not be rationalized by assuming an associative equilibrium forming $[(CH_3)_3CCH_2]_2Pt(PEt_3)_3$: a quantity of triethylphosphine which decreased the rate of decomposition of **1** by a factor of 15 increased its solubility by only 16%.[7] Examination of the ^{31}P NMR spectrum of **1** in the presence of triethylphosphine also showed no evidence of formation of a species containing three triethylphosphine moieties under conditions (0.08 M **1**, 0.3 M Et_3P,) in which 93% of **1** would have necessarily been converted into such a species to rationalize the observed decrease in k_{obsd}.

The observation of a significant kinetic isotope effect in the decomposition of **1** indicates that C-H bond breaking or bond forming occurs in or before the rate-limiting step. The rates of decomposition of **1**-d_0 and $[(CD_3)_3CCD_2]_2Pt[P(C_2D_5)_3]_2$ (**5**) were determined by comparing the yields of neopentane as a function of time. After correction for isotopic impurities, analysis of these data yielded $k_1/k_5 = k_H/k_D = 3.0-3.5$.

The most important conclusion from this work is that the cleavage of an unactivated C-H bond which takes place during the conversion of **1** into **4** proceeds by an oxidative addition to the platinum atom of a reactive (trialkylphosphine)dialkylplatinum(II) moiety. We are currently studying a number of other examples of related, unactivated C-H bond cleavage reactions involving additions to platinum:[8] most appear to involve a $LPtR_2$ moiety as the reactive intermediate, and thus to require a vacant coordination site on (formally) three-coordinate platinum(II). The available evidence is not sufficient to distinguish between oxidative addition of a C-H bond to platinum(II) (k_2) or reductive elimination of a C-H bond from platinum(IV) (k_3) as the overall rate-limiting step.[9]

Activation of C-H bonds by surface atoms of platinum metal occurs readily.[10] We note that a prominent feature of a metal surface is the availability of vacant coordination sites and suggest that explicit comparisons of the reactivity of vacant sites on soluble complexes and on metal surfaces should be one of the most useful and direct methods of establishing parallels between homogeneous and heterogeneous catalysts. The activation energy determined for the transformation **1** → **4** described here ($E_a \simeq 49$ kcal mol^{-1}) cannot be directly compared with the lower values ($E_a \simeq 10$ kcal mol^{-1}) characterizing C-H bond cleavage during surface reactions,[10] since the former is composed of contributions from the energy of dissociation of a phosphine ligand, the energy (or the energy of activation) of addition of the C-H bond to platinum, the strain energy involved in forming the platinacyclobutane ring, and (possibly) the energy of activation for reductive elimination of neopentane from **3**. Studies of other C-H oxidative additions to platinum and of systems designed to provide comparable thermodynamic parameters for homogeneous and heterogeneous activation of C-H bonds by platinum will be reported as they are completed.

References and Notes

(1) Supported by the National Science Foundation (MPS 74-20956 and 7711282CHE).

(2) Parshall, G. W. *Acc. Chem. Res.* **1975,** *8*, 113-117. Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976,** *25*, 125-183. Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977,** *24*, 97-143.

(3) Compound 1 was prepared by reaction of 1,5-cyclooctadienedichloroplatinum(II) with neopentylmagnesium bromide, followed by treatment with triethylphosphine. See Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978,** *100*, 5808-5815, for similar procedures.

(4) All isotopic analyses were obtained using a Hewlett-Packard Model 5990 A GC/MS. The accuracy of these determinations varied with the sample, but should be considered to be precise to ±2% for neopentane. For example, treatment of **1** with aqueous DCl yields neopentane (99% d_1, 1% d_0). The 13% d_1 neopentane obtained on reaction of **4** with DCl is well outside experimental error and seems to represent a real (if presently unexplained) side reaction.

(5) *Schrock*, R. R. *Acc. Chem. Res.*, in press.

(6) In principle, a plot of $(k_{obsd})^{-1}$ vs. $[P(C_2D_5)_3]$ can be used to estimate values of k_1 and k_{-1}/k_2. In practice, the uncertainty in these rate constants is so large that they are of only qualitative significance.

