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MÖSSBAUER SPECTRA OF IRON(II) HYDRIDE COMPLEXES WITH 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE

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Mössbauer parameters, δ and ΔE, for the known series of complexes, $[FeHL(dppe)_2][BPH_4]$ (dppe=1,2-bis(diphenylphosphino)ethane; L=CO, $PhCH_2NC$, $P(OMe)_3$, N_2, etc.), and a new series of complexes, $[FeHX(dppe)_2]$ ($X=CN^-$, NO_2^-, NCS^-, NCO^-, Cl^-, etc.), were obtained. From these data in combination with i.r. data, the bonding properties of the ligands L and X are discussed.

Bancroft et al. studied the bonding properties of neutral ligands from the relationship between the isomer shift, δ, and the quadrupole splitting, ΔE, for the complexes trans-$[FeHL(depe)_2][BPh_4]$ (depe=1,2-bis(diethylphosphino)ethane; L=CO, Me_3CNC, $P(OPh)_3$, N_2, etc.).$^{1)}$ The conclusions which they obtained were that σ-bonding effects are dominant in determining both the δ and ΔE in the case of most neutral ligands and that CO and N_2 have relatively much stronger π-bonding effects than the other ligands. This has been the only case where π acceptance for N_2 ligand is recognized from Mössbauer spectroscopy. To examine the result of Bancroft et al., we have obtained the Mössbauer parameters for the complexes $[FeHL(dppe)_2][BPh_4]$ (dppe=1,2-bis(diphenylphosphino)ethane; L=CO, $PhCH_2NC$, $P(OMe)_3$, N_2, PhCN, MeCN, and NH_3) most of which have been already prepared by Sacco et al.$^{2)}$ To study further the bonding properties of anionic ligands, we prepared a new series of complexes $[FeHX(dppe)_2]$ ($X=CN^-$, NO_2^-, NCS^-, NCO^-, Cl^-, N_3^-, Br^-, and I^-), and obtained their Mössbauer parameters.

The complexes $[FeHL(dppe)_2][BPh_4]$ were prepared by the method described by Sacco et al.$^{2)}$ The complexes $[FeHX(dppe)_2]$ were prepared by the reaction of $[FeHCl(dppe)_2]^{3)}$ with an excess amount of the sodium salt of each anion in a (1:1) benzene-ethanol solution at 50°C. Mössbauer spectra were recorded at ca. 80 K with a ^{57}Co source doped in palladium. Knowledges about the signs of the ΔE and the configurations of the complexes are necessary for this study. The signs of the ΔE for the complexes $[FeH(CO)(dppe)_2][BPh_4]$ and $[FeH(PhCH_2NC)(dppe)_2][BPh_4]$ were found to be negative from the patterns of their Mössbauer spectra measured under the external magnetic field. To assign the configurations of the complexes, the ΔE for each complex is plotted against the partial quadrupole splitting (p.q.s.)$^{4)}$ for the substituted ligand in Fig. 1. If all the substituted ligands were on the z-axis or xy plane of the complex, the slope of the plot should be +2 or ca. -1, respectively. Since the slope is near +2, all the

Table 1. Mössbauer parameters and analytical data.

Compound	Mössbauer parameters[a] ($mm\ s^{-1}$)		Analyses					
			Found (%)			Calcd. (%)		
	δ[b]	ΔE	C	H	N	C	H	N
$[FeH(CN)(dppe)_2]$	0.41±0.01	(-)1.77±0.01	70.5	6.3	1.4	72.4	5.6	1.6
$[FeH(NO_2)(dppe)_2]$	0.47±0.02	(-)1.34±0.01	68.8	5.6	1.6	69.4	5.5	1.6
$[FeH(NCS)(dppe)_2]$	0.52±0.01	(-)1.01±0.01	69.0	5.9	1.3	69.8	5.4	1.5
$[FeH(NCO)(dppe)_2]$	0.54±0.01	(-)1.02±0.01	70.5	6.1	1.3	71.1	5.5	1.6
$[FeHCl(dppe)_2]$	0.54±0.01	(-)0.75±0.01	69.7	5.8		70.2	5.6	
$[FeH(N_3)(dppe)_2]$	0.55±0.02	(-)0.72±0.01	69.4	5.8	4.6	69.7	5.5	4.7
$[FeHBr(dppe)_2]$	0.55±0.01	(-)0.71±0.01	66.6	5.5		66.9	5.3	
$[FeHI(dppe)_2]$	0.57±0.01	(-)0.74±0.01	63.8	5.1		63.7	5.0	
$[FeH(CO)(dppe)_2][BPh_4]$	0.28±0.01	-1.32±0.02	76.1	6.3		77.0	5.8	
$[FeH(PhCH_2NC)(dppe)_2][BPh_4]$	0.35±0.01	-1.62±0.02	76.7	5.9	1.0	78.2	5.9	1.1
$[FeH(P(OMe)_3)(dppe)_2][BPh_4]$	0.41±0.01	(-)1.51±0.02	72.9	6.1		73.2	6.1	
$[FeH(N_2)(dppe)_2][BPh_4]$[c]	0.47±0.01	(-)0.63±0.02						
$[FeH(PhCN)(dppe)_2][BPh_4]$	0.49±0.01	(-)1.01±0.01	76.3	5.7	0.9	78.2	5.8	1.1
$[FeH(MeCN)(dppe)_2][BPh_4]$	0.50±0.01	(-)0.85±0.02	76.6	6.1	1.2	77.2	6.0	1.2
$[FeH(NH_3)(dppe)_2][BPh_4]$[c]	0.54±0.01	(-)0.78±0.01						

a) At ca. 80 K. b) Relative to sodium nitroprusside. c) Unstable samples.

