an NOE experiment was performed by irradiating at signal D and at its symmetrical position with respect to E, alternately, and subtracting the FID's. In addition, a similar experiment was performed by irradiating at signal C and at its symmetrical position with respect to E. The resulting difference spectra were subtracted, in order to rule out any possible contribution of C to the NOE on E. The result of such subtraction is shown in Figure 4. Signal E is clearly apparent as a negative shoulder of the irradiated signal D and therefore demonstrates the presence of sizable NOE. Off-resonance effects are apparent on signal B and, to a lesser extent, on signal A, for which complete cancellation has not occurred. The intensity of the NOE observed on signal E is consistent with D and E being the geminal $\beta$-CH$_2$ protons of Asp-81.

The assignment of $\beta$-CH$_2$ protons of aspartic and $\gamma$-CH$_2$ protons of glutamic residues has always been a problem in the NMR spectroscopy of paramagnetic proteins, and very few documented examples are available. Some significant work had been done by Goff and Que in dinuclear iron complexes.[19]

We have now put the assignment of the protons of the cobalt domain in cobalt-substituted SOD's on a firmer basis through deuteriation and $^1$H NOE experiments: the ortho-like protons of histidines may relax much faster than the meta-like protons in tetrahedral cobalt(II) systems, and the CH$_2$ protons of Glu and Asp are quite broad and experience shifts similar to those of meta-like protons of histidines.

(19) Arafa, I. M.; Goff, H. M.; David, S. S.; Murch, B. P.; Que, L., Jr. *Inorg. Chem.* **1987,** *26,* 2779.

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## Cobalt Carbonyl Chemistry in Wet Ethereal Solutions: [Co$_6$(CO)$_{15}$]$^{2-}$ and Co$_6$(CO)$_{16}$ Cluster Formation or Stepwise Water Gas Shift Reaction

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The reduction of water by CO to form CO$_2$ and H$_2$ (water gas shift reaction (WGSR)) is an important process catalyzed in homogeneous phase by metal carbonyls.[1] Therefore, the chemistry of metal carbonyls in water or in water-containing solutions is a subject of large interest: several group 6 or group 8 metal carbonyls, precursors for WGSR, were investigated in detail in their reactions with water or with hydroxide ion.[2] From this point of view, Co$_2$(CO)$_8$ (1), promoting the WGSR under drastic conditions,[3] has been somewhat neglected. It is known that water, in which 1 is not soluble, slowly disproportionates 1;[4] from the resulting pink solution, especially when concentrated, some HCo(CO)$_4$ and Co(OH)$_2$ can be formed. Subsequently, we found

that the disproportionation–synproportionation equilibrium (1) is established at room temperature in tetrahydrofuran (THF) solutions of 1 in the presence of small amounts of water (H$_2$O/1 molar ratio <10).[5]

$$\tfrac{3}{2}Co_2(CO)_8 \xrightleftharpoons{\text{THF, H}_2\text{O}}$$
$$[Co(H_2O)_x(THF)_y]^{2+} + 2[Co(CO)_4]^- + 4CO \quad (1)$$
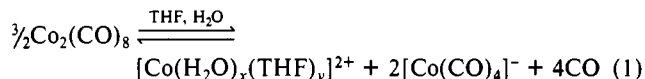
These findings indicate that the chemistry of 1 is strongly affected by water concentration. In order to better define these effects and the possibilities offered by 1 as a catalyst for the WGSR, we carried out the present study, where the electron transfers occurring in wet ethereal solutions of 1 are investigated under various H$_2$O/1 molar ratios and CO pressures.

