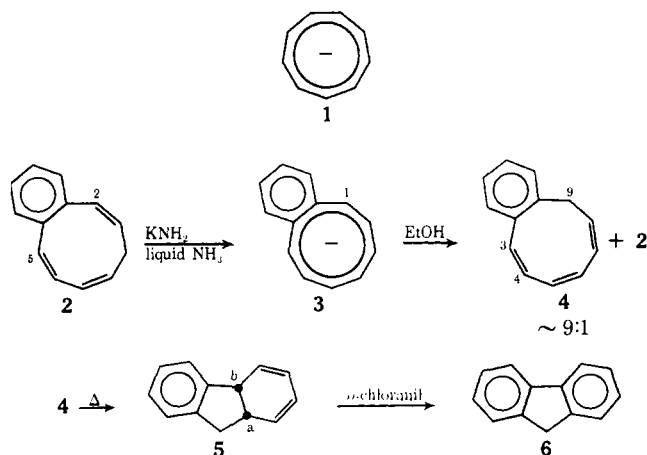


that it is the largest possible member of the series to exist in planar fully delocalized (D_{9h})¹ form and thus to be classed as "aromatic."² Nonetheless, the rather central question of how does this 10π monocycle compare with benzene in terms of π -electron delocalization or will π delocalization in this molecule persist under the perturbation of benzenoid fusion remained largely unanswered, since the obvious model compound necessary for such a study, the benzocyclononatetraenyl anion (**3**), had been unavailable.³ Presently, we describe the generation and direct observation of this substance and, in addition, its use in the preparation of the hitherto unknown benzocyclononatetraene (benzo-CNT) shown in **4**. Treatment of benzo-CNT **2** at



-55° with potassium amide in liquid ammonia, containing trimethylamine as internal standard, produces a dark solution displaying nmr signals⁴ at τ 1.78 (2 H, doublet of doublets, $J = 8$ Hz, 4.5 Hz), 2.18 (2 H, doublet, $J = 14.5$ Hz, H_1) and 2.4–3.5 (7 H, multiplet). Comparison of this spectrum to that of **2**⁵ reveals several structural features of **3**. First, we note that the two 1 H doublets present in the spectrum of **2** (H_2 at τ 3.28 and H_5 at 3.68) reduce to a single 2 H doublet in the spectrum of **3** (H_1 at τ 2.18). This change requires that **3** possess twofold symmetry and hence that the charge formally associated with the C_9 segment of the molecule be delocalized over at least seven of its centers. In fact, brief comparison of the benzenoid resonances of **2** (4 H singlet at τ 2.81)⁵ and **3** (two 2 H doublets of doublets centered at τ 1.78 and 3.04) appears to indicate that charge delocalization in **3** is not limited to the cyclononatetraenyl portion but extends into the benzene moiety as well. Moreover, judging from the significant downfield shift experienced by all protons bound to the C_9 portion of the molecule on going from **2** to **3**,⁶ and

(1) H. E. Simmons, D. B. Chesnut, and E. A. LaLancette, *J. Amer. Chem. Soc.*, **87**, 982 (1965).

(2) For a recent review on the subject, see P. J. Garratt and M. V. Sargent in "Nonbenzenoid Aromatics II," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1971, Chapter 4.

(3) A dibenzo derivative of **1**, recently prepared, was reported to exhibit nmr characteristics best ascribable to the gradual development of a delocalized π frame: P. J. Garratt and K. A. Knapp, *Chem. Commun.*, 1215 (1970).

(4) We are indebted to Professor S. W. Staley and Mr. A. W. Orvedal for their valuable assistance in the preparation of the nmr sample of **3** and the determination of its spectrum.

(5) A. G. Anastassiou, S. S. Libsch, and R. C. Griffith, *Tetrahedron Lett.*, 3103 (1973).

(6) The downfield shift of signals is especially striking in connection with the two "olefinic" doublets of **2** appearing at τ 3.28 (H_2) and 3.68 (H_5) which merge into a single "aromatic" doublet at τ 2.18 (H_1) on passing to **3**.

this in spite of the shielding effect of the added negative charge, it may safely be concluded that π -electron delocalization in **3** is attended by strong ring diamagnetism.

The nmr characteristics of the benzocyclononatetraenyl anion thus serve to securely classify the molecule as "aromatic" and one best viewed as a 14π unit rather than a benzannelated 10π system. The obvious conclusion then is that the cyclononatetraenyl anion (**1**) closely resembles benzene in its affinity toward π delocalization.

