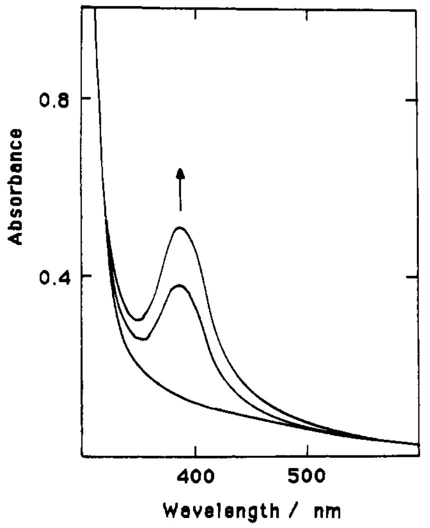

Figure 3. UV/vis spectral changes upon irradiation of mixture c of Figure 1 (10^{-1} M PPh_3 added, IR cell 0.02 cm) at 514.5 nm.

anion in the contact ion pair. Ion pairing in metal carbonyl chemistry can also be monitored by means of IR spectroscopy.[9,11,13,15,16] The IR spectra of the cobaltate solutions of Figure 1 showed hardly any difference in intensity for the strong C–O stretching vibration at about 1890 cm^{-1}. Moreover, no other band showed up in this wavenumber region, but only significantly small changes in bandwidths were observed. This is obviously due to different interactions in the ion pairs and/or their concentrations. Although the addition of TBAP decreases the IPCT absorption, see Figure 1, the bandwidth of the CO stretching vibration is not significantly altered. Thus, a similar contact ion pair seems to be formed upon replacement of $DMBP^{2+}$ by the tetra-*n*-butylammonium cation, which has, however, no low-energy IPCT transition, since a low-lying π^*-orbital is lacking in the latter cation. The solubility of $Na^+Co(CO)_4^-$ is much less than 5×10^{-3} M in CH_2Cl_2. Stirring a suspension of $Na^+Co(CO)_4^-$ and $DMBPY^{2+}(PF_6^-)_2$ gives an increasing C–O stretching mode in the solution. This indicates that the $Co(CO)_4^-$ anion dissolves by ion-pair formation with $DMBPY^{2+}$. The final relative bandwidth is increased compared with the corresponding mixture by using $PPN^+Co(CO)_4^-$ as cobaltate source. This result clearly shows that ion-pair equilibria in organic solvents are dependent on the initial ion pairs.

Thermal Reactions. The solutions of the ion-pair with $DMBPY^{2+}$ are stable for some hours so that photochemistry could be studied separately from thermal reactions, see below. On the other hand, mixing $MV^{2+}(PF_6^-)_2$ with $PPN^+Co(CO)_4^-$ or $Na^+Co(CO)_4^-$ in CH_2Cl_2 or acetone caused the color to change to blue with bands at 390 and 606 nm, indicating the formation of MV^+. In acetone, the intensity of these bands increased within 3 h at room temperature until a maximum was reached and then slowly decreased. With an absorption coefficient of 13 800 M^{-1} cm^{-1},[17] the extent of maximum conversion toward equilibrium can be estimated to be about 5%. As a plot of the increasing absorbance at 606 nm revealed approximately first order kinetics with $k_3 = 5 \times 10^{-5}$ s^{-1}, the rate-determining step is the redox reaction within the ion pair, reaction 3. The fate of the cobalt radical is not yet

$$MV^{2+}Co(CO)_4^-PF_6^- \rightarrow MV^+PF_6^- + {}^{\bullet}Co(CO)_4 \tag{3}$$

clear. Because of the strong blue color of the mixtures we did not further study the IPCT behavior and photochemistry of $MV^{2+}Co(CO)_4^-$.

Photochemical Reactions. Irradiation of a mixture of both 5×10^{-3} M $DMBPY^{2+}(PF_6^-)_2$ and $PPN^+Co(CO)_4^-$ in CH_2Cl_2 with the 514.5-nm laser line of an Ar ion laser did not cause any change in the UV/vis and IR spectra, obviously because of a fast back-reaction of the radicals formed by the charge-transfer transition. Addition of triphenylphosphine (10^{-1} M) and irradiation with 514.5-nm laser light caused the appearance of an absorption band at 390 nm (Figure 3). At the same time the $Co(CO)_4^-$ IR band at 1890 cm^{-1} decreased in intensity while two new bands showed up at 1957 and 1976 cm^{-1}, respectively. The new features at 390 nm and 1957 cm^{-1} belong to $Co_2(CO)_6(PPh_3)_2$;[7,18] the origin of the 1976-cm^{-1} band is not yet clear. $Co(CO)_3(PPh_3)_2^+$, which has a strong IR band at 2008 cm^{-1},[18] was not formed during this reaction.