(7) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972,** *94*, 5258-5270, discuss the use of solubilities to differentiate between associative and dissociate equilibria.

(8) For other examples of intramolecular C-H oxidative additions, cf. ref 2 and references cited in the following. Goel, R. G.; Montemayor, R. G. *Inorg. Chem.* **1977,** *16*, 2188-2196. Webster, D. E. *Adv. Organomet. Chem.* **1977,** *15*, 147-188. Anderson, R. A.; Jones, R. A.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Chem. Commun.* **1977,** 283-285. Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978,** *152*, 347-357.

(9) The neopentyl methyl and methylene groups of $(Et_3P)_2Pt[CD_2C(CH_3)_3]_2$ do not interchange. This observation does not guarantee the irreversibility of the step **2** → **3,** since we do not know that the methylene groups of **3** are equivalent.

(10) Biloen, P.; Dautzenberg, F. M.; Sachtler, W. M. H. *J. Catal.* **1977,** *50*, 77-86. Gault, F. G.; Rooney, J. J.; Kemball, C. *ibid.* **1962,** *1*, 255-274. Karpinski, Z.; Guczi, L. *J. Chem. Soc., Chem. Commun.* **1977,** 563-564.

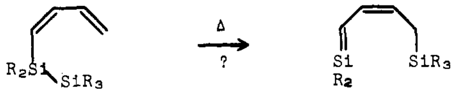
Paul Foley, George M. Whitesides*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received December 12, 1978

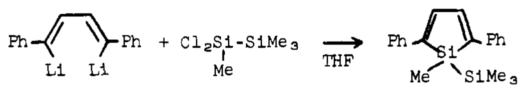
Silicon-Carbon Double-Bond Formation via 1,5-Sigmatropic Migration of Trimethylsilyl from Silicon to Carbon

Sir:

It is well established that a trimethylsilyl group will undergo 1,5 migration on a cyclopentadiene ring far more easily than will hydrogen.[1] Thus, we hoped to utilize this enhanced migratory aptitude in an attempt to observe an unprecedented 1,5 thermal migration of silicon from silicon to carbon in order to generate a 5-silyl-1-sila-1,3-butadiene.

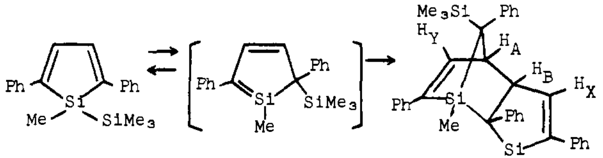


The initial test molecule, 1-methyl-1-trimethylsilyl-2,5-diphenylsilole (**1**), was conveniently prepared in 51% yield from the cyclization of 1,4-dilithio-1,4-diphenylbutadiene and 1,1-dichloro-1,2,2,2-tetramethyldisilane. Silole **1** is a bright yellow solid: mp 95-96.5 °C; NMR (CCl_4) δ 0.0 (s, 9 H, $SiMe_3$), 0.68 (s, 3 H, SiMe), 7.1-7.6 (m, 12 H, ArH + vinyl); mass spectrum calculated for $C_{20}H_{24}Si_2$ 320.14166, observed *m/e* 320.14006.



1

Heating silole **1** in an evacuated, sealed tube at 150 °C for 9 h produced a clean mixture of **1** and a white, crystalline product **2** in a 1.1:1.0 ratio, respectively. Product **2** (mp 186.5-188 °C) was assigned the dimer structure shown on the basis of its spectra: NMR (CCl_4) δ −0.78 (s, 9 H, $SiMe_3$), −0.24 (s, 9 H, $SiMe_3$), 0.03 (s, 3 H, SiMe), 1.18 (s, 3 H, SiMe!), 4.02 (t, overlapped d of d, H_B, $J_{AB} = J_{BX} = 5$ Hz), 4.35 (d of d, H_A, $J_{AY} = 2.5$ Hz, *hν* at 6.59 collapses to d), 5.90-7.35 (m, 22 H, ArH + H_X + H_Y); mass spectrum calculated for $C_{40}H_{48}Si_4$ 640.28333, observed *m/e* 640.28233 (2.3% of base peak at *m/e* 320).



