Solution Equilibria between C-Bonded CO and Π-CO Ligands in Four-Iron Clusters and Cleavage of the Π-CO Ligand

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Abstract: The interaction of the Lewis acids $[R_3PAu]^+$, $[LCu^+]$, and $[CH_3Hg]^+$ with the tetrahedral cluster $[Fe_4(CO)_{13}]^{2-}$ produces an equilibrium mixture of two isomers in solution. For one of these, the iron framework remains tetrahedral and for the other it exists as a butterfly with a Π-CO ligand between the wingtips. Multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, or ^{199}Hg) was employed to determine the position of the equilibrium between the tetrahedral and butterfly isomers. Judging from CO stretching frequencies, the proportion of the butterfly isomer is greatest when the strongest Lewis acid ligand is employed. Butterfly formation is complete when an additional electrophile is attached to the II-CO oxygen. Cleavage of the II-CO with acid to form a carbido cluster also was observed by variable-temperature NMR spectroscopy. This reaction provides convincing evidence that the Π-CO is highly activated toward CO cleavage.

Systematic methods for the formation of Π-CO ligands have been developed for dinuclear[1,2] systems and the accompanying paper[3] reports a systematic route to Π-CO formation in the four-iron cluster $[Fe_4(CO)_{13}]^{2-}$ by coordination of electron-acceptor ligands, A, to the metal framework (Table I). X-ray crystallographic results, solid-state IR, and low-temperature NMR spectroscopy reveal that the addition of a Lewis acid ligand, A^+, to $[Fe_4(CO)_{13}]^{2-}$ results in two isomeric forms of $[Fe_4(A)(CO)_{13}]^-$. In one of these isomers, the iron core retains the tetrahedral structure of the $[Fe_4(CO)_{13}]^{2-}$ starting material and the Lewis acid caps one face of this tetrahedron. The other product occurs in a four-iron butterfly geometry with the Lewis acid bridging the hinge of the butterfly. The cluster geometries observed in the solid state for the various $[Fe_4(A)(CO)_{13}]^-$ complexes are depicted in Scheme I. In this paper we report the solution equilibria between these two forms as determined by variable-temperature and multinuclear NMR spectroscopy, and we also describe the selective cleavage of C- and O-bonded CO as monitored by NMR spectroscopy.

The spectroscopic observation of individual isomers of the $[Fe_4(A)(CO)_{13}]^-$ compounds was achieved by dissolving the crystalline sample of one isomeric form at a temperature which is sufficiently low to prevent interconversion of the isomers and then obtaining multinuclear NMR spectra at this low temperature. Similarly, we found that it was possible to follow the reaction of a single isomer of $[Fe_4(A)(CO)_{13}]^-$ with a protic acid by performing all of the chemistry and spectroscopy at low temperatures.

Experimental Section

The preparation of the organometallic complexes was described in the previous paper.[3] HSO_3F (Aldrich) was purified by distillation under reduced pressure. The NMR and IR instrumentation is described elsewhere.[3]

Low-Temperature Dissolution and NMR of $[Fe_4(A)(CO)_{13}]^-$ Salts. The appropriate ^{13}CO-enriched crystalline salt of $[Fe_4(A)(CO)_{13}]^-$ was loaded in a 10-mm NMR tube in the glovebox and the tube was fitted with a rubber septum. The tube was cooled to –80 °C and solvent, which had been precooled to –80 °C, was added via syringe. The tube was then rapidly transferred to the NMR tube probe which had been precooled to –80 °C.

Low-Temperature NMR of Protonated $[Fe_4(A)(CO)_{13}]^-$. The ^{13}CO-enriched $[Fe_4(A)(CO)_{13}]^-$ complex salt was weighed in the glovebox and loaded into a 10-mm NMR tube which was fitted with a rubber septum. The NMR tube was kept at –80 °C while solvent, precooled to –80 °C, and 1 equiv of HSO_3F were added via syringe. The tube was then rapidly transferred to the precooled, –80 °C, NMR probe, and the ^{13}C, ^{1}H, and ^{31}P NMR spectra were obtained at this low temperature.

(1) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.
(2) (a) Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* **1980**, *201*, C39. (b) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.
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Table I. Infrared Stretching Frequencies[a]

compound		CH₂Cl₂ soln
1	$[PPN]_2[Fe_4(CO)_{13}]$	2018 w, 1943 vs
2	$[PPN][HFe_4(CO)_{13}]$	2014 vs, 1989 s, 1970 m sh
3	$[K(18\text{-crown-}6)][Fe_4(AuPR_3)(CO)_{13}]$ (R = Et or Ph)	2038 m, 1995 w, sh, 1973 vs
4	$[PPN][Fe_4(AuPR_3)(CO)_{13}]$ (R = Et or Ph)	2038 m, 1971 vs, 1947 sh
5	$[PPN][Fe_4(CuL)(CO)_{13}]$ (L = PPh₃ or 2,6-$(CH_3)_2C_6H_3NC$)	2036 w, 1997 sh, 1973 vs, 1910 br, sh (ν_{N-C} 2160)
6	$[PPN][Fe_4(HgCH_3)(CO)_{13}]$ (butterfly)	2052 w, 2017 m, 1993 vs. 1965 sh
6	$[PPN][Fe_4(HgCH_3)(CO)_{13}]$ (tetrahedron)	2052 w, 2017 m, 1993 vs, 1965 sh
7	$Fe_4(AuPEt_3)(CO)_{12}(COMe)$	2072 w, 2037 vs, 2011 vs, 1988 s sh, 1920 w sh

[a] vs = very strong; s = strong; m = medium; w = weak; sh = shoulder; br = broad.

