United Atom Models for Polyatomic Ligands. Part IV.[1] Trisubstituted Radical and Anion Derivatives of Group IV

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United atom theory is applied to radicals and anions AB_3 in which A is a Group IV element and B is H, CH_3, F, or Cl. Using available evidence and rules developed in previous work to predict orbital energies, the electronic structures and Lewis basicities of these fragments are discussed. Through a proposed subduction of the eigenvectors from T_d, the angular behaviour of all n/a_1 and n/e orbitals can be predicted. There are five different types of e orbitals from p, d, or f orbitals of the united atom, each implying its own natural bond angle, the smallest being associated with the orbital of lowest energy in any manifold. The affect of each type of e level on the pyramidal angle depends on its bonding character. In the hydrides this bond angle may be a measure of σ donation but in the heavier fragments it essentially reflects π basicity.

UNLIKE derivatives of Group V and VI atoms discussed in previous papers,[1] ligands which are derivatives of Group IV atoms are bonded to Lewis acids as molecular fragments. In the limits, these fragments may be considered either as radicals or anions. In order to discover trends in both geometric and electronic structures the united atom correlation diagrams for both AB_3 and $[AB_3]^-$ in which A is C, Si, Ge, or Sn and B is H, CH_3, F, or Cl have been investigated.

THEORY

A few of these radicals or anions have been observed experimentally. Many more have been analysed with various theoretical models, most of which are concerned with calculation of total energies, hyperfine splitting constants, and molecular geometry. Some recent relevant results are collected in Table 1. From this survey it is clear that there are many uncertainties and indeed direct contradictions concerning the expected structures depending on the interpretation of results or in their absence, the model adopted.

None of the theoretical treatments cited however uses the energies of occupied valence orbitals to predict molecular geometries in the manner of a Walsh diagram. Allen [22] has recently shown that one parameter models involving repulsion or electronegativity arguments are homomorphous with the Walsh diagram technique because the relative values of orbital energies are all functions of one molecular angle. The Walsh technique however has the advantage that the expected behaviour of each type of valence orbital is more easily assessed than are the angular dependences of bulk properties such as polarizability or electronegativity. As Pauling remarks,[16] the electronegativity calculations are not very reliable because the strength of the bond changes very little with changing s (and therefore ionic [23]) character. As a result, the orbital energy information available in the united atom correlations for these molecular fragments should be of use in predicting their geometries.

Construction of Diagrams.—Ideally, the diagrams could be constructed from empirical data assuming Koopmans' theorem to be correct in a first approximation. From Table 1 it is clear that this is usually not possible even by substitution of calculated data. The diagrams have in most cases been drawn using the energy levels of the separated and united atom limits,[24] electron affinity data,[25] and the apparent behaviour of orbitals in more fully defined systems.[1,26]

This experience shows that the perturbations of orbital energies can be described in terms of four major effects related to their symmetries.

(i) *The off centre atom (O.C.A.) field.* In the molecular field created by the off centre atoms the degenerate levels of the united and separated atoms must split. This is part of the standard technique in constructing the diagrams but by analogy with crystal field theory assuming the fragment solutions to be close to the united atom limit, the appropriate Hamiltonian [27] can be used to predict the energy ordering of the split levels of the united atom. For this purpose the C_{3v} molecules (including D_{3h} as a special case) studied here can be regarded as descended in symmetry from the united atom *via* the tetrahedron. This permits the unambiguous identification of each fragment

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[1] Parts (I)—(III), B. R. Hollebone, *J. Chem. Soc. (A)*, 1971, 3008, 3014, and 3021.

TABLE 1

(a) Experimental results

Radical	Technique	Orbital energies/10^3 cm^{-1} Unoccupied	Orbital energies/10^3 cm^{-1} Occupied	Geometry (Bond angle or point group)	Ref.
$CH_3^{\bullet}$	U.v.	$3sa_1$ −46·2 $3de''$ −66·5 $3da_1$ −66·8 $4sa_1$ −71·0	a''_2 −79·4	D_{3h}	2
$CH_3^{\bullet}$	U.v.	−66·6			3
$CH_3^{\bullet}$	N.m.r. J (s.s.)[a]			D_{3h}	4
$CH_3^{\bullet}$	E.s.r. h.f.s.[b]			D_{3h}	5
$CF_3^{\bullet}$	E.s.r. h.f.s.[b]			111°	6
$CF_3^{\bullet}$	P.i.[c]		$2a_1$ −74·6		7
$CCl_3^{\bullet}$	I.r.			109·5°	8
$SiH_3^{\bullet}$	E.s.r. h.f.s.[b]			C_{3v} (~115)	9, 10
$Si(CH_3)_3^{\bullet}$	E.s.r. h.f.s.[b]			110°	9
$SiF_3^{\bullet}$	E.s.r. h.f.s.[b]			C_{2v} (~109)	10
$SiCl_3^{\bullet}$	E.s.r. h.f.s.[b]			109	9

(b) Theoretical results for CH_3

Radical or anion	Technique	Orbital energies/10^3 cm^{-1} Unoccupied	Orbital energies/10^3 cm^{-1} Occupied	Total (a.u.)	Geometry	Ref.
$CH_3^{\bullet}$			a_2 82·1		D_{3h}	11
			e 126·2		D_{3h}	
			a_1 197·8		D_{3h}	
$CH_3^{\bullet}$					D_{3h}	12
$CH_3^{\bullet}$	Rydberg	a_1 43·5			120°	13
		e 53·2			120°	
		e 61·3			92°	
$CH_3^{\bullet}$	Rydberg	$3sa_1'$ 46·2 $3de''$ 66·5 $4sa_1'$ 66·8 $3da_1'$ 71·0	a_2'' 74·4		D_{3h}	14
$CH_3^{\bullet}$	LCAO MO (Gaussian)			−39·19335	D_{3h}	15
$CH_3^{\bullet}$	LCAO VB				D_{3h}	16
$CH_3^{\bullet}$	LCAO (Gaussian)		$1a_1$ $2{\cdot}4 \times 10^6$		105°	17
			$2a_1$ 132·8		105°	
			$1e$ 52·3		105°	

