# Ligand-variation Studies on the Mössbauer Effect in Low-valency Iron Organometallic Complexes: The $LFe(CO)_4$ and $L_2Fe(CO)_3$ Series

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Room-temperature Mössbauer parameters have been measured for seven $LFe(CO)_4$ compounds and fifteen complexes of the type $L_2Fe(CO)_3$ where L is an organophosphine or similar ligand. The trend in isomer shift values has been interpreted in terms of a dominant $\sigma$-interaction synergistically buttressed by $\pi$-bonding. A quasilinear correlation ($R$ = 0·92) has been found between $\delta$ and $|\Delta E_Q|$.

In recent years the Mössbauer effect has found increasing use as a technique for the structural characterisation of organometallic iron complexes.[1] For this reason it is rather surprising that there has been no extensive systematic investigation of the role of the ligand in determining the Mössbauer parameters for mononuclear $Fe^0$ complexes with unidentate ligands. We here present the initial results of such a study.

The compounds chosen for investigation were of the type $LFe(CO)_4$ and $L_2Fe(CO)_3$ where L is an organophosphine or similar unidentate ligand. The i.r. spectra of these complexes are consistent with their having $C_{3v}$ and $D_{3h}$ symmetries respectively—both series of compound being derived from the trigonal-bipyramidal[2] $Fe(CO)_5$ molecule by successive replacement of apical carbonyl groups. This geometrical arrangement has been confirmed for such compounds of the class as have been subjected to detailed crystallographic investigation.[3] The Mössbauer spectra should therefore be unperturbed by *gross* changes in geometry.

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Variations in isomer shift (δ) and quadrupole splitting ($|\Delta E_q|$) may then be interpreted in terms of changes in the interactions of the ligand σ-donor and π-acceptor orbitals with the 3*d*, 4*s*, and 4*p* orbitals of the $Fe^0$ valence shell. The data here reported extends our knowledge of the mechanism of this interaction.

Seven $LFe(CO)_4$ compounds and fifteen complexes of the type $L_2Fe(CO)_3$ have been studied. The Mössbauer parameters are summarised in Table 1 and the Figure.