### Experimental Section

Materials and procedures were used as described recently.[6]

**Co$_7$(CO)$_{15}$·2H$_2$O·6THF (2).** A 6.2-g amount (18.13 mmol) of 1 and 0.35 mL (19.44 mmol) of H$_2$O were dissolved in 600 mL of THF. The resulting dark brown solution was refluxed at 40 °C under a constant 440-mmHg pressure. Pure CO was evolved during the reaction, and after 10 h 6.0 g (89%) of 2 was obtained as black crystals. Anal. Calcd for Co$_7$(CO)$_{15}$·2H$_2$O·6THF: Co, 31.74; CO, 32.28; THF, 33.20; H$_2$O, 2.77. Found: Co, 31.27; CO, 32.12; THF, 32.80; H$_2$O, 2.85. Selected IR bands (Nujol mull): 3413 (m, br), 2045 (m), 1984 (vs), 1956 (vs), 1781 (s), 1756 (m), 1732 (m), 1722 (s), 1697 (m), 1653 (s) cm$^{-1}$.

**Carbonylation of 2 in Toluene.** A suspension of 1.45 g (1.11 mmol) of 2 in 100 mL of toluene was vigorously stirred with a magnetic bar in a 500-mL closed vessel filled with CO at atmospheric pressure. After 12 h at 20 °C a dark brown solution and a black solid, Co$_6$(CO)$_{16}$ (76%), were obtained. Anal. Calcd for Co$_6$(CO)$_{16}$: Co, 44.14; CO, 55.86. Found: Co, 43.60; CO, 55.10. $\nu$(CO) (Nujol mull): 2113 (w), 2061 (vs), 2057 (sh), 2026 (w), 2020 (w), 2018 (w), 1772 (vs) cm$^{-1}$.

**Co$_4$(OH)$_7$Co(CO)$_4$ (3).** A pink solution obtained by dissolving 3.16 g (9.2 mmol) of 1 and 2.5 mL (139 mmol) of H$_2$O in 300 mL of Et$_2$O was refluxed under atmospheric pressure. A CO/H$_2$ = 2.8 mixture of constant composition was evolved during 3 h while 3 separated out as a gray solid (96%). Anal. Calcd for Co$_5$(OH)$_7$(CO)$_4$: Co, 56.08; OH, 22.62; CO, 21.29. Found: Co, 57.03; OH, 21.63; CO, 20.84. IR (Nujol mull; cm$^{-1}$): $\nu$(OH) 3665 (m), 3640 (m), 3594 (m); $\nu$(CO) 2040 (m), 1980 (s), 1920 (vs).

**Carbonylation of 3.** A 120-mL rocking steel autoclave containing 0.96 g (1.83 mmol) of 3 suspended in 35 mL fo 0.5% H$_2$O/THF was pressurized with 80 atm of CO and warmed at 100 °C. Analysis of gases after 12 h revealed the presence of CO and CO$_2$ only. CO$_2$ was quantitatively determined by slowly bubbling the reaction gases into 50 mL of 0.106 M Ba(OH)$_2$ solution. The excess of Ba(OH)$_2$ was potentiometrically titrated against 0.1 N HCl. The end point was reached after the addition of 36 mL of HCl. The IR spectrum of the liquid phase showed absorptions due to 1 ($\nu$(CO) 2070 (vs), 2040 (vs), 1846 (s) cm$^{-1}$) and to [Co(CO)$_4$]$^-$ ($\nu$(CO) 1887 cm$^{-1}$). Quantitative determination of formed H$_2$O (3.0 mmol) was performed by IR comparison with standard H$_2$O/THF solutions. Before analysis, samples were treated with an excess of 2,2′-bipyridine.

