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Reactions of Bis[1,2-bis(dialkylphosphino)ethane]-(dihydrogen)hydridoiron(1+) with Alkynes *

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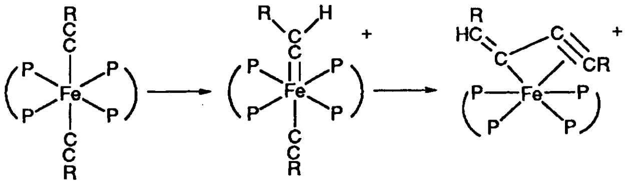
The compounds $[FeH(H_2)(dmpe)_2]BPh_4$ and $[FeH(H_2)(depe)_2]BPh_4$ (dmpe = $Me_2PCH_2CH_2PMe_2$ and depe = $Et_2PCH_2CH_2PEt_2$) reacted with terminal alkynes R′CCH (R = Me, Pr^i or Ph) to yield a variety of structures, apparently formed in sequence, bis(alkynyl), alkynyl(vinylidene) and substituted butenynyl complexes of iron(II), which also contain bis(diphosphines). The structures of *trans*-$[Fe(CCMe)(CCHMe)(dmpe)_2]BF_4$, *trans*-$[Fe(CCPr^i)(CCHPr^i)(dmpe)_2]BF_4$, $[Fe(MeCCCCHMe)(depe)_2]BPh_4$ and $[Fe(PhCCCCHPh)(dmpe)_2]BPh_4$ have been determined and the interconversions of the complexes are discussed.

We have recently commenced an intensive study of the reactions of cyclopropenes and their isomers, allenes and alkynes with iron compounds in order to clarify the observed reduction behaviour of nitrogenases with cyclopropene.[1] The reactions of alkynes with iron halides yielded chloro(alkynyl) complexes, for example, and such complexes have been discussed in some detail.[2,3] In this context, we note specifically that $[FeCl(CCPh)(dmpe)_2]$ (dmpe = $Me_2PCH_2CH_2PMe_2$) can be protonated to give vinylidene complexes $[FeCl(CCHPh)(dmpe)_2]^+$ which we formulated as iron(II) complexes of the neutral carbene :C=CHR, on the grounds of bond lengths and Mössbauer data.[2] This protonation is reversible. The complex $[FeCl(CCPh)(dmpe)_2]$ has also been described by other workers.[4]

The reactions of iron hydrides with alkynes have also been studied. The compounds $[Fe(CCR)_2(dmpe)_2]$ (R = Me, Ph, $C_6H_4C{\equiv}CH$, Bu^t, *etc.*) are apparently readily obtained by reaction of $[FeH_2(dmpe)_2]$ in methanol with the appropriate alkyne.[5] Some analogous compounds of depe ($Et_2PCH_2CH_2PEt_2$) are also known.[5] These bis(alkynyls) react very rapidly with protons to give butenynyl complexes. This formation is reversible, and a reaction mechanism has been proposed which involves an intermediate alkynyl(vinylidene) complex (Scheme 1).[6] The alkynyl(vinylidene) intermediate, for which hard evidence was not forthcoming apart from a ^{31}P NMR resonance and the colour, was suggested to isomerise *trans* ⟶ *cis* before the coupling of the alkynyl residues. However, there is clearly an alternative route to butenynyl complexes, because the reaction of $[FeCl_2(dmpe)_2]$ with PhC≡CH can also give rise to the coupled compound, supposedly by the reaction of $[FeCl(CCPh)(dmpe)_2]$ with more PhC≡CH.[4] Be that as it may, compounds $[Fe(CCR)_2(diphosphine)_2]$ are quite stable {compare also $[Fe(CCPh)_2(Bu^n{}_2PCH_2CH_2PBu^n{}_2)_2]$},[7] as are the ruthenium homologues.[8]

The dihydride $[FeH_2(dmpe)_2]$ dissolves in methanol to give a solution containing $[FeH_3(dmpe)_2]^+$,[9] and this has been taken to be the reactive species in the alkyne reactions. In the meantime, we have prepared salts such as $[FeH_3(dmpe)_2]BPh_4$[3] and have established, on the basis of T_1 experiments and general ^1H NMR data,[10] that the cation is best described as



Scheme 1

a dihydrogenhydrido-complex with an estimated H–H separation of 0.87 Å. We have also been able to carry out experiments in solvents other than alcohols, and specifically in acetone, which have yielded observations which lead us to propose a rather different mechanism from that suggested for the bis(alkynyl)–butenynyl conversion. This we describe here. Some of our data have been published in preliminary form.[3]

Results and Discussion

The reaction between $[FeH(H_2)(dmpe)_2]BPh_4$ and PhC≡CH in acetone–tetrahydrofuran (thf) yields red crystals of $[Fe(PhC{\equiv}C{-}C{=}CHPh)(dmpe)_2]BPh_4$, as established by X-ray crystallography.[3] It is clearly complex, involving a series of colour changes suggestive of yellow and green intermediates. In contrast, the reaction with $[FeH_2(dmpe)_2]$ in methanol {supposedly also essentially $[FeH_3(dmpe)_2]^+$ [9]} gives $[Fe(CCPh)_2(dmpe)_2]$.[5] This yellow complex reacts with trifluoroacetic acid in thf to form a green unisolated intermediate and finally a red product over 24 h.[6]

There is clearly a difference to be explained here, since we were never able to isolate the bis(alkynyl) complex in our reactions, and found that the bis(phenylalkynyl) complex is itself so insoluble in methanol that it could be recovered unchanged after stirring with methanol for 24 h. In fact, some of the bis(alkynyl) complexes of Field *et al.*[6] are so sensitive to acid that they can only be isolated if the methanolic solution for the reaction of $[FeH_2(dmpe)_2]$ with alkynes is made alkaline by addition of some sodium metal. This raises a doubt as to whether $[FeH_3(dmpe)_2]^+$ is really the key reactant in such cases.

Field *et al.*[6] have fully characterised other butenynyl complexes $[Fe(RC{\equiv}C{-}C{=}CHR)(dmpe)_2]^+$ with R = Me, Bu^t,

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

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C_6H_4(C≡CH)-4, or C_6H_3(C≡CH)$_2$-3,5. They have shown that the coupling process is intramolecular and have some spectroscopic evidence for green intermediates. We shall discuss this further below.

We found that the reactions of previously prepared [FeH(H_2)(depe)$_2$]BPh_4 with phenylacetylene, propyne or 3-methylbutyne in acetone also pass through a green stage, giving enynyl complexes which we have fully characterised, the product from propyne by X-ray structural analysis. Again, we saw no sign of bis(alkynyl) intermediates. Treatment of the butenynyl products with KOBu^t in thf at ambient temperature yielded no isolable products. Field *et al.*[6] report that if solutions of the diphenylbutenynyl complex are treated with KOH or KOBu^t in thf–methanol or thf, under reflux, then the bis(acetylide) complex is regenerated. No yields were quoted.

The structure of [Fe(MeC≡C–C=CHMe)(depe)$_2$]BPh_4 **A** was not determined to a high degree of precision because of disorder of the butenynyl ligands in two superimposed orientations. A representation of the molecular structure is shown in Fig. 1, and it is fully consistent with the previously described structure of [Fe(PhC≡C–C=CHPh)(dmpe)$_2$]$^+$ **B** (Fig. 2) which we have reported in preliminary form. In the structure of **B**, the diphenylbutenynyl ligand is properly ordered but the dmpe ligands are disordered. The mutually *trans* P(1) and P(4) atoms are well defined and common to both orientations of these ligands. The major occupied arrangement (*ca.* 65%) is shown in Fig. 2(*a*). The minor arrangement, Fig. 2(*b*), has one dmpe ligand chelating through P(2) and P(4), the second through P(1) and P(3y); P(3x) and P(3y) have resolved, distinct locations. The alternative arrangements of the chelating phosphine ligands are related by a pseudo-mirror plane of symmetry which includes the atoms Fe, P(2) and C(51) to C(71) of the butenynyl ligand. Contacts between the butenynyl ligand and the two arrangements are similar, but with C(7)···C(13y) at 3.08(3), C(6)···C(43y) 3.17(3) and H(70)···C(33y) 2.58(6) Å, slightly shorter than those to the major phosphine ligands. It is apparent from Figs. 1 and 2 that for a common arrangement of the diphosphine ligands the favoured alignment of the butenynyl ligand in **A** is opposite that in **B**. Selected bond dimensions for both derivatives **A** and **B** are shown in Tables 1 and 2. Tables 3 and 4 list the atomic coordinates. The new compound **A** is clearly a normal enynyl complex, as described by Field *et al.*[6] and by others.[11] Tables 2 and 4 contain our previously unpublished data for the phenyl dmpe derivative. Table 5 compares some dimensions and the spectral properties of our new butenynyl complexes and confirms that **A**, **B** and [Fe(Pr^{i}C≡C–C=CHPr^i)(depe)$_2$]BPh_4 **C** have similar structures.

We isolated enynyl complexes directly only with complexes of depe and alkynes, and with the phenylacetylene reaction with [FeH(H_2)(dmpe)$_2$][BPh_4]. With methyl- and isopropyl-acetylene and [FeH(H_2)(dmpe)$_2$]BPh_4 in acetone we obtained green crystalline solids which have been shown by X-ray structural analysis unequivocally to be alkynyl(vinylidene) complexes, examples of the intermediate in alkynyl coupling suggested by

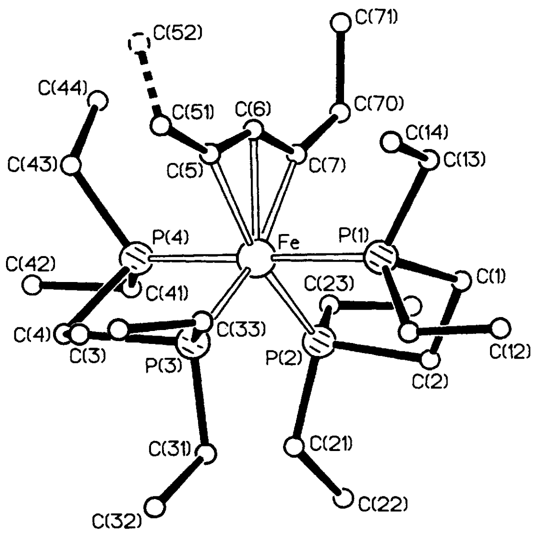

Fig. 1 The structure of the cation [Fe(MeC≡C–C=CHMe)(depe)$_2$]$^+$ in crystals of complex **A**, indicating the atom numbering scheme. The butenynyl ligand is disordered, lying in one of two opposing directions; the orientation with the higher site occupancy includes C(71), while C(52) is of the less-populated orientation

