ala)$_2$·H_2O are in good agreement with corresponding distances determined for other amino acid complexes by X-ray crystallography. Isotropic coupling constants for these molecules are not resolved in ESR spectra and our study gives the first direct measurement of these coupling constants. The sign and relative magnitude of these coupling constants can be explained by a mechanism involving spin delocalization from the $d_{x^2-y^2}$ orbital of the copper through the σ bonds of the chelate. This technique probes short-range metal-nuclei interactions without interference from more distant nuclei. It should be of value in studies of the local structure of higher molecular weight biologically important complexes in which knowledge of the ligand structure near the metal ion is of importance.

Acknowledgment. This work was supported in part by National Institutes of Health Grant GM-22793.

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Kinetic Studies of the Reactions of *N,N*-Dimethylformamide and *N,N*-Dimethylacetamide with Sodium in Liquid Ammonia[1]

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Received December 19, 1977

Abstract: The reactions of *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) with sodium in liquid ammonia were found to obey the fourth-order rate law $-d(e^-_{am})/dt = k(e^-_{am})^2(\text{amide})(Na^+)$. A negative activation energy was observed for the reaction of DMF with the ammoniated electron, while the rate of the DMA reaction was not significantly influenced by temperature. A mechanism involving ion pairing is presented to explain the results of this study.

Introduction

Dissolved metal nonaqueous solutions have long been known to constitute powerful reducing systems of considerable synthetic utility.[2] The nature of the reducing species present in these solutions has been a matter of conjecture over the years. Both solvated electrons and alkali metal anions are now recognized as reducing species in dissolved metal systems.[3-5] The equilibria which are important in the metal solutions can be described by the following:[5]

$$2M(s) \rightleftharpoons M^+ + M^- \tag{1}$$

$$M^- \rightleftharpoons M + e^-_{solv} \tag{2}$$

$$M \rightleftharpoons M^+ + e^-_{solv} \tag{3}$$

In liquid ammonia, equilibria in eq 2 and 3 are far to the right and hence for dilute metal-ammonia solutions the only significant reducing species present are the solvated electron and its ion pair.[4] Relatively few homogeneous kinetic studies have been reported for reactions involving the ammoniated electron in contrast to the extensive amount of kinetic data available for the hydrated electron.[6,7] However, based on limited data, reactions involving the ammoniated electron are generally several orders of magnitude slower than those for the hydrated electron.[6,8,9]

The reaction of *N,N*-dimethylformamide (DMF) with sodium in liquid ammonia has been reported[10] to proceed according to the equation

$$2Na + 2(CH_3)_2NCHO \rightarrow (CH_3)_2NCNaO + (CH_3)_2NCH_2ONa \tag{4}$$

Also, the electrochemical reduction of higher amides in methylamine with lithium chloride as the supporting electrolyte has been reported.[11] In the presence of a proton donor (ethanol) the product after hydrolysis and workup was the corresponding aldehyde; in the absence of a proton donor the corresponding alcohol was isolated after acid hydrolysis and workup.[11]

Using the pulse-radiolysis technique, a second-order rate constant of $(5.2 \pm 1.3) \times 10^7\ M^{-1}\ s^{-1}$ has been reported[12] for the reaction of DMF with the hydrated electron. Unfortunately, no information concerning reaction products was reported.[12] Moreover, an attempt to generate the solvated electron in DMF itself by pulse radiolysis failed.[12]

We undertook the present study to obtain more information concerning the reactivities of amides toward solvated electrons since these compounds are used extensively as solvents in electrochemical studies,[13] and to better understand the kinetics of solvated electron reactions in nonaqueous solvents.

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Table I. Kinetic Data for the Reactions of *N,N*-Dimethylformamide with Sodium in Liquid Ammonia

