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Unsymmetrically Substituted Butenynyl-Iron(II) Complexes

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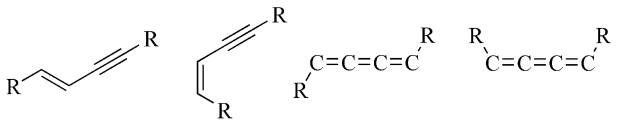
The preparation and characterisation of iron(II) complexes bearing unsymmetrically 1,4-disubstituted η^3-butenynyl ligands, *cis*-[Fe(C(C≡CR)=C(H)R′)(dmpe)$_2$][PF$_6$] (e.g. R = *t*Bu, R′ = Ph **2e**; R = Ph, R′ = *t*Bu **2e′**) are reported. The complexes were obtained as a mixture by protonation and rearrangement of the bis(acetylido)iron(II) complex *trans*-Fe(CCPh)(CC*t*Bu)(dmpe)$_2$. The complexes **2e** and **2e′** were separated by crystallisation and were both characterised crystallographically. In addition, a number of complexes with symmetrically 1,4-disubstituted butenynyl ligands *cis*-[Fe(C(C≡CR)=C(H)R)(dmpe)$_2$][PF$_6$] (R = *p*-C$_6$H$_4$-OMe **2a**; *p*-C$_6$H$_4$-Me **2b**. C$_6$H$_3$-3,5-(CF$_3$)$_2$ **2c**; 1-adamantyl **2d**) were synthesised by protonation and rearrangement of the corresponding bis(acetylido)iron(II) complexes.

Introduction

Transition-metal butenynyl complexes have been identified as key intermediates in the metal-catalysed head-to-head couplings of alkynes leading to *E*/*Z*-1,4-disubstituted 1-buten-3-ynes[1–5] and *E*/*Z*-1,4-disubstituted butatrienes.[6] Such compounds are of interest as building blocks in organic synthesis and as components of biologically active molecules.[7] The majority of alkyne dimerisation studies have focused on the homo-dimerisation of terminal alkynes; there has been relatively little attention to the cross-coupling of two *different* terminal alkynes.[8] The regioselective and stereoselective catalytic synthesis of unsymmetrically 1,4-disubstituted butenynes from alkyne mixtures could be utilised for the synthesis of more complex organic molecules.[3,9] In a manner similar to the homodimerisation of alkynes, metal-catalysed cross-coupling reactions could involve the intermediacy of unsymmetrically 1,4-disubstituted butenyne metal complexes



(*E*)-butenyne (*Z*)-butenyne (*E*)-butatriene (*Z*)-butatriene

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When used as a ligand, the but-1-en-3-yn-2-yl moiety can coordinate in either an η^3- or η^1-mode, depending on the co-ligands and metal centre, and the η^1-coordination mode of butenynyl ligands has been implicated as an important intermediate preceding σ-bond metathesis with alkynes during the metal mediated coupling of alkynes.[10] Butenynyl complexes have been studied for a range of transition metals including iron,[11–14] ruthenium,[2,5,10,15–18] osmium,[19] and platinum.[20] Various methods have been established for the synthesis of butenynyl complexes, including the addition of 1,4-disubstituted-1,3-diynes to metal hydride complexes,[2,15,21] and the addition of terminal acetylenes to either metal hydrides,[2,13,22,23] metal acetylides,[1,17,24] or metal alkenyl complexes.[22] Other methods of synthesis include the insertion of a coordinated acetylide into a metal–vinylidene bond.[2,6,12,24,25]

We have previously reported[12,18] the synthesis of symmetrical butenynyl-iron(II) and -ruthenium complexes, [M(C(C≡CR)=C(H)R)(P$_4$)]$^+$ {M = Fe, P$_4$ = 2 × dmpe [1,2-bis(dimethylphosphanyl)ethane]; M = Ru, P$_4$ = 4 × PMe$_3$} by the acidification of the corresponding bis(acetylido)-iron(II) and -ruthenium(II) complexes. The bis(acetylido) complexes were protonated at an acetylenic β-carbon to form vinylideneacetylido complexes, which rearrange with coupling of the acetylide and vinylidene ligands to form the butenynyl complexes.

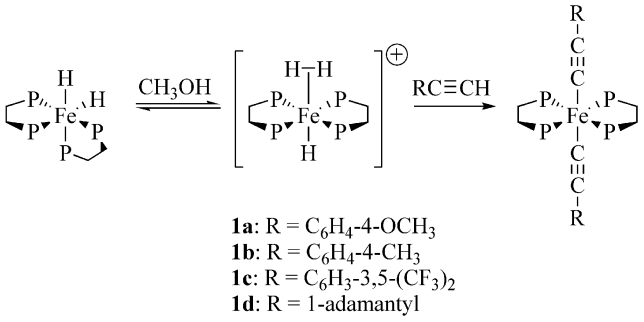
As an extension of this work, we report the synthesis and characterisation of a number of iron(II) complexes bearing both symmetrically and unsymmetrically substituted butenynyl ligands.

Results and Discussion

Synthesis of Bis(acetylido) Complexes

The reaction of terminal acetylenes with *cis*-FeH$_2$(dmpe)$_2$ in MeOH is known[12] to yield bis(acetylido)iron(II) com-

plexes (Scheme 1). This method has been used to prepare a number of iron(II) complexes **1a**–**d** of the form *trans*-$Fe(C{\equiv}CR)_2(dmpe)_2$ incorporating a variety of aryl- and alkyl-substituted acetylenes.



1a: R = C_6H_4-4-OCH_3
1b: R = C_6H_4-4-CH_3
1c: R = C_6H_3-3,5-$(CF_3)_2$
1d: R = 1-adamantyl

Scheme 1.

The NMR spectra of the resultant complexes are unremarkable, with the *trans* configuration of the ligands confirmed by the presence of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum. Crystals suitable for X-ray structure determination were grown by recrystallisation from benzene (**1a**) or toluene (**1b**, **1c**) (Figure 1); selected bond lengths [Å] and angles [°] are shown in Table 1.

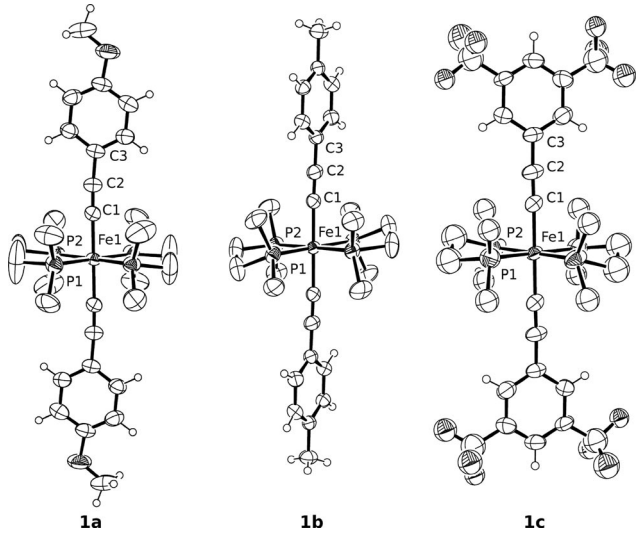


Figure 1. Molecular projection of the complexes *trans*-$Fe(C{\equiv}C{-}C_6H_4$-4-$OMe)_2(dmpe)_2$ (**1a**, left), *trans*-$Fe(C{\equiv}C{-}C_6H_4$-4-$Me)_2(dmpe)_2$ (**1b**, centre) and *trans*-$Fe(C{\equiv}C{-}C_6H_3$-3,5-$(CF_3)_2)_2(dmpe)_2$ (**1c**, right). Thermal ellipsoids are shown at the 50% probability levels, selected hydrogen atoms have been removed for clarity.

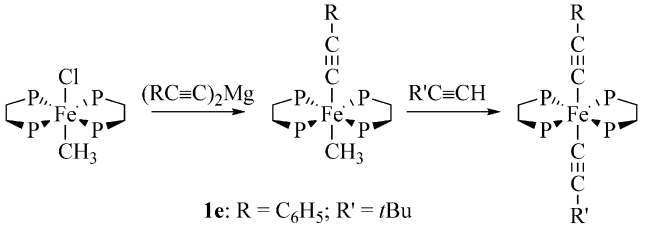
Crystallographically, the complexes **1a**–**1c** are highly symmetrical, with the asymmetric unit consisting of one half of each molecule. The structural analysis confirms the expected octahedral geometry with the two acetylide groups being disposed in a mutually *trans* fashion. The seven atoms forming the central core of the complexes (C–C≡C–Fe–C≡C–C) are essentially colinear with the acetylide groups orthogonal to the plane containing the iron and four phosphorus atoms. Comparison of the bond lengths with the

Table 1. Selected bond lengths [Å] and angles [°] for *trans*-$[Fe(C{\equiv}C{-}C_6H_4$-4-$OMe)]_2(dmpe)_2$ (**1a**), *trans*-$[Fe(C{\equiv}C{-}C_6H_4$-4-$Me)_2(dmpe)_2]$ (**1b**), and *trans*-$[Fe(C{\equiv}C{-}C_6H_3$-3,5-$(CF_3)_2)_2(dmpe)_2]$ (**1c**).

