F(3)–C(1)–Si–C(2)	55.5(3)	F(3)–C(1)–Si–C(8)	−64.9(3)

Table 5

Comparison of geometries of CF_3SiX_3 compounds

X	Si–CF_3	X–Si–X	C–F	F–C–F	Ref.
F	1.910(2)	108.9(1)	1.342(1)	107.6(1)	3
H	1.925(1)	110.3(3)	1.348(1)	106.7(2)	2
H	1.900(7)	111.69(3)	1.360(3)	105.4(3)	9
C_6H_6 [a]	1.933(4)	112.5(6) [b]	1.370(3) [b]	105.2(3) [b]	This work

[a] These values are corrected for thermal motion. [b] Average values.

structural parameters for two methyl-phenyl-diarylsilanes [22]. Their average Si–CH_3, 1.858(6) Å, and Si–C(Ph), 1.884(4) Å, bond lengths are 0.065(7) Å shorter and 0.026(5) Å longer, respectively, than the corresponding distances in CF_3SiPh_3. The difference in these Si–CH_3 and Si–CF_3 bond lengths matches that found previously [2,3], and the effect of CH_3/CF_3 substitution on Si–C(Ph) distances is similar to the 0.013(2) Å shortening of the Si–F bond length in CF_3SiF_3 [3] relative to that in CH_3SiF_3 [5]. The short Si–C(Ph) distances in CF_3SiPh_3 are accompanied by an average C(Ph)–Si–C(Ph) angle (112.5(6)°) which is not significantly smaller than the largest previously determined values for a triphenylsilane (i.e., 113.5(13)° in $Ph_3SiOClO_3$ [23]). Note that just as CF_3SiPh_3 possesses a long Si–CF_3 bond, the Si–O bond of $Ph_3SiOClO_3$ is also long.

The structures of three CF_3SiX_3 compounds are now known, and some of their geometrical parameters are compared in Table 5. The comparison shows that CF_3SiPh_3 has the longest Si–CF_3 and C–F distances, the largest X–Si–X angles, and smallest F–C–F angles.

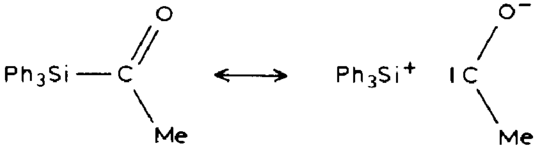
The phenyl groups are planar within experimental error, and their bond distances and angles are typical of silicon-bonded species [24].

Discussion

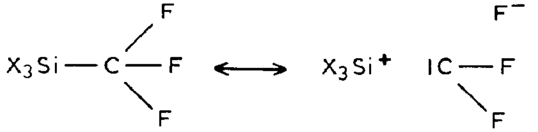
Inspection of Table 5 reveals interesting correlations of the structural parameters in CF_3SiX_3 compounds. The X–Si–X angles increase with the sequence of X = F, H, Ph. If the electron-withdrawing power of X in silanes varies as in phosphines [25] (F > H > Ph), then the trend in the X–Si–X angles is that predicted by VSEPRT [7] and isovalent hybridization theory [8]. These theories also suggest that the Si–C bonds shorten as the electron-withdrawing power of X increases, and this trend is found for the structures determined by X-ray and electron diffraction. But the Si–C bond is weakened (rather than being strengthened inductively) by fluorination at the carbon atom, and observations such as this led to the development of the polar model [6]. Assuming the above-described variations of the withdrawing powers of X, the modified polar model [3] can also rationalize these structural parameters. Nevertheless, it is desirable to see if the bonding in these compounds can be described in such a way that a dependence of bond distances on bond orders becomes apparent.