### Results and Discussion

Depending on the H$_2$O/1 molar ratio, different reactions occur on CO removal from wet THF solutions of 1. As mentioned above, in the case of H$_2$O/1 = 1 (molar ratio) the $P_{CO}$-dependent equilibrium (1) is operating at room temperature in a 0.03 M solution of 1 in THF. By reflux under reduced pressure at 40 °C, CO is lost from this solution while a black crystalline solid analyzing as Co$_7$(CO)$_{15}$·2H$_2$O·6THF (2) separates out in almost quantitative yields. While some disorder in the crystals prevented a X-ray determination of the structure, the nature of 2 can be inferred from its IR spectrum in CH$_3$OH, where 2 dissolves with a dark green color. In the CO stretching region the characteristic pattern of absorptions of the anionic cluster [Co$_6$(CO)$_{15}$]$^{2-}$ is observed[7] and the spectrum is superimposable on that of an authentic sample of Cs$_2$Co$_6$(CO)$_{15}$ in CH$_3$OH at the same concentration (Figure 1a). It is considered therefore that, in the

(1) (a) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977,** *99,* 252. (b) Cheng, C. H.; Hendersen, D. E.; Eisenberg, R. J. *J. Am. Chem. Soc.* **1977,** *99,* 2791. (c) Kang, H.; Mauldin, C.; Cole, T.; Sleigier, W.; Pettit, R. *J. Am. Chem. Soc.* **1977,** *99,* 8323. (d) Ford, P. C. *Acc. Chem. Res.* **1981,** *14,* 31 and references therein. (e) Halpern, J. *Comments Inorg. Chem.* **1981,** *1,* 1. (f) Eisenberg, R.; Hendricksen, D. E. *Adv. Catal.* **1979,** *28,* 79.

(2) (a) Laine, R. M.; Wilson, R. B. *Aspects of Homogeneous Catalysis;* Ugo, R., Ed.; D. Reidel: London, 1984; Vol. 5, p 217 and references therein. (b) Trantman, R. J.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985,** *107,* 2355. (c) Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1985,** *107,* 585. (d) Taube, D. J.; Rokicki, A.; Austock, M.; Ford, P. C. *Inorg. Chem.* **1987,** *26,* 526.

(3) Haenel, M. W.; Schanne, L.; Woestfeld, E. *Erdoel Kohle, Erdgas, Petrochem.* **1986,** *39,* 505; *Chem. Abstr.* **1987,** *106,* 20865w.

(4) Hieber, W.; Sedlmeier, J.; Abeck, W. *Chem. Ber.* **1953,** *86,* 700.

(5) Fachinetti, G.; Del Cima, F.; Braca, G.; Funaioli, T. *J. Organomet. Chem.* **1984,** *275,* C25.

(6) Fachinetti, G.; Funaioli, T.; Marcucci, M. *J. Organomet. Chem.* **1988,** *353,* 393.

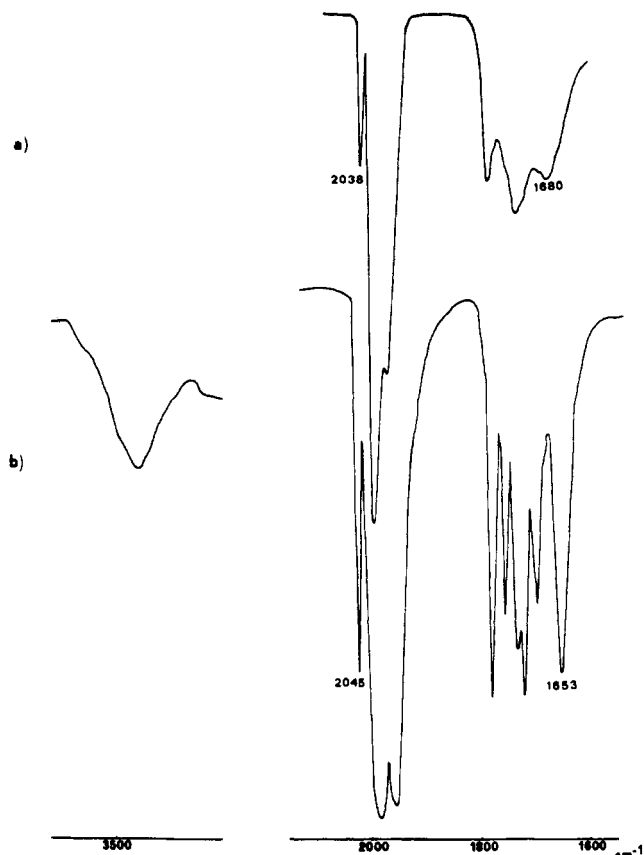(7) Chini, P.; Albano, V. *J. Organomet. Chem.* **1968,** *15,* 433.