Scheme I
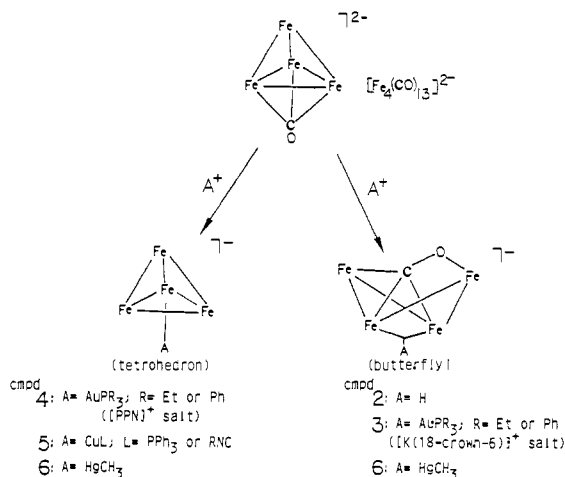
Results and Discussion

Evidence for Isomers in Solution. In the accompanying paper, a single-crystal X-ray diffraction study demonstrated that $[PPN][Fe_4(CuPPh_3)(CO)_{13}]$ (**5a**) contains a tetrahedral array of iron atoms.[3] When this compound is dissolved at –80 °C and the ^{13}C NMR spectrum is obtained at that temperature, a single sharp resonance is observed in the carbonyl region at 220.7 ppm. We concluded that the CO ligands in the tetrahedral form of

Table II. ^{13}C and ^{31}P NMR Spectroscopic Data[a-c]

| compd	$^{13}C\{^1H\}$		$^{31}P\{^1H\}$	
	I[d]	II[e]	I[d]	II[e]
1	227.8	227.8		
2	279.8 (1), 221.5 (2), 219.7 (1), 217.5 (1), 215.6 (2), 211.4 (2), 209.5 (2), 209.1 (2)	279.8, 221.5, 219.7, 217.5, 216.7, 215.6, 211.4, 209.5, 209.1		
3a	284.6 (1), 224.0 (2), 223.1 (1), 220.6 (2), 217.8 (1), 216.1 (2), 213.5 (2), 212.4 (2)	284.6, 224.5, 222.8, 220.7, 216.1, 213.8, 212.5	62.4 (1), 57.7 (14)	62.4 (6), 57.7 (1)
3b	284.7 (1), 224.0 (2), 223.0 (1), 220.9 (2), 218.4 (1), 215.6 (2), 213.3 (2), 212.0 (2)	284.7, 223.9, 222.4, 220.9, 218.4, 215.6, 213.3, 212.0	58.3	60.4 (6), 58.3 (1)
4a	222.0		57.8	
4b	221.7	284.9, 223.2, 221.6, 219.8, 217.7, 215.2, 212.4, 211.1	56.8	56.7 (6), 54.4 (1)
5a	220.7	287.9, 220.7, 210.0	3.03br	
5b	220.4	286.7, 221.5, 220.4, 217.4, 212.9, 209.7		
6 (butterfly)	282.6 (1), 221.1 (1), 220.9 (2), 216.5 (2), 215.1 (1), 212.4 (2), 210.5 (2), 207.9 (2)	282.6, 221.0, 220.1, 219.1, 216.5, 215.1, 212.4, 210.5, 207.8		
7	303.5 (1), 219.9 (2), 216.1 (2), 214.3 (1), 212.8 (2), 211.3 (1), 208.3 (2), 207.5 (2)	303.5, 219.9, 216.1, 214.3, 212.8, 211.3, 208.3, 207.5	58.1	58.1

[a] External references: ^{13}C, SiMe$_4$; ^{31}P, 85% H$_3$PO$_4$. [b] All in CD$_2$Cl$_2$ except **3a** and **3b** in (CD$_3$)$_2$CO. [c] Values in parentheses are relative intensities. [d] Spectra of samples dissolved at −80 °C and recorded at −80 °C. [e] Spectra of samples dissolved at −80 °C, warmed to room temperature, then recorded at −80 °C.

$[Fe_4(CuPPh_3)(CO)_{13}]^-$ are interchanging rapidly on the NMR time scale. Similarly, IR data indicate the presence of a Fe$_4$ tetrahedron in $[PPN][Fe_4(AuPPh_3)(CO)_{13}]$ (**4b**)[3] and again a single ^{13}C NMR signal is seen at 221.7 ppm for a sample which was dissolved and run at low temperature.

Solutions of **4** and **5** were warmed to room temperature and then recooled to −80 °C, and ^{13}C NMR spectra were obtained. For each solution a downfield resonance due to the Π-CO ligand as well as a new set of resonances in the terminal CO region were observed (Table II, Figure 1a). The resonance due to the tetrahedral isomer is still present, and judging from relative intensities this tetrahedral form predominates for both of these solutions. The isomerization process for complexes **4** and **5** can be described by eq 1. The ^{31}P NMR spectrum also is informative for the Au complex **4**. At low temperature a single ^{31}P NMR resonance is observed and this resonance is assigned to the tetrahedral form. For solutions which have been warmed to +20 °C and then cooled to −80 °C, two ^{31}P NMR resonances appear. The original peak of the tetrahedral isomer is still present and predominant, but a new upfield resonance assigned to the Π-CO isomer also appears (Table II, Figure 1b). Consistent with the ^{13}C NMR spectroscopic results, the Π-CO isomer is present in lower concentration than the tetrahedral form (1:6 butterfly:tetrahedron). This ratio does not change when PEt$_3$ replaced PPh$_3$ in **4** and does not change significantly over the temperature range investigated, −80° to +20 °C. A similar lack of temperature dependence for the concentrations of the two isomers of $[HFe_4(CO)_{13}]^-$ was reported previously.[4,5] It is difficult to determined the analogous ratio for the two isomers of $[Fe_4(CuPPh_3)(CO)_{13}]^-$ because the quadrupolar nature of Cu broadens the ^{31}P NMR signals so that there is significant overlap of signals and integration is unreliable.
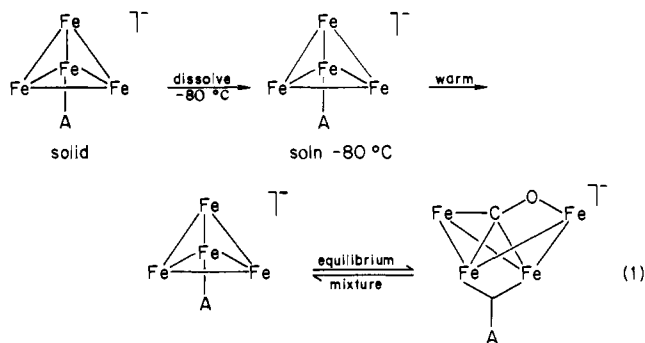
The low-temperature ^{13}C NMR spectra of $[Fe_4(HgCH_3)(CO)_{13}]^-$ (**6**(butterfly)), and $[K(18\text{-crown-6})][Fe_4(AuPR_3)(CO)_{13}]$ (**3**) both show the presence of a Π-CO ligand at low fields (Table II). These compounds also show both the appropriate number of bands, seven, in the terminal CO region as well as the correct relative intensities for a butterfly molecule.[3,4] When the solution of each compound is warmed, two ^{13}C NMR signals, of relative intensities 1 and 2 (designated by the labels a and b in Figure 2) collapse and coalesce. A rotational process involving the CO's on one of the wingtip iron atoms is indicated by the relative intensities. It appears likely that this rotational process occurs for the CO ligands on the iron which is not bonded to the oxygen of the Π-CO because this wingtip metal atom is the least sterically congested. In addition to this rotational process, a new resonance (not at a position corresponding to the weighted average of the coalesced signals) is observed for both compounds. This feature (labeled c in Figure 2) gains intensity as the solution temperature is raised. This pattern is consistent with the conversion of the butterfly isomer to a tetrahedron, (Table II and eq 2).

