Determination by Electron Diffraction of the Molecular Structures of Chloro- and Bromo-tris(trimethylsilyl)methane in the Gas Phase

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The molecular structures of chloro- and bromo-tris(trimethylsilyl)methane in the gas phase have been determined by electron diffraction. Both molecules have inner Si–C bonds which are longer than normal and wide Si–C–Si angles. Principal parameters (r_a) for $CCl(SiMe_3)_3$, with estimated standard deviations in parentheses, are r(C–Cl) 182.3(15) pm, r(Si–C_{inner}) 193.9(6) pm, r(Si–C_{outer}) 188.2(2) pm, and angles Cl–C–Si 102.7(5)° and C_{outer}–Si–C_{outer} 109.6(4)°. The three trimethylsilyl groups are twisted 14.6(7)° from the staggered positions, and tilted 1.3(6)° away from the molecular three-fold axis. For $CBr(SiMe_3)_3$ the major parameters are r(C–Br) 191.1(35) pm, r(Si–C_{inner}) 195.4(15) pm, r(Si–C_{outer}) 187.7(3) pm, Br–C–Si 106.5(6)° and C_{outer}–Si–C_{outer} 109.3(5)°. The trimethylsilyl groups are twisted 13.5(7)° from the staggered positions, but the tilt angle of these groups could not be determined.

Organometallic compounds in which the bulky ligand $C(SiMe_3)_3$, R, is bound to a metal show a wide range of novel reactions and a number of unprecedented structures.[1,2] Many of the structural data are for species RXL_n in the solid state where the configuration of R may be distorted by packing forces or by the rest of the molecule to which it is attached, XL_n. We therefore considered that it was important to obtain data for some species RXL_n in the gas phase. Since the only published electron diffraction studies are of the alkane RH,[3] the phosphine RPH_2[4] and the trichlorosilane $RSiCl_3$[5] we decided to examine the halides RCl, RBr and $CBr[SiMe_2(OMe)]_3$. The structures of the first two are reported here: that of $CBr[SiMe_2(OMe)]_3$ will be described elsewhere.

Experimental

Syntheses.—Chlorotris(trimethylsilyl)methane, RCl. A solution of LiR (4.22 mmol) in tetrahydrofuran (50 cm^3) was added dropwise to an excess (134 mmol) of CCl_4 at 0 °C.[6a] The mixture was stirred overnight at 20 °C and solvent was evaporated. The residue was extracted into light petroleum (b.p. 30–40 °C, 4 × 70 cm^3) and the oil obtained on removal of solvent from the extract was evaporated into an air condenser to give a liquid (RH) and a white solid, which was crystallised from the minimum volume of hot methanol. Yield 45%, m.p. 139 °C (lit.,[6b] 139–141 °C) (Found: C, 45.1; H, 10.3. Calc. for $C_{10}H_{27}ClSi_3$: C, 44.9; H, 10.1%).

Bromotris(trimethylsilyl)methane, RBr. The bromide RBr was made by photochemical bromination of RH,[7a] and sublimed at 80 °C at 1 Torr (*ca.* 133 Pa). M.p. 194–195 °C (lit.,[7b] 194–195 °C).

Spectroscopic data for both RCl and RBr have been given in ref. 6(*a*).

Electron Diffraction.—Electron diffraction data were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus.[8] Three plates were exposed for each compound at both the long (258 mm) and the short (96 mm) camera distances, with the samples held at *ca.* 385 K and the nozzle at 438 K. Data were also obtained for benzene at the same nozzle temperature, providing calibration of the electron wavelength and nozzle-to-plate distances. Plates were traced on the computer-controlled Joyce Loebl MDM6 microdensitometer[9] at the Daresbury Laboratory of the SERC. Data reduction[9] and least-squares refinements[10] followed standard procedures, using established programs and the complex scattering factors of Fink and co-workers.[11] The ranges of scattering data, weighting functions used in setting up the off-diagonal weight matrices for least-squares refinements, and other experimental data are listed in Table 1.

