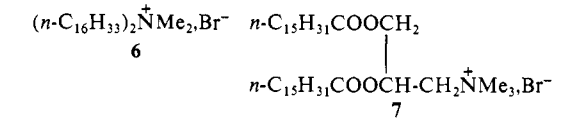
gestive of 3-4 lamellae. The drying process probably accounts for the smaller diameter, as compared to the fully hydrated vesicles studied by light scattering.

Native vesicular **2** is surprisingly unreactive toward active ester substrates such as *p*-nitrophenyl hexanoate (PNPH).[14a] At [**2**] = 1.0×10^{-3} M, k_ψ for this esterolysis is 4.2×10^{-4} s^{-1}, 27 000 times less than $k_\psi = 11.4$ s^{-1} for the analogous reaction of PNPH with vesicular **1**.[4] However, the reactivity of **2** is strongly potentiated in covesicles with nonfunctional cationic surfactants **6**



or **7**; cf., Figure 1 and Table I. Thus, at [**2**] = 3.5×10^{-4} M and [**6** or **7**] = 7.0×10^{-4} M, i.e., [total surfactant] = 1.05×10^{-3} M, k_ψ for PNPH cleavages are increased to 3.2×10^{-2} s^{-1} (by **6**) and 1.1×10^{-2} s^{-1} (by **7**). Correction for [**2**], affords second-order rate constants, k_2, of 91 M^{-1} s^{-1} (**2** + **6**) and 31 M^{-1} s^{-1} (**2** + **7**) for the covesicular cleavages of PNPH, representing kinetic enhancements of 217 and 74, respectively, over native vesicular **2** (Table I, cases 1-3).[14b] Similarly, the covesicles were also reactive (although not as reactive as native vesicular **1**) toward substrates 4-acetoxy-3-nitrobenzene sulfonate (ANBS)[4] and *p*-nitrophenyl acetate (PNPA); see Figure 1 and Table I, cases 5-10.

How is the imidazole moiety of **2** "switched on" in the covesicles? We suggest that the reactivity of vesicular **2** is controlled by the accessibility of the imidazole moieties to substrate. Phosphatidylcholine vesicles feature extensive electrostatic interactions between the N^+ and ^-O-P of adjacent headgroups; consequently, these lie parallel to the bilayer surface.[15] In native phospholipid **2**, this may "bury" the exovesicular imidazole moieties in the vesicular surface, so that they are relatively inaccessible to substrate. Additionally, in multilamellar vesicles of **2** only a small fraction of the imidazoles will be exovesicular; the good packing of the acylglycerol backbones will deny substrate access to the majority of imidazoles on interior lamellae, thus decreasing vesicular reactivity. Covesicles of **2** with **6** or **7**, in contrast, are much more permeable to substrate, their imidazole residues are consequently more accessible, and the reactivity is enhanced.

These suggestions are supported by measurements of the half-times ($\tau_{1/2}$, s) required for the development of fluorescence by added 1,8-anilinonaphthalene sulfonate (ANS) in stopped-flow experiments with vesicular **2**, (**2** + **6**) and (**2** + **7**). $\tau_{1/2}$ is inversely related to the rate constant for permeation of ANS into the vesicles[16,17] and should also reflect the accessibility of the endovesicular imidazoles of **2** toward the substrates. Native vesicles of **2** show *no* ANS permeation below 35 °C ($\tau_{1/2} = 1.63$ s at 40 °C, where T_c is 36 °C by fluorescence[11]), but 1:2 covesicular (**2** + **6**) shows "instantaneous" ($\tau_{1/2} < 5$ ms) ANS permeation at 20-40 °C, and 1:2 covesicular (**2** + **7**) has $\tau_{1/2} \sim 7$ s at 26 °C.[18]

Clearly, cationic covesicular additives **6** and **7** increase the permeability of vesicular **2** and, hence, access to the interior imidazole nucleophiles.[19] The mechanism of additive action may also involve substitution in the N^+-^-O-P headgroup association[15] of vesicular **2**, thus providing greater mobility and accessibility for the exovesicular imidazole moieties.

