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Molecular Orbital Study of Electrophilic Substitution of Allylmetal Compounds: hyperconjugation, transition states, cations and solvent effects

Clifford W Fong

Eigenenergy, Adelaide, South Australia

Summary

MO computations of “hard” (eg H^+) and “soft” (eg SO_2) electrophiles reacting with substituted cyclohex-2-enylmetals and allylmetals (Si, Ge, Sn) show:

- 1) The global electrophilicity index is a sensitive predictor of electrophilic reactions
- 2) Extensive hyperconjugative $\sigma - \pi$ stabilization in the ground state, carbocations, and transition states.
- 3) Small energy differences between carbocation intermediates and the transition states indicate that products can form via the cation or the transition state.
- 4) The C2 cations formed from protolysis of the substituted cyclohex-2-enylmetals have a bridging $H^+ - C2 = C3$ structure, whereas bridging and non-bridging cations are formed with the allylmetals.
- 5) The transition states have structures similar to the cations. Strong nucleophilic solvents cause a shift from a non-bridging to a bridging structure.
- 6) The insertion transition states have SO_2 bridging the double bond in the cyclohex-2-enyltrimethylstannane, or non-bridging in allyltrimethylstannane.

Keywords: MO computations, allylmetals, electrophilicity index, hyperconjugation, transition states, carbocations, reaction mechanisms

1. Introduction

Electrophilic substitution reactions of organometal compounds of group 14 have been widely studied, mainly via reaction rates and stereochemistry. These reactions made a significant contribution to the fundamental basis of electrophilicity that exists today. Allylmetal compounds have been noted to involve very rapid allylic rearrangement when attacked by electrophiles, ^[1-7] attributed to significant $\sigma - \pi$ hyperconjugation ^[1,2, 8-10] invoked by contribution of electron density from the C – M bond to the charged β position. Electrophilic substitution of cyclic allylmetal compounds have also been studied, but the allylic strain imposed by the cyclic ring constraint ^[11-13] has not been evaluated. The description of the reaction mechanisms, transition states and their interactions with solvents involved in these electrophilic substitution reactions needs to be revised using modern molecular orbital computations to give details which were previously not accessible. New fundamental concepts such as the global electrophilicity index, which derived from molecular orbital theory, have not been tested against reactivity data and mechanisms which formed the basis of the current theories of electrophilic substitution.

Details such as the nature of the electrophile, preferred site of electrophilic attack, the nature of transition states and reactive carbocationic intermediates, ^[5, 8] and the factors which determine final product distribution are all available from such calculations. Hyperconjugative stabilization of the ground state and transition states can also be elucidated by molecular orbital calculations.

This study will examine the following issues:

1. The ground state molecular electronic configuration of a series of closely related substituted allyltrimethylmetal and cyclohex-2-enyltrimethyl metal compounds for silicon, germanium and mainly tin metals will be examined to identify which factors might influence electrophilic substitution (Figure 1). The influence of σ - π hyperconjugation and conformation on atomic charges of the allylic moiety will be highlighted, as well as the energies of the frontier HOMO and LUMO. The theoretical global electrophilicity index of these organometals is also examined to detect if this indicator can predict reactivity.
2. The electronic configurations of the transition states for the protolysis reaction and sulphur dioxide insertion reaction will be calculated (Figure 2). The hydrogen ion is an example of a “hard” electrophile, and SO_2 is an example of a “soft” electrophile.
3. The electronic configurations of the cation intermediates possibly involved in protolysis will be investigated (Figure 2).
4. The electronic configuration of possible reaction intermediates or transition states influence final product distribution will be assessed. In particular, how nucleophilic attack by the anions formed by acid dissociation are directed to the LUMO, and how intramolecular attack by the O of SO_2 during the insertion reaction is directed by the LUMO and the orbitals of the C – M bond.

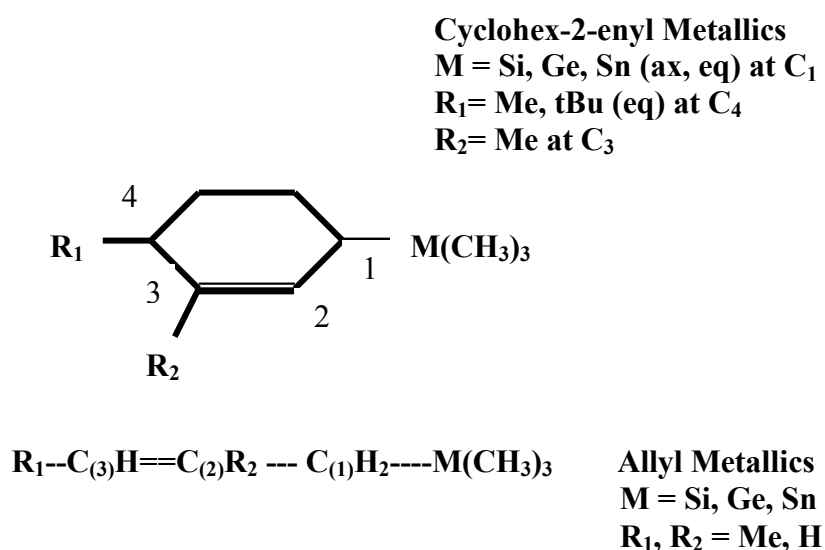
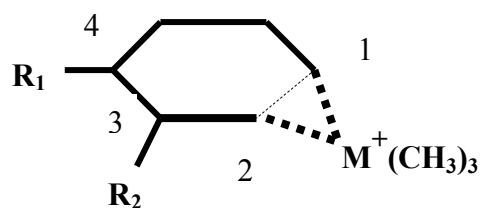
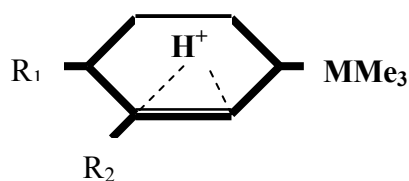


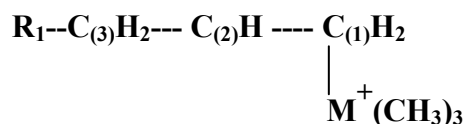
Figure 1. Substituted Cyclohex-2-enyl Metallics and Allyl Metallics



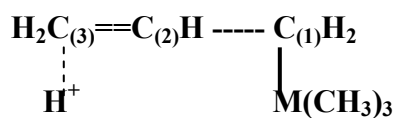
**Bridged C2 Cations from
Cyclohex-2-enyl Metallics**
M = Si, Ge, Sn at C₁
R₁ = Me at C₄
R₂ = Me at C₃



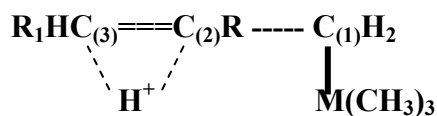
**Bridged H⁺ Protolysis
Transition States from
Cyclohex-2-enyl Metallics**
M = Si, Ge, Sn at C₁
R₁ = Me at C₄
R₂ = Me at C₃



**C2 Cations from Allyl
Metallics**
M = Si, Ge, Sn at C₁
R₁ = Me at C₃



**H⁺ Protolysis Transition States
from Allyl Metallics**
M = Si, Ge, Sn at C₁



**Bridged H⁺ Protolysis
Transition States from Allyl
Metallics**
M = Sn at C₁
R = Me, H
R₁ = Me, H

Figure 2. Cations and transition states for protolysis of allylmetallics

2. Results and Discussion

2.1 Influence of ground state configuration on electrophilic attack

The nature of the electrophile and solvent is a major factor in electrophilic reactions. Protolysis of allylmetal compounds is an example of a “hard” electrophile, and can

involve intermediate cationic species when the H^+ ion attacks the double bond. This would then be followed by nucleophilic attack by the anion formed from acid dissociation in polar solvents, typically methanol. ^[1-5, 8] The “hard” “soft” concept, structural reactivity and hyperconjugation have been previously discussed. ^{9-11]} Protolysis in less polar solvents such as chloroform have also been studied for trifluoroacetolysis in the cyclohex-2-enylstannane system. ^[6] Sulphur dioxide has been chosen as an example of a “soft” electrophile, where the “nucleophilic” component is a part of the electrophile. ^[7, 12-14]

It has been previously observed that “soft” heteroatom electrophiles usually form a cyclic bridging cation with the double bond in olefin systems, whereas “hard” electrophiles usually do not. ^[8] The bridging cation formed by “soft” heteroatom electrophiles usually have a lone pair so the bridging species notionally has 4 electrons, which are not present with “hard” electrophiles like the H^+ ion. Intermediate cationic species can be stable depending on what other substituents are present.

The molecular electronic configuration of the allylmetal species and the interaction of the HOMO on the allylmetal substrate with the LUMO of the electrophile will determine the pathway to the transition state. The energies of the HOMO, E_{HOMO} , are listed in Table 1 (as the Ionization Potential, IP, calculated from Koopmans’ theorem for the HF theory), and the energies of the LUMO, E_{LUMO} , (as the electron affinity EA) along with the natural bond orbital charges for the Sn, C1, C2 and C3 atoms. Orbital coefficients would be preferable to atomic charges, but these are difficult to accurately assess for multi-electron systems with high atomic numbers with extensive electron correlation. The values derived from Koopmans’ theorem are a good approximation of the IP and EA values. The energy of the all species studied were calculated using fully optimised geometries by the DFT B3LYP level of theory with the LANL2DZ basis set. Comparison calculations using the HF / LANL2DZ level showed that the same trends were observed although the absolute energy levels varied as expected. The object of the study (and the level of theory used) is to examine quantitative trends amongst a series of molecules, not determine the absolute accuracy of each calculation.