Structural Analysis

Molecular Model.—Although these are large molecules, with 41 atoms, only ten parameters are needed to define the geometry of each molecule. It was assumed that each $SiCH_3$ group had C_{3v} local symmetry, that each $Si(CH_3)_3$ group had C_3 local symmetry, and that the overall symmetry was C_3. Each structure was then defined by four bond lengths (C–H, Si–C and Si–C′, where C and C′ are used to indicate outer and inner carbon atoms, respectively, and C–X, where X is the halogen), the angles X–C–Si, C–Si–C and Si–C–H, twist angles about the C′–Si and Si–C bonds, and a tilt angle of the $SiMe_3$ groups, defined as the angle between the three-fold axis of a group and its adjacent C′–Si bond, a positive value indicating a tilt away from the molecular three-fold axis. Zero twist angles represented staggered conformations, and the angles were defined so that values of the same sign indicated twists in the same sense.

One problem in each study was that the C′–Si, Si–C and C–X distances were very similar, giving rise to a single peak in the radial distribution curve. The three distances were inevitably strongly correlated (Table 2), and although the mean distance was very well determined, individual distances were not so well defined. The chosen independent parameters were different for the two compounds, being appropriate combinations of the individual distances.

$CCl(SiMe_3)_3$.—The C–Cl bond is a little shorter than the two types of Si–C bond, and there were only weak correlations

Table 1 Weighting functions, correlation parameters and scale factors

Compound	Camera height/mm	Δs	s_{min}	sw_1	sw_2	s_{max}	p/h*	Scale factor	Electron wavelength, λ/pm
		nm^{-1}							
$CCl(SiMe_3)_3$	258.09	2	20	40	140	164	0.427	0.717(10)	5.691
	96.06	4	80	100	304	356	0.450	0.645(16)	5.693
$CBr(SiMe_3)_3$	258.43	2	30	50	140	164	0.461	0.823(14)	5.690
	96.07	4	80	100	268	320	0.266	0.684(20)	5.694

* Correlation parameter.

Table 2 Least-squares correlation matrices (× 100)[a]

(*a*) $CCl(SiMe_3)_3$

	p_3	p_4	p_6	p_9	p_{10}	u_6	u_{11}	u_{22}	k_1[b]	k_2[b]
p_1		−87								
p_2	95		73	−64	65	51			56	57
p_3			80	−68	53					
p_4			−61				54			
p_6				−64						
p_8							−53			
p_9							54			
p_{10}						53			58	
u_{25}								60		53

(*b*) $CBr(SiMe_3)_3$

	p_2	p_3	p_4	p_6	p_8	p_9	u_1	u_5	u_{14}	k_2[b]
p_1	−89	75	64	66		−60		−61	−55	
p_2		−90	−76	−68		61		72	63	
p_3			52	76		−67	−67	−78	−57	
p_4					−64					
p_6						−69	−53			
u_1								68		57
u_5									57	

[a] Only elements with absolute values > 50 are listed. [b] Scale factor.

Table 3 Geometrical parameters (distances, r_a/pm; angles/°)*

	Parameter	$CCl(SiMe_3)_3$	$CBr(SiMe_3)_3$
p_1	r(C–Cl)	182.3(15)	
p_2	r(Si–C)(mean)	189.6(2)	
p_1	r(C–Br/Si–C)(mean)		189.7(2)
p_2	r(C–Br) − [Si–C(1)]		−4.3(50)
p_3	Δr(Si–C)	5.7(8)	7.7(14)
p_4	Cl/Br–C–Si	102.7(5)	106.5(6)
p_5	r(C–H)	112.0(4)	113.6(7)
p_6	C(3)–Si–C(4)	109.6(4)	109.3(5)
p_7	Si–CH	111.5(7)	113.4(12)
p_8	Si–C(1) torsion	−14.6(7)	−13.5(7)
p_9	Si–C(3) torsion	38.8(23)	36.2(26)
p_{10}	$SiMe_3$ tilt	1.3(6)	2.5(fixed)

* Estimated standard deviations obtained in the least-squares refinements are quoted in parentheses.

between the C–Cl and Si–C bond lengths. The independent parameters chosen to define these distances were: p_1, r(C–Cl); p_2, the weighted mean Si–C distance; and p_3, the difference between the lengths of the inner and outer Si–C bonds. The full list of parameters is given in Table 3. All ten geometrical parameters were refined, and although there are still several quite strong correlations (Table 2), this procedure gives realistic estimates of the uncertainties in the refined parameters. Eight vibrational parameters were also refined, representing amplitudes of vibration either for individual atom pairs or for groups of related types of atom pair with similar interatomic distances. Vibrational amplitudes which could not be refined were fixed at values observed or calculated for related compounds. (It was not feasible to compute force fields for molecules of this size *ab initio*, and with 117 modes of vibration experimental force fields could not be obtained.)

