pendence that goes from first order at low pressure to less than first, and approaches zero order at ~700 Torr. Since we were unable to detect an intermediate $RhCl(CO)P_2O_2$ dioxygen complex, even at low temperatures, where their formation is thermodynamically favored,[19] a dissociative mechanism such as shown in eq 6, where L = P or Cl^-, seems likely. Testing

$$RhCl(CO)P_2 \underset{k_{-1},\ +L}{\overset{k_1,\ -L}{\rightleftharpoons}} \text{solvated Rh} + O_2 \xrightarrow{k_2} \text{products} \tag{6}$$

such a mechanism (rate law, eq 7), which requires an inverse

$$-d[O_2]/dt = k_1k_2[Rh][O_2]\,(k_{-1}[L] + k_2[O_2]) \tag{7}$$

dependence on L at lower O_2 pressures, proved impossible since the addition of chloride led to decomposition to metal and green solutions (probably[20] via $2Rh^I \rightleftharpoons Rh^0 + Rh^{II}$), while addition of phosphinite led to its catalytic oxidation (see below).

Phosphine dissociation from $RhCl(CO)(PPh_3)_2$ has been proposed recently[7] for a photoinduced O_2 oxidation; here, however, the oxidation of coordinated CO to CO_2 was photoinduced, and the isolated oxidized complex was formulated as $[RhCl(O_2)(OPPh_3)_{0.67}]_x$. This process almost certainly involves radical pathways via hydroperoxides, since Harvie and McQuillin[21] have reported the oxidation of CO in $RhCl(CO)(PPh_3)_2$ to CO_2 by reaction with hydroperoxides. Our system is a "dark" reaction and is unaffected by the presence of added hydroquinone.

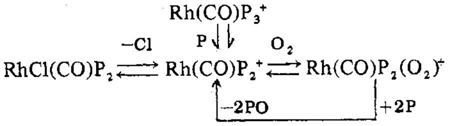
The catalytic phosphinite oxidation was very rapid at 60 °C and 1 atm of O_2; ~0.3 M phosphinite solutions being converted to the oxide in ~15 min using ~10^{-3}M $RhCl(CO)(PPh_2O\text{-}i\text{-}Bu)_2$. Kinetic studies at 30 °C show that the initial reaction rates are *independent* of the [Rh], even though the metal complex is a necessary catalyst. Such behavior indicates a radical process involving decomposition of adventitious hydroperoxides. Addition of hydroquinone (HQ) in a 1:1 ratio to Rh did not affect the oxidation rates, but increasing the [HQ] by ten to a hundred times that of the Rh (in fact, to concentrations approaching that of the phosphinite) reduced the rates by as much as a hundred. The radical mechanism could be initiated by reaction 8, where I is formed sponta-

$$Rh^I + I \xrightarrow{O_2} Rh^{II} + IOO\cdot \tag{8}$$

neously on exposing the reaction mixture to O_2; an extremely low concentration of I can result in zero-order dependence on Rh. The fact that 10^{-3} M HQ does not inhibit the reaction implies that HQ is consumed and, since the phosphinite is the reagent in large excess, this is the likely source of I. All the reagents were completely negative to tests for peroxides. A possible hydroperoxide source is hydrogen abstraction from the phosphinite by traces of a Rh–O_2 adduct.[22]

In the presence of ~10^{-1} M HQ, the efficient radical pathway is stopped, and the kinetics of the catalytic oxidation show first order in Rh and between first and zero order in O_2 and in phosphinite at 1 atm of O_2. At low O_2 pressure, an inverse phosphinite dependence is observed. Triphenylphosphine oxidation catalyzed by $Pt(PPh_3)_n$ and $RuCl_2(PPh_3)_3$ are thought to involve attack of uncoordinated phosphine on an intermediate O_2 adduct.[23,24] Reaction Scheme I for phosphinite oxidation invokes such a pathway and qualitatively accounts for the kinetics. Addition of chloride to the system again produces metal and thwarts attempts to substantiate the mechanism.

Scheme I



The main conclusion is that the catalytic phosphinite oxidation occurs mainly via a radical (or at least peroxide) pathway and not via oxygen atom transfer from coordinated dioxygen. Of interest is Halpern's[25] suggestion that the Pt(O)-catalyzed O_2 oxidation of Ph_2PMe via a molecular dioxygen complex involves free peroxide in solution.

