

provides a rapid channel for nonradiative decay in this system.²⁸

The results observed with the luminescent palladium porphyrins and DMA appear closely related to those previously obtained with long-lived but nonemitting triplets of zinc and magnesium porphyrins with acceptors such as aromatic nitro and halogen compounds.^{21,22} Here initial apparent quenching is followed by formation of relatively long-lived complexes having transient spectra very similar to the uncomplexed metalloporphyrin triplet. For these systems too it can be concluded that charge-transfer interactions play a limited role and that the exciplex is nonpolar. Since weak complex formation is a fairly general phenomenon in the ground state, there is no reason why phenomena similar to those reported in the present study should not occur for a variety of substrates having long excited-state lifetimes and that such very weak exciplexes could be frequent but masked precursors to photoproducts.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM 15238) for support of this work.

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for a preprint of this work.

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- At high [DMA] (above 4 M) there is some indication of an increase in both phosphorescence intensity and lifetime. While this could be a "solvent effect", it could also be attributable to a higher order complex as has been previously determined.^{21,22}
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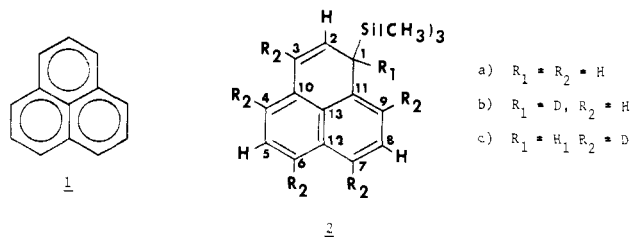
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Received September 14, 1978

Thermally and Photochemically Induced Shifts of Silicon on the Phenalene Ring System

Sir:

In recent years there has been a great deal of interest in the fluxionality and sigmatropic behavior associated with σ - and π -bonded metal derivatives of organic π ligands, among them being metal derivatives of cyclopentadienyl, indenyl, cycloheptatrienyl, cycloheptatriene, and cyclooctatetraene.¹ Su, in a theoretical paper describing the nature of several of these reactions, suggested that one could explore these reactions (metallotropic shifts) more deeply and in entirely new ways by using new organic π ligands.² We suggest that the phenalenylyl ring system (**1**) is an excellent choice for this purpose



because (1) it possesses high symmetry (D_{3h}); (2) both σ - and π -bonded metal complexes are possible;³ and (3) for a given derivative, several metal shifts, some of which are unique here, are possible. Consider, for example, the σ complex 1-trimethylsilylphenalene (**2a**). Here there are possibly three nonequivalent 1,3-silicon shifts, to C-3, -9, and -13,⁴ and two nonequivalent 1,2 shifts, to C-2 and -11. We wish to report our results pertaining to the thermally and photochemically induced sigmatropic shifts of silicon on **2**.

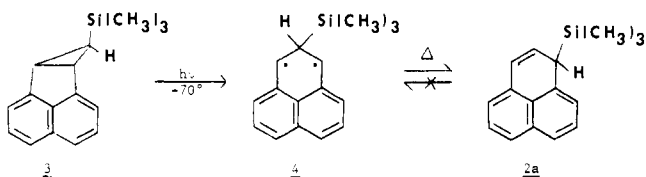
Silane **2a**,⁵ which was prepared by the reaction of the phenalenylyl anion with trimethylsilyl chloride, in C_6D_6 is non-fluxional on the NMR time scale at temperatures up to 185 °C,⁶ with studies at high temperatures being precluded by

competing irreversible hydrogen shifts.⁷ An attempt to observe a sigmatropic shift at 150 °C, where hydrogen shifts are slow, by a Forsén-Hoffman spin saturation experiment⁸ was also unsuccessful. A thermal shift of silicon was finally observed by using the deuterium-labeled silane **2b**.⁹ The reaction in C₆D₆ (unimolecular,¹⁰ $E_a \sim 27$ kcal/mol¹¹) was monitored by observing the increase in the H-1 signal in the ¹H NMR spectrum. The equilibrium value for the H-1 NMR signal at all temperatures was found to be 50% of that for H-2, which was used as an internal standard. These results rule out a cleavage recombination mechanism and indicate that a single 1,3 shift of silicon,¹² either to C-3 or -9, is occurring. The reversible shift between rings to C-9 was shown to be the correct choice by analysis of the H-2 NMR pattern as a function of time.¹³ The observed isomerization of **2**, it should be noted, represents one of the very few 1,3-sigmatropic shifts of silicon observed to date.¹²

