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MLCT[1] Spectra and Carbon Monoxide Binding to Iron(II) Difluoro(dioximato)borate Complexes in Weak Donor Solvents

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A variety of $Fe(dioxBF_2)_2W_2$ complexes, where diox equals dimethylglyoximate, naphthoquinone dioximate, and benzoquinone dioximate and W is a weak donor ligand, including tetrahydrofuran (thf), *N,N*-dimethylformamide (dmf), dimethyl sulfoxide (dmso), tetrahydrothiophene (tht), and a variety of nitriles (benzonitrile, acrylonitrile, phthalonitriles, cyanopyridines, tetracyanoethylene (tcne)), are described. Low-energy MLCT bands are observed in the visible spectrum for axial ligands with low reduction potentials (tcne, 922 nm; nitrophthalonitrile, 549 nm; methylpyrazinium, 687 nm; tetrachlorophthalonitrile, 530 nm; 4-cyanopyridine, 470 nm), and these are compared with pentacyanoferrate analogues. The kinetics of the reaction of these systems with CO were determined by flash photolysis in neat solvents or in toluene solution in the presence of excess W. The order of lability for FeN_4W_2 in either toluene or neat W is thf > dmf > dmso > nitriles ≥ tht ≫ py. Carbon monoxide binding systems with rate and equilibrium constants spanning over 6 orders of magnitude are described.

Introduction

In a previous paper,[2] we described the synthesis of *trans*-$Fe(dioxBF_2)_2(CH_3CN)_2$ (diox = dimethylglyoximate (dmg), naphthoquinone dioximate (npq), and benzoquinone dioximate (bqd)) complexes. These acetonitrile derivatives are significantly more labile than corresponding pyridine and methylimidazole complexes[3,4] yet undergo characteristic axial ligand substitution reactions by the same D mechanism previously elucidated for a variety of $Fe(dioxH)_2L_2$ complexes. To extend the lability of such systems and thereby also increase their affinity for CO (eq 1) and

$$Fe(dmgBF_2)_2W_2 + CO \rightleftharpoons Fe(dmgBF_2)_2W(CO) + W \qquad (1)$$

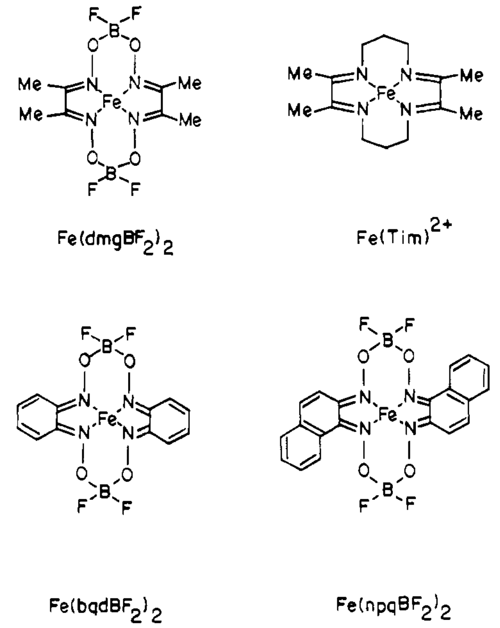
potential application to CO scrubbing,[5] we have introduced even weaker axial ligands. Depending on the particular application, high levels (low $P_{1/2}$) or rates of binding and/or release may be desirable.

The low-spin d^6 Fe(II) systems (Chart I) described here show rich visible spectra due to metal to oxime charge-transfer (MOxCT) bands whose position ranges across the entire visible region, depending upon the nature of N_4 and the axial ligands. If the axial ligand also has a low-lying vacant orbital, additional bands due to charge transfer to the axial ligand may be detected (MAxCT).[6] In this work, a large number of weak-donor complexes have been synthesized and characterized spectrally, the kinetics of the reaction of the FeN_4W_2 complexes with CO examined, and equilibrium constants for CO binding determined.

Experimental Section

Materials. The complexes $Fe(dioxBF_2)_2(CH_3CN)_2$ and Fe(Tim)$(CH_3CN)_2[PF_6]_2$ were prepared as described previously.[2,7] Methylpyrazinium iodide was prepared by the reaction of pyrazine with methyl iodide.[8] The $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ complex was synthesized from $Na_2[Fe(CN)_5NO]\cdot 2H_2O$.[13] THF was distilled from Na and benzophenone, toluene from $LiAlH_4$, and CH_2Cl_2 from P_2O_5. Dmf was Aldrich Chemicals packaged in Sure-Seal bottles; dmso, tht, and CH_3CN were reagent grade or better.

Chart I



Physical Measurements. Visible spectra were recorded on an Aminco DW-2a UV/vis or a Cary 2400 spectrophotometer. NMR spectra were obtained on a Bruker AM-300 spectrophotometer with TMS as an internal standard. Infrared spectra were obtained on a Nicolet 20 SX FTIR instrument in KBr disks. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Vancouver, BC.

Syntheses. All syntheses were performed under a CO or inert (nitrogen or argon) atmosphere.