Apparently, PPh_3 acts as a scavenger here for the ${}^{\bullet}Co(CO)_4$ radicals as in the case of the photochemical reaction of the $Co(Cp)_2^+Co(CO)_4^-$ ion pair;[6,11] see reactions 4 and 5. An initial

$${}^{\bullet}Co(CO)_4 + PPh_3 \rightarrow {}^{\bullet}Co(CO)_3PPh_3 + CO \tag{4}$$

$$2{}^{\bullet}Co(CO)_3PPh_3 \rightarrow Co_2(CO)_6(PPh_3)_2 \tag{5}$$

quantum yield of about 0.02 for the formation of $Co_2(CO)_6(PPh_3)_2$ was determined under our conditions with $[PPh_3] = 10^{-1}$ M. The irradiation of a mixture of $PPN^+Co(CO)_4^-$ with PPh_3 in the absence of $DMBPY^{2+}(PF_6^-)_2$ did not give any products.

The primary product of the charge-transfer transition is the $DMBPY^+$ radical cation, for which different lowest energy bands at 600[19] and 470 nm,[20] respectively, are given. As such an absorption band could not be detected, we conclude that $DMBPY^+$ is not formed in noticeable concentrations due to a secondary reaction of the cation radical, possibly with the solvent, re-forming the $DMBPY^{2+}$ dication. The photochemical reaction of the same mixture with added PPh_3 in acetone was much slower, also taking into account the smaller IPCT absorption. This is expected for the more polar solvent. Neither the 1957-cm^{-1} nor the 390-nm band is dominating in the spectra as found in CH_2Cl_2. Obviously acetone competes with PPh_3 for the ${}^{\bullet}Co(CO)_4$ radicals, reducing them at least in part.

These results show that IPCT occurs also in contact ion pairs without significant distortion of the tetrahedral structure of the tetracarbonylcobaltate anion. Therefore the interaction should be effected here mainly via the CO ligands and not directly by the metal, as for the ion pairs with complex cobalt cations and Tl^+. $DMBPY^{2+}/Co(CO)_4^-$ ion pairs give irreversible photochemical product formation only if the intermediate radicals are scavenged, in accordance with results on other pyridinium cations.[11]

Acknowledgment. We acknowledge the assistance of Dr. M. von Szombathely, KMU Leipzig, in nonlinear regression analysis and the preparation of the cobaltates by W. G. J. de Lange, and we are grateful for helpful discussions with Prof. Dr. A. Oskam.

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Competitive CO Attack in $Fe(CO)_5$ Using Methanolic $[Et_4N][OH]$. IR Spectral Observation and Reactivity Studies of $[Fe(CO)_4(CO_2X)^-]$ (X = OH, OMe)

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The water gas shift reaction continues to receive attention in connection with carbon dioxide reduction processes and as a method to generate hydrogen from water gas.[1] Of the many

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catalytic and model water gas shift systems examined, the vast majority deal with iron and ruthenium complexes.[2-9] A key step in many of these studies conducted under alkaline conditions is the activation of a coordinated CO ligand by hydroxide to yield an intermediate hydroxycarbonyl complex $[M(CO_2H)^-]$. Most anionic hydroxycarbonyl complexes are thermally unstable and lose CO_2 to give the corresponding anionic hydride $[MH^-]$. As part of our interest in the spectral characterization of thermally unstable $[M(CO_2H)^-]$ complexes and their possible role in catalytic reactions, we report our results on the reaction of $Fe(CO)_5$ with methanolic $[Et_4N][OH]$. Our spectral observation and reactivity studies unequivocally establish the presence of $[Fe(CO)_4(CO_2H)^-]$ and are intended to supplement the excellent seminal kinetic studies that have implicated $[Fe(CO)_4(CO_2H)^-]$ in water gas shift cycles.[3-5]

Results

The reaction between $Fe(CO)_5$ and $[Et_4N][OH]$ in THF/MeOH gives the hydroxycarbonyl and methoxycarbonyl complexes $[Fe(CO)_4(CO_2H)^-]$ ($[1^-]$) and $[Fe(CO)_4(CO_2Me)^-]$ ($[2^-]$), respectively, as determined by low-temperature IR analysis. The reactivity of these anions toward trifluoroacetic acid, Et_3N, and $[Li^+]$ is described in the sections that follow.