2.1.1 The global electrophilicity index ($GEI = [\{E_{HOMO} + E_{LUMO}\}/2]^2 / 2\{E_{HOMO} - E_{LUMO}\}$) has been used to assess the electrophilicity of molecules. ^[18] However, it has been shown that the *inverse* of GEI also describes the nucleophilicity, ^[19] or the propensity of the molecule’s HOMO to “donate” electrons to the vacant LUMO of the electrophile. Table 1 shows the calculated GEI for the allylmetal compounds under consideration, and it shows that:

- 1) For the cyclohex-2-enylmetallics where M is Si, Ge and Sn (axial or equatorial) the GEI decreases going down the periodic table, from 5.2, 5.15, 4.6 eV, so the nucleophilicity correspondingly increases. This trend is consistent with the known electrophilic reactivity of group 14 ^[1-4, 8, 13].
- 2) For the allylmetallics where M is Si, Ge and Sn, the GEI also decreases going down the periodic table, from 4.5, 4.4, 4.25eV, so the nucleophilicity correspondingly increases.
- 3) $Me_3SnCH_2CH=CH_2$ has a GEI of 4.25 eV compared to $Me_3SnCH_2C(CH_3)=CH_2$ (4.85 eV) and $Me_3SnCH_2CH=CH-Me$ (anti, syn) of 4.55 and 4.9 eV all in methanol. The methyl substituents exert a significant effect of about 0.6 eV (14

kcal/mol) in lowering the propensity to electrophilic attack compared to the allylstannane. This observation is compared with the known kinetic data for the protolysis (HCl and HClO₄) in methanol where the relative second order rates are 0.475, 24.8, 0.0274 and 0.0508 l.mol⁻¹sec⁻¹ respectively [4]. The protolysis of 2-methylprop-2-enestannane is clearly anomalous based on this data alone, and the very large rate enhancement caused by the 2-methyl substituent is not expected based on consideration of Hammett type substituent constants for the methyl group.^[20]

- 4) The axial cyclohex-2-enylstannane where R₁ and R₂ are methyl, GEI is 5.15 eV, compared to the corresponding cases where R₁ = Me and R₂ = H or R₁ = H and R₂ = H, GEI is 4.6 and 4.55 eV respectively in the gas phase. As in the allylstannane case above, substitution of a Me group at C3 has a significant effect (about 0.6 eV) in lowering the propensity to electrophilic attack.
- 5) The transition states TS for protolysis (gas phase) for the cyclohex-2-enylmetals (R₁ and R₂=H, or R₁ = Me, R₂ = H) show a decrease in GEI going down the table from Si to Sn, and hence an increased propensity to nucleophilic attack, as expected from electrophilic reactivity data.
- 6) The change in GEI going from the ground state to the TS is 4.15, 4.15 and 3.8 eV for the protolysis of cyclohex-2-enylmetals (R₁ and R₂=H) from Si, Ge to Sn (gas state). The corresponding figures for the R₁ = Me and R₂=H compounds are 4.05, 4.15 and 3.95 eV.
- 7) The change in GEI going from the ground state to the TS is 3.45, 4.40 and 3.40 eV for the protolysis of allylmetals from Si, Ge to Sn (gas state).
- 8) The changes in GEI for SO₂ insertion going from the ground state reactants to the TS are 4.0 and 3.70 eV for cyclohex-2-enylstannane and allylstannane (gas phase).
- 9) The effect of solvation on the TS for cyclohex-2-enylstannane shows an increase in GEI from gas to chloroform or methanol (PCM van der Waals continuum model) of 0.6 and 1.05 eV. The effect of solvation for the SO₂ insertion TS shows no effect going from the gas phase to chloroform solution on GEI, indicating a less polar TS, compared to the protolysis TS.
- 10) The GEI for the cations formed from protolysis of cyclohex-2-enylstannane have the following gas phase GEI values: C₃ cation 0.6 eV, C₂ cation 1.25 eV (axial Sn) and C₃ cation 0.6 eV, C₂ cation 1.25 eV (equatorial Sn). The same values are found for the 4-methyl substituted cyclohex-2-enylstannanes (equatorial and axial). For the 4 tBu-cyclohex-2-enylstannanes, the C₃ cation is 0.6 eV, C₂ cation is 1.3 eV (axial Sn). Clearly the ring conformation has little impact on the GEI.
- 11) The GEI for the most stable cations formed from protolysis of allylstannane and 2-methylpro-2-enylstannane have the following gas phase GEI values: C₂ cation 1.1 and 1.1 eV, which can be compared with the cations formed from syn and anti but-2-enylstannane which have GEI values of 1.1 (C₂ cation), 1.3 (C₃ cation) for the anti configuration, and 1.1 (C₂ cation), 0.65 (C₃ cation) for the syn configuration.

2.1.2 Summary of findings on the applicability of the global electrophilicity index (GEI):

- 1) The GEI is a relatively sensitive indicator which can differentiate among ground state reactants from different classes of compounds, such as substituted allylicmetals from group 14, transition states, and cationic intermediates.

- 2) The GEI clearly shows strong differentiation between “hard” and “soft” electrophile behaviour in the TS.
- 3) The GEI is sensitive to solvent effects on the TS.
- 4) The GEI cannot easily differentiate amongst changes to the allylic group, such as ring conformations in the cyclohexenylmetal compounds, or syn and trans isomers for allylicmetals.
- 5) The obvious advantage of utilizing the GEI (or its inverse as a measure of nucleophilicity) compared to single point molecular energies is the detail obtained about how frontier orbitals are influenced during electrophilic reaction.

2.1.3 Hyperconjugation ^[1,2, 8-10] can stabilize the ground state substituted of allylmetals, and particularly where a positive charge at the β position from the C—M bond exists. The sigma bond of C—MR₃ (Si, Ge, Sn, Pb) are powerful sigma donor orbitals as the electrons are weakly held, and polarised towards C atom. The importance of neutral σ - π hyperconjugation is expected to increase going down group 14, as the C—M bond becomes more polarized. Table 2 shows:

- 1) Comparison of the cyclohex-2-enylmetals (Si, Ge, Sn, axial configuration) with the series allylmetals (Si, Ge, Sn) shows the angles M-C1-C2-C3 changes from 117.1, 115.3, 111.8 to 108.4, 106.3 95.0 degrees correspondingly, which allows greater overlap of the C—M orbitals with the double bond orbitals for the allylmetals. This is evident by visual examination of the HOMO orbitals (double bond orbitals) with the second highest energy occupied orbitals, the C—M orbitals. The HOMO energies of the cyclohexenylmetals are -8.7, -8.6, -8.3 compared to the allylmetals where the values are -9.2, -9.0, -8.8 eV (the HOMO are “localized” around the double bond). The differences between the series are constant at 0.5 eV, indicating that geometrical constraint of the cyclohexenyl ring raises the energy of the (double bond) HOMO by 12.5 kcal/mol. Such a difference would be manifest in electrophilic reactivity mechanisms.
- 2) Comparison of the axial and equatorial conformations for the substituted cyclohex-2-enylmetals (R₁ and R₂ = H; R₁ = Me, R₂ = H; R₁ = Me, R₂ = Me) shows that for Si and Ge the more stable conformation is equatorial, but is reversed for Sn. The differences in energy are small, about 0.5 kcal/mol in single point energies, and about 4.5 kcal/mol in the energies of the HOMO. The Sn examples are indicative of more extensive hyperconjugative σ - π stabilization. It is worth noting that the inversion barriers ^[15,16] between the anti and syn cyclohexenyl molecules is about 5 kcal/mol.
- 3) Comparison of the NBO atomic charges at C1, C2 and C3 for the cyclohex-2-enylmetals and allylmetals in Table 1 also reflect the same trends as seen above for the HOMO orbitals as expected. The changes in atomic charges (although small) do indicate the sites of greatest localized electron density, and where electrophilic attack might occur if electronic factors only are involved.

2.1.4 Structure of potential carbocation intermediates involved in protolysis.

- 1) Lambert ^[21] has suggested that that silicon preferentially stabilizes β carbocations (carbonium ions) via hyperconjugative vertical stabilization rather than a bridging (non-vertical) stabilization. A β silicon carbocation has been suggested as an intermediate in the electrophilic substitution of allyl- and vinyl-silanes, which are widely used in stereo-electronic controlled (anti-S_E2') organic synthesis. ^[8]