	1a	**1b**	**1c**
Fe(1)–C(1)	1.935(4)	1.937(2)	1.917(6)
C(1)–C(2)	1.197(5)	1.205 (3)	1.219(8)
C(2)–C(3)	1.432(5)	1.437(3)	1.422(8)
Fe(1)–P(1)	2.204(1)	2.206(1)	2.207(2)
Fe(1)–P(2)	2.201(1)	2.2082(9)	2.209(2)
Fe(1)–C(1)–C(2)	178.6(4)	177.4(2)	178.2(5)
C(1)–C(2)–C(3)	175.8(4)	177.3(2)	176.3(7)

known bis(acetylido)iron(II) complex *trans*-$[Fe(C{\equiv}CPh)_2(dmpe)_2]$[26] shows that there is very little variation between the structures, with the Fe–C, C≡C and C–C bonds being essentially indistinguishable between complexes.

The bis(acetylido) complexes *trans*-$[Fe(C{\equiv}CPh)(C{\equiv}CtBu)(dmpe)_2]$ (**1e**), *trans*-$[Fe(C{\equiv}CC_6H_4$-4-$CH_3)(C{\equiv}CtBu)(dmpe)_2]$ (**1f**) and *trans*-$[Fe(C{\equiv}CPh)(C{\equiv}CSi(CH_3)_3)(dmpe)_2]$ (**1g**) were synthesised as described previously from *trans*-$Fe(CH_3)Cl(dmpe)_2$ in a two-step sequence (Scheme 2).[27]



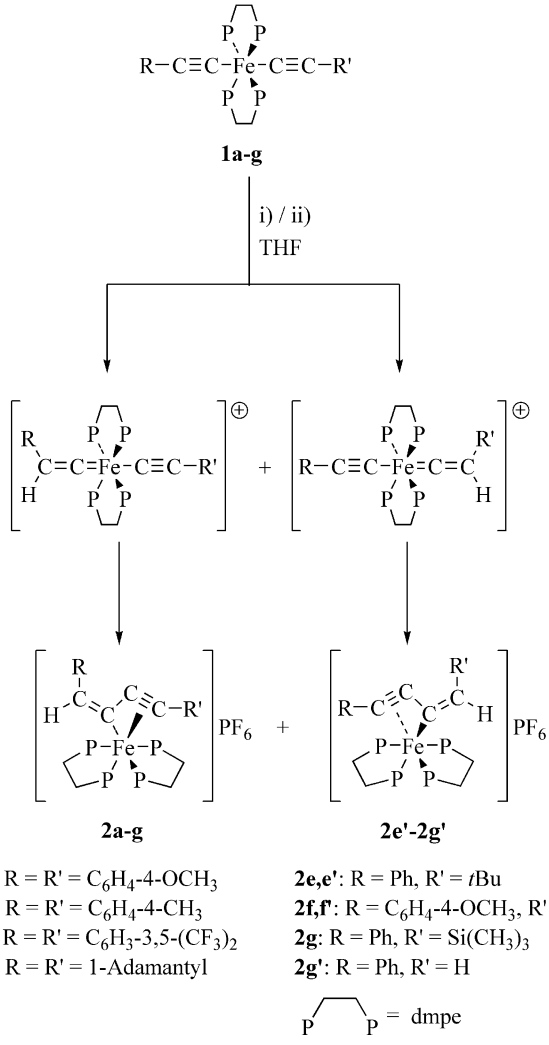
1e: R = C_6H_5; R' = *t*Bu
1f: R = C_6H_4-4-CH_3; R' = *t*Bu
1g: R = C_6H_5; R' = $Si(CH_3)_3$

Scheme 2.

Rearrangement to Butenynes

The addition of trifluoroacetic acid to **1a**–**d** in THF, followed by anion exchange and recrystallisation from ethanol led to the isolation of the complexes *cis*-$[Fe(C(C{\equiv}CR){=}CHR)(dmpe)_2][PF_6]$ (**2a**–**d**) in good yield. The synthesis of complexes bearing unsymmetrically substituted butenynyl ligands was undertaken from the known[27] bis(acetylido) complexes *trans*-$[Fe(C{\equiv}CPh)(C{\equiv}CtBu)(dmpe)_2]$ (**1e**), *trans*-$[Fe(C{\equiv}CC_6H_4$-4-$CH_3)(C{\equiv}CtBu)(dmpe)_2]$ (**1f**) and *trans*-$[Fe(C{\equiv}CPh)(C{\equiv}CSi(CH_3)_3)(dmpe)_2]$ (**1g**). Addition of either trifluoroacetic acid or ammonium hexafluorophosphate to solutions of **1e**–**g** gave mixtures of the two possible regioisomeric complexes **2e/e′**–**2g/g′** (Scheme 3).

The relative yields of the two possible regioisomers of **2e/e′**–**2g/g′** were determined by NMR spectroscopy and depended on the nature of the acetylide ligands, and in the case of **2g/g′**, on the temperature at which the reaction was performed (Table 2).



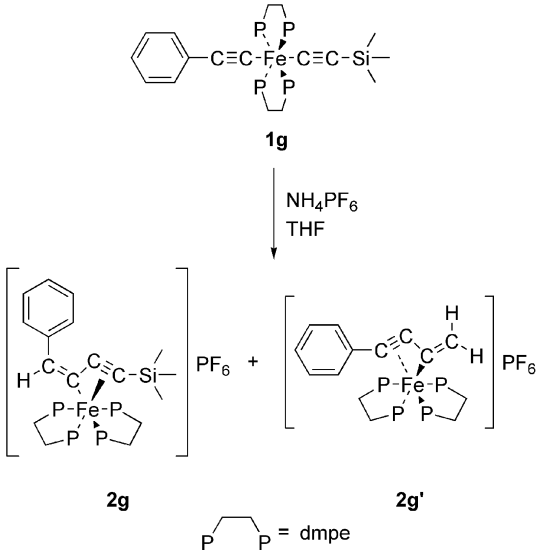
Scheme 3. Preparation of butenynyl-iron(II) complexes **2a**–**g**. Reagents: i) CF_3COOH, KPF_6 (**2a**–**2d**, **2f/f′**). ii) NH_4PF_6 (**2e/e′**, **2g/g′**).

Table 2. Yields of non-symmetric butenynyl-iron(II) complexes from bis(acetylido)iron(II) complexes.

Acetylide complex	Butenynyl complex	Relative yield [%][a]	Temp. [°C]
1e	**2e/2e′**	45:55	24
1e	**2e/2e′**	45:55	65
1f	**2f/2f′**	>98/<2[b]	24
1g	**2g/2g′**	10:90	10
1g	**2g/2g′**	23:77	65

[a] Average of two preparations. [b] At the limit of detection.

Attempts to prepare complexes incorporating a trimethylsilyl group met with limited success. The first step in butenyne formation is generally taken to be protonation at one of the acetylide β-carbon atoms to yield a mixed vinylidene/acetylide complex,[12,28] and this is followed by coupling of the two carbon-based ligands. Protonation of the β-carbon of the trimethylsilylacetylido ligand in *trans*-[Fe(C≡CC_6H_5)(C≡CSi$(CH_3)_3$)(dmpe)$_2$] (**1h**) resulted in the cleavage of the trimethylsilyl group to give *cis*-[Fe(C(C≡CC_6H_5)=CH_2)(dmpe)$_2$][PF_6] (**2g′**), while protonation at the phenylacetylido ligand resulted in retention of the trimethylsilyl group and the formation of *cis*-[Fe(C(C≡CSi$(CH_3)_3$)=C(H)C_6H_5)(dmpe)$_2$][PF_6] (**2g**) (Scheme 4).



Scheme 4.

The lability of carbon–silicon bonds is well established, and, although the cleavage of trimethylsilyl groups from trimethylsilylacetylide complexes to form the parent acetylido complexes has been reported to be particularly difficult in some cases,[29] the use of ammonium hexafluorophosphate appears to allow the isolation of vinylidene complexes bearing the C=CH_2 moiety in good yields.[30] The desilylation of **2g′** occurs early in the reaction to yield the deprotected vinylidene complex, which then undergoes ligand coupling to give the final product.

As has previously been noted for iron butenyne complexes of this type,[12,14] the butenynyliron(II) complexes generally exhibit four sharp eight-line multiplets in the $^{31}P\{^1H\}$ NMR spectrum ranging from δ = 49 ppm to 65 ppm, with the observed splittings due to either *cis* (–19 to –50 Hz) or *trans* (150 Hz to 170 Hz) phosphorus–phosphorus coupling. Second-order coupling effects arise in the $^{31}P\{^1H\}$ NMR spectrum of **2e** and **2e′** due to the close proximity of the chemical shifts. Assignment of the $^{31}P\{^1H\}$ NMR spectra of these complexes was achieved by crude extraction of coupling constants from each species by the use of ^{31}P-COSY NMR spectroscopy. The coupling constants and chemical shifts were then refined by the use of an iterative $^{31}P\{^1H\}$-NMR simulation program. The simulated spectra for each complex were obtained separately (see parts a and b in Figure 2), combined (Figure 2, c), and compared with the experimental data (Figure 2, d). The appearance of unique phosphorus resonances is entirely consistent with the structures revealed by the X-ray crystal structure analysis (vide infra).

