

These results could well suggest that all future ab initio calculations on substituted carboranes be conducted at least to the

CID/6-31G\*//6-31G or MP3/6-31G\*//6-31G level for useful information about relative stabilities. Unfortunately, this is not practical for the other derivatives discussed herein because of computer time constraints, especially upon considering that many (e.g., ethyl and trimethylamino) rotamer possibilities would need examination.

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Contribution from the Department of Chemistry and Saskatchewan Accelerator Laboratory, University of Saskatchewan, Saskatoon, SK, Canada S7N 0W0, and Bereich Strahlenchemie, Hahn-Meitner-Institut Berlin GmbH, Postfach 39 01 28, D-1000 Berlin 39, Federal Republic of Germany

## Radiolytic Study of the Reactions of Hydroxyl Radical with Cobalt(III), Iron(II), and Ruthenium(II) Complexes Containing 2,2'-Bipyridyl and Cyano Ligands

A. C. Maliyackel,<sup>1a</sup> W. L. Waltz,<sup>\*,1a</sup> J. Lilie,<sup>1b</sup> and R. J. Woods<sup>1a</sup>

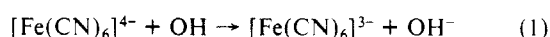
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The reactions of hydroxyl radical with the complex ions  $[\text{Co}(\text{bpy})_3]^{3+}$ ,  $[\text{Fe}(\text{bpy})_3]^{2+}$ ,  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$ ,  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{Me}_2\text{bpy})_3]^{2+}$ , and  $[\text{Ru}(\text{bpy})_3]^{2+}$  and with  $\text{bpy}$  and  $\text{Hbpy}^+$ , where  $\text{bpy}$  = 2,2'-bipyridine and  $\text{Me}_2\text{bpy}$  = 4,4'-dimethyl-2,2'-bipyridine, have been investigated in  $\text{N}_2\text{O}$ -saturated aqueous media. The results from time-resolved studies, carried out by using pulse radiolysis in conjunction with conductivity and near-UV-visible optical detection methods, show that the OH reactions occur with rate constants in the range  $(2\text{--}17) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . For the reactions of  $\text{bpy}$  and the tris(bipyridyl) complex ions, the absence of significant conductivity movements accompanying the initial optical changes demonstrates that the processes are ones involving OH addition to the systems. The products are reactive toward hexacyanoiron(III) and molecular oxygen, and the associated findings clearly implicate these species to be of a ligand-radical type; however, the evidence also indicates in several cases the occurrence of more than one initially observed product. The reaction of ferrocyanide involves electron transfer whereas for the mixed cyano-bipyridyl complexes of iron(II) both electron-transfer and OH-addition processes are encountered, and the predominant process for  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$  proceeds by an inner-sphere electron-transfer mechanism. Determinations for some of the final products arising from the pulse and  $\gamma$ -ray radiolysis of the mixed cyano-bipyridyl complexes,  $[\text{Co}(\text{bpy})_3]^{3+}$ , and  $[\text{Fe}(\text{bpy})_3]^{2+}$  have been undertaken in order to obtain insight into the overall sequence of events, and the natures of the mechanisms are discussed.

### Introduction

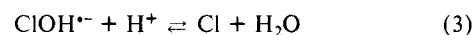
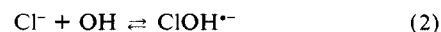
The hydroxyl radical is one of the strongest single-electron oxidizing agents ( $E^\circ(\text{OH}/\text{OH}^-) = 1.89 \text{ V}$ ) available for use in aqueous media to study oxidation-reduction processes.<sup>2–4</sup> While its occurrence is perhaps most often associated with radiolytic investigations where it is one of the primary products of water degradation, hydroxyl radical is encountered in many other contexts, notably those pertaining to photolysis, sonolysis, and thermal reactions such as the Fenton-type processes involving interactions of metal ions with hydrogen peroxide. Recent reviews indicate that studies of the OH reactions with inorganic substances, in particular metal complex ions, now number well into the several hundreds.<sup>3,4</sup> Because of the transitory existence of this free radical and the fact that it absorbs only weakly in the UV region, its reaction mechanisms with inorganic materials and the features that influence the processes are in many respects not clearly understood; however, hydroxyl radical does exhibit considerable diversity in its mechanistic behavior.

As one would expect for a single-electron oxidant, reactions of hydroxyl radical with metal complex ions are found that proceed in an overall sense by electron transfer as exemplified by its reaction with ferrocyanide (eq 1). Because of the perception that



the transformation of  $\text{OH}(\text{aq})$  to  $\text{OH}^-(\text{aq})$  engenders considerable solvent reorganization, it has been proposed that electron-transfer

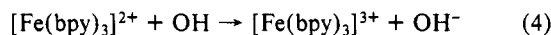
processes such as that of eq 1 proceed via inner-sphere pathways rather than by outer-sphere ones.<sup>4–6</sup> In this context, the inner-sphere terminology is being used in a somewhat broader sense than the classical definition; namely, it is meant to imply that electron transfer is promoted by strong electronic interactions (chemical bond formation) as discussed by Linck.<sup>7</sup> Evidence for inner-sphere processes for OH reactions with metal complex ions has been generally circumstantial although results obtained by using conductivity detection for metal aquo ions clearly point to this, and recently the reaction of  $[\text{IrCl}_6]^{3-}$  and OH to yield  $[\text{IrCl}_6]^{2-}$  has been shown to involve two pathways, the major one entailing OH adduct formation.<sup>4,8</sup> In contrast, inner-sphere processes encompassing formation of adducts are commonly found in the interactions of OH with simple non-metal anions such as cyanide and chloride (eqs 2 and 3).<sup>3,4,9</sup>



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\* To whom correspondence should be addressed.

With metal complexes containing unsaturated organic ligands, addition of OH to the organic moiety can prevail even though on thermodynamic grounds the complex of the same stoichiometry with the metal center in the next higher valent state is expected to be accessible: for example, the reaction of OH with tris-(2,2'-bipyridine)iron(II) (eq 4) is on the latter basis viable (see



below). Results obtained by using visible absorption detection in conjunction with pulse radiolysis indicate for this system and the analogous osmium and ruthenium complexes that the mode of reaction is OH addition, which is proposed to occur on one of the ligands (eq 5).<sup>10-12</sup>



This study reports findings, obtained by pulse and <sup>60</sup>Co γ-ray radiolysis, on the reactions of hydroxyl radical with a series of substitutionally inert cobalt(III), iron(II), and ruthenium(II) complexes containing cyano and bipyridyl ligands, and it has been undertaken with several purposes in mind. We want to compare the mechanistic behaviors of these systems along with findings reported on other low-spin d<sup>6</sup> complexes in order to obtain insight into the factors that may influence the courses of events, such as the nature of the metal center and its oxidation state, the overall charge and type of ligands contained by the system, and redox potential.<sup>4,13</sup> Extensive use has been made of conductivity detection because it is particularly well suited for detecting the occurrence of OH reactions involving charge transfer (CT) owing to the high equivalent conductance of hydroxide ion (and of proton with which it will react rapidly in acidic media).<sup>14</sup> Through a cross-comparison of the conductivity and optical signals, it seemed likely that one would be in better position to discern the competitive occurrence of electron-transfer and OH-addition processes. This aspect has been realized in the reactions of the mixed cyano-bipyridyl complexes of iron(II) where, in the case of [Fe(bpy)(CN)<sub>4</sub>]<sup>2-</sup>, the major process of electron transfer is found to proceed via an inner-sphere mechanism. In this regard, we have examined the reactions of the tris(bipyridyl)iron(II) and -ruthenium(II) ions, and the conductivity results confirm the earlier proposals, based on optical observations, that the predominant mode of reaction is OH addition (eq 5). To clarify the natures of the adducts and to discern if more than one such product occurs, their reactivities and that of the OH-addition product(s) for [Co(bpy)<sub>3</sub>]<sup>3+</sup> toward the mild oxidant [Fe(CN)<sub>6</sub>]<sup>3-</sup> and molecular oxygen have been investigated. In several cases, determinations have been made to identify the natures of the final products and the effects of dose rate (pulse radiolysis versus γ-ray irradiation), and this has assisted in characterizing the sequence of events. Even though these situations are complicated and only partially understood, particularly for the [Co(bpy)<sub>3</sub>]<sup>3+</sup> and [Fe(bpy)<sub>3</sub>]<sup>2+</sup> systems, the findings do underscore the significant roles played by the natures of the metal centers at both the primary and the secondary levels of reaction.

