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Mössbauer spectroscopy of (benzylideneacetone)Fe(CO)$_2$L complexes with L = CO, phosphites and phosphines. An analysis of ligand effects

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Abstract

The (benzylideneacetone)Fe(CO)$_2$L complexes, with L = CO, PPh$_3$, PMePh$_2$, PMe$_2$Ph, PEt$_3$, PCy$_3$, P(OPh)$_3$, P(OMe)$_3$, P(OEt)$_3$ and P(O^{i}Pr)$_3$ have been studied by Mössbauer spectroscopy. The spectra are compatible with a distorted octahedral geometry with the iron atom at the center. The isomer shifts δ and quadrupole splittings ΔE_q are correlated with the Giering electronic parameter χ_d of the phosphines and phosphites and with the ^{13}C NMR complex shifts ΔC_4 of coordinated benzylideneacetone. The results are discussed in terms of the stereoelectronic effects of the ligand L. Correlation between isomer shifts and quadrupole splittings indicates that d_π–L_{π^*} back bonding is predominant in the complexes with L = CO and phosphites and negligible in the complexes with L = phosphines.

Key words: Iron; Carbonyl; Mössbauer spectroscopy; Phosphite; Phosphine; π-Bonding

1. Introduction

Owing to the importance of phosphorus(III) in organometallic chemistry and catalysis [1], an evaluation of the stereoelectronic properties of complexes containing such ligands is of great interest as is evident from the impressive number of papers dealing with this subject [2]. A very important step towards quantification of electronic and steric contributions was the introduction of Tolman's electronic parameter (χ) and the cone angle (θ) of phosphines and phosphites [3].

Concerning the electronic parameters, separation into σ and π components has been attempted. However, this is complicated by the requirement of the concept of synergic bonding that the electronic factors be mutually dependent [4]. The χ values, derived from infrared data for Ni(CO)$_3$L complexes, are thought to reflect the collective electron donor/acceptor properties of the ligands [3]. Separation of phosphorus(III) ligands into two distinct groups, identified as pure σ-donor ligands and σ-donor/π-acceptor ligands, was accomplished by Giering *et al.* [2] for the complexes (η-Cp)FeL(CO)Me and (η-Cp')Fe(CO)COMe (η-Cp' = MeC$_5$H$_5$) by correlating the terminal stretching frequencies ν(CO) with formal reduction potentials E^0. A better parameter for measuring σ-donicity, χ_d, which is presumably free of π influence, was also proposed [5]. However, since the earliest studies [6], it seems to have been clear that phosphorus(III) ligands cannot be characterized by definite donor/acceptor capacities as these capacities depend to a great extent on the overall electron distribution of the complexes to which they are bonded.

We have previously described the structural and electronic properties of a series of (bda)Fe(CO)$_2$L complexes (bda = benzylideneacetone; L = phosphines and phosphites) obtained from ^{13}C NMR data [7] and

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molecular orbital calculations [8]. We suggested that in these complexes the σ-donation of the phosphites is more pronounced than that of the phosphines in spite of the latter having higher Lewis basicities. This is interpreted as being a consequence of the d_π–L_{π^*} back bonding from iron to phosphorus in the phosphite complexes, producing a synergic increase in σ-donation.

Here we discuss Mössbauer spectroscopic studies of almost the same series of complexes, in an attempt to detect the changes caused in the electronic environment of the iron atom arising from the different phosphorus(III) ligands. In a recent paper [9] we used this technique to study electronic effects in (sorbic acid)Fe(CO)$_2$L complexes with L = CO, P(OPh)$_3$, PPh$_3$ and PEt$_3$.

