Theoretical Studies of Polyvinyl-Substituted Carbenium and Silylenium Ions

Thanh Truong
Mark S. Gordon
Philip Boudjouk

Available at: https://works.bepress.com/mark_gordon/38/
crystalline W(CH3PMe3)(PMe3)2(CO)Cl2 was collected (53%): 1H NMR (CD3CN) δ 1.83 (d, JHP = 13.2 Hz, CH3PMe3), 1.46 (br virtual t, 18, PMe3). 13C NMR (CDCl3) δ 273.5 (t, JCP = 30 Hz, CH3PMe3), 132.2 (d, JCP = 30 Hz, PMe3), 5.5 (t, JCP = 20 Hz, PMe3) ~ 125 Hz, CH3PMe3). 31P NMR (CDCl3) δ -10.0 (d, JPP = 24 Hz, CH2PMe3). 31P NMR (CDCl3, 12.03 MHz, CH3CN) δ 1.79 (d, 9, 2JHP = 13.2 Hz, CH3PMe3). 1H NMR (CDCl3) δ 1.79 (d, JHP = 13.2 Hz, CH3PMe3), 1.38 (d, JHP = 8.3 Hz, PMe3), 1.73 (d, JHP = 9.9 Hz, PMe3). 1H NMR (CDCl3) δ 260.5 (m, CH3CN, 123.98 °C, CH3PMe3), 0.95 (m, 2, CH2PMe3). 31P NMR (CDCl3) δ 18.3 (d of q, JCP = 23 Hz, CH2PMe3), 18.6 (d of q, JCP = 23 Hz, CH2PMe3), 18.9 (d of q, JCP = 23 Hz, CH2PMe3), 16.7, 16.0, and 13.3 (each a d, JCP = 24 Hz, PMe3), 2.3 (br t, JCP = 122 Hz, CH3PMe3), -33 (m, CH3PMe3), -13 (m, CH3PMe3), -33 (m, CH3PMe3), IR (Nujol) 1895 (s, sh) 1772 cm-1 (s, sh); conductivity (CH2Cl2, 27.3 °C). It could be characterized only by comparison of its NMR spectra with those of its stable relative below.

[W(CH3PMe3)(PMe3)3(CO)Cl][CF3SO4]. [W(CH3-PMe3)3Cl][CF3SO4]. [0.42 g, 0.61 mmol] was dissolved in 5 mL of 1,2-dichloroethane, and the solution was placed under 30 psi of CO. After 24 h the red solution had become yellow. Upon concentration of the solution to 2 mL, addition of 10 mL of toluene, and cooling to ~90 °C for 1 day, 0.30 g of yellow crystals was obtained. A second crop of 0.05 g was collected from the mother liquor in a similar manner (total 0.53 g). 1H NMR (CDCl3) δ 0.05 (m, 2, CH2PMe3), 0.30 (m, 25, CH2PMe3), 0.30 (m, 2, CH2PMe3). 13C NMR (CDCl3) δ 260.5 (m, 2, CH3CN, 123.98 °C, CH3PMe3), 0.95 (m, 2, CH2PMe3). 31P NMR (CDCl3) δ 30.0 (M-1 at 0.05 MHz, CH2PMe3), A yellow solution of the pure compound in chloroform becomes brown after several hours at 25 °C. After being left standing at 25 °C for 1 h, the solution was filtered. A 31P NMR spectrum of the filtrate showed a 2:1 ratio of MP2/PCI to another phosphorus-containing species. After the NMR sample was heated at 80 °C for 1 week, the MeP2PCI remained, but the other compound had been quantitatively converted into Me2PCI: 31P NMR (H2O) δ 22.8 (s, 1, Me2PCI), -2.9 (d, JHP = 505 Hz, MeP2PCI).

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Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated factors (18 pages). Ordering information is given on any current masthead page.

Theoretical Studies of Polyvinyl-Substituted Carbenium and Silylenium Ions

Thanh Truong, Mark S. Gordon,* and Philip Boudjouk
Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105
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Ab initio (STO-2G and 3-21G) calculations have been performed to analyze the ability of one, two, and three vinyl groups to stabilize the CH3+ and SiH3+ ions. Vinyl groups appear to be quite effective at stabilizing the positive charge on the silylenium ion, and successive vinylization preferentially stabilizes the silicon relative to the carbon ion.