- 2) Examination of the cationic intermediates involved in protolysis reveals a strong stabilizing factor depending on whether the species produced by H⁺ addition to the double bond is a C2 or C3 cation. The C2 cation is the most stable cation because of hyperconjugative $\sigma - \pi$ stabilization as per Figure 2. The M⁺ moiety sits midway between the C1 and C2 positions, and is a **bridging cation** for the cyclohex-2-enylmetals. This is contrary to the finding of Lambert. The **bridging cation** is found for Si, Ge and Sn even though hyperconjugative vertical stabilization would be expected to be more likely for Sn. However, for the allylmetals, the M⁺ moiety sits more directly over C1, which indicates that vertical hyperconjugative stabilization is operating. The significant difference is that for the allylmetal cations, the {M⁺-C1-C2-C3} angles are about 95° compared to the angles for the cyclohexenylmetals which are about 110-112° for the Si and Ge, but 92° for the Sn cation. The allylic conformational ring constraints imposed by the cyclohexenyl moiety account for the differences between the two classes of cations, with the exception being the Sn cation where the longer C—Sn bond length (and increased bond polarity) means greater bridging capacity. The Sn cation is more stable than the Ge and Si cations by 8.3 and 14.5 kcal/mol respectively. *In summary, the difference between a vertical hyperconjugative stabilization and a non-vertical bridging stabilization of these cations is finely balanced, and represent a continuum rather than discrete behaviours.*
- 3) Comparison of the C2 cations formed from the cyclohex-2-enylmetals (Si, Ge, Sn, axial configuration) with the series allylmetals (Si, Ge, Sn) shows that the HOMO energies change from -14.9 to -14.7 to -14.5 eV, and from -15.9 to -15.6 then -15.3 eV for the allylmetals. The trends are consistent with the greater ability of the more polarised C—Sn bonding orbitals to engage in $\sigma - \pi$ stabilization than either the C—Si or C—Ge orbitals. The higher energy values for the cyclohex-2-enylmetals reflect ring or allylic strain^[16,17] not present in the allylmetals.
- 4) Comparison of the C2 and C3 cations of cyclohex-2-enylstannanes show that the following HOMO energy values: C2 -14.5 and C3 -13.4 eV, a difference of 1.1 eV attributed to better hyperconjugative stabilization of the C2 cation. The molecular energies of the C2 and C3 cations are -357.4983 and -357.4356 AU. The C2 cation is more stable than the C3 cation by 39 kcal/mol from the total energies or 25.4 kcal/mol from the HOMO energies
- 5) Comparison of the C2 and C3 cations of but-2-enylstannanes show that the C2 cation is more stable by 35.7 kcal/mol in molecular energies, or 29.9 kcal/mol by HOMO energies.
- 6) The energies of the HOMO of the cations that can be formed from 2-methylprop-2-enyltrimethylstannane in methanol solvent are C2 (-11.3 eV) and C3 (-11.6 eV) a difference of 7 kcal/mol, indicating that the C3 cation is the most stable. The molecular energies are -280.1300 and -280.1695 AU respectively, a difference of 25 kcal/mol. This anomalous result is the result of a molecular rearrangement of the 2-methylprop-2-enyl moiety of the C3 cation where a methyl substituted cyclopropyl ring stabilizes a Me₃Sn⁺ moiety. This is an example of *homohyperconjugation*^[10] (see Figure 3). The anomalously rapid kinetic data in methanol^[4] discussed above (see section on global electrophilicity above) is probably due to formation of cyclopropyl products rather than 2-methylpropene as the activation energy or the energy gap between the TS and the cation intermediates do not suggest unusually fast kinetics (see Table 3).

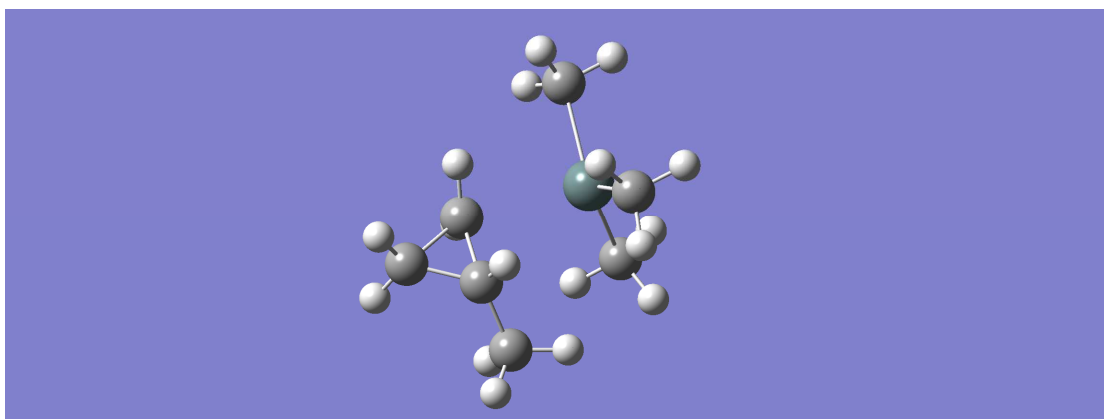


Figure 3. Cation formed from the C3 protonation of 2-methylprop-2-enyltrimethylstannane in methanol showing the molecular rearrangement to a homohyperconjugatively stabilized Sn^+ - methylenecyclopropyl cation

2.2 Transition States

2.2.1 The transition states (TS) for protolysis have been identified. As expected, H^+ attachment to the double bond occurs, and the position of the attachment varies from attachment to C3 for the allylmetals to a bridging H which can sit closer to C2 in some cyclohex-2-enylmetals. Tables 1 and 2 show:

- 1) For the cyclohex-2-enylmetals, the bridging H sits closer to the C3 for Si, and gradually sits closer to C2 going from Ge to Sn. (Figures 4)

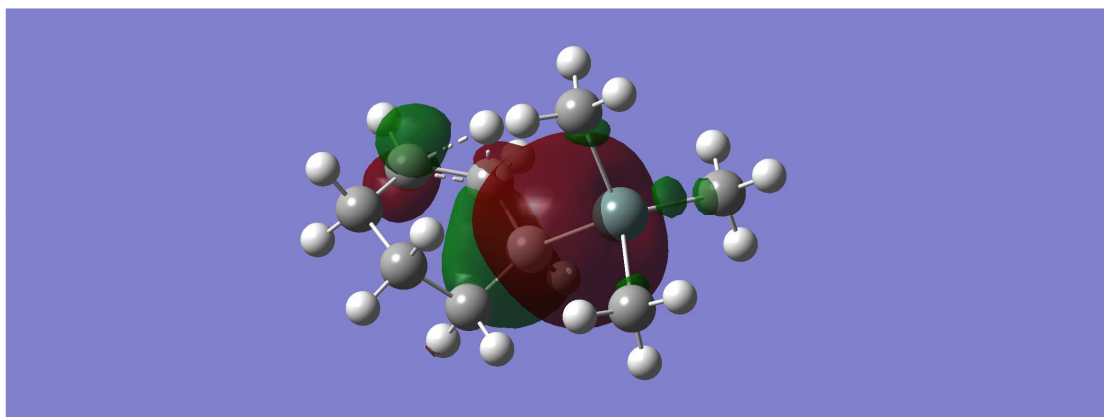


Figure 4. H^+ bridged transition state from protolysis of cyclohex-2-enyltrimethylstannane showing HOMO

- 2) For the allylmetals, (Si, Ge, Sn) the H^+ attaches to C3, and sits directly over C3 in the gas phase and chloroform. However for the allylSn compounds, the H^+ bridges the double bond in methanol. The 2 methylallyltin TS in methanol has the H^+ sitting above C2. The crotyl 3-methylallylstannanes (syn and anti) TS have a bridging H^+ sitting over the C2-C3 double bond, slightly closer to C2.
- 3) *As a general rule, the protolysis TS for all cyclohex-2-enylmetals ($R_1 = \text{Me}$, $R_2 = \text{Me}$) and SO_2 insertion TS, there is a lengthening of the C—M bond and shortening of the C1--C2 bond consistent with hyperconjugative $\sigma - \pi$ stabilization of the bridged cationic double bond centre.*

- 4) Hyperconjugative stabilization of the TS can be seen for selected examples such as the TS formed from axial and equatorial 4-methylcyclohex-2-enyltrimethylstannane where the Sn-C1-C2-C3 angles are 121 and 138.1° (gas phase) respectively. The axial conformation has greater C—M orbital overlap with the protonated double bond than the equatorial conformation. The data below for the cyclohex-2-enylstannanes (anti and syn isomers) shows that the NBO charges are sensitive to hyperconjugative changes.

{Sn ax + H ⁺ } TS gas -403.4 Vibn GEI 0.8eV	396.7407 AU	13.5 -HOMO	-3.2 EA	2.020 Sn	-0.689 C1	-0.397 C2	0.121 C3 H ⁺ 0.350
{Sneq + H ⁺ } TS gas -566.7 Vibn GEI 0.85eV	396.7406	13.5	-3.0	2.031	-0.691	-0.352	0.077 H ⁺ 0.350

- 5) Visual inspection of the HOMO and LUMO of the various protolysis TS show the following features:

Generally the HOMO for the Sn TS for both allylmetals and cyclohex-2-enylmetals are more delocalised over the M-C1-C2-C3 part of the molecule than the Si and Ge equivalents. This is consistent with the increased hyperconjugative ability of the C – Sn bond.

The HOMO for the Si and Ge molecules are usually centred mainly over the double bond and to a lesser extent over the C—M bonds.

The LUMO vary from extensive delocalisation over the molecule to localisation over the double bond or C—M bonds. The location of the LUMO will direct nucleophilic attack by the counter-ion of the acid species, eg Cl⁻, ClO₄⁻, CF₃COO⁻ etc.

2.2.2 The transition states for SO₂ insertion involve either a bridged SO₂-C2=C3 positively charged ring as in the cyclohex-3-enylstannane TS or a non-bridging SO₂-C3 linkage for the allylstannane (see Figures 2, 5). As these reactions are known to be second order reaction mechanisms,^[13-15] then the final insertion product is formed by an intramolecular process in which the LUMO of the TS centred on SO₂ “accepts” electrons from the C—Sn bond orbitals. For the allylSn TS the HOMO is centred over the double bond, and the C—Sn orbital is the 5th highest energy MO (the 2nd to 4th highest energy occupied MO are located on SO₂). For the cyclohexenylSn TS, the HOMO is delocalised over almost the whole molecule, and the LUMO is localised over the (SO₂-{C2=C3}-C1-Sn) moiety. The TS in the gas phase and CHCl₃ are essentially the same in both HOMO and LUMO. The solvent effect on the activation energies is negligible.