$Fe(dmgBF_2)_2$(thf)CO. A CO-saturated solution of 120 mg of $Fe(dmgBF_2)_2(CH_3CN)_2$ (0.26 mmol) in 50 mL of thf was reduced in volume by trap distillation at reduced CO pressure to 5 mL, whereupon 10 mL of CO-purged petroleum ether (40-60 °C) was added. The product was isolated by filtration, recrystallized from CO-saturated thf/petroleum ether, washed with ice-cold CO-purged petroleum ether, and dried in vacuo (yield: 87 mg, 70%): IR (KBr) 3040-3000 (ν_{thf}), 2034 (ν_{CO}), 1614 ($\nu_{C=N}$), 1168 (ν_{B-O}) cm^{-1}. Anal. Calcd for

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(1) Abbreviations: $dmgBF_2$, (dimethylglyoximato)difluoroborate; $bqdBF_2$, (benzoquinone dioximato)difluoroborate; $npqBF_2$, (naphthoquinone dioximato)difluoroborate; Tim, 2,3,9,10-tetramethyl-1,2,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; MeIm, 1-methylimidazole; py, pyridine; 2-CNpy, 2-cyanopyridine; 4-CNpy, 4-cyanopyridine; dcne, *trans*-1,2-dicyanoethylene; tcne, tetracyanoethylene; thf, tetrahydrofuran; tht, tetrahydrothiophene; dmf, *N,N*-dimethylformamide; dmso, dimethyl sulfoxide; TEAP, tetraethylammonium perchlorate; MLCT, metal to ligand charge transfer; MOxCT, metal to oxime charge transfer; MAxCT, metal to axial ligand charge transfer. Rate constants are designated by k_{-LT} for the dissociation of the ligand L trans to T, k_{+ET} for the addition of a ligand to a pentacoordinate ligand trans to T; equilibrium constants $K_{L,ET}$ are for replacement of L by E trans to T. The shortened forms N (MeIm) and A (CH_3CN) are used as superscripts and subscripts.

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$FeC_{13}H_{20}B_2F_4N_4O_6$: C, 32.4; H, 4.2; N, 11.6. Found: C, 33.2; H, 4.3; N, 10.8.

$Fe(dmgBF_2)_2(ROH)CO$ (ROH = H_2O and MeOH). A 76-mg amount of $Fe(dmgBF_2)_2(CH_3CN)_2$ (0.16 mmol) was dissolved with gentle heating in 40 mL of CO-purged thf containing 8 mL of ROH. The thf was removed by trap distillation, and the precipitate was collected by filtration, washed with petroleum ether, and dried in vacuo.

For $Fe(dmgBF_2)_2(H_2O)CO$ (yield: 32 mg, 47%): IR (KBr) 3448–3500 (ν_{OH}), 2041 (ν_{CO}), 1617 ($\nu_{C=N}$). Anal. Calcd for $FeC_9H_{14}B_2F_4N_4O_6$: C, 25.3; H, 3.3; N, 13.1. Found: C, 25.3; H, 3.3; N, 12.7.

For $Fe(dmgBF_2)_2(MeOH)CO$: IR (KBr) 3502 (ν_{OH}), 2046 (ν_{CO}), 1617 ($\nu_{C=N}$). Anal. Calcd for $FeC_{10}H_{16}B_2F_4N_4N_4O_6$: C, 27.2; H, 3.7; N, 12.7. Found: C, 27.0; H, 3.7; N; 12.1.

$Fe(dmgBF_2)_2(dmso)CO$. To 50 mL of CH_2Cl_2 containing 0.2 mL of dmso (1.5 mmol) was added 87 mg of $Fe(dmgBF_2)_2(CH_3CN)_2$ (0.2 mmol). The CH_2Cl_2 was removed by trap distillation. The solid was isolated by washing the flask with 8 mL of ice-cold CO-purged EtOH, filtering, washing the precipitate with 50 mL of ice-cold ether, and drying in vacuo (yield: 58 mg, 67%): ^1H NMR (acetone-d_6) δ 2.47 (dmg Me), 2.57 (dmso Me); IR (KBr) 2021 (ν_{CO}), 1612 ($\nu_{C=N}$). Anal. Calcd for $FeC_{12}H_{24}B_2F_4N_4O_6S_2$: C, 27.1; H, 3.7; N, 11.5. Found: C, 27.0: H, 3.7; N, 11.0.

$Fe(dmgBF_2)_2(dmso)_2$. To 50 mL of Ar purged CH_2Cl_2 containing 1 mL of dmso was added 140 mg of $Fe(dmgBF_2)_2(CH_3CN)_2$ (0.3 mmol). The solvent was removed in vacuo and the orange precipitate isolated by filtration (yield: 117 mg, 74%): ^1H NMR (dmso-d_6) δ 2.47 ($dmgBF_2$ Me); IR (KBr) 3015, 2932 (ν_{C-H}, dmso), 1624 ($\nu_{C=N}$), 1435 (δ_{C-H}, dmso). Anal. Calcd for $FeC_{12}H_{24}B_2F_4N_4O_6S$: C, 26.8; H, 4.5; N, 10.4; S, 11.9. Found: C, 26.2; H, 4.3; N, 9.8; S, 12.2.

