by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF (CHE81-07629) are gratefully acknowledged.

Registry No. **3**, 4646-69-9; **7**, 92012-54-9; **8**, 92012-55-0; **9**, 286-85-1; **11**, 92012-56-1; **12**, 92012-57-2; **13**, 92012-58-3; Ph_2CO, 119-61-9; $PhC(O)CH_3$, 98-86-2.

Synthesis of Dialkylruthenium Nitrosyls and Thermal Conversion to Ruthenium Oximate, Carboxamide, and Cyano Complexes

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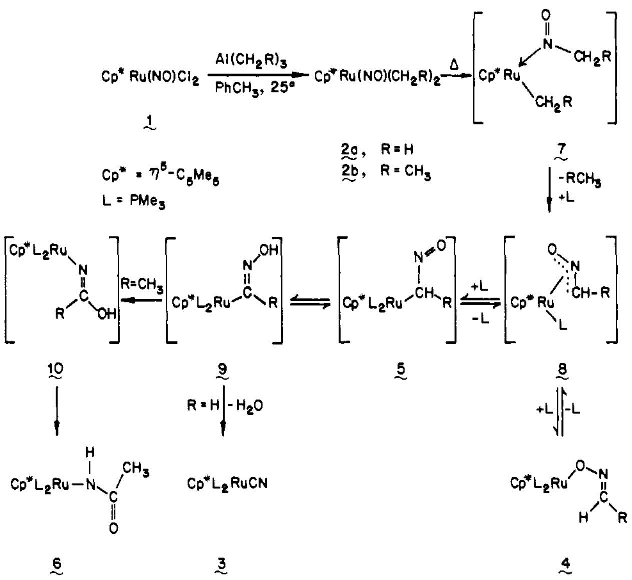
Several years ago, in search of homogeneous models for the metal-catalyzed oxidation of propylene to acrylonitrile, a group at Du Pont[1] uncovered a reaction in which an allyl group and a nitric oxide ligand underwent conversion to an oxime π-complexed to nickel. This discovery presaged a growing number of processes in which coordinated nitric oxide can be used to form new carbon–nitrogen bonds in organic molecules.[2] We wish to report here some unusual ruthenium chemistry germane to the understanding of such processes, which includes the observation of (1) the transformation of coordinated nitric oxide into oxime functionality σ-bound to the metal, (2) in one system, the rearrangement to an isomeric amide structure, and (3) in another system, dehydration of the oxime, leading to coordinated cyanide.

Our results are summarized in Scheme I. Nitric oxide was introduced into the coordination sphere of ruthenium by treating $Cp^*Ru(CO)_2Cl$ ($Cp^* = \eta^5$-C_5Me_5)[3] with NOCl[4] in methylene chloride at room temperature. After chromatography on silica gel and recrystallization from boiling toluene, air-stable dark green crystals of $Cp^*(NO)RuCl_2$ (**1**) were obtained in 53% yield.[5] After experimenting with a variety of alkylating agents, the transformation of **1** to the dialkyl complexes **2** was found to be most cleanly achieved with trialkylaluminum compounds. Thus treatment of a slurry of **1** in toluene with a dilute solution of $AlMe_3$ gave red-orange crystalline **2a** in 67% yield. The diethyl complex **2b** was prepared in a similar manner from $AlEt_3$ in 56% yield and also forms red-orange crystals. Both **2a** and **2b** are slightly air sensitive, in solution and as solids, and were purified by sublimation at 60 and 50 °C, respectively, at 10^{-4} torr.

In contrast to the closely related complex[6] $CpFe(NO)Me_2$, which slowly decomposes at room temperature, complexes **2** are remarkably thermally stable. In the absence of phosphine, dimethyl complex **2a** decomposes slowly at 120 °C over 24 h, leading to intractable products. However, thermolysis in benzene at 150 °C for 20 h in the presence of trimethylphosphine produces a new material having an intense IR absorption at 2060 cm^{-1} and resonances in the ^1H NMR spectrum at δ 1.66 (t, 15 H, J = 1.4 Hz) and 1.16 (virtual triplet, 18 H, $J + J$ = 8.4 Hz). This, as well as other spectral evidence, is consistent with the formulation of this material as the metal cyanide $Cp^*Ru(PMe_3)_2(CN)$ (**3**, Scheme I). Compound **3** is isolated as yellow crystals in 51% yield. Water and methane are also produced in this reaction (identified by GC/MS and quantified by GC and ^1H NMR). Complex **3** may be prepared independently by treatment of $Cp^*Ru(PMe_3)_2Cl$[7] with potassium cyanide in methanol.[8]