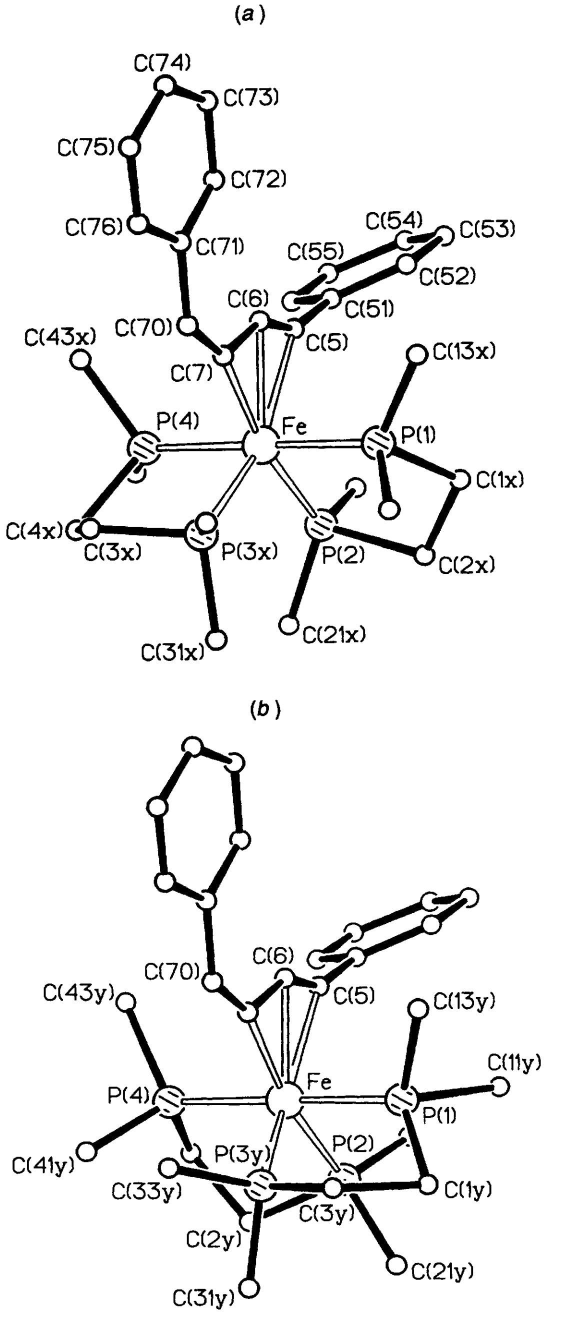

Fig. 2 The structure of the cation [Fe(PhC≡C–C=CHPh)(dmpe)$_2$]$^+$ in crystals of complex **B**, indicating the atom numbering scheme. In this complex the dmpe ligands are disordered; in identical views (and in an orientation comparable to that in Fig. 1), the major component is shown in (*a*), the minor component in (*b*)

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Table 1 Selected molecular dimensions (bond lengths in Å, angles in °) in [Fe(MeC≡C–C=CHMe)(depe)$_2$]BPh$_4$ **A** with estimated standard deviations (e.s.d.s) in parentheses

(*a*) About the Fe atom

Fe–P(1)	2.296(3)	Fe–C(5)	2.196(12)
Fe–P(2)	2.253(3)	Fe–C(6)	2.113(8)
Fe–P(3)	2.260(3)	Fe–C(7)	2.048(10)
Fe–P(4)	2.283(3)		
P(1)–Fe–P(2)	85.3(1)	P(2)–Fe–C(6)	130.8(3)
P(1)–Fe–P(3)	95.5(1)	P(3)–Fe–C(6)	124.0(3)
P(2)–Fe–P(3)	105.2(1)	P(4)–Fe–C(6)	90.6(3)
P(1)–Fe–P(4)	177.2(1)	C(5)–Fe–C(6)	34.9(4)
P(2)–Fe–P(4)	92.8(1)	P(1)–Fe–C(7)	85.8(3)
P(3)–Fe–P(4)	87.0(1)	P(2)–Fe–C(7)	93.8(3)
P(1)–Fe–C(5)	92.8(3)	P(3)–Fe–C(7)	161.0(3)
P(2)–Fe–C(5)	165.7(3)	P(4)–Fe–C(7)	92.3(3)
P(3)–Fe–C(5)	89.1(3)	C(5)–Fe–C(7)	71.9(4)
P(4)–Fe–C(5)	88.5(3)	C(6)–Fe–C(7)	37.0(4)
P(1)–Fe–C(6)	89.1(3)		

(*b*) Torsion angles in the depe ligands

P(1)–C(1)–C(2)–P(2)	52.3(9)
P(3)–C(3)–C(4)–P(4)	−48.0(10)

(*c*) In the butenynyl ligand

C(52)–C(51)	1.40(4)	C(6)–C(7)	1.321(13)
C(51)–C(5)	1.469(17)	C(7)–C(70)	1.384(14)
C(5)–C(6)	1.296(14)	C(70)–C(71)	1.466(18)
C(52)–C(51)–C(5)	108.6(19)	C(5)–C(6)–C(7)	144.8(10)
Fe–C(5)–C(51)	147.0(9)	Fe–C(7)–C(6)	74.2(6)
Fe–C(5)–C(6)	69.0(6)	Fe–C(7)–C(70)	153.5(8)
C(51)–C(5)–C(6)	144.0(12)	C(6)–C(7)–C(70)	132.3(10)
Fe–C(6)–C(5)	76.0(7)	C(7)–C(70)–C(71)	120.8(11)
Fe–C(6)–C(7)	68.8(6)		

Field *et al.* Indeed, the complex [Fe(CCMe)(CCHMe)(dmpe)$_2$]BPh$_4$ **D** in acetone shows a singlet in its ^{31}P-{^{1}H} NMR spectrum at δ −82.5, and [Fe(CCPr^i)(CCHPr^i)(dmpe)$_2$]BPh$_4$ **E** a singlet at δ −86.7. This compares with a value of *ca.* δ −82, suggested by Field *et al.*[6] for these species (never isolated).

The structure determination of compound **E** was not wholly successful (Fig. 3, and Tables 6 and 7). There is considerable disorder and the detailed bond lengths and angles are very imprecise. The iron atom unexpectedly lies on a crystallographic centre of symmetry, which implies that the two groups –C≡CPr^i and =C=CHPr^i are equivalent. This can only mean that they are aligned randomly within the crystal. There are also two independent molecules in the unit cell, and the methylene groups of the diphosphines of one of these molecules did not take up their expected staggered conformations, the FePCCP ring remaining rather flat. This is presumably also an artefact of disorder; the thermal parameters of the C atoms around P(11) are indeed significantly higher than around any other P atom. The two molecules differ principally in the orientation of the isopropyl groups with respect to the FeP$_4$ rectangular plane (Fig. 3).

The C$_\alpha$ and C$_\beta$ atoms of the alkynyl and vinylidene ligands of both molecules cannot be resolved into distinct centres for the different types of ligand; we can determine only a single carbon–carbon distance in each cation, and in each case this is clearly very short, at 1.211(8) and 1.197(9) Å. not what one might expect from the mean of a double and a triple bond. The Fe–C separations are also short, at 1.86 Å. The vinylidene ligands are clearly bent and the acetylide straight.

The structure of [Fe(CCMe)(CCHMe)(dmpe)$_2$]BPh$_4$ **D** is of rather higher quality and is well resolved. It is shown in Fig. 4, with the relevant data in Tables 8 and 9. The Fe–P separations [mean 2.229(5) Å] are entirely unexceptional for an iron(II)

Table 2 Selected molecular dimensions (bond lengths in Å, angles in °) in [Fe(PhC≡C–C=CHPh)(dmpe)$_2$]BPh$_4$·Me$_2$CO **B** with e.s.d.s in parentheses

(*a*) About the Fe atom

Fe–P(1)	2.251(3)	Fe–P(4)	2.260(3)
Fe–P(2)	2.250(2)	Fe–C(5)	2.305(7)
Fe–P(3x)	2.247(9)	Fe–C(6)	2.094(7)
Fe–P(3y)	2.160(19)	Fe–C(7)	1.987(6)
P(1)–Fe–P(2)	86.9(1)	P(4)–Fe–C(5)	89.5(2)
P(1)–Fe–P(3x)	96.2(3)	P(1)–Fe–C(6)	89.9(3)
P(2)–Fe–P(3x)	100.0(2)	P(2)–Fe–C(6)	128.0(2)
P(1)–Fe–P(3y)	79.6(8)	P(3x)–Fe–C(6)	131.9(3)
P(2)–Fe–P(3y)	97.2(5)	P(3y)–Fe–C(6)	133.1(5)
P(3x)–Fe–P(3y)	16.7(8)	P(4)–Fe–C(6)	90.9(3)
P(1)–Fe–P(4)	179.1(1)	C(5)–Fe–C(6)	32.4(3)
P(2)–Fe–P(4)	92.3(1)	P(1)–Fe–C(7)	89.7(3)
P(3x)–Fe–P(4)	83.4(3)	P(2)–Fe–C(7)	167.6(2)
P(3y)–Fe–P(4)	100.1(8)	P(3x)–Fe–C(7)	92.2(3)
P(1)–Fe–C(5)	91.1(2)	P(3y)–Fe–C(7)	93.9(5)
P(2)–Fe–C(5)	95.8(2)	P(4)–Fe–C(7)	91.1(2)
P(3x)–Fe–C(5)	162.9(3)	C(5)–Fe–C(7)	72.3(3)
P(3y)–Fe–C(5)	163.6(6)	C(6)–Fe–C(7)	40.0(3)

(*b*) Torsion angles in the dmpe ligands

P(1)–C(1x)–C(2x)–P(2)	50.2(12)
P(3x)–C(3x)–C(4x)–P(4)	−52.6(14)
P(1)–C(1y)–C(3y)–P(3y)	50.3(26)
P(2)–C(2y)–C(4y)–P(4)	−55.2(21)

(*c*) In the butenynyl ligand

C(5)–C(6)	1.243(9)	C(7)–C(70)	1.340(9)
C(6)–C(7)	1.398(10)	C(70)–H(70)	0.99(6)
C(5)–C(51)	1.427(9)	C(70)–C(71)	1.458(11)
Fe–C(5)–C(51)	142.7(5)	Fe–C(7)–C(6)	74.2(4)
Fe–C(5)–C(6)	64.4(4)	Fe–C(7)–C(70)	153.1(6)
C(6)–C(5)–C(51)	152.9(7)	C(6)–C(7)–C(70)	132.7(7)
Fe–C(6)–C(5)	83.2(5)	C(7)–C(70)–C(71)	128.8(7)
Fe–C(6)–C(7)	65.9(4)	C(7)–C(70)–H(70)	115.1(29)
C(5)–C(6)–C(7)	149.0(7)	C (71)–C(70)–H(70)	115.7(29)

compound. The carbon–carbon bond length of the alkynyl residue is 1.174(11) Å, which is a very short triple bond. The corresponding Fe–C bond is 1.963(7) Å, typical of alkynyl complexes of iron. The vinylidene moiety presents more of a problem, the formal carbon–carbon double bond has a characteristic triple bond length [1.192(15) Å], whereas the formal iron–carbon double bond is 1.853(9) Å. There is no disorder within the crystal, and the methylenes of the dmpe bridges are staggered, as expected. Corrections to the bond lengths for thermal motion have been considered, but (*i*) there is little apparent correlation between the dimensions of the ellipsoids of the atoms of the C(5) ligand, rendering such corrections difficult to apply, and (*ii*) since the thermal parameters of the atoms in the C(5) and C(6) ligands are of similar magnitude, and the dimensions in the latter ligand appear satisfactory and as expected, then we do not expect corrections to the reported dimensions in the Fe–C(5)–C(51) group for thermal motion to be significant.