$Fe(dmgBF_2)_2(tcne)_2$. To 50 mL of CH_2Cl_2 containing 168 mg of tcne (1.3 mmol) was added 288 mg of $Fe(dmgBF_2)_2(CH_3CN)_2$ (0.6 mmol). The solvent was removed and the product dried in vacuo: IR (KBr) 2338, 2239, 2204 (ν_{CN}, tcne), 1616 ($\nu_{C=N}$, $dmgBF_2$).

$Fe(dmgBF_2)_2(tcne)CO$. To 50 mL of CH_2Cl_2 was added 172 mg of $Fe(dmgBF_2)_2(tcne)_2$ (0.3 mmol). The solution was stirred with mild heating until the solid had dissolved, whereupon 10 mL of hexane was added. The excess CH_2Cl_2 was purged off, and the product was collected by filtration (yield: 93 mg, 67%): IR (KBr) 2319, 2294, 2211 (ν_{CN}, tcne), 2065 (ν_{CO}), 1620 ($\nu_{C=N}$, $dmgBF_2$).

In Situ Generation of Complexes

$Fe(CN)_5(RCN)^{3-}$. A solution of $Na_3[Fe(CN)_5NH_3]$ dissolved in H_2O was allowed to aquate for 15 min, prior to ligand addition.[13]

$Fe(dioxBF_2)_2W_2$. Solutions were prepared by dissolving $Fe(dmgBF_2)_2(CH_3CN)_2$ in Ar-purged CH_2Cl_2 containing an excess of the nitrile and diluting with toluene. Saturating the solution with CO resulted in conversion to the carbonyl complexes. In cases where the solid $Fe(dioxBF_2)_2(W)CO$ complexes were isolated and characterized, the spectra and kinetics were identical with those found for the samples prepared in situ.

Kinetics. Slow reactions ($t_{1/2} > 10$ s) were monitored by conventional visible spectroscopy and the more rapid reactions by flash photolysis on an Applied Photophysics flash photolysis apparatus.[2] For moderately fast reactions ($t_{1/2} < 100$ ms), occasional use was made of a Starblitz 200 DRX photoflash. Data were analyzed by microcomputer, as described previously.[2]

The [CO] in kinetic runs was determined by either manometric or tonometric methods. Where a detailed concentration dependence on CO was not carried out, the rate was measured in CO-saturated solvent and a qualitative demonstration of a rate dependence on [CO] was established by purging the cells with N_2 and observing a dramatic reduction in rate. For reactions of the complexes in CO-saturated toluene, [W] was typically 0.1 M and the rate was shown to display an inverse first-order dependence on [W] for a 4–10-fold variation in [W]. In the case of tcne, somewhat lower concentrations were used (0.02 M) owing to solubility restrictions.

Electrochemical measurements were performed on a PAR electrochemical instrument, as described previously.[2] The electrolyte, TEAP, was made from (TEA)Br by standard methods, recrystallized twice from H_2O, and dried in vacuo for 2 days. Reagent grade acetonitrile was distilled from P_2O_5 under a N_2 atmosphere. Cyclic voltammetry was carried out at scan rates of typically 100 mV/s, with 0.1 M TEAP and 0.01 M analyte. Solutions of tcne displayed a reversible wave at 0.27 V vs SCE in agreement with literature values.[9] For 4-nitrophthalonitrile, quasireversible waves at −0.65 and −1.28 V vs SCE were assigned successive one-electron reductions.[10,11] Tetrafluoronaphthalonitrile gave an irreversible wave at −1.4 V vs SCE as well as a feature at −1.2 V on subsequent scans associated with adsorption of some polymeric material on the electrode surface.

Table I. Visible Spectral Data[a] for $Fe(N_4)$ Systems

		λ_{max}, nm		
		FeN_4W_2		
N_4	W	MOxCT[b]	MAxCT	$FeN_4W(CO)$
$dmgBF_2$	thf	480, 402		426, 360
	dmf	480, 410		404, 366
	dmso	488, 420		414, 362
	tht	500		402, 369
	CH_3CN	444, 426		370, 350
	$CH_2{=}CHCN$	436, 415		370, 359
	dcne[c]	420	440	377, 341
	tcne[d]	388	922	376, 353
	$ClCH_2CN$	429, 416		373, 354
	C_6H_5CN	440, 420		381
	$C_6H_4(CN)_2$[c]	427		373, 351
	$C_6H_3(NO_2)(CN)_2$[c]	417	549	
	$C_6F_4(CN)_2$[c]	414	460	406, 356
	$C_6Cl_4(CN)_2$[d]	418	530	405, 369
	2-CNpy[c]	410, 431	350	372
	4-CNpy[c]	496	471, 413	404, 366
	py	510	401, 366	405
	pz[d]	493	443	
	$Mepz^+$[e]	467	687	357
$bqdBF_2$	dmso	640, 580		515
	CH_3CN[f]	599		465
	2-CNpy[d]	574		470
	4-CNpy[d]	656	485	492
	py[f]	687	404	495
	pz[d]	649	457	
$npqBF_2$	dmso	613		507
	CH_3CN[f]	568		470
	2-CNpy[d]	552		475
	4-CNpy[d]	634	479	
	py[f]	656		495
	pz[d]	625	461	
Tim^{2+}	dmso	574		464
	CH_3CN[f]	550, 516		420
	tcne[e]	495	879	449
	C_6H_5CN[g]	542, 500		420
	py[e]	649, 600	396	
	pz[e]	617, 573	478, 430	

[a] Spectra in neat solvent unless otherwise noted. [b] High-energy band often appears as a shoulder. [c] In toluene. [d] In CH_2Cl_2. [e] In acetone. [f] Reference 2. [g] Reference 5.

