

## CARBON-13 NMR STUDIES OF SOME IRON CARBONYLS: AN UNEXPECTED TREND IN THE CHEMICAL SHIFTS OF DISUBSTITUTED COMPLEXES

KENTON H. WHITMIRE \* and T. RANDALL LEE

*Department of Chemistry, Rice University, P.O. Box 1892, Houston, TX 77251 (U.S.A.)*

(Received June 4th, 1984)

### Summary

The Carbon-13 NMR spectra of a series of  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  complexes ( $\text{L} = \text{P}(\text{cyclohexyl})_3$ ,  $\text{PMe}_3$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{OMe})_3$  or  $\text{P}(\text{OPh})_3$ ) have been measured. A good correlation is observed between  $^{13}\text{C}$  chemical shift of the carbonyls and the donor-acceptor properties of the phosphorus ligand. However, an unexpected trend is observed for  $\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}(\text{CO})_4\text{L} \rightarrow \text{Fe}(\text{CO})_3\text{L}_2$  showing high field shifts of  $\delta(^{13}\text{C})$  upon successive substitution for some complexes. A variable temperature study was conducted on  $\text{H}_2\text{Fe}(\text{CO})_4$  and the axial and equatorial carbonyls have been resolved. The energy of interconversion is estimated at ca. 8.1 kcal. In addition the  $^{13}\text{C}$  spectrum of  $[\text{HFe}(\text{CO})_4]^-$  is reported for the first time.

### Introduction

Carbon-13 NMR spectroscopy is an increasingly powerful tool for studying the structure and dynamics of inorganic and organometallic complexes and, in particular, metal carbonyls [1]. Correlations between ligand donor-acceptor properties and  $^{13}\text{C}$  chemical shifts of the carbonyls have been studied in the following:  $\text{CpMn}(\text{CO})_2\text{L}$  [2],  $\text{Ni}(\text{CO})_{4-n}\text{L}_n$  [3],  $(\text{C}_6\text{H}_5\text{X})\text{Cr}(\text{CO})_3$  [4],  $\text{M}(\text{CO})_5\text{L}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) [5–8], *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$  [9] and  $\text{CpFe}(\text{CO})_2\text{X}$  [10]. The fluxionality of  $\text{M}(\text{CO})_4\text{X}_2$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) [11] and of  $\text{Co}(\text{CO})_4\text{EX}_3$  [12] has been studied and the data indicate that similar correlations are operative. Upon examining the literature for correlations involving iron carbonyls, we were surprised at the lack of data since substituted iron carbonyls are obtained as products in many reactions. We were particularly interested in NMR data for use in our studies of iron carbonyls with phosphorus ylids. While the trends were expected to be similar, it was of interest to carry out a study of the  $\text{Fe}(\text{CO})_{5-n}\text{L}_n$  ( $n = 1, 2$ ) system and some related mononuclear species. Generally, the trends observed for other correlations are followed for iron, but we have observed an unusual effect in the chemical shift trends for our series that is

unlike those for the other simple octahedral- and tetrahedral-substituted metal carbonyls. We wish to report those observations here.

## Experimental

All manipulations were carried out using standard Schlenk techniques under dry  $N_2$ . The  $^{13}C$  NMR spectra were obtained on either a Nicolet NT 360 spectrometer (5 mm tubes, University of Illinois) or a Bruker WM500 (10 mm tubes, California Institute of Technology). Non-deuterated NMR solvents were distilled by appropriate methods before usage, while the deuterated solvents were used as received after placing in a Schlenk storage tubes and freeze-thaw-pump degassing.

*$^{13}C$  enrichment of  $Fe(CO)_5$ .* Iron pentacarbonyl was  $^{13}C$  enriched after a modification of the method of John S. Bradley [13] by placing 8.0 ml  $Fe(CO)_5$ , in a 100 ml stainless steel bomb equipped with a needle valve. The bottom of the cylinder was frozen in liquid nitrogen and the cylinder evacuated. After warming the cylinder was filled with ca. 100 psi of  $^{13}CO$  (99%  $^{13}CO$ , Prochem Isotopes, Ltd.). The cylinder was closed and placed in a boiling water bath for about 6 h. At that time the bomb was cooled and reattached to the vacuum line. The  $Fe(CO)_5$  was frozen in liquid  $N_2$  and the gaseous  $CO$  (ca. 25%  $^{13}C$ ) was transferred to a gas bulb for future use. After warming, the cylinder was vented to air and the  $Fe(CO)_5$  transferred to a Schlenk storage tube and degassed under high vacuum. The carbonyl was stored in a freezer to slow decomposition. The  $Fe(CO)_5$  so produced showed C–O stretching frequencies attributable to the presence of  $^{13}CO$ . The  $^{13}C$  chemical shift of  $Fe(CO)_5$  was measured in toluene/toluene- $d_8$  under conditions identical to those used for  $Fe(CO)_4L$  and  $Fe(CO)_3L_2$ .