We have already mentioned briefly[2] the problem with formulating [FeCl(CCPh)(dmpe)$_2$]$^+$ which might *a priori* contain Fe^{II} and neutral :C=CHPh or Fe^{IV} and formal (CCHPh)$^{2-}$, and concluded that the carbon–carbon [1.268(11) Å] and iron-carbon bond lengths [1.750(7) Å] were best rationalised on the basis of an iron(II) species containing a carbene. A similar but different problem arises here.

The Mössbauer isomer shift of the isopropyl derivative is −0.12 mm s^{-1}, the spectrum being a normal quadrupole doublet with splitting 1.39 mm s^{-1}. These values compare with

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Table 3 Final atomic coordinates (fractional × 10^4) for [$Fe(MeC{\equiv}C{-}C{=}CHMe)(depe)_2$]$BPh_4$ **A** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	5514.3(4)	2435(1)	33.3(6)	B(8)	2071(5)	2500(10)	4854(6)
P(1)	6218(1)	2453(3)	−856(2)	C(81a)	2661(4)	2549(10)	5359(6)
C(11)	6774(5)	1416(12)	−856(7)	C(82a)	3159(4)	2183(9)	5068(7)
C(12)	7183(4)	1457(12)	−1569(6)	C(83a)	3659(6)	2296(14)	5475(7)
C(13)	6518(5)	3837(12)	−1195(10)	C(84a)	3655(7)	2813(15)	6184(9)
C(14)	7004(8)	4134(15)	−595(11)	C(85a)	3181(8)	3182(13)	6499(7)
C(1)	5888(5)	2064(12)	−1803(6)	C(86a)	2679(6)	3055(10)	6088(6)
C(2)	5552(5)	941(14)	−1640(7)	C(81b)	2148(4)	1453(8)	4199(5)
P(2)	5089(1)	1210(2)	−783(1)	C(82b)	1972(4)	306(9)	4308(6)
C(21)	4978(6)	−301(10)	−572(7)	C(83b)	2066(5)	−558(11)	3763(8)
C(22)	4683(7)	−1065(13)	−1189(9)	C(84b)	2323(5)	−339(12)	3086(8)
C(23)	4428(5)	1688(11)	−1205(8)	C(85b)	2510(4)	807(11)	2961(6)
C(24)	4340(5)	1644(15)	−2047(6)	C(86b)	2414(4)	1632(9)	3501(6)
P(3)	5961(1)	1289(2)	885(1)	C(81c)	1946(3)	3732(8)	4445(5)
C(31)	5957(7)	−313(10)	770(7)	C(82c)	2082(4)	4754(9)	4775(6)
C(32)	6218(8)	−1046(12)	1409(8)	C(83c)	1933(4)	5804(9)	4483(7)
C(33)	6699(5)	1621(11)	1146(7)	C(84c)	1667(4)	5898(9)	3794(7)
C(34)	6836(5)	1548(15)	2029(7)	C(85c)	1511(4)	4875(10)	3453(6)
C(3)	5610(6)	1426(12)	1833(6)	C(86c)	1643(4)	3823(10)	3776(6)
C(4)	4972(6)	1400(13)	1679(6)	C(81d)	1565(5)	2127(9)	5447(6)
P(4)	4785(1)	2429(3)	870(1)	C(82d)	1633(6)	1383(12)	6055(6)
C(41)	4111(5)	1980(15)	602(7)	C(83d)	1224(10)	1066(17)	6523(9)
C(42)	3674(6)	2025(18)	1365(10)	C(84d)	710(9)	1583(16)	6453(9)
C(43)	4665(6)	3774(13)	1447(7)	C(85d)	600(7)	2263(13)	5854(9)
C(44)	4346(7)	4658(14)	1022(11)	C(86d)	1048(5)	2584(12)	5376(7)
C(52)*	6030(16)	5550(36)	1414(22)				
C(51)	6175(6)	4394(11)	1282(7)				
C(5)	5842(4)	3955(11)	638(6)				
C(6)	5538(4)	4261(7)	58(5)				
C(7)	5228(4)	3883(9)	−516(5)				
C(70)	4935(4)	4451(10)	−1087(6)				
C(71)*	4919(6)	5718(12)	−1115(8)				

* In the disordered butenynyl ligand, C(52) and C(71) have site occupancy factors of 0.28 and 0.72 respectively.

0.04 and 1.38 mm s^{-1} for [$Fe(CCPr^i)_2(dmpe)_2$], −0.04 and 1.32 mm s^{-1} for [$FeCl(CCHPh)(dmpe)_2$]Cl,[12] and +0.16 and 0.44 mm s^{-1} for [$FeCl(CCPh)(dmpe)_2$]. Our compound looks, in these terms, to be typical low-spin octahedral iron(II). This is consistent with the Fe–P separations (see above).

The IR spectra of complexes **D** and **E** show bands at 1636 and 1636 cm^{-1}, respectively {*cf.* 2068 and 2077 cm^{-1} for [$FeCl(CCPr^i)(dmpe)_2$] and [$FeCl(CCMe)(dmpe)_2$]; 1636 cm^{-1} for [$FeCl(CCHPr^i)(dmpe)_2$]$^+$}. Unfortunately we could obtain no stable product from [$FeCl(CCMe)(dmpe)_2$] and acid so a comparison with the isopropylvinylidene derivative was not feasible. However, the isopropyl derivative shows no IR band assignable to a vibration ν(C=C).

In the ^{13}C-{^1H} NMR spectrum the two vinylidene carbon atoms resonate at δ 79.0 (Fe=C=*C*) and 348 (Fe=C) (**E**) and 78.0 (Fe=C=*C*) and 371 (Fe=C) (**D**). The corresponding alkynyl resonances are at δ 114 (Fe–C=*C*) and 150 (Fe–C) (**E**) and 115 (Fe–C≡*C*) and 155 (Fe–C) (**D**). These differ from [$FeCl(CCPr^i)(dmpe)_2$] [δ 96.8, qnt (Fe–C)], 122.7 (Fe–C≡*C*) and [$FeCl(CCMe)(dmpe)_2$] [δ 97.8, qnt (Fe–*C*), 108.2 (Fe–C≡*C*)] and [$FeCl(CCHPr^i)(dmpe)_2$]$^+$ [δ 365.9, qnt (Fe=C), 123.0 (Fe=C= *C*)]. Although the shifts are in some ways comparable, they are clearly not the same. In particular, the lack of Fe–C coupling to phosphorus in complexes **D** and **E** is not easily explicable. All the other resonances discussed above are singlets unless otherwise stated. For [$RuCl(CCMe)(Ph_2PCH_2PPh_2)_2$], P–C coupling is observed in both alkynyl carbon resonances, though the coupling constant is very small (1–2 Hz) for Ru–C≡*C*.[13]

The ^{31}P-{^1H} NMR spectra are, of course, all singlets, so that the principal differences between the alkynyl(vinylidene) and the chloro(vinylidene) complexes would appear to be that the former have shorter carbon–carbon (formally) double bonds, longer iron–carbon double bonds, and no P–C coupling. The alternative structures for the vinylidene iron system can be written as Fe←:C=CHR and $Fe\leftarrow\overset{-}{C}\equiv\overset{+}{C}HR$. We favour the triple-bond structure in this case, which means that a hypervalent carbon atom is present. There seems no obvious reason why such a structure should be excluded. The ion CH_5^+ is well established in the gas phase and is said to be remarkably stable.[14] A derivative stabilised in an organometallic complex is not to be *a priori* rejected. Clearly, further examples of this type of complex need to be investigated, and we also plan to remeasure the diffraction intensities of complex **D** under low-temperature conditions to try to improve the resolution in this ligand. The presence of the soft alkynyl in the *trans* position may help to stabilise this form. A vinylideneiron(IV) formulation does not seem to be reasonable. However, the compound [$Ru(dppm)_2${$C{=}C{=}C(OMe)CH{=}CPh_2$}$_2$]$^{2-}$ has formal double bonds with a length of 1.22(1) Å.[15] This is also of triple-bond length, though clearly formally double. In addition, [$RuCl(CCH_2)(Ph_2PCH_2CH_2PPh_2)_2$]$PF_6$ has a C=C bond length of 1.22(1) Å which is again very short, and in [$RuCl(CCH)(Ph_2PCH_2PPh_2)_2$] the C≡C length is 1.16(1) Å.[15] Our very short C=C double bond is not an isolated phenomenon.

Field *et al.*[6] identified alkynyl(vinylidene) complexes as key intermediates in the formation of enynyl derivatives. This may be the case, but the formation of such complexes is not sufficient to explain all the data. Thus the complexes [$Fe(CCR)(CCHR)(dmpe)_2$]BPh_4 react with $KOBu^t$ in thf to give an immediate change from green to yellow. Infrared and ^1H NMR spectroscopy confirmed the formation of the bis(alkynyl) complexes [$Fe(CCR)_2(dmpe)_2$]. When these complexes were treated with HCl in thf the green alkynyl(vinylidene) complexes were regenerated instantaneously. However, the addition of one

