

Figure 2. A plot of the room temperature Mössbauer effect chemical isomer shift vs. the carbonyl stretching force constant.

points and the more severe deviations of $\text{CpFe}(\text{CO})_2\text{CN}$, $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$, and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CN}$ from the best linear least-squares fit of the other 12 data points. The stretching force constants for the $\text{CpFe}(\text{CO})_2\text{X}$ complexes span a range of 16.90–16.45 mdyn/Å, representing only a 3% change in this parameter as a function of X. On the other hand the percentage change in the isomer shift (excluding the cyanide complex) is an order of magnitude greater at ca. 25%. Inclusion of the cyanide complex of course makes the difference even more dramatic. Given these differences the source of the scatter in the $\text{CpFe}(\text{CO})_2\text{X}$ data points becomes obvious.

The carbonyl stretching force constants for $\text{CpFe}(\text{CO})_2\text{CN}$ and $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$ are in the same range as for the other dicarbonyl derivatives (Table III) so that the deviation of these two complexes from the best fit of the isomer shift-stretching force constant plot (Figure 2) is the result of the comparatively low values of the isomer shift. Similarly k for $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CN}$ is essentially identical with those for the other monocarbonyls while the isomer shift is lower by ca. 0.15 mm/s. The common feature of these three complexes is the presence of three good π -acceptor ligands. While this feature is clearly evident in the Mössbauer data it is not fully reflected in the infrared absorption bands of the carbonyl ligands.

The difficulty in quantifying the relationship between the infrared and Mössbauer spectroscopic data is most likely associated with the presumption that changes in the electron density at iron will be reflected *solely* in changes in ν_{CO} . The approximate evaluation of the force constant used herein³⁴ ignores changes in dative bonding between iron and the other ligands. Such changes are indicated, for instance, by the shift in ν_{CN} which is found at 2120 cm^{-1} for $\text{CpFe}(\text{CO})_2\text{CN}$ and at 2090 cm^{-1} for $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CN}$. Further, proton NMR spectra show an upfield shift of 0.2–0.3 ppm for the cyclopentadienyl protons of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$ relative to $\text{CpFe}(\text{CO})_2\text{X}$.^{4,7} This is indicative of increased back-donation from filled iron orbitals to empty ring molecular orbitals, the upfield shift reflecting the difference in π -acceptor properties of the carbonyl and triphenylphosphine ligands.

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Registry No. $\text{CpFe}(\text{CO})_2\text{Cl}$, 12107-04-9; $\text{CpFe}(\text{CO})_2\text{Br}$, 12078-20-5; $\text{CpFe}(\text{CO})_2\text{I}$, 12078-28-3; $\text{CpFe}(\text{CO})_2\text{NCO}$, 32660-69-8; $\text{CpFe}(\text{CO})_2\text{NCS}$, 12317-60-1; $\text{CpFe}(\text{CO})_2\text{SCN}$, 12317-59-8; $\text{CpFe}(\text{CO})_2\text{SeCN}$, 33179-83-8; $\text{CpFe}(\text{CO})_2\text{CN}$, 12152-37-3;

$\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$, 12099-18-2; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{Br}$, 12099-12-6; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCN}$, 64784-33-4; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{NCS}$, 61113-76-6; $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CN}$, 32757-48-5; $[\text{CpFe}(\text{CO})_3]\text{PF}_6$, 38834-26-3; $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{PF}_6$, 12100-39-9.

Supplementary Material Available: Table of Mössbauer effect data collected by other workers, Table II (1 page). Ordering information is given on any current masthead page.

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Distinguishing Axial and Equatorial Carbonyl Groups in Iron Pentacarbonyl by ESCA

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Oxygen 1s ESCA spectra of terminally coordinated carbon monoxide in various transition metal compounds, obtained with the old Berkeley spectrometer, showed single peaks even in

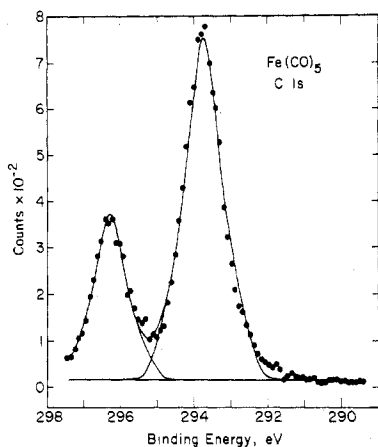
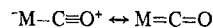


Figure 1. The carbon 1s spectrum of a mixture of $\text{Fe}(\text{CO})_5$ vapor and CO gas. The peak at higher binding energy is due to the CO reference.

