

Table III. Values of the ρ Factors

	ρ_{tot}	ρ_{str}	ρ_{el}
$[\text{Ni}_6\text{C}(\text{CO})_{17}]^{2-}$	0.80	0.81	0.99
$[\text{Re}_8\text{C}(\text{CO})_{24}]^{2-}$	0.89	1.01	0.88
$[\text{Re}_7\text{AgC}(\text{CO})_{22}]^{2-}$	0.88	0.97	0.90
$[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$	0.93	0.98	0.95
$[\text{Re}_7\text{C}(\text{CO})_{21}(\mu\text{-CO})]^-$	0.94	1.00	0.94
$[\text{Re}_6\text{C}(\text{CO})_{18}(\text{H})_2]^{2-}$	1.00	1.00	1.00

case of perfect octahedral symmetry) is a combination of a factor measuring the electronic effect ρ_{el} and of a factor measuring the structural effect ρ_{str} . The factorization of ρ_{tot} is justified by the fact that ρ_{el} can be related to the F matrix and ρ_{str} to the G matrix. ρ_{str} is easily calculated from

$$\rho_{\text{str}} = (\nu_{\text{A}})_{\text{calcd}}^2 / (\nu_{\text{E}})_{\text{calcd}}^2$$

in which $(\nu_{\text{A}})_{\text{calcd}}$ and $(\nu_{\text{E}})_{\text{calcd}}$ are the best fitting values, assuming that a unique force constant is operating.

The values of the three ρ factors are reported in Table III and clearly indicate that the most important role is played by ρ_{str} in the capped Ni complex and by ρ_{el} in the capped Re complexes.

The rationalization of the ρ values in term of molecular data of the complexes is not straightforward. Obviously, ρ_{el} varies with

the number of capping atoms from ca. 0.9 (two capping atoms) to ca. 0.95 (one capping atom) to 1 (no capping atom). In this context Ag and the $\text{Re}(\text{CO})_3$ group seem to have the same electronic effect and there is no dependence on the total free anionic charge.

A clearer relationship is found between the approximate values of the M-C force constant and the relevant structural data. When the data for the complexes are separated according to the transition series of the metal, the general trend is the greater the M-C distance, the smaller the force constant (Table II).

A plot of the apparent radius of the carbide atom r_{C} vs. the force constant (Figure 8) provides a general illustration of the above trend. A progressive decrease of force constant on increasing r_{C} is apparent, regardless of the metal transition series and the approximation adopted in calculating the force constant. These results suggest that there will be a decrease of the interaction of the carbide atom with the metals when the size of the metal cavity is increased.

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^{13}C and ^{17}O NMR and IR Spectroscopic Study of a Series of Carbonyl(4-substituted pyridine)(*meso*-tetraphenylporphinato)iron(II) Complexes. Correlations between NMR Chemical Shifts and IR Stretching Frequencies of the Carbonyl Ligand and Taft Parameters of the Pyridine Substituent

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The results of a ^{13}C and ^{17}O NMR and IR spectroscopic study of a series of carbonyl(4-substituted pyridine)(*meso*-tetraphenylporphinato)iron(II) ($\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$) complexes are presented. Good to excellent linear correlations between the ^{13}C and ^{17}O NMR chemical shifts and the IR stretching frequencies of the carbonyl ligand are observed as the pyridine substituent is varied. Good to excellent linear correlations are also observed between these NMR chemical shifts and IR stretching frequencies and the NMR chemical shifts and IR stretching force constants for the trans carbonyls of a series of *cis*- $\text{Mo}(\text{CO})_4(\text{py-4-X})_2$ complexes as the pyridine substituent is varied. The relationship between the donor ability of the pyridine ligands and the ^{13}C and ^{17}O NMR chemical shifts and IR stretching frequencies of the carbonyl ligands in the $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$ complexes has been quantitated by fitting the spectroscopic data to the single and the dual Taft substituent parameters of the pyridine substituent. Good to excellent correlations are observed. The upfield shift in the ^{13}C NMR resonance of the carbonyl ligand as the electron-donor ability of the pyridine increases is unique. This has been rationalized by using the Buchner and Schenk description of metal carbonyl ^{13}C NMR chemical shifts.