(c) Theoretical results for AB_3

Radial or anion	Calc. technique	Geometry	Ref.	Radial or anion	Calc. technique	Geometry	Ref.
CF_3	LCAO VB	112°	16	$SnH_3^{\bullet}$		D_{3h}	21
$CCl_3^{\bullet}$	LCAO VB	$109 < \alpha < 120$	18	$SnH_3^{\bullet}$	LCAO VB	C_{3v}	16
CCl_3^-	LCAO VB	<109°	18	$SnH_3^{\bullet}$		C_{3v}	21
$SiH_3^{\bullet}$	LCAO (semiempirical)	D_{3h}	12	SnF_3^-	LCAO VB	(<109)	16
				$SnCl_3^{\bullet}$	LCAO VB	C_{3v}	16
$SiH_3^{\bullet}$	LCAO VB	C_{3v}	16	$SiCl_3^{\bullet}$	LCAO VB	C_{3v}	16
$SiH_2^{\bullet}$		D_{3h}	19	$GeH_3^{\bullet}$		D_{3h}	20
$SiH_3^{\bullet}$	LCAO (semiempirical)	C_{3v}	12	$GeH_3^{\bullet}$	LCAO VB	C_{3v}	16
				GeH_3^-		C_{3v}	20
$SiF_3^{\bullet}$	LCAO VB	C_{3v} (<109)	16	$GeF_3^{\bullet}$	LCAO VB	(<109)	16
$SiCl_3^{\bullet}$	LCAO VB	C_{3v}	16	$GeCl_3^{\bullet}$	LCAO VB	C_{3v}	16
$GeH_3^{\bullet}$		D_{3h}	20	$SnH_3^{\bullet}$		D_{3h}	21
$GeH_3^{\bullet}$	LCAO VB	C_{3v}	16	SnH_3	LCAO VB	C_{3v}	16
GeH_3^-		C_{3v}	20	SnH_3^-		C_{3v}	21
$GeF_3^{\bullet}$	LCAO VB	(<109)	16	$SnF_3^{\bullet}$	LCAO VB	(<109)	16
$GeCl_3^{\bullet}$	LCAO VB	C_{3v}	16	$SnCl_3^{\bullet}$	LCAO VB	C_{3v}	16

[a] Spin-spin coupling constant observed in n.m.r. spectrum. [b] Hyperfine splitting constant observed in e.s.r. [c] Photo-ionisation spectroscopy.

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orbital from its symmetry ascent coupling coefficients,[28] calculated here for C_3 quantization.[29]

These first order wave functions are of considerable use in predictions of molecular geometry and are discussed below.

(ii) *The anisotropic potential destabilization* (*A.P.D.*) *effect*. If the off centre atoms of an AB_3 molecule have low to moderate electronegativities, the totally symmetric a_1 orbitals are much less stable than expected.[1] The effect has been described quantitatively elsewhere; [26] for assignment purposes it is sufficient to recognize that from a degenerate manifold at the separated atom limit, the a_1 orbital will usually lie highest. As a corollary the highest occupied orbital in these C_{3v} fragments is almost invariably a_1. The extent of the destabilization of the highest occupied a_1 level can be used as a measure of the Lewis σ basicity [1] of the fragment. Unoccupied a_1 orbitals also display an A.P.D. effect while a_2 orbitals, by analogy with σ_u of H_2^+ display a smaller but still significant effect. The degenerate levels situated essentially outside the nuclear framework appear to be little affected.

(iii) *The anisotropic potential stabilization* (*A.P.S.*) *effect*. For fragments having strongly electronegative substituents, the degenerate orbitals are usually more stable than expected, particularly if they originate on the off centre atoms. This usually results in early achievement of high bond stabilization ($CH_3^{\bullet}$) or in very late correlation to high lying united atom limits ($CF_3^{\bullet}$).

(iv) *Configuration interaction*. This effect tends to reinforce the O.C.A. splitting of degenerate levels. As discussed below, different orbitals may imply different molecular geometries and if because of bonding to a Lewis σ acid, orbitals of the same symmetry in the fragment are forced to cross, configuration interaction would prevent a smooth change in geometry but rather tend to cause a sudden adoption of a new geometry.

There remains a special problem in the construction of diagrams for the anions. To preserve the centre of symmetry at the separated atom limit the excess electron must be located either on the central atom or distributed on the off centre atoms. In cases where the electronegativities of A and B are very different the choice is made for the more electronegative species. However, for species like CH_3^- the choice is not clear. Placement of the whole charge on carbon results in CH_3^- apparently having no bonding orbitals, while placement on (H_3) seems more appropriate. To place the charge on the off centre atoms, the ionization potentials of the valence orbitals are taken as

$$IP_{B}^{1/3-} = IP_{B} - \tfrac{1}{3}(IP_{B} - IP_{B^-}) \qquad (1)$$

The Prediction of Molecular Geometries.—The wave functions provided by the O.C.A. field approximation for C_{3v} systems are given in Table 2. For any single orbital the assumption is made that it is most stable when its greatest density is directed at the off-centre atoms. This implied angle between the off-centre atoms can then be obtained by differentiation of the wave function and is listed for each level in Table 2. It is initially clear that unlike any LCAO model, the U.A. theory yields different resident angles for *e* orbitals depending on their *united atom parentage*. Closer examination shows that in the case of both *nd* or *nf* parentage, the descent in symmetry *via* the tetrahedron furthermore predicts that the *e* orbital giving the smallest resident angle is the most stable.

TABLE 2

Natural angles of *nle* orbitals in C_{3v} symmetry

Orbital			
U.A. Label	T_d Parentage	Wave function *	Pyramidal angle
pe	T_2	$\vert 11\rangle$	120°
de$^\beta$	T_2	$\sqrt{\frac{2}{3}}\vert 22\rangle - \sqrt{\frac{1}{3}}\vert 2-1\rangle$	114·7°
de$^\alpha$	E	$\sqrt{\frac{1}{3}}\vert 22\rangle + \sqrt{\frac{2}{3}}\vert 2-1\rangle$	100·6°
fe$^\beta$	T_2	$\sqrt{\frac{5}{6}}\vert 32\rangle + \sqrt{\frac{1}{6}}\vert 3-1\rangle$	77·0°
fe$^\alpha$	T_1	$\sqrt{\frac{1}{6}}\vert 32\rangle - \sqrt{\frac{5}{6}}\vert 3-1\rangle$	61·2°

* In each case only one of the two orthogonal functions is given.

The angular behaviour of valence *e* orbitals thus appears to be much more complicated than usually assumed in LCAO theories.[30] In some cases examined in this work there is one valence *e* orbital which is forced to be strongly bonding by the radial correlation, and by assuming that the non-bonding or anti-bonding filled *e* levels are unimportant to first order the effect of the degenerate valence levels on the molecular geometry can be assessed.

This assumption is usually too simplistic in the fragments with heavy off-centre atoms. Then there can be several degenerate orbitals each bonding to a different extent and each tending towards a different natural bond angle. Strong competition arises when the *p* valence orbitals of the ligand produce *e* orbitals correlating to *nd* and *n'p* at the united atom limit. The equilibrium bond angle is then a compromise of the natural angles of *nde*$^\alpha$, *nde*$^\beta$, and *npe* depending on the relative stability of each level. In most cases this would lead to a pyramidal angle near or greater than 109·5° which is very sensitive to bond length in the molecular fragment.