*Synthesis of substituted iron carbonyls.* The substituted iron carbonyls were prepared photochemically from enriched  $Fe(CO)_5$  (ca. 0.10 ml) and approximately 1.5 equivalents of the appropriate phosphine in about 30 ml of dry tetrahydrofuran (distilled from sodium and benzophenone and saturated with  $N_2$ ). The reaction mixtures were then left to stand in sunlight for several days or irradiated for 1 to 2 h by a 450W Ace Hanovia mercury arc lamp. Each method produced a mixture of  $Fe(CO)_4L$  and  $Fe(CO)_3L_2$  complexes which were separated by fractional crystallization or sublimation by minor modifications of literature methods [14]. The mono- and di-substituted species can be distinguished by the nature of the coupling to phosphorus; doublets are seen for the monosubstituted and triplets for the disubstituted products. Unfortunately the instrument used to measure these spectra was not capable of phosphorus–carbon decoupling; however, the assignment of these doublets and triplets to  $J(C-P)$  is reasonable based on the solid state structures of  $Fe(CO)_4L$  and  $Fe(CO)_3L_2$  complexes as well as the established stereochemical nonrigidity of these five coordinate systems. No chemically meaningful alternatives would explain the results as well as the simplest coupling interpretation. The NMR samples were prepared in 5 mm NMR tubes. The solids were loaded in a nitrogen filled dry box and then each was attached to a high vacuum line, where a toluene/toluene- $d_8$  mixture (75/25) was distilled in under vacuum after which the tubes were sealed with a flame. The temperature settings for the NT-360 were calibrated with a thermocouple inserted in the probe prior to the runs. The  $^{13}C$  chemical shift data and  $J(C-P)$  coupling constants are given in Tables 1 ( $Fe(CO)_4L$ ) and 2 ( $Fe(CO)_3L_2$ ). Chemical shifts were referenced to the methyl carbon resonance

of solvent toluene, and the deuterium signal of the solvent was used as an internal lock. The values given are for spectra measured at ambient temperature. Spectra were also examined at  $-90^{\circ}\text{C}$  and no broadening of the signals was observed. The sample of  $\text{Fe}(\text{CO})_4\text{PPh}_3$  was examined also on the Bruker WM500 after transferring the sample to a 10 mm tube.

*Preparation of [PPN][HFe(CO)<sub>4</sub>] and H<sub>2</sub>Fe(CO)<sub>4</sub>.* Enriched [PPN][HFe(CO)<sub>4</sub>] [PPN = bis(triphenylphosphine)iminium] was prepared by addition of  $\text{Fe}(\text{*CO})_5$  to cold methanolic KOH followed by warming and addition of one equivalent of [PPN]Cl dissolved in methanol. A copious white precipitate developed which was collected by filtration and dried under vacuum. This product gave an infrared spectrum characteristic of  $[\text{HFe}(\text{CO})_4]^-$  ( $\nu(\text{CO})$  2000w, 1910m, 1885vs  $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ). Approximately 0.1 g [PPN][HFe(CO)<sub>4</sub>] was placed in a Schlenk reaction vessel and an excess of gaseous HCl was distilled in under vacuum at  $-196^{\circ}\text{C}$ . The flask was allowed to warm to  $-78^{\circ}\text{C}$  for a few minutes and then the volatiles were collected in a 10 mm NMR tube which had been prefilled with pentane/toluene-*d*<sub>8</sub> (ca. 80/20). The sample thus prepared was sealed and kept at liquid nitrogen temperatures until it was placed in the precooled NMR probe ( $-110^{\circ}\text{C}$ ). The spectrum of the  $[\text{HFe}(\text{CO})_4]^-$  ion was obtained using the [PPN]<sup>+</sup> salt dissolved in  $\text{CD}_2\text{Cl}_2$  which was kept frozen until measurement on the NT-360. This salt reacts slowly with the solvent and must be kept cold to prevent conversion to  $[\text{HFe}_3(\text{CO})_{11}]^-$ .

## Results

Chemical shift data for the  $\text{Fe}(\text{CO})_{5-n}\text{L}_n$ : The <sup>13</sup>C chemical shifts and  $J(\text{C-P})$  coupling constants for the  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  complexes are given in Tables

TABLE 1  
<sup>13</sup>C NMR AND IR DATA FOR  $\text{Fe}(\text{CO})_4\text{L}$  COMPLEXES

L	$\chi$	$\delta(^{13}\text{C})$ (ppm)	$J(\text{C-P})$ (Hz)	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )
P(cyclohexyl) <sub>3</sub>	0.3	214.2	19.0	2040, 1957, 1925
PMe <sub>3</sub>	7.8	213.1	19.8	2043, 1967, 1932
PPh <sub>3</sub>	12.9	213.0	19.0	2050, 1977, 1945
P(OMe) <sub>3</sub>	23.1	211.8	23.3	2063, 1996, 1953
P(OPh) <sub>3</sub>	29.1	211.1	22.3	2063, 1992, 1960

TABLE 2  
<sup>13</sup>C NMR AND IR DATA FOR  $\text{Fe}(\text{CO})_3\text{L}_2$  COMPLEXES

L	$\chi$	$\delta(^{13}\text{C})$ (ppm)	$J(\text{C-P})$ (Hz)	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )
P(cyclohexyl) <sub>3</sub>	0.3	216.6	26.9	1840
PMe <sub>3</sub>	7.8	215.0	29.6	1870
PPh <sub>3</sub>	12.9	213.9	28.0	1890
P(OMe) <sub>3</sub>	23.1	211.3	38.7	1926
P(OPh) <sub>3</sub>	29.1	209.1	40.8	(1923, 1951)

1 and 2, respectively. In Fig. 1, the data is plotted against ligand acceptor–donor properties derived from Tolman’s  $\chi$  values [15]. Tolman’s values are given as a function of R group on the phosphorus ligand and so we have summed the effect of R to obtain an overall value for  $\text{PR}_3$ . For example, Tolman determined cyclohexyl to have a  $\chi$  value of 0.1 so we have used 0.3 as the value for  $\text{P}(\text{cyclohexyl})_3$ . The plots obtained in Fig. 1 give lines represented by eq. 1 and 2 for  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  respectively.