## Experimental Section

**Apparatus and Dosimetry.** The pulse radiolysis systems and the associated UV-visible absorption and conductivity detection apparatus have been described elsewhere.<sup>15,16</sup> Of note is that the absorption and conductivity data given here represent differences between those of the unirradiated and those of the pulsed solutions. Such differences were

calibrated against one of the following standard dosimetry solutions: ferrocyanide, thiocyanate, or tetraniotromethane.<sup>15</sup> <sup>60</sup>Co γ-ray radiolysis was performed with a Gammacell-220 source having a dose rate of 7.5 Gy/min as determined by Fricke dosimetry.<sup>17</sup> The *G* values (number of a given species formed or lost per 100 eV of energy absorbed) have been taken for the primary aqueous radicals as *G*<sub>e-</sub> = *G*<sub>H+</sub> = 2.7, *G*<sub>OH</sub> = 2.8, and *G*<sub>H</sub> = 0.55. The equivalent ionic conductivities used for the proton and hydroxide ions of 350 and 197 Ω<sup>-1</sup> cm<sup>2</sup>, respectively, are those appropriate to our room-temperature irradiation conditions.<sup>14</sup>

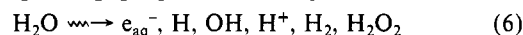
**Materials.** The compound 2,2'-bipyridine or bpy was obtained from several sources (BDH Chemicals, Fisher Scientific, G. F. Smith Chemicals) and further purified by recrystallization from methanol-water media and in some instances also by vacuum sublimation. The substance 5-hydroxy-2,2'-bipyridine (HOBpy) was synthesized by a published procedure.<sup>18</sup> Tris(2,2'-bipyridine)iron(II) perchlorate ([Fe(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>), tris(4,4'-dimethyl-2,2'-bipyridine)iron(II) perchlorate ([Fe(Me<sub>2</sub>bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>), and tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate ([Ru(bpy)<sub>3</sub>](Cl)<sub>2</sub>·6H<sub>2</sub>O) were obtained from G. F. Smith Chemicals: the ruthenium complex was converted to the perchlorate salt for use in the radiolysis studies. The iron(III) complex [Fe(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub> and the congeneric cobalt(III) compound [Co(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O were synthesized by the methods reported by Burstall and Nyholm.<sup>19</sup> Potassium hexacyanoiron(II) trihydrate (K<sub>4</sub>[Fe(CN)<sub>6</sub>]·3H<sub>2</sub>O) and the analogous iron(III) form (K<sub>3</sub>[Fe(CN)<sub>6</sub>]) were used as received from J. T. Baker or from Merck. The mixed cyano-bipyridyl compounds [Fe(bpy)<sub>2</sub>(CN)<sub>2</sub>]·3H<sub>2</sub>O, [Fe(bpy)<sub>2</sub>(CN)<sub>2</sub>](ClO<sub>4</sub>), K<sub>2</sub>[Fe(bpy)(CN)<sub>4</sub>]·3H<sub>2</sub>O, and H[Fe(bpy)(CN)<sub>4</sub>]·2H<sub>2</sub>O were prepared by literature procedures.<sup>20</sup> For the bipyridyl compounds, satisfactory elemental analyses for CHN were found, and their UV-visible absorption spectra generally agreed with those reported by others.<sup>21-25</sup> All other materials used were of reagent quality.

**Solutions and Product Analyses.** For radiolysis, deaerated solutions of the complexes that are thermally inert toward substitution were prepared from triply distilled water or from water obtained from a Millipore Super-Q system. While the cyano complexes can exhibit acid-base properties, the predominant forms under our pH conditions were the unprotonated species.<sup>26,27</sup> Changes to the alkalinity or acidity of the media were made through the addition of sodium hydroxide or perchloric acid.

Pulsed- or γ-irradiated solutions were analyzed for the presence of longer term, relatively stable products and for changes in their absorption spectra (Cary 118C spectrophotometer). The procedures cited below were generally performed within an hour of irradiation, and the determinations employed calibration curves constructed from authentic samples. The amount of uncoordinated 2,2'-bipyridine was determined by its extraction from the aqueous media with chloroform or *n*-heptane, followed by measurement of its absorbance (300 nm) in the organic phase: prior to extraction, the pH was adjusted to 2 because the hydroxybipyridyl material(s) formed upon irradiation was found to be less extractable at this pH. Subsequent to the removal of free bpy, the hydroxybipyridyl component(s) was extracted with *n*-pentyl alcohol, and the absorbance of the organic phase was measured at 330 nm. Determinations for free cyanide ion were made with an Orion cyanide ion electrode (Model 94-06A). The occurrence of aqueous cobalt(II) ion in irradiated [Co(bpy)<sub>3</sub>]<sup>3+</sup> solutions was measured colorimetrically.<sup>28</sup>

## Results

Radiolysis of dilute aqueous solutions by high-energy electrons (2–20 MeV) and γ-rays as done in this work leads initially to the generation of aqueous free radicals, hydrogen ion, and small amounts of H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (eq 6). Results reported elsewhere show



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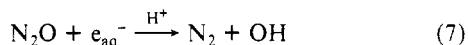
**Table I.** Optically Measured Rate Constants for OH Reactions and Thermodynamic Data for Half-Cell Couples of Metal Complex Ions

reactant ion, M <sup>a</sup>	kinetic data				thermodynamic data (M <sup>n+1/n</sup> ) <sup>a</sup>			major OH process
	pH	$\lambda$ , nm	concn, $\mu$ M	$10^{-9}k_{\text{OH}}$ , M <sup>-1</sup> s <sup>-1</sup>	E°, V	$\Delta H^\circ$ , kJ mol <sup>-1</sup>	$\Delta S^\circ$ , J mol <sup>-1</sup> K <sup>-1</sup>	
[Co(bpy) <sub>3</sub> ] <sup>3+</sup>	4.5, 6.0	415–425	98–250	2.7 ± 0.3				addition
[Fe(Me <sub>2</sub> bpy) <sub>3</sub> ] <sup>2+</sup>	6.0	310–500	10–30	17 ± 0.3	0.941	–112	–71.6	addition
[Fe(bpy) <sub>3</sub> ] <sup>2+</sup>	3.5–9.5	370–800	20–59	8 ± 1	1.120	–137	–96.6	addition
[Fe(bpy) <sub>2</sub> (CN) <sub>2</sub> ]	3.3–9.7	320–720	19–74	8.4 ± 0.6 <sup>b</sup>	0.781 <sup>c</sup>			see text
[Fe(bpy)(CN) <sub>4</sub> ] <sup>2–</sup>	4.3–9.7	295–530	20–301	9.7 ± 0.4	0.542	–114	–207	charge transfer
[Fe(CN) <sub>6</sub> ] <sup>4–</sup>	natural pH	420	80–140	11 ± 2 <sup>d</sup>	0.355	–112	–260	charge transfer
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>	4.0, 4.3	480–800	36, 52	8 ± 1	1.374	–152	–64.4	addition
[Ru(CN) <sub>6</sub> ] <sup>4–</sup>	natural pH	330–470	40–200	5.7 ± 0.8 <sup>d</sup>	0.86 <sup>e</sup>			charge transfer
[Os(bpy) <sub>3</sub> ] <sup>2+</sup>	natural pH	ca. 750	10–100	~10 <sup>f</sup>	0.878	–103	–61.9	addition
[Os(CN) <sub>6</sub> ] <sup>4–</sup>	natural pH	330, 410	50–200	10 ± 1 <sup>d</sup>	0.634 <sup>g</sup>			charge transfer
[IrCl <sub>6</sub> ] <sup>3–</sup>	3.0–4.5		100–300	13 <sup>h</sup>	0.866 <sup>i</sup>	–147	–128	charge transfer

<sup>a</sup> Half-cell couple written as reduction of M<sup>n+1</sup> to M<sup>n</sup> (relative to hydrogen couple) and unless otherwise noted data from ref 27. <sup>b</sup> Conductivity:  $k_{\text{OH}} = (6.7 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ; [Fe(bpy)<sub>2</sub>(CN)<sub>2</sub>] = 19–159  $\mu$ M. <sup>c</sup> Reference 39. Formal potential at 0.01 F H<sub>2</sub>SO<sub>4</sub>. <sup>d</sup> Reference 40. <sup>e</sup> Reference 41. <sup>f</sup> Reference 10. <sup>g</sup> Reference 42. <sup>h</sup> Reference 8. <sup>i</sup> Reference 43.

that with the exceptions of the reactions of e<sub>aq</sub><sup>–</sup> and H atom with ferrocyanide and that for H atom with bpy, these radicals react rapidly with the metal complexes studied here to yield transients, absorbing in the near-UV–visible regions.<sup>3,21,29–32</sup> This information in combination with the strategies described below have been used to minimize complications arising out of possible reactions of the hydrated electron and hydrogen atom and to optimize the interactions of the complexes with hydroxyl radical.