The reaction of *trans*-[Fe(C≡CC_6H_5)(C≡C*t*Bu)(dmpe)$_2$] (**1e**) with NH_4PF_6 at –10 °C occurred at such a rate that it could be followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. During the course of the reaction, two intermediates were

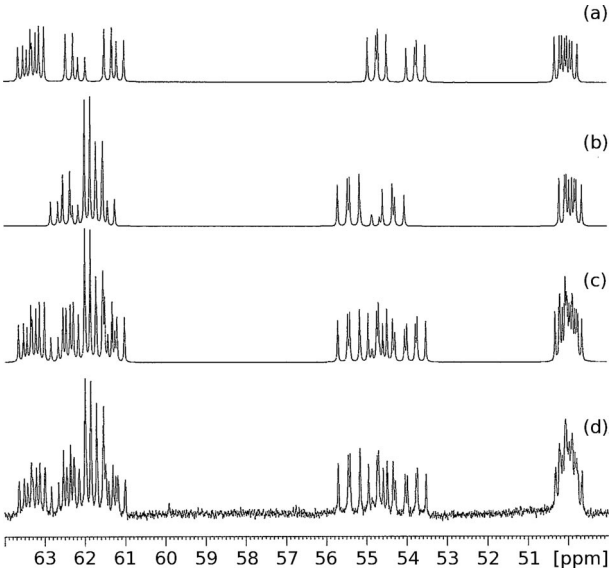
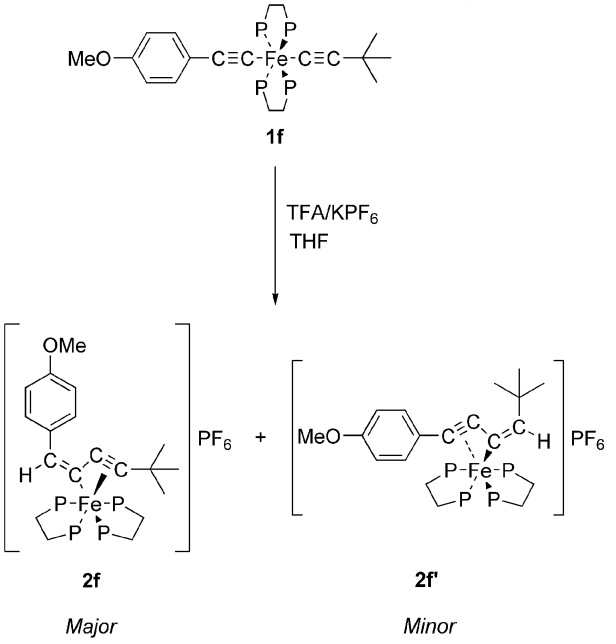


Figure 2. (a) Simulated $^{31}P\{^{1}H\}$ NMR spectrum of **2f**. (b) Simulated spectrum of **2f′**. (c) Combined simulated spectra. (d) Experimental spectrum [162 MHz, $(CD_3)_2CO$].



Scheme 5.

observed in the $^{31}P\{^{1}H\}$ NMR spectrum, with broad singlet resonances appearing at δ = 56.8 ppm and 56.7 ppm (in the ratio 45:55 respectively). Evidence allowing assignment of these intermediates as vinylidene species was provided by the ^{1}H NMR spectrum, with the appearance of resonances corresponding to vinyl protons at δ = 4.91 and 5.79 ppm. Both (acetylido)vinylidene-iron(II) complexes then slowly rearranged at room temperature to the two butenynyl-iron(II) complexes **2e** and **2e′**. The proportions of the (acetylido)vinylidene-iron(II) intermediates mirrored the final distribution of butenynyl regioisomers. Clearly then, **1e** can be protonated at the β-carbon of both acetylide ligands, with little preference for the site of protonation in this case.

In the case of **2f/f′**, there is a clear preference for protonation at the β-carbon of the 4-methoxyphenylacetylide ligand. As there are essentially no steric differences between **1e** and **1f**, this stark difference in reactivity is likely the result of the high electron-donating ability of the methoxy substituent on the aryl ring in **1f** increasing the susceptibility of the acetylenic β-carbon to electrophilic attack (Scheme 5) and stabilising the resulting cation.

Suitable crystals of **2a**, **2b**, **2e** and **2e′** were subjected to X-ray crystallographic analysis. ORTEP[31] diagrams of the crystal structures are shown in Figure 3, while selected bond lengths and bond angles are shown in Table 3.

The $Me_2PCH_2CH_2PMe_2$ ligands in **2b** show considerable disorder, which required the use of two sites for each of these atoms. The iron atom and the atoms of the $C_{18}H_{15}$ ligand have full occupancy. The major isomer has P1 linked to P2 and P3 to P4; whereas the minor isomer has P91 (near P1) linked to P92 (near P4) and P93 (near P3) linked to P94 (near P2). As the various sites frequently overlap, restraints were imposed on P–C and C–C bonded distances and on C–P–C and P–C–C angles for the minor isomer. Isotropic displacement parameters were used for the minor sites. The

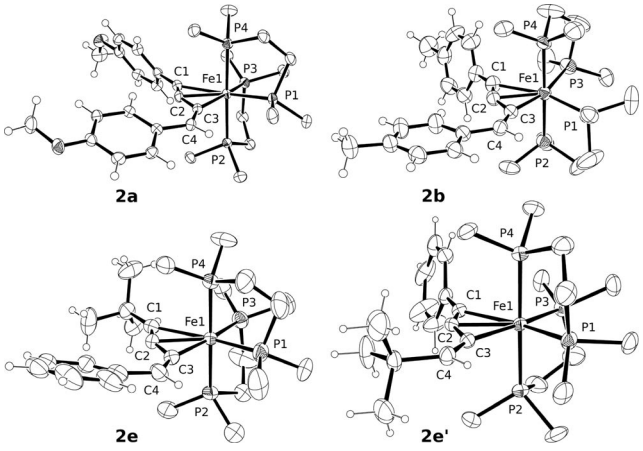


Figure 3. Molecular projection of the complex cations of **2a** (top left), **2b** (top right), **2e** (bottom left) and **2e′** (bottom right). Only one component of each of the disordered sites of **2b** and **2e** is shown.

Table 3. Selected bond lengths [Å] and angles [°] for complexes **2a**, **2b**, **2e** and **2e′**.

	2a	**2b**	**2e**	**2e′**
Fe(1)–C(3)	2.018(2)	2.005(3)	2.017(7)	2.026(7)
Fe(1)–C(2)	2.089(1)	2.081(3)	2.098(7)	2.084(6)
Fe(1)–C(1)	2.269(2)	2.300(4)	2.344(8)	2.260(7)
C(3)–C(4)	1.347(2)	1.338(5)	1.342(10)	1.334(9)
C(2)–C(3)	1.383(2)	1.388(5)	1.397(10)	1.381(8)
C(1)–C(2)	1.253(2)	1.237(5)	1.212(10)	1.234(8)
C(1)–Fe–C(3)	72.35(6)	72.0(1)	70.7(3)	71.9(3)
C(2)–C(3)–C(4)	133.3(1)	133.3(1)	132.0(7)	134.0(6)
C(1)–C(2)–C(3)	148.8(2)	148.7(2)	152.9(8)	149.6(7)
C(2)–C(1)–R	146.3(2)	150.2(4)	143.4(8)	151.4(7)
C(1)–Fe–P(2)	92.12(4)	93.7(1)	97.4(2)	95.1(2)
P(3)–Fe–C(3)	97.56(5)	93.0(1)	94.5(2)	90.6(2)

relative occupancies of the two isomers were refined. Similarly, **2e** is disordered, with two sites associated with two ligand orientations resolved for atom C18 and C20, with occupancies of the components refining to 0.4 and 0.6. The model C17 and C19 ellipsoids are large; however the atoms could not be successfully modelled with multiple sites.