the case of compounds with structurally different terminal CO groups.²⁻⁵ The measured oxygen 1s binding energies of compounds with structurally different CO groups must therefore be treated as weighted averages of the binding energies of the structurally different CO groups. From a simple valence-bond picture of back-bonding between a transition metal and coordinated carbon monoxide



it is clear that the charge of the oxygen atom should be correlated with the C–O bond strength. Therefore it is not surprising that the oxygen 1s binding energies are linearly correlated both with the multiplicity-weighted average C–O stretching frequencies of these compounds⁵ and with the weighted average stretching force constants.⁶ Using the relation between the binding energies and the weighted average force constants together with the force constants for structurally different CO groups, it is possible to calculate the expected oxygen 1s binding energy differences for these structurally different CO groups. The calculated binding energy differences, $E_{\text{B}}(\text{axial}) - E_{\text{B}}(\text{equatorial})$, for $\text{Fe}(\text{CO})_5$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Cl}_3\text{SiMn}(\text{CO})_5$, $\text{HMn}(\text{CO})_5$, and $\text{CH}_3\text{Mn}(\text{CO})_5$ are, respectively, +0.4, -0.2, -0.3, -0.4, and -0.6 eV. Quantitative theoretical data can also be used to estimate such shifts in oxygen binding energy. For example, Baerends and Ros⁷ have carried out ab initio calculations for $\text{Fe}(\text{CO})_5$ and have calculated the atomic charges. (The calculated axial and equatorial oxygen atom charges are -0.360 and -0.396, respectively, whereas the corresponding calculated carbon atom charges are practically identical, as expected from the simple valence-bond picture.) Using the atomic charges and the point-charge potential equation⁸

$$E_{\text{B}}(\text{axial}) - E_{\text{B}}(\text{equatorial}) = k\Delta Q + \Delta V \quad (1)$$

we calculate a chemical shift of +0.5 eV, in good agreement with the value calculated from the C–O force constants.⁹⁻¹¹

The half-widths of our O 1s lines from the Berkeley spectrometer were around 1.4 eV, and the electron count data were quite scattered because of a high background count; therefore our spectra could not be reliably deconvoluted into separate peaks due to the structurally different CO groups. Spectra of similar carbonyls reported by other workers also show no evidence of nonequivalent CO groups.¹² However, because the Uppsala high-resolution spectrometer¹³ is characterized by a very low background level and generally yields spectra with relatively narrow lines, we used this instrument to obtain the carbon 1s and oxygen 1s spectra of $\text{Fe}(\text{CO})_5$, with the hope of being able to resolve the oxygen 1s spectrum into

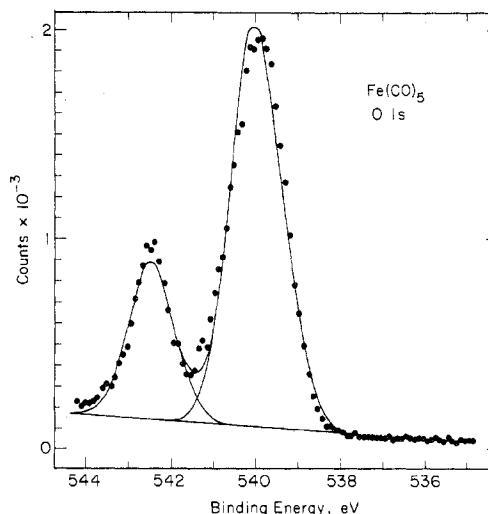


Figure 2. The oxygen 1s spectrum of a mixture of $\text{Fe}(\text{CO})_5$ vapor and CO gas. The peak at higher binding energy is due to the CO reference. The $\text{Fe}(\text{CO})_5$ spectrum has been fit with a single peak. The asymmetry of the $\text{Fe}(\text{CO})_5$ points relative to the fitted curve can be seen.

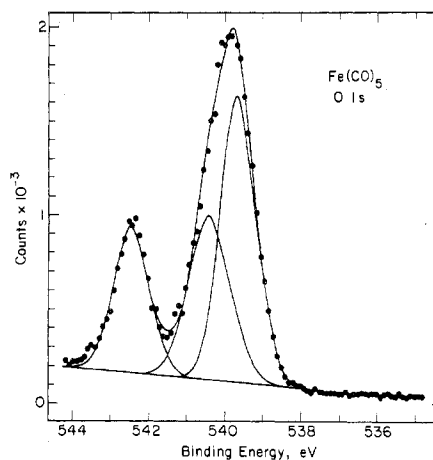


Figure 3. The oxygen 1s spectrum of a mixture of $\text{Fe}(\text{CO})_5$ vapor and CO gas. The peak at higher binding energy is due to the CO reference. The $\text{Fe}(\text{CO})_5$ spectrum has been fit with two peaks constrained to a 2:3 area ratio.

two peaks, characteristic of the axial and equatorial carbonyl groups of the molecule.

