Cationic Low-spin Bis[1,2-bis(dialkylphosphino)ethane]iron(II) Complexes†

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The complexes *trans*-$[FeCl_2(depe)_2]$ and *trans*-$[FeCl_2(dmpe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$, dmpe = $Me_2PCH_2CH_2PMe_2$) dissolve in acetonitrile and methanol to give 1 : 1 electrolytes. In methanol solution *trans*-$[FeCl_2(depe)_2]$ reacts rapidly with a variety of π-acceptor ligands to yield cations of the type *trans*-$[FeCl(L)(depe)_2]^+$ [L = CO, NO^+, RCN, $\frac{1}{2}N_2$, and $P(OMe)_3$] which have been isolated as their tetraphenylborate or chloride salts. In acetone solution the neutral complexes react much more slowly and with a reduced range of ligands L. Where reaction does take place (L = CO or RNC) a mixture of *cis* and *trans* isomers is obtained and these have been isolated. The complex *trans*-$[FeI_2(depe)_2]$ is insoluble in methanol, but a suspension of the complex in this solvent reacts slowly with CO to give a mixture of *cis*- and *trans*-$[Fe(CO)I(depe)_2]^+$. Other complexes of the type *trans*-$[FeX_2(depe)_2]$ (X = NCO or NCS) do not react with CO in methanol. I.r. and Mössbauer spectra have been recorded for some of the complexes and enable the stereochemistry of the complexes to be assigned.

WE have previously reported[1] a series of cationic complexes of the type *trans*-$[FeH(L)(depe)_2]^+$ [L = CO, N_2, RCN, RNC, or $P(OR)_3$; depe = 1,2-bis(diethylphosphino)ethane] derived from the hydrido-complex *trans*-$[FeCl(H)(depe)_2]$. These complexes were of interest in that a Mössbauer study enabled the bonding properties of dinitrogen to be compared with those of other ligands.[2] It is known that the bonding of dinitrogen in a metal complex is extremely sensitive to the nature of the other ligands present,[3] and in order to study this problem systematically it was thought to be of interest to attempt the preparation of a further series of cationic iron(II) complexes with a different ligand *trans* to L. We have therefore re-examined the properties of the complexes *trans*-$[FeCl_2(dmpe)_2]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] and *trans*-$[FeCl_2(depe)_2]$, first described by Chatt and Hayter.[4] It was hoped that these complexes would provide a suitable starting point for the synthesis of cations of the type *trans*-$[FeX(L)(P\text{–}P)_2]^+$ (P–P = depe or dmpe; X^- = Cl^-, I^-, NCO^-, *etc.*). In this paper the synthesis of a number of such complexes in which X = Cl is described and also one complex in which X = I. In some cases complexes with *cis* stereochemistry have also been isolated. Some iron(0) and ruthenium(II) nitrosyl complexes, both stabilised by depe, are also described. I.r. and Mössbauer studies have enabled the stereochemistry of the iron(II) complexes to be assigned. Since the completion of our experimental work, a paper has been published[5] in which several bis[*o*-phenylenebis(dimethylarsine)]iron(II) complexes analogous to the depe and dmpe complexes are described.

RESULTS AND DISCUSSION

Preparation and Infra-red Spectra.—In reporting the complexes *trans*-$[FeCl_2(P\text{–}P)_2]$ (P–P = dmpe or depe), Chatt and Hayter[4] stated that they were rapidly decomposed by alcohols. However, under an argon atmosphere it was found that these green complexes dissolve in methanol to give orange solutions and are 1 : 1 electrolytes in this solvent. The complexes also dissolve in acetonitrile, again as 1 : 1 electrolytes, to give purple solutions. Both solutions yielded the red iron(III) cations $[FeCl_2(P\text{–}P)_2]^+$ on exposure to the

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† No reprints available.

[1] G. M. Bancroft, M. J. Mays, B. E. Prater, and E. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2146.

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

[3] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.

[4] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 5507.