Results and Discussion

Visible Spectra. Dissolution of $Fe(dmgBF_2)_2(CH_3CN)_2$ in donor solvents results in visible spectra that we assign to the bis solvato $Fe(dmgBF_2)_2W_2$ species. In the oxygen donor solvents dmso, dmf, and thf, one observes two broad bands in the visible region, while, for the nitrogen donors CH_3CN and py and the sulfur donor tht, a single fairly sharp band is observed (for CH_3CN a distinct shoulder is present).

Spectral data for these solvato complexes are collected in Table I along with data for a variety of other new *trans*-FeN_4W_2 complexes. For ligands that are solids, spectra were obtained in toluene or CH_2Cl_2 in the presence of excess ligand. Metal to oxime charge-transfer bands (MOxCT) display characteristic shifts as a function of the axial ligands.[2-4] The nitriles listed in Table I give MOxCT bands analogous to those of CH_3CN but shifted to higher energy with electron-withdrawing substituents. In this work, ligands were specifically selected to probe potential linkage isomerism or which might display low-energy charge-transfer bands assigned to MAxCT transitions. These features are discussed below.

Spectral features for the other N_4 systems shown in Table I parallel the trends previously described for the dioxH systems[3,4] and are analogous to those described above for the $dmgBF_2$ system. In the $bqdBF_2$ and $npqBF_2$ systems, the greater intensity of MOxCT bands results in the MAxCT bands being less prominent but analogous bands are clearly evident in the spectra.

MAxCT Spectra. Previously, only a few examples of bands assigned to charge transfer to the axial ligands (MAxCT) have been described in FeN_4L_2 systems.[2-4] Pyrazine and methyl-

Table II. Ligand Reduction Potentials and Comparative MAxCT Spectral Data for $Fe(dmgBF_2)_2L_2$ and $Fe(CN)_5L^{3-}$ Complexes

ligand	$E_{1/2}{}^{0/-}$, V vs SCE[a]	λ_{max}, nm $Fe(dmgBF_2)_2$[b]	 $Fe(CN)_5$[c]
tcnc	0.27[d]	922	914
$Mcpz^+$		687	662[e]
$C_6H_3(NO_2)(CN)_2$	−0.66	549	523
4-CNpy	−1.6[f]	470	477[g]
$C_6F_4(CN)_2$	−1.4[h]	460	463
pz		443	502[e]
dcnc	−1.36[i]	440	462
$C_6H_4(CN)_2$	−1.7[f]	420	413[g]
2-CNpy		350	387[g]

[a] In CH_3CN. [b] In CH_2Cl_2. [c] In H_2O solution. [d] This work. A value of 0.24 V vs SCE is reported by Kaim.[9] [e] Reference 15. [f] Reference 11. Converted from values reported in DMF vs $Ag/AgClO_4$ by addition of 0.41 V. [g] Reference 12. [h] Irreversible. [i] Reference 9.

pyrazine, as well as some common nitrile ligands, are known to give rise to MLCT bands in pentacyanoferrate(II)[12,13] and pentaamineruthenium(II) systems.[14] Corresponding transitions found in the spectra of $Fe(dmgBF_2)_2$ complexes of these ligands are listed in the third column of Table I.

The MAxCT band positions in the $dmgBF_2$ and pentacyanoferrate systems are compared in Table II, along with the ligand reduction potentials. An excellent correlation is found between the charge-transfer energies in the $Fe(dmgBF_2)_2$ and $Fe(CN)_5{}^{3-}$ systems. A similar correlation between the pentacyanoferrate and pentaamineruthenium systems is reported by Macartney.[15] These correlations arise because the transition energy is primarily determined by the ligand reduction potential. The tcne complex gives the lowest energy MAxCT band of those examined, appearing at 922 nm, consistent with expectations based on the reduction potential of tcne.

The assignment of the bands in the pyridine-bound[16] (see below) 4-CNpy complex is not trivial because the MPyCT band falls in approximately the same region as the MOxCT band. Nevertheless, confident assignments can be made based on a careful comparison with other 4-substituted derivatives.[17] The MPyCT band is more sensitive to substituents on the py than is the MOxCT band. The plots shown in Figure 1 illustrate this dependence for both the $dmgBF_2$ and dmgH systems. Assignments based on the plots in $Fe(dmgH)_2(4\text{-CNpy})_2$ for the MPyCT and the MOxCT bands are at 530 and at 490, respectively, while in $Fe(dmgBF_2)_2(4\text{-CNpy})_2$ the MOxCT is at 496 nm and the MPyCT occurs at 471 nm. This conclusion is consistent with the general invariance of the MOxCT band on BF_2 substitution,[2] while MAxCT bands are shifted to higher energy as a result of the increased Fe(III/II) reduction potential in the BF_2 derivative.

