

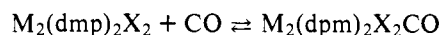
Figure 1. A view of the coordination geometry of **1**, $\text{Mo}_2(\text{OBu})_6(\text{CO})$, showing the main internuclear distances. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density. The tertiary butyl groups are omitted for clarity.

metal atom is a distorted square pyramid with the Mo to carbonyl carbon bond at the apex.

We believe the Mo-Mo bond has a formal bond order of 2. The molecule is diamagnetic and the electron counting for each molybdenum atom may be conducted as follows: the neutral Mo atom has 6 electrons, each terminal RO group contributes 1 as does the bridging CO group, and the pair of bridging RO groups contribute 3 electrons to each metal atom. Thus, before metal-metal bond formation is considered, each metal atom has 12 electrons. To account readily for diamagnetism, an Mo-Mo bond of even order should be present. With a distance of 2.489 (1) Å, the most reasonable conclusion is a bond order of 2.

Metal-metal bonds of orders 1, 3, and 4 are, of course, very numerous and well known, but not many double bonds have been observed to date. For molybdenum there have not previously been any unambiguous cases⁵ except for that in $\text{Mo}_2(\text{OPr})_8$,⁶ where the Mo-Mo distance, 2.523 (1) Å, is very similar to the one found here. It is noteworthy that in the isopropoxide also the metal atoms have formal 14-electron configurations, but the coordination polyhedron is a trigonal bipyramid.

In conclusion we emphasize the following. (1) This work provides the first synthesis and structural characterization of a compound in which a carbonyl ligand bridges a metal-metal double bond, as well as only the second unambiguous example of an Mo=Mo bond. (2) To our knowledge the only reactions comparable to (1) are the very recently reported^{7,8} reactions of platinum and palladium complexes of bis(diphenylphosphino)methane, dpm, viz.,



where X = Cl, Br. (3) The formation of $\text{Mo}(\text{CO})_6$ under the extremely mild conditions reported here is quite remarkable. Indeed, the reaction between $\text{Mo}_2(\text{OR})_6$ compounds and CO may prove synthetically useful for the synthesis of labeled compounds $\text{Mo}(\text{*CO})_6$.

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Supplementary Material Available: A table of atomic positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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 (2) Additions were made using standard vacuum line techniques.
 (3) Anal. Calcd for $\text{Mo}(\text{OCHMe}_2)_3\text{CO}$: C, 39.88; H, 7.03. Found: C, 39.88; H, 7.06.
 (4) Crystal data for $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\text{CO})$: $a = 17.827$ (3), $b = 9.335$ (2), $c = 19.447$ (4) Å; $\alpha = \beta = \gamma = 90.00^\circ$; $V = 3236$ (1) Å³; $Z = 4$. Space group $Cmcc2_1$ (No. 36). Unique data (1532 reflections) having $0.0^\circ < 2\theta$ (Mo K α) $\leq 50.0^\circ$ were collected at 22 °C using Mo K α radiation ($\lambda = 0.710730$ Å) and the 1237 reflections having $I > 3\sigma(I)$ were retained as observed. The structure was solved using standard heavy-atom methods and refined to convergence using anisotropic thermal parameters for molybdenum and oxygen atoms and isotropic thermal parameters for the carbon atoms. Hydrogen atoms were not located. Final residuals are $R = 0.067$ and $R_w = 0.085$; the esd of an observation of unit weight is 1.958.
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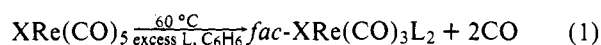
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Simultaneous Multiple Emissions from $\text{fac-XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$: $n-\pi^*$ Intraligand and Charge-Transfer Emission at Low Temperature

Sir:

