

THE PREPARATION AND MOLECULAR STRUCTURE OF THE HIGHLY STERICALLY HINDERED TRIS(TRIMETHYLSILYL)METHYLBORON COMPOUND $(\text{Me}_3\text{Si})_3\text{CB}(\text{Ph})[\text{O}(\text{CH}_2)_4\text{C}(\text{SiMe}_3)_3]$

COLIN EABORN ^{*}, NEGUSSIE RETTA, J. DAVID SMITH ^{*} and PETER B. HITCHCOCK
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ
(Great Britain)

(Received April 1st, 1982)

Summary

The reaction between $(\text{Me}_3\text{Si})_3\text{CLi}$ and BF_3 in $\text{Et}_2\text{O}/\text{THF}$ gives the fluoride $(\text{Me}_3\text{Si})_3\text{CB}(\text{F})[\text{O}(\text{CH}_2)_4\text{C}(\text{SiMe}_3)_3]$, which upon treatment with PhLi gives the corresponding phenyl compound $(\text{Me}_3\text{Si})_3\text{CB}(\text{Ph})[\text{O}(\text{CH}_2)_4\text{C}(\text{SiMe}_3)_3]$. A single crystal X-ray diffraction study has shown that in the latter the three bonds to boron lie in a plane, which is almost perpendicular to the plane of the Ph group. The C—SiMe₃ bonds (mean 1.900(12) Å) are probably longer than the Si—Me bonds (mean 1.867(15) Å), and the C—Si—Me angles (mean 113.0(13)°) are larger than the Me—Si—Me angles (mean 105.6(12)°).

Introduction

Studies of compounds in which the very bulky tris(trimethylsilyl)methyl group $(\text{Me}_3\text{Si})_3\text{C}$ (the 'trisyl' group, frequently denoted by Tsi) is attached to a metal or metalloid have shown some of them to have very unusual properties. Derivatives of Li [1], Si [1,2], Ge [3,4], Sn [5], P [6], Hg [7–9], Zn [9] and Cd [9] have previously been studied, and we now describe the first trisyl derivatives of boron.

Results and discussion

Interaction of TsiLi , prepared as usual in $\text{Et}_2\text{O}/\text{THF}$, with BF_3 in THF was found to give a compound with an elemental analysis and mass spectrum consistent with a species containing boron, two Tsi groups, a fluorine atom, and a THF molecule, but the possible structure $(\text{Tsi})_2\text{BF} \cdot \text{THF}$ for this compound was ruled out by the appearance in the ^1H NMR spectrum of two singlets of equal height from the Me_3Si protons. The compound reacted with PhLi in

Et_2O to give a product in which the fluorine atom had been replaced by a phenyl group, and again the Me_3Si protons gave two singlets of equal height in the ^1H NMR spectrum. To establish the nature of the compounds obtained, a single crystal X-ray diffraction study was carried out on the phenyl derivative, which was thus shown to be $\text{TsiB(Ph)[O(CH}_2)_4\text{C(SiMe}_3)_3]$ (I). The fluoride must thus be $\text{TsiB(F)[O(CH}_2)_4\text{C(SiMe}_3)_3]$ (II).

The way in which the fluoride II is formed is a matter for speculation. Ethers are known to react with BF_3 to give alcohols and olefins [10], but these could not lead to the observed product. Since the TsiLi solution, by its method of preparation, contained an equivalent of LiCl , it is conceivable that some B-Cl bonds were present in small amounts in equilibrium with B-F bonds, so that a species containing the $\text{BO(CH}_2)_4\text{Cl}$ system might be formed [11], and this could possibly react to give a $\text{BO(CH}_2)_4\text{Tsi}$ system. It seems more likely, however, that the THF is cleaved by TsiLi to give $\text{Tsi(CH}_2)_4\text{OLi}$, which then reacts at a B-F bond, but such cleavage does not normally occur (at least not on the scale necessary to explain the results described above) in solutions of TsiLi in $\text{Et}_2\text{O/THF}$, since there has never been any indication of the production of $\text{SiO(CH}_2)_4\text{Tsi}$ species in the reactions of TsiLi with silicon halides in this medium [2]. We suggest that the cleavage of the THF by TsiLi is promoted by complexing of the ether with BF_3 or TsiBF_2 .