[5] T. E. Nappier, R. D. Feltham, J. H. Enemark, A. Kruse, and M. Cooke, *Inorg. Chem.*, 1975, **14**, 806.

slightest amount of oxygen. We previously [6] described the purple salt *trans*-[FeCl(NCMe)(depe)$_2$][BPh$_4$], and hence interpret the solution behaviour of the complexes in terms of equilibrium (1) (S = MeOH or MeCN).

$$\textit{trans}\text{-}[\mathrm{FeCl_2(P{-}P)_2}] \underset{-\mathrm{S}}{\overset{+\mathrm{S}}{\rightleftharpoons}} \textit{trans}\text{-}[\mathrm{FeCl(S)(P{-}P)_2}]^+ + \mathrm{Cl}^- \quad (1)$$

This was partially confirmed by the fact that the original green complexes were regenerated from the coloured solutions on removal of the solvents *in vacuo*. The position of equilibrium lies far to the right in all cases and the dissociation is presumably facilitated by the combined cation- and anion-solvating abilities of acetonitrile and methanol.[7] The complexes do not dissolve in water but were soluble in acetone and in the non-polar solvents benzene and light petroleum to give non-conducting green solutions. The orange methanol solutions of *trans*-[FeCl$_2$(depe)$_2$] reacted rapidly with π-acceptor ligands under an atmosphere of argon. Thus passage of CO for 10 min followed by removal of the solvent *in vacuo* gave yellow *trans*-[Fe(CO)Cl(depe)$_2$]Cl. The ν(CO) i.r. band for this complex at 1 906 cm^{-1} (Table 1) is 4 cm^{-1} higher than that for the corresponding iodo-complex (see below), and this is consistent with the greater electron-withdrawing ability of Cl$^-$ as the *trans* ligand. The corresponding hydrido-complex [1] shows a band at 1 915 cm^{-1} attributable mainly to ν(CO), but this vibration is almost certainly coupled to ν(Fe–H) [8] and is therefore not directly comparable.

TABLE 1

Conductivities, microanalytical data, and i.r. spectra

Complex	Λ [a]	I.r. bands [b] (cm^{-1})	Analysis (%) Found C	H	N	Calc. C	H	N
trans-[{FeCl(depe)$_2$}$_2$N$_2$][BPh$_4$]$_2$	134	ν(N$_2$) 2 081w	64.2	8.2	1.6	63.2	8.2	1.6
trans-[FeCl{P(OMe)$_3$}(depe)$_2$][BPh$_4$]		ν(PO) 1 190m	59.9	8.2		59.6	8.1	
trans-[FeCl(NO)(depe)$_2$][BPh$_4$]$_2$	141	ν(NO) 1 839	69.7	7.3	1.2	69.6	7.5	1.2
trans-[FeCl(NO)(depe)$_2$][[FeCl$_4$]$_2$		ν(NO) 1 843	26.0	5.4	1.4	25.8	5.2	1.5
[Fe(NO)(depe)$_2$][BPh$_4$]	74	ν(NO) 1 683	64.4	8.2	1.7	64.6	8.3	1.7
trans-[RuCl(depe)$_2$][PF$_6$]$_2$	172	ν(NO) 1 843	27.8	5.3	1.7	27.7	5.5	1.6
trans-[Fe(CO)Cl(depe)$_2$]Cl	81	ν(CO) 1 906	36.1	7.9		37.0	8.5	
trans-[Fe(CO)Cl(dmpe)$_2$][BPh$_4$]		ν(CO) 1 938	60.1	7.3		60.0	7.1	
cis-[Fe(CO)Cl(dmpe)$_2$][BPh$_4$]	50	ν(CO) 1 979	59.9	7.2		60.0	7.1	
trans-[Fe(CNBu^t)Cl(dmpe)$_2$][BPh$_4$]	53	ν(NC) 2 091	62.7	8.3	1.9	62.2	7.7	1.8
cis-[Fe(CNBu^t)Cl(dmpe)$_2$][BPh$_4$]		ν(NC) 2 124	62.1	8.2	1.3	62.2	7.7	1.8
trans-[Fe(CO)I(depe)$_2$]I	79	ν(CO) 1 902	28.6	6.2		28.0	6.4	
cis-[Fe(CO)I(depe)$_2$]I		ν(CO) 1 935						

[a] In units of S cm^2 mol^{-1}; measured on 10^{-3} mol dm^{-3} solutions in nitromethane at 298 K. [b] Nujol mulls. All bands were strong unless otherwise indicated.

