

Table I. Cu/CH<sub>4</sub> Photoproducts and Infrared Frequencies (cm<sup>-1</sup>)

product <sup>a,c</sup>		assignment <sup>b</sup>
CuH	CuCH <sub>3</sub> (II) HCuCH <sub>3</sub> (I) CH <sub>3</sub>	
		ν(CH <sub>3</sub> ), (ref 11)
	2929	asym ν(CH <sub>3</sub> )
1850	2880	sym ν(CH <sub>3</sub> )
		ν(CuH); ν(CuD) 1333 cm <sup>-1</sup>
	1697	ν(CuH); ν(CuD) 1229 cm <sup>-1</sup>
		i.p. δ(CH <sub>3</sub> ) (ref 10, 11)
	1344 } <sup>d</sup>	asym δ(CH <sub>3</sub> ); asym δ( <sup>13</sup> CH <sub>3</sub> )
	1328 }	1338 and 1320 cm <sup>-1</sup>
	1196	sym δ(CH <sub>3</sub> ); sym δ( <sup>13</sup> CH <sub>3</sub> )
		1189 cm <sup>-1</sup>
	1011	sym δ(CH <sub>3</sub> ); sym δ( <sup>13</sup> CH <sub>3</sub> )
		1003 cm <sup>-1</sup> ; sym δ( <sup>12</sup> CD <sub>3</sub> )
		786 cm <sup>-1</sup>
	611	o.p. δ(CH <sub>3</sub> ) (ref 10, 11)

<sup>a</sup> 320-nm control photolyses of pure CH<sub>4</sub> at 12 K in the absence of Cu atoms showed none of the effects described in the text.

<sup>b</sup> Band III in Figure 2 may be ascribed to a perturbed methyl radical by comparison with alkali metal-methyl halide matrix IR data (ref 15). <sup>c</sup> Bands associated with I and II were also observed at 433, 414, 351, and 275 cm<sup>-1</sup> (see text). <sup>d</sup> Assigned to the asymmetric δ(CH<sub>3</sub>) mode subject to either a site symmetry or a multiple trapping site effect.

The assignments were confirmed by isotopic substitution experiments involving CH<sub>n</sub>D<sub>4-n</sub> (where n = 0-4) matrices. The infrared bands not associated with CuH or CH<sub>3</sub> can be grouped into two categories, depending on whether they persist as final products or first grow in and then decay with further irradiation. Two bands in the latter category apparently associated with the same species are denoted I in Figure 2, in which the initial growth and subsequent decay behavior is illustrated. The species I band at 1697 cm<sup>-1</sup> was found to shift to 1229 cm<sup>-1</sup> in the case of CD<sub>4</sub> matrices and was invariant to <sup>12</sup>C/<sup>13</sup>C substitution of methane. In addition, the spectrum for a 1:1 CH<sub>4</sub>/CD<sub>4</sub> matrix was found to be a simple superposition of the CH<sub>4</sub> and CD<sub>4</sub> spectra. We therefore assign species I as a monohydride with 1697 cm<sup>-1</sup> corresponding to ν<sub>Cu-H</sub>, shifted to lower energy from the corresponding band of CuH at 1850 cm<sup>-1</sup>. The species I band at 1011 cm<sup>-1</sup> was found to be sensitive to both H/D and <sup>12</sup>C/<sup>13</sup>C substitution of methane (Table I). These results strongly suggest that I is the Cu(II) species HCuCH<sub>3</sub>, with the vibrational assignments listed in Table I. The frequencies and isotopic shifts of the species II bands are closely similar to those observed for isotopically substituted LiCH<sub>3</sub> molecules isolated in rare-gas matrices.<sup>12</sup> We therefore identify species II as CuCH<sub>3</sub>, and list tentative assignments of the observed infrared bands in Table I.<sup>13</sup> A more detailed analysis of the infrared spectrum of CuCH<sub>3</sub> will be presented in the full paper. It is interesting to note that all of the products described above could also be produced in ~1:10 CH<sub>4</sub>/Ar matrices.