**Figure 1.** (a) IR spectrum of a 8 × 10⁻³ M solution of **2** or Cs₂Co₆(C-O)₁₅ in CH₃OH. (b) IR spectrum of solid **2** (Nujol mull).

present case, CO removal brings about [Co₆(CO)₁₅]²⁻ formation with Co²⁺ as the countercation. The latter presumably coordinates water, which in turn may bind THF through hydrogen bonding. Additional THF, clathrated in the solid, is presumably responsible for the observed disorder. In view of our interest in the chemistry of carbonyl metalates with countercations of the same metal, we examined the spectroscopic and chemical properties of **2** in some detail. Its IR spectrum in the solid state (Figure 1b) strongly differs from that in CH₃OH solution; a comparison between the two shows that, in the solid state, stretching vibrations for terminal CO groups are at higher wavenumber with respect to those in CH₃OH solution. Moreover, only in the solid state are absorptions at very low wavenumber. These are suggestive of face-bridging CO groups associated with an acidic countercation.[8] Thus, we can account for the differences between the two spectra of Figure 1 by assuming that in the solid state **2** is a Co²⁺,[Co₆(CO)₁₅]²⁻ tight homonuclear ion pair (HNIP) through oxygen atoms of face-bridging CO groups. In CH₃OH solutions, the basic solvent brings about the separation of ions, giving solvent-surrounded Co²⁺ cations and unperturbed [Co₆(CO)₁₅]²⁻ anions. Concerning the chemical properties of **2**, it reacts with CO at atmospheric pressure both in CH₃OH solutions and as a suspension in toluene or Et₂O. Depending on the medium, two different reactions occur. In CH₃OH solution the reaction consists of the carbonylation of the [Co₆(CO)₁₅]²⁻ anionic cluster and, according to Chini,[7] unperturbed [Co(CO)₄]⁻ and solvent-surrounded Co²⁺ cations are formed. In a different way, neutral cobalt carbonyls, namely Co₆(CO)₁₆ and **1**, are obtained on reacting **2** with CO in toluene or Et₂O (eq 2). Co₆(CO)₁₆ can be isolated in 76% yields so that

$$\underset{\mathbf{2}}{Co_7(CO)_{15}\cdot 2H_2O\cdot 6THF} + 5CO \xrightarrow[-H_2O, -THF]{toluene}$$

$$\underset{\mathbf{1}}{\tfrac{1}{2}Co_2(CO)_8} + Co_6(CO)_{16} \quad (2)$$
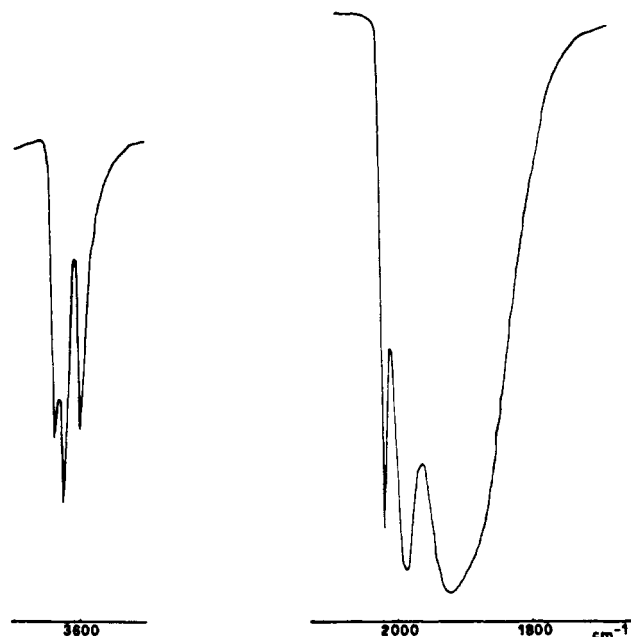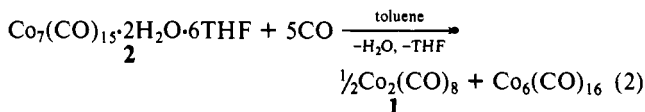