At the end of the refinements the *R* factor (R_G) was 0.081, and the parameters listed in Table 3 and distances and vibrational amplitudes listed in Table 4 were obtained. The observed and final difference radial distribution and combined molecular scattering intensity curves are shown in Figs. 1(*a*) and 2(*a*) respectively, and Fig. 3(*a*) is a perspective view of the structure of the molecule, showing the atomic numbering used in Tables 3 and 4.

$CBr(SiMe_3)_3$.—Strong correlations between the three parameters defining the C–Br and Si–C distances persisted, although many permutations were tried. In principle, a completely uncorrelated set of parameters can be defined, but in this case such a set was not physically very meaningful. Eventually, the parameters were chosen to be: p_1, the mean length of all Si–C and C–Br bonds; p_2, the difference between the C–Br and Si–C_{inner} distances; and p_3, the difference between the outer and inner Si–C bond lengths. Correlations between these, and other, parameters (Table 2) were greater than for the chloro compound, but all geometrical parameters other than the tilt of the trimethylsilyl groups were refined, as well as six vibrational parameters. The results of the final refinement, for which R_G was 0.109, are given in Tables 3 and 4, and radial distribution and scattering intensity curves are presented in Figs. 1(*b*) and 2(*b*). Fig. 3(*b*) is a view of the molecule along the C–Br bond, showing the three-fold symmetry.

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

		CCl(SiMe$_3$)$_3$		CBr(SiMe$_3$)$_3$	
	Atom pair	Distance	Amplitude	Distance	Amplitude
r_1	C–X	182.3(15)	5.0^b	191.1(35)	5.0(4)
r_2	Si–C(1)	193.9(6)	5.0^b	195.4(15)	
r_3	Si–C(3)	188.2(2)	5.0^b	187.7(3)	
r_4	C–H	112.0(4)	8.2(5)	113.6(7)	9.7(7)
r_5	Si···X	293.9(6)	11.1(7)	309.7(9)	11.2(5)
r_6	C(1)···C(3)	314.1(13)	9.5(8)	317.6(10)	
r_7	C(1)···C(4)	311.1(7)		311.6(10)	
r_8	C(1)···C(5)	310.0(10)		309.6(9)	
r_9	C(3)···C(4)	307.5(6)		306.2(12)	
r_{10}	Si(C)H	251.8(8)	13.5(6)	255.1(15)	16.3(13)
r_{11}	Si(2)···Si(6)	327.6(13)	12.3(8)	324.4(20)	11.2^c
r_{12}	X···C(5)	323.8(22)		338.2(15)	12.1^b
r_{13}	X···C(4)	365.1(15)	11.5^b	376.9(17)	16.3^b
r_{14}	X···C(3)	461.9(7)	10.3(9)	477.8(19)	13.3(8)
r_{15}	Si(2)···C(9)	482.5(6)		482.6(18)	
r_{16}	Si(2)···C(12)	488.6(5)		486.4(17)	
r_{17}	Si(2)···C(7)	415.6(20)	16.0^b	405.8(13)	16.3^b
r_{18}	Si(2)···C(8)	355.8(9)	16.0^b	355.9(13)	16.3^b
r_{19}	Si(2)···C(11)	378.6(17)	16.0^b	371.4(23)	16.3^b
r_{20}	Si(2)···C(13)	387.4(12)	16.0^b	386.9(20)	16.3^b
r_{21}	C(3)···C(11)	382.3(32)	15.0^b	365.0(34)	15.0^b
r_{22}	C(3)···C(12)	569.3(14)	17.1(24)	560.0(19)	16.3(24)
r_{23}	C(5)···C(11)	562.0(12)		555.0(18)	
r_{24}	C(5)···C(12)	618.2(19)		620.6(21)	
r_{25}	C(3)···C(13)	513.8(26)	19.3(27)	505.7(26)	20.3^b
r_{26}	C(4)···C(12)	538.6(11)		538.4(13)	20.3^b
r_{27}	C(5)···C(13)	524.2(26)		530.1(21)	20.3^b
r_{28}	C(4)···C(11)	394.4(33)	15.0^b	393.9(42)	15.0^b
r_{29}	C(4)···C(13)	324.8(25)	15.0^b	325.9(25)	15.0^b

^{a} Estimated standard deviations obtained in least-squares refinements are given in parentheses. Other Si···H, C···H, X···H and H···H atom pairs, included in the refinements, are not listed here. ^{b} Fixed. ^{c} Tied to u_5.

