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Butenynyl complexes of iron(II) containing the tripodal tetraphosphine ligand $P(CH_2CH_2PMe_2)_3$

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The preparation and characterisation of iron(II) η^3-but-1-en-3-yn-2-yl complexes $[Fe(\eta^3\text{-}RC{\equiv}C\text{–}C{=}CHR)L]^+$ [L = $P(CH_2CH_2PMe_2)_3$, R = Ph **1**; R = Bu^t **2**; R = *p*-HC≡CC_6H_4 **3**] is reported. The phenyl substituted butenynyl complex **1** was prepared by the reaction of $FeCl_2L$ **5**, FeH(Cl)L **6** or $[FeH(H_2)L]^+$ **7** with phenylacetylene in alcohol solvent. The coordinated but-1-en-3-yn-2-yl fragment is bound as a σ-vinyl/π-acetylenic ligand. In solution, complex **1** exists as a pair of equilibrating isomers (**1a** and **1b**) which differ in the anchoring mode of the butenynyl ligand *i.e.* depending on whether the π-bound acetylenic group is *cis* or *trans* to the apical phosphorus of L in the octahedral coordination sphere. Assignment of the relative stereochemistry of **1a** and **1b** was achieved by analysis of the 2D NOESY spectrum. Exchange peaks in the NOESY spectrum also provided information on the mechanism of exchange between **1a** and **1b**. The crystal structure of **1** showed the solid state structure to be that of the major solution state isomer **1a** (π-bound acetylenic group is *cis* to the apical phosphorus of L). Complex **1** catalyses the stereospecific head-to-head dimerisation of phenylacetylene to *Z*-1,4-diphenylbut-1-en-3-yne.

Introduction

The reaction of metal complexes with terminal alkynes to afford butenynyl complexes is an important C–C bond forming reaction. In a number of cases, the free butenyne is subsequently liberated, effectively completing the catalytic cycle of head-to-head dimerisation of the alkyne.[1,2] As part of a wider study examining the dimerisation (and oligomerisation) of acetylenes, we have examined a range of metal complexes where alkyne coupling occurs. Octahedral complexes containing tripodal tetradentate ligands appear particularly suited to alkyne dimerisation since the two sites available for alkyne coordination are constrained by the nature of the ligand to be mutually *cis*, facilitating the coupling of the alkyne fragments. Indeed, both the formation of butenynyl complexes and catalytic head-to-head coupling of terminal alkynes have been reported for complexes containing the tripodal tetraphosphine ligands $P(CH_2CH_2PPh_2)_3$ (L^1) **8**[2] and $P(CH_2CH_2CH_2PMe_2)_3$ (L^2) **9**.[3]

The preparation and characterisation of a number of butenynyl complexes containing bi- and tetra-dentate phosphine ligands have been reported. Iron(II) dihydrogen hydrido complexes containing the bidentate phosphines 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diethylphosphino)ethane (depe) react with terminal alkynes to form bis(acetylide) complexes in good yield.[4] The bis(acetylide) complexes are protonated to initially form metal vinylidene complexes which rearrange and couple to form complexes containing coordinated butenynes. For some bis(acetylide) complexes, methanol employed as a reaction solvent is sufficiently acidic to carry out the protonation, in others, a stronger acid (*e.g.* trifluoroacetic acid) is required.[5] The dichloro complex $FeCl_2(dmpe)_2$ also reacts with phenylacetylene in the presence of hexafluorophosphate to give the corresponding butenynyl complex.[6]

Reaction of the ruthenium dihydrogen hydrido complex $[RuH(H_2)L^1]^+$ with terminal alkynes proceeds *via* two isolable intermediates, the σ-alkenyl complex $[Ru(CH{=}CHR)L^1]^+$ and the σ-alkynyl complex $[Ru(C{\equiv}CR)L^1]^+$, to eventually give the corresponding butenynyl complex $[Ru(\eta^3\text{-}RC{\equiv}C\text{–}C{=}CHR)L^1]^+$.[2a–c,e] Reaction of the osmium dinitrogen hydrido complex $[OsH(N_2)L^1]^+$ with terminal alkynes also yields butenynyl complexes.[2d] The reaction proceeds *via* the vinylidene hydride complex $[OsH(C{=}CHR)L^1]^+$ and one equivalent of $RCH{=}CH_2$ is produced as the reaction progresses. Butenynyl complexes of osmium can also be prepared directly from the dichloro complex $OsCl_2L^1$.[2d]

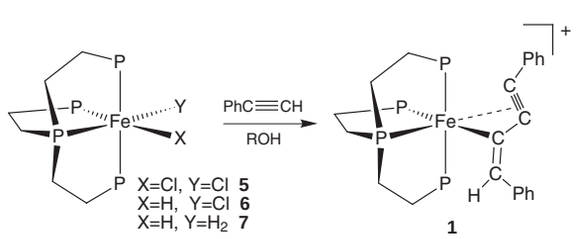
The reaction of the iron complexes $[FeH(X)L^1]^+$ (X = N_2, H_2) with terminal alkynes affords σ-alkenyl complexes $[Fe(HC{=}CHR)L^1]^+$ and σ-alkynyl complexes $[Fe(C{\equiv}CR)L^1]^+$, but these do not react further to give the corresponding butenynyl complexes.[7]

We have recently reported[8] an efficient and high-yielding synthesis of the tetradentate ligand $P(CH_2CH_2PMe_2)_3$ (L) **4**, which has facilitated investigation of iron complexes containing **4**.[9] Here, we report the synthesis of the iron(II) butenynyl complexes, $[Fe(\eta^3\text{-}RC{\equiv}CC{=}CHR)L]^+$ [R = Ph **1**, Bu^t **2**, *p*-HC≡CC_6H_4 **3**] and their characterisation by NMR spectroscopy and X-ray crystallography.