Although the reactivity of nucleophilic, imidazole-functionalized, vesicular **2** can be "adjusted" by covesicalization with **6** or **7**,[20] the reactivity of the covesicles remains inferior to that of native vesicular **1**. Partly, this may reflect greater accessibility of the imidazole residues in vesicles constructed solely with the dialkylammonium ion backbone. There could also be intrinsic, structure-based reactivity differences between the imidazole groups of **2** and **1**. However, the pK_a for ($ImH^+ \rightleftharpoons Im + H^+$) of covesicular (**2** + **7**) is ~5.3[21] (vs. ~5.5 for **1**[4]), and the solvent isotope effect (k_{H_2O}/k_{D_2O}) is 1.25 for the 1:2 (**2** + **6**) covesicular cleavage of ANBS. These results implicate the neutral imidazole moiety of **2** (perhaps assisted by hydroxide ion at N-H) in the nucleophilic cleavages of the ester substrates, as is also the case for vesicular **1**.[4]

Acknowledgment. We are grateful to the U.S. Army Research Office for support of this work and to Professor L. D. Simon (Waksman Institute) for electron microscopy.

(14) (a) Kinetic conditions: 0.01 M Tris buffer, pH 8.0 ± 0.1, $\mu = 0.01$ (KCl), 4 vol % EtOH, 25 °C, [substrate] = 1.0×10^{-5} M. k_ψ was determined by monitoring *p*-nitrophenoxide ion at 400 nm. Reproducibilities of k_ψ were generally <±2%, although one case featured ±7%. All runs in Table I or Figure 1 conformed to *good* pseudo-first-order kinetics with $r > 0.998$ over >90% of reaction. (b) Vesicles of **6** or **7** are not particularly reactive toward PNPH. Under the standard buffer conditions,[14a] PNPH is cleaved with $k_\psi = 5.43 \times 10^{-5}$ s^{-1}. With 1×10^{-3} M vesicular **6** or **7**, k_ψ increases to 1.34×10^{-4} or 1.18×10^{-4} s^{-1}, respectively, representing enhancements of 2.5 (**6**) or 2.2 (**7**). In contrast, the kinetic enhancements in PNPH cleavage (relative to buffer) are 589 (**2** + **6**) or 203 (**2** + **7**) for the covesicular systems. The differences between (**2** + **6**) and (**2** + **7**) are real and far beyond the reproducibilities of the kinetic data.

(15) Yeagle, P. L. *Acc. Chem. Res.* **1978**, *11*, 321.

(16) Moss, R. A.; Swarup, S.; Wilk, B.; Hendrickson, T. F. *Tetrahedron Lett.* **1985**, *26*, 4827.

(17) Haynes, D. H.; Simkowitz, P. *J. Membr. Biol.* **1977**, *33*, 63.

(18) T_c's for vesicular phase transitions from the "rigid" gel to the more fluid liquid crystalline phases were determined both by fluorescence polarization[11] and from discontinuities in Arrhenius plots (k_ψ vs. $1/T$) for PNPH cleavage. For native vesicles of **2**, $T_c = 36$ °C (fluorescence) or 31 °C (Arrhenius); for 1:2 covesicles of (**2** + **6**) or (**2** + **7**), $T_c = 27$ or 47 °C, respectively, by either method. Plots of fluorescence polarization vs. temperature[11] for (**2** + **6**) or (**2** + **7**) showed significant changes in T_c (in comparison to **2**) but only single, sharp, gel-to-liquid crystal transitions, suggesting both efficient intravesicular mixing of **6** or **7** with **2** and the absence of surfactant "sorting". Neither pure vesicular **2** nor **7** permits ANS permeation below their respective T_c's of 36 or 52 °C. Vesicular **6** is readily permeable at temperatures as low as 15 °C.

(19) The esterolytic reactivities of vesicular (**2** + **6**) and (**2** + **7**) increase by factors of 18 and 6, respectively, at T_c ± 3 °C, further implicating permeability of the substrate and fluidity of the vesicle interiors as reactivity controlling factors. Significantly, the reactivity of holovesicular **2** increases much less (factor of 2.5) at T_c ± 5 °C.

(20) A 2:1 ratio of **6** or **7** to **2** appears optimum for this purpose.