Introduction

Metalloproteins containing an iron-porphyrin active site have diverse biological functions, many of which involve coordination to and/or reaction with a dioxygen ligand.¹⁻⁶ The differences in the reactivity of the iron-porphyrin proteins toward dioxygen are surprising in view of the great similarities between the active

sites in these proteins. It has been suggested that these differences are due, in part, to the differences in the axial ligands that are coordinated to the iron-porphyrin active site.⁷

The electron-donor ability of the axial ligand may have a significant effect on the reactivity of a dioxygen ligand coordinated to an iron-porphyrin center. As the electron-donor ability of the axial ligand increases, the electron density at the iron increases. This, in turn, should increase the donation of electron density into the π^* orbitals of an η^1 -dioxygen ligand and weaken the O-O double bond, increasing the reactivity of the ligand. Unfortunately, it is difficult to study this relationship using simple iron-porphyrin complexes of dioxygen as model systems since these complexes are unstable.⁸

Carbonyl complexes of simple iron porphyrins may be an acceptable alternative to the dioxygen complexes as models for the relationship between the electron-donor ability of the axial ligand

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Table I. NMR Instrument Parameters and Standards

nucleus	center of spectrum, MHz	data point resolu., Hz	spectrum width, Hz	pulse delay	pulse angle, deg/ μ s	no. of pulses	line broadening, Hz	ref
^{13}C	75.476	1.2	20000	6.0 s	75/15	1.2×10^5	4.0	int Me_4Si
^{17}O	40.696	9.7	20000	0.5 ms	90/27	1.0×10^6	30.0	ext H_2O

and the ability of iron-porphyrin enzymes to activate dioxygen. Although the coordination geometries of the ligands are different (linear for the carbonyl vs. bent for η^1 -dioxygen), both ligands are good π -acceptor ligands (accept electron density from the partially filled d orbitals of the iron into their $\pi^*(2p)$ orbitals).⁹ Thus, changes in electron-donor abilities of the axial ligands in iron porphyrins should have qualitatively similar effects on the bond strengths of the carbonyl and η^1 -dioxygen ligands.

It should be possible to probe the relationship between the electron-donor ability of the axial ligand and the bond strength of the carbonyl ligand in simple iron-porphyrin complexes by using both multinuclear NMR and IR spectroscopy. These techniques have been used to study similar relationships in a variety of other transition-metal carbonyl complexes.¹⁰⁻²⁵ Quantitative relationships between the electron-donor ability of group 15 ligands and the carbonyl bond strengths have been reported for complexes in which the change in the electron-donor ability of the ligand results from variation of the para substituent of an aromatic ring.^{23,25} Infrared spectroscopic studies of carbonyl ligands coordinated to the active sites of iron-porphyrin proteins have also provided significant insight into the electronic effects that occur in these active sites.²⁶⁻³⁶

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Table II. Carbonyl ^{13}C and ^{17}O NMR Chemical Shifts and IR Stretching Frequencies of the Fe(TPP)(CO)(py-4-X) Complexes and the Taft Substituent Parameters of the X Groups

X	$\delta(^{13}\text{C})^a$	$\delta(^{17}\text{O})^a$	ν_{CO} , cm^{-1}	σ_p^b	σ_R^c	σ_I^c
<i>t</i> -Bu	204.67	<i>d</i>	1976	-0.15	-0.18	-0.01
Et	204.72	<i>d</i>	1976	-0.15	-0.14	-0.01
Me	204.74	377.6	1976	-0.17	-0.16	-0.01
H	204.77	378.4	1976	0.00	0.00	0.00
Ph	204.78	378.6	1977	-0.01	-0.11	0.12
CO_2Me	205.04	381.7	1980	0.39	0.11	0.32
COMe	205.03	383.6	1981	0.50	0.20	0.30
CN	205.27	384.9	1984	0.66	0.08	0.57

^a Singlet. ^b Reference 38. ^c Reference 39. ^d Not observed.