Introduction
Carbenium ions, R3C+, are readily accessible species in all three phases and possess a well-developed chemistry. In contrast, the silicon analogues, silylenium ions, R3Si+, are far more elusive. They are easily produced only as a gas, typically in the mass spectrometer, and only very recently was the first silylenium ion detected in a condensed phase.2 The difficulty in obtaining stable R3Si+ species in solution is probably because silicon has energetically very favorable reaction paths involving pentavalent or hexavalent intermediates that ensure a short life.

* Present address: Department of Chemistry, University of California, Berkeley, Berkeley, CA 94709


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time for the species or completely suppress its formation.\(^3\)

In the gas, \(R_3 Si^+\) is easily formed but is also kinetically unstable with a strong tendency to undergo self-association reactions.\(^4\)

There have recently been several studies of silylenium (\(SiH_2 X^+\)) ions using theoretical methods\(^5,6\) in order to determine substituents \(X\) that might particularly stabilize trivalent silicon relative to trivalent carbon cations. Particularly important is a moiety that will help to stabilize the positive charge, presumably by delocalizing the charge throughout the system. A simple classic example in hydrocarbon chemistry is the allyl cation, in which vinyl substitution into \(CH_3^+\) produces a rather stable species. Earlier we reported that vinyl-substituted silanes exhibited significantly lower ionization potentials for the \(RR'ViSiMe\) → \(RR'ViSi^+\) reaction than for similar transformations on non-vinylated silanes.\(^7\) This suggests the possibility that vinyl substitution will similarly stabilize \(SiH_3^+\) by donating \(\pi\)-electron density into the empty \(p_\pi\) orbital of silicon. Indeed, Apeloig and co-workers\(^5\) have found the \(\pi\) donor \(NH_2\) to be the most effective stabilizing substituent.

In the present work the stabilizing effect of successive vinyl substitution is compared for \(CH_3^+\) and \(SiH_3^+\). All calculations were carried out by using an IBM version of the GAUSSIAN80 program\(^8\) and the ST0-2G\(^9\) and 3-21G\(^10\) basis sets. The ST0-2G basis set has previously been demonstrated\(^11\) to provide reliable estimates of molecular structures, as well as trends in isodesmic\(^12\) reactions.

![Figure 1. Predicted structures for monovinyl cations. Bond lengths are given in angstroms and angles in degrees.](image1)

![Figure 2. Predicted structures for divinyl cations. Bond lengths are given in angstroms and angles in degrees.](image2)

![Figure 3. Predicted structures for trivinyl cations. Bond lengths are given in angstroms and angles in degrees.](image3)

<table>
<thead>
<tr>
<th>Table I. Mulliken Populations in X p(_\pi) MO</th>
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\(n\) = the number of vinyl groups attached to \(X\).

Results and Discussion

The ST0-2G and 3-21G structures for \(XH_2 Vi^+ (X = C\) or Si, \(Vi = \text{vinyl}\) are displayed in Figure 1. Both basis sets predict the allyl cation to be symmetric with \(C_2v\) symmetry, and the two structures are in good agreement with each other. The latter is also true for the silicon analogue, except for the somewhat longer \(SiH\) bonds predicted by ST0-2G. Comparison of the CC bond lengths suggests greater delocalization stabilization in the hydrocarbon. Since the ST0-2G \(C\equiv C\) and \(C\equiv Si\) bond lengths in ethylene and methylsilane are 1.32 and 1.93 Å, respectively, the silicon ion has acquired considerable delocalization as well.

In view of the good agreement between the ST0-2G and 3-21G structures and the computer time saved by using the smaller basis set, geometries for the di- and trivinyl...
The foregoing discussion has been largely qualitative. One can imagine several quantitative measures of cation stabilization. The use of approximate quantum mechanical methods requires that any such measure be based on isodesmic reactions. The various approaches will differ in the point of reference used. With use of Vi to represent a vinyl group, the simplest isodesmic reaction is the bond separation reaction shown in eq 1 introduced by Pople et al.,\textsuperscript{13} where \( X = C \) or \( Si \).

\[ \text{Reaction 1: } [XVi,H_3-n]+ + nCH_4 \rightarrow XH_3^+ + nXH_3Vi \]  

\[ \text{Reaction 2: } XVi,H_3-n^+ + nXH_4 \rightarrow XH_3^+ + nXH_3Vi \]  

\[ \text{Reaction 3: } XVi,H_3-n^+ + nCH_3H_4 \rightarrow XH_3^+ + nXH_3Vi \]  

An additional indicator of \( \pi \) delocalization effects is the electron density acquired by the \( p_x \) orbital on the central, formally positive, atom. The appropriate Mulliken populations are listed in Table I. Although the numbers differ for the two basis sets, it is clear that more \( \pi \)-electron density is donated to the formerly empty \( p_x \) orbital on carbon than on silicon. It is striking, however, that the third vinyl group provides a much larger increase in \( \pi \) density on the silicon than on the carbon.