2. Experimental details

The (bda) Fe(CO)$_2$L complexes with L = CO, P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$, PPh$_3$, PMePh$_2$, PMe$_2$Ph, PEt$_3$ and PCy$_3$ were prepared and purified as described previously [7,10,11]. The new complex (bda)Fe(CO)$_2$P(O^{i}Pr)$_3$ was prepared by thermal substitution of one CO group per molecule of (bda)Fe(CO)$_3$ by P(O^{i}Pr)$_3$. The tricarbonyl complex (292 mg, 1.02 mmol) and triisopropylphosphite (207 mg, 1.00 mmol) were dissolved in benzene (30 ml) and the solution was heated under reflux for 15 min. Further triisopropylphosphite (0.025 mmol) in benzene solution (2 ml) was then added, drop by drop, until all bands of the starting materials had vanished from the infrared spectrum of the reaction mixture [12]. The solvent was removed under vacuum, and the resulting material was chromatographed on silica gel. Elution with 10% ethyl ether–petroleum ether (40–60°C) gave, after recrystallization, the product as an orange powder [264 mg, 52% yield based on (bda)Fe(CO)$_3$]. Anal. Calcd. for $C_{21}H_{31}FeO_6P$: C, 54.1; H,6.65; P, 6.65. Found: C, 52.7; H, 6.49; P 6.70% ^{13}C NMR (benzene): δ 21.2 (C$_1$); δ 142.0 (C$_2$); δ 78.3 (C$_3$); δ 57.1 (C$_4$); δ 208.5, 213.5 (CO). IR: ν(CO) (cyclohexane) 2000, 1947 cm^{-1}.

The Mössbauer spectra were recorded (1024 channels) with a Hewlett-Packard multichannel analyzer with a drive unit which imparts a sinusoidal motion to the ^{57}Co source. The data were collected at room temperature and at 4.2 K — the source and absorber were kept at the same temperature. Data folding and linearization were carried out with an IBM 370/175 computer. The isomer shifts were referred to a ^{57}Co/Rh source. A superconductor solenoid (Oxford Instruments) was used to determine the Mössbauer spectra in a longitudinal external magnetic field. The absorber is microcrystalline with density of natural iron of 10 mg cm^{-2}.

3. Results and discussion

3.1. Mössbauer data

The isomer shifts δ and the quadrupole splittings ΔE_q obtained from the least-squares fitting of a pair of Lorentzian lines to the experimental data, are reported in Table 1. In the series of complexes studied, δ is in the range −0.144 to −0.083 mm s^{-1}, as expected for iron(0) compounds. The ΔE_q values, from 1.81 to 2.02, are consistent with the octahedral point symmetry revealed by the X-ray study of some of the compounds of this series [11].

Analyzing a series of complexes, in which a ligand is systematically changed, reveals the effect of the ligand on the chemical bond to the central iron atom. The modifications induced by the different ligands in the s-electron density at the iron nucleus, shown by changes in δ, do not make possible unequivocal assignment of σ-bonding or π-back bonding effects. Forward σ-donation and π-back donation both increase the s-electron density at the iron nucleus with a consequent decrease in the isomer shift ($\Delta R/R < 0$ for ^{57}Fe) [13]. Through σ-bonding, electron density is transferred from the ligand to appropriate iron orbitals hybridized as required by geometry that has, at least, partial s-character. The π-back donation transfers d-electron density from the iron atom to appropriate ligand molecular orbitals and consequently decreases the shielding of the 3s electrons. So, δ measures the effect of σ + π bonding on the total s-electron density at the iron nucleus and ΔE_q, which is related to the electric field gradient at the iron nucleus and involves only p or d electrons, measures the effect of σ–π bonding. Therefore, in a closely related series of compounds, it is possible to distinguish the contributions to the electri-