The molecular structure of $\text{TsiB(Ph)[O(CH}_2)_4\text{Tsi}]$ (I)

The structure of I is depicted in Fig. 1, which shows the atom numbering system used, and bond lengths and angles are given in Table 1.

Since atoms C(17) and C(18) are apparently disordered (see Experimental section), data referring to these and nearby atoms cannot be regarded as significant. When such data are omitted, there are no surprising features in the structure. The three bonds to boron lie in a plane (Table 2), and this plane is almost perpendicular to that of the aromatic ring, this arrangement presumably minimizing the steric interaction between the phenyl and the nearer trisyl group at

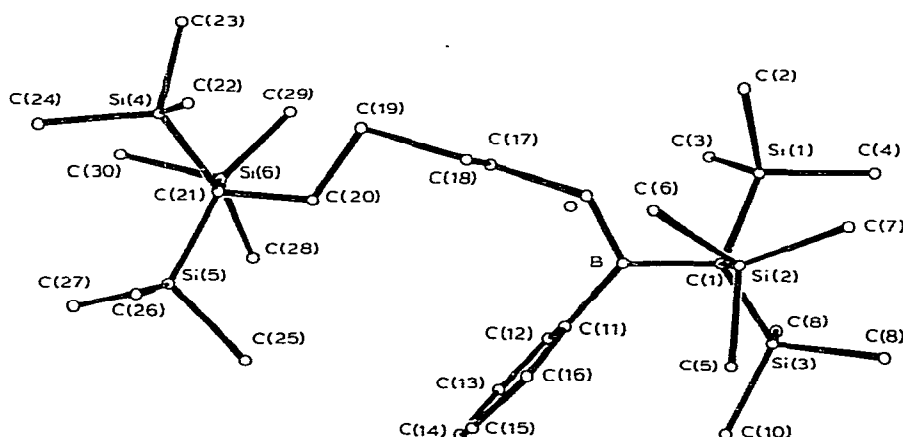


Fig. 1. Structure of $(\text{Me}_3\text{Si})_3\text{CB(Ph)[O(CH}_2)_4\text{C(SiMe}_3)_3]$.