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Table 4 Final atomic coordinates (fractional × 10^4) for $[Fe(PhC{\equiv}C\text{–}C{=}CHPh)(dmpe)_2]BPh_4 \cdot Me_2CO$ **B** with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Fe	5 853.0(9)	1 830.6(9)	1 981.9(6)	C(4x)	4 295(15)	1 044(14)	3 090(10)
P(1)	6 565(2)	3 044(2)	1 793(1)	C(41x)	6 112(13)	−952(12)	2 468(8)
C(1x)	8 199(14)	2 287(14)	2 064(11)	C(43x)	4 134(15)	495(15)	1 403(9)
C(11x)	6 092(17)	4 344(16)	2 418(10)	C(4y)	6 484(25)	−775(23)	2 695(16)
C(13x)	6 323(15)	3 737(14)	861(9)	C(41y)	3 976(23)	1 081(21)	2 808(16)
C(1y)	6 591(30)	3 980(28)	2 598(19)	C(43y)	4 585(25)	88(25)	1 264(16)
C(11y)	8 202(29)	2 357(29)	1 536(22)	C(51)	7 378(7)	80(6)	474(4)
C(13y)	5 804(25)	4 070(23)	845(15)	C(52)	8 082(8)	291(8)	39(5)
P(2)	7 601(2)	701(2)	2 717(1)	C(53)	9 041(9)	−611(10)	−272(6)
C(2x)	8 457(12)	1 561(13)	2 873(9)	C(54)	9 261(9)	−1 713(10)	−161(6)
C(21x)	7 810(12)	230(13)	3 752(8)	C(55)	8 554(10)	−1 955(9)	262(6)
C(23x)	8 734(13)	−590(14)	2 320(9)	C(56)	7 601(8)	−1 039(7)	571(5)
C(2y)	7 189(25)	−340(25)	3 296(17)	C(5)	6 422(7)	996(6)	806(4)
C(21y)	8 286(27)	1 129(27)	3 502(19)	C(6)	5 415(7)	1 848(7)	760(4)
C(23y)	8 904(21)	−299(21)	2 207(14)	C(7)	4 513(6)	2 703(6)	1 138(4)
P(3x)	4 761(8)	2797(9)	2 936(6)	C(70)	3 423(7)	3 547(7)	872(5)
C(3x)	3 645(15)	2 331(16)	3 036(10)	H(70)	2 910(50)	3 938(48)	1 286(33)
C(31x)	5 393(18)	2 644(18)	3 957(12)	C(71)	2 850(7)	3 882(7)	59(5)
C(33x)	3 784(15)	4 375(15)	2 790(10)	C(72)	3 416(9)	3 347(8)	−587(5)
P(3y)	5 059(19)	3 053(17)	2 864(11)	C(73)	2 840(10)	3 712(9)	−1 356(6)
C(3y)	5 186(33)	4 317(32)	2 765(22)	C(74)	1 687(12)	4 609(10)	−1 467(8)
C(31y)	5 269(32)	3 034(33)	3 914(21)	C(75)	1 106(10)	5 138(9)	−821(8)
C(33y)	3 312(22)	3 854(22)	2 808(14)	C(76)	1 695(8)	4 770(7)	−79(6)
P(4)	5 155(2)	604(2)	2 190(1)				
The BPh_4^- anion							
B(8)	3 050(8)	8 274(8)	3 449(5)	C(81c)	2 948(7)	7 695(6)	2 612(4)
C(81a)	2 226(6)	9 686(6)	3 320(4)	C(82c)	2 080(7)	7 372(7)	2 403(4)
C(82a)	1 813(7)	10 242(7)	2 567(5)	C(83c)	1 925(8)	6 969(8)	1 686(5)
C(83a)	1 182(7)	11 435(8)	2 440(6)	C(84c)	2 665(8)	6 801(7)	1 143(5)
C(84a)	917(8)	12 135(8)	3 070(7)	C(85c)	3 536(8)	7 095(8)	1 306(5)
C(85a)	1 283(8)	11 641(8)	3 812(7)	C(86c)	3 678(7)	7 539(7)	2 025(4)
C(86a)	1 920(7)	10 440(8)	3 949(5)	C(81d)	2 558(7)	7 777(7)	4 111(4)
C(81b)	4 448(7)	7 941(7)	3 778(4)	C(82d)	3 237(8)	6 637(8)	4 420(5)
C(82b)	4 748(8)	8 649(8)	4 255(5)	C(83d)	2 834(9)	6 153(9)	4 943(5)
C(83b)	5 891(9)	8 347(10)	4 554(5)	C(84d)	1 758(11)	6 782(11)	5 191(5)
C(84b)	6 816(10)	7 315(10)	4 391(6)	C(85d)	1 064(10)	7 895(11)	4 893(5)
C(85b)	6 566(8)	6 616(9)	3 933(6)	C(86d)	1 450(8)	8 380(8)	4 367(5)
C(86b)	5 403(8)	6 909(7)	3 638(5)				
The unresolved, disordered acetone (?) molecule							
C(90)	175(26)	5 366(21)	3 621(16)	C(93)	670(17)	5 043(25)	2 789(18)
C(91)	−623(15)	5 022(13)	3 458(12)	C(94)	−327(18)	6 638(14)	3 189(14)
C(92)	979(28)	4 820(24)	4 200(17)				

Atoms in the iron complex cation with the suffix x have a refined site occupancy factor of 0.65(1), those with suffix y have the factor 0.35(1).

drop of trifluoroacetic acid to a solution of $[Fe(CCMe)(CCHMe)(dmpe)_2]BPh_4$ in acetone gave a rapid colour change to red, characteristic of the enynyl complex. Field *et al.*[6] showed that trifluoroacetic acid in thf converts the bis(acetylido)-complexes into enynyl complexes during periods ranging from seconds to hours. However, they did not report data for depe complexes. The complex $[Fe(CCMe)_2(dmpe)_2]$ is exceptionally labile in methanol and could only be isolated in the presence of base.[5] We were not able to isolate depe alkynyl(vinylidene) complexes under any conditions because they rearranged too rapidly.

These data are best reconciled by assuming that protonation to acetylidovinylidene complexes is not the key step in the formation of enynyl complexes, rather it is the subsequent opening of a diphosphine chelate ring. Presumably this occurs spontaneously in the reaction of PhC≡CH with $[FeH(H_2)(dmpe)_2]BPh_4$ with no extra acid needed. The ring opening should enable the hydrocarbon residues to couple, and the diphosphine to rechelate, but in a *cis* arrangement. The evidence for this is circumstantial. Henderson[16] has demonstrated the temporary diphosphine ring opening during the reaction of $[FeH(N_2)(depe)_2]^+$ with HCl to give $[FeCl_2(depe)_2]$. This is promoted by transient protonation of one phosphorus of a diphosphine. The same could happen in this case.

We cannot be specific about the reaction mechanisms involved here. The fact that Field *et al.*[5,6] only observe an initial di(alkynyl) complex, whereas we can only isolate an initial alkynyl(vinylidene) complex, suggests that more than one route may be involved in enynyl complex formation. We have evidence to show that the dihydrogen is the most labile ligand in these complexes.[17] However, that may not always be the case. Bianchini *et al.*[18,19] have shown that the reaction of $[FeH(H_2)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$ with alk-1-ynes requires two molecules of alkyne to give the final product, and that no H_2 is generated. This they take to imply that the formation of $[FeH(CCPh)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$, for example, proceeds *via* deco-ordination of one arm of the phosphine, complexing of alkyne and insertion into an Fe–H bond, elimination of alkene, and subsequent formation of a σ-alkenyl complex with more alkyne. We and others[9] have also observed styrene formation in our reactions with PhC≡CH, and we know that $[FeH(H_2)(dmpe)_2]^+$ can reduce cyclopropenes and allenes without the presence of dihydrogen.[1] Consequently, the Bianchini mechanism may well also apply in our case.

Bianchini *et al.*[18] also observed dimerisation of certain alkynyl residues to give butadienes, but their systems would presumably require the reactive centres always to be *cis* because $P(CH_2CH_2PPh_2)_3$ imposes this when it co-ordinates. In our

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Table 5 A comparison of selected spectral and structural parameters of [Fe(MeC≡C–C=CHMe)(depe)$_2$]BPh$_4$ **A**, [Fe(PhC≡C–C=CHPh)(dmpe)$_2$]BPh$_4$ **B** and [Fe(Pr^{i}C≡C–C=CHPr^i)(depe)$_2$]BPh$_4$ **C**[a]

	A	**B**	**C**
Fe–P (mean)	2.273(10)	2.252(4)	
Fe–C(5)	2.196(12)	2.305(7)	
Fe–C(6)	2.113(8)	2.094(7)	
Fe–C(7)	2.048(10)	1.987(6)	
C(51)–C(5)	1.469(17)	1.427(9)	
C(5)–C(6)	1.296(14)	1.243(9)	
C(6)–C(7)	1.321(13)	1.398(10)	
C(7)–C(70)	1.384(14)	1.340(9)	
C(5)–Fe–C(6)	34.9(4)	32.4(3)	
C(6)–Fe–C(7)	37.0(4)	40.0(3)	
C(51)–C(5)–C(6)	144.0(12)	152.9(7)	
C(5)–C(6)–C(7)	144.8(10)	149.0(7)	
C(6)–C(7)–C(70)	132.3(10)	132.7(7)	
C(7)–C(70)–C(71)	120.8(11)	128.8(7)	
Fe–C(5)–C(51)	147.0(9)	142.7(5)	
Fe–C(7)–C(70)	153.5(8)	153.1(6)	
^{31}P-{^{1}H} NMR[b]	P$_A$ −77.6, $^2J_{AB}$ = 155, $^2J_{AC}$ = 35.5, $^2J_{AD}$ = 40.1 P$_B$ −75.3, $^2J_{BC}$ = 43.5, $^2J_{BD}$ = 24.6 P$_C$ −66.5, $^2J_{CD}$ = 21.8 P$_D$ −74.6	P$_A$ −77.4, $^2J_{AB}$ = 42.9, $^2J_{AC}$ = 180.5, $^2J_{AD}$ = 28.9 P$_B$ −77.7, $^2J_{BC}$ = 49.5, $^2J_{BD}$ = 23 P$_C$ −84.4, $^2J_{CD}$ = 40.3 P$_D$ −91.1	P$_A$ −82.8, $^2J_{AB}$ = 150, $^2J_{AC}$ ≡ $^2J_{AD}$ = 36.8 P$_B$ −78.3, $^2J_{BC}$ = 43.6, $^2J_{BD}$ = 26.0 P$_C$ −65.9, $^2J_{CD}$ = 18.0 P$_D$ −76.9
^{13}C-{^{1}H} NMR[b]	78.0 (s) C(70) 154.0 (s) C(7) 36.0 (s), 101.0 (s) } C(5), C(6) 12.0 (s), 27.0 (s) } C(51), C(71)	133.5 (s) C(70) 153.0 (s) C(7) 51.0 (s), 106.0 (s) } C(5), C(6)	77.7 (s) C(70) 147.8 (s) C(7) 41.5 (s), 111.8 (s) } C(5), C(6)
^{1}H NMR[b]	2.29 (d), $^3J_{HH}$ = 15, C(71)H$_3$ 2.36 (s) C(51)H$_3$ 6.11 (d), $^2J_{HH}$ = 15, C(70)H	6.11 (s) C(70)H[c]	5.97 (s) C(70)H[d]

[a] Bond lengths in Å, angles in °; NMR in ppm relative to SiMe$_4$ or P(OMe)$_3$, J in Hz. The atom numbering is consistent for all three compounds, and is shown in Fig. 1. [b] In CD$_2$Cl$_2$ unless otherwise stated. [c] Product from [FeD(D$_2$)(dmpe)$_2$]$^+$ had 1:1:1 triplet, $^1J_{CD}$ = 31.6 Hz. [d] Other signals obscured by depe resonances.

case, coupling would have to occur within the co-ordination sphere rather than by attack of alkyne upon alkynyl, and this implies a *trans* ⟶ *cis* isomerisation of the iron complex.

We propose the reaction paths in Scheme 2 for the species involved in these reactions, based upon all the observations,[6,18,19] including our own. This scheme provokes two final comments. It is likely that the intermediate in the Bianchini system[19] which gives rise to a butadiene may well be an enynyl complex which, under H$_2$, yields the final product. This is currently being tested. Finally, the coupling reactions seem to vary in facility, requiring stronger or weaker acids depending on the circumstances. Complexes of depe seem particularly labile. This could be due to weaker Fe–P bonds, or it may be because dmpe is a weaker proton base than depe. We suspect the latter to be the case. It should be noted that [FeH(H$_2$){PPh(OEt)$_2$}$_4$]BPh$_4$ and alk-1-ynes have recently been reported[20] to give rise to enynyl complexes, whereas the analogous complex of P(OEt)$_3$ gives a σ-acetylide. Clearly the influences at work are very subtle.