Table 5 Geometrical parameters of some tris(trimethylsilyl)methyl derivatives^a

XL$_n$	r(Si–C)/pm	r(Si–Me)/pm	Si–C–X/°	Si–C–Si/°	C–Si–C/°	E	Ref.
BPh$_2$	193.4(2)	187.3(6)	110.3(16)	108.6(2)^b	105(2)	2.0	12
Cl	193.9(6)	188.2(2)	102.6(5)	115.1(5)	109.6(4)	3.2	*c*
Br	195.4(15)	187.7(3)	106.1(15)	112.2(5)	109.3(5)	3.0	*c*
SiMe$_2$Ph	191.6(7)	187.7(16)	109.5(9)	109.5(9)	105.0(11)	1.9	13
H	188.7(6)	187.3(3)	101.2(1)	116.3(4)	105.8(3)	2.2	3
MgR	187.7(3)	188.1(4)	106.1(1)	112.6(1)	105.4(2)	1.3	14
MnR	188.1(8)	187.7(3)	106.5(2)	112.3(2)	105.6(17)	1.6	15
HgR	188.7(4)	187.1(3)	106.2(2)	112.6(2)	106.1(2)	2.0	16
ZnR	189.0(3)	188.5(4)	107.7(1)	111.1(1)	106.4(2)	1.7	17
K	182.2(10)	187.3(13)	90	120.0(5)	102.8(7)	0.8	18
Rb	181.5(7)	188.0(8)	90	120.0(4)	102.9(4)	0.8	19
Cs	181.8(10)	188.6(13)	99.6(4)	117.3(5)	103.0(3)	0.8	19
PH$_2$	194.1(5)	188.3(2)	111.9(13)	106.9(13)	104.3(4)	2.2	4
BH$_2$	190.4(6)	187.8(6)	107.8^d	111.2(3)	106.0(3)	2.0	20
SnPh$_2$F	190.6(10)	186.6(15)	107.1(5)	111.7(5)	106.2(8)	2.0	21
BPhO(CH$_2$)$_4$R	190.0(6)	186.7(8)	108.4^e	110.4(3)	105.6(4)	2.0	22
(CH$_2$)$_4$OBRPh	190.0(6)	186.7(8)	107.9^f	110.8(3)	105.7(4)	2.6	22
YbR	183.8(11)	188.1(12)	103.9^g	114.4(5)	104.8(5)	1.3	1
SiCl$_3$	191.4(8)	187.8(6)	110.9(6)	108.0(6)	107.0(11)	1.9	5
	Mean	187.5					

^{a} R = C(SiMe$_3$)$_3$; E = Pauling electronegativity. ^{b} Mean of 109.0, 110.7 and 106.2°. ^{c} This work. ^{d} Mean of 114.9, 106.1 and 101.7°. ^{e} Mean of 105.5, 106.6 and 113.4°. ^{f} Mean of 111.4, 103.1 and 109.4°. ^{g} Mean of 125.6, 89.7 and 96.6°.

Discussion

A survey (Table 5) of X-ray and electron diffraction data shows that the conformation of the tris(trimethylsilyl)methyl group undergoes a range of adjustments depending on the group to which it is attached. The present discussion is confined to neutral species L$_n$XC(SiMe$_3$)$_3$; intraligand parameters in complexes[23] are not considered.

There is little variation in the outer, *i.e.* Si–Me, bond lengths. In the 19 compounds listed in Table 5 the mean outer Si–C bond length is the same as that, 187.5(2) pm, in SiMe$_4$.[24] That is, the outer Si–C bonds are 'normal'.