The iron centre exhibits a distorted octahedral coordination sphere, in which the butenynyl fragment binds in a trihapto fashion to the metal centre. A similar arrangement has been reported previously for the related complex *cis*-[FeC(C≡CC_6H_5)=C(H)C_6H_5(dmpe)$_2$]BPh_4.[14] The bond lengths of the complexes show subtle changes in the binding of the butenynyl fragment between the four butenynyl-iron(II) complexes; notably the Fe(1)–C1 bond length for **2e** [2.344(8) Å] is significantly longer than for **2a** and **2e′** [2.269(2) and 2.260(7) Å, respectively]. The analogous bond lengths in **2c** and *cis*-[FeC(C≡CC_6H_5)=C(H)C_6H_5(dmpe)$_2$]-PF_6 [2.300(4) and 2.309(8) Å, respectively] are midway between these two extremes. Additionally, the C(1)–C(2) bond is shortened in **2e** [1.212(10) Å] compared to **2a**, **2b** and **2e′** [1.253(2), 1.237(5) and 1.234(8) Å, respectively]. Noteworthy changes in bond angles include an increase in the C(1)–C(2)–C(3) angle of **2e** [152.9(8)°] relative to the other complexes [*e.g.*, 149.6(7)° for **2e′**] and reductions in the C(1)–Fe–C(3) [70.7(3)° (**2e**) vs. 71.9(3)° (**2e′**)] and C(2)–C(1)–R angles [143.4(8)° (**2e**) vs. 151.4(7)° (**2e′**)]. The crystallographic results suggest that the alkyne group in *cis*-[FeC(C≡C*t*Bu)=C(H)C_6H_5(dmpe)$_2$]PF_6 (**2e**) is less strongly bound to the metal centre than in the other complexes studied. The interaction of the sterically demanding *tert*-butyl substituent with the methyl groups of the *cis* phosphane ligand almost certainly accounts for this observation.

Conclusions

Butenynyl-iron(II) complexes of the general formula *cis*-[FeC(C≡CR)=C(H)R′(dmpe)$_2$]PF_6 (R = R′, **2a**–**d**; R ≠ R′, **2e/e′**–**g/g′**) have been prepared by the reaction of bis(acetylido)iron(II) complexes under mildly acidic conditions. The use of unsymmetrically substituted bis(acetylido)-iron(II) complexes results in a mixture of products in which both possible regioisomeric butenynyl products are formed. In the rearrangement of arylacetylides, the major product is that derived from the more stable vinylidene intermediate. X-ray structure analysis of a pair of regioisomeric butenynyl-iron(II) complexes show that the ligand binds in an η^3-manner, with some significant differences in the bond lengths and angles.

Experimental Section

General: All syntheses and manipulations involving air-sensitive compounds were performed under an inert atmosphere in a nitrogen-filled box or by using standard Schlenk techniques. All solvents used with air-sensitive compounds were either distilled under nitrogen or degassed using three to five freeze-pump-thaw cycles. Phenylacetylene, (trimethylsilyl)acetylene, 4-ethynyltoluene and (*tert*-butyl)acetylene were obtained from Aldrich and degassed prior to use. 1,2-Bis(dimethylphosphanyl)ethane (dmpe) was obtained from Strem and used as supplied. (4-Methoxyphenyl)acetylene,[32] (1-adamantyl)acetylene,[33] and *cis*-FeH_2(dmpe)$_2$[34] were prepared according to literature methods. The unsymmetrical bis(acetylido) complexes *trans*-[Fe(C≡C*t*Bu)(C≡CC_6H_5)(dmpe)$_2$] (**1e**), *trans*-[Fe(C≡C*t*Bu)(C≡C$C_6H_4OCH_3$)(dmpe)$_2$] (**1f**) and *trans*-[Fe(C≡CPh)(C≡CSi$(CH_3)_3$)(dmpe)$_2$] (**1g**) were prepared as described previously.[27]

NMR spectra were recorded on a Bruker AMX or DRX 400 spectrometer at 300 K unless otherwise stated, fitted either with a broadband or multinuclear probe tuned to 100.61, 400.13 and 162.00 MHz for ^{13}C, ^{1}H and ^{31}P nuclei, respectively. Chemical shifts (δ) are reported in ppm. ^{13}C and ^{1}H NMR spectra were referenced to residual solvent resonances whilst ^{31}P NMR spectra were referenced to external, neat, trimethyl phosphite taken to be 140.85 ppm at 300 K. Infrared spectra were recorded on a Perkin–Elmer 1600 Series FTIR. Electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer by direct infusion of a methanol or THF solution of the complexes into the source. Chemical ionisation (CI) mass spectra of organic compounds were recorded on a Hewlett–Packard 5989 A mass spectrometer "engine" using CH_4 as the ionization gas. Liquid secondary ion mass spectra (LSIMS) were recorded at the Central Science Laboratory, University of Tasmania, on a Kratos Concept ISQ mass spectrometer using a *m*-nitrobenzyl alcohol matrix.

Preparation of Bis(acetylido)iron(II) Complexes:[35] An excess of the appropriate acetylene was added to a solution of FeH_2(dmpe)$_2$ in methanol (3 mL). The mixture was stirred at room temperature for 17 h, before the resultant precipitate was isolated by filtration, washed with methanol and dried.

***trans*-Fe(C≡C$C_6H_4OCH_3$)$_2$(dmpe)$_2$ (1a):** Prepared from (4-methoxyphenyl)acetylene (0.28 g, 2.1 mmol) and FeH_2(dmpe)$_2$ (0.070 g, 0.20 mmol). The product was recrystallised from benzene to afford a yellow crystalline solid of *trans*-Fe(C≡C$C_6H_4OCH_3$)$_2$(dmpe)$_2$ (**1a**); yield 0.076 g (63%). $\nu_{C\equiv C}$ (Nujol): 2043 cm^{-1} (w). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 69.1 (s) ppm. $^{1}H\{^{31}P\}$ NMR (C_6D_6): δ = 1.66 (br. s, 24 H, CH_3), 1.77 (br. s, 8 H, CH_2), 3.57 (s, 6 H, OCH_3), 7.02 (AA′ of AA′XX′, 4 H, Ar*H*), 7.49 (XX′ of AA′XX′, 4 H, Ar*H*) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 16.6 (*C*H_3), 31.2 (*C*H_2), 55.2 (O*C*H_3), 114.5 (Ar*C*H), 114.7 (C≡C*C*), 125.0 (FeC≡*C*), 131.5 (Ar*C*H), 133.4 (Fe*C*≡C), 156.7 (*C*OCH_3) ppm. MS (C.I.): *m/z* (%) = 619 (100) [M + 1], 487 (53). $C_{30}H_{46}FeO_2P_4$ (618.398): calcd. C 58.26, H 7.50; found C 58.36, H 7.50.

***trans*-Fe(C≡C$C_6H_4CH_3$)$_2$(dmpe)$_2$ (1b):** Prepared from 4-ethynyltoluene (0.20 g, 1.7 mmol) and FeH_2(dmpe)$_2$ (0.030 g, 0.084 mmol). *trans*-Fe(C≡C$C_6H_4CH_3$)$_2$(dmpe)$_2$ (**1b**) was obtained as a yellow crystalline solid that was recrystallised from toluene; yield 0.037 g (76%). $\nu_{C\equiv C}$ (Nujol): 2047 cm^{-1}. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 68.9 (s) ppm. $^{1}H\{^{31}P\}$ NMR (C_6D_6): δ = 1.65 (s, 24 H, CH_3), 1.75 (br. s, 8 H, CH_2), 2.39 (s, 6 H, ArCH_3), 7.23 (AA′ of AA′XX′, 4 H, Ar*H*), 7.51 (XX′ of AA′XX′, 4 H, Ar*CH*) ppm. $^{13}C\{^{1}H,^{31}P\}$ NMR (C_6D_6): δ = 16.9 (*C*H_3), 21.9 (Ar*C*H_3), 31.6 (*C*H_2), 129.5 (C≡C*C*), 115.9 (FeC≡*C*), 129.7 (Ar*C*H), 130.9 (Ar*C*H), 132.5 (*C*CH_3), 133.0 (Fe*C*≡C) ppm. MS (C.I.): *m/z* (%) = 586 (100) [MH_3^+]. $C_{30}H_{46}FeP_4$ (586.398): calcd. C 61.44, H 7.91; found C 61.18, H 7.95.

***trans*-Fe[C≡CC_6H_3-3,5-$(CF_3)_2$]$_2$(dmpe)$_2$ (1c):** Prepared from 3,5-bis(trifluoromethyl)phenylacetylene (0.18 g, 0.76 mmol) and FeH_2(dmpe)$_2$ (0.060 g, 0.17 mmol). The product was recrystallised

from benzene to afford a yellow crystalline solid of *trans*-Fe[C≡CC$_6$H$_3$-3,5-(CF$_3$)$_2$]$_2$(dmpe)$_2$ (**1c**); yield 0.117 g (84%). $\nu_{C\equiv C}$ (Nujol): 2030 cm^{-1}. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 67.0 (s) ppm. ^{1}H{^{31}P} NMR ([D$_8$]THF): δ = 1.60 (br. s, 24 H, CH_3), 1.88 (br. s, 8 H, CH_2), 7.38 (s, 2 H, Ar*H*), 7.41 (s, 4 H, Ar*H*) ppm. ^{13}C{^{31}P,^{1}H} NMR ([D$_8$]THF): δ = 16.1 (P*C*H$_3$), 31.2 (P*C*H$_2$), 114.8 (FeC≡*C*), 115.3 (Ar*C*H), 124.8 (q, $^1J_{CF}$ = 272 Hz, *C*F$_3$), 129.9 (Ar*C*H), 132.0 (q, $^2J_{CF}$ = 32 Hz, *C*CF$_3$), 132.9 (Ar*C*), 153.4 (Fe*C*) ppm. MS (C.I.): *m*/*z* (%) = 831 (100) [M + 1], 537 (45). C$_{32}$H$_{38}$F$_{12}$FeP$_4$ (830.354): calcd. C 46.29, H 4.61; found C 46.57, H 4.82.