Experimental

The compounds [FeCl$_2$(dmpe)$_2$],[2] [FeBr$_2$(dmpe)$_2$][2] and [FeCl$_2$(depe)$_2$][21] were prepared as described elsewhere, and NaBH$_4$, KBH$_4$ and NaBD$_4$ were obtained commercially from Aldrich, as were the alkynes.

All operations were carried out under dry dinitrogen or argon, following standard Schlenk techniques. All solvents were distilled under N$_2$ from the appropriate drying agents prior to use. Where exclusion of N$_2$ was required, the solvent was saturated with argon by bubbling through immediately before use.

Infrared spectra were recorded on a Perkin Elmer 882 instrument as Nujol mulls, NMR spectra on a JEOL GSX-270 spectrometer in the appropriate deuteriated solvents using, as references, SiMe$_4$ for ^{1}H and ^{13}C and P(OMe)$_3$ for ^{31}P. Elemental analyses were carried out in this Laboratory by Mr. C. J. Macdonald, using a Perkin Elmer 2400 CHN elemental analyser. Mössbauer spectra were recorded by Dr. D. J. Evans on an ES technology MS-105 spectrometer with a 25 mCi (9.25 × 10^8 Bq) ^{57}Co source in a rhodium matrix at 77 K and referenced against iron foil at 298 K.

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](*dihydrogen*)*hydridoiron*(II) *Tetraphenylborate*.—A suspension of [FeCl$_2$(dmpe)$_2$] (1 g, 2.42 mmol) in argon-purged ethanol (80 cm^3) was treated with NaBH$_4$ (0.09 g, 2.5 mmol) in ethanol (10 cm^3). An orange solution was obtained which was stirred under argon for 0.5 h. Then NaBPh$_4$ (0.9 g, 2.6 mmol) in ethanol (10 cm^3) was added, which resulted in the immediate formation for an orange precipitate. This was stirred for 1 h before being filtered off, washed with EtOH and dried *in vacuo*. The product needed no further purification. Yield: 1.18 g (75%) (Found: C, 64.1; H, 8.4. C$_{40}$H$_{65}$BFeP$_4$ requires C, 63.7; H, 8.1%). IR: ν(Fe–H) 1856 cm^{-1}. ^{1}H NMR (−80 °C), [^{2}H$_8$]thf: δ −17.15 (qnt, $^2J_{HP}$ = 51.0 Hz, FeH) and −11.85 (br s, FeH$_2$).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*deuterio*(*dideuterium*)*iron*(II) *Tetraphenylborate*.—To [FeCl$_2$(dmpe)$_2$] (3.0 g, 7.04 mmol) in argon-purged CH$_3$OD (80 cm^3) was added NaBD$_4$ (0.3 g, 7.0 mmol) in CH$_3$OD (5 cm^3). The solution was allowed to react for 30 min before NaBPh$_4$ (2.4 g, 7.0 mmol) was added. A light beige precipitate formed and the

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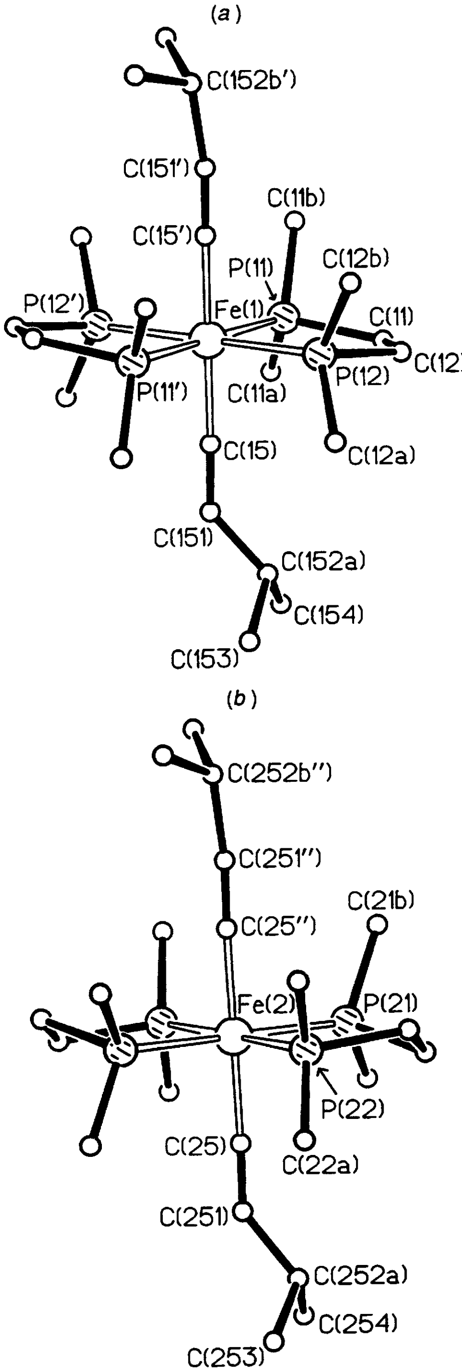

Fig. 3 The structures of the two independent cations of *trans*-[Fe(CCPr^i)(CCHPr^i)(dmpe)$_2$]$^+$ in crystals of complex **E** showing the atom numbering schemes

solution was allowed to stir for 2 h before the precipitate was filtered off and dried *in vacuo*. Yield: 3.76 g (70%). IR: ν(Fe–D) 1341 cm^{-1}. ^{2}H NMR (−80 °C, thf): δ −16.88 (qnt, $^2J_{DP}$ = 8 Hz, FeD) and −11.84 (br s, FeD_2).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(*propyn*-1-*yl*)*iron*(II).—Propyne was bubbled through a solution of [$FeCl_2$(dmpe)$_2$] (0.31 g, 0.7 mmol) in methanol (30 cm^3) to yield a dark purple solution. Then KBH_4 (0.05 g, 0.9 mmol) was added, producing an immediate change from purple to orange and evolution of a gas. The solution was stirred overnight. The solution was then filtered and taken to dryness to yield an orange solid. Yield: 0.1 g (30%) (Found: 39.4; H, 7.9. $C_{15}H_{35}ClFeP_4$ requires C, 41.8; H, 8.2%). IR: ν(C≡C) 2077 cm^{-1}. ^{13}C NMR (CD_2Cl_2): δ 13.0 (s, C*C*H_3), 13.8, 16.0 (qnt, $^1J_{CP}$ = 4–7, PCH_3), 30.5 (qnt, $^1J_{CP}$ = 13.1, PCH_2), 97.8 (qnt, $^2J_{CP}$ = 29.1 Hz, FeC) and 108.2 (s, *C*CH_3).

Table 6 Selected molecular dimensions (bond lengths in Å, angles in °) in *trans*-[Fe(CCPr^i)(CCHPr^i)(dmpe)$_2$]BPh_4 **E** with e.s.d.s in parentheses

(*a*) About the Fe atom

Fe(1)–P(11)	2.231(2)	Fe(2)–P(21)	2.239(1)
Fe(1)–P(12)	2.233(2)	Fe(2)–P(22)	2.234(2)
Fe(1)–C(15)	1.858(5)	Fe(2)–C(25)	1.873(5)
P(11)–Fe(1)–P(12)	85.6(1)	P(21)–Fe(2)–P(22)	86.2(1)
P(11)–Fe(1)–C(15)	88.0(2)	P(21)–Fe(2)–C(25)	88.4(2)
P(12)–Fe(1)–C(15)	89.2(2)	P(22)–Fe(2)–C(25)	89.9(2)

(*b*) Torsion angles in the dmpe ligand

P(11)–C(11)–C(12)–P(12)	5.8(17)
P(21)–C(21)–C(22)–P(22)	43.9(7)

(*c*) In the *trans*-C ligands

C(15)–C(151)	1.211(8)	C(25)–C(251)	1.197(9)
C(151)–C(152a)	1.466(24)	C(251)–C(252a)	1.504(19)
C(151)–C(152b)	1.537(21)	C(251)–C(252b)	1.502(22)
C(152a)–C(153)	1.521(24)	C(252a)–C(253)	1.534(21)
C(152a)–C(154)	1.654(22)	C(252a)–C(254)	1.456(24)
C(152b)–C(153)	1.561(26)	C(252b)–C(253)	1.487(24)
C(152b)–C(154)	1.554(25)	C(252b)–C(254)	1.412(28)

Fe(1)–C(15)–C(151)	178.4(6)
C(15)–C(151)–C(152a)	136.6(10)
C(15)–C(151)–C(152b)	171.0(12)
C(151)–C(152a)–C(153)	114.2(16)
C(151)–C(152a)–C(154)	111.2(14)
C(153)–C(152a)–C(154)	110.8(12)
C(151)–C(152b)–C(153)	108.2(13)
C(151)–C(152b)–C(154)	112.9(14)
C(153)–C(152b)–C(154)	114.2(16)
Fe(2)–C(25)–C(251)	178.0(5)
C(25)–C(251)–C(252a)	141.5(8)
C(25)–C(251)–C(252b)	173.8(10)
C(251)–C(252a)–C(253)	111.2(13)
C(251)–C(252a)–C(254)	113.2(13)
C(253)–C(252a)–C(254)	106.8(12)
C(251)–C(252b)–C(253)	113.9(16)
C(251)–C(252b)–C(254)	115.9(14)
C(253)–C(252b)–C(254)	111.7(16)

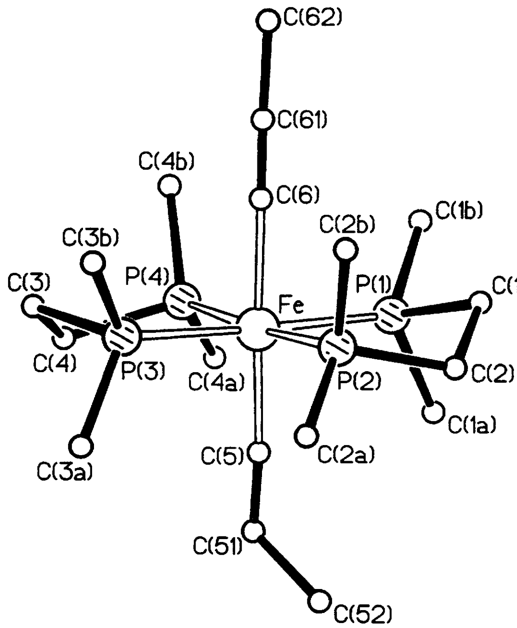

Fig. 4 The structure of the cation *trans*-[Fe(CCMe)(CCHMe)(dmpe)$_2$]$^+$ in crystals of complex **D**, showing the atom numbering scheme

