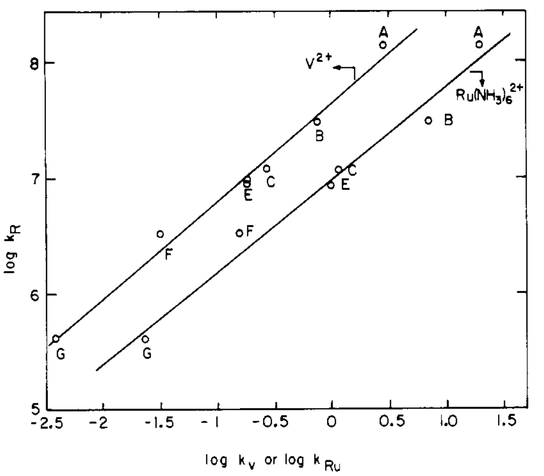

Figure 3. Plots of logarithm of the rate constants for the reductions of $(NH_3)_5Co(NC_5H_4X)^{3+}$ complexes by 2-hydroxy-2-propyl radicals (k_R) vs. log (k_V) for the reductions of the same complexes by hexaaquovanadium(II) ions and vs. log (k_{Ru}) for the reductions by hexaammineruthenium(II) ion at 25 °C, $\mu = 1.0$ M ($HClO_4 + LiClO_4$). The pyridine substituents are (A) 3-CN, (B) 3-Cl, (C) H, (E) 4-$C(CH_3)_3$, and (F) 4-$N(CH_3)_2$; point G refers to $Co(NH_3)_6^{3+}$.

nation of whether or not the rates of reduction of a given series of complexes by two different metals (M and N) are correlated. This correlation, when it is successful, often takes the form of a relation such as $\log k_M = m \log k_N + b$. This treatment permits the inclusion of related oxidants that are not members of the family of substituted pyridine derivatives, such as $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$. Thus data applying to these complexes, otherwise not part of the Hammett relation, can be included as a part of the analysis of the mechanism.

Figure 3 shows such correlations for the present series of reactions in terms of plots of log k_R vs. log k_V and log k_{Ru}. Both sets of data define reasonable straight lines, which are given by

$$\log k_R = (0.84 \pm 0.05) \log k_V + 7.65 \pm 0.07 \qquad (11)$$

$$\log k_R = (0.80 \pm 0.06) \log k_{Ru} + 6.99 \pm 0.06 \qquad (12)$$

Mechanism and Conclusion. The following facts are germane to the assignment of a reaction mechanism: (1) All of the electron donors show strikingly similar substituent effects as expressed by the Hammett equation. (2) The rates of electron transfer from the aliphatic radical, although much faster than from the metal ion donors, are very successfully correlated with one another in terms of LFER relations. (3) The latter treatment readily and quantitatively incorporated kinetic data for complexes with an "innocent" ligand in place of the pyridine, for which electron transfer to the ligand is clearly impossible. (4) Reduction of free pyridinium ions by $\cdot C(CH_3)_2OH$ occurs at rates which are also correlated by the Hammett expression with $\rho = 8.5$ for a limited series of substituents.[15] The difference in the sensitivity of the reactions of free and complexed pyridines to substituent effects implies a mechanistic difference between the two series.

These facts, considered as a whole, suggest to us that each of the reactions proceeds by rate-limiting electron transfer to the cobalt itself. The comparisons cited above would appear to rule out a pathway consisting of a "chemical mechanism" by which electron transfer occurs first to pyridine. These results do suggest further experiments, however, which are presently in progress; in that work we plan to investigate reactions in which the pyridine is bound to a metal center that is not capable of further reduction, (e.g., $(NH_3)_5Ru(py)^{2+}$) or to one that can be reduced only at much more negative potentials, (e.g., $(H_2O)_5Cr(py)^{3+}$). Reduction of the pyridine ring will necessarily be involved if reaction occurs in the former case, and it may also occur in the latter. As such, the rates would be expected to respond to substituents differently, perhaps more in parallel to the trends reported[15] for $C_5H_4NH^+$ and $C_5H_4NCH_3^+$. Such a duality of mechanisms, i.e. outer-sphere electron transfer vs. attack at the ligand, has been observed recently in the reaction of alkyl radicals with $M(phen)_3^{3+}$ (M = Fe, Ru, Os; phen = 1,10-phenanthroline).[32,33]

