nance[16] is highly indicative of the presence of h^2-**3**, because this configuration, in which the ligands are positioned in a pseudotetrahedral arrangement about Ti, appears to be the only possible monomeric structure containing magnetically equivalent nitrogen nuclei.[17] The large ^{15}N nmr chemical-shift difference for h^1-**3** and h^2-**3** is gratifying and augurs well for ^{15}N nmr spectroscopy for studies of soluble dinitrogen complexes.

The infrared spectrum of **3** in heptane at −65°[18] provides quite convincing evidence for two distinct isomers which differ in their modes of nitrogen coordination to Ti. There is a band at 2056 cm^{-1} of medium intensity and a strong band at 2023 cm^{-1}, which may be attributed to the N≡N stretching frequencies of h^2-**3** and h^1-**3**. Although we are unable to make specific assignments, the observation of two bands is clearly consistent with eq 4. Furthermore, the relatively small separation of these ir bands indicates that the edge-on and end-on nitrogen coordinations involve comparable changes of the N≡N bond order.

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(16) The possibility of the singlet resonance arising from free $^{15}N_2$ seems remote because its solubility at −60° is at least 200 times less than the experimental concentration of **3**.

(17) An alternative interpretation of the data can be based on the assumption that **3** is an equilibrium mixture of h^1-**3** and a dimer such as $[C_5(CH_3)_5]_2Ti(\mu\text{-(di-}h^1)N_2)_2Ti[C_5(CH_3)_5]_2$; however, the small temperature dependence of the equilibrium, observed in the ^1H and ^{13}C nmr and ir experiments,[4] is more indicative of the intramolecular process, $h^1\text{-}\mathbf{3} \rightleftharpoons h^2\text{-}\mathbf{3}$.

(18) The ir spectra were obtained on a Perkin-Elmer 225 spectrophotometer in a vacuum-tight solution cell equipped with sapphire windows. Except for small frequency shifts, identical results were observed in toluene; however, this solvent was less suitable than heptane due to the interference of several weaker solvent peaks in the region of interest.

John E. Bercaw,* Edward Rosenberg, John D. Roberts
Contribution No. 4765
Noyes and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received September 26, 1973

Thermolysis of Silacyclobutanes in the Presence of Imines. Definitive Evidence for a p_π–p_π Silicon–Nitrogen Double-Bonded Reaction Intermediate

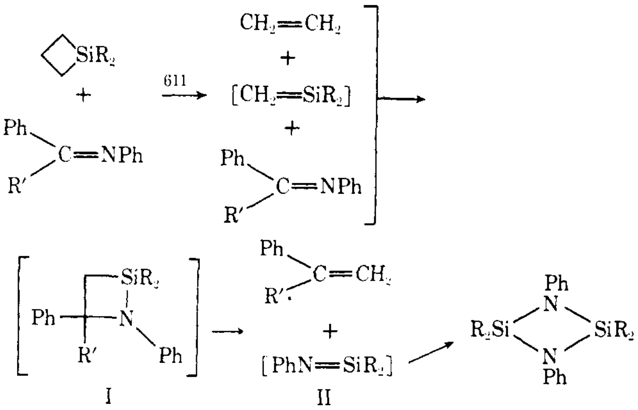
Sir:

In recent years evidence for the formation of intermediates containing p_π–p_π silicon–carbon,[1] silicon–silicon,[2] and silicon–oxygen[3] double bonds has appeared in the literature. However, only two reports[4,5] have considered the possibility of formation of a transient silicon–nitrogen doubly bonded species. In both of these,[4,5] the only evidence comprised isolation of a cyclodisilazane from reactions which may easily be envisaged as proceeding by pathways not involving a silicon–nitrogen double-bonded intermediate.

Based upon previous work showing formation of $R_2Si{=}CH_2$ as an intermediate in the gas-phase pyrolysis of silacyclobutanes, we believe that the experiments described below provide strong evidence for the existence of intermediates containing p_π–p_π silicon–nitrogen double bonds.

Gas-phase pyrolysis[6] of benzene solutions of a 1,1-disubstituted silacyclobutane and an *N*-phenylimine,[7] afforded roughly comparable yields (see Table I) of olefinic product and the corresponding cyclodisilazane. Considering the nature of the reactants, isolation of cyclodisilazane and olefinic products is reasonably accommodated by the mechanism outlined in Scheme I.

Scheme I



Glpc analysis of the crude pyrolysates indicated that these were reasonably clean reactions. Volatile byproducts, other than the imine decomposition products,[7] were not formed in appreciable quantities (<5%).