The addition of trimethyl phosphite to an orange solution of *trans*-[FeCl$_2$(depe)$_2$] in methanol resulted in an immediate red colouration. Addition of Na[BPh$_4$] in methanol gave red needles of the complex *trans*-[FeCl{P(OMe)$_3$}(depe)$_2$][BPh$_4$]. The complex *trans*-[FeCl$_2$(depe)$_2$] dissolves in nitrogen-saturated methanol to give a red solution. Addition of Na[BPh$_4$] in methanol to this solution slowly resulted in red-orange needles of the air-sensitive complex *trans*-[{FeCl(depe)$_2$}$_2$N$_2$][BPh$_4$]$_2$ which was shown to be a 2 : 1 electrolyte in nitromethane solution. The rather high carbon analysis for this salt (Table 1) may be due to trace amounts of Na[BPh$_4$], which are difficult to wash away without loss of nitrogen from the complex. A weak ν(N$_2$) band (Nujol mull) in the i.r. spectrum of this complex must arise from solid-state effects, since a centrosymmetric bridged dinitrogen complex would otherwise show no such absorption. However, attempts at obtaining a Raman spectrum were unsuccessful because of decomposition. Although H$^-$ is a better σ donor than Cl$^-$, the ν(N$_2$) i.r. band at 2 081 cm^{-1} observed for *trans*-[{FeCl(depe)$_2$}$_2$N$_2$][BPh$_4$]$_2$ is at a lower wavenumber than that for *trans*-[FeH(N$_2$)(depe)$_2$]$^+$ (2 090 cm^{-1}). This can be explained in terms of the bridging character of the dinitrogen ligand in the former complex, but it may also be that ν(N$_2$) in the hydrido-complex is anomalously high due to ν(Fe–H)–ν(N$_2$) coupling.

On passage of NO through a solution of *trans*-[FeCl$_2$(depe)$_2$] in methanol containing Na[BPh$_4$] a green colouration developed after a few minutes. A golden-yellow precipitate analysing for [FeCl(NO)(depe)$_2$][BPh$_4$]$_2$* then formed and was filtered off. This moderately air-sensitive complex showed an i.r. band at 1 839 cm^{-1} due to ν(NO), suggesting that it is analogous to the complex *trans*-[Fe(pdma)$_2$Cl)][ClO$_4$]$_2$ reported recently by Nappier *et. al.*[5] [pdma = *o*-phenylenebis(dimethylarsine)]. For this latter complex ν(NO) is at 1 860 cm^{-1}. The designation of the depe complex as an octahedral {FeNO}^{6} system [9] containing Fe$^{\mathrm{II}}$ and a linearly co-ordinated nitrosyl group is strongly supported by its Mössbauer spectrum (see below). The depe complex was also prepared as an [FeCl$_4$]$^-$ salt by refluxing a mixture of iron(III) chloride, sodium nitrite, and depe in ethanol–chloroform (1 : 3) solution. The slightly higher ν(NO) wavenumber (1 843 cm^{-1}) for this salt is probably the result of anion interference.[10] The tetraphenyl-

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* The cation of this complex was incorrectly written as [FeCl(NO)(depe)$_2$]$^+$ in a previous paper (ref. 6).

[6] J. M. Bellerby and M. J. Mays, *J.C.S. Dalton*, 1975, 1281.

[7] A. J. Parker, *Chem. Rev.*, 1969, 69.

[8] L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 4100.

[9] R. D. Feltham and J. H. Enemark, *Co-ordination Chem. Rev.*, 1973, **13**, 339.