Acknowledgment. We thank the National Research Council of Canada for financial support and Johnson Matthey Ltd. for loan of the rhodium.

Registry No. *trans*-$RhCl(CO)[PPh_2(O\text{-}i\text{-}Bu)]_2$, 64740-76-7; *trans*-$RhCl(CO)(PPhEt_2)_2$, 15691-93-7; *trans*-$RhCl(CO)(PEt_3)_2$, 15631-52-4; *trans*-$RhCl(CO)(PPh_3)_2$, 15318-33-9; *trans*-$RhCl(CO)(poly\text{-}OPPh_2)_2$, 64740-85-8; O_2, 7782-44-7; $Rh_4Cl_4(CO)_4(O_2)_2(PPh_3)_2$, 64740-77-8; $Rh_4Cl_4(CO)_4(O_2)_2[PPh_2(O\text{-}i\text{-}Bu)]_2$, 64740-78-9; $Rh_4Cl_4(CO)_4(O_2)_2(poly\text{-}OPPh_2)_2$, 64740-83-6; $Rh_4Cl_4(CO)_4(O_2)_2(PPhEt_2)_2$, 64740-79-0; $Rh_4Cl_4(CO)_4(O_2)_2(PEt_3)_2$, 64740-80-3; **2**, 64740-81-4.

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A Mössbauer Effect Study of the Bonding in η^5-Cyclopentadienyliron Carbonyl Complexes[1]

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The series of complexes $CpFe(CO)_2X$, where Cp is η^5-C_5H_5 and X is a one-electron ligand such as a halide, an alkyl group, or $SiCl_3$, etc., undergoes substitution reactions in which either

Table I. Mössbauer Effect Parameters[a]

	78 K				Room temperature			
Compd	δ	ΔE_Q	Γ_1	Γ_2	δ	ΔE_Q	Γ_1	Γ_2
$CpFe(CO)_2Cl$	0.2277 (9)	1.863 (9)	0.27 (1)	0.27 (1)	0.1415 (6)	1.83 (1)	0.23 (2)	0.25 (2)
$CpFe(CO)_2Br$	0.227 (1)	1.87 (1)	0.36 (3)	0.34 (3)	0.1496 (8)	1.84 (2)	0.28 (3)	0.27 (3)
$CpFe(CO)_2I$	0.215 (1)	1.84 (1)	0.28 (2)	0.28 (2)	0.1329 (8)	1.82 (2)	0.25 (3)	0.22 (3)
$CpFe(CO)_2NCO$	0.2113 (9)	1.880 (7)	0.29 (1)	0.30 (1)	0.1258 (6)	1.84 (1)	0.22 (2)	0.25 (2)
$CpFe(CO)_2NCS$	0.2015 (8)	1.878 (7)	0.28 (1)	0.28 (1)	0.1227 (6)	1.87 (1)	0.24 (2)	0.23 (2)
$CpFe(CO)_2SCN$	0.1858 (7)	1.811 (8)	0.29 (1)	0.32 (1)	0.1138 (6)	1.80 (1)	0.23 (2)	0.27 (3)
$CpFe(CO)_2SeCN$	0.1867 (9)	1.75 (1)	0.28 (2)	0.26 (2)	0.1057 (5)	1.72 (1)	0.25 (2)	0.23 (2)
$CpFe(CO)_2CN$	0.0696 (3)	1.899 (3)	0.29 (1)	0.30 (1)	−0.0097 (4)	1.89 (2)	0.25 (2)	0.22 (2)
$CpFe(CO)(PPh_3)I$	0.308 (1)	1.87 (1)	0.27 (2)	0.28 (2)	0.233 (1)	1.85 (1)	0.26 (3)	0.25 (3)
$CpFe(CO)(PPh_3)Br$	0.290 (1)	1.89 (1)	0.25 (3)	0.28 (3)	0.231 (1)	1.88 (2)	0.24 (3)	0.26 (3)
$CpFe(CO)(PPh_3)SCN$	0.262 (1)	1.789 (8)	0.26 (1)	0.26 (1)	0.184 (1)	1.81 (1)	0.26 (3)	0.27 (3)
$CpFe(CO)(PPh_3)NCS$	0.256 (1)	1.936 (9)	0.28 (2)	0.27 (2)	0.1782 (9)	1.92 (1)	0.24 (2)	0.25 (2)
$CpFe(CO)(PPh_3)CN$	0.1347 (6)	1.93 (1)	0.32 (2)	0.32 (2)	0.0576 (3)	1.89 (2)	0.24 (3)	0.24 (3)
$[CpFe(CO)_3]PF_6$	0.0459 (2)	1.884 (8)	0.27 (1)	0.26 (1)	−0.0047 (8)	1.85 (1)	0.24 (2)	0.24 (2)
$[CpFe(CO)_2(PPh_3)]PF_6$	0.0851 (4)	1.82 (1)	0.26 (1)	0.30 (1)	0.0013 (8)	1.80 (2)	0.24 (4)	0.31 (4)

