Isolation and Characterisation of Iron(II) Complexes with Dinitrogen, and of other Derivatives, especially from Phenylacetylene†

David L. Hughes, G. Jeffery Leigh,* Manuel Jimenez-Tenorio and Adrian T. Rowley
AFRC Institute of Plant Science Research Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK

The complex [$FeCl_2(dmpe)_2$] (dmpe = $Me_2PCH_2CH_2PMe_2$) dissolves in alcohols under dinitrogen to yield the dinitrogen complex [$FeCl(N_2)(dmpe)_2$]$^+$. Reactions of [$FeCl_2(dmpe)_2$] with PhC≡CH yield the interconvertible acetylide and vinylidene complexes [FeCl(C≡CPh)(dmpe)$_2$] and [FeCl(C=CHPh)(dmpe)$_2$]$^+$, the structures of which have been determined. Related complexes of $Et_2PCH_2CH_2PEt_2$ have been prepared, as well as similar complexes containing ligands such as MeNC, CO, *etc*.

Iron complexes containing dinitrogen have been known for a considerable time, but they have generally failed to produce interesting dinitrogen chemistry.[1] The exceptions, where ammonia is produced, involve heavily reduced systems and reagents such as lithium dihydronaphthylide, and such systems are far removed from the circumstances which might prevail in an aqueous enzyme.[2] Nevertheless, the characterisation of a nitrogenase apparently containing only iron of the transition metals[3] does suggest that iron in oxidation states normally accessible in aqueous media should be able to mediate the reduction of dinitrogen. This paper describes part of a search for such systems.

We have worked with iron(II) complexes because there are several reports of iron(II)-containing dinitrogen complexes. For example, reduction of $FeCl_2\cdot 2H_2O$ with $NaBH_4$ in the presence of tertiary phosphines PR_3 (R_3 = $EtPh_2$ or Bu^nPh_2) in ethanol produces tetrahydrides [$FeH_4(PR_3)_3$] which react with N_2 to yield [$FeH_2(N_2)(PR_3)_3$].[4] The parent complexes are now believed to be better represented as dihydridodihydrogen compounds, [$FeH_2(H_2)(PR_3)_3$].[5] In addition, [$FeH_2(N_2)(PMePh_2)_3$] has been mentioned but not fully characterised.[5]

Complexes with diphosphines are more stable on storage under N_2 than those with monophosphines, and several have been described. Thus, [FeH(Cl)(depe)$_2$] (depe = $Et_2PCH_2CH_2PEt_2$) reacts with $NaBPh_4$ in acetone under N_2 to yield [$FeH(N_2)(depe)_2$]$^+$.[6] On the other hand, [$FeH(N_2)(dppe)_2$]$^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$) was obtained by reaction of the five-co-ordinate species [FeH(dppe)$_2$]$^+$ with N_2 in tetrahydrofuran (thf)[7] and is apparently more stable than its depe homologue. The complexes [$FeH(N_2)\{P(CH_2CH_2PPh_2)_3\}$]$^+$,[8] [$FeH(N_2)\{N(CH_2CH_2PPh_2)_3\}$]$^+$,[8] and [$FeH(N_2)\{(Ph_2PCH_2CH_2PPhCH_2)_2\}$]$^+$ [9] have been described. Of all these hydrido(dinitrogen) complexes, just two, [$FeH_2(N_2)(PEtPh_2)_3$][10] and [$FeH(N_2)\{(Ph_2PCH_2CH_2PPhCH_2)_2\}$]$^+$,[9] have been structurally characterised.

Analogous complexes in which the H is replaced by Cl are apparently not so easy to prepare. However, it has been observed that green [$FeCl_2(depe)_2$] dissolves in methanol under N_2 to give an orange solution, from which a complex of supposed composition [$Fe_2Cl_2(N_2)(depe)_4$][BPh_4]$_2$ was isolated.[11] This shows a weak IR band at 2081 cm^{-1}, but it was found impossible to obtain satisfactory Raman or Mössbauer spectra.

We decided to reinvestigate the systems [FeH_2(diphosphine)$_2$] and [$FeCl_2$(diphosphine)$_2$] as possible precursors to dinitrogen complexes of iron with dinitrogen reactivity. This paper deals with halogeno-complexes. Some of this work has been published in preliminary form.[12]

Results and Discussion

We attempted to reproduce the observations reported for [$FeCl_2(depe)_2$] and found that its solutions in methanol do indeed take up dinitrogen. We were able to isolate beautiful orange crystals after addition of $NaBPh_4$, but the nitrogen content varied from preparation to preparation. Our best analyses corresponded to [$\{FeCl(depe)_2\}_2N_2$][BPh_4]$_2$, but these samples exhibited a strong ν(N_2) band at 2081 cm^{-1}. This is not typical of symmetrical bridging-dinitrogen compounds. We suspected that a complex [$FeCl(N_2)(depe)_2$][BPh_4] is involved, but were never able to prove this. The Mössbauer spectrum at 77 K (centre shift 0.26, quadrupole splitting 1.42 mm s^{-1}) indicates a single low-spin octahedral iron(II) centre.[13] This is clearly of no value for distinguishing between bridging and singly bound end-on dinitrogen complexes.

However, data obtained using the diphosphine dmpe ($Me_2PCH_2CH_2PMe_2$) were entirely unequivocal. The green, octahedral complex [$FeCl_2(dmpe)_2$][14] dissolves in tetrahydrofuran (thf) under N_2 to give a green solution. However, in alcohols, the colour ranges from orange to purple, depending upon concentration. Addition of $NaBPh_4$ in alcohol to such an alcoholic solution under N_2 gives a red crystalline solid, shown by microanalysis and ^{31}P NMR spectroscopy to be *trans*-[$FeCl(N_2)(dmpe)_2$][BPh_4]. This has a strong IR band at 2105 cm^{-1}, assignable to ν(N_2), which compares with 2090 cm^{-1} for [$FeH(N_2)(depe)_2$][BPh_4],[6] 2081 cm^{-1} for the supposed [$FeCl(N_2)(depe)_2$][BPh_4],[11] and 2130 cm^{-1} for [$FeH(N_2)(dppe)_2$][BPh_4].[7] The complex [$FeBr(N_2)(dmpe)_2$][BPh_4], ν(N_2) 2107 cm^{-1}, was synthesised analogously from [$FeBr_2(dmpe)_2$]. Neither of our new dinitrogen complexes produced ammonia upon treatment with acid.

The role of the solvent in facilitating the uptake of dinitrogen is striking. Chatt and Hayter[15] reported that [$FeCl_2(dmpe)_2$] and [$FeCl_2(depe)_2$] are rapidly decomposed by alcohols. However, we have found that these green complexes dissolve in alcohols under argon to give orange-purple solutions, and they behave then as 1:1 electrolytes. The original green solid

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

complexes are regenerated upon removing the solvent *in vacuo*. The preparation of $[FeCl(MeCN)(dmpe)_2]BPh_4$ in MeOH has been proposed to proceed *via* the intermediate $[FeCl(MeOH)(depe)_2]^+$.[16] If this is so, because we can isolate $[FeCl(N_2)(depe)_2]^+$ from such solutions then presumably N_2 can displace co-ordinated MeOH. Previously we had tried to prepare $[FeCl(N_2)(dmpe)_2]^+$ by reaction of $[FeCl_2(dmpe)_2]$ with either $AgBF_4$ or $TlBF_4$ in thf or toluene under N_2, but without success.[17] Clearly the solvent is of prime importance.

We have attempted to throw more light on this problem using ^{31}P-$\{^1H\}$ NMR spectroscopy. In thf or toluene at room temperature, under either Ar or N_2, $[FeCl_2(dmpe)_2]$ gives rise to a sharp singlet in the ^{31}P-$\{^1H\}$ NMR spectrum at δ −84.6, consistent with its formulation as *trans*-$[FeCl_2(dmpe)_2]$. The same complex in methanol at room temperature under Ar shows a broad band at δ −84.6, half-width 400 Hz. On cooling to −50 °C the spectrum changes reversibly to a sharp singlet at δ −80.4, half-width 14 Hz. An explanation could be that $[FeCl_2(dmpe)_2]$, like $[FeCl_2(depe)_2]$, apparently undergoes a spin-state change.[18] The mechanism, as discussed by Baker *et al.*,[18] could involve high-spin/low-spin cross-over, reversible loss of halide in solution, and partial or complete dissociation of a diphosphine. Apparently $[FeCl_2(dmpe)_2]$ is diamagnetic in $[^2H_8]$toluene at temperatures where $[FeCl_2(depe)_2]$ becomes paramagnetic. Baker *et al.*[18] suggest phosphine dissociation is likely. In our case, we believe that the non-appearance of line broadening with $[FeCl_2(dmpe)_2]$ in toluene or thf, and the line-broadening in methanol, are consistent with halide loss giving a labile five-co-ordinate species at room temperature, which changes to a five-co-ordinate square-pyramidal structure at −50 °C.