1 3 2

0002-7863/79/1501-2733$01.00/0

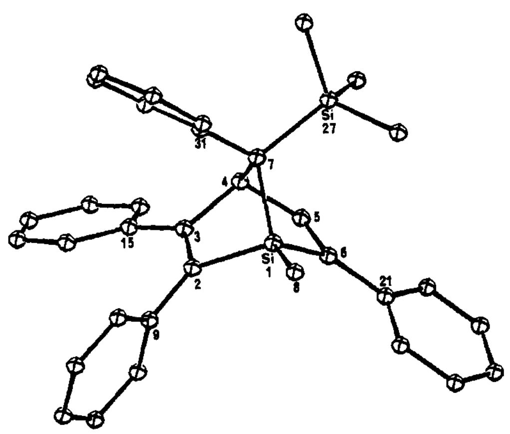
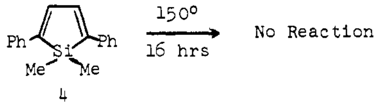


Figure 1. A computer-generated drawing of 1-silanorbornadiene (**5**). Hydrogens are omitted for clarity.

The obvious explanation for the origin of **2** is that silole **1** is undergoing the desired 1,5-trimethylsilyl migration to generate the rearranged silole **3** which, in turn, reacts in a Diels-Alder fashion with starting material **1**. Even more important is the observation that heating either **1** or **2** at 150 °C for any length of time >20 h produces essentially the same ratio of **1**:**2**. Thus, we are clearly dealing with an equilibrium process. That the initial reaction is not simply a Diels-Alder reaction between two molecules of **1**, followed by rearrangement, was shown by heating the analogous 1,1-dimethyl-2,5-diphenylsilole (**4**) under the same conditions for 16 h with *no* change.



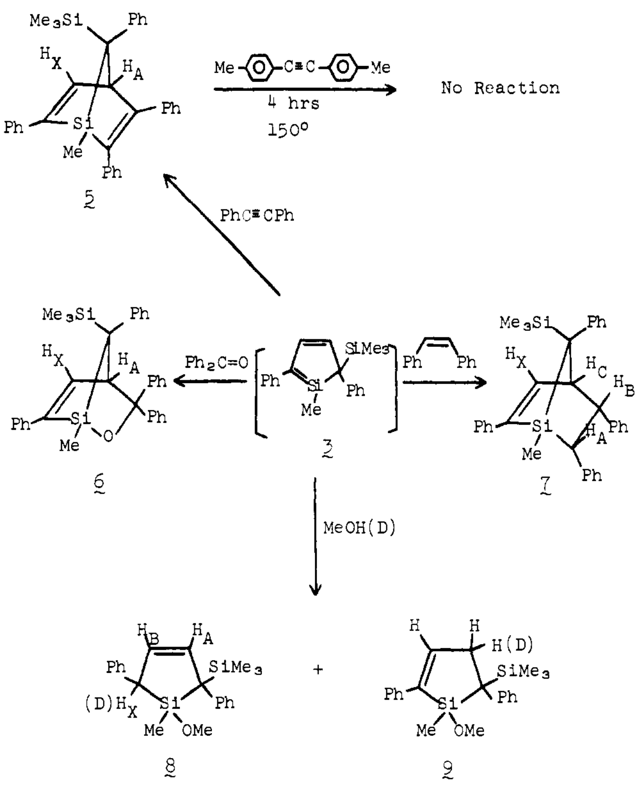
4

If indeed **3** is present in an equilibrium concentration, it should be possible to siphon it out through the addition of a dienophilic alternative to **1**. This was first attempted with diphenylacetylene. Heating equimolar amounts of silole **1** and diphenylacetylene for 12 h at 150 °C produced a reaction mixture, which by NMR analysis contained only one product. The white, crystalline product (mp 164-168 °C, 63% isolated) was inferred to be 1-silanorbornadiene (**5**) from its spectral characteristics: NMR (CCl_4) δ −0.07 (s, 9 H, $SiMe_3$), 1.01 (s, 3 H, SiMe), 4.53 (d, H_A, J_{AX} = 5.6 Hz), 6.5-7.4 (m, 20 ArH), 7.75 (d, H_X, J = 5.6 Hz, collapses to s when $h\nu$ at 4.67 and vice versa); mass spectrum calculated for $C_{34}H_{34}Si_2$ 498.21992, observed *m/e* 498.22007, base peak *m/e* 129.

