Bonding Properties of Ligands: A Mössbauer Study of Carbonyl Complexes of Iron(II)

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The Mössbauer spectra of a large number of previously prepared and new iron(II) low-spin compounds are reported. We have derived partial quadrupole splittings (p.q.s.) and partial centre shifts (p.c.s.) for many of the common neutral ligands. The p.q.s. values and carbonyl i.r. stretching frequencies have been used to assign the stereochemistry of compounds of the type $FeA_2B_2C_2$ and $FeAB_3C_2$ (A = neutral ligand, B = CO, C = halide).

P.c.s. and p.q.s. values are used to estimate qualitatively the σ-donor and π-acceptor abilities of the ligands in this study. The variable bonding properties of CO are discussed. Trimethyl phosphite is the strongest σ-donor and π-acceptor of the tertiary phosphorus ligands in this study, and is very similar to isocyanides in its bonding properties. All phosphites are found to be better π-acceptors than their corresponding phosphines.

The general correlation between p.c.s. and p.q.s. values suggest that σ bonding is usually dominant in determining the c.s. and q.s. Mössbauer parameters for CO are also correlated with theoretical calculations of carbonyl orbital populations and carbonyl stretching frequencies.

PREVIOUS Mössbauer studies of Fe^{II} low-spin compounds have shown that partial quadrupole splitting (p.q.s.) and partial centre shift (p.c.s.) parameters can be derived and subsequently used for both predicting and rationalizing bonding properties of ligands in terms of σ and π effects.[1-3] P.q.s. values have also been recently used successfully to assign the stereochemistry of these Fe^{II} compounds,[1] and to predict signs and magnitudes of quadrupole parameters for other $t_{2g}{}^6$ species such as Co^{III}, Ru^{II}, and Mn^{I}.[4-6]

In this paper we greatly enlarge upon our previous studies by preparing a large number of compounds containing many of the common neutral ligands. P.q.s. values have been derived, and these values have

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[1] G. M. Bancroft, M. J. Mays, and B. E. Prater, *Discuss. Faraday Soc.*, 1969, **47**, 136; *J. Chem. Soc.* (*A*), 1970, 956.

[2] G. M. Bancroft, R. E. B. Garrod, and A. G. Maddock, *J. Chem. Soc.* (*A*), 1971, 3165.

[3] G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, B. E. Prater, *J. Amer. Chem. Soc.*, 1972, **94**, 647.

[4] G. M. Bancroft, *Chem. Phys. Letters*, 1971, **10**, 449.

[5] G. M. Bancroft, K. D. Butler, and E. T. Libbey, *J.C.S. Dalton*, 1972, 2643.

[6] G. M. Bancroft, H. C. Clark, R. G. Kidd, A. T. Rake, and H. G. Spinney, *Inorg. Chem.* 1973, **12**, 728.

been of value in assigning the stereochemistry of a number of $FeA_2B_2C_2$ and $FeAB_3C_2$ type compounds (A = neutral ligand, B = CO, C = halide). We then use the p.q.s. and p.c.s. values to rationalize bonding characteristics of ligands. In particular, we discuss the variable bonding properties of CO, and the surprising bonding properties of $P(OMe)_3$ and $P(OEt)_3$ compared with other tertiary phosphines and phosphites.

EXPERIMENTAL

Preparations.—All preparations were carried out under dry nitrogen, by use of standard techniques. Commercial analytical grade solvents were deaerated, but not specially dried, before use. *p*-Methoxyphenyl isocyanide was prepared by the method of Hertler and Corey.[7]

cis- and *trans*-di-iododicarbonylbis(trimethyl phosphine)-iron(II) were a gift of M. Bigorgne and M. Pankowski of the Laboratoire de Chemie minérale de l'Ecole Nationale Supérieure de Chemie, Paris.[8] The preparations of the trimethyl phosphite, triethyl phosphite, and trimethylphosphine complexes are described elsewhere.[9]

TABLE 1

Analyses

Compound	Found (Calc.) C (%)	Found (Calc.) H (%)	Found (Calc.) N (%)	Colour	Recrystallization solvent
cis-$Fe(NCS)_2(dppe)_2$	66·9 (66·9)	5·9 (5·0)	2·7 (2·9)	Purple	
$Fe(CO)_3I_2(ArNC)$	26·1 (25·0)	1·5 (1·3)	2·3 (2·6)	Red-brown	
$Fe(CO)_2I_2(ArNC)_2$	34·1 (34·1)	2·2 (2·2)	4·5 (4·4)	Dark red	
$Fe(CO)_2Cl_2(PPh_2Me)_2$	57·5 (57·6)	4·4 (4·5)		Yellow	Acetone
$Fe(CO)_2Br_2(PPh_2Me)_2$	49·8 (50·0)	3·6 (3·9)		Orange-brown	Acetone
$Fe(CO)_2I_2(PPh_2Me)_2$	43·3 (43·7)	3·5 (3·4)		Dark red	Acetone
$Fe(CO)_3I_2(PPh_2Et)$	33·7 (33·4)	2·5 (2·5)		Crimson red	
$Fe(CO)_3Br_2[P(OPh)_3]$	41·2 (41·3)	2·3 (2·5)		Orange	
$Fe(CO)_3I_2[P(OPh)_3]$	35·8 (35·7)	2·2 (2·1)		Dark red	Ether
$Fe(CO)_2Cl_2[P(OPh)_3]_2$	56·6 (56·8)	3·6 (3·7)		Yellow	Acetone
$Fe(CO)_2Br_2[P(OPh)_3]_2$	51·4 (51·1)	3·5 (3·4)		Orange	CH_2Cl_2–pentane; or acetone
$Fe(CO)_2I_2[P(OPh)_3]_2$	46·3 (46·1)	3·1 (3·2)		Dark red	$CHCl_3$–light petroleum
$Fe(CO)_2Br_2(dppe)$	49·4 (50·1)	4·0 (3·7)		Orange	
$Fe(CO)_2I_2(dppe)$	44·1 (43·9)	3·1 (3·1)		Dark red	CH_2Cl_2–ether
$Fe(CO)_2Br_2[P(OMe)_3]_2$	18·7 (18·5)	3·4 (3·5)		Orange	Methanol

cis-Tetracarbonyliron dihalides were prepared in ether (n-pentane for the chloride) at −30 °C, at which temperature the products precipitate.[10,11] These were dried at room temperature (0 °C for the chloride) under vacuum for a few hours [to ensure conversion of $Fe(CO)_5X_2$ into $Fe(CO)_4X_2$]. They were used subsequently without further purification.

Some isocyanide, phosphine, and phosphite-substituted derivatives of $Fe(CO)_4X_2$ and their analogues have been reported, prepared by various routes.[11–16] We allowed the $Fe(CO)_4X_2$ to react in ether or dichloromethane with a stoicheiometric amount of phosphine, phosphite, or isocyanide. Recrystallization from ether, acetone, methanol, or dichloromethane–pentane gave the desired products (this was sometimes unsuccessful, leading to loss of carbon monoxide). *cis*- and *trans*-Dichlorodicarbonyl-(1,2-bisdiphenylphosphinoethane)iron(II) were made by the methods of Manuel.[13] Our preparation apparently gives the same product as his *cis*-isomer.

We were unable to obtain many monosubstituted derivatives pure. Except for one bromide, all the monosubstituted derivatives are iodides.