Discussion

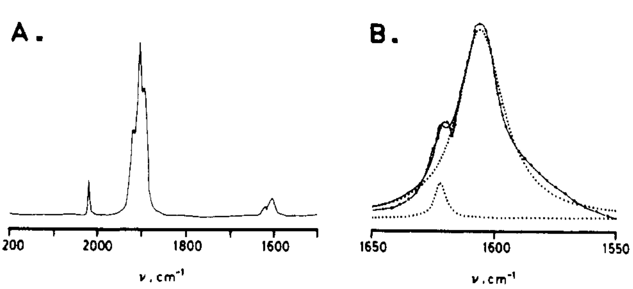
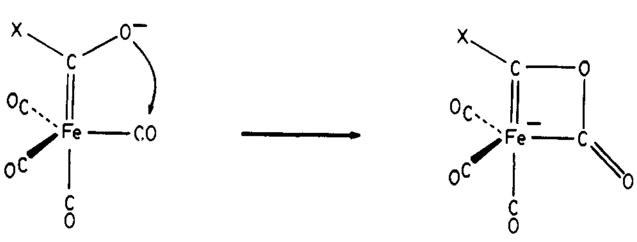


Figure 1. Infrared spectra of the carbonyl region for $[Fe(CO)_4(COX)][Et_4N]$ (where X = OH and OMe): (A) full spectrum of $[Fe(CO)_4(COX)^-]$ (3.8×10^{-3} M); and (B) expanded view (1.9×10^{-2} M) of the acid/ester C–O stretching region for the experimental spectrum (–·–), resolved bands (···), and the theoretical curve (—) for both the acid and the ester. Both spectra were recorded in THF at −70 °C.

Treatment of $Fe(CO)_5$ in THF at −78 °C with 1.0 equiv of $[Et_4N][OH]$ (1.3 M in MeOH) affords $[Fe(CO)_4(CO_2H)^-]$ and $[Fe(CO)_4(CO_2Me)^-]$ immediately and in essentially quantitative yield (combined yield). Low-temperature IR analysis revealed the presence of terminal carbonyl stretching bands at 2022 (m), 1922 (m), 1908 (vs), and 1897 (s) cm^{-1} indicative of an axially substituted $[Fe(CO)_4(COX)^-]$ complex (X = OH or OMe)[10] in addition to two weaker intensity bands at 1621 (vw) and 1604 (w) cm^{-1} ascribed to the C–O bands of the ester and acid functionalities, respectively. $[1^-]$ and $[2^-]$ are analogous to axially substituted $LFe(CO)_4$ compounds that possess idealized C_{3v} symmetry and are predicted to exhibit three terminal CO bands ($2A_1$ + E). Four bands are observed due to a splitting of the E vibrational mode.[11] An unlikely alternative that would give rise to four CO bands involves formation of a metalloanhydride-derived complex formed via intramolecular carboxylate/ester attack on an equatorial CO, i.e.



A similar process has been invoked in the oxide transfer reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CO_2)^-]$ and in the formation of iron arylphosphonate complexes.[12] Figure 1A shows the low-temperature IR spectrum of the mixture of $[1^-]$ and $[2^-]$.

Unequivocal proof for the presence of $[2^-]$ derives from its independent synthesis. The reaction of $Fe(CO)_5$ in THF with [MeO][Li] (1.3 M in MeOH) gives **[2]**[Li], which exists as contact ion pairs in solution similar to **[2]**[Na].[5c] The contact ion pairs of **[2]**[Li] were next disrupted through the addition of HMPA or 15-crown-5 in order to allow for a direct spectral comparison with the solvent-separated ions of $[\mathbf{2}][Et_4N]$.[13,14] The resulting spectrum of $[2^-]$ revealed an ester C–O stretch at 1621 cm^{-1}, providing confirmatory proof of its existence in the $[Et_4N][OH]$ reaction. Accordingly, the band at 1604 cm^{-1} is assigned to the acid C–O stretch of $[1^-]$.