The affect of occupied a_1 levels is important but appears to arise in a different way. From Table 1, $CH_3^{\bullet}$ is flat so that the geometric effect of the 2*pe* orbital appears to be dominant if $2pa_1$ is unstable and only half filled. This can be compared to the geometry [2] of NH_3^+ or indeed all the single electron excited states of NH_3 in which $2pa_1$ is half filled. In CH_3^- or ground state NH_3 however the filled and very unstable $2pa_1$ requires a pyramidal form. If the concept that bonding orbitals are primarily responsible for geometry is maintained, then this geometry change can be

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seen as a specific response to the presence of totally symmetric antibonding charge density at the cost of some bonding energy. As discussed elsewhere, the formation of a three dimensional Gaussian volume is an efficient way to trap a charge density.[26] If the Gaussian volume is naturally present *via nde* or *nfe* orbitals then the addition of an a_1 antibonding electron costs little energy and its destabilization and hence Lewis σ basicity will be low. If on the other hand the three dimensional shape is not natural but formed with the loss of bonding energy from an *npe* orbital then the destabilization will be high and may go to the extreme that the electron cannot be held as appears to be the case with CH_3^-.[31]

Prediction of Chemical Behaviour.—The chemical behaviour of these fragments towards Lewis σ acids such as metal ions or derivatives of Group III depends primarily on the availability of the electrons in the totally symmetric orbitals. The Lewis basicity of these electrons seems to depend on two factors,[1] their localization in the ligand and their destabilization.

Electrons in a totally symmetric orbital on the central atom are easily available to the Lewis acid. This availability is also a function of the U.A. azimuthal quantum number of the orbital because the higher the l value the more concentrated the charge becomes on the z axis. Alternatively, electrons in totally symmetric orbitals localized on the substituents are poorly located for donation. They are first of all concentrated on the opposite side of the ligand from its direction of donation since it is often possible that the location of this orbital does not reflect the sense of the molecular dipole. Moreover, a totally symmetric orbital only implies rotational and reflection symmetry about the axis but does not necessarily imply that the maximum concentration of charge resides on the z axis. Indeed the $2pa_1$ orbital of $CH_3^{\cdot}$ from the group of $1s$(H) levels is a ring of charge around the axis and the minimum density is found on the axis.

It was clear in earlier work[1] that the second factor governing basicity is the A.P.D. effect. The analysis of the foregoing section has added further understanding and permits a more detailed interpretation of a special group of derivatives. Three radicals discussed here display a highest occupied a_1 orbital (HOa_1) correlating rapidly downwards to *ns* of the united atoms. At the same time the HOe orbital correlates up from an initially more stable condition to the *np* level. The two levels cross at shorter bond length than the equilibrium distance. Since in most heavy united atoms there is a large energy separation of the highest lying *ns* and *np* orbitals, this correlation leads to a very large A.P.D. for the HOa_1 and a prediction of high Lewis σ basicity.

The analysis of Allen[22] of the homomorphism between orbital energy and bulk property arguments concerning molecular angles applies equally to bond lengths. Since both the U.A. and Walsh diagrams represent the same orbital energy situation for any geometry, any prediction of a bulk property in one model must be reflected by the same prediction from the other. In this case, the corresponding prediction of high Lewis σ basicity from the Walsh diagram is plainly evident. In this latter model, the molecular fragment tends towards planar geometry because of the *npe* orbital and must coincidentally destabilize the a_1 orbitals producing a high Lewis σ basicity. The converse situation in which a prediction of low Lewis basicity because of a low A.P.D. is confirmed by the Walsh diagram (using the data of Table 2) is also observed in other fragments discussed below.

These factors of orbital localization and destabilization can also be used to predict the Lewis π acidity of these species. Orbitals of the *nde* or *nfe* type can achieve much greater overlap than the *npe* type with any Lewis π base. Localization on the central atom also promotes this overlap.

The most effective π acid orbitals also require a low destabilization. A high A.P.D. reflects a strong penetration by the e orbital of the Gaussian volume. Occupation of this orbital must tend to destabilize the molecular fragment and increase bond lengths. Thus in energy requirements, the best π acid orbital is one which has a low A.P.D., that is, it is essentially a Rydberg level, which does not correlate rapidly downwards towards the separated atom limit. This rapid stabilization with increasing bond length is a common property of HOe orbitals however, and if such an orbital is occupied, its antibonding nature must be overcome by an increase in stability of bonding orbitals to prevent dissociation. Examples of this are discussed below.

RESULTS AND DISCUSSION

The thirty-two drawings for all the AB_3 radicals and anions have been prepared and a few representative diagrams are presented here. The complete results are summarized in Table 3 in which the united atom quantum numbers for the highest occupied a_1 and e orbitals, together with their separated atom limits and destabilizations, are given. All available ionization data have been used.[32]

The Hydride Derivatives.—In all but one case the highest occupied a_1 (HOa_1) originates on the off centre atom group (H_3) or $(H_3)^-$. The exception is SnH_3 in which HOa_1 originates from $5s$ of Sn. In all cases this orbital correlates to the *np* orbital of the next rare gas atom or ion. Similarly, in all cases the HOe correlates to *np* of the united atom and originates on the $1s$ of (H_3) or $(H_3)^-$.

There is only one occupied valence e orbital, the *npe* level which tends to produce a planar fragment. In $CH_3^{\cdot}$ this effect is apparently dominant.[2] The other radicals $AH_3^{\cdot}$ are also expected to be planar and while there is some disagreement on the literature,[16,19] even the valence bond model predicts the hydrides to be the most nearly planar of the series $AB_3^{\cdot}$. This is also the conclusion from the magnitudes of hyperfine splitting constants in the $SiB_3^{\cdot}$ series.[10]

The HOa_1 is destabilized in all the radicals but in the lightest three it originates on (H_3). Weak σ basicity is therefore expected except for $CH_3^{\cdot}$ in which the destabilization is very large leading to moderate donor power. The π acidity is also expected to be weak since in each case the LUe correlates to *np* at the U.A. limit and downwards to *np* of the central atom at the separated atom limit. This stabilization with increasing bond length which is smallest in $SnH_3^{\cdot}$ is only counteracted by an increase in stability of HOa_1.

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[31] D. K. Bohme, personal communication.

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The hydride anions are all expected to be pyramidal because of the Gaussian volume effect. There will be a tendency for the pyramidal angle to remain above 109·5° although the angle in CH_3^- has been calculated as 105°.[17] In all these ions the HOa_1 orbital appears to be very unstable but only in CH_3^- (assuming the electron originally on carbon) does this orbital originate on the central atom and imply strong Lewis basicity. This basicity indeed may be too great, for even sophisticated attempts reacting gas phase NO^- with $CH_3^{\cdot}$ have failed to produce CH_3^-.[31] This may as well extend to the heavier congeners.