The new compounds were prepared as follows.

cis-*Di-isothiocyanatobis-*(1,2-*bisdiphenylphosphinoethane*)-*iron*(II).—The diphosphine (0·8 g, 2 mmol) in dichloromethane (25 cm^3) was added slowly with shaking to a solution of $FeCl_2,4H_2O$ (0·2 g, 1 mmol) and NH_4NCS (0·25 g, *ca.* 4 mmol) in methanol. The product, as a purple powder, was filtered off and washed well with dichloromethane, methanol, and ether, and dried under vacuum. Recrystallization was not possible owing to its insolubility in all common solvents; yield 0·85 g (*ca.* 90%).

Di-iodotricarbonyl(*diphenylethylphosphine*)*iron*(II). To $Fe(CO)_4I_2$ (0·61 g, 1·5 mmol) in ether (50 cm^3) was added diphenylethylphosphine (0·3 g, 1·3 mmol) in ether (10 cm^3). The volume was reduced in the nitrogen stream to about half, and a crimson powder separated. This was filtered off and washed with cold ether and vacuum dried; yield 0·6 g (*ca.* 70%).

Dibromotricarbonyl(*triphenyl phosphite*)*iron*(II). To $Fe(CO)_4Br_2$ (0·42 g, 1·3 mmol) in ether was added triphenyl phosphite (0·8 g, *ca.* 2·7 mmol) with stirring at *ca.* 15 °C. After a few minutes an orange powder separated which was filtered off and washed with cold ether, and vacuum dried. This solid showed three i.r. bands in the 2000—2100 cm^{-1} region as expected for the monosubstituted derivative. Subsequently, on cooling the filtrate, crystals of the expected disubstituted product were obtained. The yield of the tricarbonyl complex was 0·4 g (*ca.* 50%).

Some microanalyses were carried out by the Microanalytical Department at the University of Cambridge. Satisfactory analyses were obtained for all new compounds. These results and a summary of preparative details are in Table 1.

Spectra.—I.r. spectra were recorded on Perkin-Elmer 257, 457, and 621 and Beckman IR7 and IR10 instruments, calibrated with carbon monoxide and polystyrene. Carbon

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[7] W. R. Hertler and E. J. Corey, *J. Org. Chem.*, 1958, **23**, 1221.

[8] M. Bigorgne and M. Pankowski, *Compt. rend.*, 1966, *C*, **263**, 239.

[9] G. M. Bancroft and E. T. Libbey, *Canad. J. Chem.*, 1973, **51**, 1482.

[10] W. Hieber and G. Bader, *Z. anorg. Chem.*, 1930, **190**, 193.

[11] I. A. Cohen and F. Basolo, *J. Inorg. Nuclear Chem.*, 1966, **28**, 511.

[12] W. Hieber and A. Thalhofer, *Angew Chem.*, 1956, **68**, 679.

[13] T. A. Manuel, *Inorg. Chem.*, 1963, **2**, 854.

[14] R. C. Taylor and W. D. Horrocks, jun., *Inorg. Chem.*, 1964, **3**, 584.

[15] G. Booth and J. Chatt, *J. Chem. Soc.*, 1962, 2099.

[16] W. Hieber, V. Frey, and P. John, *Chem. Ber.*, 1967, **100**, 1961.

monoxide stretching frequencies are believed accurate to ± 2 cm^{-1} (Table 2). Other prominent i.r. bands and probable assignments are shown in Table 3. Where these compounds have been reported previously, our data is in substantial agreement.

TABLE 2

I.r. data for carbonyl derivatives

Compound	Frequencies/cm^{-1} $\pm$ 2 cm^{-1} Nujol mulls			Chloroform solution		
$Fe(CO)_2Cl_2(PPh_2Me)_2$	2037	1988		2040 (2040)	1988 (1989)	
$Fe(CO)_2Br_2(PPh_2Me)_2$	2034	1986		2037 (2039)	1985 (1989)	
$Fe(CO)_2I_2(PPh_2Me)_2$	2029	1982		2029 (2028)	1977 (1979)	
$Fe(CO)_2Cl_2(PPh_2Et)_2$	2040	1976		2040	1988	
$Fe(CO)_2Br_2(PPh_2Et)_2$	2035	1971		2037	1985	
$Fe(CO)_2I_2(PPh_2Et)_2$	2026	1968		2027	1976	
$Fe(CO)_2Cl_2[P(OPh)_3]_2$				2069	2025	
$Fe(CO)_2Br_2[P(OPh)_3]_2$				2064	2020	
$Fe(CO)_2I_2[P(OPh)_3]_2$				2056	2013	
$Fe(CO)_2Cl_2(PPh_3)_2$				(2042)	(1994)	
$Fe(CO)_2Br_2(PPh_3)_2$	2033	1984		2038	1989	
$Fe(CO)_2Br_2(dppe)$				2053	1998	
$Fe(CO)_2I_2(dppe)$				2037	1991	
$Fe(CO)_2Br_2[P(OMe)_3]_2$				2062	2013	
cis-$Fe(CO)_2I_2(PMe_3)_2$				2022 2017*	1971 1967*	
trans-$Fe(CO)_2I_2(PMe_3)_2$				1976 1977*		
$Fe(CO)_3I_2(PPh_2Et)$	2086m	2045	2030m, sh	2090m	2046	2027m
$Fe(CO)_3Br_2[P(OPh)_3]$	2132m	2087br		(2125m)	(2087)	(2071m, sh)
$Fe(CO)_3I_2[P(OPh)_3]$	2112m	2060	2056m	(2109m)	(2061)	(2050m)
$Fe(CO)_3I_2(PPh_3)$	2091m	2046	2031m, sh	2094m	2045	2033m, sh

Frequencies in parentheses are in dichloromethane solution. All bands strong and sharp unless otherwise indicated; br = broad, sh = shoulder.

* n-Hexane solution, ref. 8.

^{1}H N.m.r. spectra of the trimethyl phosphite and diphenylmethylphosphine derivatives were recorded on Varian HA100 and T60 spectrometers at *ca.* 30 °C.

TABLE 3

I.r. stretching frequencies for (NCS) derivatives

Compound	Nujol mulls, ± 4 cm^{-1} Frequencies/cm^{-1} and assignments	
trans-$Fe(NCS)_2[P(OMe)_3]_4$	2114s	ν(CN)
	815s, sharp	ν(CS)
trans-$Fe(NCS)_2[P(OEt)_3]_4$	2118s	ν(CN)
cis-$Fe(NCS)_2[PMe_3]_4$	2120m 2100s, broad 2049m	ν(CN)
	805m, multiplet	ν(CS)
cis-$Fe(NCS)_2(dppe)_2$	2112s 2101s	ν(CN)
	815m, multiplet	ν(CS)

Mössbauer spectra were recorded at *ca.* 80 K (some also at room temperature) on an Austin Science Associates Spectrometer with a ^{57}Co in Cu source. Spectra were calibrated by use of an iron foil absorber and centre shifts are quoted relative to sodium nitroprusside (Table 4). All compounds were sufficiently air-stable to be sealed in a Perspex holder immediately before being cooled in liquid nitrogen.

All spectra were fitted without constraints to Lorentzian line shapes by use of a programme written by A. J. Stone.[17] Standard deviations in the centre shift and quadrupole splittings were less than $\pm 0{\cdot}01$ mm s^{-1} (except in a few cases where the lines were poorly resolved or where the γ-ray beam caused loss of CO). Reproducibility of the parameters was within 0·01 mm s^{-1}. χ^2 values for all spectra were 500 ± 50 with *ca.* 500 degrees of freedom. Line-widths for all spectra were less than 0·30 mm s^{-1}.

