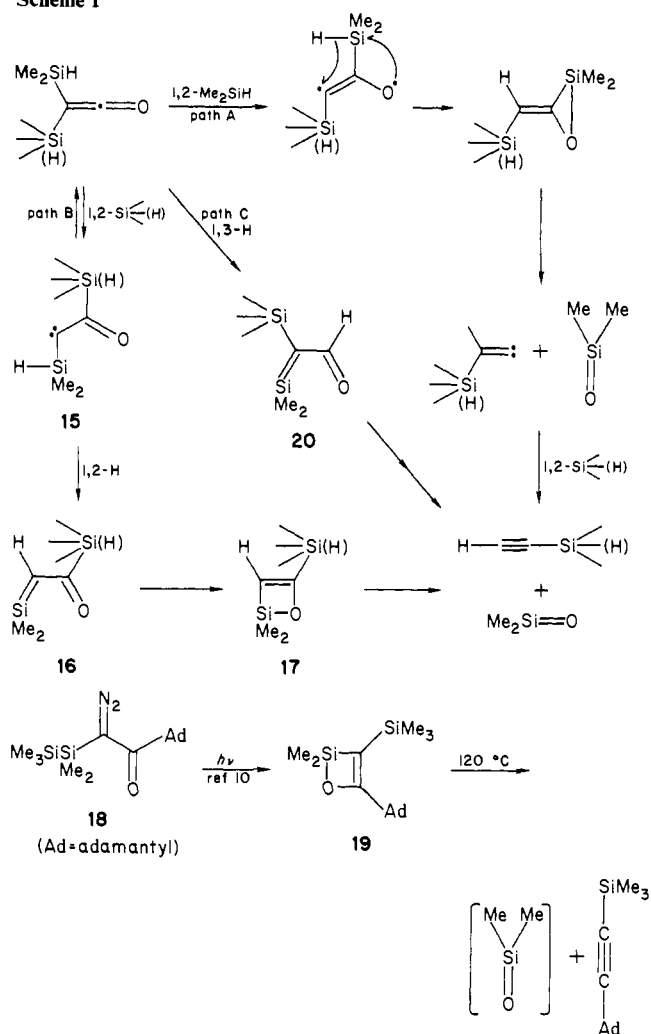
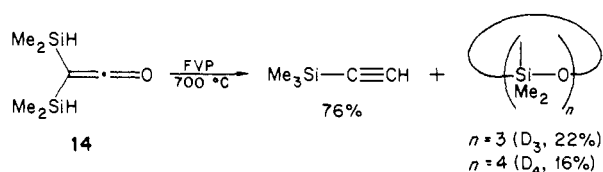


Scheme I



FVP of **14** at 700 °C (67% completion) afforded (trimethylsilyl)acetylene in 76% yield along with permethylcyclotrisiloxane ( $D_3$ , 22%) and permethylcyclotetrasiloxane ( $D_4$ , 16%), the usual



products from oligomerization of  $\text{Me}_2\text{Si}=\text{O}$ . Thus, it is clearly established that hydridosilylketenes thermally decompose by extrusion of silanone.

As to *how* (hydridosilyl)ketenes thermally extrude silanones, we can offer two mechanistic possibilities (Scheme I) which originate with a 1,2-shift to the central carbon of the ketene to produce a diradical which may be viewed as an  $\alpha$ -keto carbene (**15**). Although the oxasilacyclopropane ring system is known,<sup>14</sup> we tend to disfavor path A largely due to the excellent precedents for each of the proposed steps from **15** to dimethylsilanone in path B. Ando has reported<sup>15</sup> that a disilanyl analogue of **15**, photochemically generated from the corresponding diazo ketone **18**, rearranges by a similar route to afford an isolable silaoxetene, **19**, which extrudes  $\text{Me}_2\text{Si}=\text{O}$  at 120 °C (Scheme I, bottom equation).

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Without question, the most exciting aspect of the decomposition of (hydridosilyl)ketenes is that the first step appears to correspond to what is, to our knowledge, the first example of a retro-Wolff rearrangement. As such, two key factors attributable to silicon are involved in promoting the rearrangement—the superb migratory characteristics of silyl groups<sup>16</sup> and the excellent carbene trapping ability of the Si-H bond. Conversion of **15** to **16** via a 1,2-shift is well preceded on both experimental<sup>17</sup> and theoretical grounds,<sup>18</sup> while the reaction of silenes and ketenes (**16** → **17**) is one of the first silene reactions discovered.<sup>19</sup> However, definite invocation of a retro-Wolff rearrangement must be tempered by recognition that isomerization of the silylketene to **20**, a positional isomer of silene **16**, could occur via a single, unprecedented 1,3-H shift from silicon to carbon (Scheme I, path C).<sup>20</sup> Studies are currently in progress to make a definitive distinction between paths A, B, and C and to probe more subtle questions such as the possible involvement of oxirene intermediates.