The preliminary results of an ESR study of the Cu/CH<sub>4</sub> photochemical reaction are consistent with the above assignments. In particular, the characteristic spectrum of methyl radical is readily identified, and the assignment of I as the Cu(II) species HCuCH<sub>3</sub> is strongly supported both by the overall appearance of the spectrum, which is of the form expected for a randomly oriented <sup>2</sup>Σ<sup>+</sup> axial system split by a I = 3/2 (<sup>63</sup>Cu/<sup>65</sup>Cu, natural abundance 69%/31%) nucleus,<sup>14</sup> and the hyperfine pattern caused by the hydride, deuteride, or carbon-13 nucleus when using <sup>12</sup>CH<sub>4</sub>,

(12) Andrews, L. *J. Chem. Phys.* 1967, 47, 4834.

(13) In the case of Cu/CH<sub>4</sub>, where the reactions were induced by broad band photolysis either during or after matrix formation, Billups et al. find infrared bands at 1855.7, 1200.1, 613.8, 433.9, and 417.4 cm<sup>-1</sup>, which they assign to the species HCuCH<sub>3</sub>. However, we prefer the assignments listed in Table I, for reasons explained in the text. Thus the products observed by Billups et al. include CuH (1855.7 cm<sup>-1</sup>), CuCH<sub>3</sub> (1200.1 cm<sup>-1</sup>, 433.9 cm<sup>-1</sup>, 417.4 cm<sup>-1</sup>), and CH<sub>3</sub> (613.8 cm<sup>-1</sup>) but not HCuCH<sub>3</sub>, although this latter species was observed as an intermediate in the present study.

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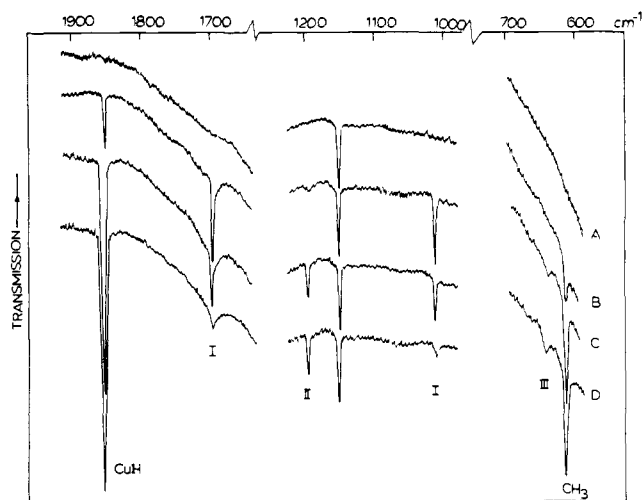


Figure 2. Infrared spectra of Cu/CH<sub>4</sub> ≈ 1/10<sup>4</sup> matrices at 12 K, showing the effects of 320-nm photolysis. (A) Freshly deposited matrix, (B) 10 min, 320-nm irradiation, (C) 50 min, 320-nm irradiation, (D) 70 min, 320-nm irradiation. All regions of the IR spectrum were scanned. Only selected regions are illustrated in this figure.

<sup>12</sup>CD<sub>4</sub>, and <sup>13</sup>CH<sub>4</sub> matrices, respectively. Interestingly, the ESR spectra reveal the presence of significant amounts of H atoms as photoproducts.

We feel that the overall photochemical reaction may be best described in terms of an initial insertion of an optically excited copper atom into a C-H bond of methane, followed by secondary photolysis of HCuCH<sub>3</sub> to form mainly CuH and CH<sub>3</sub> but also CuCH<sub>3</sub> and H atoms as illustrated in Scheme I. Matrix kinetic experiments designed to probe the mechanistic details of this important photochemical reaction are presently underway in this laboratory.

