

ior of heat release or thermalization of photofragments. This kind of quantum interference effects are to be found even in the cell experiment,<sup>16</sup> where the different dissociation channels can be investigated by detection of photoacoustic or photothermal signals.

### Summary

We have shown that the acoustic wave generated by multiphoton dissociation of chlorine molecules in argon can be detected by PBD. Since PBD is a noncontact technique, this detection method can be used in the corrosive environment where the diaphragm of microphone can be easily destroyed. Detection of acoustic wave or heat release by PBD can be an alternative choice of studying photodissociation of molecules with high sensitivity and even quantum interference effect in the cell may have good reason to be studied by PBD.

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## Effect of Electrolyte and Solvent in Axial Ligation of Tetrakis(2,6-dichlorophenyl)porphyrinato Manganese(III) and -(II) Complexes

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Manganese porphyrins have several interesting aspects of physical, chemical, and biological properties which distinguish them from other metalloporphyrins.<sup>1-3</sup> Manganese porphyrins are of interest as catalysts for the epoxidation of olefins and for hydrocarbon oxygenation,<sup>4-8</sup> as models for the behavior of cytochrome P-450,<sup>9</sup> photosystem II,<sup>10</sup> and superoxide dismutase.<sup>11</sup> Particularly axial ligation of manganese porphyrins coupled with their redox chemistry is very crucial in diverse biological functions.<sup>12-17</sup> Recently we investigated the redox chemistry and autoreduction of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl by hydroxide ion.<sup>18</sup> Electrochemistry, spectrophotometry, and conductometry were used for determining the state of axial ligation of Mn<sup>III</sup>(TPP)Cl in solutions, they reveal that the axial Cl<sup>-</sup> ligand is bound to Mn<sup>III</sup> and Mn<sup>II</sup> oxidation states in non-ligating solvents, but Cl<sup>-</sup> is dissociated from Mn<sup>III</sup>(TPP)Cl in stronger ligating solvents.<sup>19-23</sup> In this study, thin-layer spectroelectrochemistry has been used to probe the effect of electrolyte and solvent on axial ligation of manganese substituted tetra-phenyl porphyrins [Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl and Mn<sup>III</sup>(Me<sub>12</sub>TPP)Cl].

### Experimental

**Reagents.** Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl and Mn<sup>III</sup>(Me<sub>12</sub>TPP)Cl were synthesized by literature procedures.<sup>16,24</sup> Anhydrous acetonitrile (MeCN), methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), dimethyl formamide (DMF), and dimethylsulfoxide (DMSO) were used as received from Aldrich. As supporting electrolytes, tetrabutyl ammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) and tetrabutyl ammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) were used as received from Aldrich, and tetrabutyl ammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) and tetraethyl ammonium chloride (Et<sub>4</sub>NCl) were purchased from Tokyo Chemical Inc. and vacuum desiccated before use.

**Equipment and Procedures.** Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell containing a Pt mesh working electrode *via* controlled potential electrolysis using three electrode potentiostat (Bioanalytical Systems, Model CV-27). A platinum-wire electrode separated from the analyte compartment by a medium porosity glass frit was used as an auxiliary elec-

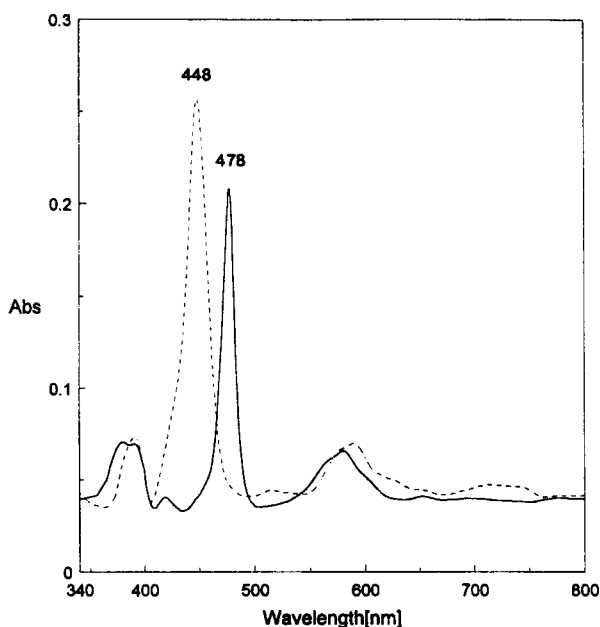
trode. A Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.00 V vs SCE)<sup>25</sup> with a solution junction *via* a Pyrex-glass tube closed with a cracked-glass bead (soft glass). Absorption spectra were recorded on a Jasco V-530 spectrophotometer equipped with a HMC-358 constant temperature cell holder, and an optical path length is 0.2 mm. All experiments are carried out under anaerobic conditions and at room temperature.