[10] C. A. Reed and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 3054.

borate salt was characterised as a 2 : 1 electrolyte in nitromethane and was additionally prepared in almost quantitative yield from the tetrachloroferrate salt by addition of Na[BPh_4] to *trans*-[FeCl(NO)(depe)$_2$][$FeCl_4$]$_2$ in methanol.

The corresponding ruthenium complex *trans*-[RuCl(NO)(depe)$_2$][PF_6]$_2$ was prepared by refluxing an NO-saturated solution of $RuCl_3 \cdot 3H_2O$ with depe under nitrogen for 2 d. The yellow complex (a 2 : 1 electrolyte in nitromethane) precipitated out following the addition of [NH_4][PF_6] in methanol. The ν(NO) frequency at 1 843 cm^{-1} is very close to that of the analogous iron complex (see above) and suggests that the cations have identical structures. Refluxing a methanol solution of *trans*-[$FeCl_2$(depe)$_2$] with sodium nitrite for 10 min produced a pale brown solution. Addition of Na[BPh_4] in methanol then gave a precipitate which analysed for [Fe(NO)(depe)$_2$][BPh_4] and was shown to be a 1 : 1 electrolyte in nitromethane. The 1,2-bis(diphenylphosphino)ethane (dppe)[11] and pdma[4] analogues of this complex are both known and the latter has been designated as an {FeNO}[8] system. The position of the ν(NO) band in the i.r. spectrum of the depe complex (1 683 cm^{-1}) is close to that of the same band in [Fe(pdma)$_2$(NO)]$^+$ (1 710 cm^{-1}) and in [Ru(NO)(dppe)$_2$]$^+$ (1 673 cm^{-1}). The structure of the last complex has been determined[12] and the similarity of the i.r. spectra suggests that [Fe(NO)(depe)$_2$]$^+$ also has a trigonal-bipyramidal structure with a linearly co-ordinated nitrosyl group in an equatorial position. The complexes *trans*-[FeX_2(depe)$_2$] (X = I, NCO, and NCS)[13] did not undergo substitution by NO in methanol to give nitrosyl derivatives. Instead they were oxidised to the corresponding iron(III) cations [FeX_2(depe)$_2$]$^+$.

The reactions of the complexes *trans*-[$FeCl_2$(P–P)$_2$] with π-acceptor ligands were slower in acetone than in methanol. The ligands N_2, RCN, and P(OMe)$_3$ did not react with *trans*-[$FeCl_2$(depe)$_2$] in this solvent. Passage of CO through a solution of *trans*-[$FeCl_2$(dmpe)$_2$] and Na[BPh_4] in acetone, however, produced a bright yellow colouration after *ca.* 1 h. Following removal of the solvent and recrystallisation, yellow plates of *cis*-[Fe(CO)Cl(dmpe)$_2$][BPh_4] were isolated together with a small amount of the red *trans* isomer. The latter was obtained in greater yield by refluxing a solution of *trans*-[$FeCl_2$(dmpe)$_2$] under CO in acetone for 5 h, followed by the addition of Na[BPh_4] in acetone. The isomers were distinguished by their i.r. and Mössbauer spectra (see below). The ν(CO) band appeared at 1 979 cm^{-1} in the i.r. spectrum of the yellow *cis* isomer and at 1 938 cm^{-1} in that of the red *trans* isomer. This is in keeping with the relative π-acceptor abilities of the ligands *trans* to CO in each case (phosphine and chloride respectively). The two isomers could not be interconverted suggesting that, once co-ordinated, the ligands are non-labile. Such inertness is not unexpected for iron(II) low-spin complexes. Both *cis*- and *trans*-[Fe(CNBu^t)Cl(dmpe)$_2$]-[BPh_4] were obtained by the action of Bu^{t}NC on a solution of *trans*-[$FeCl_2$(dmpe)$_2$] and Na[BPh_4] in acetone. The mixture was stirred under nitrogen for 2 h and, following removal of the solvent and the subsequent recrystallisation, crystals of the two isomers were separated by hand-picking. The ν(NC) band appeared at 2 091 cm^{-1} in the i.r. spectrum of the orange *trans* isomer and at 2 124 cm^{-1} in that of the golden-yellow *cis* isomer; this separation in frequencies is less than for the carbonyl isomers. Mono- and di-substituted organo-nitrile derivatives of *trans*-[$FeCl_2$(depe)$_2$], some analogous to the complexes described herein, have already been reported.[6]

