In conclusion, ring opening of dimetallacyclopropanes of the type discussed in this communication points to a promising new synthetic entry to the hitherto little investigated class of dinuclear organometals having alkyl and halide groups bound to adjacent metal centers.[17] This simple preparative route and its mechanistic implications are presently under active investigation in our laboratories.

Supplementary Material Available: List of atomic, population, and thermal parameters of **3b** (1 page). Ordering information is given on any current masthead page.

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(17) In this context, the reader's attention is drawn to related homodinuclear dimethyl complexes of type $[(\mu\text{-CO})(CH_3)\{(\eta^5\text{-}C_5H_5)Co\}]_2$ reported by Bergman et al., which exhibit some fascinating decomposition pathways: I. E. Schore, C. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 7436 (1976); H. E. Bryndza and R. G. Bergman, *ibid.*, **101**, 4766 (1979); M. A. White and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, 1056 (1979).

(18) Karl Winnacker Scholarship Recipient, 1979–1984.

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Selective Reductions of Ammineruthenium(III) Complexes by Hydrogen Sulfide

Sir:

Due to more stringent pollution regulations, hydrogen sulfide is being recovered in increasing amounts. Hydrogen sulfide is an effective reducing agent, as exemplified by the Claus process[1] in which oxygen is reduced to water (eq 1). We have become

$$2H_2S + O_2 \rightarrow 2S^0 + 2H_2O \tag{1}$$

interested in a modification of this reaction which would allow us to use hydrogen sulfide for partial reduction of oxygen to hydrogen peroxide (compare eq 1 and 2). A logical starting point

$$H_2S + O_2 \rightarrow H_2O_2 + S^0 \tag{2}$$

for this chemistry is the observation by Taube and co-workers that ammineruthenium(II) complexes[2] serve as specific reducing agents for oxygen to produce hydrogen peroxide (eq 3).[3] It occurred

$$2(NH_3)_6Ru^{II} + O_2 + 2H^+ \rightarrow 2(NH_3)_6Ru^{III} + H_2O_2 \tag{3}$$

to us that it might be possible to reduce the oxidized ruthenium complexes with hydrogen sulfide without the incorporation of sulfur ligands since these complexes are nonlabile and coordinatively saturated. Herein we report our preliminary results in this area which demonstrate that hydrogen sulfide can indeed function as a selective and potent outer-sphere reductant for these coordinatively saturated complexes.

In a typical procedure $[(NH_3)_5Ru^{III}py]_2(S_2O_6)_3$[4] (py ≡ pyridine) is dissolved in deoxygenated water. Hydrogen sulfide is bubbled through the clear solution, resulting in an immediate color change to bright yellow. This transformation is accompanied by the formation of a fine, off-white precipitate which can be filtered. Analysis of this material shows it to be elemental sulfur. Examination of the filtrate by UV-vis spectroscopy reveals that a quantitative reduction of the ruthenium(III) complex to $[(NH_3)_5Ru^{II}py](S_2O_6)$ has taken place. A solid can also be isolated by addition of excess anion. Microanalysis confirms it to be the expected ruthenium(II) complex. Overall, the reaction can be represented by eq 4.

$$2(NH_3)_5Ru^{III}py + H_2S \rightarrow 2(NH_3)_5Ru^{II}py + S^0 + 2H^+ \tag{4}$$

The reduction proceeds equally well with $(NH_3)_4Ru^{III}py_2$[5] and $(NH_3)_4Ru^{III}bpy$[6] (bpy ≡ 2,2′-bipyridine). Quantitative amounts of the corresponding ruthenium(II) complexes are formed in seconds. In the case of $(TMED)_2Ru^{III}bpy$[7] [TMED ≡ $NH_2C(CH_3)_2C(CH_3)_2NH_2$], the reaction is much slower, on the order of hours to go to completion. This finding is corroborated by the fact that the same complex is slow to disproportionate into a mixture of the corresponding ruthenium(II) and ruthenium(IV) species.[8]

The reduction of the aquo complex $(NH_3)_5Ru^{III}OH_2$[9] is also facile. The corresponding ruthenium(II) complex may be trapped quantitatively by isonicotinamide (ISN) to give $(NH_3)_5Ru^{II}ISN$.[10] If isonicotinamide is not present, the known hydrogen sulfide complex is formed.[11] In the presence of oxygen, this complex is rapidly oxidized to yield the well-characterized disulfide-bridged dimer $[(NH_3)_5RuS\text{–}SRu(NH_3)_5]^{4+}$.[12] Thus, sulfur incorporation can be avoided only if coordinatively saturated complexes are employed.