Furthermore, we found that treatment of $[FeCl_2(dmpe)_2]$ in methanol under Ar with $NaBPh_4$ gives low yields of a purple species analysing as $[FeCl(dmpe)_2]BPh_4$. This is consistent with the presence in methanol of the five-co-ordinate species $[FeCl(dmpe)_2]^+$, homologues of which have been already reported, *viz.* $[FeCl\{P(CH_2CH_2PPh_2)_3\}]^+$ and $[FeCl\{N(CH_2CH_2PPh_2)_3\}]^+$.[8] The alcohols might promote the formation of such species because they are stronger acids than HCl in these circumstances, and thus act as chloride-ion abstractors. It should be noted that the acid character of methanol, evident in the protonation of $[FeH_2(dmpe)_2]$ to give $[FeH_3(dmpe)_2]^+$,[19] has been very well substantiated.

We attempted to make iron–dinitrogen complexes with sulfur ligands by reaction of $K(S_2CNEt_2)$ in ethanol under N_2 with $[FeCl_2(dmpe)_2]$. In fact, we isolated not the hoped-for $[Fe(N_2)(S_2CNEt_2)(dmpe)_2]^+$, but $[Fe(S_2CNEt_2)(dmpe)_2]BPh_4$. ^{31}P-$\{^1H\}$ NMR spectroscopy (A_2B_2 system) confirmed that the diphosphines are here stereochemically *cis*.

The complexes $[FeX(N_2)(dmpe)_2]^+$ can be used to produce further complexes, by reactions involving loss of dinitrogen. Thus, CO in acetone yields a mixture of the known complexes *cis*- and *trans*-$[FeCl(CO)(dmpe)_2]^+$.[11] Previously these were prepared by direct reaction of CO with $[FeCl_2(dmpe)_2]$. We were never able to separate these isomers completely by crystallisation, though the characteristic ν(CO) bands in the IR spectrum at 1941 (*trans*) and 1969, 1979 cm^{-1} (*cis*) were clearly assignable. This latter splitting may be due to solid-state effects. The product of the reaction of CO with $[FeBr(N_2)(dmpe)_2]^+$ seems to be a single isomer, *trans*-$[FeBr(CO)(dmpe)_2]^+$. The tetraphenylborate salt shows a sharp singlet in the ^{31}P-$\{^1H\}$ NMR spectrum and a clean Mössbauer doublet, so that the two bands observed in the solid-state IR spectrum, 1942vs and 1967m (sharp) cm^{-1}, are likely to be due again to solid-state effects.

The reaction of $[FeCl(N_2)(dmpe)_2]BPh_4$ with MeNC likewise produces $[FeCl(CNMe)(dmpe)_2]BPh_4$. Consequently, the dinitrogen complexes are good starting materials for established and new iron(II) bis(diphosphine) derivatives.

Reactions of iron(II) complexes with acetylenes are also of interest to us in the context of nitrogenase chemistry. We have therefore also looked at the reaction of $[FeCl_2(dmpe)_2]$ with phenylacetylene in ethanol. Under N_2 or Ar, and in the presence of 1 molar equivalent of $NaBH_4$, the product was $[FeCl(CCPh)(dmpe)_2]^+$. This complex has been described by us in a preliminary communication,[12] and since has also been reported by others.[20] Its formulation was established by IR [ν(C≡C) at 2044 cm^{-1}] and ^{31}P-$\{^1H\}$ NMR (singlet at δ −75.5) spectroscopies, microanalysis, and finally by X-ray structure analysis. In analogous fashion we prepared $[FeBr(CCPh)(depe)_2]$ and $[FeCl(CCPr^i)(dmpe)_2]$.

The complex $[FeCl(CCPh)(dmpe)_2]$ is a yellow-orange solid, soluble in common organic solvents with the exception of hexane and alcohols. In contrast, $[FeBr(CCPh)(depe)_2]$ is red and, as might be expected, is more soluble in organic solvents. The methyl groups of the dmpe complex are not all equivalent since the methyl protons give rise to two signals in the ^1H NMR spectrum which, from the ^{31}P spectrum, are not due to P–H coupling. The Mössbauer parameters are consistent with the presence of low-spin octahedral iron(II). Both complexes are thermochromic, changing reversibly to bright yellow or yellow-green on cooling to −196 °C. There is no obvious change in the Mössbauer spectra between −196 °C and room temperature, so that the origin of this phenomenon presumably lies in the acetylide ligand.

The function of the borohydride in the preparative reactions is not clear. It is possible that $[FeH(Cl)(dmpe)_2]$, for example, is generated, and that this reacts with the acetylene to produce the acetylide and H_2. However, we do not know whether $[FeH(Cl)(dmpe)_2]$ is involved in the reaction of $[FeCl_2(dmpe)_2]$ with borohydride in methanol, which ultimately generates $[FeH_3(dmpe)_2]^+$. Probably in this system the borohydride produces an acetylide which then displaces chloride from the iron.

When $[FeCl_2(depe)_2]$ is treated with PhC≡CH in methanol the vinylidene complex $[FeCl(C{=}CHPh)(depe)_2]^+$ forms, apparently by a 1,2-hydrogen shift. We have prepared new iron–vinylidene complexes, $[FeCl(C{=}CHPh)(dmpe)_2]^+$, $[FeCl(C{=}CHPr^i)(dmpe)_2]^+$ and $[FeBr(C{=}CHPh)(depe)_2]^+$, by reaction of the corresponding acetylides with HCl or HBF_4. These green complexes were isolated as the chloride, iodide, or tetrafluoroborate salts.

The dmpe vinylidene complexes show IR bands at 1615 and 1593 cm^{-1}, assigned to ν(C=C) of the vinylidene and of the phenyl ring, respectively, and at 1636 cm^{-1} in the *iso*-propyl derivative. The corresponding values in the phenyl bromo-depe complex are *ca.* 1614 and 1587 cm^{-1}, which compare well with those in the chloro-depe complex (1609 and 1572 cm^{-1}).

The ^1H NMR spectrum of the phenyl dmpe complex as a tetrafluoroborate salt shows resonances assignable to all the protons, but the β-carbon proton of the vinylidene is observed as a quintet ($^4J_{PH}$ = 8.4 Hz) in CD_2Cl_2, and is not observable at all in CD_3OD. Evaporation of the solvent from such a solution leaves a green solid which has IR bands at 2080 and 2050 cm^{-1}, assignable to ν(CD). Clearly there is facile H/D exchange. The position of the ^1H resonance depends upon the solvent and the counter anion, a phenomenon which has been observed in compounds such as $[ReCl(C{=}CHPh)(dppe)_2]$.[21] For $[FeCl(C{=}CHPh)(dmpe)_2]Cl$ in CD_2Cl_2 the vinylidene proton resonates at δ 6.26, $^4J_{PH}$ = 7.8 Hz. The corresponding values for $[FeCl(C{=}CHPh)(depe)_2]^+$ are δ 4.29 (qnt), $^4J_{PH}$ = 4 Hz. In contrast, $[FeBr(C{=}CHPh)(depe)_2]^+$ shows only a broad resonance at δ 5.51, with no resolved coupling. The effective magnetic moment in solution in CD_2Cl_2 changes from 1.0 to 1.8 in the temperature range 223–293 K, so it is possible that there is a diamagnetic–paramagnetic equilibrium in this temperature range, similar to that observed for $[FeCl_2(depe)_2]$.[18]

The deprotonation of these vinylidene complexes can be effected with bases such as $LiBu^n$, to regenerate the acetylido-compounds. We were not able to alkylate the acetylides.