The Methyl Derivatives.—The diagrams of these species are considerably more complicated and unlike the hydrides, do not all correlate to one group of the periodic table at the U.A. limit. In these systems the energy levels of the substituent methyl group are taken from the U.A. diagram of the $CH_3^{\cdot}$ radical (Figure 1), while those of the anion are taken from Figure 2, and inserted in equation (1). The group orbitals of the $2pe$ levels produce an nfa_2 orbital which in the lighter derivatives is unlikely to be occupied because it correlates very rapidly towards the ionization limit with decreasing bond length.

In $C(CH_3)_3^{\cdot}$ (Figure 3) the HOa_1 originates in the $2pa_1$ group orbitals of $(CH_3)_3$ while the HOe originates on the slightly more stable $2p$ orbital of the central carbon. The HOe however correlates upward to $4p$ and is much less stable than the lower valence e levels which correlate to $3d$. The $3de^{\beta}$ is probably non-bonding, suffering configuration interaction with $3de^{\alpha}$ so that the pyramidal angle results from the $3de^{\alpha}$ in competition with $4pe$. The equilibrium angle is probably greater than 109° and the flattening gives substantial A.P.D. to the HOa_1. The Lewis basicity will be moderate in spite of this because the HOa_1 is not localized on the donor.

In $Si(CH_3)_3^{\cdot}$ (Figure 4) the opposite situation is found. Here the HOa_1 originates on the central atom, is weakly destabilized, and correlates to the more constricted $4d$ orbital. The HOe is $4de^{\alpha}$ implying that the pyramidal geometry is natural rather than forced and

TABLE 3

Origin and behaviour of valence orbitals; radicals

		HOa_1				HOe				LUe			
A	X_3	UA [a]	SA [b]	ΔE_D [c]	D [d]	UA	SA	ΔE_D	D	UA	SA	ΔE_D	A [e]
C	H	$2p$	$1s$(H)	55	m	$2p$	$1s$(H)	−7	w	$3p$	$2p$(C)	25	w
Si	H	$3p$	$1s$(H)	30	w	$3p$	$1s$(H)	−5	w	$4p$	$3p$(Si)	15	w
Ge	H	$4p$	$1s$(H)	25	w	$4p$	$1s$(H)	−5	w	$5p$	$4p$(Ge)	10	w
Sn	H	$5p$	$5s$(Sn)	30	s	$5p$	$1s$(H)	−5	w	$6p$	$5p$(Sn)	15	w
C	CH_3	$4s$	$2pa_1$(CH_3)	45	m	$4p$	$2p$(C)	−7	w	$5p$	$2p$(CH_3)	20	w
Si	CH_3	$4d$	$3p$(Si)	12	m	$4d$	$2pa_1$(CH_3)	−7	w	$4d$	$3p$(Si)	45	s
Ge	CH_3	$5p$	$2pa_1$(CH_3)	37	m	$4f$	$2pa_1$(CH_3)	−12	w	$4f$	$4p$(Ge)	30	m
Sn	CH_3	$5d$	$5p$(Sn)	20	m	$5d$	$5p$(Sn)	−10	w	$6p$	$5p$(Sn)	30	w
C	F	$4s$	$2p$(C)	40	s	$4p$	$2p$(F)	−12	w	$5p$	$2p$(C)	30	w
Si	F	$4d$	$3p$(Si)	−10	w	$4d$	$2p$(F)	−20	w	$4d$	$3p$(Si)	35	s
Ge	F	$5p$	$4s$(Ge)	35	s	$4f$	$2p$(F)	−15	w	$4f$	$4p$(Ge)	15	m
Sn	F	$5d$	$5s$(Sn)	20	m	$5d$	$2p$(F)	15	m	$6p$	$5p$(Sn)	20	w
C	Cl	$5s$	$2p$(C)	80	s	$5d$	$3p$(Cl)	−25	w	$5d$	$2p$(C)	30	m
Si	Cl	$4f$	$3p$(Si)	20	m	$4f$	$3p$(Cl)	10	m	$5d$	$3p$(Si)	20	m
Ge	Cl	$6s$	$4p$(Ge)	50	s	$6p$	$3p$(Cl)	−10	w	$7p$	$4p$(Ge)	20	w
Sn	Cl	$5f$	$5s$(Sn)	30	m	$6d$	$3p$(Cl)	5	m	$6d$	$5p$(Sn)	30	m

Anions

		HOa_1				HOe		
A	X_3	UA [a]	SA [b]	ΔE_D [c]	D [d]	UA	SA	ΔE_D [c]
C	H	$2p$	$2s$(C)	40	s	$2p$	$1s$(H)	0
Si	H	$3p$	$1s$(H)	40	m	$3p$	$1s$(H)	0
Ge	H	$4p$	$1s$(H)	35	m	$4p$	$1s$(H)	0
Sn	H	$5p$	$1s$(H)	35	m	$5p$	$1s$(H)	0
C	CH_3	$4s$	$2pa_1$(CH_3)	55	s	$4p$	$2p$(C)	−5
Si	CH_3	$4p$	$3p$(Si)	25	s	$4d$	$3p$(Si)	−10
Ge	CH_3	$5p$	$2pa_1$(CH_3)	40	m	$4f$	$2pa_1$(CH_3)	0
Sn	CH_3	$5d$	$2pa_1$(CH_3)	30	m	$5d$	$2pa_1$(CH_3)	−5
C	F	$4s$	$2p$(C)	20	s	$4p$	$2p$(F)	−20
Si	F	$4d$	$3p$(Si)	15	m	$4d$	$2p$(F)	−10
Ge	F	$5p$	$2p$(F)	35	m	$4f$	$2p$(F)	−20
Sn	F	$5d$	$5s$(Sn)	35	s	$5d$	$2p$(F)	10
C	Cl	$5s$	$2p$(C)	70	s	$5d$	$3p$(Cl)	−15
Si	Cl	$4f$	$3p$(Si)	40	s	$4f$	$3p$(Cl)	5
Ge	Cl	$6s$	$4p$(Ge)	55	s	$6p$	$3p$(Cl)	−10
Sn	Cl	$5f$	$3p$(Cl)	30	m	?	$3p$(Cl)	?

[a] UA is the united atom limit of a molecular orbital. [b] SA is the separated atom origin of a molecular orbital. [c] ΔE_D is the energy destabilization of an orbital at the equilibrium geometry. [d] D is the predicted donor ability of a filled orbital; s, strong; m, moderate; w, weak. [e] A is the predicted acceptor ability of an empty orbital.