$$\text{(2)}$$
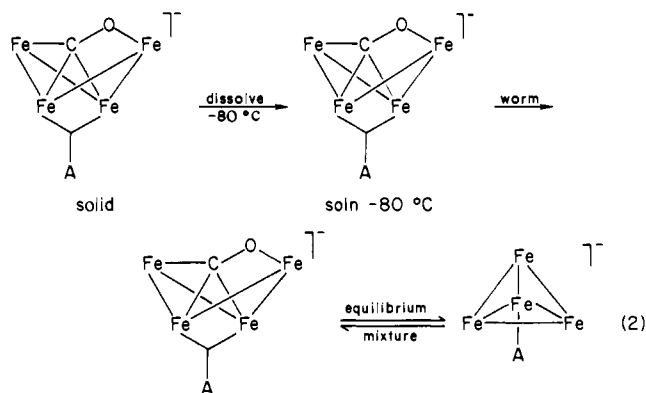
The isomerization process is easily monitored for compound **3** by $^{31}P\{^1H\}$ NMR spectroscopy. Only a single resonance is observed for the solid dissolved at low temperatures, but raising the temperature results in the generation of a new downfield resonance (Table II). The variable-temperature ^{31}P NMR spectrum of $[K(18\text{-crown-6})][Fe_4(AuPR_3)(CO)_{13}]$ shows a decrease in intensity for the butterfly isomer as the temperature is increased, while a concurrent increase in the resonance for the tetrahedral form is observed in (Figure 3). At −35 °C and above equilibrium is established between tetrahedral and butterfly isomers for both the $[K(18\text{-crown-6})]^+$ and $[PPN]^+$ salts of $[Fe_4(AuPR_3)(CO)_{13}]^-$. When this equilibrium mixture is cooled, the rate of equilibration between the tetrahedral and butterfly isomers becomes quite slow and no change in the intensities of the signals for these two isomers is seen down to −80 °C. At none of the

$$\text{(1)}$$

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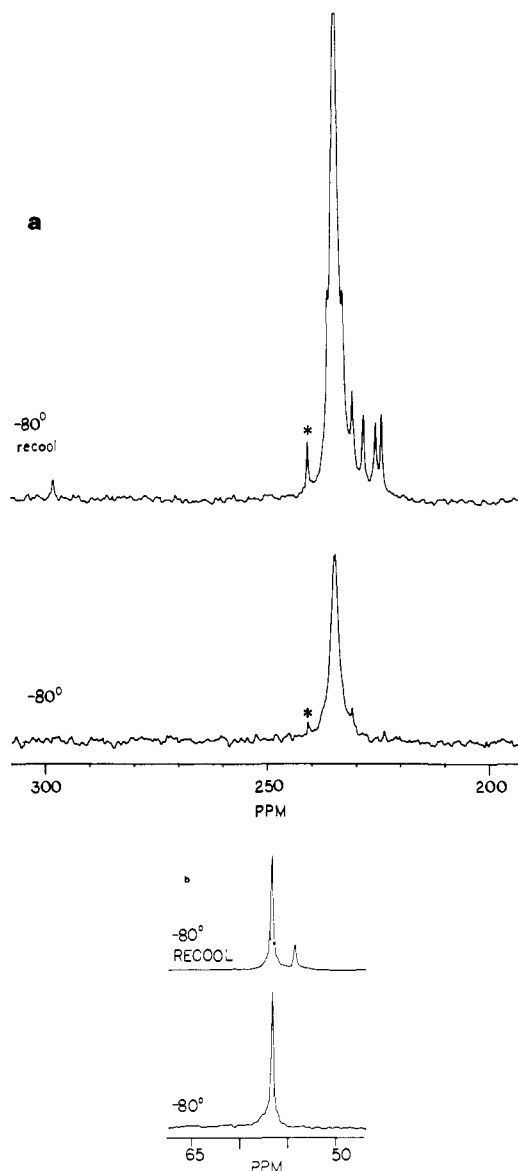(5) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc. Chem. Commun.* **1976**, 919.

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Figure 1. Variable-temperature NMR spectra of [PPN][Fe₄-(AuPPh₃)(CO)₁₃] (4b) for the solid dissolved at -80 °C (lower trace) and of the solution after warming to room temperature and then recooling to -80 °C (upper trace); (a) $^{13}C\{^1H\}$ and (b) $^{31}P\{^1H\}$. An asterisk denotes [Fe₄(CO)₁₃]²⁻ impurity.

Figure 2. ^{13}C NMR spectra of [Fe₄(HgCH₃)(CO)₁₃]⁻ (6(butterfly)) dissolved at -80 °C. Spectra were obtained at -80 °C and the successively higher temperatures indicated in the figure. Resonances denoted a and b are involved in a rotational process and c denotes the appearance of the tetrahedral isomer of 6. The upper trace, -80 °C recool, refers to solid dissolved at -80 °C, warmed to room temperature, and then recooled to -80 °C. an asterisk denotes [Fe₄(CO)₁₃]²⁻ impurity.

temperatures employed in the present work was the rate of equilibration between tetrahedral and butterfly isomers sufficiently rapid to bring about broadening or coalescence of the NMR signals for the individual isomers.

Similarly, the equilibration process between butterfly and tetrahedral forms is evident in the $^{199}Hg\{^1H\}$ NMR spectrum of 6. The sample of 6(butterfly) dissolved at -80 °C shows a single ^{199}Hg resonance, and somewhere between -60 and -50 °C a second resonance arising from 6(tetrahedron) appears. When this equilibrated sample is recooled to -80 °C, the two isomers remain in an approximate 1:1 ratio [1353 ppm (Fe₄ butterfly) and 1449 ppm (Fe₄ tetrahedron) downfield of 0.1 M CH₃HgCl]. Acceptable spectra were not obtained above 0 °C because the compound decomposes during the long data acquisition times.