TABLE 1. Data for (benzylideneacetone)Fe(CO)$_2$L complexes

L	δ [a] (mm s^{-1})	ΔE_q [b] (mm s^{-1})	χ_d [c] (cm^{-1})	ΔC_4 [d] (ppm)	E_r [e] (kcal mol^{-1})
CO	−0.097	2.02	–	−81.8	7
P(OPh)$_3$	−0.109	1.96	22.05	−82.6	65
P(OMe)$_3$	−0.117	1.93	16.70	−85.0	52
P(OEt)$_3$	−0.127	1.92	15.51	−84.6	59
P(O^{i}Pr)$_3$	−0.135	1.89	12.90	−85.4	74
PPh$_3$	−0.083	1.81	13.25	−79.5	75
PCy$_3$	−0.087	1.81	1.40	−85.7	116
PMePh$_2$	−0.105	1.86	12.10	−81.7	57
PMe$_2$Ph	−0.109	1.86	10.60	−83.1	44
PEt$_3$	−0.144	1.93	6.30	−85.1	61

[a] This work. [b] This work. [c] Ref. 5. [d] $\Delta = \delta_{complex} - \delta_{BDA}$, ref.7. [e] Ref. 18.

cal field gradient, EFG, of the σ-bonding and π-back bonding, providing the sign (+ or −) of ΔE_q is known, by plotting δ *vs.* ΔE_q [14]. In this work the octahedral symmetry of the series of complexes studied is so distorted that it is not possible to define a direction of higher symmetry at the iron atom which would determine the sign of ΔE_q.

3.2. Stereoelectronic effects of the phosphorus(III) ligands on the Mössbauer parameters

The basicities of the phosphorus ligands, quantified in terms of pK_a or half-wave neutralization potentials, ΔHNP [15], have been used as a measure of the σ-donicity of these ligands towards transition metals [16]. However, these parameters are not quite appropriate since they measure the proton–phosphorus σ interactions. In bonding with transition metals the d_π–L_{π^*} back bonding to the phosphorus would produce a synergic increase in σ-donation [7]. The effect is expected to be bigger in the phosphites compared to the phosphines owing the presence of the electronegative oxygen atoms bonded to phosphorus. Extended Hückel molecular orbital calculations in model complexes [8] showed that the HOMO is more destabilized in the $Fe(CO)_2P(OH)_3$ fragment than in the $Fe(CO)_2PH_3$ fragment, reflecting the higher energy of the phosphite lone pair and implying a greater σ-donor capacity. It was also shown [5] that pK_a and ΔHNP include an effect of solvation that increases the basicity of smaller ligands. A better measure of σ-donicity is the Giering electronic parameter χ_d [5] which is not affected by solvation. The values of χ_d for the ligands studied in this work are in Table 1.

The electronic effects discussed above are clearly seen in Figs. 1 and 2 where $-\delta$ and ΔE_q respectively are plotted *vs.* χ_d. Figure 1 shows that except for PCy_3 the s-electron density at the iron nucleus in the phosphine series increases with the σ-donor capacity of the phosphorus(III) ligand, *i.e.*, $PPh_3 < PMePh_2 < PMe_2Ph < PEt_3$. The values of δ for the phosphite complexes are higher than would be expected from its χ_d values. This is a consequence of iron to phosphorus π-back bonding in the phosphites since $-\delta$ measures the effect of $\sigma + \pi$ bonding. The deviation of $-\delta$ for PCy_3 from the regular linear behaviour shown by other phosphines is *ca.* 0.090 mm s^{-1} possibly due to a steric effect associated with its exceptionally large cone angle [3]. The same explanation is given for the deviation of PCy_3 from the linear plot shown by other phosphines of $h\nu(\sigma \rightarrow \sigma^*)$ *vs.* ΔHNP, used for measuring σ-bonding interactions between the metals in $Mn_2(CO)_8L_2$ and $Co_2(CO)_6L_2$ complexes [17].

