Organonitriles as Ligands in Low-spin Di[1,2-bis(diethylphosphino)-ethane]iron Complexes

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The complex *trans*-[$FeCl_2(depe)_2$] [depe = 1,2-bis(diethylphosphino)ethane] reacts with organonitriles, RCN, to give 1 : 1 complexes of the type *trans*-[FeCl(NCR)$(depe)_2$]$^+$ which have been isolated as their tetraphenylborate salts. When R = alkyl the 2 : 1 complexes *trans*-[$Fe(NCR)_2(depe)_2$]$^{2+}$ are also formed. The reaction of the dinitriles, malononitrile (maln), 1,2-dicyanobenzene (dcb), and succinonitrile (sucn) have also been studied. I.r. and Mössbauer spectra for a selection of these complexes have been recorded and are discussed in an attempt to assess the relative importance of the σ-donor and π-acceptor properties of the various ligands in determining their co-ordinating ability.

ORGANONITRILES, RCN, generally co-ordinate to transition-metal ions *via* σ donation of the lone pair of electrons on the nitrile nitrogen atom and the i.r. frequency due to the nitrile group, ν(CN), is generally raised (by up to 50 cm^{-1}) on co-ordination.[1] Certain metals in low oxidation states, however, form bonds in which back donation of electrons from metal *d* orbitals into orbitals of π symmetry on the nitrile ligands is thought to play an important part. In such complexes ν(CN) is generally lowered on co-ordination.[2-6] In this latter type of complex, organonitriles exhibit rather similar bonding properties to dinitrogen, and organonitrile analogues of dinitrogen complexes can generally be prepared.[5,6] A recent n.m.r. study, however, showed that different organonitriles vary quite considerably in their ability to accept π-electron density from metal atoms, depending on the nature of the group R.[7] In order to explore these bonding differences further we have studied the reaction of a number of different organonitriles with the complex *trans*-[$FeCl_2(depe)_2$] [depe = 1,2-bis(diethylphosphino)-ethane]. This complex was chosen because it was known to form a stable dinitrogen complex,[8] [{$(depe)_2ClFe$}$_2$-N_2]$^{2+}$, and because the resulting organonitrile complexes could be studied by Mössbauer spectroscopy, a technique which is capable of yielding information about the relative importance of σ- and π-bonding properties of ligands.[9-11]

RESULTS AND DISCUSSION

Preparation and I.r. Spectra of the Complexes.—The reaction between MeCN and *trans*-[$FeCl_2(depe)_2$] in the mol ratio 1 : 1 produced purple *trans*-[FeCl(NCMe)-$(depe)_2$]$^+$, the tetraphenylborate salt of which was characterised as a 1 : 1 electrolyte. The ν(CN) peak appeared in the i.r. spectrum (Table 1) at 2 242 cm^{-1} which represents a reduction of 12 cm^{-1} from the free-ligand value. This is fairly typical of the reduction found in other organonitrile complexes for which dinitrogen analogues can be prepared.[3]

TABLE 1

Colours, conductivities, and i.r. spectra (cm^{-1}) [a] of the complexes

Complex [b]	Colour	Λ [c]	ν(CN) (complex)	ν(CN) (free ligand)	ν(CN) [d]
trans-[FeCl(NCMe)$(depe)_2$]$^+$	Purple	71	2 242m	2 254	−12
trans-[FeCl(NCPh)$(depe)_2$]$^+$	Orange	71	2 179m	2 231	−52
trans-[FeCl(dcb)$(depe)_2$]$^+$	Red	68	2 170m, 2 230w	2 230	−60, 0
trans-[$Fe(NCMe)_2(depe)_2$]$^{2+}$	Yellow	146	2 254w	2 254	0
trans-[$Fe(NCCH_2CO_2Me)_2(depe)_2$]$^{2+}$	Yellow	144	2 255w	2 256	−1
trans-[$Fe(NCCH_2Ph)_2(depe)_2$]$^{2+}$	Yellow	143			
trans-[FeCl(maln)$(depe)_2$]$^+$	Pink	74	2 224m, 2 157m	2 278	−54, −121
trans-[{$(depe)_2ClFe$}$_2$(sucn)]$^{2+}$	Purple	115 [e]	2 217	2 257	−40
trans-[$Fe(sucn)_2(depe)_2$]$^{2+}$	Cream	137	2 236w, 2 222 (sh)	2 257	−21, −35

[a] Nujol mull. [b] All as the [BPh_4]$^-$ salt. [c] In units of S cm^2 mol^{-1} measured on 10^{-3}M solutions in nitromethane at 298 K. [d] ν(CN) (complex) − ν(CN) (free ligand). [e] Λ = 185 S cm^2 mol^{-1} in acetone.