We wish to report some interesting results concerning the excited-state decay of $\text{fac-XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$ (X = Cl, Br, I). These organometallics exhibit both long-lived and short-lived emissions at 77 K which are associated with an $n-\pi^*$ intraligand triplet excited state and a $\text{Re} \rightarrow 3\text{-benzoylpyridine CT}$ excited state, respectively. Aside from the fact that these are the first examples of species that exhibit $n-\pi^*$ intraligand emission, it is unusual that two emissions are observed at a similar energy. A similar phenomenon was observed in $\text{Ir}(1,10\text{-phenanthroline})_2\text{Cl}_2^+$ where two decay times were observed and associated with two states of different orbital configuration.¹ In another example of multiple emissions,² complexes of the type $\text{Rh}(2,2'\text{-bipyridine})_2(1,10\text{-phenanthroline})^{3+}$ exhibit two intraligand $\pi-\pi^*$ emissions associated with the two different ligands. Study of the excited-state decay of intraligand states is necessary for the development of phototemplate reactions of coordinated molecules.

Complexes $\text{fac-XRe}(\text{CO})_3\text{L}_2$ (L = 3-benzoylpyridine, 4-benzoylpyridine; X = Cl, Br, I) can be synthesized according to



following literature procedures for other pyridine complexes.³ Isolation of the solid product is by addition of *n*-pentane to concentrated C_6H_6 solutions. Repeated washing of the solid with alkane serves to remove any excess L or unreacted $\text{XRe}(\text{CO})_5$. Elemental analyses for two representative complexes are satisfactory. Calcd for $\text{ClRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$: C, 48.25; H, 2.70; N, 4.17. Found: C, 48.13; H, 2.78; N, 4.08. Found for $\text{ClRe}(\text{CO})_3(4\text{-benzoylpyridine})_2$: C, 48.41; H, 2.79; N, 4.25. All of the complexes exhibit the characteristic three-band infrared spectrum in the CO stretching region: 2030-2032, 1929-1932, 1894-1900 cm^{-1} . Further, the complexes exhibit a ketone carbonyl stretch with an integrated intensity twice (within 10%) that for the free ligand at the same concentration.

Table I. Excited-State Properties of *fac*-XRe(CO)₃(benzoylpyridine)₂ Complexes (X = Cl, Br, I)

Compd	Temp, K	Solvent	Total emission, ^a band max, cm ⁻¹ × 10 ⁻³ (lifetime, μs)	Long-lived emission, ^b band max, cm ⁻¹ × 10 ⁻³ (lifetime, μs)
ClRe(CO) ₃ (3-benzoylpyridine) ₂	298	Benzene	18.3 (≤0.5)	19.5, 21.1, 22.7, 24.2 (1400)
	77	EPA	19.5, 21.1, 22.6, 24.2 (18.0 and 1400)	
BrRe(CO) ₃ (3-benzoylpyridine) ₂	298	Benzene	18.3 (≤0.5)	19.3, 20.9, 22.6, 24.2 (1300)
	77	EPA	20.9, 22.5, 24.2 (12.5 and 1300)	
IRe(CO) ₃ (3-benzoylpyridine) ₂	298	Benzene	17.9 (≤0.5)	19.5, 21.0, 22.7, 24.2 (1200)
	77	EPA	20.8, 24.2 (14.5 and 1200)	
ClRe(CO) ₃ (4-benzoylpyridine) ₂	298	Benzene	16.7 (≤0.5)	19.5, 21.0, 22.7, 24.2 (1200)
	77	EPA	19.38 (39)	
BrRe(CO) ₃ (4-benzoylpyridine) ₂	298	Benzene	16.62 (≤0.5)	19.5, 21.0, 22.7, 24.2 (1200)
	77	EPA	19.49 (38)	
IRe(CO) ₃ (4-benzoylpyridine) ₂	298	Benzene	16.56 (≤0.5)	19.5, 21.0, 22.7, 24.2 (1200)
	77	EPA	19.05 (36)	
3-Benzoylpyridine	77	EPA	18.1, 19.7, 21.3, 22.9, 24.6 (5000)	Same as total emission
4-Benzoylpyridine	77	EPA	16.9, 19.2, 20.7, 22.3, 24.0 (3200)	Same as total emission

^a Total emission spectra were obtained from Aminco-Bowman spectrofluorometer; room temperature spectra are corrected for variation in response of detector; 77 K spectral maxima represent raw data; the detector sensitivity varies by less than a factor of 2 over the wavelength range of interest and band maxima are within 200 cm⁻¹. ^b Long-lived component of emission spectra obtained from Aminco-Bowman spectrofluorometer using the phosphoroscope attachment. Lifetimes represent the long-lived component of the emission.

