

the basis for a facile analysis of the porphyrin content of the complexes. Treatment of the complexes with hydroxide ion in water-organic solvent mixtures produces minor but definite spectral changes similar to those which occur upon μ -oxo dimer formation by octaethylporphyrin complexes of iron(III) and scandium(III).²³ We tentatively assign these changes to this cause.

The nmr spectra confirm the formation of paramagnetic metalloporphyrins with the metal ion considerably displaced from the porphyrin plane.^{5, 24-26} The proton nmr spectrum of the tetra-*p*-tolyl derivative, Eu(*p*-CH₃)TPPacac, at -21° exhibits peaks (ppm from TMS) at -13.31 d (*ortho-endo*), -9.33 d (*meta-endo*), -8.30 (pyrrole), -8.13 (*ortho-* and *meta-exo*), -3.44 (*p*-CH₃), and 0.88 (acac-CH₃), with areas consistent with this assignment. These may be compared with diamagnetic free-base resonances at -9.22 (pyrrole), -8.43 d (*ortho*), -7.80 d (*meta*), and -2.82 (*p*-CH₃) (d signifies a doublet with 8 Hz splitting). The signals shift linearly with T^{-1} as expected for isotropically shifted resonances. Shift ratios for the phenyl protons (*ortho-endo*:*meta-endo*:*ortho-exo*:*meta-exo*:*p*-CH₃ = -10.00:-3.14:0.61:-0.68:-1.28) agree well with those calculated²⁷ assuming axial symmetry (-10.00:-3.09:0:80:-0.68, -1.23). The ratios agree best for a model with the europium atom 2.0 Å out of the porphyrin plane. This implies a Eu-N distance of 2.83 Å which is 0.18 Å larger than the pyridine nitrogen to europium distance in a shift reagent system.²⁸ No attempt was made to account for phenyl ring oscillation, porphyrin skeleton doming, or Fermi contact contributions, so the above estimate, which is extremely sensitive to the small *ortho-endo* and *meta-endo* shifts, must be considered highly uncertain and is probably too large. The same structural parameters predict a relative dipolar shift of -4.77 for the pyrrole protons, while this resonance is observed to shift *upfield* by 0.92 ppm at -21°. We attribute this to a sizeable Fermi contact interaction. It is for the pyrrole protons that contact shifts are particularly evident in both low- and high-spin iron(III) porphyrin systems.⁵ Preliminary nmr spectra of Pr(*p*-CH₃)TPPacac and Yb(*p*-CH₃)TPPacac show well-resolved signals with the *p*-CH₃ resonances shifted by +1.15 and -3.28 ppm, respectively, at -21°. These shifts may be compared with the -0.63 ppm shift for this resonance in the analogous europium complex. The observed sign changes are entirely consistent with the results in shift reagent systems.¹¹ The shift observed for the ytterbium complex implies that its dipolar shifting ability is about 2.4 times that of the low-spin, d⁵, iron(III) hemin moiety in metmyoglobin cyanide.⁶

These preliminary findings, and particularly the ob-

served stability of lanthanide porphyrin complexes toward water suggest that the analogous complexes of naturally occurring porphyrins may serve as potent and specific nmr shift and broadening probes in biological systems.²⁹ Lanthanide porphyrin complexes may find application as heavy-atom probes for electron microscopy and X-ray structure determination. Gadolinium derivatives are potential epr spin labels. Work on various aspects of this new area is in progress in these laboratories.

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(29) Spectroscopic evidence from preliminary experiments with the dimethyl esters of proto- and mesoporphyrin IX reveals that lanthanide complexes of these ligands have been synthesized.

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Mechanism of 1,4-Disilacyclohexa-2,5-diene Formation from Acetylenes and Silylenes

Sir:

One of the best known and most perplexing problems in organosilicon chemistry is the nature of the reaction of silylenes (R₂Si:) with acetylenes. In 1962 it was reported¹ that dimethylsilylene, generated either from pyrolysis of polysilane or from sodium and dimethyldichlorosilane, reacted with diphenylacetylene to produce silacyclopentene, **1**. Soon after this report a variety of methods² were employed to show that the product was actually the 1,4-disilacyclohexadiene, **2**. The mechanism for formation of **2** was suggested³ to involve π -dimerization of **1**. However, generation of dimethylsilylene in the presence of both diphenylacetylene and 2-butyne afforded none of the mixed disilacyclohexadiene (**3**) of the type demanded by such a mechanism.⁴ The possibility of **1** opening to a 1,3-diradical followed by a head-to-tail dimerization was excluded since even in the presence of a large excess of diphenylacetylene, no silacyclopentadiene (**4**) was formed. Thus it has been assumed that "the formation of the disilacyclohexadienes proceeds by a rather specific dimerization of silacyclopentene intermediates with rupture of the carbon-silicon ring bonds."⁴