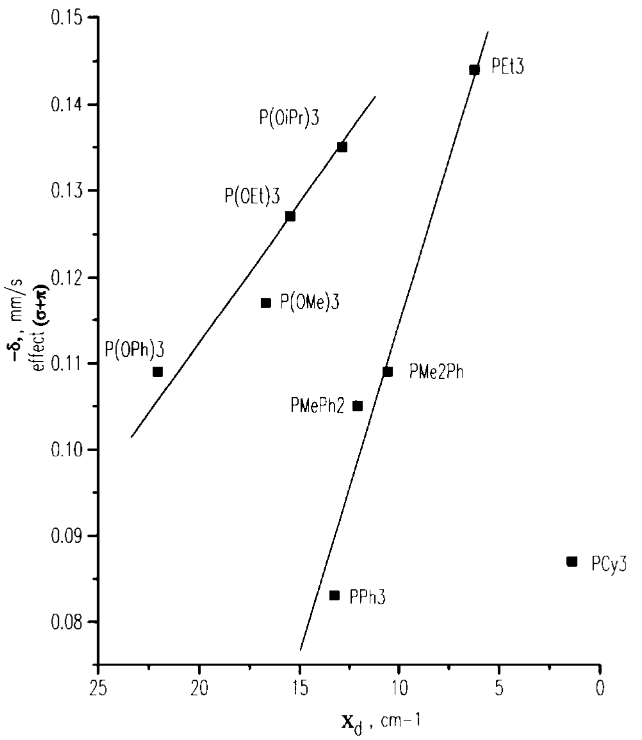


Fig. 1. Plots of isomer shifts (δ, mm s^{-1}) *vs.* electronic parameter (χ_d, cm^{-1}) for the series of (benzylideneacetone)Fe(CO)$_2$L complexes.

Giering *et al.* [5] suggested that in the complexes $L_2Mo(CO)_4$ and $L_3Mo(CO)_3$, steric congestion may prevent potential π-acid ligands from approaching close enough to form a metal–phosphorus π-bond. Brown *et al.* [18] have shown by molecular mechanics that the Cr–P bond is longer in $(CO)_5Cr(PR_3)$ complexes when PR_3 is bulky. In the complexes studied in this work the Fe–P distance may be affected by steric interaction between the ligands and the organometallic fragment. In BDAFe(CO)$_2$L with L = PEt_3 and $PPhMe_2$ the Fe–P bond distance is slightly longer in the PEt_3 complex (2.235 Å) than in the $PPhMe_2$ complex (2.228 Å) [11]. The PEt_3 ligand is more basic than $PPhMe_2$ and the Fe–P distance would be shorter if a steric effect were not in operation.

An estimation of the relative importances of steric contributions to $-\delta$ has been made using a similar approach to that of Poë and Jackson for $Mn_2(CO)_8L_2$ and $Co_2(CO)_6L_2$ complexes [17]. Here the steric effect assumed to be responsible for the deviation in $-\delta$ of *ca.* 0.090 mm s^{-1} for L = PCy_3 from the regular linear behaviour shown by other phosphines is quantified in terms of Brown's steric parameter, E_R [19], as reported in Table 1. The value of E_R for PCy_3 is 55 kcal mol^{-1} larger than that of PEt_3 and the value of E_R for PPh_3 is 14 kcal mol^{-1} larger than that of PEt_3. If the relative steric deviations are proportional to E_R, the deviation for PPh_3 will be (0.090 mm s^{-1}) × (14/55) = 0.023 mm