TABLE 1

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

Bonds			
Si(1)—C(1)	1.917(6)	Si(1)—C(2)	1.868(8)
Si(1)—C(3)	1.873(8)	Si(1)—C(4)	1.887(8)
Si(2)—C(1)	1.904(6)	Si(2)—C(5)	1.875(8)
Si(2)—C(6)	1.862(9)	Si(2)—C(7)	1.864(8)
Si(3)—C(1)	1.904(7)	Si(3)—C(8)	1.844(8)
Si(3)—C(9)	1.874(8)	Si(3)—C(10)	1.870(9)
Si(4)—C(21)	1.878(7)	Si(4)—C(22)	1.859(8)
Si(4)—C(23)	1.892(8)	Si(4)—C(24)	1.868(8)
Si(5)—C(21)	1.903(7)	Si(5)—C(25)	1.862(9)
Si(5)—C(26)	1.886(9)	Si(5)—C(27)	1.869(8)
Si(6)—C(21)	1.891(6)	Si(6)—C(28)	1.825(10)
Si(6)—C(29)	1.859(8)	Si(6)—C(30)	1.875(9)
O—B	1.363(10)	O—C(17)	1.817(14)
B—C(1)	1.567(11)	B—C(11)	1.540(11)
C(11)—C(12)	1.386(10)	C(11)—C(16)	1.392(10)
C(12)—C(13)	1.365(11)	C(13)—C(14)	1.348(13)
C(14)—C(15)	1.345(13)	C(15)—C(16)	1.412(12)
C(17)—C(18)	1.210(13)	C(18)—C(19)	1.88(2)
C(19)—C(20)	1.521(10)	C(20)—C(21)	1.588(9)
Angles			
C(1)—Si(1)—C(2)	114.3(3)	C(1)—Si(1)—C(3)	110.9(3)
C(1)—Si(1)—C(4)	113.4(3)	C(2)—Si(1)—C(3)	106.8(4)
C(2)—Si(1)—C(4)	104.7(4)	C(3)—Si(1)—C(4)	106.1(4)
C(1)—Si(2)—C(5)	112.7(4)	C(1)—Si(2)—C(6)	112.3(3)
C(1)—Si(2)—C(7)	113.5(3)	C(5)—Si(2)—C(6)	103.9(4)
C(5)—Si(2)—C(7)	107.3(4)	C(6)—Si(2)—C(7)	106.4(4)
C(1)—Si(3)—C(8)	112.1(3)	C(1)—Si(3)—C(9)	112.9(3)
C(1)—Si(3)—C(10)	115.7(3)	C(8)—Si(3)—C(9)	106.4(4)
C(8)—Si(3)—C(10)	104.6(4)	C(9)—Si(3)—C(10)	104.2(4)
C(21)—Si(4)—C(22)	112.2(4)	C(21)—Si(4)—C(23)	113.6(3)
C(21)—Si(4)—C(24)	114.0(4)	C(22)—Si(4)—C(23)	105.4(4)
C(22)—Si(4)—C(24)	105.3(4)	C(23)—Si(4)—C(24)	105.4(4)
C(21)—Si(5)—C(25)	111.6(4)	C(21)—Si(5)—C(26)	111.5(4)
C(21)—Si(5)—C(27)	114.7(3)	C(25)—Si(5)—C(26)	104.0(4)
C(25)—Si(5)—C(27)	107.4(4)	C(26)—Si(5)—C(27)	107.0(4)
C(21)—Si(6)—C(28)	111.6(4)	C(21)—Si(6)—C(29)	115.1(3)
C(21)—Si(6)—C(30)	112.7(3)	C(28)—Si(6)—C(29)	103.8(4)
C(28)—Si(6)—C(30)	107.1(5)	C(29)—Si(6)—C(30)	105.8(4)
B—O—C(17)	129.2(7)	O—B—C(1)	114.3(7)
O—B—C(11)	117.1(7)	C(1)—B—C(11)	128.6(8)
Si(1)—C(1)—Si(2)	110.6(3)	Si(1)—C(1)—Si(3)	110.6(3)
Si(1)—C(1)—B	105.5(4)	Si(2)—C(1)—Si(3)	110.0(3)
Si(2)—C(1)—B	106.6(4)	Si(3)—C(1)—B	113.4(5)
B—C(11)—C(12)	121.8(8)	B—C(11)—C(16)	123.5(8)
C(12)—C(11)—C(16)	114.7(7)	C(11)—C(12)—C(13)	123.5(8)
C(12)—C(13)—C(14)	120.4(9)	C(13)—C(14)—C(15)	119.7(9)
C(14)—C(15)—C(16)	120.3(9)	C(11)—C(16)—C(15)	121.3(8)
O—C(17)—C(18)	83(1)	C(17)—C(18)—C(19)	85(1)
C(18)—C(19)—C(20)	103.3(6)	C(19)—C(20)—C(21)	117.1(6)
Si(4)—C(21)—Si(5)	110.2(4)	Si(4)—C(21)—Si(6)	112.3(3)
Si(4)—C(21)—C(20)	111.4(5)	Si(5)—C(21)—Si(6)	110.0(3)
Si(5)—C(21)—C(20)	103.1(4)	Si(6)—C(21)—C(20)	109.4(5)

TABLE 2

DEVIATIONS (Å) OF ATOMS FROM MEAN PLANES. ATOMS MARKED * WERE NOT USED IN THE CALCULATION OF THE PLANE

(a)	B 0.01, O 0.00, C(1) 0.00, C(11) 0.00; Si(1)* -1.12, Si(2)* 1.79, Si(3)* -0.66
(b)	C(11) -0.01, C(12) 0.00, C(13) 0.01, C(14) 0.00, C(15) -0.02, C(16) 0.02; B* -0.07

Angle between planes a and b is 95°

the expense of overlap between the π -orbitals of the ring and the vacant p -orbital on boron. The C(1)—B—C(11) angle is significantly larger than the other two bond angles at boron. As in all the trisyl compounds for which the structures have been determined, the C—SiMe₃ bonds of the C(SiMe₃)₃ group (mean length 1.900(12) Å) are probably longer than the Si—Me bonds (mean length 1.867(15) Å), and the C—Si—Me angles of the group (mean 113.0(13)°) are distinctly larger than the Me—Si—Me angles (mean 105.6(12)°).