(21) This value comes from a rate constant vs. pH profile for the cleavage of PNPH by 1:2 covesicular (**2** + **7**).

Dimethylsilylene Insertion into Tantalum-Hydride Bonds

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Received May 29, 1987

The insertion of silylenes into heteronuclear single bonds is the most well-established type of reaction for these divalent intermediates.[1] As part of our studies of silylene transfer to transition-metal substrates we recently reported the synthesis of dimethylsilyl complexes from molybdenum hydrides by using hexamethylsilacyclopropane (HMS),[2] a source of dimethylsilylene under mild conditions.[3] The apparent insertion of dimethylsilylene into the Mo-H bonds, however, was found to be the net result of a radical chain mechanism, which does not involve dimethylsilylene. We now report the silylation of tantalum hydride complexes with HMS, which apparently proceeds via the insertion

(1) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley: New York, 1978; Vol. 1, p 229; 1981; Vol. 2, p 335; 1985; Vol. 3, p 333.

(2) Berry, D. H.; Mitstifer, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 3777-3778.

(3) Seyferth, D.; Annarelli, D. C.; Duncan, D. *Organometallics* **1982**, *1*, 1288-1294, and references therein.

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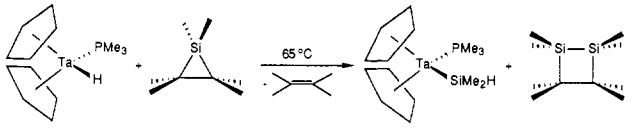
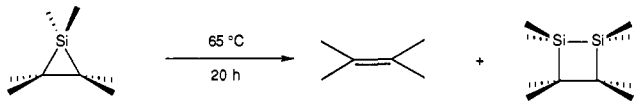
of dimethylsilylene into Ta–H bonds.

Treatment of $Cp_2Ta(PMe_3)(H)$ with a stoichiometric amount of HMS in benzene results in no reaction after several days at room temperature. After 15 h at 65 °C, however, silylation is observed according to eq 1.



(1)

Although the hydride and a new dimethylsilyl complex, $Cp_2Ta(PMe_3)(SiMe_2H)$ (**1**), are the only metal-containing compounds observed, a substantial amount of octamethyl-1,2-disilacyclobutane is also produced ($\mathbf{1}/Me_8Si_2C_2 \sim 1$). Seyferth has reported this disilacyclobutane and tetramethylethylene as the primary products in the thermolysis of HMS, arising from extrusion of dimethylsilylene and subsequent insertion into a Si–C bond of HMS (eq 2).[4]

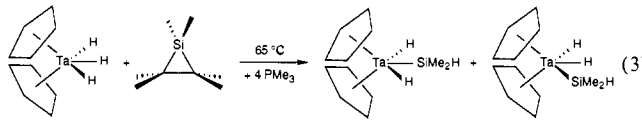


(2)

Significantly, addition of a radical initiator to the reaction has no effect on the qualitative rate of silylation at tantalum.[5] In contrast, radical chain silylation of $CpMo(CO)_3H$ at 25 °C with HMS is extremely sensitive to initiation.[2] We suggest, therefore, that **1** arises from the insertion of extruded dimethylsilylene into a Ta–H bond but that Si–C insertion is competitive, leading to concurrent formation of the disilacyclobutane.

The selectivity of silylene insertion is dramatically improved by the addition of trimethylphosphine. When the silylation is run in the presence of 4 equiv of PMe_3, formation of **1** is nearly quantitative, with less than 5% of the disilacyclobutane detected. No other products are observed. In this manner **1** has been prepared and isolated in 86% yield.[6]

The role of phosphine in the silylation was probed by treating Cp_2TaH_3 with HMS and 4 equiv of PMe_3 (eq 3). After 15 h