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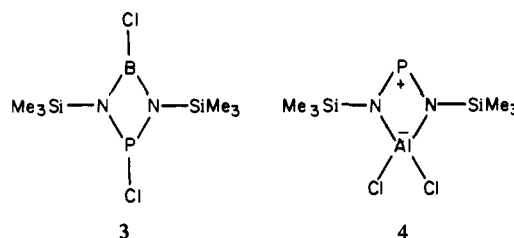
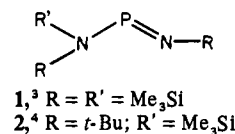
### Reaction of Two-Coordinate Phosphorus Compounds with Group 3A Alkyls: A Novel Double Group Shift and Concomitant Cyclization

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The two-coordinate phosphorus compound **1** reacts with BCl<sub>3</sub> and Al<sub>2</sub>Cl<sub>6</sub> to afford the heterocycles **3**<sup>1</sup> and **4**,<sup>2</sup> respectively. We



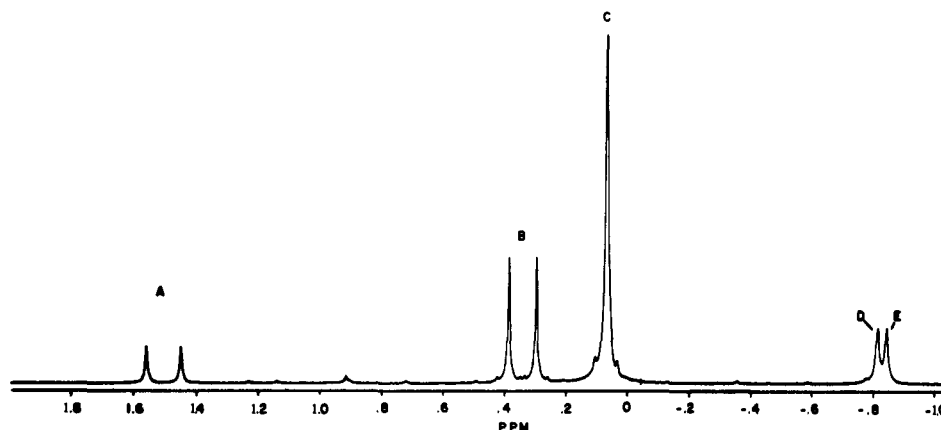


Figure 1.  $^1\text{H}$  NMR spectrum of **5** recorded at 90 MHz, 30 °C in  $\text{CH}_2\text{Cl}_2$ .

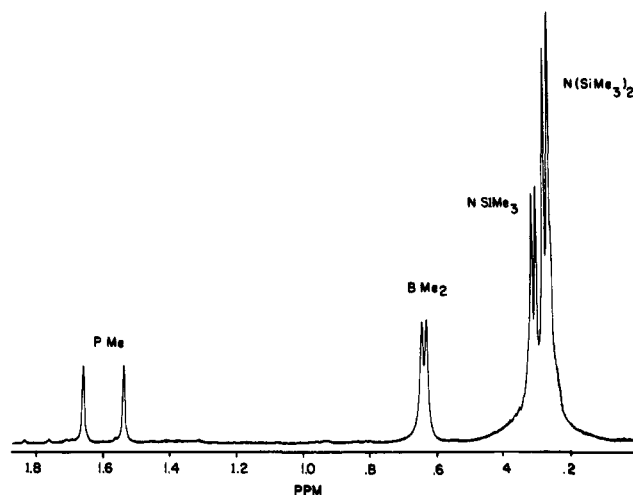
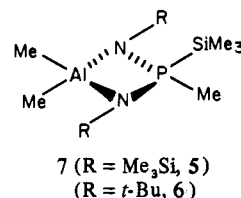


Figure 2.  $^1\text{H}$  NMR spectrum of **8** recorded at 90 MHz, 30 °C in  $\text{CH}_2\text{Cl}_2$ .