Unlike *trans*-[$FeCl_2$(depe)$_2$], the yellow complex *trans*-[FeI_2(depe)$_2$] did not dissolve in methanol. However, prolonged reaction (12 h) of CO with a suspension of the complex in methanol gave a bright yellow solution. Removal of the solvent gave a solid, the i.r. spectra of which showed ν(CO) bands at 1 902 and 1 935 cm^{-1} which are presumably due to the *cis* and *trans* isomers respectively of [Fe(CO)I(depe)$_2$]I. No attempt was made to separate the isomers, but microanalytical results for the mixture were consistent with this formulation. In addition, the mixture behaved as a 1 : 1 electrolyte in nitromethane. Neither *trans*-[Fe(NCS)$_2$(depe)$_2$] nor *trans*-[Fe(NCO)$_2$(depe)$_2$] reacted with CO in methanol even under reflux.

Mössbauer Spectra.—The usefulness of Mössbauer spectroscopy in determining the stereochemistry of octahedral low-spin iron(II) complexes has been demonstrated in recent years.[14] The concept of partial quadruple splittings (p.q.s) developed in the early work of Bancroft *et al.*[13] has enabled values for the quadrupole splittings (q.s.) of new complexes to be calculated from tabulated p.q.s. values for the constituent ligands.[14] In favourable cases a comparison of this calculated value with the observed value can lead to an assignment of the stereochemistry of the complex. This is particularly useful in a series of isomeric complexes (*e.g.* $FeA_2B_2C_2$) where i.r. studies are unable to distinguish between isomers.[15] In other cases the Mössbauer results can provide corroborative evidence.

In complexes of the type $FeABC_4$ a comparison of observed and calculated quadrupole splittings can provide an unambiguous method for distinguishing between *cis* and *trans* isomers in cases where the difference between the q.s. magnitudes for the two isomers is greater than the margin of error in their calculation (±0.2 mm s^{-1}). For *cis* complexes $\eta \neq 0$ * and it is necessary to determine this for each complex from a knowledge of V_{zz}, V_{xx}, and V_{yy} derived from p.q.s. values of the ligands A, B, and C (see ref. 16). Once

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* η (the asymmetry parameter) = $(|V_{yy}| - |V_{xx}|)/V_{zz}$, where V_{yy} is the component of the electric-field gradient along the *y*-axis, *etc.* By convention the axes are chosen so that $V_{zz} \geqslant V_{yy} \geqslant V_{xx}$.

[11] B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1972, 1268.

[12] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1088.

[13] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

[14] G. M. Bancroft, *Co-ordination Chem. Rev.*, 1973, **11**, 247.

[15] G. M. Bancroft and E. T. Libbey, *J.C.S. Dalton*, 1973, 2103.

[16] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

this is done it is possible to calculate q.s.(*cis*) using the formula (2). The calculation of q.s.(*trans*) is simplified

$$\text{q.s.} = V_{zz}[1 + (\eta^2/3)]^{\frac{1}{2}} \qquad (2)$$

by the fact that for *trans* complexes $\eta = 0$ and hence q.s.(*trans*) $= V_{zz}$. Using Bancroft's argument,[6] q.s.(*trans*) can be expressed as in equation (3).

$$\text{q.s.}(\textit{trans}) = V_{zz} = 2(\text{p.q.s.})_A + 2(\text{p.q.s.})_B - 4(\text{p.q.s.})_C \qquad (3)$$

Table 2 presents data for several new complexes of the type *cis*- and *trans*-$[FeCl(L)(P{-}P)_2]^+$ prepared in this study. In cases where only one isomer has been isolated ($L = NO^+$ or PhCN; P–P = depe) a comparison of the calculated and observed q.s. values strongly supports the *trans* formulation in each case. There is good agreement, in both cases within ±0.2 mm s^{-1}, and q.s.(*cis*) is considerably less than q.s.(*trans*) in both examples. No attempt was made to measure the signs of the observed quadrupole splittings. However, we feel that agreement between the magnitudes of the observed and calculated values is sufficiently good to justify our assuming that the sign for all the complexes is positive.