However, the chemical shift of the lone methyl group (δ 1.01) is unusually low for a methyl on silicon. This generates the vexing possibility that the methyl rather than the trimethylsilyl migrated in **1**. A single-crystal X-ray determination of **5** was undertaken to unequivocally eliminate this possibility. Figure 1 is a computer-generated drawing of the final X-ray model.[2]

Diels-Alder adduct **5**, the first reported example of the 1-silanorbornadiene ring system,[3] proved to be remarkably stable. In an attempt to observe retro-Diels-Alder decomposition, **5** was heated for 4 h at 150 °C with an excess of di-*p*-tolylacetylene with no acetylene exchange and no decomposition.

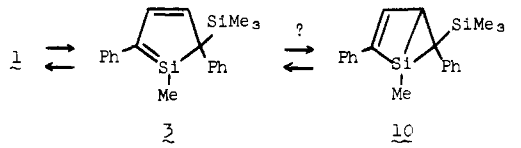
Since the carbonyl group is well known to be an excellent trap for the silicon-carbon double bond, **1** was heated for 10 h at 150 °C with an equimolar quantity of benzophenone in degassed benzene solution. By NMR analysis adduct formation was *quantitative* and a single crystallization afforded a 61% yield of white, crystalline **6**: mp 188-189.5 °C; NMR (CCl_4) δ −0.23 (s, 9 H, $SiMe_3$), 1.14 (s, 3 H, SiMe), 4.77 (d, H_A, J = 5 Hz, $h\nu$ at ~6.83 collapses to s), 6.31-7.51 (m, 21 H, ArH + H_X); mass spectrum calculated for $C_{33}H_{34}OSi_2$ *m/e* 502.21483, observed *m/e* 502.21658 (83% of base peak at *m/e* 128).[4]



In a similar fashion (150 °C, 26.5 h, neat) *cis*-stilbene reacted with silole **1** to quantitatively (by NMR, 69% isolated) produce white, crystalline **7**: mp 117.5-119 °C; NMR (CCl_4) δ −0.11 (s, 9 H, $SiMe_3$), 0.85 (s, 3 H, SiMe), 3.01 (d, H_A, J_{AB} = 11 Hz, collapses to s when $h\nu$ at 7.5), 4.17 (m, H_B and H_C, simultaneous irradiation at 3.01 and 7.50 produces an AB quartet, J_{BC} = 3.5 Hz), 6.39-7.57 (m, 21 H, ArH + d at 7.5, H_X, J_{CX} = 5 Hz, collapses to s when $h\nu$ at ~4.25); mass spectrum calculated for $C_{34}H_{36}Si_2$ 500.23557, observed *m/e* 500.23530, base peak *m/e* 320.

The hydroxyl group has long been known to be an excellent trap for the silicon-carbon double bond.[6] Thus heating **1** with an 8-fold excess of MeOH (146 °C, 3 h, C_6H_6) afforded in quantitative yield a 1:1 mixture of two adducts **8** and **9**. Adduct **8**, which formally results from a 1,2 addition of MeOH to **3**, was identified from its spectral characteristics: NMR (CCl_4) δ −0.03 (s, 9 H, $SiMe_3$), 0.06 (s, 3 H, SiMe), 2.89 (s, 3 H, OMe), 3.42 (m, H_X, collapses to s when $h\nu$ at 6.33), 6.33 (center of two overlapped d of d, J_{AX} = J_{BX} = 1.7, J_{AB} = 8 Hz, collapses to AB quartet when $h\nu$ at 3.38 or when MeOD employed as reactant), 7.01-7.24 (m, 10 H, ArH); mass spectrum calculated for $C_{21}H_{23}Si_2O$ 352.16788, observed *m/e* 352.16673 (20% of base peak at *m/e* 248). Likewise the 1,4-addition product **9** was identified from NMR (CCl_4): δ −0.08 (s, 9 H, $SiMe_3$), 0.60 (s, 3 H, SiMe), 2.80 (s, 3 H, OMe), 3.10 (m, CH_2, collapses to apparent d, J = 0.8 Hz when $h\nu$ at ~7.1), 7.0-7.45 (m, 11 H, arH and vinyl); mass spectrum, observed molecular ion *m/e* 352.1652 (15% of base peak at *m/e* 248). Separation of **8** and **9** could not be effected by GC, but was accomplished by LC (C-18 μ-Bondapak, 85% MeOH/H_2O).