The sign of the quadrupole splitting for *trans*-$Fe(CO)_2I_2(PMe_3)_2$ was measured by P.C.M.U., Harwell, England.

RESULTS AND DISCUSSION

Infrared Spectra.—The use of i.r. spectra in the 1900—2200 cm^{-1} region to elucidate the stereochemistry of carbonyl compounds by comparing observed numbers of bands and their intensities with predictions based on idealised point-group symmetry has been well established.[18,19] Most of the disubstituted compounds $Fe(CO)_2L_2X_2$ used in this work showed the expected two bands for the *cis*-configuration of carbonyls; those compounds showing one band are assigned as *trans*-carbonyls. Similarly, the monosubstituted derivatives, $Fe(CO)_3LX_2$, showed three medium to strong i.r.-active bands, characteristic of a *fac*-configuration of three carbonyls [8,14,16] (Table 2).

There are few systematic trends in the stretching frequencies. Usually in a given Cl, Br, I series, ν(CO) increases in the order I < Br < Cl, and for the disubstituted products two sharp bands of approximately equal intensity were observed at *ca.* 2035 ± 10 cm^{-1} and 1980 ± 10 cm^{-1}. The exceptions are the trimethyl phosphite and triphenyl phosphite derivatives where there is a shift to higher wavenumbers of *ca.* 30—40 cm^{-1}, largely as a result of the increased π-acceptor ability of the phosphites compared with phosphines (*viz.* Mössbauer discussion below). Graham noted that $P(OMe)_3$ was a strong π-bonding ligand.[20]

However, the $Fe(CO)_2X_2L_2$ series of compounds can

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[17] A. J. Stone, appendix to G. M. Bancroft, W. K. Ong, A. G. Maddock, R. H. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.

[18] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.* 1962, **84**, 4432.

[19] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

[20] W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

exist in five possible geometric isomers, which clearly cannot all be distinguished by carbonyl i.r. stretching modes since three of these will give two bands of approximately equal intensity and the other two just one band. In the series of isocyanide derivatives, Taylor and Horrocks[14] had additional structural data in C–N stretching modes but were unable to definitely choose one isomeric form.

Hieber *et al.*,[16,21] studying the closely related series of ruthenium compounds (and a few iron and osmium analogues), used a combination of i.r. and dipole moment data to define stereochemistry. Using such data they were able to distinguish between the three isomers with *cis*-carbonyls. Booth and Chatt[15] used this method too for $Fe(CO)_2X_2(PR_3)_2$, but they only isolated one isomer. Such data can only be obtained in solution, whereas the Mössbauer effect is normally used in the solid state (*cf.* below).

TABLE 4

Mössbauer parameters for Fe^{II} low-spin compounds

[C.s. given with respect to sodium nitroprusside; spectra obtained at *ca.* 80 K (room-temperature data in parentheses), ±0·01 unless otherwise given.]

		C.s.	Q.s.
1	*cis*-$Fe(NCS)_2(dppe)_2$	0·62	0·33
2	*cis*-$Fe(NCS)_2(PMe_3)_4$	0·58	0·31
3	*cis*-$Fe(NCS)_2(ArNC)_4$	0·38	0·42
4	[a] *trans*-$Fe(NCS)_2[P(OMe)_3]_4$	0·46	0·56
5	*trans*-$Fe(NCS)_2[P(OEt)_3]_4$	0·48	0·49
6	[b] *cis*-$Fe(CO)_2I_2(PMe_3)_2$*	0·32	0·90
7	[b] *trans*-$Fe(CO)_2I_2(PMe_3)_2$*	0·45	+1·32
8	$Fe(CO)_2Br_2[P(OMe)_3]_2$	0·29	0·93
9	$Fe(CO)_3I_2(ArNC)$	0·29	0·58
10	$Fe(CO)_2I_2(ArNC)_2$	0·29	0·79
11	*cis*-$Fe(CO)_2Cl_2(dppe)$*	0·32 (0·28)	0·61 (0·56)
12	*trans*-$Fe(CO)_2Cl_2(dppe)$*	†0·41	†0·33
13	*cis*-$Fe(CO)_2Br_2(dppe)$*	0·38	0·63
14	*cis*-$Fe(CO)_2I_2(dppe)$*	0·38 (0·29)	0·64 (0·57)
15	$Fe(CO)_3I_2(PPh_2Et)$	0·34 (0·27)	0·46 (0·46)
16	$Fe(CO)_2Cl_2(PPh_2Et)_2$	0·32	0·62
17	$Fe(CO)_2Br_2(PPh_2Et)_2$	0·35 (0·28)	0·55 (0·47)
18	$Fe(CO)_2I_2(PPh_2Et)_2$	0·37 (0·34)	0·37 (0·32)
19	$Fe(CO)_2Cl_2(PPh_2Me)_2$	0·31	0·60
20	$Fe(CO)_2Br_2(PPh_2Me)_2$	0·33 (0·27)	0·56 (0·51)
21	$Fe(CO)_2I_2(PPh_2Me)_2$	0·36 (0·29)	0·39 (0·36)
22	$Fe(CO)_3I_2PPh_3$	0·33 (0·28)	0·44 (0·44)
23	$Fe(CO)_2Cl_2(PPh_3)_2$	0·34	0·40
24	$Fe(CO)_2Br_2(PPh_3)_2$	0·35	0·34
25	$Fe(CO)_3Br_2P(OPh)_3$	0·31	0·27
26	$Fe(CO)_3I_2P(OPh)_3$	0·33	0·33
27	$Fe(CO)_2Cl_2[P(OPh)_3]_2$	0·28	0·50
28	$Fe(CO)_2Br_2[P(OPh)_3]_2$	0·29	0·48
29	$Fe(CO)_2I_2[P(OPh)_3]_2$	†0·33	†0·31
30	$Fe(CO)_3I_2AsPh_3$	0·37	0·54
31	$Fe(CO)_2Cl_2(AsPh_3)_2$	†0·39	†0·34
32	$Fe(CO)_2Br_2(AsPh_3)_2$	0·42	0·26
33	$Fe(CO)_2Cl_2(SbPh_3)_2$	0·40	0·30
34	$Fe(CO)_2Br_2(SbPh_3)_2$	‡0·44	‡0·27
35	*cis*-$Fe(CO)_4Cl_2$	0·29	0·24
36	*cis*-$Fe(CO)_4Br_2$	0·31	0·30
37	*cis*-$Fe(CO)_4I_2$	0·31	0·30
38	[c] *trans*-$Fe(CO)_4(SnCl_3)_2$	0·26	0·46

* *cis* and *trans* refers to configuration of carbonyl groups.
† ±0·02 mm s^{-1}.
‡ ±0·03 mm s^{-1}.

[a] G. M. Bancroft and E. T. Libbey, ref. 9. [b] Compounds kindly donated by M. Bigorgne and M. Pankowski. [c] N. Dominelli, E. Wood, P. Vasudev, and C. H. W. Jones, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1077.

The i.r. spectra of the thiocyanate derivatives show strong absorptions in the 2000—2200 cm^{-1} region, assignable to the N–C stretching mode (Table 3). The *trans*-isomers show a sharp resonance while the *cis*-isomers show a broader band or doublet. Owing to overlapping bands from the isocyanide, assignment for *cis*-$Fe(NCS)_2(ArNC)_4$ is not possible.