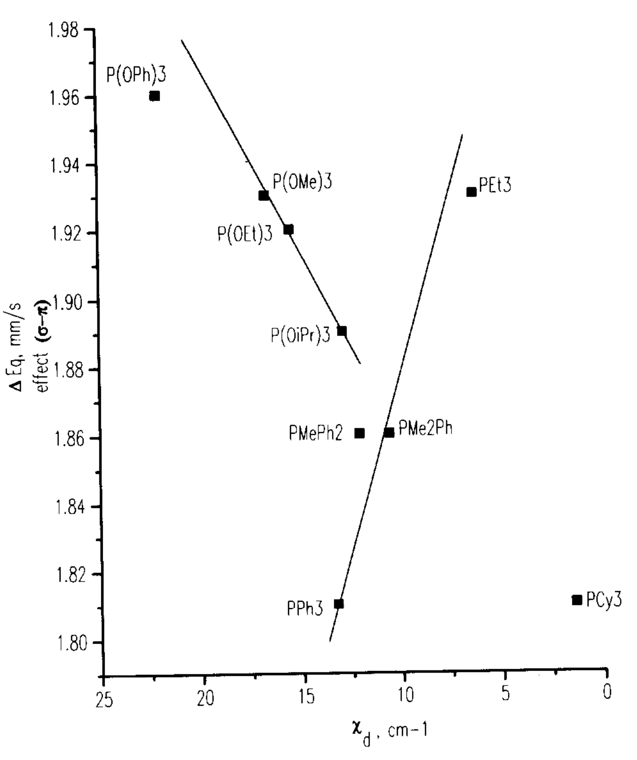


Fig. 2. Plots of quadrupole splittings (ΔE_q, mm s^{-1}) *vs.* electronic parameter (χ_d, cm^{-1}) for the series of (benzylideneacetone)Fe(CO)$_2$L complexes.

s^{-1}; *i.e.*, of the increase of 0.059 mm s^{-1} in $-\delta$ from L = PPh$_3$ to L = PEt$_3$, *ca.* 39% is due to the decreasing E_R, the remaining 0.036 mm s^{-1} being due to increasing basicity. The steric contribution of 0.023 mm s^{-1} estimated for PPh$_3$ is an upper limit since the steric effects would increase with the cone angle more sharply at large cone angles than at small ones [17]. For example, the change in steric effect from PEt$_3$ to PPh$_3$ probably is proportionally less (per unit of E_R) than that from PPh$_3$ to PCy$_3$. The influence of E_R in the s-electron density at the iron nucleus is significant for large ligands and probably reflects sensitivity of the Fe–L bond to the size of L.

The ligands P(O^{i}Pr)$_3$ and PPh$_3$ show a difference in χ_d of -0.35 and a difference in $-\delta$ of -0.052 mm s^{-1}. Accepting a similar dependence on σ basicity to that found for the phosphines, only *ca.* -0.003 mm s^{-1} or 6% of the difference in $-\delta$ can be due to this. No steric effect is expected since the difference in E_R is only 1 kcal mol^{-1} and the most reasonable hypothesis is that a π-effect is in operation. More than 90% of the difference in $-\delta$ can, therefore, be ascribed to the π-acidity of P(O^{i}Pr)$_3$.

Plots of ΔE_q *vs.* χ_d (Fig. 2) show the slope to be positive for the σ-donor phosphines but negative for the π-acid phosphites, providing a much more sensitive indication of π-acidity. We have seen that ΔE_q measures the effect of σ–π bonding and the negative slope for the phosphites indicates increasing π-bonding along the series P(O^{i}Pr)$_3$ < P(OEt)$_3$ < P(OMe)$_3$ < P(OPh)$_3$. The steric effect of the PCy$_3$ ligand is again apparent and its contribution estimated to be 40% of the difference in ΔE_q for PPh$_3$.

The relative importance of σ-bonding and π-back bonding is clearly seen in the correlation between δ and ΔE_q shown in Fig. 3, which includes the exceptional π-acid CO. Since δ and ΔE_q measure $(\sigma + \pi)$ and $(\sigma - \pi)$ bonding, respectively, this permits separation of σ and π effects. It is important to notice that the PCy$_3$ ligand lies on the correlation line and, therefore, its steric effect is not apparent.