expt no.	temp, °C	concn of sodium metal, 10^3 M	concn of amide, 10^2 M	concn of sodium ion, 10^3 M	k_{obsd}, $M^{-2} s^{-1}$	$10^{-5} k_{obsd}/(Na^+)_t$ $M^{-3} s^{-1}$
Y1-36	−34	1.93	1.92	1.93	191 ± 9	1.0
Y1-40	−34	0.403	2.14	0.403	61 ± 7	1.5
Y1-50	−34	1.51	1.32	1.51	180 ± 15	1.2
Y1-54	−34	1.92	1.30	1.92	204 ± 17	1.1
Y1-66	−34	2.66	1.43	2.66	292 ± 21	1.1
D33	−34	0.588	0.766	13.4[a]	2090 ± 100	1.6
D37	−34	1.97	2.46	30.1[a]	3750 ± 150	1.3
D71	−34	0.640	4.05	25.2[a]	2770 ± 200	1.2
						av 1.3 ± 0.2
Y1-22	−45	1.74	1.59	1.74	341 ± 27	2.0
Y1-58	−45	0.501	0.888	0.501	136 ± 8	2.7
Y1-62	−45	0.881	0.685	0.881	175 ± 8	2.0
Y1-86	−45	2.01	1.66	2.01	326 ± 26	1.6
Y1-88	−45	3.11	0.599	3.11	534 ± 28	1.7
D34	−45	1.12	0.915	15.4[a]	3950 ± 300	2.5
D36	−45	0.407	0.920	9.65[a]	2810 ± 200	2.9
						av 2.2 ± 0.4
Y1-26	−65	0.779	3.42	0.779	601 ± 34	7.7
Y1-32	−65	0.956	1.20	0.956	789 ± 45	8.3
D31	−65	1.82	0.619	33.4[a]	25 400 ± 1000	7.6
D38	−65	0.587	6.44	7.24[a]	6 440 ± 300	8.9
						av 8.1 ± 0.5

[a] The sodium ion concentration in these experiments is equal to the sum of added NaCl and sodium metal.

Experimental Section

Ammonia (Matheson 99.99%) was purified by being left in contact with sodium in an evacuated stainless steel tank for at least 3 days at room temperature. The purified ammonia was next distilled and stored in another evacuated stainless steel tank. Sodium (United Mineral and Chemical Co.) was obtained in the highest purity commercially available. Sodium samples were prepared by distilling the metal twice under high vacuum into sealed capillary tubes. Quantities of sodium, estimated from the size of the capillary tubes, were distilled into the reaction systems as needed. *N,N*-Dimethylformamide (Mallinckrodt analytical reagent 4929) was purified by vacuum distillation from barium oxide into break-seal tubes. *N,N*-Dimethylacetamide (K&K 2370) was purified by vacuum distillation first from barium oxide and then from sodium metal into break-seal tubes. Weighed samples were prepared by high-vacuum distillation into tared fragile glass ampules or break-seal tubes. (2,2,2)Cryptand (PCR Inc.) and reagent grade NaCl were used as received. All work was carried out in a sealed borosilicate glass high-vacuum system (pressure less than 5×10^{-6} Torr). All glassware was washed by previously reported procedures.[14]

The stoichiometry of the reaction of *N,N*-dimethylformamide (DMF) with sodium in liquid ammonia was verified and the stoichiometry of the reaction of DMA with sodium was established by having the respective amides react with an excess of sodium in liquid ammonia. After the reactions of the amides with sodium were complete (readily determined by resistance measurements) an excess of ammonium chloride was added to the reaction mixture. The hydrogen evolved from the reaction

$$e^-_{am} + NH_4^+ \rightarrow NH_3 + \tfrac{1}{2}H_2 \qquad (5)$$

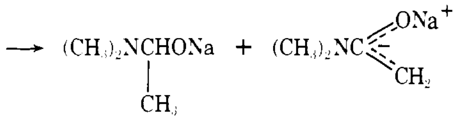
was quantitatively collected as described previously.[15] In other experiments, DMA and DMF were also permitted to react with excess amounts of sodium after which excess amounts of ammonium chloride were again added. DMA and DMF, identified by their NMR spectra, were isolated from the reaction mixtures.

The progress of the reactions was studied utilizing conventional conductometric and spectrophotometric techniques by following procedures outlined in detail elsewhere.[16] The equipment used and experimental manipulations have also been described previously.[16] The concentration of the ammoniated electron as a function of time was calculated from published conductance data[17] using procedures described elsewhere.[18] Optical data, collected as a function of time, were analyzed to yield ammoniated electron concentration vs. time data by assuming Beer's law to be valid in the concentration range of the experiments.[19]

Results and Discussion

When excess sodium was used, 0.370 mmol was required to react completely with 0.368 mmol of DMF, confirming the reported stoichiometry.[10] In the same way it was found that 0.405 mmol of sodium was needed to react completely with 0.413 mmol of DMA, thus establishing that 1 mol of sodium reacted with 1 mol of amide for this reaction also. The isolation of DMA from a protonated mixture of DMA with excess sodium is consistent with the presence of enolate anion. The presence of enolate anion and the stoichiometry are consistent with the following equation for the reaction of DMA with sodium in liquid ammonia:

