$C_5H_5Fe(CO)_2R$ ($R = CH_3$ and $CH_2C_6H_5$) do not react with $ClSO_2NCO$ under comparable conditions. This shows that the formation of **21** from h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ and $ClSO_2NCO$ is almost certainly related to the allylic nature of the metal complex.

In principle, this type of dualistic behavior with respect to rearrangement should also extend to V. However, a recent study on nucleophilic reactions of h^5-$C_5H_5Fe(CO)_2(h^5$-$CH_2{=}C{=}CHR)^+$ ($R = CH_3$ or C_6H_5) has demonstrated that the coordinated allene is rather inert to displacement.[39] Consistent with this observation, we note herein that rearrangement of the intermediates V invariably affords products containing a Δ^3-pyrrolinone ring (II).

Registry No. $ClSO_2NCO$, 1189-71-5; h^5-$C_5H_5Fe(CO)_2$-$CH_2CH{=}C(CH_3)_2$, 38905-70-3; h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, 31798-46-6; h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$, 40199-87-9; $C_6H_5NH_2$, 62-53-3; $(C_2H_5)_2NH$, 109-89-7; C_6H_5COCl, 98-88-4; h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, 34822-36-1; h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; $Mn(CO)_5$-$CH_2C{\equiv}CC_6H_5$, 23626-46-2; h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$, 32877-62-6; h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5$-$C_5H_5)$, 40199-91-5; CH_3OH, 67-56-1; $NaBH_4$, 16940-66-2; Na-$[h^5$-$C_5H_5Fe(CO)_2]$, 12152-20-4; C_6H_5CHO, 100-52-7; h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$, 31781-60-9; p-$CH_3C_6H_4$-NH_2, 106-49-0; $Mn(CO)_5CH_2CH{=}CHC_6H_5$, 23108-58-9; **1**, 38599-33-6; **2**, 39015-07-1; **3**, 40196-20-1; **4**, 40196-21-2; **5**, 40196-22-3; **6**, 40196-23-4; **7**, 40196-24-5; **8**, 40196-25-6; **9**, 40196-26-7; **10**, 40196-27-8; **11**, 40196-28-9; **12**, 40196-29-0; **13**, 40196-30-3; **14**, 40196-31-4; **15**, 40330-49-2; **16**, 40196-32-5; **17**, 40196-33-6; **18**, 40196-34-7; **19**, 40187-04-0; **20**, 40187-05-1; **21**, 38905-68-9; **22**, 38905-69-0; **23**, 40199-84-6.

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Metal Complexes as Probes of Donor-Acceptor Interaction. Vibrational Spectra of (π-C_5H_5)$Fe(CO)_2(CNMX_3)$ ($M = B$, $X = H$, F, Cl, Br, or CH_3; $M = Al$ or Ga, $X = Cl$ or CH_3)

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The change in the asymmetric CO stretching frequency, $\Delta\nu_{CO}{}^{asym}$, which occurs upon coordination of an acid to (π-C_5H_5)$Fe(CO)_2(CN)$ provides a convenient probe for the electron pair acceptor strength of the acid. In contrast with previous attempts to employ frequency shifts as probes of Lewis acids, the present method is not affected by spurious kinematic coupling between the probe oscillator and other oscillators in the adduct. Values of $\Delta\nu_{CO}{}^{asym}$ were determined for group III Lewis acids, and from these, relative electron pair acceptor strengths were deduced: $BH_3 < BF_3 < BCl_3 \approx BBr_3$, $BCl_3 > GaCl_3 > AlCl_3$, and $Al(CH_3)_3 > B(CH_3)_3 \approx Ga(CH_3)_3$. Comparison of trends in electron pair acceptor strength with acidity trends yields valuable insight into the details of Lewis acid-base interaction. For example, such a comparison provides experimental evidence for the distortion energy of BH_3 being less than that of BF_3.

Introduction

Assessment of the extent of donor-acceptor electron transfer is a central problem in the understanding of bonding in complexes. While the relative acidity of an acceptor as judged by ΔG_f° or ΔH_f° is important in describing the extent of complex formation, these thermodynamic data usually do not provide specific information on the donor-acceptor bond because a variety of other bonds are altered upon complex formation. For example, the interaction of a donor with BF_3 leads to considerable change in B-F bond lengths and angles, indicating significant changes in the B-F bond energies. More specific information on the donor-acceptor bond is available from interatomic distances and from force constants, both of which are difficult and sometimes impossible to determine with the required precision. These difficulties have prompted the use of simple spectroscopic criteria for the extent of donor-acceptor interaction, the foremost being nmr chemical shift and infrared absorption frequencies. However, these methods have serious limitations.[1] For example, the complex factors which determine nmr chemical shifts lead to considerable uncertainty in the application of this technique to a study of acceptor character.[1a] Infrared absorption frequencies associated with either the donor-acceptor bond stretch or with the stretch of an adjacent bond, *e.g.*, ν_{CN} in nitrile adducts, are of limited value because these modes generally include large contributions from atom motions other than the ones of primary interest.[1b,c]

In the present work we explore the use of shifts in ν_{CO} as criteria for the extent of donor-acceptor interaction with the nitrogen end of cyanide in (π-C_5H_5)$Fe(CO)_2(CN)$. The attractive features of the metal carbonyl cyanide as a probe for donor-acceptor interaction are the sensitivity of CO stretching frequencies to the nature of the group attached to cyanide and negligible kinematic coupling of extraneous motions with the CO stretch.