Table III. Results of the Linear Correlations between the Carbonyl NMR Chemical Shifts and IR Stretching Frequencies for the Fe(TPP)(CO)(py-4-X) Complexes

correln	<i>r</i>	level of confidence, %
$\delta(^{13}\text{C})$ vs. $\delta(^{17}\text{O})$	0.967	99.8
$\delta(^{13}\text{C})$ vs. ν_{CO}	0.990	99.9
$\delta(^{17}\text{O})$ vs. ν_{CO}	0.984	99.9

Table IV. Results of the Linear Correlations between the Carbonyl NMR Chemical Shifts or IR Stretching Frequencies (Force Constants) of the Fe(TPP)(CO)(py-4-X) and *cis*-Mo(CO)₄(py-4-X)₂ Complexes

correln	<i>r</i>	level of confidence, %
$\delta(^{13}\text{C})$	-0.965	99.8
$\delta(^{17}\text{O})$	0.967	99.8
ν_{CO} or k_1	0.987	99.9

Table V. Results of the Linear Regression Analysis of the Correlation between the Carbonyl NMR Chemical Shifts and IR Stretching Frequencies of the Fe(TPP)(CO)(py-4-X) Complexes and the Taft σ_p Substituent Parameters

correln	ρ_p	$\delta_{\text{H}}/\nu_{\text{H}}$	<i>r</i>	level of confidence, %
$\delta(^{13}\text{C})$	0.622	204.79	0.976	99.9
$\delta(^{17}\text{O})$	9.023	378.75	0.992	99.9
ν_{CO}	8.833	1977.2	0.984	99.9

Table VI. Results of the Linear Regression Analysis of the Correlation between the Carbonyl Chemical Shifts and IR Stretching Frequencies of the Fe(TPP)(CO)(py-4-X) Complexes and the Taft σ_R and σ_I Substituent Parameters

correln	ρ_R	ρ_I	$\delta_{\text{H}}/\nu_{\text{H}}$	<i>r</i> ²	level of confidence, %
$\delta(^{13}\text{C})$	0.227	0.848	204.75	0.991	99.9
$\delta(^{17}\text{O})$	7.935	9.580	378.58	0.986	99.5
ν_{CO}	3.700	11.650	1976.6	0.989	99.9

In this paper, we report the results of a ^{13}C and ^{17}O NMR and IR spectroscopic study of a series of Fe(TPP)(CO)(py-4-X) (TPP = *meso*-tetraphenylporphyrinato, py-4-X = 4-substituted pyridine) complexes. The relationships between the NMR chemical shifts and IR stretching frequencies of the carbonyl ligands and the electron-donor abilities of the pyridine ligands are discussed. These relationships are compared to those that have been reported for a series of *cis*-Mo(CO)₄(py-4-X) complexes. The results of linear

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regression analyses of the relationships between the spectroscopic data and the Taft single or dual substituent parameters for the pyridine substituents are also presented.

Experimental Section

(A) Reagents. Substituted pyridines were obtained from Aldrich Chemical Co., Milwaukee, WI, and required no purification. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine (TPPH₂) was purchased from Sigma Chemical Co., St. Louis, MO. Chloroform was dried by distillation from calcium hydride under nitrogen. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

(B) Syntheses. The Fe(TPP)(CO)(py-4-X) complexes were prepared by the method of Peng and Ibers³⁷ as outlined below. The reactions were run under an inert atmosphere of either argon or dinitrogen.

Fe(TPP)(CO)(py-4-X)·H₂O. Fresh saturated iron(II) acetate solution was prepared by boiling 1.00 g of iron powder in 180 mL of degassed glacial acetic acid until the iron(II) acetate precipitated. Next, 135 mL of this solution was transferred to a pressure-equalizing dropping funnel and added dropwise to a solution containing 50 mL of chloroform, 500 mg of TPP, and an excess of the desired 4-substituted pyridine. When the addition was completed, the reaction mixture was heated at 57 °C for 2.5 h, after which the temperature was reduced to 0 °C and research grade carbon monoxide slowly bubbled through the solution for 1 h. The solution was then sealed under a carbon monoxide atmosphere and refrigerated overnight. The resulting purple crystalline product was collected by filtration, washed with diethyl ether to remove excess acetic acid and 4-substituted pyridine, and dried under vacuum at ambient temperature. Elemental analyses were run on two of the complexes, R = Et and CO₂Me. Anal. Calcd for R = Et: C, 76.00; H, 4.78; N, 8.52. Found: C, 76.08; H, 4.74; N, 8.58. Calcd for R = CO₂Me: C, 73.33; H, 4.38; N, 8.22. Found: C, 73.52; H, 4.39; N, 8.22.