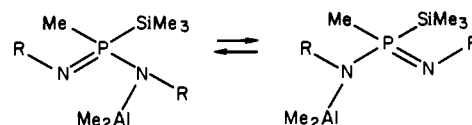
have found that the group 3A alkyls,  $\text{Me}_3\text{B}$  and  $\text{Me}_6\text{Al}_2$ , react with **1** and **2** to yield quite different products. This has led to the discovery of an unprecedented double group migration and a new method of synthesizing four-membered heterocycles.

Treatment of **1** and **2** with  $\text{Me}_6\text{Al}_2$  in  $\text{CH}_2\text{Cl}_2$  solution results in clear colorless liquids **5** [bp 90 °C ( $10^{-2}$  torr)] and **6** [bp 115 °C ( $10^{-2}$  torr)], respectively, which solidify slightly below room temperature. Elemental analyses indicate the compositions  $\text{C}_{12}\text{H}_{36}\text{AlN}_2\text{PSi}_3$  (**5**) and  $\text{C}_{14}\text{H}_{36}\text{AlN}_2\text{PSi}_3$  (**6**), and the mass spectra of both compounds exhibit low-intensity molecular ions and intense M–Me peaks. The 90-MHz  $^1\text{H}$  NMR spectrum of **5** ( $\text{CH}_2\text{Cl}_2$  solution) consists of five resonances, as shown in Figure 1: A (d, 3 H,  $\delta$  1.50), B (d, 9 H,  $\delta$  0.34), C (s, 18 H,  $\delta$  0.07), D (s, 3 H  $\delta$  –0.81), and E (s, 3 H,  $\delta$  –0.84). Resonances A and B collapse to singlets in a  $^1\text{H}\{^{31}\text{P}\}$  experiment. On the basis of their chemical shifts, resonances A–E are assigned to  $\text{PMe}$  ( $J_{\text{PCH}} = 19.9$  Hz),  $\text{PSiMe}_3$  ( $J_{\text{PSiCH}} = 8.2$  Hz),  $\text{NSiMe}_3$ , and two  $\text{AlMe}$  groups, respectively. The separation between the two resonances D and E increases from 3.6 to 8.0 Hz when the spectrometer frequency is increased from 90 to 200 MHz. We attribute these resonances to anisochronous Me groups on an  $\text{AlMe}_2$  moiety. The 90-MHz  $^1\text{H}$  NMR spectrum of **6** and its assignments are very similar to those of **5**:  $\text{PMe}$  (d, 3 H,  $\delta$  1.59,  $J_{\text{PCH}} = 10.1$  Hz),  $\text{N}-t\text{-Bu}$  (d, 18 H,  $\delta$  1.20,  $J_{\text{PNCC}} = 0.9$  Hz),  $\text{PSiMe}_3$  (d, 9 H,  $\delta$  0.42,  $J_{\text{PSiCH}} = 6.9$  Hz),  $\text{AlMe}$  (s, 3 H,  $\delta$  –0.83), and  $\text{AlMe}$  (s, 3 H,  $\delta$  –0.85). The 36.43-MHz  $^{31}\text{P}\{^1\text{H}\}$  spectra of **5** and **6** exhibit singlets at 42.05

and 37.36 ppm,<sup>5</sup> respectively. The 20.0-MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{Me}_4\text{Si}$ ) spectra of **5** and **6** consist of the following resonances.<sup>6</sup> **5**:  $\text{PMe}$  (d,  $\delta$  23.43,  $J_{\text{PC}} = 31.4$  Hz),  $\text{NSiMe}_3$  (d,  $\delta$  3.32,  $J_{\text{PNSiC}} = 2.7$  Hz),  $\text{PSiMe}_3$  (d,  $\delta$  –2.58,  $J_{\text{PSiC}} = 13.8$  Hz). **6**:  $\text{NC}$  (s,  $\delta$  50.77),  $\text{NCMe}_3$  (d,  $\delta$  34.80,  $J_{\text{PNCC}} = 6.6$  Hz),  $\text{PMe}$  (d,  $\delta$  23.91,  $J_{\text{PC}} = 25.0$  Hz), and  $\text{PSiMe}_3$  (d,  $\delta$  –0.53,  $J_{\text{PSiC}} = 12.4$  Hz). On the basis of the foregoing evidence, the only satisfactory structure for **5** and **6** is **7**.



