Thus a Pt center would be expected to bond more strongly to other soft ligands, such as phosphines. One could alternatively view these differences in metal–ligand distances as an effect of the different bonding capabilities of strongly σ-bonding (i.e., alkyls, halides) and π-bonding (phosphines) ligands. Phosphines are π-acceptors; therefore Pt–P bonding should be stronger than Pd–P bonding. If bond strength can be correlated with bond distance, stronger Pt–P bonds would be expected. A more quantitative discussion of the nature of the bonding in these complexes has been presented.[73] Differences in ability to undergo reductive elimination between the Pd and Pt species may be accounted for by the M–P bond distances. A mechanism for reductive elimination for *cis*-dialkyls has been presented for Pd[6] and Pt.[74] It is believed that prior dissociation of one phosphine ligand is necessary before coupling of the alkyl groups can occur. The Pd–P bonds are longer and therefore expected to be weaker and more likely to dissociate. Thus the postulated mechanism for reductive elimination is supported by the structural data presented here.

Acknowledgment. We are indebted to Prof. Robert L. Burwell, Jr., for calling our attention to the lack of structural data on comparable Pd and Pt alkyl systems. T.J.B. gratefully acknowledges a leave from the Institute of General Chemistry, Technical University of Łódź, Poland. This work was kindly supported by the National Science Foundation (Grant No. CHE83-08076).

Registry No. *cis*-$Pd(CH_3)_2(P(C_6H_5)_2CH_3)_2$, 60885-30-5; *cis*-$Pt(CH_3)_2(P(C_6H_5)_2CH_3)_2$, 24917-50-8.

Supplementary Material Available: Tables of thermal parameters, positions of hydrogen atoms, and bond distances and angles within phenyl groups for Pd and Pt compounds (9 pages); listings of structure amplitudes for Pd and Pt compounds (52 pages). Ordering information is given on any current masthead page.

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[73] Wisner, J. M.; Bartczak, T. J.; Ibers, J. A.; Law, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 347–348.

[74] (a) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403. (b) Nuzzo, R. G.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3404–3410.

Gas-Phase Ion Chemistry of Dimethylsilene

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A pyrolysis port fitted to the flowing afterglow instrument has been used to prepare dimethylsilene. Its ion–molecule chemistry has been explored by using fluoride and amide ions. Fluoride ion adds to dimethylsilene giving an adduct anion which has been characterized by reaction with nitrous oxide; however, complications make the use of some other characterizing anion more desirable. Thus, amide ion abstraction from dimethylsilene has been used to characterize dimethylsilene. The resulting M − 1 ion reacts sluggishly compared to its carbon analogue, the M − 1 of isobutene. The gas-phase acidity of dimethylsilene is greater than that of isobutene (390 kcal/mol); thus, the M − 1 of dimethylsilene is considerably more stable than the isobutene ion. Carbanions have been reacted with dimethylsilene to explore the possibility of carbanion addition to the carbon end of the Si=C bond. Allyl addition can be interpreted as such an addition. Cycloaddition reactions of dimethylsilene have also been studied.

Dimethylsilene, $Me_2Si{=}CH_2$ has been studied in great detail over the last 20 years.[2] From its initial discovery in 1966 as a transient intermediate in the pyrolysis of dimethylsilacyclobutane (DMSCB), its physical properties, chemical reactivity, and theoretical characterization have been detailed.[2] A variety of other silenes have also been characterized including stable ones.[2,3] Perhaps the greatest impetus for these studies has been the desire to understand the differences between the ability of carbon and silicon to participate in multiple bonding. Indeed, experimental estimates of the π-bond strength of dimethylsilene suggest that silicon forms considerably weaker π-bonds than carbon (approximately 38 vs. 65 kcal/mol for ethylene).[4] Theoretical estimates give similar results.[5]

Our interest in dimethylsilene has focused on its reactions with anionic reagents in the gas phase. In previous work, we have demonstrated that the flowing afterglow (FA) technique gives a variety of interesting results in organosilicon chemistry; in addition, silicon compounds have been useful in studying important problems fundamental to gas-phase chemistry and in preparing gas-phase species for study.[6] Thus, in early studies we reported on

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[1] (a) University of Colorado at Denver. (b) University of Colorado at Boulder. (c) The University, Leicester.