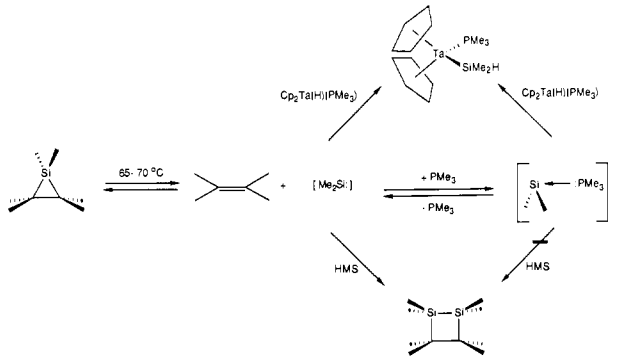


(3)

at 65 °C, $Cp_2Ta(SiMe_2H)H_2$ is formed as a mixture of isomers (**2a,b**, 9:1). Less than 5% of octamethyldisilacyclobutane is produced. More importantly, $Cp_2Ta(PMe_3)(H)$ and **1** are not detected by ^1H NMR (<1%), suggesting that silylene transfer occurs without phosphine coordination to an intermediate unsaturated tantalum(III) complex. In contrast, $Cp_2Ta(PR_3)(H)$ is readily formed from Cp_2TaH_3 and tertiary phosphines at 110 °C via Cp_2TaH.[7] Compound **1** is stable under the silylation conditions.

The increased selectivity for silylation at tantalum in the presence of PMe_3 can be traced to the highly electrophilic nature of silylenes. Recent experimental[8-10] and theoretical[11] results

Scheme I. Proposed Mechanism for Dimethylsilylene Transfer with and without Added Phosphine



indicate that silylenes form adducts with Lewis bases such as PH_3, NH_3, THF, etc. prior to subsequent reactions. In the case of the H_2Si–PH_3 adduct, the stabilization is calculated to be on the order of 18 kcal/mol.[11] Silylene–phosphine adduct formation has also been proposed by Seyferth and Lim to explain the catalytic role of tertiary phosphines in reactions of HMS with certain ketones.[8] Furthermore, Steele and Weber have shown that photochemically generated dimethylsilylene is more selective in THF than cyclohexane, which they attribute to formation of the silylene–tetrahydrofuran adduct.[9] Most recently, West and co-workers have reported the spectroscopic observation of a silylene–ether complex in frozen matrices.[10]

In the present instance we propose that dimethylsilylene forms an analogous phosphine adduct, Me_2SiPMe_3. The adduct is unreactive toward the Si–C bonds of HMS but retains activity for silylation of tantalum hydrides. The proposed mechanism is summarized in Scheme I. The silylation of the hydride by Me_2SiPMe_3 resembles the net transfer of CH_2 from methylene trimethylphosphorane into a zirconium hydride bond of $Cp^*_2ZrH_2$ to yield the methyl derivative.[12]

An alternative mechanism in which dimethylsilylene extrusion from HMS is initiated by nucleophilic attack by PMe_3 cannot be ruled out, although this would not explain silylation in the absence of phosphine. This and other possibilities will be addressed in future mechanistic studies.

Other Lewis bases can be employed to increase the selectivity of silylation at tantalum. Triethylamine and tetrahydrofuran are effective in amounts ranging from 5 to 100 equiv. For preparative reactions it is most convenient to simply use THF as solvent. For example, silylation of $Cp_2Ta(CO)H$ using a 5–10% excess of HMS in THF leads to $Cp_2Ta(CO)(SiMe_2H)$, **3**, in 82% isolated yield (eq 4).[13] Similarly, $Cp_2Ta(SiMe_2H)H_2$ (a mixture of **2a,b**, 9:1) has been prepared in 83% yield from Cp_2TaH_3.[14] A variety of

(4) Seyferth, D.; Goldman, E. W.; Escudie, J. *J. Organomet. Chem.* **1984**, *271*, 337–352.

(5) The tantalum hydrides do, however, react with $Ph_3C^\bullet$ to produce Ph_3CH and as yet uncharacterized paramagnetic materials. These compounds do not undergo radical chain silylene transfer with HMS.