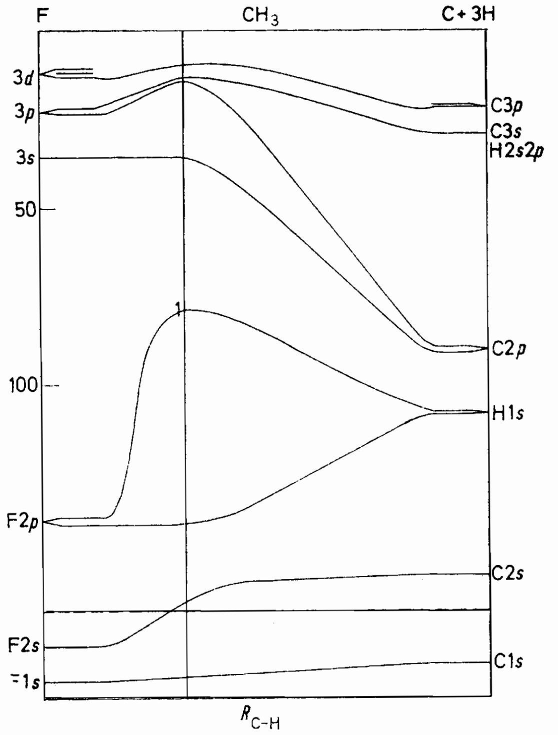

FIGURE 1 Methyl radical, HOMO is $2pa_1$ (vertical line indicates the order of eigenvalues at the equilibrium internuclear separation)

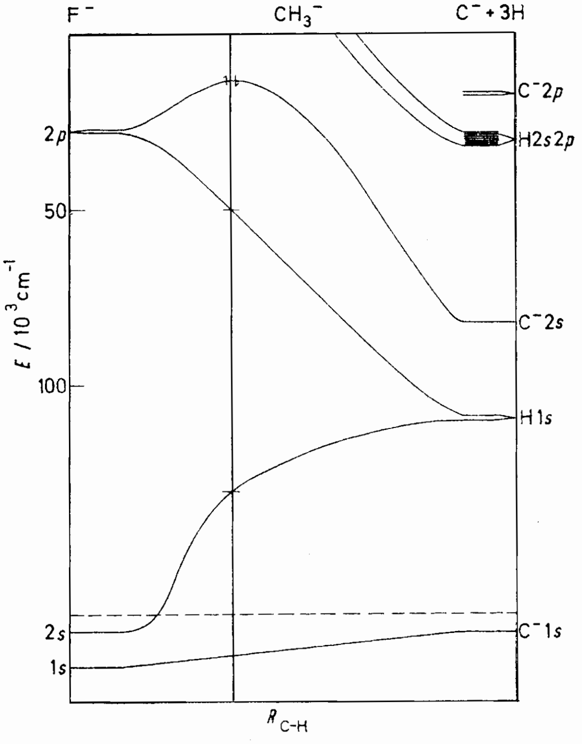

FIGURE 2 Methyl carbanion, HOMO is $2pa_1$ from C⁻

this is reflected in the low A.P.D. of HOa_1. The lowest unoccupied e is $4de^{\beta}$ also originating on silicon. It has both the best localization and angular distribution for overlap with a π base. As well the $4pe$ stabilizes with increasing bond length counteracting the anti-bonding influence of electrons in $4de^{\beta}$. Therefore the radical can act as a Lewis π acid and since both $4da_1$ and $4de^{\beta}$ originate on silicon $3p$ it can act as a synergic ligand.[1]

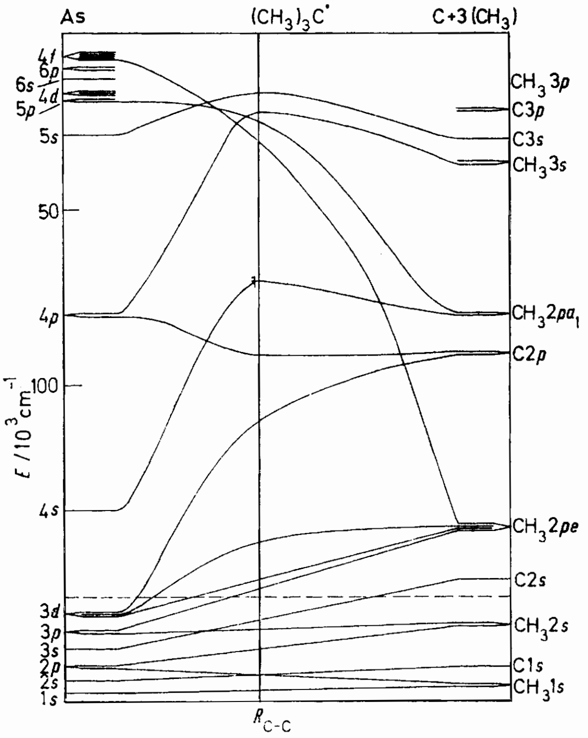

FIGURE 3 t-Butyl radical, HOMO is $4sa_1$

The radical $Ge(CH_3)_3^{\bullet}$ (Figure 5) correlates to praseodymium, permitting the $4fa_2$ orbital to become occupied. Thus, in spite of the further slight decrease in electronegativity from silicon to germanium, the HOa_1 originates from the $2pa_1$ of $(CH_3)_3$. The HOe is $4fe^{\alpha}$ and also originates in these group orbitals. However, both it and the $5pe$ are slightly anti-bonding and the geometry is probably a function of $4de^{\beta}$ implying a more open pyramid (Table 2) than the analogous carbon or silicon derivatives.

The Lewis σ basicity of this radical will be substantially less than that of the silicon derivative but should closely resemble that of the analogous carbon compound. This alternation in the origin of the HOa_1 caused by the filling of the $4fa_2$ orbital is a plausible explanation of the oft-cited[33] apparent alternation of electronegativities in Group IV. This alternation can be expected on this basis in derivatives in which the substituents are bound to the central atom by valence

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[33] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, 1972, p. 310.

p orbitals and the ionization potential of the pa_1 group varies between 91 10^3 cm^{-1}, the ionization potential of carbon, and 66 10^3 cm^{-1}, the ionization potential of silicon.

The ionization potentials of most organic substituents fall in this range. However for those which are more complex than the methyl group, it is probably inappropriate to attempt a condensation to a single atom.[1] Rather in the present model such substituent groups can be regarded as perturbed methyl groups retaining essentially p-like valence orbitals with modified $2pa_1$ and $2pe$ eigenvalues. Thus the derivatives of Group IV should display an alternation in Lewis σ basicity, not because of an alternation of electronegativity in the Mulliken sense but because the ligand centred $4fa_2$ orbital is filled in the germanium compounds.