ligands may be on the z-axis. This is consistent with the fact that the X-ray powder patterns of all the complexes $[FeHX(dppe)_2]$ were analogous to each other. The compounds $[FeHL(dppe)_2]$-$[BPh_4]$ did not show any X-ray diffraction patterns.

The plot of ΔE against δ for the complexes are shown in Fig. 2. The δ and ΔE values may be related to the ligand bonding properties as follow.[5] δ is decreased by the increase in either σ-donor or π-acceptor ability of the ligand. ΔE changes to the more negative or more positive value with the increase in σ-donor or π-acceptor ability of the ligand, respectively, when the ligand is on the z-axis as is the case for this study. A straight line can be fitted to the complexes of the type $[FeHL(dppe)_2][BPh_4]$, excluding the complexes with CO, N_2 and $PhCH_2NC$. Since this line has a positive slope, it is realized that

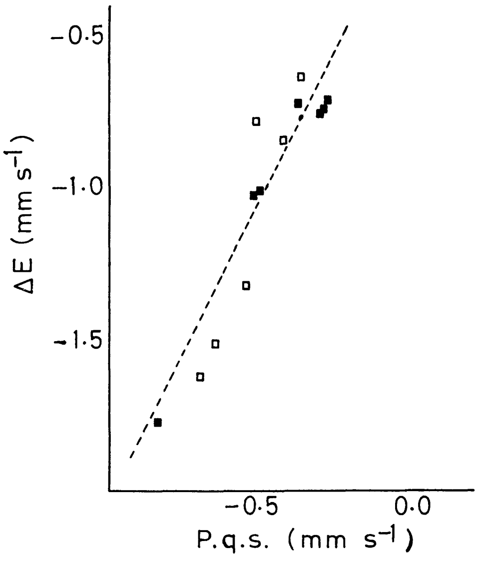

Fig. 1. Correlation between the quadrupole splitting, ΔE, for the complexes $[FeHX(dppe)_2]$ (■) and $[FeHL(dppe)_2]$-$[BPh_4]$ (□) and the partial quadrupole splitting (p.q.s.) for X and L. The dotted line is one of the straight lines with slope equal to +2. The values of p.q.s. are cited from ref. 4.