In an effort to trap the proposed silicon–nitrogen bonded species (II) directly, a pyrolysis using a second trapping reagent (benzophenone) was carried out. Pyrolysis of a solution of 1,1-dimethylsilacyclobutane (5.06 mmol), *N*-phenylbenzaldimine (20.0 mmol),[8]

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(1) (a) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1969); (b) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7926 (1972). (c) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 54 (1973), and references therein; (d) D. N. Roark and L. H. Sommer, *ibid.*, 167 (1973); (e) C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, *J. Organometal. Chem.*, in press; (f) R. D. Bush, C. M. Golino, D. V. Roark, and L. H. Sommer, *J. Organometal. Chem.* **59**, C17 (1973).

(2) D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, **94**, 5837 (1972).

(3) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971). See also ref 1d and e.

(4) W. T. Reichle, *Inorg. Chem.*, **3**, 402 (1964). Thermal decomposition of triphenylsilyl azide at 680° gave up to 60% yields of hexaphenylcyclodisilazane with the remainder being the corresponding linear polymer.

(5) W. Fink, *Helv. Chim. Acta*, **49**, 1408 (1966). Much of this material is summarized in an earlier review: W. Fink, *Angew. Chem., Int. Ed. Engl.*, **5**, 760 (1966). Reaction of diorganosilanes with primary amines using catalytic amounts of alkali metals or their hydrides gave high yields of cyclodisilazanes.

$$2RNH_2 + 2H_2SiR_2' \xrightarrow{-2H_2} 2RN(H)Si(H)R_2' \xrightarrow{-2H_2} (R_2'SiNR)_2$$

(6) Identical pyrolysis conditions (nitrogen flow system, 760 Torr, 611°) were used for all of the reactions discussed below.

(7) When either *N*-phenylbenzaldimine or benzophenone phenylimine was pyrolyzed alone (0.4 *M* in benzene) glpc analysis of the pyrolysates using internal standards indicated 22 and 40% decomposition, respectively: *N*-phenylbenzaldimine yielded comparable amounts of benzonitrile and biphenyl; benzophenone phenylimine gave comparable amounts of biphenyl and benzophenone imine, $Ph_2C{=}NH$. Both reactions also produced small quantities of high molecular weight products. It is unlikely that decomposition products of the imines are precursors to the observed products and many of the isolated product yields in Table I are larger (50 *vs.* 22–40%) than the amount of decomposition of the corresponding imine.

(8) It was necessary to use a large excess of *N*-phenylbenzaldimine relative to benzophenone since the latter is a much more efficient trap for the silicon–carbon double bond.

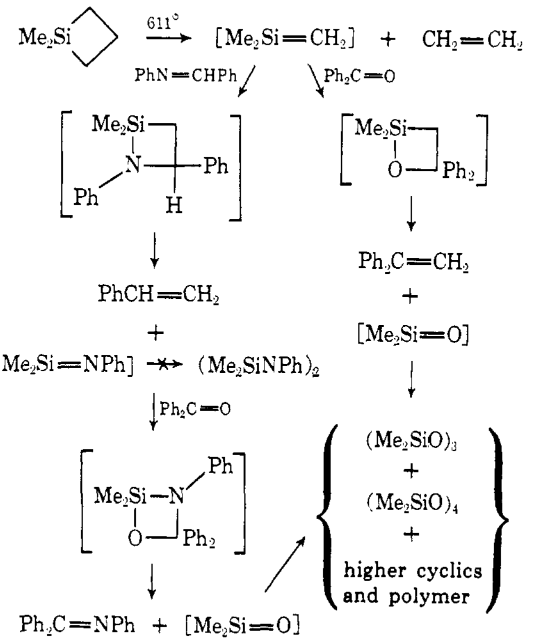
Table I. Pyrolysis of Silacyclobutane–Imine Solutions at 611°

Silacyclobutane (mmol)	Imine (mmol)	Benzene (mmol)	Products (% yield)[a]	
$(CH_2)_3SiMe_2$ (21.2)	$PhCH{=}NPh$ (14.5)	(59)	$(Me_2SiNPh)_2$ (41)	$PhCH{=}CH_2$ (32)
$(CH_2)_3SiMe_2$ (13.2)	$Ph_2C{=}NPh$ (5.20)	(55)	$(Me_2SiNPh)_2$ (30)	$Ph_2C{=}CH_2$ (56)
$(CH_2)_3SiPh_2$ (6.33)	$Ph_2C{=}NPh$ (3.03)	(62)	$(Ph_2SiNPh)_2$ (25)[b,c]	$Ph_2C{=}CH_2$ (33)[b]