However, it is clearly necessary to ascertain whether all our NCS compounds are isothiocyanates (Fe–NCS) or thiocyanates (Fe–SCN). Several authors[22-26] have tried to define characteristic frequencies assignable to the N–C and C–S stretching modes and the N–C–S bending modes for the two linkage isomers, though no definitive method has yet been suggested. The C–S stretch usually comes in the 780—860 cm^{-1} region for N-bonded and the 690—720 cm^{-1} region for S-bonded structures. Unfortunately $P(OMe)_3$ and 1,2-bis(diphenylphosphino)ethane have absorptions in the latter region which could mask these bands. However, all of our thiocyanate compounds have a medium to strong band at *ca.* 800 cm^{-1} which is probably the C–S stretching mode. This evidence is consistent then with N-bonded thiocyanate. The C–N stretching mode at *ca.* 2100 cm^{-1} (Table 3) is also consistent with N-bonded thiocyanate. In common with previous authors who suggest that Fe^{II} complexes are generally isothiocyanates, we assign all of our compounds as isothiocyanates.

N.m.r. Spectra.—The ^1H n.m.r. spectra of *trans*- and *cis*-$Fe(NCS)_2[P(OMe)_3]_4$ and *cis*-$Fe(NCS)_2[PMe_3]_4$ have been reported.[9] The *cis*-compounds both show a pair of chemically inequivalent triplets.

The ^1H n.m.r. spectra of the $P(OMe)_3$ and PPh_2Me carbonyl derivatives show strong 'virtual coupling' patterns, a sharp triplet, $^3J(P\text{–}H) + {}^5J(P\text{–}H)$ and $^2J(P\text{–}H) + {}^4J(P\text{–}H)$, respectively, equal to *ca.* 10 Hz. Such observations are usually ascribed to a *trans*-configuration of phosphines or phosphites, but in light of our previous work[9] such information should be interpreted with caution.

Mössbauer Spectra.—Derivation of p.q.s. values. The use of partial quadrupole splittings (p.q.s.) for predicting and correlating Mössbauer quadrupole splittings has been discussed.[1,2] To help in the assignment of the structures, and to indicate the structural use of Mössbauer quadrupole splittings, we have derived the electric field gradient components in terms of partial field gradients (p.f.g.) (Table 5) for all the $FeA_2B_2C_2$ and $FeAB_3C_2$ isomers, and used derived partial quadrupole splittings (p.q.s.) * (Table 6) to predict the quadrupole splittings of 28 compounds (Table 7).

Many of the p.q.s. values in Table 6 have been derived

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* p.q.s. = $\frac{1}{2}e^2Q[L]$, where [L] = p.f.g.

[21] W. Hieber and P. John, *Chem. Ber.*, 1970, **103**, 2161, 2178.

[22] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1960, 1912.

[23] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.

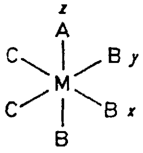
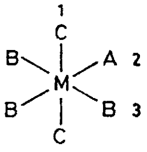
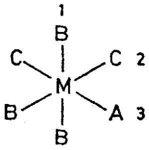
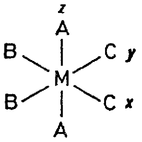
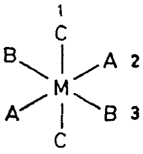
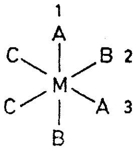
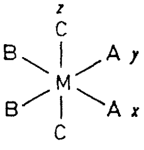
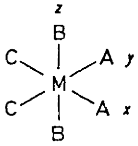
[24] R. A. Bailey, S. L. Kozak, T. W. Michelson, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

[25] M. Aslam and W. H. J. Massie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 961.

[26] A. H. Norbury and A. T. P. Sinka, *Quart. Rev.*, 1970, **25**, 69.

TABLE 5

Electric-field gradient components and *EFG* axes for compounds of the type MAB_3C_2 and $MA_2B_2C_2$ *

	Species	Components of the *EFG* tensor
1		$V_{zz} = \{2[A] - 2[C]\}e$ $V_{yy} = \{[C] - [A]\}e$ $V_{xx} = \{[C] - [A]\}e$ $\eta = 0$
2		$V_{11} = \{4[C] - 3[B] - [A]\}e$ $V_{22} = \{2[A] - 2[C]\}e$ $V_{33} = \{3[B] - 2[C] - [A]\}e$ $\eta \neq 0$
3		$V_{11} = \{3[B] - [A] - 2[C]\}e$ $V_{22} = \{[C] - [A]\}e$ $V_{33} = \{2[A] + [C] - 3[B]\}e$ $\eta \neq 0$
4		$V_{zz} = \{4[A] - 2[B] - 2[C]\}e$ $V_{yy} = \{[C] + [B] - 2[A]\}e$ $V_{xx} = \{[C] + [B] - 2[A]\}e$ $\eta = 0$
5		$V_{11} = \{4[C] - 2[B] - 2[A]\}e$ $V_{22} = \{4[A] - 2[B] - 2[C]\}e$ $V_{33} = \{4[B] - 2[C] - 2[A]\}e$ $\eta \neq 0$
6		$V_{11} = \{[A] + [B] - 2[C]\}e$ $V_{22} = \{[B] + [C] - 2[A]\}e$ $V_{33} = \{[A] + [C] - 2[B]\}e$ $\eta \neq 0$
7		$V_{zz} = \{4[C] - 2[A] - 2[B]\}e$ $V_{yy} = \{[A] + [B] - 2[C]\}e$ $V_{xx} = \{[A] + [B] - 2[C]\}e$ $\eta = 0$
8		$V_{zz} = \{4[B] - 2[A] - 2[C]\}e$ $V_{yy} = \{[A] + [C] - 2[B]\}e$ $V_{xx} = \{[A] + [C] - 2[B]\}e$ $\eta = 0$

* A = phosphine, phosphite, isocyanide, arsine, or stibine; B = CO; C = X (=Cl, Br, or I). Axes are defined for the above case only where $\eta = 0$. In other cases unambiguous assignment is not possible as the choice of axes depends upon the relative p.q.s. values of A, B, and C.

from our previous study.[2] We have used the previously derived [1,2] value of −0·30 mm s^{-1} for the p.q.s. of Cl^- as the reference point for the p.q.s. scale. Because much better spectra can be obtained at 80 K and more data are now available at this temperature, we have derived our p.q.s. values wherever possible at 80 K instead of 295 K. Because quadrupole splittings of Fe^{II} low-spin compounds never vary by more than 0·1 mm s^{-1} over this temperature range, partial quadrupole splittings derived at 80 K will not differ by more than *ca.* 0·02 mm s^{-1} from those derived at 295 K.

Wherever possible, the p.q.s. values in Table 6 have been derived from *trans*-compounds not containing the carbonyl ligand. The variable bonding properties of carbonyl could cause a variation in any derived p.q.s. value for CO, and recent theoretical work [27] suggests that the additivity model may break down for strong π-acceptors. It is clearly important to assess whether the model will break down for such a ligand.

TABLE 6

Partial quadrupole splittings/mm s^{-1} at 80 K *

Ligand	P.q.s.	Footnote	Ligand	P.q.s.	Footnote
NO^+*	+0·01	*a*	$P(OPh)_3$	−0·55	*c*
Br^-	−0·28	*a*	CO	−0·55	*d*
I^-	−0·29	*a*	PPh_2Et	−0·58	*c*
Cl^-	−0·30	*a*	PPh_2Me	−0·58	*c*
N_2*	−0·37	*b*	depb/2	−0·59	*a*
N_3^-	−0·38	*a*	$P(OEt)_3$	−0·63	*e*
MeCN*	−0·43	*b*	depe/2	−0·65	*a*
$SnCl_3$	−0·43	*a*	$P(OMe)_3$	−0·65	*e*
H_2O*	−0·45	*a*	PMe_3	−0·66	*f*
$SbPh_3$	−0·50	*c*	dppe/2	−0·68	*f*
NCS^-	−0·51	*a*	dmpe/2	−0·70	*a*
$AsPh_3$	−0·51	*c*	ArNC	−0·70	*a*
NH_3*	−0·52	*a*	CN^-*	−0·84	*a*
NCO^-	−0·52	*a*	H^-	−1·04	*a*
PPh_3	−0·53	*c*			

* Those ligands asterisked had their p.q.s. values derived from room-temperature data.