Experimental Section

Materials. (π-C_5H_5)$Fe(CO)_2CN$ was prepared by a modification of Piper, Cotton, and Wilkinson's procedure[2] in which the refluxing step was replaced by stirring at room temperature for 1.5 hr (yield 40–50%). The compound was judged pure by C, H, and N analyses and infrared spectra. $AlCl_3$ (Matheson, Coleman and Bell) was

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[1] (a) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83, 4138 (1961); (b) R. C. Taylor, *Advan. Chem. Ser.*, No. 42 (1964); (c) D. F. Shriver and B. Swanson, *Inorg. Chem.*, 10, 1354 (1971). (d) By contrast, a very promising spectroscopic probe for donor-acceptor interaction involves the esr of free-radical bases; see T. B. Eames and B. M. Hoffman, *J. Amer. Chem. Soc.*, 93, 3141 (1971).

[2] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1, 165 (1955).

sublimed *in vacuo* at 125° before use. $GaCl_3$ was synthesized and purified by previously reported procedures.[3] BF_3, BCl_3, BBr_3, B_2H_6, $B(CH_3)_3$, and $Ga(CH_3)_3$ were purified by trap-to-trap distillation until their vapor pressures agreed with literature values.[4] Trimethylaluminum (Ethyl Corp.) was purified by vacuum distillation. All solvents were distilled prior to use and were stored over Linde 4A molecular sieves.

General Procedures. Except for aluminum trichloride and gallium trichloride, all Lewis acids were manipulated on a preparative high vacuum line. Reaction of these acids with the metal compound was carried out in grease-free o-ring sealed equipment. For BF_3, BCl_3, B_2H_6, and $B(CH_3)_3$ the stoichiometry of interaction was followed by PVT measurement of initial and unused Lewis acid, as well as weight gain of the solid. The $GaCl_3$ adduct was prepared in a grease-free vacuum line filtration apparatus.[5] Aluminum trichloride complexes were prepared in standard Schlenk equipment. A nitrogen-filled drybox was used for solids transfer. Conductance of 7×10^{-3} *M* (π-C_5H_5)Fe$(CO)_2$(CNGaCl_3) solution in nitrobenzene was measured in an air-tight cell having a cell constant of 0.919 cm^{-1}. Analyses were performed by Dornis and Kolbe Micro-Analytical Laboratories, Mulheim-Ruhr, West Germany, and in some cases were verified by the Northwestern Analytical Services Laboratory.

(π-C_5H_5)Fe$(CO)_2$(CNBF_3). A tensimetric titration of 0.423 mmol of (π-C_5H_5)Fe$(CO)_2$CN suspended in *ca.* 1.5 ml of CH_2Cl_2 at 0° was carried out with BF_3. A break in the titration curve occurred at 1:1.15 mole ratio of (π-C_5H_5)Fe$(CO)_2$CN:BF_3, while weight gain indicated a ratio of 1:1.05. In a similar experiment with $^{10}BF_3$ the mole ratio was 1:1.02 from PVT measurement of initial and unused BF_3. In both cases the compound was pale yellow and air-sensitive. *Anal.* Calcd for (C_5H_5)Fe$(CO)_2$CNBF_3: C, 35.48; H, 1.86; N, 5.19. Found: C, 35.42; H, 1.81; N, 5.20.

(π-C_5H_5)Fe$(CO)_2$(CNBCl_3). An excess of BCl_3 was added to a suspension of 0.710 mmol of the iron compound in *ca.* 1.5 ml of chlorobenzene at 0°. After 4 hr of stirring, excess BCl_3 was removed. Weight gain data indicated a ratio of 1:1.09 for (π-C_5H_5)Fe$(CO)_2$-(CN):BCl_3 and in a similar but separate preparation a ratio of 1:1.07 was obtained by PVT measurement of the initial and unconsumed BCl_3. The product is off-white and appears to be somewhat more stable to air and hydrolysis than the BF_3 adduct. *Anal.* Calcd for (C_5H_5)Fe$(CO)_2$(CNBCl_3): C, 30.01; H, 1.57; N, 4.37. Found: C, 31.61; H, 1.75; N, 4.68.

(π-C_5H_5)Fe$(CO)_2$(CNBBr_3). An excess of BBr_3 was added to a stirred suspension of 0.438 mmol of the parent iron compound in *ca.* 1.5 ml of benzene. After 3 hr at *ca.* 0° excess BBr_3 and solvent were removed to yield a pale yellow compound which is stable in air for short periods of time. From the weight gain the ratio of (π-C_5H_5)-Fe$(CO)_2$(CN):BBr_3 was 1:1.01. *Anal.* Calcd for (C_5H_5)Fe(CO)-(CNBBr_3): C, 21.18; H, 1.11; N, 3.08. Found: C, 21.77; H, 0.97; N, 2.95.

(π-C_5H_5)Fe$(CO)_2$(CNBH_3). Excess B_2H_6 was added to 0.429 mmol of the parent iron compound in 1.5 ml of chlorobenzene. After stirring for 8 hr, excess B_2H_6 was removed and determined by PVT measurement to yield an iron complex to BH_3 ratio of 1:1.15. The compound is pale yellow and appears to be more stable toward hydrolysis and air than the boron halide adducts. *Anal.* Calcd for (C_5H_5)Fe$(CO)_2$(CNBH_3): C, 44.31; H, 3.72; N, 6.46. Found: C, 43.90; H, 4.00; N, 5.85.

(π-C_5H_5)Fe$(CO)_2$(CNAlCl_3). Equal volumes of a 0.1 *M* nitrobenzene solution of (π-C_5H_5)Fe$(CO)_2$(CN) and a nitrobenzene solution 0.1 *M* in $AlCl_3$ were mixed under an N_2 atmosphere and in the dark. The resulting mixture was directly examined by ir techniques.