The ratio of $[1^-]$ to $[2^-]$ present from the reaction of $[Et_4N][OH]$ and $Fe(CO)_5$ was determined by measuring the area under the overlapping low-frequency C–O stretching bands as shown in the experimental and resolved spectra in Figure 1B. The ratio of $[1^-]$ to $[2^-]$, calculated to be ca. 95:5, is of interest when one considers the $[OH^-]/[MeO^-]$ equilibrium in eq 1, which has

$$MeOH + [OH^-] \rightleftarrows [MeO^-] + H_2O \qquad (1)$$

a $K_{eq} \approx 7.7$ in aqueous MeOH.[15] Since the 1.3 M methanolic $[Et_4N][OH]$ solution used exists in >99% as the $[MeO^-]$ ion, $[\mathbf{2}][Et_4N]$ would have been predicted as the major product given

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(14) (a) $[Fe(CO)_4(CO_2Me)][Li]$ (THF, −70 °C) ν_{CO}: 2028 (m), 1932 (m), 1916 (vs), 1903 (s), 1574 (w, ester) cm^{-1}. (b) $[Fe(CO)_4(CO_2Me)^-]$ (THF/HMPA {10 equiv}, −70 °C) ν_{CO}: 2018 (m), 1912 (sh), 1906 (vs), 1898 (sh), 1621 (w, ester) cm^{-1}.

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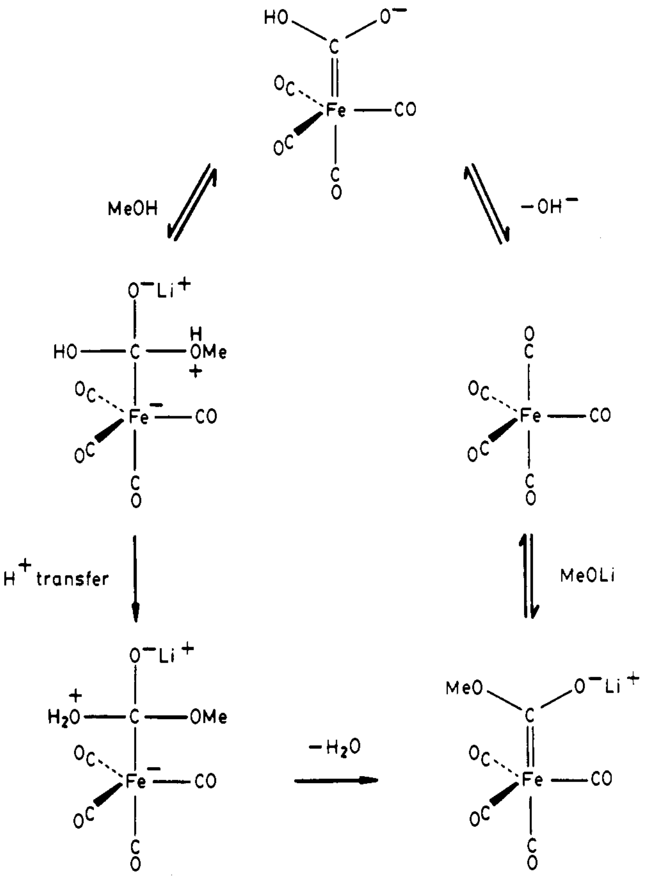
the greater nucleophilicity of [MeO$^-$] relative to [OH$^-$][16] coupled with the exothermic nature of this reaction,[10] which should not lead to substantial nucleophile discrimination. While the effect of THF on the equilibrium in eq 1 has not been determined, Ford and co-workers indicate that the K_{eq} should, if anything, increase upon the addition of THF.[5c] Such deviation in the product distribution from the equilibrium concentrations of [MeO$^-$] and [OH$^-$] suggests that the nature of both the initial carbonyl complex and the gegencation play an important role in determining the relative ratio of [**1**$^-$] to [**2**$^-$] in this reaction (vide infra the reactivity between [**1**][Et$_4$N] and [Li$^+$]).[17]

Having established the identity of [**1**$^-$] and [**2**$^-$] in the [Et$_4$N][OH] reaction, we conducted several low-temperature IR studies in order to better define the reactivity of these anions. Addition of trifluoroacetic acid (slight excess) to [**1**$^-$] and [**2**$^-$] at −78 °C led immediately to the regeneration of Fe(CO)$_5$ in quantitative yield[18] according to the stoichiometry given by eq 2 while added Et$_3$N had no effect on the solution mixture.[19] This