Acknowledgment. This work was supported in part by the U.S. Department of Energy through the Joint U.S.-Yugoslav Board for Scientific Cooperation, by the Research Council (SIZ-II) of S.R. Croatia, and by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $Co(NH_3)_5(NC_5H_4\text{-}3\text{-}CN)^{3+}$, 80041-64-1; $Co(NH_3)_5(NC_5H_4\text{-}3\text{-}Cl)^{3+}$, 99618-38-9; $Co(NH_3)_5(NC_5H_5)^{3+}$, 31011-67-3; $Co(NH_3)_5(NC_5H_4\text{-}4\text{-}CH_3)^{3+}$, 33248-50-9; $Co(NH_3)_5(NC_5H_4\text{-}4\text{-}C(CH_3)_3)^{3+}$, 99618-39-0; $Co(NH_3)_5(NC_5H_4\text{-}4\text{-}N(CH_3)_2)^{3+}$, 99618-40-3; $\cdot C(CH_3)_2OH$, 5131-95-3; $V(H_2O)_6^{2+}$, 15696-18-1; $Ru(NH_3)_6^{2+}$, 19052-44-9.

Supplementary Material Available: Tables of kinetic data for each reaction (4 pages). Ordering information is given on any current masthead page.

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(32) Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.
(33) We are grateful to a reviewer for bringing this point to our attention.

Contribution from the Department of Chemistry,
University of Hong Kong, Hong Kong

A High-Valent Dioxoruthenium(VI) Complex of 2,2′-Bipyridine (bpy)—Preparation and Characterization of *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$

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The preparation and characterization of *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ (bpy = 2,2′-bipyridine) are described. The observed high $E_f°$ value (1.25 V vs. NHE) for the *trans*-$[Ru^{VI}(bpy)_2O]_2^{2+}$/*trans*-$[Ru^{IV}(bpy)_2O(OH_2)]^{2+}$ couple indicates that *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ is potentially useful for the photocatalytic splitting of water to oxygen.

Introduction

High-valent oxo complexes of ruthenium, especially those containing polypyridyl ligands, are of current interest in view of their potential usefulness as oxidative catalysts.[1] Although monooxoruthenium(IV) species are well-known,[2] the existence of dioxoruthenium(VI) species of 2,2′-bipyridine (bpy), namely *cis*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ [3a] and *trans*-$[Ru^{VI}(bpy)O_2Cl_2]$,[3b] has been reported only on several occasions. However, no detailed spectroscopic characterizations on this class of dioxo complexes have

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(1) See, for example: Gerstein, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029–4030.
(2) See, for example: Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106–4115.
(3) (a) Takeuchi, K. J.; Samuels, G. J.; Gerstein, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407–1409. (b) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315–1320.

ever been reported. Recent works of Damme and co-workers[4] showed that high-valent ruthenium oxo species derived from *trans*-$[Ru^{II}(bpy)_2(H_2O)_2]^{2+}$ played an important role in the photocatalytic splitting of water. Here the synthesis, electrochemistry, and spectroscopic properties of *trans*-$[Ru^{VI}(bpy)_2O_2][ClO_4]_2$ are described. This species, previously communicated by Meyer and co-workers,[3a] has incorrectly been formulated as $[Ru^{IV}(bpy)_2O(OH_2)[ClO_4]_2$.

Experimental Section

$RuCl_3$ (Johnson and Matthey) and 2,2′-bipyridine (bpy) (Strem) were used as supplied. All chemicals and solvents used were of analytical grade.

***trans*-$[Ru(bpy)_2O_2][ClO_4]_2$.** A mixture of *trans*-$[Ru(bpy)_2(OH)(OH_2)][ClO_4]_2$[5] (0.25 g) and excess $[NH_4]_2[Ce(NO_3)_6]$ (1 g) in water (50 mL) was stirred for 20 min. A yellow solid, *trans*-$[Ru(bpy)_2O_2][ClO_4]_2$, slowly deposited upon standing. Yields were usually greater than 85%. Anal. Calcd for *trans*-$[Ru(bpy)_2O_2][ClO_4]_2$: C, 37.3; H, 2.5; N, 8.7; Cl, 11.0. Found: C, 37.53; H, 2.67; N, 9.03; Cl, 11.2. IR: ν(Ru=O) 850 cm^{-1} (Nujol mull). μ_{eff}: ~0 μ_B at 25 °C. UV-vis spectral data (λ_{max}/nm ($\epsilon/M^{-1}\ cm^{-1}$) in CH_3CN_4): 395 (780), 300 (12200), 206 (29600).