TABLE 2

Iron-57 Mössbauer parameters (mm s^{-1})

Complex[a]	Q.s. obs.[b]	Q.s. calc.[c]	Remarks
trans-$[FeCl(NCPh)(depe)_2]^+$	1.12	1.02[d]	q.s.(*cis*) calc. = 0.62 (η 0.52)
trans-$[FeCl(NO)(depe)_2]^{2+}$	2.15	2.02	q.s.(*cis*) calc. = −1.14 (η 0.92)
trans-$[Fe(CO)Cl(dmpe)_2]^+$	0.88	1.10	
cis-$[Fe(CO)Cl(dmpe)_2]^+$	0.72	0.70	(η 0.70)

[a] All as $[BPh_4]^-$ salts. [b] Measured at 77 K. [c] From p.q.s. values in ref. 14. [d] From ref. 6.

For the complexes *cis*- and *trans*-$[Fe(CO)Cl(dmpe)_2]^+$ the situation is not so clear cut since the observed q.s. values differ by less than 0.2 mm s^{-1}. However, it is possible to argue that since the value of $(\text{p.q.s.})_{CO}$ used in calculating the q.s. value was derived from data on *trans*-$[Fe(CO)_4(SnCl_3)_2]$,[15] then this value (−0.55 mm s^{-1}) is strictly applicable only in complexes where CO is *trans* to itself or another good π acceptor. This is the situation in *cis*-$[Fe(CO)Cl(dmpe)_2]^+$ (where CO is *trans* to phosphine) and therefore it is perhaps not surprising that there is excellent agreement between the observed and calculated q.s. values for this complex. Where CO is *trans* to a poor π acceptor {*e.g.* Cl^- in *trans*-$[Fe(CO)Cl(dmpe)_2]^+$} there will be a change in its p.q.s. value. It is possible to show[15] that there is a decrease in $(\text{p.q.s.})_{CO}$ relative to cases where it is *trans* to a good π acceptor. In such instances Bancroft suggested that a value of −0.6 mm s^{-1} for $(\text{p.q.s.})_{CO}$ might be more appropriate. Using such a value in recalculating q.s.(*trans*) from equation (3) gives 1.0 mm s^{-1} which is closer to the observed value of 0.88 mm s^{-1} (Table 2). While perhaps in itself not unambiguous, the assignment of the *cis* and *trans* isomers of $[Fe(CO)Cl(dmpe)_2]^+$ made on the basis of Mössbauer data is clearly in support of the i.r. evidence (see above). Unfortunately the Mössbauer spectrum of the bridged dinitrogen complex *trans*-$[\{FeCl(depe)_2\}_2N_2]^{2+}$ was impossible to interpret because of the broadness of the peaks.

EXPERIMENTAL

All preparations and reactions were carried out under an atmosphere of argon using degassed methanol as solvent, unless otherwise stated. In all cases AnalaR solvents were used without further purification. 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}. Iron-57 Mössbauer spectra were obtained with a ^{57}Co source in palladium and an experimental arrangement already described.[17] All spectra were fitted without constraints to Lorentzian lineshapes by techniques already described.[18] Conductivities were measured in nitromethane using a Wayne–Kerr Universal Bridge.

