

(e.g., Cu) complexes would not be, but we cannot yet explain the peculiarity of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ . Solutions of  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  without PBP, or their complexes with tyrosine, or mixtures of metal and PBP without base are ineffective for pyrene transport. The binding ability of the self-assembled  $\text{Co}^{2+}$  complex is destroyed by addition of EDTA, which sequesters the metal; pyrene transport returns to the background rate. A Job's plot<sup>14</sup> (data not shown) at  $[\text{PBP}] + [\text{Co}^{2+}] = 1.74 \text{ mM}$  confirms that the species responsible for transport has a 1:1 ratio of PBP: $\text{Co}^{2+}$ , as expected for a 2:2 PBP: $\text{Co}^{2+}$  complex.

The pyrene transport rate (Figure 2) is directly proportional to the concentration of 1:1  $\text{Co}^{2+}$  and PBP added.<sup>15</sup> We have measured (see below) an 8-fold increase in the concentration of pyrene in water at equilibrium with 10 mM pyrene in isoctane due to the presence of  $9.6 \times 10^{-4} \text{ M}$  each of  $\text{Co}^{2+}$  and PBP. This nicely matches the 8-fold increase in transport rate of the regression line.

The transport rate depends on the amount of pyrene dissolved in the aqueous phase, which in turn depends on the concentration of host and on the binding constant of the host for pyrene. The concentration of host complex is related to the concentration of  $\text{M}(\text{amino acid})_2$ , which we have estimated from known stability constants<sup>13</sup> for metal complexes of phenylalanine; these are displayed in Table I. They are minimal estimates of  $\text{ML}_2$  formation for the macrocyclic case. The transport rate does not correlate with stability, which suggests that transport rate is dependent not only on the amount of host complex formed but also, as we expected, on the geometry of the complex.

If the binding species is of composition  $\text{Co}_2\text{PBP}_2$ , its concentration must be  $\leq 4.8 \times 10^{-4} \text{ M}$  at  $9.6 \times 10^{-4} \text{ M}$  added  $\text{Co}^{2+}$ . An upper limit for the dissociation constant for pyrene may be calculated on the basis of concentrations of pyrene measured (by extraction<sup>7a</sup>) in water with and without  $\text{Co}_2\text{PBP}_2$  ( $2.07 \times 10^{-6}$  and  $2.60 \times 10^{-7}$ , respectively). A value of  $K_D \leq 6.9 \times 10^{-5} \text{ M}$  is obtained, which favorably compares with the value of  $5.5 \times 10^{-7} \text{ M}$  observed by Diederich<sup>7a</sup> for pyrene binding by a related host bearing eight ortho methyl groups. Our self-assembled structure appears to bind within an order of magnitude as well as would a covalent host without methyl groups.<sup>16</sup>

The  $\text{Co}^{2+}$ /PBP complex transports pyrene selectively.  $\text{Co}^{2+}$ /PBP solutions ( $9.6 \times 10^{-4} \text{ M}$ ) transport aromatic compounds at the following rates ( $\pm 20\%$ ), relative to background: pyrene, 10; acenaphthene, 2.3; naphthalene, 1.2; 9-bromoanthracene, 1.3, *p*-iodotoluene, 1.0; biphenyl, 0.94. Bromoanthracene has a shape incompatible with the expected cavity, but naphthalene does not show enhanced transport even though it is expected to fit into the cavity. The background transport rate for naphthalene exceeds the facilitated pyrene rate, so that even if binding occurs, it may not manifest itself as measurably enhanced transport. Consistent with this interpretation, addition of  $7.1 \times 10^{-4} \text{ M}$  *N*-methylquinolinium iodide to  $8.1 \times 10^{-4} \text{ M}$   $\text{Co}^{2+}$  and PBP causes a 46% decrease in pyrene transport rate, presumably by competing for well-defined binding sites.

