Bridge Addition Compounds. III. The Influence of Boron-Containing Lewis Acids on Electronic Spectra, Vibrational Spectra, and Oxidation Potentials of Some Iron–Cynanide Complexes

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Abstract: Charge-transfer spectra were determined for a series of metal–cyanide adducts, $Fe(phen)_2(CNBX_3)_2$ (X = CH_3, H, F, Cl, and Br), and some of these were also studied by oscillopolarography in methylene chloride solution. The observed changes in spectra and oxidation potentials are interpreted in terms of a decrease in metal–ligand σ bonding and an increase in π bonding upon addition of the Lewis acid. This explanation is also supported by the change in the NO stretching frequency upon BF_3 addition to $Na_2Fe(CN)_5NO$ and the change in the charge-transfer spectrum of $[Fe(phen)_2(CN)_2][PF_6]$ upon BF_3 addition. Similarly, semiempirical SCF–MO calculations show that addition of a proton (and presumably any acid) to the nitrogen end of cyanide leads to a reduction in σ and π energies which is consistent with the above interpretation. As judged by charge-transfer spectra, the inductive effects of boron-containing Lewis acids fall in the order $BBr_3 > BCl_3 > BF_3 > BMe_3 > BH_3$.

Dicyanobis(1,10-phenanthroline)iron(II) displays a visible charge-transfer spectrum which is strongly dependent on the hydrogen-bonding propensity of the solvent in which it is dissolved.[1,2] This absorption is thought to involve a metal to 1,10-phenanthroline π^* charge transfer,[2,3] and a qualitative physical model for the spectral shift upon protonation has been given by Hamer and Orgel.[3] These authors postulate that upon protonation the cyanide ligand becomes a very strong π acceptor and thus stabilizes the ferrous state relative to the ferric. This stabilization of the ground state leads to a blue shift in the charge-transfer (oxidation–reduction) spectrum.

Recently, it was shown that compounds containing metal —C≡N—BX_3 linkages may be formed (X = H or F).[4] In this work we have prepared additional compounds of the type $Fe(phen)_2(CNBX_3)_2$ (X = Br, Cl, Me) and studied properties such as charge-transfer spectra which are directly related to their electronic structures.

Experimental Section

General Procedures. Dicyanobis(1,10-phenanthroline)iron(II) was prepared according to Schilt's procedure[2] and dehydrated under high vacuum ($<10^{-4}$ mm). Boron trifluoride was manipulated in a preparative high-vacuum system for which Kel-F grease was used as a stopcock lubricant. Boron trichloride and boron tribromide were handled in a grease-free vacuum system equipped with O-ring joints and O-ring needle valve stopcocks. The solid adducts were manipulated in a nitrogen-filled glove bag; however, except for $[Fe(phen)_2(CNBF_3)_2{}^+][PF_6{}^-]$, brief exposure of these compounds to the atmosphere did not lead to significant decomposition. The preparation of $Fe(phen)_2(CNBF_3)_2$ and $Fe(phen)_2(CNBH_3)_2$ by direct addition of the acid to the dry cyanide complex has been discussed previously.[4a]

$Fe(phen)_2(CN)_2$ plus BCl_3. Matheson CP grade BCl_3 was purified by several distillations through a trap maintained at −78° and was collected at −112°; the vapor pressure of the fractionated material was 476.0 mm at 0° (lit 476 mm).[5] Reaction of BCl_3 gas with $Fe(phen)_2(CN)_2$ was initially rapid and highly exothermic with the consequence that moderation of the reaction was necessary to avoid side reactions; therefore 0.291 mmole of $Fe(phen)_2(CN)_2$ was cooled to 0° and BCl_3 was admitted slowly. After standing overnight excess BCl_3 was removed and *PVT* measurement of the unreacted acid indicated the mole ratio of BCl_3 absorbed to initial $Fe(phen)_2(CN)_2$ was 2.17; however, further removal of BCl_3 under high vacuum gave a value of 2.05 BCl_3 per $Fe(phen)_2(CN)_2$ by *PVT* measurement of BCl_3 and 2.03 by weight gain. This yellow-orange solid is slightly soluble in halogenated hydrocarbons.

$Fe(phen)_2(CN)_2$ plus BBr_3. Boron tribromide obtained from the Anderson Chemical Division of Stauffer Chemical Co. was distilled through a 250-mm Vigreux column (bp 87.0–88.0° uncor), shaken with mercury, and introduced into the grease-free vacuum line by trap-to-trap distillation. The parent cyanide complex was maintained at 0° and BBr_3 was slowly introduced. After 20 hr excess BBr_3 was removed. The weight gain of the solid indicated an excess of BBr_3 had been absorbed (BBr_3 per $Fe(phen)_2CN_2$ = 2.25), but a constant weight was reached after several hours under high vacuum. The final mole ratio of reactants, determined by weight gain, was 2.01.