The carbon 1s and oxygen 1s spectra of mixtures of CO and $\text{Fe}(\text{CO})_5$ are shown in Figures 1–3. Each spectrum consists of a broad band at low binding energy due to the $\text{Fe}(\text{CO})_5$ and a narrower band at high binding energy due to the free CO reference gas. The spectra have been least-squares fitted with mixed Gaussian–Lorentzian curves. The C 1s spectrum (Figure 1) is fit quite well using just one curve for the $\text{Fe}(\text{CO})_5$ band ($\chi^2 = 255$). A slightly better fit of the $\text{Fe}(\text{CO})_5$ band is obtained using two curves constrained to an area ratio of 2:3 ($\chi = 244$), but application of the F test¹⁴ to the data indicates that the improved fit is statistically significant with a confidence level of only 92%. We reject the improved fit because we feel the confidence level should be greater than about 99%.¹⁵ However, the O 1s $\text{Fe}(\text{CO})_5$ spectral points, shown in Figures 2 and 3, are obviously asymmetric. In Figure 2, the $\text{Fe}(\text{CO})_5$ points have been fit to one curve; the points on the left side have a lower slope than that of the fitted curve, and the points on the right side have a greater slope than that of the fitted curve. ($\chi^2 = 553$.) In Figure 3, the O 1s $\text{Fe}(\text{CO})_5$ points have been fit with two curves constrained to an area ratio of 2:3. The F test shows that the improved fit ($\chi^2 = 210$)

Table I. Carbon and Oxygen Core Binding Energies for Fe(CO)₅

	$E_B,^a$ eV	FWHM, ^a eV
C 1s		
{Fe(CO) ₅	293.72 (4)	1.17 (4)
{CO reference	296.24 ^b	1.05 (8)
O 1s		
{Fe(CO) ₅ (treated as 1 peak)	540.02 (5)	1.42 (4)
{CO reference	542.57 ^b	1.27 (11)
{Fe(CO) ₅ (treated as 2 peaks) ^c	539.71 (4)	1.09 (5)
{CO reference	540.50 (6)	1.27 (14)
{CO reference	542.57 ^b	1.10 (7)

^a The uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. ^b For the binding energies of the carbon

monoxide reference we use the values of S. R. Smith and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 45 (1976).

^c Area ratio constrained to 2:3.

is statistically significant with an acceptable confidence level of >99.999%. The spectral parameters are summarized in Table I.

The conclusion that the C 1s peak cannot be deconvoluted, whereas the O 1s peak can be deconvoluted, is reasonable in view of the simple valence-bond picture of back-bonding, which indicates that back-bonding causes a change in the formal charge of the oxygen atom but no change in the formal charge of the carbon atom. The conclusion is also consistent with the calculations which show essentially identical charges for the equatorial and axial carbon atoms but significantly different charges for the equatorial and axial oxygen atoms.

The fact that the deconvoluted peak of higher intensity in the O 1s Fe(CO)₅ spectrum (the peak due to the equatorial CO groups) is of lower binding energy than the deconvoluted peak of lower intensity is in qualitative agreement with the prediction that the equatorial oxygen atoms are more negatively charged than the axial oxygen atoms. The result indicates that the back-bonding to the equatorial CO groups is greater than that to the axial CO groups and is consistent with the well-established rule that, in trigonal-bipyramidal d⁸ complexes, strong π-acceptor ligands preferentially coordinate at equatorial positions.¹⁶⁻¹⁸ The magnitude of the binding energy shift between the deconvoluted peaks (0.8 eV) is higher than the predicted values, but the agreement is satisfactory in view of the uncertainties associated with the measured and predicted values.

Experimental Section

The gas phase spectra were obtained using the Uppsala high-resolution spectrometer.¹³ Carbon monoxide gas was introduced into the ionization chamber as a reference, and its O 1s and C 1s spectra were recorded simultaneously with those of Fe(CO)₅. The raw spectral data were analyzed using the nonlinear least-squares fitting program GAMET.¹⁹ Each data point (counts per channel) was weighted by the reciprocal of its magnitude. A mixed Gaussian-Lorentzian function

$$f(x) = \frac{h}{\alpha \left[1 + \left(\frac{x - \mu}{\lambda} \right)^2 \right] + (1 - \alpha) \left[\exp \left(\frac{x - \mu}{\lambda} \right)^2 \right]}$$

was used to represent each core-level line. Combinations of two or three of these lines plus a linear background were used to fit the experimental spectra. The parameters μ , λ , h , and α measure the peak position, line width, peak height, and "mixing ratio", respectively. For the C 1s spectrum the best fit was obtained using $\alpha = 0.97$ (97% Lorentzian character) for all peaks. For the O 1s spectrum the best fit was obtained using $\alpha = 0.60$ for all peaks. We believe that the different mixing ratios required for the oxygen and carbon lines may be attributed to differences in vibrational broadening.²⁰

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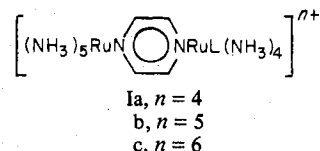
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Solubility of the Dithionates of Binuclear Ions

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The binuclear ions Ia-c were first described by Creutz and



Taube.² These workers prepared the ions Ia-c, where ammonia L was one of several ligands, e.g., water, chloride, pyrazine, etc. Only the symmetric ions, where L was ammonia, have been isolated as solid salts. Those compounds were isolated as tosylates or perchlorates from quite concentrated mother liquors. The general method of synthesis for ions of the kind Ia is the reaction between the pyrazinepenta-