These complexes have many interesting features, not least the open coordination sites on the octahedral metal ions available for catalysis of reactions of bound substrates and the capability for oxidation to substitutionally inert and diamagnetic  $\text{Co}^{3+}$ , which should make isolation and characterization of the isomer(s) responsible for the binding possible.

In conclusion, we have shown that binding of aromatic hydrocarbons from water by a binding site self-assembled by metal-ligand interactions is feasible and that significant variation of binding propensity may be achieved by choice of metal. The structures of these complexes remain to be elucidated.

**Acknowledgment.** We thank the donors of the Caldwell Fellowship for support of this work.

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## Synthesis and X-ray Crystallographic Analysis of Pentacoordinate 1,2-Oxasiletanides, Intermediates of the Peterson Reaction

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The Peterson reaction has been widely utilized for olefin synthesis as a silicon analog of the Wittig or Horner-Emmons reaction.<sup>1</sup> One of the features of this reaction is that (*E*) and (*Z*) olefins can be obtained stereospecifically from a single diastereomer of ( $\beta$ -hydroxyalkyl)silanes by changing reaction conditions (acidic vs basic).<sup>1b,d,2</sup> From analogy with the Wittig reaction and from studies on the stereochemistry of the reaction (syn-elimination),<sup>2</sup> a pentacoordinate 1,2-oxasiletanide has been considered as a reaction intermediate or transition state, but neither isolation nor spectroscopic observation of such a species has been reported. Very recently, we succeeded in the synthesis of isolable pentacoordinate 1,2-oxaphosphetanes bearing the Martin ligand, i.e., intermediates of the Wittig reaction.<sup>3</sup> We now report the first synthesis and X-ray crystallographic analysis of 1,2-oxasiletanides, intermediates of the Peterson reaction.

Sequential treatment of vinylsilane **1**<sup>4</sup> bearing the Martin ligand with 1.5 equiv of *t*-BuLi (THF,  $-78^\circ\text{C}$ ), 5 equiv of hexamethylphosphoric triamide (HMPA), and then excess carbonyl compounds (**2a,b**) (THF,  $-78^\circ\text{C}$ , 1 h) gave a diastereomeric mixture of the corresponding  $\beta$ -hydroxy silanes **3a** (34%) and **3b** (56%), together with olefins **4** and byproducts **5** and **6** (Scheme I).<sup>5</sup> During purification by chromatography on silica gel, the more reactive diastereomer(s) decomposed to give olefins and only the less reactive one remained (recovery: **3a** (67%) and **3b** (38%)).<sup>6</sup>

Deprotonation of a single diastereomer of **3a** thus obtained with *n*-BuLi in THF was monitored by <sup>19</sup>F and <sup>29</sup>Si NMR spectroscopy to show that 1,2-oxasiletanide **7a** was formed quantitatively and that two sets of double quartets with centers of  $\delta_{\text{F}} -77.77$ ,  $-74.63$  ( $^4J_{\text{FF}} = 9.5 \text{ Hz}$ ) and  $-76.13$ ,  $-73.89$  ( $^4J_{\text{FF}} = 9.8 \text{ Hz}$ ) and a singlet ( $\delta_{\text{Si}} -72.45$  at  $-50^\circ\text{C}$ ) in the <sup>19</sup>F and <sup>29</sup>Si NMR spectra, respectively, for **7a** were unchanged from  $-50^\circ\text{C}$  to room temperature. The large upfield shift in  $\delta_{\text{Si}}$  from **3a** ( $\delta_{\text{Si}} 10.66$ )<sup>7</sup> to **7a** strongly supports the structure of a pentacoordinate silicate.<sup>8</sup>

It was found by <sup>19</sup>F NMR spectroscopy that **7a** provided olefin **4a** and lithium silanoxide **9** in 86% yield together with unreacted **7a** (14%) upon heating ( $40^\circ\text{C}$ , THF, 24 h), indicating that **7a** is a real intermediate of the Peterson reaction. Treatment of **7a** with acetic acid at room temperature resulted in the quantitative recovery of **3a**.<sup>9</sup>

