Determination by Electron Diffraction of the Molecular Structure of Bromotris(methoxydimethylsilyl)methane in the Gas Phase

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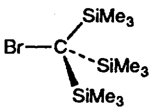
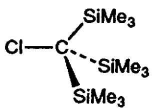
The molecular structure of bromotris(methoxydimethylsilyl)methane in the gas phase has been determined by electron diffraction. The molecules have C_3 symmetry, adopting a conformation in which the Si–O bonds are *gauche* with respect to the C–Br bond, and the O–C bonds are *anti* with respect to the inner Si–C bonds. This arrangement avoids conflict between the sterically demanding methoxydimethylsilyl groups and minimises interactions between lone pairs of electrons on the methoxy groups, which are widely separated from each other, on the periphery of the molecule. The Br–C–Si–O and C_{inner}–Si–O–C dihedral angles are 38.5(5) and 169.9(28)° respectively. Other principal parameters (r_a) are r(C–Br) 196.0(21) pm, r(Si–C_{inner}) 190.6(10) pm, r(Si–C_{outer}) 188.3(4) pm, r(Si–O) 167.4(4) pm, r(O–C) 141.9(5) pm, and angles Br–C–Si 106.2(6)°, C_{inner}–Si–C_{outer} 114.7(5)°, C_{inner}–Si–O 107.3(9)°, C_{outer}–Si–O 106.4(8)° and Si–O–C 121.4(13)°.

We recently described the determination by electron diffraction of the molecular structures of the halides $CBr(SiMe_3)_3$ **1** and $CCl(SiMe_3)_3$ **2**, and commented on the subtle variations in the conformation of the silicon-substituted alkyl group R [$=C(SiMe_3)_3$] in a wide range of species RXL_n.[1] For comparison we have obtained data on the methoxy derivative $CBr[SiMe_2(OMe)]_3$ **3**.



1



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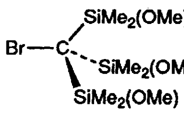


3

Experimental

Synthesis of Bromotris(methoxydimethylsilyl)methane.—A solution of ICl (54 g, 0.334 mol) in CCl_4 (50 cm^3) was added dropwise to a solution of bromotris(trimethylsilyl)methane **1** (11 g, 0.035 mol) in CCl_4 (20 cm^3) at a rate such that gentle reflux was maintained. When the addition was complete the mixture was stirred for a further 4 h and a mixture of MeOH (125 cm^3) and NEt_3 (14.8 cm^3, 0.108 mol) was added during 2 h. The mixture was stirred for a further 36 h and then shaken with aqueous $Na_2S_2O_5$. Light petroleum (b.p. 60–80 °C) was added and the organic layer was washed with water and then dried over $MgSO_4$. Solvent was removed under reduced pressure to leave a pale yellow oil, which was sublimed at 100 °C at 10^{-3} Torr (*ca.* 0.133 Pa) to give bromotris(methoxydimethylsilyl)methane (6.8 g, 54%, m.p. 77–80 °C) (Found: C, 33.1; H, 7.3. $C_{10}H_{27}BrO_3Si_3$ requires C, 33.4; H, 7.6%); $\delta_H(CDCl_3)$ 0.32 (18 H, s, $SiMe_2$), 3.46 (9 H, s, OMe); $\delta_C(CDCl_3)$ −0.5 ($SiMe_3$), 35.1 (Si_3C), 51.2 (OMe); $\delta_{Si}(CDCl_3)$ 13.9; m/z (electron impact, only peaks with ^{79}Br indicated, relative intensities in parentheses) 343 (90, M − Me), 327 (30, M − Me − CH_4), 238 (100, M − Me − $SiMe_3O_2$), 223 (50, M − Me − $SiMe_4O_2$), 207 (50, M − Me − $SiMe_4O_3$), 159 (70, Si_2CMe_5O), 89 (70), 59 (60).

Electron Diffraction.—Electron scattering intensity data for $CBr[SiMe_2(OMe)]_3$ were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[2] The sample was maintained at 410 K and the inlet nozzle at 439 K during the experiments, in which three plates were taken at the long camera distance (259 mm) and three at the short distance (97 mm), giving data over the range 20–320 nm^{-1} in the scattering variable, s. Scattering data for benzene were recorded concurrently and used to calibrate the camera distances and electron wavelength. Data were obtained in digital form using the Joyce Loebl MDM6 microdensitometer[3] at the SERC Daresbury Laboratory.