Experimental

Spectra. The ¹¹B and ¹⁹F NMR spectra were recorded on a Brüker Multi-nuclear WP 80SY FT spectrometer. The shifts (downfield positive) for the ¹¹B spectra (recorded at 25.7 MHz) are relative to BF₃·Et₂O and for the ¹⁹F spectra (at 75.4 MHz) relative to CFCl₃.

Mass spectra were recorded at 70 eV.

Preparation of fluoro[tris(trimethylsilyl)methyl] [5,5,5-tris(trimethylsilyl)-pentoxy] borane

A solution of TsiH (2 g, 8.7 mmol) in anhydrous THF (30 cm³) was added to MeLi (9.6 mmol, prepared from MeCl) in ether (8 cm³), and the mixture was stirred for 20 h at room temperature, then refluxed for 0.5 h (cf. ref. 1). The solution was added dropwise to a gently refluxing solution of BF₃·Et₂O (1.42 g, 10 mmol of BF₃; dried by distillation from CaH₂) in anhydrous Et₂O (30 cm³). Refluxing was continued for 4 h, then the solvent was removed and the residue was extracted with pentane. The pentane extract was evaporated to leave a thick liquid residue, which upon washing with MeOH gave white crystals of [(Me₃Si)₃C][(Me₃Si)₃C(CH₂)₄O]BF (1.34 g, 55% based on TsiH taken). A sample for analysis, m.p. 189–191°C, was obtained by sublimation (Found: C, 51.4; H, 11.3. C₂₄H₆₂BFOSi₆ calcd.: C, 51.1; H, 11.1%); ¹H NMR (C₆D₆, with CH₂Cl₂ as reference) δ (ppm) 0.13 (s, 27 H, Me₃Si), 0.18 (s, 27 H, Me₃Si), 1.47–1.76 (unresolved m, 6 H, CH₂), 3.84 (m, 2 H, CH₂O); ¹⁹F NMR (C₆D₆) -75.0 ppm; ¹¹B NMR, 29.8–31.1 ppm (br, s). (As with the related compounds EtBF(OBu-t) [12] and s-Bu₃CBF(OCe₃) [13], coupling between fluorine and boron was not observed.) The mass spectrum showed a base peak at m/e 73 (abundance 100), and the expected strong peak at 549 (32) (M - Me) and a significant peak at 545 (10) (M - F).

Similar results were obtained when reverse addition was used, and when the TsiLi/BF₃ mol ratio was increased to 3/1.

Preparation of phenyl[tris(trimethylsilyl)methyl] [5,5,5-tris(trimethylsilyl)-pentoxyl] borane

A solution of PhLi (8 ml of 1.24 *M* solution in Et₂O; prepared from PhBr) was added dropwise with stirring to a solution of (Tsi)(Tsi(CH₂)₄O)BF (0.50 g, 0.89 mmol) in anhydrous ether (20 cm³) at room temperature. The mixture was refluxed for 16 h, then the solvent was removed and pentane was added, followed by water. The organic layer was separated and combined with further pentane extracts of the aqueous layer. The combined extracts were washed with water, dried (MgSO₄) and filtered, and the solvent was evaporated to leave a thick liquid, which was crystallized from CH₂Cl₂/MeOH to give [(Me₃Si)₃C]-[(Me₃Si)₃C(CH₂)₄O](Ph)B (0.4 g, 73%), m.p. 122°C (decomp.) (Found: C, 57.7; H, 10.7. C₃₀H₆₇BOSi₆ calcd.: C, 57.9; H, 10.8%); ¹H NMR (CCl₄ with CH₂Cl₂ as reference), δ(ppm) 0.13 (s, 27 H, Me₃Si), 0.19 (s, 27 H, Me₃Si), 1.43–1.55 (unresolved m, 6 H, CH₂), 3.52 (m, 2 H, CH₂O), 7.03–7.38 (m, 5 H, Ph); ¹¹B NMR ca. –10 ppm (very br.; width ca. 3900 Hz). The mass spectrum showed the expected [*M* – Me] peak at *m/e* 607.