Results and discussion

Preparation of butenynyl complexes

The iron(II) diphenylbutenynyl complex $[Fe(\eta^3\text{-}PhC{\equiv}C\text{–}C{=}CHPh)L]^+$ **1** was prepared by the reaction of phenylacetylene with the dichloro complex **5**, the chloro hydrido complex **6** or the dihydrogen hydrido complex **7** in alcohol solvent (Scheme 1). In the reactions of phenylacetylene with **6** and **7**, styrene was observed as a by-product.



Scheme 1

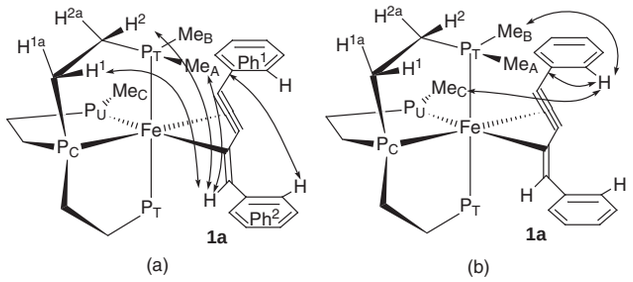


Fig. 1 Schematic representation of cross peaks observed between L and butenynyl ligands in the NOESY spectrum of the major diphenylphenylbutenynyl isomer **1a**. (a) Cross peaks between the vinylic proton and Me_A, backbone protons H^1 and H^2, and between the *ortho* protons of Ph^2 and Me_A indicate that Ph^2 lies near to the central phosphorus P_C; (b) cross peaks between the *ortho* proton of Ph^1 and Me_A, Me_B and Me_C, indicate that Ph^1 lies near the terminal phosphorus P_U.

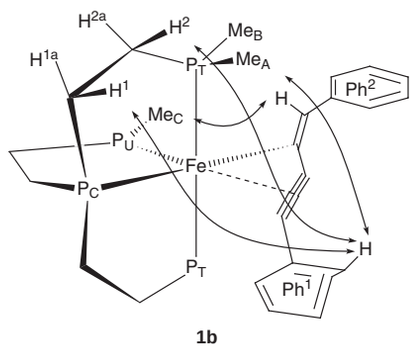
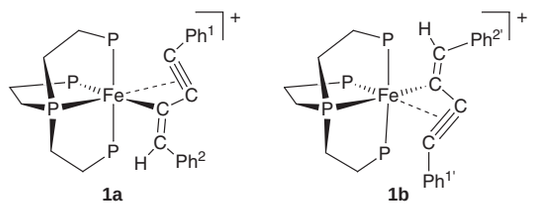


Fig. 2 Schematic representation of cross peaks observed between L and butenynyl ligands in the NOESY spectrum of the minor diphenylbutenynyl isomer **1b**. Cross peaks between the vinylic proton and Me_C, indicate that Ph^2 lies near the terminal phosphorus P_U. Cross peaks between the *ortho* protons on Ph^1 and the ligand backbone protons H^1 and H^2, and also Me_A indicate that Ph^1 lies near to the central phosphorus P_C.

Reaction of phenylacetylene with **6** and **7** was rapid and no intermediates were detected (by ^{31}P NMR) in either case. Reaction of **5** with phenylacetylene was significantly slower, and a number of (uncharacterised) intermediate complexes were visible if the course of the reaction was followed by ^{31}P NMR. The addition of an ethanol solution of sodium tetraphenylborate to an ethanol solution of **1** resulted in the immediate precipitation of the red tetraphenylborate salt of **1**. The tetrafluoroborate salt of **1** was also prepared by the addition of sodium tetrafluoroborate, however, the BF_4^- salt was more soluble in methanol and ethanol, resulting in incomplete precipitation. Both the tetrafluoroborate and tetraphenylborate salts of **1** were soluble in acetone.