The pH dependence of the reduction can be demonstrated in reactions of hydrogen sulfide with hexaammineruthenium(III). In 0.1 M trifluoroacetic acid solution, no reduction takes place. On the basis of the potentials of the redox couples shown below, this is readily understandable (eq 5–7).[13] As the pH is raised

$$(NH_3)_6Ru^{III} + 1e^- = (NH_3)_6Ru^{II} \quad E^\circ = 50\ \text{mV} \tag{5}$$

$$H_2S = S^0 + 2H^+ + 2e^- \quad E^\circ = -141\ \text{mV} \tag{6}$$

$$HS^- + OH^- = S^0 + H_2O + 2e^- \quad E^\circ = 478\ \text{mV} \tag{7}$$

to approximately 4, $(NH_3)_6Ru^{II}$ and elemental sulfur start to appear.

In preliminary attempts to define the scope and limitations of this reaction, it has been found that methyl mercaptan also reduces the pentaammineruthenium(III)–pyridine complex. In analogy to other oxidants, the oxidation product of methyl mercaptan is believed to be dimethyl disulfide.[14] The reaction is not as rapid as with hydrogen sulfide and proceeds to only approximately 70% completion.

Coordinatively saturated ferric complexes behave analogously to the ruthenium complexes. Thus, tris(*o*-phenanthroline)ferric ion is rapidly and quantitatively reduced to ferrous ion, and hy-

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(1) Gamson, B. W.; Elkins, R. H. *Chem. Eng. Prog.* **1953**, *49*, 203–215. Palm, J. W. *Hydrochem. Process.* **1972**, *51*(3), 105–108.

(2) All of the complexes discussed herein are cationic, containing six neutral ligands. The molecular formulas of the ruthenium(III) complexes (with the associated anions) are $[(NH_3)_5Ru(py)]_2(S_2O_6)_3$, $[(NH_3)_4Ru(py)_2](ClO_4)_3$, $[(NH_3)_4Ru(bpy)](PF_6)_3$, $[(TMED)_2Ru(bpy)](PF_6)_3$, $[(NH_3)_5Ru(OH_2)](CF_3SO_3)_3$, and $[(NH_3)_6Ru]Cl_3$.

(3) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639–643. Stanbury, D. M.; Haas, O.; Taube, H. *Ibid.* **1980**, *19*, 518–524.

(4) Ford, P.; Rudd, DeF. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187–1194.

(5) Ford, P. C.; Sutton, C. *Inorg. Chem.* **1969**, *8*, 1544–1546.

(6) Alvarez, V. E.; Allen, R. J.; Matsubaru, T.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 7686–7692. The corresponding ruthenium(III) complex may be prepared by ceric oxidation of the ruthenium(II) complex.

(7) This complex was prepared by displacement of the ammonia ligands from $(NH_3)_4Ru^{II}bpy$ by TMED followed by ceric oxidation.

(8) The slow rates of reduction and disproportionation are anomalous in view of the fact that these complexes are expected to undergo an adiabatic electron transfer via the bipyridyl ligand. Thus, the rates of reduction of $(NH_3)_4Ru^{III}bpy$ and $(TMED)_2Ru^{III}bpy$ are expected to be very similar. The discrepancy between the expected and observed behavior of $(TMED)_2Ru^{III}bpy$ cannot be explained at this time. For disproportionation of other ruthenium(III) complexes, see: Rudd, DeF. P.; Taube, H. *Inorg. Chem.* **1971**, *7*, 1543–1544.

(9) Diamond, S. E. Ph.D. Thesis, Stanford University, Stanford, CA, 1975.

(10) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392–1401.

(11) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689–702.