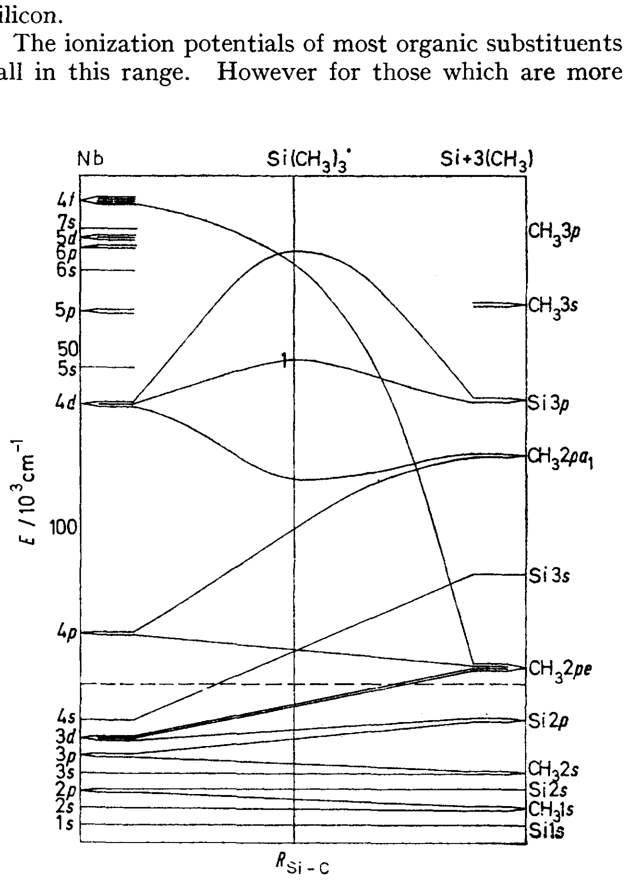

FIGURE 4 Trimethylsilyl radical, HOMO is $4da_1$

The HOa_1 in $Sn(CH_3)_3^{\bullet}$ is $5da_1$ and originates again on the $(CH_3)_3$ group because $4fa_2$ is filled. The Lewis σ basicity is likely higher than that of the germanium radical however because the underlying $4fa_1$ from Sn $5s$ is much less stable than $5sa_1$ from Ge $4s$. The two highest e orbitals, $5de^{\alpha}$ and $5de^{\beta}$, are both anti-bonding and as before the geometry is probably a function of $4fe^{\beta}$ from the $(CH_3)_3$ $2pe$ levels.

The methyl substituted anions, constructed in each case from the limit $A + (CH_3)_3^-$, follow a somewhat different pattern from the radicals. The decreased ionization potential of the CH_3 $2pa_1$ orbitals shifts the HOa_1 from Si in the radical to CH_3 in the anion and the HOe is changed in the opposite sense. In the tin derivative, both HOa_1 and HOe are changed from originating on the substituent to the central atom. The Lewis basicity of all the anions is higher than the radicals but the destabilizations are not as large as in the hydride series because the pyramidal form which stabilizes a_1 charge density is already present in all but the $C(CH_3)^-$ ion. The effective change in the basicity of the $Si(CH_3)_3$ fragment as it acquires charge is probably very small since the charge is moved onto the substituents in the anion.

The Fluoride Derivatives.—Because the ionization potential of fluorine is much larger than that of any Group IV central atom, the HOa_1 originates on the central atom of the radical in each case. In spite of this the occupation of $4fa_2$ in $GeF_3^{\bullet}$ and $SnF_3^{\bullet}$ again causes an alternation in Lewis basicity. In $CF_3^{\bullet}$ (Figure 6) and $SiF_3^{\bullet}$ (Figure 7) the HOa_1 originates on np of the central atom. In $CF_3^{\bullet}$ HOa_1 correlates to $4s$ with an underlying HOe $4pe$ and thus has a very large A.P.D. and high basicity. In $SiF_3^{\bullet}$ HOa_1 and HOe both correlate to $4d$ and the Lewis σ basicity is much reduced. The Lewis π acidity however should be very strong. Any anti-bonding effects in $4de^{\beta}$ are counterbalanced by increasing stability in $4de^{\alpha}$ and since both HOa_1 and HOe originate on $3p$ of silicon the ligand is synergic. In $GeF_3^{\bullet}$ the HOa_1 originates on $4s$ of Ge since $4fa_2$ is occupied and correlates to $5p$. However underlying the HOe which is $4fe^{\alpha}$ is the $5pe$ from the

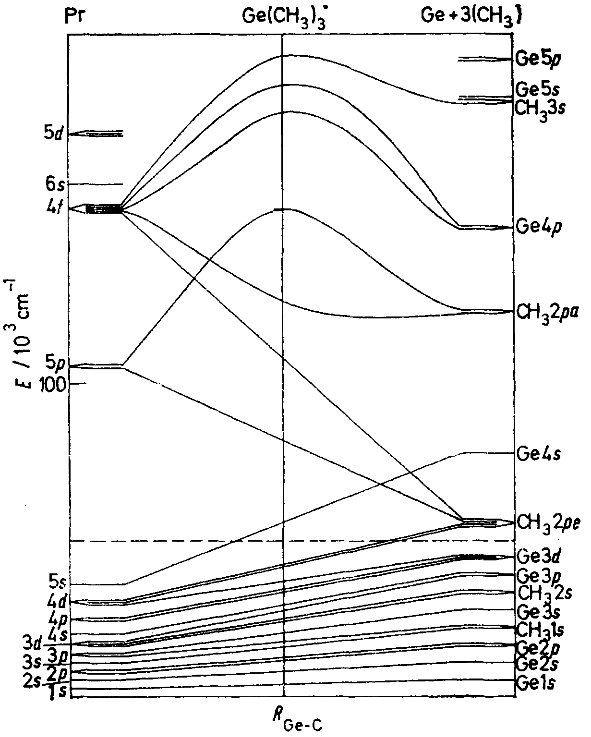

FIGURE 5 Trimethylgermyl radical, HOMO is $5pa_1$ (note filled $4fa_2$)

$2p$ levels of (F_3) which again forces the HOa_1 to be destabilized as in the carbon derivative. In $\mathrm{SnF_3}^{\bullet}$ the $5pe$ has become a core orbital and the HOa_1 which is $5da_1$ is not destabilized. Thus, as in the methyl derivative the occupation of $4fa_2$ at germanium causes an increased Lewis basicity which is not related to a reversal of the electronegativity trend in the group. All of these radicals are probably pyramidal but both $\mathrm{CF_3}^{\bullet}$ and $\mathrm{GeF_3}^{\bullet}$ are most likely flatter than $\mathrm{SiF_3}^{\bullet}$ or $\mathrm{SnF_3}^{\bullet}$ since the HOe's of the former correlate to np.