Attempts to isolate a crystalline adduct (in Schlenk equipment) by addition of low polarity solvents were unsuccessful. However, nmr spectra revealed a resonance due to parent (π-C_5H_5)Fe$(CO)_2$(CN) and one due to the adduct for mole ratios of cyanide complex to $AlCl_3$ greater than 1:1. At the 1:1 stoichiometry a single adduct resonance is observed, which reverts to the shift of parent cyanide complex upon introduction of excess triethylamine.

(π-C_5H_5)Fe$(CO)_2$(CNGaCl_3). To 2 ml of diethyl ether containing 0.460 mmol of $GaCl_3$, 0.410 mmol of (π-C_5H_5)Fe$(CO)_2$(CN) was added, and the suspension was stirred for 24 hr at 0°. The light yellow chalky product was filtered off. *Anal.* Calcd for (C_5H_5)Fe-$(CO)_2$(CNGaCl_3): C, 25.34; H, 1.32; N, 3.71; Cl, 28.05; Ga, 18.39. Found: C, 25.25; H, 1.80; N, 3.72; Cl, 27.91; Ga, 18.26.

(π-C_5H_5)Fe$(CO)_2$(CNAl$(CH_3)_3$). To a suspension of 0.572 mmol of (π-C_5H_5)Fe$(CO)_2$(CN) in 2 ml of xylene was added 2.5 mol of $Al(CH_3)_3$. The pale yellow suspension gradually changed to a yellow-brown solution. After 12 hr at 0°, xylene and excess $Al(CH_3)_3$ were removed leaving the yellow-brown compound. The determination of active methyl by hydrolysis gave 1.05:1 for the (π-C_5H_5)Fe$(CO)_2$CN-$Al(CH_3)_3$ ratio.

(π-C_5H_5)Fe$(CO)_2$(CNB$(CH_3)_3$). A suspension of 0.514 mmol of (π-C_5H_5)Fe$(CO)_2$(CN) in 2 ml of xylene was titrated tensimetrically with $B(CH_3)_3$ at 0°. After each addition, a slight increase in pressure was noted, as well as a large increase in solubility. The titration indicated a $B(CH_3)_3$/Fe ratio of 1.02. The yellow solution was allowed to warm to room temperature, followed by separation of $B(CH_3)_3$ from xylene by trap-to-trap fractionation. An infrared spectrum of the remaining solid was identical with that of the parent compound, demonstrating that the adduct readily loses $B(CH_3)_3$ under vacuum at room temperature. Samples used for infrared spectroscopy were prepared with a slight excess of trimethylboron, followed by syringing the cold solution directly into the infrared cell.

(π-C_5H_5)Fe$(CO)_2$(CNGa$(CH_3)_3$). To a suspension of 0.615 mmol of (π-C_5H_5)Fe$(CO)_2$CN in 2 ml of C_6H_6 was added an excess of $Ga(CH_3)_3$. Upon addition, a yellow-brown solution resulted. After 5 hr at ≈10°, excess $Ga(CH_3)_3$ and benzene were removed under vacuum yielding a light-yellow chalky product. *Anal.* Calcd for (π-C_5H_5)Fe$(CO)_2$(CNGa$(CH_3)_3$): C, 41.57; H, 4.44: N, 4.40; Ga, 21.93; Fe, 17.57. Found: C, 47.60; H, 4.86; N, 4.25; Ga, 21.43; Fe, 16.98.

Spectra. All medium infrared spectra were obtained with a Beckman IR 9. CO and CN band positions were determined with slow scans on an expanded scale and 2-cm^{-1} resolution. The reported values represent averages from several scans, with an observed reproducibility for solution spectra of ±0.5 cm^{-1}. Calibration of the instrument was periodically checked with polystyrene film. Solution spectra of the halide adducts were obtained with 0.05 *M* nitrobenzene solutions using 0.05-mm path length Irtran-2 windowed cells. Far-infrared spectra were obtained with a Beckman IR 11 on Nujol mulls between polyethylene windows. For the trimethyl adducts infrared spectra were obtained under identical conditions for 0.02 *M* solutions of the adducts in toluene using 0.10-mm NaCl cells. Nmr spectra were obtained with a Varian T-60 on 0.5 *M* samples in nitrobenzene-d_5 solution.

Results and Discussion

Characterization of the Adducts. As with previous reports of Lewis acid interaction with carbonyl containing cyanides,[6] the formation of adducts produced an increase in ν_{CN} of 30–80 cm^{-1}, characteristic of M–CN– acid linkages.[7] Furthermore, smaller increases in *both* CO stretching frequencies are observed in comparison to the parent (π-C_5H_5)-Fe$(CO)_2$(CN), thereby eliminating the possibility of Fe–CO–acid linkages, Figure 1 and Table I. (Although M–CO– acid linkages have been reported,[8] such interactions have always produced a decrease in ν_{CO} of the C and O bonded CO and an increase in ν_{CO} of the remaining groups of the parent compound.) The possibility of substitution on the C_5H_5 ring was eliminated by nmr spectra which yielded a single sharp H resonance for the 1:1 adducts examined.

