(e.g., Cu) complexes would not be, but we cannot yet explain the peculiarity of Co²⁺ and Ni²⁺. Solutions of Co²⁺ or Ni²⁺ 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 Co²⁺ complex is destroyed by addition of EDTA, which sequesters the metal; pyrene transport returns to the background rate. A Job's plot¹⁴ (data not shown) at [PBP] + $[Co^{2+}] = 1.74$ mM confirms that the species responsible for transport has a 1:1 ratio of PBP:Co²⁺, as expected for a 2:2 PBP:Co²⁺ complex.

The pyrene transport rate (Figure 2) is directly proportional to the concentration of 1:1 Co^{2+} and PBP added.¹⁵ We have measured (see below) an 8-fold increase in the concentration of pyrene in water at equilibrium with 10 mM pyrene in isooctane due to the presence of 9.6 \times 10⁻⁴ M each of Co²⁺ 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 $M(amino acid)_2$, which we have estimated from known stability constants¹³ for metal complexes of phenylalanine; these are displayed in Table I. They are minimal estimates of ML₂ 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 Co_2PBP_2 , its concentration must be $\leq 4.8 \times 10^{-4}$ M at 9.6×10^{-4} M added Co²⁺. An upper limit for the dissociation constant for pyrene may be calculated on the basis of concentrations of pyrene measured (by extraction^{7a}) in water with and without Co_2PBP_2 (2.07 × 10⁻⁶ and 2.60 \times 10⁻⁷, respectively). A value of $K_D \leq 6.9 \times 10^{-5}$ M is obtained, which favorably compares with the value of 5.5×10^{-7} M observed by Diederich^{7a} 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.¹⁶

The Co^{2+}/PBP complex transports pyrene selectively. Co^{2+}/PBP solutions (9.6 × 10⁻⁴ 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 7.1×10^{-4} M N-methylquinolinium iodide to 8.1×10^{-4} M Co²⁺ 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 Co³⁺, 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.

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(15) Expected deviations from linearity due to dissociation of ML₂ complexes at low concentrations are minor

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

Takayuki Kawashima,* Naoshi Iwama, and Renji Okazaki*

Department of Chemistry, Faculty of Science The University of Tokyo, 7-3-1 Hongo Bunkyo-ku, Tokyo 113, Japan Received April 21, 1992

The Peterson reaction has been widely utilized for olefin synthesis as a silicon analog of the Wittig or Horner-Emmons reaction.¹ 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).^{1b,d,2} From analogy with the Wittig reaction and from studies on the stereochemistry of the reaction (syn-elimination),² 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.³ We now report the first synthesis and X-ray crystallographic analysis of 1,2-oxasiletanides, intermediates of the Peterson reaction.

Sequential treatment of vinylsilane 1⁴ bearing the Martin ligand with 1.5 equiv of t-BuLi (THF, -78 °C), 5 equiv of hexamethylphosphoric triamide (HMPA), and then excess carbonyl compounds (2a,b) (THF, -78 °C, 1 h) gave a diastereomeric mixture of the corresponding β -hydroxy silanes 3a (34%) and 3b (56%), together with olefins 4 and byproducts 5 and 6 (Scheme I).⁵ 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%)).6

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

It was found by ¹⁹F NMR spectroscopy that 7a provided olefin 4a and lithium silanoxide 9 in 86% yield together with unreacted 7a (14%) upon heating (40 °C, THF, 24 h), indicating that 7a is a real intermediate of the Peterson reaction. Treatment of 7awith acetic acid at room temperature resulted in the quantitative recovery of 3a.9

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⁽⁵⁾ In the ¹H 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.



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).



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 hexanedichloromethane. Its ¹⁹F and ²⁹Si 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).^{10,11} 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.¹² The structure of the Martin ligand moiety is very similar to that of pentacoordinate compounds such as 10^{8a} and 11.³ 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 ususually long C-C and Si-C bonds.12



Similarly, a single benzaldehyde adduct 3b reacted with n-BuLi and KH to give 7b (δ_{Si} -66.69) and 8b (δ_{Si} -66.31), which decomposed slowly at room temperature and 50 °C, respectively, to give exclusively (Z)-4b.^{13,14} Since the benzaldehyde adduct 12 prepared from triphenylvinylsilane instead of 1 gave no upfield signal characteristic of a pentacoordinate siletanide in ²⁹Si 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 ¹⁹F NMR spectra of 7b and 8b showed two sets of double quartets (2:1), indicating the presence of two diastereomers. For the ¹H and ¹⁹F 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

Mohammad Mahroof-Tahir and Kenneth D. Karlin*

Department of Chemistry The Johns Hopkins University Baltimore, Maryland 21218 Received May 21, 1992

In this report, we describe a dinuclear mixed-valence Cu(I)/Cu(II) complex, which reversibly reacts with dioxygen (O₂) 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.¹⁻⁴ The latter include O₂ transport by hemocyanin (Hc),^{5,6} substrate

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