Nitrous oxide is a facile scavenger of e<sub>aq</sub><sup>–</sup>, and for our N<sub>2</sub>O-saturated solutions, greater than 90% of the electron will have reacted with nitrous oxide (eq 7), essentially eliminating con-



tributions from the electron reactions with the complexes.<sup>3</sup> This rapid scavenging process (nanosecond time scale) has two further advantages: the proton generated with the same yield as that of e<sub>aq</sub><sup>–</sup> during irradiation will be consumed via eq 7 so that, in acidic media on our time scales, it will not contribute to any conductivity movements, and near the end of the pulse, approximately 90% of the aqueous radicals will be hydroxyl radical with the remaining 10% being hydrogen atom. The latter reacts slowly with *tert*-butyl alcohol whereas this alcohol is highly reactive toward hydroxyl radical.<sup>3</sup> The resulting  $\beta$ -hydroxy alcohol radical does not absorb above 300 nm nor does it appear to be reactive toward the complexes studied here.<sup>33</sup> On addition of 0.11–1.8 M *tert*-butyl alcohol (conditions under which hydroxyl radical but not hydrogen atom will be scavenged), the absorption changes described below were reduced to generally 5% or less of their values in the absence of the alcohol, and similar levels of reduction were found with the conductivity signals occurring on irradiation of the mixed cyano–bipyridyl complexes. These results indicate that contributions arising from H atom reactions are generally minor and that the origin of the observed changes resides with the reactions of OH and the starting materials. Because the associated absorption changes are measured relative to the unirradiated solutions and the iron and ruthenium complex ions have intense absorption bands, this can give rise on irradiation to negative values of the observed absorbances.

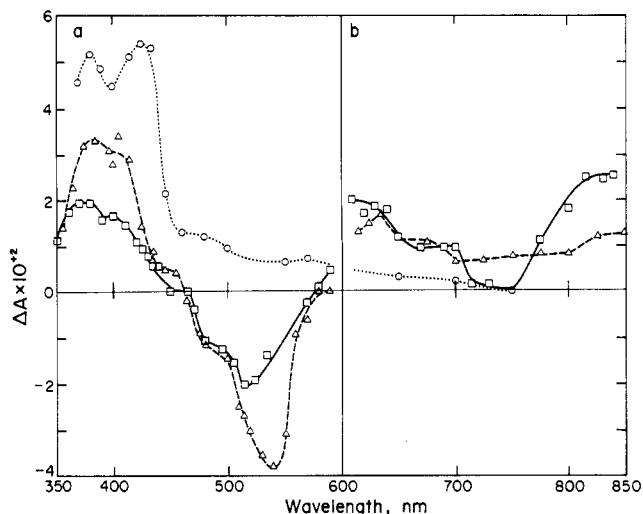
**Reactions of Uncoordinated 2,2'-Bipyridine.** Results of an earlier study at pH 9.3 using optical detection have shown that bpy is itself highly reactive toward hydroxyl radical ( $k = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), resulting in a transitory absorption spectrum with two maxima at 305 and 365 nm.<sup>34</sup> To obtain further information about this reaction, we have carried out conductivity measure-

ments, complemented by appropriate optical determinations, under the following conditions: 100–210  $\mu$ M bpy, pH 2.7–10.1. Pulse irradiation led to the rapid development in basic or natural pH (ca. 6.5) solutions of spectra closely matching that found by Simić and Ebert,<sup>34</sup> and the results also showed that the absorption is negligible between 600 and 850 nm, a region where significant absorption does occur for reactions involving the iron and ruthenium complexes (see below). No conductivity changes accompany the optical growths in acidic or basic media. At pH 10, where the unprotonated form of bpy prevails, the subsequent decay of absorption obeys a second-order rate law with  $2k = (1.5 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and without any accompanying conductivity change. In contrast at pH 3.6, where both monoprotonated and unprotonated forms of bpy are present, the optical decay exhibits mixed-order kinetic behavior, accompanied by a small conductivity increase ( $70 \Omega^{-1} \text{ cm}^2$ ). For pH 2.7, where the dominant form is Hbpy<sup>+</sup> ( $\text{p}K_a = 4.5$ ),<sup>35</sup> the nascent growth of the absorption at 350 nm is slower ( $k = (2.0 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) than that for reaction of unprotonated bpy as cited above, and the subsequent decay that is second-order is also slower with  $2k = (5 \pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . These features are consistent with the nascent process being one of OH addition, followed by the radical product (bpy(OH)• or Hbpy(OH)•<sup>+</sup>) undergoing self-reactions (dimerization or disproportionation), and they closely parallel the optical results found for the OH reactions of 1,10-phenanthroline.<sup>36</sup> Selvarajan and Raghavan have used ferricyanide, a mild oxidant, to oxidize the products of OH addition to pyridine to form hydroxypyridines.<sup>37</sup> In this context, measurements were carried out at 360 nm on the decay of the hydroxybipyridyl transient(s) at pH 10.1 on addition of 0.96–2.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]; however, the rate of decay in the presence of ferricyanide was not markedly different from that in its absence. (The use of ferricyanide concentrations in excess of 2 mM was precluded as the absorbance of the starting solution would then have been too large.) Because the second-order decay in the absence of ferricyanide does not lead to a conductivity change, conductivity detection proved to be the more feasible approach to study the reaction of ferricyanide: here a decrease in conductivity transpires, yielding a maximum change of  $-100 \Omega^{-1} \text{ cm}^2$ . The rate increases with increasing ferricyanide concentration with a second-order rate constant of about  $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and this indicates that the hydroxybipyridyl radical(s) is a moderately strong reducing agent.

**Reactions of Tris(bipyridyl)metal Complexes.** Our studies have focused on the reactions of [Co(bpy)<sub>3</sub>]<sup>3+</sup> and [Fe(bpy)<sub>3</sub>]<sup>2+</sup> with hydroxyl radical; however, in view of the results found for these systems, we also extended the investigations to the related complexes [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and [Fe(Me<sub>2</sub>bpy)<sub>3</sub>]<sup>2+</sup>. Figure 1 shows the initial absorption spectra developed on pulsed irradiation of so-

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**Figure 1.** Absorption changes for the reactions of hydroxyl radical (ca. 8  $\mu\text{M}$ ) with  $[\text{Co}(\text{bpy})_3]^{3+}$ ,  $[\text{Fe}(\text{bpy})_3]^{2+}$ , and  $[\text{Fe}(\text{Me}_2\text{bpy})_3]^{2+}$  in  $\text{N}_2\text{O}$ -saturated solutions at natural pH (ca. 6.0): (O)  $[\text{Co}(\text{bpy})_3]^{3+}$  (96  $\mu\text{M}$  complex, 4-cm light path, 10  $\mu\text{s}$ ); (□)  $[\text{Fe}(\text{bpy})_3]^{2+}$  (10  $\mu\text{M}$  complex, 1-cm light path; (b) 97  $\mu\text{M}$ , 4-cm light path); (Δ)  $[\text{Fe}(\text{Me}_2\text{bpy})_3]^{2+}$  (5  $\mu\text{M}$  complex, 1-cm light path; (a) 45  $\mu\text{M}$  complex, 1-cm light path; (b) 91  $\mu\text{M}$  complex, 4-cm light path).

lutions containing the cobalt and iron ions at natural pHs (ca. 6–7). The specific conditions used are given in Table I along with the second-order rate constants for the reactions of OH with the complexes: the values have been calculated from the slopes of the linear plots for the optically measured pseudo-first-order rate constants versus the concentrations of the complexes.<sup>8,10,27,38–43</sup> The absorption by  $[\text{Co}(\text{bpy})_3]^{3+}$  in the region shown in Figure 1 is weak so that the observed difference spectrum will closely approximate that obtained after correction for loss in the starting material. The situation for  $[\text{Fe}(\text{bpy})_3]^{2+}$  is more complicated, partly because this complex exhibits considerable absorption for wavelengths below about 600 nm (as does that for  $[\text{Fe}(\text{Me}_2\text{bpy})_3]^{2+}$ ). An additional feature to those shown in Figure 1 for  $[\text{Fe}(\text{bpy})_3]^{2+}$  is the occurrence of an intense peak near 300 nm. Correction of the spectrum for loss of starting complex yields a spectrum markedly different from that of  $[\text{Fe}(\text{bpy})_3]^{3+}$ : the latter has two relatively weak bands with peaks at 372 nm ( $\epsilon = 745 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 600 nm ( $\epsilon = 150 \text{ M}^{-1} \text{ cm}^{-1}$ ) whereas the corrected spectrum shows two intense bands at 350 and 530 nm ( $\epsilon$ 's near  $5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ;  $\epsilon_{350}/\epsilon_{530} = 1.2/1$ ).<sup>21</sup> Furthermore, neither the starting complex nor  $[\text{Fe}(\text{bpy})_3]^{3+}$  absorbs in the 650–850-nm range as found for the product(s) of the OH reaction. Although the iron(III) complex is stable on pulse radiolysis time scales, the spectrum of Figure 1 is transitory: slight enhancements to the  $\Delta A$  values occur over the first 50  $\mu\text{s}$ , followed by major changes in the millisecond time frame (see below).