All of the adducts with halide acceptors display M–X stretching frequencies in the region characteristic of four-coordinate group III metals (Table II), an observation again consistent with simple molecular adducts, (π-C_5H_5)Fe$(CO)_2$-(CNMX_3). For the $GaCl_3$ adduct, where the ionic structure $[((\pi\text{-}C_5H_5)Fe(CO)_2(CN))_2MX_2]^+[MX_4]^-$ must be considered,[9]

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Table I. CO and CN Stretching Frequencies (cm^{-1}) for $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ Adducts[a]

	ν_{CN}		ν_{CO}^{sym}		ν_{CO}^{asym}	
Adduct	Mull	Soln	Mull	Soln	Mull	Soln
Parent[b]	2117.4	2121.0	2058	2054.7	2000.0	2006.9
$AlCl_3$	2172.1	2168.1	2063.7	2068.3	2014.5	2025.9
BF_3	2195.9	2201.0	2076.0	2073.0	~2025	2030.8
$^{10}BF_3$	2196.5	2201.2	2077.5	2073.3	~2025	2031.1
BCl_3	2205.4	2191.4	2071.2	2076.5	2023.7	2037.4
BBr_3	2190.5	2182.5	2071.0	2077.0	2026.6	2038.9
BH_3	2194.2		2070		2016.9	
$GaCl_3$	2151.7	2152.1	2072.4	2073.2	2034.0	2035.1
Parent[c]		2026.5		2054.5		2008.2
$B(CH_3)_3$		2194.5		2066.1		2023.1
$Al(CH_3)_3$	2164.9	2166.2	2068.9	2069.1	2032.3	2027.8
$Ga(CH_3)_3$	2155.8	2157.3	~2058	2064.7	2012.2	2022.0

[a] Solution spectra of the halide adducts were obtained on 0.05 *M* solutions in nitrobenzene. For the group III trimethyl adducts 0.02 *M* solutions in toluene were employed. [b] Solution spectra obtained using nitrobenzene as solvent. [c] Solution spectra obtained using toluene as solvent.

Table II. Far-Infrared Data

Compound	Frequencies, cm^{-1}
$(\pi\text{-}C_5H_5)Fe(CO)_2CN$	358 mw, 379 m, 410 m, 462 m, 482 w, 501 mw, 520 m, 561 s, 599 s, 607 s, 614 vs
$(\pi\text{-}C_5H_5)Fe(CO)_2(CNBF_3)$	343 w, 375 mw, 390 mw, 402 m, 442 w, 489 m, 507 m, 525 m, 546 mw, 568 vs, 596 vs, 598 sh, 608 sh
$(\pi\text{-}C_5H_5)Fe(CO)_2(CNBCl_3)$	374 mw, 406 w, 418 m, 468 w, 493 m, 518 vs, 561 vs, 594 vs, b, 600 s, 605 s
$(\pi\text{-}C_5H_5)Fe(CO)_2(CNBBr_3)$	290 mw, 371 w, 400 w sh, 404 mw, 451 mw, 475 mw, 491 m, 514 s, 559 vs, 588 vs, 596 m, 603 m

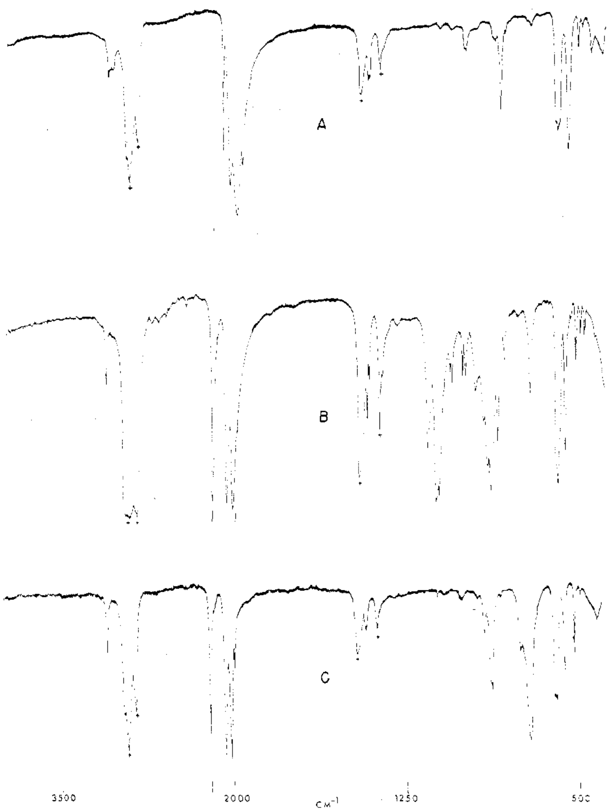

Figure 1. Infrared spectra of A, $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$, B, $(\pi\text{-}C_5H_5)Fe(CO)_2(CNBF_3)$, and C, $(\pi\text{-}C_5H_5)Fe(CO)_2(CNBCl_3)$. The 2000- and 2200-$cm^{-1}$ positions are indicated by vertical lines below each spectrum. Nujol peaks are indicated by +.

the molar conductance for a 7×10^{-3} *M* solution in nitrobenzene was found to be 1.64 ohm^{-1} cm^{-2}. This value is much lower than the molar conductance obtained for a similar tetraphenylarsonium chloride solution (18.7 ohm^{-1} cm^{-2}) as well as values reported for known 1:1 electrolytes in nitrobenzene,[10] indicating that the molecular $GaCl_3$ adduct is the predominant, if not exclusive form in nitrobenzene solution.