The data analysis followed standard procedures, using established data reduction[3] and least-squares refinement[4] programs, and the scattering factors of Fink and co-workers.[5] Table 1 lists experimental data, including the weighting points needed to set up the off-diagonal weight matrices used in the least-squares refinements.

Structural Analysis

The key issue which had to be addressed in analysing the structure of compound **3** was the conformation adopted by the three methoxydimethylsilyl groups. Even if orientations of individual methyl groups are ignored, there are six torsion angles (three about Si–C bonds and three about Si–O bonds) to be considered, and there is the possibility that the gas consists of a mixture of conformers. For each methoxydimethylsilyl group there were therefore two torsion angles, about the Si–C_{inner} and Si–O bonds, to be determined. The zero positions were defined to be those in which the Si–O bond was *anti* with respect to the C–Br bond, with the three possible conformations labelled A, G and G′, and in which the Si–C_{inner} bond was *anti* to the O–C bond, with conformations labelled a, g and g′. For all torsion angles values of the same sign represent twists in the same sense, and similarly G and g correspond to torsions having the same sign, while G′ and g′ have the opposite sign.

Table 1 Weighting functions and other experimental data

Camera height/mm	Δs	s_{min}	sw_1	sw_2	s_{max}	Correlation parameter	Scale factor	Wavelength λ/pm
	nm^{-1}							
258.72	2	20	40	140	164	0.355	0.672(11)	5.691
96.68	4	80	100	268	320	0.084	0.542(21)	5.694

Table 2 Geometrical parameters (distances, r_a/pm; angles/°)[a]

p_1	r(C–Br/C–Si)$_{mean}$	189.8(1)
p_2	r(C–Br) − (Si–C$_{inner}$)	5.4(30)
p_3	r(Si–C$_{inner}$) − (Si–C$_{outer}$)	2.3(14)
p_4	r(C–H)	111.7(5)
p_5	r(Si–O)	167.4(4)
p_6	r(O–C)	141.9(5)
p_7	Br–C–Si	106.2(6)
p_8	O–C–H	112.4(fixed)
p_9	Si–C–H	113.5(fixed)
p_{10}	C$_{inner}$–Si–C$_{outer}$	114.7(5)
p_{11}	C$_{inner}$–Si–O	107.3(9)
p_{12}	C$_{outer}$–Si–O	106.4(8)
p_{13}	Si–O–C	121.4(13)
p_{14}	Si–C$_{inner}$ twist[b]	−141.5(5)
p_{15}	Si–O twist[b]	−10.1(28)
p_{16}	O-methyl twist[b]	20.0(fixed)
p_{17}	Si-methyl twist[b]	39.8(fixed)

[a] Estimated standard deviations obtained in the least-squares refinements are quoted in parentheses. [b] For definition see text.

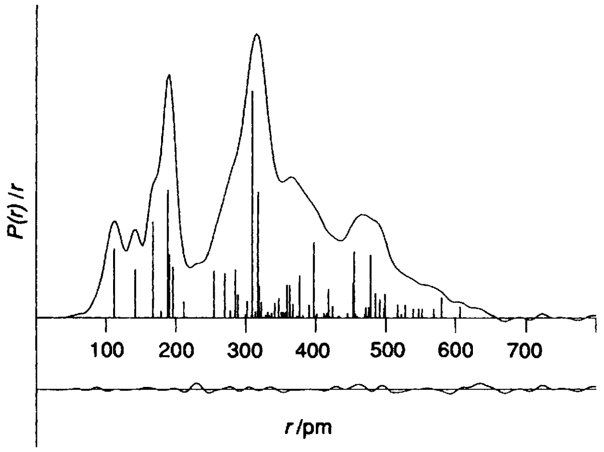


Fig. 1 Observed and final weighted difference radial distribution curves, $P(r)/r$, for $CBr[SiMe_2(OMe)]_3$. Before Fourier inversion the data were multiplied by $s\cdot\exp(-0.000\,02s^2)/(Z_{Br} - f_{Br})(Z_C - f_C)$

It was assumed that all methyl groups had C_{3v} local symmetry and that all C–H bonds were of equal length. However, the O–C–H and Si–C–H angles were distinct, and the O–Me and Si–Me groups had separate torsion angles, each defined so that a value of zero represented a staggered conformation. The two methyl groups bound to a common silicon atom were assumed to rotate in the same direction, so that the $SiMe_2$ fragment had C_2 local symmetry. Neither of these torsion angles, nor the O–C–H or Si–C–H angles, would refine: all were eventually fixed at optimum values obtained from series of refinements in which they were fixed at various positions covering their whole reasonable ranges.