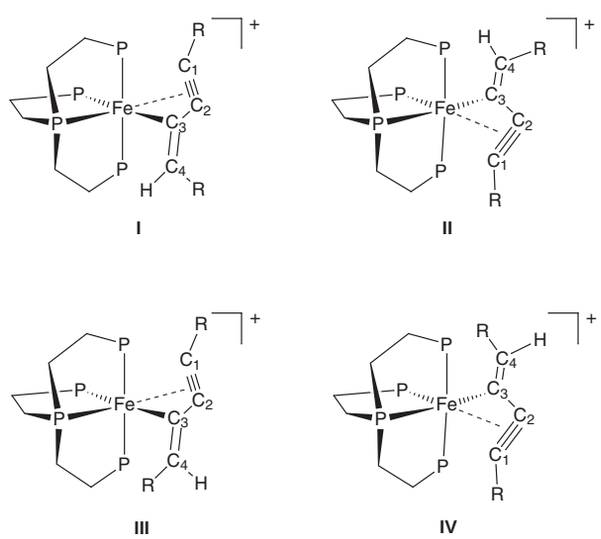
The ^{31}P NMR spectrum of **1** (BPh_4^- salt in acetone) at room temperature contains sharp resonances at δ 171.9 (t, P_C), 64.4 (t, P_U) and 49.5 (dd, P_T). For the purposes of identifying the phosphorus nuclei of the coordinated ligand L, mutually *trans* terminal phosphorus nuclei were labelled P_T, the central phosphorus from which the three arms radiate was labelled P_C and the remaining terminal phosphorus was labelled P_U (see Figs. 1 and 2 for a labelled diagram). In complex **1**, no spin–spin coupling was detected between the terminal phosphines, P_T and P_U, in contrast with most complexes of L which have been characterised.[9] A smaller set of broadened resonances arising from a second, minor product, was observed at δ 165.4 (P_C), 78.9 (P_U) and 54.1 (P_T). At 233 K both species gave rise to sharp resonances in the ^{31}P NMR spectrum. The major species gave rise to signals at δ 171.7 (t, P_C), 65.1 (t, P_U) and 50.5 (dd, P_T); the minor species gave rise to resonances at δ 164.8 (dt, P_C), 79.3 (dt, P_U) and 55.4 (dd, P_T). The coupling constant between P_T and P_U for the minor species was also small (12.9 Hz). The ratio of major to minor species was *ca.* 11 : 1 at 233 K. The broadness of the resonances of the minor species at 300 K is due to exchange between the two products at this temperature. The two species were identified (*vide infra*) as the isomeric complexes **1a** and **1b** which differ in the orientation of the butenynyl ligand with respect to the rest of the molecule. For convenience, the exchanging mixture of isomeric butenynyl complexes **1a** and **1b** is referred to as **1**.



Reaction of the chloro hydrido complex FeH(Cl)L **6** with *tert*-butylacetylene afforded the corresponding butenynyl complex **2**. In contrast to **1**, only one set of resonances was observed in the 233 K ^{31}P NMR spectrum of **2**. This may be due to the absence of appreciable quantities of the minor product corresponding to **1b**, or fast exchange between isomers even at this temperature. Reaction of the chloro hydrido complex FeH(Cl)L **6** with 1,4-diethynylbenzene also afforded the corresponding butenynyl complexes **3a** and **3b**. The ^{31}P NMR spectrum of **3a**,**b** at both 300 and 233 K were similar to those of the phenylbutenynyl complexes, with two products observed at 233 K in the ratio of approximately 8 : 1. The ^{31}P NMR spectra of **3** and **1** are almost identical and the major and minor isomers of **3** would therefore correspond to those of the phenylbutenynyl complex.

Assignment of stereochemistry in butenynyl complexes

Isomeric butenynyl complexes have been observed for the ruthenium and osmium systems with L. In these cases no exchange is apparent in the 300 K ^{31}P NMR spectrum. As discussed by Bianchini *et al.*,[2b] octahedral complexes of L offer two different sites for the unsymmetrical bidentate butenynyl ligand and hence two isomers are possible, with the triple bond *trans* to either P_C or *trans* to P_U. There is also the possibility of *E*/*Z* isomers about the butenynyl double bond, resulting in a total of four possible isomers (**I**–**IV**). A *trans* stereochemistry



about the double bond of the ruthenium[2b] and osmium[2d] complexes of L was assigned (structures **I** and **II**) on the basis of the size of the long range coupling constant $^3J_{C(2)-H(C4)}$.[18]

The relative stereochemistry of the butenynyl ligand with respect to L and the stereochemistry about the double bond for **1a** and **1b** was determined using 2D NMR COSY and

NOESY experiments. These spectra were recorded on the tetrafluoroborate salt (to avoid complication of ^{1}H spectra by resonances of the tetraphenylborate counter ion). Both the major and the minor isomers exhibited strong cross peaks between the vinylic proton and the relevant (see below) protons of L in the NOESY spectrum and were hence assigned a *Z* configuration about the butenyne double bond. The major isomer **1a** was found to have structure **I** whilst the minor isomer **1b** was assigned structure **II**.

In complex **1a**, strong NOESY cross peaks from the *ortho* protons on Ph^1 to Me_A, Me_B and Me_C indicated that the triple bond was *trans* to P_C. Cross peaks from the olefinic proton, to Me_A, H^1 and H^2 and from the *ortho* protons on Ph^2 to Me_A confirmed this assignment (Fig. 1). The expected cross peak from the vinylic proton H to the *ortho* proton of Ph^2 was obscured by the stronger cross peak between the *ortho* and *meta* protons on Ph^2 (δ 7.57 (Ph^2 H_{meta}), 7.56 (Ph^2 H_{ortho})).

The stereochemistry of the minor isomer **1b** was also determined from the NOESY spectrum and a full spectral assignment of the ^{1}H NMR spectrum of **1b** was achieved despite the large excess of **1a**. The ^{1}H resonances of L were assigned using the same methodology as was used for other octahedral complexes of L.[9] A strong NOESY cross peak between the resonance of the vinylic proton and Me_C indicated that the double bond is located *trans* to P_C. This stereochemistry was confirmed by the presence of strong NOESY cross peaks between the resonances of the *ortho* protons on Ph^1 and H^1 and H^2 on the backbone of the PP_3 ligand (Fig. 2).

Exchange between isomers 1a and 1b

Exchange processes on a timescale similar to the mixing time of the NOESY experiment (usually 1–10 s) give rise to exchange cross peaks in the NOESY spectrum. These cross peaks are easily differentiated from the 'real' NOESY cross peaks in small molecules as they are characteristically of opposite sign. The NOESY spectrum of the diphenylbutenynyl complexes **1a** and **1b** acquired at 303 K contains exchange peaks as well as the expected NOESY cross peaks.

