

crystalline $W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2$ was collected (53%): 1H NMR ($CDCl_3$) δ 1.83 (d, 9, $^2J_{HP} = 13.2$ Hz, CH_2PMe_3), 1.46 (br virtual t, 18, PMe_3), 0.80 (m, 2, CH_2PMe_3); ^{13}C NMR ($CDCl_3$) δ 273.5 (t, $^2J_{CP} = 39$ Hz, CO), 237.5 (s, CO), 15.3 (d of q, $J_{CH} = 131$ Hz (q), $J_{CP} = 55$ Hz (d), CH_2PMe_3), 14.5 (d, $J_{CP} = 32$ Hz, PMe_3), 13.2 (d, $J_{CP} = 23$ Hz, PMe_3), 3.5 (t of t, $J_{CP} = 29$ Hz, $J_{CH} \approx 125$ Hz, CH_2PMe_3); ^{31}P NMR (CH_2Cl_2) δ -10.0 (d, $^2J_{PP} = 24$ Hz, $J_{PW} = 168$ Hz, PMe_3), 35.2 (t, $^2J_{PP} = 23$ Hz, CH_2PMe_3); IR (Nujol) 1895 (s, sh) 1772 cm^{-1} (s, sh); conductivity (CH_2Cl_2 , 273 K) $\Lambda = 0.49 \Omega^{-1} cm^{-1} M^{-1}$ at $1.02 \times 10^{-3} M$.

This product is unstable in the solid state; the yellow crystals become brown after 12 at 25 °C. A yellow solution of the pure compound in chloroform becomes brown after several hours at 25 °C. It could be characterized only by comparison of its NMR spectra with those of its stable relative below.

$[W(CH_2PMe_3)(PMe_3)_3(CO)_2Cl][CF_3SO_3]$. $[W(CH_2)(PMe_3)_4Cl][CF_3SO_3]$ (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 -30 °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 0.35 g, 78%): 1H NMR ($CDCl_3$) δ 1.79 (d, 9, $^2J_{HP} = 13.2$ Hz, PMe_3), 1.38 (d, 9, $^2J_{HP} = 8.3$ Hz, PMe_3), 1.73 (d, 9, PMe_3), 1.66 (d, 9, PMe_3), 0.95 (m, 2, CH_2PMe_3); ^{13}C NMR ($CDCl_3$) δ 250.8 (m, CO), 228 (m, CO), 120.9 (q, $J_{CF} = 319$ Hz, CF_3SO_3), 18.6 (d, $J_{CP} = 34.5$ Hz, PMe_3), 16.7, 16.0, and 13.2 (each a d, $J_{CP} = 24$ Hz, PMe_3), 2.3 (br t, $J_{CH} = 122$ Hz, CH_2PMe_3); ^{31}P NMR ($CDCl_3$) δ 33 (m, PMe_3), -5 (m, PMe_3), -11 (m, PMe_3), -33 (m, PMe_3); IR (Nujol) 1895 (s, sh), 1790 cm^{-1} (s, sh); conductivity ($C_2H_4Cl_2$) $\Lambda = 17.3 \Omega^{-1} cm^{-1} M^{-1}$ at $0.72 \times 10^{-3} M$. Anal. Calcd for $WC_{16}H_{38}ClF_3O_5P_4S$: C, 25.90; H, 5.12. Found: C, 26.10; H, 5.28. The structure was positively identified by X-ray methods.²³

$[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. $W(CH)(PMe_3)_4Cl$ (2.5 g, 4.7 mmol) was dissolved in 20 mL of chlorobenzene, and $AlCl_3$ (1.24 g, 9.3 mmol) was added rapidly as a solid. The mixture was stirred for 5 min at 25 °C. Hexachloroethane (2 equiv) was then added slowly, as a solid, over a period of 5 min. A white powder and a brown oily solid formed immediately. The mixture was stirred for 12 h, and the solvent was decanted away from the solid. The solid was dissolved in acetonitrile. The solution was concentrated, toluene was added, and the mixture was cooled to -30 °C. After 1 day some yellow crystals were collected. After a second crystallization by the same procedure, 0.53 g of product was collected (17%): 1H NMR (CD_3CN) δ 2.03 (m, 18, PMe_3), 1.47