Physical Measurements. Elemental analyses of the newly prepared complexes were performed by the Australian National Laboratory. IR spectra were measured in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (4000–200 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Gouy method with mercury tetrakis(thiocyanato)cobaltate(II) as the calibrant.

Cyclic voltammograms were obtained with Princeton Applied Research (PAR) instruments: Model 175 universal programmer and Model 173 potentiostat-galvanostat. Pyrolytic graphite and glassy-carbon electrodes were used as appropriate as the working electrodes. The reaction cell was a standard PAR Model K64 three-electrode jacketted polarographic cell, which was maintained to ±0.1 °C by thermostated water. Cyclic voltammograms were recorded with a Houston Model 2000# X-Y recorder at slow scan rates (<1 V s^{-1}) and with a Tektronix Model 5103N storage oscilloscope at high scan rates (1 V s^{-1}). Controlled-potential coulometric electrolysis was carried out with a PAR Model 9610 coulometric cell system, which was supplied with a PAR Model 377 synchronous stirring motor. A vitreous carbon crucible electrode was used as the working electrode during controlled-potential electrolysis experiments. All reaction solutions were deaerated before the CV scans and during the constant-potential electrolysis process.

Results and Discussion

Meyer and co-workers previously communicated that Ce(IV) oxidation of *trans*-$[Ru^{III}(bpy)_2(OH)(OH_2)][ClO_4]_2$ in water produced *trans*-$[Ru(bpy)_2(OH_2)O][ClO_4]_2$.[3a] The assignment of this species as a monooxo-Ru(IV) complex was probably inferred from the electrochemical behavior of *trans*-$[Ru(bpy)_2(OH_2)_2]^{2+}$. At pH 1.5 two couples, each involving the loss of one proton and one electron, at $E_{1/2}$ = 0.45 and 1.01 V vs. SSCE were assigned by these authors as the Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples, respectively.[3a] Our electrochemical studies showed that the cyclic voltammograms of *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ and *trans*-$[Ru^{III}(bpy)_2(OH)(OH_2)]^{2+}$ in 0.1 M CF_3SO_3H (pH 1.14) are very similar (Figure 1). Three quasi-reversible couples, I–III (ΔE_p ~ 30–70 mV) at 1.01, 0.88, and 0.44 V vs. SCE, respectively were observed at slow scan rates (20 mV s^{-1}). Controlled-potential reductions of *trans*-$[Ru(bpy)_2O_2]^{2+}$ at 0.95 V vs. SCE showed that n = 1.90, where n is the electrochemical stoichiometry. This result, together with the 30-mV peak-to-peak separation (ΔE_p) of couple I, strongly suggests that this is a reversible two-proton–two-electron-transfer process and disproves previous assignment of a Ru(IV)/Ru(III) couple to I. The observation that the $E_f°$ values shift by 60 mV for every change of 1 pH unit (Figure 2) is consistent with the electrode reaction

$$\text{(I)}\quad trans\text{-}[Ru^{VI}(bpy)_2O_2]^{2+} + 2H^+ + 2e^- \rightarrow trans\text{-}Ru^{IV}(bpy)_2O(OH_2)]^{2+} \quad (1)$$