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Table 7 Final atomic coordinates (fractional × 10^4) for *trans*-[Fe(CCPr^i)(CCHPr^i)(dmpe)$_2$]BPh$_4$ **E** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	5 000	5 000	0	B(7)	3 604(1)	9 919(5)	575(3)
P(11)	4 902.0(4)	6 900(2)	410.8(9)	C(71a)	3 706(1)	9 401(5)	−52(2)
C(11a)	5 212(2)	7 656(10)	1 018(5)	C(72a)	3 660(1)	8 118(5)	−264(2)
C(11b)	4 753(3)	8 287(7)	−76(5)	C(73a)	3 751(1)	7 675(7)	−777(3)
C(11)	4 565(4)	6 615(11)	756(9)	C(74a)	3 894(1)	8 532(9)	−1 107(3)
C(12)	4 395(3)	5 563(11)	657(6)	C(75a)	3 949(2)	9 794(8)	−918(3)
P(12)	4 535.7(3)	4 304(2)	210.7(7)	C(76a)	3 854(1)	10 206(6)	−400(2)
C(12a)	4 548(2)	2 828(10)	662(5)	C(71b)	3 541(1)	11 509(5)	518(3)
C(12b)	4 171(1)	4 048(9)	−402(4)	C(72b)	3 668(1)	12 380(5)	993(3)
C(15)	5 237(1)	4 482(6)	784(3)	C(73b)	3 613(2)	13 731(7)	926(5)
C(151)	5 398(2)	4 159(7)	1 292(3)	C(74b)	3 420(2)	14 231(7)	378(5)
C(152a)*	5 332(5)	3 858(20)	1 887(9)	C(75b)	3 291(2)	13 405(6)	−89(4)
C(152b)*	5 556(5)	3 820(21)	1 972(10)	C(76b)	3 349(1)	12 097(5)	−23(3)
C(153)	5 419(3)	2 462(12)	2 109(5)	C(71c)	3 913(1)	9 606(5)	1 175(2)
C(154)	5 515(3)	4 930(13)	2 419(4)	C(72c)	4 241(1)	9 799(5)	1 170(3)
Fe(2)	2 500	2 500	2 500	C(73c)	4 505(2)	9 649(7)	1 676(3)
P(21)	2 457.1(3)	2 884(1)	1 501.8(5)	C(74c)	4 459(2)	9 303(8)	2 216(4)
C(21a)	2 823(1)	3 003(8)	1 219(3)	C(75c)	4 144(2)	9 085(8)	2 261(3)
C(21b)	2 194(1)	1 840(6)	930(2)	C(76c)	3 873(2)	9 254(7)	1 751(3)
C(21)	2 272(2)	4 503(6)	1 326(3)	C(71d)	3 264(1)	9 156(4)	613(2)
C(22)	2 025(3)	4 739(9)	1 656(3)	C(72d)	2 950(1)	9 684(5)	416(2)
P(22)	2 162.6(4)	4 217(2)	2 454.6(6)	C(73d)	2 659(1)	8 998(6)	415(2)
C(22a)	2 311(2)	5 651(7)	2 909(3)	C(74d)	2 679(2)	7 740(6)	635(2)
C(22b)	1 757(2)	4 027(10)	2 601(5)	C(75d)	2 979(2)	7 172(6)	841(3)
C(25)	2 866(1)	3 628(5)	2 694(2)	C(76d)	3 267(1)	7 860(5)	834(2)
C(251)	3 102(2)	4 335(8)	2 836(3)				
C(252a)*	3 233(4)	5 611(16)	2 660(8)				
C(252b)*	3 385(5)	5 289(20)	2 946(9)				
C(253)	3 316(3)	6 567(11)	3 205(7)				
C(254)	3 533(3)	5 458(16)	2 454(6)				

* Site occupancy 0.5.

Table 8 Selected molecular dimensions (bond lengths in Å, angles in °) in *trans*-[Fe(CCMe)(CCHMe)(dmpe)$_2$]BPh$_4$ **D** with e.s.d.s in parentheses

(*a*) About the Fe atom

Fe–P(1)	2.219(2)	Fe–P(4)	2.242(2)
Fe–P(2)	2.229(2)	Fe–C(5)	1.853(9)
Fe–P(3)	2.228(2)	Fe–C(6)	1.963(7)
P(1)–Fe–P(2)	85.9(1)	P(3)–Fe–C(5)	91.3(3)
P(1)–Fe–P(3)	177.6(1)	P(4)–Fe–C(5)	93.0(2)
P(2)–Fe–P(3)	95.5(1)	P(1)–Fe–C(6)	88.2(2)
P(1)–Fe–P(4)	92.4(1)	P(2)–Fe–C(6)	87.6(2)
P(2)–Fe–P(4)	176.2(1)	P(3)–Fe–C(6)	90.0(2)
P(3)–Fe–P(4)	86.1(1)	P(4)–Fe–C(6)	88.9(2)
P(1)–Fe–C(5)	90.6(3)	C(5)–Fe–C(6)	177.8(3)
P(2)–Fe–C(5)	90.4(2)		

(*b*) Torsion angles in the dmpe ligand

P(1)–C(1)–C(2)–P(2)	−51.5(8)
P(3)–C(3)–C(4)–P(4)	−48.5(9)

(*c*) In the *trans*-C ligands

C(5)–C(51)	1.192(15)	C(6)–C(61)	1.174(11)
C(51)–C(52)	1.505(20)	C(61)–C(62)	1.467(14)
Fe–C(5)–C(51)	174.7(8)	Fe–C(6)–C(61)	176.0(7)
C(5)–C(51)–C(52)	125.5(11)	C(6)–C(61)–C(62)	177.7(9)

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(3-*methylbut*-1-*yn*-1-*yl*)*iron*(II).—To [FeCl$_2$(dmpe)$_2$] (0.30 g, 0.70 mmol) in ethanol (30 cm^3) was added 3-methylbut-1-yne (0.1 cm^3, 1.0 mmol) and the mixture was stirred for 5 min. Then NaBH$_4$ (0.025 g, 0.70 mmol) in ethanol (5 cm^3) was added and there was a change from purple to orange with the evolution of a gas. The solution was stirred for 2 h before being reduced *in vacuo* until a precipitate appeared. The solution was stored at −20 °C to crystallise the product which was filtered off and dried *in vacuo*. Yield: 0.11 g (35%) (Found: C, 42.0; H, 8.2. $C_{17}H_{39}ClFeP_4$ requires C, 44.4; H, 8.5%). IR: ν(C≡C) 2068 cm^{-1}. NMR: ^{1}H (CD_2Cl_2), δ 1.38, 1.48 (s, 24 H, PCH$_3$), 1.85 (br s, 8 H, PCH$_2$), 2.25 (br s, 1 H, CH) and 0.82 [d, $^3J_{HH}$ = 6.1 Hz, 6 H, C(CH$_3$)$_2$]; ^{31}P (acetone), δ 75.49 (s); ^{13}C (CD_2Cl_2), δ 13.4 (qnt, $^1J_{CP}$ = 4.5, PCH$_3$), 15.6 (qnt, $^1J_{CP}$ = 6.7, PCH$_3$), 24.1 [s, *C*H(CH$_3$)$_2$], 25.6 [s, C(*C*H$_3$)$_2$], 30.4 (qnt, $^1J_{CP}$ = 13.3, PCH$_2$), 96.8 (qnt, $^2J_{CP}$ = 28.5 Hz, FeC) and 122.7 (s, *C*Pr^i).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*bromo*(3-*methylbut*-1-*yn*-1-yl)*iron*(II).—The procedure was as described for [FeCl(CCPr^i)(dmpe)$_2$] but using [FeBr$_2$(dmpe)$_2$] (0.51 g, 1.0 mmol). Yield: 0.15 g (32.1%) (Found: C, 36.8; H, 7.5. $C_{17}H_{39}BrFeP_4$ requires C, 40.6; H, 7.8%). IR: ν(C≡C) 2069 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 0.82 [d, $^3J_{HH}$ = 6.8 Hz, C(CH$_3$)$_2$], 1.48, 1.50 (s, PCH$_3$), 1.88 (br s, PCH$_2$) and 2.34 (br, CH).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*chloro*(3-*methylbut*-1-*ene*-1,1-*diyl*)*iron*(II) *Chloride*.—To [FeCl(CCPr^i)(dmpe)$_2$] (0.46 g, 1.0 mmol) in diethyl ether (20 cm^3) was added anhydrous HCl (generated from SiMe$_3$Cl in methanol). An off-white precipitate was formed which was filtered off and dried *in vacuo*. Yield: 0.21 g (43%) (Found: C, 39.3; H, 7.8. $C_{17}H_{40}Cl_2FeP_4$ requires C, 41.2; H, 8.1%). IR: ν(C≡C) 1636 cm^{-1}. NMR: ^{1}H (CD_2Cl_2), δ 0.98 [d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$], 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 (acetone), δ −86.5 (s); ^{13}C (CD_2Cl_2), δ 12.9 (qnt, $^1J_{CP}$ = 6.7, PCH$_3$), 15.9 (qnt, $^1J_{CP}$ = 6.7, PCH$_3$), 23.6 [s, *C*(CH$_3$)$_2$], 25.3 [s, C(*C*H$_3$)$_2$], 29.3 (qnt, $^1J_{CP}$ = 11.1, PCH$_2$), 123.0 (s, Fe=C=*C*) and 365.9 (qnt, $^2J_{CP}$ = 31.2 Hz, Fe=C).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*(*prop*-1-*ene*-1,1-*diyl*)(*propyn*-1-*yl*)*iron*(II) *Tetraphenylborate*.—Propyne was bubbled through a solution of [FeH(H$_2$)(dmpe)$_2$]BPh$_4$ (0.75 g, 1.11 mmol) in acetone (25 cm^3) for 5 min. This was then