The results of the spectroscopic studies for complexes 3 through 6 are summarized in Scheme II. Even though these compounds adopt either the Fe₄ butterfly or Fe₄ tetrahedral configuration in the solid state, both isomers exist in solution. The detection of two isomers in solution appears to be a general phenomenon in these [Fe₄(A)(CO)₁₃]⁻ systems. There are only a few other well documented examples of clusters undergoing similar polytopal rearrangements.[6]
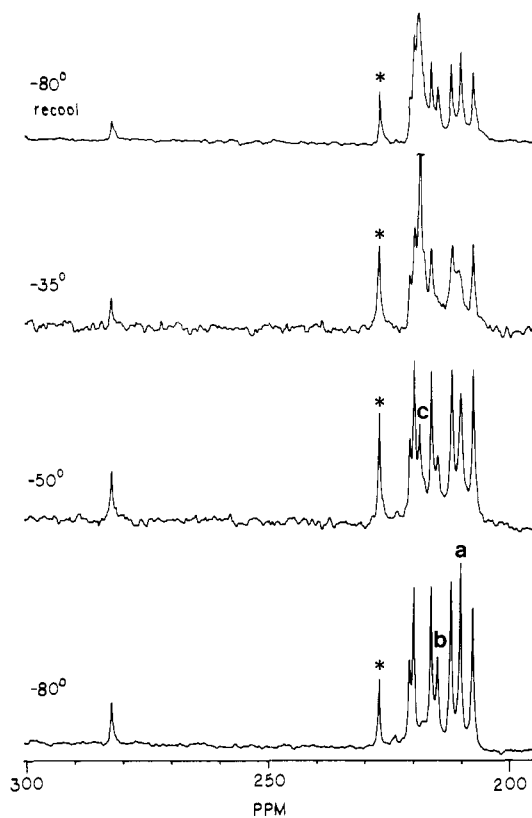

Figure 3. ^{31}P NMR spectra of [K(18-Crown-6)][Fe₄(AuPEt₃)(CO)₁₃], (3a) dissolved at -80 °C. Spectra were obtained at -80 °C and the successively higher temperatures indicated in the figure.
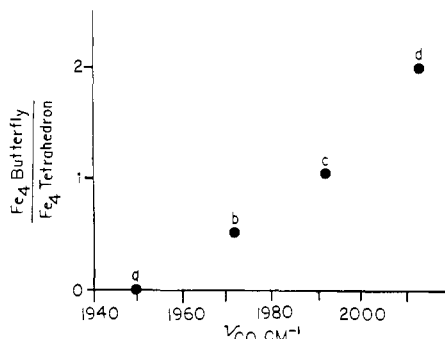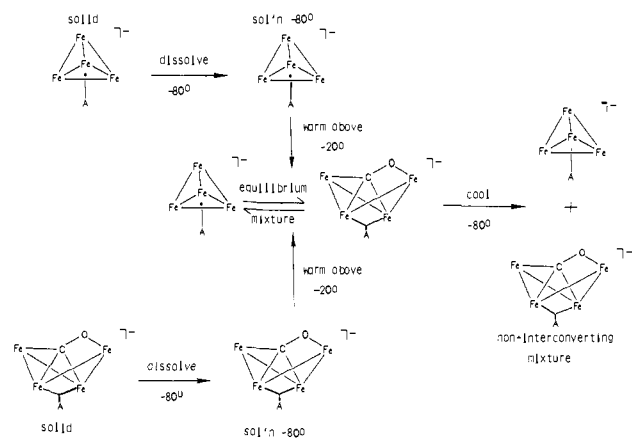
Figure 4. A plot of Fe_4 (butterfly)/Fe_4(tetrahedron), determined by NMR spectroscopy at $-80\ °C$, vs. the strongest CO stretching frequency in solution: (a) $[Fe_4(CO)_{13}]^{2-}$, (b) $[Fe_4(AuPR_3)(CO)_{13}]^-$, (c) $[Fe_4(Hg-CH_3)(CO)_{13}]^-$, and (d) $[HFe_4(CO)_{13}]^-$.

Scheme II

Electronic Origin of the Skeletal Rearrangement. There is strong evidence from previous work that the position of the terminal CO-stretching frequencies for a cluster reflect the amount of electron density within the metal framework available for π-back-bonding.[7] The CO-stretching frequencies are thus dependent on the overall charge on the cluster. The position of the most intense CO stretching frequency for each of the complexes in Table I indicates that the acceptor strength increases in the order CuL^+ $\approx AuPR^+_3 < CH_3Hg^+ < H^+$. In Figure 4 these CO-stretching frequencies are plotted against the ratio of Fe_4 butterfly:Fe_4 tetrahedron. It can be seen that the relative concentration of the Fe_4 butterfly isomer increases monotonically as the CO stretching frequency increases. This suggests that the greatest stabilization of the butterfly relative to the capped tetrahedron is achieved when the strongest acceptor is coordinated to the cluster.