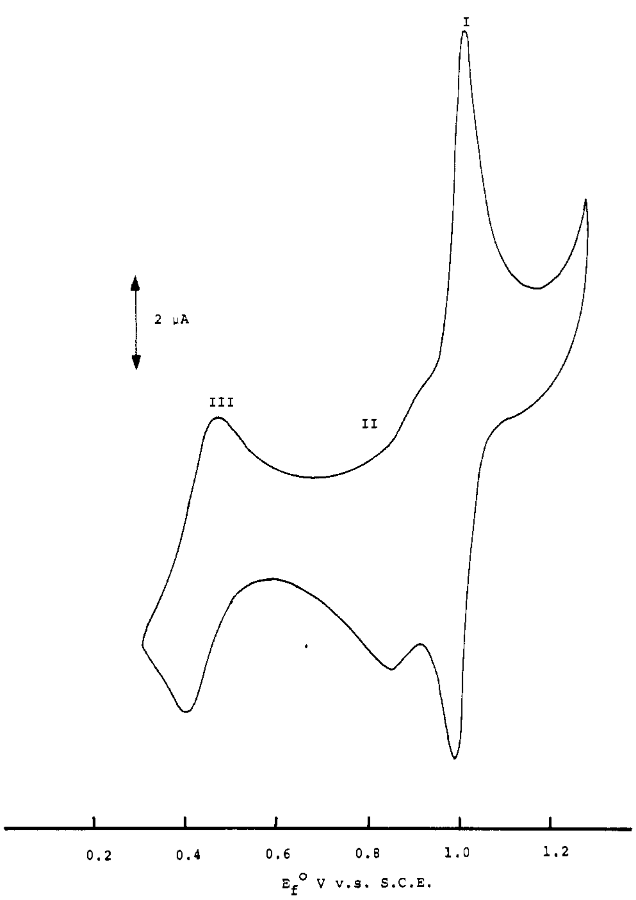

Figure 1. Cyclic voltammogram of *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ in 0.1 M CF_3SO_3H: Working electrode, pyrolytic graphite; scan rate, 20 mV s^{-1}.

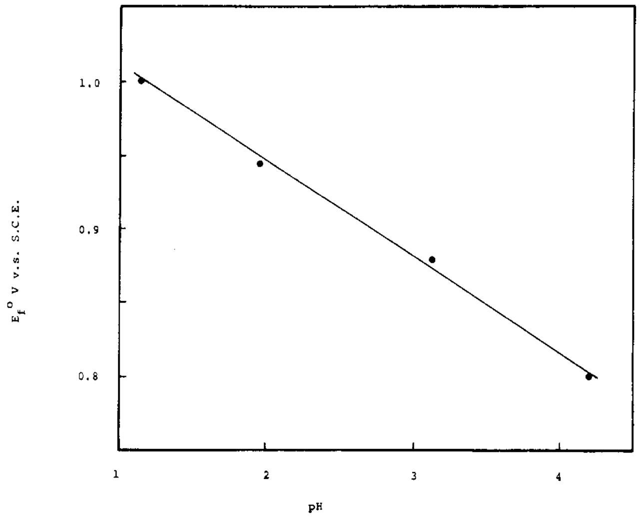

Figure 2. The $E_f°$ vs. pH plot for the *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$/*trans*-$[Ru^{IV}(bpy)_2O(OH_2)]^{2+}$ couple.

with $E°_{298} = E_f° + 0.059(pH)$.

It should be noted that from the electrochemical studies above, it is not possible to assign the Ru(IV) species as either *trans*-$[Ru^{IV}(bpy)_2O(OH_2)]^{2+}$ or *trans*-$[Ru(bpy)_2(OH)_2]^{2+}$. Couples II and III could be assigned to reactions 2 and 3, respectively.

$$\text{(II)}\quad trans\text{-}[Ru^{IV}(bpy)_2O(OH_2)]^{2+} + H^+ + e^- \rightarrow trans\text{-}[Ru^{III}(bpy)_2(OH)(OH_2)]^{2+} \quad (2)$$

$$\text{(III)}\quad trans\text{-}[Ru^{III}(bpy)_2(OH)(OH_2)]^{2+} + H^+ + e^- \rightarrow trans\text{-}[Ru^{II}(bpy)_2(OH_2)_2]^{2+} \quad (3)$$

Controlled-potential coulometry experiments on *trans*-$[Ru^{IV}(bpy)_2O(OH_2)]^{2+}$ in 0.1 M CF_3SO_3H at 0.6 V vs. SCE established

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[4] Nijs, H.; Cruz, M.; Fripiat, J.; Damme, H. V. *J. Chem. Soc., Chem. Commun.* **1981**, 1026–1027.

