Journal of Organometallic Chemistry, 269 (1984) 235–238
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CRYSTAL STRUCTURE OF TRIS(PHENYLDIMETHYLSILYL)METHANE

COLIN EABORN*, PETER B. HITCHCOCK, and PAUL D. LICKISS

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received March 7th, 1984)

Summary

The structure of $(PhMe_2Si)_3CH$ has been determined by X-ray diffraction. The central Si–C–Si bond angles (113.99(6)°) are somewhat smaller than those in $(Me_3Si)_3CH$ (116.3(8)°) as measured by electron diffraction in the gas phase.

Introduction

There is considerable interest in the structures of simple compounds in which two or three bulky groups are attached to a central carbon atom, as, for example, in $(Me_3C)_2CH_2$ [1], $(Me_3C)_3CH$ [2], $(Me_3Si)_2CH_2$ [3], and $(Me_3Si)_3CH$ [4], all of which were studied by electron diffraction. It therefore seemed to us appropriate to determine the structure of the related species $(PhMe_2Si)_3CH$, which as a solid could be studied by X-ray diffraction. A second aspect is that the ligand $(Me_3Si)_3C$ (the 'trisyl' ligand) is being increasingly used in organometallic chemistry, often bestowing very unusual properties [5]. These properties arise mainly, but by no means exclusively, from the bulk of the ligand, and it was thus of interest to see whether the $(PhMe_2Si)_3C$ ligand would have even greater bulk, as at first sight might be expected.

Experimental

Preparation of $(PhMe_2Si)_3CH$

This was prepared from CCl_4, $Me_2PhSiCl$ and Mg in THF as described by Ma and Liu [6], but use of ultrasonic activation (Sonicor SC-52 laboratory glassware cleaner) reduced the reaction time from 48 to 6 h and increased the yield from 15 to 22%. M.p. 105 °C (lit. [6], 105–106 °C); ^1H NMR (CCl_4) δ 0.18 (s, 18 H, $SiMe_2$), 0.38 (s, 1H, CH), 7.1–7.2 (unres. m., 15 H, arylH) (lit. [11], δ 0.18, 0.38, 7.16); m/z 403 (68%, $[M - Me]^+$), 325 (23, $[M - C_6H_6 - Me]^+$), 197(20), 135 (100, $[Me_2PhSi]^+$) 105 (18), 73 (23, $[Me_3Si]^+$). The crystal for X-ray study was obtained by recrystallization from pentane.

0022-328X/84/$03.00

Crystal data. $C_{25}H_{34}Si_3$, $M = 418.81$, trigonal, a 15.206(5), c 6.625(4) Å, U 1326.6 Å^3, $Z = 2$, D_c 1.05 g cm^{-3}, $F(000) = 452$. Mo-K_α radiation, λ 0.71069 Å, μ 1.9 cm^{-1}. Space group $P\bar{3}$ from successful structure refinement.

Data were measured on an Enraf–Nonius CAD4 diffractometer using a crystal of size ca. $0.5 \times 0.5 \times 0.3$ mm. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting anles for 25 reflections with $0 \approx 15°$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (1.0 + 0.35 \tan \theta)°$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ, at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.04 subject to a maximum scan time of 120 seconds. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lp effects but not for absorption, and after averaging of any equivalent reflections 2463 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + 0.04(I)^2]^{1/2}/\mathrm{Lp}$.

The space group was initially assumed to be $P3$, and Si and C atoms of the molecules were located by routine heavy atom methods. Since the two molecules in the unit cell were related by an inversion centre the space group was then taken to be $P\bar{3}$. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least squares. A low angle difference map showed the phenyl H atoms and H(1), which were included in the least squares with isotropic temperature factors. A subsequent difference map using the full data clearly showed the methyl H atoms, which were held fixed at positions from the map. Refinement converged at

