

of ethane, and trapping by phosphine leads to η^3 -oximate intermediate **8**. Reaction with an additional mole of phosphine may now force conversion of the oximate ligand to one of its η^1 isomers **4** or **5**; apparently formation of **4** is favored, and this complex is isolated.

Formation of the cyanide and *N*-ruthenium amide complexes **3** and **6** is more complex, and less well-precedented, processes. We suggest these reactions may be related by the mechanism outlined at the bottom of Scheme I. Reversible interconversion of O- and C-bound oximate complexes **4** and **5** could occur thermally on phosphine loss in **4**. As **5** is simply a ruthenium-substituted nitrosoalkane, it should undergo rapid prototropic isomerization to the corresponding oxime **9**, as is typical of this class of compounds. When R = H, elimination of water in this complex leads to isolated ruthenium cyanide **6**. When R = Me, this elimination is prevented, and we suggest that the ruthenium analogue of a Beckmann rearrangement converts oxime **9** to **10**. Complex **10** should quickly rearrange to its more stable, isolable carboxamide tautomer **6**.

Experiments are currently under way aimed at testing these mechanistic hypotheses and exploring further the chemistry of the O- and N-bound ruthenium(II) derivatives reported here.¹²

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Registry No. **1**, 90419-99-1; **2a**, 91993-47-4; **2b**, 91993-48-5; **3**, 91993-49-6; **4**, 91993-50-9; **6**, 91993-51-0; Cp*Ru(CO)₂Cl, 77488-50-7; AlMe₃, 75-24-1; AlEt₃, 97-93-8; NOCl, 2696-92-6.

Supplementary Material Available: Proton, carbon, and phosphorus NMR, infrared, mass spectra, elemental analysis, and melting point data for **1**, **2a**, **2b**, **3**, **4**, and **6** (4 pages). Ordering information is given on any current masthead page.

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Stable Potassium Complex of a Pyridine-Fused Hexaaza[18]annulene. A New Rival for 18-Crown-6

Thomas W. Bell* and Frieda Guzzo

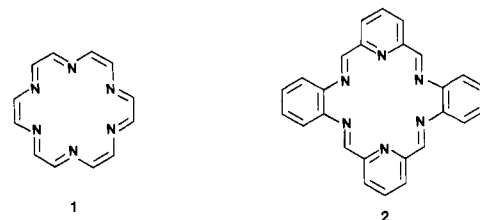
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

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The crown ethers¹ are of increasing importance as complexing agents for the biologically relevant alkali metal ions, potassium and sodium. In recent years, considerable synthetic effort has been directed toward surpassing the ion affinities of crown ethers, notable achievements being cryptands² and spherands.³ Most simple structural modifications of 18-crown-6, such as benzanellation and heteroatom replacement, lead to decreased potassium complex stability.^{4,5} We report here a potassium complex of a nitrogen analogue of 18-crown-6 having a stability constant 1 order

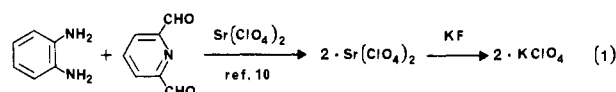
of magnitude greater than that of 18-crown-6.

The dominant interaction between alkali metal ions and oxygen or nitrogen ligand sites is generally considered to be an ion/dipole electrostatic attraction.⁶ Reduced stability constants observed in saturated nitrogen analogues⁴ of crown ethers are consistent with this analysis, since the dipole moment of trimethylamine (0.61 D) is smaller than that of dimethyl ether (1.30 D).⁷ The sizeable dipole moment of (methylimino)methane (1.53 D) suggests the hexaaza[18]annulene **1**⁸ as the parent for a new family of alka-



li-metal complexing agents. Fusion of **1** with pyridine rings (2.19 D) should afford even better macrocyclic ligands, assuming a planar conformation. The dibenzo dipyrrodo hexaaza[18]annulene **2**⁹ has been found in complexes with alkaline-earth and some transition-metal ions,¹⁰ although the free ligand has not been reported. An earlier report¹¹ of a metal-free synthesis of the tetramethyl derivative of **2** has been found in error.^{12,13}

Alkaline earth perchlorate complexes of tetraimine **2** may be prepared by the metal-templated condensation¹⁰ shown in eq 1.



We have found that when the strontium complex **2**·Sr(ClO₄)₂¹⁰ is treated with potassium fluoride monohydrate in refluxing methanol, the corresponding potassium perchlorate complex is obtained. Recrystallization from acetonitrile afforded analytically pure (C, H, N, K) yellow needles (69%, mp 386–388 °C dec), exhibiting infrared absorptions¹⁴ consistent with the proposed structure (**2**·KClO₄). The proton NMR chemical shifts of this material in Me₂SO-*d*₆ are given in Table I (entry 3) in comparison with the chemical shifts of **2**·Sr(ClO₄)₂¹⁰ and the 2:1 sandwich complex of **2** with barium perchlorate¹⁰ (entries 1 and 2).