[2] (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (b) Bertrand, G.; Trinquier, G.; Mazerolles, P. *J. Organomet. Chem. Libr.* **1981**, *12*, 1. (c) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (d) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[3] Brook, A. G.; Nyburg, S. C.; Abedesaken, F.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. C.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

[4] (a) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329. (b) Walsh, R. *Acc. Chem. Res.* **1982**, *14*, 246.

[5] (a) Schmidt, M. W.; Gordon, M. S.; Depuis, M. *J. Am. Chem. Soc.* **1985**, *107*, 2585. (b) Schaefer, H. F., III *Acc. Chem. Res.* **1982**, *15*, 283.

[6] (a) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480. (b) Damrauer, R.; DePuy, C. H. *Organometallics* **1984**, *3*, 362. (c) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051. (d) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385. (e) Damrauer, R.; DePuy, C. H.; Davidson, I. M. T.; Hughes, K. J., *Organometallics*, following paper in this issue.

the preparation of several new pentacoordinate silicon anions as well as the characterization of isomeric anionic silicon species using nitrous oxide.[6a,b] More recently, we have been able to use silicon compounds to measure the acidity of weakly acidic hydrocarbons as well as to generate the acetyl anion.[6c,d] We sought, then, to apply this powerful gas-phase technique to dimethylsilene and to study its reactions with anions and neutral molecules as well as its acid–base behavior.

Experimental Section

These experiments were performed in a flowing afterglow system at 298 K as previously described[7] with one modification. A port has been added to allow the introduction of neutral pyrolysates. Neutrals are passed through a 9.5-mm quartz tube wrapped with 8 turns of 26-gauge nichrome wire. A stainless-steel flange fashioned with feed-throughs for both the resistance wire and the pyrolysis tube is permanently attached to the flow tube at a distance of 90 cm from the sampling orifice. A sample flask is attached to the pyrolysis tube through an on–off vacuum stopcock. It should be emphasized that a sophisticated experimental setup is not required. We have tried a variety of designs and found a simple, straight pyrolysis tube to work as well as other more complicated designs.

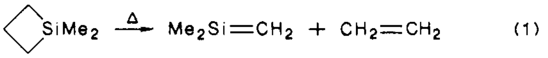
The resulting pyrolysis mixture is swept into the flow tube by the normal flow of helium bath gas. The resistance heater is controlled by a variable transformer and approximate temperatures are measured by using a chromel–alumel thermocouple inserted in a small indentation at the end of the quartz tube. We gauge the extent of reaction not from the crude temperature measurements but by monitoring differences in product distribution as a function of temperature.

Amide and fluoride ions were made by electron impact on NH_3 and NF_3, respectively, HO^- was made by dissociative electron attachment to N_2O followed by hydrogen atom abstraction from CH_4, and CH_3O^- was made by reaction of H_2N^- and dimethoxyethane. Typical helium pressures and flow rates were 0.4 torr and 140 STP cm^3/s, respectively. Neutral reactants were obtained from commercial suppliers; their flow rates were measured by monitoring the pressure increase with time into a calibrated volume. Rate constants were measured by following reactant ion counts as a function of distance.

The identity of product ions was determined not only from mass-to-charge ratios but also by reaction with various neutral molecules like N_2O, CO_2, CS_2, and COS (see Results and Discussion and ref 6b for additional details). Since neutral products are not detected in the FA, their identity has been inferred from knowledge of the reactants and the observed anionic products.

Results and Discussion

Dimethylsilene has been produced in the FA by the pyrolysis of dimethylsilacyclobutane (eq 1). Because of



(1)

the configuration of the pyrolyzer it was not possible to determine the exact temperature at which pyrolysis was occurring. Therefore, we began by introducing DMSCB into the flow tube with the pyrolyzer turned off and examined its ambient-temperature ion–molecule reactions. We raised the temperature until new product ions which could be ascribed to dimethylsilene could be detected by reaction with F^- or H_2N^-. We are presently unable to decide whether the neutral pyrolysis products react in vibrationally excited states or whether they are cooled by reaction with helium buffer gas before reaction.