$$\delta(^{13}\text{C}) = -0.104\chi + 214.2 \quad (1)$$

$$\delta(^{13}\text{C}) = -0.256\chi + 216.9 \quad (2)$$

The correlation factors in each case were greater than 99% for a least squares plot. We have treated Bodner’s data [3] for  $\text{Ni}(\text{CO})_{4-n}\text{L}_n$  ( $n = 1, 2$ ;  $\text{L} = \text{PBu}_3, \text{PEt}_3, \text{PPh}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3$ ) similarly and obtained eq. 3 and 4 for the mono- and disubstituted complex, respectively:

$$\delta(^{13}\text{C}) = -0.151\chi + 197.9 \quad (3)$$

$$\delta(^{13}\text{C}) = -0.278\chi + 203.4 \quad (4)$$

Correlation factors were  $> 99\%$  and  $98\%$  respectively. Similar treatment of Gansow’s data for  $\text{W}(\text{CO})_5\text{L}$  yielded eq. 5 (correlation factor  $> 98\%$ ).

$$\delta(^{13}\text{C}) = -0.201\chi + 200.8 \quad (5)$$

One can estimate a  $\chi$  value for CO from these lines for comparison to Tolman’s data on the phosphines by substituting the chemical shift of the unsubstituted carbonyl for  $\delta(^{13}\text{C})$ . This gives  $\chi \sim 45$  for Fe,  $\sim 42$  for Ni and  $\sim 43$  for W which is

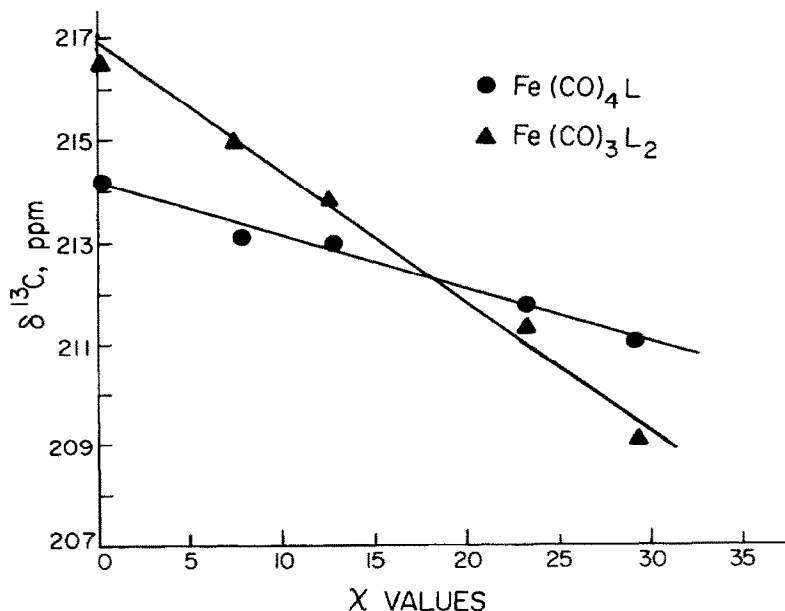


Fig. 1. Chemical shift data for the monosubstituted and disubstituted iron carbonyls plotted as a function of the  $\chi$  values for the ligand donor–acceptor properties.

remarkably good agreement considering that these values were measured in different solvents on different instruments. A similar process can be carried out for the disubstituted case giving  $\chi = 42.8$  for Ni but 28.8 for Fe. The nickel system agrees well with expectations but the iron system is obviously anomalous.

A correlation is observed in the pairwise comparison of chemical shift data for  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  species. When the change in Carbon 13 chemical shift obtained by taking  $\delta(^{13}\text{C}[\text{Fe}(\text{CO})_3\text{L}_2]) - \delta(^{13}\text{C}[\text{Fe}(\text{CO})_4\text{L}])$  is plotted vs.  $\chi$  (Fig. 2), a linear plot is obtained (least squares correlation  $> 98\%$ ).

*Fluctonality of  $\text{H}_2\text{Fe}(\text{CO})_4$ .* Vancea and Graham [11] previously reported the high fluctonality of  $\text{H}_2\text{Fe}(\text{CO})_4$  but did not achieve a limiting spectrum. The  $^1\text{H}$  decoupled variable temperature spectrum of  $\text{H}_2\text{Fe}(\text{CO})_4$  is shown in Fig. 3, while Fig. 4 shows the coupled spectrum at  $-110^\circ\text{C}$ . The coalescence temperature is determined to be ca.  $-103^\circ\text{C}$  and the separation between the two resolved singlets (decoupled) at  $-110$  is 57 Hz. The  $\Delta G_C^\ddagger$  of activation from this process can be estimated from the eq. 7 and 8.

$$\Delta G_C^\ddagger = 2.3RT_C \left( 10.32 + \log \frac{T_C}{k_C} \right) \quad (7)$$

$$K_C = \frac{\pi \Delta \nu}{2^{1/2}} \quad (8)$$

where  $\Delta \nu$  is the separation in Hz of the peaks at the slow exchange limit and  $T_C$  is the coalescence temperature. The  $-110^\circ\text{C}$  spectrum may not be exactly at the slow