Shifts in ν_{CO}. It is well documented that an increase in ν_{CO} occurs upon a decrease of electron availability from other ligands in a mixed carbonyl complex. For example, the carbonyl stretching frequencies of $LW(CO)_5$ complexes increase as the basicity of L decreases.[11,12] There is some difference of opinion on the detailed interpretation of this effect. Some workers either assume or conclude that back π bonding to L is the primary mechanism by which ν_{CO} is increased,[13,14] while others attribute this increase in ν_{CO} among a series of substituted carbonyls to both decreases in σ donation and increases in back π bonding by L.[15] In addition, recent molecular orbital calculations provide evidence for the perturbation of the CO bond by direct donation from L to cis carbonyls.[16] Fortunately, all of these mechanisms should give rise to the same trend in predicted shift so their relative importance does not have to be resolved for the interpretation of $(\pi\text{-}C_5H_5)Fe(CO)_2(CNMX_3)$ carbonyl stretching frequencies. Upon coordination of a Lewis acid to the nitrogen end of a metal cyanide complex, both spectroscopic evidence and molecular orbital calculations reveal that the cyanide in a metal complex becomes a potentially poorer σ donor and better π acceptor.[7b] Therefore, within any of the current interpretations of CO stretching frequencies for substituted carbonyls, ν_{CO} should increase with increased electron pair acceptance by a Lewis acid attached to the cyano nitrogen.

As described in the Introduction, most previous correlations between vibrational frequencies and donor-acceptor interaction are highly suspect owing to the inadequacy of a localized description for the modes of interest. The question naturally arises as to whether the trends observed for ν_{CO} of $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ adducts are substantially influenced by coupling with other coordinates in the adducts. To provide a quantitative answer to this question, $\delta\nu_{CO}$ is defined as the change occurring in ν_{CO} upon adduct formation due entirely to changes in frequency of other oscillators within the molecules which are coupled to the CO oscillator.

The application of perturbation methods to the problem of a system of oscillators coupled to the CO oscillator yields a value for the CO frequency parameter λ_{CO} given in eq 1.[17]

$$\lambda_{CO} = H_{11} - \sum_{i=2}^{n} \frac{H_{1i}H_{i1}}{H_{ii} - H_{11}} \tag{1}$$

In the present case the summation in eq 1 extends over all

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the stretching and deformation coordinates of either A′ or A″ symmetry for the $Fe(CO)_2CN$ moiety, exclusive of the CO coordinate, for which $i = 1$.[18a] To a good approximation, both H_{ii} and H_{11} in the denominator can be replaced by the corresponding observed frequency parameters λ_i and λ_1. Utilizing the observed λ_{CO} for the parent compound, H_{11} was determined. Then, using primed quantities for the adduct and unprimed for the parent, $\delta\nu_{CO}$ is given by eq 2.

$$\delta\nu_{CO} = 1303\left[\left(H_{11} - \sum_{i=2}^{n}\frac{H_{1i}H_{i1}}{\lambda_i - \lambda_1}\right)^{1/2} - \left(H_{11} - \sum_{i=2}^{n}\frac{H_{1i}H_{i1}}{\lambda'_i - \lambda_1}\right)^{1/2}\right] \tag{2}$$

Off-diagonal matrix elements in eq 2 are calculated from the product of the kinetic energy and force constant matrices, $\mathbf{H} = \mathbf{GF}$.

The **G** matrix was calculated[18b] using bond distances and angles from closely related molecules:[19] ∠(OCFeCO) = ∠(NCFeCO) = 90°; r(Fe-C) = 1.76 Å; r(CO) = 1.14 Å. The **F** matrix was constructed from a list of typical force constants given by Jones for $M(CO)_6$ species.[20] (This procedure is reasonable in view of the transferability of interaction constants from $M(CO)_6$ to $Fe(CO)_5$.[20]) When a range of force constants was quoted, the extreme values were used which led to the greatest influence in $\delta\nu_{CO}$. Another measure taken to assure that $\delta\nu_{CO}$ would not be underestimated was the assumption that force constants involving CN are the same as those for CO.

The transformation from an internal to a symmetry coordinate basis yields two blocks each for $\mathbf{F}_s$ and $\mathbf{G}_s$, one 9 × 9 for A′ coordinates and one 6 × 6 for A″ coordinates. The corresponding **H** matrix for the A′ block contains nonzero values for all matrix elements of the type H_{1i} and H_{i1}. Therefore by eq 2, shifts in all of the symmetric $Fe(CO)_2(CN)$ modes will influence the symmetric CO stretch, but, judging from the magnitude of these elements, most of the symmetric modes will exert relatively little influence on $\nu_{CO}{}^{sym}$. As had been anticipated, mixing is much less extensive in the A″ block with all products $H_{i1}H_{1i}$ ($i = 3, 4, \ldots, 6$) equal to zero; consequently, eq 1 leads to the conclusion that the asymmetric CO stretch is only influenced by the asymmetric FeC stretch ($i = 2$).

Previous studies by Wade and coworkers have shown that ν_{FeC} is relatively insensitive to adduct formation on the cyano nitrogen.[7d] For example, the T_{1u} FeC stretch shifts from 417 cm^{-1} in $K_4[Fe(CN)_6]$ to 422 cm^{-1} in $K_4[Fe(CNBF_3)_6]$. Judging from Manning's assignments for $(\pi\text{-}C_5H_5)Fe(CO)_2X$ compounds,[21] a 462-cm^{-1} absorption for $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ is most likely the asymmetric Fe-CO stretch. This band shifts to 442, 468, and 451 cm^{-1} for the BF_3, BCl_3, and BBr_3 adducts, respectively. From eq 2 these shifts lead to very small kinematic perturbations of ν_{CO}: $\delta\nu_{CO} = +0.04, -0.01, +0.02$ cm^{-1}, respectively, for BF_3, BCl_3, and BBr_3 adducts. Even if this particular assignment is incorrect, the small shift ($\leqslant 10$ cm^{-1}) for all of the bands in the 400-500 cm^{-1} range indicates that $\delta\nu_{CO}{}^{asym}$ is less than 1 cm^{-1} for all of the adducts. We conclude that $\Delta\nu_{CO}{}^{asym}$ for $(\pi\text{-}C_5H_5)Fe(CO)_2CN$ upon adduct formation arises almost exclusively from electronic effects. Therefore, shifts in this infrared band provide a reliable guide to the relative electron pair acceptor strength of the added Lewis acid.