The ^{1}H NMR spectrum of **1** (303 K, 600 MHz) contained resonances due to the two isomers **1a** and **1b**, although the resonances for the minor isomer **1b** were significantly broadened by exchange. The NOESY spectrum acquired at 303 K indicated that exchange processes were occurring within as well as between the two isomeric complexes. Each of the isomers **1a** and **1b** has three methyl resonances and exchange peaks are present between all of the methyl resonances of L (a six site exchange). Exchange peaks were also observed within and between the methylene resonances of L of both isomers.

In the aromatic region of the 2D NOESY spectrum acquired at 303 K (Fig. 3), more specific exchange was observed. An exchange peak was observed between the vinylic proton of the major isomer and the corresponding vinylic proton in the minor isomer. Exchange peaks were also observed between the alkyne-bound phenyl group in the major isomer (Ph^1) and the alkyne-bound phenyl group in the minor isomer (Ph$^{1'}$), and between the corresponding alkene-bound phenyl groups Ph^2 and Ph$^{2'}$ (Fig. 4).

The most probable mechanism for the exchange involves the decoordination of the acetylene of the butenynyl ligand to give complex **10** (where the butenyne is coordinated by the σ-bond to the vinylic carbon) followed by rotation around the metal–carbon bond and re-coordination of the alkyne to give the other stereoisomer (Scheme 2). There is ample precedent for the existence of η^1-bound butenynyl complexes, including X-ray crystal structures.[1a,b]

X-Ray crystallography of [FeL(η^3-PhC≡C–C=CHPh)]BPh$_4$ 1a

Diffraction quality crystals were obtained by slow evaporation of a saturated acetone solution of the tetraphenylborate salt of

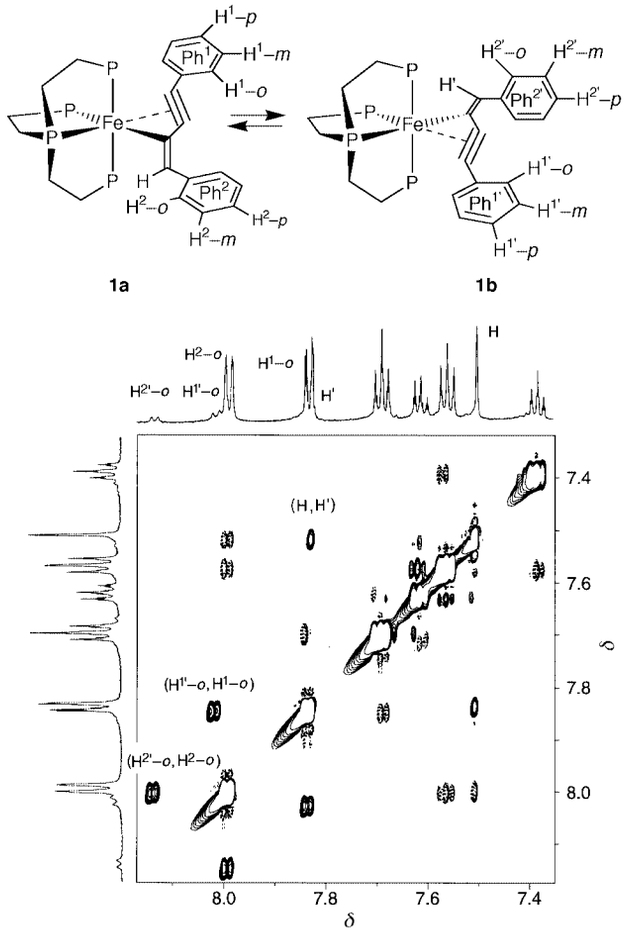


Fig. 3 Aromatic region of the NOESY spectrum (600 MHz, 303 K, acetone-d_6) of [Fe(η^3-PhC≡C–C=CHPh)L]$^+$ **1** (BPh_4 salt). Negative cross peaks are represented by dashed contours, positive peaks (due to exchange) are represented as solid contours.

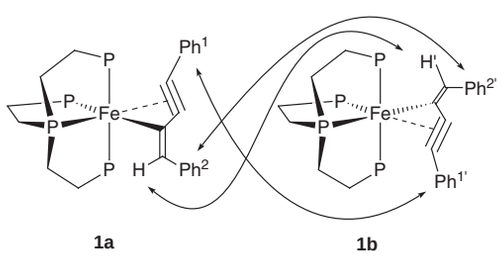
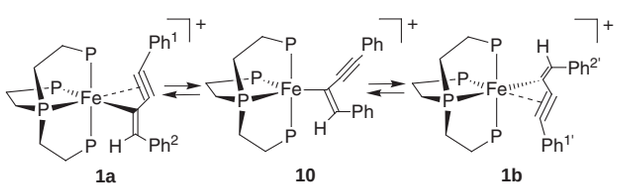


Fig. 4 Schematic representation showing the exchange observed in the 303 K NOESY spectrum between H-*o* of **1a** and H′-*o* of **1b**, Ph^1 of **1a** and Ph$^{1'}$ of **1b**, and Ph^2 of **1a** and Ph$^{2'}$ of **1b**.