(6) A solution of $Cp_2Ta(PMe_3)H$ (120 mg, 0.31 mmol), HMS (65 μL, 0.36 mmol), and PMe_3 (1.72 mmol) in 5 mL of benzene was heated at 65 °C for 15 h under argon. Volatiles were removed in vacuo, and the residue was sublimed at 70 °C and 10^{-3} Torr to yield orange crystals of $Cp_2Ta(PMe_3)(SiMe_2H)$ (118 mg, 86%). **1**: ^1H NMR (C_6D_6) δ 4.85 (1 H, septet, $^3J_{HH}$ = 4.1 Hz, Si*H*), 4.11 (10 H, d, $^3J_{PH}$ = 2.0 Hz, C_5H_5), 0.97 (9 H, d, $^3J_{PH}$ = 7.3 Hz, PCH_3), 0.64 (6 H, d, $^3H_{HH}$ = 4.1 Hz, $SiCH_3$); IR (Nujol) ν (SiH) = 1970 cm^{-1}; mass spectrum calcd 446.102, found 446.103. Anal. Calcd for $C_{15}H_{26}PSiTa$: C, 40.36; H, 5.87. Found: C, 39.73; H, 5.70.

(7) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793–3795.

(8) Seyferth, D.; Lim, T. F. O. *J. Am. Chem. Soc.* **1978**, *100*, 7074–7075.

(9) Weber, W. P.; Steele, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095–6097.

(10) (a) West, R.; Gillette, G. R.; Noren, G. H. Eighth International Symposium on Organosilicon Chemistry, St. Louis, MO, June 7–12, 1987; Abstract no. B2. (b) West, R.; Gillette, G. R.; Noren, G. H., submitted for publication to *J. Am. Chem. soc.*

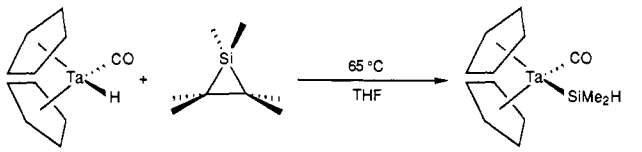
(11) Raghavachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5853–5859.

(12) (a) Bercaw, J. E.; Moore, E. J., private communication. (b) Moore, E. J. Ph.D. Thesis, CIT, 1984.

(13) A solution of $Cp_2Ta(CO)H$ (330 mg, 0.97 mmol) and HMS (210 μL, 1.08 mmol) in 10 mL of THF was heated at 65 °C for 7 h under argon. Volatiles were removed in vacuo, and the residue was sublimed at 55–60 °C and 10^{-3} Torr to yield dark purple crystals of $Cp_2Ta(CO)(SiMe_2H)$ (317 mg, 82%). **3**: ^1H NMR (C_6D_6) δ 4.91 (1 H, septet, $^3J_{HH}$ = 4.0 Hz, Si*H*), 4.27 (10 H, s, C_5H_5), 0.59 (6 H, d, $^3J_{HH}$ = 4.0 Hz, $SiCH_3$); IR (Nujol) ν (SiH) = 2000 cm^{-1}, ν (TaCO) = 1899 cm^{-1}; mass spectrum calcd 398.053, found 398.050. Anal. Calcd for $C_{13}H_{17}OSiTa$: C, 39.20; H, 4.30. Found: C, 39.39; H, 4.46.

(14) $Cp_2TaH_2(SiMe_2H)$ was prepared as a mixture of isomers (**2a,b**, 9:1) in 85% yield by a similar procedure.[15] **2a**: ^1H NMR (C_6D_6) δ 5.38 (1 H, septet, $^3J_{HH}$ = 4.1 Hz, Si*H*), 4.52 (10 H, s, C_5H_5), 0.79 (6 H, d, $^3J_{HH}$ = 4.1, $SiCH_3$), −4.50 (2 H, s, TaH_2). **2b**: ^1H NMR δ 5.32 (1 H, septet, $^3J_{HH}$ = 3.6 Hz, Si*H*), 4.51 (10 H, s, C_5H_5), 0.63 (6 H, d, $^3J_{HH}$ = 3.6, $SiCH_3$), −3.33 (1 H, d, $^3J_{HH}$ = 7.5 Hz, Ta*H*), −4.72 (1 H, d, $^3J_{HH}$ = 7.5 Hz, Ta*H*). **2a,ib**: IR (Nujol) ν (SiH) = 2025 cm^{-1}, ν (TaH) = 1800 cm^{-1}. Mass spectrum (CI) calcd for $[M + 1]^+$ 373.0814, found 373.0772. Anal. Calcd for $C_{12}H_{19}SiTa$: C, 38.71; H, 5.14. Found: C, 38.66; H, 5.27.