The most striking observation on the reaction of **1** and methanol is that *only* one isomer of **8** and one of **9** are formed. Thus, for example, adduct **8** has three chiral centers; yet only one diastereomer is formed. Formally this corresponds to addition of methanol to only one face of **3**. It is possible that the bulky trimethylsilyl group on **3** blocks addition from one face (indeed, only one isomer each of **2, 5, 6,** and **7** are formed), but this seems a bit unlikely. In addition the ratio of **8:9** moves to 2:1 when a huge excess of MeOH is employed in the reaction. If MeOH were only reacting with **3** to produce **8** and **9**, the product ratio should be independent of the methanol concentration. Thus, it would appear that we have at least one intermediate other than **3**. While further study is obviously called for, we must consider the possibility that **3** is in equilibrium with silabicyclo[2.1.0]pentene (**10**).[7] It is therefore possible that adducts **2, 5, 6** and **7** arise from addition to **10**. This would be in keeping with the well-established stereospecific additions of multiple bonds to bicyclo[2.1.0]pentanes,[10] if the bulk of the trimethylsilyl group forces **3** to fold in only one direction in closing to **10**. This and other possibilities are being experimentally checked at this time.



Acknowledgment. The partial support of this work by a grant from Dow Corning Corporation is much appreciated. The diffractometer used in this work was purchased with a grant from the National Science Foundation.

Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Larrabee, R. B. *J. Organomet. Chem.* **1974,** *74*, 313, and references therein.

(2) Crystals of **5** belong to the orthorhombic crystal class with $a = 9.509$ (2), $b = 17.394$ (3), and $c = 17.545$ (3) Å. Systematic extinctions indicated the chiral space group $P2_12_12_1$ and density measurements indicated one molecule of $C_{34}H_{34}Si_2$ per asymmetric unit. All unique diffraction maxima within a Mo Kα sphere of 0.93 Å were collected and 2074 (96%) were judged observed ($F_o \geq 3\sigma(F_o)$). Solution and refinement were uneventful and the current crystallographic residual is 0.036 for the observed data. All crystallographic calculations were done on a Prime 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were REDUCE and UNIQUE, data reduction programs, M. E. Leonowicz, Cornell University, 1978; BLS, block-diagonal least-squares refinement, K. Hirotsu, Cornell University, 1978; ORFLS (modified), full matrix least squares, W. R. Busing, K. O. Martin, and H. S. Levy, Oak Ridge, ORNL-TM-305; ORTEP, crystallographic illustration program, C. Johnson, Oak Ridge, ORNL-3794; BOND, structural parameters and errors, K. Hirotsu, Cornell University, 1978; MULTAN-76, direct methods and fast fourier transform, G. Germain, P. Main and M. Woolfson, University of York.

(3) The parent 1-methyl-1-silanorbornadiene has been prepared from an unexpected C–H insertion by the carbene produced upon photolysis of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene: Barton T. J.; Banasiak, D. S., unpublished results.

(4) While adduct **6** formally represents a 1,4 addition of the carbonyl group across **3,** we have no way of knowing whether or not the initial cycloaddition was "[2 + 2]" followed by rearrangement to **6.**[5]

(5) A similar mechanistic dilemma exists in the work of Weber: Valkovich P. B.; Weber, W. P. *Tetrahedron Lett.* **1975,** 2153; *J. Org. Chem.* **1975,** *40*, 229.