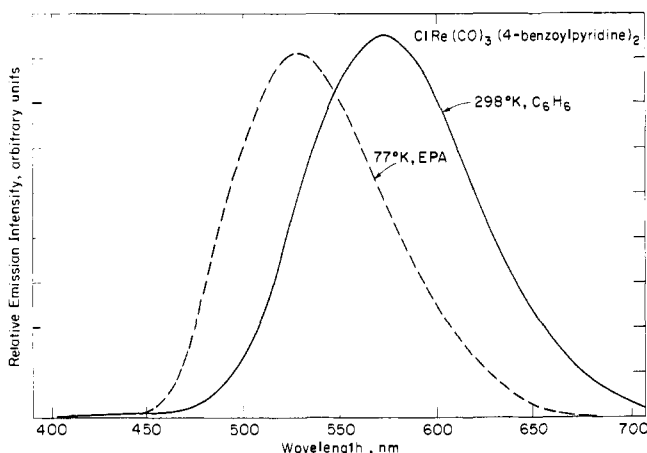


Figure 1. Total emission spectra in solution excited at 330 nm; concentration is $\sim 10^{-4}$ M. The 298 and 77 K emissions are not shown at the same sensitivity.

As found earlier for a number of other *fac*-XRe(CO)₃L₂ complexes,^{4,5} we find that the 3- and 4-benzoylpyridine complexes are emissive in 298 K fluid solution (Figures 1 and 2 and Table I). The structureless emission with a lifetime of $\sim 10^{-6}$ s is typical of emission associated with the Re \rightarrow L CT transition in absorption. Generally, such transitions are at lower energy for L = 4-benzoylpyridine than for L = 3-benzoylpyridine; e.g., in the d⁶ complexes W(CO)₅L⁶ and (η^5 -C₅H₅)-Re(CO)₂L⁷, the 298 K M \rightarrow L CT absorption maximum is ~ 2000 cm⁻¹ lower in energy in the 4- compared with the 3-benzoylpyridine. Here we find lower energy 298 K emission and absorption in the *fac*-XRe(CO)₃L₂ species for the 4-benzoylpyridine (Table I). Thus, we assign the 298 K emission in the complexes to a CT transition. Consistent with these results, the absorption spectra of the complexes are in accord with a lower energy Re \rightarrow L CT in the 4-benzoylpyridine complex. Generally, the 4-benzoylpyridine complexes exhibit a fairly well-resolved first absorption at ~ 330 nm (ϵ 10 000) in benzene. By way of contrast the 3-benzoylpyridine complexes exhibit a higher energy first absorption which appears as a shoulder at ~ 295 nm on the π - π^* intraligand absorption tail.

The unusual feature of these complexes is found in the 77 K emission properties. The 4-benzoylpyridine complexes exhibit the usual effect:^{4,5} the emission blue shifts, intensifies, and becomes somewhat longer lived, but remains featureless. However, the 3-benzoylpyridine complexes behave differently.