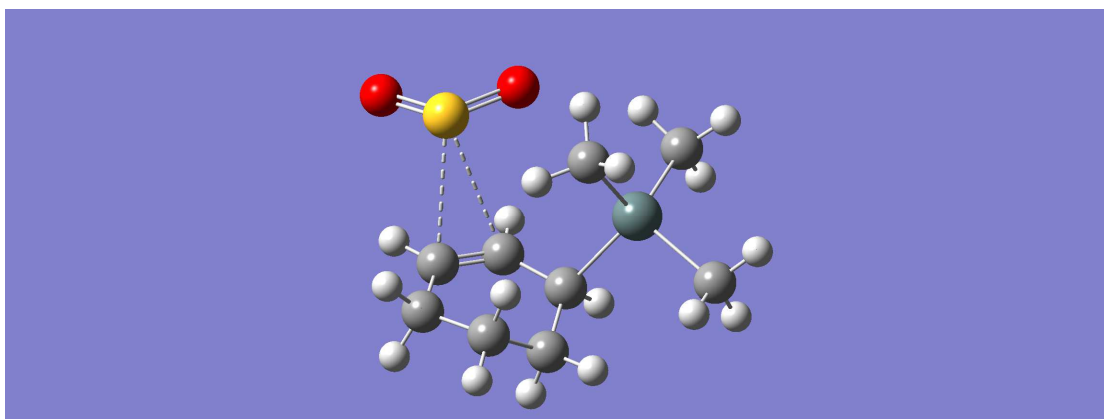


Figure 5. Transition state for the insertion reaction of SO₂ with cyclohex-2-enyltrimethylstannane showing bridging O₂S—C=C structure

2.2.3 Transition states and possible cation intermediates in the protolysis reaction can be assessed by identifying the initial TS energies for H⁺ addition to the double bond and comparing such energies to the energies of the possible cation molecules. The carbocations intermediates in the protolysis reactions have been identified. Only small energy difference between the most stable C2 intermediates and the transition states have been found, and in some cases, notably the Si and Ge allyls, and the cyclohexenylSi, the gap is negligible, indicating that these carbocations do not play any role in the reaction mechanism. However, where TS have a bridged H⁺ - C2=C3 structure, two possible cations can form, the most stable C2 cation or the less stable C3 cation. The energy gaps between the C3 cations and the TS are very small, about 2-3 kcal/mol, (and much smaller than the gap between the C2 cation and the TS), indicating that products can form directly from the TS equally as fast as from the less stable C3 cation.

2.2.4 The activation energies (E_a) for the transition states for the allylmetals and the cyclohex-3-enylmetals are shown in Table 3 for a notional HCl reaction with the organometals, and for the SO₂ insertion reaction. These E_a for the protolysis reaction are nominal in that details of what the exact processes that lead to the electrophile H⁺ attacking the organometal substrate are not addressed. HCl in the gas phase and in chloroform solution is not dissociated. In methanol, it is known^[4] that HCl forms the protonated species CH₃OH₂⁺, so the E_a values in methanol solution are calculated for the reaction of the CH₃OH₂⁺ species with the organometals to give the TS and methanol.

The following key features are seen in Table 3:

- 1) The E_a for SO₂ insertion are over 100 kcal/mol lower than for those for protolysis for the tin TS. This reflects the difference between a “soft” electrophile where the large polarisable S atom of SO₂ can more easily “accept” electrons into the LUMO from the HOMO of the double bond compared to the smaller “harder” H⁺ species. The charge separation that occurs in the TS of the protolysis reactions, but not so in the insertion reactions, is clearly a major factor in the difference values for E_a. The insertion reaction rates are correspondingly much faster than for protolysis.
- 2) There is a large solvent effect for the methanol E_a values compared to the gas phase and chloroform solution. This can be attributed to the labile H⁺ species

available from the CH_3OH_2^+ species. The E_a values for the cyclohexenylSn and allylSn are very low, and consistent with their known reactivity data.^[1-4] The strong solvent effect in methanol is due to the specific nucleophilic solvation of the C—Sn bond through the LUMO of the activated species.^[14]

- 3) The E_a values for the protolysis (in the gas phase or chloroform) of the allylmetals are similar to those for the cyclohexenylmetals. Allylic ring strain does not appear to be significant factor in the protolysis TS. The calculated gas phase E_a values are surprisingly high, similar to those for proton affinities. The cation $\text{H}_2\text{C}^+-\text{CH}_2-\text{SnH}_3$ formed from the gas phase protonation of the vinylstannane has a proton affinity of 212 kcal/mol^[23], propylene and isobutene have proton affinities of 179.5 and 195.9 kcal/mol respectively.^[24] The calculated gas phase E_a values are then entirely consistent with the strong electron donor ability of the CH_2MR_3 substituent to enhance the basicity of the allyl- and cyclohexenyl-metallics in the ground state.
- 4) Methyl substituents at C3 or C4 on the cyclohex-3-enyltrimethylstannanes have no effect on the E_a with the exception of the 4-tertiary-butyl substituent which raises the E_a by about 30 kcal/mol from the equivalent methyl substituent. This effect may be steric in origin, since the inductive or field effect of the methyl and t-butyl substituents^[20] are 0.01 and -0.02.
- 5) As discussed above, the protolysis (HCl or HClO_4) of $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ and the crotyl $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CH}-\text{Me}$ (anti and syn) in 4% aqueous methanol have relative second order rates of 0.475, 0.0274 and 0.0508 $\text{l.mol}^{-1}\text{sec}^{-1}$ respectively^[4]. Kochi^[3] has suggested that the varying product distribution of 1-butene and 2-butene (mainly syn, some anti) obtained from various carboxylic acids in various solvents may be due to rapid equilibrium between the crotyl isomer and the α -methallyl isomer, and that protolysis only occurs by a $\text{S}_{\text{E}}2'$ rearrangement mechanism. The structure of the TS for both syn and anti crotylstannanes in methanol has a **bridging** H^+ sitting over the double bond, with the H^+ slightly closer to the C2 position. The LUMO of the anti TS is delocalised over the Sn-C1-C2 moiety while the LUMO of the syn TS is more localised over the C3 position of the double bond, which explains the lower E_a for the anti-isomer. As the TS for these isomers have a bridging cationic structure, then both C2 and C3 intermediate carbocations can be formed. The energy gap between the TS and the C3 cation intermediate in methanol is very small, 2-3 kcal/mol, indicating that products can form from the less stable C3 cation intermediate as fast as they can from the TS directly.

3. Conclusions

MO computations of the reaction of “hard” (eg H^+) and “soft” (eg SO_2) electrophiles for a closely related series of substituted cyclohex-2-enylmetals and allylmetals (Si, Ge, Sn) have demonstrated that:

- 1) The global electrophilicity index and its inverse, the nucleophilicity index, are sensitive predictors of electrophilic attack
- 2) Comparison of the NBO atomic charges at C1, C2 and C3 for the cyclohex-2-enylmetals and allylmetals in Table 1 also reflect the same trends as seen above for the HOMO orbitals as expected. The changes in atomic charges (although small) do indicate the sites of greatest localized electron density, and where electrophilic attack might occur if electronic factors only are involved.

- 3) There is evidence of allylic ring strain in the ground state of the cyclo-hexen-2-enylmetal molecules.
- 4) Hyperconjugative $\sigma - \pi$ stabilization (at the β position to the metal) is extensive in the ground state organometallic reactants, carbocations formed by protonation of the substituted cyclohex-2-enylmetals and allylmetals, and the transition states for protolysis and SO_2 insertion.
- 5) The carbocations intermediates in the protolysis reactions have been identified. Only small energy difference between the most stable C2 intermediates and the transition states have been found, and in some cases, notably the Si and Ge allyls, and the cyclohexenylSi, the gap is negligible, indicating that these carbocations do not play any role in the reaction mechanism. However, where the TS have a bridged $\text{H}^+ - \text{C}2 = \text{C}3$ structure, two possible cations can form, the most stable C2 cation or the less stable C3 cation. The energy gaps between the C3 cations and the TS are very small, about 2-3 kcal/mol, (and much smaller than the gap between the C2 cation and the TS), indicating that products can form directly from the TS equally as fast as from the less stable C3 cation.
- 6) The C2 cations formed from protolysis of the double bond of the substituted cyclohex-2-enylmetals have a bridging structure, whereas both bridging and non-bridging cations are formed from protolysis of the allylmetals. The difference between a vertical hyperconjugative stabilization and a non-vertical bridging stabilization of these cations is finely balanced, and represent a continuum rather than discrete behaviours.
- 7) The C3 cation formed by the protonation of 2-methylprop-2-enyltrimethylstannane is more stable than the C2 cation as a result of a molecular rearrangement where a methyl substituted cyclopropyl ring stabilizes a Me_3Sn^+ moiety. This is an example of *homohyperconjugation* and explains the anomalously rapid protolysis kinetic data in methanol. ^[4]
- 8) The transition states (TS) for the protolysis of the substituted cyclohex-2-enylmetals and allylmetals have been identified and their structures detailed. The substituted cyclohex-2-enylmetals TS have structures where the H^+ bridges the double bond, whereas both bridging and no-bridging TS are found for the substituted allylmetals, with the former being most prevalent for Sn. Strong nucleophilic solvents can cause a shift from a non-bridging structure (gas phase or chloroform) to a bridging structure in methanol.
- 9) The insertion TS has SO_2 bridging the double bond in the cyclohex-2-enyltrimethylstannane, or non-bridging over the C3 in allyltrimethylstannane.
- 10) The activation energies (E_a) of the TS have been calculated, with the protolysis TS showing large solvent effects between methanol and the gas phase or chloroform. The E_a in the gas phase or chloroform are similar to the gas phase proton affinities of similar molecules.
- 11) The E_a for the SO_2 insertion TS have very low values, generally much lower than the protolysis TS in methanol.
- 12) The product distribution from the protolysis (the kinetics in HCl or HClO_4 were identical) of the crotyl isomers $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CH}-\text{Me}$ (anti and syn) in 4% aqueous methanol have been portrayed in the literature ^[3] as being due to a rapid equilibrium between the crotyl isomer and the α -methallyl isomer, and that protolysis only occurs by a $\text{S}_{\text{E}}2'$ rearrangement mechanism. The structure of the TS for both syn and anti crotylstannanes has a **bridging** H^+ sitting over the $\text{C}2=\text{C}3$ double bond. As the TS for these isomers have a bridging cationic structure, then both C2 and C3 intermediate carbocations can be formed. The energy gap between