tertiary silyl derivatives of tantalum and niobium have recently been prepared by other methods.[15]



(4)

The 9:1 ratio of isomers **2a** and **2b** does not reflect the kinetic preference for silylene insertion into the two types of Ta–H bonds of Cp_2TaH_3. A sample depleted in **2a** (2:1) regains the original ratio within 1 h at 65 °C.[16] Therefore, the 9:1 mixture obtained from the silylation represents a thermodynamic distribution.

In conclusion, if the proposed mechanism proves correct, this will represent the first report of silylene trapping with a transition-metal substrate. In any event, the reaction of hexamethylsilacyclopropane (HMS) with hydride complexes is a convenient route to silyl–tantalum compounds containing α-hydrogens.

Acknowledgment. We thank the Research Corporation for an Exxon Education Foundation Grant, the University of Pennsylvania Research Fund, and the National Science Foundation (MRL Program, under Grant No. DMR-8519059) for support of this research. We also thank Professor Robert West for disclosing his results prior to publication.

(15) (a) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701–707. (b) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037–2044. (c) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 473–479.

(16) Photolysis of $Cp_2Ta(H)(CO)$ with excess Me_2SiH_2 in toluene-d_8 at −40 °C cleanly produces a 2:1 mixture of **2a** and **2b**. The mechanism of the isomerization will be the subject of a separate report.

A New Mg^{2+} Ion Receptor. Macrocyclic Polyamines Bearing an Intraannular Phenolic Group

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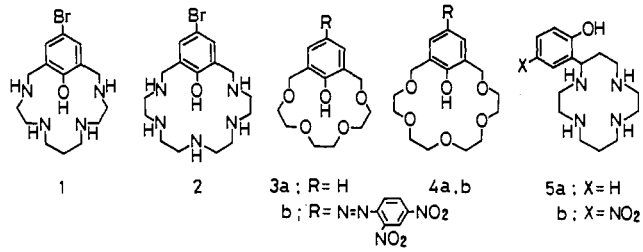
Received March 26, 1987

It is a general preception that inclusion of alkali and alkaline earth metal ions is best achieved with polyether macrocycles ("crown ethers"), while polyamine counterparts are exclusively for heavy and transition-metal ions. Few aza crowns[1-3] were developed as selective sequestering agents for harder metal ions.

To explore a new potential of macrocyclic polyamines, we now have synthesized intraannular phenol-containing derivatives **1** and **2**,[4] which were discovered to possess novel uptake features for



(1) Kodama, M.; Kimura, E.; Yamaguchi, S. *J. Chem. Soc., Dalton Trans.* **1980**, 2536–2538.
(2) Fujioka, H.; Kimura, E.; Kodama, M. *Chem. Lett.* **1982**, 737–740.
(3) Review Article: Kimura, E. *Top. Curr. Chem.* **1985**, *128*, 113–141.

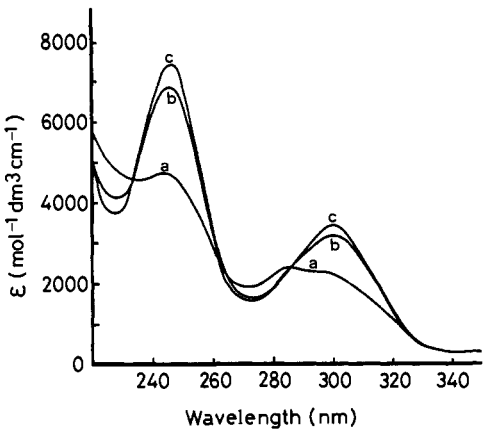
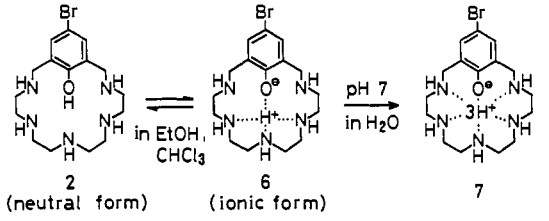


Figure 1. UV absorption spectra of **2** in EtOH at 25 °C: (a) 0.50 mM **2** only; (b) in the presence of 0.25 mM $MgCl_2$; (c) in the presence of 0.5 mM $MgCl_2$.

alkaline earth metal ions. Homologous bifunctional host molecules **3**, **4**,[5-9] and **5**[10-13] have recently been reported, and comparison with those congeners sheds light on the unique properties of the present phenol azamacrocycles.