[a] Refs. 1 and 2. [b] Reference 5. [c] From the $Fe(CO)_2Cl_2L_2$ (L = phosphine, phosphite, arsine, or stibine) compound in Table 4. [d] From ref. *c* of Table 4. [e] From the *trans*-$(NCS)_2$ compounds in Table 4. [f] From *cis*-$Fe(NCS)_2(PMe_3)_4$ and *cis*-$Fe(NCS)_2(dppe)_2$.

A p.q.s. value for CO of −0·55 mm s^{-1} has been derived from the q.s. for *trans*-$Fe(CO)_4(SnCl_3)_2$ [27] (Table 4, compound 38) and our results support the use of this value as a first approximation. For example, the measured positive sign of the q.s. for *trans*-$Fe(CO)_2I_2(PMe_3)_2$ † is in agreement with the signs predicted from use of the −0·55 mm s^{-1} p.q.s. value for CO. In addition, there is generally very satisfactory agreement between predicted and observed magnitudes (Table 7). We take ±0·20 mm s^{-1} as being satisfactory agreement, compared with the value of ±0·40 mm s^{-1} taken for Sn^{IV} compounds.[27] Five of the observed nine discrepancies in Table 7 depend on the assignment of structure, and these will be discussed in the next section.

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† In isomers of $Fe(CO)_2X_2L_2$, *cis-trans* refers to configuration of carbonyl groups.

[27] M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

It is apparent from Table 7 that, even for strong π-acceptors such as CO, there is a considerable correlative use of p.q.s. values. The generally good agreement between observed and calculated values suggest that localized orbitals[27] are not essential for the useful derivation and application of p.q.s. values. However, in an effort to improve agreement between predicted and observed values, especially for the *cis*-$\mathrm{Fe(CO)_4X_2}$ (X = Cl, Br, or I) compounds, it is illuminating to calculate two p.q.s. values for carbonyl; [CO_t] for carbonyls *trans* to each other, and [CO_c] for *cis*-carbonyls, *i.e.*, *trans* to some other ligand, which in this study is invariably halide. Taking the quadrupole splittings of *cis*-$\mathrm{Fe(CO)_4I_2}$, *cis*-$\mathrm{Fe(CO)_2I_2(PMe_3)_2}$, and *trans*-$\mathrm{Fe(CO)_2I_2(PMe_3)_2}$ to be (—)0·30 mm s^{-1}, (—)0·90 mm s^{-1},‡ and +1·32 mm s^{-1} respectively, and taking the usual p.q.s. value of iodide as —0·29 mm s^{-1}, we can obtain p.q.s. values for CO_c, CO_t, and $\mathrm{PMe_3}$ of —0·60 mm s^{-1}, —0·53 mm s^{-1} and —0·68 mm s^{-1} respectively. The p.q.s. value for $\mathrm{PMe_3}$ is in good agreement with the p.q.s. value for that ligand derived from *cis*-$\mathrm{Fe(NCS)_2[PMe_3]_4}$ (Table 6). These two values for CO of course improve the agreement between predicted and observed values for the *cis*-$\mathrm{Fe(CO)_4X_2}$ compounds, but they do not substantially affect the predicted values for the other substituted compounds. The significance of these two values for the p.q.s. of CO will be discussed further below.

TABLE 7

Predicted and observed values of quadrupole splittings/mm s^{-1}

Compound	Structure*	Quadrupole splitting Predicted	Observed
1 $\mathrm{Fe(NCS)_2(ArNC)_4}$	*cis*	+0·38	0·42
2 $\mathrm{Fe(CO)_2I_2(PMe_3)_2}$	4 [b]	—0·96	0·90
3 $\mathrm{Fe(CO)_2I_2(PMe_3)_2}$	5 [b]	+1·31	+1·32
		(η = 0·52)	
4 $\mathrm{Fe(CO)_2Br_2[P(OMe)_3]_2}$	4	—0·94	0·93
5 $\mathrm{Fe(CO)_3I_2ArNC}$	1 [c]	—0·82†	0·58
	3	+0·45	
		(η = 0·80)	
6 $\mathrm{Fe(CO)_2I_2(ArNC)_2}$	4 [c]	—1·12†	0·79
	6	—0·71	
		(η = 0·67)	
7 $\mathrm{Fe(CO)_2Cl_2(dppe)}$	6 [d]	—0·67	0·61
		(η = 0·62)	
8 $\mathrm{Fe(CO)_2Cl(dppe)}$	8 [d]	—0·24	0·33
9 $\mathrm{Fe(CO)_2Br_2(dppe)}$	6	—0·71	0·63
		(η = 0·60)	
10 $\mathrm{Fe(CO)_2I_2(dppe)}$	6	—0·69	0·60
		(η = 0·61)	
11 $\mathrm{Fe(CO)_4(SnCl_3)_2}$	*cis*	+0·24	0·20 [a]
12 $\mathrm{Fe(CO)_3I_2PPh_2Et}$	1	—0·52	0·46
13 $\mathrm{Fe(CO)_2Br_2(PPh_2Et)_2}$	4 [e]	—0·66	0·55
14 $\mathrm{Fe(CO)_2I_2(PPh_2Et)_2}$	4 [e]	—0·64†	0·37
	6	—0·56	
		(η = 0·16)	
15 $\mathrm{Fe(CO)_2Br_2(PPh_2Me)_2}$	4 [e]	—0·66	0·56
16 $\mathrm{Fe(CO)_2I_2(PPh_2Me)_2}$	4	—0·64†	0·39
	6	—0·56	
		(η = 0·16)	
17 $\mathrm{Fe(CO)_3I_2PPh_3}$	1	—0·48	0·43
18 $\mathrm{Fe(CO)_2Br_2(PPh_3)_2}$	4	—0·56†	0·34
	6	—0·52	
		(η = 0·12)	
19 $\mathrm{Fe(CO)_3Br_2P(OPh)_3}$	1	—0·54†	0·27
	3	—0·54†	
20 $\mathrm{Fe(CO)_3I_2P(OPh)_3}$	1	—0·52	0·33
21 $\mathrm{Fe(CO)_2Br_2[P(OPh)_3]_2}$	4	—0·54	0·45
22 $\mathrm{Fe(CO)_2I_2[P(OPh)_3]_2}$	4	—0·52	0·32
	6	—0·52	
23 $\mathrm{Fe(CO)_4Cl_2}$	*cis*	—0·50† [f]	0·24
24 $\mathrm{Fe(CO)_4Br_2}$	*cis*	—0·54† [f]	0·30
25 $\mathrm{Fe(CO)_4I_2}$	*cis*	—0·52† [f]	0·30
26 $\mathrm{Fe(CO)_3I_2AsPh_3}$	1	—0·44	0·54
27 $\mathrm{Fe(CO)_2Br_2(AsPh_3)_2}$	4	—0·38	0·26
28 $\mathrm{Fe(CO)_2Br_2(SbPh_3)_2}$	4	—0·34	0·27

* See Table 5 for diagram of suggested structures

† Predicted quadrupole splittings deviate from observed by more than 0·20 mm s^{-1}. η = 0 Unless otherwise shown.

