Table II. Qualitative Observations on the Dissociative Loss of Phosphines (L) from *cis*-$Mo(CO)_4L_2$ Derivatives[a]

L	cone angle,[b] deg	rate of L dissocn
$P(OCH_2)_3CEt$	101	very slow
$PN_3(CH_2)_6$	102[c]	very slow
$PPhMe_2$	122	very slow
$P(OPh)_3$	128	very slow
$P(n\text{-}Bu)_3$	132	very slow[d]
PPh_3	145	fast[e]
$PPhCy_2$	162[f]	very fast

[a] Reactions carried out in CO saturated tetrachloroethylene at 55 °C. Very slow defined as $t_{1/2}$ greater than 48 h. [b] Taken from C. A. Tolman, *Chem. Rev.*, 77, 313 (1977), unless otherwise noted. [c] J. R. DeLerno, L. M. Trefonas, M. Y. Darensbourg, and R. J. Majeste, *Inorg. Chem.*, **15**, 816 (1976). [d] This derivative undergoes isomerization to the trans isomer much faster than phosphine loss with formation of $Mo(CO)_5P(n\text{-}Bu)_3$. [e] $t_{1/2}$ for this reaction is ~30 min. [f] Weighted average of Tolman's PPh_3 and PCy_3 cone angles.

production of the readily identifiable $Mo(CO)_5L$ species. Table II contains a qualitative comparison of the ease of ligand (L) dissociation in the cis-disubstituted molybdenum tetracarbonyl derivatives. As illustrated in Table II, the dissociative loss of phosphine closely parallels the steric requirement of the phosphine ligand as determined by its cone angle;[25] i.e., bulky ligands are readily lost whereas small ligands do not undergo dissociative loss easily. It should as well be noted that an additional driving force for the dissociation of phosphine in *cis*-$Mo(CO)_4L_2$ derivatives is the formation of $[Mo(CO)_4L]$ intermediates where L is in an equatorial position (the C_s isomer), that is, Brown's cis-labilization arguments.[26,27]

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Registry No. *cis*-$Mo(CO)_4(PPhCy_2)_2$, 66966-52-7; *cis*-$Mo(CO)_4(P(n\text{-}Bu)_3)_2$, 16244-54-5; *cis*-$Mo(CO)_4(PPhMe_2)_2$, 24554-47-0; *cis*-$Mo(CO)_4(PPh_2Me)_2$, 37438-49-6; *cis*-$Mo(CO)_4(PN_3(CH_2)_6)_2$, 66966-51-6; *cis*-$Mo(CO)_4(PPh_3)_2$, 16742-93-1; *cis*-$Mo(CO)_4(SbPh_3)_2$, 16742-98-6; *cis*-$Mo(CO)_4(P(OPh)_3)_2$, 59599-01-8; *cis*-$Mo(CO)_4(P(OCH_2)_3CEt)_2$, 66966-50-5; *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$, 65337-26-0; *cis*-$W(CO)_4[NHC_5H_{10}]_2$, 56083-13-7; $W(CO)_4[NHC_5H_{10}]PPh_3$, 67010-37-1; *trans*-$Mo(CO)_4[PPh_3]_2$, 16244-53-4; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $W(CO)_4[NHC_5H_{10}]P(n\text{-}Bu)_3$, 66966-49-2.

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Photochemistry of Carbon Monoxide and Benzyl Isocyanide Complexes of Heme Models

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In view of the well-known photodissociation of carbon monoxide and alkyl isocyanides from hemoglobin[1,2] it is of interest to determine if a similar photolability of these π-acceptor ligands is possible in simple iron complexes analogous to the iron porphyrin in hemoglobin. Photoaquation of $[Fe(CN)_5CO]^{-3}$ has a reported quantum yield of 0.9.[3] A quantum yield of 0.14 is reported for photoaquation of $Fe(CNCH_3)_4(CN)_2$ (the isocyanide ligand is aquated).[4] We have previously reported that benzyl isocyanide (BzNC) complexes of ferrous phthalocyanine are photochromic.[5] We have now investigated several macrocyclic complexes of iron including ferrous phthalocyanine[5,6], ferrous 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (Fe(TIM)),[7,8] and ferrous bis(dimethylglyoxime).[9] All of these systems undergo a photochromic reaction based on the shift of the equilibrium

$$Fe(N_4)L_2 + X \rightleftharpoons Fe(N_4)(L)(X) + L \qquad (1)$$

where L is a nitrogen base, X is CO or BzNC, and N_4 is the tetradentate macrocycle. We report on the synthesis, characterization, and thermal kinetics of these complexes elsewhere. Herein we report measurements of the quantum yield for photodissociation of CO and BzNC from these complexes (the reverse of eq 1). While this work was being considered for publication, Incorvia and Zink[10] published their independent study which overlaps in part with this report.