Photolysis of the above thermally equilibrated sample led to an increase in the H-1 NMR signal until an equilibrium value close to 85% of that for H-2 was attained.¹⁴ The deuterium label had clearly been randomized at all six corner sites on **2**. Three mechanisms can be invoked to explain the results: (1) a cleavage recombination mechanism, (2) a photochemically induced 1,3 shift of silicon to C-13 followed by a thermal (and random) 1,3 shift back to the corner carbons, and (3) competing 1,3 shifts to C-3 and -9. The photolysis of **2c**¹⁵ indicates that only this last possibility is correct.

The photolysis of **2c** could be followed by observing the disappearance of the H-1 signal in the ¹H NMR spectrum and the appearance of the corresponding H-3 and H-9 signals. In the very first part of the reaction, where the buildup of the H-3 and H-9 signals¹⁶ should give a good estimate of relative amounts of shifts to C-3 and -9, respectively, the H-9 signal increased much more sharply than the H-3 signal.¹⁷ One can deduce from these observations that both silicon shifts occur, with the shift to C-9 proceeding at least five times more rapidly than the shift to C-3.

1,2 shifts of silicon on the phenalenyl ring system are also possible. Photolysis of **3**¹⁸ at -70 °C yields **2a** cleanly. Based



on the work of Michl¹⁹ on the unsubstituted cyclopropane, it is clear that this reaction occurs by initial photochemical cleavage of the central cyclopropane bond to yield the biradical **4** followed by a thermal 1,2 shift of silicon.²⁰ Interestingly, the reverse 1,2 shift, i.e., **2** → **4**, during the thermolysis of **2** can be ruled out on energy considerations.²¹

The above results on **2** can be interpreted, at least in part, in terms of an admixture of the Woodward-Hoffmann rules and steric considerations. Thermally, a 1,3 shift of silicon should occur with inversion at the silicon, with the shift between rings to C-9 yielding less steric interaction between the phenalenyl ring and the methyl groups attached to the silicon than the corresponding shift within the ring to C-3. Photochemically, the silicon should migrate with retention of configuration, with the shifts between rings and within the ring having comparable steric requirements. The regioselectivity observed in the photochemical case, of course, cannot be explained as simply as in the thermal case. We will reserve discussion of this point to our full paper.

It is clear from the above that σ -bonded metal derivatives of **1** can be used to study the regioselectivity of thermally and photochemically induced metallotropic shifts. It is also clear that to attain a fluxion or ring whizzing phenalene will require

metals which will undergo a 1,3 shift with a low energy of activation, and uranium and thorium seem to fit this requirement.²³ Studies in this area are continuing.

Acknowledgment. J.A.B. wishes to thank the Tennessee Eastman Co. for a fellowship. The Fourier transform NMR used in some of our work was purchased with funds provided by the National Science Foundation. Both authors would like to thank M. Lietzke, J. Q. Chambers, B. M. Benjamin, E. D. Hagaman, and L. L. Brown for help and advice during the course of this project.

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- (14) The H-2 pattern changed exactly as expected.
- (15) Silane **2c** was prepared from 1,1,3,4,6,7,9-heptadeuteriophenalene by methods described above. Silane **2c** contained some residual hydrogen at the corner positions (at C-3, -4, -6, -7, and -9). The data were corrected to take this into account.
- (16) The ¹H NMR signal for H-9 and H-4 overlap.⁵ If only 1,3 shifts occur, the buildup of the H-4/-9 signal at the very beginning of the reaction can only be due to H-9.
- (17) H-2 was used as the internal standard. In addition to observing the H-1, H-3, and H-4/-9 signals as a function of time, one could dissect the H-4/-9 signal into its components by making certain reasonable assumptions. At equilibrium, H-3, H-4, and H-9 were all approximately 18% of the value for H-2, while H-1 was 7% of that for H-2. Possible origins for this isotope effect will be discussed in our full paper.
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Received January 18, 1979