Silyl Halide Radical Anions

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Ab initio molecular orbital theory using diffuse-augmented basis sets and a second-order Møller–Plesset correction for electron correlation has been used to investigate the $SiH_3F^{-\bullet}$ and $SiH_3Cl^{-\bullet}$ radical anions. $SiH_3F^{-\bullet}$ is calculated not to be bound with respect to loss of an electron, whereas $SiH_3Cl^{-\bullet}$ is suggested to be bound at its minimum energy geometry, a C_s structure derived from a trigonal bipyramid, but not with respect to optimised SiH_3Cl. The thermodynamics and bonding in $SiH_3Cl^{-\bullet}$ are discussed and the performance of this level of theory for radical anions is assessed.

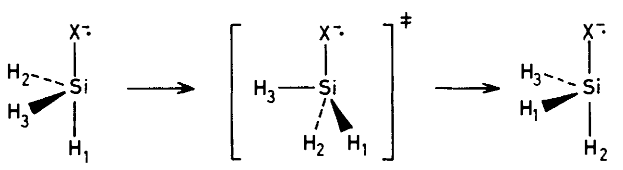
A FASCINATING structural problem in modern organic chemistry is the nature of radicals with nine electrons in the valence shell of the central atom.[1] These species may either form σ^* radicals,[2] in which the extra electron occupies a σ antibonding orbital which would be the LUMO of the neutral eight-electron closed shell equivalent, or they may adopt a structure which is best regarded as being derived from a pentavalent trigonal bipyramid (TBP) in which one ligand is replaced by the radical centre.[3] A useful generalisation is that first row radicals, such as $CH_3Cl^{-\bullet}$[4] or $NX_3X^\bullet$,[5] adopt a σ^* (in this case C_{3v}) structure, whereas their second row equivalents, $SiH_3X^{-\bullet}$ [6] and $PH_3X^\bullet$,[7] prefer TBP structures. Hypervalency has often been attributed to the involvement of low-lying *d*-orbitals [8] although preliminary work on the $SiH_3X^{-\bullet}$ radical anions [9] revealed a strong tendency to form the TBP structure even without *d*-orbitals in the basis set. The purpose of this work is not only to investigate the structure and bonding in such species, but also to test the effects of *d*-orbitals on silicon. In view of the recent advances in *ab initio* methods for closed shell anions [10-12] the performance of relatively economical levels of *ab initio* MO theory for radical anions is also of interest.

METHOD

All calculations employed the GAUSSIAN 76 series of programs.[13] Open shell calculations used the unrestricted Hartree–Fock (UHF) and closed shell the restricted Hartree–Fock (RHF) formalisms. This combination is denoted HF throughout. Optimisations were performed using analytically evaluated atomic forces [14] in a Davidon–Fletcher–Powell multiparameter search.[15] The 3-21G and 6-21G basis sets [16] (33-21G and 66-21G for silicon and chlorine) [17] were supplemented by an additional set of diffuse *s* and *p* functions on all heavy atoms to give 3-21+G [18] and further with diffuse *s* functions on hydrogens [18] and polarisation functions on silicon and chlorine [19] to give 6-21++G*. Single point calculations including the second-order Moller–Plesset correction for electron correlation (MP2) [20] did not include the core orbitals (frozen core approximation).[21] Molecular orbital plots were produced using Jorgensen's program [22] on the UHF/STO-3G wave function. The α orbitals were plotted as if they were doubly occupied.