Relative Affinity of Other Clusters for Lewis Acids. The simple relationship between the CO stretching frequency and the ratio of isomeric species in solution which we have observed and described above may be somewhat fortuitous. For example, formation constants, K_f, were measured for H^+, Cu^+, Hg^{2+}, and Ag^+ adducts of Ru_3 $(dppm)_2(CO)_8$ (dppm is $Ph_2PCH_2PPh_2$)[8] and the K_f increases in the order $H^+ < Ag^+ < Hg^{2+} < Cu^+$. However, the average CO-stretching frequency for these adducts increases in the order $Cu^+ < H^+ < Hg^{2+} < Ag^+$. Thus the relative Lewis acidity of these ligands may depend on the identity of the metal cluster with which they interact.
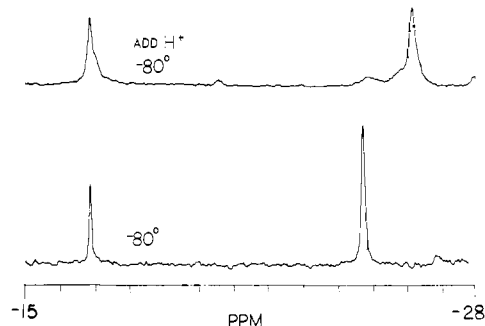
Influence of Π-COR on Butterfly Formation. Since a Π-CO moiety appears to readily interconvert with simple C-bonded CO in these $[Fe_4(A)(CO)_{13}]^-$ clusters, we were interested in attempting to find systems for which the equilibrium was displaced entirely toward the butterfly isomer. This goal was achieved by addition of an electrophile, in this instance CH_3^+, to the oxygen of the Π-CO ligand. The two clusters $HFe_4(CO)_{12}(COCH_3)$[9] and $Fe_4(AuPEt_3)(CO)_{12}(COCH_3)$ (7)[3] have both been shown crystallographically to adopt Fe_4 butterfly cores with Π-COCH$_3$ groups bridging the wingtips. Evidence for the presence of only a single isomeric species in solution was established for $Fe_4(Au-PEt_3)(CO)_{12}(COCH_3)$ by observation of a single resonance in the ^{31}P NMR spectrum over the temperature range -90 to $+25\ °C$. A recent Fenske–Hall molecular orbital calculation on $[HFe_4-(CO)_{13}]^-$[10] indicates that the Π-CO is a net electron donor from a CO orbital to the wingtip iron; however, there also is a component of π-backbonding. Presumably, the addition of a CH_3^+ group to the oxygen of the CO enhances the electron-accepting character of the Π-CO ligand and causes the equilibrium to shift completely toward the butterfly form.

Selective Protonation of Π-CO. The Π-CO ligand was previously suggested as an important intermediate in the reductive cleavage of CO to form cluster carbides and ultimately CH_4.[11,12,13] The present systems provide an opportunity for further confirmation of the activating influence on CO of the Π-CO interaction. It has been demonstrated that reaction of $[HFe_4(CO)_{13}]^-$ with H^+ at low temperature, $-80\ °C$, results in protonation of the Π-CO oxygen to form a Π-COH moiety (eq 3).[11] However, this experiment was performed on a crystalline sample of $[HFe_4(CO)_{13}]^-$ which had been dissolved at a sufficiently low temperature so that only the butterfly isomer was present in solution. Thus it was

$$[HFe_4(CO)_{13}]^- + H^+ \xrightarrow{-80\ °C} HFe_4(CO)_{12}(COH) \quad (3)$$
$$\Pi\text{-CO} \qquad\qquad\qquad\qquad \Pi\text{-CO-H}$$
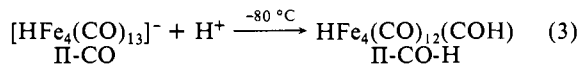
of interest to determine the site or sites of protonation when both the tetrahedral and butterfly isomers are present in solution. An experiment was performed by dissolving $[PPN][HFe_4(CO)_{13}]$ at room temperature in CD_2Cl_2, followed by cooling the sample to $-80\ °C$, a temperature at which the two isomers interconvert very slowly, and then adding 1 equiv, based on starting iron cluster, of HSO_3F at this temperature. The reaction was monitored by ^{13}C and ^1H NMR spectroscopy.

Following addition of HSO_3F to this solution at $-80\ °C$, the ^1H NMR spectrum shows that the resonance at -16.9 ppm of the Fe_4 tetrahedron is essentially unaffected, the -24.9-ppm resonance of the Fe_4 butterfly is strongly diminished, and a new resonance

Figure 5. ^1H NMR spectra for the reaction of HSO_3F with $[HFe_4(C-O)_{13}]^-$ at $-80\ °C$. The lower trace is of a solution prepared at $+25\ °C$ and then cooled to $-80\ °C$ (no acid added). The upper trace is of this same solution after the addition of 1 equiv of HSO_3F at $-80\ °C$.

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(12) Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 1456.

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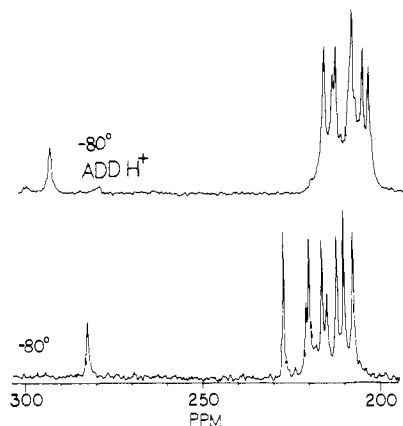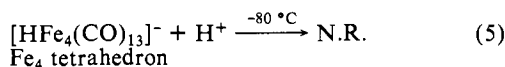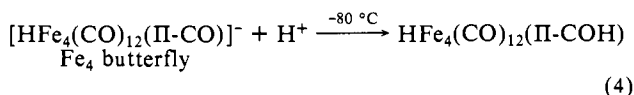
Figure 6. ^{13}C NMR spectrum of the reaction of $[Fe_4(HgCH_3)(CO)_{13}]^-$ (**6**(butterfly)), with HSO_3F. The lower spectrum is of the solid dissolved at -80 °C with no added acid. The upper trace is of this same solution after 1 equiv of HSO_3F was added at -80 °C.

at -26.3 ppm is present (Table III, Figure 5). The -26.3-ppm resonance has been previously assigned to the species $HFe_4(CO)_{12}(COH)$,[11] and appearance of a downfield resonance at 13.2 ppm supports coordination of the acid to an oxygen. Further confirmation of the selective protonation of the Π-CO containing isomer is provided by the ^{13}C NMR spectrum. Coordination of H^+ to the Π-CO oxygen shifts the Π-CO carbon resonance from 279.8 to 294.0 ppm. In addition, all of the terminal CO ligands assigned to the butterfly isomer shift to slightly higher field positions. However, the resonance at 216.7 ppm for the Fe_4 tetrahedron is still present (Table III). These observations can be described by eq 4 and 5.[14]

$$[HFe_4(CO)_{12}(\text{Π-CO})]^- + H^+ \xrightarrow{-80\ °C} HFe_4(CO)_{12}(\text{Π-COH})$$
$$\text{Fe}_4 \text{ butterfly}$$

$$\text{(4)}$$

$$[HFe_4(CO)_{13}]^- + H^+ \xrightarrow{-80\ °C} \text{N.R.}$$
$$\text{Fe}_4 \text{ tetrahedron}$$ (5)

The butterfly isomers of $[Fe_4(HgCH_3)(CO)_{13}]^-$ (**6**) and $[Fe_4(AuPPh_3)(CO)_{13}]^-$ (**4**) also show reactivity of the Π-CO with HSO_3F at -80 °C (Figure 6). Both compounds display Π-CO-H resonances in a region similar to that of $HFe_4(CO)_{12}(COH)$ (Table III). In addition, resonances are observed at 12.0 and 11.5 ppm in the ^1H NMR spectrum for **6** and **4**, respectively, indicating the formation of an O–H bond. In addition, resonances are observed at 12.0 and 11.5 ppm in the ^1H NMR spectrum for **6** and **4**, respectively, indicating the formation of an O–H bond.