***trans*-Fe(C≡CC$_{10}$H$_{15}$)$_2$(dmpe)$_2$ (1d):** Prepared from (1-adamantyl)-acetylene (0.270 g, 1.67 mmol) and FeH$_2$(dmpe)$_2$ (0.060 g, 0.167 mmol). The product was recrystallised from toluene to afford a yellow crystalline solid of *trans*-Fe(C≡CC$_{10}$H$_{15}$)$_2$(dmpe)$_2$ (**1d**); yield 0.088 g (78%). $\nu_{C\equiv C}$ (Nujol): 2067 cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = 68.3 (s) ppm. ^{1}H{^{31}P} NMR ([D$_8$]THF): δ = 1.58 (br. s, 24 H, P*CH*$_3$), 1.70 (br. s, 12 H, CH_2), 1.75 (br. s, 8 H, P*CH*$_2$), 1.82 (br. s, 12 H, CH_2), 1.89 (br. s, 6 H, C*H*) ppm. ^{13}C{^{1}H,^{31}P} NMR ([D$_8$]THF): δ = 17.7 (P*C*H$_3$), 31.5 (*C*H), 32.9 (P*C*H$_2$), 34.1 (*C*-C≡C), 39.3 (*C*H$_2$), 48.4 (*C*H$_2$), 112.4 (Fe–C≡*C*), 123.0 (Fe–*C*≡C) ppm. MS (CI): *m*/*z* (%) = 675 (100) [M + 1], 515 (21). C$_{36}$H$_{62}$FeP$_4$·C$_7$H$_8$ (766.72): calcd. C 67.36, H 9.20; found C 67.01, H 9.44.

***cis*-[Fe{C(C≡C–C$_6$H$_4$-4-OMe)=C(H)C$_6$H$_4$-4-OMe}(dmpe)$_2$]PF$_6$ (2a):** Trifluoroacetic acid (approx. 8 drops, 200 μL) was added to a THF solution of *trans*-Fe(C≡CC$_6$H$_4$-4-OMe)$_2$(dmpe)$_2$ (**1a**) (0.200 g, 0.324 mmol) in THF (20 mL). A colour change from yellow to red via green and orange occurred over 2 h. Potassium hexafluorophosphate (0.11 g, 0.60 mmol) was added to precipitate the product, which was recrystallised from acetone/pentane and dried in vacuo. *cis*-[Fe{C(C≡C–C$_6$H$_4$-4-OMe)=C(H)C$_6$H$_4$-4-OMe}(dmpe)$_2$]PF$_6$ (**2a**) was obtained as a red crystalline solid, suitable for X-ray crystallography; yield 0.205 g (83%). ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 50.9 (ddd, $^2J_{P1P2}$ = 40, $^2J_{P1P3}$ = 28, $^2J_{P1P4}$ = 21 Hz, 1 P, P1), 56.7 (ddd, $^2J_{P2P3}$ = 179, $^2J_{P2P4}$ = 47 Hz, 1 P, P2), 63.4 (ddd, $^2J_{P3P4}$ = 48.5 Hz, 1 P, P3), 63.5 (ddd, 1 P, P4) ppm. ^{1}H{^{31}P} NMR ([D$_6$]-acetone): δ = 0.80 (s, 3 H, P*CH*$_3$), 0.92 (s, 3 H, P*CH*$_3$), 1.40 (br. s, 6 H, 2× P*CH*$_3$), 1.52 (s, 3 H, P*CH*$_3$), 1.55 (s, 3 H, P*CH*$_3$), 1.65–1.85 (m, 4 H, P*CH*$_2$), 1.71 (s, 3 H, P*CH*$_3$), 1.98 (s, 3 H, P*CH*$_3$), 2.10–2.25 (m, 4 H, PCH$_2$), 3.79 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.92 (AA′ of AA′XX′, 2 H, Ar*H*), 7.04 (AA′′ of AA′′XX′′′, 2 H, Ar*H*), 7.40 (Ar*H*, 2 H, XX′ of AA′XX′), 7.73 (XX′′ of AA′′XX′′′, 2 H, Ar*H*), 7.35 (s, 1 H, =C*H*) ppm. ^{13}C{^{1}H,^{31}P} NMR ([D$_6$]acetone): δ = 8.5 (P*C*H$_3$), 9.1 (P*C*H$_3$), 15.2 (P*C*H$_3$), 16.8 (P*C*H$_3$), 18.5 (P*C*H$_3$), 19.1 (2× *P*CH$_3$), 20.0 (P*C*H$_3$), 26.3 (P*C*H$_2$), 27.6 (P*C*H$_2$), 31.7 (P*C*H$_2$), 32.6 (P*C*H$_2$), 48.0 (Ph*C*≡C), 54.3 (O*C*H$_3$), 54.6 (O*C*H$_3$), 104.6 (*C*≡CPh), 113.7 (Ar*C*H), 114.6 (Ar*C*H), 120.1 (Ar*C*), 126.4 (Ar*C*H), 131.1 (Ar*C*H), 131.5 (Ar*C*), 131.7 (=*C*H), 150.1 (Fe*C*), 159.5 (*C*OCH$_3$), 160.7 (*C*OCH$_3$) ppm. MS (ES): *m*/*z* (%) = 619 (29) [M$^+$], 489 (34); m.p. 257 °C (dec). C$_{30}$H$_{47}$F$_6$FeO$_2$P$_5$·(CH$_3$)$_2$CO (822.454): calcd. C 48.19, H 6.50; found C 48.11, H 6.55.

***cis*-[Fe{C(C≡C–C$_6$H$_4$-4-Me)=C(H)C$_6$H$_4$-4-Me}(dmpe)$_2$]PF$_6$ (2b):** Prepared as described for **2a** from *trans*-Fe(C≡CC$_6$H$_4$CH$_3$)$_2$-(dmpe)$_2$ (**1b**). *cis*-[Fe{C(≡CC$_6$H$_4$CH$_3$)C=C(H)C$_6$H$_4$CH$_3$}(dmpe)$_2$]-PF$_6$ (**2b**) was obtained as a red crystalline solid after recrystallisation from ethanol. These crystals were suitable for X-ray crystallography; yield 0.227 g (91%). ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 49.8 (ddd, $^2J_{P1P2}$ = 40, $^2J_{P1P3}$ = 22, $^2J_{P1P4}$ = 29 Hz, 1 P, P1), 56.6 (ddd, $^2J_{P2P3}$ = 49, $^2J_{P2P4}$ = 182 Hz, 1 P, P2), 63.0 (ddd, $^2J_{P3P4}$ = 49 Hz, 1 P, P3), 63.4 (ddd, 1 P, P4) ppm. ^{1}H{^{31}P} NMR ([D$_6$]-acetone): δ = 0.65 (s, 3 H, P*CH*$_3$), 0.77 (s, 3 H, P*CH*$_3$), 1.24 (s, 6 H, 2× P*CH*$_3$), 1.38 (s, 3 H, P*CH*$_3$), 1.42 (s, 3 H, P*CH*$_3$), 1.57 (s, 3 H, P*CH*$_3$), 1.57–1.70 (m, 8 H, P*CH*$_2$), 1.92 (s, 3 H, P*CH*$_3$), 2.14 (s, 3 H, ArCH_3), 2.23 (s, 3 H, ArCH_3), 7.02 (Ar*H*, 2 H, AA′ of AA′XX′), 7.17 (Ar*H*, 2 H, A′′A′′′ of A′′A′′′X′′X′′′), 7.22 (Ar*H*, 2 H, X′′X′′′ of A′′A′′′X′′X′′′), 7.25 (s, 1 H, C=C*H*), 7.54 (Ar*H*, 2 H, XX′ of AA′XX′) ppm. ^{13}C{^{1}H,^{31}P} NMR ([D$_6$]acetone): δ = 8.5 (P*C*H$_3$), 9.1 (P*C*H$_3$), 15.2 (P*C*H$_3$), 16.8 (P*C*H$_3$), 18.8 (P*C*H$_3$), 19.0 (2× P*C*H$_3$), 19.9 (2× Ar*C*H$_3$), 20.3 (P*C*H$_3$), 26.3 (P*C*H$_2$), 27.6 (P*C*H$_2$), 31.7 (P*C*H$_2$), 32.6 (P*C*H$_2$), 49.4 (Ph*C*≡C), 106.0 (PhC≡*C*), 125.4 (Ar*C*H), 126.1 (*C*C≡C), 129.0 (Ar*C*H), 129.4 (Ar*C*H), 129.7 (Ar*C*H), 132.1 (=*C*H), 135.6 (2× Ar*C*), 138.4 (Ar*C*), 152.5 (Fe*C*) ppm. MS (E.S.): *m*/*z* (%) = 587 (100) [M$^+$], 471 (37), 356 (19). C$_{30}$H$_{47}$F$_6$FeP$_5$ (732.376): calcd. C 49.20, H 6.47; found C 49.17, H 6.42.