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## Layer Cross-Linking in Pillared Clays

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Recent <sup>29</sup>Si and <sup>27</sup>Al magic angle spinning (MAS) NMR studies by Plee et al.<sup>1</sup> have indicated that two mechanisms operate for the pillaring of smectite clays by polyoxoaluminum oligomers. For pillared montmorillonite and Laponite (Laporte, Ltd.), the layers retained their constitution even after calcination at 350 °C. However, for calcined pillared beidellite, the tetrahedral sheets of the layers reacted chemically with the gallery oligomers. It was concluded that layer reactivity is dependent on the origin of layer charge (octahedral layer charge for montmorillonite and Laponite, tetrahedral layer charge for beidellite<sup>2</sup>).

Our own <sup>29</sup>Si and <sup>27</sup>Al MAS NMR results for alumina pillared clays confirm the existence of two mechanisms for the pillaring of smectite clays. However, our results also show that the mechanisms are not differentiated *solely* on the basis of the origin of layer charge. Although calcined alumina pillared montmorillonite and Laponite exhibit no evidence for layer reaction, we

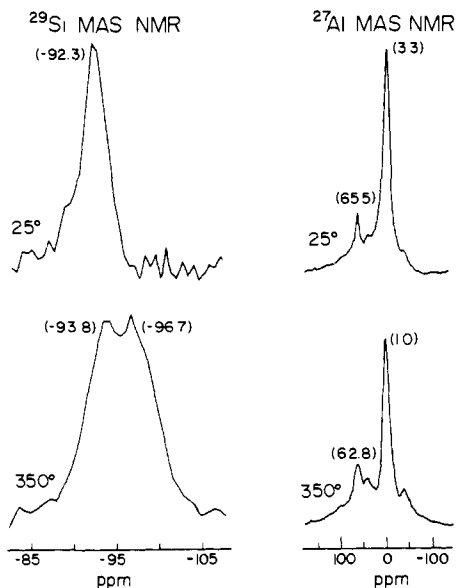
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(2) In octahedrally charged clays such as montmorillonite and Laponite with typical unit cell formulas of  $\text{M}_{0.7/n}^{n+}[\text{Mg}_{0.7}\text{Al}_{1.3}]\text{Si}_{8.0}\text{O}_{20}(\text{OH})_4$  and  $\text{M}_{0.4/n}^{n+}[\text{Li}_{0.4}\text{Mg}_{5.6}]\text{Si}_{8.0}\text{O}_{20}(\text{OH})_4$ , respectively, the layer charge results from metal ion substitutions in the octahedral sheet (e.g., Mg replacing Al or Li replacing Mg). For a tetrahedrally charged clay like beidellite,  $\text{M}_{0.9/n}^{n+}[\text{Al}_{4.0}](\text{Si}_{7.1}\text{Al}_{0.9})\text{O}_{20}(\text{OH})_4$ , the layer charge results from ion substitutions in the tetrahedral sheet (e.g., Al replacing Si).

**Table I.** Properties of Calcined (350 °C, 2 h) Fluorohectoric Clay Reaction Products

prod	aluminum reagent	gallery Al ions per unit cell	$d_{001}$ , Å	surf area, <sup>a</sup> m <sup>2</sup> /g	chemical shifts, <sup>b</sup> ppm	
					<sup>29</sup> Si	<sup>27</sup> Al
I	ACH	3.63	18.5	230	-93.8, -96.7	62.8, 1.0
II	AlCl <sub>3</sub> (OH/Al = 2.4)	4.12	18.5	166	-94.5, -98.0	63.0, 2.0
III	AlCl <sub>3</sub> (OH/Al = 0.0)	0.47	13.6	17	-92.0	11.0

<sup>a</sup>N<sub>2</sub>BET surface areas. <sup>b</sup>The <sup>29</sup>Si and <sup>27</sup>Al MAS NMR chemical shifts are relative to SiMe<sub>4</sub> and AlCl<sub>3</sub>·6H<sub>2</sub>O, respectively.