A plot of the lengths of the inner Si–C bonds, *i.e.* those within the CSi$_3$ skeleton, with error bars equal to twice the estimated standard deviations, against the Pauling electronegativity of the

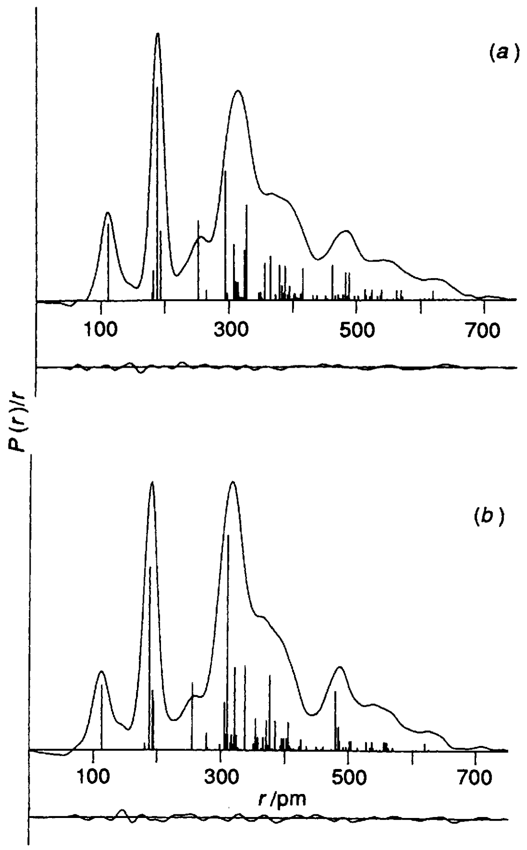

Fig. 1 Observed and final weighted difference radial distribution curves, $P(r)/r$, for (*a*) $\mathrm{CCl(SiMe_3)_3}$ and (*b*) $\mathrm{CBr(SiMe_3)_3}$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.000\,02s^2)/(Z_{Si}-f_{Si})(Z_X-f_X)$, where X is Cl or Br

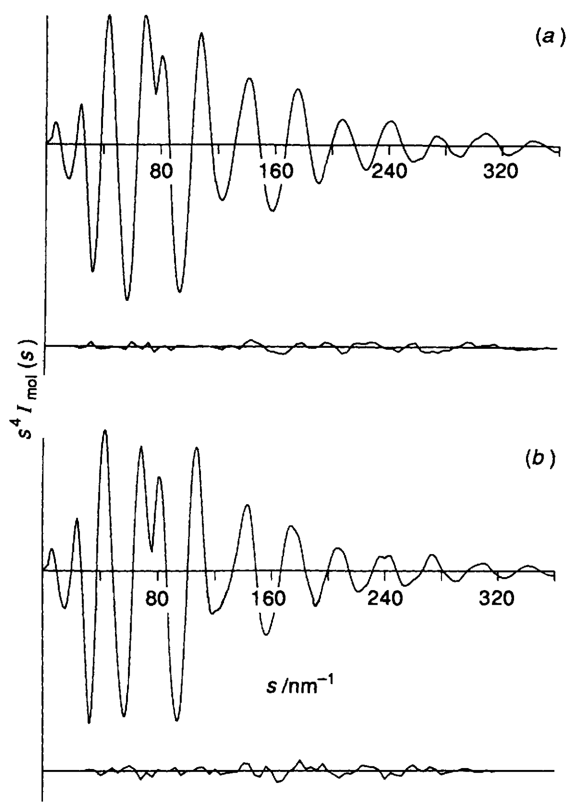

Fig. 2 Experimental and final weighted-difference combined molecular scattering intensity curves for (*a*) $\mathrm{CCl(SiMe_3)_3}$ and (*b*) $\mathrm{CBr(SiMe_3)_3}$. Theoretical data have been added in those regions for which there are no experimental data