In formal terms, these vinylidene compounds contain

Table 1 Final atomic coordinates (fractional $\times 10^4$) for *trans*-[FeCl(CCPh)(dmpe)$_2$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Fe	1378.0(1)	2639.3(4)	86.8(4)
C(11)	952(1)	3328(4)	3470(3)
C(12)	613(1)	5230(3)	1116(4)
P(1)	863.6(2)	3388.7(8)	1458.6(7)
C(1)	383.7(9)	2152(3)	1069(3)
C(2)	335.1(8)	1784(3)	−582(3)
P(2)	868.5(2)	1147.2(7)	−1053.5(8)
C(21)	773(1)	1086(4)	−3062(3)
C(22)	860(1)	−849(3)	−571(4)
C(31)	2132(1)	3929(4)	2990(3)
C(32)	1759(1)	6265(3)	1160(4)
P(3)	1876.3(2)	4254.1(8)	1112.5(8)
C(3)	2348.5(9)	4221(4)	43(4)
C(4)	2422.2(9)	2603(3)	−420(4)
P(4)	1893.4(2)	1843.1(8)	−1254.1(8)
C(41)	1888(1)	2460(4)	−3175(3)
C(42)	2010(1)	−161(3)	−1410(4)
Cl(5)	1609.8(2)	754.7(8)	1891.7(8)
C(6)	1199.6(8)	4122(3)	−1366(3)
C(60)	1087.3(8)	5027(3)	−2305(3)
C(61)	966.6(9)	6088(3)	−3487(3)
C(62)	528(1)	6335(3)	−4017(3)
C(63)	416(2)	7329(4)	−5161(4)
C(64)	724(2)	8092(5)	−5801(4)
C(65)	1155(2)	7877(4)	−5310(4)
C(66)	1276(1)	6893(3)	−4167(3)

Table 2 Final atomic coordinates (fractional $\times 10^4$) for *trans*-[FeCl(C=CHPh)(dmpe)$_2$]I·EtOH with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Fe	2016(1)	1135.9(5)	2586.9(9)
P(1)	3648(2)	1788(1)	2540(2)
C(11)	3849(12)	2291(5)	3610(9)
C(12)	3767(12)	2225(5)	1363(9)
C(1)	5238(9)	1412(5)	2593(9)
C(2)	5125(11)	876(5)	1888(9)
P(2)	3630(3)	495(1)	2247(2)
C(21)	4252(12)	46(5)	3324(9)
C(22)	3360(13)	3(5)	1132(9)
P(3)	391(3)	486(1)	2763(2)
C(31)	668(12)	−140(5)	3555(9)
C(32)	−418(13)	226(5)	1566(8)
C(3)	−992(10)	834(5)	3422(9)
C(4)	−1144(10)	1414(5)	2996(9)
P(4)	439(2)	1776(1)	2998(2)
C(41)	458(13)	2108(6)	4299(8)
C(42)	120(11)	2368(4)	2104(8)
Cl(5)	2473(3)	1023(1)	4424(2)
C(6)	1574(7)	1217(3)	1239(6)
C(60)	1156(11)	1294(4)	289(7)
C(61)	1831(10)	1253(3)	−765(6)
C(62)	3203(8)	1174(3)	−834(7)
C(63)	3805(10)	1144(4)	−1809(7)
C(64)	3039(10)	1172(4)	−2720(7)
C(65)	1675(11)	1253(4)	−2684(7)
C(66)	1047(10)	1294(3)	−1677(7)
H(60)	58(102)	1382(37)	111(70)
I	7324.5(7)	3277.0(4)	4815.9(6)
Solvent (ethanol) molecule			
O(7)	7371(13)	3735(6)	2223(9)
C(7)	7014(17)	3313(6)	1598(15)
C(71)	6611(17)	3489(7)	562(10)

iron(IV), although this is not altogether expected for iron in a phosphine environment, and is discussed further in structural terms below. The Mössbauer centre shift is -0.04 mm s^{-1}, compared to $+0.16$ and $+0.22$ mm s^{-1} for the dmpe and depe acetylide complexes, respectively. Similarly, the quadrupole splitting is $+1.32$ mm s^{-1}, compared to $+0.44$ and $+0.32$ mm s^{-1}. The acetylido-complexes are in Mössbauer terms typical low-spin octahedral iron(II) compounds. The vinylidene complex is clearly different in terms of its quadrupole splitting, but this is more likely to be due to the vinylidene ligand than to a change at iron. There are no suitable literature data on iron(IV) species to make valid comparisons.

Table 3 Selected molecular dimensions (distances in Å, angles in °) in *trans*-[FeCl(CCPh)(dmpe)$_2$] with e.s.d.s in parentheses; angles marked with an asterisk have an e.s.d. less than 0.05°

(*a*) About the Fe atom

Fe–P(1)	2.219(1)	Fe–P(4)	2.216(1)
Fe–P(2)	2.215(1)	Fe–Cl(5)	2.389(1)
Fe–P(3)	2.222(1)	Fe–C(6)	1.897(3)
P(1)–Fe–P(2)	85.9*	P(3)–Fe–Cl(5)	91.4*
P(1)–Fe–P(3)	94.2*	P(4)–Fe–Cl(5)	88.6*
P(2)–Fe–P(3)	176.1*	P(1)–Fe–C(6)	90.7(1)
P(1)–Fe–P(4)	178.7*	P(2)–Fe–C(6)	87.5(1)
P(2)–Fe–P(4)	93.8*	P(3)–Fe–C(6)	88.6(1)
P(3)–Fe–P(4)	86.2*	P(4)–Fe–C(6)	90.5(1)
P(1)–Fe–Cl(5)	90.1*	Cl(5)–Fe–C(6)	179.1(1)
P(2)–Fe–Cl(5)	92.5*		

(*b*) In the acetylide ligand

C(6)–C(60)	1.192(3)	C(62)–C(63)	1.373(5)
C(60)–C(61)	1.442(4)	C(63)–C(64)	1.345(6)
C(61)–C(62)	1.398(4)	C(64)–C(65)	1.362(6)
C(61)–C(66)	1.386(4)	C(65)–C(66)	1.373(5)
Fe–C(6)–C(60)	178.4(2)	C(61)–C(62)–C(63)	120.6(3)
C(6)–C(60)–C(61)	177.1(3)	C(62)–C(63)–C(64)	121.3(4)
C(60)–C(61)–C(62)	121.0(3)	C(63)–C(64)–C(65)	119.6(4)
C(60)–C(61)–C(66)	122.3(3)	C(64)–C(65)–C(66)	120.4(4)
C(62)–C(61)–C(66)	116.7(3)	C(61)–C(66)–C(65)	121.4(3)

(*c*) Torsion angles in the dmpe ligands

P(1)–C(1)–C(2)–P(2)	50.0(2)
P(3)–C(3)–C(4)–P(4)	49.5(2)

One final reaction of [FeCl$_2$(dmpe)$_2$] and an acetylene is worthy of mention. With methyl propiolate in ethanol in the presence of NaBH$_4$ it yields a complex which we formulate as [Fe(CH=CHCOOMe)(dmpe)$_2$]$^+$. In this case the acetylene is reduced to a vinyl group, and the reaction is more characteristic of those of [FeH$_3$(dmpe)$_2$]$^+$ with acetylenes. These will be discussed elsewhere.

The structure of [FeCl(CCPh)(dmpe)$_2$] has already been reported by us in preliminary form[12] and subsequently reported in detail by others.[20] The structure of [FeCl(C=CHPh)(dmpe)$_2$]I·EtOH is reported here for the first time. Atomic coordinates for the two molecules are presented in Tables 1 and 2, and Tables 3 and 4 contain selected bond lengths and angles. Both molecules contain iron in an approximately octahedral co-ordination with the iron in the plane of the four ligating phosphorus atoms, and chloride *trans* to the acetylene residue (Figs. 1 and 2). The most obvious difference is that the acetylide residue is linear [Fe–C(6)–C(60) 178.4(2)°], with Fe–C(6) and C(6)–C(60) 1.897(3) and 1.192(3) Å, respectively, compared to the corresponding values of 174.9(7)°, 1.750(7), and 1.268(11) Å in the vinylidene residue. Further, upon protonation C(6)–C(60)–C(61) and C(60)–C(61) change from 177.1(3)° and 1.442(4) Å to 132.3(10)° and 1.498(12) Å, respectively. This is fully consistent with protonation converting the acetylide into vinylidene, causing a bend in the carbon skeleton from linear to a value approaching 120° and with corresponding shortening in the iron–carbon bond by about 0.15 Å as it becomes a double rather than single