Linkage Isomerism. For the dmso, tcne, and cyanopyridine ligands, it is necessary to consider more than one potential mode of ligand binding to the iron. Both σ and π complexes of tcne with metal complexes are known.[9,18-20] Infrared evidence has been used to distinguish between these binding modes in metal carbonyl derivatives of tcne;[21] however, the features observed in the CN and CC stretching regions are not considered definitive in our systems. The kinetic and spectral characteristics of the tcne complexes described here are not especially different from the other nitriles investigated and are therefore presumed to involve coordination via the nitrile nitrogen.

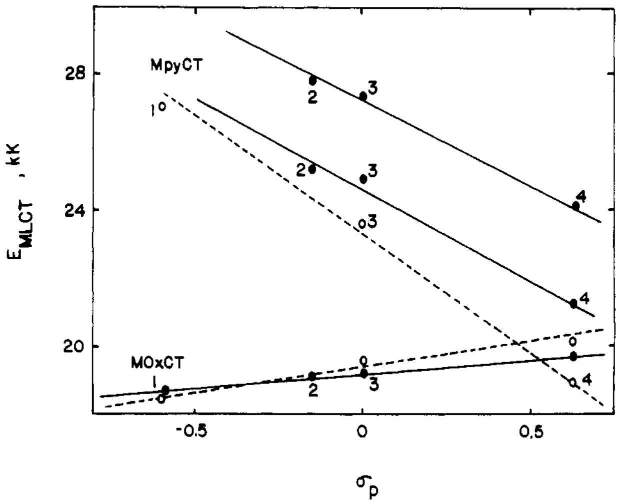

Figure 1. Hammett plot of MOxCT and MPyCT for the 4-substituted pyridine complexes $Fe(dmgBF_2)_2L_2$ (●) and $Fe(dmgH)_2L_2$ (○) for L = (1) 4-N(Me)_2py, (2) 4-*tert*-butylpy, (3) py, and (4) 4-CNpy.

The cyanopyridine ligands exhibit spectral characteristics fully consistent with nitrile coordination in the 2-CNpy case and pyridine coordination in the 4-CNpy case, as previously found by Haim for the pentacyanoferrate system.[12] The nitrile substituent in 2-CNpy introduces severe steric problems that disfavor coordination through the normally more basic pyridine nitrogen. Its spectrum is seen to be similar to other nitrile complexes. In the 4-CNpy case, the spectrum resembles that of pyridine derivatives that give rise to a MOxCT in the 500-nm range, as well as additional bands assigned to charge transfer to pyridine.

The question of S- vs O-bonded dmso[22,23] is not resolved by the IR spectra, which contain several bands in the 1000–1100-cm^{-1} region; however, we favor the O-bonded formulation because of the similarity in visible spectra to other oxygen-donor ligands and the anticipated steric effects associated with the S-bonded form. Both S- and O-bonded dmso are found in other Fe complexes (S bonded in $FePc(dmso)_2$,[24] O bonded in $Fe(dmso)_4Cl_2{}^+$ [25]).

Our ability to handle Fe(II) complexes of these quite labile weak-donor ligands is attributed to the very high oxidation potentials in the $Fe(dioxBF_2)_2$ systems (0.95 V vs SCE for $Fe(dmgBF_2)_2(CH_3CN)_2$).[2] The complexes become increasingly air-sensitive with decreasing concentration or strength of the axial ligands. Details of reactions with oxygen will be reported elsewhere.

Carbon Monoxide Binding. The FeN_4W_2 complexes undergo the characteristic axial substitution reactions previously described in detail for W = CH_3CN.[2] Under 1 atm of CO, solutions of FeN_4W_2 in neat solvent W react rapidly and completely, giving visible spectra assigned to the $Fe(N_4)(W)CO$ complexes (W = thf, dmf, dmso, and CH_3CN). The carbonyls display MLCT bands in the region 350–430 nm with a substantial splitting of the band for oxygen-donor ligands. The carbonyl complexes were more inert, more soluble, and more stable than corresponding bis(solvato) precursors. The carbonyl stretching frequencies parallel closely those of the analogous weak-donor phthalocyanine