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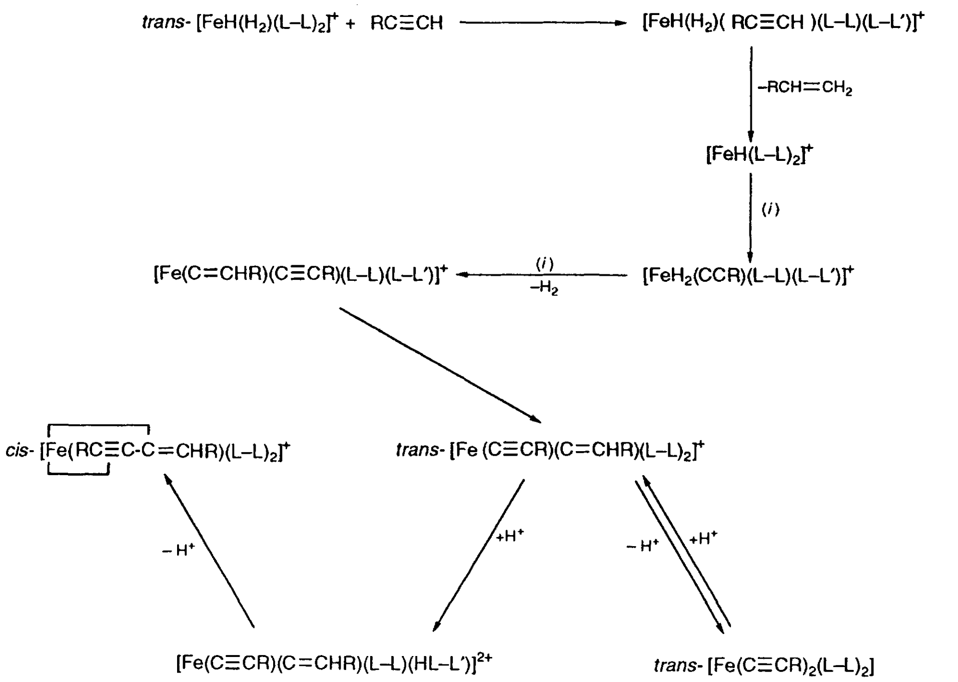
Table 9 Final atomic coordinates (fractional × 10^4) for *trans*-[Fe(CCMe)(CCHMe)(dmpe)$_2$]BPh$_4$ **D** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	2230.9(5)	4602.2(4)	2972.4(6)	B(7)	7070(5)	3502(3)	1797(5)
P(1)	1073(1)	3898(1)	2802(2)	C(71a)	6887(4)	3224(3)	2858(4)
C(1a)	1310(8)	2987(4)	2918(10)	C(72a)	6149(5)	2872(4)	3038(5)
C(1b)	125(5)	3989(5)	3445(7)	C(73a)	6061(7)	2612(5)	3969(7)
C(1)	515(7)	3981(6)	1531(6)	C(74a)	6710(7)	2707(4)	4690(6)
C(2)	1252(7)	4043(5)	891(7)	C(75a)	7441(6)	3049(4)	4550(5)
P(2)	1994(2)	4703(1)	1382(1)	C(76a)	7528(5)	3316(3)	3660(5)
C(2a)	2941(8)	4682(8)	689(7)	C(71b)	7885(4)	3048(3)	1434(4)
C(2b)	1412(10)	5462(5)	901(8)	C(72b)	8414(4)	2566(3)	1976(5)
P(3)	3365(2)	5334(1)	3187(2)	C(73b)	9102(4)	2223(3)	1646(6)
C(3a)	4452(5)	5085(7)	2843(10)	C(74b)	9309(5)	2337(3)	750(6)
C(3b)	3230(9)	6180(5)	2728(13)	C(75b)	8814(5)	2796(3)	175(5)
C(3)	3643(8)	5482(6)	4521(8)	C(76b)	8102(5)	3132(3)	517(5)
C(4)	3481(7)	4839(7)	5062(8)	C(71c)	6186(4)	3432(3)	979(4)
P(4)	2378(1)	4531(1)	4575(1)	C(72c)	5846(5)	2789(4)	708(5)
C(4a)	2344(8)	3716(4)	5140(6)	C(73c)	5084(6)	2703(5)	10(6)
C(4b)	1629(6)	5006(4)	5239(6)	C(74c)	4699(6)	3249(5)	−450(6)
C(5)	3015(5)	3892(4)	2867(5)	C(75c)	5012(6)	3879(5)	−211(6)
C(51)	3549(8)	3447(6)	2874(8)	C(76c)	5752(4)	3962(4)	486(5)
C(52)	3598(10)	2947(7)	2078(13)	C(71d)	7361(4)	4299(3)	1920(4)
C(6)	1375(5)	5345(3)	3035(5)	C(72d)	6764(4)	4768(3)	2230(4)
C(61)	851(6)	5772(4)	3122(6)	C(73d)	6951(5)	5454(3)	2303(5)
C(62)	175(8)	6297(5)	3195(11)	C(74d)	7746(5)	5693(3)	2111(5)
				C(75d)	8363(5)	5250(3)	1846(5)
				C(76d)	8176(4)	4564(3)	1745(4)



Scheme 2 L–L = dmpe or depe; L–L′ = monodentate L–L. (*i*) RC≡CH

allowed to stir at room temperature for 2 h before being filtered through Celite and concentrated to one-half the original volume. The solution was stored at −20 °C overnight. Green crystals formed, and were filtered off and dried *in vacuo*. Yield: 0.24 g (29%) (Found: C, 67.0; H, 7.9. $C_{42}H_{59}BFeP_4$ requires C, 66.9; H, 8.0%). NMR: ^{1}H (CD_2Cl_2), δ 1.47, 1.52 (s, 24 H, PCH_3), 1.63 (s, 3 H, CC–CH_3), 1.66 [s, 3 H, C=C(H)C*H*$_3$], 1.86 (br m, 8 H, PCH_2) and 4.13 (m, 1 H, C=CH); ^{13}C (CD_2Cl_2), δ 11.5 (s, CC–*C*H_3), 12.5, 15.6 (qnt, $^1J_{CP}$ = 6–8, PCH_3), 26.8 [s, C=C(H)*C*H_3], 29.0 (qnt, $^1J_{CP}$ = 12.2 Hz, PCH_2), 78.0 (s, Fe=C=*C*), 115.0 (s, Fe–C*C*), 155.0 (s, FeC) and 371.0 (s, Fe=C); ^{31}P (acetone), δ −86.7 (s).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](3-*methylbut*-1-*ene*-1,1-*diyl*)(3-*methylbut*-1-*yn*-1-*yl*)*iron*(II) *Tetraphenylborate*.—To [FeH(H_2)(dmpe)$_2$]BPh$_4$ (0.93 g, 1.37 mmol) in acetone (25 cm^3) was added 3-methylbut-1-yne (0.5 cm^3, 5.15 mmol) and the solution was stirred at room temperature for 2 h. It was filtered through Celite, concentrated to one-half the original volume then stored at −20 °C overnight. Green crystals formed which were filtered off and dried *in vacuo*. Yield: 0.27 g (25%) (Found: C, 67.9; H, 7.3. $C_{46}H_{67}BFeP_4$ requires C, 68.2; H, 8.3%). IR: ν(C=C) 1636 cm^{-1}. NMR: ^{1}H (CD_2Cl_2), 1.02 [d, $^3J_{HH}$ = 6.1, 12 H, C(CH_3)$_2$], 1.06 [d, $^3J_{HH}$ = 6.7, C(CH_3)$_2$], 1.60, 1.68 (s, 24 H, PCH_3), 1.85 (br, 8 H, PCH_2), 2.58 [m, 2 H, C*H*(CH_3)$_2$] and 4.30 (m, 1 H, C=CH); ^{13}C (CD_2Cl_2); δ 79.0 (s, Fe=C=*C*), 114.0 (s, Fe–C*C*), 150.0 (s, Fe–C) and 348.0 (s, Fe=C); the isopropyl and dmpe signals were not resolved; ^{31}P (acetone) δ −82.5 (s).

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Reaction of [Fe(CCPr^i)(C=CHPr^i)(dmpe)$_2$]BPh$_4$ *with KOBu^t*.—To a solution of [Fe(CCPr^i)(C=CHPr^i)(dmpe)$_2$]BPh$_4$ (0.06 g, 0.07 mmol) in [^{2}H$_8$]thf (5 cm^3) was added KOBu^t (0.09 g, 0.7 mmol). An immediate change from green to yellow was observed along with the formation of a white precipitate of KBPh$_4$. This was filtered off and the yellow solution was transferred to an NMR tube for analysis. IR: ν(C≡C) 2064 cm^{-1}. ^{1}H NMR ([^{2}H$_8$]thf): δ 0.95 [d, ^3J = 6 Hz, CH(C*H*$_3$)$_2$], 1.15 (s, 24 H, PCH$_3$), 1.40 (br s, 8 H, PCH$_2$) and 1.67 [br s, 2 H, C*H*(CH$_3$)$_2$].

The data should be compared with those for bis(alkynyl)-iron(II) complexes from ref. 5.

Reaction of [Fe(CCMe)(C=CHMe)(dmpe)$_2$]BPh$_4$ *with* KOBu^t.—The procedure was as described above using the analogous complex [Fe(CCMe)(C=CHMe)(dmpe)$_2$]BPh$_4$ (0.13 g, 0.2 mmol) and KOBu^t (0.03 g, 0.2 mmol) in thf (10 cm^3). IR: ν(C≡C) 2075 cm^{-1}.

Reaction of [Fe(CCMe)(C=CHMe)(dmpe)$_2$]BPh$_4$ *with* CF$_3$CO$_2$H.—To [Fe(CCMe)(C=CHMe)(dmpe)$_2$]BPh$_4$ (0.13 g, 0.2 mmol) in acetone (5 cm^3) was added one drop of trifluoroacetic acid. An immediate change from green to red was observed, indicating the formation of the butenyne complex. No crystalline solid was isolated from the reaction mixture. This observation should be compared with the data of ref. 6.

trans-*Bis*[1,2-*bis(diethylphosphino)ethane*](*dihydrogen*)-*hydridoiron*(II) *Tetraphenylborate*.—To a solution of [FeCl$_2$-(depe)$_2$] (2.4 g, 4.5 mmol) in ethanol (50 cm^3) was added NaBH$_4$ (0.17 g, 4.5 mmol) in ethanol (5 cm^3). There was an immediate change from purple to orange accompanied by the evolution of a gas. After 15 min NaBPh$_4$ (1.5 g, 4.5 mmol) in ethanol (5 cm^3) was added and a precipitate formed. This was allowed to stir for 2 h before being filtered off and dried *in vacuo*. Yield: 2.16 g (62%). IR: ν(Fe–H) 1884 cm^{-1}.

Bis[1,2-*bis(diethylphosphino)ethane*](1,4-*dimethylbut*-1-*en*-3-*yn*-2-*yl*)*iron*(II) *Tetraphenylborate*.—Propyne was bubbled through a solution of [FeH(H$_2$)(depe)$_2$]BPh$_4$ (0.78 g, 1.0 mmol) in acetone (30 cm^3) for *ca*. 5 min. The solution immediately turned green and after stirring for 30 min changed to dark red. It was filtered through Celite, the filtrate concentrated to one-half volume, and stored at −20 °C overnight. Dark red crystals that formed were filtered off and dried *in vacuo*. Yield: 0.34 g (39%) (Found: C, 68.7; H, 8.8. C$_{50}$H$_{75}$BFeP$_4$ requires C, 69.3; H, 8.7%).

Bis[1,2-*bis(diethylphosphino)ethane*](1,4-*diisopropylbut*-1-*en*-3-*yn*-2-*yl*)*iron*(II) *Tetraphenylborate*.—To a solution of [FeH-(H$_2$)(depe)$_2$]BPh$_4$ (0.5 g, 0.65 mmol) in acetone (20 cm^3) was added an excess of 3-methylbut-1-yne (0.35 cm^3, 3.5 mmol). The solution was allowed to stir for 2 h and turned dark red. After filtration through Celite, the filtrate was concentrated to one-half the original volume and stored at −20 °C overnight. The red solid that had formed was filtered off and dried *in vacuo*. Yield: 0.17 g (28%) (Found: C, 69.0, H, 9.1. C$_{53}$H$_{82}$BFeP$_4$ requires C, 70.2; H, 9.0%).