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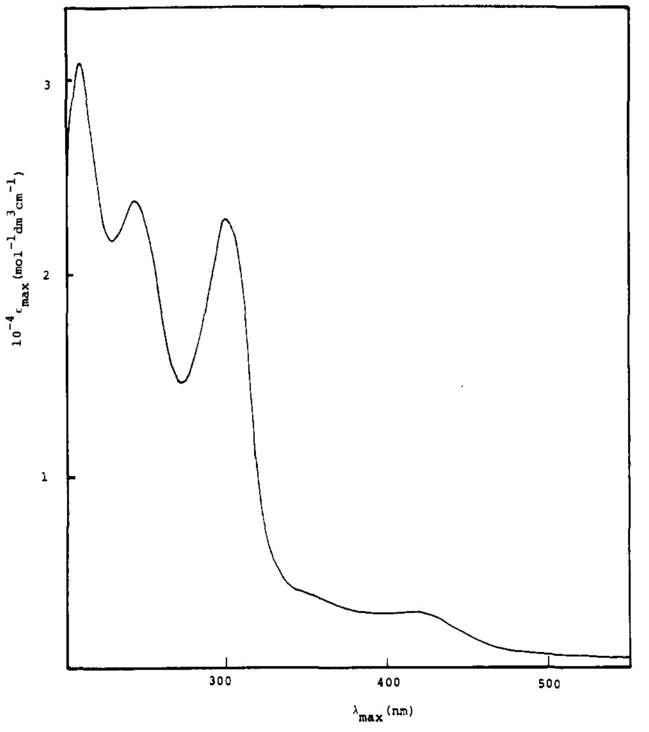

Figure 3. UV–vis absorption spectrum of *trans*-[Ru^{IV}(bpy)$_2$O(OH$_2$)]$^{2+}$ (generated by controlled-potential reduction of *trans*-[Ru^{VI}(bpy)$_2$O$_2$]$^{2+}$ at 0.95 V vs. SCE) in 0.1 M CF$_3$SO$_3$H.

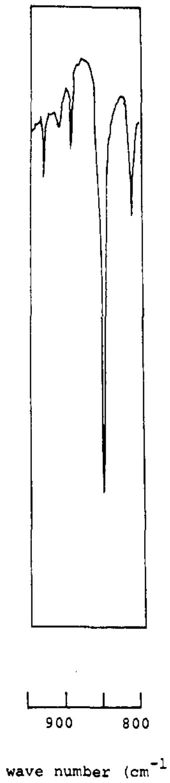

Figure 4. IR absorption spectrum (Nujol mull) of *trans*-[Ru(bpy)$_2$O$_2$][ClO$_4$]$_2$ in the 800–900-cm^{-1} region.

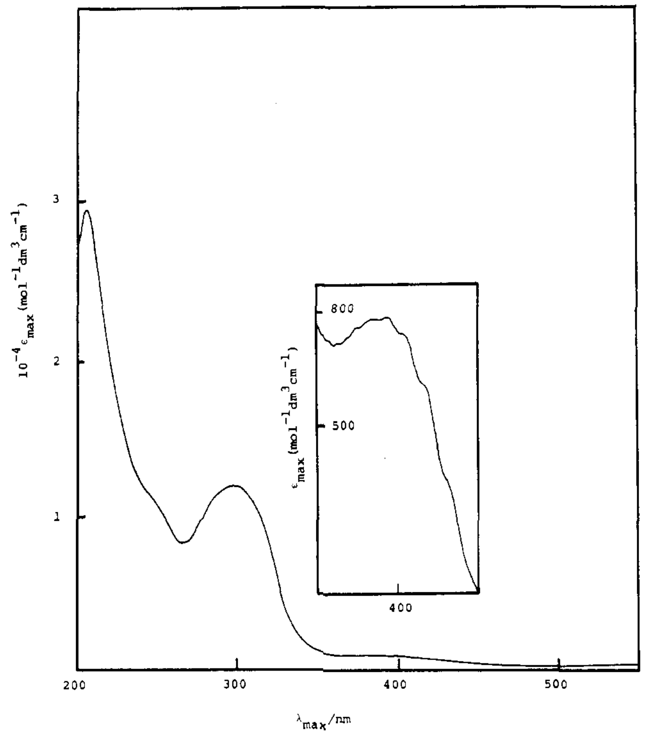

Figure 5. UV–vis absorption spectrum of *trans*-[Ru^{VI}(bpy)$_2$O$_2$]ClO$_4$ in CH$_3$CN.