For both the iron and cobalt systems, the initial spectra observed on irradiation of acidic solutions were essentially the same as those shown in Figure 1 for natural pHs; however, in alkaline media, differences arose, and in the case of  $[\text{Co}(\text{bpy})_3]^{3+}$ , the peak at 420 nm (natural pH) appears as a shoulder of lesser intensity with  $\epsilon_{420}/\epsilon_{380}$  now being less than 1 (ratio = 0.6/1). With  $[\text{Fe}(\text{bpy})_3]^{2+}$ , the absorption near 370 nm is enhanced by a factor of 2 and the extent of bleaching near 515 nm is about halved relative to the values at natural pH: correction for loss of starting material indicates that the intensity of the longer wavelength band has decreased compared to that of the shorter wavelength one in a manner similar to that for the  $[\text{Co}(\text{bpy})_3]^{3+}$  case. These effects are not attributable to absorption changes for the starting com-

plexes as their spectra remain unaltered over the interval pH 3.5–9.5. Furthermore, the optically measured rate constants (Table I) are not markedly affected by changes in pH. These features indicate that while the reactions of hydroxyl radical with the complexes are probably rate limiting, subsequent fast processes occur to yield the observed products.

The conductivity measurements provide a new viewpoint to the nascent interactions. For the reaction of  $[\text{Co}(\text{bpy})_3]^{3+}$ , no conductivity movement ( $\Delta\Lambda < 10^{-1} \text{ cm}^2$ ) accompanies the spectral growth (Figure 1), demonstrating the absence of a CT process of the type given by eq 4: this result is that expected on the basis that the cobalt(IV) form of the tris(bipyridyl) complex is unknown. In contrast for acidic solutions of  $[\text{Fe}(\text{bpy})_3]^{2+}$ , a decrease of  $-47 \pm 5 \text{ } \Omega^{-1} \text{ cm}^2$  transpired; this shows a net consumption of proton that can arise from the formation of hydroxide ion as in eq 4. However, the extent of this decrease should be compared to that anticipated if charge transfer was the sole process. The equivalent conductivities of the metal ions participating in eq 4 will be about  $70 \text{ } \Omega^{-1} \text{ cm}^2$ , and thus in acidic solutions, the full measure of decrease associated with eq 4 will be near  $-280 \text{ } \Omega^{-1} \text{ cm}^2$ . The observed decrease is less than 20% of the anticipated value, so that a charge-transfer reaction such as that to yield  $[\text{Fe}(\text{bpy})_3]^{3+}$  is a minor facet. This feature in association with the spectral changes show the major type of process to be OH addition (eq 5).

These initial conductivity and absorption features were followed for both complexes by at least two further stages of reaction, the first taking place on the 500- $\mu\text{s}$  scale and the second in the 5–10-ms domain. The first stage for the cobalt system is marked by a general decrease in the absorption spectrum (but with a slight increase at 420 nm), described by a first-order rate law, and accompanied by an increase in conductivity ( $\Delta\Lambda = 100 \text{ } \Omega^{-1} \text{ cm}^2$ ). The rate constants for both phenomena are the same ( $k = (1.1 \pm 0.1) \times 10^3 \text{ s}^{-1}$ ). The optically measured value is independent of complex concentration (50–110  $\mu\text{M}$ ), wavelength (370–425 nm), and dose (7-fold), but in basic solution (pH 9.0), the rate constant is a factor of 100 larger than that in acidic or natural pH media. The second phase (5–10 ms) shows a further decay in absorption and a slight additional increase in conductivity, but the movements were too small for us to identify the rate law(s). Over these time spans, no absorption increases around 300 nm that would signify the formation of the reduced form  $[\text{Co}(\text{bpy})_3]^{2+}$  (or a related cobalt(II) species) have been observed.<sup>29</sup>

In the case of  $[\text{Fe}(\text{bpy})_3]^{2+}$ , the first stage is associated with decreases to the original absorption in the regions near 380 and 850 nm (Figure 1) with the changes obeying a first-order rate law, independent of complex concentration (32–100  $\mu\text{M}$ ); however, the values of the rate constants vary between  $0.8 \times 10^3$  and  $1.7 \times 10^3 \text{ s}^{-1}$  in a nonsystematic way with wavelength. In the region near 500 nm, some enhancement to the original bleaching transpired, but the rate law is neither first order nor second order. The enhancement to the bleaching is opposite to the diminution reported by Dimitrijević and Mičić.<sup>11</sup> While we have no explanation for this apparent discrepancy, we do agree with their findings that at 520 nm mixed-order kinetics prevail whereas at 400 nm the absorption decrease obeys first-order behavior with  $k = 1.35 \times 10^3 \text{ s}^{-1}$ . We also find a first-order rate law applies to the conductivity movements with  $k = (1.0 \pm 0.1) \times 10^3 \text{ s}^{-1}$  (pH 4.0, 9.0). In acidic solution, this is described by a decrease from the original change of  $-47$  to  $-85 \text{ } \Omega^{-1} \text{ cm}^2$ , but at pH 9.0, a small reduction to the nascent increase of  $35 \text{ } \Omega^{-1} \text{ cm}^2$  occurs. These directions of movement do not appear to be consistent with the occurrence of only one process giving rise to the changes. At even longer times (5–10 ms), some further changes to the absorption transpired, now including some diminishing of the bleaching at 500 nm, although these were too small to determine the rate law(s).

The foregoing results indicate that the principal transients are ligand-based free radicals. Molecular oxygen is known to be reactive toward OH-addition products such as that for pyridinium ion, and similarly,  $[\text{Fe}(\text{CN})_6]^{3-}$  exhibits reactivity toward carbon-based radicals as exemplified above for the OH-addition

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**Table II.** Rate Constants for Reactions of Transients with Additives

complex ion	additive		wavelength, nm	$k$ , M <sup>-1</sup> s <sup>-1</sup>
	agent	concn		
[Co(bpy) <sub>3</sub> ] <sup>3+</sup> <sup>a</sup>	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	100–200 μM	370–440	(2.1 ± 0.3) × 10 <sup>8</sup>
	O <sub>2</sub>	600 μM	375, 425	(5.5 ± 0.6) × 10 <sup>5</sup>
	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	800 μM	375, 620	(2.1 ± 0.5) × 10 <sup>5</sup>
[Fe(bpy) <sub>3</sub> ] <sup>2+</sup> <sup>a</sup>	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	0.8–2.0 mM	825	(8 ± 2) × 10 <sup>5</sup>
	O <sub>2</sub> <sup>b</sup>	600 μM	400	(4.0 ± 4) × 10 <sup>6</sup>
	O <sub>2</sub> <sup>b</sup>	600 μM	525	(7.6 ± 0.3) × 10 <sup>6</sup>
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup> <sup>c</sup>	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	0.1–0.6 mM	479, 800	(4.1 ± 0.4) × 10 <sup>6</sup>

<sup>a</sup> Natural pH (ca. 6). <sup>b</sup> O<sub>2</sub> sensitive at 620 and 825 nm. <sup>c</sup> pH 9.7.**Table III.** Yields of Long-Term Products from Reactions of OH with Fe(II) and Co(III) Complex Ions<sup>a</sup>

complex ion	irradn source	$G$ values <sup>b</sup>		
		loss of start complex	formn of Fe(III) or Co(II)	uncoord bpy
[Co(bpy) <sub>3</sub> ] <sup>3+</sup>	electron	1.3	1.6 <sup>c</sup>	5.4
	γ-ray	5.0	4.5 <sup>c</sup>	13.2
[Fe(bpy) <sub>3</sub> ] <sup>2+</sup>	electron	1.1		0.7
	γ-ray	0.7		0.8
[Fe(bpy) <sub>2</sub> (CN) <sub>2</sub> ]	γ-ray	5.2		see text
[Fe(bpy)(CN) <sub>4</sub> ] <sup>2-</sup>	γ-ray	4.7	5.1 <sup>d</sup>	see text

<sup>a</sup> Conditions: N<sub>2</sub>O-saturated solutions; natural pHs (6–7); complex concentrations, 100–200 μM. Dose rates: electron irradiation, ca. 100 Gy/pulse; γ-ray radiolysis, 75 Gy/min. <sup>b</sup> Estimated error ±10%. <sup>c</sup> Product is [Co(aq)]<sup>2+</sup>. <sup>d</sup> Product is [Fe(bpy)(CN)<sub>4</sub>]<sup>-</sup>.

product(s) for uncoordinated bpy.<sup>44–46</sup> Addition of these reagents at concentrations in excess of those for the transients caused enhanced rates of optical decay. The conditions used along with the calculated second-order rate constants are given in Table II. In addition to the demonstration of the sensitivity of the transients toward these additives, two specific features are noteworthy. For the cobalt system, ferricyanide shows greater reactivity than does O<sub>2</sub>, but the reverse trend is found for the [Fe(bpy)<sub>3</sub>]<sup>2+</sup> case. For the latter complex, the rate constants also exhibit variation with wavelength: this is a further indication of the occurrence of more than one product arising from the reaction of OH with the iron(II) complex.