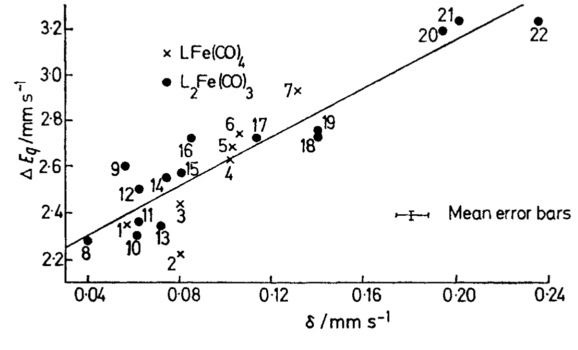
TABLE 1

Mössbauer parameters [a] for $LFe(CO)_4$ complexes

| No. | Compound | Isomer shift | Quadrupole splitting |
|---|---|---|---|
| (1) | $(MTPB)Fe(CO)_4$ | 0·057 ± 0·005 | 2·35 ± 0·010 |
| (2) | $(Me_2N)_3PFe(CO)_4$ | 0·080 ± 0·008 | 2·22 ± 0·017 |
| (3) | $(Ph_3P)Fe(CO)_4$ | 0·080 ± 0·005 | 2·44 ± 0·011 |
| (4) | $(Ph_3Sb)Fe(CO)_4$ | 0·102 ± 0·010 | 2·63 ± 0·022 |
| (5) | $(Ph_3As)Fe(CO)_4$ | 0·103 ± 0·005 | 2·68 ± 0·022 |
| (6) | $(o\text{-}MeC_6H_4)_3PFe(CO)_4$ | 0·106 ± 0·006 | 2·74 ± 0·016 |
| (7) | $(o\text{-}MeC_6H_4)_3AsFe(CO)_4$ | 0·131 ± 0·005 | 2·93 ± 0·016 |
| | Mössbauer parameters [a] for $L_2Fe(CO)_3$ complexes | | |
| (8) | $\{(MeO)_3P\}_2Fe(CO)_3$ | 0·039 ± 0·007 | 2·28 ± 0·014 |
| (9) | $\{(PhO)_3P\}_2Fe(CO)_3$ | 0·056 ± 0·009 | 2·60 ± 0·019 |
| (10) | $\{(Me_2N)_3P\}Fe(CO)_3$ | 0·061 ± 0·007 | 2·30 ± 0·013 |
| (11) | $(Ph_2POMe)_2Fe(CO)_3$ | 0·062 ± 0·005 | 2·36 ± 0·01 |
| (12) | $(Ph_2POPh)_2Fe(CO)_3$ | 0·062 ± 0·006 | 2·50 ± 0·07 |
| (13) | $(MTPB)_2Fe(CO)_3$ | 0·072 ± 0·004 | 2·34 ± 0·008 |
| (14) | $(Ph_2PMe)_2Fe(CO)_3$ | 0·074 ± 0·008 | 2·55 ± 0·016 |
| (15) | $(Ph_2PH)_2Fe(CO)_3$ | 0·081 ± 0·005 | 2·57 ± 0·010 |
| (16) | $\{(p\text{-}FC_6H_4)_3P\}Fe(CO)_3$ | 0·085 ± 0·006 | 2·72 ± 0·012 |
| (17) | $(Ph_3P)Fe(CO)_3$ | 0·114 ± 0·008 | 2·71 ± 0·017 |
| (18) | $(Ph_2PC_6H_{11})_2Fe(CO)_3$ | 0·140 ± 0·010 | 2·73 ± 0·020 |
| (19) | $\{(C_6H_{11})_3P\}_2Fe(CO)_3$ | 0·140 ± 0·005 | 2·75 ± 0·010 |
| (20) | $(Ph_3As)_2Fe(CO)_3$ | 0·194 ± 0·015 | 3·19 ± 0·016 |
| (21) | $(Ph_2AsMe)_2Fe(CO)_3$ | 0·210 ± 0·010 | 3·23 ± 0·020 |
| (22) | $(Ph_3Sb)_2Fe(CO)_3$ | 0·235 ± 0·011 | 3·22 ± 0·024 |

[a] Measured (mm $s^{-1}$) at room temperature and referred to sodium nitroprusside standard. Compounds are listed in order of increasing isomer shift. MTPB = 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

The isomer shift data will be considered first. Although irregularities are apparent (and these will be discussed later) it will be noted that $|\psi_{s(o)}|^2$ for the $^{57}Fe$ nucleus increases (*i.e.* decreasing δ value) in the general sequence: triaryl stibine < triarylarsine < trialkylphosphine < triarylphosphine < aminophosphine ≈ phosphite. The *s*-electron density at the $^{57}Fe$ nucleus thus increases in step with the generally accepted sequence of increasing ligand π-acceptor character. An increase in $|\psi_{s(o)}|^2$ may be due to either (*a*) an increase in the effective population of the iron 4*s* orbital consequent on an increase in L→M σ-bonding, or (*b*) a decrease in the shielding of the iron *s* orbitals by the 3*d* orbitals due to increasing involvement of the latter in M → L π-bonding. In the case of (*a*) above it should be mentioned that since σ-bonding in $Fe^0$ complexes involves orbitals of approximate $dsp^3$ character, an increase in σ-bonding will involve some augmentation of iron 3*d* electron density. By analogy with other work, however, this effect is assumed to be small.[4] A decrease in δ may thus be caused by either an increase in σ- or in π-bonding—or both.



Any interpretation of the trend in δ-values shown by our compounds depends on the model adopted to dedescribe the metal-ligand interaction. One such model assumes that the σ-donor and π-acceptor character of the complexed ligand may be expected to parallel those of the free ligand. It has been suggested that the ligand p$K_a$ value may be used as a measure of relative σ-donor ability.[5] Thus for ligands involving any one group V element the donor ability will decrease with increasing electronegativity of the groups attached to the donor atom [6]—which increase in electronegativity will have the effect of simultaneously increasing the ligand π-acceptor character.[7] Good σ-donor ligands will thus be poor π-acceptors; the converse is also true. An alternative description postulates that on complex formation the ligand σ- and π-bonding capacities are synergistically related.[8] According to this model, *in the complexed ligand*, good π-acceptors are also good σ-donors.