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(16) Evidence for a transient nitrile bound linkage isomer of 4-CNpy is found in the flash photolysis study of the $Fe(dmgBF_2)_2(4\text{-CNpy})(CO)$ complex in toluene. When the system is monitored at 500 nm, biphasic kinetics are observed consistent with a fast reaction ($k = 15\ s^{-1}$) assigned to dissociative isomerization of $Fe(dmgBF_2)_2(4\text{-CNpy})(4\text{-CNpy}^*)$ to $Fe(dmgBF_2)_2(4\text{-CNpy})_2$ at a rate independent of both [CO] and [4-CNpy] (4-CNpy* refers to the nitrile bound form). The slower subsequent reaction of the py-bound complex with CO then proceeds normally at a rate inverse in [4-CNpy] and first order in [CO]. The rate constant assigned to the isomerization step is similar to that reported previously for replacement of CH_3CN trans to py in toluene.[2] From the absorbance changes, we estimate about 33% of the initial photoproduct is trapped with the 4-CNpy bound through the nitrile group, consistent also with relative rates of addition of py vs CH_3CN of 2.5 reported previously.[2]

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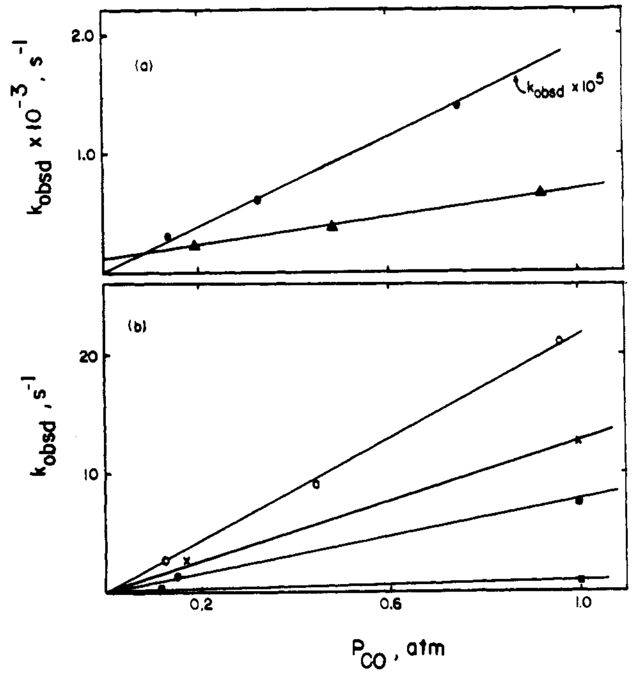

Figure 2. (a) Kinetic data for the reaction $Fe(dmgBF_2)_2W_2 + CO \rightarrow Fe(dmgBF_2)_2(W)CO + W$ in neat solvent at 25 °C, for W = thf (●), and tht (▲). Note, for thf, $k_{obsd} \times 10^5$ is plotted. (b) Kinetic data for the reaction $FeN_4(dmso)_2 + CO \rightarrow Fe(N_4)(dmso)CO + dmso$ in dmso at 25 °C, for Tim (○) bqdBF₂ (×) npqBF₂ (●), and dmgBF₂ (■).

derivatives reported by Calderazzo and James.[26] The existence of a large chemical shift for the dmso methyl resonances is sometimes taken as evidence for S bonding.[22] In $FeN_4(dmso)CO$, the position of the dmso methyl resonance is distinct from that of free dmso but only shifted −0.07 ppm. This is taken as weak evidence for O bonding.

Kinetics. The kinetics of the reactions with CO (eq 1) were measured by the flash photolysis method previously described for the CH_3CN systems.[2] In this method, the FeN_4W intermediate generated via Fe–CO photodissociation is rapidly trapped as the bis(solvato) species. The slower (millisecond to minutes) subsequent reaction of FeN_4W_2 is monitored by visible spectroscopy. The kinetics are consistent with a dissociative mechanism in which CO and W compete for the FeN_4W intermediate generated via thermal dissociation of W from FeN_4W_2. Under the conditions of pseudo-first-order [CO], one observes a first-order dependence on CO:

$$k_{obs} = k_f[CO] + k_{-CO} \qquad (2)$$

Only in the cases of tht and py (ligands of better donor strength than CH_3CN) is the second term in eq 2 significant (k_{-CO}). For tht, k_f corresponds to the slope of the plot in Figure 2 and k_{-CO}, to the intercept. For the extreme case of neat pyridine, the reaction proceeds very slowly, going only 15% to completion. The approximate value for py in Table III is estimated based on the rate of approach to equilibrium, the extent of the reaction at equilibrium, and an independent determination of the reverse reaction at low [CO].

In terms of the D mechanism, the rate constant k_f is given by eq 3 for the case $k_{-W}[W] \gg k_{+CO}[CO]$.

$$k_f = k_{-W}k_{+CO}/k_{+W}[W] \qquad (3)$$

The forward rate constant then depends upon the lability of W (k_{-W}) and the relative constants for addition to the pentacoordinate intermediate (k_{+CO}/k_{+W}).

The relative values of k_f in thf, dmf, dmso, nitriles, tht, and py are most simply explained in terms of the changes in k_{-W} as a function of the donor ability of the solvent. The stronger binding of CH_3CN compared to dmso is also apparent in the data for npqBF₂, bqdBF₂, and Tim systems.