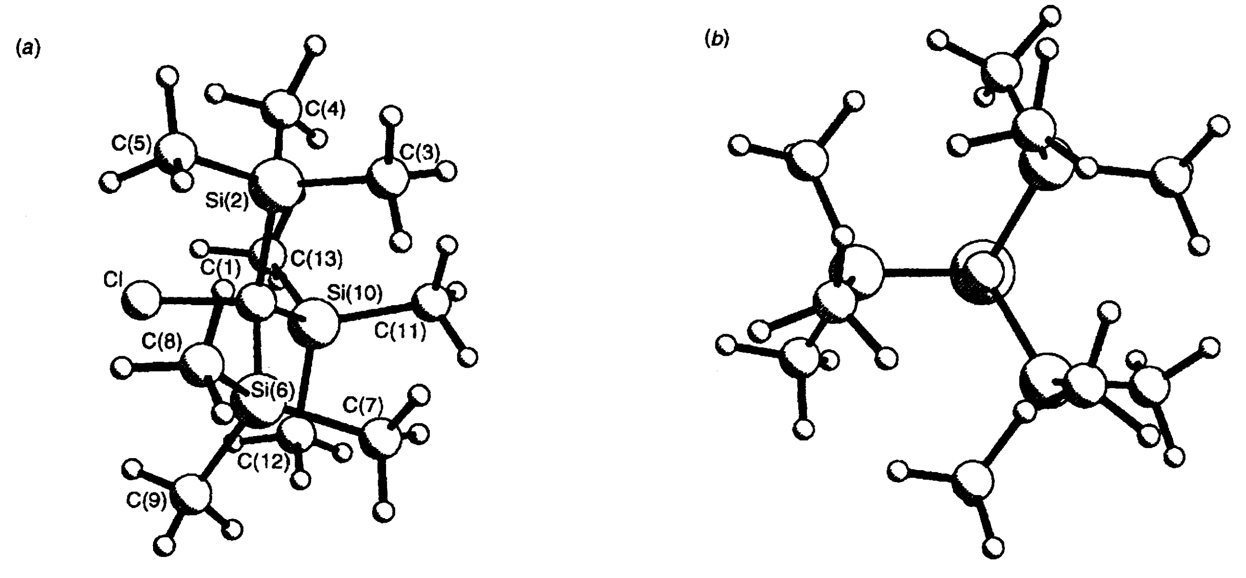

Fig. 3 (*a*) A perspective view of $\mathrm{CCl(SiMe_3)_3}$, showing the atom numbering. (*b*) A view of $\mathrm{CBr(SiMe_3)_3}$ along the C–Br bond, showing the molecular symmetry

atom X, is shown in Fig. 4. There is a systematic decrease in bond length as the electronegativity of X decreases. Lengthening of Si–C bonds associated with the presence of electronegative substituents on C can also be seen in X-ray diffraction data for $\mathrm{Me(Bu^tCH_2)PhSiCHPhOCOC_6H_4Br}$-*p*[25] and $\mathrm{Me(Bu^tCH_2)PhSiCHMeBr}$[26]. A similar effect on C–C bonds was observed in a very old electron diffraction study of $\mathrm{Me_3CCH_2Cl}$ and attributed to the inductive withdrawal of electron density from the C–C bond to the chlorine.[27] The simplest explanation for the shortening when X is electropositive is in terms of contributions by structures of the type $\mathrm{Me_3Si^-{=}C(SiMe_3)_2}$ involving delocalisation of charge into d orbitals on Si, or $\mathrm{Me^-Me_2Si{=}C(SiMe_3)_2}$, arising from hyperconjugation, or both.[28]

There is no clear separation in Fig. 4 between points derived from electron and X-ray diffraction data. However, points for a