the TS and the C3 cation intermediate in methanol is very small, 2-3 kcal/mol, indicating that products can form from the less stable C3 cation intermediate as fast as they can from the TS directly.

Experimental Section

Computational molecular orbital calculations were conducted with the Gaussian 09 with Gaussview 5.0 suite of programs. All geometries were fully optimised using the DFT B3LYP level with the LANL2DZ basis set. Transition state calculations were confirmed by identifying in all cases, the singular negative vibration which was always a mode involving the H⁺ or SO₂. Visual animation of the mode (observing the link between the H⁺ and SO₂ moiety and allylic double bond was conducted before or after final optimization to confirm the negative vibration was the relevant vibration. In some cases where solvent free optimisations were run, it was found that the solvent had a small effect on the negative vibration.

The validity of the DFT B3LYP / LANL2DZ calculations were tested against experimental data: (1) the first ionization potential of allyltrimethylsilane, benzyltrimethylgermane and allyltrimethylstannane were evaluated using Koopmans' Theorem for the Hartree-Fock theory to gauge the electron correlation error using the LANL2DZ basis set for Si, Ge and Sn: the calculated ionization potentials for the HOMOs were 9.19, 8.75 and 8.77 eV, compared to the literature values of 9.00, 8.36 and 8.70 eV taken from the NIST data base^[22] a reasonable agreement, indicating the LANL2DZ basis set is applicable to the organometallic compounds used in this study. The corresponding calculated first ionization potential (HOMO) and electron affinity (LUMO) for the trimethylstannane radical was 7.7 and 1.25 eV (or 7.0 and 3.3 eV by the SCF difference method) compared to the experimental values^[25] of 7.10 and 1.70 eV.

DFT B3LYP / LANL2DZ calculations have been widely applied to studies of organostannanes.^[26-30]

References

- [1] Smith, M.B., March, J., March's Advanced Organic Chemistry, Reactions, Mechanisms and Structure, 6th ed., Wiley Interscience, 2007, Chapter 12.
- [2] Davies, A.G., Organotin Chemistry, 2nd ed., 2004, Wiley-VCH, Chapter 9.
- [3] Kochi, J., Organometallic Mechanisms and Catalysis, 1978, Academic Press New York, page 311.
- [4] (a) Bamford, C.H., Tipper, C.F.H., Electrophilic Substitution at Saturated Carbon, Chemical Kinetics, Volume 12, 1973, Elsevier, London. (b) Pratihari, S., Roy, S., Organometallics, 2011, 30, 3257.
- [5] Wikipedia, Electrophilic Substitution of Unsaturated Silane, http://en.wikipedia.org/wiki/Electrophilic_substitution_of_unsaturated_silanes. Allylsilanes and allylstannanes are known to react with electrophiles by an **anti-S_E2'** mechanism. http://en.wikipedia.org/wiki/Allylic_stannane_addition.
- [6] Wickham, G., Kitching, W., J. Org. Chem., 1983, 48, 612.
- [7] Young, D., Kitching, W., J. Org. Chem., 1983, 48, 614.
- [8] Fleming, I., Molecular Orbitals and Organic Chemical Reactions: Reference Edition, 2011, Wiley, Chapter 5. Fleming, I., Dunoguès, J., Smithers, R., The Electrophilic Substitution of Allylsilanes and Vinylsilanes, Organic Reactions, 2004, John Wiley & Sons
- [9] Galabov, B., Ilieva, S., Koleva, G., Allen, W.D., Schaeffer, H.F., Schleyer, P.V.R., WIREs Comput. Mol. Sci. 2013, 3, 37.
- [10] Albugin, I.V., Gilmore, K.M., Peterson, P.W., WIREs Comput. Mol. Sci. 2011, 1, 109.
- [11] Pearson, R.G., J. Chem. Sci., 2005, 117, 369.
- [12] Fong, C.W., Kitching, W., J. Organomet. Chem., 1973, 59, 213.
- [13] W. Kitching, C.W. Fong., Organometallic Chemical Reviews, Sect. 1970, A 5, 281.
- [14] Fong, C.W., Kitching, W., J. Phys. Org. Chem., 2014, 27, 204.
- [15] Kalsi, P.S., Stereochemistry, Conformation and Mechanism, 2005, 6th ed New Age Int Ltd Publishers, chapter 4.18

- [16] Shishkin, O.V., Shishkina, S.V., Conformational Analysis of Cyclohexene, Chapter 12 in Practical Aspects of Computational Chemistry I, 2012, Springer.
- [17] Hoffmann, R. W., Chem. Rev. **1989**, 89, 1841.
- [18] Parr, R.G., Szentpaly, L.V., Liu, S., J. Am. Chem. Soc., 1999, 121, 1922.
- [19] Domingo, E., Chamorro, P., Perez, P., J. Org. Chem., 2008, 73, 4615.
- [20] Hansch, C., Leo, A., Taft, R.W., Chem. Revs. 1991, 91, 165
- [21] Lambert, J. B., Acc. Chem. Research, 1999, 32, 183.
- [22] NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>
- [23] Mó, O., Gal, M. Y., Maria, P. C., Guillemin, J. C., J. Phys. Org. Chem., 2002, **15**, 509.
- [24] Lias, S.G., Liebman, J.F., Levin, R.D., J. Phys. Chem. Ref. Data 1984, 13, no. 3.

Table 1. Molecular orbital parameters for substituted cyclohex-2-enylmetal compounds, substituted allylmetal, cations and transition states for protolysis and sulphur dioxide insertion reactions

M	R ₁	R ₂	Energy - AU	IP eV -HOMO	EA eV	Charge M	Charge C ₁	Charge C ₂	Charge C ₃
Si ax GEI 5.2eV	H	H	357.6540	8.7	4.5	1.748	-0.698	-0.222	-0.217
{Si ax + H ⁺ } TS gas -141.2 Vibn GEI 1.05eV			358.0060	14.9	-2.8	1.798	-0.425	0.010	-0.475 H ⁺ 0.257
Si ax cation C2 GEI 1.1 eV	H	H	358.0081	14.9	-2.3	1.791	-0.333	-0.079	-0.467
Si eq GEI 5.2eV	H	H	357.6548	8.9	4.5	1.756	-0.705	-0.220	-0.210
Ge ax GEI 5.05eV	H	H	357.5308	8.6	4.4	1.794	-0.694	-0.225	-0.219
{Ge ax + H ⁺ } TS gas -516.5 Vibn GEI 0.9eV			357.8397	14.1	-3.1	1.777	-0.668	-0.348	0.083 H ⁺ 0.349
Ge ax cation C2 GEI 1.6 eV	H	H	357.8948	14.7	-1.7	1.843	-0.252	-0.181	-0.457
Ge eq GEI 5.15eV	H	H	357.5311	8.8	4.5	1.802	-0.701	-0.224	-0.212
Sn ax GEI 4.6eV	H	H	357.1210	8.3 (7.1)	4.1 (3.3)	2.034	-0.725	-0.233	-0.225
{Sn ax + H ⁺ } TS gas -391.5 Vibn GEI 0.8eV			357.4313	13.6 (12.0)	-3.3 (-5.0)	2.019	-0.692	-0.399	0.115 H ⁺ 0.351
{Sn ax + H ⁺ } TS CHCl ₃ - 528.6 Vibn GEI 1.4eV			357.4910	10.7	0.1	2.044	-0.704	-0.353	0.086 H ⁺ 0.359
{Sn ax + H ⁺ } TS MeOH - 551.5 Vibn GEI 1.85eV			357.5064	10.2	1.3	2.054	-0.706	-0.342	0.078 H ⁺ 0.365
Sn ax CHCl ₃	H	H	357.1228			2.044	-0.726	-0.236	-0.234
Sn ax MeOH	H	H	357.1236			2.040	-0.727	-0.237	-0.238