RESULTS AND DISCUSSION

$SiH_3F^{-\bullet}$.—Earlier work[9] at the 3-21G basis set level indicated the C_s structure (I) to be favoured by 9.7 kcal mol^{-1} over the C_{3v}, pure σ^*, structure (II). Diagonalisation of the Hessian (force constant) matrix at 3-21G showed, however, that (II) is neither a minimum nor a transition state at this level. The ligand exchange transition state was found to be the C_s structure (III), in which the fluorine occupies an equatorial position and in which an axial position remains vacant. The ligand exchange activation energy (Scheme 1) is 8.4 kcal mol^{-1} at 3-21G. The inclusion of diffuse functions, however, reverses the stability of (II) and (III), the former now being 5.4 kcal mol^{-1} more stable than (III) (3-21 + G). Structure (I) is, however, still the most stable structure at this level. Surprisingly the inclusion of diffuse functions on hydrogen and *d*-orbitals on silicon (6-21 ++G*) strongly favours the C_{3v} σ^* structure (II), making this the most stable form at 6-21 ++G*//3-21+G, although MP2 reverses the stability order. It is unlikely that (II) or (III) are minima at this level. $SiH_3F^{-\bullet}$ is, however, indicated not to be a bound species (see below) and the above results are therefore not reliable. The energies obtained for (I)—(III) and for related species are shown in Table 1 and their 3-21G and 3-21+G optimised geometries in Table 2.



SCHEME 1 The ligand exchange process in SiH_3X radical anions

$SiH_3Cl^{-\bullet}$.—$SiH_3Cl^{-\bullet}$ is found to prefer the TBP structure (IV) at all levels of theory. The C_{3v} structure (V) is consistently found to be the least stable of the three investigated, whereas the alternative C_s structure (VI) lies intermediate in energy between (IV) and (V). Diagonalisation of the Hessian matrix for (VI) at 3-21G shows this structure to be a transition state, as for $SiH_3F^{-\bullet}$ at this level. The energy ordering for $SiH_3Cl^{-\bullet}$ suggests, however, that the ligand exchange mechanism shown in

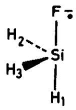
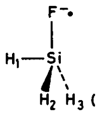
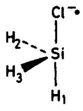
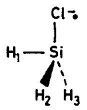
TABLE 1

Total (a.u.) and relative (kcal mol^{-1} in parentheses) energies

	3-21G//3-21G	3-21 + G//3-21 + G	6-21 + + G*//6-21 ++ G*	MP2/6-21 ++ G*// 3-21 + G
H·	−0.496 20	−0.496 20	−0.497 80	−0.497 80
H^-	−0.400 42	−0.400 42	−0.485 56	−0.498 71
F·	−98.845 01	−98.876 07	−99.259 66	−99.348 73
F^-	−98.772 14	−98.933 66	−99.315 34	−99.470 47
Cl·	−457.276 55	−457.284 63	−459.439 87	−459.547 92
Cl^-	−457.353 58	−457.380 86	−459.531 78	−459.665 78
SiH_3·	−289.080 54	−289.085 48	−290.599 62	−290.670 13
SiH_3^-	−289.084 50	−289.100 46	−290.608 30	−290.698 16
SiH_2F·	−387.458 97	−387.501 75	−389.409 59	−389.607 18
SiH_2F^-	−387.469 78	−387.538 05	−389.430 74	−389.648 46
SiH_2Cl·	−745.850 09	−745.863 73	−749.544 63	−749.742 56
SiH_2Cl^-	−745.901 34	−745.922 53	−749.580 24	−749.793 78
SiH_3F	−388.074 06	−388.111 96	−390.031 39	−390.242 43
$SiH_3F^{-\bullet}$ (I)	−387.990 24 (0.0)	−388.067 25 (0.0)	−389.974 54 (0.0)	−390.196 57 (0.0)
$SiH_3F^{-\bullet}$ (II)	−387.974 82 (9.7)	−388.062 08 (3.2)	−389.975 04 (−0.3)	−390.196 15 (0.3)
$SiH_3F^{-\bullet}$ (III)	−387.976 79 (8.4)	−388.053 50 (8.6)	−389.962 74 (7.4)	−390.217 36 (3.8)
SiH_3Cl	−746.457 79	−746.470 87	−750.163 33	−750.375 00
SiH_3Cl^- (IV)	−746.452 19 (0.0)	−746.477 20 (0.0)	−750.140 33 (0.0)	−750.349 08 (0.0)
$SiH_3Cl^{-\bullet}$ (V)	−746.443 08 (5.7)	−746.471 67 (3.5)	−750.135 63 (2.9)	−750.343 38 (3.6)
$SiH_3Cl^{-\bullet}$ (VI)	−746.448 13 (2.5)	−746.474 89 (1.4)	−750.136 97 (2.1)	−750.345 19 (2.4)