3.3. Bonding between the BDA ligand and the Fe(CO)$_2$L moieties

Carbon-13 NMR measurements over almost the same series of complexes as that studied here suggest transmission of electronic effects from phosphorus(III) ligands to BDA [7]. The main evidence is the highly

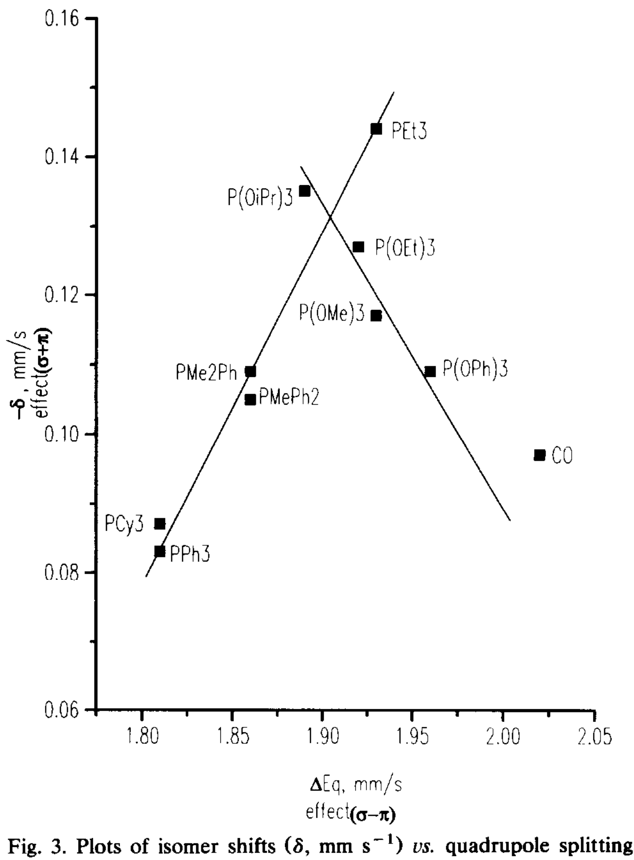
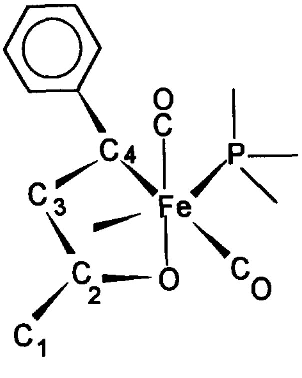


Fig. 3. Plots of isomer shifts (δ, mm s^{-1}) *vs.* quadrupole splittings (ΔE_q mm s^{-1}) for the series of (benzylideneacetone)Fe(CO)$_2$L complexes.



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negative complex shifts Δ [20] on carbons C_2, C_3 and C_4, **1**, pointing to very large upfield shifts of these carbons. Accordingly, electron density is transferred from the Fe(CO)$_2$L moiety to BDA through a π^* interaction, causing a net shielding effect on the BDA carbon atoms bonded to Fe(CO)$_2$L. A proposed bonding model [8] comprises donation of electrons from the HOMO of BDA (mainly π_1 localized on O atom) to the LUMO of the iron fragment and back-donation from the HOMO of this fragment to the LUMO of BDA (mainly π_3 localized on C_4).