We consider a dynamic exchange process such as



to be highly unlikely for the following reasons: (i) no  $\text{NSiMe}_3$  or  $\text{N}-t\text{-Bu}$  anisochrony is detectable in the low temperature (–100 °C)  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra of **5** or **6** and (ii) the maintenance of Me nonequivalence in the  $\text{AlMe}_2$  moiety would imply an unreasonably high barrier to N–Al rotation.

Treatment of **1** and **2** with  $\text{BMe}_3$  for 3–4 days at room temperature in  $\text{CH}_2\text{Cl}_2$  solution produced colorless liquid compounds **8** [bp 69–70 °C ( $5 \times 10^{-3}$  torr)] and **9** [bp 100 °C ( $10^{-2}$  torr)], respectively. Both compounds solidified to glassy solids at  $\sim 25$  °C.

The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **9**<sup>7,8</sup> are very similar to those of **5** and **6**; thus a structure of type **7** is assigned to this product. The NMR spectra of **8**, however, are quite distinct from those of **5**, **6**, and **9**. The most striking difference is that the 36.43-MHz  $^{31}\text{P}\{^1\text{H}\}$  resonance of **8** (s,  $\delta$  103.54) is  $\sim 52$  ppm

(5) Positive  $^{31}\text{P}$  chemical shifts are downfield from 85%  $\text{H}_3\text{PO}_4$ .

(6) The methyl carbons of  $\text{AlMe}_2$  and  $\text{BMe}_2$  were generally not detected, presumably because of relaxation effects.

(7) Spectroscopic data for **9**:  $^1\text{H}$  (200 MHz)  $\text{PMe}$  (d, 3 H,  $\delta$  1.68,  $J_{\text{PCH}} = 9.9$  Hz),  $\text{N}-t\text{-Bu}$  (d, 18 H,  $\delta$  1.13,  $J_{\text{PNCC}} = 0.7$  Hz),  $\text{PSiMe}_3$  (d, 9 H,  $\delta$  0.42,  $J_{\text{PSiCH}} = 6.9$  Hz),  $\text{BMe}_2$  (s, 3 H,  $\delta$  0.079), and  $\text{BMe}_2$  (s, 3 H,  $\delta$  0.055);  $^{13}\text{C}\{^1\text{H}\}$  (20.0 MHz) ( $\text{Me}_4\text{Si}$ )  $\text{PNC}$  (d,  $\delta$  51.0,  $J_{\text{PNC}} = 1.3$  Hz),  $\text{NCMe}_3$  (d,  $\delta$  34.02,  $J_{\text{PNCC}} = 6.6$  Hz),  $\text{PMe}$  (d,  $\delta$  24.83,  $J_{\text{PC}} = 18.8$  Hz),  $\text{PSiMe}_3$  (d,  $\delta$  –0.17,  $J_{\text{PSiC}} = 12.9$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  (36.43 MHz)  $\delta$  51.3. Mass spectrum reveals molecular ion, intense M–Me peak.

(8) The possibility that B–N rotation may not be fast enough to rule out the acyclic structure was considered, since the analogous compounds such as  $\text{Me}(\text{Ph})\text{NBMe}_2$ ,  $\text{Et}(\text{Ph})\text{NBMe}_2$ ,  $i\text{-Pr}(\text{Ph})\text{NBMe}_2$ , and  $t\text{-Bu}(\text{Ph})\text{NBMe}_2$  have rotational barriers of 18.8, 19.1, 19.1, and 17.6 kcal/mol, respectively.<sup>9</sup> However, the high temperature ( $\sim 75$  °C) 200-MHz ( $^1\text{H}$ ) NMR spectrum of **9** showed no significant difference from that of the room temperature spectrum, thus discrediting the acyclic structure.