(d, 9, $^2J_{HP} = 14$ Hz, $WCPMe_3$); ^{13}C NMR (CD_3CN , 270 K) δ 241.9 (br s, $WCPMe_3$), 20.8 (virtual t of q, $J_{CH} = 120$ Hz, $J_{CP} = 16$ Hz, PMe_3), 13.1 (d of q, $J_{CH} = 130$ Hz, $J_{CP} = 61$ Hz, $WCPMe_3$); ^{31}P NMR (CH_3CN) δ 6.8 (s, $J_{PW} = 166$ Hz, $WCPMe_3$), -18.7 (s, $J_{PW} = 300$ Hz, PMe_3); ^{27}Al NMR (CH_3CN) δ 102.5 (sharp s, $AlCl_4^-$). The crystal for the X-ray study was selected from a homogeneous, crystalline sample.

Hydrolysis of $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. A 1-mL sample of aqueous 1 N HCl was shaken for a few minutes with approximately 0.05 g of $[W_2(CPMe_3)_2(PMe_3)_4Cl_4][AlCl_4]_2$. After being left standing at 25 °C for 1 h, the solution was filtered. A ^{31}P NMR spectrum of the filtrate showed a 2.2:1 ratio of Me_3PHCl to another phosphorus-containing species. After the NMR sample was heated at 80 °C for 1 week, the Me_3PHCl remained, but the other compound had been quantitatively converted into Me_4PCl : ^{31}P NMR (H_2O) δ 22.8 (s, 1, Me_4PCl), -2.9 (d, 2, $J_{HP} = 505$ Hz, Me_3PHCl).

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Registry No. $W(CH)(PMe_3)_4Cl$, 76642-46-1; $W(CH)(PMe_3)_4I$, 87862-02-0; $W(CH)(PMe_3)_4(CF_3SO_3)$, 87862-03-1; Me_3SiI , 16029-98-4; $Me_3Si(OTf)$, 27607-77-8; $[W(CH_2)(PMe_3)_4I][CF_3SO_3]$, 87862-05-3; $[W(CH_2)(PMe_3)_4(CF_3SO_3)][CF_3SO_3]$, 87869-37-2; $W(CH)(PMe_3)_4(BH_4)$, 87862-06-4; $W(CH)(C_2H_4)(PMe_3)_3(CF_3SO_3)$, 87862-07-5; C_2H_4 , 74-85-1; $W(CHAlMe_3)(PMe_3)_3Cl$, 76657-21-1; $AlMe_3$, 75-24-1; $W(CHAlMe_2Cl)(PMe_3)_3Cl$, 76642-47-2; $AlMe_2Cl$, 1184-58-3; $W(CAl_2Me_4Cl)(PMe_3)_2(C_2H_4)$, 79255-12-2; $W(CHCOAlCl_3)(PMe_3)_3(CO)Cl$, 81391-10-8; $AlCl_3$, 7446-70-0; $W(CHCOAlMe_3)(PMe_3)_3(CO)Cl$, 81371-73-5; CO , 630-08-0; $W(CH^{13}COAlMe_3)(PMe_3)_3(^{13}CO)Cl$, 87862-08-6; $W(CH_2PMe_3)(PMe_3)_2(CO)_2Cl_2$, 87869-38-3; $W(CH)(H)(PMe_3)_3Cl_2$, 79197-72-1; $[W(CH_2PMe_3)(PMe_3)_3(CO)_2Cl][CF_3SO_3]$, 82880-78-2; $[W(CH_2)(PMe_3)_4Cl][CF_3SO_3]$, 79197-71-0; $[W_2(CPMe_3)(PMe_3)_4Cl_4][AlCl_4]_2$, 87862-10-0.