(C) NMR Spectroscopy. Multinuclear (¹³C and ¹⁷O) NMR spectra were taken of saturated 3.0-mL CDCl₃ solutions of the Fe(TPP)(CO)(py-4-X) complexes to which approximately 0.1 mL of the appropriate pyridine was added. All solutions were purified by filtration through Celite into the NMR tubes under a carbon monoxide atmosphere. Spectra were obtained on a Nicolet 300 MHz wide-bore NMR spectrometer. The instrumental parameters for data acquisition and workup and the standards used are summarized in Table I. Chemical shift data of the ¹³C and ¹⁷O NMR resonances are summarized in Table II. The chemical shifts of the ¹⁷O resonances were determined by using the line-fitting routine of the spectrometer.

(D) IR Spectroscopy. IR spectra of CH₂Cl₂ solutions of the Fe(TPP)(CO)(py-4-X) complexes were taken in the 2050–1900-cm⁻¹ region on a Perkin-Elmer Model 283B IR spectrometer using matched 0.2-mm NaCl solution cells. These spectra were calibrated with a polystyrene film, and the carbonyl IR stretching frequencies are given in Table II.

(E) Linear Regression Analyses. Linear regression analyses were run for correlations between the NMR chemical shift and IR stretching frequency data of the Fe(TPP)(CO)(py-4-X) complexes (Table III), for correlations between the NMR chemical shift and IR data for the Fe(TPP)(CO)(py-4-X) complexes and those for the *cis*-Mo(CO)₄(py-4-X)₂ complexes (Table IV), and for the correlations of either the Taft single or dual substituent parameters with either the NMR chemical shift or the IR stretching frequency data of the Fe(TPP)(CO)(py-4-X) complexes (Tables V and VI). All linear regression analyses were run by using the ABSTAT release 4 program of Anderson-Bell, which calculates the regression coefficients and correlation coefficients and also performs an analysis of the variance of the data, using the *F* test to obtain a level of confidence (LoC). This level of confidence is a measure of the validity of the linear correlations and was used to evaluate the goodness of the correlation which was observed: excellent (LoC ≥ 99.9%), good (99.9% > LoC ≥ 99.5%), fair (99.5% > LoC > 99.0%).

The correlations between either the NMR chemical shift or IR stretching frequency data and either the Taft single (σ_p) or dual (σ_R and σ_I) substituent parameters were studied by linear regression analyses of eq 1 and 2, respectively, where δ_X = the chemical shift of the resonance

$$\delta_X(\nu_X) = \rho_p \sigma_p + \delta_H(\nu_H) \quad (1)$$

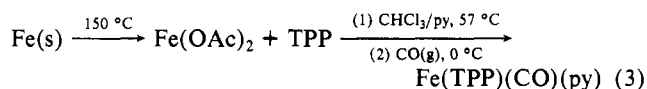
$$\delta_X(\nu_X) = \rho_R \sigma_R + \rho_I \sigma_I + \delta_H(\nu_H) \quad (2)$$

with substituent X, ν_X = the carbonyl IR stretching frequency with substituent X, ρ_p = the single parameter regression coefficient, σ_p = the Taft single parameter for the X substituent,³⁸ ρ_R = the regression coefficient for resonance, ρ_I = the regression coefficient for inductive effect,

σ_R = the Taft resonance parameter for the X substituent,³⁹ σ_I = the Taft inductive parameter for the X substituent,³⁹ δ_H = chemical shift of the resonance with the substituent H, and ν_H = the carbonyl IR stretching frequency with substituent H.

Results

Syntheses of the Fe(TPP)(CO)(py-4-X) Complexes. The Fe(TPP)(CO)(py-4-X) complexes were synthesized by the method of Peng and Ibers³⁷ as shown in eq 3. It is necessary to use freshly



prepared, saturated Fe(OAc)₂ solution in order to obtain the desired products because the use of a solution prepared by the addition of Fe(OAc)₂ (Alfa; freshly opened) to glacial acetic acid did not produce any of the desired product. The reasons for this are not obvious as the concentrations of the reagents were the same in both cases.

Carbonyl ¹³C NMR Spectra. The carbonyl ligands of the Fe(TPP)(CO)(py-4-X) complexes give rise to singlets in the ¹³C NMR spectra, and the chemical shifts of these resonances are summarized in Table II. The resonances are broad in the absence of excess pyridine, and this is probably due to a small degree of dissociation of the pyridines from the complexes. This broadening has a very small effect upon the chemical shifts of the carbonyl resonance (<0.05 ppm). The six-coordinate complex is the only major species in solution as evidenced by the presence of a single IR absorption for the carbonyl ligand whose frequency is constant in the presence or absence of free pyridine.