Table 4 Selected molecular dimensions (distances in Å, angles in °) in *trans*-[FeCl(C=CHPh)(dmpe)$_2$]I·EtOH with e.s.d.s in parentheses

(*a*) About the Fe atom

Fe–P(1)	2.255(3)	Fe–P(4)	2.260(3)
Fe–P(2)	2.268(3)	Fe–Cl(5)	2.355(2)
Fe–P(3)	2.259(3)	Fe–C(6)	1.750(7)
P(1)–Fe–P(2)	86.8(1)	P(3)–Fe–Cl(5)	87.3(1)
P(1)–Fe–P(3)	175.9(1)	P(4)–Fe–Cl(5)	88.7(1)
P(2)–Fe–P(3)	94.0(1)	P(1)–Fe–C(6)	93.9(3)
P(1)–Fe–P(4)	92.7(1)	P(2)–Fe–C(6)	93.5(3)
P(2)–Fe–P(4)	177.6(1)	P(3)–Fe–C(6)	90.1(3)
P(3)–Fe–P(4)	86.4(1)	P(4)–Fe–C(6)	88.9(3)
P(1)–Fe–Cl(5)	88.7(1)	Cl(5)–Fe–C(6)	176.6(3)
P(2)–Fe–Cl(5)	88.9(1)		

(*b*) In the vinylidene ligand

C(6)–C(60)	1.268(11)	C(63)–C(64)	1.365(12)
C(60)–C(61)	1.498(12)	C(64)–C(65)	1.378(13)
C(61)–C(62)	1.387(12)	C(65)–C(66)	1.424(12)
C(61)–C(66)	1.378(12)		
C(62)–C(63)	1.374(12)	C(60)–H(60)	1.14(10)
Fe–C(6)–C(60)	174.9(7)	C(63)–C(64)–C(65)	121.3(9)
C(6)–C(60)–C(61)	132.3(10)	C(64)–C(65)–C(66)	119.4(8)
C(60)–C(61)–C(62)	121.6(8)	C(61)–C(66)–C(65)	118.6(9)
C(60)–C(61)–C(66)	118.0(9)		
C(62)–C(61)–C(66)	120.3(8)	C(6)–C(60)–H(60)	120.8(46)
C(61)–C(62)–C(63)	120.8(8)	H(60)–C(60)–C(61)	106.7(46)
C(62)–C(63)–C(64)	119.6(9)		

(*c*) In the ethanol molecule

O(7)–C(7)	1.319(15)	O(7)–C(7)–C(71)	112.8(14)
C(7)–C(71)	1.417(21)		

(*d*) Torsion angles in the dmpe ligands

P(1)–C(1)–C(2)–P(2)	−50.2(9)
P(3)–C(3)–C(4)–P(4)	−49.3(9)

(*e*) Proposed hydrogen bonds

O(7)···I	3.431(11)	C(7)–O(7)···I	108.2(10)
C(60)···I′	3.995(11)		
H(60)···I′	2.87(10)	C(60)–H(60)···I′	173(6)

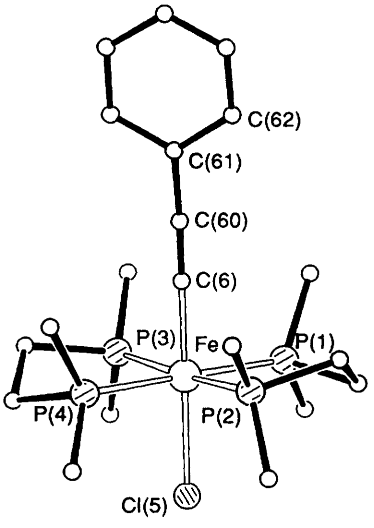


Fig. 1 View of the molecule *trans*-[FeCl(CCPh)(dmpe)$_2$]

bond, and a lengthening in the C(6)–C(60) bond by 0.07 Å as it changes from a triple towards a double bond. In the limit this implies that the acetylide complex contains iron(II) but that the vinylidene complex contains iron(IV), an unusually high oxidation state for iron in a phosphine environment.

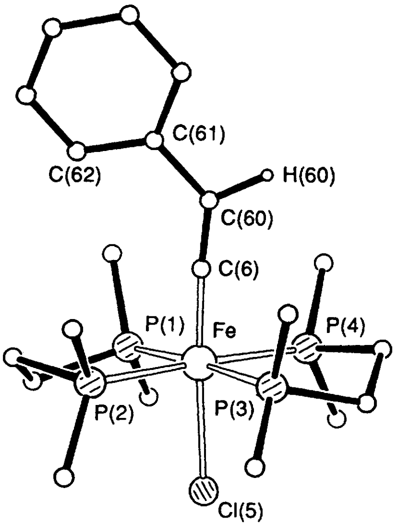
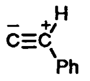


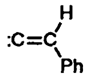
Fig. 2 View of the complex cation in *trans*-[FeCl(CCHPh)-(dmpe)$_2$]I·EtOH

Nevertheless, the vinylidene hydrogen atom must be significantly positive. This hydrogen atom, H(60), which was refined independently and well, is 2.87(10) Å from the iodide (a distance rather shorter than the sum of van der Waals radii, 3.35 Å) and forms an almost linear C–H–I group; its distance from C(60), 1.14(10) Å, connotes a normal covalent C–H bond. The H–I contact should therefore be considered a hydrogen bond. The iodide–ethanol contact forms a more traditional hydrogen bond.

The bond lengths in other acetylide complexes allow some more general comparisons to be made. In [Fe(CCPh)$_2$(dmpe)$_2$] they are as follows: Fe–C 1.918(3), C≡C 1.222(4); Fe–P (mean of two values) 2.227(5) Å,[22] and an independent analysis of [FeCl(CCPh)(dmpe)$_2$][20] has given values of 1.880(5), 1.216(8) and (mean of four) 2.215(1) Å for the analogous bond lengths.

The change in the acetylide upon protonation in our complexes is also reflected in other bond lengths within the molecules. Thus, Fe–Cl in the acetylide [2.389(1) Å] changes to 2.355(2) Å in the vinylidene complex. This shortening is in the sense expected during an oxidation, but is not dramatic. However, we have already noted how insensitive iron–chlorine bond lengths are to changes in the rest of the molecule.[23] The values for [FeCl$_2$(diphosphine)$_2$] are all quite close to 2.35 Å.[23] Upon protonation, the Fe–P bond increases from *ca.* 2.22 to *ca.* 2.26 Å. This is not at all what one might expect, and seems to imply that the iron is still rather closer to iron(II) than iron(IV). The problem with identifying the iron as iron(II) is that the vinylidene moiety then has to be regarded either as a neutral ligand containing hypervalent carbon or as a neutral carbene.





The C(6)–C(60) separation in the vinylidene complex, 1.268(11) Å, compares with literature values of 1.31(2) Å in [ReCl(C=CHPh)(dppe)$_2$][24] and 1.327(7) Å in [MoBr-(C=CHPh){P(OMe)$_3$}$_2$(C$_5$H$_5$)].[25] The usual range in complexes of this kind is 1.29–1.38 Å, which must connote a carbon–carbon double bond.[26] Although marginally shorter in our case, it is still considerably longer than in the acetylide precursor, and therefore we conclude that the complex contains a formal double bond. The complex is therefore best descibed as an iron(II) complex containing a neutral carbene. The enhanced quadrupole splitting in the Mössbauer spectrum can then be

Table 5 $^{13}C-\{^1H\}$ NMR spectral data for acetylene and vinylidene complexes in CD_2Cl_2

	δ, *J*/Hz	
Complex	Fe–C–*C*	Fe–*C*–C
$[FeCl(CCPh)(dmpe)_2]$	130.3 (s)	119.7 (s)
$[FeCl(CCPr^i)(dmpe)_2]$	122.7 (s)	96.8 (qnt, $^2J_{CP}$ = 28.5)
$[FeCl(CCHPh)(dmpe)_2]BF_4$	128.6 (qnt, $^3J_{CP}$ = 4.5)	368.7 (s)
$[FeCl(CCDPh)(dmpe)_2]Cl$	128.8 (br s)	369.2 (s)
$[FeCl(CCHPr^i)(dmpe)_2]Cl$	123.0 (s)	365.9 (qnt, $^2J_{CP}$ = 31.2)

s = Singlet, qnt = quintet, br = broad.