$Na_2Fe(CN)_5NO$ plus BF_3. A 0.453-mmole sample of reagent grade $Na_2Fe(CN)_5NO \cdot 2H_2O$ was dehydrated under high vacuum and then sealed in a tube with 4.086 mmoles of BF_3. After 2 years the sample was opened to the vacuum system and *PVT* measurement of the unconsumed BF_3 showed that 5.08 moles of acid were absorbed per mole of $Na_2Fe(CN)_5NO$. An infrared spectrum of the recovered BF_3 agreed with the spectrum of the pure compound. The weight gain of the solid phase also indicated a mole ratio of 5.08 for the reactants.

$[Fe(phen)_2(CN)_2][PF_6]$ plus BF_3. Dicyanobis(1,10-phenanthroline)iron(III) nitrate was prepared by the oxidation of $Fe(phen)_2(CN)_2$ with nitric acid.[2] Because of the reactivity of $NO_3{}^-$ with BF_3,[6] a metathesis was performed in hot water between KPF_6 and $Fe(phen)_2(CN)_2NO_3$. Upon cooling a finely divided red precipitate of $Fe(phen)_2(CN)_2PF_6 \cdot xH_2O$ was formed. *Anal.* (dried compound): Calcd: C, 50.91; H, 2.63; N, 13.71. Found: C, 52.22; H, 2.59; N, 12.93. An infrared spectrum of this material revealed a very weak band in the C≡N stretch region at 2132 cm^{-1}; a low CN stretch intensity is also observed in ferricyanide. In addition, the sample displayed a strong absorption at *ca.* 847 cm^{-1}, which presumably corresponds to the strong absorption at 860–920 cm^{-1} for $PF_6{}^-$ in KPF_6; none of the characteristic $NO_3{}^-$ infrared absorptions was present.

Direct reaction of boron trifluoride gas with a dehydrated sample of $[Fe(phen)_2(CN)_2][PF_6]$ produced a vivid color change from deep red to green. In a typical preparation, 0.136 mmole of the metal

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[1] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

[2] A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

[3] N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

[4] (a) D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963); (b) *ibid.*, **84**, 4610 (1962).

[5] H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).

[6] R. N. Scott and D. F. Shriver, *Inorg. Chem.*, **5**, 158 (1966).

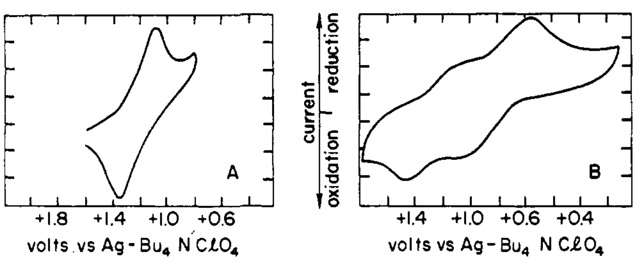

Figure 1. Oscillopolarogram of (A) $Fe(phen)_2(CNBBr_3)_2$ in methylene chloride, and (B) a mixture of $Fe(phen)_2(CNBF_3)_2$ and $Fe(phen)_2(CN)_2 \cdot BF_3$ in methylene chloride.

complex was exposed to 0.488 mmole of BF_3 for 24 hr and 0.290 mmole of BF_3 was absorbed. This corresponds to $2.13BF_3$ per $Fe(phen)_2(CN)_2][PF_6]$. The absorption of a slight excess of BF_3 was analogous to the Fe(II) systems, but, in contrast to those systems, the Fe(III) complex appears to have a noticeable dissociation pressure which was evident from the observation that 15 min under high vacuum reduced the BF_3 to $[Fe(phen)_2(CN_2)][PF_6]$ ratio to 1.96, after 45 min to 1.83, and after 1.75 hr to 1.75. Exposure of this sample to BF_3 for 3 hr followed by removal of excess BF_3 for 5 min under vacuum ($<10^{-4}$ mm) produced a net reabsorption of boron trifluoride, 1.98 BF_3 per $[Fe(phen)_2(CN)_2][PF_6]$. This green solid decomposes rapidly on exposure to air, but it may be handled without apparent decomposition in a nitrogen-filled glove bag. An infrared spectrum of the compound displayed the expected increase in C≡N stretch frequency to 2232 cm^{-1}. In contrast to the uncomplexed material this absorption was strong. Broad absorptions at 1160 (s), 1110 (sh), and 840 (s) cm^{-1} were evident; these general absorptions are found in all BF_3–metal cyanide adducts.[4]

Displacement Reactions. Approximately 0.27 mmole of trimethylboron was added to an excess of $Fe(phen)_2(CN)_2$ in the presence of 1,2-dichloroethane, the solvent was removed, and a small excess of BF_3 was added to the solid. After several hours the original red complex had turned bright yellow and 0.19 mmole of BMe_3 was separated from the excess gas by trap-to-trap distillation.