The ¹³C resonance of the carbonyl ligand shifts downfield as the electron-withdrawing ability of the pyridine substituent increases with a total chemical shift range of 0.60 ppm. This insensitivity of the carbonyl ¹³C NMR chemical shift to variation in the iron-porphyrin site has been noted in previous studies.^{40–46} The downfield shift with the increasing electron-donor ability of the trans ligand is unique since all previous studies of transition-metal carbonyl complexes have reported an upfield shift in this resonance.^{10–25}

Carbonyl ¹⁷O NMR Spectra. The carbonyl ligands of the Fe(TPP)(CO)(py-4-X) complexes give rise to singlets in the ¹⁷O NMR spectra, and the chemical shifts of these resonances are summarized in Table II. The resonance shifts downfield as the electron-withdrawing ability of the pyridine substituent increases with a total range of 7.3 ppm. This range is 12 times that of the ¹³C NMR resonance, and this suggests that the ¹⁷O NMR chemical shift of the carbonyl ligand is a more sensitive probe of changes in the electron-donor ability than is the ¹³C NMR chemical shift. The resonance is broad with a peak half-height ranging from 70 to 190 Hz, and the exact chemical shift was calculated by using the internal line-fitting program of the spectrometer. Due to the broadness of the peaks and the low sensitivity of ¹⁷O NMR nucleus, a minimum of 1 million transients was required for observation of the spectra. The ¹⁷O NMR resonances of the X = Et and *t*-Bu complexes could not be observed due to the lower chloroform-*d* solubilities and dynamic range problems that were encountered. An attempt is currently under way to observe the resonances by using alternative pulse sequences that minimize acoustic ringing and reduce dynamic range problems.⁴⁷

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Solution Infrared Spectra. Single IR absorptions are observed in the 2050–1900-cm⁻¹ region for the Fe(TPP)(CO)(py-4-X) complexes, and the absorption frequencies are summarized in Table II. The absorbance shifts to higher frequency as the electron-withdrawing ability of the pyridine substituent increases. However, the total range observed for the carbonyl absorption frequency is only 8 cm⁻¹, which means that this parameter is relatively insensitive to changes in the electron-donor abilities of the pyridine ligand. The total range and the direction of the frequency shift as the electron-withdrawing ability of the pyridine substituent increases are in good agreement with those reported by Alben and Caughey for the carbonyls in a series of carbonyl(4-substituted pyridine)(dimethyl 2,4-diacetyldeuteroporpinato IX)iron(II) complexes as the pyridine substituent is varied.²⁶

Discussion

Rationalization of the Carbonyl ¹³C and ¹⁷O NMR Chemical Shifts. A theoretical explanation for the variation in the carbonyl ¹³C and ¹⁷O NMR resonances in most transition-metal carbonyl complexes as the electron-donor properties of the ligand substituents are changed has been proposed by Buchner and Schenk.⁴⁸ These authors suggest that the variable in the Karplus and Pople equation for paramagnetic shielding, shown in eq 4,⁴⁹ which

$$\sigma_p^A = -\frac{e^2 h^2}{2m^2 c^2 \Delta E} \langle r_{2p}^{-3} \rangle (Q_{AA} + Q_{AB}) \quad (4)$$

dominates the paramagnetic screening for both the carbonyl ¹³C and ¹⁷O nuclei is the (Q_{AA} + Q_{AB}) term. Evaluation of this expression for the ¹³C and ¹⁷O nuclei considering both C–O and M–C multiple bonding yields eq 5 and 6, respectively.

$$Q_{CC} + Q_{CO} + Q_{MC} = \frac{1}{3}(1 - P_{ZCZO}P_{YCYO} - 3^{1/2}P_{ZCZM}P_{YCYM}) \quad (5)$$