Experimental Section

The complexes and their spectral features are given in Table I. Stirred solutions of the complexes were irradiated using a 200-W quartz–halogen lamp in 5-cm optical glass cells contained in a close-fitting brass block thermostated at 20 °C by means of a Lauda circulator. Wavelengths were isolated with interference filters of 100 Å band-pass (Optically Thin Films, North Andover, Mass.). Incident light intensities were typically 10^{-7} einstein/min as determined by

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Table I. Spectral Data

complex	λ_{max}, nm ($\epsilon \times 10^{-4}$)
$Fe(DMGH)_2(BzNC)_2$[a]	392 (0.6)
$Fe(DMGH)_2(CH_3Im)(BzNC)$[b]	445 (0.59)
$Fe(DMGH)_2(CH_3Im)(CO)$[b]	385 (0.4)
$Fe(DMGH)_2(CH_3Im)_2$[b]	531 (0.69)
$Fe(Pc)(CH_3Im)\cdot(BzNC)$[c]	660 (11), 590 sh (2.8)
$Fe(Pc)(CH_3Im)_2$[a]	660 (13), 590 sh (3.2), 425 (1.8)
$[Fe(TIM)(CH_3CN)(CO)][PF_6]_2$[c]	430 (0.5)
$[Fe(TIM)(CH_3CN)_2][PF_6]_2$[c]	550 (0.89)
$[Fe(TIM)(CH_3Im)_2][PF_6]_2$[d]	667 (1.1)
$[Fe(TIM)(CH_3Im)(BzNC)][PF_6]_2$[d]	555 (0.89)

[a] Toluene. [b] Chloroform. [c] Acetonitrile. [d] Acetone.

Reineckate actinometry.[11] All solutions had absorbances greater than 2 at the wavelength irradiated. Complexes were irradiated for 2–30 min. The extent of reaction was determined from the visible spectrum by analysis at an absorption maximum of the reactant or product. The reactions could be conveniently driven to 100% completion by irradiation with white light for a few minutes. Corrections were made for the thermal dark reactions. Each quantum yield reported is typically the average of three or more experiments carried out on different days.

Results and Discussion

In all cases spectra of solutions of the carbonyl and benzyl isocyanide complexes successively irradiated in the presence of excess methylimidazole (or acetonitrile in the case of $Fe(TIM)(CH_3CN)(CO)^{2+}$) show clean isosbestic points indicative of the two absorbing species $FeN_4(L)(X)$ and FeN_4L_2. At low concentrations of methylimidazole, the photoproduct spontaneously reverts back to the $FeN_4(L)(X)$ giving rise to the photochromism described previously. Quantum yields were determined at high concentration of methylimidazole where the thermal reverse reaction does not occur. The simplest explanation for the photochemical reaction involves dissociation of CO and BzNC from a photoexcited state giving rise to a pentacoordinate intermediate (the same intermediate postulated in the dissociative thermal substitution reactions of these complexes) which rapidly adds methylimidazole to give FeN_4L_2. At the high concentrations of methylimidazole and low concentration of carbon monoxide or benzyl isocyanide in solution, the addition of X to the intermediate is not important.

Quantum yields are given in Table II. Complexes were irradiated at or near the maximum of the carbonyl and benzyl isocyanide complexes at short wavelength and the extent of reaction determined from the absorbance of photolyzed solutions at the maximum of the FeN_4L_2 complex at longer wavelength. In the Pc system, both reactant and product absorb at 650–550 nm. The amount of $FePc(CH_3Im)_2$ formed is determined at 425 nm where only the product has a maximum. In the case of the $Fe(TIM)(CH_3CN)(CO)^{2+}$ complex, the thermal contribution to the formation of the $Fe(TIM)(CH_3CN)_2{}^{2+}$ was comparable to the photochemical contribution. In view of this large correction, this value is considered less reliable. Incorvia and Zink[10] report $\Phi = 0.60$ for this reaction under slightly different conditions.