The addition of an excess of acetonitrile to the dichloride complex gave the same purple solution from which the monocation had been isolated. With this quantity of ligand, however, the addition of Na[BPh_4] in methanol gave an immediate yellow precipitate of the complex *trans*-[$Fe(NCMe)_2(depe)_2$][BPh_4]$_2$ which was recrystallised from acetone and shown to be a 2 : 1 electrolyte. The appearance of a single weak band in the i.r. spectrum at 2 254 cm^{-1} attributable to ν(CN) suggested the *trans* configuration for the complex, and this assignment is confirmed by its Mössbauer spectrum (see below). The fact that the value of ν(CN) in this complex is higher than that in the monocation can be attributed in part at least to the greater formal charge on the metal ion. Di(nitrile) complexes of Ru^{II} such as *trans*-[$Ru(NH_3)_4(NCPh)_2$]$^{2+}$ also show higher values of ν(CN)

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than corresponding mono(nitrile) complexes,[2] however, and, since in this case the mono and bis complexes carry the same positive charge, the higher values in the bis complexes probably also reflect increased competition for metal *d* electrons.

The cations *trans*-$[Fe(NCR)_2(depe)_2]^{2+}$ (R = $PhCH_2$ or $MeO_2C{\cdot}CH_2$) were prepared in a similar way to the corresponding MeCN complex by addition of an excess of the ligand to a methanol solution of *trans*-$[FeCl_2(depe)_2]$ under argon. In the case of the phenylacetonitrile adduct no absorption occurred in the i.r. spectrum at *ca.* 2 250 cm^{-1}, although microanalysis and conductivity data confirmed the complex as a di(nitrile) and 2 : 1 electrolyte. The low intensity or even absence of the ν(CN) absorption in organonitrile complexes, however, is a feature which has been observed previously.[12]

The addition of an excess of PhCN to a solution of *trans*-$[FeCl_2(depe)_2]$ gave *trans*-$[FeCl(NCPh)(depe)_2]^+$ rather than the dications obtained under these conditions with R = alkyl. This difference in behaviour can be attributed in part to the greater π-acceptor strength when R = aryl, as evidenced by the greater reduction in ν(CN) on co-ordination, and by n.m.r. data on related organonitrile complexes of ruthenium.[7] The Mössbauer data, however, indicate that differences in σ-donor properties when R = alkyl or aryl are probably more important than differences in π-acceptor properties. It may be, therefore, that the fact that dications are only formed when R = alkyl reflects the greater ability of such nitriles to neutralise the increased formal charge on the metal atom.

The reaction of succinonitrile (sucn) with *trans*-$[FeCl_2(depe)_2]$ in 1 : 2 mol ratio gave *trans*-$[\{(depe)_2ClFe\}_2(sucn)]^{2+}$, whereas an excess of the ligand gave *trans*-$[Fe(sucn)_2(depe)_2]^{2+}$. Malononitrile (maln), however, gave only the monosubstituted cation *trans*-$[FeCl(depe)_2(maln)]^+$ at all ligand : complex ratios. The failure to give a bridged complex may be steric in origin, but the inability of this ligand to form a disubstituted complex is more difficult to account for. In this context, however, the i.r. spectrum of the monosubstituted complex is probably significant. The two ν(CN) peaks appeared at 2 224 (free) and 2 157 cm^{-1} (co-ordinated), which represent reductions of 54 and 121 cm^{-1} respectively from the free-ligand value. This is by far the largest reduction recorded for a σ-bonded nitrile complex and suggests that it might well exhibit unusual bonding properties. Reductions of up to 200 cm^{-1} have been reported but these are postulated to result from π bonding of the nitrile through the C≡N triple bond.[13] The Mössbauer data for this complex, however, are not markedly different from those recorded for the other complexes investigated by this technique.

The reaction of 1,2-dicyanobenzene (dcb) with *trans*-$[FeCl_2(depe)_2]$ in 1 : 1 mol ratio (or with excess of ligand) gave red *trans*-$[FeCl(dcb)(depe)_2]^+$. A 1 : 2 ratio failed to give a bridged binuclear complex, presumably again for steric reasons.