The chemical shifts of **2**·KClO₄ were found to be dependent on concentration and on the presence of added potassium complexing agents (Table I). The imine methine resonance (Hm), which occurs at δ 8.887 for a 2×10^{-2} M solution (entry 3), shifts to lower field with dilution, e.g., 8.962 ppm at 4×10^{-3} M (entry 6). The effect of added [2.2.2]cryptand is also dependent on the initial concentration of **2**·KClO₄. Thus, incremental addition of

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Table I. 300-MHz Proton NMR Chemical Shifts for Ligand **2** in MeSO-*d*₆ (δ)

entry	sample	H _m	H ₄	H ₃	H _a , H _b
1	2·Sr(ClO ₄) ₂ ^a	9.195	8.436 ^b	8.197 ^c	7.60-7.86
2	(2) ₂ ·Ba(ClO ₄) ₂ ^a	8.528	8.061 ^b	7.659 ^c	7.1-7.2
3	2·KClO ₄ (2 × 10 ⁻² M)	8.887	8.206 ^b	7.952 ^c	7.42-7.56
4	2·KClO ₄ (2 × 10 ⁻² M) ^d + [2.2.2]cryptand (2 × 10 ⁻³ M) ^d	8.815	8.138 ^b	7.876 ^c	7.36-7.47
5	2·KClO ₄ (2 × 10 ⁻² M) + 18-crown-6 (1 × 10 ⁻² M)	8.815	8.136 ^b	7.874 ^c	7.36-7.46
6	2·KClO ₄ (4 × 10 ⁻³ M)	8.962	8.262 ^b	8.015 ^c	7.47-7.62
7	2·KClO ₄ (4 × 10 ⁻³ M) + [2.2.2]cryptand (4 × 10 ⁻² M)	9.224	(8.05-8.08) ^e		7.35-7.55

^aReference 10. ^bTriplet, $J = 7.7$ Hz. ^cDoublet, $J = 7.7$ Hz. ^dConcentration approximate. ^eAB₂ multiplet.

[2.2.2]cryptand to a 4 × 10⁻³ M solution of 2·KClO₄ led to a downfield shift of the H_m resonance, which finally, in the presence of excess cryptand, occurred at δ 9.224 (entry 7). In contrast, the addition of small increments of [2.2.2]cryptand to 2 × 10⁻² M 2·KClO₄ produced upfield shifts of all resonances of ligand **2** (entry 4).¹⁵ Much larger quantities of added 18-crown-6 were required to produce these shifts (entry 5). The opposite ligand shifts observed when potassium is sequestered from different concentrations of 2·KClO₄ indicate rapid equilibration among at least three species containing **2**. A simple explanation is that the chemical shifts listed in entry 7 of the table are due to the presence of metal-free **2**, whereas the upfield resonances at higher concentration (entries 4 and 5) may arise from significant amounts of a 2:1 complex analogous to the barium perchlorate complex.¹⁰

In order to estimate the stability constant (K_1) of 2·KClO₄, we have used proton NMR to examine the uptake of potassium by 18-crown-6 when added to solutions of 2·KClO₄ in Me₂SO-*d*₆. This process may be followed using the observed 18-crown-6 chemical shift, which is the population-weighted average of the shifts of the two species, 18-crown-6 and its potassium complex, in rapid equilibrium. To calibrate this marker, we first examined the concentration dependence of the NMR spectrum of 18-crown-6·KClO₄. Using δ 3.494 as the chemical shift for free 18-crown-6, it was calculated¹⁶ that the chemical shift of the fully associated potassium complex is δ 3.543 and that the logarithm of the stability constant ($\log K_1$) of 18-crown-6·KClO₄ is approximately 3.4. This is within experimental error of the potentiometrically determined value of 3.21 for $\log K_1$ of 18-crown-6·KClO₄ in Me₂SO.¹⁷ In the competition experiments, increments of solid 18-crown-6 were added to 2 × 10⁻² M 2·KClO₄ solutions in Me₂SO-*d*₆, causing slight upfield shifts of the resonances of **2**, as exemplified in entry 5 of the table. The concentration of "free" (solvated) potassium ion was calculated¹⁸ from the observed 18-crown-6 chemical shift, which was also used with the integral ratio of 2/18-crown-6 to determine the concentration of 18-crown-6·KClO₄. The concentrations of 2·KClO₄ and free **2** were calculated by difference, resulting in a $\log K_1$ for 2·KClO₄ of at least 4.1.¹⁹

We have estimated that the stability constant for 2·KClO₄ is an order of magnitude greater than that of the corresponding 18-crown-6 complex in the same solvent. This effect is consistent with the larger dipole moment of imines and pyridines relative to ethers and contrasts with the reduced metal ion affinities observed in some pyridine-annelated crown ethers.²⁰ The difference may be largely conformational in nature,²¹ since pyridine rings in the latter systems are relatively free to rotate their electric

dipoles away from the molecular cavity. A similar effect could operate in sexipyridine,²² making more rigid systems, such as azakekulenes,²³ particularly attractive candidates for strong and selective complexation of alkali metal ions.

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Reaction of a Carbon Analogue of Iodosylbenzene with Iron Porphyrins: Isolation and X-ray Structure of an Iron(II) Complex with O-C-C Moieties Inserted between Two Trans Iron-Nitrogen Bonds

Daniel Mansuy,*^{1a} Jean-Paul Battioni,^{1a} Irèna Akhrem,^{1a} Daniel Dupré,^{1a} Jean Fischer,^{1b} Raymond Weiss,*^{1b} and Irène Morgenstern-Badarau^{1c}

Laboratoire de Chimie
de l'Ecole Normale Supérieure
LA 32, 75231 Paris Cedex 05, France
Laboratoire de Cristalochimie, ERA 08
Université Louis Pasteur
67070 Strasbourg Cedex, France
Laboratoire de Spectrochimie des éléments
de Transition, ERA 672, Université de Paris-Sud
91405 Orsay Cedex, France

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High-valent Fe(IV)- or Fe(V)-oxo^{2,3} complexes have been prepared upon reaction of iron porphyrins with potential oxygen atom donors. They are believed to be the active species involved in alkane hydroxylation and alkene epoxidation by iodosylbenzene catalyzed by cytochrome P-450⁴ or iron porphyrins.⁵ Their nitrogen analogues, Fe(IV)- or Fe(V)-imido (or iron(II) or iron(III) nitrene) complexes, seem to be formed upon oxidation of 1,1-dialkylhydrazines by cytochrome P-450,⁶ and porphyrin-

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