The dissociation of the CO and BzNC could come from the charge-transfer state or as suggested by Condorelli[4] from a triplet ligand field state reached by a rapid nonradiative decay from the CT state. Incorvia and Zink have made a very similar argument, independently, for the Fe(TIM) systems.[10] The lower quantum yield for photodissociation of BzNC from the $Fe(DMGH)_2(BzNC)_2$ complex compared to the $Fe(DMGH)_2(CH_3Im)(BzNC)$ complex is also in agreement with diminished relative importance of π bonding vs. σ bonding for BzNC trans to BzNC.

The relative quantum yield for CO vs. BzNC dissociation is seen to be about 10:1. This order correlates well with the idea that it is the weakening of the π bonding in the excited state which gives rise to the photolability of π-acceptor ligands in these systems.

Table II. Quantum Yields

	λ_{irrad}	% photolysis	Φ[a]
$Fe(Pc)(CH_3Im)\cdot(BzNC)$[b]	550	1.6–8.3	0.039 (4)
	600	3.6–7.1	0.037 (1)
$Fe(TIM)(CH_3Im)(BzNC)[PF_6]_2$[c]	500	2.6–3.9	0.064 (5)
	550	5.8–18.5	0.077 (5)
$Fe(DMGH)_2(CH_3Im)(BzNC)$[d]	450	3.6	0.053 (5)
$Fe(TIM)(CH_3CN)(CO)[PF_6]_2$[e]	400	6.1–8.1	0.77 (8)
$Fe(DMGH)_2(CH_3Im)(CO)$[d]	400	2.4–6.3	0.41 (10)
$Fe(DMGH)_2(BzNC)_2$[d]	400	2.4–6.0	0.033 (5)
HbCO[f]			0.7–0.4
Hb(EtNC)[f]			0.05

[a] Average deviation of three or more experiments. [b] 1.2 M CH_3Im in toluene. [c] Φ independent of CH_3Im (0.2 M CH_3Im in acetone or neat CH_3Im). [d] Neat CH_3Im. [e] Acetonitrile; a large correction is required for the thermal reaction. [f] Reference 1, EtNC = ethyl isocyanide.

For the series of analogous $FeN_4(CH_3Im)(BzNC)$ complexes the quantum yields are in the order Pc < DMGH < TIM. The lower values for the Pc system may reflect the different nature of the bands irradiated. The bands at long wavelength in the phthalocyanine complexes are ligand bands[12] while those in the TIM and DMGH are charge-transfer bands.[13] The charge-transfer excited state is expected to have considerably diminished π bonding to the axial ligands.

The quantum efficiency for photodissociation of CO vs. BzNC in these systems is similar to that reported for hemoglobin.[14] Values somewhat lower than 1.0 are reported for modified proteins and depend on ionic strength for HbCO.[1,2] The similarity in results on these heme models and those on the proteins indicates that these relative quantum efficiencies for carbon monoxide and isocyanide dissociation are a characteristic property of low-spin tetragonal Fe(II) and are not restricted to the proteins or the heme group. While the photochemical reactivities of these systems are similar to the heme group, the thermal reactivities of Pc, TIM, and DMGH systems are vastly different from that of the heme group.[5,6,8,9]

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Registry No. $Fe(DMGH)_2(BzNC)_2$, 59575-75-6; $Fe(DMGH)_2(CH_3Im)(BzNC)$, 59575-74-5; $Fe(DMGH)_2(CH_3Im)(CO)$, 61395-33-3; $Fe(DMGH)_2(CH_3Im)_2$, 57804-36-1; $Fe(Pc)(CH_3Im)\cdot(BzNC)$, 62006-60-4; $Fe(Pc)(CH_3Im)_2$, 55925-76-3; $[Fe(TIM)(CH_3CN)(CO)][PF_6]_2$, 43223-43-4; $[Fe(TIM)(CH_3CN)_2][PF_6]_2$, 43223-41-2; $[Fe(TIM)(CH_3Im)_2][PF_6]_2$, 67114-10-7; $[Fe(TIM)(CH_3Im)(BzNC)][PF_6]_2$, 67114-11-8.

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