We suggest here an alternative mechanism and present the results of initial experiments which are consistent with this suggestion. Our interest in molecules containing the silicon-carbon (p-p) π double bond produced the suggestion that disilacyclohexadiene formation might arise from the Diels-Alder reaction be-

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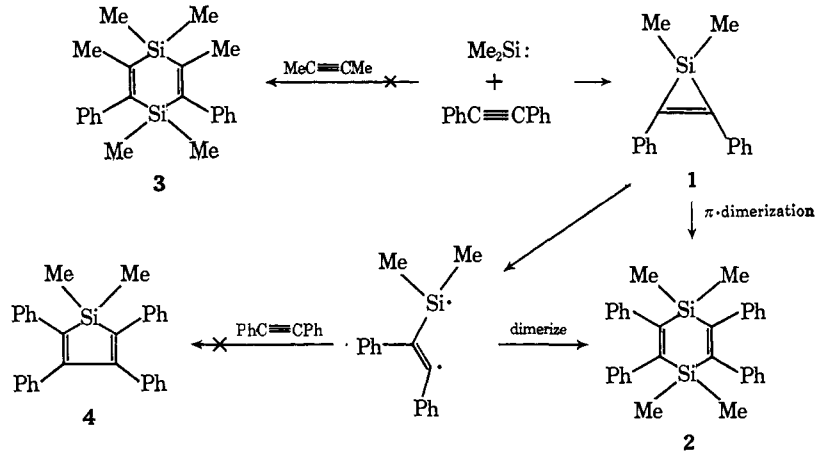
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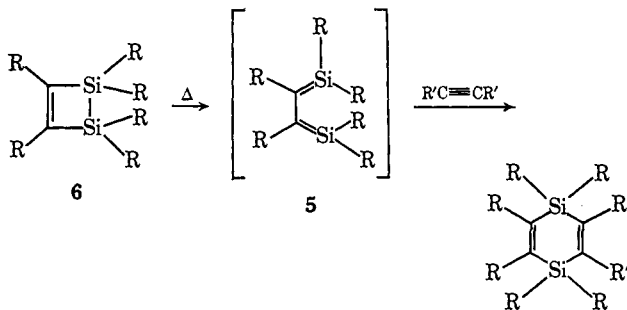
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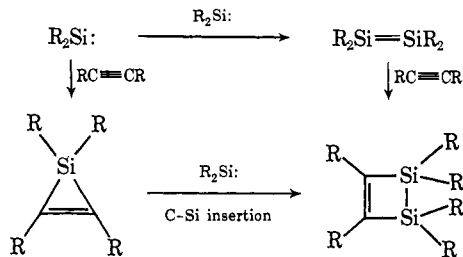
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tween a 1,4-disila-1,3-butadiene (**5**) and an acetylene. Diene **5** could be reversibly formed from the opening of a 1,2-disilacyclobutene (**6**) and if $R \neq R'$ this would account for the absence of isomer **3** in the mixed acetylene experiments.



One can envision the formation of **6** by at least two separate routes—insertion of silylene into a silicon-carbon bond of an initially formed silacyclopipene (a route recently suggested by Atwell⁵ or dimerization of silylene followed by addition of the resulting disilylene to an acetylene.