n = 0.9 for reaction 2. In both reactions 2 and 3, the same linear plots of $E_f°$ vs. pH (over the pH range 1–4) with a slope of 60 mV/pH are also observed, and this is taken to support the formulation of *one-electron–one-proton-transfer processes.* *trans*-[Ru^{IV}(bpy)$_2$O(OH$_2$)]$^{2+}$ has also been characterized spectroscopically. Its UV–vis absorption spectrum (Figure 3) is similar to that of *cis*-[Ru^{IV}(bpy)$_2$(py)O]$^{2+}$[6] (py = pyridine). The above results clearly indicate that *trans*-[Ru(bpy)$_2$O$_2$]$^{2+}$ is a powerful oxidant and is thermodynamically feasible for the splitting of water into oxygen ($E_f°$ = [O$_2$/H$_2$O] = 1.23 V vs. NHE, 1 M acid). In the observed photocatalytic oxidation of water by *trans*-[Ru^{II}(bpy)$_2$(OH$_2$)$_2$]$^{2+}$/Ru(bpy)$_3$$^{2+}$/Co(NH$_3$)$_5$Cl^{2+} system,[4], the involvement of Ru^{IV}=O complex as an active intermediate in the oxidation process is therefore unlikely in view of its low potential.

As shown above, the electrochemical oxidation of *trans*-[Ru^{III}(bpy)$_2$(OH)(OH$_2$)][ClO$_4$]$_2$ in 0.1 M CF$_3$SO$_3$H yielded *trans*-[Ru(bpy)$_2$O$_2$][ClO$_4$]$_2$. However the best method to prepare this species is the direct oxidation of *trans*-[Ru(bpy)$_2$(OH)(OH$_2$)][ClO$_4$]$_2$ by *[NH$_4$]$_2$[Ce(NO$_3$)$_6$] in water.* Other oxidants, such as H$_2$O$_2$ and *tert*-butyl hydroperoxide were not effective to bring about the oxidation. As expected, *trans*-[Ru(bpy)$_2$O$_2$][ClO$_4$]$_2$ is diamagnetic with $^1A_{1g}$ $(d_{xy})^2$ ground state. It exhibits only *one* intense IR band at 850 cm^{-1} (Figure 4), which is indeed too high for a ν(Ru^{IV}=O) stretch but is typical of ν_{as}(Ru^{VI}=O) as observed in the structurally characterized *trans*-[Ru^{VI}(15-TMC)O$_2$]$^{2+}$ and *trans*-[Ru^{VI}(16-TMC)O$_2$]$^{2+}$ species[7] (15-TMC = 1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane and 16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) and *trans*-[Ru(bpy)$_2$O$_2$Cl$_2$][3b] and *trans*-dioxoruthenium(VI) porphinate species.[8] These findings, together with the observation that the electrochemical behavior of this species is very similar to that of *trans*-[Ru^{III}(bpy)$_2$(OH)(OH$_2$)]$^{2+}$ indicate a trans configuration for this dioxoruthenium(VI) species. The low solubility and the instability of *trans*-[Ru(bpy)$_2$O$_2$][ClO$_4$]$_2$ in solutions preclude a detailed NMR analysis on the complex. Similar to *trans*-[Ru(15-TMC)O$_2$][ClO$_4$]$_2$ and *trans*-[Ru(16-TMC)O$_2$][ClO$_4$]$_2$, this Ru(VI)–dioxo–bpy species has been found to be stable in the dark and under cold conditions but it slowly deteriorated to a green substance upon exposure to UV light at room temperature.

The UV–vis absorption spectrum of *trans*-[Ru(bpy)$_2$O$_2$][ClO$_4$]$_2$ in CH$_3$CN with a characteristic weak vibronically structured absorption band at ~400 nm is shown in Figure 5. The 400-nm vibronic structured band similarly present in *trans*-[Ru(NH$_3$)$_4$O$_2$]$^{2+}$ and *trans*-[Ru(TMC)O$_2$]$^{2+}$[9] (TMC = 1,4,8,11-

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Inorg. Chem. **1986,** *25,* 348–355

tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been assigned as the $(d_{xy})^2 \rightarrow (d_{xy})^1(d\pi)^1[d\pi = (d_{xz}, d_{yz})]$ transition ($^1A_{1g} \rightarrow {}^1E_g$), which is vibronically coupled to the A_{2u}(Ru–O) vibrational stretching mode. This kind of vibronic structured d–d transition that is also commonly encountered in other d^2 *trans*-dioxo complexes[10] should be regarded as an essential characteristic spectral feature for *trans*-Ru(VI)–dioxo species. The relative insensitivity of this 400-nm band of *trans*-[Ru^{VI}LO$_2$]$^{2+}$ [L = (NH$_3$)$_4$, TMC, (bpy)$_2$] with the nature of L[9] is in accordance with its formulation as *the electronic transition is primarily within the dπ levels.* The observed decrease in the ν(Ru–O) stretch (~620–650 cm^{-1}) in the excited state clearly indicates a weakening of the Ru–O bond in these dioxo species upon UV–vis excitation. This result together with its high oxidizing power ($E_f° = 1.25$ V vs. NHE) strongly implies the potential usefulness of these species as *powerful photochemical oxidative catalysts.*