TABLE 2

3-21G and 3-21+G optimised geometries

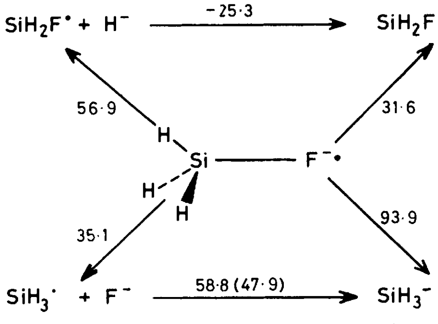
Species	Parameter	3-21G	3-21 + G
$SiH_3^{\bullet}$, C_{3v}	SiH (Å)	1.486	1.486
	$\widehat{HSiH}$ (°)	111.6	111.7
SiH_3^-, C_{3v}[a]	SiH (Å)	1.562	1.555
	$\widehat{HSiH}$ (°)	95.2	96.7
$SiH_2F^{\bullet}$, C_s	SiF (Å)	1.640	1.679
	SiH (Å)	1.483	1.483
	$\widehat{FSiH}$ (°)	109.9	107.3
	$\widehat{HSiH}$ (°)	110.7	112.8
SiH_2F^-, C_s	SiF (Å)	1.704	1.770
	SiH (Å)	1.572	1.560
	$\widehat{FSiH}$ (°)	99.7	94.7
	$\widehat{HSiH}$ (°)	92.2	94.7
$SiH_2Cl^{\bullet}$, C_s	SiCl (Å)	2.195	2.207
	SiH (Å)	1.480	1.480
	$\widehat{ClSiH}$ (°)	107.7	107.5
	$\widehat{HSiH}$ (°)	112.6	112.9
SiH_2Cl^-, C_s	SiCl (Å)	2.461	2.472
	SiH (Å)	1.546	1.542
	$\widehat{ClSiH}$ (°)	93.4	93.3
	$\widehat{HSiH}$ (°)	94.8	94.8
SiH_3F, C_{3v}c[b]	SiF (Å)	1.635	1.675
	SiH (Å)	1.478	1.477
	$\widehat{FSiH}$ (°)	109.2	107.3
 (I) C_s	SiF (Å)	1.726	1.836
	SiH_1 (Å)	1.661	1.615
	SiH_2 (Å)	1.531	1.516
	$H_1\widehat{Si}H_3$ (°)	92.2	96.0
	$H_1\widehat{Si}F$ (°)	165.6	164.5
	$H_2\widehat{Si}H_3$ (°)	104.2	108.0
$SiH_3Cl^{-\bullet}$ (V) C_{3v}	SiF (Å)	1.704	1.795
	SiH (Å)	1.569	1.500
	$\widehat{FFSiH}$ (°)	91.4	93.1
 (III) C_s	SiF (Å)	1.728	1.853
	SiH_1 (Å)	1.547	1.515
	SiH_2 (Å)	1.580	1.550
	$H_1\widehat{Si}H_3$ (°)	87.5	98.8
	$H_1\widehat{Si}F$ (°)	88.9	88.6
	$H_2\widehat{Si}H_3$ (°)	104.6	102.3
SiH_3Cl, C_{3v}[b]	SiCl (Å)	2.191	2.203
	SiH (Å)	1.475	1.475
	$\widehat{ClSiH}$ (°)	107.1	106.8
 (IV) C_s	SiCl (Å)	2.915	3.091
	SiH_1 (Å)	1.536	1.525
	SiH_2 (Å)	1.496	1.492
	$H_1\widehat{Si}H_2$ (°)	103.1	105.1
	$H_1\widehat{Si}Cl$ (°)	158.7	156.8
	$H_2\widehat{Si}H_3$ (°)	108.3	109.8
SiH $Cl^{-\bullet}$ (V) C_{3v}	SiH (Å)	1.480	1.479
	SiCl (Å)	3.246	3.380
	$\widehat{ClSiH}$ (°)	78.6	77.6
 (VI) C_s	SiCl (Å)	3.062	3.266
	SiH_1 (Å)	1.494	1.491
	SiH_2 (Å)	1.515	1.510
	$H_1\widehat{Si}H_2$ (°)	105.0	107.1
	$H_1\widehat{Si}Cl$ (°)	88.5	88.5
	$H_2\widehat{Si}H_3$ (°)	104.2	105.8