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

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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 CH_3^+ and SiH_3^+ 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, R_3C^+ , are readily accessible species in all three phases and possess a well-developed chemistry. In contrast, the silicon analogues, silylenium ions, R_3Si^+ , are far more elusive.¹ 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 R_3Si^+ species in solution is probably because silicon has energetically very favorable reaction paths involving pentavalent or hexavalent intermediates that ensure a short life-

(1) Olah, G. A.; Field, L. D. *Organometallics* 1982, 1, 1485. For reviews of the silylenium question see: Corriu, R. J. P.; Henner, M. J. *J. Organomet. Chem.* 1974, 74, 1. Boe, B. *Ibid.* 1976, 107, 139.

(2) Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* 1983, 105, 1672.

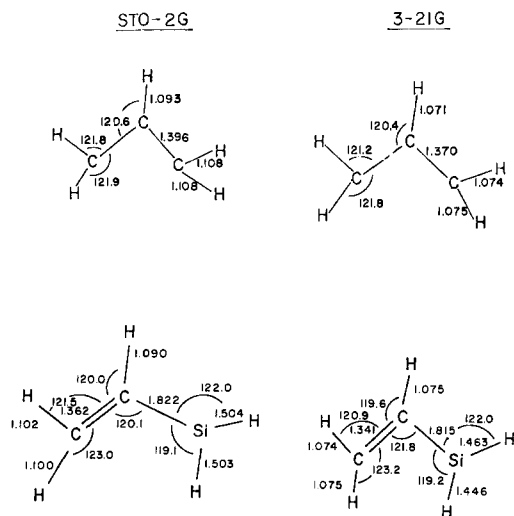


Figure 1. Predicted structures for monovinyl cations. Bond lengths are given in angstroms and angles in degrees.

time for the species or completely suppress its formation.³ In the gas, R_3Si^+ 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_2X^+) 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 $RR'ViSiMe \rightarrow RR'ViSi^+$ reaction than for similar transformations on non-vinylated silanes.⁷ This suggests the possibility that vinyl substitution will similarly stabilize SiH_3^+ by donating π -electron density into the empty p_π orbital of silicon. Indeed, Apeloig and co-workers⁵ have found the π 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 program⁸ and the STO-2G⁹ and 3-21G¹⁰ basis sets. The STO-2G basis set has previously been demonstrated¹¹ to provide reliable estimates of molecular structures, as well as trends in isodesmic¹² reactions.

(3) O'Brien, D. H.; Hairston, T. J. *Organomet. Chem. Rev., Sect. A* 1971, 7, 95.

(4) George, C.; Morris, M. L.; Gordon, M. S.; Koob, R. D. "Abstracts of Papers"; 17th Organosilicon Symposium, Fargo, ND, Poster 16.

(5) Apeloig, Y.; Schleyer, P. v. R. *Tetrahedron Lett.* 1977, 4642-4645. Apeloig, Y.; Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Ibid.* 1981, 22, 3297.

(6) Godleski, S. A.; Heacock, D. J.; McKelvey, J. M. *Tetrahedron Lett.* 1982, 23, 4453.

(7) Boudjouk, P.; Gordon, M. S.; Han, B.-H.; Sooriyakumaran, R.; Feil, V. J. "Abstracts of Papers", 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983; American Chemical Society: Washington, D. C. 1983; Abstract No. ORGN 223.

(8) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Kahn, L. R.; Pople, J. A. *QCPE* 1980, 13, 406.

(9) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* 1969, 51, 2657.

(10) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* 1980, 102, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* 1982, 104, 2797.

(11) Gordon, M. S.; Boudjouk, P.; Anvari, F. *J. Am. Chem. Soc.* 1983, 105, 4972.