Investigations into the relatively stable products for the cobalt and iron systems have been carried out following radiolysis by electron pulses (three to five successive pulses) and by <sup>60</sup>Co γ-rays where conversions have been limited to less than 15% of the concentrations of the starting materials. The  $G$  values determined for the formation of uncoordinated bpy and [Co(aq)]<sup>2+</sup> and for the loss of starting complex are presented in Table III. The yields for losses of [Co(bpy)<sub>3</sub>]<sup>3+</sup> and of [Fe(bpy)<sub>3</sub>]<sup>2+</sup> have been measured from the linear reductions with time of irradiation of the major absorption peaks at 222 and 515 nm, respectively, while, in the pulse radiolysis experiments, the values have been determined from absorption decreases following several pulses of irradiation. Spectral measurements following γ-ray radiolysis of the iron complex show decreases in absorption of the intense peaks at 295 and 515 nm, small increases at 265, 315, and 600 nm, and isosbestic points at 280, 300, and 500 nm. For [Co(bpy)<sub>3</sub>]<sup>3+</sup>, electron and γ-ray irradiations result in absorption decreases of the peaks at 222 and 318 nm and the development of a new peak near 306 nm with isosbestic points at 265 and 312 nm. The amounts of free bpy have been determined by measuring the near-UV absorption spectra of the organic extractant phase (see Experimental Section); however, in addition to the absorption attributable to bpy, there is for both the cobalt and iron systems a band at longer wavelengths (near 325 nm). This feature is not observed for unirradiated solutions that have been doped with 2,2'-bipyridine whereas the addition of 5-hydroxy-2,2'-bipyridine

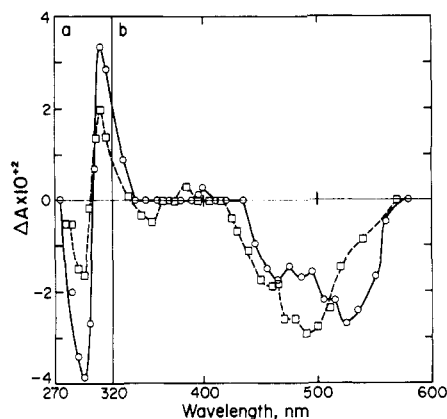
does result in this type of feature, and as such this indicates the presence of the 5-hydroxy substance or related isomers in the irradiated solutions.

Our optical observations for [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (similar to those above for [Fe(bpy)<sub>3</sub>]<sup>2+</sup>) agree with those reported previously as does our value for the second-order rate constant for the OH reaction given in Table I.<sup>10,12,47</sup> In addition, we find that essentially no conductivity alteration ( $\Delta\Lambda < 10 \Omega^{-1} \text{ cm}^2$ ; pH 4.0 and 9.7) accompanies the initial optical changes: this eliminates the possibility of significant contributions from a CT process. This supports the original proposal made by Creutz and Sutin on the basis of absorption results, for the formation of an OH adduct.<sup>10</sup> Their results also show that the band at 750 nm decays by a second-order process with  $2k = (1-2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and our findings at pH 9.7 agree with this for the decay of the absorption at 800 nm and for the return of bleaching at 479 nm. These movements are accompanied by a slight decrease in conductivity ( $\Delta\Lambda = -44 \pm 10 \Omega^{-1} \text{ cm}^2$ ). The situation is substantially altered in the presence of [Fe(CN)<sub>6</sub>]<sup>3-</sup> ((1.32–5.97) × 10<sup>-4</sup> M) where the rates of absorption change at 479 and 800 nm are enhanced and are now described by a pseudo-first-order rate law: the calculated values of the second-order rate constants are the same within experimental error for both wavelengths (Table II). Concurrently, there is a substantial decrease in conductivity ( $\Delta\Lambda = -155 \pm 9 \Omega^{-1} \text{ cm}^2$ ), having the same calculated second-order rate constant ( $k = (3.4 \pm 0.4) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) as that for the optical behavior. The foregoing features suggest that, in contrast to the OH reaction of [Fe(bpy)<sub>3</sub>]<sup>2+</sup>, the reaction of the congeneric ruthenium complex yields primarily one type of product.

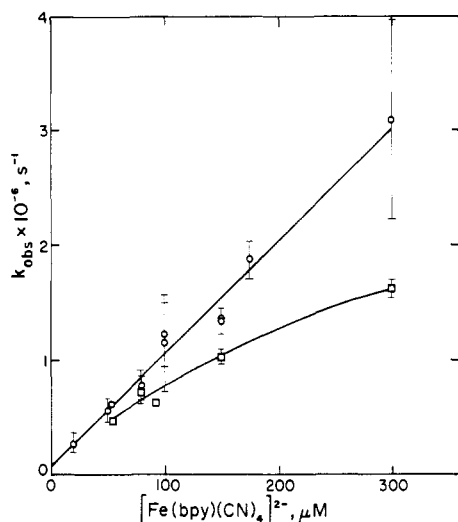
Earlier workers have proposed that OH addition to coordinated bpy may occur preferentially at the 4- and 6-positions.<sup>10,11</sup> In view of this and the fact that substitution on pyridine can alter the position of OH-addition, the reaction of OH with the 4,4'-dimethyl-substituted complex [Fe(Me<sub>2</sub>bpy)<sub>3</sub>]<sup>2+</sup> has been examined at pH 3.8. The spectrum arising from this reaction and the associated second-order rate constant are given in Figure 1 and Table I, respectively. Accompanying the development of the absorption spectrum is a small conductivity decrease of  $-50 \Omega^{-1} \text{ cm}^2$ . These features closely match those found for the reaction of the unsubstituted [Fe(bpy)<sub>3</sub>]<sup>2+</sup>. The implication is that the 4-position of the ligand is not the only site of OH attack.

**Reactions of Iron(II) Cyano Complexes.** Results obtained by absorption methods have shown that the reaction of [Fe(CN)<sub>6</sub>]<sup>4-</sup> and OH involves charge transfer to yield the stable ferricyanide complex (eq 1).<sup>1,3,5,40</sup> Our experiments, carried out at pH 8.8 with 192 μM ferrocyanide, indicate that this process is accompanied by a conductivity increase of  $60 \pm 14 \Omega^{-1} \text{ cm}^2$ , and this value is within experimental error the same as that calculated for eq 1, based upon the known equivalent conductivities of the participating species.<sup>14</sup> The situations for the mixed cyano-bipyridyl complexes [Fe(bpy)<sub>2</sub>(CN)<sub>2</sub>] and [Fe(bpy)(CN)<sub>4</sub>]<sup>2-</sup> are by contrast more complicated. The absorption changes following their pulse irradiation are presented in Figure 2, and their developments obey first-order rate laws. The associated rate constants increase linearly with complex concentrations as exemplified in Figure 3 for [Fe(bpy)(CN)<sub>4</sub>]<sup>2-</sup>, and the calculated second-order rate constants

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**Figure 2.** Absorption changes for the reactions of hydroxyl radical (ca. 4–7  $\mu\text{M}$ ) with  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$  and  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$  in  $\text{N}_2\text{O}$ -saturated solutions at natural pH (6–7), 1-cm light path: (O)  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$  ((a) 10  $\mu\text{M}$  complex, 25  $\mu\text{s}$ ; (b) 47–52  $\mu\text{M}$  complex, 7  $\mu\text{s}$ ); ( $\square$ )  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$  ((a) 20  $\mu\text{M}$  complex, 10  $\mu\text{s}$ ; (b) 100  $\mu\text{M}$  complex, 9  $\mu\text{s}$ , 18  $\mu\text{M}$  OH).



**Figure 3.** Plot of observed first-order rate constant versus the concentration of  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$  for its reaction with hydroxyl radical: (O) optical detection (295–530 nm; pH 4.3–4.5, 6.0, 9.7); ( $\square$ ) conductivity decrease (pH 3.8–4.5).

are cited in Table I. The occurrence of negative  $\Delta A$  values in the region near 500 nm and of positive ones at 310 nm are qualitatively consistent with the transformations of the starting complexes into their analogous iron(III) forms, but there are quantitative discrepancies. Relative to the amount of hydroxyl radical reacting with  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ , the extent of bleaching at 485 nm is 70% of that anticipated if the only product was  $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$  whereas at 310 nm, the observed value is close to that expected. Similarly for the reaction of  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$  to yield exclusively  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]^+$ , the bleaching at 490 nm and the growth at 310 nm are 60% and 40% of the expected values, respectively. In addition for this system, a low-intensity broad band occurs in the 600–800-nm region where neither the starting complex nor its iron(III) form absorb: the situation here is analogous to those for the tris(bipyridyl)iron(II) ions shown in Figure 1. Alterations to pH (4.0–9.5) do not markedly affect the spectral features although, for the tetracyano ion, the  $\Delta A$ -values of the 310-nm peak in acidic and basic media are about half that encountered at natural pH.