[a] Taken from G. W. Spitznagel, Diplomarbeit, Universität Erlangen-Nürnberg, 1981. [b] 3-21G values taken from R. A. Whiteside, J. S. Binkley, P. Krishnan, D. J. DeFrees, H. B Schlegel, and J. A. Pople, 'Carnegie-Mellon Quantum Chemistry Archive,' Carnegie-Mellon University, 1980.

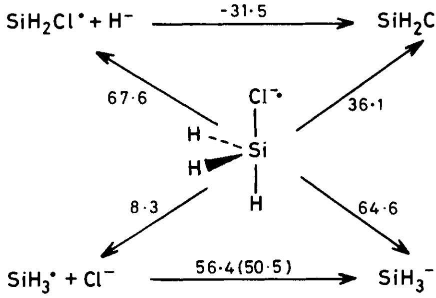
Scheme 1 is correct for this radical anion. The best estimate for the barrier to ligand exchange in $SiH_3Cl^{-\bullet}$ (MP2/6-21++G*//3-21+G) is therefore 2.4 kcal mol^{-1}, a not unreasonable value when compared with isoelectronic $PX_4^{\bullet}$ radicals,[23] although ligand exchange was not observed for $SiH_3Cl^{-\bullet}$ on the e.s.r. time scale at 77 K[6] or before the radical begins to decompose at 113 K.[24]

Energies and structures for (IV)—(VI) and related compounds are also shown in Tables 1 and 2, respectively.

Thermodynamic Stability.—Schemes 2 and 3 show the possible bond dissociation reactions for $SiH_3F^{-\cdot}$ and $SiH_3Cl^{-\cdot}$, respectively, with MP2/6-21++G* energies for each reaction.



SCHEME 2 Calculated (MP2/6-21 + + G*//3-21 + G) bond dissociation energies for $SiH_3F^{-\cdot}$ (kcal mol^{-1}). The experimental value is shown in parentheses



SCHEME 3 Calculated (MP2/6-21 + + G*//3-21 + G) bond dissociation energies for $SiH_3Cl^{-\cdot}$ (kcal mol^{-1}). The experimental value is shown in parentheses