Mössbauer Spectra.—In octahedral low-spin Fe^{II} complexes the isomer shift (i.s.) can be expressed qualitatively as a function of the σ-donor and π-acceptor properties of the ligands,[11,14] and it can be shown that i.s. $\propto -(\sigma + \pi)$. For complexes of the type *trans*-$[FeABC_4]$ the quadrupole splitting (q.s.) can be expressed similarly in the form q.s. $\propto (\pi - \sigma)$. In a series of complexes, such as *trans*-$[FeClL(depe)_2]^+$, where only one ligand, L, is varying these two equations can in principle be used to assess the relative importance of σ and π effects for different L ligands. Before this can be done, however, it is necessary to ascertain the sign of the quadrupole splittings for each complex in the series. Although we have not attempted to measure any signs it is possible to deduce these by a comparison of the magnitude of observed quadrupole splittings with those calculated making use of the concept of partial quadrupole splittings (p.q.s.).[9,11] This comparison is presented in Table 2 with the calculated values being obtained using the p.q.s. values given in ref. 11. We assumed that dcb may be assigned the same p.q.s. value as PhCN and that sucn may be assigned the same value as MeCN. The greatest difference between the observed and calculated values is 0·1 mm s^{-1}, with the exception of the dcb complex. This represents extremely good agreement, particularly in view of the fact that previous work has indicated that the agreement between observed and calculated values is generally not as good for cationic and anionic as for neutral complexes.[14] The discrepancy in the case of the dcb complex suggests, perhaps not unreasonably, that the assumption that its p.q.s. value is the same as that of PhCN is not valid. Since the sign of the calculated q.s. values is in each case positive, the close agreement with the observed values provides convincing evidence that these also are positive. It also shows that the complexes do possess the assumed *trans* configuration. In the case of $[Fe(NCMe)_2(depe)_2]^{2+}$ the calculated q.s. value for the *cis* form is 0·44 mm s^{-1}, which differs by nearly 0·5 mm s^{-1} from the observed value for the *trans* form.

TABLE 2

^{57}Fe Mössbauer parameters (mm s^{-1}) [a]

Complex	δ	Obs.	Calc.[b]
trans-$[\{(depe)_2ClFe\}_2(sucn)]^{2+}$	0·58	1·17	+1·14
trans-$[FeCl(NCPh)(depe)_2]^+$	0·55	1·12	+1·02 [c]
trans-$[FeCl(dcb)(depe)_2]^+$	0·51	0·74	+1·02 [d]
trans-$[Fe(NCMe)_2(depe)_2]^{2+}$	0·53	0·93	+0·88
trans-$[FeCl(maln)(depe)_2]^+$	0·55	0·90	
trans-$[FeCl(NO)(depe)_2]^+$	0·26	2·15	+2·04

[a] All isomer-shift values are quoted relative to $Na_2[Fe(CN)_5NO]$ at 295 K with the sample at *ca.* 80 K. Linewidth at half height *ca.* 0·3 mm s^{-1}. [b] From p.q.s. values at 80 K given in ref. 11. [c] P.q.s. value for PhCN calculated from data in ref. 13. [d] P.q.s. value for dcb assumed to be the same as for PhCN.

Previous work on the series of complexes $[FeHL(depe)_2]^+$ [L = RCN, $(RO)_3P$, or RNC] revealed a positive linear correlation between i.s. and q.s. values for the

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different L ligands, suggesting that σ effects were dominant in determining the i.s. and q.s.[10,11] For N_2 and CO the observed parameters indicated that π effects were relatively more important. Our work shows that there is also a positive correlation between i.s. and q.s. in the related series $[FeClL(depe)_2]^+$ where L is a series of organonitrile ligands. For comparative purposes Mössbauer data for $[FeCl(NO)(depe)_2]^+$ are also included in Table 2. This complex, which contains the very good π-acceptor ligand NO^+, has the lowest i.s. and highest q.s. value in the Table. Thus again π effects are relatively much more important for this type of ligand than for the different organonitriles studied. It would have been of considerable interest to compare also the Mössbauer parameters for the organonitrile complexes with those of the dinitrogen complex *trans*-$[\{(depe)_2ClFe\}_2N_2]^{2+}$. Unfortunately, the Mössbauer spectrum of this latter complex gave only a broad unresolvable peak from which meaningful data could not be obtained.