Since the tetrahedral form of $[HFe_4(CO)_{13}]^-$ did not react at -80 °C with HSO_3F, it was of interest to determine if analogous lack of reactivity would be observed for the tetrahedral form of $[Fe_4(AuPR_3)(CO)_{13}]^-$ (**4**). Thus a protonation experiment was performed on a solution which contained only the tetrahedral form of $[PPN][Fe_4(AuPR_3)(CO)_{13}]$ and the reaction was monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Addition of acid at -80 °C causes a slight, ca. 2 ppm, upfield shift in the ^{13}C NMR spectrum of the CO resonances from the unprotonated tetrhedron (Figure 7), and for R = Et, **4a**, a resonance at 354 ppm is also observed. A broad resonance appears downfield at 13.7 ppm in the ^1H NMR spectrum and the ^{31}P NMR spectrum shows a broadening of the resonance due to the tetrahedral isomer (Figure 7b). These spectra suggest that protonation has occurred on a carbonyl oxygen to form a Σ-CO-H compound.[1] The formation

Figure 7. Variable-temperature NMR spectra of the reaction of $[PPN][Fe_4(AuPPh_3)(CO)_{13}]$ (**4**) with HSO_3F. The lower traces are of the solid dissolved at -80 °C before addition of acid. The subsequent spectra are for solutions to which had been added 1 equiv of HSO_3F at -80 °C. These spectra were obtained at -80 °C and the successively higher temperatures indicated in the figure. The top right of the figure denoted $+2$° 30 min refers to solid protonated at -80 °C, warmed to $+2$ °C and maintained at this temperature for 30 min. (a) ^{13}C NMR spectra; (b) ^{31}P NMR spectra. An asterisk denotes $[Fe_4(CO)_{13}]^{2-}$ impurity. The symbol ‡ denotes $[Fe_4(CO)_{12}(C)\cdot AuPPh_3]^-$ impurity.

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(14) The $HFe_4(CO)_{12}(\text{Π-COH})$ species is unstable above approximately -30 °C and decomposes to a smaller cluster, $HFe_3(CO)_{10}CH$, which was characterized at -80 °C by a hydride signal at -20.3 ppm and a methylidyne carbon resonance at 265 ppm.[15] In contrast with this fragmentation reaction in methylene chloride solution, the analogous reaction in neat HSO_3CF_3 yields $HFe_4(CO)_{12}(CH)$[16] as the major cluster product.[11,12] The origin of the effect of the reaction medium on the course of the reaction is still unclear.
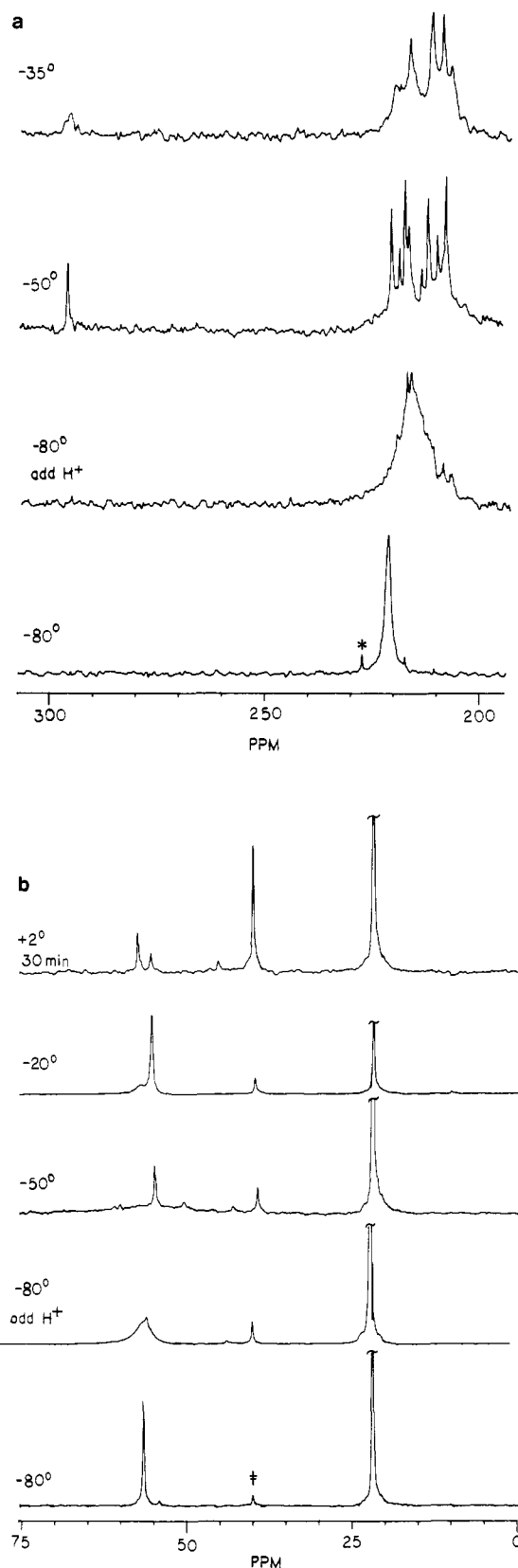
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Table III. ^{13}C and ^1H NMR Spectra of Acid Reactions[a,b]

| compd	$^{13}C\{^1H\}$ (−80 °C) no H$^+$	add H$^+$	^1H (−80 °C) no H$^+$	add H$^+$
2 butterfly only[c]	279.8, 221.5, 219.7, 217.5, 215.6, 211.4, 209.5, 209.1	294.0, 219.1, 214.1, 212.6, 207.5, 206.5	−24.6	−26.3, +13.2
2 both isomers[d]	279.8, 221.5, 219.7, 217.5, 216.7, 215.6, 211.4, 209.5, 209.1	294.0, 219.1, 216.8, 214.1, 212.6, 207.5, 206.5	−16.9, −24.9	−16.9, −26.3, +13.2
4b tetrahedron only[c]	221.7	218 (broad)		+13.7
4b both isomers[d]	284.9, 223.2, 221.6, 219.8, 217.7, 215.1, 212.4, 211.1	296.5, 220.5, 217.4, 212.2, 210.6, 209.7, 207.8		+11.5 (II-COH)
6 butterfly only[c]	282.6, 221.1, 220.9, 216.5, 215.1, 212.4, 210.5, 207.9	294.9, 217.8, 215.4, 214.5, 210.0, 207.0, 205.2		+12.0
both isomers[d]	282.6, 221.0, 220.1, 219.1, 216.5, 215.1, 221.4, 210.5, 207.8	294.6, 217.3, 214.1, 209.5, 206.4, 204.8		