**Figure 2.** IR spectrum of solid **3** (Nujol mull).

the carbonylation of solid **2** in poorly coordinating solvents (eq 2) constitutes an improvement of its known synthesis: Co₆(CO)₁₆ has only been obtained in very low yields by Fe(III) or Hg(II) oxidation of the [Co₆(CO)₁₅]²⁻ anion in aqueous solution.[9] In reaction, Co²⁺ cations insufficiently solvated by bases act as oxidizing agents under CO.

The addition of excess water to 0.03 M solutions of **1** in THF or Et₂O (H₂O/**1** = 15 (molar ratio)) brings about a fast, complete disproportionation reaction (eq 1): in both solvents, pink solutions stable at room temperature under CO were obtained. When these solutions are refluxed under atmospheric pressure, H₂ is lost in addition to CO, while a gray solid separates out. The nature of the ether affects the reaction: in refluxing THF, the reaction requires 2 days to be complete and the solid product contains variable amounts of ferromagnetic cobalt metal; in refluxing Et₂O, no more carbonyls can be detected in solutions after 3 h of reflux. During this time, a CO/H₂ = 2.8 gas mixture of constant composition is evolved, while cobalt metal does not contaminate the solid product analyzing as Co₄(OH)₇Co(CO)₄ (**3**). As suggested by its insolubility, **3** is probably a polymeric substance. Its IR spectrum as a Nujol mull (Figure 2) shows three bands in the OH stretching region (ν(OH) 3665 (m), 3640 (m), 3594 (m) cm⁻¹) and three bands in the CO stretching region (ν(CO) 2040 (m), 1980 (s), 1920 (vs) cm⁻¹). Owing to their relative intensity and wavenumber, the last three bands can be attributed to a [Co(C-O)₄]⁻ anion in a metal–metal HNIP with an acidic Co²⁺ countercation.[10] In order to confirm the presence of the [Co(CO)₄]⁻ anion, **3** was treated with 5% H₂O in THF: a solution showing the IR absorption of unperturbed [Co(CO)₄]⁻ (1887 cm⁻¹) was obtained together a pink residual of Co(OH)₂. Concerning the absorptions of **3** in the OH stretching region, none of the three corresponds to the wavenumber for OH stretching of solid Co(OH)₂ in the pink form (3623 cm⁻¹). We therefore suggest that no free Co(OH)₂ is present in **3** but rather that oxygen atoms of the Co(OH)₂ are in the coordination sphere of a central [Co(OH)]⁺ cation, together with the cobalt atom of a [Co(CO)₄]⁻ anion. Thus, on the refluxing of a fully disproportionated wet ethereal solution of **1**, [Co(CO)₄]⁻ anions reduce H₂O to H₂ and OH⁻, with the H₂O/[Co(CO)₄]⁻ molar ratio being 11. Such a reduction does not occur on refluxing a wet ethereal solution of NaCo(CO)₄ with an identical H₂O/[Co(CO)₄]⁻ molar ratio. Clearly, in the [Co(CO)₄]⁻ water reduction reported here, the

(8) Adams, H. N.; Fachinetti, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 404.
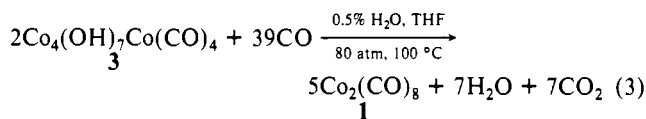
(9) Chini, P. *Inorg. Chem.* **1969**, *8*, 1206.

