

nance¹⁶ is highly indicative of the presence of $h^2\text{-}3$, 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 ¹⁵N nmr chemical-shift difference for $h^1\text{-}3$ and $h^2\text{-}3$ is gratifying and augurs well for ¹⁵N nmr spectroscopy for studies of soluble dinitrogen complexes.

The infrared spectrum of **3** in heptane at -65°C 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 $\text{N}\equiv\text{N}$ stretching frequencies of $h^2\text{-}3$ and $h^1\text{-}3$. 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 $\text{N}\equiv\text{N}$ bond order.

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(16) The possibility of the singlet resonance arising from free ¹⁵N₂ 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 $h^1\text{-}3$ and a dimer such as $[\text{C}_5(\text{CH}_3)_5\text{Ti}(\mu\text{-}(\text{di-}h^1)\text{N}_2)_2\text{Ti}(\text{C}_5(\text{CH}_3)_5)_2]$; however, the small temperature dependence of the equilibrium, observed in the ¹H and ¹³C nmr and ir experiments,⁴ is more indicative of the intramolecular process, $h^1\text{-}3 \rightleftharpoons h^2\text{-}3$.

(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.

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Thermolysis of Silacyclobutanes in the Presence of Imines. Definitive Evidence for a $p_\pi\text{-}p_\pi$ Silicon-Nitrogen Double-Bonded Reaction Intermediate

Sir:

In recent years evidence for the formation of intermediates containing $p_\pi\text{-}p_\pi$ silicon-carbon,¹ silicon-silicon,² and silicon-oxygen³ double bonds has ap-

(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).

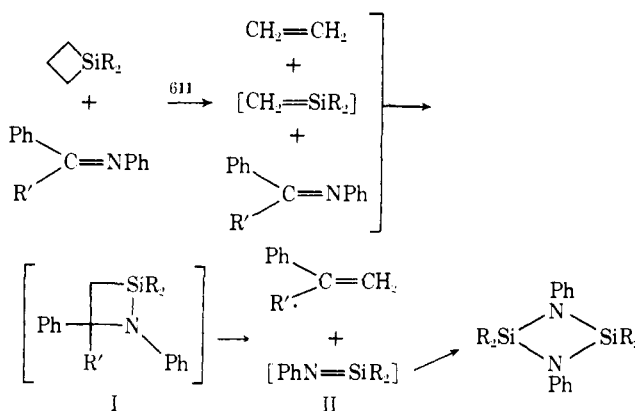
(3) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971). See also ref 1d and e.

peared 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 $\text{R}_2\text{Si}=\text{CH}_2$ 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 $p_\pi\text{-}p_\pi$ silicon-nitrogen double bonds.

Gas-phase pyrolysis⁶ 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



Gpc analysis of the crude pyrolysates indicated that these were reasonably clean reactions. Volatile by-products, 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

(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.



(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) gpc 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, $\text{Ph}_2\text{C}=\text{NH}$. 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.