If we apply the former bonding description to our compounds we are forced to the conclusion that the M–L interaction is predominantly π- in nature since $|\psi_{s(o)}|^2$ is greatest for those ligands which are the most powerful π-acceptors (*i.e.* phosphites, *etc.*) and least for those ligands such as $Ph_3Sb$ which have little π-acceptor character. A dominant σ-interaction would be expected to reverse the sequence of δ-values within the group of phosphorus compounds. The position of the As and Sb compounds, *vis-à-vis* the phosphorus compounds as a group, would remain unchanged since σ-donor ability is thought to decrease in the order P > As > Sb.[9]

The concept of a dominant π-interaction is however at variance with information available from other sources. Bowen *et al.*[10] have determined the $^{121}Sb$ and $^{57}Fe$ Mössbauer parameters for $(Ph_3M)Fe(CO)_4$

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and $(Ph_3M)_2Fe(CO)_3$ (M = Sb, As, P) and argue convincingly from their data that the predominant transfer of electron density is *via* a $\sigma$-bonding mechanism. In a related study Bigorgne[11] has investigated the i.r. spectra of complexes of the type $(R_3P)_nNi(CO)_{4-n}$ and comes to the conclusion that the major metal-phosphorus interaction is $\sigma$ in nature.

Thus our conclusions and the external evidence are at variance if we adopt the convention that ligand $\sigma$-donor strength decreases with increasing $\pi$-acceptor character.

It is nonetheless possible to reconcile our data and that of Bowen[10] if the synergistic relationship[8] of ligand $\sigma$- and $\pi$-capacity is assumed. Here a dominant $\sigma$-interaction would be increasingly buttressed by a synergistic mechanism as $\pi$-bonding comes into play. Since both effects will cause a decrease in $\delta$ this mechanism would therefore lead one to predict exactly the broad trend in isomer shift values evident from our data. Conversely our data may be considered to provide additional evidence for the synergistic bonding model.

Turning now to the $|\Delta E_q|$ values we are faced with a more difficult interpretative problem. Previous workers[12] have pointed out that the inherently large contribution to the electric field gradient (e.f.g.) at the $^{57}$Fe nucleus from the nonspherically symmetric $d^8$ valence shell of $Fe^0$ makes a detailed analysis of $|\Delta E_q|$ values very difficult. In particular the point-charge approximation—which has been used with considerable success in other systems[12a,13-15]—cannot be applied here. A further problem arises from the difficulty of separating the contributions of $\sigma$- and $\pi$-interactions to the e.f.g.[12b] since both processes involve transfer of electron density into (or from) orbitals of at least partial $d$-character. For the present series of compounds we may note that the magnitude of $|\Delta E_q|$ increases as the $\pi$-acceptor ability of the ligand decreases. However, since we have at this stage no way of estimating the contribution of $\sigma$-bonding to the $|\Delta E_q|$ values it would be unwise to assume that $|\Delta E_q|$ values bear any simple relationship to ligand $\pi$-acceptor ability. It may however be mentioned that a similar dependence of $|\Delta E_q|$ on $\pi$-bonding was reported by Cullen[12b] for a series of tetrahedral $d^{10}$ Fe($-$II) compounds in which $\sigma$-bonding plays little or no part in determining the e.f.g. value.

Of greater interest is the good quasi-linear relationship between $\delta$ and $|\Delta E_q|$ ($R = 0{\cdot}92$), which is illustrated in the Figure. Linear or near-linear $\delta/|\Delta E_q|$ correlations have been encountered previously for organometallic iron complexes.[16a,17,18] Since the factors which determine isomer shift and quadrupole splitting (*i.e.* the donor and acceptor capacities of the ligands) are themselves interdependent it is hardly surprising that, in the absence of external factors such as geometric changes, $\delta$ and $|\Delta E_q|$ should be related in a systematic fashion. Just why this relationship should be linear is, however, far from clear. Of particular significance for the present work are the linear $\delta/|\Delta E_q|$ relationships reported by Collins and Pettit[16a] and Korecz and Burger.[17] The compounds involved were of the general type $LFe(CO)_4$ where L is an alkyl phosphite,[16a] aryl phosphine,[16a] alkene,[16a,17] allyl cation,[16a] or $I_2$.[16a] Both these investigations showed that a plot of $\delta$ *vs.* $|\Delta E_q|$ defined a straight line of slope opposite in sign to that resulting from our data. Despite a correlation coefficient of 0·98 the data of Collins and Pettit[16a] has some ambiguous aspects. The present work confirms an earlier suggestion by Dessy and his co-workers[19] that the correlation of data for the apical[3] phosphine and phosphite derivatives with that for the equatorial[20-24] alkene complexes (an equatorial geometry also seems reasonable for the allyl compounds[25]) is 'most fortuitous'. This correlation can now be seen to be due to a coincidental intersection of the lines defined by the Mössbauer data for our compounds and those of Collins and Pettit[16a] respectively. The latter workers have interpreted the correlation of the parameters for the *cis*-octahedral $Fe(CO)_4I_2$ with the other $LFe(CO)_4$ compounds as indicating that $I_2$ is complexed to the trigonal bipyramidal $Fe(CO)_4$ fragment as a single molecular iodine unit rather than *via* two $\sigma$-bonds. This suggestion seems of questionable validity in view of the reported ease of solid-state *cis–trans* isomerisation of this compound[26] and the results of an *X*-ray crystallographic investigation[27] of the related molecule $(PH_3)_2Fe(CO)_2I_2$. From the published structural data for the latter compound a minimum iodine–iodine distance of 3·95 Å may be calculated. This is very much longer than the 2·66 Å recorded[28] for the free iodine molecule. A more recent study of the $^{129}$I Mössbauer spectrum of $Fe(CO)_4I_2$, which has been interpreted[16b] in terms of the $LFe(CO)_4$ model, would appear to be equally consistent