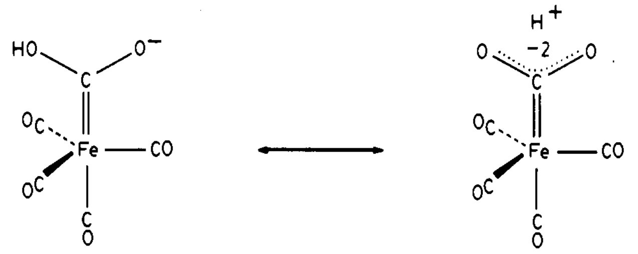
$$[Fe(CO)_4(CO_2H)^-]/[Fe(CO)_4(CO_2Me)^-] \xrightarrow{TFA} Fe(CO)_5 + H_2O + MeOH \quad (2)$$

latter observation suggests that a comparison between [**1**$^-$] and organic carboxylic acids, RCO$_2$H (where R = alkyl), is inappropriate. Organic carboxylic acids are sufficiently acidic (pK_a $\approx$ 4–5) and are readily deprotonated by Et$_3$N; however, on the basis of the absence of an observable reaction between [**1**$^-$] and Et$_3$N and the knowledge of the pK_a value for Et$_3$N (as [Et$_3$NH$^+$]) reported as ca. 11,[20] it is concluded that the hydroxycarbonyl moiety in [**1**$^-$] must possess a pK_a value in excess of 11. Mixtures of [**1**$^-$] and [**2**$^-$] were observed to be stable and their ratio unchanged for a period of 2 weeks when maintained at −70 °C. Decomposition to [HFe(CO)$_4$$^-$] occurs upon warming to room temperature.[21]

Scheme I



The ratio of [**1**$^-$] to [**2**$^-$] is extremely sensitive to the nature of the gegencation. Treatment of the original solution containing [**1**$^-$] and [**2**$^-$] (95:5 ratio) at −78 °C with 10 equiv of [Li$^+$] (as [CF$_3$SO$_3$][Li]) led immediately to [**2**][Li] in quantitative yield. Under similar conditions the reaction between Fe(CO)$_5$ and [Li][OH] (1.3 M in MeOH) led to [**2**][Li] as the sole product in accordance with the equilibrium in eq 1. We believe that the observed product distribution is driven by maximum delocalization of the anionic charge, which, in turn, is strongly influenced by the cation. For example, use of [Et$_4$N][OH] leads to anions that exist in an unperturbed, symmetrical environment since the [Et$_4$N$^+$] ion is a nonspecific, charge-delocalized cation.[22] The IR frequencies of [**1**][Et$_4$N] and [**2**][Et$_4$N] are not affected upon the addition of HMPA, supporting the absence of [Et$_4$N$^+$] ion pairing. The salt [**2**][Et$_4$N] is expected to exhibit high charge density on the ester/iron center relative to [**1**][Et$_4$N], which can delocalize the anionic charge more effectively through the carboxylate-like resonance structure



Addition of [Li$^+$] gives the thermodynamically more stable complex [**2**][Li] exclusively. Contact ion pairing between the anionic ester oxygen and the [Li$^+$] ion (vide supra) is apparently so stabilizing that no [**1**][Li] is observed. Whether this [Li$^+$]-induced transformation of [**1**][Et$_4$N] to [**2**][Li] proceeds through a methanol addition/water elimination or a hydroxide dissociation/methoxide addition sequence as shown in Scheme I remains open for speculation. However, the former pathway would seem to be favored given the low K^{-1} value observed in the equilibrium between Fe(CO)$_5$/[Fe(CO)$_4$(CO$_2$H)$^-$] and Fe(CO)$_5$/[Fe(CO)$_4$(CO$_2$Me)$^-$]. Here [Li$^+$] coordination to the anionic oxygen of [**1**$^-$] should render the acid carbon more susceptible to MeOH attack as demonstrated in related organic acid/ester hydrolysis reactions.[23]

Experimental Section

Materials and Methods. Fe(CO)$_5$ was purchased from Pressure Chemical Co. and was used as received. [Et$_4$N][OH] (20% aqueous solution) was obtained from Lancaster Synthesis and dried under high vacuum to give solid [Et$_4$N][OH]. The 1.3 M methanolic solutions of [Et$_4$N][OH] were subsequently prepared under argon and transferred to a Schlenk storage vessel. THF and HMPA were distilled from so-