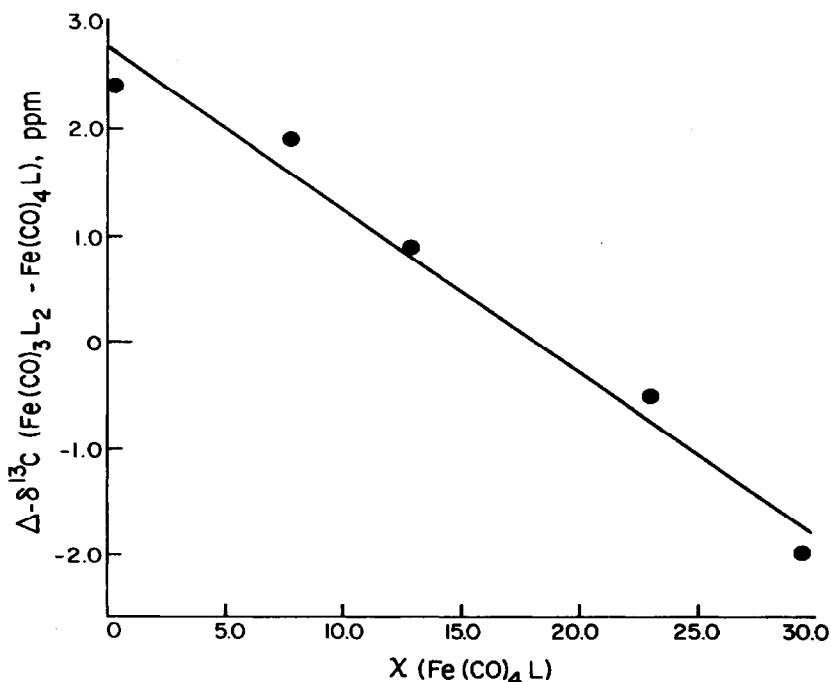


Fig. 2. The difference in chemical shift values on successive addition of  $\text{PR}_3$  plotted against the  $\chi$  values for the monosubstituted species.

exchange limit but lower temperatures were not attempted for the sake of the instrument. This value is the lowest measured for a fluxional octahedral complex. Values in excess of 11 kcal/mol have been observed for a series of  $\text{H}_2\text{FeL}_4$  (L = phosphine) [17]. In those complexes a "tetrahedral jump" mechanism was proposed for the exchange mechanism. As can be seen in the  $-110^\circ\text{C}$  spectrum (Fig. 4), two signals of equal intensity are obtained as expected for the *cis* dihydride

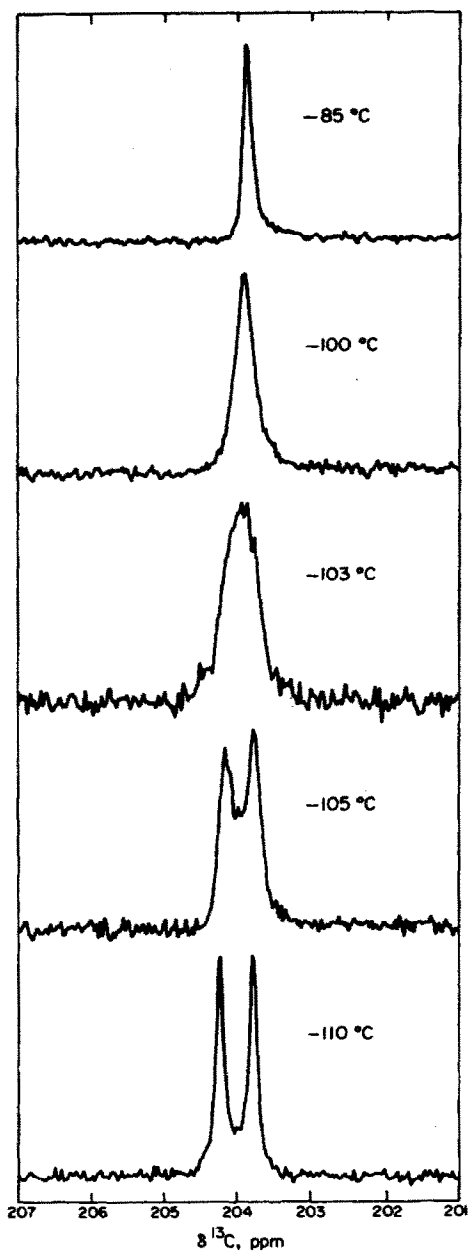


Fig. 3. The variable temperature  $^{13}\text{C}$  spectrum of  $\text{H}_2\text{Fe}(\text{CO})_4$  obtained on a Bruker WM500 spectrometer (decoupled) in pentane/toluene- $d_3$ .

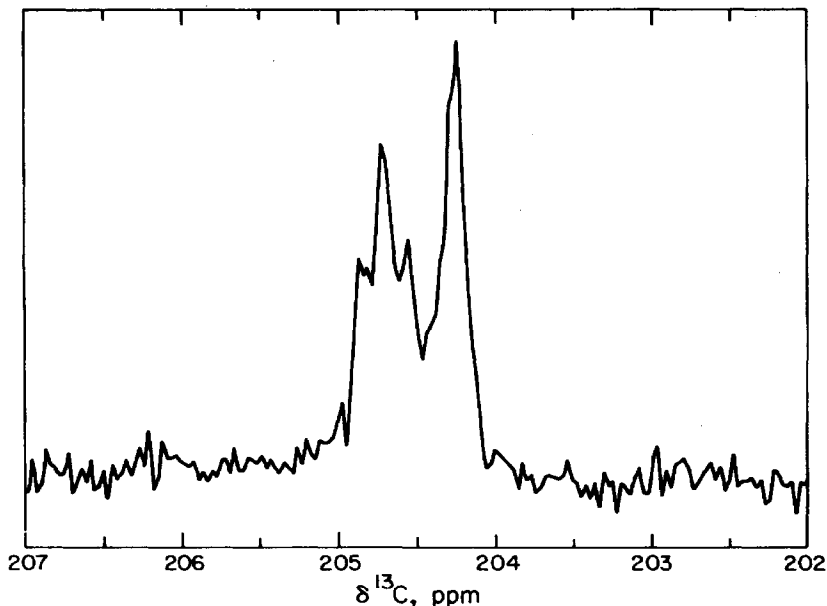
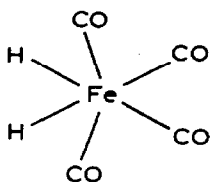


Fig. 4. The non-decoupled  $^{13}\text{C}$  spectrum of  $\text{H}_2\text{Fe}(\text{CO})_4$  taken at  $-110^\circ\text{C}$ .

structure (I). The coupling expected for this molecule would be as follows. The two equivalent axial CO's would be split into a triplet by the two equivalent hydrides. An equatorial CO, on the other hand, sees two magnetically inequivalent hydrides and should be a doublet of doublets. The coupled spectrum shows that the lower field peak is obviously split into a triplet ( $J(\text{C}-\text{H})$  6.6 Hz), while the higher field signal is broadened but the coupling is not resolved. This could arise from two possible causes. One is that residual exchange may obscure the  $J(\text{C}-\text{H})$ , or secondly the coupling constants may be too small to be resolved under the spectral resolution available (ca. 4 Hz).