[a] Ref. *c* of Table 4. [b] Ref. 8. [c] See ref. 14 for discussion of structures of analogous compounds. [d] Ref. 13. [e] See refs. 15 and 16 for discussion of structures of analogous compounds. [f] See ref. 33.

For some of the neutral ligands in this study, we did not have reference compounds not containing carbonyl to derive p.q.s. values. In fact, no neutral six-co-ordinate $\mathrm{Fe^{II}}$ compound containing ligands such as $\mathrm{PPh_3}$, $\mathrm{SbPh_3}$, or $\mathrm{AsPh_3}$, and not containing carbonyl, has yet been prepared. For these ligands, we have derived p.q.s. values from the $\mathrm{Fe(CO)_2X_2L_2}$ compounds containing *trans*-L groups. The agreement between predicted and observed q.s. values for the $\mathrm{Fe(CO)_2X_2L'_2}$ [L′ = $\mathrm{PMe_3}$, $\mathrm{P(OMe)_3}$, and (dppe)/2] compounds indicates that meaningful p.q.s. values can be derived from carbonyl containing compounds.

Structure.—It is noteworthy (Table 8) that, using the combination of i.r. and Mössbauer spectra, we can distinguish between all the five possible isomers of $\mathrm{FeX_2(CO)_2(PR_3)_2}$ if the p.q.s. values of $\mathrm{PR_3}$ and CO are reasonably different, say *ca.* 0·1 mm s^{-1}. By use of the p.q.s. values [$\mathrm{I^-}$] = —0·29 mm s^{-1}, [CO] = —0·55 mm s^{-1}, and [$\mathrm{PMe_3}$] = —0·66 mm s^{-1}, those isomers with *cis*-carbonyls give predicted quadrupole splittings of —0·96, +1·26, and —0·65 mm s^{-1}, while the *trans*-carbonyl isomers give values of +1·31 and —0·30 mm s^{-1}. Thus, our observed q.s. of +1·32 mm s^{-1} can be assigned confidently to the all-*trans*-isomer, while our observed q.s. of (—)0·90 mm s^{-1} can be safely assigned to structure 4, Table 5 (*trans*-$\mathrm{PMe_3}$, *cis*-CO's and I's). These structural assignments are as given previously.[8] Similarly, the predicted quadrupole splittings for the three possible isomers of $\mathrm{Fe(CO)_2Cl_2(dppe)}$ are +1·26 mm s^{-1} (structure

TABLE 8

Magnitudes and signs of quadrupole splittings for the five possible $\mathrm{Fe(CO)_2(PMe_3)_2I_2}$ isomers

Isomer *	Quadrupole splitting/mm s^{-1} Predicted	Observed	Predicted
4 (*cis*-CO's)	—0·96	0·90	0
5 (*trans*-CO's)	+1·31	+1·32	0·52
6 (*cis*-CO's)	—0·65		0·52
7 (*cis*-CO's)	+1·26		0
8 (*trans*-CO's)	—0·30		0

* See Table 5.

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‡ The signs in parentheses are assumed. A recently measured sign, for $\mathrm{Fe(CO)_2I_2(PEt_3)_2}$, [28], is negative, strongly supporting our assignment.

[28] B. W. Fitzsimmons and A. C. Sawbridge, personal communication.

7, Table 5), $-0{\cdot}67$ ($\eta = 0{\cdot}62$) (structure 6, Table 5) and $-0{\cdot}24$ mm s^{-1} (structure 8, Table 5). The observed q.s. values of 0·61 mm s^{-1} and 0·33 mm s^{-1} lead to an unambiguous assignment of isomers to structures 6 and 8 respectively.

However, our calculated p.q.s. value of $-0{\cdot}68$ mm s^{-1} for (dppe)/2 [from *cis*-$Fe(NCS)_2(dppe)_2$] should be viewed as somewhat uncertain in light of the Mössbauer quadrupole splittings for *trans*-$Fe(phen)_2(CN)_2$, *cis*-$Fe(phen)_2(CN)_2$, and $K_2[Fe(phen)(CN)_4]$ of 0·63 mm s^{-1}, 0·62 mm s^{-1}, and 0·61 mm s^{-1} respectively.[29] Magnetic spectra of the above three compounds [30] strongly indicate that all three compounds have the same sign of the quadrupole splitting, again in contradiction to expectations from our partial quadrupole splitting treatment. Observed chemical properties of dppe, and a correlation given shortly between p.c.s. and p.q.s., suggest that the p.q.s. of (dppe)/2 should be closer to that of PPh_3. All of these results indicate that much more work on chelating ligands is necessary before accurate p.q.s. values can be assigned to them, especially from *cis*-compounds.

Also it should be realized that as the p.q.s. value of ligand A approaches that of CO, then the predicted q.s. values converge to those of *cis*- and *trans*-$Fe(CO)_4X_2$ (or FeA_4X_2). Thus for ligands like PPh_2Me (p.q.s. = $-0{\cdot}58$ mm s^{-1}) it is difficult to distinguish between isomers. For example, as seen in Table 7, compound 16, the difference in predicted q.s. for structures 4 and 6 is less than 0·10 mm s^{-1}.

Apart from the *cis*-$Fe(CO)_4X_2$ compounds discussed previously, the major area of disagreement between predicted and observed quadrupole splittings concerns the $Fe(CO)_2I_2L_2$ compounds (L = ArNC, PPh_2Et, and PPh_2Me; Table 7, compounds 6, 14, and 16), all of which have substantially smaller quadrupole splittings than those predicted. For PPh_2Me and PPh_2Et, the iodide has a quadrupole splitting which is *ca.* 0·2 mm s^{-1} smaller than the analogous chloride and bromide. The very similar p.q.s. values for Cl, Br, and I, and the very similar quadrupole splittings for the $Fe(CO)_2X_2(dppe)$ compounds [q.s. = 0·61 (Cl), 0·63 (Br), and 0·64 (I)] suggest that large differences in q.s. between analogous halide compounds would not be expected unless there is a substantial structural change.

This structural change is made more apparent by the series $Fe(CO)_4I_2$, $Fe(CO)_3I_2PPh_2Et$, and $Fe(CO)_2I_2(PPh_2Et)_2$ [q.s. = (—)0·30 mm s^{-1}, (—)0·46 mm s^{-1}, and (—)0·37 mm s^{-1} respectively] in which successive substitution of CO by PPh_2Et along the *Z*-axis of the electric-field gradient would lead one to expect a consistent increase in magnitude of V_{zz}. Instead, we obtain a marked decrease for the disubstituted derivative. Using $P(OPh)_3$ as a ligand, we obtained both the bromide and iodide monosubstituted derivatives $Fe(CO)_3X_2[P(OPh)_3]$ which have very similar quadrupole splittings of 0·27 mm s^{-1} and 0·33 mm s^{-1} respectively. However, the disubstituted derivatives still show the same pronounced difference: for X = Cl, Br, and I, q.s. = 0·50 mm s^{-1}, 0·48 mm s^{-1}, and 0·31 mm s^{-1} respectively.

These results indicate that the disubstituted iodides have the all-*cis*-structure (Table 5, structure 6) rather than the *trans*-phosphine structure (Table 5, structure 4) of the chlorides and bromides. *If* this is so, the agreement between predicted and observed quadrupole splittings for compounds 6, 14, and 16 in Table 7 is satisfactory.