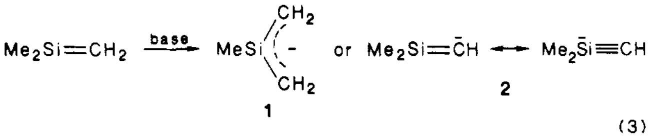
Because we have had considerable experience with reactions of F^- and DMSCB, we began our study of dimethylsilene generation by using F^-. The room-temperature reaction of DMSCB and F^- has been shown to be quite complex.[6b] An anion at m/z 91 forms as does one at mass 119. The m/z 119 signal is actually two species whose relative amounts depend on the flow tube conditions. One of these is the F^- adduct of DMSCB, and the other is $CH_3CH_2CH_2(Me)Si(F)CH_2^-$. The latter and the m/z 91 ion which is $Me_2Si(F)CH_2^-$ form from $Me_2Si(F)CH_2CH_2CH_2^-$ with the m/z 91 ion predominating. The other m/z 119 ion forms by F^- transfer from the m/z 91 ion to excess DMSCB. The characterization of these ions as well as all others in this and its companion paper[6e] has been made by reaction with various neutral reactants like N_2O. The details of such characterizations will be described shortly.

Because the m/z 91 ion has the same structure as that we expected to obtain from F^- and dimethylsilene and because of the complexity of the room-temperature reaction of F^- and DMSCB, we found that F^- had limited utility in characterizing the DMSCB pyrolysis even though we were able to demonstrate a clear enhancement of the m/z 91 signal upon pyrolysis (although signals of 1000–2000 counts were far below what we normally see). Therefore, we turned our attention to better means of characterizing the pyrolysis products of DMSCB.

When strong bases like H_2N^- and HO^- flowed past the pyrolysis tube exit, there was a dramatic difference between the products formed at low and high temperature. For example, H_2N^- reacts with DMSCB at ambient temperature to give M − 1 and M + 16 ions in roughly equal amounts (15 000–20 000 counts each). As the temperature is increased, these signals disappear as new ones emerge. The major new signal appears at m/z 71 and is the M − 1 ion of dimethylsilene (eq 2). This ion could form by

$$Me_2Si{=}CH_2 \xrightarrow{H_2N^- \text{ or } HO^-} \underset{m/z\ 71}{M-1} \qquad (2)$$

proton abstraction from methyl giving the silaallyl species 1 or by vinyl proton abstraction giving 2 (eq 3). To dis-



(3)

tinguish between these possibilities (as well as others like $EtSiCH_2^-$ which might arise in more complex processes), we reacted the m/z 71 ion with N_2O, CO_2, CS_2, and COS by introducing the appropriate neutral further down the flow tube. Reactions of N_2O have been used previously[6] to characterize anionic silicon species, differentiating between silyl anions, where an oxygen is transferred to silicon with a net m/z change of 16, and α-silyl carbanions, where oxygen is transferred to silicon, neutral diazomethane is extruded, and a net m/z change of 2 occurs (eq 4 and 5).

$$\underset{m/z\ 73}{Me_3Si^-} \xrightarrow{N_2O} \underset{m/z\ 89}{Me_3SiO^-} + N_2 \qquad (4)$$

$$\underset{m/z\ 73}{Me_2Si(H)CH_2^-} \xrightarrow{N_2O} \underset{m/z\ 75}{Me_2(H)SiO^-} + CH_2N_2 \qquad (5)$$

Reactions of CO_2, CS_2, and COS have also been studied[6,8] and allow characterization of α-silyl carbanions, which typically react by loss of CH_2 while either O or S is transferred to silicon (eq 6 and 7). We have also noted

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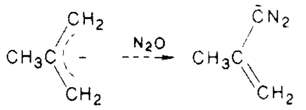
[7] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229.

[8] Bierbaum, V. M.; Grabowski, G. G.; DePuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389.