Structure determination

Crystal data. C₃₀H₆₇BOSi₆, *M* = 623.2, monoclinic, *a* 9.003(8), *b* 28.219(6), *c* 15.664(3) Å, β 91.28(5)°, *U* 3978.5 Å³, *Z* = 4, *D_c* 1.04 g cm^{–3}, *F*(000) = 1376. Mo-*K*_α radiation, λ 0.71069 Å, μ 2.3 cm^{–1}. Space group *P*2₁/*n* from systematic absences of 0*h*0 for *h* odd and *h*0*l* for (*h* + *l*) odd.

Crystals of the title compound from pentane solution were transparent needles whose diffraction pattern decayed on exposure to air. The data crystal, ca. 0.5 × 0.3 × 0.18 mm, cut from a longer piece, was sealed in a capillary tube and was then stable, although it did not diffract above θ = 20°. Data were measured on an Enraf-Nonius CAD4 diffractometer. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting reflections for 25 strong reflections with θ ≈ 15°. Intensities for *h**k*±*l* reflections with 2 < θ < 20° were measured by a θ/2θ scan with a scan width of Δθ = (1.0 + 0.35 tan θ)°. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{–1} in θ at which point any reflections with *I* < σ(*I*) were coded as unobserved. The remaining reflections were re-scanned at such a speed as to give σ(*I*)/*I* of 0.05 subject to a maximum scan time of 120 s. Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarization (Lp) effects but not for absorption, and, after averaging equivalent data, 1955 reflections with |*F*²| > σ(*F*²) were used in the structure refinement. The values of σ(*F*²) were taken as [σ²(*I*) + (0.05 *I*)²]^{1/2}/Lp.

A partial structure was found by direct methods using the MULTAN program [14] and the remaining non-hydrogen atoms found on a Fourier map. After refinement with anisotropic temperature factors by full matrix least squares it was apparent that C(17) and C(18) had peculiar temperature factors and bond lengths and were probably disordered. A difference map calculated after omitting these atoms showed both to have very elongated electron density peaks but with no obvious division into alternative sites. The matter was not therefore taken further, and atoms C(17) and C(18) were each left on a single site. Hydrogen atoms except for those on C(17) and C(18) were placed at calculated positions

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Si(1)	9529(3)	1977(1)	835(2)
Si(2)	9382(4)	2469(1)	-963(2)
Si(3)	12322(3)	1985(1)	-332(2)
Si(4)	9181(4)	5260(1)	2514(2)
Si(5)	12226(4)	5263(1)	1627(2)
Si(6)	11944(4)	4776(1)	3396(2)
O	9916(8)	2983(2)	959(5)
B	10997(14)	2814(4)	445(7)
C(1)	10614(10)	2328(3)	8(5)
C(2)	7549(12)	2163(4)	933(7)
C(3)	10416(14)	2035(4)	1923(6)
C(4)	9438(13)	1321(4)	602(7)
C(5)	10474(15)	2650(4)	-1915(6)
C(6)	8135(14)	2983(4)	-777(8)
C(7)	8160(12)	1966(4)	-1301(7)
C(8)	13352(11)	1729(4)	588(8)
C(9)	11858(13)	1479(4)	-1066(8)
C(10)	13743(13)	2334(4)	-917(7)
C(11)	12430(10)	3110(3)	388(6)
C(12)	13569(11)	3073(4)	995(7)
C(13)	14836(12)	3338(4)	979(8)
C(14)	15034(12)	3660(5)	356(10)
C(15)	13974(13)	3720(4)	-252(9)
C(16)	12683(12)	3436(4)	-259(7)
C(17)	10038(16)	3436(5)	1783(8)
C(18)	9260(15)	3658(5)	1287(9)
C(19)	9341(12)	4141(4)	2113(7)
C(20)	10643(12)	4444(4)	1837(6)
C(21)	10945(10)	4920(3)	2353(5)
C(22)	7890(14)	5220(5)	1574(8)
C(23)	8077(11)	5044(4)	3452(7)
C(24)	9467(14)	5908(4)	2702(8)
C(25)	13567(14)	4865(5)	1093(8)
C(26)	11161(15)	5549(5)	714(7)
C(27)	13326(13)	5742(4)	2171(7)
C(28)	13838(14)	4573(5)	3225(9)
C(29)	11104(13)	4291(4)	4026(7)
C(30)	12073(15)	5299(4)	4133(6)