(6) Gusel'nikov L. E.; Flowers, M. C. *Chem. Commun.* **1967,** 864 (1967).

(7) Closure of 1-sila-1,3-butadienes to silacyclobutenes has been reported by Block[8] and by Sakurai.[9] The intermediate dienes in these reports did not possess C-5 hydrogens.

(8) Block C.; Revelle, L. K. *J. Am. Chem. Soc.* **1978,** *100*, 1630.

(9) Nakadaira, Y.; Kanouchi, S.; Sakurai, H. *J. Am. Chem. Soc.* **1974,** *96*, 5621.

(10) Gassman, P. G. *Acc. Chem. Res.* **1971, 4,** 128.

Thomas J. Barton,* William D. Wulff
Department of Chemistry, Iowa State University
Ames, Iowa 50011

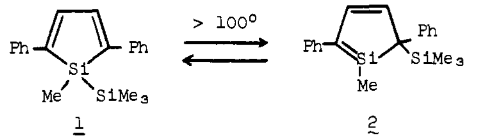
Edward V. Arnold, Jon Clardy*
Department of Chemistry, Cornell University
Ithaca, New York 14853

Received July 20, 1978

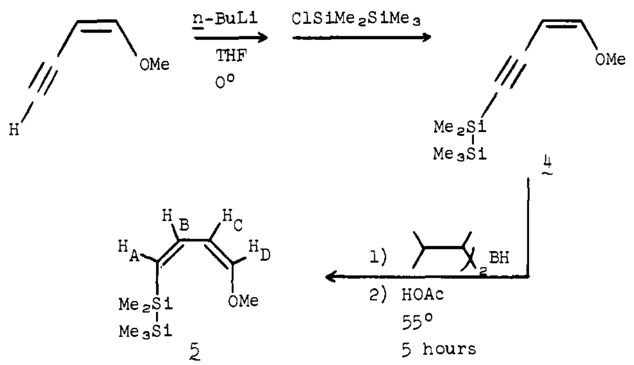
Serendipitous Synthesis of a Sila-α-pyran—Convenient, Penultimate Precursor to Dimethylsilanone

Sir:

Recently we established that 1-disilanyl-1,3-butadienes undergo thermal rearrangement via 1,5-silyl migration to produce 1-sila-1,3-butadienes.[1] For example, 2,5-diphenyl-1-trimethylsilylsilole (**1**) undergoes reversible rearrangement to **2** at temperatures above 100 °C.



We thought to put this rearrangement to use in a synthesis of silole **3** which would be the first example of a silole with all the ring-carbons unsubstituted. To this end we prepared (*Z*)-1-pentamethyldisilanyl-4-methoxybut-1-yn-3-ene (**4**) from *n*-butyllithium-induced coupling of pentamethylchlorodisilane and (*Z*)-4-methyoxybut-1-yn-3-ene in 76% yield.[2] Attempted cis reduction of the triple bond with hydrogen and Lindlar's catalyst afforded only mixtures of randomly reduced **4**. However, hydroboration with disiamylborane followed by acidic cleavage of the vinyl borane in acetic acid[3] provided (*Z,Z*)-1-pentamethyldisilanyl-4-methoxy-1,3-butadiene (**5**) in 37% yield.[4]



Our hope was that thermal rearrangement of **5** to silene **6** would be followed by α elimination of trimethylmethoxysilane to produce carbene **7** which would cyclize to the desired silole **3**. However, flow pyrolysis of **5** (760 °C at 10^{-3} Torr) afforded in 52% yield a product which resulted from the loss of the elements of tetramethylsilane[5] from **5**. This product was identified as 2,2-dimethyl-1-oxo-2-silacyclohexa-3,5-diene (**9**, oxasilin) on the basis of its spectra: NMR (CCl_4) δ 0.29 (6 H, s), 5.07 (H_C, t of d, $J_{CD} = J_{CB} = 6, J_{AC} = 1.0$ Hz), 5.54 (H_A,