The three $SiMe_2(OMe)$ groups were assumed to be identical, with C_s symmetry for each SiC_3O skeletal fragment, and C_{3v} symmetry for the $BrCSi_3$ core. A total of 17 parameters then defined the molecular geometry, six relating to bond lengths, seven to inter-bond angles and four to torsion angles, as listed in Table 2.

All of these parameters, other than the four relating to the positions of hydrogen atoms, were eventually refined, in addition to nine amplitudes of vibration. However, there were strong correlations between some refining parameters (Table 3), particularly those defining the Si–C and C–Br bond lengths. These correlations were reduced by choosing one parameter to be the mean length of all Si–C and C–Br bonds, and the other two to be the differences between the C–Br and Si–C$_{inner}$ distances, and between the inner and outer Si–C distances. The first of these three parameters was then very well determined, but the standard deviations of the other two are quite large, as are those for two of the individual distances. Other permutations of these three distances could be chosen to be the independent parameters, but one advantage of those we have selected is that they allow direct comparison with the parameters used in the study of bromotris(trimethylsilyl)methane.[1]

The study of the conformation was difficult, but ultimately unambiguous. Initially, to reduce the problem to manageable proportions, the overall symmetry was assumed to be C_3, and it was subsequently shown that this assumption was justified. Two approaches were then used. First, the two torsion angles were systematically varied stepwise over their entire ranges, and all minima in the two-dimensional R-factor space were investigated further. Secondly, the nine combinations of A/G and a/g conformations, which give five distinct overall conformations, were used as starting points, torsion angles being allowed to refine once minima had been identified. These two methods indicated that four conformations should then be considered in detail. The Aa conformation, for which parameter 14 (p_{14}, Table 2) was −20° and p_{15} was close to 0°, did not give a R factor (R_G) below 0.30, and was immediately rejected. The Gg′ conformation with p_{14} −100° and p_{15} 120° also gave a minimum value of R_G exceeding 0.30, but when p_{14} was refined from −140° instead of −100°, the R factor reduced to 0.17. However, the conformation involved a non-bonded distance of only 280 pm between the methoxy carbon atoms and bromine, and was rejected as being physically impossible.

The final conformation, Ga, with torsion angles of *ca.* −140 and 0° for p_{14} and p_{15} respectively, allowed R_G to fall to 0.099. Consideration of molecular models confirmed our belief that this is the only conformation which is physically reasonable and, in particular, that structures which do not have three-fold symmetry are extremely unlikely to occur. The parameters listed in Table 2, and inter-atomic distances and amplitudes of vibration given in Table 4, are all reasonable, and the quality of fit to the experimental intensity data (Fig. 1) and radial distribution curve (Fig. 2) is excellent. Therefore no attempt was made to investigate the possible coexistence of two or more conformers.

Fig. 3 includes a perspective view of the molecule, showing the atom numbering scheme which is needed to interpret Table 4, and a view along the three-fold axis, so that the molecular symmetry may be seen.

Discussion

The C–Br bond in compound **3** appears to be longer than that in **1** [191.1(35) pm] but in view of the large uncertainties the difference cannot be regarded as significant. The outer Si–C bond length in **1** is the same, within experimental error, as those in **3** and a wide range of related compounds.[1] The inner Si–C

Table 3 Least-squares correlation matrix for $CBr[SiMe_2(OMe)]_3 \times 100$*

	p_3	p_5	p_7	p_{10}	p_{11}	p_{12}	p_{15}	u_7	u_{16}	u_{17}	u_{18}
p_1		54									
p_2	−82		−82		79						
p_3			58		−78			−52			52
p_7				57	−74			−65			62
p_{10}						−55		−66	−65		
p_{11}											−55
p_{13}								−58			
p_{14}							55				
p_{15}									−55		
u_7									51	−60	−77
u_{11}										−53	−56
u_{17}											82

* Only elements with absolute values > 50 are listed.