ascribed to the π-electron-withdrawing power of the carbene ligand.[27] Certainly vinylidene groups are recognised to be good π acceptors. Phenylvinylidene on $Mn(CO)_2(C_5H_5)$ is exceeded in π-acceptor ability only by CS and SO_2.[28]

Another direct probe of the state of the carbon atom in the carbene/vinylidene is the C–H/D coupling constant, which might be determinable in $[FeCl(CCHPh)(dmpe)_2]^+$ and $[FeCl(CCHPr^i)(dmpe)_2]^+$ from ^{13}C and ^2H NMR spectra. Table 5 contains selected resonances from the $^{13}C-\{^1H\}$ NMR spectra of some of the new compounds. In general, the chemical shifts of vinylidene complexes are somewhat variable, but our values fall into the ranges exhibited by other compounds.[24,25] Note that Field *et al.*[20] were unable to detect resonances assignable to the acetylide carbon atoms in $[FeCl(CCPh)(dmpe)_2]$ or any ^{31}P and ^1H resonances, for that matter. This is not obviously explicable. We have observed all the ^{13}C resonances as well as ^{31}P and ^1H NMR spectra, but prefer not to rationalise the shifts in detail. The signal assigned to the C*C*DPh resonance in $[FeCl(CCDPh)(dmpe)_2]Cl$ is broad, due to coupling to both D and to the phosphine phosphorus atoms. The width at half-height is about 30 Hz. Since it already contains $^3J_{CP}$ of 4.5 Hz (from the ^1H analogue) it is unlikely that $^1J_{CP}$ is of a different order, and is probably less. This is not very useful diagnostically.

Were the other, dipolar, canonical form to predominate, the compound would be related to CH_5^+, a species which is stable in the gas phase though it has not yet been identified in organometallic derivatives.[29] We shall report further data on this matter from related compounds in the near future.

Experimental

All operations were carried out under a dry dinitrogen or argon atmosphere, following standard Schlenk techniques. All the solvents were distilled under N_2 from appropriate drying agents prior to use. When exclusion of N_2 was required, the solvent was saturated with argon by bubbling it through the solution immediately before use.

Infrared spectra were recorded on a Perkin Elmer 882 instrument in Nujol mulls or in solution, NMR spectra on JEOL GSX-270 equipment, in the appropriate deuteriated solvents, using as references $SiMe_4$ for ^1H, $P(OMe)_3$ for $^{31}P-\{^1H\}$ and $MeNO_2$ for ^{15}N. Analyses were by Mr. C. J. Macdonald of this Laboratory, using a Perkin Elmer 2400 CHN elemental analyser. Mössbauer spectra were recorded on an ES technology MS-105 spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix, courtesy of Dr. D. J. Evans. Spectra were recorded at 77 K and referenced against iron foil at 298 K.

1,2-Bis(dimethylphosphino)ethane and 1,2-bis(diethylphosphino)ethane were prepared by literature methods.[30] The complexes $[FeCl_2(dmpe)_2]$[14] and $[FeCl_2(depe)_2]$[15] were also prepared by published methods, slightly modified. Sodium tetraphenylborate and tetrahydroborate were purchased from Aldrich Chemical Co. Potassium diethyldithiocarbamate was purchased from BDH Chemicals Co. and used without purification. Phenylacetylene and methyl propiolate (methoxycarbonylacetylene) were purchased from Aldrich and used as received. Tetrafluoroboric acid diethyl etherate was purchased from BDH.

Anhydrous Iron(II) *Chloride*.—Iron powder (30 g) was placed into a three-necked flask (1 l), equipped with a mechanical stirrer and a condenser with a nitrogen inlet and a bubbler. Dioxygen-free dry methanol (500 cm³) was added, then a slow stream of anhydrous hydrogen chloride was bubbled through the stirred mixture. An exothermic reaction took place. Hydrogen chloride was passed through until all the iron had dissolved, and a dark solution was obtained. This solution was filtered under dinitrogen to remove carbon and other impurities. The filtered solution was concentrated to one-half volume and cooled to −20 °C overnight. White crystals of $[Fe(MeOH)_x]Cl_2$ were obtained. These were filtered off, washed with Et_2O and dried *in vacuo*. Then they were heated at 180 °C *in vacuo* for several hours to constant weight, in order to remove all the methanol. A porous plate was placed between the solid and the vacuum line during the heating *in vacuo* to avoid mechanical carriage of solids. Yield: 50 g (74%).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichloroiron*(II) **1**.—Anhydrous iron(II) chloride (3.57 g, *ca.* 28 mmol) was suspended in toluene (*ca.* 150 cm³). Then dmpe (10 cm³, *ca.* 66 mmol, an excess) was added dropwise *via* syringe, yielding a bright green solution. Gradually a green microcrystalline precipitate was formed. The mixture was stirred for 2–3 h, then the volume was reduced to one-half. The green product was filtered off and washed with hexane. Further crops were obtained by concentrating and cooling to −20 °C the mother-liquor. Yield: 10 g (85%).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*dichloroiron*(II) **2**.—Iron(II) chloride (1 g, *ca.* 11.5 mmol) was suspended in dichloromethane. Then depe (5.4 cm³, *ca.* 23 mmol) was added dropwise to this mixture *via* syringe. The solid gradually dissolved, yielding a bright green solution, which was stirred for 1 h at room temperature. Solvent removal *in vacuo* yielded green crystalline $[FeCl_2(depe)_2]$, which was washed with ethanol and hexane, and dried *in vacuo*. Yield: 100%.

Dinitrogenbis{*bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*chloroiron*(II)} *Bis*(*tetraphenylborate*).—Compound **2** (2.61 g, 4.84 mmol) was dissolved in refluxing methanol (50 cm³), yielding an orange-brown solution. The reflux was maintained for several minutes, and then a methanolic solution of sodium tetraphenylborate (1.65 g, *ca.* 4.85 mmol) was added to the hot solution, dropwise, *via* syringe, without stirring. On cooling, orange crystals formed. They were filtered off, washed with MeOH and hexane and dried *in vacuo*. Yield: 2.1 g (52%) (Found: C, 62.4; H, 8.2; N, 1.5. $C_{88}H_{136}B_2Cl_2Fe_2N_2P_8$ requires C, 63.2; H, 8.2; N, 1.6%). IR: $\nu(N_2)$ 2081s cm⁻¹.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(*dinitrogen*)*iron*(II) *Tetraphenylborate*.—Compound **1** (0.8 g, 1.87 mmol) was dissolved in methanol or slurried in ethanol under dinitrogen. Sodium tetraphenylborate (0.68 g, *ca.* 2 mmol) in methanol was added dropwise to the stirred mixture. Immediately a red-orange precipitate appeared, which was stirred under dinitrogen for 1 h, then filtered off, washed with methanol and diethyl ether and dried *in vacuo*. Recrystallisation from thf–EtOH under dinitrogen afforded nice red prisms of the dinitrogen complex. Yield: 1.0 g (72%) (Found: C, 58.5; H, 7.1; N, 3.6. $C_{36}H_{52}BClFeN_2P_4$ requires C, 58.5; H, 7.0; N, 3.8%). IR: ν(N_2) at 2105 cm^{-1}. ^{31}P-{^{1}H} NMR (CD_2Cl_2–CH_2Cl_2): δ −85.0 (sharp singlet).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloroiron*(II) *Tetraphenylborate*.—Essentially the same procedure was followed for the preparation of [FeCl(N_2)(dmpe)$_2$]BPh_4, but under an argon atmosphere (Found: C, 60.0; H, 7.2. $C_{36}H_{52}BClFeP_4$ requires C, 60.8; H, 7.3%). Yield: *ca*. 10%.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bromo*(*dinitrogen*)*iron*(II) *Tetraphenylborate*.—To a stirred suspension of [$FeBr_2$(dmpe)$_2$] (1 g, 1.9 mmol, prepared by reaction between $FeBr_2$ and dmpe in toluene) in ethanol under dinitrogen, an ethanolic solution of $NaBPh_4$ (1 g, *ca*. 3 mmol, an excess) was added. A greenish grey product precipitated. The mixture was stirred for 1 h under dinitrogen, then it was filtered, and the olive-green solid washed with EtOH and Et_2O and dried *in vacuo*. Yield: 1.29 g (87%) (Found: C, 55.0; H, 6.5; N, 3.1. $C_{36}H_{52}BBrFeN_2P_4$ requires C, 54.9; H, 6.6; N, 3.5%). IR: ν(N_2) at 2107 cm^{-1}. ^{31}P-{^{1}H} NMR [Me_2CO–$(CD_3)_2CO$]: δ −86.0 (sharp singlet).

