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Hypercoordination in SiH_5^- and $SiH_5^•$. An Electron-Count Dependence

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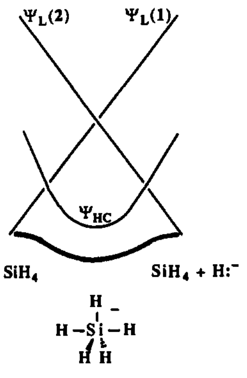
SiH_5^- with 10 valence electrons is a stable hypercoordinated species of D_{3h} symmetry.[1] Removal of just one electron causes a profound change and generates a highly unstable 9-valence electron species,[2] $SiH_5^•$. This is all the more puzzling as the isoelectronic analogues of these species, CH_5^- and $CH_5^•$, display the opposite (and expected) tendency: CH_5^- is a high-energy transition state, more than 50 kcal/mol[1a,f,3] above $CH_4 + H^-$, even more unstable than $CH_5^•$, the transition state for the inversion substitution of $CH_4 + H^•$, which only lies 37 kcal/mol[4] above the reactants. More so, no d orbitals are required to reproduce the stability of SiH_5^-,[1g,i] while $SiH_5^•$ remains an unstable transition state despite d-orbital participation.[2b,c] What could be the root cause of this profound dependency of the stability of hypercoordination on electron count? This paper provides a valence bond (VB) model that projects the essential differences between hypercoordination in SiH_5^- and $SiH_5^•$, and a comparison is made with the carbon analogues.

The key configurations for describing SiH_5^- are displayed in Figure 1A as obtained in a recent VB ab initio study.[1h] The two configurations $\Psi_L(1)$ and $\Psi_L(2)$ are the Lewis structures that form positive (Ψ_L^+) and negative (Ψ_L^-) combinations, with the energy splitting (ΔE) reflecting the four-electron/three-center stabilization energy due to the resonance between the constituent Lewis structures. The ab initio calculations show that the lowermost configuration is the hypercoordinated (Ψ_{HC}) structure where one bond is sustained by the p AO of silicon and the second bond is sustained by the σ^* fragment orbital of the central SiH_3 moiety.[1h,i]

The ground state of SiH_5^- is obtained by mixing of the positive Lewis combination, Ψ_L^+, into the hypercoordinated structure, as schematized by the VB mixing diagram in part B of Figure 1. The relationship between the two Lewis and the hypercoordinated structures is shown in **1** across an exchange reaction coordinate that generates the hypercoordinated species. This drawing further illustrates the profound impact of Ψ_{HC} on the properties of SiH_5^-.



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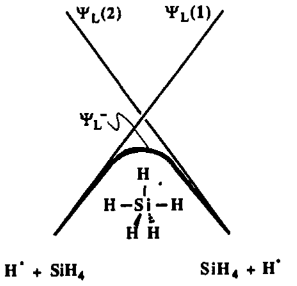

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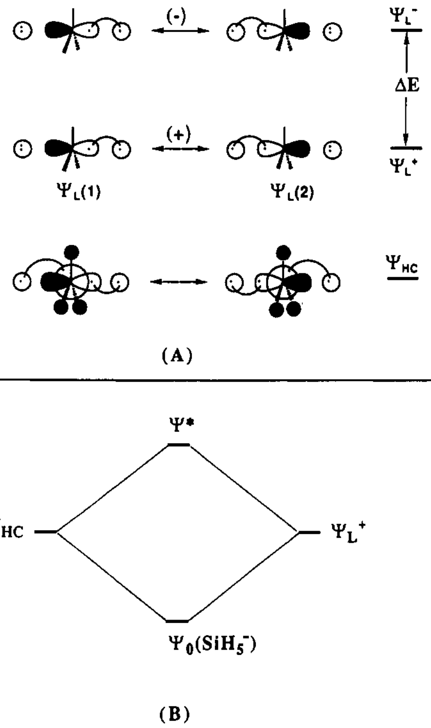

Figure 1. (A) Key VB configurations for SiH_5^-. (B) VB mixing of Ψ_{HC} and Ψ_{L^+} to generate the ground state of SiH_5^- and a corresponding antibonding combination as in **1**.