## Results and Discussion

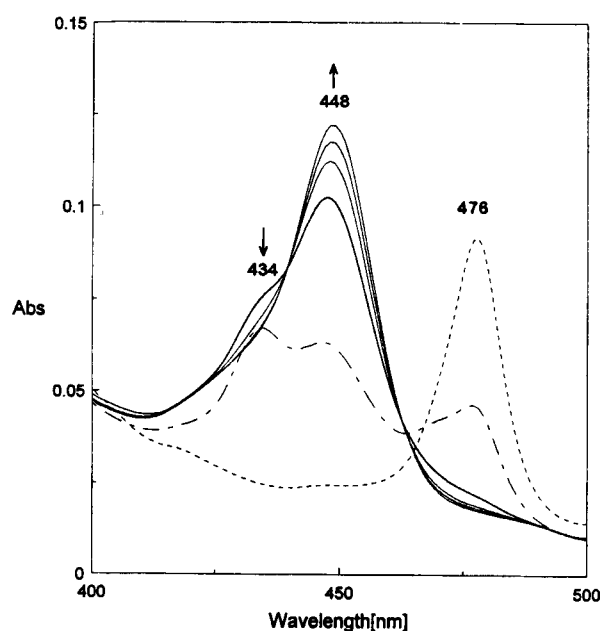
**Spectroelectrochemical studies for Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub>.** The electronic absorption spectra of Mn<sup>III</sup> and Mn<sup>II</sup> porphyrins were measured over the range of 340–800 nm. Figure 1 illustrates the absorption spectra of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl and its spectroelectrochemical reduction product in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Et<sub>4</sub>NCl. The spectrum of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl exhibits a Soret band maximum at 478 nm and Q band at 580 nm. The spectrum of reduced Mn<sup>II</sup> complex is obtained by holding the potential of the working electrode at -0.3 V vs SCE. When Et<sub>4</sub>NCl or Bu<sub>4</sub>NClO<sub>4</sub> is used as a supporting electrolyte, the optical spectra of the reduced Mn<sup>II</sup> form reveals that the Soret maximum shifts slightly in energy to 448 nm and intensifies relative to that of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl, and Q band shows at 589 nm. The result suggests the formation of [Mn<sup>II</sup>(TPP)Cl]<sup>-</sup> as Mn<sup>II</sup> form by electrochemical reduction of Mn<sup>III</sup>(TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Et<sub>4</sub>NCl or Bu<sub>4</sub>NClO<sub>4</sub> as an electrolyte. It was recently reported that the axial Cl<sup>-</sup> ligand is bound to the metal in both oxidation states of Mn<sup>III</sup>(TPP)Cl and [Mn<sup>II</sup>(TPP)Cl]<sup>-</sup> in non-ligating solvents such as CH<sub>2</sub>Cl<sub>2</sub> and ClCH<sub>2</sub>CH<sub>2</sub>Cl containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>. This result described the direct formation of [Mn<sup>II</sup>(TPP)Cl]<sup>-</sup> by reduction of Mn<sup>III</sup>(TPP)Cl without any exchange at axial position.<sup>19</sup>