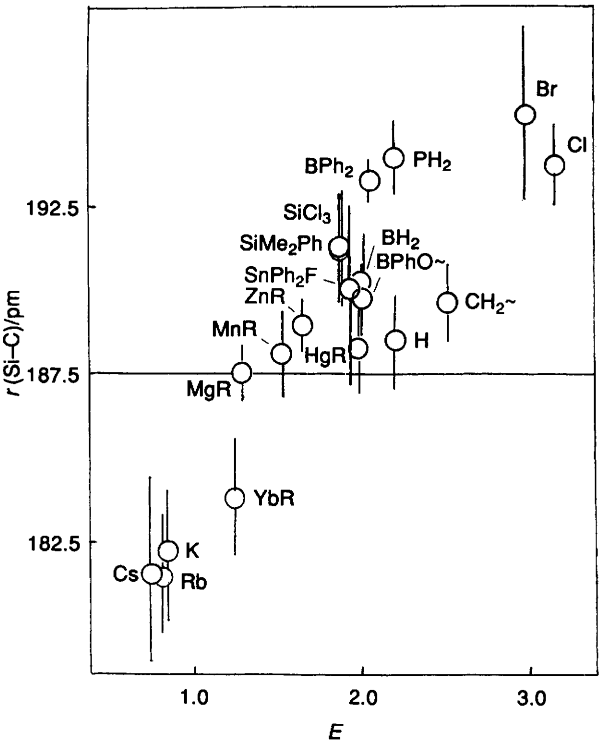

Fig. 4 Variation of inner Si–C bond lengths with the Pauling electronegativity, *E*, of the atom X, where R = $C(SiMe_3)_3$

number of compounds with sterically demanding groups L_nX lie above and to the left of the mean line, and it is possible that in these compounds the size of L_nX results in a longer Si–C bond than is appropriate for the electronegativity of X. This effect may show up also in the halides RCl and RBr: from the electronegativities of the halogens the longer inner Si–C bond is expected in the chloride, whereas it is found in the bromide. However, there is a rather large uncertainty in the C–Si bond length in the bromide.

Fig. 5 shows that the inner Si–C bond length is strongly correlated with the Si–C–X angle. However, points for four compounds (X = Cl, Br, H or K) lie off the line determined by the rest of the data. The 90° Si–C–X angle in the potassium derivative probably results from the unusual solid-state structure[18] in which there are potassium cations symmetrically disposed on either side of the $[C(SiMe_3)_3]^-$ anion, but the configurations of the other three compounds are those adopted in the gas phase. The inference seems to be that, although electronic effects dominate in determining the inner Si–C distances and Si–C–X bond angles, additional intraligand strain is imposed by the group L_nX. This usually contains several atoms and so is itself bulky; in this case the data for *r*(Si–C) and Si–C–X give points which fall near the line in the right part of Fig. 5. When L_nX consists of only one atom X, the Si–C–X angle is able to narrow beyond the value normally associated with the measured Si–C distance. This allows the outer C–Si–C angles in the $SiMe_3$ groups of the chloride and bromide to be much closer to the tetrahedral value than is usual in $C(SiMe_3)_3$ derivatives (Table 5). The electron diffraction data indicate that the PH_2 group is more sterically demanding than is Cl. Indeed, in RPH_2 the Si–C–P angle [111.9(13)°] is uncharacteristically large and the Si–C–Si angle, as well as the C–Si–C angle, is compressed below the tetrahedral value. Fig. 4 also shows that the inner Si–C bond is longer than expected from the electronegativity of phosphorus.

Intraligand 1,3 interactions cause the $SiMe_3$ groups to twist *ca.* 13–20° from the staggered positions about the Si–C bonds: the values for RCl and RBr, 14.6(7) and 13.5(7)° respectively, are at the lower end of the observed range. This twisting is evident in both electron diffraction and X-ray data, and is thus characteristic of both gas and solid phases.

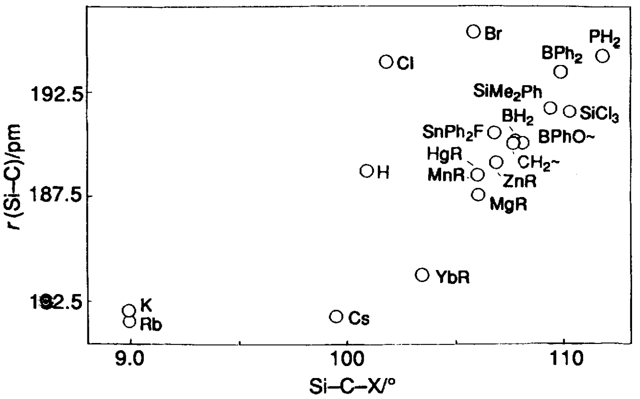

Fig. 5 Variation of inner Si–C bond lengths with Si–C–X angles

In all the electron diffraction studies it has been assumed that the $C(SiMe_3)_3$ group has a C_3 axis making all Si–C–X angles equal. In the solid state, however, there are often considerable variations in Si–C–X angles, indicating that these are easily distorted to adjust to the shape of the group L_nX. Even in these cases, however, the mean Si–C–X angles correlate well with Si–C distances.

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