[a] All data in mm/s relative to natural α-iron foil.

CO or X is replaced by a two-electron donor nucleophile (eq 1 and 2). The product depends upon the nature of X and the

$$CpFe(CO)_2X + L \rightarrow CpFe(CO)(L)X + CO \quad (1)$$

$$CpFe(CO)_2X + L \rightarrow [CpFe(CO)_2(L)]X \quad (2)$$

entering nucleophile.[3-11] Infrared,[6-9] proton,[6-9,12] and carbon-13 nuclear magnetic resonance[13,14] spectra have shown that bonding to the cyclopentadienyl ring and the carbonyl ligands is affected by the nature of X and, for carbonyl substituted derivatives, by the σ-donor and π-acceptor properties of the two electron donor ligand.

In conjunction with studies of the photochemical reactions of the above series of complexes,[15,16] we needed information on their differing bonding and electronic distributions and hence undertook a study of their Mössbauer effect spectra. Although Mössbauer data have been reported for several of these complexes,[14,17-20] no comprehensive data for the entire series exists. Our results and their relationship to the bonding and to other spectroscopic data are discussed herein.

Experimental Section

The complexes $CpFe(CO)_2Cl$[21] (-Br,[22] -I,[22] -CN,[21] -NCS,[23] -SCN,[23] -SeCN,[24] -NCO[25]), $CpFe(CO)(PPh_3)Br$[7] (-I,[7] -CN[26]), $[CpFe(CO)_3]PF_6$,[27] and $[CpFe(CO)_2(PPh_3)]PF_6$[7] were prepared by the literature methods cited and were characterized by infrared, NMR, and mass spectral data. $CpFe(CO)(PPh_3)NCS$ and $CpFe(CO)(PPh_3)SCN$ were prepared by thermal or photochemical substitution reactions of $CpFe(CO)_2NCS$ or $CpFe(CO)_2SCN$ as described elsewhere.[16] Both new products gave satisfactory elemental analyses.

Infrared spectra were measured on a Perkin-Elmer 521 spectrophotometer. The reported frequencies are accurate to ±2.0 cm^{-1}. Mössbauer spectra were obtained on an Austin Sciences Associates constant acceleration spectrometer which was equipped with a copper matrix source (maintained at room temperature) and was calibrated with natural α-iron foil. Both room temperature and low-temperature spectra were obtained on unground polycrystalline samples and were measured with a constant source-absorber-detector geometry. All samples had approximately the same absorber thickness.

Results

Each of the compounds studied in this work gave a clean, well-resolved quadrupole doublet spectrum as is shown for $CpFe(CO)(PPh_3)SCN$ in Figure 1. The Mössbauer effect parameters at room temperature and 78 K are presented in Table I.[28] All of the results were calculated from a computer optimized parabola and Lorentzian fit obtained by using the National Bureau of Standards PARLOR computer program.[29,30] The error limits have been calculated from the variance of the peak position and half-width determined in the final computer iteration of the numerical fitting procedure.[31] Standard error propagation formulas, which took into account the standard errors in the calibration factors, were then used to calculate the errors given in Table I. In order to further determine the accuracy of the Mössbauer effect isomer shift data, we have measured five separate room temperature spectra on three separate preparations of $CpFe(CO)_2Cl$. The average value and standard deviation from the mean of these measurements is 0.142 (2) mm/s for the chemical isomer shift and 1.831 (5) mm/s for the quadrupole interaction. On the basis of these average values and the errors given in Table I, we have concluded that the values of the chemical isomer shift are accurate to at least ±0.005 mm/s and that we are observing real and reproducible relative differences in the chemical isomer shifts. The small variation in these isomer shift values does, however, point up the necessity of measuring the Mössbauer spectra under as nearly identical conditions as possible.