$2Na + 2(CH_3)_2NCOCH_3$



$$\longrightarrow (CH_3)_2NCH(CH_3)ONa + (CH_3)_2NC(=CH_2)ONa^+ \qquad (6)$$

Tables I and II give summaries of the kinetic data for the reactions of the ammoniated electron with DMF and DMA, respectively. The pseudo-rate constants (k_{obsd}) tabulated were calculated using the 1:1 stoichiometry and following a third-order rate law, that is, first order in amide and second order in ammoniated electron:

$$-\frac{d(e^-_{am})}{dt} = \frac{dx}{dt} = k_{obsd}(e^-_{am})^2(\text{amide}) = k_{obsd}(a_0 - x)^2(b_0 - x) \qquad (7)$$

where a_0 and b_0 are the initial concentrations of ammoniated electron and amide, respectively. The curve-fitting program of Dye and Nicely[20] was used to evaluate the pseudo-third-order rate constants.

While the third-order computer plots gave excellent matches of theoretical to experimental data, the third-order constants tabulated in Tables I and II were found to vary directly with sodium ion concentration. Typical log-log plots of k_{obsd} vs. total sodium ion concentration are shown in Figure 1. The sodium dependence was confirmed by performing experiments with added NaCl (see Figure 1 and Tables I and II) and by performing a qualitative experiment in which DMF was per-

Table II. Kinetic Data for the Reactions of *N,N*-Dimethylacetamide with Sodium in Liquid Ammonia

		concn of				
expt no.	temp, °C	sodium metal, 10^3 M	amide, 10^2 M	sodium ion, 10^3 M	k_{obsd}, $M^{-2} s^{-1}$	$10^{-3} k_{obsd}/(Na^+)_t$, $M^{-3} s^{-1}$
Y1-76	−34	4.74	3.45	4.74	7.6 ± 0.2	1.6
Y1-80	−34	4.86	2.97	4.86	10 ± 0.3	1.8
Y1-92	−34	6.26	3.96	6.26	10 ± 0.3	1.6
Y3-4	−34	1.97	10.9	1.97	3.8 ± 0.2	1.9
D28	−34	0.399	4.55	72.9[a]	122 ± 10	1.7
D29	−34	1.72	1.05	64.5[a]	106 ± 10	1.6
						av 1.7 ± 0.1
Y1-74	−45	3.66	4.58	3.66	9.2 ± 0.5	2.5
Y1-90	−45	5.73	4.94	5.73	9.7 ± 0.3	1.7
Y2-4	−45	2.49	6.50	2.49	6.7 ± 0.5	2.7
Y2-96	−45	3.57	10.6	3.57	6.6 ± 0.3	1.9
D26	−45	6.87	6.19	62.5[a]	107 ± 10	1.7
D27	−45	5.42	4.92	39.4[a]	75 ± 6	1.9
						av 2.1 ± 0.4
Y1-82	−65	5.33	2.33	5.33	8.7 ± 0.2	1.6
Y1-84	−65	2.37	4.51	2.37	6.8 ± 0.2	2.8
Y2-5	−65	8.48	5.54	8.48	12 ± 0.5	1.4
D30	−65	3.43	10.7	40.1[a]	60 ± 4	1.5
						av 1.8 ± 0.5

[a] The sodium ion concentration in these experiments is equal to the sum of the added NaCl and sodium metal.

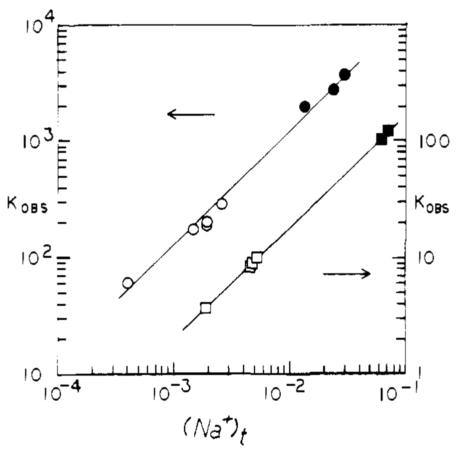


Figure 1. Log-log plot of k_{obsd} vs. the total sodium ion concentration for the reactions of DMF (circles) and DMA (squares) with sodium and liquid ammonia at −34 °C. The closed circles and squares represent experiments with added sodium chloride.