Bis[1,2-*bis(dimethylphosphino)ethane*](1,4-*diphenylbut*-1-*en*-3-*yn*-2-*yl*)*iron*(II) *Tetraphenylborate*.—To [FeH(H$_2$)(dmpe)$_2$]BPh$_4$ (0.68 g, 1 mmol) in thf–acetone, PhC≡CH (1 cm^3, excess) was added. The mixture was stirred for 3 h at room temperature. During this time the solution became orange. It was then filtered through Celite, concentrated, and cooled to −20 °C, affording red-orange crystals of the product in 40% yield (containing one acetone molecule of crystallisation [Found: C, 69.5; H, 7.3. C$_{52}$H$_{63}$BFeP$_4$·(CH$_3$)$_2$CO requires C, 70.5; H, 7.35%). IR: ν(C=C) 1589, ν(C=O) 1716 cm^{-1}. ^{1}H NMR ([^{2}H$_6$]acetone): δ 0.798 (d, $^2J_{HP}$ = 8.07, 3 H), 0.914 (d, $^2J_{HP}$ = 8.74 Hz, 3 H), 1.382 (d, $^2J_{HP}$ = 6.72, 6 H), 1.527 (d, $^2J_{HP}$ = 8.07, 6 H), 1.713 (d, $^2J_{HP}$ = 7.39 Hz, 6 H) [all (C*H*$_3$)$_2$-PCH$_2$CH$_2$P(C*H*$_3$)$_2$], 2.831 (s, 1 H, C*H*Ph), 6.760 (t), 6.909 (t), 7.185 (t), 7.322 (s), 7.342 (t), 7.471(s) and 7.780 (d) (30 H, all aromatic H).

Crystal Structure Analyses.—The X-ray analysis of [Fe(MeC≡C–C=CHMe)(depe)$_2$]BPh$_4$ **A** is described below. The analyses of complexes **B**, **D** and **E** followed similar courses. The crystal data for the four complexes are in Table 10, and experimental details of the analyses are in Table 11.

The translucent red crystals of complex **A** have approximately cubic shape. One was mounted on a glass fibre and, after preliminary photographic examination, transferred to a Enraf-Nonius CAD4 diffractometer (with monochromated Mo-Kα radiation, λ 0.710 69 Å) for determination of accurate cell parameters by refinement from the goniometer settings of 25 reflections with θ *ca*. 10.5°, each centred in four orientations. Diffraction intensities were measured to $θ_{max}$ = 22°.

During processing, the intensities were corrected for Lorentz and polarisation effects, slight absorption effects (by semi-empirical ψ-scan methods), and to ensure no negative nett intensities (by Bayesian statistical methods). No deterioration of the crystal was detected during the analysis.

Table 10 Crystal data

Complex	A	B	D	E
Complex formula	[Fe(MeC≡C–C=CHMe)-(depe)$_2$]BPh$_4$	[Fe(PhC≡C–C=CHPh)-(dmpe)$_2$]BPh$_4$·Me$_2$CO	*trans*-[Fe(C≡CMe)-(C=CHMe)(dmpe)$_2$]BPh$_4$	*trans*-[Fe(C≡CPr^i)-(C=CHPr^i)(dmpe)$_2$]BPh$_4$
Elemental formula	C$_{50}$H$_{75}$BFeP$_4$	C$_{55}$H$_{69}$BFeOP$_4$	C$_{42}$H$_{59}$BFeP$_4$	C$_{46}$H$_{67}$BFeP$_4$
M	866.7	936.7	754.5	810.6
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$P2_1/n$ (equiv. to no. 14)	$I2/c$ (equiv. to no. 15)
Cell dimensions				
a/Å	24.105(2)	12.954(2)	15.019(1)	41.832(5)
b/Å	11.564(1)	13.283(1)	19.816(1)	10.197(1)
c/Å	17.388(2)	17.081(2)	14.078(1)	22.489(1)
α/°	90	90.704(9)	90	90
β/°	90	96.796(10)	97.527(6)	105.183(8)
γ/°	90	61.238(8)	90	90
U/Å^3	4847.0	2554.9	4153.8	9257.9
Z	4	2	4	8
D_c/g cm^{-3})	1.188	1.217	1.206	1.163
F(000)	1864	996	1608	3472
μ(Mo-Kα)/cm^{-1}	4.7	4.5	5.4	4.9

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Table 11 Crystallographic experimental details, data collection and structure refinement

Complex	A	B	D	E
Crystal shape, colour	Translucent, red cubes	Thick red plates	Green rhombs	Green trapezoids
Crystal size (mm)	*ca.* 0.24 × 0.33 × 0.36	0.12 × 0.25 × 0.25	*ca.* 0.21 × 0.21 × 0.43	*ca.* 0.50 × 0.14 × 0.16
Crystal mounting	On glass fibre	On glass fibre, coated with silicone grease	On glass fibre	On glass fibre
On diffractometer: θ_{max}	22	22.5	22	22
No. of unique reflections measured	3347	6679	5069	5654
Diffraction intensities corrected for:				
Lorentz-polarisation effects	Yes	Yes	Yes	Yes
Deterioration	No	No	Yes	No
Absorption (with minimum, maximum transmission factors)	Yes (0.37/0.39)	Yes (0.95/0.99)	Yes (0.88/0.92)	Yes (0.47/0.50)
To eliminate negative intensities	Yes	Yes	Yes	Yes
No. of reflections used in refinement having $I > n\sigma_I$	2910	4313	4063	4881
n	2	1	1	1
Hydrogen atoms in the refinement process	Phenyl H included in idealised positions with free U_{iso}	As for **A**. Olefinic H butenynyl ligand refined freely	Methylene and phenyl H riding on parent C; methyl H refined with constraints. All with freely refined U_{iso}	As for **D** except that no H were included in the alkynyl and vinylidene ligands
Final R	0.068	0.076	0.079	0.065
Final R' value[22,*]	0.075	0.081	0.087	0.070
Final R_g value[22,*]	0.094	0.098	0.101	0.078
Weighting scheme w	$(\sigma_F^2 + 0.001\,47F^2)^{-1}$	$(\sigma_F^2 + 0.003\,20F^2)^{-1}$	$(\sigma_F^2 + 0.001\,92F^2)^{-1}$	$(\sigma_F^2 + 0.001\,97F^2)^{-1}$
Atoms refined anisotropically	Fe, P, B, C (except minor occupancy in disordered butenynyl ligand)	Fe, P (except for minor disordered atom), B, C (except for disordered atoms in dmpe ligands	All non-hydrogen atoms	Fe, P, B, C (except disordered γ-C in alkynyl and vinylidene ligands)
Highest peaks in final difference map/e Å^{-3}	0.7 among depe ligands	0.5 in disordered dmpe ligand region	0.55 amongst dmpe ligands	0.45 amongst dmpe and alkynyl/vinylidene ligands

* $R' = \Sigma(w^{\frac{1}{2}}\Delta)/\Sigma w^{\frac{1}{2}}|F_o|$; $R_g = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, where $\Delta = ||F_o| - |F_c||$ and w = weight as shown.

Of 3347 independent reflections input to the SHELX program suite,[22] 2910 were considered 'observed', having $I > 2\sigma_I$. The coordinates of the iron atom were derived from a Patterson synthesis. Subsequent electron-density and Fourier difference syntheses revealed the positions of all remaining non-hydrogen atoms. Refinement by full-matrix least-squares methods was concluded with $R = 0.068$ and $R' = 0.075$ for the observed data weighted $w = (\sigma_F^2 = 0.001\,47\,F^2)^{-1}$.

In the butenynyl ligand, disordered in two overlapping orientations, C(71) has a site occupancy of 0.72 and C(52) of 0.28. The C(52) atom was refined isotropically; all the other non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included only in the BPh_4^- anion, in idealised positions; their isotropic thermal parameters were refined freely.

The highest peaks in a final difference map were *ca.* 0.70 e Å^{-3} and were close to atoms in the phosphine ligands.

Scattering factors for neutral atoms were taken from ref. 23. All computer programs used in this analysis have been noted above or in Table 4 of ref. 24, and were run on a Dec MicroVAX II computer in this Laboratory.

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

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References

1 A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh, C. A. McGeary, A. T. Rowley, M. Bravo, C. E. McKenna and M.-C. McKenna, *J. Chem. Soc., Chem. Commun.*, 1991, 522.
2 D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 75
3 A. Hills, D. L. Hughes, M. Jimenez-Tenorio and G. J. Leigh, *J. Organomet. Chem.*, 1990, **391**, C41.
4 L. D. Field, A. V. George and T. W. Hambley, *Inorg. Chem.*, 1990, **29**, 4565.
5 L. D. Field, A. V. George, E. Y. Malouf, I. H. M. Slip and T. W. Hambley, *Organometallics*, 1991, **10**, 3842.
6 L. D. Field, A. V. George, G. R. Purches and I. H. M. Slip, *Organometallics*, 1992, **11**, 3019.
7 J. Lewis, M. S. Khan, A. K. Kahkov and P. R. Raithby, *J. Organomet. Chem.*, 1992, **443**, 135.
8 N. Pirio, D. Touchard, P. H. Dixneuf, M. Fettouhi and L. Ouahab, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 651.
9 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1988, 546; L. D. Field, A. V. George, T. W. Hambley, E. Y. Malouf and D. J. Young, *J. Chem. Soc., Chem. Commun.*, 1990, 931.
10 A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, **20**, 3041.
11 G. Jia, A. L. Rheingold and D. W. Meek, *Organometallics*, 1989, **8**, 1380; Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh and J. Y. Satoh, *J. Am. Chem. Soc.*, 1991, **113**, 9604; G. Jia, J. C. Gallucci, A. L. Rheingold, B. S. Haggerty and D. W. Meek, *Organometallics*, 1991, **10**, 3459; A. Dobson, D. S. Moore and S. D. Robinson, *J. Organomet. Chem.*, 1979, **177**, C8; J. Gotzig, H. Otto and H. Werner, *J. Organomet. Chem.*, 1985, **287**, 247; A. K. McMullen, J. P. Selegne, and J.-G. Wang, *Organometallics*, 1991, **10**, 3421; G. Albertin, P. Amendola, S. Antoniutti, S. Ianelli, G. Pelizzi and E. Bordignon, *Organometallics*, 1991, **10**, 2876; N. W. Alcock, A. F. Hill and R. P. Melling, *Organometallics*, 1991, **10**, 3898; G. Albertin, S. Antoniutti, E. Del Ministro and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1992, 3203; C. Bianchini, C. Bohanna, M. A. Esteruelas, P. Frediani, A. Meli, L. A. Oro and M. Peruzzini, *Organometallics*, 1992, **11**, 3837.
12 D. J. Evans, M. Jimenez-Tenorio and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1991, 1785.
13 P. H. Dixneuf, personal communication.
14 K. Hiraokaana and P. J. Kebarle, *J. Am. Chem. Soc.*, 1976, **98**, 6119;

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D. K. Bohme, G. I. Mackay and H. I. Schiff, *J. Chem. Phys.*, 1980, **73**, 4978.
15 N. Pirio, D. Touchard, P. H. Dixneuf, M. Fettouhi and L. Ouahab, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 651.
16 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1988, 509, 515.
17 M. Basallotte and G. J. Leigh, unpublished work.
18 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, F. Zanobini and P. Frediani, *Organometallics*, 1989, **8**, 2080.
19 C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics*, 1992, **11**, 138.
20 G. Albertin, S. Antoniutti, E. Del Ministro and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1992, 3203.
21 J. E. Barclay, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1988, 2865.
22 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
23 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
24 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

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