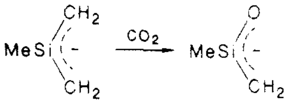
$$Me_3SiCH_2^- \xrightarrow{CO_2} Me_3SiO^- + CH_2C{=}O \quad (6)$$

$$Me_3SiCH_2^- \xrightarrow{CS_2 \text{ or } COS} Me_3SiS^- + CH_2C{=}S \text{ or } CH_2C{=}O \quad (7)$$

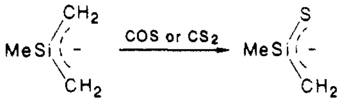
that N_2O is typically the least reactive of the neutrals ($N_2O < CO_2 < COS \approx CS_2$) and that delocalized anions and/or ones with lower basicity are less reactive with these neutrals. On the other hand, the carbon analogue of 1, the anion of isobutene, reacts with N_2O to extrude water and produce a diazo anion (eq 8).[9] The m/z 71 ion reacts with CO_2, COS, and CS_2 (eq 9 and 10), but not with N_2O (eq 11). We have formulated m/z 71 as 1 since these neutral reagents give either oxygen or sulfur transfer with the loss of CH_2 as we expect from α-silyl carbanions. The product of reaction 9 is the M − 1 ion arising from silaacetone, an anion recently reported by Squires and co-workers,[10] who have studied its reactivity in detail. One reaction reported by these authors involves the further reaction of the anion of silaacetone with CO_2 forming $MeSiO_2^-$. We did not observe this probably both because our product signals were small, and we operated without a large excess of CO_2. We rule out the alternate structure 2 because there seems to be no simple way that it could lose CH_2. Another alternate structure, $EtSiCH_2^-$, also seems unlikely since $MeSiCH_2^-$, prepared in the companion paper,[6e] has quite different reactivity from 1 reacting only with CS_2. The presence of the silicon atom in 1 makes it quite different from its carbon analogue since we do not see diazo anion formation (eq 8). Nevertheless, its other reactions (eq 9 and 10) indicate that enough negative charge is localized on carbon for reaction with these more reactive neutrals.



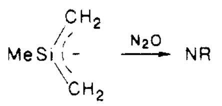
(8)



(9)



(10)



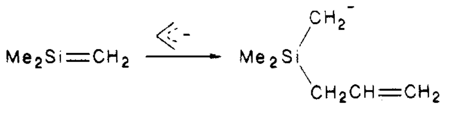
(11)

Attempts To Measure the Acidity of Dimethylsilene. We have attempted to measure the acidity of dimethylsilene by reacting it with a series of bases of varying strength. Both HO^- (ΔH°_{acid} = 391 kcal/mol) and H_2N^- (403 kcal/mol) abstract a proton from dimethylsilene while the addition of D_2O neither readily decreases the signal of 1 nor causes any H–D exchange. Reaction of MeO^- (379 kcal/mol) with dimethylsilene gives a small amount of 1, but reaction of 1 with MeOD eliminates 1 and gives a MeO^- signal which is far larger than the original amount of 1. This is likely caused by reaction between various basic anion impurities and MeOD (an occurrence which cannot be eliminated with our present experimental setup). When, however, *t*-BuOH (373 kcal/mol) reacts with 1, *t*-BuO^- is produced in approximately the same amount as that of the 1 we began with. These results limit our ability to accurately determine the acidity of dimethylsilene; however, it is clear that dimethylsilene is quite a bit more acidic than water and isobutene (390 kcal/mol). This result, coupled with the reactivity studies described in the last section, indicates that 1 is considerably stabilized relative to the isobutene anion.

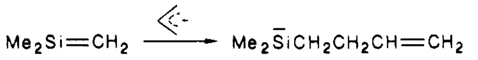
The uncertainty in the acidity of dimethylsilene points out a difficulty in these experiments that can be addressed in subsequent work. With the current experimental setup a variety of neutral and anionic species are present in the flow tube. These acidity experiments could be greatly simplified if 1 could be produced in the flow tube without any extranous neutral or anionic species. The selective ion flow tube (SIFT) currently under construction will permit a more exact determination of the acidity of dimethylsilene. In addition, the SIFT will allow us to address other questions which are now difficult to consider because some signals are weaker than in typical nonpyrolytic experiments. The greater sensitivity and simplicity of the SIFT should allow us, for example, to consider whether 1 undergoes behavior analogous to that of the deprotonated dimethylsilanone discovered by Squires and co-workers.[10] That anion, $Me(CH_2^-)Si{=}O$, undergoes reaction with deuterated alcohols possessing a β-hydrogen giving $Me_2Si(OD)O^-$ by a fairly complex addition–elimination pathway. Because of the inherent difficulties of our acidity experiments, we have not looked at this very interesting possibility for 1. When the SIFT becomes available, we will be able to consider this in detail.