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ FOR Si AND C, $\times 10^3$ FOR H) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
Si(1)	2139.2(6)	6691.3(6)	1323 3(14)
C(1)	3333	6667	2037(7)
C(2)	1032(2)	5838(3)	2902(6)
C(3)	1802(2)	6362(3)	−1361(6)
C(4)	2295(2)	7989(2)	1753(6)
C(5)	2253(3)	8317(3)	3680(6)
C(6)	2377(3)	9262(3)	4056(7)
C(7)	2507(3)	9884(3)	2493(7)
C(8)	2557(3)	9601(2)	556(7)
C(9)	2472(2)	8680(2)	195(6)
H(1)	333	667	329(7)
H(5)	214(3)	798(3)	466(6)
H(6)	244(2)	941(2)	520(6)
H(7)	256(2)	1027(2)	251(4)
H(8)	273(2)	1001(3)	−34(6)
H(9)	265(2)	867(2)	−118(6)
H(2A)	68	508	250
H(2B)	51	594	250
H(2C)	119	576	416
H(3A)	135	645	−166
H(3B)	168	576	−168
H(3C)	221	662	−209

TABLE 2. INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bonds			
Si(1)-C(1)	1.895(1)	Si(1)-C(2)	1.851(2)
Si(1)-C(3)	1.849(2)	Si(1)-C(4)	1.887(2)
C(4)-C(5)	1.384(3)	C(4)-C(9)	1.400(2)
C(5)-C(6)	1.376(3)	C(6)-C(7)	1.349(4)
C(7)-C(8)	1.368(4)	C(8)-C(9)	1.362(3)
(b) Angles			
C(1)-Si(1)-C(2)	112.93(9)	C(1)-Si(1)-C(3)	111.9(1)
C(1)-Si(1)-C(4)	111.23(6)	C(2)-Si(1)-C(3)	108.78(9)
C(2)-Si(1)-C(4)	104.05(8)	C(3)-Si(1)-C(4)	107.53(9)
Si(1)-C(1)-Si(1)	113.99(6)	Si(1)-C(4)-C(5)	120.8(1)
Si(1)-C(4)-C(9)	123.4(1)	C(5)-C(4)-C(9)	115.8(2)
C(4)-C(5)-C(6)	122.5(2)	C(5)-C(6)-C(7)	119.3(2)
C(6)-C(7)-C(8)	120.8(2)	C(7)-C(8)-C(9)	119.8(2)
C(4)-C(9)-C(8)	121.8(2)		

$R = 0.091$, $R' = 0.131$, when the maximum shift/error was 0.3 and the weighting scheme was $w = 1/\sigma^2\,(F)$. The final difference map contained unresolved electron density along the three-fold axis at 0.0, z rising to a maximum of 2.0 eÅ^{-3}. Attempts to include solvent (pentane) atoms at partial occupancy in the least squares always resulted in physically unreasonable temperature factors and bond lengths, and were abandoned.

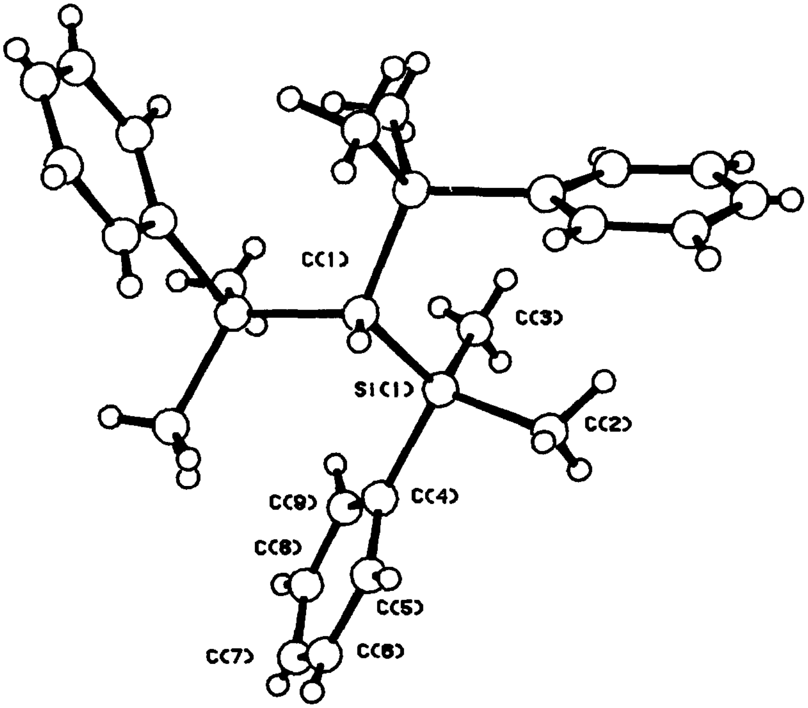

Fig. 1. An ORTEP [8] drawing showing the molecular structure of $(PhMe_2Si)_3CH$ and the atom numbering scheme. The numbering of the H atoms follows that of the C atoms.