[a] External reference for ^{13}C and ^1H, SiMe$_4$. [b] CD$_2$Cl$_2$ solution; acid HSO$_3$F. [c] Solid dissolved and spectrum obtained at −80 °C. [d] Solid dissolved at +20 °C and then cooled to −80 °C.

of Σ-CO-H compounds has previously been observed in [HM$_3$-(CO)$_{11}$]$^-$, M = Fe[16] or Ru,[17] clusters as well as Co$_3$(CO)$_9$(COH).[18] Further warming of the solution to −50 °C results in the appearance of a Π-CO-H resonance at 296.5 ppm, as well as a series of new resonances in the terminal region of the ^{13}C NMR spectrum.[19] At −50 °C the ^{31}P NMR spectrum displays a resonance at 54.9 ppm due to the Π-CO-H containing complex and the ^1H NMR spectrum shows a new resonance at 11.5 ppm. Resonances arising from the Σ-CO-H compound are no longer observed in the ^{31}P or ^1H NMR spectra; so the cluster has been completely converted to the butterfly form by protonation of the carbonyl oxygen (eq 6). The detection of only the butterfly form is analogous to the result observed for the methylated compound HFe$_4$(CO)$_{12}$(Π-COCH$_3$) which exists exclusively as the butterfly isomer. Thus, addition of an electrophile to the Π-CO oxygen strongly favors butterfly formation.

(6)
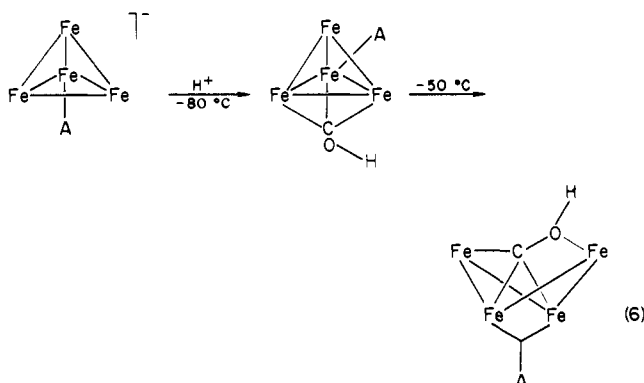
The tendency for both isomers of [Fe$_4$(AuPPh$_3$)(CO)$_{13}$]$^-$, as well as those of [Fe$_4$(HgCH$_3$)(CO)$_{13}$]$^-$ (Table III), to react with proton sources at −80 °C provides an interesting contrast to the result observed for attempted protonation of both isomers of [HFe$_4$(CO)$_{13}$]$^-$. It seems likely that these differences have their origin in the relative acceptor strengths of the Lewis acid ligands. Thus, for the strongest Lewis acid, H$^+$, only the Π-CO oxygen is basic enough to be protonated at low temperature.

Π-CO-H Cleavage. The Π-COH ligand is unstable with respect to cleavage of the C-O bond when the butterfly iron compounds

Scheme III
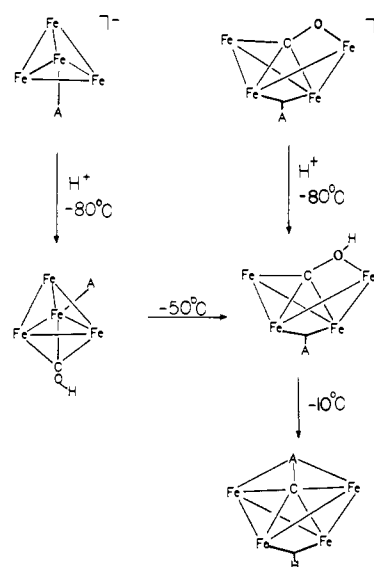
are warmed. For the Fe$_4$(AuPPh$_3$)(CO)$_{12}$(Π-CO-H) cluster this cleavage process is conveniently monitored by ^{31}P NMR spectroscopy. Between −50 and −20 °C little change is observed in the ^{31}P NMR spectrum. However, upon warming the solution to −10 °C a peak at 40 ppm slowly grows in and the resonance of the unprotonated tetrahedron also begins to appear. A concomitant decrease in the butterfly form is also noticeable. The upper spectrum in Figure 7b was obtained after the solution was held at +2 °C for 30 min. This spectrum shows the presence of both isomers of [Fe$_4$(AuPPh$_3$)(CO)$_{13}$]$^-$, confirmed by ^{13}C NMR spectroscopy, as well as the new resonance at 40.2 ppm which is due to HFe$_4$(CO)$_{12}$(C)AuPPh$_3$. The formation fo the carbide cluster involves three protons and two electrons, a process which is approximately described by eq 7. The identity of this carbide-containing compound was verified by comparison of spectra with those of HFe$_4$(CO)$_{12}$(C)AuPPh$_3$[20] which was prepared according to either reaction 8[21] or 9.[22,23] The reaction of H$^+$ with the tetrahedral gold adduct, **4**, can be described by Scheme III.

(15) Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

(16) (a) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485. (b) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541.

(17) Hodali, H. A.; Shriver, D. F.; Ammlung, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5239.

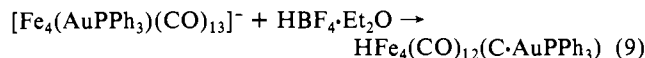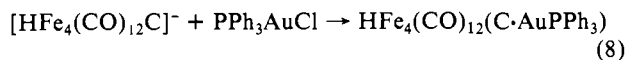(18) Keister, J. B. *J. Organomet. Chem.* **1980**, *190*, C36.