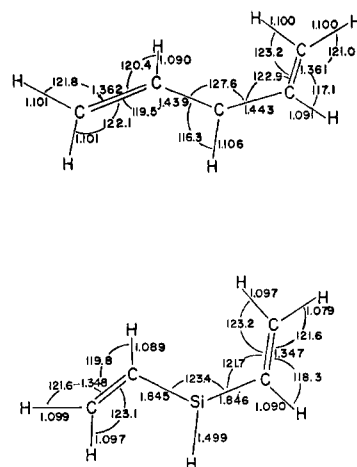


Figure 2. Predicted structures for divinyl cations. Bond lengths are given in angstroms and angles in degrees.

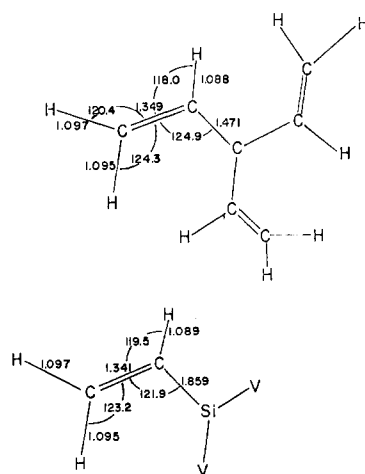


Figure 3. Predicted structures for trivinyl cations. Bond lengths are given in angstroms and angles in degrees.

Table I. Mulliken Populations in X p_π MO

| n^a | STO-2G | | 3-21G | |
|-------|--------|--------|-------|--------|
| | X = C | X = Si | X = C | X = Si |
| 1 | 0.468 | 0.340 | 0.459 | 0.266 |
| 2 | 0.540 | 0.440 | 0.533 | 0.339 |
| 3 | 0.565 | 0.502 | 0.554 | 0.395 |

^a n = the number of vinyl groups attached to X.

Results and Discussion

The STO-2G and 3-21G structures for XH_2Vi^+ (X = C or Si, Vi = 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 STO-2G. Comparison of the CC bond lengths suggests greater delocalization stabilization in the hydrocarbon. Since the STO-2G C=C and C—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 STO-2G and 3-21G structures and the computer time saved by using the smaller basis set, geometries for the di- and trivinyl

(12) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* 1979, 101, 6814.

Table II. Energy Stabilization of Vinyl-Substituted Ions^{a, b}

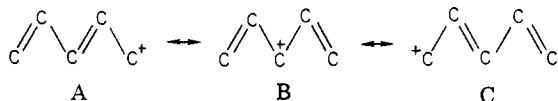
| | n = 1 | | | n = 2 | | | n = 3 | | |
|---|-------|------|------|-------|------|------|-------|------|------|
| | C | Si | R | C | Si | R | C | Si | R |
| A. Bond Separation ^c | | | | | | | | | |
| STO-2G | 43.6 | 26.2 | 0.60 | 56.5 | 42.2 | 0.75 | 56.0 | 53.8 | 0.96 |
| 3-21G | 36.9 | 21.0 | 0.57 | 39.2 | 32.6 | 0.83 | 30.6 | 42.5 | 1.39 |
| B. Ion Replacement ^d | | | | | | | | | |
| STO-2G | 62.3 | 39.9 | 0.64 | 97.3 | 61.4 | 0.63 | 121.2 | 77.1 | 0.64 |
| 3-21G | 57.4 | 26.8 | 0.47 | 80.5 | 43.0 | 0.53 | 100.5 | 58.6 | 0.58 |
| C. Partial Bond Separation ^e | | | | | | | | | |
| STO-2G | 62.3 | 39.9 | 0.64 | 94.0 | 69.7 | 0.74 | 112.3 | 94.9 | 0.85 |
| 3-21G | 57.4 | 26.8 | 0.47 | 80.2 | 44.4 | 0.55 | 92.1 | 60.2 | 0.65 |

^a Energies in kcal/mol. ^b For a definition of R, see eq 4 of text. ^c Equation 1 of text. ^d Equation 2 of text. ^e Equation 3 of text.