The Reactions of Anions with Dimethylsilene. Typically dimethylsilene undergoes addition reactions with a variety of neutral polar reactants with the more nucleophilic of the polar partners adding to silicon.[2] We have studied the anionic additions of allyl and cyanide ion to dimethylsilene to explore both the ion–molecule analogue of such additions and to assess the related question of the addition of these anions at the carbon end of the double bond (reverse addition).

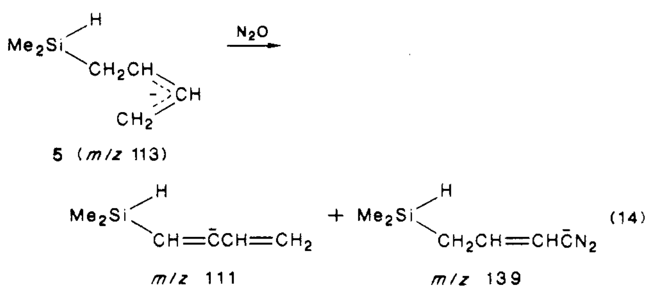
Addition of allyl anion to a stream of dimethylsilene gave an adduct signal (m/z 113) which we expected to be either the α-silyl carbanion 3 or the silyl anion adduct 4 (eq 12 and 13). Subsequent downstream reaction with N_2O indicated that this was not the case as signals at m/z 111 and 139 were observed. These were consistent with the formation of an allylic anion (**5**) and its subsequent reaction with N_2O (eq 14).[9] This allylic ion could arise either


(12)

3 (m/z 113)


(13)

4 (m/z 113)



5 (m/z 113)

(14)

m/z 111 m/z 139

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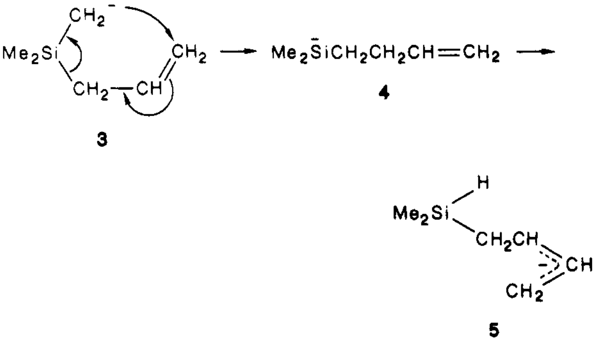
[9] Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849.

[10] Froehlicher, S. W.; Freiser, B. S.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 6863.

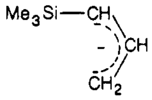
from 3 by migration of the allyl group from silicon to carbon (giving 4) followed by proton migration to silicon (eq 15) or directly from 4 followed by proton migration (eq 15). That is, the allylic anion 5 could plausibly form from either silicon or carbon addition of the allyl anion. An alternative possibility, the prototropic rearrangement of 3 to has been ruled out since this anion, when produced from $Me_3SiCH_2CH{=}CH_2$ and H_2N^-, reacts with N_2O to give $Me_2Si(CH_2CH{=}CH_2)O^-$ as the major and Me_3SiO^- as the minor product.


3

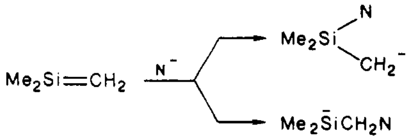
4

5

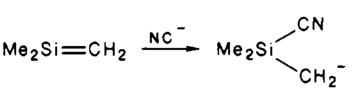
(15)



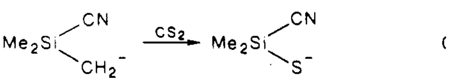
The potential for reverse addition depends on the relative stability of the α-silyl carbanion and the silyl anion (eq 12, 13, and 16). Additional experimental results designed to measure the Si–H and C–H acidity of methyl silanes address this matter. These suggest that the silyl anion is the more stable isomer. Furthermore, recent MP2/6-31++G** calculations by Gordon[11] on methylsilane reveal that the silyl anion is more stable than the α-silyl carbanion by approximately 20 kcal/mol. Thus, with anions which can bond nearly as strongly to carbon as to silicon,[4b] it seems reasonable to anticipate that the large difference in stability between silyl carbanions and silyl anions would favor reverse addition.