(I)

## Discussion

*Chemical shifts of the substituted mononuclear iron carbonyls.* The factors influencing the bonding of CO to metals have been under discussion for some time. An important aspect of this bonding is the ability of the  $\pi^*$  orbital of CO to act as an electron acceptor which has the effect of strengthening M-C and weakening C-O. Substitution of phosphine ligands for CO shows the expected correlation between the C-O infrared stretching frequencies of the remaining carbonyls and the

donor/acceptor properties of the phosphine. There was controversy over the relative effects of the  $\sigma$  donor– $\pi$  acceptor capabilities of the phosphines, but it is now generally believed that some phosphines can act as good  $\pi$  acceptors. This is in accord with the bonding changes that occur in  $\text{Cr}(\text{CO})_5\text{L}$  upon going from  $\text{PPh}_3$  to  $\text{P}(\text{OPh})_3$  [18]. Phosphorus trifluoride is one of the few phosphines whose  $\pi$  acceptor strength is comparable to that of CO. Most others are much weaker acceptors. The carbon-13 chemical shifts of the carbonyl ligands show a good correlation to C–O stretching frequencies or force constants in a number of cases [2–10]. This relationship is attributed to a relationship between metal–CO  $\pi$ -backbonding and the paramagnetic contribution,  $\sigma_p$ , to the chemical shift. Karplus and Pople [19] have shown  $\sigma_p$  to have the form:

$$\sigma_p^A = \frac{e^2 \hbar^2}{2m^2 c^2 \Delta E} \langle r^{-3} \rangle_{2p} \left[ Q_{AA} + \sum_{B \neq A} Q_{AB} \right] \quad (6)$$

where  $\Delta E$  is the average excitation energy,  $\langle r^{-3} \rangle_{2p}$  is the mean inverse cube of the distance a carbon  $2p$  electron is from the nucleus and  $Q_{AA}$  and  $Q_{AB}$  contain the elements of the charge density, bond order matrix. It was shown that this term is the one primarily responsible for the observed changes in  $\delta(^{13}\text{C})$  for multiply bonded carbon. For a more in depth discussion of the relative magnitudes of the various components of the  $\sigma_p$  term, the reader is referred to ref. 9, 20 and 21. The total chemical shift contains a diamagnetic term, whose magnitude is small compared to  $\sigma_p$ , and terms for the effects of the presence of other atoms such as anisotropy, ring currents, solvent effects, etc. In our work we have attempted to hold these latter effects constant by considering a system in which the gross geometry and solvent are constant. We cannot completely eliminate neighboring group anisotropy effects on the  $^{13}\text{C}$  chemical shift; however, such effects are generally found to be small for  $^{13}\text{C}$  NMR [22]. That this assumption is valid is supported by the high correlation of  $^{13}\text{C}$  data to the donor–acceptor properties of the phosphines used, which we would not expect to parallel the anisotropy effects for the series of ligands chosen.

Our data at first glance appears to agree well with literature precedents. Plots of  $\delta(^{13}\text{C})$  versus Tolman's  $\chi$  values for the various phosphines are linear with high correlation coefficients as seen for the substituted nickel and tungsten carbonyls. It is gratifying that the hypothetical  $\chi$  value for CO obtained from eq. 1, 3 and 5 is in good agreement for all three metals: W, 43; Fe, 45; Ni, 42. Comparing this to Tolman's scale, CO is then comparable in its donor–acceptor properties to  $\text{PCl}_3$ , and  $\text{PF}_3$  would be a slightly better acceptor–poorer donor.

The more interesting observation lies in comparison of the effect on  $\delta(^{13}\text{C})$  in the series  $\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}(\text{CO})_4\text{L} \rightarrow \text{Fe}(\text{CO})_3\text{L}_2$ . Since the phosphines used in this study are all recognized to be poorer  $\pi$  acceptors–better  $\sigma$  donors than CO, one would expect substitution of CO by a phosphine to encourage increased  $\pi$  backbonding to the residual carbonyls. This is consistent with the observed CO stretching frequencies and, by previous precedent, this should result in low field shifts for the carbon-13 resonances of the carbonyls. Likewise a further shift on disubstitution is also predicted. This is clearly not what we observe in the cases of  $\text{P}(\text{OMe})_3$  and  $\text{P}(\text{OPh})_3$ . In fact, the observed chemical shift of  $\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$  is slightly high field of that for  $\text{Fe}(\text{CO})_5$ . One might postulate that there is something unusual about phosphites as opposed to phosphines, but it is obvious from Fig. 2 that this observation is part of a general, well-behaved trend. For all the data on the



$\text{Ni}(\text{CO})_{4-n}\text{L}_n$  species shifts to low field are observed on successive substitution. In one respect, however, the trends observed for Ni are similar to that for Fe. If one constructs a plot for the Ni complexes as in Fig. 2 then one sees that a line with a similar slope is obtained, i.e. the difference  $\Delta\delta(^{13}\text{C}[\text{Ni}(\text{CO})_2\text{L}_2] - \delta(^{13}\text{C}[\text{Ni}(\text{CO})_3\text{L}])$  becomes smaller as  $\chi$  becomes larger, the same as observed here. If Bodner's data as per Fig. 2 is extrapolated, then  $\Delta\delta(^{13}\text{C})$  crosses 0 at  $\chi = 43$ , which is the  $\chi$  value (within error) found for CO. Another way of noting this difference is to examine the  $\chi$  value predicted for CO from the disubstituted correlations (eq. 2, 4). For nickel, a value of 42.8 is obtained which agrees well with the values already seen for CO. For Fe, however,  $\chi = 29$  which is very different from that expected.