Sn ax cation C3 GEI 0.6eV	H	H	357.4356	13.4	-4.3	2.023	-0.669	-0.526	0.226
Sn ax cation C2 GEI 1.25eV	H	H	357.4982	14.5	-1.7	2.100	-0.261	-0.220	-0.455
{Snax + SO ₂ } TS gas - 43.7 Vibn GEI 0.6eV			517.5320	8.7 (7.4)	-1.7 (-2.9)	2.053	-0.709	-0.178	-0.234 S 1.286
{Snax + SO ₂ } TS CHCl ₃ -30.2 Vibn GEI 0.6eV			517.5418	8.5	-1.5	2.066	-0.705	-0.172	-0.222 S 1.309
Sn eq GEI 4.9eV	H	H	357.1205	8.5	4.3	2.042	-0.734	-0.231	-0.219
{Sneq + H ⁺ } TS gas -603.8 Vibn GEI 0.8eV			357.4346	13.5	-3.2	2.042	-0.672	-0.497	0.086 H ⁺ 0.365
Sn eq cation C2 GEI 1.25eV	H	H	357.4983	14.5 (13.3)	-1.7 (-2.8)	2.100	-0.220	-0.261	-0.457
Sn eq cation C3 GEI 0.6eV	H	H	357.4371	13.4 (11.9)	-4.3 (-6.1)	2.043	-0.648	-0.532	0.228
Si ax GEI 5.2eV	Me	H	396.9625	8.7	4.5	1.748	-0.693	-0.220	-0.212
{Si ax + H ⁺ } TS gas -88.0 Vibn GEI 1.15eV			397.3160	14.8	-2.2	1.792	-0.321	-0.086	-0.462 H ⁺ 0.249
Si eq GEI 5.1eV	Me	H	396.9633	8.9	4.5	1.757	-0.700	-0.218	-0.205
Ge ax GEI 5.05eV	Me	H	396.8392	8.6	4.4	1.794	-0.689	-0.224	-0.214
{Ge ax + H ⁺ } TS gas - 621.4 Vibn GEI 0.9eV			397.1490	14.1	-3.0	1.779	-0.665	-0.342	0.085 H ⁺ 0.348
Ge eq GEI 5.2eV	Me	H	396.8397	8.7	4.5	1.803	-0.696	-0.222	-0.208
Sn ax GEI 4.55eV	Me	H	396.4295	8.4	4.1	2.035	-0.721	-0.231	-0.221
Sn ax MeOH GEI 4.75eV	Me	H	396.4322	8.3	4.2	2.049	-0.723	-0.234	-0.234
{Sn ax + H ⁺ } TS gas -403.4 Vibn GEI 0.8eV			396.7407	13.5	-3.2	2.020	-0.689	-0.397	0.121 H ⁺ 0.350
{Sn ax + H ⁺ } TS MeOH - 53.4 Vibn GEI 1.25eV			396.8178	10.1	0.04	2.045	-0.695	-0.526	0.301 H ⁺ 0.301
Sn ax cation C3	Me	H	396.7451	13.4	-4.2	2.023	-0.666	-0.524	0.236

GEI 0.6eV									
Sn ax cation C2 GEI 1.25eV	Me	H	396.8075	14.5	-1.7	2.100	-0.260	-0.214	-0.452
Sn eq GEI 4.65eV	Me	H	396.4290	8.5	4.3	2.044	-0.729	-0.229	-0.214
Sn eq MeOH GEI 4.65eV	Me	H	396.4319	8.5	4.3	2.058	-0.731	-0.233	0.228
{Sneq + H ⁺ } TS gas -566.7 Vibn GEI 0.85eV			396.7406	13.5	-3.0	2.031	-0.691	-0.352	0.077 H ⁺ 0.350
Sn eq cation C3 GEI 0.55eV	Me	H	396.7468	13.3	-4.3	2.045	-0.643	-0.532	0.226
Sn eq cation C2 GEI 1.25eV	Me	H	396.8037	14.5	-1.7	2.102	-0.287	-0.101	-0.450
Sn ax GEI 5.15eV	Me	Me	435.7419	8.1	4.3	2.034	-0.712	-0.246	0.002
{Sn ax + H ⁺ } TS gas -745.9 Vibn GEI 1.1 eV			436.0642	13.5	-1.9	2.027	-1.225	-0.252	0.149 H ⁺ 0.347
Sn eq GEI 5.15eV	Me	Me	435.7415	8.3	4.4	2.044	-0.722	-0.245	0.008
Si ax GEI 5.2eV	tBu	H	514.8778	8.7	4.5	1.747	-0.687	-0.210	-0.207
Si eq GEI 5.15eV	tBu	H	514.8793	8.8	4.5	1.756	-0.703	-0.205	-0.220
Ge ax GEI 5.15eV	tBu	H	514.7546	8.6	4.4	1.793	-0.684	-0.223	-0.209
Ge eq GEI 5.0eV	tBu	H	514.7557	8.7	4.4	1.802	-0.699	-0.209	-0.223
Sn ax GEI 4.75eV	tBu	H	514.3450	8.3	4.2	2.035	-0.715	-0.230	-0.216
{Snax + H ⁺ } TS gas - 1565.1 Vibn GEI 1.3eV			514.6080	13.8	-1.3	2.109	-0.160	-0.877	-0.111 H ⁺ 0.305
Sn ax cation C3 GEI 0.60eV	tBu	H	514.6633	13.3	-4.1	2.094	-0.700	-0.526	0.466
Sn ax cation C2 GEI 1.3eV	tBu	H	514.7246	14.4	-1.6	2.101	-0.233	-0.237	-0.455

Sn eq GEI 4.7eV	tBu	H	514.3450	8.5	4.2	2.042	-0.743	-0.215	-0.229
Me ₃ SiCH ₂ CH=CH ₂ GEI 4.5eV			240.9403	9.2 (7.9)	4.2 (3.2)	1.735	-0.911	-0.186	-0.437
{Me ₃ SiCH ₂ CH=CH ₂ + H ⁺ } TS gas -1196.4 Vibn GEI 1.05eV			241.2190	14.6	-2.5	1.763	-0.902	-0.015	-0.519 H ⁺ 0.319
[Me ₃ SiCH ₂ CH—CH ₃] ⁺ GEI 1.0 eV			241.2891	15.9	-3.4	1.784	-0.713	0.107	-0.699
Me ₃ GeCH ₂ CH=CH ₂ GEI 4.4eV			240.8168	9.0 (7.8)	4.1 (3.2)	1.778	-0.910	-0.190	-0.440
{Me ₃ GeCH ₂ CH=CH ₂ + H ⁺ } TS gas -185.6 Vibn GEI 1.0eV			241.1715	15.6	-3.2	1.836	-0.676	0.063	-0.696 H ⁺ 0.261
[Me ₃ GeCH ₂ CH—CH ₃] ⁺ GEI 1.0eV			241.1745	15.6	-3.1	1.837	-0.673	0.052	-0.694
Me ₃ SnCH ₂ CH=CH ₂ GEI 4.25eV			240.4071	8.8 (7.6)	4.0 (3.2)	2.014	-0.949	-0.197	-0.449
Me ₃ SnCH ₂ CH=CH ₂ CHCl ₃ GEI 4.25eV			240.4093	8.8	4.0	2.026	-0.953	-0.196	-0.446
Me ₃ SnCH ₂ CH=CH ₂ MeOH GEI 4.25eV			240.4104	8.8	4.0	2.032	-0.953	-0.196	-0.474
[Me ₃ SnCH ₂ CH=CH ₂] ⁺ GEI 1.25eV			240.1304	14.5 <u>15.3</u>	-1.7 <u>-4.6</u>	2.076	-0.611	-0.189	-0.208
[Me ₃ SnCH ₂ CH—CH ₃] ⁺ GEI 1.1eV			240.7769	15.3 <u>(13.9)</u>	-2.8 <u>(-4.1)</u>	2.084	-0.657	-0.008	-0.689
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS -1314.22 Vibn GEI 1.85 eV			240.7076	13.8 (12.6)	0.25 (-3.7)	2.058	-0.902	-0.014	-0.564 H ⁺ 0.285
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS CHCl₃ -1369.80 Vibn GEI 1.6eV			240.7674	10.7	0.6	2.099	-0.902	-0.017	-0.570 H ⁺ 0.290
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS MeOH -282.4 Vibn GEI 1.7 eV			240.7684	10.7	0.5	2.036	-0.942	-0.510	0.211 H ⁺ 0.337
{Me ₃ SnCH ₂ CH=CH ₂ + SO₂ } TS gas -57.5 Vibn GEI 0.55eV			400.8093	9.1 (5.7)	-2.1 (-3.1)	2.015	-0.950	-0.184	-0.477 S 1.339
{Me ₃ SnCH ₂ CH=CH ₂ + SO₂ } TS CHCl₃ -52.8 Vibn GEI 0.55eV			400.8176	8.9	-2.1	2.030	-0.951	-0.189	-0.485 S 1.391
Me ₃ SnCH ₂ CH=CH-Me (anti) GEI 4.75eV			279.7181	8.4	4.2	2.013	-0.944	-0.217	-0.213
Me ₃ SnCH ₂ CH=CH-Me MeOH (anti) GEI 4.55eV			279.7073	8.4	4.1	1.984	-0.942	-0.216	-0.218
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (anti) gas -226.2 Vibn GEI 0.75eV			280.0228	13.9	-3.7	2.001	-0.925	-0.410	-0.185 H ⁺ 0.352
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (anti) MeOH -529.0 Vibn GEI 1.85eV			280.1012	10.7	1.2	2.035	-0.934	-0.318	0.100 H ⁺ 0.367
[Me ₃ SnCH ₂ CH-CH ₂ - Me] ⁺ (anti) GEI 1.1eV			280.0856	15.2	-2.7	2.082	0.664	-0.008	-0.465
[Me ₃ SnCH ₂ CH ₂ -CH- Me] ⁺ (anti) GEI 1.3eV			280.0287	13.9	-4.3	2.010	-0.892	-0.498	0.234
Me ₃ SnCH ₂ CH=CH-Me			279.7173	8.4	4.2	2.017	-0.953	-0.221	-0.217