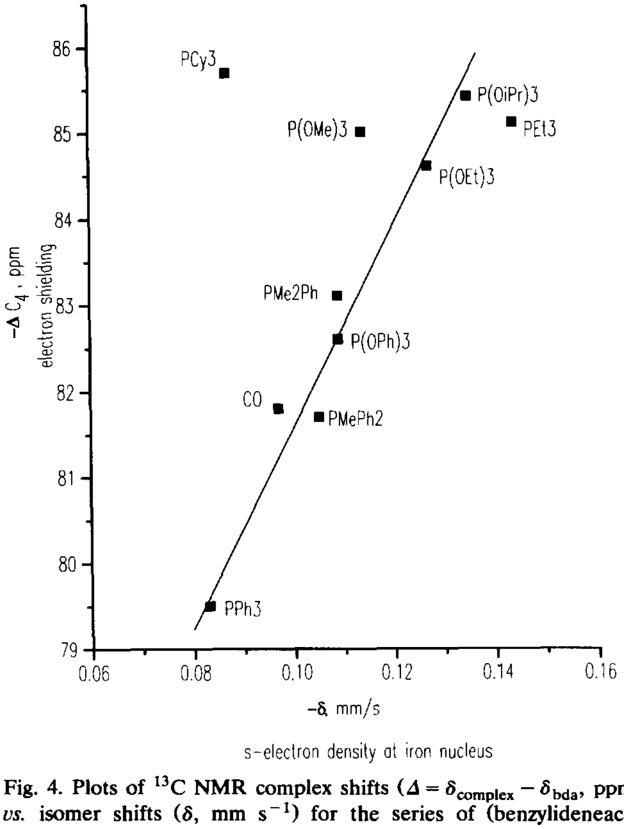

Fig. 4. Plots of ^{13}C NMR complex shifts ($\Delta = \delta_{\text{complex}} - \delta_{\text{bda}}$, ppm) *vs.* isomer shifts (δ, mm s^{-1}) for the series of (benzylideneacetone)Fe(CO)$_2$L complexes.

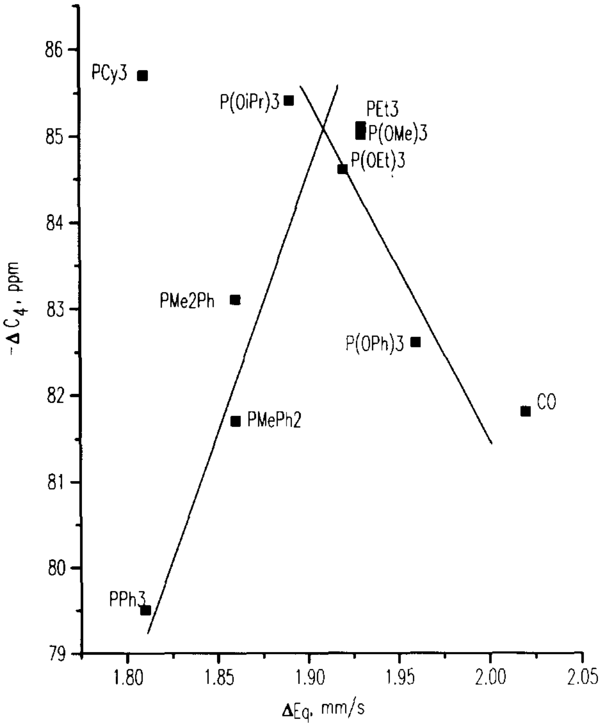

Fig. 5. Plots of ^{13}C NMR complex shifts ($\Delta = \delta_{\text{complex}} - \delta_{\text{bda}}$, ppm) *vs.* quadrupole splittings (ΔE_q, mm s^{-1}) for the series of (benzylideneacetone)Fe(CO)$_2$L complexes.

Plots of the values of $-\Delta C_4$, reported in Table 1, *vs.* $-\delta$ (Fig. 4) support the interpretation of the ^{13}C NMR results outlined above. In spite of points being scattered both σ-donors — except the bulky PCy$_3$ — and π-acids including CO lie around the same correlation line. This shows that shielding at the C_4 atom increases with increasing s-electron density at the iron nucleus ($\sigma + \pi$ effect). This also supports our theoretical prediction [8] that π-back donation from the HOMO of the Fe(CO)$_2$L fragment to the empty π_3 orbital localized mainly at the C_4 atom of BDA is stronger than σ-donation from filled π_1 and π_2 orbitals localized mainly at the O and C_2 atoms of BDA, respectively.

The competition between BDA and the π-acidic ligands for the iron dsp-electrons may be evaluated by plotting $-\Delta C_4$ *vs.* E_q (Fig. 5). The electron shielding at C_4 increases with ΔE_q (σ–π effect) in the phosphine series where iron to phosphorus π-back bonding is not significant. The contrary is observed in the phosphite series, including CO, where ΔC_4 decreases from the lesser π-acidic P(O^{i}Pr)$_3$ to the higher π-acidic P(OPh)$_3$.