***cis*-[Fe{C(C≡C–C$_6$H$_4$-3,5-(CF$_3$)$_2$)=C(H)C$_6$H$_3$-3,5-(CF$_3$)$_2$}(dmpe)$_2$]-PF$_6$ (2c):** Prepared as described for **2a** from *trans*-Fe(C≡CC$_6$H$_3$-3,5-(CF$_3$)$_2$)$_2$(dmpe)$_2$ (**1c**) (200 mg, 0.241 mmol). *cis*-[Fe{C(≡CC$_6$H$_3$-(CF$_3$)$_2$)C=C(H)C$_6$H$_3$(CF$_3$)$_2$}(dmpe)$_2$]PF$_6$ (**2c**) was obtained as a red crystalline solid; yield 0.206 g (84%). ^{31}P{^{1}H} NMR ([D$_6$]acetone): δ = 48.9 (ddd, $^2J_{P1P2}$ = 41, $^2J_{P1P3}$ = 29, $^2J_{P1P4}$ = 29 Hz, 1 P, P1), 55.7 (ddd, $^2J_{P2P3}$ = 35, $^2J_{P2P4}$ = 169 Hz, 1 P, P2), 60.0 (ddd, $^2J_{P3P4}$ = 46 Hz, 1 P, P3), 63.9 (ddd, 1 P, P4) ppm. ^{1}H{^{31}P} NMR ([D$_6$]acetone): δ = 0.76 (s, 3 H, P*CH*$_3$), 0.84 (s, 3 H, P*CH*$_3$), 1.40 (s, 3 H, P*CH*$_3$), 1.44 (s, 3 H, P*CH*$_3$), 1.57 (s, 3 H, P*CH*$_3$), 1.80–2.40 (m, 8 H, P*CH*$_2$), 1.83 (s, 3 H, P*CH*$_3$), 1.96 (s, 3 H, P*CH*$_3$), 2.18 (s, 3 H, P*CH*$_3$), 7.87 (s, 2 H, Ar*H*), 8.07 (s, 2 H, Ar*H*), 8.14 (s, 1 H, C=C*H*), 8.48 (s, 2 H, Ar*H*) ppm. ^{13}C{^{1}H,^{31}P} NMR ([D$_8$]THF): δ = 9.7 (P*C*H$_3$), 11.2 (P*C*H$_3$), 15.7 (P*C*H$_3$), 17.8 (P*C*H$_3$), 19.9 (P*C*H$_3$), 20.0 (P*C*H$_3$), 20.3 (P*C*H$_3$), 23.1 (P*C*H$_3$), 27.0 (P*C*H$_2$), 28.2 (P*C*H$_2$), 33.1 (P*C*H$_2$), 33.2 (P*C*H$_2$), 61.0 (Ar*C*≡C), 115.4 (ArC≡*C*), 119.7 (Ar*C*H), 122.1 (ArCH), 123.8 (q, $^1J_{CF}$ = 272 Hz, CF$_3$), 124.4 (q, $^1J_{CF}$ = 272 Hz, CF$_3$), 126.0 (Ar*C*H), 128.9 (Ar*C*), 130.4 (Ar*C*H), 130.9 (=*C*H), 132.4 (q, $^2J_{CF}$ = 32 Hz, *C*-CF$_3$), 132.8 (q, $^2J_{CF}$ = 32 Hz, *C*-CF$_3$), 140.6 (Ar*C*), 162.1 (Fe*C*) ppm. MS (ES): *m*/*z* (%) = 831 (100) [M$^+$], 682 (12); m.p. 277 °C (dec). The BPh$_4$ salt of this complex was synthesised as follows: A mixture of *cis*-[FeH(H$_2$)(dmpe)$_2$]BPh$_4$[14] (0.1069 g, 0.158 mmol) and 1,4-bis[3,5-bis(trifluoromethyl)phenyl]butadiyne[36] (0.0915 g, 0.193 mmol) was suspended in acetone (2.5 mL), sonicated for 40 min, and the solvent removed in vacuo. The residual solid was washed with pentane (3× 10 mL) and recrystallised from acetone/diethyl ether; yield 0.0893 g (49%). The NMR spectra were identical those previously described. C$_{56}$H$_{59}$BF$_{12}$FeP$_4$ (1150.572): calcd. C 58.46, H 5.17; found C 58.80, H 5.68.

***cis*-[Fe{C(C≡C–C$_{10}$H$_{15}$)=C(H)C$_{10}$H$_{15}$}(dmpe)$_2$]PF$_6$ (2d):** Prepared as described for **2a** from *trans*-Fe(C≡CC$_{10}$H$_{15}$)$_2$(dmpe)$_2$ (**1d**). *cis*-[Fe{C(≡CC$_{10}$H$_{15}$)C=C(H)C$_{10}$H$_{15}$}(dmpe)$_2$]PF$_6$ (**2d**) was obtained as a red crystalline solid; yield 0.022 g (86%). ^{31}P{^{1}H} NMR ([D$_7$]-DMF): δ = 51.4 (ddd, $^2J_{P1P2}$ = 39, $^2J_{P1P3}$ = 29, $^2J_{P1P4}$ = 20 Hz, 1 P, P1), 53.4 (ddd, $^2J_{P2P3}$ = 161, $^2J_{P2P4}$ = 37 Hz, 1 P, P2), 60.8 (ddd, $^2J_{P3P4}$ = 49 Hz, 1 P, P3), 63.3 (ddd, 1 P, P4) ppm. ^{1}H NMR ([D$_6$]-acetone): δ = 0.67 (d, $^2J_{PH}$ = 9.0 Hz, 3 H, P*CH*$_3$), 0.81 (d, $^2J_{PH}$ = 8.8 Hz, 3 H, P*CH*$_3$), 1.25 (d, $^2J_{PH}$ = 8.1 Hz, 3 H, P*CH*$_3$), 1.36 (d, $^2J_{PH}$ = 7.7 Hz, 3 H, P*CH*$_3$), 1.44 (d, $^2J_{PH}$ = 7.7 Hz, 3 H, P*CH*$_3$), 1.6–1.7 (m, 4 H, P*CH*$_2$), 1.70 (d, $^2J_{PH}$ = 7.1 Hz, 3 H, P*CH*$_3$), 1.72–1.97 (br. m, 30 H, adamantyl-*H*), 1.83 (d, $^2J_{PH}$ = 9.0 Hz, 3 H, P*CH*$_3$), 2.0–2.1 (m, 4 H, P*CH*$_2$), 2.33 (d, $^2J_{PH}$ = 7.7 Hz, 3 H, P*CH*$_3$), 6.11 (apparent p, splitting = 2.0 Hz, 1 H, =C*H*) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ = 8.43 (d, $^1J_{PC}$ = 22.6 Hz, P*C*H$_3$), 9.53 (d, $^1J_{PC}$ = 20.1 Hz, P*C*H$_3$), 15.2 (d, $^1J_{PC}$ = 23.5 Hz, P*C*H$_3$), 18.8 (m, P*C*H$_3$), 19.2 (m, P*C*H$_3$), 19.6 (d, $^1J_{PC}$ = 19.3 Hz, P*C*H$_3$), 21.0 (d, $^1J_{PC}$ = 20.1 Hz, P*C*H$_3$), 26.6 (dd, $^1J_{PC}$ = 28.0, $^2J_{PC}$ = 12.0 Hz, P*C*H$_2$), 28.6 (dd, $^1J_{PC}$ = 26.4, $^2J_{PC}$ = 10.7 Hz, P*C*H$_2$), 28.7

(Ad*C*H), 29.0 (Ad*C*H), 29.1 (P*C*H$_3$) 32.5–33.4 (m, 2× P*C*H$_2$), 35.2 (Ad*C*), 36.0 (Ad*C*H$_2$), 36.8 (Ad*C*H$_2$), 38.6 (Ad*C*), 43.1 (Ad*C*H$_2$), 44.4 (Ad*C*H$_2$), 47.0 (Ad*C*≡C), 114.3 (m, AdC≡*C*), 143.3 (br. m, Fe*C*), 143.4 (C=*C*H) ppm. MS (ES): *m/z* (%) = 675 (22) [M$^+$], 515 (32); m.p. 300 °C (dec.). HRMS (LSIMS): 675.3225. Req. for $C_{36}H_{63}P_4{}^{56}Fe$: 675.3230.

***cis*-[Fe{C(C≡C*t*Bu)=C(H)Ph}(dmpe)$_2$]PF$_6$ (2e) and *cis*-[Fe{C(C≡CPh)=C(H)*t*Bu}(dmpe)$_2$]PF$_6$ (2e′):** Ammonium hexafluorophosphate (0.030 g, 0.186 mmol) was added to a THF solution of *trans*-[Fe(C≡C*t*Bu)(C≡CC$_6$H$_5$)(dmpe)$_2$] (**1e**) (100 mg, 186 μmol). The colour of the solution immediately changed from yellow to green then slowly over 2 h at 65 °C to dark brown. The solvent was removed and the residue found to contain a 55:45 mixture of **3a** and **3b**, which were recrystallised from THF (0.5 mL) as red cubes and yellow needles, (112 mg, 88%). MS (E.S.): *m/z* (%) = 539 (8) [M + 1]$^+$, 389 (100) [(M + 1) – dmpe]$^+$, 237 [(M + 1) – 2 dmpe]$^+$. $C_{26}H_{47}F_6FeP_5$ (684.336): calcd. C 45.60, H 6.93; found C 45.9, H 7.2.