The geometries of these complexes must be considered in any attempt to understand the effects observed. It has been well established by IR [22] and X-ray crystallography [24–30] that an axial carbonyl of the parent trigonal bipyramidal pentacarbonyliron is replaced on monosubstitution. Both axial carbonyls are replaced upon disubstitution. In the octahedral  $\text{W}(\text{CO})_5\text{L}$  complexes, two things which bear upon this discussion have been noted. First the *trans* carbonyls show a poorer correlation than the *cis* carbonyls, and secondly the *trans* carbonyls are always shifted to lower field than the *cis* carbonyls [5,9]. One might postulate that selective replacement of the *trans* carbonyl could explain the trend we observe in carbon-13 shifts. In order for this to explain these results, the effect on the *trans* carbonyl must be very much larger than that on the *cis* carbonyls. For the sake of illustration, assume that the effect of L on the  $\delta(^{13}\text{C})$  of the *cis* carbonyls in  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  would be a shift of 1 ppm per L, that the effect on the *trans* CO is  $x$  ppm, and that the effect upon successive substitution is additive. The chemical shift of CO's in  $\text{Fe}(\text{CO})_3\text{L}_2$  will be 211.5 ppm. The average chemical shift of the carbonyls in  $\text{Fe}(\text{CO})_4\text{L}$  will then lie to low field of that of  $\text{Fe}(\text{CO})_3\text{L}_2$  when  $x < 5$  ppm and to high field when  $x > 5$  ppm. While the *trans* CO's are shifted to lower field than the *cis* carbonyls, in the  $\text{W}(\text{CO})_5\text{L}$  species the effect is never so large as five times that of the *cis* CO's. Furthermore, for this to be consistent with the experimental observations, the relative ratio of the effect on *trans* to *cis* ligands would have to be larger for the ligands with higher  $\chi$  (better acceptors—poorer donors) which is opposite the trend observed for  $\text{W}(\text{CO})_5\text{L}$ . Put more succinctly, a plot as in Fig. 2 would be predicted to have a slope of opposite sign to that observed. Also, this does not explain why shifts high field of  $\text{Fe}(\text{CO})_5$  should be observed. For these reasons, we believe that such a simple explanation as the effect of replacing a *trans*-CO rather than a *cis*-CO is insufficient. One problem in making a definite statement concerning this effect is that the  $\text{Fe}(\text{CO})_4\text{L}$  species are all highly fluxional and the relative effects on the *cis* and *trans* carbonyls have not been separated. In addition, the *trans*- $\text{Cr}(\text{CO})_4\text{L}_2$  species might be expected to show behavior similar to the iron system but observations are normal there, e.g.  $\text{Cr}(\text{CO})_6$  (212.5 ppm)  $\rightarrow$   $\text{Cr}(\text{CO})_5\text{P}(\text{OPh})_3$  (ave. 214.3 ppm)  $\rightarrow$  *trans*- $\text{Cr}(\text{CO})_4[\text{P}(\text{OPh})_3]_2$  (216.6 ppm). In the tetrahedral nickel complexes, the carbonyls are all equivalent by symmetry even with successive substitution and no geometrical effect as described above is possible.

The available structural data have been examined to see if there is any unusual bonding to which we may ascribe our chemical shift trends. Data are available for  $\text{Fe}(\text{CO})_4\text{L}$  ( $\text{L} = \text{P}(\text{t-Bu})_3$  [24],  $\text{PPh}_2\text{H}$  [25],  $\eta'$ -diphos [26],  $\text{PPh}_3$  [27],  $\text{PPh}_2\text{-C}=\text{C}(\text{AsMe}_2)\text{CF}_2\text{CF}_2$  [28] and  $\text{PFN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}$  [29]) and  $\text{Fe}(\text{CO})_3[\text{P}(\text{OMe})_3]_2$  [30]. The variations in M–C and C–O bond lengths within the  $\text{Fe}(\text{CO})_4\text{L}$  series

indicate no obvious trends. The only significant changes seen are for  $L = P(t-Bu)_3$  where *trans*-Fe-C is short as expected for the best donor-poorest acceptor phosphine in the series. Unfortunately, only one disubstituted structure has been reported, and, while the Fe-C distances seem shorter than expected (comparable to *trans*-Fe-C in  $Fe(CO)_4P(t-Bu)_3$ ), there are no values available for comparison so further comments cannot be made.

The carbon-13 spectra of a number of substituted iron carbonyls have been mentioned in the literature [1] but we have been hesitant to include these in our discussion as the conditions under which they were measured may be significantly different from ours and may lead to erroneous conclusions. For example, values differing by a few ppm have been reported for  $Fe(CO)_5$  and such differences could make a correlation such as ours meaningless. Often the conditions and instrumentation are not mentioned, although data obtained from a consistent source shows trends similar to ours. Thus the series  $Fe(CO)_4(PR_xR'_{3-x})$  ( $R = Et, R' = Ph$ ) shows a good correlation to Tolman  $\chi$  values but these points define a line slightly different from ours [1].