(10) Fachinetti, G.; Fochi, G.; Funaioli, T.; Zanazzi, P. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 680.

highly polarizing $Co^{2+}$ cations play a crucial rôle. The water excess of the present case prevents the interaction of $Co^{2+}$ and $[Co(CO)_4]^-$ to form tight HNIPs, which are intermediates in equilibrium 1 in the presence of CO and in the formation of **2** on CO removal. Only water molecules are in the first coordination sphere of $Co^{2+}$ cations. The poorer Lewis base $[Co(CO)_4]^-$ is presumably able to replace a THF or $Et_2O$ molecule in the second coordination sphere of $Co^{2+}$ giving a $H_2O$ separated ion pair[11] $[(H_2O)_nCo-O(H)-H\cdots(OC)_3CoCO]^+$. Hydrolysis can then occur with formation of $HCo(CO)_4$ and $[(H_2O)_nCoOH]^+$. $HCo(CO)_4$ decomposes to $H_2$ and **1**, the latter one being disproportionated by $H_2O$, and the sequence continues until the formation of insoluble **3**.

The here reported water reduction promoted by $Co^{2+}$ and $[Co(CO)_4]^-$ formally resembles that performed by $Zn[Co(CO)_4]_2$ in toluene, with the $H_2O/Zn[Co(CO)_4]_2$ molar ratio being 1.[12] In this latter case, the reaction presumably occurs through an intramolecular proton transfer from Zn-coordinated water to the Zn-bonded $Co(CO)_4$ unit in the $H_2OZn[Co(CO)_4]_2$ intermediate.

The achievement of water reductions using **1** instead of $Zn[Co(CO)_4]_2$ has the important consequence that the hydroxocobalt **3** can be reduced by CO. In anhydrous THF, **3** remains unchanged under 80 atm of CO and 150 °C. In the presence of added water, however, reaction 3 is observed. No $H_2$ is produced

$$2Co_4(OH)_7Co(CO)_4 + 39CO \xrightarrow[\text{80 atm, 100 °C}]{\text{0.5\% H}_2\text{O, THF}}$$
$$\mathbf{3}$$
$$5Co_2(CO)_8 + 7H_2O + 7CO_2 \quad (3)$$
$$\mathbf{1}$$

during reaction 3. The water reduction described above and reaction 3 constitute a stepwise WGSR where no promoters are required and $H_2$ and $CO_2$ are formed in two separate steps.

Finally, we examined the behavior of a 0.03 M solution of **1** in 5% $H_2O/THF$. During 20 h of reflux at 65 °C no gas was evolved and the 1887-$cm^{-1}$ band of $[Co(CO)_4]^-$ remained unchanged. The lack of reaction supports our view of HNIPs as intermediates in electron-transfer reactions occurring in wet ethereal solutions of **1**: as a large excess of water prevents both the tight and water-separated $Co^{2+}$,$[Co(CO)_4]^-$ HNIP, stable solutions are obtained.

(11) Edgell, W. F.; Lyford, J.; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403.
(12) Burlitch, J. M.; Hayes, S. E.; Withwell, G. E. *Organometallics* **1982**, *1*, 1074.