species have been predicted with STO-2G followed by single-point 3-21G calculations (denoted 3-21G//STO-2G). These structures are shown in Figures 2 and 3. If the C=C and X—C bond lengths may be used as an indicator, successive vinyl substitution appears to result in successive localization of the π electrons, since the C=C bonds become shorter and the X—C bonds become longer. This effect is more pronounced when X = C, and it is readily understood when one considers likely contributing "resonance" structures. There are two of these for the allyl cation



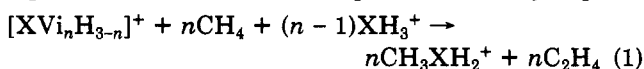
and since they are equivalent, one expects the CC bond lengths to be about halfway between single and double bond lengths. For the divinyl-substituted cation, there are three contributing structures:



Here, one expects structure B to make a greater contribution than A and C. Both of these expectations are substantiated by the calculated structures (Figures 1–3), and similar arguments may be made for the trivinyl and analogous silicon species.

An additional indicator of π 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 π -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 π density on the silicon than on the carbon.

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.,¹³ where X = C or Si. Reaction 1 measures the stability

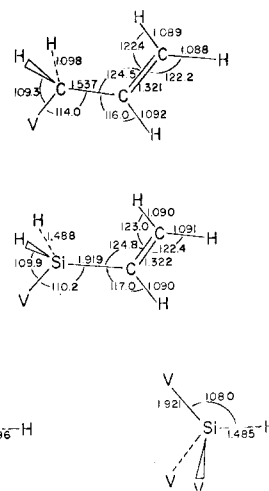
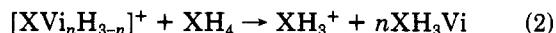
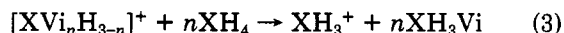


Figure 4. Predicted structures for neutral reference molecules. Bond lengths are given in angstroms and angles in degrees.

of the ion relative to the simplest isolated prototype bonds—in this case C—X, C=C, CH, and X—H bonds. An alternative measure, which has been used by other authors⁵ to estimate effects of substituents on ion stabilities, relates the stability of the ion of interest to that of the unsubstituted parent (eq 2). Finally, one might im-



agine 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).

$$R = \Delta E (\text{X} = \text{Si}) / \Delta E (\text{X} = \text{C}) \quad (4)$$

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_{3v} symmetry was assumed. Furthermore, in the latter molecules, the internal vinyl structures were held constant at the corresponding divinyl

angles and bond lengths. This is clearly justified on the basis of the constancy exhibited in Figure 4.

The energetics for reactions 1-3 are summarized in Table II. Particularly at the 3-21G level of computation, all three measures of delocalization stabilization of the ions agree that systematic vinylization successively increases the stability of the silicon ion more than the carbon ion. The differences are primarily quantitative due to the different reference points as discussed above. For the bond separation reactions (1) the ratio R steadily increases as the number of vinyl groups is increased. In fact, according to the 3-21G results trivinylsilylenium ion is more stable relative to its isolated component bonds than is its carbon analogue. This may well be a result of the strain introduced by the presence of three coplanar vinyl groups. Because the C-Vi bond length is shorter than its Si-Vi counterpart, this is likely to be more of a problem for C than for Si. To investigate the possibility that this strain may cause the vinyl groups be non-coplanar, the three vinyls were rotated out of coplanarity for both trivinyl ions. In each case the 10° rotation caused a substantial energy increase (4.2 and 2.5 kcal/mol for carbon and silicon, respectively).