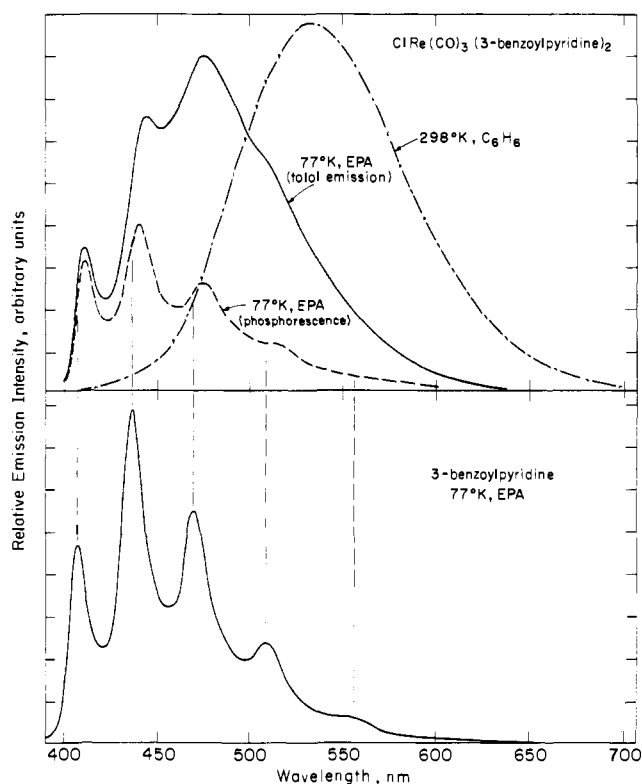
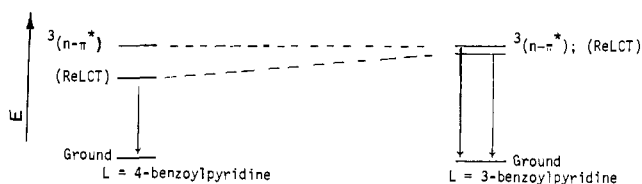


Figure 2. Emission spectra excited at 330 nm for 10^{-4} M solutions. The spectra are not shown at the same sensitivity. All spectra are total emission spectra except that one marked "phosphorescence" which was recorded with the phosphoroscope in place in the Aminco-Bowman emission spectrophotometer. The phosphoroscope allows only the detection of emissions longer than ~ 1.0 ms.

The total emission spectrum exhibits some structure (Figure 2) and, by using the phosphoroscope attachment of our Aminco-Bowman spectrofluorometer, a long-lived, very well-structured, component of the emission can be observed. The phosphorescence of the complexes and that of free 3-benzoylpyridine⁸ are very similar, but two facts unequivocally rule out the possibility that the long-lived emission of the complexes is due to free ligand impurity. First, the relative intensities and the position of the emission peaks are different (Figure 2) and the emission lifetimes are different (Table I). Subtraction of the long-lived emission from the total emission leaves a featureless spectrum. This shorter lived emission of

Scheme I. 77 K State Diagram



the 3-benzoylpyridine complexes at 77 K is longer lived than the 298 K emission, as usual, and we assign this component of the emission to the same CT transition as at 298 K. The long-lived, structured emission is attributable to a slightly perturbed $n-\pi^*$ triplet state of the 3-benzoylpyridine. In every case the total emission quantum yield is high, but the relative amount of CT and $n-\pi^*$ emission depends on X. For X = Cl and Br the relative yields are roughly equal, whereas for X = I the CT emission is much more prominent. It is noteworthy that the CT state is slightly lower for X = I than for X = Cl and Br from the emission data at 298 or 77 K for both 3- and 4-benzoylpyridine complexes (Table I).

The state orderings for the 3- and 4-benzoylpyridine complexes are shown in Scheme I. The facts that the CT state is at lower energy and that we observe no long-lived emission from the 4-benzoylpyridine under conditions used for the 3-benzoylpyridine complexes are consistent. For the 3-benzoylpyridine complexes it is apparent that the lowest Re L CT and $n-\pi^*$ states are not thermally equilibrated at 77 K. Non-interconvertibility of the two emissive states is likely a consequence of significant differences in their geometry. Excitation spectra for the $n-\pi^*$ and the Re L CT emission of the 3-benzoylpyridine complexes show that upper states relax to both of the emitting states; i.e., the relative efficiency of the $n-\pi^*$ and the Re L CT emissions is independent of the excitation wavelength and the corrected excitation spectrum strongly parallels the absorption spectrum of the complex. The relatively weak $n-\pi^*$ absorption associated with the diaryl ketone is just barely perceptible on the side of the Re \rightarrow L CT absorption in the 3-benzoylpyridine complex, and likewise is not a well-defined feature in the excitation spectrum of the complex. The excitation spectrum of the free ligand is beautifully structured in the ~ 350 -nm region, under the same measurement conditions.