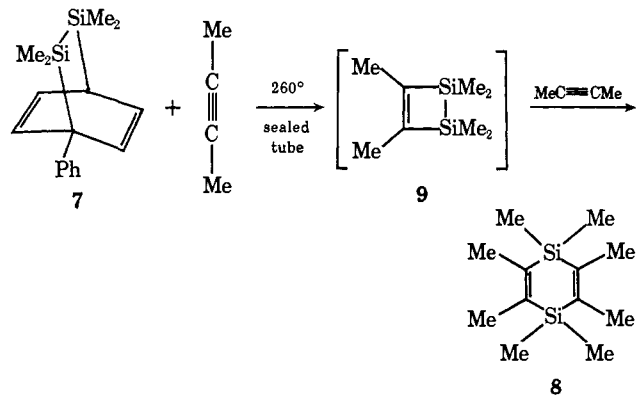
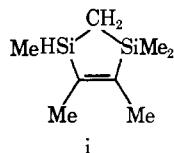
The synthesis of disilylene precursors and evidence of their thermal extrusion of disilylene has been reported.⁶ We find that under the reported⁴ conditions for silylene addition to acetylenes (sealed tube, 250°, 18 hr) disilylene precursor **7** does indeed react with 2-butyne to afford octamethyl-1,4-disilacyclohexadiene (**8**) (20%).^{7,8}

The recent discovery by Atwell⁵ that the vapor phase thermolysis of 1,2-dimethoxytetramethyldisilane

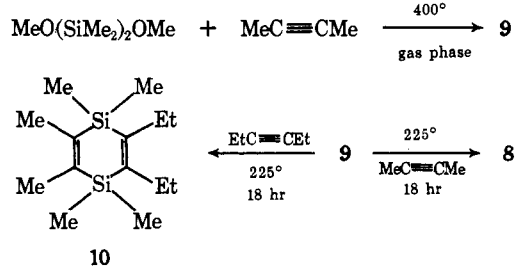
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(7) This reaction proceeds in a different fashion when performed in the gas phase (N_2 flow, 500°) and affords **i** as the major product. Com-



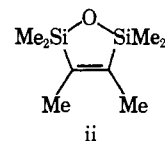
in the presence of 2-butyne gives hexamethyl-1,2-disila-3-cyclobutene (**9**) makes possible a test of this mechanism. Indeed we find that pyrolysis of **9** in the presence of excess 2-butyne (sealed tube, 225°, 18 hr) does afford **8** in 31%⁸ yield. Perhaps more importantly copyrolysis of **9** and 3-hexyne provides disilacyclohexadiene **10** (39%) as the only isomer.^{8,9}



Thus disilacyclohexadiene formation through the Diels-Alder addition of an acetylene to a 1,4-disila-1,3-butadiene (**5**) appears to be a viable route. Whether or not disilylenes add directly to acetylenes to form 3,4-disilacyclobutenes or this too is a silylene reaction should be answered by use of unsymmetrically silicon-

compound **i** presumably arises from 1,3-hydrogen migration and ultimate addition of $\text{MeHSiCH}_2\text{SiMe}_2$ to 2-butyne. Similar rearrangements have been proposed.⁶ Interestingly a minor product is **ii**, *vide infra*.

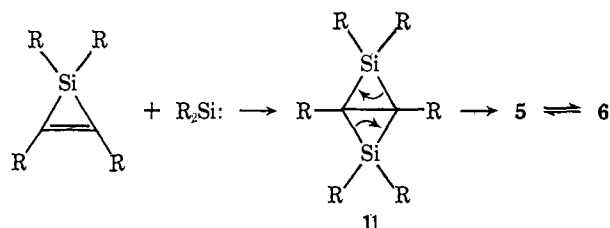
(8) Yields are from calibrated gas chromatograph traces and, for products arising from use of **9** as a starting material, have been corrected for the presence of **ii**, the product of **9**, and O_2 . Product identification



was made by gas chromatography, mass spectral, and nmr comparison with authentic samples.

(9) An authentic sample of **10** was prepared by the copyrolysis of 1,2-dimethoxytetramethyldisilane, 2-butyne, and 3-hexyne.

substituted disilylene generators and work toward this goal is now in progress. A final problem concerns the origin of **6**. It is possible that silylene adds to the π -bond of a silacyclopropene to produce an intermediate disilabicyclo[1.1.0]butane (**11**). Such a molecule could thermally rearrange to **5**, and we are experimentally checking this possibility at this time.