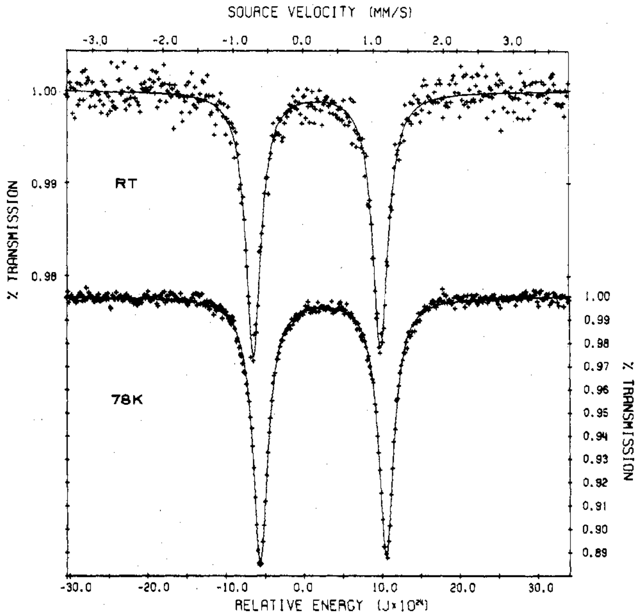

Figure 1. The Mössbauer effect spectrum of $CpFe(CO)(PPh_3)SCN$ at room temperature and 78 K.

In some instances the observed Mössbauer effect spectra exhibited a small (less than 10%) asymmetry in the areas of the two quadrupole split lines. This asymmetry is, no doubt, the result of preferential crystal orientation in these polycrystalline materials. No effort was made to eliminate such orientation effects. The percent effect observed for most of the compounds increased by a factor of from 3 to 5 between room temperature and 78 K. This increase is indicative of the

Table III. Solution Infrared Spectral Data[a]

Compd	ν_{CO}, cm^{-1}	k, mdyn/Å	k_i, mdyn/Å
$CpFe(CO)_2Cl$	2050, 2002	16.59	0.38
$CpFe(CO)_2Br$	2045, 1999	16.52	0.37
$CpFe(CO)_2I$	2038, 1998	16.45	0.33
$CpFe(CO)_2NCO$	2065, 2015	16.82	0.40
$CpFe(CO)_2NCS$	2068, 2023	16.90	0.37
$CpFe(CO)_2SCN$	2050, 2005	16.61	0.38
$CpFe(CO)_2SeCN$	2045, 2000	16.52	0.37
$CpFe(CO)_2CN$	2060, 2015	16.77	0.37
$CpFe(CO)(PPh_3)I$	1955	15.44	
$CpFe(CO)(PPh_3)Br$	1960	15.52	
$CpFe(CO)(PPh_3)SCN$	1975	15.75	
$CpFe(CO)(PPh_3)NCS$	1980	15.83	
$CpFe(CO)(PPh_3)CN$	1975	15.75	
$[CpFe(CO)_3]PF_6$[b]	2125, 2079	17.71	0.26
$[CpFe(CO)_2(PPh_3)]PF_6$[b]	2055, 2010	16.74	0.35

[a] Measured in chloroform solution in matched 0.10-mm KBr cells. [b] Measured in methylene chloride solution.

low Debye temperature expected for this type of material.[32] The exceptions are $CpFe(CO)_2I$ and $[CpFe(CO)_3]PF_6$ in which the percent effect is essentially independent of temperature.

Various authors[14,17–20] have reported Mössbauer effect parameters for certain of the compounds reported herein. Their results are summarized in Table II.[33] In general our results are in qualitative agreement with previous results and excellent agreement is found with the results of Bancroft et al.,[14] Herber et al.,[17] and Mays and Sears.[19] The observed variations indicate the importance of obtaining chemical isomer shift data under closely controlled experimental and calibration conditions if comparisons are to be made of relative isomer shift values.