Protonation of **3** provides chemical evidence for its [7.4.0] frame and serves, in addition, as a convenient source of the novel benzo-CNT, **4**. Specifically, slow addition of ethanol to **3** in liquid ammonia at -70° leads to a two-component mixture consisting (nmr) of ca. 90% **4** [nmr (60 MHz, CDCl_3 , -25°) τ 2.85 (4 H, narrow multiplet), 3.28 (1 H, doublet, H_3 , $J_{34} = 11.5$ Hz), 3.76 (1 H, doublet H_4 , $J_{43} = 11.5$ Hz), 4.28 (2 H, narrow multiplet), 4.50 (2 H, narrow multiplet), and 6.43 (2 H, doublet, H_9 , $J \sim 3$ Hz)] and 10% **2** (nmr).^{5,7} Unlike **2**, which is thermally quite stable, isomer **4** is heat sensitive, rapidly ($k_{20.6} = 1.30 \pm 0.12 \times 10^{-4}$ sec⁻¹, $\Delta G^\ddagger = 22.4$ kcal/mol) and cleanly rearranging to benzobicyclic **5** [colorless oil, λ_{max} (C_8H_{14}) 253 nm(sh) (ϵ 2900), 260.5 (3600), 267.5 (4100), 273.5 (3700), and 279(sh) (2000); nmr (60 MHz, CDCl_3) τ 2.79 (4 H, narrow multiplet), 4.20 (4 H, singlet), 6.05 (1 H, broad doublet, $J = 9$ Hz) and 6.6–7.3 (3 H, multiplet); m/e 168 (P^+ ; 86%)]. The structure of **5** follows clearly from the spectral data (the magnitude of J_{ab} (9 Hz) attesting to the presence of cis fusion) and receives added confirmation from its conversion to fluorene (**6**) (mmp, ir, nmr) on exposure to *o*-chloranil.

Finally, we note that the electrocyclicization of **4** to **5**, which is of course permitted by orbital symmetry, does not appreciably differ in rate from that of *cis*⁴-CNT itself ($\Delta G^\ddagger_{20.6} = 22.9$ kcal/mol)⁸ and are thus forced to conclude that benzannelation does not appreciably affect the thermal sensitivity of the CNT frame.

Acknowledgment. We are grateful to the National Science Foundation (GP-38553X) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(7) The proportion in which these two isomers are formed is a sensitive function of the rate of protonation, with increasingly larger quantities of **2** being produced on faster addition of the alcohol. This finding is fully consistent with the lower electron density at C_1 compared to C_3 of the anion indicated by the respective nmr chemical shifts of the protons associated with these positions.

(8) This value was calculated from the activation terms (ΔH^\ddagger and ΔS^\ddagger) given by G. Boche, H. Bohme, and D. Martens, *Angew. Chem.*, **81**, 565 (1969).

(9) National Science Foundation Graduate Trainee 1969–1973.

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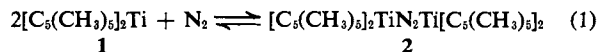
¹H, ¹³C, and ¹⁵N Nuclear Magnetic Resonance Studies of a Dinitrogen Complex of Permethyltitanocene. Evidence for Molecular Nitrogen Coordinated "Edge-on" to a Transition Metal

Sir:

In connection with the current interest in transition metal dinitrogen complexes and their possible roles in

nitrogen-fixing reaction systems, we have obtained results which bear on the structure of a titanium dinitrogen complex in solution. We report here successful application of ^{15}N nmr spectroscopy to studies of a transition metal dinitrogen complex which provides a potentially powerful technique for elucidation of the structure of such complexes.¹

In the synthesis of permethyltitanocene, $[\text{C}_5(\text{CH}_3)_5]_2\text{Ti}$ (**1**), a rapid and reversible reaction (eq 1) with di-



nitrogen was observed.^{2,3} The product, **2**, has recently been successfully isolated as a paramagnetic crystalline solid through exposure of pentane solutions of **1** to nitrogen at 0° .⁴ Crystalline **2** is moderately soluble in toluene at room temperature, and quantitatively, but slowly, releases its nitrogen under reduced pressure, as expected from eq 1. On cooling solutions of **2** in toluene below -10° under 1 atm of nitrogen, more dinitrogen is absorbed and there is a color change from dark blue to intense purple-blue. At -80° , the absorbed nitrogen is entirely retained, even under reduced pressure. Measurements of the nitrogen released on reversion to **1** at room temperature are in close agreement with the stoichiometry $[\text{C}_5(\text{CH}_3)_5]_2\text{TiN}_2$ (**3**), for the low-temperature stable, purple-blue dinitrogen complex.