In a similar experiment 0.488 mmole of $Fe(phen)_2(CN)_2 \cdot 1.74\ BH_3$ was exposed to 0.892 mmole of BF_3 gas for 2 days at room temperature. The pressure in the system slowly fell, which is in accordance with a displacement. Assuming the final product was a mixture of $Fe(phen)_2(CN)_2 \cdot 2BH_3$ and $Fe(phen)_2(CN)_2 \cdot 2BF_3$, the pressure change corresponded to 92% displacement of BH_3 by BF_3. Weight change of the product indicated 90% displacement. Infrared spectra of the solid product revealed little coordinated BH_3 (medium weak B-H absorption at 2310 cm^{-1}) but strong BF absorptions at *ca.* 1100 cm^{-1}. Infrared spectra of the gas showed the presence of B_2H_6 and a small amount of BF_3.

A 0.452-mmole sample of $Fe(phen)_2(CN)_2 \cdot 2BF_3$ was exposed to 0.90 mmole of BCl_3 for 2 days at room temperature. An infrared spectrum of the gas showed the presence of BCl_3, BCl_2F, BF_2Cl, and BF_3 whose spectra have been described by Lindeman and Wilson.[7] Another 5 days at room temperature led to a substantial reduction in the amount of BCl_3 in the gas phase. Weight change of the solid indicated 98% displacement, and weak infrared absorption at *ca.* 1100 cm^{-1} confirmed that only a trace of coordinated BF_3 remained in the solid.

Polarography. A three-electrode configuration was used with an instrument based on operational amplifier circuitry to obtain oscillopolarograms.[8] This instrumentation is necessary because of the high resistance of the dichloromethane solutions. The working electrode was a short platinum wire, another platinum wire served as auxiliary electrode, and the reference electrode was a silver wire in a Luggin probe containing 0.10 *M* tetrabutylammonium perchlorate in dichloromethane. The solvent, reagent grade dichloromethane, was dried over calcium hydride and distilled under dried nitrogen. Tetrabutylammonium perchlorate (0.10 *M*) was used as a supporting electrolyte. The surface of the working electrode was adequately cleaned by a brief period of reduction at negative potentials. Oscillopolarograms indicated all the systems were reversible or nearly reversible (Figure 1), and the oxidation potential was taken as the potential at half-peak height on an oscilloscope tracing.

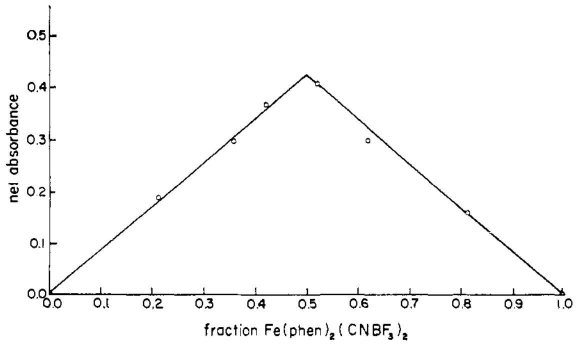

Figure 2. Continuous variations plot for the system $Fe(phen)_2(CN)_2$–$Fe(phen)_2(CNBF_3)_2$. The data for this plot were collected at 520 mμ, but similar plots are obtained at other wavelengths.

Spectral Measurements. A Cary Model 14 was used to obtain visible spectra on methylene chloride and 1,2-dichloroethane solutions of the various compounds. There was agreement between the positions of maxima in the solution spectra with mull transmittance and with reflectance spectra of corresponding compounds. Therefore, dissociation of the complexes and reaction with solvent or impurities can be ruled out.

A continuous variations study (Figure 2) was carried out between 1.0×10^{-4} *M* $Fe(phen)_2(CN)_2$ and 1.0×10^{-4} *M* $Fe(phen)_2(CNBF_3)_2$ in 1,2-dichloroethane. Prolonged contact with atmospheric moisture was avoided by carrying out most of the operations under a dry nitrogen atmosphere.

Direct reaction of boron trimethyl with $Fe(phen)_2(CN)_2$ was very sluggish; however, a complex of presumed composition $Fe(phen)_2(CNBMe_3)_2$ was prepared by exposing a 4.07×10^{-5} *M* solution of $Fe(phen)_2(CN)_2$ in $C_2H_4Cl_2$ to a large excess of BMe_3. This was accomplished by using a specially constructed evacuable cell which was attached to the vacuum line for introduction of boron trimethyl and subsequently sealed by means of an O-ring needle valve stopcock.

For the purpose of correlations, positions of overlapping bands were determined by the following procedure. The most intense band was mirrored around its maximum, and the leg most free from overlap was subtracted from the overlapping side. If overlap was quite serious, this process was repeated starting now with the weaker of the two bands which had been resolved on the first cycle.

Infrared spectra were recorded for Nujol mulls with a Beckman IR-9.