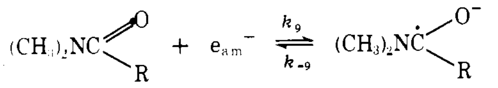
mitted to react with a sodium in liquid ammonia solution to which (2,2,2)cryptand had been added to complex the sodium ion. In the latter experiment, the half-time of the reaction was found to be approximately 50 times larger than in a comparable experiment without added complexing agent.

Unfortunately, the sodium salts which are produced in the reaction precipitate to an undetermined extent[1,10] and hence the sodium ion concentration is not completely constant throughout the reaction. However, the results of those experiments in which a large excess of NaCl was added (having an essentially constant value of sodium ion concentration) are in good agreement with those without added NaCl (see Figure 1). This agreement indicates that the precipitation of the reaction products was not extensive enough to have a serious effect on the value of the calculated rate constants. Values of $k_{obsd}/(Na^+)_t$ are also tabulated in Tables I and II. Here, $(Na^+)_t$ represents the total sodium concentration, i.e., both the ion paired and unpaired sodium cation concentration. We chose this representation because the appropriate ion pairing dissociation constants needed to calculate the unassociated sodium ion concentration are not known. Since the free sodium cation concentration should be approximately proportional to the total sodium cation concentration, our procedure will not obscure the dependence of the rate on the sodium ion concentration, as shown in Figure 1. The rate law, then, can be written

$$-\frac{d(e^-_{am})}{dt} = k(Na^+)(e^-_{am})^2(\text{amide}) \qquad (8)$$

The simplest interpretation of the above fourth-order rate law would be the sequence of reactions shown in eq 9–13. Steps 1 and 2 represent rapid equilibrium in which the concentration of products for both reactions 9 and 10 would be expected to be very small. We propose that the ion pairing, reaction 10,

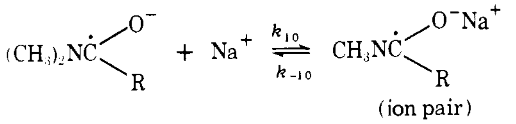
step 1



(9)

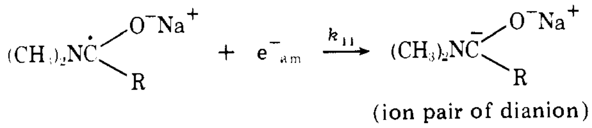
where R = H, CH_3

step 2



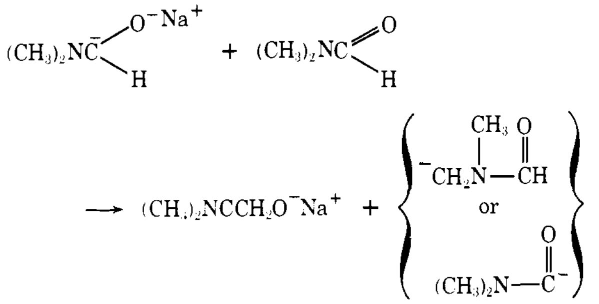
(10)

step 3



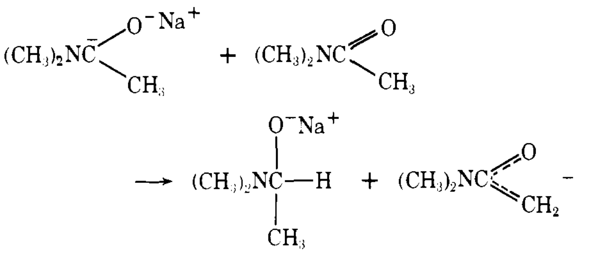
(11)

step 4 for DMF



(12)

step 4 for DMA



(13)

facilitates the formation of the dianion (step 3) by reducing coulombic repulsion. If step 3 (reaction 11) is rate limiting, that is, k_{12}/k_{11} and k_{13}/k_{11} are at least 10^3, the following rate law is obtained:

$$-\frac{d(e^-{}_{am})}{dt} = \frac{k_9k_{10}k_{11}}{k_{-9}k_{-10}}(e^-{}_{am})^2(\text{amide})(Na^+) \qquad (14)$$

Moreover, it appears reasonable to suggest that the ion pair formed in step 2 (reaction 10) can equally well result from reaction of the radical anion formed in step 1 with a nonreducible ion pair such as $Na^+{\cdot}Cl^-$. Our results do not permit us to distinguish which deprotonated form of DMF is produced in reaction 12. Also, the carbonyl anion was not proven in the earlier work where the products were acidified for analysis.[10]