Scheme 2

1. The structure determination shows the solid state structure to be the same as that determined for the major isomer **1a** by 2D NMR methods (Fig. 5). The crystal data parameters are summarised in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

Comparison of the structure of **1a** with that of the triphenylphosphine chloro complex [FeCl(PPh$_3$)L]BPh$_4$ **11**[9a] shows the Fe–L fragment to be similar for both complexes, despite the different co-ligands (Table 2). Fe–P bond lengths

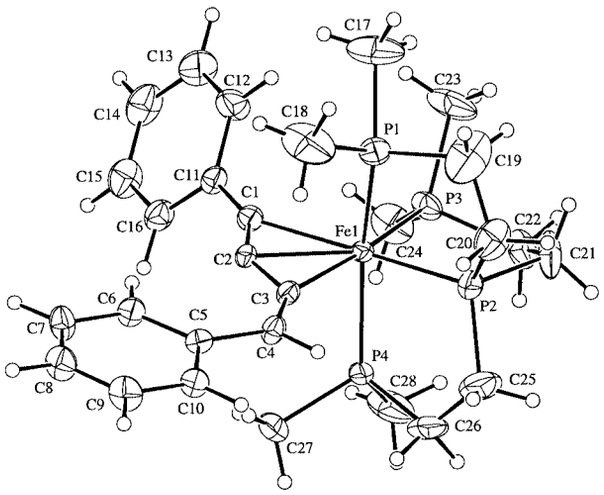


Fig. 5 ORTEP plot (25% thermal ellipsoids, non-hydrogen atoms) of $[Fe(\eta^3\text{-PhC}{\equiv}C{-}C{=}CHPh)L]^+$ **1a** (BPh_4 salt).

Table 1 Crystallographic data for $[Fe(\eta^3\text{-PhC}{\equiv}C{-}C{=}CHPh)L]^+$ **1a** (BPh_4 salt)

Empirical formula	$C_{52}H_{61}BFeP_4$
Formula weight	876.61
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
Lattice Parameters:	
a/Å	13.459(4)
b/Å	13.517(6)
c/Å	13.843(6)
α/°	76.75(4)
β/°	74.45(4)
γ/°	78.76(4)
V/Å^3	2337(2)
T/°C	21.0
μ(Mo-Kα)/cm^{-1}	4.935
No. of reflections measured	
Total	8595
Unique	8218
R_{int}	0.030
Residuals: R, R_w	0.053, 0.043

for **1a** are slightly shorter than those of **11**. The bond angles are similar, with deviations from the octahedral angles of 90 and 180° brought about by the small natural bite angle of L.

A number of η^3-butenynyl complexes have been reported in the literature, including X-ray structures of complexes of tungsten,[19] iron,[5b,c] ruthenium[2a,20] and osmium.[21] The most relevant structures to compare with that of **1a** are the iron(II) η^3-1,4-diphenylbutenynyl complex **12**,[5b,c] containing two dmpe ligands, and the ruthenium(II) η^3-1,4-bis(trimethylsilyl)-butenynyl complex **13**[2a] containing the tripodal tetradentate phosphine L^1 **8** (Table 3). The structures of **1a** and **12** are very similar. The Fe–C_1 bond is slightly longer in **12**, as is the C_2–C_3 bond. The C_1–C_2–C_3 bond angle is smaller in **1a** than in **12**.

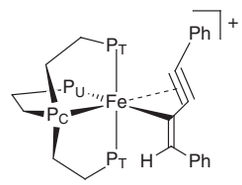
The ruthenium butenynyl complex **13** exhibits the same regio- and stereo-chemistry as **1a**, with the alkyne *trans* to the central phosphorus and the metal *trans* to the non-hydrogen substituent on the double bond. The metal–butenynyl bonds are longer for **13**, as would be expected for the larger second-row metal. Bond lengths in the butenynyl fragment in **13** are similar to those of **1a** and **12**, however, **13** has a smaller R–C_1–C_2 bond angle and a larger C_1–C_2–C_3 bond angle.

Catalytic dimerisation of phenylacetylene

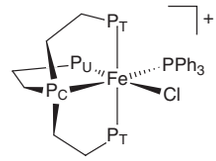
A number of transition metal complexes are catalysts for the head-to-head dimerisation of terminal alkynes to 1,4-disubstituted butenynes,[1,2] including the ruthenium complex **13**.

Reaction of **1** with an excess of phenylacetylene results in the slow formation of 1,4-diphenylbut-3-en-1-yne, which was identified by GC–MS and by ^{1}H NMR. Only the Z isomer[2c] was formed in the reaction and the butenynyl complex **1a** was the only iron complex detected by ^{31}P NMR during the course of the reaction. The reaction rate for this reaction at 80 °C was approximately one turnover per day (from the ^{1}H NMR spectrum). This turnover rate is slow compared with other systems, and the reaction was not further investigated.