(12) Brulet, C. R.; Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758–4759.

(13) Note that the reduction potentials for the complexes containing aromatic nitrogen heterocycles are all greater than 300 mV. The overall reaction with hydrogen sulfide is highly favored. This is not true for the hexaammineruthenium(III) ion: Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460–1466. Matsubaru, T.; Ford, P. C. *Ibid.* **1976**, *15*, 1107–1110.

(14) Many oxidizing agents are known to convert mercaptans to disulfides. See, for example: Collman, J. P.; Sorrell, T. N.; Hoffman, B. M. *J. Am. Chem. Soc.* **1975**, *97*, 913–914.

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drogen sulfide is oxidized to sulfur.

The mechanism of these reactions most probably involves initial outer-sphere electron transfer from the sulfide to ruthenium (eq 8). This may then be followed by rapid reduction of a second

$$L_6Ru^{III} + H_2S \rightarrow L_6Ru^{II} + HS\cdot + H^+ \qquad (8)$$

molecule of ruthenium(III) by HS· or by dimerization to dihydrogen disulfide which may disproportionate (eq 9 and 10).

$$L_6Ru^{III} + HS\cdot \rightarrow L_6Ru^{II} + S^0 + H^+ \qquad (9)$$

$$2HS\cdot \rightarrow H_2S_2 \rightarrow H_2S + S^0 \qquad (10)$$

The ruthenium(II) complexes obtained by the reduction of the ruthenium(III) analogues with hydrogen sulfide can be oxidized by oxygen to produce hydrogen peroxide. This cycle has been demonstrated in the case of $(NH_3)_5Ru^{III}py$ at pH 4. This complex was reduced by hydrogen sulfide to produce its ruthenium(II) analogue quantitatively. After isolation, this complex was oxidized by oxygen to yield the expected amount of hydrogen peroxide.[3] Thus, a two-step, partial reduction of oxygen by hydrogen sulfide to hydrogen peroxide has been demonstrated.

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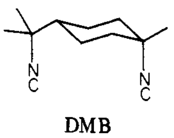
A Binuclear Nickel(II) Encapsulating Agent for Chloride and Bromide Ions

Sir:

The complexation of small cations by using crown ethers and cryptates has found a wide variety of applications in both organic[1] and inorganic chemistry.[2] On the other hand, selective complexation of small anions is relatively unknown, although Lehn and co-workers[3] have found that halides bind strongly to certain protonated cryptates. Here we report experiments that show that a binuclear isocyanide nickel species related to rhodium complexes studied[4,5] previously has the ability to bind chloride and bromide selectively in the presence of larger anions such as thiocyanate. Each halide-containing complex exhibits a fascinating electronic absorption spectrum and also undergoes a one-electron oxidation, producing a mixed-valence Ni(II),Ni(III) binuclear species.

The binuclear Ni(II) complex was prepared by addition of 0.86 g of *p*-1,8-diisocyanomenthane (0.0045 mol), or DMB, dissolved in 30 mL of methanol to a methanol solution of $NiCl_2{\cdot}6H_2O$ (0.54 g, 0.0023 mol). To the resulting orange-red solution was added a filtered methanol solution of KPF_6 (1.1 g, 0.006 mol). The product, a stable orange crystalline solid, was obtained in 84% yield. The IR spectrum of the diamagnetic complex exhibits a band at 2240 cm^{-1} (KBr disk) attributable to $\nu(C{\equiv}N)$; the frequency is similar to those found in the IR spectra of complexes of the type $Ni(CNR)_4^{2+}$.[6,7] The electronic absorption spectrum of the complex (Figure 1), however, is quite different from that of $Ni(CN)_4^{2-}$ [8] or $Ni(CNR)_4^{2+}$,[7] the most striking feature being the very intense (ϵ = 39 400 M^{-1} cm^{-1}) and extremely sharp ($\nu_{1/2}$ = 960 cm^{-1}) band at 320 nm. Chemical analysis supports the formulation $[Ni_2Cl(DMB)_4](PF_6)_3$.[9] A 10^{-3} M nitromethane solution of $[Ni_2Cl(DMB)_4](PF_6)_3$ exhibits a molar conductivity of 260 $\mu\Omega^{-1}$, which is consistent with our formulation of the compound as a 3:1 electrolyte.[10] The analogous bromo complex, $[Ni_2Br(DMB)_4](PF_6)_3$,[11] is obtained by using $NiBr_2$ as starting material.[12]