Radical anions such as those proposed in step 1 (reaction 9) have been reported in pulse radiolysis studies[21] and by ESR studies utilizing a low-temperature modification of the rapid-flow reduction technique incorporating $e^-{}_{am}$ as the reactant.[22] ESR evidence for complexes similar to the ion pairing suggested in step 2 (reaction 10) of alkali metal cations with various ketyl radical anions has been reported.[23-27] Our data is consistent with protonation occurring via the dianions.[28] This is also in agreement with other reports[29] that suggest that dianions may be the sole agents of protonation in a variety of other reactions. Evidence for dianion participation in electrochemical reduction of aliphatic carbonyl compounds to glycols, or pinacols, has also been advanced.[30]

The kinetic data presented in this study are not in agreement with other proposed mechanisms,[2,31,32] largely to account for reaction products, for the reduction of saturated carbonyls by dissolved metal systems. House[31] proposed that the reduction proceeds via the sequence: (1) reduction of the ketone to the ketyl radical anion; (2) protonation of the radical anion to the ketyl radical; (3) reduction of the ketyl radical to the α-hydroxy carbanion; (4) protonation of the α-hydroxy carbanion to the alcohol. However, the kinetic data of this study are in agreement with protonation of the ion pair of the dianion.[28] Recently, Rautenstrauch and Geoffroy[32] hypothesized a pathway in which the ketyl ion pair undergoes association to the ketyl ion quadruplet which upon disproportionation yields the enolate and the alcoholate. Again this scheme is not in accord with our kinetic data. Moreover, the reaction products reported by Rautenstrauch and Geoffroy can also readily be explained if deuterium scrambling occurred prior to reduction, which is a likely possibility especially in the presence of base produced by the reaction of the alkali metal with the solvent. The reaction sequence of our proposed mechanism may also be the route of decomposition of some recently observed metal solutions.[33-35]

Upon combination of the Arrhenius equation with the equation for the temperature dependence of the equilibrium constant the following expression for the observed activation energy ($E_{a_{obsd}}$) is obtained:

$$E_{a_{obsd}} = E_{a_{11}} + \Delta H°_9 + \Delta H°_{10} \qquad (15)$$

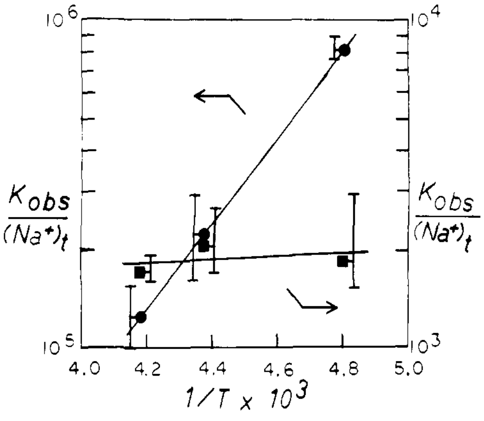


Figure 2. Semilog plots of $k_{obsd}/(Na^+)_t$ vs. $1/T$ for the reactions of sodium with DMF (circles) and DMA (squares) in liquid ammonia.

Semilogarithmic plots of $k_{obsd}/(Na^+)_t$ vs. $1/T$ for the DMF and DMA reactions are shown in Figure 2. $E_{a_{obsd}}$ for the reaction of DMF with sodium in liquid ammonia is equal to −6.0 ± 0.5 kcal/mol and is essentially negligible for the DMA reactions. The most likely reason for the low or negative temperature dependence of these reactions is the stabilization of the free radical in step 1 (reaction 9) at lower temperatures. In other words, step 1 is exothermic and $\Delta H°_9$ is negative. Moreover, $\Delta H°_{10}$ is also expected to be negative.[36] The lack of temperature effect on the rate of the reaction of DMA, contrasted to DMF, is probably due to a larger activation energy in step 3 (reaction 11). It seems reasonable to suggest that $E_{a_{11}}$ would be 5-6 kcal greater for the DMA sodium reaction than for the DMF sodium reaction owing to the expected inductive effect of the methyl group.[16,37] Similar trends in activation energies attributed to inductive effects have been observed previously for other reactions involving the ammoniated electron.[2,16] When an attempt was made to extend this study to *N,N*-diethylacetamide (DEA) it was found that this compound did not react at an observable rate with sodium in liquid ammonia. We then found that sodium would dissolve in DEA and other structurally related compounds. These results have been reported elsewhere.[33]

Acknowledgment. We wish to thank Mr. Cliff L. King for his assistance in processing the data.