Discussion

Syntheses and Characterizations. In the course of this work the following new bridge addition compounds were prepared and/or identified: $Fe(phen)_2(CNBCl_3)_2$, $Fe(phen)_2(CNBBr_3)_2$, $[Fe(phen)_2(CNBF_3)_2^+][PF_6^-]$, $Na_2FeNO(CNBF_3)_5$, and $Fe(phen)_2(CN)_2 \cdot BF_3$. The composition of all but the last of these was clearly established by measurement of the uptake of Lewis acid. Also, these adducts displayed the characteristic[4] increase in C≡N stretch frequency (Table I). This evidence and analogy with previous work[4] leaves little doubt that they are correctly formulated as metal–cyanide bridge addition compounds containing Fe—C≡N—BX_3 linkages. Evidence for the 1:1 adduct $Fe(phen)_2(CN)_2 \cdot BF_3$ came from two sources: (1) a continuous variations treatment using $Fe(phen)_2(CN)_2$ and $Fe(phen)_2(CNBF_3)_2$ solutions (Figure 2), and (2) the appearance of a new oxidation wave in the oscillopolarogram (Figure 1).

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(7) L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956).

(8) A more complete description of the instrument and pertintent references are given in the following paper: D. F. Shriver, D. E. Smith, and P. Smith, *J. Am. Chem. Soc.*, **86**, 5153 (1964).

Table I. Spectral Data and Half-Wave Potentials

Compound	ν_{CN}, cm^{-1}	Charge-transfer bands		
		Apparent,[a] mμ	Resolved, cm^{-1}	$E_{1/2}$,[e] v
$Fe(phen)_2(CN)_2$	2067 (s)[c]	599 [9.67]	16.7 × 10^3	0.52
	2079 (s)[c]	~540 (sh)	19.1	
$Fe(phen)_2(CNBH_3)_2$	2145 (s)[c]	510	18.9	
	2165 (ms)[c]	459	21.9	
$Fe(phen)_2(CNBMe_3)_2$		484 [6.76]	20.4	
		448 [6.66]	22.4	
$Fe(phen)_2(CN)_2 \cdot BF_3$		~515 (sh)	18.8	+0.8
		473 [8.15]	21.3	
$Fe(phen)_2(CNBF_3)_2$	2153 (s)[c]	~450 (sh)	21.3	1.12
	2173 (ms)[c]	419 [6.37]	24.3	
$Fe(phen)_2(CNBCl_3)_2$	2130 (s)	~445 (sh)	21.7	1.18
	2155 (ms)	408 [6.39]	24.5	
$Fe(phen)_2(CNBBr_3)_2$	2127 (s)	~440 (sh)	21.9	1.21
	2158 (ms)	405 [6.58]	24.7	
$[Fe(phen)_2(CN)_2^+][PF_6^-]$	2132 (vw)	~523[b]		
$[Fe(phen)_2(CNBF_3)_2^+][PF_6^-]$	2230 (s)	~630[b]		
$Na_2Fe(CN)_5NO \cdot 2H_2O$	2145 (s)[d] (1943, ν_{NO})	~395[b]		
$Na_2Fe(CNBF_3)_5NO$	2261 (s) (2015, ν_{NO})	~395[b]		

[a] Molar extinction coefficients are enclosed in brackets. [b] Obtained from transmittance of a mull. [c] These values are from ref 4a. [d] Under good resolution the CN stretch region is much more complex than previously reported: 2099 (s), 2110 (mw), 2115 (w), ~2130 sh, ~2145 (vs), 2159 (ms), 2162 (ms), and 2174 (s). [e] Half-peak potential.

A Qualitative Model for the Transmission of Inductive Effects through Cyanide. Hamer and Orgel's explanation for the shift in the charge-transfer spectrum of $Fe(phen)_2(CN)_2$ upon protonation attributes the apparent stabilization of the Fe(II) to back π bonding.[3] The data now at hand indicate that changes in σ bonding must also be considered to explain both charge-transfer spectra and d–d transitions. The ligand in question, C≡N—H, should be intermediate in both σ-donor and π-acceptor strength between CO and CN^-. Carbon monoxide is a poor σ donor, as evidenced by its lack of affinity for BF_3, or protons, but infrared spectra and a variety of evidence indicate it is a good π acceptor. In contrast, CN^- is a good base and therefore a good σ donor but less efficient than CO as a π acceptor. Therefore, addition of a proton or BF_3 to the nitrogen end of cyanide should decrease σ bonding and increase π bonding to a metal.