(syn) GEI 4.85eV							
Me ₃ SnCH ₂ CH=CH-Me MeOH (syn) GEI 4.9eV	279.7203	8.4	4.3	2.034	-0.958	-0.226	-0.230
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS gas (syn) - 194.1 Vibn GEI 0.75eV	280.0231	13.9	-3.7	2.004	-0.925	-0.421	-0.179 H ⁺ 0.350
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS MeOH (syn) -521.8 Vibn GEI 1.85eV	280.1013	10.7	1.2	2.039	-0.937	-0.337	0.108 H ⁺ 0.354
[Me ₃ SnCH ₂ CH-CH ₂ - Me] ⁺ (syn) GEI 1.1eV	280.0850	15.2	-2.7	2.082	-0.664	-0.014	-0.468
[Me ₃ SnCH ₂ CH ₂ -CH- Me] ⁺ (syn) GEI 0.65eV	280.0282	13.9	-4.2	2.012	-0.902	-0.495	0.220
Me ₃ SnCH ₂ C(CH ₃)=CH ₂ GEI 4.85eV	279.7192	8.6	4.3	2.020	-0.955	0.022	-0.465
Me ₃ SnCH ₂ C(CH ₃)=CH ₂ MeOH GEI 4.85eV	279.7225	8.6	4.3	2.039	-0.959	0.027	-0.493
[Me ₃ SnCH ₂ C(CH ₃)- CH ₃] ⁺ GEI 1.1eV	280.0982	15.1	-2.7	2.093	-0.740	0.248	-0.693 CH ₃ -0.693
[Me ₃ SnCH ₂ CH(CH ₃)- CH ₂] ⁺ MeOH GEI 2.4eV	280.1300	11.6	1.9	2.218	-0.680	-0.176	-0.332
[Me ₃ SnCH ₂ C(CH ₃)- CH ₃] ⁺ MeOH GEI 1.8 eV	280.1695	11.3	1.1	2.136	-0.745	0.254	-0.692 CH ₃ -0.692
{Me ₃ SnCH ₂ C(CH ₃)=CH ₂ + H ⁺ } TS MeOH -492.2 Vibn GEI 1.2eV	280.0766	10.8	-0.5	2.042	-0.932	-0.303	0.190 H ⁺ 0.379

Footnotes to Table 1:

Ionization Potential (Energy) values of IP were calculated from Koopmans' Theorem (Hartree Fock theory) using electron propagator theory OVGf as -HOMO eV.

Values in parentheses are IP calculated by the SCF difference method: E(M⁺) - E(M)

Electron Affinity (EA) values were calculated from Koopmans' Theorem (Hartree Fock theory) using electron propagator theory OVGf as LUMO eV.

Values in parentheses are EA calculated by the SCF difference method: E(M⁻) - E(M)

GEI is the Global Electrophilicity Index = $\{[E_{\text{HOMO}} + E_{\text{LUMO}}]/2\}^2 / 2 [E_{\text{HOMO}} - E_{\text{LUMO}}]$

Atomic charges are Natural Bond Orbital charges

Energies are sum of electronic and thermal energies + thermal corrections

Table 2. Calculated structural parameters for selected cyclohex-2-enyl and allyl metallics, cations and transition states.

Cyclohex-2-enyl Metallics M = Si, Ge, Sn (ax, eq) at C ₁ R ₁ , R ₂ = H (Figures 1,2)							
Si ax R₁, R₂ = H Bond Length A° Angle Sn-C1-C2-C3	Si-C1, 1.937	C1-C2 1.518	C2-C3 1.353			117.1°	
{Si ax + H⁺} R₁, R₂ = H TS gas Bond Length A° Angle Si-C1-C2-C3 (Angle Si-C1-C2-H ⁺)	Si-C1 2.299	C1-C2 1.390	C2-C3 1.501	C2-H ⁺ 2.133	C3-H ⁺ 1.104	108.8°	(na) ^o
Si ax R₁, R₂ = H Cation							

C2 Bond Length A° Angle Si-C1-C2-C3	Si-C1, 2.373, Si- C2 2.621	C1-C2 1.387	C2-C3 1.507					109.7°	
Ge ax R1, R2 = H Bond Length A° Angle Sn-C1-C2-C3	Ge-C1, 2.014	C1-C2 1.515	C2-C3 1.354					115.3°	
{Ge ax + H⁺} R1, R2 = H TS gas Bond Length A° Angle Ge-C1-C2-C3 (Angle Ge-C1-C2-H ⁺)	Ge-C1 2.061	C1-C2 1.508	C2-C3 1.433	C2-H ⁺ 1.225	C3-H ⁺ 1.568			123.6°	(41.7°)
Ge ax R1, R2 = H Cation C2 Bond Length A° Angle Ge-C1-C2-C3	Ge-C1, 2.533, Ge- C2 2.607	C1-C2 1.382	C2-C3 1.514					111.9°	
Sn ax R1, R2 = H Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, 2.189	C1-C2 1.512	C2-C3 1.355					111.8°	
{Sn ax + H⁺} R1, R2 = H TS gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.248	C1-C2 1.509	C2-C3 1.440	C2-H ⁺ 1.201	C3-H ⁺ 1.637			119.0°	(32.2°)
{Sn ax + H⁺} R1, R2 = H TS CHCl₃ Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.231	C1-C2 1.507	C2-C3 1.432	C2-H ⁺ 1.223	C3-H ⁺ 1.561			119.5°	(37.4°)
{Snax+H⁺} R1, R2 = H TS MeOH Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.221	C1-C2 1.507	C2-C3 2.169	C2-H ⁺ 1.228	C3-H ⁺ 1.540			121.1°	(40.2°)
Sn ax R1, R2 = H Cation C3 Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn- C2 2.695, 2.741	C1-C2 1.381	C2-C3 1.517					111.4°	
Sn ax R1, R2 = H Cation C2 Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn- C2 2.232, 3.106	C1-C2 1.537	C2-C3 1.464					91.9°	
{Snax + SO₂} R1, R2 = H TS gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-S)	Sn-C1 2.229	C1-C2 1.489	C2-C3 1.372	C2-S 3.126	C3-S 2.961			110.5°	(23.2°)
{Snax + SO₂} R1, R2 = H TS CHCl₃ Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-S)	Sn-C1 2.229	C1-C2 1.488	C2-C3 1.372	C2-S 3.126	C3-S 2.961			110.5°	(23.2°)
Sn eq R1, R2 = H Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, 2.181	C1-C2 1.516	C2-C3 1.355					131.6°	
{Sn eq + H⁺} R1, R2 = H TS gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.254	C1-C2 1.505	C2-C3 1.438	C2-H ⁺ 1.205	C3-H ⁺ 1.605			114.7°	(161.0°)

Sn eq R1, R2 = H Cation C2 Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.741, 2.695	C1-C2 1.381	C2-C3 1.516	110.1°			
Sn eq R1, R2 = H Cation C3 Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.477, 3.055	C1-C2 1.630	C2-C3 1.534	95.6°			
Allyl Metallics (Figures 1,2)							
Me ₃ SiCH ₂ CH=CH ₂ Bond Length A° Angle Si-C1-C2-C3	Si-C1 1.925	C1-C2 1.511	C2-C3 1.352	108.4°			
{Me ₃ SiCH ₂ CH=CH ₂ + H ⁺ } TS gas Bond Length A° Angle Si-C1-C2-C3 (Angle Si-C1-C2-H ⁺)	Si-C1 1.954	C1-C2 1.478	C2-C3 1.384	C2-H ⁺ 1.950	C3-H ⁺ 1.553	75.9°	(32.2°)
[Me ₃ SiCH ₂ CH—CH ₃] ⁺ Bond Length A° Angle Si-C1-C2-C3	Si-C1, Si-C2 2.200, 2.861	C1-C2 1.391	C2-C3 1.488	94.3°			
Me ₃ GeCH ₂ CH=CH ₂ Bond Length A° Angle Si-C1-C2-C3	Ge-C1 2.002	C1-C2 1.508	C2-C3 1.353	106.3°			
{Me ₃ GeCH ₂ CH=CH ₂ + H ⁺ } TS gas Bond Length A° Angle Ge-C1-C2-C3 (Angle Ge-C1-C2-H ⁺)	Ge-C1 2.321	C1-C2 1.385	C2-C3 1.500	C2-H ⁺ 2.159	C3-H ⁺ 1.100	97.5°	(na)
[Me ₃ GeCH ₂ CH—CH ₃] ⁺ Bond Length A° Angle Ge-C1-C2-C3	Ge-C1, Ge-C2 2.326, 2.912	C1-C2 1.384	C2-C3 1.492	94.5°			
Me ₃ SnCH ₂ CH=CH ₂ Bond Length A° Angle Ge-C1-C2-C3	Sn-C1 2.176	C1-C2 1.505	C2-C3 1.354	95.0°			
[Me ₃ SnCH ₂ CH—CH ₃] ⁺ Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.516, 3.023	C1-C2 1.367	C2-C3 1.496	95.0°			
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.235	C1-C2 1.459	C2-C3 1.394	C2-H ⁺ 2.012	C3-H ⁺ 1.475	73.0°	(na)
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS CHCl₃ Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.122	C1-C2 2.235	C2-C3 1.459	C2-H ⁺ 2.012	C3-H ⁺ 1.475	73.0°	(na)
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS MeOH Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 3.017	C1-C2 2.144	C2-C3 1.507	C2-H ⁺ 3.089	C3-H ⁺ 3.016	109.9°	(na)
{Me ₃ SnCH ₂ CH=CH ₂ + SO ₂ } TS gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-S)	Sn-C1 2.177	C1-C2 2.144	C2-C3 1.504	C2-S 4.299	C3-S 3.456	109.2°	(na)