***cis*-[Fe{η^3-C(C≡C*t*Bu)=C(H)Ph}(dmpe)$_2$][PF$_6$] (2e):** $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 49.89 (ddd, $^2J_{P1P2}$ = 42, $^2J_{P1P3}$ = 30, $^2J_{P1P4}$ = 20 Hz, 1 P, P1), 54.23 (ddd, $^2J_{P2P3}$ = 158, $^2J_{P2P4}$ = 36 Hz, 1 P, P2), 61.68 (ddd, $^2J_{P3P4}$ = 50 Hz, 1 P, P3), 63.26 (ddd, 1 P, P4) ppm. $^1H\{^{31}P\}$ NMR ([D$_8$]THF): δ = 0.59 (s, 3 H, PC*H*$_3$), 0.74 (s, 3 H, PC*H*$_3$), 1.26 (s, 3 H, PC*H*$_3$), 1.36 (s, 3 H, PC*H*$_3$), 1.43 (s, 3 H, PC*H*$_3$), 1.51 (s, 9 H, C(C*H*$_3$)$_3$), 1.60–1.80 (m, 4 H, PC*H*$_2$), 1.71 (s, 3 H, PC*H*$_3$), 1.90–2.20 (m, 4 H, PC*H*$_2$), 1.91 (s, 3 H, PC*H*$_3$), 2.24 (s, 3 H, PC*H*$_3$), 7.20 (s, 1 H, =C*H*), 7.13 (m, 1 H, Ar*H*), 7.30 (m, 2 H, Ar*H*), 7.75 (m, 2 H, Ar*H*) ppm. $^{13}C\{^1H,^{31}P\}$ NMR ([D$_6$]acetone): δ = 9.8 (P*C*H$_3$), 10.7 (P*C*H$_3$), 16.2 (P*C*H$_3$), 19.2 (2× P*C*H$_3$), 20.15 (P*C*H$_3$), 20.19 (P*C*H$_3$), 21.4 (P*C*H$_3$), 27.4 (P*C*H$_2$), 29.3 (P*C*H$_2$), 32.9 [C(*C*H$_3$)$_3$], 33.5 [*C*(CH$_3$)$_3$], 33.6 (P*C*H$_2$), 33.9 (P*C*H$_2$), 48.1 (C≡*C*t Bu), 120.0 (Ar*C*), 126.3 (Ar*C*H), 126.8 (Ar*C*H), 129.3 (Ar*C*H), 132.6 (=*C*H), 139.5 (*C*≡CtBu), 154.8 (Fe*C*) ppm.

***cis*-[Fe{η^3-C(C≡CPh)=C(H)*t*Bu}(dmpe)$_2$][PF$_6$] (2e′):** $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 49.89 (ddd, $^2J_{P1P2}$ = 39, $^2J_{P1P3}$ = 22, $^2J_{P1P4}$ = 29 Hz, 1 P, P1), 54.87 (ddd, $^2J_{P2P3}$ = 37, $^2J_{P2P4}$ = 170 Hz, 1 P, P2), 61.87 (ddd, $^2J_{P3P4}$ = 49 Hz, 1 P, P3), 61.97 (ddd, 1 P, P4) ppm. $^1H\{^{31}P\}$ NMR ([D$_8$]THF): δ = 0.75 (s, 3 H, PC*H*$_3$), 0.88 (s, 3 H, PC*H*$_3$), 1.26 (s, 3 H, PC*H*$_3$), 1.27 (s, 3 H, PC*H*$_3$), 1.28 (s, 3 H, PC*H*$_3$), 1.43 (s, 3 H, PC*H*$_3$), 1.48 [s, 9 H, C(C*H*$_3$)$_3$], 1.60 (s, 3 H, PC*H*$_3$), 1.60–1.80 (m, 4 H, PC*H*$_2$), 1.87 (s, 3 H, PC*H*$_3$), 1.90–2.20 (m, 4 H, PC*H*$_2$), 6.37 (s, 1 H, =C*H*), 7.28–7.39 (m, 5 H, Ar*H*) ppm. $^{13}C\{^1H,^{31}P\}$ NMR ([D$_6$]acetone): δ = 9.2 (P*C*H$_3$), 10.0 (P*C*H$_3$), 16.2 (P*C*H$_3$), 18.1 (P*C*H$_3$), 20.0 (P*C*H$_3$), 20.4 (P*C*H$_3$), 20.5 (P*C*H$_3$), 21.2 (P*C*H$_3$), 27.5 (P*C*H$_2$), 28.8 (P*C*H$_2$), 30.4 [C(*C*H$_3$)$_3$], 32.9 (P*C*H$_2$), 33.8 (P*C*H$_2$), 37.9 [*C*(CH$_3$)$_3$], 52.4 (C≡*C*Ph), 103.7 (*C*≡CPh), 128.8 (Ar*C*H), 130.0 (Ar*C*H), 130.4 (Ar*C*H), 131.5 (Ar*C*), 145.0 (Fe*C*), 145.2 [=*C*(H)Ph] ppm.

***cis*-[Fe{C(C≡CC$_6$H$_4$OCH$_3$)=C(H)*t*Bu}(dmpe)$_2$]PF$_6$ (2f) and *cis*-[Fe{C(C≡C*t*Bu)=C(H)C$_6$H$_4$OCH$_3$}(dmpe)$_2$]PF$_6$ (2f′):** Prepared as described for **2a** from *trans*-[Fe(C≡C*t*Bu)(C≡CC$_6$H$_4$OCH$_3$)(dmpe)$_2$] (**1f**) (0.020 g, 0.035 mmol) and trifluoroacetic acid (2.7 μL). The solution was allowed to stand at room temperature for 16 h in which time it changed colour from yellow to green to dark orange. Potassium hexafluorophosphate (20 mg) was added, the solvent was removed and the residue recrystallised from ethanol to give an orange-brown solid containing 98% **2f** and 2% **2f′**, (12 mg, 41%). MS (LSIMS) *m/z* (%): 569.2 (50), 519.2 (78), 465.1 (47), 419.2 (73), 369.2 (100), 287.1 (63). HRMS (LSIMS): 569.20879. Required for $C_{27}H_{49}{}^{56}FeOP_4$: 569.2083.

***cis*-[Fe{η^3-C(C≡C*t*Bu)=C(H)C$_6$H$_4$OCH$_3$}(dmpe)$_2$][PF$_6$] (2f):** $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 50.55 (ddd, $^2J_{P1P2}$ = 40.3, $^2J_{P1P3}$ = 29.2, $^2J_{P1P4}$ = 21.0 Hz, 1 P, P1), 54.23 (ddd, $^2J_{P2P3}$ = 159.5, $^2J_{P2P4}$ = 35.4 Hz, 1 P, P2), 61.47 (ddd, $^2J_{P3P4}$ = 49.2 Hz, 1 P, P3), 63.33 (ddd, 1 P, P4) ppm. $^1H\{^{31}P\}$ NMR ([D$_8$]THF): δ = 0.53 (s, 3 H, PC*H*$_3$), 0.65 (s, 3 H, PC*H*$_3$), 1.21 (s, 3 H, PC*H*$_3$), 1.32 (s, 3 H, PC*H*$_3$), 1.42 (s, 3 H, PC*H*$_3$), 1.46 [s, 9 H, C(C*H*$_3$)$_3$], 1.60–1.70 (m, 4 H, PC*H*$_2$), 1.69 (s, 3 H, PC*H*$_3$), 1.85–2.10 (m, 4 H, PC*H*$_2$), 1.86 (s, 3 H, PC*H*$_3$), 2.20 (s, 3 H, PC*H*$_3$), 3.73 (s, 3 H, OC*H*$_3$), 6.85 (AA′ of AA′XX′, 2 H, Ar*H*), 7.65 (XX′ of AA′XX′, 2 H, Ar*H*), 7.07 (s, 1 H, C=*C*H) ppm. $^{13}C\{^1H,^{31}P\}$ NMR ([D$_8$]THF): δ = 9.6 (P*C*H$_3$), 10.5 (P*C*H$_3$), 16.2 (P*C*H$_3$), 19.1 (P*C*H$_3$), 20.0 (P*C*H$_3$), 20.2 (P*C*H$_3$), 21.2 (P*C*H$_3$), 27.4 (P*C*H$_2$), 28.4 (P*C*H$_3$), 29.3 (P*C*H$_2$), 33.0 [C(*C*H$_3$)$_3$], 33.6 (P*C*H$_2$), 33.9 (P*C*H$_2$), 48.2 [*C*(CH$_3$)$_3$], 55.4 (O*C*H$_3$), 114.5 (Ar*C*H), 119.3 [(CH$_3$)$_3$C*C*≡C], 127.2 (Ar*C*H), 131.8 (Ar*C*), 132.0 (C=*C*H), 144.4 [(CH$_3$)$_3$CC≡*C*], 151.2 (Fe*C*), 159.4 (Ar*C*O) ppm.