Table I shows that the trends in $\Delta\nu_{CO}{}^{sym}$ parallel those for $\Delta\nu_{CO}{}^{asym}$ implying that $\Delta\nu_{CO}{}^{sym}$ might also be diagnostic of the Lewis acid. It is true that the symmetric modes are influenced by much the same electronic factors as the asymmetric modes, and it is highly likely that purely kinematic perturbations of $\Delta\nu_{CO}{}^{sym}$ are small because the CO internal coordinate is remote from the BX_3 and separated from it by a relatively massive central atom. However, because of the greater number of symmetry coordinates which may couple with $\nu_{CO}{}^{sym}$, and lack of detailed assignments, it is not possible at present to justify the use of $\Delta\nu_{CO}{}^{sym}$ by eq 2.

$\nu_{CO}{}^{asym}$ for $(\pi\text{-}C_5H_5)Fe(CO)_2(CNBX_3)$, X = F, Cl, Br. $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ was tested as a probe toward the boron halides BF_3, BCl_3, and BBr_3, for which considerable information is available. Donor-acceptor bond lengths for acetonitrile adducts of BF_3 and BCl_3 demonstrate a stronger bond in the case of the chloride.[22] Similarly, detailed vibrational analyses show that the B-N force constants of acetonitrile adducts follow the order $BBr_3 \sim BCl_3 > BF_3$.[1c] We expect a similar trend with the reference base $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ because cyanide nitrogen donors are involved in both series. The data of Table I show that the shift in carbonyl asymmetric stretch from that of the parent, $\Delta\nu_{CO}{}^{asym}$, follows the order BBr_3 (32 cm^{-1}) ~ BCl_3 (31 cm^{-1}) > BF_3 (25 cm^{-1}). The agreement with the order found for the acetonitrile complexes constitutes good empirical evidence for the utility of $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ as a probe for Lewis acids.

Trends in Acceptor Strength. The iron carbonyl cyanide probe was applied to a series of group III Lewis acids. For the diborane adduct, solution spectra were not obtainable because of rapid decomposition of the adduct in nitrobenzene. There is, however, a good indication from a comparison of data obtained for mulls that $\Delta\nu_{CO}{}^{asym}$ is less for BH_3 (17 cm^{-1}) than for BF_3 (25 cm^{-1}), implying a similar order for the electron pair acceptor strengths. Even though different solvents are involved, it is clear from the magnitude of the solvent effects that $B(CH_3)_3$ ($\Delta\nu_{CO}{}^{asym} = 15$ cm^{-1}) has a lower electron pair acceptor strength than BF_3. Variation in the group III acceptor in the trihalide series leads to the following order for $\Delta\nu_{CO}{}^{asym}$: BCl_3 (31 cm^{-1}) > $GaCl_3$ (28 cm^{-1}) > $AlCl_3$ (19 cm^{-1}). However, the group III trimethyl derivatives show a much smaller variation and different order: $Al(CH_3)_3$ (20 cm^{-1}) > $B(CH_3)_3$ (15 cm^{-1}) ≈ $Ga(CH_3)_3$ (14 cm^{-1}).

Comparison of Electron Pair Acceptor Strengths with Acidities. We have consistently referred to the quantity being measured by $\Delta\nu_{CO}{}^{asym}$ as the relative electron pair acceptor strength and not the relative acidity. While the point has been made previously,[1c,23] it is worth stressing that spectroscopic probes in general measure the *relative strength* of the donor-acceptor bond but *not the acidity*. The term acidity, in our view, is best reserved for thermodynamic data such as $\Delta H°$ or $\Delta G°$ of complex formation. Even when the

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(18) (a) The BX_3 coordinates are not included in this summation as second-order perturbation theory and simple physical reasoning shows that direct kinematic interaction of BX_3 and CO coordinates will be nil. Also, it is reasonably assumed that negligible changes will occur in the π-cyclopentadiene-metal vibrations and therefore coordinates involving the ring are neglected. (b) Program GMAT: J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules V," Report 231-64, Shell Development Co., Emeryville, Calif.

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thermodynamic data is corrected for possible variations in physical state and degree of association of the acid (*e.g.*, $B_2H_6 \rightarrow 2BH_3$), the resulting acidities will not necessarily parallel the electron pair acceptor strengths. The reason lies in the fact that, in contrast with the spectral probe which provides a measure of the donor–acceptor bond interaction, the enthalpy or free energy of reaction includes contributions from changes in other bonds as well. The classic example is provided by the reorganization of the boron halides from planar triangular with short B–X bonds in the free state to a pyramidal geometry with longer B–X bonds in the adduct, eq 3. It is clear from this cycle that the heat of com-

$$\begin{tikzcd}
 & \begin{array}{c}D + BX_3\\ \text{pyramidal}\end{array} \arrow[dr, "\Delta H_{DB}"] & \\
\begin{array}{c}D{:} + BX_3\\ \text{planar}\end{array} \arrow[ur, "\Delta H_R"] \arrow[rr, "\Delta H_c"'] & & D{:}BX_3
\end{tikzcd} \qquad (3)$$