On the same time scale as for the developments of the optical spectra, substantial movements to the conductivity occur with the directions of change indicating the formation of hydroxide ion. With  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$ , the observed first-order rate constants increase linearly with complex concentrations (19–159  $\mu\text{M}$ ; pH 3.3–4.2, 9.5); however, the calculated second-order rate constant of  $(6.7 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the conductivity is somewhat

smaller than the optical one (Table I). At high concentrations (74 and 159  $\mu\text{M}$  complex) in acidic solutions, the initial conductivity decrease is quickly followed by a second stage of decrease. The latter movement exhibits a first-order rate law with  $k = (1.6 \pm 0.3) \times 10^5 \text{ s}^{-1}$ , independent of complex concentration and of dose (2-fold). No discernible optical change accompanies this second stage, but the amount of this process is only 20% of the total short-term change of  $-220 \pm 20 \Omega^{-1} \text{ cm}^2$ . At pH 9.5, just one stage of conductivity increase ( $\Delta A = 94 \pm 4 \Omega^{-1} \text{ cm}^2$ ) was encountered. These conductivity movements demonstrate the occurrence of charge transfer, but the observed  $\Delta A$  value in acidic medium is only about 70% of that anticipated. In addition, the absolute ratio of  $\Delta A(\text{acid})/\Delta A(\text{base}) = 2.3/1$  is considerably larger than that of 0.7/1 predicted if only one CT process (analogous to eq 1) was contributing to the conductivity alterations. Clearly at least two short-term processes are involved, and because the initial rate constant for the conductivity change appears to be smaller than that for the optical case (Table I), there is the distinct possibility that both short-term processes occur at secondary stages.

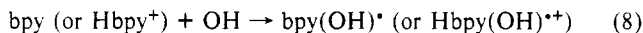
For the reaction of the tetracyano complex with hydroxyl radical, one conductivity step occurs and the level attained at pH 4.5 is  $-280 \pm 50 \Omega^{-1} \text{ cm}^2$ . The absolute ratio of  $\Delta A(\text{acid})/\Delta A(\text{base}) = (2.7 \pm 0.1)/1$  is consistent with a single CT process transpiring; however, the magnitudes of change in acidic and basic media are only 70% of those anticipated. This percentage is also that encountered above for the optical bleaching at 485 nm. The associated rate law is first-order, but as shown in Figure 3, the plot of the observed rate constant (conductivity) versus complex concentration exhibits definite curvature. This aspect demonstrates that the charge-transfer reaction arises at the secondary level. Little, if any, further alterations to the spectral and conductivity signals occur at times up to 1 s, and subsequent spectra recorded on a Cary 118C spectrophotometer are quite similar to that of Figure 2. For  $\gamma$ -irradiated solutions, the  $G$  values for loss of starting material and formation of an iron(III) product have been measured from the amount of bleaching at 480 nm and the growth of the 310-nm peak, respectively, and these are given in Table III. The values are within about 10% of those expected if the radiolysis leads eventually to the quantitative formation of  $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$  even though on the pulse radiolysis time frame a somewhat lesser amount occurs. Consistent with the occurrence of this iron(III) complex as the major final product are the observations that addition to an irradiated solution of hydroxylamine, which reduces  $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$  to its iron(II) form, generates an absorption spectrum nearly identical with that for the unirradiated solution and that neither free cyanide nor bpy are detectable (<20% relative to the amount of OH generated).

Following the initial changes described above for  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$ , two further stages of reaction occur with the first one (500- $\mu\text{s}$  scale) being signified by a general reduction to the nascent absorption (30–40%) and conductivity (35–45%) movements. The larger percentages are associated with the behaviors found in basic solutions (pH 9.0, 9.5) where the rates were not describable by either first- or second-order rate laws. While similar changes occur at pH 4.0 and natural pH, first-order behavior prevails: the optically measured rate constant is  $(3 \pm 1) \times 10^3 \text{ s}^{-1}$ , independent of complex concentration (31 and 56  $\mu\text{M}$ ), wavelength (310, 330, 515–530 nm) and dose (12-fold), and that for conductivity is  $4 \times 10^3 \text{ s}^{-1}$ . At even longer times, further reductions took place, but these changes were too small to establish the associated rate law(s). Spectra recorded within an hour of pulse or  $\gamma$ -ray irradiation show the presence of a new peak at 310 nm and decreases in the visible absorption (482-nm peak) with the latter indicating extensive loss of the starting complex (Table III). Radiolysis did not produce detectable amounts of free cyanide. Because the uncharged  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$  is to some extent extractable into organic media, determination for liberated bpy was not attempted; however, the absorption spectrum of an irradiated aqueous solution that had been subjected to repeated extractions (seven times with chloroform) closely approximated that for the iron(III) complex  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]^+$ .



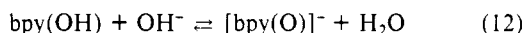
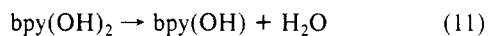
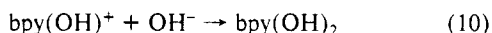
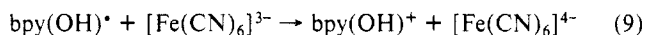
### Discussion

The absences of major conductivity changes in the pulse-radiolysis experiments show in an unambiguous manner that the nascent reactions of hydroxyl radical with the tris(pyridyl) complexes of Co(III), Fe(II), and Ru(II) and with bpy and Hbpy<sup>+</sup> do not involve significant CT processes (eq 4), but instead OH adduct formations transpire (eqs 5 and 8). The conductivity



findings are consistent with the optical results presented here and in earlier reports for the iron and ruthenium complexes and for the related phenanthroline complex [Fe(phen)<sub>3</sub>]<sup>2+</sup> that indicate the absences as nascent products of the corresponding iron(III) and ruthenium(III) tris(bipyridyl) substances.<sup>10-12,47,48</sup> In principle, the reaction of eq 8 can generate four isomeric carbon-based adducts, and findings from ab initio SCF MO calculations suggest that, for bpy, the isomeric products are energetically similar (unlike the reaction of OH and pyridine where there is considerable specificity toward attack at the meta position) and that addition at the nitrogen position is unfavorable.<sup>21,37</sup> Simić and Ebert have proposed that two isomeric adducts arise on the basis of the observation of two absorption bands in the reaction of 2,2'-bipyridine but only one band in the case of 4,4'-bipyridine, and our conductivity results for the reaction of ferricyanide with bpy(OH)<sup>•</sup> may be an indication of multiple-product formation (see below).<sup>34</sup> For the reactions of the metal complexes, not only can addition occur at the carbon sites but also the possibility exists for attack at the metal center (or at the metal-nitrogen interface). Given the potential number of possible adducts that can be formed in the OH reactions and the complicated decay patterns, particularly in the cases of the cobalt(III) and iron(II) complexes as described in the Results Section, it is difficult to specify the exact nature(s) of the OH-addition products. Notwithstanding this limitation, a number of features clearly emerge from our findings.

The reactivities of the intermediates for the cobalt, iron, and ruthenium systems and for uncoordinated bpy toward [Fe(CN)<sub>6</sub>]<sup>3-</sup> indicate that these species are moderately strong reducing agents. The sensitivity of the cobalt and iron transients toward molecular oxygen implies a free-radical character. Recently it has been found that [Ru(bpy)<sub>3</sub>(OH)]<sup>•2+</sup> reacts with organic radicals resulting in polymer molecules with covalently bound [Ru(bpy)<sub>3</sub>]<sup>2+</sup> residues.<sup>47</sup> These features argue that at least part of the products are carbon-based radicals. More to this point is that the reactions of the ruthenium adduct and of bpy(OH)<sup>•</sup> with ferricyanide in basic media give rise to decreases in conductivity whereas in the absence of the iron oxidant little or no conductivity change occurs. This suggests the following possible sequence of reactions as exemplified for the free bipyridyl case with the first step (eq 9) being rate



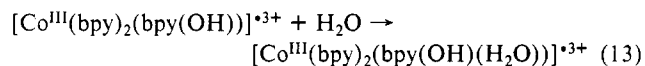
determining (here bpy(OH)<sup>•</sup> represents a radical moiety and bpy(OH) aromatized hydroxy-2,2'-bipyridine). The overall conductivity change, assuming that eq 12 lies to the left as seems likely at pHs near 10, is expected to approach -200 Ω<sup>-1</sup> cm<sup>2</sup> for the foregoing set of reactions and also for the analogous set for the ruthenium adduct. For the case of bpy(OH)<sup>•</sup>, the observed ΔA value is about half of that predicted. This disparity can be accounted for in part by the fact that under our conditions the self-reaction of bpy(OH)<sup>•</sup> is very competitive with that of eq 9: in the absence of ferricyanide, essentially no conductivity change transpires, and this tends to favor the interpretation that the self-reaction is one of dimerization rather than disproportionation as the latter would lead to the occurrence of some conductivity

movement via eq 12. The possibility also exists that more than one isomeric form of the adduct is present and that the isomers have different levels of reactivity toward ferricyanide such as found for the reactions with HO adducts of pyridine.<sup>37</sup> The conductivity change associated with the reaction of ferricyanide and [Ru(bpy)<sub>3</sub>(OH)]<sup>•2+</sup> is close to the predicted value (within 20%). In the absence of ferricyanide, the second-order decay of the ruthenium transient(s) does lead to a small amount of decrease (ca. -45 Ω<sup>-1</sup> cm<sup>2</sup>) whereas one might expect a conductivity level of about -100 Ω<sup>-1</sup> cm<sup>2</sup> if the self-reaction only involved disproportionation, and this apparent difference suggests that dimerization (yielding a diol-like substance) is in competition with disproportionation.