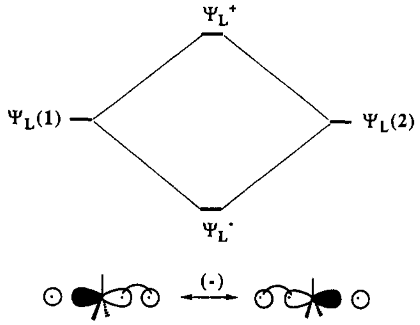

Figure 2. Mixing of the Lewis structures for $SiH_5^•$ as in **2**.

Removal of one electron from SiH_5^- generates $SiH_5^•$ and changes drastically the bonding features. The hypercoordinated structure now disappears from the set of low-lying structures, and the bonding must be sustained by resonance of the two Lewis

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Table I. Axial (R_{ax}) and Equatorial (R_{eq}) Optimized Bond Lengths (Å) of the Radicals and Anions of Planar XH_3 and Hypercoordinated XH_5 Species (X = C, Si)[a]

	SiH_5^-	$SiH_5^\bullet$	$SiH_3^\bullet$	SiH_3^-	CH_5^-	$CH_5^\bullet$	$CH_3^\bullet$	CH_3^-
R_{ax}	1.625	1.589			1.692	1.337		
R_{eq}	1.521	1.488	1.460	1.471	1.062	1.079	1.072	1.076

[a] The radicals have been calculated with the RHF open-shell Davidson Hamiltonian.[7]

structures only,[2a] as shown in Figure 2. The major consequential change arises in the energy of the species, which, as schematized in **2**, is converted to a high-energy transition state relative to its normal coordinated species.

Let us turn to discuss the carbon analogues. As shown previously,[1h] the hypercoordinated structure Ψ_{HC} is so stable owing to (a) the good overlap capability of the a_s' σ^* orbital of the SiH_3 fragment with an axial hydrogen, and to (b) the low promotion energy required to populate the $\sigma^*(SiH_3)$ orbital and prepare it thereby for bonding. In CH_5^-, on the other hand, the a_s' $\sigma^*(CH_3)$ orbital is too high in energy and overlaps too weakly with an axial ligand to be able to stabilize efficiently a structure like Ψ_{HC}. Consequently, CH_5^- remains a transition state just like $CH_5^\bullet$. In conclusion, $SiH_5^\bullet$, CH_5^-, and $CH_5^\bullet$ are described by the same bonding mechanism, the resonance hybrid of the Lewis structures, as in **2**, which differs from the hypercoordinated bonding mechanism of SiH_5^- in Figure 1B and in **1**.

It is interesting to examine the coherence of the above-described bonding mechanisms in the geometric features of the radicals and anions of CH_5 and SiH_5. First, the axial bond lengths of CH_5^- are expected to be longer than those of $CH_5^\bullet$, since four electrons undergo more exchange repulsion than three in the axial three-orbital system, much like H_3^- having longer H–H bond lengths[5] than $H_3^\bullet$. Second, the equatorial C–H bond lengths for CH_5^- and $CH_5^\bullet$ should be almost identical, and roughly equal to the C–H bond lengths of planar CH_3^- or $CH_3^\bullet$.

On the other hand, the dominance of Ψ_{HC} in the wave function of SiH_5^- leaves only three electrons in the axial three-orbital system, just as in the $SiH_5^\bullet$ radical, so that no significant lengthening of the axial bonds is expected as an electron is added to $SiH_5^\bullet$. Moreover, while the equatorial bonds of $SiH_5^\bullet$ are expected to be close to those of the planar SiH_3^- or $SiH_3^\bullet$ species, the equatorial bonds of SiH_5^- are expected to be significantly longer since their antibonding σ^* orbital is populated in the Ψ_{HC} structure.