plex formation, ΔH_c, will be less than the donor–acceptor bond enthalpy, ΔH_{DB}, owing to the endothermic process of reorganization, ΔH_R. Thus, comparison of acidities ($\approx \Delta H_c$) with electron pair acceptor strengths ($\sim \Delta H_{DA}$) will, in certain cases, provide information on the reorganization processes (ΔH_R). A good illustration of such an influence is provided by comparison of heats of complex formation of BH_3 and BF_3 toward a nitrogen donor, eq 4.[24] The similarity in these

$$\begin{aligned}
&BH_3(g) + N(CH_3)_3(g) = H_3BN(CH_3)_3(g)\\
&\qquad \Delta H_c{}^\circ = -31.3 \text{ kcal/mol}\\
&BF_3(g) + N(CH_3)_3(g) = F_3BN(CH_3)_3(g)\\
&\qquad \Delta H_c{}^\circ = -30.9 \text{ kcal/mol}
\end{aligned} \qquad (4)$$

heats of reaction is to be contrasted with the order of electron pair acceptor strengths, $BF_3 > BH_3$, found in the present work. This comparison provides direct experimental evidence that ΔH_R is more positive for BF_3 than for BH_3. Therefore, BH_3 is the easier of the two to distort, in agreement with the reorganization energy estimates of Parry and Alton.[25]

The relative electron pair acceptor strengths for the group III chlorides, BCl_3, $AlCl_3$, and $GaCl_3$, are of particular interest because of the frequent application of these acids as catalysts. Satchell and Satchell have argued from the relative radii of B, Al, and Ga that there should be a monotonic decrease in the affinity for hard bases in the order $B > Al \gtrsim Ga$,[26] and enthalpy data in a coordinating solvent tend to support this order.[27] Toward pyridine as a reference base, the enthalpy data indicate a different order of acidity[28] $AlCl_3 > BCl_3 > GaCl_3$. While the position of BCl_3 relative to $GaCl_3$ may be somewhat variable, there is agreement that BCl_3 is the stronger acid of the two. Given this higher acidity of BCl_3 (more negative ΔH_c) and the expected higher reorganization energy of BCl_3 (more positive ΔH_R), it follows from eq 3 that the donor-acceptor bond energy should be greater for BCl_3 (more negative ΔH_{DB}) than for $GaCl_3$ adduct formation. This conclusion agrees with the relative electron pair acceptor strengths which were determined for BCl_3 and $GaCl_3$ in the present work.

The unusually low electron pair acceptor strength for $AlCl_3$, below that of $GaCl_3$, does not have a ready explanation. We have, however, confirmed that this order is paralleled by relative affinities for $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ by a competition experiment in which a stoichiometric quantity of $AlCl_3$ in nitrobenzene was added to a nitrobenzene solution of $(\pi\text{-}C_5H_5)Fe(CO)_2(CNGaCl_3)$. Judging from ν_{CO}, $GaCl_3$ was not displaced. It will be recalled that the $AlCl_3$ adduct could not be isolated as a solid and therefore was not characterized as completely as the other trihalide adducts. It is possible that unlike the other members of this series, the $AlCl_3$ complex is not a simple MX_3 adduct. Two reasonable alternate formulations are an ionic complex $[((\pi\text{-}C_5H_5)_2Fe(CO)_2(CN))_2AlCl_2{}^+][AlCl_4{}^-]$ or a solvent-coordinated species $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)AlCl_3O_2NC_6H_5$.

The enthalpies of formation for trimethylamine adducts of $B(CH_3)$, $Al(CH_3)_3$, and $Ga(CH_3)_3$ demonstrate the acidity order $Al > Ga \gtrsim B$,[29] which is to be compared with the order of electron pair acceptor strength, $Al > B \approx Ga$, based on $\Delta\nu_{CO}{}^{asym}$. The rather small change in position for trimethylboron in these two series may result from the smaller steric hindrance to trimethylboron complex formation with $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ than with $N(CH_3)$.[30] In line with this argument $B(CH_3)_3$ and $Ga(CH_3)_3$ are equally acidic toward $P(CH_3)_3$ which is less sterically encumbered than $N(CH_3)_3$.[29d,30]

Conclusion

Relative values of $\Delta\nu_{CO}{}^{asym}$ for Lewis acid adducts of $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ form a convenient and reliable guide to trends in electron pair acceptor strengths of acids. In addition to convenience, the probe has the advantage that it can be applied to studies on the influences of different acceptor atoms (*e.g.*, BCl_3 *vs.* $GaCl_3$) as well as studies on the influence of ligands in a single acceptor (*e.g.*, BF_3 *vs.* BCl_3). By contrast, bond length and force constant variations for the donor–acceptor bond provide information on the relative electron pair acceptor strengths only when comparison is being made between acids having the same acceptor atom. While the present work was confined to group III acceptors, $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ or similar metal carbonyl cyanides should be generally applicable probes for main group and transition metal acceptor molecules as well as acceptor sites on surfaces.

Fruitful comparisons can be made between electron pair acceptor strengths measured by spectral probes and acidities measured by thermochemical data. In general, electron pair acceptor strengths will parallel acidities because the donor–acceptor bond strength usually dominates the heat of adduct formation. However, where the two are not parallel, the disparities provide good indications of factors other than the donor–acceptor bond enthalpy which contribute to the enthalpy of complex formation. One such factor which is difficult, if not impossible, to assess by any other means is the energy necessary to distort the acid to the geometry it possesses in the complex (reorganization energy).