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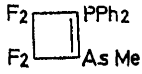
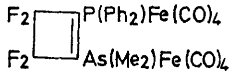
with the *cis*-octahedral structure. It seems more than likely that the correlation of $\delta$ and $|\Delta E_q|$ for $Fe(CO)_4I_2$ with the data for the other compounds is also purely coincidental. The remaining compounds involved in the Collins and Pettit [16a] and Korecz and Burger [17] correlations all involve formal equatorial substitution of the $Fe(CO)_5$ trigonal bipyramid. Even so, bearing in mind the known sensitivity of the Mössbauer effect to metal oxidation state [29] and co-ordination number [30] it is surprising that the correlation holds for such a wide variety of compounds. (For instance is the allyl ligand realistically regarded as uni- rather than bi- or tridentate? Again, it would certainly seem more logical to describe compounds of the type $[(\pi\text{-}C_3H_5)Fe(CO)_4]^+$ as derivatives of $Fe^I$ rather than $Fe^0$.) Assuming, however, that it is meaningful to describe all these compounds as belonging to the $LFe(CO)_4$ class—and although we are unable at this stage of our investigation to comment upon the significance of the linear relationship itself—we may extract some information from the difference in sign between the slopes of the two lines. Collins and Pettit [16a] have reasonably interpreted their data in terms of dominant $\sigma$-bonding from the unsaturated ligand to iron and noted that for their compounds, as for ours, the magnitude of $|\Delta E_q|$ decreases with increasing $\pi$-acceptor character of the ligand L. (We prefer to reject the alternative interpretation of Korecz and Burger [17] which neglects the contribution of $\sigma$-bonding to the isomer shift value and involves an oversimplified interpretation of changes in quadrupole splitting.) The difference in sign of the slope then implies that while the L–M interaction in our compounds is synergistic in nature, bonding in the unsaturated organic ligands investigated by Collins and Pettit [16a] or Korecz and Burger [17] is non-synergistic. It is not clear whether this difference in bonding is characteristic of the two classes of ligands themselves or reflects the differing bonding capacities of the apical and equatorial $Fe(CO)_4$ fragments. Work is currently in progress with equatorial $LFe(CO)_4$ compounds involving unambiguously unidentate ligands which we hope will clarify this point.