Table 4 Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)[a]

	Atom pair	Distance	Amplitude
r_1	C–Br	196.0(21)	5.4(3)
r_2	Si–C(2)	190.6(10)	
r_3	Si–C(4)	188.3(4)	
r_4	Si–O	167.4(4)	5.2(4)
r_5	O–C	141.9(5)	3.7(7)
r_6	C–H	111.7(5)	8.9(5)
r_7	Br ··· Si	309.2(9)	15.3(16)
r_8	C(2) ··· O(6)	288.7(12)	10.5(9)
r_9	C(2) ··· C(4)	319.1(12)	
r_{10}	Si(3) ··· C(7)	270.0(16)	
r_{11}	Si ··· Si	317.1(13)	
r_{12}	C(5) ··· O(6)	285.0(13)	
r_{13}	C(4) ··· C(5)	302.3(17)	
r_{14}	Si(C)H	254.4(5)	13.6[b]
r_{15}	O(C)H	211.4(6)	11.0[b]
r_{16}	Br ··· C(5)	478.3(11)	10.3(19)
r_{17}	Br ··· C(4)	397.3(16)	11.2(19)
r_{18}	Br ··· O	317.8(14)	12.4(17)
r_{19}	C(2) ··· C(7)	424.3(12)	
r_{20}	C(5) ··· C(7)	322.4(29)	
r_{21}	C(4) ··· C(7)	341.8(34)	
r_{22}	Si(3) ··· C(10)	418.5(18)	
r_{23}	Si(3) ··· C(9)	359.2(18)	
r_{24}	Si(3) ··· C(15)	363.1(12)	
r_{25}	Si(3) ··· C(14)	385.5(10)	
r_{26}	Si(3) ··· O(11)	453.3(8)	
r_{27}	Si(3) ··· O(16)	377.4(15)	
r_{28}	Br ··· C(7)	455.1(14)	13.1[c]
r_{29}	Si(3) ··· C(12)	580.0(17)	14.0[b]
r_{30}	Si(3) ··· C(17)	498.9(22)	14.0[b]
r_{31}	O(11) ··· C(5)	527.8(13)	14.0[b]
r_{32}	O(11) ··· C(4)	606.4(12)	14.0[b]
r_{33}	O(11) ··· C(15)	517.1(25)	14.0[b]
r_{34}	O(11) ··· C(14)	347.5(25)	14.0[b]
r_{35}	O(11) ··· O(6)	491.5(18)	14.0[b]
r_{36}	C(5) ··· C(10)	390.6(33)	14.0[b]
r_{37}	C(5) ··· C(9)	367.5(19)	14.0[b]
r_{38}	C(4) ··· C(10)	568.9(21)	14.0[b]
r_{39}	C(4) ··· C(9)	547.2(17)	14.0[b]

[a] Estimated standard deviations obtained in least-squares refinements are given in parentheses. Other Br ··· H, Si ··· H, C ··· H, O ··· H and H ··· H atom pairs, included in the refinements, are not listed here. [b] Fixed. [c] Tied to u_{16}.

bond length in compound **3** [190.6(10) pm] is, however, significantly shorter than that in **1** [195.4(15) pm]. A similar shortening of Si–C bonds associated with the presence of alkoxy substituents on silicon is found in compounds $[(MeO)Me_2Si](Me_3Si)_2CSiPh_2Cl$, **4**, $[(EtO)Me_2Si](Me_3Si)_2CSiPh_2(OMe)$ **5**[6] and possibly also, though the uncertainty is large, in $SiMe(OMe)_3$,[7] in which the Si–C bond length is 184.2(13) pm, compared with 187.5(2) pm in $SiMe_4$.[8]