Table 2 Comparison of selected bond lengths (Å) and angles (°) in the FeL fragments of $[Fe(\eta^3\text{-PhC}{\equiv}C{-}C{=}CHPh)L]BPh_4$ **1a** and $[FeCl(PPh_3)L]BPh_4$ **11**[9a]



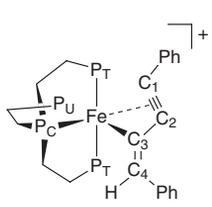
1a



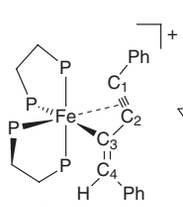
11

	1a	**11**[9a]
Fe–P_C	2.140(2)	2.202(2)
Fe–P_U	2.218(2)	2.234(2)
Fe–P_T(P1)	2.266(2)	2.312(2)
Fe–P_T(P4)	2.280(2)	2.312(2)
P_C–Fe–P_U	87.45(8)	83.85(9)
P_C–Fe–P_T(P1)	83.32(7)	83.66(9)
P_C–Fe–P_T(P4)	83.58(7)	83.24(9)
P_U–Fe–P_T(P1)	99.38(7)	98.71(9)
P_U–Fe–P_T(P4)	93.84(7)	93.40(9)
P_T–Fe–P_T	160.91(7)	161.07(9)

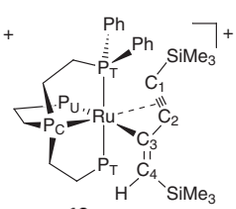
Table 3 Comparison of bond lengths (Å) and angles (°) in the metal–butenynyl fragments of $[Fe(\eta^3\text{-PhC}{\equiv}C{-}C{=}CHPh)L]BPh_4$ **1a**, $[Fe(\eta^3\text{-PhC}{\equiv}C{-}C{=}CHPh)(dmpe)_2]BPh_4$ **12**[5b,c] and $[Ru(\eta^3\text{-Me}_3SiC{\equiv}C{-}C{=}CHSiMe_3)L^1]BPh_4$ **13**[2a]



1a



12



13

	1a	**12**[5b,c]	**13**[2a]
M–C_1	2.176(6)	2.309(8)	2.485(3)
M–C_2	2.071(5)	2.093(7)	2.234(3)
M–C_3	1.986(5)	1.985(7)	2.144(3)
C_1–C_2	1.250(7)	1.249(9)	1.247(5)
C_2–C_3	1.380(7)	1.396(10)	1.392(5)
C_3–C_4	1.340(7)	1.338(9)	1.335(5)
R–C_1–C_2	150.7(7)	152.9(7)	142.0(3)
C_1–C_2–C_3	144.4(6)	149.1(7)	154.0(3)
C_2–C_3–C_4	136.7(5)	132.5(7)	133.5(3)

Conclusions

The iron(II) butenynyl complexes $[Fe(\eta^3\text{-RC}{\equiv}C{-}C{=}CHR)L]^+$ (R = Ph **1**; R = Bu^t **2**; R = *p*-HC≡CC_6H_4 **3**) have been prepared. Complex **1** exists as a pair of isomers (**1a** and **1b**) which differ in the stereochemistry of binding of the butenynyl ligand. Assignment of the relative stereochemistry of **1a** and **1b** was achieved by analysis of the 2D NOESY spectrum. The stereoisomers **1a** and **1b** are in equilibrium and exchange peaks in the NOESY spectrum provided information on the mechanism of exchange. A crystal structure of **1a** showed the solid state

structure to be that of the major solution state isomer. Complex **1** catalyses the stereospecific head-to-head dimerisation of phenylacetylene to *Z*-1,4-diphenylbut-1-en-3-yne.

Experimental

All synthetic manipulations involving air sensitive materials were carried out under an inert atmosphere of argon in an argon filled dry box or under a nitrogen atmosphere using standard Schlenk techniques. THF, benzene and hexane were dried over sodium before distillation from sodium and benzophenone under nitrogen. Ethanol and methanol were distilled from magnesium under nitrogen. The iron(II) dichloride complex $FeCl_2L$ **5**,[9a] the iron(II) chloro hydrido complex FeH(Cl)L **6**[9a] and the iron(II) dihydrogen hydrido complex $[FeH(H_2)L]^+$ **6**[9c] were prepared using previously reported methods. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AMX400 or AMX600 spectrometers at the temperatures quoted. ^1H and ^{13}C chemical shifts were internally referenced to residual solvent resonances. ^{31}P spectra were referenced to external neat trimethyl phosphite at δ 140.85. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. Mass spectra were recorded on a Finnigan MAT TSQ-46 (San Jose, CA, USA) spectrometer equipped with a desorption probe, with a source temperature of 140 °C and an electron energy of 100 eV. Chemical ionisation (CI) was used, with methane (>99.999%) as the ionisation gas. Elemental analyses were carried out at the Joint Elemental Analysis Facility, The University of Sydney. Melting points were recorded on a Gallenkamp heating stage and are uncorrected.

Crystal structure determination

The crystallographic data for **1a** (BPh_4 salt) are summarised in Table 1. A red–orange crystal of **1a** having approximate dimensions $0.42 \times 0.32 \times 0.07$ mm was mounted on an Enraf-Nonius CAD4 diffractometer employing graphite monochromated Mo-Kα radiation. Triclinic cell constants were obtained from a least-squares refinement against the setting angles of 25 reflections in the range $16 < 2\theta < 27°$. Diffraction data were collected at a temperature of 21 ± 1 °C using ω–θ scans to a maximum 2θ value of 50°. The intensities of three representative reflections measured every hour did not change significantly during the course of the data collection. The data were corrected for Lorentz, polarisation and absorption (analytical) effects.

All calculations were performed using the teXsan[10] crystallographic software package. The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] Neutral atom scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in the structure factor calculation,[14] and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[15] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[16] Non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the full matrix least squares refinement at calculated positions with group temperature factors. An ORTEP[17] representation of the complex is shown in Fig. 5.

CCDC reference number 186/1518.

See http//www.rsc.org/suppdata/dt/1999/2557/ for crystallographic files in .cif format.