The conclusion to be drawn from the Mössbauer results presented here is that changes in σ-donor properties of the different organonitrile ligands studied are important in accounting for the observed differences in their coordinating ability. However, the relative sensitivity of the Mössbauer parameters to changes in σ- and π-bonding properties of ligands has not yet been determined satisfactorily, and the i.r. results suggest that changes in the π-acceptor properties of the ligands must also be taken into account.

TABLE 3

Analytical data (%)

Complex	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
trans-$[FeCl(NCMe)(depe)_2][BPh_4]$	64·1	8·1	1·6	64·0	8·2	1·6
trans-$[FeCl(NCPh)(depe)_2][BPh_4]$	66·4	8·1	1·4	66·0	7·9	1·5
trans-$[FeCl(dcb)(depe)_2][BPh_4]$	65·9	7·6	2·7	65·8	7·6	2·9
trans-$[Fe(NCMe)_2(depe)_2][BPh_4]_2$	72·2	7·7	2·3	72·2	7·8	2·3
trans-$[Fe(NCCH_2CO_2Me)_2(depe)_2][BPh_4]_2$	69·7	7·4	2·1	70·0	7·5	2·1
trans-$[Fe(NCCH_2Ph)_2(depe)_2][BPh_4]_2$	75·6	7·5	2·3	75·8	7·7	2·1
trans-$[FeCl(maln)(depe)_2][BPh_4]$	64·3	7·6	2·9	64·0	7·9	3·2
trans-$[\{(depe)_2ClFe\}_2(sucn)][BPh_4]_2$	63·7	7·7	1·9	64·0	8·1	1·6
trans-$[Fe(sucn)_2(depe)_2][BPh_4]_2$	72·3	7·8	4·9	72·0	7·6	4·4

EXPERIMENTAL

All preparations and reactions were carried out under an atmosphere of argon using degassed methanol (AnalaR) as solvent. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer with carbon monoxide as calibrant and are quoted to an accuracy of ±1 cm^{-1}. ^{57}Fe Mössbauer spectra were obtained with a ^{57}Co source in palladium and an experimental arrangement already described.[15] I.s. values are quoted relative to disodium pentacyanonitrosylferrate(2−). All spectra were fitted without constraints to Lorentzian line shapes by techniques already described.[16]

Preparations.— (*Acetonitrile*)*di*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloroiron tetraphenylborate*. The complex *trans*-$[FeCl_2(depe)_2]$ (0·10 g, 0·19 mmol) was dissolved in MeOH (20 cm^3) under argon with rigorous exclusion of air. Acetonitrile (0·01, 0·2 mmol) was added from a microsyringe whereupon the orange solution immediately became pale purple. The solution was stirred for 5 min and $Na[BPh_4]$ (0·15 g, 0·44 mmol) in degassed methanol (5 cm^3) was then added quickly. A purple *solid* was slowly deposited and this was centrifuged off and dried *in vacuo*. The air-sensitive complex was stored under nitrogen, yield 0·123 g, (77%). The analogous complexes containing the ligands benzonitrile, 1,2-dicyanobenzene, and malononitrile were prepared in an identical manner. The yields were respectively 94, 81, and 44%.

trans-μ-*Succinonitrile-bis*{*di*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloroiron*} *bistetraphenylborate*. This was prepared in an identical manner to *trans*-$[FeCl(NCMe)(depe)_2][BPh_4]$ except that succinonitrile (0·008 g, 0·1 mmol) was added to *trans*-$[FeCl_2(depe)_2]$ (0·1 g, 0·19 mmol) to give a 1 : 2 mol ratio of reactants, yield 83%.

trans-*Di*(*acetonitrile*)*di*[1,2-*bis*(*diethylphosphino*)*ethane*]*iron bistetraphenylborate*. A ten-fold excess of acetonitrile (0·10 g, 2 mmol) was added to the orange solution formed by dissolving *trans*-$[FeCl_2(depe)_2]$ (0·10 g, 0·10 mmol) in methanol (20 cm^3). This resulted in an immediate purple colouration. After stirring for 5 min under argon, $Na[BPh_4]$ (0·20 g, 0·58 mmol) in methanol (10 cm^3) was added, bringing about immediate precipitation of a cream solid. This was filtered off and recrystallised from acetone to give air-stable yellow *plates* of the complex, yield 0·172 g (78%). The analogous complexes containing the ligands phenylacetonitrile, methoxycarbonylacetonitrile, and succinonitrile were prepared in an identical manner. The respective yields were 84, 77, and 55%. The ligands benzonitrile, 1,2-dicyanobenzene, and malononitrile gave only the 1 : 1 complexes under these conditions.

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