The foregoing features clearly point to the involvement of the bipyridyl ligand, but at the same time, our findings also show the importance of the presence and nature of the metal center throughout all phases of reaction. The rate constants for the OH reactions (Table I) are large and perhaps in some instances at diffusion-controlled levels; nevertheless, there seems to be evidence for a chemical component, based upon the order of reactivity: [Fe(Me<sub>2</sub>bpy)<sub>3</sub>]<sup>2+</sup> > [M(bpy)<sub>3</sub>]<sup>2+</sup> (M = Fe, Os, Ru) > bpy > [Co(bpy)<sub>3</sub>]<sup>3+</sup> ≈ Hbpy<sup>+</sup>. The lower reactivities of Hbpy<sup>+</sup> and the cobalt(III) complex relative to that of uncoordinated bpy can be rationalized within the context of withdrawal of electron density from the aromatic ring (with little, if any, d-π\* back-bonding for the cobalt complex) giving rise to a decreased rate of ligand attack.<sup>13,49</sup> A Lewis acid effect will also be present for systems of the iron triad; however, d-π\* back-bonding (a significant ground-state factor for these types of complexes) can contribute to enhanced reactivity of the bpy ligand.<sup>13,49,50</sup>

The influence of the metal center is also manifested at the longer term stages of reaction where the ruthenium adduct(s) decays relatively slowly via a second-order rate law. In contrast, the cobalt and iron adducts disappear in several stages with the initial phases exhibiting first-order behavior. This latter aspect along with the apparent absences of reactivities toward the starting materials suggest that the initial decay processes observed in pulse radiolysis are of an intramolecular character. However, even given these similarities, differences arise between the cobalt and iron cases. For the iron bipyridyl complex, the changes are wavelength-dependent, and this dependency is also encountered in the reactions of O<sub>2</sub> and [Fe(CN)<sub>6</sub>]<sup>3-</sup>, implicating the occurrence of more than one product, whereas these features are not found with the cobalt complex and where in fact the reverse order of reactivity toward the aforementioned additives is found. The conductivity changes in acidic media are also different with the disappearance of the iron transients giving rise to conductivity decreases, indicating consumption of proton: this may be an indication of release of bpy at one coordination site although final product analysis shows that the amount of uncoordinated bpy formed is quite small (Table III).

For the cobalt system, an increase of 100 Ω<sup>-1</sup> cm<sup>2</sup> (at 500-μs time frame) transpires, and some [Co(aq)]<sup>2+</sup>, bpy and, hydroxybipyridyl-type product(s) are found as final products (Table III). An explanation for the observed spectral decrease and accompanying conductivity increase (*k* = 1.1 × 10<sup>3</sup> s<sup>-1</sup>) is that the dearomatized ligand adduct undergoes modification such as hydrate formation (eq 13) in a manner similar to that proposed for



the ligand adduct produced in the reaction between OH and [Co(NH<sub>3</sub>)<sub>5</sub>(py)]<sup>3+</sup>.<sup>51,52</sup> Partial loss of the proton from the hydrate product of eq 13 could then account for the increase in conductivity in slightly acidic media and for the much enhanced decay rate

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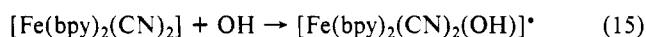
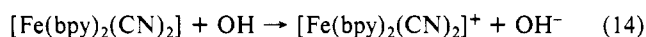
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for the reactant in basic media. The decay of the proposed product of eq 13 may in part lead to formation of the small amount of observed  $[\text{Co}(\text{aq})]^{2+}$  (and to bpy products) as given in Table III. The low  $G$  value of 1.6 for  $[\text{Co}(\text{aq})]^{2+}$  is one indication that an intramolecular electron-transfer mechanism (IET) is of minor consequence. Further to this point is that we would have expected to see in pulse radiolysis the cobalt(II) product of an IET reaction on the basis that  $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$ , formed by the hydrated electron reaction with the congeneric cobalt(III) complex, is stable on pulse-radiolysis time scales and readily detectable by its intense absorption peak at 300 nm.<sup>29</sup> In addition, one does encounter in the reaction of H atom and  $[\text{Co}(\text{bpy})_3]^{3+}$ , where the initial product spectrum is similar to that of the OH reaction (Figure 1), the development on the millisecond scale of an intense absorption band with a peak at 305 nm and a full width at half-maximum close to that for  $[\text{Co}(\text{bpy})_3]^{2+}$ .<sup>21,53</sup> The variation of yields for the final products with dose (Table III) does indicate that several pathways to the longer term products exist, and the much higher  $G$  values found in  $\gamma$ -ray radiolysis point toward contributions from an intermolecular electron-transfer mechanism under conditions of low dose rate.

In contrast, the yields for bpy and loss of starting material on irradiation of  $[\text{Fe}(\text{bpy})_3]^{2+}$  are smaller although spectral evidence for hydroxybipyridyl-type product(s) is also found as in the cobalt case. In addition, the  $G$  values are relatively insensitive to dose rate, and these aspects suggest in a general sense that one ligand adduct may serve as a multiple source of electrons for repair of other adducts: similar situations are encountered in the thermal reductions of  $[\text{Ru}(\text{bpy})_3]^{3+}$  and analogous systems by hydroxide ion.<sup>54,55</sup>

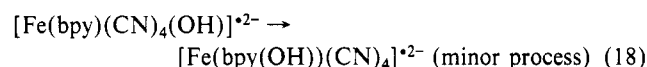
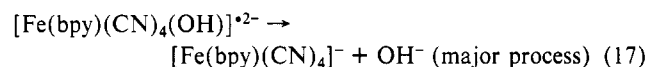
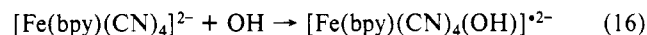
The progressive replacement of bpy ligand by two cyano ligands, which leads to iron(II) complexes having overall zero or negative electrostatic charges and lower redox potentials (Table I), gives rise to substantial differences in radiolytic behavior from those of iron(II) tris(bipyridyl) type. Notable in this regard is the detection of the congeneric iron(III) forms. No detectable amounts of free bpy and cyanide ion are found for the radiolysis of  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ , nor is free cyanide observed on irradiation of  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$ . Several authors have proposed that the CT reaction of OH and  $[\text{Fe}(\text{CN})_6]^{4-}$  proceeds by way of an OH adduct (one involving addition either to the metal center or to a cyanide ligand) followed by release of hydroxide ion to form ferricyanide ion.<sup>5,6</sup> Comparison of the conductivity and optical changes gives no clear indication of an intermediate within our time resolution; however, the conductivity increase attained in basic media of  $60 \pm 14 \Omega^{-1} \text{ cm}^2$  certainly supports the occurrence of electron transfer (eq 1). In the reaction of OH and  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]$ , the formation of an intermediate preceding electron transfer is also difficult to establish unambiguously because while substantial conductivity changes occur (showing charge transfer) the rate of the initial conductivity change is only marginally slower than that for the optical movement. Nevertheless, the findings clearly demonstrate that at least two types of products are formed in a competitive fashion (eqs 14 and 15). The level of the initial



conductivity change implies that eq 14 represents the major path; however, there is also a minor second component (20%) in acidic media that complicates the picture. The product of eq 15 could also well be representative of several different types of ligand adducts because its absorption in the 800-nm region and its subsequent kinetic behavior are close to those features encountered with the iron(II) tris(bipyridyl) system.

The reaction of  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$  and OH represents a much more straightforward situation to interpret, in part, because as a final product  $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$  is formed to an extent in excess

of 90% (relative to the amount of OH reacting) even though on the pulse radiolysis time scales the yield appears somewhat lower (ca. 70%). In the latter experiments, only one stage of conductivity is found. The striking feature of this change as shown in Figure 3 is that the conductivity movement is slower than that for the initial optical one. This difference is a clear indication that although CT via formation of hydroxide ion is the major process, it occurs at a secondary stage; i.e., the OH reaction generates a precursor(s) to charge transfer. Several schemes are consistent with the data, and the mechanism given by eqs 16–18 involves



formation of a common intermediate. An alternative scheme entails direct competitive generation of two adducts such as one to the bpy ligand ( $\text{Fe-bpy-OH}$ ) and the other to a cyanide group ( $\text{Fe-CN-OH}$ ) with the latter subsequently releasing hydroxide ion. In either scheme, the rate constant associated with release of  $\text{OH}^-$  is about  $(1-2) \times 10^6 \text{ s}^{-1}$ . The discernment here of a relatively long-lived precursor to CT is a clear demonstration that the electron-transfer process proceeds via an inner-sphere type of mechanism.