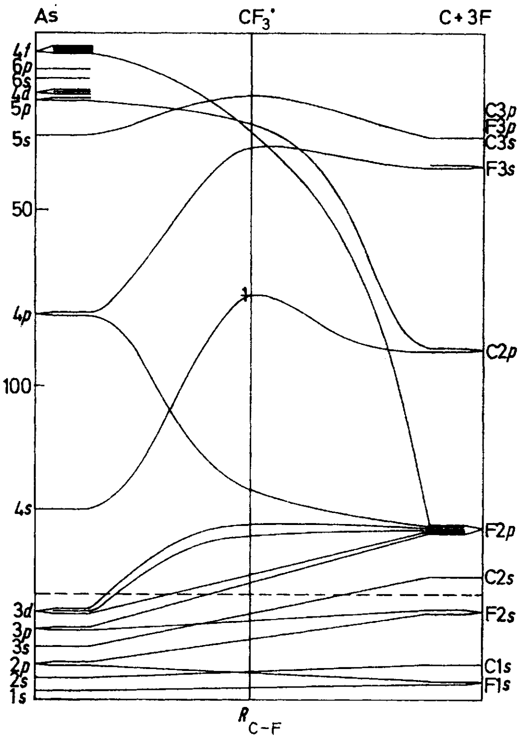

FIGURE 6 Trifluoromethyl radical, HOMO is $4sa_1$

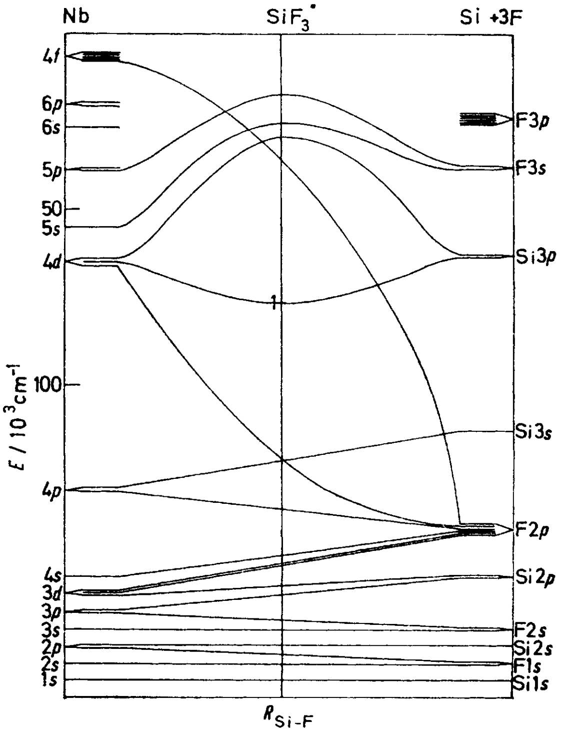

FIGURE 7 Trifluorosilyl radical, HOMO is $4da_1$

In the anions the situation is very similar. There is one change of importance at germanium where the valence orbitals of $(\mathrm{F}_3)^-$ fall above $4s$ of Ge and HOa_1 and HOe both originate on fluorine. Thus in spite of the upward correlation of HOe to $5p$ and the consequent high destabilization of HOa_1, the Lewis basicity of $\mathrm{GeF_3}^-$ is probably not significantly different from $\mathrm{GeF_3}^{\bullet}$ because as in the $\mathrm{SiMe_3}^-$ anion, the charge migrates to the substituents.

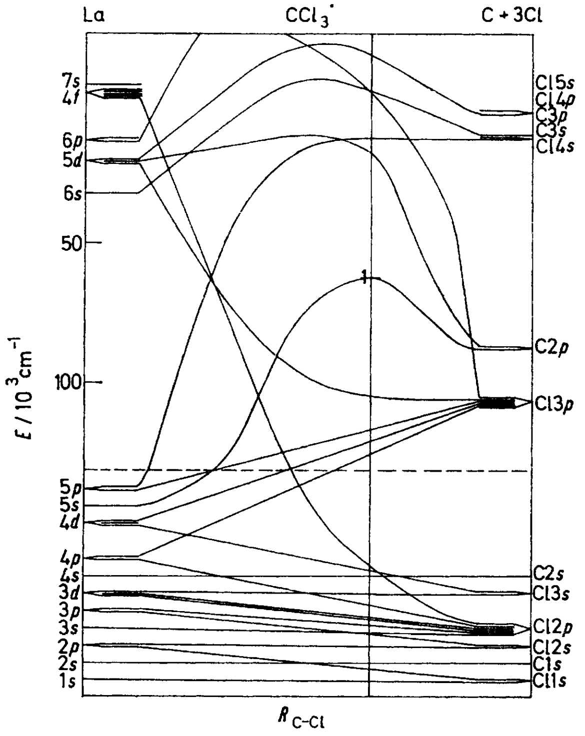

FIGURE 8 Trichloromethyl radical, HOMO is $5sa_1$

The Chloride Derivatives.—As in the fluoride substituted radicals all the HOa_1 orbitals are found on the central atom. The electronic structure of the first two members of this series $\mathrm{CCl_3}^{\bullet}$ (Figure 8) and $\mathrm{SiCl_3}^{\bullet}$ (Figure 9) are very similar to the fluoride analogues. The radical $\mathrm{CCl_3}^{\bullet}$ correlates to lanthanum and assuming that $2pa_2$ is occupied but that $3pa_2$ is unoccupied the HOa_1 originating on $2p$ of carbon is $5sa_1$. The second highest degenerate level is $5pe$ which at the equilibrium bond length causes both a flattening of the geometry[8] away from the angle implied by the HOe $5de^{\alpha}$ orbital and a strong destabilization of $5sa_1$. The Lewis σ basicity of the radical should be very high because both the destabilization and localization of the HOa_1 are favourable. The radical should also act as a strong π acid since the LUe is $5de^{\beta}$ originating on $2p$ of carbon. Moreover the HOe probably stabilizes with increasing bond length counteracting the anti-bonding $5de^{\beta}$ electrons. Since both $5sa_1$ and $5de^{\beta}$ originate on carbon the radical should act synergically.

The $SiCl_3$ radical is very different. The HOe orbital originating on silicon correlates to $4f$ as do the highest and second highest occupied degenerate levels. As a result the destabilization of the HOa_1 is much reduced and the pyramidal angle is expected to be determined by the $4fe^{\alpha}$ orbital. The Lewis σ basicity should be moderate since the HOa_1 is again on the central atom. The LUe is $5de^{\alpha}$ from $3p$ of silicon and its occupation can be counteracted by the HOe orbital $4fe^{\beta}$. This radical should also act synergically.

The radical $GeCl_3^{\bullet}$ (Figure 10) correlates to bismuth. While the $5fa_2$ remains unoccupied, the electronic structure of the valence levels is very similar to that of $CCl_3^{\bullet}$ and the chemical alternation is again observed. In this case the HOa_1 is $6sa_1$ underlain by the HOe, $6pe$.