cis- *and* trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*carbonylchloroiron*(II) *Tetraphenylborate*.—The dinitrogen complex [FeCl(N_2)(dmpe)$_2$]BPh_4 (0.36 g, *ca*. 0.5 mmol) was dissolved in acetone (25 cm^3), yielding a dark red solution. Carbon monoxide was bubbled through the solution, and a colour change to orange was immediately observed. The mixture was stirred for 10 min, then the solvent was removed *in vacuo* and the orange residue dried. This residue contains a mixture of both *cis*- and *trans*-[FeCl(CO)(dmpe)$_2$]$^+$. It was recrystallised from concentrated dichloromethane solutions at −20 °C. Yield: 0.28 g (77%) (Found: C, 59.8; H, 7.2. $C_{37}H_{52}BClFeOP_4$ requires C, 60.1; H, 7.0%). IR: ν(CO) at 1941 (*trans* isomer) and 1969, 1979 cm^{-1} (*cis* isomer). Isomer ratio *cis*/*trans* ≈ 1:3. ^{31}P-{^{1}H} NMR (CH_2Cl_2–C_6D_6): δ −84.8 (sharp singlet, *trans* isomer); −95.4 (m), −79.3 (m) and −81.1 (m) (*cis* isomer).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(*methyl isocyanide*)*iron*(II) *Tetraphenylborate*.—This was obtained from [FeCl(N_2)(dmpe)$_2$]BPh_4 (0.45 g, 0.61 mmol) by reaction with MeNC (0.1 cm^3, an excess) in acetone (25 cm^3). The pure yellow-orange product was obtained by recrystallisation from acetone–hexane. Yield: 0.42 g (92%) (Found: C, 60.3; H, 7.3; N, 1.7. $C_{38}H_{55}BClFeNP_4$ requires C, 60.7; H, 7.3; N, 1.8%). IR: ν(N≡C) at 2113; 2157w cm^{-1}. ^{31}P-{^{1}H} NMR (Me_2CO–$CDCl_3$): δ −80.1 (sharp singlet).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bromocarbonyliron*(II) *Tetraphenylborate*.—This complex was obtained from [FeBr(N_2)(dmpe)$_2$]BPh_4 (0.3 g, 0.38 mmol) by reaction with CO in dichloromethane and recrystallisation from dichloromethane–ethanol as a bright green microcrystalline solid which dissolves in dichloromethane, yielding dichroic solutions (green to transmitted light and brown to reflected light). Yield: 0.26 g (87%) (Found: C, 56.8; H, 6.5. $C_{37}H_{52}BBrFeOP_4$ requires C, 56.8; H, 6.6%). IR: ν(CO) at 1942s and 1967 cm^{-1} (sharp). ^{31}P-{^{1}H} NMR [CH_2Cl_2–$(CD_3)_2CO$]: δ −86.5 (sharp singlet).

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](*diethyldithiocarbamato*-S,S′)*iron*(II) *Tetraphenylborate*.—Compound **1** (0.45 g, *ca*. 1 mmol) in ethanol was treated with solid K(S_2CNEt_2) (0.19 g, *ca*. 1 mmol) under a dinitrogen atmosphere. A dark brown-orange solution was obtained. After stirring for *ca*. 15 min, $NaBPh_4$ (0.36 g, *ca*. 1 mmol) in EtOH was added, yielding a yellow precipitate. This was filtered off, washed with ethanol and diethyl ether and dried *in vacuo*. Recrystallisation from acetone or dichloromethane–hexane afforded yellow-orange crystals. Yield: 0.64 g (78%) (Found: C, 59.0; H, 7.4; N, 1.6. $C_{41}H_{62}BFeNP_4S_2$ requires C, 59.8; H, 7.5; N, 1.7%). IR: ν(C=N) 1505 cm^{-1}. ^{31}P-{^{1}H} NMR [Me_2CO–$(CD_3)_2CO$]: A_2B_2 spin system, δ(P_A) −75.5 (t), δ(P_B) −78.4 (t), $^2J_{PP}$ = 38.1 Hz.

This material was the only product characterised from a series of reactions carried out to attempt the preparation of complexes [FeX(N_2)(dmpe)$_2$]BPh_4. In a typical test, [$FeCl_2$(dmpe)$_2$] (0.5 mmol) in EtOH was treated with KX or NaX (X = S_2CNEt_2, N_3 or I) under dinitrogen. Addition of $NaBPh_4$ in ethanol precipitated materials, which, after filtration, did not show any ν(N_2) in their IR spectra. No further attempts were made to purify these derivatives.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(*phenylethynyl*)*iron*(II).—Compound **1** (0.44 g, *ca*. 1 mmol) in absolute ethanol (20 cm^3) was treated with phenylacetylene (0.6 cm^3, an excess). A dark brown, clean solution was obtained a few minutes after addition, and then $NaBH_4$ (0.04 g, *ca*. 1 mmol) in ethanol was added. The mixture changed from brown to light brown, red and then orange or orange-yellow, together with copious gas evolution. A yellow-orange precipitate was obtained after stirring for 2 h. This was filtered off, washed with ethanol and hexane and dried *in vacuo*. Recrystallisation from dichloromethane–hexane afforded yellow crystals. Yield: 0.4 g (81%) (Found: C, 49.0; H, 7.2. $C_{20}H_{37}ClFeP_4$ requires C, 48.7; H, 7.5%). IR: ν(C≡C) 2044, 1992 (sh) cm^{-1}. NMR: ^{1}H (CD_2Cl_2), δ 1.45(s), 1.533(s) (PCH_3), 1.89 (br s, PCH_2), 6.81(d), 6.99(t) (C_6H_5); ^{31}P-{^{1}H} (thf–CD_2Cl_2), δ −75.5 (sharp singlet); ^{13}C-{^{1}H} (CD_2Cl_2), δ 130.3 (s, FeC≡*C*), 130.6, 129.9, 128.1, 122.5 (all s, C_6H_5), 119.7 (s, Fe–*C*≡C), 30.4 (q, $^1J_{CP}$ = 12.5 Hz, PCH_2), 15.7, 13.4 (s, PCH_3).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*phenylethynyl*)*iron*(II).—Compound **2** (0.63 g, 1 mmol) in EtOH (25 cm^3) was treated with HC≡CPh (1 cm^3, an excess), and then with $NaBH_4$ (0.04 g, *ca*. 1 mmol) in ethanol. The colour changed to red. The mixture was finally warmed slightly with an air-blower. After stirring for 30 min, a red-orange precipitate began to form. The mixture was then concentrated and diethyl ether was added in order to dissolve all the solid material. Cooling to −20 °C overnight afforded beautiful red crystals of [FeBr(C≡CPh)(depe)$_2$]. Yield: 0.29 g (45%) (Found: C, 52.4; H, 8.4. $C_{28}H_{53}BrFeP_4$ requires C, 51.8; H, 8.2%). IR: ν(C≡C) 2041 cm^{-1}. NMR: ^{1}H (C_6D_6), δ 1.11 (br s, 24 H, PCH_2CH_3), 1.75 (pseudo-octet, 16 H, J_{HH} = 7.33, PCH_2CH_3), 2.42 and 2.57 (8 H, pseudo-sextets, $^2J_{HH}$ = 7.33 Hz, PCH_2), 6.870 (m), 7.14 (m, overlapping with solvent signal, C_6H_5); ^{31}P-{^{1}H} (C_6H_5Me–C_6D_6), δ −70.85 (sharp singlet).