tion.<sup>19</sup>

Spectroelectrochemical studies for the reduction of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl is executed in non-ligating solvents containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> or Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte. The electronic spectra of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl obtained from a series of supporting electrolytes (Et<sub>4</sub>NCl, Bu<sub>4</sub>NClO<sub>4</sub>, Bu<sub>4</sub>NBF<sub>4</sub>, and Bu<sub>4</sub>NPF<sub>6</sub>) are almost identical in CH<sub>2</sub>Cl<sub>2</sub>. Visible spectral changes observed for the spectroelectrochemical reduction of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> is shown in Figure 2 over the range of 400–500 nm. The similar result is obtained when Bu<sub>4</sub>NBF<sub>4</sub> is used as a supporting electrolyte. Examination of Figure 2 describes that the absorption band gives initially rise to 434 and 446 nm during thin-layer electrolysis, and then the band at 434 nm slowly disappears, and 446 nm shifts to 448 nm and intensifies relative to that of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl. The Q bands have at 577 and 621 nm. There are seen isosbestic points (417, 439, 463 and 495 nm) which demonstrate the absence of any long-lived intermediates. On the basis of its Soret band, the absorbance at 434 nm may be assigned to Mn<sup>II</sup>(Cl<sub>8</sub>TPP) as a dissociation form of chloride ion, and the Soret band at 448 nm may be assigned to [Mn<sup>II</sup>(Cl<sub>8</sub>TPP)Cl]<sup>-</sup>. These assignments are comparable to the results reported from the literature.<sup>16,26</sup> Although the direct formation of [Mn<sup>II</sup>(TPP)Cl]<sup>-</sup> by electrochemical reduction of Mn<sup>III</sup>(TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Et<sub>4</sub>NCl or Bu<sub>4</sub>NClO<sub>4</sub> is apparently dominant, it has been demonstrated that Cl<sup>-</sup> is lost in the reduction process to Mn<sup>II</sup>(Cl<sub>8</sub>TPP), and then Mn<sup>II</sup>(Cl<sub>8</sub>TPP) may slowly recombine with the Cl<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> or Bu<sub>4</sub>NBF<sub>4</sub>. Effect of supporting electrolytes for Mn<sup>III</sup>(Me<sub>12</sub>TPP)Cl is not observed in CH<sub>2</sub>Cl<sub>2</sub> containing any electrolytes, and the result is similar to that of Mn<sup>III</sup>(TPP)Cl solution. Spectroelectrochemical reduction of Mn<sup>III</sup>(TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub> gives the direct formation of [Mn<sup>II</sup>(TPP)Cl]<sup>-</sup> without any intermediates. These



**Figure 1.** Spectroelectrochemical reduction of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Et<sub>4</sub>NCl. Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl (—) and Mn<sup>II</sup> form (---).



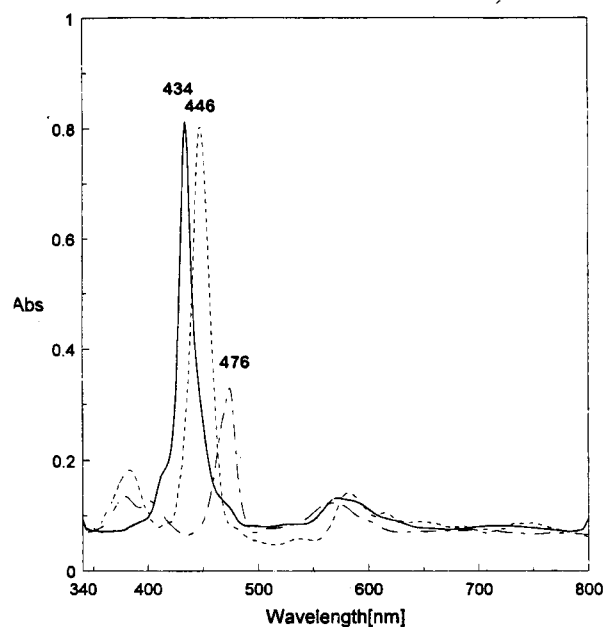
**Figure 2.** Visible spectral changes observed for the spectroelectrochemical reduction of Mn<sup>III</sup>(Cl<sub>8</sub>TPP)Cl in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>.

results indicate that the reduced  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})$  of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  having electron withdrawing substituted phenyl group bonded to *meso*-position of porphyrin ring may be somewhat metastable under conditions which are not contained chloride or perchlorate ion, that can be easily coordinated to manganese center.