The results for the bond replacement reaction 2 may be directly compared with the earlier results of Apeloig and co-workers.⁵ These authors, using STO-3G⁹ wave functions, find Li and planar NH_2 to be the most effective substituents for stabilizing both SiH_3^+ and CH_3^+ . According to our STO-2G results, ΔE for reaction 2 is about the same for vinyl and planar NH_2 when $X = \text{Si}$. In contrast, vinyl is only about two-thirds as effective as planar NH_2 when $X = \text{C}$. Similar results apply for 3-21G

wave functions, although here planar NH_2 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. $^+\text{CH}_2(\text{CH}=\text{CH}_2)_2$, 1724-44-3; $^+\text{CH}(\text{CH}=\text{CH}_2)_2$, 54963-17-6; $^+\text{C}(\text{CH}=\text{CH}_2)_3$, 54963-18-7; $^+\text{SiH}_2(\text{CH}=\text{CH}_2)_2$, 64840-94-4; $^+\text{SiH}(\text{CH}=\text{CH}_2)_2$, 87999-58-4; $^+\text{Si}(\text{CH}=\text{CH}_2)_3$, 87999-59-5.

Communications

Alkylidenebis(perthiolates): A New Class of Organosulfur Ligands Prepared from $(\text{RC}_5\text{H}_4)_2\text{TiS}_5$

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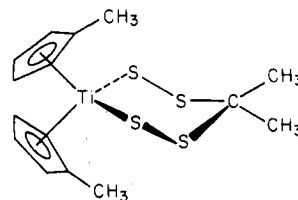
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Summary: In the presence of $(\text{NH}_4)_2\text{S}$, $(\text{RC}_5\text{H}_4)_2\text{TiS}_5$ ($R = \text{H}, \text{Me}, i\text{-Pr}$) reacts with aliphatic ketones and CH_2Br_2 to give 1,4- $(\text{RC}_5\text{H}_4)_2\text{TiS}_4\text{CR}_2$ ($R_2 = \text{Me}_2, \text{Me}, \text{Et}, \text{c-C}_6\text{H}_{10}, \text{H}_2$) and 1,3- $(\text{RC}_5\text{H}_4)_2\text{TiS}_4\text{CH}_2$. The new compounds were purified chromatographically and were characterized spectroscopically including DNMR spectroscopy. Single-crystal X-ray crystallography confirmed the structure of $(i\text{-PrC}_5\text{H}_4)_2\text{TiS}_4\text{CH}_2$.

Bis(cyclopentadienyl)titanium pentasulfide (1) is the most thoroughly studied metal polysulfido chelate.¹⁻³ According to the method described by Köpf and Schmidt,

1 is prepared from the reaction of Cp_2TiCl_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and ammonium polysulfide in acetone.¹ Close examination of one such preparation employing $(\text{MeCp})_2\text{TiCl}_2$ 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 Cp_2TiS_5 .⁴

The red product **3b** was found to have the formula $(\text{MeCp})_2\text{TiS}_4\text{CMe}_2$.⁵ Its ^1H NMR spectrum featured



3b

(4) For the compound numbers in this paper, the letters a, b and c indicate the Cp, MeCp, and $i\text{-PrCp}$ derivatives, respectively. The nomenclature for these compounds has been questioned by a reviewer. The staff at Chemical Abstracts suggests naming these compounds as derivatives of sulfenic acids. For example, 1,4- $(\text{C}_5\text{H}_5)_2\text{TiS}_4\text{C}(\text{CH}_3)_2$ (3a) and 1,3- $(\text{C}_5\text{H}_5)_2\text{TiS}_4\text{CH}_2$ (7a) would be named bis(η^5 -2,4-cyclopentadien-1-yl)[2,2-propanedisulfeno(2-)]titanium and bis(η^5 -2,4-cyclopentadien-1-yl)[1-mercapto-1-methanosulfeno(dithioperoxoate)(2-)]titanium, respectively.

(1) Köpf, H.; Block, B.; Schmidt, M. *Chem. Ber.* 1968, 101, 272.
 (2) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* 1982, 21, 3947.
 (3) (a) Schmidt, M.; Block, B.; Block, H. D.; Köpf, H.; Wilhelm, E. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 632. (b) Sandow, T.; Steidel, J.; Steudel, R. *Ibid.* 1982, 21, 794. (c) Schmidt, M.; Wilhelm, E. *J. Chem. Soc., Chem. Commun.* 1970, 1111.