Registry No. *trans*-[Ru(bpy)$_2$O$_2$][ClO$_4$]$_2$, 99664-14-9; *trans*-[Ru(bpy)$_2$(OH)(OH$_2$)][ClO$_4$]$_2$, 72174-11-9; [NH$_4$]$_2$[Ce(NO$_3$)$_6$], 16774-21-3; *trans*-[Ru(bpy)$_2$O(OH$_2$)]$^{2+}$, 85114-19-8.

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Preparation, Characterization, and Chemistry of Activated Cobalt

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When anhydrous cobalt chloride or iodide was treated with solutions of lithium or potassium naphthalide in glyme at low temperature, slurries of very finely divided cobalt metal were obtained. The solid material obtained was a complex mixture of cobalt microparticles intimately mixed with the alkali halide coproduct and a carbonaceous material from solvent decomposition. X-ray photoelectron spectroscopy and the materials' chemical properties confirm the presence of metallic cobalt. The cobalt powder by itself or on alumina support was found to be a methanation and Fischer–Tropsch catalyst. Under some conditions high selectivity for formation of methanol and ethanol or methyl acetate was observed. Iodobenzene reacted with cobalt powders to give a low yield of biphenyl, while benzyl bromide gave a 63% yield of bibenzyl. Geminal dihalides such as dichlorodiphenylmethane reacted to give high yields of the unsaturated coupling product, tetraphenylethylene. Cobalt powders converted nitrobenzene to azobenzene in 37% yield.

Introduction

Highly dispersed and reactive metal powders have commanded a great deal of interest for their applications in catalytic and stoichiometric chemical syntheses as well as their uses in materials science. Numerous methods exist for the preparation of metal powders. Hydrogen reduction of metal oxides is one common method[37,54] as is reduction of metal salts by other chemical means.[54a,55] Pyrolysis of metal carboxylate derivatives has been used in some cases,[54a,56] and condensation of metal atom vapors in a frozen solvent or other matrix[25,26,42,57] is one of the more modern methods. A far-ranging review of unsupported metal particles and their preparation, reactivity, and physical properties has appeared.[27]

Since 1972 we have published several reports describing convenient methods for the generation of reactive metal slurries in ethereal solvents and their use in organic synthesis.[1-22] Our research on reactive cobalt was first reported in detail only recently.[21,22] We have since developed a modified preparation for activated cobalt that gives a more reactive material, which we have used to prepare Co$_2$(CO)$_8$.[1] Further details of the nature of this new form of cobalt are the subject of this report. Included are the results of our attempts to form carbon–carbon bonds from organic halides using activated cobalt and the results of treating aromatic nitro compounds with activated cobalt.

Cobalt is an important constituent of some Fischer–Tropsch catalysts and, not surprisingly, our activated cobalt also displayed modest catalytic activity, which we shall describe.

Results

Preparation and Properties of Active Cobalt Powders. We have used two general approaches in preparing cobalt powders. The first method, reported previously,[21,22] used a slight excess of lithium, usually 2.1–2.3 equiv in glyme (1,2-dimethoxyethane), to reduce anhydrous cobalt chloride to a dark gray powder, **1**. Use of cobalt bromide or iodide gave a somewhat less reactive form of **1**.[22] These reductions also required the addition of a catalytic quantity of naphthalene, which acted as an electron carrier. This greatly shortened the time necessary for reduction and improved the reactivity of the metal. Slurries of **1** were very reactive toward strongly electrophilic aryl halides such as C$_6$F$_5$X (X = Br, I), yielding the solvated species Co(C$_6$F$_5$)$_2$ and CoX$_2$. The former was isolated as the bis(triethylphosphine) adduct. Attempts to extend this reaction to less reactive aryl halides met with disappointing results. In order to increase the reactivity of our cobalt powders, a new method of preparation was devised using a modification of a previously reported method.[56g] This reactive cobalt, **2**, was prepared by dissolving lithium in glyme containing

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