These qualitative arguments were further substantiated by semiempirical LCAO–MO–SCF calculations on CO, CNH, and CN^-. The method used was recently formulated by Pople, Santry, and Segal, who have shown that it gives a good approximation to *a priori* calculations.[9] The zero-differential overlap approximation is used, and basis orbitals are 1s for hydrogen and 2s, $2p_x$, $2p_y$, and $2p_z$ for second-period atoms. Diagonal matrix elements of the Hamiltonian are given by

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - {}^1/_2P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} Q_{BB}\gamma_{AB} \quad (1)$$

The quantity $U_{\mu\mu}$ is the valence-state ionization potential[10] plus the change in electron repulsion upon ionization. P_{AA} is the total valence electron density on atom A and $P_{\mu\mu}$ is the electron density in the μth orbital of A. In our calculation one-center two-electron integrals were taken proportional to the Slater exponent in accordance with Paoloni's approximation:[11] $\gamma_{AA} = 3.29Z_A$ for second-period atoms, and $\gamma_{AA} = 8.00Z_A$ for hydrogen. Q_{BB} is the net charge on atom B. The two-center two-electron integral γ_{AB} was found by the Mataga–Nishimoto approximation.[12]

Off-diagonal elements are given by

$$F_{\mu\nu} = \beta_{AB}S_{\mu\nu} - {}^1/_2P_{\mu\nu}\gamma_{AB} \quad (2)$$

$$\beta_{AB} = \beta_A{}^\circ + \beta_B{}^\circ$$

The empirical parameters $\beta_X{}^\circ$ were 4.5, 6.5, 7.5, 8.5, and 9.5 for H, B, C, N, and O, respectively. These values appear to give reasonable calculations on a variety of molecules. Other terms in eq 2 are $S_{\mu\nu}$, which is the overlap integral between orbitals μ and ν, and $P_{\mu\nu}$, which is the μ–ν bond order.

The calculation was programmed for the CDC 3400. After each diagonalization of the F matrix, a new set of charge densities and bond orders was calculated and used to generate an F matrix for the next round. It was found that the rate of convergence to self-consistent charge densities could be approximately doubled by a weighted average of matrix elements from the previous, *i*th, round with the newly calculated values, *j*th round

$$F_{\mu\nu} = 0.4F_{\mu\nu}{}^i + 0.6F_{\mu\nu}{}^j$$

Our confidence in the results is reinforced by the observation that the ordering of levels for CO agrees with much more exact calculations, and the orbital energies agree rather well with experimental ionization potentials:[13a] $\epsilon(\sigma_z) = 13.69$ ev, observed ionization

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(9) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965). It should be noted that the sum term in eq 1 is different from that of Pople, *et al.*, owing to our assumption that the two-center two-electron integral is equal to the two-center electron-core integral.

(10) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(11) (a) L. Paoloni, *Nuovo Cimento*, **4**, 410 (1956); (b) R. D. Brown, *Mol. Phys.*, **1**, 304 (1958).

(12) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957).

(13) (a) W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965); (b) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Inc., Englewood Wood Cliffs, N. J., 1965, p 313.

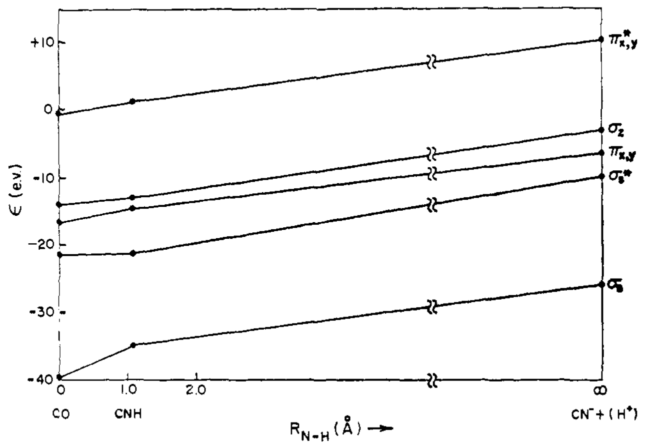

Figure 3. Correlation diagram of orbital energies for CO, CNH, and $CN^- + H^+$.

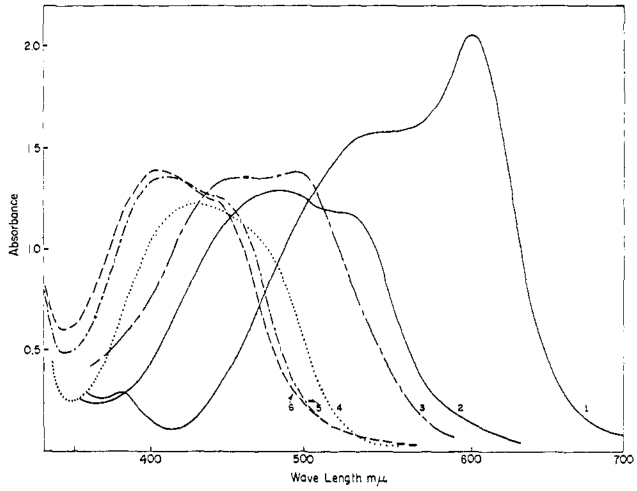

Figure 4. Charge-transfer spectra: (1) $Fe(phen)_2(CN)_2$; (2) $Fe(phen)_2(CN){\cdot}BF_3$; (3) $Fe(phen)_2(CNBMe_3)_2$; (4) $Fe(phen)_2(CNBF_3)_2$; (5) $Fe(phen)_2(CNBCl_3)_2$; (6) $Fe(phen)_2(CNBBr_3)_2$. The concentrations are not equal.

potential to $^2\Sigma^+ = 14.01$ ev; $\epsilon(\pi_{x,y}) = 16.50$ ev, observed ionization potential to $^2\Pi = 16.92$. Furthermore the σ_z orbital energy, 13.61, and ionization potential for HCN, 13.73, are in good agreement.[13b] The total energy of HCN is lower than that of CNH, which agrees with the fact that HCN is the chemically stable form.