DMB

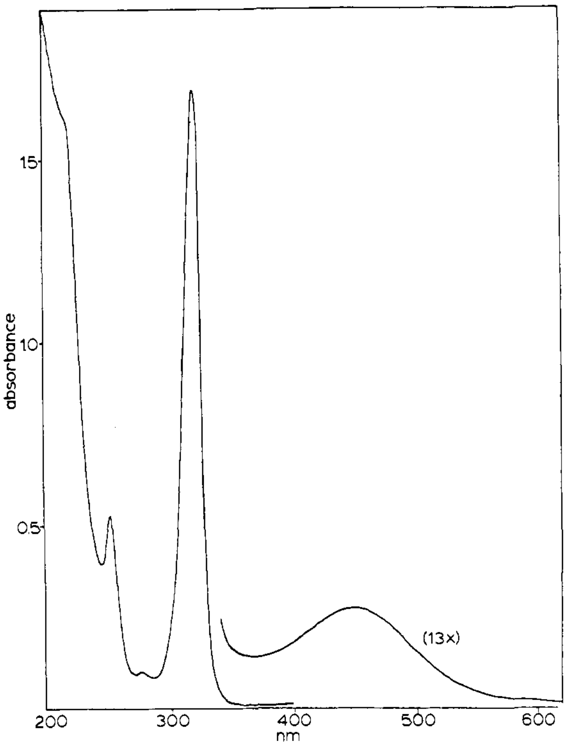


Figure 1. Electronic absorption spectrum of 0.043 mM $[Ni_2Cl(DMB)_4](PF_6)_3$ in acetonitrile solution at 25 °C.

The geometry of DMB as a bridging ligand is such that the two metals are far enough apart to encapsulate a Cl$^-$ or Br$^-$. In $Ni_2(CN)_4(DMB)_2$, the Ni-Ni distance is 4.33 Å[13] whereas in $Rh_2(DMB)_4^{2+}$ the Rh-Rh distance is 4.48 Å.[14] Far-infrared spectra of several salts of the $Ni_2X(DMB)_4^{3+}$ complexes exhibit sharp, intense bands attributable to Ni-X stretches at 210 (X = Cl) and 158 cm^{-1} (X = Br). The fact that the IR bands are observable in the $Ni_2X(DMB)_4^{2+}$ complexes supports our placement of the halide in a bridging position.[15] Further evidence that the system is effectively centrosymmetric comes from Raman spectral measurements on $Ni_2Cl(DMB)_4^{3+}$; an intense band due to the symmetric Ni–Cl–Ni stretch is observed at 284 cm^{-1}.

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(9) All analyses were performed by the Caltech Microanalytical Laboratory. Anal. Calcd for $[Ni_2Cl(DMB)_4](PF_6)_3$: C, 42.73; H, 5.39; N, 8.31. Found: C, 42.51; H, 5.17; N, 8.05.

(10) Geary, W. J. *Coord. Chem. Rev.* **1971**, *1*, 81.

(11) Anal. Calcd for $[Ni_2Br(DMB)_4](PF_6)_3$: C, 41.37; H, 5.22; N, 8.04. Found: C, 41.64; H, 5.35; N, 8.10.

(12) Preliminary experiments indicate that fluoride also forms a complex. Iodide, however, tends to substitute readily for the isocyanide ligands, initially forming dark blue $[Ni_2I_3(DMB)_3]BPh_4$ and ultimately brown $Ni_2I_4(DMB)_2$. Details of these reactions will be reported later.

(13) Gray, H. B.; Gladfelter, W. L., to be submitted.

(14) Mann, K. R., personal communication.

(15) The IR spectra of $[NiX(diphos)_2]ClO_4$ (X = Cl, Br) complexes do not exhibit Ni-X bands; we assume they are extremely weak.

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