tertiary silyl derivatives of tantalum and niobium have recently been prepared by other methods.<sup>15</sup>



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<sub>2</sub>TaH<sub>3</sub>. A sample depleted in 2a (2:1) regains the original ratio within 1 h at 65 °C.<sup>16</sup> 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 hexamethyl-silacyclopropane (HMS) with hydride complexes is a convenient route to silyl-tantalum compounds containing  $\alpha$ -hydrogens.

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## A New Mg<sup>2+</sup> Ion Receptor. Macrocyclic Polyamines Bearing an Intraannular Phenolic Group

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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<sup>1-3</sup> 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



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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<sub>2</sub>; (c) in the presence of 0.5 mM MgCl<sub>2</sub>.

alkaline earth metal ions. Homologous bifunctional host molecules 3, 4,<sup>5-9</sup> 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 ( $\lambda_{max}$  294 nm) and ionic phenoxide absorptions ( $\lambda_{max}$  301 and 250 nm) are observed in their electronic spectra of 1 and 2 in EtOH and CHCl<sub>3</sub> 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<sub>3</sub>, on the basis of the UV absorptions for the sole phenol form (generated with CCl<sub>3</sub>CO<sub>2</sub>H,  $\epsilon$  2200 at 283 nm) and phenolate form (with NaOEt,  $\epsilon$  4400 at 301 nm and  $\epsilon$  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<sub>4</sub>NClO<sub>4</sub>) to be 11.2, 10.3, 9.6, 4.8 (phenol, confirmed spec-

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<sup>(16)</sup> 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.

<sup>(4)</sup> 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<sub>2</sub> contaminated in concentrated HBr solution. Neutralization with aqueous NH<sub>3</sub> and extraction into CH<sub>2</sub>Cl<sub>2</sub> afforded crystalline 1 (300 mg, mp 165 °C from CH<sub>3</sub>CN-MeOH) and 2 (500 mg, mp 179 °C from CH<sub>3</sub>CN) as free forms. The final products 1 and 2 were identified by elemental analysis, <sup>1</sup>H NMR and mass spectroscopic techniques.

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Table I. 1:1 Metal Complexation Constants (log K)

metal ion (ionic diamtr, Å)	1 <sup><i>a.c</i></sup>	2 <sup><i>a.d</i></sup>	15-crown-5 <sup>b,e</sup>	18-crown-6 <sup>b,f</sup>
$Mg^{2+}(1.30)$	3.3	3.1	noncomplxtn	unreported
$Sr^{2+}$ (2.26)	2.9	2.9	2.6	>5.5
$Ba^{2+}$ (2.70)	1.6	2.4	unreported	7.0

 ${}^{a}K = [M^{2+}-complex]/[M^{2+}][H_{-1}L] (M^{-1}) in EtOH at 25 °C.$ Standard deviation is  $\pm 0.1$ .  ${}^{b}K = [M^{2+}-L]/[M^{2+}][L] (M^{-1}) in$ MeOH at 25 °C (Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, 85, 271-339). <sup>c</sup> Cavity size (1.4-2.0 Å). <sup>d</sup> Cavity size (1.8-2.2 Å). <sup>e</sup> Cavity size (1.7-2.2 Å). <sup>f</sup> Cavity size (2.6-3.2 Å).

trophotometrically), <2, and <1.<sup>14</sup> The phenol  $pK_a$  value of 4.8 is much lower than 8.8 of p-bromophenol alone, presumably under the strong influence of +3 charge of the N<sub>5</sub> macrocycle. We could isolate crystalline triprotonated (on  $N_5$ ) phenolate species 7 (as 2ClO<sub>4</sub><sup>-</sup> salt) out of pH 7 aqueous solution containing excess NaClO<sub>4</sub>. Its UV spectrum (in H<sub>2</sub>O) of  $\lambda_{max}$  309 nm ( $\epsilon$  3900) supports the phenolate form of 7. On the other hand, the ratio of the phenolate species is minor (1:0.25) with tetraamine homologue 1 in EtOH. Its  $pK_a$  values in 0.1 M Et<sub>4</sub>NClO<sub>4</sub> are 10.7, 10.5, 8.3 (phenol), 4.2, and 3.7. The phenol  $pK_a$  of 8.3 is not as low as 4.8 of 2, under the lesser influence of +2 charge of the N<sub>4</sub> macrocycle. For the sake of comparison,  $pK_a$  values of the relevant phenol macrocycles are 11.8, 10.5, 8.9 (phenol), <2, and <2 for 5a,<sup>10</sup> 11.8, 10.4, 6.4 (phenol), <2, and <2 for 5b,<sup>11</sup> 10.8 for 3a, and 10.6 for 4a.<sup>5</sup> Apparently, self dissociation of the phenol protons should be negligible with 3 and 4 in EtOH<sup>5</sup> and with 5a in CHCl<sub>3</sub> and EtOH.<sup>11</sup> Thus, an enormous influence of the azacrowns on reactivity of the intraannular phenol protons is revealed.