Orbital energies of CO, CNH, and CN^- are presented graphically in Figure 3, where it is evident that removal of a proton from the oxygen nucleus to produce CNH has little effect on the highest σ, the π, and the π^* levels, which are the orbitals primarily involved in ligand–metal bonds. Thus, CNH like CO is expected to be a poor σ donor but a good π acceptor. The complete removal of the proton to produce CN^- leads to much higher σ- and π-orbital energies which implies good σ-donor and poor π-acceptor properties for cyanide.

Both the empirically observed differences between CO and CN^- and the molecular orbital calculations indicated *an electron-withdrawing substituent on the nitrogen end of cyanide will* (*1*) *decrease the energy of the lone pair on carbon and therefore decrease its availability for donor–acceptor bond formation, and* (*2*) *decrease the* π *and* π^* *energies, thereby increasing the* π*-acceptor character.* As outlined below, this model affords an explanation for a wide variety of phenomena including charge-transfer spectra, d–d transitions, oxidation potentials, and NO vibration frequencies of cyanide bridge adducts.

d–d Transitions. Previously we have found that the energies of d–d transitions for a cyanide complex are only weakly influenced by BF_3 addition.[4] Actually, there is some variability in this regard. Upon formation of a BF_3 adduct, $K_4Mo(CN)_8$ shows practically no change in its d–d spectrum,[2] but BF_3 increases the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition of $K_4Fe(CN)_6$ by 1000 cm^{-1}.[14] Similarly, this transition is increased by 1600 cm^{-1} upon formation of the Prussian blue analog $K_2Fe(CN)_6Zn$, which involves Fe—C≡N—Zn linkages.[14] These shifts are about fourfold less than changes in the charge-transfer bands of $Fe(phen)_2(CN)_2$ upon formation of $Fe(phen)_2(CNBF_3)_2$. Their smallness is understandable when it is noted that an electron-withdrawing substituent on nitrogen produces two opposing effects on the ligand field of CN^-. The substituent decreases σ donation, which diminishes the ligand field, but it increases back π bonding which enhances the ligand field.

Charge-Transfer Bands. From the effect of substituents on the visible spectra of iron(II) tris-2,2′-bipyridine and tris-1,10-phenanthroline complexes, Williams has concluded that these spectra involve metal-to-ligand(π^*) transitions.[15] By analogy, Schilt[2] and Hamer and Orgel[3] argue that the intense band of $Fe(phen)_2(CN)_2$ at 600 mμ involves an iron→phen(π^*) transition.

Upon protonation, or formation of a BX_3 adduct, electrons primarily localized on iron will be reduced in energy because of an increase in back π bonding and a decrease in negative charge on the metal. This decrease in negative charge should arise from the enhanced π bonding and the diminished σ bonding. However, the π^* energy of phenanthroline should be virtually unaffected.[16] Thus, metal-to-phenanthroline(π^*) transitions should shift to higher energy, and the data collected in Table I and Figure 4 bear this out.

When BF_3 was added to $[Fe(phen)_2(CN)_2^+][PF_6^-]$, a striking color change occurred from deep red to green, caused by a red shift in the 525-mμ absorption band of the parent compound to 630 mμ for the adduct $[Fe(phen)_2(CNBF_3)_2^+][PF_6^-]$. This bathochromic shift had been anticipated, because it appeared likely the visible bands of the iron(III) compound involve a charge transfer which is in the reverse sense from its iron(II) analog. Trivalent iron complexes with 1,10-phenanthroline display strong visible absorption bands which Jørgensen suggests are best described as phen(π)→iron transitions.[17] Similarly, Williams believes that these bands are intermediate between transfer character and d–d character.[15] Analogy with the trisphenanthroline complexes suggests the visible bands of Fe-

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[14] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

[15] R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

[16] Good evidence for the lack of influence of bridge adduct formation on the π levels of phenanthroline comes from the observation that the ultraviolet $\pi \rightarrow \pi^*$ transition energies and relative intensities for this ligand are essentially unaffected by addition of BF_3 to $Fe(phen)_2(CN)_2$.