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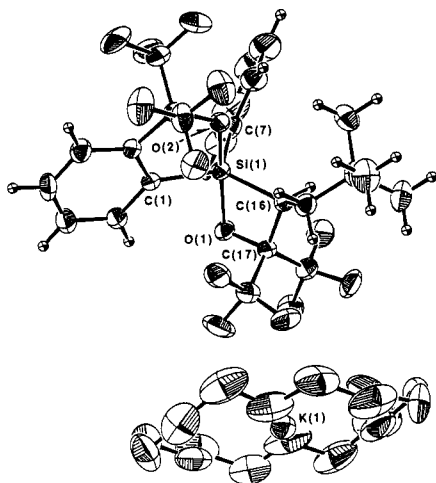
(4) Vinylsilane **1** was prepared from dichlorophenylvinylsilane by modifying the reported method: Yamamoto, Y.; Takeda, Y.; Akiba, K.-Y. *Tetrahedron Lett.* 1989, 30, 725.

(5) In the <sup>1</sup>H NMR spectra, two and four singlets due to *tert*-butyl groups were observed in the ratios of 21:79 and 1:14:20:65 for **3a** and **3b**, respectively, although the stereochemistry of the diastereomers was not determined. Yields of **4**, **5**, and **6** were 0, 21, and 21% for **2a** and 9, 27, and 8% for **2b**, respectively.

(6) In the case of **3b**, the *E:Z* ratio of olefin **4b** thus obtained was 87:13.

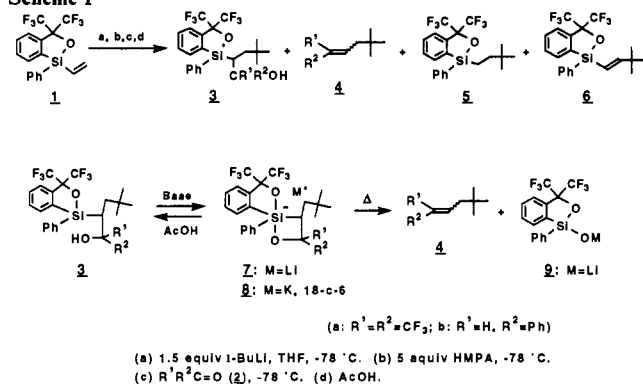
(7) The <sup>29</sup>Si NMR spectrum of **3a** was taken at  $-50^\circ\text{C}$ ; no signal could be observed at room temperature.

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**Figure 1.** ORTEP drawing of **8a**. Selected bond lengths (Å) and bond angles (deg): Si(1)–O(1), 1.844 (4); Si(1)–O(2), 1.798 (4); Si(1)–C(16), 1.913 (5); O(1)–Si(1)–O(2), 166.3 (2); C(1)–Si(1)–C(7), 115.4 (2); C(1)–Si(1)–C(16), 132.7 (2); C(7)–P(1)–C(16), 111.1 (2); O(1)–Si(1)–C(16), 73.9 (2); O(2)–Si(1)–C(1), 85.6 (2).

### Scheme I



The use of KH instead of *n*-BuLi as base in the presence of 18-crown-6 in THF gave potassium 1,2-oxasiletanide **8a** in 91% yield as colorless needles after recrystallization from hexane-dichloromethane. Its  $^{19}F$  and  $^{29}Si$  NMR spectra are very similar to those of the lithium salt **7a**.