Table III. Rate and Equilibrium Data for CO Binding for

$$FeN_4(W)_2 + CO \underset{k_{-CO}^{W}}{\overset{k_f}{\rightleftharpoons}} FeN_4(W)CO + W$$

W	k_f with different solvents[a] W	k_f with different solvents[a] toluene	k_{-CO}^{W}, s^{-1}	$k_{W,CO}^{W}$, atm^{-1}
$N_4 = (dmgBF_2)_2$				
thf	160		0.018	8900
dmf	3.5	3.1	3×10^{-4}	12000
dmso	0.8	1.4	5×10^{-4}	1600
CH_3CN[b]	0.025	0.075	1.5×10^{-4}	170
tht	0.0057	0.098	1.1×10^{-3}	5.1
$CH_2{=}CHCN$	0.011	0.065		
dcne		0.060		
tcne		0.075[c]		
$ClCH_2CN$	0.061	0.47		
C_6H_5CN	0.006	0.065		
$C_6H_4(CN)_2$		0.031		
$C_6H_3(NO_2)(CN)_2$		0.02		
$C_6F_4(CN)_2$		0.04		
2-CNpy		0.11		
4-CNpy		0.0012		
py	5×10^{-6}	1.3×10^{-4}[b]	3×10^{-5}	0.2
$N_4 = (bqdBF_2)_2$				
dmso	12		0.2	60
CH_3CN[b]	0.088		0.042	2.1
$N_4 = (npqBF_2)_2$				
dmso	8		0.026	320
CH_3CN[b]	0.017		4.3×10^{-3}	4.0
N_4 = Tim				
dmso	21		5×10^{-4}	42000
CH_3CN[b]	2.7×10^{-3}		4.9×10^{-4}	5.5
C_6H_5CN[d]	7.7×10^{-4}		3.3×10^{-4}	2.3

[a] Units for k_f in W are $atm^{-1}\ s^{-1}$ and in toluene are $M\ atm^{-1}\ s^{-1}$. [b] Calculated from data in ref 2. [c] Measured in CH_2Cl_2. [d] Calculated from data in ref 5.

The values of k_f in toluene[27] for the various nitriles listed in Table III are all fairly similar. A few trends are worth noting.

(1) k_f increases with electron-withdrawing substituents, reflecting an increase in k_{-W} as the donor ability of W decreases. The largest effect is found for $ClCH_2CN$. In the aromatic nitriles, substituents in the ring have a smaller effect on the nitrile basicity.

(2) A statistical effect is present in k_f for nitriles with multiple –CN groups, which leads to values 2 (phthalonitriles, dcne) or 4 (tcne) times that expected for a comparable mononitrile. The statistical effect arises in the contribution of k_{+CO}/k_{+W} in eq 3. A ligand with two nitrile groups will compete with CO twice as effectively as a mononitrile. Data reported by Haim[12] for benzo- vs phthalonitriles in the pentacyanoferrate(II) system do not include this effect since, in their work, k_{-W} is measured.

(3) In cyanopyridines, the value of k_f is 100 times slower when the py is coordinated (4-CNpy) than when a nitrile group is bound (2-CNpy). Haim[12] obtained a similar result.

While it was not possible to obtain values of k_{-W} experimentally, reasonable estimates of k_{-W} can be made on the basis of the experimental values for k_f in toluene, the solubility of CO (0.007 $M\ atm^{-1}$), and an assumed value of k_{+CO}/k_{+W}. Previous work[2,3] suggests values between 10 and 100 for the discrimination ratio in toluene. This leads to estimates for k_{-W} between 10^3–10^4 times the values of k_f in Table IV. Thus, k_{-A} is estimated at 1000 s^{-1} corresponding values for dmso and dmf are an order of magnitude greater, and for k_{-thf} the value is as high as $10^6\ s^{-1}$.

CO Dissociation. Owing to the large affinities of these systems for CO, the reverse reaction (eq 4) could not be studied directly

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(26) Calderazzo, F.; Frediani, S.; James, B. R.; Pampaloni, G.; Reimer, K. J.; Sams, J. R.; Serra, A. M.; Vitali, D. *Inorg. Chem.* **1982**, *21*, 2302.

(27) Rate constants for reaction of $Fe(dmgBF_2)_2W_2$ in CO-saturated toluene at concentrations [W] = 0.05, 0.10, 0.60, and 1.2 M are 48, 29, 6, and 7.2 s^{-1} for W = dmf and 28, 15, 4.3, and 3.5 s^{-1} for W = dmso, respectively.

Table IV. Comparative Reactivity of Weak-Donor Complexes

W	donor parameters				k_f for different N_4, atm s^{-1}		$k_{-W} \times 10^{-3}$, s^{-1}	$k_{aq} \times 10^{-7}$, s^{-1}
	DN[a]	CP[b]	*E*[c]	*C*[c]	$(dmgBF_2)_2$	Tim	$Fe(CN)_5W^{3-}$[e]	$Co(NH_3)_5W^{3+}$[f]
NH_3	59.0						15.8	
py	33.1	2.24	1.17	6.4	5×10^{-6}		1.10	
tht			0.34	7.9	0.0057			
dmso	29.8	1.24	1.34	2.85	0.8	21	0.075	180
dmf	26.6	0.72			3.5			16
thf	20.0		0.98	4.27	160			
H_2O	18.0	0.79				1.7×10^4[d]		
CH_3CN	14.1	0.0	0.89	1.34	0.025	0.003		0.2