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Crystal and Molecular Structure of an Osmium Bispyridine Ester of Adenosine

Sir:

Organic complexes of osmium(VI), apart from their inherent interest as metal-organic complexes in inorganic chemistry, have become of biochemical interest because they have been reported to form a heavy atom derivative of transfer ribonucleic acid (tRNA).¹ We wish to report the X-ray diffraction structure determination of a bis(pyridine)osmate(VI) ester of adenosine.² We believe that the stereochemistry observed in this compound may serve as a model of one mode of binding of osmium to tRNA in the heavy atom derivatives used in the structure determination of tRNA.^{1b,3,4}

The preparation of crystals of the adenosine bis(pyridine)osmate complex proceeded from the observation that ribonucleosides, as well as other cis diols, form 1:1 addition complexes with OsO₃py₂ in water-pyridine solution.^{5,6} OsO₃py₂ (118.7 mg), prepared from OsO₄ by reduction with ethanol according to Criegee, *et al.*,⁶ and 80.1 mg of adenosine (Sigma) were dissolved in 4.5 ml of water-pyridine (2:1, v/v) and kept for several hours at 4° in the dark. The progress of the reaction was followed by thin-layer chromatography on Merck Cellulose F plates in 2-propanol-concentrated ammonium hydroxide-water (50:1:49, v/v). The osmate ester appeared after drying of the plate as a gray-brown spot ($R_f = 0.21$). After completion of the reaction the

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(2) The IUPAC name for the compound is *ab*-[adenosinato(2-)-O²,O³]-*ce*-dioxo-*df*-bis(pyridine)osmium according to Dr. K. L. Loening, Director of Nomenclature at the Chemical Abstracts Service.

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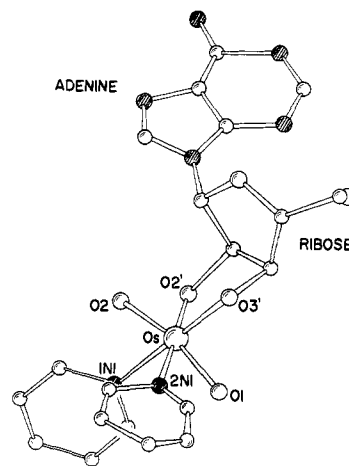


Figure 1. Molecular structure of bis(pyridine)osmate(VI) ester of adenosine. Selected distances (Å) and angles (deg) are listed with errors in parentheses: O(3')-Os, 1.99 (5); O(2')-Os, 1.91 (5); O(1)-Os, 1.78 (4); O(2)-Os, 1.78 (4); 1N(1)-Os, 2.24 (6); 2N(1)-Os, 2.11 (7); 1N(1)-Os-2N(1), 91 (3)°; 1N(1)-Os-O(3'), 178 (3)°; 2N(1)-Os-O(3'), 87 (3)°; O(2')-Os-O(3'), 90 (3)°; O(2)-Os-1N(1), 90 (3)°; O(2')-Os-2N(1), 178 (3)°; O(1)-Os-O(2), 164 (3)°. The nitrogen atoms have diagonal shading.

product was isolated by evaporation of the solvent. It was redissolved in a few drops of water-pyridine (1:1) and crystallized on cooling in the form of brown lamellar plates and needles (yield 125 mg, 65%).

The problem of finding a suitable crystal for data collection proved extremely difficult despite repeated recrystallizations; the crystals formed tight aggregates, were quite brittle, and exhibited a high degree of mosaic spread as well as thermal diffuse scattering. During preliminary X-ray photographic investigations, no crystal could be found which failed to exhibit both undue mosaic spread and thermal diffuse scattering; however, we decided to attempt data collection anyway. The diffraction photographs indicated that the crystal belongs to the orthorhombic space group $P2_12_12_1$, as determined by its systematic absences; the cell constants were $a = 7.84$, $b = 12.28$, and $c = 23.71$ Å. Data were collected using a modified Picker FACS I diffractometer at 8° with an ω -stepscan; 2243 unique reflections were collected to a resolution of approximately 0.7 Å. In at least one direction the mosaic spread caused some reflections to be appreciably wider than the counter (528 mm from crystal) could accommodate, hence these reflections were "clipped" to substantially less than their true value.

The osmium atom was located by Patterson methods, and all other atoms were placed in subsequent Fourier refinements. Least-squares refinement of the structure using anisotropic temperature factors for the osmium atom and isotropic temperature factors for all other atoms lowered the crystallographic R factor to 0.108. The use of anisotropic temperature factors on all atoms does not improve this figure significantly according to the Hamilton R test.⁷ The final structure is depicted in Figure 1, with the packing of the structure in the unit cell depicted in Figure 2.⁸

A few structural observations are immediate; the osmium binds as an osmate ester to the 2'-3' cis diol of

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