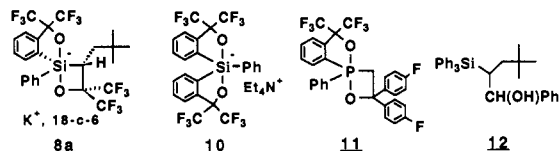
The X-ray crystallographic analysis of **8a** indicated that it has a distorted TBP (trigonal bipyramide) structure (Figure 1).<sup>10,11</sup> The phenyl group on silicon is trans to the neopentyl group, and as expected, two oxygen and three carbon atoms occupy apical and equatorial positions, respectively. The bond angle O(1)–Si(1)–O(2) between two apical bonds deviates by 13.7 (2)° from 180°. The bond length of Si–O(1) (1.844 (4) Å) is slightly longer than that of Si–O(2) (1.798 (4) Å), although both bonds are substantially longer than that of the Si–O bond (1.696 (6) Å) of a tetracoordinate 1,2-oxasiletane.<sup>12</sup> The structure of the Martin ligand moiety is very similar to that of pentacoordinate compounds such as **10**<sup>8a</sup> and **11**.<sup>3</sup> The strain of the four-membered ring seems to be reduced by elongating the apical Si–O(1) bond in contrast to a tetracoordinate oxasiletane with usually long C–C and Si–C bonds.<sup>12</sup>

(9) The signals due to **7a** were also observed in the reaction mixture of the preparation of **3a**.

(10)  $C_{36}H_{45}F_7O_3Si$ , FW = 900.91, crystal dimensions (mm) 0.560 × 0.650 × 0.440, triclinic, space group *P*1, *a* = 14.063 (2) Å, *b* = 14.919 (2) Å, *c* = 11.451 (2) Å,  $\alpha$  = 97.78 (1)°,  $\beta$  = 114.27 (1)°,  $\gamma$  = 74.45 (1)°, *V* = 2104.8 (6) Å<sup>3</sup>, *Z* = 2,  $D_{\text{calc}}$  = 1.421 g/cm<sup>3</sup>, *R* = 0.057 (*R*<sub>w</sub> = 0.069). Full details of the crystallographic structure analysis are described in the supplementary material.

(11) The percentage (TBP → SP) was calculated to be 37.4% by a reported method: Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

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Similarly, a single benzaldehyde adduct **3b** reacted with *n*-BuLi and KH to give **7b** ( $\delta_{Si}$  –66.69) and **8b** ( $\delta_{Si}$  –66.31), which decomposed slowly at room temperature and 50 °C, respectively, to give exclusively (*Z*)-**4b**.<sup>13,14</sup> Since the benzaldehyde adduct **12** prepared from triphenylvinylsilane instead of **1** gave no upfield signal characteristic of a pentacoordinate siletanide in  $^{29}Si$  NMR under the same conditions, the Martin ligand is considered to play an important role in stabilizing a 1,2-oxasiletanide structure.

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**Supplementary Material Available:** Listing of physical and spectral data of **1**, **3a**, **4a**, **5**, **6**, **8a**, and **8b** and tables of X-ray crystallographic data including thermal and positional parameters, bond lengths, and bond angles for **8a** (14 pages). Ordering information is given on any current masthead page.

(13) Unexpectedly, the  $^{19}F$  NMR spectra of **7b** and **8b** showed two sets of double quartets (2:1), indicating the presence of two diastereomers. For the  $^1H$  and  $^{19}F$  NMR spectra of **8b**, see the supplementary material.

(14) A single diastereomer **3b** was treated with a few drops of concentrated  $H_2SO_4$  in THF at room temperature to give mainly (*E*)-**4b** (*E*:*Z*, 75:25), indicating that anti-elimination probably occurs under acidic conditions as with the usual Peterson reaction.

## A Dinuclear Mixed-Valence Cu(I)/Cu(II) Complex and Its Reversible Reaction with Dioxygen: Generation of a Superoxodicopper(II) Species

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In this report, we describe a dinuclear mixed-valence Cu(I)/Cu(II) complex, which *reversibly* reacts with dioxygen ( $O_2$ ) to form a  $Cu_2O_2$  adduct, formally a superoxodicopper(II) complex.

The reaction of  $O_2$  with copper(I) ion is of fundamental importance in a variety of chemical and biological processes.<sup>1–4</sup> The latter include  $O_2$  transport by hemocyanin (Hc),<sup>5,6</sup> substrate

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