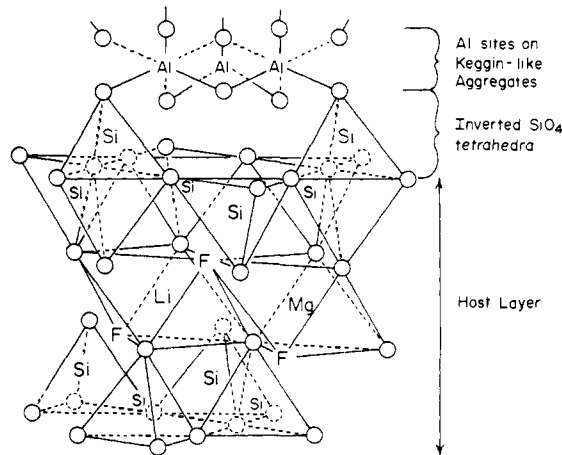
**Figure 1.** <sup>29</sup>Si (79.41 MHz) and <sup>27</sup>Al (104.3 MHz) MAS NMR spectra for uncalcined (25 °C) and calcined (350 °C) forms of pillared fluorohectorite I. MAS frequency, 4.0 KHz; pulse width, 2.0 μs; pulse delay, 2.0 s; number of transients, 800–1200; line broadening, 80–100 Hz.

find that the calcined pillared form of a related octahedrally charged fluorohectorite does undergo structurally significant transformations. Thus, *layer composition* also plays an important role in determining layer reactivity. In addition, we demonstrate that layer cross-linking is dependent on the *structure* of the gallery aluminum ions.

Synthetic fluorohectorite with a unit cell composition of Li<sub>1.6</sub>[Li<sub>1.6</sub>Mg<sub>4.4</sub>]Si<sub>8.0</sub>O<sub>20</sub>F<sub>4</sub> was allowed to react at 25 °C with an aqueous aluminum chlorohydrate (ACH) solution (Chlorhydrol, Reheis Chemical Co.) according to previously described methods<sup>3</sup> to form pillared product I. ACH solutions,<sup>4</sup> which are prepared by reaction of AlCl<sub>3</sub> with Al and have a OH/Al (mol/mol) ratio of 2.50, contain a large fraction of the total Al in the form of the Keggin-like [Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>7+</sup> ion. Hydrolyzed analogues of this Al<sub>13</sub> ion are believed to function as the initial pillaring species.<sup>1,3,5,6</sup>

A second pillared product (II) was prepared by using base-hydrolyzed AlCl<sub>3</sub> (OH/Al = 2.42) as the source of Al<sub>13</sub> cations.<sup>3,4,7</sup> For purposes of comparison, a simple, nonpillared Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> exchange form of the clay III was synthesized by ion exchange with 0.1 M AlCl<sub>3</sub> (OH/Al = 0.0). Table I provides the number of gallery Al ions per unit cell, the basal spacings, and N<sub>2</sub> BET surface areas for each product following calcination at 350 °C.

The <sup>29</sup>Si MAS NMR spectrum of the parent clay exhibits a single line at -92.8 ppm. This line is indicative of Si in a Q<sup>3</sup>(OAl)-type environment in which three oxygen atoms of the SiO<sub>4</sub> tetrahedron are bridging adjacent tetrahedral all occupied by silicon. Analogous Si sites in related phyllosilicates exhibit chemical shifts in the range -93 to -98 ppm.<sup>8</sup> A single <sup>29</sup>Si

**Chart I**

resonance also is observed for the parent clay after calcination at 350 °C.

As shown in Figure 1, the uncalcined form of I exhibits a single <sup>29</sup>Si resonance indicative of unaltered Q<sup>3</sup>(OAl) sites, as expected for the electrostatic binding of Al<sub>13</sub> cations to the negatively charged layers. Also, the <sup>27</sup>Al MAS NMR spectrum of uncalcined I (cf., Figure 1) exhibits lines at 65.5 and 3.3 ppm due to Al in tetrahedral and octahedral environments, respectively. This latter result, as noted previously,<sup>1</sup> is consistent with the presence of partially hydrolyzed Al<sub>13</sub> cations in the galleries. When I is calcined at 350 °C, a second resonance appears in the <sup>29</sup>Si spectrum, indicating the formation of a new Si environment due to reaction between the host layer and the pillar. Since the calcination of I does not significantly alter the positions of the <sup>27</sup>Al resonances, the initial Al<sub>13</sub> cations and alumina oligomers formed by their dehydration/dehydroxylation are structurally similar. In agreement with Plee et al.,<sup>1</sup> we observe <sup>27</sup>Al MAS NMR spectra analogous to I for uncalcined and calcined versions of pillared montmorillonites and Laponites, but, unlike I, these derivatives exhibit only a single Q<sup>3</sup>(OAl) <sup>29</sup>Si resonance indicative of unaltered layers.

The <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra for II are similar to those described for I (cf. Table I). Thus, the layer rearrangement which occurs upon calcination is independent of the source of the Al<sub>13</sub> cations. It is significant that the MAS NMR results for the nonpillared product III (cf., Table I) differ from those for I and II. The presence of simple mononuclear aluminum ions in the galleries in the case of III results in a single Q<sup>3</sup>(OAl) <sup>29</sup>Si resonance and a single octahedral <sup>27</sup>Al resonance even when calcined at 350 °C. Thus, the reaction that takes place upon calcination of pillared products I and II also is dependent on the *structure of the gallery aluminum ions*.