Preparations.—trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]-*carbonylchloroiron*(II) *chloride*. The complex *trans*-$[FeCl_2(depe)_2]$ (0.050 g, 0.09 mmol) was dissolved in CO-saturated methanol (20 cm^3) under an atmosphere of carbon monoxide to give a bright yellow solution. Carbon monoxide was passed through this solution for another 10 min after which the solution was filtered and the solvent removed *in vacuo* to yield yellow crystals of the product, yield 0.040 g (77%).

trans-μ-*Dinitrogen-bis*{*bis*[1,2-*bis*(*diethylphosphino*)*ethane*]-*chloroiron*(II)} *bis*(*tetraphenylborate*). The complex *trans*-$[FeCl_2(depe)_2]$ (0.20 g, 0.37 mmol) was dissolved with stirring in methanol (25 cm^3) under nitrogen to give a red solution. While maintaining the nitrogen atmosphere, $Na[BPh_4]$ (0.150 g, 0.44 mmol) in methanol was added slowly to this solution and after a few minutes red-orange needles of the complex began to separate out. These were removed by centrifuging and dried *in vacuo*. The air-sensitive crystals could be stored without decomposition under dry nitrogen, yield 0.203 g (67%).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloro*(*trimethyl phosphite*)*iron*(II) *tetraphenylborate*. The complex *trans*-$[FeCl_2(depe)_2]$ (0.170 g, 0.32 mmol) was dissolved with stirring in methanol (25 cm^3). When all the solid had dissolved to give an orange solution, trimethyl phosphite (0.2 cm^3) was added and the solution was stirred for another 0.5 h. Sodium tetraphenylborate (0.150 g, 0.44 mmol) in methanol (5 cm^3) was then added to the now red solution and on cooling red needles were deposited. The air-sensitive crystals were removed by centrifuging and dried *in vacuo*, yield 0.123 g (41%).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloronitrosyl*-*iron*(II) *bis*[*tetrachloroferrate*(III)]. Iron(III) chloride (0.50 g,

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[17] G. M. Bancroft, A. G. Maddock, and J. Ward, *Chem. and Ind.*, 1965, 423.

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

3 mmol) was suspended in a mixture of ethanol (15 cm^3) and chloroform (45 cm^3) under nitrogen. Sodium nitrite (0.069 g, 1 mmol) was added followed by depe (0.4 cm^3, 2 mmol), this final addition resulting in a deep magenta colour. The mixture was heated under reflux under nitrogen for 2.5 h, after which time the colour had become dull yellow. The solution was then filtered quickly under nitrogen while still hot, and on cooling the filtrate yellow crystals separated out. These were filtered off and dried *in vacuo*. The moderately air-sensitive complex was stored under an atmosphere of dry nitrogen, yield 0.610 g (84%).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloronitrosyliron*(II) *bis*(*tetraphenylborate*). *Method* (*a*). The salt *trans*-$[\text{FeCl(NO)(depe)}_2][\text{FeCl}_4]_2$ (see above) (0.150 g, 0.2 mmol) was dissolved in methanol (20 cm^3) under nitrogen. Sodium tetraphenylborate (0.30 g, 0.88 mmol) in methanol (10 cm^3) was added whereupon an immediate yellow precipitate was obtained. This was filtered off and recrystallised from acetone to yield orange plates of the complex. The solid slowly decomposes in air but is stable under an atmosphere of nitrogen, yield 0.231 g (96%).

Method (*b*). The complex *trans*-$[\text{FeCl}_2(\text{depe})_2]$ (0.150 g, 0.28 mmol) was dissolved with stirring in methanol (30 cm^3). Sodium tetraphenylborate (0.250 g, 0.73 mmol) in methanol (10 cm^3) was added and NO was immediately bubbled through the solution (before any precipitate could form). After a few minutes the solution became green and a yellow solid precipitated out. This was filtered off and the complex was recrystallised from acetone as before, yield 0.129 g (39%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*nitrosyliron*(0) *tetraphenylborate*. The complex *trans*-$[\text{FeCl}_2(\text{depe})_2]$ (0.10 g, 0.19 mmol) was dissolved in methanol (20 cm^3). Sodium nitrite (0.020 g, 0.29 mmol) was added and the solution was heated under reflux under argon for 10 min. After cooling to room temperature, the solution was centrifuged and $\text{Na[BPh}_4]$ (0.150 g, 0.44 mmol) in methanol (5 cm^3) was added. Brown platelets of the complex separated out on cooling and were filtered off and stored under nitrogen, yield 0.097 g (64%).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloronitrosylruthenium*(II) *bis*(*hexafluorophosphate*). The salt $\text{RuCl}_3{\cdot}3\text{H}_2\text{O}$ (0.260 g, 1 mmol) was dissolved in methanol (50 cm^3) and NO was bubbled through the mixture for 12 h, resulting in a plum-red solution. 1,2-Bis(diethylphosphino)ethane (0.4 cm^3, 2 mmol) was added from a syringe and the mixture was heated under reflux under nitrogen for 2 d. After cooling to room temperature the solution was filtered and the volume reduced by half by removing some of the solvent *in vacuo*. Ammonium hexafluorophosphate (0.50 g, 3 mmol) in methanol (10 cm^3) was then added slowly to this solution and a yellow solid separated out. After further cooling the solid was filtered off and the complex recrystallised from methanol to give yellow needles, yield 0.780 g (90%).