The most favourable dissociation for $SiH_3F^{-\cdot}$ is to the fluorosilyl anion SiH_2F^- and the hydrogen atom, although this is endothermic by 31.6 kcal mol^{-1}. The splitting off of F^- (35.1 kcal mol^{-1}) is competitive. The only radical product observed on irradiation of SiH_3F was $SiH_2F\cdot$.[6] The reaction $SiH_3^- + F\cdot \rightarrow SiH_3\cdot + F^-$ allows a check of the reliability of the calculations. Experimentally,[25] this reaction is exothermic by 47.9 kcal mol^{-1}, compared with 58.8 kcal mol^{-1} calculated. As the heats of formation of $SiH_3\cdot$, $SiH_3^{-\cdot}$, $F\cdot$, and F^- are known [25,26] the heat of formation of $SiH_3F^{-\cdot}$ can be calculated from Scheme 2 to be -55 ± 5 kcal mol^{-1}. The heat of formation of SiH_3F is quoted as -105 ± 15 kcal mol^{-1} in the JANAF tables,[27] and extrapolation from the SiF_4 and SiF_3H values [26] gives a value of -107 kcal mol^{-1}. The electron affinity of SiH_3F therefore appears to be of the order of -2 eV (*i.e.* the radical anion is not bound), in accord with the fact that $SiH_3F^{-\cdot}$ could not be observed experimentally.[6] The validity of *ab initio* calculations for unbound radical anions, is, naturally, extremely doubtful and may explain the extreme basis set dependency of the $SiH_3F^{-\cdot}$ results. Larger basis sets allow the extra electron to essentially dissociate and so the calculations reflect more and more the geometrical preference of the neutral molecule as the basis set is made larger. The 6-21++G* population analysis for C_{3v} $SiH_3F^{-\cdot}$ confirms this interpretation, the SOMO being unbound by 5 kcal mol^{-1} and localised almost exclusively on the diffuse functions. The calculations therefore strongly suggest that $SiH_3F^{-\cdot}$ is not a bound anion.

The situation for the experimentally known[6] $SiH_3Cl^{-\cdot}$ is, however, different. The possible bond dissociation pathways (Scheme 3) are all calculated to be endothermic, the most favourable being the dissociation of Cl^-, which has a calculated heat of reaction of 8.3 kcal mol^{-1}. The electron transfer reaction from SiH_3^- to $Cl\cdot$ is calculated to be exothermic by 56.4 kcal mol^{-1}, compared with the experimental value of 50.5 kcal mol^{-1}.[25] Using a similar procedure to that used above to calculate a heat of formation for $SiH_3Cl^{-\cdot}$ we obtain a value of -22 ± 5 kcal mol^{-1}. The JANAF [27] heat of formation for SiH_3Cl is -48 ± 15 kcal mol^{-1}, whereas an incremental approach based on the $(CH_3)_nSiH_{4-n}$ series and on $(CH_3)_3SiCl$ [26] yields a value of -36.5 kcal mol^{-1}, which is probably more reliable. The $SiH_3Cl^{-\cdot}$ radical anion is thus suggested to be thermodynamically unbound by 0.6—1.1 eV. The directly calculated (MP2/6-21++G*) electron affinity of SiH_3Cl is -0.7 eV, in good agreement with the value obtained from the heat of formation. The MP2/6-21++G* energy for SiH_3Cl at the 3-21+G geometry of (IV) is $-750.246\,80$ a.u., giving a vertical ionisation potential for the radical anion of 2.8 eV. The TBP radical anion is therefore kinetically bound, although adiabatic electron capture by SiH_3Cl is endothermic. In contrast to $SiH_3F^{-\cdot}$ the SOMO of $SiH_3Cl^{-\cdot}$ is bound at 6-21++G* and is localised largely on the outer of the two normal valence shells, rather than on the diffuse functions.