{Me ₃ SnCH ₂ CH=CH ₂ + SO ₂ } TS CHCl ₃ Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-S)	Sn-C1 2.178	C1-C2 1.503	C2-C3 1.356	C2-S 4.417	C3-S 3.564	109.2°	(na)
Me ₃ SnCH ₂ CH=CH-Me (anti) Bond Length A° Angle Sn-C1-C2-C3	Sn-C1 2.173	C1-C2 1.508	C2-C3 1.354	104.8°			
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (anti) gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.221	C1-C2 1.512	C2-C3 1.440	C2-H ⁺ 1.190	C3-H ⁺ 1.685	130.5°	(40.8°)
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (anti) gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.221	C1-C2 1.512	C2-C3 1.440	C2-H ⁺ 1.190	C3-H ⁺ 1.685	130.5°	(40.8°)
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (anti) MeOH Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.196	C1-C2 1.505	C2-C3 1.426	C2-H ⁺ 1.232	C3-H ⁺ 1.531	129.6°	(50.0°)
[Me ₃ SnCH ₂ CH-CH ₂ -Me] ⁺ (anti) Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.504, 3.011	C1-C2 1.380	C2-C3 1.499	95.9°			
[Me ₃ SnCH ₂ CH ₂ -CH-Me] ⁺ (anti) Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.215, 3.136	C1-C2 1.537	C2-C3 1.448	81.1°			
Me ₃ SnCH ₂ CH=CH-Me (syn) Bond Length A° Angle Sn-C1-C2-C3	Sn-C1 2.174	C1-C2 1.508	C2-C3 1.357	100.8°			
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (syn) gas Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.229	C1-C2 1.507	C2-C3 1.445	C2-H ⁺ 1.188	C3-H ⁺ 1.701	127.2°	(34.2°)
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS (syn) MeOH Bond Length A° Angle Sn-C1-C2-C3 (Angle Sn-C1-C2-H ⁺)	Sn-C1 2.2011	C1-C2 1.501	C2-C3 1.431	C2-H ⁺ 1.226	C3-H ⁺ 1.554	123.5°	(40.4°)
[Me ₃ SnCH ₂ CH-CH ₂ -Me] ⁺ (syn) Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.511, 3.009	C1-C2 1.380	C2-C3 1.502	98.0°			
[Me ₃ SnCH ₂ CH ₂ -CH-Me] ⁺ (syn) Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, Sn-C2 2.225, 3.149	C1-C2 1.522	C2-C3 1.450	87.4°			
Me ₃ SnCH ₂ C(CH ₃)=CH ₂ Bond Length A° Angle Sn-C1-C2-C3	Sn-C1, 2.179	C1-C2 1.512	C2-C3 1.359	95.5°			
Me ₃ SnCH ₂ C(CH ₃)=CH ₂ MeOH	Sn-C1,	C1-C2	C2-C3				

Bond Length A°	2.179	1.512	1.359				
Angle Sn-C1-C2-C3				95.5°			
{Me ₃ SnCH ₂ C(CH ₃)=CH ₂ + H ⁺ } TS MeOH	Sn-C1	C1-C2	C2-C3	C2-H ⁺	C3-H ⁺		
Bond Length A°	2.185	1.578	1.432	1.150	1.864		
Angle Sn-C1-C2-C3						167.9°	
(Angle Sn-C1-C2-H ⁺)							(69.5°)

Table 3. Activation Energies and Molecular Parameters for Protolysis and Sulphur Dioxide Insertion Transition States

Transition State Cyclohex-2-enylmetals (see Figure 1)	Energy - AU	Ionization Potential (IP) eV -HOMO	Electron Affinity (EA) eV	Energy Gap: TS and Cation Intermed. kcal/mol	Activation Energy kcal/mol
{Si ax + H ⁺ } R ₁ =H R ₂ =H TS gas GEI 1.05eV	358.0060	14.9	-2.8	1.3	116.5
{Ge ax + H ⁺ } R ₁ =H R ₂ =H TS gas GEI 0.9eV	357.8397	14.1	-3.1	34.6	145.6
{Sn ax + H ⁺ } R ₁ =H R ₂ =H TS gas GEI 0.8eV	357.4313	13.6 (12.0)	-3.3 (-5.0)	42.0 (C2 cation) [C3 cation 2.7]	144.7
{Sn ax + H ⁺ } R ₁ =H R ₂ =H TS CHCl₃ GEI 1.4eV	357.4910	10.7	0.1		108.4
{Sn ax + H ⁺ } R ₁ =H R ₂ =H TS MeOH GEI 1.85eV	357.5064	10.2	1.3		(14.1)*
{Snax + SO ₂ } R ₁ =H R ₂ =H TS gas GEI 0.6eV	517.5320	8.7 (7.4)	-1.7 (-2.9)		7.2
{Snax + SO ₂ } R ₁ =H R ₂ =H TS CHCl₃ GEI 0.6eV	517.5418	8.5	-1.5		7.4
{Sneq + H ⁺ } R ₁ =H R ₂ =H TS gas GEI 0.8eV	357.4346	13.5	-3.2	40.0 (C2 cation) [C3 cation 1.6]	142.3
{Si ax + H ⁺ } R ₁ =Me R ₂ =H TS gas GEI 1.15eV	397.3160	14.8	-2.2		117.6
{Ge ax + H ⁺ } R ₁ =Me R ₂ =H TS gas GEI 0.9eV	397.1490	14.1	-3.0		145.0
{Sn ax + H ⁺ } R ₁ =Me R ₂ =H TS gas GEI 0.8eV	396.7407	13.5	-3.2	42.0 (C2 cation) [C3 cation 2.8]	144.1
{Sn ax + H ⁺ } R ₁ =Me R ₂ =H TS MeOH GEI 1.25eV	396.8178	10.1	0.04		(12.8)*
{Sneq + H ⁺ } R ₁ =Me R ₂ =H TS gas GEI 0.85eV	396.7406	13.5	-3.0	39.6 (C2 cation) [C3 cation 3.9]	143.9
{Sn ax + H ⁺ } R ₁ =Me R ₂ =Me TS gas GEI 1.1 eV	436.0642	13.5	-1.9		137.2
{Snax + H ⁺ } R ₁ =tBu R ₂ =H TS gas GEI 1.3eV	514.6080	13.8	-1.3	73.2 (C2 cation) [C3 cation]	174.4

				34.7]	
Transition States Allylmetals (see Figure 1)					
{Me ₃ SiCH ₂ CH=CH ₂ + H ⁺ } TS gas GEI 1.05eV	241.2190	14.6	-2.5	0.1	174.9
{Me ₃ GeCH ₂ CH=CH ₂ + H ⁺ } TS gas GEI 1.0eV	241.1715	15.6	-3.2	2.0	116.9
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS gas GEI 1.85 eV	240.7076	13.8 (12.6)	0.25 (-3.7)	43.5	150.9
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS CHCl ₃ GEI 1.6eV	240.7674	10.7	0.6		114.7
{Me ₃ SnCH ₂ CH=CH ₂ + H ⁺ } TS MeOH GEI 1.5eV	240.8280	9.7	0.8		(30.1)*
{Me ₃ SnCH ₂ CH=CH ₂ + SO ₂ } TS gas GEI 0.55eV	400.8093	9.1 (5.7)	-2.1 (-3.1)		1.7
{Me ₃ SnCH ₂ CH=CH ₂ + SO ₂ } TS CHCl ₃ GEI 0.55eV	400.8176	8.9	-2.1		0.7
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS gas (anti) GEI 0.75eV	280.0228	13.9	-3.7	39.4 (C2 cation) [3.7 C3 cation]	99.0
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS MeOH (anti) GEI 1.85eV	280.1012	10.7	1.2	35.5 (C2 cation) [C3 cation 2.8]	(7.6)*
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS gas (syn) GEI 0.75eV	280.0231	13.9	-3.7	38.8 (C2 cation) [C3 cation 3.2]	147.5
{Me ₃ SnCH ₂ CH=CH-Me + H ⁺ } TS MeOH (syn) GEI 1.85eV	280.1013	10.7	1.2	35.1 (C2 cation) [C3 cation 2.3]	(15.7)*
{Me ₃ SnCH ₂ C(CH ₃)=CH ₂ + H ⁺ } TS MeOH GEI 1.2eV	280.0766	10.8	-0.5	58.3 (C2 cation) [C3 cation 33.5]	(32.6)*

Footnotes to Table 3:

Activation energies are for the reaction of H-Cl + organometal → {organometal—H⁺} + Cl⁻ in the gas phase and chloroform solution.

Activation energies in parentheses (xx)* are for the reaction of CH₃OH₂⁺ + organometal → {organometal—H⁺} + MeOH in methanol solution.

Energy Gap is the difference between the transition state and the most stable cation intermediate (C2 cation) for the protolysis reaction. For some cases, both the energy differences between the C2 and C3 cations and their transition states are given, as indicated by [xx C3 cation].