(19) Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1979**, 379.

(20) At −50 °C resonances are observed in the ^{13}C NMR spectrum at 296.5, 220.6, 218.8 217.5, 216.4, 212.1, 209.8, and 207.8 ppm.

(21) Horwitz, C. P., unpublished observations.

(22) Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Rosales, M. J. *J. Organomet. Chem.* **1982**, *238*, C73.

(23) This hydride resonance was originally reported to be at −24.1 ppm (ref 22) in CD$_2$Cl$_2$ but we have found this resonance at −27.3 ppm in CD$_2$Cl$_2$ for compounds prepared by either reaction 8 or 9.

$$3Fe_4(AuPPh_3)(CO)_{12}(\Pi\text{-}COH) \rightarrow HFe_4(CO)_{12}(C\cdot AuPPh_3)$$
$$+ [Fe_4(AuPPh_3)(CO)_{13}]^- \text{ both isomers} + H_2O + CO +$$
$$\text{oxidized Fe species} \quad (7)$$

$$[HFe_4(CO)_{12}C]^- + PPh_3AuCl \rightarrow HFe_4(CO)_{12}(C\cdot AuPPh_3)$$
$$(8)$$

$$[Fe_4(AuPPh_3)(CO)_{13}]^- + HBF_4\cdot Et_2O \rightarrow$$
$$HFe_4(CO)_{12}(C\cdot AuPPh_3) \quad (9)$$
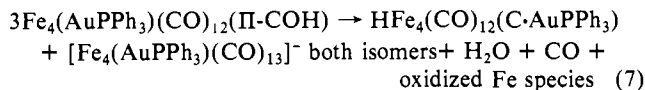
It is interesting to compare the results obtained for the low-temperature protonation reaction described in Scheme III with reaction 9 which normally was performed at room temperature. From NMR spectroscopic data described above, it has been demonstrated that complex **4** exists in solution primarily as a capped Fe$_4$ tetrahedron (Figure 1). However, in order to form the carbide cluster HFe$_4$(CO)$_{12}$(C·AuPPh$_3$) in reaction 9, conversion of the tetrahedral isomer to the butterfly isomer must presumably occur prior to C–O bond cleavage.

Conclusion

Formation and stabilization of the butterfly cluster [Fe$_4$-(A)(CO)$_{13}$]$^-$ is promoted by the presence of a Lewis acid ligand bridging the hinge of the butterfly. All examples of [Fe$_4$(A)-(CO)$_{13}$]$^-$ molecules exhibit two isomeric forms in solution (Fe$_4$ butterfly and Fe$_4$ tetrahedron) and it was possible to demonstrate that strong acceptors favor the butterfly form. The butterfly form can be further stabilized by the addition of an electrophile to the Π-CO oxygen. In this instance the butterfly form is the only cluster species in solution.

The low-temperature protonation reactions suggest that the Π-CO ligand possesses a more basic oxygen than even a face-capping CO ligand. The subsequent C–O bond cleavage of these Π-CO ligands to form a cluster carbide species clearly indicates the importance of Π-CO ligands in the activation of CO.
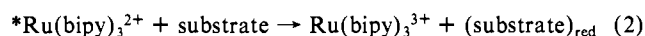
Study of Intramolecular Sensitization and Other Excited-State Pathways in Orthometallated Azobenzene Complexes of Palladium(II)

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Abstract: Reported are structural, spectral, and photochemical studies of several complexes of the type (Azb')PdBr(L) and (Azb'')PdBr(L), where Azb' is orthometallated 4-nitro-4'-(dimethylamino)azobenzene, Azb'' is orthometallated 4-methoxyazobenzene, and L is *cis*- or *trans*-4-stilbazole, pyridine, or 3-methylpyridine. In room-temperature solutions containing an equimolar amount of free L, these square-planar complexes undergo both rapid exchange of free and coordinated L and cis-trans isomerization at the Pd center. The low-energy region in the absorption spectra of the complexes is dominated by transitions that are localized largely on the orthometallated azobenzene chromophore. Neither free 4-nitro-4'-(dimethylamino)azobenzene nor 4-methoxyazobenzene luminesce in room-temperature fluid solution; upon metallation by Pd, however, intraligand fluorescence is observed. Irradiation of the complexes at a wavelength that populates an azobenzene-localized excited state causes isomerization of the 4-stilbazole ligand. Although this result demonstrates that low-energy photons absorbed by the azobenzene chromophore can be used to sensitize a photochemical reaction of a remotely located nonabsorbing ligand, the quantum yields are disappointingly low ($<10^{-3}$). The mechanism of this intramolecular sensitization and possible reasons for its inefficiency are considered.

During the past 15 years, numerous coordination compounds have been investigated as photosensitizers for organic and inorganic reactions.[1] Much of the recent impetus in this area has arisen from the desire to convert sunlight into stored chemical energy and the attendant need to extend the threshold of photoreactivity to wavelengths above 500 nm. Metal complexes containing conjugated ligands such as 2,2'-bipyridine (bipy), 1,10-phenanthroline, and various porphyrins are potentially attractive in this regard, since they absorb well into the visible spectral region owing to the presence of low-lying electronic excited states of charge-transfer or intraligand character. Moreover, many of these complexes can activate suitable substrates via pathways that involve intermolecular energy transfer and/or electron transfer.[2] These types of interactions are outlined for the specific case of Ru(bipy)$_3^{2+}$ in eq 1–3, where the subscripts red and ox denote

$$*Ru(bipy)_3^{2+} + substrate \rightarrow Ru(bipy)_3^{2+} + *substrate \quad (1)$$

$$*Ru(bipy)_3^{2+} + substrate \rightarrow Ru(bipy)_3^{3+} + (substrate)_{red} \quad (2)$$

$$*Ru(bipy)_3^{2+} + substrate \rightarrow Ru(bipy)_3^{+} + (substrate)_{ox} \quad (3)$$

the reduced and oxidized forms, respectively, of some generic substrate and the asterisk signifies an electronically excited species.

An alternative, though less-explored approach to sensitization involves the intramolecular transfer of energy from a strongly absorbing, unreactive chromophore ("antenna fragment") situated in one part of a complex to a reactive substrate located some

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(1) For a review of basic principles and much of the early work in this area, see: Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 32.

(2) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, *44*, 83.