The azacrown rings here are anticipated to be efficient acceptors of the phenol protons. Indeed, both the neutral phenol (λ_{max} 294 nm) and ionic phenoxide absorptions (λ_{max} 301 and 250 nm) are observed in their electronic spectra of **1** and **2** in EtOH and $CHCl_3$ solutions (see Figure 1a). The ratios for the neutral phenol form **2** to ionic phenolate form **6** with the pentaamine are estimated



to be 1:1 in anhydrous EtOH and 1:0.75 in $CHCl_3$, on the basis of the UV absorptions for the sole phenol form (generated with CCl_3CO_2H, ϵ 2200 at 283 nm) and phenolate form (with NaOEt, ϵ 4400 at 301 nm and ϵ 8600 at 250 nm). In aqueous solution protonation constants of the five nitrogens and the phenol group of **2** were determined pH metrically at 25 °C and I = 0.1 M (Et_4NClO_4) to be 11.2, 10.3, 9.6, 4.8 (phenol, confirmed spec-

(4) Synthesis of **1** and **2** involves cyclization of 2,6-bis(bromomethyl)anisole (6.1 g, 20.8 mmol) with the corresponding tetraamine tetratosylate (16.1 g, 20.8 mmol) and pentaamine pentatosylate (20.0 g, 20.8 mmol), respectively, in the presence of 2 equiv of NaH in DMF (300 mL) at 100 °C for 24 h. The detosylation and demethylation of the resulting tetratosylate (7.0 g) and pentatosylate (11.8 g) were achieved in AcOH–48% aqueous HBr (1:1 in volume) at 140 °C for 48 h, whereby *p*-bromination accompanied, probably due to Br_2 contaminated in concentrated HBr solution. Neutralization with aqueous NH_3 and extraction into CH_2Cl_2 afforded crystalline **1** (300 mg, mp 165 °C from CH_3CN–MeOH) and **2** (500 mg, mp 179 °C from CH_3CN) as free forms. The final products **1** and **2** were identified by elemental analysis, ^1H NMR and mass spectroscopic techniques.
(5) Browne, G. M.; Fergeson, G.; McKervey, M. A.; Mulholland, D. L.; O'Connov, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703–2712.
(6) Kaneda, T.; Sugihara, K.; Kamiya, H.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 4407–4408.
(7) Nakashima, K.; Nakatsuji, S.; Akiyama, S.; Kaneda, T.; Misumi, S. *Chem. Lett.* **1982**, 1781–1782.
(8) Nakashima, K.; Yamawaki, Y.; Nakatsuji, S.; Akiyama, S.; Kaneda, T.; Misumi, S. *Chem. Lett.* **1983**, 1415–1418.
(9) Nakashima, K.; Nakatsuji, S.; Akiyama, S.; Kaneda, T.; Misumi, S. *Chem. Pharm. Bull.* **1986**, *34*, 168–173.
(10) Kimura, E.; Koike, T.; Takahashi, M. *J. Chem. Soc., Chem. Commun.* **1985**, 385–386.
(11) Kimura, E.; Koike, T.; Uenishi, K.; Hediger, M.; Kuramoto, M.; Joko, S.; Arai, Y.; Kodama, M.; Iitaka, Y. *Inorg. Chem.*, in press.
(12) Iitaka, Y.; Koike, T.; Kimura, E. *Inorg. Chem.* **1986**, *25*, 402–404.
(13) Kimura, E. *Pure Appl. Chem.* **1986**, *58*, 1461–1466.

0002-7863/87/1509-6212$01.50/0