Bis[1,2-bis(diethylphosphino)ethane]chloro(phenylethynyl)-*iron*[II) was obtained following the same procedure, starting from [$FeCl_2$(depe)$_2$], but it was always mixed with some *trans*-bis[1,2-bis(diethylphosphino)ethane]bis(phenylethynyl)-iron(II).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(3-*methylbut*-1-*ynyl*)*iron*(II).—To [$FeCl_2$(dmpe)$_2$] (0.30 g, 0.70 mmol) in ethanol (20 cm^3) was added HC≡CPr^i (0.1 cm^3, 1.0 mmol) and the mixture stirred for 5 min. Then $NaBH_4$ (0.025 g) in ethanol (5 cm^3) was added. The colour changed to orange, gas was evolved, and the mixture was allowed to stir for 2 h. The volume was reduced *in vacuo* until a solid appeared, and the ethanolic solution allowed to crystallise at 0 °C. The crystals were filtered off and dried *in vacuo*. This compound deteriorates even at room temperature under dinitrogen, and the microanalysis was never entirely satisfactory. Yield 0.11 g, 35% (Found: C, 42.0; H, 8.15. $C_{17}H_{39}ClFeP_4$ requires C, 44.6; H, 8.5%). IR: ν(C≡C) 2068

cm^{-1}. NMR: ^1H (CD_2Cl_2), δ 0.82 [d, $^3J_{HH}$ = 6.1 Hz, 6 H, $C(CH_3)_2$], 1.38 (s), 1.48 (s) (24 H, PCH_3), 1.85 (br s, 8 H, PCH_2) and 2.25 (br s, 1 H, CH); ^{31}P-{^1H} (Me_2CO), δ −75.49 (s); ^{13}C-{^1H} (CD_2Cl_2), δ, 122.7 (s, Fe–C≡*C*), 96.8 (q, $^3J_{CP}$ = 28.5, Fe–C), 30.4 (q, $^1J_{CP}$ = 13.3, PCH_2), 25.6 [s, $C(CH_3)_2$], 24.1 (s, C≡C–*C*), 15.6 (q, $^1J_{CP}$ = 6.7), 13.4 (q, $^1J_{CP}$ = 4.5 Hz, PCH_3).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(*phenylvinylidene*)*iron*(II) *Tetrafluoroborate*.—The chloro(phenylethynyl) complex $[FeCl(C{\equiv}CPh)(dmpe)_2]$ (0.55 g, 1.1 mmol) in thf (20 cm^3) was treated with $HBF_4{\cdot}OEt_2$ (0.4 cm^3). A green precipitate was obtained. The mixture was stirred for 1 h, then the product was filtered off, washed with hexane and Et_2O and dried *in vacuo*. Recrystallisation from methanol afforded several crops of green needles of the complex, containing methanol of crystallisation. Yield: 0.42 g (63%) (Found: C, 40.8; H, 6.9. $C_{20}H_{38}BClF_4FeP_4{\cdot}CH_3OH$ requires C, 40.9; H, 6.8%). IR: ν(C=C) 1615, ν(C=C) (phenyl ring) 1593, ν(OH) 3571 cm^{-1}. NMR: $^1H(CD_2Cl_2)$, δ 1.62 (br s, 24 H, PCH_3), 1.99 (br m, 8 H, PCH_2), 3.42 (s, 3 H, CH_3OH), 5.21 (qnt, $^2J_{HP}$ = 8.4 Hz, C=C*H*Ph), 6.86 (d), 7.20 (t) and 7.27 (t), (5 H, C_6H_5); ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2): δ −87.9 (s); ^{13}C-{^1H} (CD_2Cl_2), δ 368.7 (s, Fe=*C*=C), 128.6 (q, $^3J_{CP}$ = 4.5, Fe=C=*C*), 129.5, 126.9, 126.2, 119.6 (all s, C_6H_5), 29.4 (q, $^1J_{CP}$ = 13.5 Hz, PCH_2), 13.0, 15.6 (s, PCH_3).

The chloride salt was obtained following a similar procedure, using HCl generated from MeOH plus $SiMe_3Cl$ in ether instead of HBF_4. The iodide salt used in structure analyses was obtained serendipitously from a solution of the attempted reaction of the phenylacetylide with methyl iodide in thf. This did not occur. Addition of MeOH + $SiMe_3Cl$ produced beautiful crystals of $[Fe(C{=}CHPh)Cl(dmpe)_2]I{\cdot}MeOH$ on standing over several days.

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*phenylvinylidene*)*iron*(II) *Chloride*.—The bromo(phenylethynyl) complex $[FeBr(C{\equiv}CPh)(depe)_2]$ (0.45 g, *ca*. 0.65 mmol) in diethyl ether was treated with methanol (0.5 cm^3) and $SiMe_3Cl$ (0.5 cm^3). Immediately upon addition of $SiMe_3Cl$ a pale yellow precipitate was formed. This was filtered off, washed with diethyl ether and hexane and dried *in vacuo*. The product was dissolved in dichloromethane, the green-yellow solution filtered through Celite and then the product precipitated by addition of hexane. Yield: 100% (Found: C, 48.7; H, 7.8. $C_{27}H_{54}BrClFeP_4$ requires C, 49.0; H, 7.9%). IR: ν(C=C) 1614; ν(C=C) (phenyl ring) 1587, 1572 cm^{-1}. The complex is paramagnetic, yielding broad, unresolved signals in the ^1H NMR spectrum. μ_{eff} = 1.8 at 293 K in dichloromethane solution (Evans method).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(3-*methylbut*-1-*enylidene*)*iron Chloride*.—To the chloro(3-methylbut-1-ynyl) complex (0.46 g, 1 mmol) in diethyl ether (20 cm^3) was added anhydrous HCl (generated from $SiMe_3Cl$ in methanol). This produced an off-white precipitate, which was filtered off and dried *in vacuo*. Yield 0.21 g, 43% (Found: C, 39.3; H, 7.75. $C_{17}H_{40}Cl_2FeP_4$ requires C, 41.2; H, 8.05%). IR: ν(C=C) 1636 cm^{-1}. NMR: ^1H (CD_2Cl_2), δ 0.98 [d, $^3J_{HH}$ = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.56 (br m, 24 H, PCH_3), 1.85, 2.03 (br m, 8 H, PCH_2), 2.47 (br m, 1 H, C*H*$(CH_3)_2$] and 4.07 (m, 1 H, C=CH); ^{31}P-{^1H} (Me_2CO), δ −86.5 (s); ^{13}C-{^1H} (CD_2Cl_2), δ 365.9 (q, $^2J_{CP}$ = 31.2, Fe=*C*=C), 123.0 (s, Fe=C=*C*), 29.3 (q, $^1J_{CP}$ = 11.1, PCH_2), 25.3 [s, $C(CH_3)_2$], 23.6 (s, C=C–*C*), 15.9 (q, $^1J_{CP}$ = 6.7) and 12.9 (q, $^1J_{CP}$ = 6.7 Hz, PCH_3).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*](*carboxyethynyl*-C,O)-*iron*(II) *Tetraphenylborate*.—Complex **1** (0.71 g, 1.66 mmol) in ethanol (30 cm^3) under nitrogen or argon was treated with an excess of methyl propiolate (1 cm^3). Sodium tetrahydroborate (0.07 g, *ca*. 2 mmol) in ethanol was added. A red-orange solution was obtained. Addition of $NaBPh_4$ (0.57 g, 1.66 mmol) in ethanol produced a red-orange crystalline precipitate, which was filtered off, washed with Et_2O and dried *in vacuo*. Recrystallisation from CH_2Cl_2–MeOH afforded red crystals of the product. Yield: 0.86 g (68%) (Found: C, 62.1; H, 7.5. $C_{40}H_{57}BFeO_2P_4$ requires C, 63.1; H, 7.5%). IR: no ν(Fe–H) or ν(C≡C) bands, ν(C=O) 1565 cm^{-1}. NMR: ^1H (CD_2Cl_2), $(CH_3)_2PCH_2CH_2P(CH_3)$, 8 non-equivalent groups, 3 H each, δ 0.78 (d, $^2J_{HP}$ = 8.07), 1.03 (d, $^2J_{HP}$ = 8.74), 1.07 (d, $^2J_{HP}$ = 9.41), 1.28 (d, $^2J_{HP}$ = 7.39), 1.32 (d, $^2J_{HP}$ = 8.07), 1.45 (d, $^2J_{HP}$ = 6.73), 1.53 (d, $^2J_{HP}$ = 8.07), 1.59 (d, $^2J_{HP}$ = 7.39 Hz); 3.51 (s, 3 H, $HC{=}CHCO_2CH_3$), 6.18 (br s, 1 H, *H*C=CHCO$_2$CH$_3$) and 7.12 (br s, overlapping with BPh_4^- resonances, HC=C*H*CO$_2$CH$_3$); ^{31}P-{^1H} (Me_2CO–CD_2Cl_2), ABCD spin system, δ(P_A) −71.69, δ(P_B) −80.99, δ(P_C) −63.67, δ(P_D) −83.66, $^2J_{AB}$ = 127, $^2J_{AC}$ = 53, $^2J_{AD}$ = 21, $^2J_{BC}$ = 36, $^2J_{BD}$ = 36, $^2J_{CD}$ = 25 Hz.