The infrared spectra in the carbonyl stretching region are characterized by two intense absorption bands for $CpFe(CO)_2X$, $[CpFe(CO)_3]PF_6$, and $[CpFe(CO)_2(PPh_3)]PF_6$ and a single absorption band for the substituted covalent derivatives, $CpFe(CO)(PPh_3)X$. Data, which were collected in solution to permit calculation of approximate carbonyl stretching force constants according to the Cotton–Kraihanzel method,[34] are presented in Table III. The trends observed in the solid-state infrared data are consistent with those observed for the solution spectra.

Discussion

For the series of compounds, $CpFe(CO)_2X$, the Mössbauer effect isomer shift measured at 78 K decreases in the order Cl ~ Br > I ~ NCO > NCS > SCN ~ SeCN > CN (Table I). Essentially the same trend is observed at room temperature. Although the differences in the isomer shift values are small, they are, we believe, real. The decreasing isomer shift values reflect an increasing s-electron density at the iron nucleus.[32] The latter is increased by ligand to iron σ donation and by retrodative π bonding from filled iron to vacant ligand orbitals. Additionally, if the ligand donor atom possesses unshared electron pairs, these may be donated into *empty* iron d orbitals, leading to an increase in the isomer shift.[32] The above ordering of X is consistent with these concepts. The complexes with halide ligands (good σ donors and π donors) give the highest isomer shift values whereas the complex with cyanide (a good σ donor and π acceptor) exhibits the lowest value. For the pseudohalide complexes, retrodative bonding into vacant ligand π^* orbitals is possible in all cases and contributes to a lowering of the isomer shift relative to the halide complexes. For the pair of linkage isomers $CpFe(CO)_2NCS$ and $CpFe(CO)_2SCN$, the former gives the higher isomer shift value, indicating lower s-electron density at iron in the N-bonded isomer. The N-bonded isomer is expected to have a more "ionic" iron–ligand bond than $CpFe(CO)_2SCN$[35] so that the observed difference in isomer shifts could reflect a greater σ donation for $CpFe(CO)_2SCN$. The isomer shift values for $CpFe(CO)_2NCO$ and $CpFe(CO)_2SeCN$ can be rationalized similarly.

The isomer shift values for $CpFe(CO)(PPh_3)Br$, –I, –NCS, –SCN, and –CN are significantly higher (0.05–0.10 mm/s) than for the corresponding neutral derivatives, $CpFe(CO)_2X$. This indicates decreased s-electron density at the iron nucleus upon replacement of the carbonyl group with triphenylphosphine and is consistent with the weaker π-acceptor properties of the phosphorus ligand.[4–9] The isomer shifts in the $CpFe(CO)(PPh_3)X$ series measured at 78 K decrease in the order I > Br > SCN ≳ NCS > CN. This order which is also observed at room temperature is qualitatively consistent with that observed for the neutral dicarbonyl derivatives (Table I). The cationic derivatives $[CpFe(CO)_3]PF_6$ and $[CpFe(CO)_2(PPh_3)]PF_6$ exhibit smaller isomer shifts than the neutral complexes. This can be rationalized in terms of the positive charge on the $CpFeL_3$ moiety which reduces iron–ligand back-bonding[4,5,7] and thus increases the s-electron density at the iron nucleus. Alternatively, the ionic derivatives may be viewed as the formal result of replacing the anionic ligand by the much stronger π-acceptor ligand, carbon monoxide, with the conclusions regarding isomer shift differences being the same. The effect of phosphine substitution on isomer shift is evident in the cationic complexes as well, a point made previously by Bancroft et al[14] for a series of ionic derivatives.

The quadrupole splitting parameter, ΔE_Q, is relatively invariant in the series of compounds studied here, in contrast to the results[36] obtained for low-spin iron(II) complexes of the general formula $[trans\text{-}FeH(L)(depe)_2]BPh_4$. Bancroft et al.[14] have attributed this invariance to the ability of the cyclopentadienyl and carbonyl ligands to substantially change their bonding properties so as to neutralize the changes in electron asymmetry. It is interesting to note that in all instances the $CpFe(CO)_2SCN$, $CpFe(CO)_2SeCN$, and $CpFe(CO)(PPh_3)SCN$ complexes have the lowest quadrupole interaction values in the series. These low values may be related to the coordination geometry of the thiocyanate and selenocyanate group. It is now well accepted[35] that in N-bonded thiocyanate complexes the metal–nitrogen–carbon angle is at most only slightly reduced from 180°. In contrast, most S-bonded thiocyanate complexes exhibit a metal–sulfur–carbon bond angle in the range of 90–120°.[35] The additional bonding freedom associated with the sulfur or selenium nonlinearly bonded complexes must permit the pseudohalide to bond in a geometry which reduces the electric field gradient at the iron nucleus relative to that observed for the linear N-bonded pseudohalides and other halides.