(16)

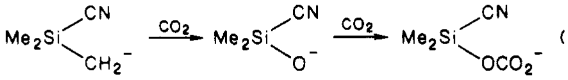
Reaction of dimethylsilene with cyanide ion gives a much clearer result; addition at silicon is the only path. An adduct forms (eq 17) which reacts with CO_2 and CS_2, but not with N_2O (we write it as addition at the carbon end of the cyanide anion recognizing both the possibility of nitrogen addition and the implication that nitrogen addition may alter the delicate balance between addition to carbon or silicon). Thus, CS_2 gives S transfer with the concomitant loss of thioketene (eq 18), and CO_2 reacts in an analogous way with the complication that, after CO_2 transfers O to silicon with ketene loss, further reaction with CO_2, a common reaction of siloxides and CO_2,[6b] also competes (eq 19). When the flow of CO_2 is varied either product can be the major one.



$$Me_2Si{=}CH_2 \xrightarrow{NC^-} Me_2Si(CN)CH_2^- \quad (17)$$



$$Me_2Si(CN)CH_2^- \xrightarrow{CS_2} Me_2Si(CN)S^- \quad (18)$$



$$Me_2Si(CN)CH_2^- \xrightarrow{CO_2} Me_2Si(CN)O^- \xrightarrow{CO_2} Me_2Si(CN)OCO_2^- \quad (19)$$

Cycloaddition Reactions of Dimethylsilene. Dimethylsilene undergoes a variety of cycloaddition reactions, the most pervasive of which is its self-condensation to 1,1,3,3-tetramethyl-1,3-disilacyclobutane. In addition, the cycloaddition reactions with O_2, carbonyl compounds, and imines as well as olefins and conjugated dienes have not only helped define the reactivity patterns of silenes but also made available a number of other multiply bonded reactive intermediate silicon species.[2,12]

We have been able to demonstrate the self-condensation of dimethylsilene by both reaction with F^- and H_2N^- (yielding the F^- adduct and the M − 1 ions of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, respectively). The signal intensities in these experiments are again much smaller than normal. This, however, appears to be a property of this disilacyclobutane not the pyrolysis setup, since, when it is directly introduced into the flow tube, it gives very small product signals with F^- and H_2N^- under a variety of conditions.

We have attempted to carry out two other cycloaddition reactions with dimethylsilene. Reaction with O_2 was carried out in the presence of H_2N^- by adding O_2 and DMSCB simultaneously through the pyrolysis port. A small amount of the known[10] deprotonated dimethylsilanone $Me(CH_2^-)Si{=}O$ was detected, but efforts to increase the signal and to simplify the reaction (there were several other reaction products) proved futile. In a related experiment, we have shown that dimethylsilanone, generated independently from 1,3,3-trimethyl-6-oxa-3-silabicyclo[3.1.0]hexane (6),[13] could be deprotonated to but a small extent, although larger amounts of the M − 1 anion of its trimer, D_3, were detected. Although it seems clear that dimethylsilanone forms from the bicyclic precursor 6, it is less certain whether it forms by cycloaddition of the silene with O_2. Even though both reactions gave small amounts of the M − 1 anion of dimethylsilanone, we have not pursued this chemistry further both because of our experimental difficulties and because Squires and coworkers[10] have reported both a superior method for its production and an exhaustive study of its reactivity.

Attempted cycloaddition of dimethylsilene and butadiene was even more problematic. While butadiene and DMSCB were being added through the pyrolysis port, attempts were made to convert any possible cycloaddition product to an anionic species by flowing H_2N^-, HO^-, and F^- past the pyrolizer. Neither H_2N^- nor HO^- gave any evidence that cycloaddition had occurred, while F^- gave only a very small peak corresponding to a fluoride adduct of the cycloaddition product. We, thus, have only a faint indication of a cycloaddition reaction with butadiene.