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The Nature of the Lowest Excited State in *fac*-Tricarbonylhalobis(4-phenylpyridine)rhenium(I) and *fac*-Tricarbonylhalobis(4,4′-bipyridine)rhenium(I): Emissive Organometallic Complexes in Fluid Solution[1]

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Abstract: Electronic absorption and emission spectral studies are reported for *fac*-$XRe(CO)_3L_2$ (X = Cl, Br, I; L = 4-phenylpyridine, 4,4′-bipyridine) complexes in solution at 298 and 77 K. All complexes are emissive at 298 K from a state which is assigned as a Re → LCT state having considerable triplet character, and in every case the emission intensifies, blue shifts, and becomes longer lived at 77 K. For L = 4-phenylpyridine the complexes have a 77 K emissive state which has considerable intraligand (IL) (π–π^*) triplet character, whereas the 4,4′-bipyridine complexes exhibit emission which is dominated by Re → LCT character at any temperature between 77 and 298 K. The temperature dependence, over the range 30–300 K, of the emission lifetime and quantum yield in EPA, 2-propanol, and as a solid for *fac*-$ClRe(CO)_3$(4-phenylpyridine)$_2$ shows that both temperature and medium rigidity significantly influence the emission properties. The temperature dependence of the emission properties shows that both the nonradiative and radiative decay constants change with temperature, in accord with a variable admixture of IL and ReLCT character of the emissive state. Quenching of the excited *fac*-$XRe(CO)_3$(4-phenylpyridine)$_2$ complexes by *trans*-stilbene occurs at a diffusion-controlled rate and produces the spectroscopic *trans*-stilbene triplet which decays to the characteristic ratio of *cis*- and *trans*-stilbene. This result supports the conclusion that the emissive state has considerable triplet character.

Elaboration of the known bimolecular reactions of electronic excited organometallic complexes hinges on the discovery of excited species which persist in fluid solution long enough to suffer some reactive quenching process. Often the lowest excited states of mononuclear organometallics involve orbitals of termination and/or origin which are very consequential with respect to metal–ligand bonding. Lowest lying excited states which are ligand field (d–d) in character are believed to be responsible for the extreme photosensitivity of metal carbonyl complexes with respect to ligand dissociation.[2] Metal–metal bonded complexes often exhibit lowest lying excited states which involve depopulation of the σ_b (with respect to the metal–metal framework) orbital and/or population of the σ^* orbital.[3] Such excited states undergo dissociative-type metal–metal bond homolysis; dinuclear species in particular are efficiently fragmented with optical excitation. To design molecules which have long-lived excited states in solution, one must seemingly avoid introduction of lowest excited states involving transitions which terminate in orbitals which are σ^* in character.

At the present time there are a number of transition-metal complexes which exhibit optically excited luminescence in fluid solution under conditions where photochemistry is possible. Observation of luminescence is an indicator that the excited species is long lived enough to suffer bimolecular reaction in competition with dissociative excited-state reactions. And importantly, the observation of emission allows some key excited-state properties (energy, lifetime, one-electron character) to be determined directly and relatively easily. The solution emission properties of certain Cr(III) complexes are under intense study,[4] in connection to photosubstitution. Detectable luminescence from excited $[Ru(2,2'\text{-}bpy)_3]^{2+}$ and related complexes[5] has certainly been a key to the prevailing interest in its solution photochemistry; examples of simple collisional electronic energy transfer,[6] oxidation–reduction,[7] proton transfer,[8] and medium effects such as those resulting from ion pairing[9] and solvent deuteration[10] have been reported. Other examples of low-spin d^6 emitters in fluid solution are Os(II) and Ir(III) complexes of 1,10-phenanthroline[11] and related ligands.

Organometallics $M(CNPh)_6$ (M = Cr, Mo, W) have been found[12] to be luminescent in solution and have been found to undergo bimolecular reactions in the excited state. Recently, the dinuclear system Rh_2(1,3-diisocyanopropane)$_4^{2+}$ has been found to be emissive[13] in solution and has been shown to undergo excited-state electron-transfer reactions which yield H_2 from acidic aqueous solutions.[14] The only metal carbonyls known to be emissive in fluid solution are *fac*-$ClRe(CO)_3$(phen) and related complexes.[15] A study of the excited-state electron-transfer properties of this species has recently been completed.[16] A preliminary account[17] describes the emission behavior of *fac*-$XRe(CO)_3$(benzoylpyridine)$_2$ representing a set of metal carbonyl complexes which are emissive in fluid solution but involve no chelating ligand system.

0002-7863/79/1501-2888$01.00/0