Acknowledgment. We thank the National Science Foundation for support of this work.

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Importance of Apolar Binding in Complex Formation of Cyclodextrins with Adamantanecarboxylate

Sir:

We wish to report here the importance of apolar binding in complex formation of cyclodextrins (CDs). CDs have served as enzyme models for many years, mainly because they form complexes with substrates prior to reaction; this is consistent with enzymatic reactions.^{1,2} Furthermore, complex formation of CDs with guest compounds such as drugs, insecticides, etc., causes new physicochemical features, leading to practical usages.² Thus, information on the binding forces of complex formation is obviously very important. The binding forces between CDs and guest compounds, however, are still the subject of controversy involving four proposals: (1) van der Waals interactions;^{3,4} (2) hydrogen bonding;⁵ (3) release of high energy water molecules from the cavity of CD;^{3,6} and (4) release of strain energy in the macromolecular ring of CD.⁷ Several studies were made to evaluate the contribution of the four kinds of binding forces.^{4b,8} However, apolar binding, which is operative in the formation of enzyme-substrate complexes, was regarded as unimportant in the formation of CD-guest complexes, since complexation is usually associated with a favorable enthalpy change and an unfavorable (or slightly favorable) entropy change.^{2,6} Usually apolar binding is characterized by a very favorable entropy change.⁹ In this paper, we evaluate the role of apolar binding in complexation of CDs with guest compounds.

Complexation of 1-adamantanecarboxylate (**1**) with α -cyclodextrin (α -CD) is a good system to examine the contribution of apolar binding in complexation. A molecular model study in a previous paper³ showed that **1** is too bulky to be included in the cavity of α -CD; rather **1** sits *on top* of the cavity. Thus, factors 1-4 can be minimized in complexation of **1** with α -CD. In the present paper, the enthalpy change (ΔH) and the entropy change (ΔS) for complexation of **1** with α -CD are determined. For comparison, the values of ΔH and ΔS for complexation of **1** with β -cyclodextrin (β -CD), which has a cavity large enough to almost completely accommodate **1** *inside*, are also measured.

The values of ΔH and ΔS were evaluated from the dissociation constants of the CD-**1** complexes (K_d) at different temperatures. K_d 's were determined by competitive inhibition of the CD-accelerated cleavage of *m*-nitrophenyl acetate by **1**. As shown in a literature,³ the *Y* intercept in the plot of $[1]$ vs. $(k_2 - k_{\text{obsd}})/(k_{\text{obsd}} - k_{\text{un}})$, keeping $[\text{CD}]$ constant, gave K_d .¹⁰ Here, k_2 and k_{un} are the rate constants of the CD-*m*-nitrophenyl acetate complex and that of the ester in the absence of CD, both of which can be determined in the absence of **1**.

Table I shows K_d 's of CD-**1** complexes at different temperatures, and the enthalpy and entropy changes for complexation of CDs with **1**. Experimental errors in K_d 's (and in ΔH and ΔS) were estimated by consideration of the errors in k_2 's as well as the deviations in the plots of $[1]$ vs. $(k_2 - k_{\text{obsd}})/(k_{\text{obsd}} - k_{\text{un}})$ (see note 11). The errors in Table I are maximal errors.

Complexation of **1** with α -CD exhibited a quite favorable ΔS but only a small favorable ΔH ; this is in contrast to a large favorable ΔH reported for many inclusion complexes of CDs.^{2,6} The stabilization energy due to a favorable ΔS is >70% of the total stabilization energy, whereas a (favorable) ΔH showed <30% contribution. The large favorable ΔS can be attributed to a transfer of **1** from aqueous medium to more apolar medium such as the cavity of CD. This transfer requires breakdown of structural water molecules around **1**, resulting in a large favorable ΔS and a small unfavorable ΔH . This is obviously apolar binding.

On the other hand, complexation of **1** with β -CD, in which **1** can be almost perfectly included in the larger cavity of β -CD,