**Spectroelectrochemical studies for  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  in ligating solvents.** Figure 3 illustrates the spectroelectrochemical reduction of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  in MeCN containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  and 0.1 M  $\text{Et}_4\text{NCl}$ , respectively. The spectrum of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  exhibits a Soret band maximum at 476 nm and Q band maxima at 581 nm, and is similar in solutions containing  $\text{Bu}_4\text{NClO}_4$  or  $\text{Bu}_4\text{NBF}_4$ . From the results of spectroscopic and conductometric methods, there is no evidence that  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  dissociates the chloride ion in MeCN as a weakly ligating solvent. On the basis of its Soret band, presumably  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  retains the chloride ion as five coordinate, or the chloride ion and MeCN as mixed-ligand six coordinate. The dissociation of chloride ion from  $\text{Mn}^{\text{III}}(\text{Me}_2\text{TPP})\text{Cl}$  was observed,<sup>16</sup> but does not occur for  $\text{Mn}^{\text{III}}(\text{TPP})\text{Cl}$  in MeCN.<sup>19</sup>

Examination of Figure 3 suggests that the optical spectra of reduced  $\text{Mn}^{\text{II}}$  complex are different in the electrolyte solutions. The spectrum of reduced  $\text{Mn}^{\text{II}}$  complex shows a Soret maximum at 434 nm and Q band at 575 nm in 0.1 M  $\text{Bu}_4\text{NPF}_6$  solution, whereas a Soret band at 446 nm and Q band at 580 nm in 0.1 M  $\text{Bu}_4\text{NCl}$  solution. According to the position of Soret band the formation by reduction of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  is apparently  $[\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})\text{Cl}]^-$  as five-coordinate in 0.1 M  $\text{Bu}_4\text{NCl}$  solution. A band at 434 nm is probably ascribed to  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})$  or  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})(\text{MeCN})_n$  ( $n=1$  to 2) as ligation of solvent in 0.1 M  $\text{Bu}_4\text{NPF}_6$  or  $\text{Bu}_4\text{NBF}_4$  solution. In  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{Bu}_4\text{NPF}_6$ , the absorption band at 434 nm observed from the reduction of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  is assigned to  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})$ , but it is unstable and slowly converts to  $[\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})\text{Cl}]^-$ . However in MeCN,  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})$  seems to be stable and it may be ligated with ligating solvent to form  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})(\text{MeCN})_n$ . The product assigned as  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})(\text{MeCN})_n$  is not observed in MeCN solutions having  $\text{Bu}_4\text{NClO}_4$  or  $\text{Bu}_4\text{NCl}$ , whereas  $[\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})\text{Cl}]^-$  is predominant product.

The spectrum of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  exhibits a Soret band maximum at 464 nm and Q bands at 566 and 605 nm in DMF containing 0.1 M  $\text{Bu}_4\text{NPF}_6$ . The spectrum of reduced  $\text{Mn}^{\text{II}}$  complex shows a Soret band at 438 nm and intensifies relative to that of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$ . Table 1 summarizes Soret bands measured from spectroelectrochemical method as a function of solvents for  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  and its  $\text{Mn}^{\text{II}}$  form in the solution containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  as a supporting electrolyte. To infer the identity of the axial ligands of manganese complexes in solvent employed, the shift of Soret band may be used under these conditions. The Soret band in ligating solvents gives blue shift relative to that in non-ligating solvents. Considering the relationship between the donor number of solvent and the extent of blue shift of Soret band for  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{II}}$  complexes, the shift extent for  $\text{Mn}^{\text{III}}$  complex is presumably proportional to the donor number of solvent. This result indicates that the  $\text{Mn}^{\text{III}}$  complex can be strongly ligated with solvent having higher value of donor number, and makes larger blue shift of Soret band. Adding ligating solvent to  $\text{Mn}^{\text{III}}$  complex may give



**Figure 3.** Spectroelectrochemical reduction of  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  in MeCN containing 0.1 M  $\text{Bu}_4\text{NPF}_6$  and 0.1 M  $\text{Bu}_4\text{NCl}$ .  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  (---),  $\text{Mn}^{\text{II}}$  form in  $\text{Et}_4\text{NCl}$  (---), and  $\text{Mn}^{\text{II}}$  form in  $\text{Bu}_4\text{NPF}_6$  (—).