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## Dinuclear Ruthenium Complexes with Bridging 1,4,5,8-Tetraoxonaphthalene: Redox Properties and Mixed-Valence Interactions

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Dinuclear ruthenium complexes are the focus of active research aimed at understanding the mechanism of electron transfer between metal centers in mixed-valence states.[1-12] The studies of

the intervalence transition occurring in the electronic spectra and the analysis of the spectral parameters of the band have provided considerable information about the interaction between the two metal centers.[13-17]

Recently, mononuclear ruthenium dioxolene complexes were reported showing at least five different oxidation states, which provided evidence of the noninnocent nature of the dioxolene ligands toward ruthenium.[18] Since the extent of the overlap between ruthenium(II) and ruthenium(III) in dinuclear complexes, which determines the nature of the mixed-valence species, is expected to depend on the mixing of the metal and bridging ligand orbitals, the use of noninnocent ligands may favor the formation of class III complexes. $[Ru(bpy)_2]^{n+}$ (bpy = 2,2'-bipyridine) cations appear to be particularly suitable to this purpose because of their stability toward disproportionation. Kaim et al. recently reported[19] dinuclear ruthenium complexes bridged by *o*- and *p*-quinoid molecules, in which borderline behavior between radical and metal-centered mixed-valence character was observed. This observation in fact showed that in principle it is possible to tune the metal–ligand delocalization by using appropriate quinoid molecules. With this in mind, we decided to investigate dinuclear ruthenium complexes with 1,4,5,8-tetraoxonaphthalene (tetrox), which potentially can bridge two different metal ions in five different oxidation states, as shown in Scheme I. We wish to report here the cations $[Ru_2(bpy)_4(tetrox)]^{n+}$ with $n$ = 2–4, which we could isolate as polycrystalline solids, and show that the complex with $n$ = 3 is a genuine example of class III ruthenium mixed-valence compounds with unprecedented spectral features.

### Experimental Section

**Chemicals.** *cis*-$Ru(bpy)_2Cl_2$ was prepared by using a published procedure.[20] 5,8-Dihydroxy-1,4-naphthoquinone (Fluka) was used as received. All other reagents were purchased commercially and used without further purification.

$[Ru_2(bpy)_4(tetrox)](PF_6)_2\cdot2H_2O$ **(2).** A 2-mmol sample of $Ru(bpy)_2Cl_2$ was suspended in 60 mL of methanol and heated for 0.5 h with stirring. Solid 5,8-dihydroxy-1,4-naphthoquinone (1 mmol) and a sodium hydroxide (2 mmol) solution in methanol were added. The reaction mixture was refluxed for 4 h, and the deep blue solution turned green. Upon the addition of 40 mL of a saturated potassium hexafluorophosphate aqueous solution, a black precipitate was formed. It was filtered out, washed several times with water, and then recrystallized from acetone/water and acetonitrile/diethyl ether mixtures. Anal. Calcd for $C_{50}H_{40}F_{12}N_8O_6P_2Ru_2$: C, 44.78; H, 2.98; N, 8.34. Found: C, 44.93; H, 2.66; N, 8.03.

$[Ru_2(bpy)_4(tetrox)](PF_6)_3$ **(3).** A sample of **2** (268 mg, 0.2 mmol) was dissolved in 30 mL of freshly distilled acetonitrile, and then $(NH_4)_2Ce(NO_3)_6$ (111 mg, 0.2 mmol) in 20 mL of water was added. The blue solution turned green. Upon addition of a saturated aqueous solution of

(3) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
(4) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.
(5) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
(6) Furholz, O.; Bürgi, H. B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121.
(7) Joss, S.; Bürgi, H. B.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 949.
(8) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015.
(9) Geselowitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015.
(10) Sahai, R.; Baucom, D. A.; Rillema, D. P. *Inorg. Chem.* **1986**, *25*, 3843.
(11) Hage, R.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. C. *Inorg. Chem.* **1988**, *27*, 2185.
(12) Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1174.
(13) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.
(14) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996.
(15) Wang, K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *28*, 369.
(16) Ko, J.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1985**, *107*, 6161.
(17) Piepho, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 6319.
(18) Lever, A. B. Pp.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.-A.; Liu, W.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076.
(19) Ernst, S.; Hanel, P.; Jordanov, J.; Kaim, W.; Kasack, V.; Roth, E. *J. Am. Chem. Soc.* **1989**, *111*, 1733.
(20) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(1) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.
(2) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984.