[a] DN = donor number, from ref 26 and references within. [b] CP = coordination power, from ref 31. [c] Drago *E* and *C* parameters, from ref 30. [d] Butler, A.; Linck, R. G.; *Inorg. Chem.* **1984**, *23*, 4545. Converted to appropriate units using 10^{-3} M/atm for the solubility of CO in H_2O. [e] Reference 15. [f] Curtis, N. J.; Lawrance, G. A. *Inorg. Chem.* **1986**, *25*, 1033.

since W does not readily displace CO except for the better donor W = py or tht. However, the reaction with MeIm in eq 5 affords

$$Fe(dmgBF_2)_2(W)CO + W \rightarrow Fe(dmgBF_2)_2(W)_2 + CO \qquad (4)$$

$$FeN_4(W)CO + 2\ MeIm \rightarrow FeN_4(MeIm)_2 + W + CO \qquad (5)$$

the information sought. This reaction proceeds cleanly with isobestic points at a pseudo-first-order rate constant that is independent of [MeIm] in the range 0.03–0.3 M. These results are good evidence that the rate-determining step for reaction 5 is loss of CO trans to W ($k_{-CO}{}^{W}$). Complications arising from the formation of $FeN_4(MeIm)CO$ via the "base-off" pathway are not significant when [W] ≫ [MeIm]. Examples where this is not the case will be presented elsewhere.

The equilibrium constant for CO binding is calculated from the ratio of the forward- and reverse-reaction rate constants and verified by titration in favorable cases.

$$K_{CO} = k_f / k_{-CO} \qquad (6)$$

Hemes, whose weak-donor complexes are high-spin and pentacoordinate, bind CO via addition to a vacant site, and therefore the equilibrium constant for CO binding is relatively insensitive to the nature of the weak-donor ligand ($10^{-6}K_{CO}{}^{W}$ = 2.8, 4.3, and 2.5 M^{-1} for thf, dmf, and 2-MeIm for deuteroheme in benzene[28]). In contrast, the FeN_4W_2 systems are clearly six coordinate, and the CO binding is very sensitive to the nature of W, spanning 5 orders of magnitude for the $dmgBF_2$ systems shown.

The relative affinities of different FeN_4 systems for CO primarily reflect trends in the values of k_{-CO} previously elucidated.[2,4] One should also note that there are significant differences in the relative value of k_f for dmso and CH_3CN in the different FeN_4 systems. Steric effects may account for the fact that $FeTim^{2+}$ has the highest value of k_f for dmso and the lowest for CH_3CN.

Relative Donor Ability of Ligands. The relative ability of donor solvents to coordinate to metal ions is a subject of continuing interest. The donor number concept of Gutmann[29] is the most widely used scale for this purpose. It is well-known that the donor number, being based on the heat of reaction of $SbCl_5$, includes not only the metal solvent bonding but factors related to solvation as well. The *E* and *C* number scale of Drago[30] is designed to measure only the metal ligand bond enthalpy and deliberately excludes solvation effects. Unfortunately, it is primarily based on non-transition-metal acid–base interactions and does not take π bonding and other d-orbital effects into account. The coordinating power of a solvent is defined by Munakata[31] on the basis of equilibria for solvato nickel(II) complexes and is scaled relative to acetonitrile being 0. These parameters are given in Table IV, along with kinetic data for replacement of the coordinated solvent in several systems.

While differences in the solvent, as well as other ligands present (trans effects), are undoubtedly of some importance, it is noteworthy that the relative binding order thf < dmf < dmso < CH_3CN < py is generally maintained, except for the case of dmso in the pentacyanoferrate(II) system. Here, the postulate of S coordination[22] or some other effect is required.

In all of the d^6 metal complexes shown, CH_3CN is several orders of magnitude better as a ligand than would be inferred from any of the reported scales of solvent donor ability. The enhanced binding of CH_3CN compared to the other weak donors may be related to its small size or the π-acceptor character of nitriles. The kinetic data for the $dmgBF_2$ system clearly shows the same relative binding order for these weak donors in toluene solution. Therefore, the kinetic data, unlike some of the donor parameter scales, reflect the metal–ligand bond component largely uncomplicated by other "solvation" effects.

Molecular Engineering of CO Binding. One of the goals of this work was to obtain CO binding systems in which both the kinetic and thermodynamic characteristics for CO binding could be systematically engineered over a large range by choice of the ligands N_4 and W. The data in Table IV show the extent to which CO binding to $Fe(dmgBF_2)_2$ can be varied as a function of the donor solvent used. Equilibrium constants vary over 5 orders of magnitude. The CO pressure required to half-form the carbonyl, $P_{1/2}$, is only a few parts per million in thf, a few Torr in CH_3CN, and several atmospheres in pyridine. The rate of response of the complex to CO at a level of 1 Torr ranges from half-lives of seconds in thf to minutes for CH_3CN. The distinct color changes in these systems make them useful in visual detectors for CO.

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