The same complex was obtained by reaction between $[FeH(H_2)(dmpe)_2]BPh_4$ and an excess of $HC{\equiv}CCO_2Me$ in thf–acetone. Addition of ethanol and concentration were used for precipitation of the product.

X-*Ray Structure Analysis of* trans-$(FeCl(CCPh)(dmpe)_2]$.—Orange-brown crystals were obtained by recrystallisation from dichloromethane–hexane as a mixture of rectangular plates and thin diamond-section prisms.

Crystal data. $C_{20}H_{37}ClFeP_4$, *M* = 492.7, monoclinic, space group $P2_1/n$ (equivalent to no. 14), *a* = 30.731(2), *b* = 8.861(1), *c* = 9.059(1), β = 96.423(6)°, *U* = 2451.5 Å^3, *Z* = 4, D_c = 1.335 g cm^{-3}, *F*(000) = 1040, μ(Mo-Kα) = 9.9 cm^{-1}, λ(Mo-K$\bar{\alpha}$) = 0.710 69 Å.

Photographic examination of both types showed that they have the same diffraction patterns except that the latter are twinned crystals. One of the single-crystal plates (*ca*. 0.04 × 0.21 × 0.31 mm) was transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation). Accurate cell parameters were determined from the goniometer settings of 25 reflections (θ *ca*. 11°), each centred in four orientations, and diffraction intensities were measured to θ_{max} = 23°. During processing, intensities were corrected for Lorentz-polarisation effects, absorption (from ψ-scan measurements) and to eliminate negative intensities (by Bayesian statistical methods). No deterioration of the crystal was observed.

3394 Unique reflections were entered into the SHELX system[31] for structure determination (by the heavy-atom method) and refinement (by full-matrix least-squares methods). Hydrogen atoms were included in idealised positions, with methyl groups in staggered orientations; in the final cycles of refinement the CH_3 groups were included as rigid groups (free to move by translation or rotation) and the parameters of the remaining hydrogen atoms were set to ride on those of their bonded C atoms. All atoms other than hydrogens were allowed anisotropic thermal parameters. At convergence, $R = R_g$ = 0.032[31] for 3172 reflections (*i.e*. those with $I > \sigma_I$) weighted $w = \sigma_F^{-2}$. There were no features of significance in the final difference map, with all peaks and troughs in the range −0.27 to +0.25 e Å^{-3}.

The scattering factors for neutral atoms used in both this structure determination and the one that follows were taken from ref. 32. Computer programs (in addition to SHELX) used in both analyses are listed in Table 4 of ref. 33, and were run on the MicroVAX II computer in this Laboratory.

X-*Ray Structure Analysis of* trans-$[FeCl(C{=}CHPh)(dmpe)_2]$-$I{\cdot}EtOH$.—*Crystal data*. $C_{22}H_{44}ClFeIOP_4$, *M* = 666.7, monoclinic, space group $P2_1/c$ (no. 14), *a* = 9.987(1), *b* = 23.849(5), *c* = 12.539(3) Å, β = 91.051(2)°, *U* = 2986.1 Å^3, *Z* = 4, D_c = 1.483 g cm^{-3}, *F*(000) = 1360, μ(Mo-Kα) = 18.4 cm^{-1}.

The crystals were very dark green, well formed plates with good diamond-shaped faces. After photographic examination, one (*ca*. 0.10 × 0.29 × 0.43 mm), mounted on a glass fibre in air, was transferred to our CAD4 diffractometer for determination of cell dimensions and measurement of diffraction intensities as described above. Diffraction data ($\theta_{max} = 22.5°$) were corrected as previously and also for deterioration of the crystal (*ca.* 25% overall). The structure was determined and refined from 3892 unique reflections in the SHELX program in procedures paralleling those described above. The vinylidene hydrogen atom was located and refined freely; all other hydrogen atoms were treated as before but with independent isotropic thermal parameters. At convergence, $R = 0.067$ and $R_g = 0.084$[31] for 3501 reflections (those with $I > \sigma_I$) weighted $w = (\sigma_F{}^2 + 0.000\,43F^2)^{-1}$. The major features in the final difference map were peaks of *ca.* 0.64 e Å^{-3} in the region of the iodide ion and ethanol molecule.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We acknowledge financial support from the EEC Stimulation Programme under contract ST2*410.

References

1 R. A. Henderson, G. J. Leigh and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1987, **23**, 197.

2 T. A. Bazenova, A. K. Shilova, E. Deschamps, M. Gruselle, G. Levy and M. Tchoubar, *J. Organomet. Chem.*, 1981, **222**, C1.

3 See R. R. Eady, *Adv. Inorg. Chem.*, 1991, **36**, 77.

4 A. Sacco and M. Rossi, *Chem. Commun.*, 1967, 326; M. Aresta, P. Giannocaro, M. Rossi and A. Sacco, *Inorg. Chim. Acta*, 1971, **5**, 115.

5 R. H. Crabtree and D. G. Hamilton, *J. Am. Chem. Soc.*, 1986, **108**, 3124.

6 G. M. Bancroft, M. J. Mays, B. E. Prater and F. P. Stefanini, *J. Chem. Soc. A*, 1970, 2146.

7 P. Giannocaro, M. Rossi and A. Sacco, *Coord. Chem. Rev.*, 1972, **8**, 77.

8 P. Stoppioni, F. Main and L. Sacconi, *Inorg. Chim. Acta*, 1974, **11**, 227.

9 G. A. Ghillardi, S. Midollini, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, 1981, **205**, 193.

10 G. J. Kubas, K. G. Caulton, L. D. Van der Sluys, J. C. Huffman, S. A. Jackson, T. F. Koetzee and P. J. Vergamini, *J. Am. Chem. Soc.*, 1990, **112**, 4831.

11 J. M. Bellerby, M. J. Mays and P. L. Sears, *J. Chem. Soc., Dalton Trans.*, 1976, 1232.

12 A. Hills, D. L. Hughes, M. Jimenez-Tenorio and G. J. Leigh, *J. Organomet. Chem.*, 1990, **391**, C41.

13 N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, 1971.

14 G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339.

15 J. Chatt and R. J. Hayter, *J. Chem. Soc.*, 1961, 5507.

16 J. M. Bellerby and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 1975, 1281.

17 J. E. Barclay and G. J. Leigh, unpublished work.

18 M. V. Baker, L. D. Field and T. W. Hambley, *Inorg. Chem.*, 1988, **27**, 2872.

19 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1988, 546.

20 L. D. Field, A. V. George and T. W. Hambley, *Inorg. Chem.*, 1990, **29**, 4565.

21 A. J. L. Pombeiro, J. C. Jeffery, C. J. Pickett and R. L. Richards, *J. Organomet. Chem.*, 1984, **277**, C7.

22 L. D. Field, A. V. George, E. Y. Malouf, I. H. M. Slip and T. W. Hambley, *Organometallics*, 1991, **10**, 3842.

23 J. E. Barclay, A. Hills, D. L. Hughes and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1988, 2871.

24 A. J. L. Pombeiro, S. S. P. R. Almeida, M. F. C. G. Silva, J. C. Jeffrey and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1988, 2381.

25 R. G. Beevor, M. Green, A. G. Orpen and I. D. Williams, *J. Chem. Soc., Chem., Commun.*, 1983, 673.

26 M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 59.

27 D. J. Evans, M. Jimenez-Tenorio and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1991, 1785.

28 A. B. Antosova, N. E. Kolobova, P. V. Petrousky, B. V. Lokshin and N. S. Obezyuk, *J. Organomet. Chem.*, 1977, **137**, 55.

29 For a review see P. van Ragué Schleyer, B. Tidor, E. D. Jemmis, J. Chandrasekhar, E.-U. Würtheim, A. J. Kos, B. T. Luke and J. A. Pople, *J. Am. Chem. Soc.*, 1983, **105**, 484.

30 R. A. Henderson, W. Hussain, G. J. Leigh and F. B. Normanton, *Inorg. Synth.*, 1985, **23**, 141.

31 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

32 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

33 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 21*st May* 1992; *Paper* 2/02651A