[17] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

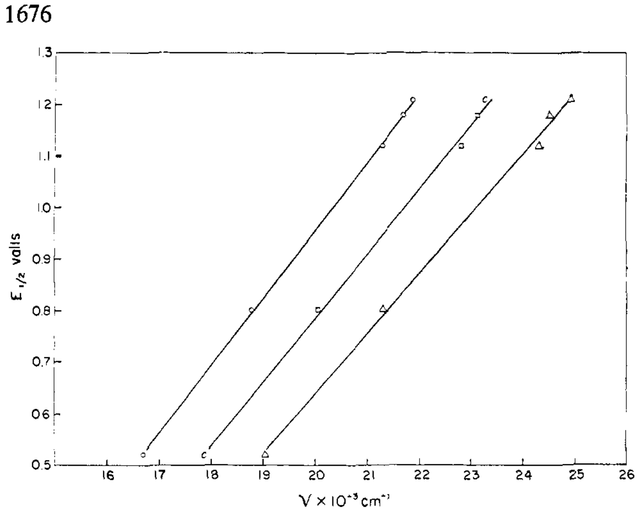

Figure 5. Half-peak potential *vs.* position of charge-transfer bands: ○, first charge-transfer band; △, second charge-transfer band; □, average of first and second bands.

$(phen)_2(CN)_2^+$ involve phen(π)→Fe(III) charge transfer. In terms of our model a red shift is expected for this transition because BF_3 addition to $Fe(phen)_2(CN)_2^+$ tends to stabilize electrons localized on the metal; thus the excited state is lowered in energy relative to the ground state.

There is one piece of spectral data which does not fall neatly into line with the interpretations presented here. It was found that the 25,320-cm^{-1} band of $Na_2Fe(CN)_5NO$ is virtually unaffected upon formation of the adduct $Na_2Fe(CNBF_3)_5NO$. Therefore, we concluded that the band was primarily d–d in character, an interpretation which agreed with the analysis of the nitroprusside spectrum published several years ago.[18a] This agreement is spoiled by a very recent reinterpretation of this spectrum which has led to the reassignment of the band as primarily charge transfer in character.[18b]

Oxidation Potentials. The foregoing arguments attribute the shifts in charge-transfer bands of the iron(II) complexes to changes in energy of the highest-filled orbitals in the *ground state* of the complex upon addition of an acid. Accordingly, a check on this aspect of the model is afforded by oxidation-potential data for a series of $Fe(phen)_2(CN)_2$ bridge adducts. In the absence of unusual variations in free energies of solvation, the oxidation potential of the complex should be a measure of the energy of the highest-filled level in the molecule. Thus, a linear relation is expected between the charge-transfer shifts and oxidation potentials; this is clearly evident in the excellent correlation shown in Figure 5. The fact that there is not a 1-v change in oxidation potential for each electron-volt change in the charge-transfer spectrum is probably due to the fact that the latter obey the Franck–Condon principle while the former do not. Also, the double-layer charging current and the portion of the solution resistance which is uncompensated by the instrument will contribute a bias to the correlation.

Methylene chloride appears to be an excellent solvent for molecular energy correlations. With tetrabutylammonium perchlorate as supporting electrolyte and a platinum working electrode it affords a wide potential range, *ca.* 3.9 v. Equally important is its low dielectric constant, 8.93, which is a desirable property when correlations are sought between molecules of different polarity.[8]

NO Stretching Frequency. The bridge adduct $Na_2Fe(CNBF_3)_5NO$ has an NO vibration absorption at 2015 cm^{-1} which is considerably higher than the 1943-cm^{-1} absorption of the parent $Na_2Fe(CN)_5NO$. This observation has a straightforward explanation.

Spectra, bond lengths, and semiempirical molecular orbital calculations indicate the NO group in the nitroprusside ion is strongly σ- and π-bonded to the metal.[18,19] Upon formation of the bridge adduct the cyanide ion becomes a more effective competitor for π electrons, so a reduction of Fe–N bond order is expected. This reduction in Fe–N bond order will result in an increased NO π-bond order and NO stretching frequency. Beck and Lottes have shown that this line of reasoning applies to a large number of NO complexes where it is found that the NO stretching frequency is highly sensitive to π-bonding competition from other ligands.[20]

Alternate Model. Long-range electrostatic forces, which are sometimes invoked to explain inductive effects in organic chemistry, do not appear capable of explaining the inductive effects observed by us. For example, Van Vleck's equations[21] for crystal-field splitting predict a 20-cm^{-1} *decrease* in 10*Dq* upon complete protonation of $Fe(CN)_6^{-4}$; this is at variance with data on $Zn_2Fe(CN)_6$ and $Fe(CNBF_3)_6^{-4}$, for which an *increase* is observed.

The Acceptor Strengths of BX_3 Acids. Relative Lewis acidities are generally found by comparison of heats or free energies of Lewis salt formation for a series of acids with a common base. In lieu of these quantitative data, acid-displacement experiments serve to establish an order of acidity. In this study the displacement experiments indicate the relative acidities $B_2H_6 < BF_3$ and $BMe_3 < BF_3 < BCl_3$. These orders show no peculiarities and are similar to observations with more conventional nitrogen-containing bases such as trimethylamine.