To verify these qualitative arguments, we have optimized the geometries of $SiH_5^\bullet$, SiH_5^-, $CH_5^\bullet$, CH_5^-, $SiH_3^\bullet$, SiH_3^-, $CH_3^\bullet$, and CH_3^- at a consistent level of theory, ab initio Hartree–Fock with the 6-31++G** basis set,[6] including polarization functions and diffuse orbitals on all atoms. The results, displayed in Table I, nicely confirm all of the above expected tendencies and are as follows: (i) The equatorial bond lengths exhibit no significant differences in the bonding types of $SiH_5^\bullet$ and $CH_5^\bullet$, being close to the bond lengths of the planar XH_3 species. On the other hand, while the equatorial bond lengths are slightly *shorter* in CH_5^- relative to CH_3, the same bonds are *longer* in SiH_5^- relative to SiH_3. While the lengthening (0.050–0.061 Å) may seem to be modest, it should be remembered that, in the hypercoordinated structure Ψ_{HC}, only one equatorial σ^* orbital (the a_s' combination) out of the available three is populated. (ii) While the C-H axial bond lengths increase by 0.355 Å from $CH_5^\bullet$ to CH_5^-, the corresponding increase in the Si–H bond lengths is an order of magnitude less, only 0.036 Å, from $SiH_5^\bullet$ to SiH_5^-. The effect of Ψ_{HC} on SiH_5^- is so profound that the axial Si–H distance ends up being *shorter* than the corresponding C–H distance.

In summary, hypercoordination in SiH_5^- is an efficient delocalization mechanism of the 10-electron/6-center type. This efficient mechanism is made possible by a hypercoordinated resonance structure, Ψ_{HC}, whose involvement allows delocalization of the fifth electron pair into both axial and equatorial Si–H bonds in SiH_5^-. Removal of one electron results also in the disappearance of this hypercoordinated configuration and generates an unstable $SiH_5^\bullet$ species in which electron delocalization is restricted to the axial H···Si···H linkage which is the conventional three-electron/three-center delocalized system. While the analogy between $SiH_5^\bullet$ and $CH_5^\bullet$ holds, SiH_5^- with its Ψ_{HC} structure displays very different bonding features from CH_5^- and this is reflected in both energetic and geometric features of these species. It should be noted that other arguments have been put forward by Gronert, Glaser, and Streitwieser,[8] who explained the stability of SiH_4F^- by the importance of ionic contributions to bonding. We do not believe, however, that the ionic model can be extended to the SiH_5^- case. Indeed, all the ionic contributions are included, with their optimized coefficients, in our calculations of Lewis structures, and despite this, SiH_5^- is not found to be stable in the absence of the hypercoordinated Ψ_{HC} structure.[1h,i]

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Single-Crystal EPR Study of Copper(II) Trinuclear Compounds: Exchange-Averaging Effects

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Three years ago, we described two copper(II) trinuclear compounds with dithiooxamide derivative ligands.[2] Their formula is $\{Cu_3[C_2S_2(NCH_2CH_2CH_2SCH_2CH_2OH)_2]_2\}X_2$ with X = ClO_4 (**1**) and NO_3 (**2**). The crystal structure of **1** has been solved and is recalled in Figure 1. It consists of trinuclear cations and noncoordinated perchlorate anions. The central copper atom is in a square-planar CuS_4 chromophore, and the terminal copper atoms are in $CuS_2N_2O_2$ chromophores with a 4 + 2 coordination. The crystal structure of **2** has not been properly refined because of a disorder of the lateral chains of the dithiooxamide derivatives. The available crystal data, however, indicate that the molecular structure of the trinuclear cation is very similar to that found in **1**. The central copper atom in **2**, however, is located on an inversion center. As far as the packings are concerned, both compounds have S···S intermolecular contacts of the order of 3.5 Å.

The magnetic properties for **1** and **2**, measured in the 50–300 K temperature range, have revealed a strong intramolecular antiferromagnetic interaction between nearest-neighbor copper(II) ions.[2] The doublet ground state is stabilized by ca. 480 and 720 cm^{-1} with regard to the doublet and quartet excited states, re-

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