Bonding in $SiH_3Cl^{-\cdot}$.—The original calculations [9] on $SiH_3F^{-\cdot}$ and $SiH_3Cl^{-\cdot}$ suggested that low-lying σ^* SiH orbitals were responsible for the preferred hypervalent structures. An electropositive central atom therefore favours TBP structures as the σ orbitals are concentrated on hydrogen, leading to the opposite polarisation in the σ^* orbitals. The present, more complete, calcuations allow a critical examination of this proposal. The great advantage of calculations in this respect is that *d*-orbitals can be added to the basis set in order to assess their effect. A stabilisation of the TBP species by *d*-orbitals should be observable either as a stabilisation of (IV) relative to (VI) on inclusion of *d*-orbitals or of (IV) relative to $SiH_3^{\cdot} + Cl^-$ at the four levels of theory used in this work. Also included is the energy for the reaction $SiH_3^{\cdot} + Cl^- \rightarrow SiH_3Cl + e^-$. The inclusion of both diffuse functions and *d*-orbitals has the effect of decreasing the stability of the radical anion relative to its components, and neither has a large effect on the relative energies of the three $SiH_3Cl^{-\cdot}$ structures. The inclusion of electron correlation, however, stabilises all three $SiH_3Cl^{-\cdot}$ structures and SiH_3Cl by a similar amount. It has previously been noted [28] that the inclusion of a correlation correction strengthens the three-electron bond in strongly bound σ^* radical complexes. This effect is similar to the role played by correlation in determining the NN bond length in N_2O_4,[29] where the $(\sigma^2{}_u)$ state contributes strongly. In the case of σ^* radicals the $(\sigma^1{}_g,\sigma^2{}_u)$ state appears to be important and presumably in TBP radicals the corresponding singly excited state. The destabilisation of $SiH_3Cl^{-\bullet}$ relative to $SiH_3^{\bullet}$ and Cl^- upon inclusion of diffuse functions or *d*-orbitals is probably better regarded as a more effective stabilisation of Cl^-. Figure 1, therefore, indicates that *d*-orbitals do not play a significant role in the bonding in $SiH_3Cl^{-\bullet}$ but that σ^* orbitals are important, especially at the post SCF level. Howell and Olsen[8b] reached similar conclusions regarding the non-involvement of *d*-orbitals in the TBP $PX_4^{\bullet}$ radicals. In order to check that the *d*-orbitals in 6-21++G* were not responsible for the large MP2 stabilisation the calculations were repeated using the 6-21++G basis set without *d*-orbitals. The results are essentially identical, not surprisingly as diffuse functions on neighbouring atoms can take over the polarisation role usually attributed to *d*-functions.

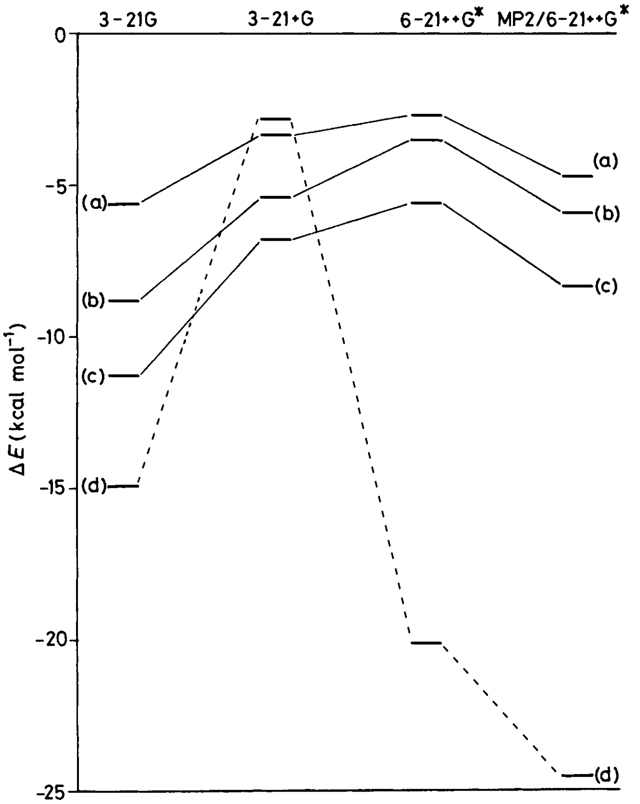


FIGURE 1 Basis set dependence of the energy for the reactions $SiH_3^{\bullet} + Cl^- \longrightarrow X$ where X = (a) $SiH_3Cl^{-\bullet}$ (V), C_{3v}; (b) $SiH_3Cl^{-\bullet}$ (VI), C_s; (c) $SiH_3Cl^{-\bullet}$ (IV), C_s; (d) $SiH_3Cl + e^-$