$$Q_{OO} + Q_{CO} = \frac{1}{3}(1 - P_{ZCZO}P_{YCYO}) \quad (6)$$

Equations 5 and 6 provide a basis for rationalizing the behavior of the ¹³C and ¹⁷O NMR chemical shifts of the carbonyl ligands both in the previously studied complexes^{10–25} and in the Fe(TPP)(CO)(py-4-X) complexes of this study. For the ¹⁷O nuclei, an increase in the electron-donor ability of the other ligands will result in a reduction in the C–O π-bond order, P_{YCYO}. Since the C–O σ-bond order, P_{ZCZO}, is negative (due to the choice of the coordinate system⁴⁸), this will result in a decrease in the (Q_{OO} + Q_{CO}) term and a shielding contribution in eq 4. For the ¹³C nuclei, an increase in the electron-donating ability of the other ligands will result in a linear decrease in the C–O π-bond order, P_{YCYO}, and a linear increase in the M–C π-bond order, P_{YCYM}. Since the σ bond orders, P_{ZCZO} and P_{ZCZM} are negative, this will result in a linear decrease in the –P_{ZCZO}P_{YCYO} term and a linear increase in the –P_{ZCZM}P_{YCYM} term. If there is relatively little π bonding between the metal and the carbonyl ligand, the decrease will be larger than the increase, and there will be a shielding contribution in eq 4. In contrast, if there is significant π bonding between the metal and the carbonyl ligand, the increase will be larger than the decrease, and there will be a deshielding contribution in eq 4. These arguments suggest that there is significantly less π bonding between the carbonyl ligand and the metal in the Fe(TPP)(CO)(py-4-X) complexes than in the previously studied complexes such as *cis*-Mo(CO)₄(py-4-X)₂. This is consistent with the current theories of bonding between metals and π-acceptor ligands, which indicate that π bonding is most extensive with low-valent second- and third-row transition metals.

The Buchner and Schenk interpretation of the ¹³C and ¹⁷O NMR chemical shifts of carbonyl ligands in transition-metal complexes can also be used to explain why the carbonyl ¹⁷O NMR chemical shift is more sensitive to variations in the electron-donor abilities of other ligands than is the carbonyl ¹³C NMR chemical shift. As the electron-donor abilities of the other ligands increase, the increase in shielding of the ¹⁷O nucleus of a carbonyl ligand

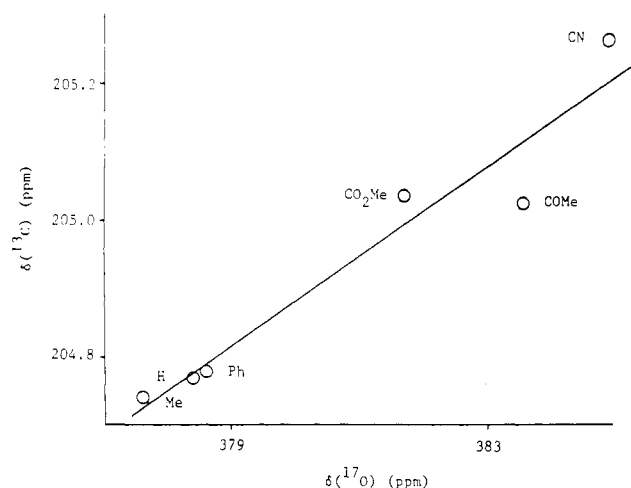


Figure 1. Plot of the carbonyl ¹³C NMR chemical shift vs. the carbonyl ¹⁷O NMR chemical shift of the Fe(TPP)(CO)(py-4-X) complexes.

is directly proportional to the decrease in the C–O π-bond order, P_{YCYO}. The variation in the shielding of the ¹³C nucleus as the electron-donor abilities of the other ligands increases will be much smaller than that of the ¹⁷O ligand because the increase in shielding due to the decrease in the C–O π-bond order, P_{YCYO}, is counteracted by the decrease in shielding due to the increase in the M–C π-bond order, P_{YCYM}. Thus, assuming that the ΔE and ⟨r_{2p}⁻³⟩ terms in eq 4 are approximately the same for the ¹³C and ¹⁷O nuclei, the variation in the shielding of the ¹³C nucleus NMR shift will equal that in the shielding of the ¹⁷O nucleus only if no M–C π bonding occurs (P_{YCYM} = 0).

Correlations between the NMR Chemical Shifts and IR Stretching Frequencies of the Carbonyl Ligand in Fe(TPP)(CO)(py-4-X). Good to excellent linear correlations between the ¹³C and ¹⁷O NMR chemical shifts and IR stretching frequencies of the carbonyl ligand in the Fe(TPP)(CO)(py-4-X) complexes are observed as the X group is varied as shown in Table III. A plot of the ¹³C NMR chemical shift of the carbonyl vs. the ¹⁷O NMR chemical shift of the carbonyl is given in Figure 1. The good correlations are due to the facts that the X group is distant from the nuclei of interest and that variation in the X group does not affect the cone angles of the pyridine ligands but does affect their electron-donor ability.^{21–25} The positive correlations between the ¹³C NMR chemical shifts and either the ¹⁷O NMR chemical shifts or the IR stretching frequencies of the carbonyl ligands are highly unusual as negative correlations have been reported for all other metal carbonyl complexes that have been studied.^{10–25} The positive correlations are due to the unusual downfield shift in carbonyl ¹³C NMR resonance as electron-donor ability of the pyridine substituent decreases.