A comparison of the infrared spectra of pairs of $CpFe(CO)_2X$ and $CpFe(CO)(PPh_3)X$ derivatives led to conclusions similar to those cited above for the Mössbauer effect data. Replacement of a carbonyl group by the weaker π-acceptor ligand triphenylphosphine leads to a lowering of the carbonyl stretching frequency (see Table III), indicating an increased π donation from iron to the remaining carbonyl ligand.[6,7,12,13] The same effects are noted in the infrared spectra of $[CpFe(CO)_3]PF_6$ and $[CpFe(CO)_2(PPh_3)]PF_6$, in that the phosphine substituted derivative has the lower ν_{CO}. Figure 2 shows a plot of the Mössbauer effect isomer shift vs. the carbonyl stretching force constant for the complexes studied. There is an inverse relationship between these parameters as they respond in opposite directions to the changing electron density at iron. This relationship is evident in Figure 2, but the correlation between isomer shift and stretching force constant is far from quantitative. The most obvious examples of this breakdown are the scatter in the $CpFe(CO)_2X$ data

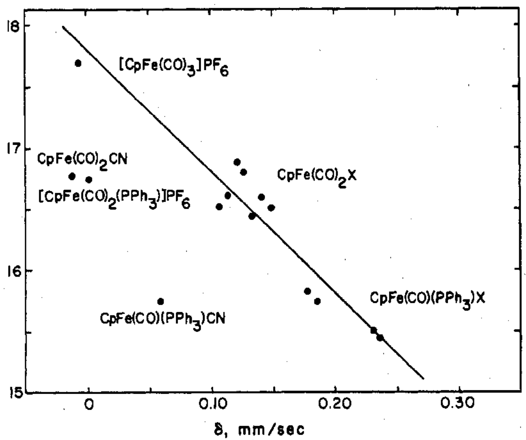

Figure 2. A plot of the room temperature Mössbauer effect chemical isomer shift vs. the carbonyl stretching force constant.

points and the more severe deviations of $CpFe(CO)_2CN$, $[CpFe(CO)_2(PPh_3)]PF_6$, and $CpFe(CO)(PPh_3)CN$ from the best linear least-squares fit of the other 12 data points. The stretching force constants for the $CpFe(CO)_2X$ 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 $CpFe(CO)_2X$ data points becomes obvious.

The carbonyl stretching force constants for $CpFe(CO)_2CN$ and $[CpFe(CO)_2(PPh_3)]PF_6$ 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 $CpFe(CO)(PPh_3)CN$ 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 herein[34] 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 $CpFe(CO)_2CN$ and at 2090 cm^{-1} for $CpFe(CO)(PPh_3)CN$. Further, proton NMR spectra show an upfield shift of 0.2–0.3 ppm for the cyclopentadienyl protons of $CpFe(CO)(PPh_3)X$ relative to $CpFe(CO)_2X$.[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. $CpFe(CO)_2Cl$, 12107-04-9; $CpFe(CO)_2Br$, 12078-20-5; $CpFe(CO)_2I$, 12078-28-3; $CpFe(CO)_2NCO$, 32660-69-8; $CpFe(CO)_2NCS$, 12317-60-1; $CpFe(CO)_2SCN$, 12317-59-8; $CpFe(CO)_2SeCN$, 33179-83-8; $CpFe(CO)_2CN$, 12152-37-3; $CpFe(CO)(PPh_3)I$, 12099-18-2; $CpFe(CO)(PPh_3)Br$, 12099-12-6; $CpFe(CO)(PPh_3)SCN$, 64784-33-4; $CpFe(CO)(PPh_3)NCS$, 61113-76-6; $CpFe(CO)(PPh_3)CN$, 32757-48-5; $[CpFe(CO)_3]PF_6$, 38834-26-3; $[CpFe(CO)_2(PPh_3)]PF_6$, 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