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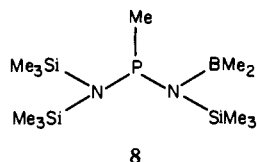
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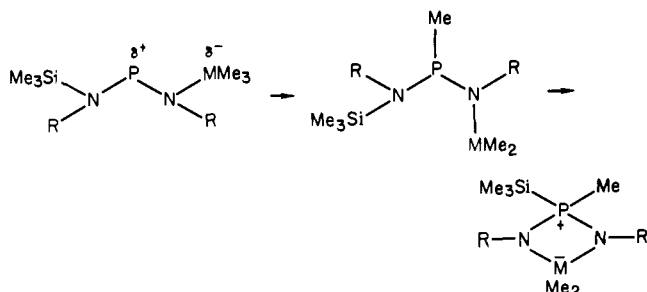
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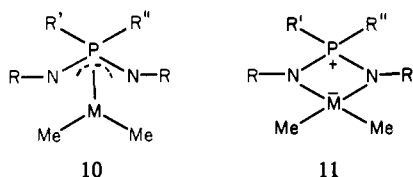
downfield from that of **9** and in the region expected for di-amidoalkylphosphines.<sup>10,11</sup> The <sup>1</sup>H NMR of **8** (Figure 2) consists of four resonances assignable as follows: PMe (d, 3 H, δ 1.60, *J*<sub>PCH</sub> = 11.3 Hz), BMe (d, 6 H, δ 0.63, *J*<sub>PNBCH</sub> = 1.2 Hz), BNSiMe<sub>3</sub> (d, 9 H, δ 0.31, *J*<sub>PNSiCH</sub> = 1.2 Hz), and N(SiMe<sub>3</sub>)<sub>2</sub> (d, 18 H, δ 0.30, *J*<sub>PNSiCH</sub> = 1.5 Hz). The separation between the two BMe resonances remains constant at 1.5 Hz when the spectrometer frequency is increased from 90 to 200 MHz, thus indicating the BMe doublet is due to coupling with the phosphorus. It is clear that in **8** all Me<sub>3</sub>Si groups are attached to nitrogen. This fact is confirmed by the <sup>13</sup>C{<sup>1</sup>H}, (Me<sub>4</sub>Si) spectrum of **8** which also gives no indication of a P-SiMe<sub>3</sub> moiety. PMe (d, δ 25.6, *J*<sub>PC</sub> = 32.8 Hz), BMe (br, δ 12-20.0), N(SiMe<sub>3</sub>)<sub>2</sub> (d, δ 5.64, *J*<sub>PNSiC</sub> = 8.1 Hz), and BNSiMe<sub>3</sub> (d, δ 5.34, *J*<sub>PNSiC</sub> = 4.0 Hz). The 70-eV mass spectrum of **8** exhibits no molecular ion; the 100% peak is at *m/e* 279, which corresponds to loss of NBMe<sub>2</sub>. The foregoing data indicate that the structure of **8** is



In turn, the isolation of **8** suggests that the most likely reaction pathway leading to the cyclic compounds **5**, **6**, and **9** is



Two canonical forms, **10** and **11**, can be written for the cyclic compounds **5**, **6**, and **9**.



In **10** a neutral (RN)<sub>2</sub>PR'<sub>2</sub> ligand behaves in a trihapto manner toward an Me<sub>2</sub>M moiety,<sup>12</sup> while **11** implies formation of a zwitterion via electron transfer from P to M. The <sup>31</sup>P chemical shifts of **5**, **6**, and **9** fall in the range of 30-60 observed for dialkylamino, alkyl-substituted phosphonium cations,<sup>13</sup> thus indicating considerable zwitterionic character. The possibility that (RN)<sub>2</sub>PR'<sub>2</sub> ligands can coordinate to transition metals is under active investigation.