Correlations between the ¹³C and ¹⁷O NMR Chemical Shifts and IR Stretching Frequencies of the Fe(TPP)(CO)(py-4-X) Complexes with Those of the *cis*-Mo(CO)₄(py-4-X)₂ Complexes. The linear correlations that are observed between the ¹³C and ¹⁷O NMR chemical shifts and IR stretching frequencies of the carbonyl ligand in the Fe(TPP)(CO)(py-4-X) complexes and the ¹³C and ¹⁷O NMR chemical shifts and IR stretching force constants of the *cis*-Mo(CO)₄(py-4-X)₂ complexes²⁵ as the X group is varied are summarized in Table IV. The good to excellent positive correlations between the ¹⁷O NMR chemical shifts and the IR data suggest that the variation in the pyridine substituent has similar effects on the ¹⁷O NMR chemical shift and bond strength of the carbonyl in the two sets of complexes. The correlation between the ¹³C NMR chemical shifts of the carbonyl ligands in the two sets of complexes is also good but negative, as shown in Figure 2. The negative correlation is consistent with the Buchner and Schenk interpretation of ¹³C and ¹⁷O NMR chemical shifts discussed above. The shielding of the carbonyl ¹³C nuclei is dominated by the decrease in the C–O π-bond order in the Fe(TPP)(CO)(py-4-X) complexes and by the increase in the M–C π-bond order

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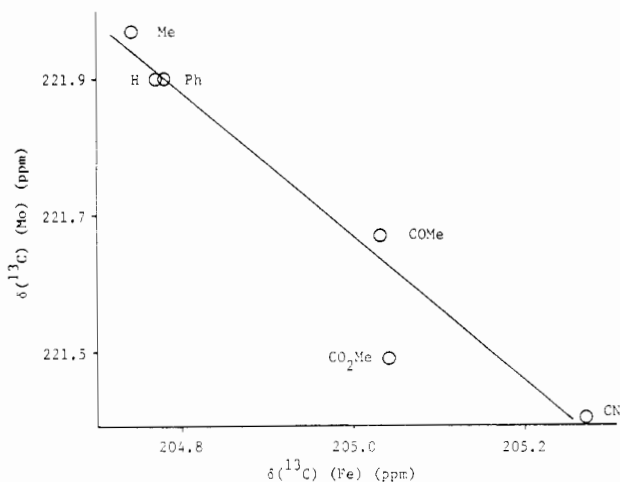


Figure 2. Plot of the carbonyl ^{13}C NMR chemical shift of the $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$ complexes vs. the trans carbonyl ^{13}C NMR chemical shift of the $\text{cis-Mo}(\text{CO})_4(\text{py-4-X})_2$ complexes.

in the $\text{cis-Mo}(\text{CO})_4(\text{py-4-X})_2$ complexes. Because these terms are linearly related to each other, a negative linear correlation between the carbonyl ^{13}C NMR chemical shifts is expected.

Correlations of the Taft Parameters with either NMR Chemical Shifts or IR Stretching Frequencies. The relationship between the electron-donor abilities of the pyridine substituents and both the ^{13}C and ^{17}O NMR chemical shifts and IR stretching frequencies of the carbonyl ligands of the $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$ complexes provides insight into the relationship between the electron-donor ability of the pyridine and the ability of the Fe to weaken the carbonyl C–O triple bond. A linear regression analysis of the relationship between the electron-donor ability of the pyridine ligands as measured by the Taft single substituent parameter (σ_p) of the X group and both the NMR chemical shifts and the IR stretching frequencies has been carried out, and the results are summarized in Table V. A plot of the ^{17}O NMR chemical shift of the carbonyl ligand vs. σ_p for the X substituent is shown in Figure 3. These results indicate that as the electron-donor ability of the pyridine increases (σ_p decreases), the Fe donates more electron density into the π^* orbital of the carbonyl, which weakens the C–O triple bond.