The solubility of **3** in hydrocarbon solvents is high, and the ^1H nmr spectrum in toluene- d_6 at -52° shows a single, somewhat broadened, resonance centered on δ 1.78 ppm.⁸ On cooling to -62° , the signal splits into two resonances of approximately equal intensity at 1.88 and 1.68 ppm. Further cooling to -72° results in no substantial further change, whereas warming to above -45° leads to severe broadening of the signal, probably due to the onset of dissociative exchange with **1** (eq 2), and/or with **2** (eq 3). Below -45° , **1** and **2**

(1) Previous attempts to obtain ^{15}N nmr spectra of dinitrogen complexes of ruthenium (cf. J. A. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 2560 (1970)) have been uniformly unsuccessful although the shifts of complexes of the type Ru-N₂-Ru are easily obtained (unpublished work by Drs. R. L. Lichter and J. P. Warren in collaboration with Professors J. A. Armor and H. Taube).

(2) J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2045 (1971).

(3) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

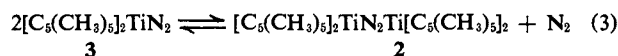
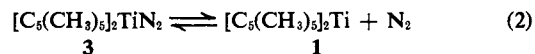
(4) Recent studies have revealed that samples of **1** prepared as described previously^{1,2} were contaminated with considerable amounts of the titanium(III) hydride complex, $[\text{C}_5(\text{CH}_3)_5]_2\text{TiH}$. Analytically pure samples of **1** are most conveniently obtained from crystalline samples of **2**. Detailed synthetic procedures for **1** and **2** together with their physical and chemical properties will appear in an article in preparation: J. E. Bercaw, unpublished work.

(5) Although no molecular weight studies on **3** have been undertaken because of its instability with respect to conversion to **2** at ambient temperatures, monomeric **3** appears most likely for the following reasons: (a) with the exception of **2**, molecular weight determinations have established a definite preference for monomeric permethyltitanocene derivatives,⁴ undoubtedly due to unfavorable steric crowding of bulky pentamethylcyclopentadienyl ligands in polymeric species (for example, $[\text{C}_5(\text{CH}_3)_5]_2\text{TiH}$ and $[\text{C}_5(\text{CH}_3)_5]_2\text{Ti}$ are exclusively monomeric in benzene solution, whereas their $(\text{C}_5\text{H}_5)_2\text{Ti}$ counterparts have been shown to be dimeric);^{3,5} (b) the infrared spectra to be discussed below.

(6) J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **91**, 7301 (1969).

(7) A total of 210 mg of **2** in 3.3 ml of $\text{C}_6\text{D}_6\text{CD}_3$ was stirred under 1 atm nitrogen, filtered into a 10-mm nmr tube, and sealed off under N_2 , with all operations being carried out at -80° . The spectra were recorded on a Varian XL-100 spectrometer operating in the Fourier transform mode.

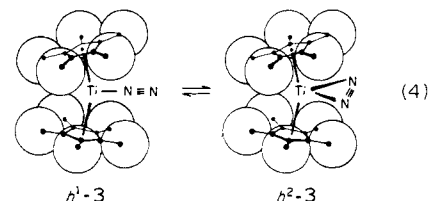
(8) The ^1H chemical shifts were calculated from their positions relative to the residual aromatic protons in toluene- d_6 and converted to values relative to (and downfield of) TMS at δ 0.



do not appear to be present to a significant extent as judged by the absence of their characteristic ^1H nmr signals.⁹ The results thus imply the presence of two forms of **3** which are in rapid equilibrium on the nmr time scale above -62° .

This interpretation is supported by ^{13}C nmr spectra of the same sample. Below -45° , two resonances of approximately equal intensity are observed at 28.0 and 29.4 ppm,¹⁰ attributable to the ring carbons of the two forms of **3**. At higher field, a single, slightly broadened resonance attributable to the methyl carbons of **3** appears at 125.5 ppm. These assignments were confirmed by comparison with the ^{13}C shifts of $[\text{C}_5(\text{CH}_3)_5]_2\text{Ti}(\text{CH}_3)_2$,¹² and by the spectrum at -58° without proton decoupling, the highest field signal being then the expected quartet. Clearly, the two forms of **3** differ slightly in structure because only the ring carbons exhibit resolvable chemical-shift differences.