Scheme I



Additional insight as to how this cyanide complex may be formed is provided by thermolysis of the corresponding diethyl complex **2b** in the presence of trimethylphosphine. This reaction proceeds, under somewhat milder conditions (85 °C in benzene), with extrusion of 0.82 equiv of ethane (as determined by GC/MS and quantified by GC; 0.09 equiv of ethylene is also formed); it gives as the organometallic product a yellow crystalline material analyzing correctly for the formula $C_{18}H_{37}NOP_2Ru$ in 76% isolated yield. In addition to resonances for one Cp* and two trimethylphosphine ligands in the ^1H NMR (δ 1.55 (t, 15 H, J = 1.4 Hz), 1.28 (virtual triplet, 18 H, $J + J$ = 8.2 Hz)), it exhibits resonances characteristic of one vinylic hydrogen and methyl group (δ 6.43 (q, 1 H), 2.17 (d, 3 H)) weakly coupled to one another (J = 5.2 Hz). We therefore propose a ruthenium oximate (aza enolate) ($Cp^*L_2Ru(ONCHCH_3)$) formulation for this complex. That the carbon attached to nitrogen is in fact sp^2 hybridized is confirmed by the ^{13}C–H coupling constant of 172.7 Hz measured in the gated carbon spectrum. This requires that the ruthenium oximate has the unusual[9] (at least for a late-transition-metal complex) oxygen–metal bound structure **4** rather than the analogous carbon–metal bound structure **5**. Thermolysis of **4** at 75 °C for 4.5 h in benzene leads (35%) to an isomeric crystalline yellow material containing an exchangeable, rather than vinylic, hydrogen, which spectral data demonstrate to be the *N*-ruthenium amide complex **6**. Confirmation of this assignment was obtained by independent synthesis of **6** from $Cp^*Ru(PMe_3)_2Cl$ and $CH_3CONHLi$ in Me_2SO. The transformation of **4** to **6** is strongly inhibited by added phosphine. This explains why **6** is not formed at the higher temperature at which **4** is prepared. Furthermore, if dimethylphenylphosphine is added instead of trimethylphosphine, phosphine substitution is observed before isomerization.[10]

We propose the pathways outlined in Scheme I to explain these observations. The process is presumably initiated by migratory insertion of NO into one of the metal alkyl bonds,[6,11] leading to nitrosoalkane intermediate **7**. Transfer of a hydrogen to the metal center from the carbon adjacent to nitrogen (this can be viewed either as β-elimination cyclometallation), reductive elimination

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(4) Nitrosyl chloride was prepared from thionyl chloride and isoamyl nitrite according to Stryker et al.: Stryker, J. M. Ph.D. Dissertation, Columbia University, New York, 1983.

(5) (η^5-C_5H_5)$Ru(NO)Cl_2$ has been prepared in a similar manner. See: Connelly, N. G. *Inorg. Chim. Acta Rev.* **1972**, *6*, 47.

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(7) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

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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)$_2$Cl, 77488-50-7; AlMe$_3$, 75-24-1; AlEt$_3$, 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

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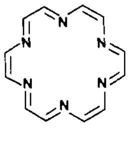
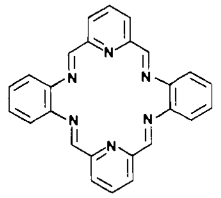
The crown ethers[1] are of increasing importance as complexing agents for the biologically relevant alkali metal ions, potassium and sodium. In recent years, considerable synthetic effort has been directed toward surpassing the ion affinities of crown ethers, notable achievements being cryptands[2] and spherands.[3] Most simple structural modifications of 18-crown-6, such as benzannelation 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 analogues[4] 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 alkali-metal complexing agents. Fusion of **1** with pyridine rings (2.19 D) should afford even better macrocyclic ligands, assuming a planar conformation. The dibenzo dipyrido 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 report[11] of a metal-free synthesis of the tetramethyl derivative of **2** has been found in error.[12,13]

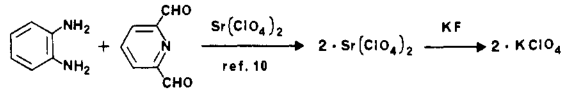


1



2

Alkaline earth perchlorate complexes of tetraimine **2** may be prepared by the metal-templated condensation[10] shown in eq 1.



(1)

We have found that when the strontium complex **2**·Sr(ClO$_4$)$_2$[10] 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 absorptions[14] consistent with the proposed structure (**2**·KClO$_4$). The proton NMR chemical shifts of this material in Me$_2$SO-d_6 are given in Table I (entry 3) in comparison with the chemical shifts of **2**·Sr(ClO$_4$)$_2$[10] and the 2:1 sandwich complex of **2** with barium perchlorate[10] (entries 1 and 2).

The chemical shifts of **2**·KClO$_4$ wre 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**·KClO$_4$. Thus, incremental addition of

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(8) Systematic name for **1**: 1,4,7,10,13,16-hexaazacyclooctadecine.

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(13) The reported failure of the tetramethyl derivative of **2** to extract alkali metal ions must also be disregarded: Ramdani, A.; Tarrago, G. *Tetrahedron* **1981**, *37*, 991–1000.

(14) IR (KBr) 3050 (w), 3000 (w), 1620 (m), 1580 (s), 1480 (m), 1440 (m), 1365 (w), 1255 (m), 1080 (br, s), 800 (m), 725 (m) cm^{-1}.

(15) An equimolar ratio of the cryptand to **2** could not be obtained for 2×10^{-2} M solutions of **2**·KClO$_4$, due to low solutility.

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