The above analysis does not provide any information as to the relative magnitudes of the inductive and resonance effects of the X group on the NMR chemical shifts and IR stretching frequencies. In order to determine this, a linear regression analysis of the relationship between both the ^{13}C and ^{17}O NMR chemical shifts and IR stretching frequencies of the carbonyl ligand in the $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$ complexes and the Taft σ_R and σ_I parameters has been carried out, and the results are summarized in Table VI. These results indicate that the inductive effect of the X group is significantly greater than the resonance effect for both the ^{13}C NMR chemical shift and the IR stretching frequency of the carbonyl ligand. The results are in contrast to those obtained from a similar study of a series of $\text{cis-Mo}(\text{CO})_4(\text{py-4-X})_2$ complexes²⁵ in which the resonance effect of the X group on the ^{13}C and ^{17}O NMR chemical shifts and the IR stretching force constant of the trans carbonyl ligand was significantly larger than was the inductive effect of the X group. The difference in these correlations may be explained by the degree of M–C π bonding in the two sets of complexes. As previously discussed, there should be significantly less $\text{Fe}(\text{II})\text{--C}$ π bonding than $\text{Mo}(\text{O})\text{--C}$ π bonding both because Fe has the higher oxidation state and because Fe

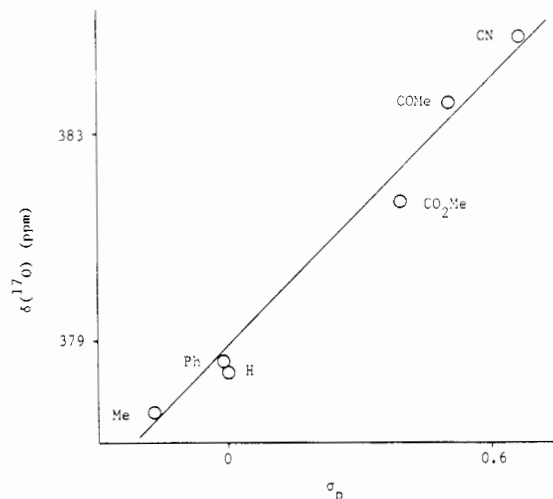


Figure 3. Plot of the carbonyl ^{17}O NMR chemical shift of the $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$ complexes vs. the Taft σ_p substituent parameter for the X group.

is in the first transition series. Thus, the smaller resonance contribution reflects the lower degree of Fe–C π bonding.

Conclusion

This study has demonstrated that it is possible to use both multinuclear NMR and IR spectroscopy to probe the relationship between the electron-donor ability of pyridine ligands in a series of $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-X})$ complexes and the ability of the Fe to donate electron density into the π^* orbitals of the carbonyl ligands. The ^{17}O NMR chemical shift of the carbonyl ligand appears to be the most sensitive of the three spectroscopic parameters to the variation in the electron-donor ability of the pyridine ligand. This relationship has been quantitated by fitting the NMR and IR data to both the single and dual Taft substituent parameters of the pyridine substituent. The results of these studies suggest that the axial ligands that will cause the Fe to donate the most electron density into the π^* antibonding orbitals of the carbonyl ligand are those that are good σ donors. These results are consistent with the observation that hemoglobin, which does not react with O_2 , has a poor σ donor, imidazole, as the axial ligand¹ while cyt P450, which catalyzes the cleavage of the O_2 double bond, has an excellent σ donor, a thiolate anion, as the axial ligand.²

A positive correlation between the ^{13}C and ^{17}O NMR chemical shifts of a carbonyl ligand in a transition-metal complex is reported for the first time in this study. This correlation can be rationalized by using the Buchner and Schenk interpretation of carbonyl chemical shifts. This rationalization is consistent with the results from the correlations with the Taft σ_R and σ_I parameters, and it also explains, at least in part, why the ^{17}O NMR chemical shift is more sensitive than the ^{13}C NMR chemical shift to changes in the electron-donor properties of the pyridine ligands in these complexes.

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Registry No. $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-}t\text{-Bu})$, 109434-13-1; $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-Et})$, 109434-14-2; $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-Me})$, 109434-15-3; $\text{Fe}(\text{TPP})(\text{CO})(\text{py})$, 53470-09-0; $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-Ph})$, 109434-16-4; $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-CO}_2\text{Me})$, 109434-17-5; $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-COMe})$, 109434-18-6; $\text{Fe}(\text{TPP})(\text{CO})(\text{py-4-CN})$, 109434-19-7.