Conclusion

We have generated dimethylsilene by pyrolysis of dimethylsilacyclobutane. It undergoes addition reactions with allyl anion and cyanide ion. The addition of cyanide occurs at the silicon end of the polar Si–C bond while the results with allyl are consistent with either silicon or carbon

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[11] Gordon, M. S., personal communication.

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addition. Proton abstraction from this silene yields the silicon analogue of the isobutene anion. Its chemical behavior indicates that it is more highly stabilized than either the isobutene anion or $Me_3SiCH_2^-$. Attempts to measure the acidity of dimethylsilene, while not wholly successful, have established that it is more acidic than isobutene.

Cycloaddition reactions of dimethylsilene with O_2 and butadiene have been attempted. Oxygen appears to react to give dimethylsilanone, which has been detected as its deprotonated anion. Reaction with butadiene may occur, but products have only been detected in a stream of F^-.

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Note Added in Proof. A recent report on $Me(CH_2^-)Si{=}O$ has been published: Tumas, W.; Saloman, K. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2541.

Registry No. $Me_2Si{=}CH_2$, 4112-23-6.

Gas-Phase Ion Chemistry of Dimethylsilylene

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A pyrolysis port fitted to the flowing afterglow instrument has been used to prepare dimethylsilylene. Its ion–molecule chemistry has been explored by reaction with fluoride and amide ions. Fluoride ion adds to dimethylsilylene giving an adduct anion which has been characterized by reaction with nitrous oxide. Amide ion abstracts a proton from dimethylsilylene. Characterization of the resulting M − 1 ion has been made by reaction with carbon disulfide and various acids. The gas-phase acidity of this anion has been determined to be near that of methanol (379 kcal/mol). The isomerization of dimethylsilylene and methylsilene has been probed by fluoride ion followed by nitrous oxide reaction. We have also demonstrated at the highest temperatures we can study that methylsilene slightly predominates over dimethylsilylene. Reaction of dimethylsilylene and butadiene has also been studied.

Introduction

Silylene chemistry has been actively pursued since the mid-1960s, undoubtedly the result of the tremendous interest in the chemistry of carbenes.[2] One of the first indications of the preparation of dimethylsilylene was provided by Gilman and co-workers in its reverse Diels–Alder extrusion from several bicyclic precursors.[3] Subsequently, dimethylsilylene has been prepared by a variety of methods with its extrusion from disilanes being one of the most reliable preparative methods for thermal generation.[2-4] Studies of silylenes of recent vintage have examined in detail their reactivity, structure, and theoretical characterization,[2] culminating most recently in the resolution of the conflicting reports on the equilibrium between dimethylsilylene and methylsilene.[5]

Our interest in dimethylsilylene focuses on its chemistry with anionic reagents in the gas phase. Previous work using the flowing afterglow (FA) techniques has provided a wealth of novel chemistry of organosilicon compounds.[6] We have not only examined the reactivity of organosilicon compounds but also utilized them both to prepare unusual gas-phase species and to examine important fundamental questions in gas-phase chemistry. We sought, then, to apply the powerful FA technique to the chemistry of dimethylsilylene and to study its reactions with anions and neutral molecules as well as its acid–base behavior.

Experimental Section

These experiments were performed in a flowing afterglow system at 298 K as previously described[7] with one modification. A port at 90 cm has been added to allow the introduction of neutral pyrolysates. Thus, neutral reactants are passed through a quartz tube wrapped with resistance wire. The resulting pyrolysis mixture is swept into the flow tube by the normal flow of helium bath gas although additional helium flow can be directed through the quartz tube when necessary. The resistance heater is controlled by a variable transformer, and approximate temperatures are measured by using a chromel–alumel thermocouple inserted in a small indentation at the end of the quartz tube. Further details of the pyrolysis system are reported in the companion paper.[6e]

Amide and fluoride ions were produced by electron impact on NH_3 and NF_3, respectively, HO^- was produced by dissociative electron attachment to N_2O followed by hydrogen atom ab-

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