**Table 1.** Absorption Soret bands measured from spectroelectrochemical method as a function of solvents for  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  and its  $\text{Mn}^{\text{II}}$  form (0.1 M  $\text{Bu}_4\text{NPF}_6$ )

| Solvent                             | DN <sup>a</sup> | $\lambda_{\text{max}}[\text{Mn}^{\text{III}}](\text{nm})$ | $\lambda_{\text{max}}[\text{Mn}^{\text{II}}](\text{nm})$ |
|-------------------------------------|-----------------|-----------------------------------------------------------|----------------------------------------------------------|
| $\text{CH}_2\text{Cl}_2$            |                 | 478                                                       | 448                                                      |
| $\text{ClCH}_2\text{CH}_2\text{Cl}$ |                 | 478                                                       | 448                                                      |
| MeCN                                | 14.1            | 476                                                       | 434                                                      |
| THF                                 | 20.0            | 469                                                       | 436                                                      |
| DMF                                 | 26.6            | 464                                                       | 438                                                      |
| DMSO                                | 29.8            | 464                                                       | 438                                                      |

<sup>a</sup> DN: Donor Number, from ref. 27.

mixed six-coordinate  $\{\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})(\text{L})\text{Cl}\}$  or bisligated six-coordinate  $\{\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})(\text{L})_2\}^+$  structure. The red shift extent of Soret band for  $\text{Mn}^{\text{II}}$  form seems to be proportional to the donor number of solvent based on the chloride dissociated form  $[\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})]$  which is shown Soret band at 434 nm in  $\text{CH}_2\text{Cl}_2$ . The suggestion on the red shift of Soret band in the  $\text{Mn}^{\text{II}}$  form may also be donation effect of solvent, and the coordination of chloride ion to  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})$  to produce  $[\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})\text{Cl}]^-$  shifts to 448 nm from 434 nm as Soret band of  $\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})$ . Finally, we conclude that the dissociation of chloride ion is dependent on solvent as well as electrolyte used for the spectroelectrochemical studies, and the dissociation of chloride ion from  $\text{Mn}^{\text{III}}(\text{Cl}_8\text{TPP})\text{Cl}$  is more difficult than from  $[\text{Mn}^{\text{II}}(\text{Cl}_8\text{TPP})\text{Cl}]^-$ .

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## Thermal Generation of 2-Silanaphthalene Intermediates

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There have been many reports of the generation and reaction of silabenzene intermediate, an attractive molecule in silicon chemistry, from the readily available chloro or allyl precursors.<sup>1</sup> The first generation of silatoluene intermediate formed *via* a thermally induced retro-ene extrusion of propene from 1-methyl-1-allyl-1-silacyclohexa-2,4-diene was reported by the Barton group,<sup>2</sup> and the existence was confirmed by matrix isolation method at low temperature.<sup>3</sup> Thermal fragmentation of 1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl-diazomethane to give silatoluene was reported by Ando and Sekiguchi.<sup>4</sup> West and Rich reported evidence for the existence of hexamethyl-1,4-disilabenzene intermediate produced by photochemical or thermal extrusions of anthracene from the precursor.<sup>5</sup> The attempted generation of 9-silaanthracene from the suitable precursors has been reported.<sup>6,7a</sup> However, in solution, the necessary elimination for formation of 9-silaanthracene from the chloro precursors fails to occur and reaction proceeds *via* intermolecular substitution leading to dimeric or polymeric products.<sup>6a,b</sup> No evidence for the generation of 9-silaanthracene intermediate from photolysis of 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene in methanol<sup>7a</sup> and flash vacuum thermolysis

of 9,10-dibenzyl-9,10-diphenyl-9,10-dihydro-9-silaanthracene<sup>6c</sup> was observed. There is a precedent for the unsuccessful approach to generate 2-silanaphthalene intermediate from the thermolysis or photolysis of diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene (**4**) in the presence of methanol.<sup>7</sup>

Recently, we reported the results of a thermolytic reaction of 2-allyl-2-methyl-1,2-dihydro-2-silanaphthalene (**1**) with methanol or methanol-*d*<sub>1</sub> in which appeared to involve generation of, an aromatic silicon-containing analogue of naphthalene, 2-methyl-2-silanaphthalene intermediate (**2**).<sup>8</sup>



We now wish to report the generation and trapping of 2-allyl- (**9**) and 2-methoxy-2-silanaphthalene (**11**) intermediates which could arise from the thermolytic reaction of 2,2-diallyl-1,2-dihydro-2-silanaphthalene (**7**) with methanol or methanol-*d*<sub>1</sub>.