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(10) For example, MeP(NMe<sub>2</sub>)<sub>2</sub> (+86.4),<sup>11</sup> EtP(NMe<sub>2</sub>)<sub>2</sub> (+99.9),<sup>11</sup> C<sub>6</sub>H<sub>11</sub>P(NMe<sub>2</sub>)<sub>2</sub> (+107.1).<sup>11</sup>

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(12) R<sub>2</sub>Al moieties are known to coordinate in a trihapto manner to cyclopentadiene and permethylcyclopentadiene rings. See: Schonberg, P. R.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1979**, *101*, 7726-7728.

(13) For example: [Me<sub>2</sub>P(NH<sub>2</sub>)(NMe<sub>2</sub>)]Cl (+39),<sup>11</sup> [MeP(NMe<sub>2</sub>)<sub>3</sub>]Cl (+44),<sup>11</sup> [(*n*-Bu)P(NMe<sub>2</sub>)<sub>3</sub>]Br (+62).<sup>11</sup>

## Nature of Species Present in an Aqueous Solution of Potassium Silicate

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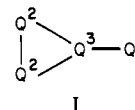
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We wish to report definitive evidence for the structures of 11 species present in an aqueous solution of potassium silicate. These include five ions which involve a ring containing three siloxy units.

Aqueous silicate solutions are important in the detergent industry<sup>1</sup> and geochemistry<sup>2</sup> and have some biochemical significance.<sup>3</sup> Stable solutions of moderate concentration can only be achieved at high pH. Although these solutions might appear to be simple, in practice they are complex because the orthosilicate ion polymerizes in such a fashion as to yield a variety of species in dynamic equilibrium. Until recently, information about the nature of these species was obtained only indirectly, for instance, by trimethylsilylation followed by chromatographic separation.<sup>4</sup> <sup>29</sup>Si NMR has given promise of more direct information,<sup>5-9</sup> since a variety of peaks can be resolved in the spectra, but unfortunately there has been no clear way of assigning the peaks to given structures. Rapid proton exchange ensures that no (Si,H) coupling can be observed, and the natural abundance of <sup>29</sup>Si (4.7%) means that (Si,Si) coupling is also absent. Limited progress has, however, been achieved, and bands due to the monomeric orthosilicate species (Q<sup>0</sup>), end groups (Q<sup>1</sup>), middle groups (Q<sup>2</sup>), and branching positions (Q<sup>3</sup>) have been recognized.<sup>5,6</sup> Two further bands are the subject of dispute but have been tentatively assigned to Q<sup>2</sup> and Q<sup>3</sup> units in three-membered rings.<sup>7</sup> The Q designation refers to silicons bonded to four oxygen atoms, and the superscript number indicates how many of these bonds are part of siloxy bridges. Assignments of individual lines have been very sparse, only the monomer (Q<sup>0</sup>) and dimer (Q<sup>1</sup>Q<sup>1</sup>) peaks being recognized definitively.<sup>8</sup> [The designations *n*-mer and *n*-membered ring refer to the condensed species containing *n* siloxy (SiO) groups plus the appropriate number of additional oxygen atoms. Throughout this discussion the states of protonation of the species present are ignored.] A third peak has been assigned to the cyclic trimer (Q<sup>2</sup>), and Harris and Newman<sup>7</sup> have also tentatively assigned peaks to the linear trimer (Q<sup>1</sup>Q<sup>2</sup>Q<sup>1</sup>), the linear tetramer (Q<sup>1</sup>Q<sup>2</sup>Q<sup>2</sup>Q<sup>1</sup>), and a substituted cyclic trimer (I). Recently, we have begun



studies by using material enriched in <sup>29</sup>Si and have obtained some information from splitting patterns.<sup>8</sup> In particular, five peaks were found to be unsplit, including those assigned as Q<sup>0</sup>, Q<sup>1</sup>, and Q<sup>2</sup>. Moreover, splitting evidence tended to confirm the existence of I but fell short of clear proof. Since the chemical likelihood of

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