Preparations

$[Fe(\eta^3\text{-PhC}{\equiv}C\text{–}C{=}CHPh)L]^+$ 1. Phenylacetylene (33 mg, 320 μmol) was added to a stirred solution of FeH(Cl)L **6** (34 mg, 87 μmol) in methanol (10 ml), resulting in a colour change from yellow to red. On addition of sodium tetraphenylborate (40 mg, 120 μmol) in methanol (5 ml), a red precipitate formed. The crude product was isolated by filtration, washed with methanol (20 ml) and dried *in vacuo* to yield $[Fe(\eta^3\text{-PhC}{\equiv}C\text{–}C{=}CHPh)L]^+$ **1** (BPh_4 salt) (72 mg, 94%), mp 242–244 °C.

The tetrafluoroborate salt of **1** was also prepared in an analogous way using sodium tetrafluoroborate in the place of sodium tetraphenylborate. MS (+ CI, CH_4) *m*/*z* (>150): 558 (M + 1, 14), 557 (M, 36), 388 (10), 363 (30), 233 (14), 206 (17), 205 (95), 165 (100). IR ν_{max} (Nujol): 1578w, 1592w.

Major isomer **1a**. $^{31}P\text{-}\{^1H\}$ NMR (BF_4 salt, 162 MHz, acetone-d_6, 300 K): δ 171.9 (t, 1P, P_C, $^2J_{P(C)\text{–}P(T)} = 26.2$), 49.5 (dd, 2P, P_T, $^2J_{P(T)\text{–}P(U)} = 34.8$ Hz), 64.4 (t, 1P, P_U). $^{31}P\text{-}\{^1H\}$ NMR (BF_4 salt, 162 MHz, acetone-d_6, 233 K): δ 171.7 (t, 1P, P_C, $^2J_{P(C)\text{–}P(T)} = 25.8$), 50.5 (dd, 2P, P_T, $^2J_{P(T)\text{–}P(U)} = 35.3$ Hz), 65.1 (t, 1P, P_U).

$^1H\text{-}\{^{31}P\}$ NMR spectrum (600 MHz, acetone-d_6, 303 K): δ 1.95, 2.56 (2 × m, 2 × 2H, $\text{–}P_CCH_2CHHP_T\text{–}$), 2.61, 2.86 (2 × m, 2 × 2H, $\text{–}P_CCHHCH_2P_T\text{–}$), 2.27 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 2.10 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 0.92, 1.29 [2 × s, 2 × 6H, 2 × $P_T(CH_3)$], 1.85 [s, 6H, $P_U(CH_3)_2$], 7.51 (s, 1H, C=CH), 7.84 (d, 2H, $CCPh_{ortho}$), 7.70 (d, 2H, $CCPh_{meta}$), 7.62 (t, 1H, $CCPh_{para}$), 7.99 (d, 2H, $C{=}CHPh_{ortho}$), 7.57 (d, 2H, $C{=}CHPh_{meta}$), 7.39 (t, 1H, $C{=}CHPh_{para}$).

$^1H\text{-}\{^{31}P\}$ NMR (BF_4 salt, 600 MHz, acetone-d_6, 240 K): δ 1.91, 2.51 (2 × m, 2 × 2H, $\text{–}P_CCH_2CHHP_T\text{–}$), 2.57, 2.84 (2 × m, 2 × 2H, $\text{–}P_CCHHCH_2P_T\text{–}$), 2.24 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 2.05 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 0.87, 1.26 [2 × s, 2 × 6H, 2 × $P_T(CH_3)$], 1.81 [s, 6H, $P_U(CH_3)_2$], 7.56 (s, 1H, C=CH), 7.84 (d, 2H, $CCPh_{ortho}$), 7.69 (d, 2H, $CCPh_{meta}$), 7.61 (t, 1H, $CCPh_{para}$), 7.99 (d, 2H, $C{=}CHPh_{ortho}$), 7.56 (d, 2H, $C{=}CHPh_{meta}$), 7.37 (t, 1H, $C{=}CHPh_{para}$).

$^{13}C\text{-}\{^1H\}$ NMR (chloride salt, 101 MHz, methanol-d_4, 300 K) δ 10.0 [t, $\text{–}P_T(CH_3)$, $^1J_{P(T)\text{–}C} = 11.4$], 19.0 [t, $\text{–}P_T(CH_3)$, $^1J_{P(T)\text{–}C} = 7.6$], 21.2 [d, $\text{–}P_U(CH_3)_2$, $^1J_{P(U)\text{–}C} = 22.9$], 26.3 (dt, $\text{–}P_TCH_2CH_2P_C\text{–}$, $^1J_{P(C)\text{–}C} = 21.6$, $^2J_{P(T)\text{–}C} = 7.6$), 32.9 (dt, $\text{–}P_TCH_2CH_2P_C\text{–}$, $^1J_{P(T)\text{–}C} = 16.5$, $^2J_{P(C)\text{–}C} = 13.4$), 29.1 (dd, $\text{–}P_UCH_2CH_2P_C\text{–}$, $^1J_{P(C)\text{–}C} = 24.2$, $^2J_{P(U)\text{–}C} = 15.9$), 34.2 (dd, $\text{–}P_UCH_2CH_2P_C\text{–}$, $^1J_{P(U)\text{–}C} = 29.2$, $^2J_{P(C)\text{–}C} = 11.4$), 42.6 (m, $PhC{\equiv}C\text{–}$, $J_{P\text{–}C} < 2.5$), 122.1 (dd, $PhC{\equiv}C\text{–}$, $J_{P(C)\text{–}C} = 10.1$, $J_{P(U)\text{–}C} = 7.0$), 165.4 (ddt, Fe-$C{=}CHPh$, $J_{P(C)\text{–}C} = 10.2$, $J_{P(U)\text{–}C} = 10.2$, $J_{P(T)\text{–}C} = 16.5$), 134.2 (d, Fe-$C{=}CHPh$, $J_{P\text{–}C} = 1.3$), 131.3 (s, $\text{–}C{\equiv}CPh_{ortho}$), 130.5 (s, $\text{–}C{\equiv}CPh_{meta}$), 129.6 (s, $\text{–}C{\equiv}CPh_{para}$), 126.7 (s, $\text{–}C{=}CHPh_{ortho}$), 130.3 (s, $\text{–}C{=}CHPh_{meta}$), 128.0 (s, $\text{–}C{=}CHPh_{para}$), 133.0 (d, Ph_{ipso}, $J_{P\text{–}C} = 2.5$), 139.1 (apparent q, Ph_{ipso}, $J_{P\text{–}C} = 1.9$ Hz).