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dium/benzophenone and CaH$_2$, respectively, and stored under argon in Schlenk vessels. All reactions were conducted under argon by using Schlenk techniques.[24]

Low-temperature infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer with a Specac Model P/N 21.000 variable-temperature cell equipped with inner and outer CaF$_2$ windows. Solutions for analysis were transferred to the precooled IR cell via cannulation from an external Schlenk vessel maintained at −78 °C. The transfer cannula was wrapped in dry ice to prevent undue warming. Dry ice/acetone was used as coolant, and the reported cell temperature, taken to be accurate to ±1 °C, was determined with a copper-constantan thermocouple. The ^{13}C NMR spectrum was recorded at 75 MHz on a Varian 300-VXR spectrometer.

Since the acid and ester carbonyl stretching bands exhibit partial overlap, the infrared band shapes of these CO bands were calculated by using a numerical procedure in order to determine the ratio of their areas. Absorbances were digitized from 1650 to 1550 cm^{-1} at 1-cm^{-1} intervals and entered into files on the university VAX 11/85 computer. Following baseline correction, the spectra were fit by a model consisting of Lorentzian band shapes, each characterized by a peak frequency (ν), maximum intensity (I), and half-width [fwhh] (Δ). Since the instrument resolution (2 cm^{-1}) is far less than the observed bandwidths (~20 cm^{-1}), it was unnecessary to convolute the model spectrum with a resolution (slit) function. The parameters were varied to minimize the squared deviation between the experimental and calculated intensities by using a nonlinear regression procedure.[25] A representative experimental and calculated spectrum of [**1**$^-$] and [**2**$^-$] at −70 °C is shown in Figure 1B. Given that the area of a Lorentzian peak is proportional to the product of the bandwidth and the maximum intensity, the area ratio of the different anions is calculated easily as $A_2/A_1 = (I_2\Delta_2)/(I_1\Delta_1)$.

Reaction of Fe(CO)$_5$ with [Et$_4$N][OH]. To 5.0×10^{-3} mL of Fe(CO)$_5$ (0.038 mmol) in 10 mL of THF at −78 °C was added 2.9×10^{-2} mL of a 1.3 M methanolic [Et$_4$N][OH] solution. The reaction leading to [**1**][Et$_4$N] and [**2**][Et$_4$N] was instantaneous based on low-temperature IR analysis. IR (−70 °C, THF) ν_{CO}: 2022 (m), 1922 (m), 1908 (vs), 1897 (s), 1621 (vw, ester), 1604 (w, acid) cm^{-1}. ^{13}C{^{1}H} NMR [−78 °C, THF/C$_6$D$_6$ 3:1 (v/v)]: δ 213.8 (1 C, COOH), 220.2 (4 C, broad, terminal carbonyls). Note: the resonances associated with [**2**][Et$_4$N] were not observed due to their low concentration relative to [**1**][Et$_4$N].

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Crossover from Metal-Centered to Ligand-Centered Emission in Rhodium(III) Polypyridine Complexes: Rh(phen)$_2$(NH$_3$)Cl^{2+}, Rh(phen)$_2$(NH$_3$)$_2^{3+}$, Rh(phen)$_2$(CN)$_2^+$

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With respect to the enormous amount of work performed in recent years on the photophysics of ruthenium(II) polypyridine compounds,[1] relatively little attention has been devoted to analogous complexes of rhodium(III).[2-11]

Among Rh(III) polypyridine complexes, the best studied case is that of the tris(1,10-phenanthroline)rhodium(III) ion, Rh(phen)$_3^{3+}$, which exhibits in 77 K matrices an intense ($\Phi \simeq 1$)[3] structured ligand-centered (LC) phosphorescent emission.[2-5] An interesting observation (first made by Bolletta et al.[6] and later confirmed in other laboratories[7,8]) is that the exceedingly weak emission detectable in room-temperature solutions of this complex consists mainly of a broad band assignable to a metal-centered (MC) d–d transition. This was explained on the basis of fast equilibration at room temperature between the lowest LC triplet state and a thermally accessible upper MC state.[6-8] This experimental result was subsequently questioned by Watts,[9] who attributed the broad-band emission observed by the other groups to impurities.