The effects involved in determining the chemical shift of metal bound carbonyls are complex, and the effect observed is a subtle combination of many factors which cannot be easily disentangled. The  $\sigma$  donor and  $\pi$  acceptor properties of the phosphines used will each have their own effects on the overall electronic structure of the complex. These influences will change the positioning of the metal *d* orbitals with respect to both the  $\sigma$  and  $\pi$  system of the bound C-O and the totality will give rise to the carbon chemical shifts observed. It may be significant that the first ionization potential of Fe is higher than that for either Cr or Ni whose  $\delta(^{13}C)$  trends are normal, and this may be related to some influence on the M-L bonding that would give rise to our observed trends. One thing that can be said with a reasonable degree of certainty is that whatever is affecting  $\delta(^{13}C)$  is also affecting related C-O parameters and this is the source of the good correlations between these observables. This work simply serves to reinforce the idea that those relationships are not simple and probably represent a subtle balancing of  $\sigma$  donor and  $\pi$  acceptor effects of L on the complexes.

*The mononuclear iron hydrides.* The carbon-13 NMR spectra were obtained for  $[HFe(CO)_4]^-$  and  $H_2Fe(CO)_4$  in order to give some empirical idea of what charge effects might be in the iron system. As expected,  $[HFe(CO)_4]^-$  shows a low field signal (220.8 ppm) for the average carbonyl chemical shift. As in  $Fe(CO)_4L$  ( $L =$  phosphine or phosphite) the monohydride is fluxional under the conditions studied. This fits well with the trends observed for better donating ligands; the effect of hydride is simpler since it has no  $\pi$  bonding capabilities to mitigate electron density build-up on the metal due to charge. Similar chemical shifts have been noted for other mono-anionic iron carbonyls:  $[Fe(CO)_4Me]^-$  (223.0 ppm);  $[Fe(CO)_4C(O)Me]^-$  (220.5 ppm) [31]. The observation that  $\delta^{13}C$  for the acetyl complex is slightly higher field of that of the methyl analogue might be due to a small contribution from the former's oxycarbene resonance structure which would tend to remove charge from iron and localize it on the acetyl oxygen. In  $H_2Fe(CO)_4$  the shift is to high field (203.2 ppm) of  $Fe(CO)_5$  and may indicate substantial positive charge at iron. This is supported by comparison to  $\delta^{13}C$  for  $Fe(CO)_4I_2$  (201.5 ppm average) [11] and observation that the CO stretching frequencies are consistent with this analysis [31]. Similar trends are seen for Ru  $[Ru(CO)_5, 200.4 ppm [33];$

$\text{H}_2\text{Ru}(\text{CO})_4$ , 191.5 ppm average [11];  $\text{Ru}(\text{CO})_4\text{I}_2$ , 178.0 ppm average [11]] and Os [ $\text{Os}(\text{CO})_5$ , 182.6 ppm [32,11];  $\text{H}_2\text{Os}(\text{CO})_4$ , 172.6 ppm average [11];  $\text{Os}(\text{CO})_4\text{I}_2$ , 157.8 ppm average [11]]. Bodner has seen correlations with charge for the isoelectronic series [ $\text{CpCr}(\text{CO})_3$ ]<sup>-</sup> (246.7 ppm),  $\text{CpMn}(\text{CO})_3$  (225.1 ppm) and [ $\text{CpFe}(\text{CO})_3$ ]<sup>+</sup> (202.9 ppm) as well as [ $\text{V}(\text{CO})_6$ ]<sup>-</sup> (225.7 ppm) and  $\text{Cr}(\text{CO})_6$  (212.5 ppm) [4]. In general the charge effects seem to be larger than the more indirect effects observed in the substituted species.

*Fluctuality of  $\text{H}_2\text{Fe}(\text{CO})_4$ .* The high fluctuality of dihydridotetracarbonyliron [11] has now been resolved as seen in Fig. 3 and 4.

An activation energy of 8.1 kcal/mol is estimated for this process which is the lowest yet measured for a fluctional octahedral system. Values in excess of 11 kcal/mol have been reported for dihydridotetrakisphosphineiron complexes [17]. The low field resonance in the <sup>1</sup>H coupled spectrum shows the expected triplet for coupling to two equivalent hydrides and is therefore assigned to the axial carbonyls. The coupling of the equatorial CO's is not resolved under these conditions. The chemical shift assignments are consistent with the inductive effects observed for *trans*-carbonyls in  $\text{W}(\text{CO})_5\text{L}$  species as discussed earlier. Here the two hydrogens accept electron density from the metal which should promote shifts to higher field. The largest high field shift is experienced by the carbonyls *trans* to the hydrides. The spectrum is therefore in agreement with the gas phase structure found by electron diffraction [34]. The large distortion of the carbonyl ligands observed has been noted as being consistent with the high degree of fluctuality observed [11].

## Conclusions

The chemical shifts of the substituted iron carbonyls show good correlation within the  $\text{Fe}(\text{CO})_3\text{L}_2$  and  $\text{Fe}(\text{CO})_4\text{L}$  series with the donor acceptor properties of L. The chemical shift trend on comparing  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$ , however, is anomalous showing high field shifts for good acceptor-poor donor ligands. This effect, however, is still well correlated to the donor-acceptor properties of L and indicates that while the relationship exists it is not simple or easily understood. Charge effects are as predicted, showing shifts to low field for increased charge at iron.

## Acknowledgments

We wish to acknowledge the financial support of The Robert A. Welch Foundation, the American Chemical Society Petroleum Research Fund and Rice University. Randall Lee also acknowledges The Welch Foundation for an undergraduate fellowship. The high field NMR spectra were obtained at the University of Illinois NSF Regional NMR Facility (Nicolet NT360) or at the NSF Regional NMR Facility at the California Institute of Technology. The Cal Tech facility provided some travel support for this work. We also wish to thank Professor John Bercaw for allowing us to prepare the sample of  $\text{H}_2\text{Fe}(\text{CO})_4$  in his laboratories. We are also grateful for helpful discussions with Professors Thomas Albright and Richard Fenske.