Spin Densities.—The UHF total spin densities for $SiH_3Cl^{-\bullet}$ do not reproduce the observed[6] values well, the spin being concentrated far too much on silicon. The electron densities calculated from the SOMO, however, show excellent agreement with experiment (Table 3), the only significant deviation being the large spin density calculated for the chlorine *p*-orbitals. As the experimental work[6] located only 86% of the spin, however, the calculations may be more reliable. Extensive investigation of spin densities with large polarisation basis sets[30] suggests that the electron density in the SOMO may be a better approximation for the experimental results than UHF total spin densities.

TABLE 3

$SiH_3Cl^{-\bullet}$ Spin densities

		Experimental[a]	SOMO[b,c]	UHF Total[c,d]
Si	*s*	0.250	0.234	0.286
	p	0.314	0.304	0.754
Cl	*s*	0.021	0.023	−0.022
	p	0.150	0.357	0.032
H_1		0.106	0.067	0.010
$H_{2,3}$		0.009	0.009	−0.035

[a] From ref. 6. [b] Electron density of the α-SOMO. [c] UHF-6-21 + + G*//3-21 + G. [d] $<S^2> = 0.7555$.

It appears that the UHF procedure may overemphasise spin polarisation with large, flexible basis sets as spin densities appear to deviate more and more from experiment with increasing size of the basis set. This may also reflect a problem in assigning electrons with large basis sets where diffuse or polarisation functions extend into regions which would normally be assigned to other atoms. At present, however, it appears to be an acceptable alternative to use electron densities from the SOMO in place of UHF total spin densities for radicals in which spin polarisation is not dominant.

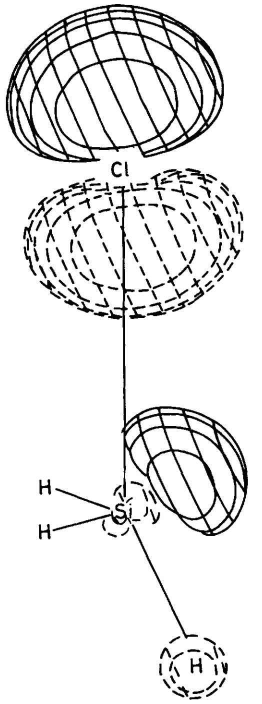


FIGURE 2 The SOMO of $SiH_3Cl^{-\bullet}$. Note that the STO-3G basis set used for this plot overemphasises the chlorine contribution in comparison to larger basis sets

The SOMO of $SiH_3Cl^{-\bullet}$ is shown in Figure 2. As expected from the experimental results[6] and from a qualitative MO analysis[9] this orbital resembles a radical centre directed towards the empty valence of a pentaco-ordinate trigonal bipyramidal silicon. There are significant antibonding contributions from chlorine and from the axial hydrogen. Such hypervalent radicals can be regarded as three-centre σ^* radicals, comparable with the more conventional two-centre σ^* species.[2,4,5] Similarly structures (III) and (VI) may be regarded as four-centre σ^* radicals.[31]

Conclusions.—The $SiH_3F^{-\bullet}$ radical anion is not a bound species. Large basis set calculations for such radical anions tend towards the neutral molecule geometry with an extra electron which is dissociated as far as possible.

$SiH_3Cl^{-\bullet}$ is a kinetically bound anion (*i.e.* at its equilibrium geometry it has a positive ionisation potential), the electron affinity of SiH_3Cl being of the order of 0.5 eV. The radical anion has a C_s structure derived from a trigonal bipyramid with the chlorine axial and one equatorial site vacant. Ligand exchange occurs *via* an alternative trigonal bipyramidal transition state in which chlorine is equatorial and the vacant site axial.

d-Orbitals do not contribute significantly to the bonding in $SiH_3Cl^{-\bullet}$ but correlation is important, as in σ^* radicals.

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