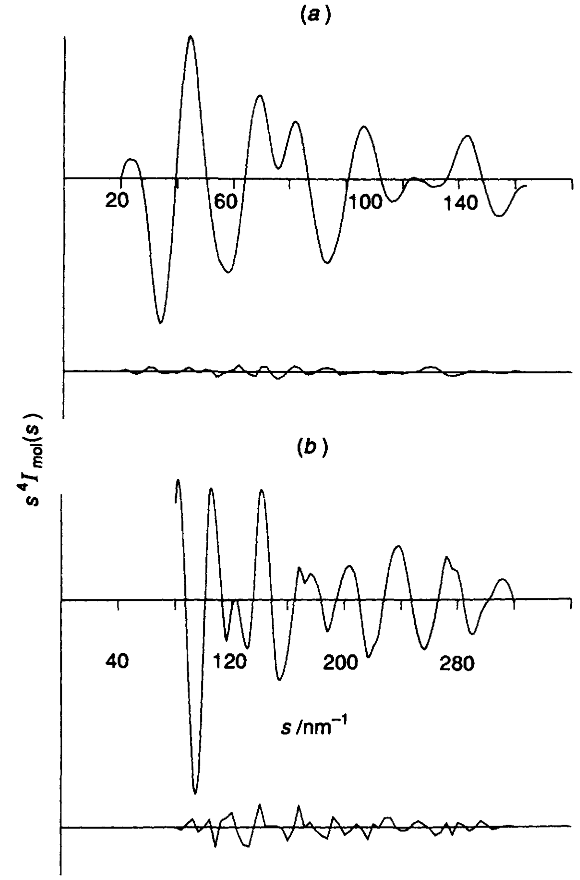


Fig. 2 Experimental and final weighted-difference molecular scattering intensity curves for $CBr[SiMe_2(OMe)]_3$, recorded with nozzle-to-plate distances of (*a*) 259 and (*b*) 97 mm

The Br–C–Si angles in **1** and **3** are almost the same in spite of the fact that shorter Si–C bonds in compounds $(Me_3Si)_3CXL_n$ are normally associated with narrower X–C–Si angles.[1] The short inner C–Si bonds in the bromide **3** are accompanied by Si–O bonds which are longer than the average, *ca.* 162 pm, for Si–O–C systems,[9] but similar to those in **4** [165.7(3) pm], **5** [166.8(3) pm] and the organozinc compound $Zn[C(SiMe_3)_2\{SiMe_2(OMe)\}]_2$ [167.4(3) pm].[10] The C–Si–O angles are narrower and the C–Si–C angles wider than the tetrahedral value, suggesting that the Si–O bonds contain less and the Si–C more s than required for sp^3 hybridisation. The wide Si–O–Me angle found in **3** is common in methoxysilanes.[7]

As in derivatives of the ligand $C(SiMe_3)_3$, the three $SiMe_2(OMe)$ groups in **3** were twisted, all in the same sense, by *ca.* 20° from the fully staggered conformations[1,11] and this

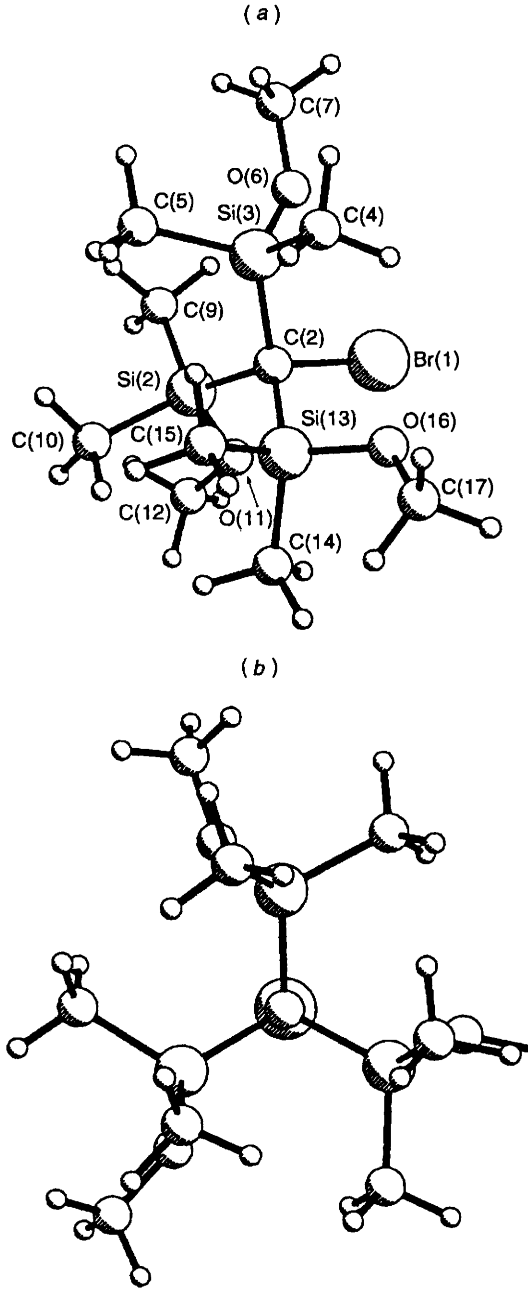
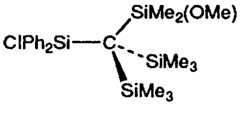