Kinetic information on the reactions of OH with the systems studied here and for related low-spin  $d^6$  metal complexes is presented in Table I along with pertinent thermodynamic data, which are cited relative to the standard hydrogen couple for the half-reaction of the metal complex being written for the reduction process, for example, the reduction of ferricyanide to ferrocyanide. For each of the lower valent metal complexes listed in column one, there is a corresponding complex of the same stoichiometry for the metal in the next higher valent state: the exception is that of  $[\text{Co}(\text{bpy})_3]^{3+}$ . Under the assumption that the reactions of hydroxyl radical ( $E^\circ(\text{OH}/\text{OH}^-) = 1.89 \text{ V}$ ) and these metal complexes in their standard states are reasonable approximations to those under the pulse-radiolysis conditions (dilute aqueous media), then on thermodynamic grounds one would anticipate that electron-transfer processes (such as that of eq 4) are viable possibilities. The situations encountered differ from this, notably in the cases of the positively charged complexes where OH adduct formation prevails. For the negatively charged ions, electron transfer does predominate; however, for  $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ , the mechanism is an inner-sphere type. Selvarajan and Raghavan in their pulse-radiolysis study of the OH reaction with  $[\text{IrCl}_6]^{3-}$  found two pathways to the formation of  $[\text{IrCl}_6]^{2-}$  and  $\text{OH}^-$ .<sup>8</sup> The minor route (35%) is proposed to involve outer-sphere electron transfer on the basis that the nascent optical and conductivity changes occur within experimental error at the same rate. The major, but slower, pathway proceeds via an inner-sphere process where the intermediate is considered to be  $[\text{Cl}_5\text{Ir-Cl-OH}]^{3-}$  with this species subsequently decaying to the final product by a process that is first order in proton concentration. Uncoordinated cyanide ion undergoes reaction with hydroxyl radical by addition, and thus it seems likely that, in the electron-transfer reactions of the iron(II) mixed cyano-bipyridine cases, these also occur via OH addition to the cyanide ligand.<sup>3</sup> A logical extension to this is that all of the OH reactions for the hexacyano complexes listed in Table I also proceed by inner-sphere mechanisms (as proposed earlier by others for the electron-transfer reaction of OH and ferrocyanide) even though the intermediates are too short-lived to be detected for time scales at or slightly below a microsecond.

The OH reactions under discussion do not seem to reflect in a direct fashion the energetics of these situations when one considers the following three features. The half-cell reduction potentials for  $[\text{Os}(\text{bpy})_3]^{3+/2+}$ ,  $[\text{Fe}(\text{bpy})_2(\text{CN})_2]^{3+/2+}$ , and  $[\text{Ru}(\text{CN})_6]^{3-/4-}$  differ by less than 0.1 V, but the lower valent state complexes react with OH differently (Table I). The reactions of OH and the positively charged tris(bipyridyl) complexes of the

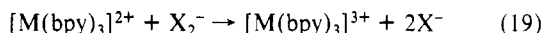
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iron(II) triad yield relatively stable adducts whereas the reactions of these systems with dihalogen or pseudodihalogen radicals  $X_2^-$  such as  $Br_2^-$  and  $(SCN)_2^-$ , which have reduction potentials near that for OH, occur rapidly and without apparent intermediates to yield the corresponding complex for the metal in the next higher valent state (eq 19).<sup>2,11,12,56</sup> Furthermore, the M(II)/M(III)



couples are well noted for their very large self-electron exchange rate constants (in the range  $10^8$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>56,57</sup> The implication is that there is a significant barrier to the transformation of neutral OH(aq) to the negatively charged  $OH^-(aq)$ , i.e. to the occurrence of electron transfer.

In this context, it is germane to consider the process in eq 20 in order to consider in more detail the thermodynamic features associated with the reactions of OH and the complexes cited in



Table I. The  $\Delta S^\circ$  value for eq 20 is estimated to be ca.  $-110 \text{ J/(K mol)}$  (based upon reported thermodynamic information along with the estimate made by Berdinkov and Bazhin of  $-84 \text{ J/(K mol)}$  for the entropy of hydration of OH(g) to OH(aq)).<sup>58-60</sup> Electron-transfer processes involving the positively charged bipyridyl complexes as in eq 4 are anticipated to exhibit negative values of  $\Delta S^\circ$  (ca.  $-15$  to  $-50 \text{ J/(K mol)}$ ) whereas for  $[IrCl_6]^{3-}$ ,  $[Fe(CN)_6]^{4-}$ , and  $[Fe(bpy)(CN)_4]^{2-}$ , where electron transfer is re-

alized, the entropic values are positive (ca.  $15$  to  $150 \text{ J/(K mol)}$ ); in all instances, the corresponding enthalpies are exothermic (ca.  $-60$  to  $-110 \text{ kJ/mol}$ ) with no discernible reactivity trend. While overall entropies and enthalpies represented but one contribution to activation processes for electron transfer, the negative  $\Delta S^\circ$  values for the tris(bipyridyl) complexes are one indication of a barrier to net charge exchange, and mechanistically one perceives substantial solvent reorganization around positively charged ions prior to the transformation of the neutral OH group to the hydroxide anion. In this regard, one can view the OH-bipyridine adducts as potential precursors to electron transfer even though more facile channels involving ligand modification-degradation predominate in the actual disappearance of the adducts. The occurrence of the adducts for the iron(II) bipyridyl complexes may in the first instance be favored by the presence of  $d-\pi^*$  back-bonding (this is also expected of the hexacyano systems) and by the conversion of the hydrophobic bipyridyl ligand to a less hydrophobic hydroxyl containing entity.<sup>61</sup> The potential loss of the hydrophilic OH group may consequently act as one of the impediments toward subsequent electron transfer. A further clue to a barrier may be indicated by the presence of charge-transfer bands for the OH adducts of the iron triad-bipyridyl complexes in the 700–850-nm region with molar extinction coefficients in the range  $(0.5\text{--}2.1) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  (Figure 1 and ref 10). On the presumption that these bands are of an intervalent character ( $M(II) \rightarrow OH$ ), their optical features would imply a considerable barrier to the corresponding thermal electron transfer: notably, these bands are absent for the OH-addition products for  $[Co(bpy)_3]^{3+}$  (where the corresponding cobalt(IV) is unknown) and for uncoordinated bipyridine.

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## Notes

Contribution from the Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, and Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Federal Republic of Germany

### Preparation and Crystal Structure of $(NEt_4)[Fe_2(CO)_8(\mu-AuPPh_3)]$

Oriol Rossell,\*† Miquel Seco,† and Peter G. Jones†

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As a part of our continuing studies on complexes containing metal-metal bonds, we have recently shown that the  $[HFe(CO)_4]^-$  anion is a very useful reagent for the synthesis of complexes containing Fe-M ( $M = Zn, Cd, Hg$ ),<sup>1</sup> Fe-Sb,<sup>2</sup> and Fe-Sn<sup>3</sup> bonds. We are now investigating the potential use of the related metal carbonylate  $[Fe_2(CO)_8]^{2-}$  in similar preparative processes, since this dianion could give rise to polymetallic chains longer than the three-membered ones reported so far. Although the initial expectations have not been fully confirmed, we obtained the anionic triangular cluster  $[Fe_2(CO)_8(\mu-AuPPh_3)]^-$  (**1**), the first triangular

cluster with an  $Fe_2Au$  skeleton. The preparation and structure of **1** are reported in this paper.

### Experimental Section

All solvents were dried by standard methods, and all manipulations were performed in Schlenk-type flasks under nitrogen. Elemental analyses of C, H, and N were carried out at the Institut de Bio-Organica de Barcelona. The  $^{31}P\{^1H\}$  NMR spectra were obtained on a Bruker WP 80SY spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. The compounds  $(Et_4N)_2[Fe_2(CO)_8]^{4-}$  and  $[ClAuPPh_3]^{5-}$  were prepared as described previously.

**Synthesis of  $(NEt_4)[Fe_2(CO)_8(\mu-AuPPh_3)]$  (**1**).** To a slurry of 0.44 g of  $(Et_4N)_2[Fe_2(CO)_8]$  (0.74 mmol) in 80 mL of THF was added 0.36 g of  $[ClAuPPh_3]$  (0.74 mmol) at room temperature. The solution became deep orange within about 1 min, and all the carbonylmetalate dissolved. After being stirred for an additional 1 h, the mixture was filtered and hexane was added dropwise to the filtrate until orange microcrystals precipitated. This product was recrystallized from acetone-hexane to give 0.57 g of  $(NEt_4)[Fe_2(CO)_8(\mu-AuPPh_3)]$  (0.61 mmol, 83% yield). IR (THF,  $cm^{-1}$ ):  $\nu_{CO}$  stretch 2000 m, 1950 s, 1915 s, 1750 br. IR (KBr

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\* Universitat de Barcelona.

† Technische Universität Braunschweig.