In order to contribute to the understanding of the photophysical behavior of Rh(III) polypyridine complexes, we have now studied some mixed-ligand complexes of the type *cis*-Rh(phen)$_2$XY^{n+} (X = Y = CN, n = 1; X = Y = NH$_3$, n = 3; X = NH$_3$, Y = Cl, n = 2). The approach is that of using the X and Y ligands (hereafter called ancillary ligands) to change the energy of the MC states in a predictable way without substantially affecting that of the LC state and to look for qualitative effects of the change in the LC–MC energy difference on the emission properties of these complexes.

Experimental Section

Materials. Rhodium(III) chloride hydrate, 1,10-phenanthroline, hydrazine hydrate, and ethylene glycol were commercial products (Fluka) of reagent grade. Tetradistilled water was used throughout.

Syntheses. The starting material for the synthesis of the complexes, [Rh(phen)$_2$Cl$_2$]Cl, was prepared according to literature procedures.[12]

[Rh(phen)$_2$(CN)$_2$]Cl. This complex was prepared and purified with the procedure described by Gillard.[12] Anal. Calcd for [Rh(phen)$_2$(CN)$_2$]Cl·2H$_2$O: C, 53.21; H, 3.44; N, 14.32. Found: C, 52.38; H, 3.41; N, 13.83.

[Rh(phen)$_2$Cl(NH$_3$)](PF$_6$)$_2$ and [Rh(phen)$_2$(NH$_3$)$_2$](PF$_6$)$_3$. These two complexes were synthesized by the Gillard method[12] with appropriate modifications, particularly concerning purification procedures.

[Rh(phen)$_2$Cl(NH$_3$)](PF$_6$)$_2$. To an aqueous solution (10 mL) containing 0.15 g of [Rh(phen)$_2$Cl$_2$]Cl was added 0.5 mL of NH$_3$ (25%). The reaction mixture was boiled for 30 min. An excess of NaClO$_4$ (0.2 g) was added to the cooled solution, which was concentrated until crystallization. The product was redissolved in water and purified by ion-exchange chromatography with cationic CM-Sephadex C-25 resin. Some unreacted Rh(phen)$_2$Cl$_2^+$ was first eluted with 0.05 M NaHCO$_3$; then the desired product was collected with 0.2 M NaHCO$_3$ as eluant. The eluted solution was concentrated, and precipitated NaHCO$_3$ was eliminated by filtration. Then the product was precipitated by addition of NH$_4$PF$_6$ to the solution. Finally, the resulting pale yellow product was recrystallized from water; 70% yield. Anal. Calcd for [Rh(phen)$_2$Cl(NH$_3$)](PF$_6$)$_2$: C, 35.78; H, 2.38; N, 8.69. Found: C, 34.70; H, 2.27; N, 8.51.

[Rh(phen)$_2$(NH$_3$)$_2$](PF$_6$)$_3$. To an aqueous solution (10 mL) containing 0.15 g of [Rh(phen)$_2$Cl$_2$]Cl were added a large excess (2 mL) of NH$_3$ (25%) and a catalytic amount of hydrazine hydrate (0.001 g). The reaction mixture was boiled for 5 min. To the cooled solution was added 0.2 g of NaClO$_4$, and the resulting solution was allowed to stand at 5 °C for a few days. The resulting brown precipitate was removed by filtration and dissolved in water, and the solution was loaded onto a cationic CM-Sephadex C-25 column. Uncharged impurities were first eluted with water; then elution was continued with successive aliquots of 0.05 and 0.2 M NaHCO$_3$ solutions to remove Rh(phen)$_2$Cl$_2^+$ and Rh(phen)$_2$Cl(NH$_3$)$^{2+}$, respectively. Finally, the desired colorless product was eluted with 0.5 M NaHCO$_3$, precipitated with NH$_4$PF$_6$, and recrystallized from water; 50% yield. Anal. Calcd for [Rh(phen)$_2$(NH$_3$)$_2$](PF$_6$)$_3$: C, 30.92; H, 2.38; N, 9.01. Found: C, 29.91; H, 2.21; N, 8.70.

The values of the elemental analyses for C, N, and H are all somewhat low but are in the correct ratio, suggesting the presence of some ($\leq$4%) NaCl or NaPF$_6$ in the analyzed samples. The spectra (λ_{max} and ϵ_{max})

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