Fig. 3 The molecular structure of $CBr[SiMe_2(OMe)]_3$: (*a*) a perspective view showing atomic numbering and (*b*) a view along the C–Br bond to show the molecular symmetry

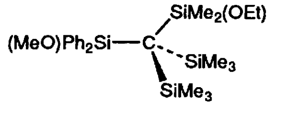
Table 5 Mean bond lengths (pm) in tris(methoxydimethylsilyl)-methyl derivatives RXL_n[a]

	XL_n		
	Br^b	$SiPh_2H^c$	Li^d
Inner Si–C	190.6(10)	188.7(5)	180.5(4)
Outer Si–C	188.3(4)	188.2(3)	185.0(2)
Si–O	167.4(4)	164.0(2)	167.2(2)

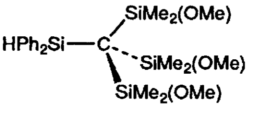
[a] R = $C[SiMe_2(OMe)]_3$. [b] This work. [c] Ref. 12. [d] Dimeric, ref. 13.


$ClPh_2Si{-}C(SiMe_2(OMe))(SiMe_3)_2$

4


$(MeO)Ph_2Si{-}C(SiMe_2(OEt))(SiMe_3)_2$

5


$HPh_2Si{-}C[SiMe_2(OMe)]_3$

6

minimises unfavourable interactions between methyl groups in a 1,3-disposition. Though distortions from C_3 symmetry are not observed in the gas phase, deviations are found in solid-state structures, *e.g.* that of **6**, in which intramolecular interactions between one methoxy oxygen atom and a remote silicon become important. The significance of these in understanding reactions mechanisms has been discussed.[12]

Average bond lengths in some $C[SiMe_2(OMe)]_3$ derivatives are compared in Table 5. Whereas the Si–O and outer Si–C bonds are similar in all three compounds, the inner Si–C bonds are much shorter in the organolithium compound than in the halide **3**, reflecting the delocalisation of charge away from the carbanionic central atom to the adjacent $SiMe_2(OMe)$ groups.

Acknowledgements

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References

1 P. T. Brain, M. Mehta, D. W. H. Rankin, H. E. Robertson, C. Eaborn, J. D. Smith and A. D. Webb, *J. Chem. Soc., Dalton Trans.*, 1995, 349.
2 C. M. Huntley, G. S. Laurenson and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.
3 S. Cradock, J. Koprowski and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.
4 A. S. F. Boyd, G. S. Laurenson and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.
5 A. W. Ross, M. Fink and R. Hilderbrandt, *International Tables for X-Ray Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, Boston and London, 1992, vol. C, p. 245.
6 N. H. Buttrus, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and S. J. Najim, *J. Chem. Soc., Perkin Trans. 2*, 1987, 891, 1753.
7 E. Gergo, I. Hargittai and G. Schultz, *J. Organomet. Chem.*, 1976, **112**, 29.
8 B. Beagley, J. J. Monaghan and T. G. Hewitt, *J. Mol. Struct.*, 1971, **8**, 401.
9 S. Shambayati, J. F. Blake, S. G. Wierschke, W. L. Jorgensen and S. L. Schreiber, *J. Am. Chem. Soc.*, 1990, **112**, 697.
10 F. I. Aigbirhio, S. S. Al-Juaid, C. Eaborn, A. Habtemariam, P. B. Hitchcock and J. D. Smith, *J. Organomet. Chem.*, 1991, **405**, 149.
11 N. H. Buttrus, C. Eaborn, M. N. A. El-Kheli, P. B. Hitchcock, J. D. Smith, A. C. Sullivan and K. Tavakkoli, *J. Chem. Soc., Dalton Trans.*, 1988, 381.
12 F. I. Aigbirhio, S. S. Al-Juaid, C. Eaborn, P. B. Hitchcock and P. D. Lickiss, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1407.
13 F. I. Aigbirhio, N. H. Buttrus, C. Eaborn, S. H. Gupta, P. B. Hitchcock, J. D. Smith and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1992, 1015.

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