The phenol ionization in EtOH is further promoted by addition of neutral alkaline earth metal salts MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub>, and  $Ba(SCN)_2$ , as illustrated by the increase in the phenolate form or accompanying decrease in the phenol form in the UV absorptions (see Figure 1b,c).<sup>15</sup> In varying the [ligand]/ $[M^{2+}]$  ratio  $([ligand] + [M^{2+}] = 1 \text{ mM})$ , the total phenolate concentration reaches maximum at  $[ligand]/[M^{2+}] = 1$  with all the metals. The degree of 1:1 association uniformly varies with the size of metal ions, i.e., Mg > Ca > Sr > Ba, for 1 and 2. Monovalent alkaline metal salts (LiCl, NaCl, KCl, CsCl), on the other hand, do not dispel the phenolic protons of 1 and 2. With crown homologues 3 and 4 basic conditions are needed to displace the phenol protons for  $M^+$  and  $M^{2+,5-9}$  The phenol-pendant  $N_4$  homologues 5a and 5b do not interact with alkaline earth metal salts in EtOH solution.<sup>11</sup> Evidently, synergism between the macrocyclic N donors and intraannular phenolate donor is essential for uptake of divalent metal ions in the nonbasic conditions. The pH metric titration indicates the complexation of 2 with Mg<sup>2+</sup> to occur above pH 9 in aqueous solution (at 25 °C, I = 0.1 M Et<sub>4</sub>NClO<sub>4</sub>).

The apparent constants for the 1:1 complexation between 1 (or 2) and  $M^{2+}$  in EtOH are calculable in terms of  $K = [M^{2+}-complex]/[M^{2+}][H_{-1}L]$  ( $M^{-1}$ ) (where  $H_{-1}L$  is a free ligand in phenolate anion form, and  $[M^{2+}-complex]$  is the [total phenolate anion] -  $[H_{-1}L]$ ) with use of the UV spectral data. The results



(14) The standard deviation for  $pK_a$  values of 1 and 2 is  $\pm 0.05$ . The titration curves of 1 and 2 in 0.1 M Et<sub>4</sub>NClO<sub>4</sub> completely overlap those in 0.1 M NaClO<sub>4</sub>. These facts indicate that Na<sup>+</sup> has no interaction with 1 and 2.

(15) With 3 and 4,  $M^+$  and  $M^{2+}$  ion size correlate linearly with wave numbers of the phenolate absorption maxima, suggesting some degree of ion pairing in nonaqueous solvents.<sup>5-9</sup> On the other hand, the absorption maxima (300 nm) remain practically the same regardless of  $M^{2+}$  with 1 and 2. are summarized in Table I, in comparison with reported K values for crown ether complexes.<sup>16</sup> Very interestingly,  $Mg^{2+}$  uptake is more favored with smaller macrocyclic 1 than with larger 2, despite the fact that the self dissociation of the former phenol hydrogen is less feasible. As the  $M^{2+}$  size increases, complexation becomes more favorable with larger macro ligand 2. These size effects suggest that the metal inclusion into the size-fitted polyamine hole is a determining factor for the selective uptake. It is to be emphasized that the macrocyclic polyamine ligands are most appropriate for the smallest  $Mg^{2+}$ , while crown ethers favor larger  $M^{2+}$ .

Furthermore, in EtOH the complexation of  $Mg^{2+}$  and  $Ca^{2+}$  with 1 or 2 is proved stronger than with 15-crown-5 or 18-crown-6,<sup>17</sup> while that of  $Sr^{2+}$  and  $Ba^{2+}$  with 1 or 2 proved to be weaker than with 18-crown-6. This is revealed by the change of the phenolate UV absorptions upon addition of crown ethers (1 equiv) to a 1:1 mixture of 1 (or 2) and MX<sub>2</sub> in EtOH.

Finally, the 1:1 complexation of 1 with Mg<sup>2+</sup> was proven by isolation of its monoperchlorate salt, Mg<sup>2+</sup>-H<sub>1</sub>L·ClO<sub>4</sub>·H<sub>2</sub>O (as light yellow powder), out of aqueous EtOH solution. The structure was characterized by elemental analysis (C, H, N), UV spectra ( $\lambda_{max}$  301 nm,  $\epsilon$  3800 in EtOH at 25 °C), and analysis of Mg by atomic absorption technique.

The present results have thus revealed new potentials of macrocyclic polyamines for selective receptors of hard metal ions.

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(in MeOH) is greater than 2.9 for 1 and 2 in EtOH, see Table I.

Enantioface Differentiation in Cis Dihydroxylation of C-C Double Bonds by Osmium Tetroxide with Use of a Chiral Diamine with  $D_2$  Symmetry

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Molecules with a high symmetry have been shown to be effective auxiliary ligands in asymmetric reactions.<sup>1,2</sup> Here we describe extremely efficient enantioface differentiation in the dihydroxylation of C-C double bonds by osmium tetroxide using a chiral diamine with  $D_2$  symmetry.<sup>2</sup> Virtually complete asymmetric induction was observed in the reaction of *trans*-1phenylpropene.

We used the  $D_2$  symmetric chiral diamine 1, which consists of two *trans*-3,4-diphenylpyrrolidine units with  $C_2$  symmetry at the both ends of the ethylene chain.<sup>3</sup> A typical experimental pro-

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