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\[ \text{Reaction 3: } XVi,H_3-n^+ + nCH_3H_4 \rightarrow XH_3^+ + nXH_3Vi \]  

Alternatively, one might imagine a partial bond separation reaction, eq 3. Here, the vinyl linkage is retained and the ion of interest is again related to the unsubstituted parent. Note that reactions 2 and 3 are identical for \( n = 1 \). Each of the above measures is useful, and for each the greater the endothermicity, the more stable the ion. In each case, one may define a ratio, \( R \), which measures the stabilization of the silicon relative to the carbon ion (eq 4).

\[ R = \frac{\Delta E (X = Si)}{\Delta E (X = C)} \]  

The structures of the reference species needed to evaluate reactions 1 and 2 have been published previously. Those required for reaction 3 are shown in Figure 4. For the divinyl species, \( C_{2v} \) symmetry was assumed during the STO-2G geometry optimization. Subsequent rigid rotation of one vinyl group resulted in little energy change. For the trivinyl species \( C_{2v} \) symmetry was assumed. Furthermore, in the latter molecules, the internal vinyl structures were held constant at the corresponding divinyl...
Alkylidenebls(perthiolates): A New Class of Organosulfur Ligands Prepared from (RC₅H₅)₂TiS₄

Dean M. Giolando and Thomas B. Rauchfuss*

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

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Summary: In the presence of (NH₄)₂S, (RC₅H₅)₂TiS₄ (R = H, Me, i-Pr) reacts with alliphatic ketones and CH₂Br₂ to give 1,4-(RC₅H₅)₂TiS₄CO₂ (R₂ = Me₂; Me, Et; c-C₅H₁₀; H₂) and 1,3-(RC₅H₅)₂TiS₂CH₂. The new compounds were purified chromatographically and were characterized spectroscopically including DNMR spectroscopy. Single crystal X-ray crystallography confirmed the structure of (i-PrC₅H₅)₂TiS₂CH₂.

Bis(cyclopentadienyl)tin(tetrasulfido) 1 is prepared from the reaction of Cp₂TiCl₄ (Cp = η⁵-C₅H₅) and ammonium polysulfide in acetone. Close examination of one such preparation employing (MeCp)₂TiCl₂ revealed two previously unnoticed products, a small amount of a red compound, and a substantial quantity of a colorless species. This paper describes our characterization of these compounds and their bearing on the chemistry of Cp₂TiS₄.

The red product 3b was found to have the formula (MeCp)₂TiS₂CMe₂. Its ¹H NMR spectrum featured wave functions, although here planar NH₂ has a slightly larger ΔE. The addition of three vinyl groups produces the greatest stabilization yet calculated. Finally, the predictions of reaction 3 are qualitatively similar to those of (1) and (2).

Conclusions

Successive vinylization of carbenium and silylenium ions provides increasing stabilization of these ions, suggesting that these substituents may lead to isolable silylenium ions, an approach now under investigation in our laboratories. Each additional vinyl group provides less additional stabilization than the last. The latter is more true for carbon than for silicon, so that successive vinylization preferentially stabilizes the silicon. The bond separation reactions, in particular, predict the trivinyl silylenium ion to be more stable than its carbenium analogue. This is likely to be due, at least in part, to the strain of having three coplanar vinyl groups and will have a greater effect for carbon than for silicon due to the shorter C–Vi bond lengths.

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Registry No. *CH₂(CH=CH₂) 1724-44-3; *CH(CH=CH₂) 54963-17-6; *C(CH=CH₂) 54963-18-7; *SiH₂(CH=CH₂) 64840-94-4; *SiH(CH=CH₂) 87999-58-4; *Si(CH=CH₂) 87999-59-5.

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Communications

(4) For the compound numbers in this paper, the letters a, b and c indicate the Cp, MeCp, and i-PrCp derivatives, respectively. The nomenclature for these compounds has been questioned by a reviewer.

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