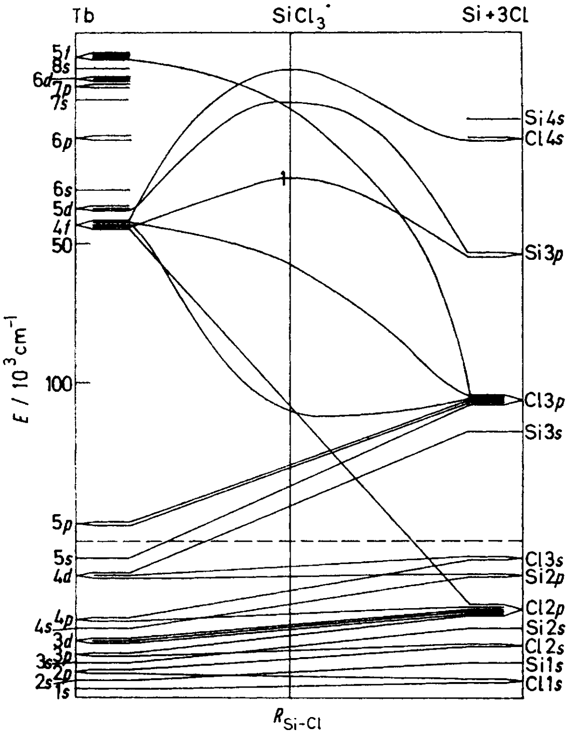

FIGURE 9 Trichlorosilyl radical, HOMO is $4fa_1$

The predicted flattening of the molecule and destabilization of the HOa_1 imply very similar chemistry to that of the carbon analogue.

In $SnCl_3$ the electronic structure reverts to one very similar to $SiCl_3$. The HOa_1 and HOe correlate to $5f$ and $5d$ respectively giving a low A.P.D. for the HOa_1 and a small pyramidal angle. The LUe is $6de^{\beta}$ counteracted by the increased stabilization of $6de^{\alpha}$.

The anions are in general similar but some important changes occur. In CCl_3^- the $3p$ levels of $(Cl_3)^-$ lie above $2p$ of carbon and the HOe and HOa_1 become centred on the substituents. In spite of retaining a large A.P.D. the Lewis basicity may decrease. In $SiCl_3^-$ the orbitals retain their origins but the $4f$ levels of the united atom move very close to the ionization limit greatly increasing the A.D.P. of HOa_1 and the σ basicity. There is no essential change in the germanium case but in the tin system, the $3p$ levels of $(Cl_3)^-$ move above $5s$ of tin and HOa_1 moves to the substituents reducing the basicity in spite of an increased A.P.D.

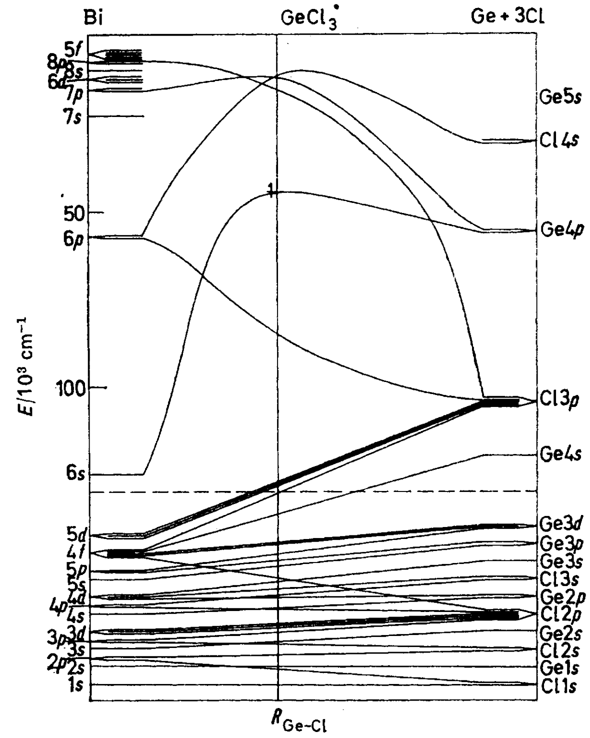

FIGURE 10 Trichlorogermyl radical, HOMO is $6sa_1$

CONCLUSIONS

This study of Group IV molecular fragments was undertaken to derive first order wave functions and eigenvalues of the orbitals responsible for donation or acceptance of charge to or from a transition metal atom or ion. For infinitely long dative bonds, the probable limits of electronic structures of these ligands are the radical and anion forms discussed here. As in the previous treatment of Group V and VI ligands,[1] the donor and acceptor properties can be predicted in each case. The degree of certainty depends to some extent on the availability of empirical data but the regularities of constructing U.A. diagrams are quite clear and sufficient for a first approximation model.

Few criteria are available to help in assessing the ionic character of the dative bond but in the Group IV derivative it may be possible to use the change in angle on co-ordination. Such changes must reflect changing relative stabilities of the valence orbitals and must be carefully interpreted.

There appear to be three primary effects which could be caused by a co-ordinated transition metal ion. These are: (i) Withdrawal of σ charge from the ligand can have one of two consequences. If the ligand is pyramidal because of *nde* or *nfe* orbitals little change in angle would be expected. If the ligand is pyramidal only because of the a_1 charge however its removal would tend to open the angle.

(ii) Withdrawal of π charge from the ligand would tend to stabilize the HO*e*. This would in turn make the natural angle of that orbital more favourable so that the molecular angle would approach the appropriate values listed in Table 2.

(iii) Donation of π charge tends to destabilize the accepting orbital but this would have little direct effect on the molecular angle. Secondary effects might be observed if the bond length readjusted to accommodate the charge input changing the relationships of the HO*e* levels. Some specific predictions can be made in individual cases using these general rules.

In complexes of CF_3 withdrawal of pure σ charge would have little effect on the angle since it is determined primarily by competition of 4*pe* and 3*de*$^{\alpha}$. Withdrawal of π charge however would have a marked effect. The 3*de*$^{\alpha}$ orbital having the smallest natural angle is best able to achieve overlap with a π acid. Therefore it should be the most stabilized and the molecular geometry should approach its natural angle, that is be reduced. A similar situation exists in many other cases including complexes of $SiCl_3^{\bullet}$ in which these predictions can be confirmed.[34]

Since this change of angle *via* withdrawal of π electrons appears to be the largest effect, most observed decreases in angle are probably due to π basicity in the ligand. Changes due to pure σ effects could only be confidently predicted in AB_3^- systems in which the natural angle was 120° determined by an isolated *npe* orbital. With the exception of this rare case, it appears that angle changes cannot reflect ionic character but are sensitive to ligand to metal dative double bonding.

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[34] L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 447; K. W. Muir and J. A. Ibers, *ibid.*, p. 440.