The structure solution and refinement was carried out on a PDP 11/34 computer using the Enraf–Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 7. Final atom coordinates are listed in Table 1, and bond lengths and angles are listed in Table 2. Tables of temperature factors and final structure factors are available from the authors.

The molecular structure is depicted in Fig. 1, which also gives the atom numbering scheme. The molecules have crystallographically-imposed C_3 symmetry.

Discussion

The main features of the structure are as expected from the results for $(Me_3Si)_3CH$ [4]. In particular, the strain is relieved mainly by opening of the Si–C(1)–Si (113.99(6)°) and the C(1)–Si–C angles (mean 112.0(7)°) and closing of the other C–Si–C angles (mean 106.8(13)°), and the Si–C(1) bonds (1.895(1)°) are slightly longer than the other Si–C bonds (mean 1.862(13)°). The most interesting feature is that the central Si–C(1)–Si angles, 113.99(6)°, are smaller than those (116.3(8)°) in $(Me_3Si)_3CH$, as determined by electron diffraction in the gas phase, implying that the $(PhMe_2Si)_3C$ ligand may have a smaller effective bulk than the $(Me_3Si)_3C$ ligand. (The observation that $(PhMe_2Si)_3CSiMe_2X$ compounds are generally a little more reactive than the corresponding $(Me_3Si)_3CSiMe_2X$ compounds [9] is consistent with this.) This is made possible by the ability of the phenyl groups to present the face of the ring to the nearest methyl groups on the other silicon atoms, so that the interaction is less than that for a methyl group in the same position. The atoms C(4) and C(7) are 0.29 and 0.78 Å, respectively, out of the plane of the three silicon atoms, and the mean plane of the Ph carbon atoms (maximum deviation 0.02 Å) makes an angle of 85° with the Si_3 plane.

There is a significant distortion of the phenyl ring, of the type commonly observed when a more electropositive element is attached to one of the carbon atoms [10]. Thus the internal angle at the ipso carbon atom, C(5)–C(4)–C(9), is only 115.8(2)°, and the lengths of the ring bonds to this carbon (mean 1.392 Å) are larger than those of the other ring C–C bonds (mean 1.363 Å).

Acknowledgments

We thank the S.E.R.C. for support of this work, and for the award of a Research Studentship to P.D.L..

References

1 L.S. Bartell and W.F. Bradford, J. Mol Struct., 37 (1977) 113.
2 H.B. Burgi and L.S. Bartell, J. Am. Chem Soc, 94 (1972) 5236.
3 T. Fjeldberg, R Seip, M.F Lappert, and A.J. Thorne, J. Mol. Struct., 99 (1983) 295
4 B. Beagley, R.G. Pritchard, C. Eaborn, and S.S. Washburne, J. Chem. Soc., Chem. Commun., (1981) 710; B. Beagley and R.G. Pritchard, J. Mol. Struct, 84 (1982) 129.
5 See, for example, A.H. Cowley, J.E. Kilduff, E.A.V. Ebsworth, D W.H Rankin, H E. Robertson, and R. Seip, J. Chem. Soc, Dalton Trans., (1984) 689, and refs. therein
6 S.-L. Liu and M.-M. Ma, J. Organomet. Chem., 24 (1970) 89
7 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.
8 C K. Johnson, Report ORNL-3794 (1965), Oak Ridge National Laboratory, Oak Ridge, Tennessee
9 C. Eaborn and A.I. Mansour, unpublished results.
10 A. Domenicano, A Vaciago, and C.A Coulson, Acta. Cryst B, 31 (1975) 221
11 G Fritz and U. Finke, Z. Anorg Allg. Chem., 430 (1977) 121