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Registry No. $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNBF}_3)$, 40199-93-7; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNBCl}_3)$, 40199-94-8; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNBBr}_3)$, 40199-95-9; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNBH}_3)$, 40199-96-0; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNAlCl}_3)$, 40199-97-1; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNGaCl}_3)$, 40330-51-6; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNAl(CH}_3)_3)$, 40199-98-2; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CNB(CH}_3)_3)$, 40199-99-3; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{(CO)}_2\text{(CNGa(CH}_3)_3)$, 40200-00-8; $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{CN}$, 12152-37-3; BF_3, 7637-07-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; B_2H_6, 19287-45-7; AlCl_3, 7446-70-0; GaCl_3, 13450-90-3; $\text{Al(CH}_3)_3$, 75-24-1; $\text{B(CH}_3)_3$, 593-90-8; $\text{Ga(CH}_3)_3$, 1445-79-0.

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Electronic Ground States of Dicyanobis(diimine)iron(III) Compounds

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Epr, nmr, and magnetically perturbed Mossbauer spectral data for $\text{Fe(phenanthroline)}_2\text{(CN)}_2^+$ and $\text{Fe(bipyridine)}_2\text{(CN)}_2^+$ are compared to similar data for the corresponding tris(diimine) systems. The principal component of the electric field gradient (V_{zz}) is positive for all of these compounds and consistent with an orbital ground state corresponding to a hole in d_{z^2}. Fits to epr spectra in various media are discussed and an axial (trigonal) model with splittings of $\sim$1000 cm^{-1} in the ground $^2T_2$ term is favored; *i.e.*, the basic trigonal field of the tris(diimine) systems appears to persist in the bis analogs. This is also supported by proton nmr data. Perturbed Mossbauer results for the low-spin ferrous systems $[\text{Fe(bipyridine)}_3](\text{ClO}_4)_2$ (V_{zz} negative) and $[\text{Fe(bipyridine)}_2\text{(CN)}_2]$ (V_{zz} positive) are considered in relation to the magnitude of the quadrupole splittings of the corresponding ferric systems.

Introduction

The electronic structure of low-spin iron(III) complexes has been the subject of several recent investigations. Much of the effort expended toward the understanding of these complexes has focused on the more symmetric molecules of the type M(chelate)_3^{n+}. In particular, studies of the Fe(NN)_3^{3+} complexes[2] have been most fruitful while investigations of sulfur-donor compounds such as $\text{Fe(dithioacetylacetonate)}_3$,[3-5] though providing equally interesting results, have proven much more difficult to interpret in terms of a unified model of bonding. In this paper we present the results of an nmr, epr, and magnetically perturbed Mossbauer study of the low-symmetry ferric complexes $[\text{Fe(diimine)}_2\text{(CN)}_2]\text{X}$ [diimine = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)] as well as the perturbed Mossbauer data for the low-spin ferrous analogs.

The reduction in symmetry resulting from substitution of two CN$^-$ ligands for a chelating diimine of a tris(diimine) complex is expected to lower the symmetry to less than threefold, the highest remaining symmetry axis being the C_2 which bisects the CN-M-CN angle. What is not apparent is whether this has a significant effect on the dominant trigonal distortion imposed by the chelate rings and, if so, to what factors the distortion is most sensitive. It is with these problems that the present study is concerned.

Experimental Section

The Mossbauer apparatus has been described previously.[6] Magnetically perturbed Mossbauer spectra were determined at ambient temperature using a Varian Associates Model 4500 magnet (transverse geometry) and accompanying power supply. The applied fields for cylindrical, tapered pole faces at 0.5-in. gap were nominally of the order of 20 kG, while the γ-ray source (50 mCi ^{57}Co in Cu) was maintained in a fringing field of less than 300 G.

Nmr spectra were recorded on a Jeolco C-60H nmr spectrometer at 30° in DMSO-d_6.[7] No evidence for coordination of DMSO was indicated. Spectra were calibrated relative to tetramethylsilane as internal standard.

Epr spectra were obtained on a Varian E-4 spectrometer system at X-band frequency. Samples of the bis complexes were prepared as dilute solutions in *N,N*-dimethylacetamide–H_2O and frozen rapidly in liquid nitrogen before reduction to the ferrous complexes could occur. Spectra were run in helium-cooled liquid N_2 at $\sim$73°K in a standard low-temperature dewar. Calibration was relative to diphenylpicrylhydrazyl (DPPH), $g = 2.0036$. All complexes were prepared as outlined in the literature.[8]

Results and Discussion

Nmr. Nmr spectra of $[\text{Fe(phen)}_2\text{(CN)}_2]^+$ and $[\text{Fe(bipy)}_2\text{(CN)}_2]^+$ in DMSO-d_6 clearly show two sets of nonequivalent protons due to the inequality of the chelate rings and unambiguously identify the compounds as the cis isomers (Figure 1). In the bipyridine complex, only the 6,6′ resonance remains degenerate, while in the phenanthroline complex, both the 2,9 and 5,6 proton resonances remain degenerate as in the tris complex (Table I).[7] Interestingly, if one averages the two inequivalent resonances in the bis complexes and compares the result to the value found in the tris complexes, the difference is generally quite small. This would indicate that there is no great change in the net amount of spin density reaching the protons as one goes from tris to bis complexes. One has a situation where due to the CN$^-$ ligands, less spin density is placed on one half of the diimine and more on the other half. While the situation involving spin delocalization is complicated by several unknown factors, and is undoubtedly exceedingly complex, it seems reasonable to conclude that lowering of the symmetry in these bis complexes takes place without gross distortion of the basic symmetry of the tris complexes. Were this not

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