(C—H 1.08 Å) and held fixed with a common isotropic temperature factor of B 5.0 Å² [15]. Further refinement converged at $R = 0.074$, $R' = 0.088$, where the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure was solved and refined using a PDP11/34 computer with the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 15. Final atomic coordinates are given in Table 3, and lists of temperature factors, H atom positions, and structure factors may be obtained from the authors.

Acknowledgement

N.R. thanks the University of Addis Ababa for granting him study leave and the British Council for financial support. We are grateful to the Dow Corning Co., Ltd., for a gift of trimethylchlorosilane, and to the SERC for provision of X-ray equipment.

References

- 1 M.A. Cook, C. Eaborn, A.E. Jukes and D.R.M. Walton, *J. Organometal. Chem.*, **24** (1970) 529.
- 2 S.S. Dua, C. Eaborn, D.A.R. Happer, S.P. Hopper, K.D. Safa and D.R.M. Walton, *J. Organometal. Chem.*, **178** (1979) 75; C. Eaborn, D.A.R. Happer, P.B. Hitchcock, S.P. Hopper, K.D. Safa, S.S. Washburne and D.R.M. Walton, *ibid.*, **186** (1980) 309; C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, *ibid.*, **188** (1980) 179; C. Eaborn and S.P. Hopper, *ibid.*, **192** (1980) 27; S.S. Dua and C. Eaborn, *ibid.*, **204** (1981) 21; C. Eaborn and K.D. Safa, *ibid.*, **204** (1981) 169; C. Eaborn and F.M.S. Mahmoud, *ibid.*, **220** (1981) 139; C. Eaborn, P.B. Hitchcock and K.D. Safa, *ibid.*, **222** (1981) 187; C. Eaborn and F.M.S. Mahmoud, *J. Chem. Soc. Perkin II*, (1981) 1309; C. Eaborn, K.D. Safa, A. Ritter and W. Binder, *J. Chem. Soc. Chem. Comm.*, (1981) 175.
- 3 C. Eaborn and N.P.Y. Siew, *J. Organometal. Chem.*, **202** (1980) 157.
- 4 I.V. Borisova, N.N. Zemlyanskii, N.D. Kolosova, Yu.A. Ustynyuk and I.P. Beletskaya, *Bull. Acad. Sci., U.S.S.R.*, **28** (1979) 2222.
- 5 F. Glockling, P. Harriott and W.K. Ng, *J. Chem. Research*, (1979) S12, M275; F. Glockling and W.K. Ng, *ibid.*, (1980) S230, M3128; *idem*, *J. Chem. Soc. Dalton Trans.*, (1981) 1101.
- 6 K. Issleib, H. Schmidt and C. Wirkner, *Z. Chem.*, **20** (1980) 153, 419; *Z. Anorg. Allgm. Chemie*, **473** (1981) 85.
- 7 A.R. Bassindale, A.J. Bowles, M.A. Cook, C. Eaborn, A. Hudson, R.A. Jackson and A.E. Jukes, *Chem. Commun.*, (1970) 559.
- 8 F. Glockling, N.S. Hosmane, V.B. Mahale, J.J. Swindall, L. Magos and T.J. King, *J. Chem. Res.* (1977), S116, M1201.
- 9 C. Eaborn, N. Retta and J.D. Smith, *J. Organometal. Chem.*, **190** (1980) 101.
- 10 E.F. Mooney and M.A. Qaseem, *Chem. Commun.*, (1967) 230.
- 11 W. Gerrard and M.F. Lappert, *Chem. Revs.*, **58** (1958) 1081.
- 12 H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99** (1966) 1049.
- 13 H.C. Brown and B.A. Carlson, *J. Organometal. Chem.*, **54** (1973) 61.
- 14 G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.*, **A27** (1971) 360.
- 15 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.