Unfortunately we have not been able to obtain other evidence for this structural change. *X*-Ray powder photographs of the three $Fe(CO)_2X_2(PPh_2Me)_2$ (X = Cl, Br, or I) compounds were taken: all three compounds gave different line patterns and no relevant information could be obtained. As stated previously, all three compounds gave similar ^1H n.m.r. triplet patterns in $CHCl_3$ and benzene, presumably indicating *trans*-PPh_2Me groups for all three compounds in solution. A frozen solution (in benzene) Mössbauer spectrum of $Fe(CO)_2I_2(PPh_2Me)_2$ gave the same quadrupole splitting as in the solid state. The last two pieces of evidence indicate that the above compound has the *trans*-PPh_2Me structure both in the solid state and in solution. However, the triplet n.m.r. pattern could be due to *cis*-phosphines or phosphites,[9] and it is possible that a true glass was not formed in benzene, *i.e.*, microcrystals were formed. The structure of these iodides must thus be considered somewhat of an open question at present though the p.q.s. treatment does indicate the all-*cis*-structure.

Predicted and observed quadrupole splittings for compound 5 and compound 19 are also not in satisfactory agreement. The CO i.r. spectrum indicates that these compounds have structure 1 in Table 5. It is noteworthy that agreement between predicted and observed quadrupole splittings is improved for compound 5 if it had structure 3, Table 5; however, the agreement is not improved for compound 19. The latter results show that discrepancies of up to 0·30 mm s^{-1} can occur and that structural assignments must be made in conjunction with other techniques.

Finally, the close agreement between predicted and observed quadrupole splittings for *cis*-$Fe(NCS)_2(ArNC)_4$ and the internal consistency of the quadrupole splittings for our NCS compounds strongly support the suggestion made previously that the NCS derivatives are all the same linkage isomer, *i.e.*, isothiocyanates. Further, the excellent agreement between predicted and observed quadrupole splittings for the PMe_3 compounds (compounds 3 and 4, Table 7) confirm the p.q.s. assignment of $-0{\cdot}66$ mm s^{-1} from *cis*-$Fe(NCS)_2[PMe_3]_4$, and also support the assignment of the above compound as *cis* from the i.r. spectra (Table 3).

Bonding.—As we have discussed previously [1] partial centre shifts (p.c.s.) can usually be derived and successfully used to correlate centre shift values. Because we

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[29] N. E. Erickson, Ph.D. Thesis, University of Washington, 1964.

[30] R. E. B. Garrod, Ph.D. Thesis, University of Cambridge, 1970.

have derived our centre shifts at 80 K with respect to sodium nitroprusside, we use the expression (1).

$$\text{c.s.} = 0{\cdot}22 + \sum_{i=1}^{6} (\text{p.c.s.})_i\,* \qquad (1)$$

Before deriving p.c.s. for a number of the neutral ligands in this study, it is desirable to have a p.c.s. value for CO. If *trans*-$Fe(CO)_4(SnCl_3)_2$ is used as a standard reference compound, the p.c.s. of carbonyl = —0·01 mm s^{-1}. The use of this value to predict the c.s. of the substituted carbonyl compounds $Fe(CO)_2X_2[PR_3]_2$ is unsuccessful, since the observed values are significantly (0·15—0·30 mm s^{-1}) smaller than the predicted ones. Thus the effective p.c.s. of CO is now —0·10($\pm$ 0·05) mm s^{-1}, a measure of the significant increase in π-back-bonding and σ-donation of carbonyl in $Fe(CO)_2X_2[PR_3]_2$ type compounds compared with *trans*-$Fe(SnCl_3)_2(CO)_4$. Indeed the variation of the p.c.s. of carbonyl is comparable with the difference in p.c.s. of the halogens and, for example isocyanide, ligands of widely differing bonding characteristics. We thus take the $(\text{p.c.s.})_{CO}$ of —0·01 as an upper limit.

For the ligands PPh_2Me, PPh_2Et, PPh_3, $P(OPh)_3$, $AsPh_3$, and $SbPh_3$ we cannot obtain p.c.s. values directly from the c.s. values of the carbonyl compounds because of the widely varying bonding characteristics of CO and $(\text{p.c.s.})_{CO}$. However, we infer approximate p.c.s. values for these ligands by comparison of the $Fe(CO)_2X_2(dppe)$ (X = Cl, Br, or I) and $Fe(CO)_2X_2(ArNC)_2$ c.s. values with the analogous compounds of the above neutral ligands. The $AsPh_3$ and $SbPh_3$ compounds always give substantially larger c.s. values than the dppe analogues, and the p.c.s. value for these ligands must be substantially larger than 0·07 mm s^{-1}. We set a lower limit of 0·09 mm s^{-1}. On the other hand the PPh_2Me, PPh_2Et, and PPh_3 compounds give very similar c.s. values to their dppe analogues and we assign them the same p.c.s. value as dppe, 0·07 mm s^{-1}. The $Fe(CO)_2X_2[P(OPh)_3]_2$ compounds give c.s. values between the ArNC and dppe analogues, and we arbitrarily set a p.c.s. value of 0·05 mm s^{-1} for $P(OPh)_3$, although it may well be lower than this.

Both p.q.s. and p.c.s. values can now be related qualitatively to the σ- and π-bonding characteristics of ligands [1] by proportionalities (2) and (3).

$$\text{p.c.s.} \propto -(\sigma + \pi) \qquad (2)$$

$$\text{p.q.s.} \propto -(\sigma - \pi) - q_{\text{lattice}} \qquad (3)$$

A plot of p.c.s against p.q.s. for the neutral ligands in Tables 6 and 9 is shown in the Figure. Since this is a plot of $-(\sigma + \pi)$ against $(\pi - \sigma)$ (neglecting q_{lattice} for the neutral ligands) a slope in the positive sense indicates σ-dominance, whereas a negative slope shows π-dominance. (A correlation in either sense may arise through a greater sensitivity of the Mössbauer experiment to π- or σ-effects, or chemically because one is the dominant bonding interaction.) The Figure shows an approximately straight-line correlation of positive slope for most of the neutral ligands, with the clear exceptions of carbonyl, isocyanide, and the phosphites, which deviate in the direction expected for more prominent π effects. This line is not a least-squares fit since there is no *a priori* reason to expect a linear correlation between $(\sigma + \pi)$ and $(\sigma - \pi)$, and we have simply drawn a line with minimum slope which would be expected for a σ dependence plot. Thus we may conclude that π-back-bonding is much more important for the ligands CO, ArNC, and phosphites than for the other ligands in this study, but that generally σ-bonding is dominant in determining both the c.s. and q.s. Indeed, the bonding characteristics of trimethyl and triethyl phosphite are distinctly different from any other phosphine and phosphite used in this work. $P(OMe)_3$ and $P(OEt)_3$ appear to be strong π-acceptors and strong σ-donors, closely resembling isocyanide rather than other tertiary phosphines and $P(OPh)_3$. Further chemical consequences of this will be discussed elsewhere.[31]

TABLE 9

Partial centre shifts/mm s^{-1} at 80 K

Ligand	P.c.s.	Footnote	Ligand	P.c.s.	Footnote
NO^+	—0·20	*a*	PMe_3	0·06	*d*
H^-	—0·08	*a*	NH_3	0·07	*a*
CO	$<$ —0·01	*b*	dppe/2	0·07	*e*
ArNC	0·00	*a*	PPh_2Me	~0·07*	*e*
CN^-	0·01	*a*	PPh_2Et	~0·07*	*f*
$P(OMe)_3$	0·03	*c*	PPh_3	~0·07*	*f*
$P(OEt)_3$	0·04	*c*	N_3^-	0·08	*a*
$SnCl_3^-$	0·04	*a*	$AsPh_3$	$>$0·09	*f*
$P(OPh)_3$	~0·05*	*f*	$SbPh_3$	$>$0·09	*f*
(dmpe)/2	0·05	*a*	H_2O	0·10	*a*
NCS^-	0·05	*a*	Cl^-	0·10	*a*
NCO^-	0·06	*a*	Br^-	0·13	*a*
(depe)/2	0·06	*a*	I^-	0·13	*a*
(depb)/2	0·06	*a*			

* Error at least 0·02 mm s^{-1}. The other values should have an error of 0·01 mm s^{-1}.