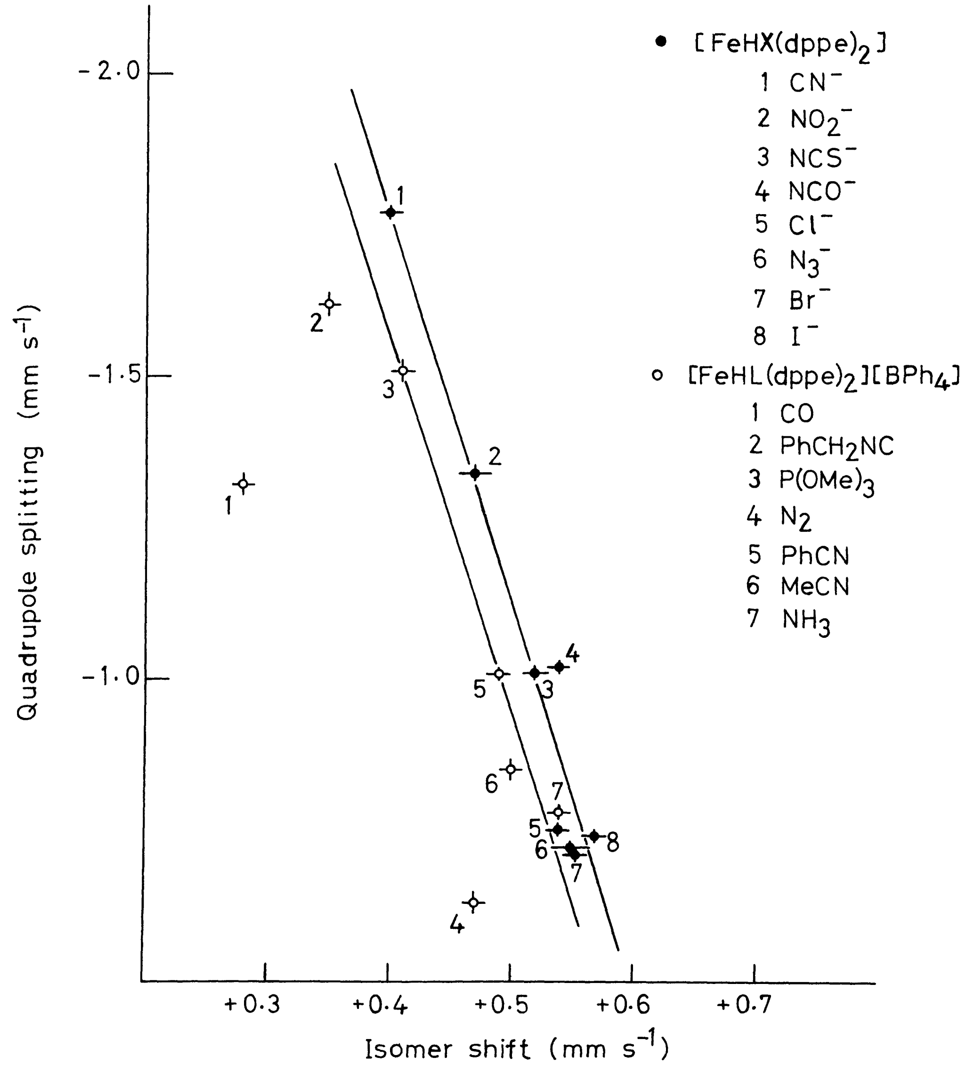

Fig. 2. Plot of quadrupole splitting against isomer shift for the iron(II) complexes, [FeHX(dppe)$_4$] and [FeHL(dppe)$_2$][BPh$_4$].

σ donation is dominant in determining both the δ and ΔE for the neutral ligands such as P(OMe)$_3$, PhCN, MeCN, and NH$_3$. The fact that complexes with CO, N$_2$ and PhCH$_2$NC deviate to the left of the line, indicates that π acceptance is relatively more important for these three ligands than for the others. The deviation increases in the order L=PhCH$_2$NC$\ll$N$_2$$\simeq$CO. The magnitude of the deviation is supposed to be corresponded to the intensity of the π acceptance of the ligand. Therefore, it is realized that π-acceptor ability of the ligand increases in the order PhCH$_2$NC$\ll$N$_2$$\simeq$CO. This order of the π-acceptor ability derived from Mössbauer spectra well agreed with the order of the magnitude of the lowerings in the i.r. streching frequencies for these three ligands (Table 2).

The whole members of the complexes [FeHX(dppe)$_2$] show a quasi-linear correlation between δ and ΔE to which a straight line of a positive slope can be fitted (Fig. 2). Since it has been reported that the q_{lattice} contribution to EFG is unimportant,$^{6)}$ we can safely neglect the effect of the negative charge of

Table 2. Changes in i.r. frequencies (cm^{-1}) from free ligands to complexed ligands.[a)]

	CO	$PhCH_2NC$	N_2	PhCN	MeCN
free ligand	ν(CO)2143	ν(NC)2150	$\nu(N_2)$2330	ν(CN)2232	ν(CN)2255
complexed ligand[b)]	1950 (-193)	2090 (-60)	2112 (-218)	2200 (-32)	2244 (-11)

	CN^-	NCS^-	NCO^-	N_3^-
free ligand	ν(CN)2080[d)]	ν(NC)2053[e)]	ν(NC)2165[e)]	ν(NN)2041[e)]
complexed ligand[c)]	2060 (-20)	2090 (+37)	2220 (+55)	2040 (-1)

a) Frequencies for the complexes are all taken from the spectra in KBr disks. Figures in parentheses are {ν(complexed ligand)-ν(free ligand)}. b) In the complexes $[FeHL(dppe)_2][BPh_4]$. c) In the complexes $[FeHX(dppe)_2]$. d) Free CN^- ion in aqueous solution. e) Potassium salts.

the ligands X on the ΔE of the complexes $[FeHX(dppe)_2]$. Thus it can be said that σ donation rather than π acceptance for the above anionic ligands is dominant in determining both the δ and ΔE, although the differences in δ for various iron(II) complexes have been attributed to the different π-acceptor abilities of the anionic ligands.[7)] In particular, CN^- ligand is a strong σ-donor rather than a strong π-acceptor, because the complex $[FeH(CN)(dppe)_2]$ has the most decreased δ and ΔE among the series of complexes $[FeHX(dppe)_2]$. The greater σ-donor ability of CN^- ligand has also been suggested in ref. 8. Of course we can not exclude the existence of the π acceptance of the anionic ligands X. Actually, a lowering in the streching frequency for the complexed CN^- ligand relative to the free CN^- ligand is seen in Table 2. In order to estimate the intensity of the π acceptance of the strong σ-donor such as CN^- from the Mössbauer spectroscopy, it is desirable to obtain the Mössbauer parameters for a complex such as trans-$[FeH_2(dppe)_2]$.[9)] If the effect of π acceptance of CN^- on Mössbauer parameters were significant, the complex trans-$[FeH_2(dppe)_2]$ might deviate to the right of the straight line fitted to the complexes of the type $[FeHX(dppe)_2]$, including the complex $[FeH(CN)(dppe)_2]$, in Fig. 2. Unfortunately the complex $[FeH_2(dppe)_2]$ which has been prepared is defined as to be the cis-isomer,[3)] and seems not to be appropriate to the above purpose.

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