cis- *and* trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*carbonyliodoiron*(II) *iodide*. The complex *trans*-$[\text{FeI}_2(\text{depe})_2]$ (0.050 g, 0.07 mmol) was dissolved in methanol (20 cm^3) during the course of 12 h under a slow stream of carbon monoxide. The solution was filtered and the solvent removed under a stream of nitrogen to yield an orange solid comprising a mixture of the isomers, as deduced from micro-analytical and i.r. data. No attempt was made to separate the isomers, total yield 0.031 g (60%).

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*carbonylchloroiron*(II) *tetraphenylborate*. The complex *trans*-$[\text{FeCl}_2(\text{dmpe})_2]$ (0.40 g, 0.94 mmol) was dissolved in acetone (50 cm^3) which had been saturated with carbon monoxide. Sodium tetraphenylborate (0.30 g, 0.94 mmol) dissolved in CO-saturated acetone (10 cm^3) was added to the solution with continued passage of CO. The green colour gave way immediately to bright yellow and a cloudiness developed. The CO was bubbled for another hour after which the solution was filtered and the solvent removed *in vacuo*. The yellow complex was recrystallised from acetone–light petroleum to give a mixture containing predominantly the *cis* isomer, crystals of which were isolated by hand-picking, yield 0.37 g (*cis* complex only) (54%).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*carbonylchloroiron*(II) *tetraphenylborate*. The complex *trans*-$[\text{FeCl}_2(\text{dmpe})_2]$ (0.40 g, 0.9 mmol) was dissolved in refluxing acetone (30 cm^3) which had been saturated with carbon monoxide and through which the gas was still being passed. Refluxing was continued for another 5 h during which time the solution changed colour from green to orange. The solution was cooled to room temperature and $\text{Na[BPh}_4]$ (0.30 g, 0.94 mmol) dissolved in CO-saturated acetone (10 cm^3) was added slowly. An immediate cloudiness developed but the colour of the solution remained the same. After filtering, the solvent was removed *in vacuo* and the residue recrystallised from dichloromethane to give red plates of the *trans* complex plus a small amount of the *cis* complex, yield 0.426 g (*trans* complex only) (62%).

cis- *and* trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(t-*butyl isocyanide*)*iron*(II) *tetraphenylborate*. The complex *trans*-$[\text{FeCl}_2(\text{dmpe})_2]$ (0.40 g, 0.94 mmol) was dissolved in acetone (50 cm^3) under nitrogen. t-Butyl isocyanide (0.8 cm^3, 1 mmol) was added to the solution and no immediate colour change was detectable. Sodium tetraphenylborate (0.30 g, 0.94 mmol) in acetone (10 cm^3) was added whereupon the green colour gave way to yellow and a cloudiness developed. The solution was stirred under nitrogen for a further 2 h and then filtered. The solvent was removed *in vacuo* and the residue recrystallised from acetone–light petroleum to give a mixture of crystals comprising the yellow *trans* complex and the red *cis* complex. The crystals were separated by hand-picking, total yield 0.637 g (86%).

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