The ^{15}N nmr studies of **3** were undertaken using a sample prepared as described above, except substituting 1 atm doubly labelled $^{15}\text{N}_2$ ¹³ for ordinary dinitrogen. This material gave ^{13}C spectra identical with those described above. The ^1H -decoupled ^{15}N nmr spectrum¹⁴ at -61° showed two clear doublets centered on 84.6 and 134.0 ppm, respectively, upfield of a third, rather sharp, singlet resonance. These signals, taken in conjunction with the ^1H and ^{13}C nmr data, are indicative of an "end-on" ($h^1\text{-N}_2$) \rightleftharpoons "edge-on" ($h^2\text{-N}_2$) equilibrium for **3** (eq 4), with the forms having com-



parable concentrations at this temperature. The two doublets are attributed to $h^1\text{-3}$ wherein the non-equivalent ^{15}N nuclei are magnetically coupled with $^1J_{^{15}\text{N}-^{16}\text{N}} = 7 \pm 2$ Hz.¹⁵ The remaining singlet reso-

(9) The ^1H nmr spectrum of **2** exhibits a resonance which is shifted to 60.9 ppm downfield of TMS at -55° while **1** shows a similarly shifted resonance at 86.2 ppm at -51° : J. E. Bercaw, unpublished results.

(10) The spectra were obtained at 15.09 MHz with a DFS-60 spectrometer, described earlier,¹¹ operating in the Fourier transform mode. The ^{13}C chemical shifts are relative to (and upfield of) the C_1 resonance of toluene- d_6 .

(11) J. D. Roberts, F. H. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970); B. L. Hawkins and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **70**, 1027 (1973).

(12) The ^1H -decoupled ^{13}C nmr spectrum (toluene- d_6):¹⁰ $[\text{C}_5(\text{CH}_3)_5]_2\text{Ti}(\text{CH}_3)_2$, s, δ 17.8 ppm; $[\text{C}_5(\text{CH}_3)_5]_2\text{Ti}(\text{CH}_3)_2$, s, δ 118.8; $[\text{C}_5(\text{CH}_3)_5]_2\text{Ti}(\text{CH}_3)_2$, s, δ 88.6 ppm.

(13) Merck Sharpe and Dohme " $^{15}\text{N}_2$ " with a composition from the mass spectrum of $^{16}\text{N}^{15}\text{N}$, 91.6; $^{16}\text{N}^{14}\text{N}$, 7.6; $^{14}\text{N}^{14}\text{N}$, 0.87%.

(14) The ^{15}N nmr spectra were obtained at 6.08 MHz with a DFS-60 spectrometer¹¹ operating in the Fourier transform mode. Due to experimental limitations, no internal ^{15}N reference compound appeared to be compatible with **3**. The low-field signal, however, comes about 615 ppm downfield of the signal observed for a separate sample of 11 M aqueous $(\text{C}_2\text{H}_5)_4^{15}\text{NCl}$.

(15) When account is taken of the difference in gyromagnetic ratios, this coupling is comparable to the ^{13}C - ^{16}N coupling of 19.8 Hz observed for $\text{HC}\equiv\text{N}$: G. Binsch and J. D. Roberts, *J. Phys. Chem.*, **72**, 4310 (1968).

nance¹⁶ 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 ¹⁵N nmr chemical-shift difference for *h*¹-3 and *h*²-3 is gratifying and augurs well for ¹⁵N nmr spectroscopy for studies of soluble dinitrogen complexes.

The infrared spectrum of **3** in heptane at -65°C¹⁸ 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.

Acknowledgment. This work has been supported by the Ford Motor Co., the Public Health Service through Research Grant No. GM-11072, Division of Medical Sciences, and by the National Science Foundation. We wish to thank Professors H. B. Gray and J. G. Gordon for helpful discussions.

(16) The possibility of the singlet resonance arising from free ¹⁴N₂ seems remote because its solubility at -60°C 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 [C₅(CH₃)₅]₂Ti(μ-(di-*h*¹)N₂)₂Ti[C₅(CH₃)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*¹-3 ⇌ *h*²-3.

(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_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-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).

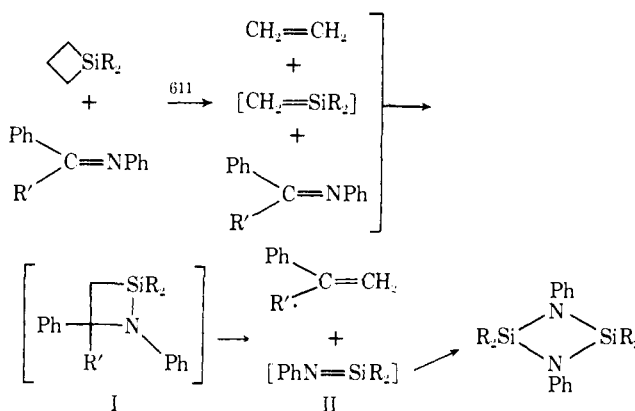
(3) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971). See also ref 1d and e.

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 R₂Si=CH₂ 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 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°C 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°C) 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, Ph₂C=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.