## References

- 1 B.E. Mann and B.F. Taylor, (Eds.), <sup>13</sup>C NMR Data for Organometallic Compounds, Academic Press, New York, 1981; G.M. Bodner, *Inorg. Chem.*, 13 (1974) 2563.
- 2 G.M. Bodner, *Inorg. Chem.*, 14 (1975) 1932.
- 3 (a) G.M. Bodner and L.J. Todd, *Inorg. Chem.*, 13 (1974) 1335; (b) G.M. Bodner, C. Gagnon and D.N. Whitten, *J. Organomet. Chem.*, 243 (1983) 305.
- 4 O.A. Gansow, B.Y. Kimura, G.R. Dobson and R.A. Brown, *J. Am. Chem. Soc.*, 93 (1971) 5922.
- 5 P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, *J. Chem. Soc. Dalton Trans.*, (1973) 1027.
- 6 G.M. Bodner, S.B. Kahl, K. Bock, B.N. Storhoff, J.E. Waller and L.J. Todd, *Inorg. Chem.*, 12 (1973) 1071.
- 7 B.E. Mann, *J. Chem. Soc. Dalton Trans.*, (1973) 2012.
- 8 W. Buchner and W.A. Schenk, *Inorg. Chem.*, 23 (1984) 132.
- 9 G.M. Gray and C.S. Kraihanzel, *J. Organomet. Chem.*, 241 (1983) 201.
- 10 O.A. Gansow, D.A. Schexnayder and B.Y. Kimura, *J. Am. Chem. Soc.*, 94 (1972) 3406.
- 11 L. Vancea and W.A.G. Graham, *J. Organomet. Chem.*, 134 (1977) 219.
- 12 D.L. Lichtenberger and T.L. Brown, *J. Am. Chem. Soc.*, 99 (1977) 8187.
- 13 J.S. Bradley, private communication.
- 14 (a) W. Strohmeier and F.-J. Müller, *Chem. Ber.*, 102 (1969) 3613; (b) S.B. Butts and D.F. Shriver, *J. Organomet. Chem.*, 169 (1979) 191; (c) A.F. Clifford and A.K. Mukherjee, *Inorg. Chem.*, 2 (1963) 151; (d) H.L. Conder and M.Y. Darensbourg, *J. Organomet. Chem.*, 67 (1974) 93.
- 15 C.A. Tolman, *J. Am. Chem. Soc.*, 92 (1970) 2953.
- 16 (a) G. Binsch and H. Kessler, *Angew. Chem. Int. Ed. Engl.*, 19 (1980) 411; (b) G. Binsch, in L.M. Jackman and F.A. Cotton (Eds.), *Dynamic Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York (1975).
- 17 P. Meakin, E.L. Muettterties and J.P. Jesson, *J. Am. Chem. Soc.*, 95 (1973) 75.
- 18 H.J. Plastas, J.M. Stewart and S.O. Grim, *J. Am. Chem. Soc.*, 91 (1969) 4326.
- 19 M. Karplus and J.A. Pople, *J. Chem. Phys.*, 38 (1963) 2803.
- 20 W. Buchner and W.A. Schenk, *J. Magn. Reson.*, 48 (1982) 148.
- 21 R.F. Fenske, *The Interpretation of Carbon-13 NMR Chemical Shifts and Their Correlation with the Reaction Chemistry of Organometallic Carbenes, Carbonyls and Related Species*, in B.L. Shapiro (Ed.), *Organometallic Compounds, Proceedings of the First Symposium of the Industry-University Cooperative Program of the Department of Chemistry, Texas A and M University, Texas A and M Press*, 1983.
- 22 G.C. Levy, R.L. Lichter and G.L. Nelson, *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, John Wiley and Sons, New York, 1980.
- 23 (a) M. Bigorgne, *J. Organomet. Chem.*, 24 (1970) 211; (b) F.A. Cotton and Parrish, *J. Chem. Soc.*, (1960) 1440; (c) D.J. Darensbourg, H.H. Nelson, III and C.L. Hyde, *Inorg. Chem.*, 13 (1974) 2135.
- 24 J. Pickardt, L. Rosch and H. Schumann, *J. Organomet. Chem.*, 107 (1976) 241.
- 25 B.T. Kilbourn, U.A. Raeburn and D.T. Thompson, *J. Chem. Soc. A*, (1969) 1906.
- 26 R.L. Keiter, A.L. Rheingold, J.J. Hamerski and C.K. Castle, *Inorg. Chem.*, 2 (1983) 1635.
- 27 P.E. Riley and R.E. Davis, *Inorg. Chem.*, 19 (1980) 159.
- 28 F.W.B. Einstein and R.D.G. Jones, *J. Chem. Soc. Dalton Trans.*, (1972) 442.
- 29 D.W. Bennett, R.J. Neustadt, R.W. Parry and F.W. Cagle, *Acta Cryst. B.*, 34 (1978) 3362.
- 30 D. Ginderow, *Acta Cryst. B*, 30 (1974) 2798.
- 31 J.P. Collman, R.K. Rothrock, R.G. Finke and F. Rose-Munch, *J. Am. Chem. Soc.*, 99 (1977) 7381.
- 32 (a) K. Farmery and M. Kilner, *J. Chem. Soc. A*, (1979) 634; (b) C.C. Barraclough, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, (1961) 2582.
- 33 P. Rushman, G.N. Van Buuren, M. Shiralian and R.R. Pomeroy, *Organometallics*, 2 (1983) 693.
- 34 E.A. McNeil and F.R. Scholor, *J. Am. Chem. Soc.*, 99 (1977) 624.