[a] These are based on the amounts of material actually isolated (either by preparative glpc or crystallization) and are probably 10–20% lower than the quantities actually present. All reaction products are known compounds and, except as noted, were completely characterized by their ir and nmr spectra and, where applicable, melting points. [b] Calculated after correction for a 24% recovery of limiting reagent. [c] Material was impure (mp 335–343°, lit.[5] mp 355.5°). Further recrystallization did not afford a purer sample.

benzophenone (4.73 mmol), and benzene (66.7 mmol) afforded a homogeneous, yellow pyrolysate which, after resolution by preparative glpc afforded benzophenone phenylimine (0.79 mmol), styrene (0.78 mmol), 1,1-diphenylethylene (1.95 mmol), octamethylcyclotetrasiloxane (0.04 mmol), hexamethylcyclotrisiloxane (trace), benzophenone (1.74 mmol), and *N*-phenylbenzaldimine (12.7 mmol). Glpc analysis of the pyrolysate did not detect any 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane, $(Me_2SiNPh)_2$. Isolation of benzophenone phenylimine provides definitive evidence for the formation of $Me_2Si{=}NPh$ and its reaction with benzophenone since pyrolysis of equimolar quantities of either benzophenone and *N*-phenylbenzaldimine or benzophenone and $(Me_2SiNPh)_2$ did not produce detectable quantities of this material. An explanation which accommodates all of these observations is outlined in Scheme II. Assuming quantitative formation of $Me_2Si{=}CH_2$ and correcting, on the basis of the isolated yield of 1,1-diphenylethylene, for the fact that 38.5% of the $Me_2Si{=}CH_2$ produced reacted with benzophenone, then the 0.79 mmol of benzophenone phenylimine isolated represents a 25.4% yield of trapped $Me_2Si{=}NPh$. This is a minimum value since isolated yields were used and factors such as decomposition of the trapping reagents and products and other side reactions were ignored. The absence of significant side reactions and the relatively high yield of benzophenone phenylimine indicate that reaction schemes more complex than II are unlikely.

Scheme II



The absence of $(Me_2SiNPh)_2$ and the comparable quantities of styrene and benzophenone phenylimine observed indicate that benzophenone is a very efficient trapping reagent for silicon–nitrogen doubly bonded intermediates. This is in accord with our observation[1e] that benzophenone is an excellent trapping reagent for intermediates containing silicon–carbon double bonds.

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C. M. Golino, R. D. Bush, L. H. Sommer*
Department of Chemistry, University of California
Davis, California 95616
Received September 20, 1973

Mechanisms of Unimolecular Gas-Phase γ-Hydrogen Rearrangements of Radical Cations. The Influence of Entropy as Opposed to Energy

Sir:

Those γ-hydrogen rearrangements commonly referred to as McLafferty-type rearrangements have probably attracted more attention than any other rearrangement encountered in mass spectrometry;[1] yet there is still considerable contention as to whether these ubiquitous rearrangements occur in a concerted or a stepwise manner.[2–6] We have sought to elucidate this persistent question by applying the powerful capabilities of field ionization kinetics (FIK)[7–9] to a study of two complementary γ-hydrogen rearrangements in hexanal.[10,11] The FIK technique[7–9] allows rates of unimolecular gas-phase reactions of (radical-) cations to be measured over a time range extending from 10^{-12} or 10^{-11} sec to 10^{-6} or 10^{-5} sec.

The rates of formation of *m/e* 45 (C_2H_3DO) and *m/e* 57

(1) (a) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956); (b) *ibid.*, **31**, 82 (1959).

(2) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 7239 (1968).

(3) C. Fenselau, J. L. Young, S. Meyerson, W. R. Landis, E. Selke, and C. Leitch, *J. Amer. Chem. Soc.*, **91**, 6847 (1969).

(4) P. B. Fairweather and F. W. McLafferty, *Org. Mass. Spectrom.*, **2**, 755 (1969).

(5) P. Brown, A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970).

(6) G. S. Smith and F. W. McLafferty, *Org. Mass Spectrom.*, **5**, 483 (1971).

(7) (a) H. D. Beckey, *Z. Naturforsch. A*, **16**, 505 (1961); *ibid.*, **21**, 1920 (1965); H. D. Beckey, H. Hey, K. Levsen, and G. Tenschert, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 101 (1969).

(8) P. J. Derrick and A. J. B. Robertson, *Proc. Roy. Soc., Ser. A.*, **324**, 491 (1971).

(9) A. M. Falick, P. J. Derrick, and A. L. Burlingame, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 101 (1973).

(10) R. J. Leidtke and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 6814 (1969).

(11) S. Meyerson, C. Fenselau, J. L. Young, W. R. Landis, E. Selke, and L. C. Leitch, *Org. Mass Spectrom.*, **3**, 689 (1970).