For the compounds under study, as mentioned earlier, the broad trend observed is for isomer shift to increase with decreasing ligand $\pi$-acceptor character. This trend, however, is not obeyed in detail—among the more obvious anomalies being the unexpectedly low $\delta$-value for $(Ph_2PMe)_2Fe(CO)_3$ and the coincidence of the values for $(Ph_2PC_6H_{11})_2Fe(CO)_3$ and $\{(C_6H_{11})_3P\}_2Fe(CO)_3$. It is tempting to suggest that these anomalies may be due to slight deviations of the structures of the compounds from ideal $C_{3v}$ and $D_{3h}$ symmetries due to internal asymmetries in the ligands themselves. A similar explanation has been advanced to account for anomalies in the i.r. spectra of $L_2Fe(CO)_3$ complexes.[31] Of interest in this regard are the results obtained for the complexes $(o\text{-}MeC_6H_4)_3MFe(CO)_4$ (M = P, As). The differences in isomer shift between these complexes and the analogous $(Ph_3M)Fe(CO)_4$ compounds seems unlikely to be due simply to the electronic effect of the *o*-methyl groups. We prefer to regard it as being due, at least in part, to a geometric effect of the type mentioned above. That the iron atom in these complexes interacts sterically with the *o*-Me groups is not to be disputed since, unlike the latter, the *o*-tolyl compounds will not react further with the phosphine to give $L_2Fe(CO)_3$ complexes. Steric hindrance is also reflected in the chemistry of these compounds.[32] Further evidence for the importance of steric effects is provided by the recent work of Cullen and his co-workers [33] on complexes derived from the potentially trifunctional ligand 1-(diphenylphosphino)-2-(dimethylarsino)-3,3,4,4-tetrafluorocyclobut-1-ene [$f_4$AsP, (I)]. The ligand $f_4$AsP forms $LFe(CO)_4$ and $L_2Fe(CO)_3$ derivatives in which co-ordination is *via* the diphenyl phosphino-group. Mössbauer data for both compounds [33] correlates fairly well with the data reported here. In contrast, while $\delta$ and $|\Delta E_q|$ for the arsenic-bound iron atom in (II) defines a point near our line that defined by $\delta$ and $|\Delta E_q|$ for the phosphorous-bound iron nucleus (0·13, 2·12 mm s$^{-1}$) deviates very considerably. Here steric crowding due to the bulky $Fe(CO)_4$ units is to be expected and the effect is evidently felt most by the nucleus bonded to the phosphorus atom.



(I)



(II)

In order to probe the consequences of asymmetry at the ligand donor atom we are currently carrying out accurate low-temperature studies on such restricted series as $\{(Ph)_nP(OR)_{3-n}\}_2Fe(CO)_3$. This study should also reveal whether the concept of ' partial ' $\delta$ and $|\Delta E_q|$ values can be applied to compounds of this type.

## EXPERIMENTAL

Mössbauer spectra were determined using a commercial drive unit and transducer, TMC model 305/306 in conjunction with a TMC Gammascope II multichannel analyser. The source was $^{57}$Co in Pd and was of 5 mCi nominal strength. Absorbers were made up in Al foil and were of ~50 mg cm$^{-2}$ in thickness. All spectra were run at room temperature. A non-linear curve-fitting programme was used and the data processed on an IBM 1130 computer. All data are referred to the spectrum of sodium nitroprusside at room temperature as standard.

*Synthesis of the Iron Complexes* $LFe(CO)_4$ *and* $L_2Fe(CO)_3$.—Most of the compounds used in this study were prepared

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by established literature procedures.[34] For those compounds which are new or for which explicit experimental details were not available the following procedure was used.

A mixture of the ligand (24—30 mmol) and $Fe_3(CO)_{12}$ (4 mmol) in dry benzene (120 ml) was refluxed with stirring in a nitrogen atmosphere for 4—8 h. The reaction mixture was cooled, filtered, and the solvent removed *in vacuo*. Generally the crude oily material thus obtained was solidified by treatment with methanol or pentane. The product was recrystallized several times from $CH_2Cl_2$–hexane, $CH_2Cl_2$–methanol, or benzene–hexane. Yields were in the range 25—50%.

Analytical data for compounds prepared in this fashion are collected in Table 2.

TABLE 2

Microanalytical data

| Complex | Found (%) | | Calc. (%) | | M.p. |
|---|---|---|---|---|---|
| | C | H | C | H | ($t$/°C) |
| $(Ph_2POMe)_2Fe(CO)_3$ [a] | 59·3 | 4·7 | 59·8 | 4·5 | 141—143 |
| $(Ph_2POPh)_2Fe(CO)_3$ [b] | 67·85 | 4·25 | 67·25 | 4·35 | >220 (d.) |
| $(Ph_2PMe)_2Fe(CO)_3$ [b] | 64·5 | 4·95 | 64·45 | 4·85 | >165 (d.) |
| $(Ph_2PC_6H_{11})_2Fe(CO)_3$ [a] | 70·1 | 6·4 | 69·25 | 6·25 | >200 (d.) |
| $(o\text{-}MeC_6H_4)_3PFe(CO)_4$ [a] | 63·05 | 4·15 | 63·55 | 4·5 | >180 (d.) |
| $(Ph_2AsMe)_2Fe(CO)_3$ [a] | 55·25 | 4·3 | 55·4 | 4·15 | 150 |
| $(o\text{-}MeC_6H_4)_3AsFe(CO)_4$ [a] | 57·5 | 3·8 | 58·15 | 4·1 | >160 (d.) |

Recrystallised from: [a] $CH_2Cl_2$–methanol. [b] $CH_2Cl_2$–hexane.

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