References and notes

1 E.C. Alyea (ed.), *Catalytic Aspects of Metal Phosphine Complexes*, Advances in Chemistry Series 196, American Chemical Society, Washington, DC, 1982.

2 M.M. Rahaman, H.Y. Liu, K. Eriks, A. Prock and W.P. Giering, *Organometallics*, *8* (1989) 1 and references therein.

3 C.A. Tolman, *Chem. Rev.*, *77* (1977) 313.

4 J.D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole, Monteray, CA, 1985.

5 H.Y. Liu, K. Eriks. A. Prock and W. Giering, *Organometallics*, *9* (1990) 1758.

6 (a) F.A. Cotton and C.S. Kraihenzel, *J. Am. Chem. Soc.*, *84* (1962) 4432; (b) F.A. Cotton, *Inorg. Chem.*, *3* (1964) 702; (c) W.A.G. Graham, *Inorg. Chem.*, *7* (1968) 315; (d) M. Bigorgne, *J. Inorg. Nucl. Chem.*, *26* (1964) 107; M. Bigorgne *J. Organomet. Chem.*, *2* (1964) 101; (e) R.J. Angelici and M.D. Malone, *Inorg. Chem.*, *6* (1967) 1731.

7 E.J.S. Vichi, F.Y. Fujiwara and E. Stein, *Inorg. Chem.*, *24* (1985) 286.

8 M.J. Calhorda and E.J.S. Vichi, *Organometallics*, *9* (1990) 1060.

9 E.H. Santos, E. Stein, E.J.S. Vichi and E.B. Saitovitch, *J. Organomet. Chem.*, *375* (1989) 197.

10 B.F.G. Johnson, J. Lewis, G.R. Stephenson and E.J.S. Vichi, *J. Chem. Soc., Dalton Trans.*, (1978) 369.

11 E.J.S. Vichi, P.R. Raithby and M. McPartlin, *J. Organomet. Chem.*, *256* (1983) 111.

12 The 2 ml of the triisopropylphosphite solution must be added very carefully because after substitution of 1 mol of CO in BDAFe(CO)$_3$ the reaction proceeds with a second CO substitution giving the diphosphite derivative.

13 N. Erickson, *Adv. Chem. Series*, *68* (1969) 86.

14 G.M. Bancroft, *Mössbauer Spectroscopy*, McGraw-Hill, Maidenhead, 1973, Chapter 6, p. 143.

15 (a) C.A. Streuli, *Anal. Chem.*, *31* (1959) 1642; (b) W.A. Henderson and C.A. Streuli, *J. Am. Chem. Soc.*, *82* (1960) 5791; (c) T. Allman and R.G. Goel, *Can. J. Chem.*, *60* (1982) 716; (d) R.A. Jackson, R. Kanluen and A.J. Poë, *Inorg. Chem.*, *23* (1984) 523.

16 (a) M.N. Golovin, M.M. Rahman, J.E. Belmonte and W.P. Giering, *Organometallics*, *4* (1985) 1981; (b) M.M. Rahman, H.Y. Liu, A. Prock and W.P. Giering, *Organometallics*, *6* (1987) 650; (c) K. Dahlinger, F. Falcone and A.J. Poë, *Inorg. Chem.*, *25* (1986) 2654.

17 A.J. Poë and R.A. Jackson, *Inorg. Chem.*, *17* (1978) 2330.

18 T.L. Brown, *Inorg. Chem.*, *31* (1992) 1286.

19 The quantity E_R can be interpreted as the energy required to move the ligands to a distance r_e against a constant force equal to the repulsive force it experiences at the equilibrium distance, r_e; see ref. 18.

20 Complex shift, Δ, is the difference between the chemical shifts of complexed and free BDA; see ref. 7.