The donor–acceptor bond energy is a quantity not directly relatable to heats of coordination (or relative acidities) because these include reorganization energies,[22–24] which are defined as the energy necessary to distort a Lewis acid into the configuration it has in the adduct. However, no means exist to determine the reorganization energy experimentally. For diborane both the heat of BH_3 dimerization and reorganization are included in the heat of formation of the complex. Attempts have been made to obtain directly relative measures of the inherent acceptor strengths by spectroscopic measurements on Lewis salts, and it is interesting to compare this previous work with ours.

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Chemical shifts of methyl protons in trimethylamine adducts decrease in the order $BBr_3 > BCl_3 > BH_3 \geq BF_3 > BMe_3$.[25,26] The simplest interpretation of these results is that they reflect relative electron-withdrawing ability of the acids, but it is well known that with other compounds such a simple explanation often fails. Miller and Onyszchuk show good correlations between the chemical shifts and heats of coordination, dipole moments, and C=O stretching frequencies of corresponding methyl acetate complexes.

From a study of dipole moments Bax, Katritzky, and Sutton have arrived at the following relative order of B–N moments in Me_3NBX_3 adducts: $BF_3 < BH_3 \leq BCl_3 < BBr_3$.[27] In contrast to the greater acceptor strength of BH_3 than BF_3 which was deduced from the dipole and nmr results, Taylor finds the B–N valence force constant much larger for H_3NBF_3 (4.14 mdynes/A) than for H_3NBH_3 (2.90 mdynes/A).[28] The inference of relative bond strengths from force constants involves an assumption about the form of the potential, but this is a much less drastic assumption than those inherent in the above interpretations of nmr spectra and dipole moments. Within the framework of the model which has been presented in this paper, the charge-transfer spectra and polarographic data may be interpreted in terms of the electron-withdrawing power of the acid. It is gratifying that these data agree with Taylor's by indicating BF_3 is a stronger acceptor than BH_3.

Like the nmr and bond moment measurements, the present charge-transfer spectra and oxidation potentials indicate the acceptor order $BBr_3 > BCl_3 > BF_3$. As Miller and Onyszchuk point out, this order was determined for the adducts and cannot be interpreted in terms of reorganization energies, which had been used to explain a similar order for heats of coordination.

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Aminophosphine Chains of CH_3N and CF_3P Units[1]

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Abstract: The new volatile compounds $CF_3P(NHCH_3)_2$ (I, mp −29°; bp estd 135°), $CF_3P(NHCH_3)Cl$ (II, bp estd 102°), and $CH_3N(CF_3PCl)_2$ (III, mp near −50°; bp estd 148°) were made as possible precursors of polymers of the CH_3NPCF_3 unit, and their vapor-phase infrared spectra were accurately recorded. I is stable up to *ca.* 200°, in contrast to the rapid self-aminolysis of a product seeming to be $CF_3P(NH_2)_2$. II is easily aminolyzed to I, and its easy thermal condensation yields CF_3PCl_2 and a slightly volatile product regarded as the P–N–P–N chain compound $CF_3PCl(CH_3NPCF_3)NHCH_3$. I and II are easily cleaved to CF_3PCl_2 by HCl, but III requires a temperature of 140° for such a result, and it is thermally stable above 200°. Aminolysis of III apparently forms the very slightly volatile $CH_3N(CF_3PNHCH_3)_2$, representing the open chain N–P–N–P–N. Numerous combinations of such compounds failed to yield evidence for the formation of $(CH_3NPCF_3)_n$ ring polymers.

The high stability of the compounds $HN[P(CF_3)_2]_2$ and $CH_3N[P(CF_3)_2]_2$, and their resistance to cleavage by dry ammonia or hydrogen chloride,[2] suggested that some stability might be retained in analogous compounds having more labile groups replacing CF_3. In fact, the new volatile compound $CH_3N(CF_3PCl)_2$ proved to be stable and quite resistant to cleavage by HCl, and it could be aminolyzed at the P–Cl bonds without extensive cleavage of the central P–N–P chain.

Also interesting was the quest for the yet unknown $(HNPCF_3)_n$ and $(CH_3NPCF_3)_n$, in view of the reported existence of analogous PN dimer or trimer rings with other side groups.[3] However, at least eight different approaches toward $(CH_3NPCF_3)_n$, including low-pressure vapor-flow methods (to favor small rings), led to no success. The dimer or trimer should be volatile but neither could be obtained by sublimation from the reaction mixtures, nor could anything intelligible be extracted by solvents. However, certain new compounds intended as polymer precursors seem worthy of description.

For example, the diaminophosphine $CF_3P(NHCH_3)_2$ proved to be stable at 180°, resisting the expected aminolytic action (observed at 210°) of the N–H bond to cleave off HCF_3. Such resistance to a reaction analogous to basic hydrolysis would imply a lack of nitrogen-base action, presumably affected by N_{2p} to P_{3d} π bonding.

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