***cis*-[Fe(η^3-C{C≡CSi(CH$_3$)$_3$}=C(H)C$_6$H$_5$)(dmpe)$_2$][PF$_6$] (2 g) and *cis*-[Fe(η^3-C(C≡CC$_6$H$_5$)=CH$_2$)(dmpe)$_2$][PF$_6$] (2g′):** Ammonium hexafluorophosphate (6.0 mg, 0.037 mmol) was added to an acetone solution (0.5 mL) of *trans*-[Fe(C≡CPh)(C≡CSi(CH$_3$)$_3$)-(dmpe)$_2$] (**1g**) (19.5 mg, 0.035 mmol). The solution was heated at 65 °C for 1.5 h during which time it changed colour from green to orange to red. The solvent was removed and the brown residue recrystallised from ethanol to give a red/brown crystalline solid containing 23% *cis*-[Fe(η^3-C{C≡CSi(CH$_3$)$_3$}=C(H)C$_6$H$_5$)(dmpe)$_2$]-[PF$_6$] **(2g)** and 77% *cis*-[Fe(η^3-C(C≡CC$_6$H$_5$)=CH$_2$)(dmpe)$_2$][PF$_6$] (**2g′**); yield 24 mg (92%).

***cis*-[Fe(η^3-C{C≡CSi(CH$_3$)$_3$}=CHC$_6$H$_5$)(dmpe)$_2$]PF$_6$ (2g):** $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = 54.2 (ddd, $^2J_{P1P2}$ = 37, $^2J_{P1P3}$ = 44, $^2J_{P1P4}$ = 14 Hz, 1 P, P1), 57.0 (ddd, $^2J_{P2P3}$ = 161, $^2J_{P2P4}$ = 40 Hz, 1 P, P2), 62.1 (ddd, $^2J_{P3P4}$ = 46 Hz, 1 P, P3), 64.9 (ddd, 1 P, P4) ppm. $^1H\{^{31}P\}$ NMR ([D$_6$]acetone): δ = 0.46 (s, 3 H, PC*H*$_3$), 0.57 (s, 3 H, PC*H*$_3$), 1.34 (s, 3 H, PC*H*$_3$), 1.36 (s, 3 H, PC*H*$_3$), 1.52 (s, 3 H, PC*H*$_3$), 1.60–1.77 (m, 4 H, PC*H*$_2$), 1.81 (s, 3 H, PC*H*$_3$), 1.95–2.20 (m, 4 H, PC*H*$_2$), 2.01 (s, 3 H, PC*H*$_3$), 2.28 (s, 3 H, PC*H*$_3$), 6.82 (s, 1 H, =C*H*), 7.21 (m, 1 H, Ar*H*), 7.36–7.39 (m, 2 H, Ar*H*), 7.79 (m, 2 H, Ar*H*) ppm. $^{13}C\{^1H,^{31}P\}$ NMR ([D$_6$]acetone): δ = 1.6 (Si*C*H$_3$), 9.3 (P*C*H$_3$), 10.0 (P*C*H$_3$), 15.8 (P*C*H$_3$), 18.3 (P*C*H$_3$), 19.7 (P*C*H$_3$), 20.1 (P*C*H$_3$), 20.3 (P*C*H$_3$), 27.1 (P*C*H$_2$), 29.0 (P*C*H$_2$), 29.4 (P*C*H$_3$), 33.2 (P*C*H$_2$), 33.6 (P*C*H$_2$), 55.7 (Si-*C*≡C), 103.6 (Si-C≡*C*), 126.5 (Ar*C*H), 127.2 (Ar*C*H), 129.3 (Ar*C*H), 130.0 (Ar*C*), 134.1 (=*C*H), 155.5 (Fe*C*) ppm.

***cis*-[Fe(η^3-C(C≡CC$_6$H$_5$)=CH$_2$)(dmpe)$_2$]PF$_6$ (2g′):** $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = (AA′BC) 48.20 (ddd, $^2J_{P1P2}$ = 40, $^2J_{P1P3}$ = 29, $^2J_{P1P4}$ = 21 Hz, 1 P, P1), 54.29 (ddd, $^2J_{P2P3}$ = 161, $^2J_{P2P4}$ = 37 Hz, 1 P, P2), 62.08 (ddd, $^2J_{P3P4}$ = 49 Hz, 1 P, P3), 63.17 (ddd, 1 P, P4) ppm. $^1H\{^{31}P\}$ NMR ([D$_6$]acetone): δ = 0.95 (s, PC*H*$_3$), 1.09 (s, 3 H, PC*H*$_3$), 1.38 (s, 3 H, PC*H*$_3$), 1.39 (s, 3 H, PC*H*$_3$), 1.47 (s, 3 H, PC*H*$_3$), 1.48 (s, 3 H, PC*H*$_3$), 1.60–1.77 (m, 4 H, PC*H*$_2$), 1.66 (s, 3 H, PC*H*$_3$), 1.93 (s, 3 H, PC*H*$_3$), 1.95–2.20 (m, 4 H, PC*H*$_2$), 6.23 (s, 1 H, =C*H*H), 6.79 (s, 1 H, =CH*H*), 7.42–7.46 (m, 5 H, ArH) ppm. Selected ^1H NMR ([D$_6$]acetone): δ = 6.23 (p, $^3J_{PH}$ = 2.0 Hz, =C*H*H), 6.79 (p, $^3J_{PH}$ = 3.0 Hz, =CH*H*) ppm. $^{13}C\{^1H,^{31}P\}$ NMR ([D$_6$]acetone): δ = 9.1 (P*C*H$_3$), 9.7 (P*C*H$_3$), 16.0 (P*C*H$_3$), 17.9 (P*C*H$_3$), 19.7 (P*C*H$_3$), 20.0 (P*C*H$_3$), 20.2 (P*C*H$_3$), 21.1 (P*C*H$_3$), 27.4 (P*C*H$_2$), 28.7 (P*C*H$_2$), 32.6 (P*C*H$_2$), 33.7 (P*C*H$_2$), 50.6 (Ph*C*≡C), 82.6 (PhC≡*C*), 119.5 (=*C*H$_2$), 129.4 (Ar*C*H), 130.1 (Ar*C*H), 130.6 (Ar*C*H), 139.5 (Ar*C*), 166.1 (Fe*C*) ppm.

CCDC-768332 to 768336 (see Table 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystallographic and structure refinement data for **1a**, **1b**, **1c**, **2a**, **2b**, **2e** and **2e′**.

	1a	**1b**	**1c**	**2a**	**2b**	**2e**	**2e′**
Chemical formula	$C_{30}H_{46}FeO_2P_4$	$C_{30}H_{46}FeP_4$	$C_{32}H_{38}F_{12}Fe_1P_4$	$C_{33}H_{53}F_6FeO_3P_5$	$C_{30}H_{47}F_6FeP_5$	$C_{26}H_{47}F_6FeP_5$	$C_{26}H_{47}F_6FeP_5$
Formula mass	618.43	586.44	830.36	822.45	732.41	684.34	684.34
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
a [Å]	9.416(3)	9.0517(1)	12.7683(11)	12.934(3)	10.7074(3)	9.3617(17)	9.7692(16)
b [Å]	12.313(4)	18.2658(4)	12.5370(11)	12.974(3)	23.5921(5)	19.4957(17)	18.966(4)
c [Å]	13.988(5)	9.5129(2)	13.4907(13)	13.818(3)	14.0345(3)	18.0126(11)	18.393(4)
α [°]				101.713(5)			
β [°]	90.22(3)	90.0265(13)	117.013(4)	105.265(5)	91.3765(14)	91.922(9)	102.182(15)
γ [°]				113.250(5)			
Unit cell volume/Å^3	1621.81(3)	1572.83(5)	1923.9(3)	1928.1(7)	3544.23(14)	3285.7(7)	3331.3(11)
Temperature [K]	294(2)	200	273(2)	173(2)	200	293(2)	294(2)
Space group	$P2_1/c$	$P2_1/a$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	2	2	4	2	4	4	4
Reflections measured	25322	27967	25482	11328	54324	6147	6372
Independent reflections	6026	3608	2761	8235	6248	5764	6001
R_{int}	0.0277	0.035	0.0376	0.0165	0.062	0.0964	0.0489
Final R_1 values [$I > 2\sigma(I)$]	0.0211	0.0280	0.0765	0.0300	0.0364	0.0595	0.0530
Final $wR(F^2)$ values [$I > 2\sigma(I)$]	0.0504	0.0687	0.1954	0.0840	0.0810	0.1484	0.1367
Final R_1 values (all data)	0.0227	0.0339	0.0900	0.0370	0.0722	0.2452	0.2264
Final $wR(F^2)$ values (all data)	0.0512	0.0743	0.2093	0.0862	0.1052	0.2052	0.1879
CCDC number	768332	768333	768334	768335	768336	768337	768338

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