In this context, the structural similarity of the $CSiPh_3$ fragments of CF_3SiPh_3 and $MeC(O)SiPh_3$ (Si–C(O)Me, 1.93(1) Å, mean Si–C(Ph), 1.864(8) Å; mean

C(Ph)–Si–C(Ph), 111.3(8)° [26]) is noteworthy. The long Si–C(O)Me bond was attributed to resonance with a no-bond structure; that is:



This resonance was justified by noting that silicon is more electropositive than carbon and that carbon is more electropositive than oxygen [27]. While the latter criterion finds no analogy in the Si–CH_3 moiety, it does in the Si-CF_3 fragment:



Thus such resonance would explain not only the greater length of Si–CF_3 bonds but also the positive correlation of the Si–CF_3 and C–F bond distances in the structures determined by X-ray and electron diffraction (Table 5). Furthermore, an increase in the electron withdrawing power of X should destabilize the no-bond resonance structure and thus hinder the resonance, and so this effect could account for the variations of the Si–CF_3 bond length with X. In short, resonance with no-bond structure appears to be a viable alternative to the modified polar interaction model for explaining substitution effects in trifluoromethylsilanes.

Acknowledgements

We wish to thank the Fonds der Chemie for financial support.

References

1 K.G. Sharp and T.D. Coyle, J. Fluorine Chem., 1 (1971/72) 249.
2 H. Beckers, H. Bürger, R. Eujen, B. Rempfer and H. Oberhammer, J. Mol. Struct., 140 (1986) 281.
3 B. Rempfer, G. Pfafferott, H. Oberhammer, H. Beckers, H. Bürger, R. Eujen and J.E. Boggs, Rev. Chim. Miner., 23 (1986) 551.
4 M. Wong, I. Ozier and W.L. Meerts, J. Mol. Spectrosc., 102 (1983) 89.
5 B. Rempfer, H. Oberhammer and N. Auner, J. Am. Chem. Soc., 108 (1986) 3893.
6 H. Oberhammer, J. Fluorine Chem., 23 (1983) 147.
7 R.J. Gillespie, Angew. Chem., 79 (1967) 885; Angew. Chem., Int. Ed. Engl., 6 (1967) 819.
8 H.A. Bent, Chem. Rev., 61 (1961) 275.
9 J.R. Durig, G. Attia, P. Groner, H. Beckers and H. Bürger, J. Chem. Phys., 88 (1988) 545.
10 H. Beckers, H. Bürger, P. Bursch and I. Ruppert, J. Organomet. Chem., 316 (1986) 41.
11 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974; Tables 2.3.1 and 2.2B.
12 G.M. Sheldrick, SHELX-76: Program for crystal structure determination, University of Cambridge, England, 1976.
13 E. Huber-Buser and K.N. Trueblood, THMA: Program for thermal motion analysis, ETH Zürich, 1987.
14 C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
15 F_o, F_c lists, tables of hydrogen and anisotropic thermal parameters may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, by quoting the deposit number CSD 53193, the names of the authors and the literature reference.

16 A. Bondi, J. Phys. Chem., 68 (1964) 441.
17 V. Schomaker and K.N. Trueblood, Acta Crystallogr., B, 24 (1968) 63.
18 J.D. Dunitz and D.N.J. White, Acta Crystallogr., A, 29 (1973) 93.
19 K.N. Trueblood and J.D. Dunitz, Acta Crystallogr., B, 39 (1983) 120.
20 D.R. Lide, Jr., D.R. Johnson, K.G. Sharp and T.D. Coyle, J. Chem. Phys., 57 (1972) 3699.
21 A.I. Kiss and I. Hargittai, Z. Naturforsch A, 37 (1982) 134.
22 E.R. Corey, J.Y. Corey and M.D. Glick, J. Organomet. Chem., 129 (1977) 17.
23 G.K.S. Prakash, S. Keyaniyan, R. Anisfeld, L. Heiliger, G.A. Olah, R.C. Stevens, H.-K. Choi and R. Bau, J. Am. Chem. Soc., 109 (1987) 5123.
24 A. Domenicano, A. Vaciago and C.A. Coulson, Acta Crystallogr., B, 31 (1975) 1630.
25 C.A. Tolman, J. Am. Chem. Soc., 92 (1970) 2953.
26 P.C. Chieh and J. Trotter, J. Chem. Soc. A, (1969) 1778.
27 R.W. Harrison and J. Trotter, J. Chem. Soc. A, (1968) 258.