[a] Ref. 1. [b] From the c.s. of *trans*-$Fe(CO)_4(SnCl_3)_2$. [c] From the c.s. of *trans*-$Fe(NCS)_2[P(OR)_3]_4$. [d] From the c.s. of *cis*-$Fe(NCS)_2(PMe_3)_4$. [e] From the c.s. of *cis*-$Fe(NCS)_2(dppe)_2$. [f] By comparison of $Fe(CO)_2X_2L_2$ (L = PPh_2Me, PPh_2Et, PPh_3, $P(OPh)_3$, $AsPh_3$, and $SbPh_3$) centre shifts with $Fe(CO)_2X_2(dppe)$ and $Fe(CO)_2X_2(ArNC)_2$ centre shifts.

The suggestion earlier that (dppe)/2 should have a more positive p.q.s. than —0·68 is made more apparent by the fact that by use of this value dppe deviates significantly from the plot of p.c.s. against p.q.s.

Since p.q.s. $\propto -(\sigma - \pi)$, an *increase* in π-back-bonding or *decrease* in σ-donation will lead to a more positive value of the p.q.s. If, in $Fe(CO)_4X_2$, the carbonyls *trans* to iodide become better π-acceptors relative to those *trans* to carbonyl, then the relative magnitudes of the p.f.g. (and p.q.s.) values for CO_c and CO_t should be $[CO_c] > [CO_t]$, whereas if the carbonyls *trans* to carbonyl

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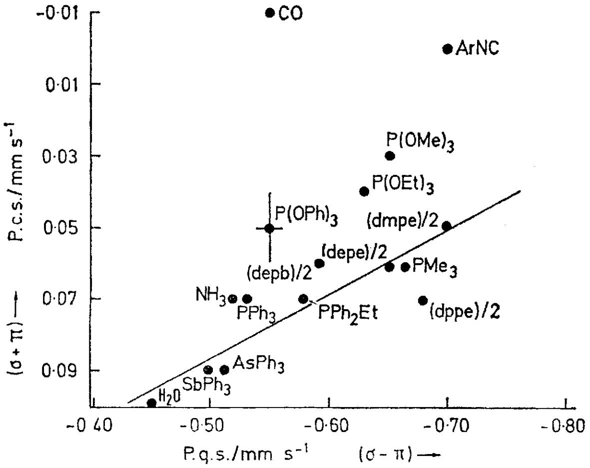
* The previous values were derived at room temperature w.r.t. stainless steel. Sodium nitroprusside has become the usual standard (add 0·16 mm s^{-1}) and for most of our compounds the chemical sift increases 0·06 $\pm$ 0·02 mm s^{-1} from 295 °K to 80 °K. To keep the same p.c.s. values as given previously, we thus use the 0·06 + 0·16 = 0·22 mm s^{-1} as a standardizing factor.

[31] G. M. Bancroft and E. T. Libbey, *J.C.S. Dalton*, in the press.

are poorer σ-donors than those *trans* to iodide, then $[CO_t] > [CO_c]$. Clearly, the usual π-bonding arguments do not explain the p.q.s. values for CO_c and CO_t (= $-0{\cdot}60$ mm s^{-1} and $-0{\cdot}53$ mm s^{-1} respectively). Fenske *et al.*[32] have studied *cis*-$Fe(CO)_4I_2$ and the variation of the 5σ and $2\pi_x, 2\pi_y$ orbital populations on the two distinguishable pairs of carbonyls. They have shown that the carbonyls *trans* to iodide have smaller 5σ (1·293) and larger 2π (0·252 + 0·285) populations than the carbonyls *trans* to themselves ($5\sigma = 1{\cdot}337$, $2\pi_x + 2\pi_y = 0{\cdot}221 + 0{\cdot}221$). Thus, CO_t is a poorer σ-donor *and* poorer π-acceptor than CO_c. The p.q.s. values for *cis*- and *trans*-CO groups indicate that the variation in σ donation of the CO groups is dominant in determining the more positive p.q.s. value for *trans*-CO. This result is consistent with the rationalization of the Figure given above in terms of dominant σ-effects. A recent paper[33] discusses further the bonding in $Fe(CO)_4I_2$.



Plot of partial centre shift (p.c.s.) against partial quadrupole splitting (p.q.s.) for neutral ligands. The errors on both are at least ±0·01 mm s^{-1} (see Tables), represented by the bars on the $P(OPh)_3$ position

In Table 10, we have calculated Cotton–Kraihanzel[18] force constants for some compounds of the type $Fe(CO)_2X_2L_2$. The force constant should increase with increased π-acceptor ability of L and decrease with increased σ-donor ability of L.[20,32] The higher values for phosphites probably indicate their more pronounced π-acceptor ability relative to phosphines as postulated earlier by Graham[20] and as suggested by the correlation of p.c.s. with p.q.s. given in the Figure.

Finally, it is interesting to comment on the comparatively invariable nature of p.q.s. values compared with p.c.s. values of strong π-acceptor ligands such as CO. As noted above, the p.q.s. values are proportional to σ — π. Since an increase in σ-donation causes an increase in π-acceptance (and *vice versa*), the two effects will tend to cancel out to give a reasonably constant p.q.s. value no matter what other ligands are present. In contrast, p.c.s. values decrease with both increased σ-donation and π-acceptance, and the above synergic bondings reinforce each other in decreasing the p.c.s. of CO markedly.

TABLE 10

Cotton–Kraihanzel force constants

Compound	Force constant/ mdyn/Å ±0·02
$Fe(CO)_2Cl_2(P(OPh)_3)_2$	16·92
$Fe(CO)_2Br_2(P(OPh)_3)_2$	16·84
$Fe(CO)_2Br_2(P(OMe)_3)_2$	16·77
$Fe(CO)_2I_2(P(OPh)_3)_2$	16·72
$Fe(CO)_2Cl_2(PPh_3)_2$	16·45
$Fe(CO)_2Cl_2(PPh_2Me)_2$	16·38
$Fe(CO)_2Br_2(PPh_3)_2$	16·37
$Fe(CO)_2Br_2(PPh_2Me)_2$	16·34
$Fe(CO)_2I_2(PPh_2Me)_2$	16·20
cis-$Fe(CO)_2I_2(PMe_3)_2$	16·10

Conclusion.—Mössbauer spectroscopy has proved valuable in discussing structure and bonding in iron(II) compounds containing three different ligands. The position of carbonyl, in particular, has been studied and its bonding characteristics related to theoretical calculations and i.r. stretching frequencies.

It has been possible to show that trimethyl phosphite and isocyanide have very similar bonding properties, thus suggesting further experimental work in the field of preparative chemistry.[31]

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[3/230 *Received, 2nd February*, 1973]

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