Plee et al.<sup>1</sup> have proposed a model for layer cross-linking in tetrahedrally charged beidellite. In this model some of the AlO<sub>4</sub> tetrahedra in the host layers are altered and coupled to the pillaring alumina aggregates. An analogous model is capable of explaining layer cross-linking in fluorohectorite, except that SiO<sub>4</sub> rather than AlO<sub>4</sub> units are inverted (see Chart I). The inverted tetrahedra place Si in a Q<sup>4</sup>(1Al) environment in which three of the oxygens

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of the SiO<sub>4</sub> unit are linked to Si and the fourth is linked to Al. The shifts observed for the inverted SiO<sub>4</sub> tetrahedra are in the range normally observed for Q<sup>4</sup>(1Al) sites in zeolites (-96 to -107 ppm).<sup>9</sup> Deconvolution of the <sup>29</sup>Si MAS NMR spectrum for I indicates that 40% of the SiO<sub>4</sub> tetrahedra in the layers have reacted. Presumably, the Al centers to which the layers couple retain the octahedral environment of a Keggin-like structure, because there is little change in the <sup>27</sup>Al MAS NMR spectrum upon layer cross-linking.

The reaction of SiO<sub>4</sub> units in alumina pillared fluorhectorite but not alumina pillared montmorillonite or Laponite apparently is related to the presence of F in the former clay which stabilizes Si-O bonds and promotes coupling. In montmorillonite and Laponite the layers are unreactive and pillaring presumably involves van der Waals interactions or, more likely, simple dative bond formation between the layer oxygens and coordinatively unsaturated sites on the alumina aggregates.

Cross-linking mechanisms that involve structural rearrangements of the host layers should be of fundamental importance in understanding the thermal stability and catalytic properties of the pillared clay. Future studies will relate changes in structural properties with differences in stability and catalytic activity.

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### Highly Conductive Metallomacrocyclic Assemblies. Synthesis via Electrocrystallization and Single-Crystal Properties of a Phthalocyanine "Molecular Metal" without Halogen Counterions

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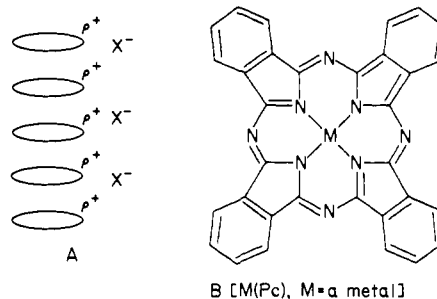
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The structural, electrical, magnetic, and optical properties of many low-dimensional molecular conductors<sup>1</sup> are a sensitive function of the interactions taking place between the band-forming molecular arrays and charge-compensating, off-axis counterions (e.g., A). To varying, largely unquantified degrees, such in-



teractions likely influence crystal structure,<sup>1,2</sup> band-filling ( $\rho^+$ ),<sup>1-3</sup> Coulombic screening,<sup>1,3,4</sup> and charge and spin density wave phenomena,<sup>1,5</sup> as well as the onset of superconductivity.<sup>1,5</sup> Despite recent advances that have been achieved in modifying the M and Pc components of phthalocyanine (B) molecular conductors,<sup>2a,6</sup> materials having counterions other than halogens (usually I<sub>3</sub><sup>-</sup>)<sup>2a</sup> are conspicuous in their paucity.<sup>7</sup> We communicate here the single-crystal synthesis via high-temperature electrocrystallization<sup>8</sup> and some of the interesting properties of the first non-halogenated phthalocyanine "molecular metal", Ni(Pc)(BF<sub>4</sub>)<sub>0.33</sub> (1).<sup>9</sup>

Because of severe solubility limitations, fragile, needlelike, golden crystals of 1 were necessarily grown at high temperatures (>100 °C), galvanostatically (0.5  $\mu$ A, Pt wire anode) from solutions of rigorously purified Ni(Pc), Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup>, and 1-chloronaphthalene under anaerobic/anhydrous conditions. Larger quantities in powder form (identical spectroscopically, analytically, and diffractometrically) can be prepared from Ni(Pc) and NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>9</sup> Preliminary work<sup>10a</sup> indicates that this electrochemical approach is generalizable to a wide range of counterions (e.g., PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, etc.) and phthalocyanines. Although BF<sub>4</sub><sup>-</sup> and I<sub>3</sub><sup>-</sup> differ substantially in spatial requirements, single-

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