Minor isomer **1b**. $^{31}P\text{-}\{^1H\}$ NMR (BF_4 salt, 162 MHz, acetone-d_6, 300 K): δ 165.4 (br, 1P, P_C), 54.1 (dd, 2P, P_T, $^2J_{P(C)\text{–}P(T)} = 30.5$, $^2J_{P(T)\text{–}P(U)} = 39.1$ Hz), 78.9 (br, 1P, P_U).

$^{31}P\text{-}\{^1H\}$ NMR (BF_4 salt, 162 MHz, acetone-d_6, 233 K): δ 164.8 (t, 1P, P_C, $^2J_{P(C)\text{–}P(T)} = 30.5$, $^2J_{P(C)\text{–}P(U)} = 12.9$), 55.4 (dd, 2P, P_T, $^2J_{P(T)\text{–}P(U)} = 39.1$ Hz), 79.3 (t, 1P, P_U).

$^1H\text{-}\{^{31}P\}$ NMR (BF_4 salt, 600 MHz, acetone-d_6, 303 K): δ 2.00, 2.31 (2 × m, 2 × 2H, $\text{–}P_CCH_2CHHP_T\text{–}$), 3.02, 3.12 (2 × m, 2 × 2H, $\text{–}P_CCHHCH_2P_T\text{–}$), 2.44 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 2.10 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 0.68, 1.14 [2 × s, 2 × 6H, 2 × $P_T(CH_3)$], 2.01 [s, 6H, $P_U(CH_3)_2$], 7.84 (s, 1H, C=CH), 8.02 (d, 2H, $CCPh_{ortho}$), 7.68 (d, 2H, $CCPh_{meta}$), 7.52 (t, 1H, $CCPh_{para}$), 8.14 (d, 2H, $C{=}CHPh_{ortho}$), 7.63 (d, 2H, $C{=}CHPh_{meta}$), 7.42 (t, 1H, $C{=}CHPh_{para}$).

$^1H\text{-}\{^{31}P\}$ NMR (BF_4 salt, 600 MHz, acetone-d_6, 240 K): δ 1.97, 2.29 (2 × m, 2 × 2H, $\text{–}P_CCH_2CHHP_T\text{–}$), 3.00, 3.09 (2 × m, 2 × 2H, $\text{–}P_CCHHCH_2P_T\text{–}$), 2.39 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 2.05 (m, 2H, $\text{–}P_CCH_2CH_2P_U\text{–}$), 0.64, 1.12 [2 × s, 2 × 6H, 2 × $P_T(CH_3)$], 2.07 [s, 6H, $P_U(CH_3)_2$], 7.85 (s, 1H, C=CH), 8.02 (d, 2H, $CCPh_{ortho}$), 7.68 (d, 2H, $CCPh_{meta}$), 7.52 (t, 1H, $CCPh_{para}$), 8.14 (d, 2H, $C{=}CHPh_{ortho}$), 7.67 (d, 2H, $C{=}CHPh_{meta}$), 7.50 (t, 1H, $C{=}CHPh_{para}$).

$[Fe(\eta^3\text{-Bu}^tC{\equiv}C\text{–}C{=}CHBu^t)L]^+$ 2. *tert*-Butylacetylene (10 mg, 120 mmol) was added to a stirred solution of FeH(Cl)L **6** (*ca.* 10 mg, 26 μmol) in methanol (5 ml), resulting in a change from yellow to dark orange. On addition of sodium tetraphenylborate (20 mg, 60 μmol) in methanol (5 ml), an

orange precipitate formed. The crude product was isolated by filtration, washed with methanol (10 ml) and dried *in vacuo* to yield $[Fe(\eta^3\text{-}Bu^tC{\equiv}C{-}C{=}CHBu^t)L]^+$ **2** (BPh_4 salt).

$^{31}P\text{-}\{^1H\}$ NMR (BPh_4 salt, 162 MHz, acetone-d_6, 300 K): δ 174.5 (t, 1P, P_C, $^2J_{P(C)-P(T)} = 25.3$), 48.2 (dd, 2P, P_T, $^2J_{P(T)-P(U)} = 35.3$), 60.40 (t, 1P, P_U). $^{31}P\text{-}\{^1H\}$ NMR spectrum (BPh_4 salt, 162 MHz, acetone-d_6, 233 K): δ 174.0 (t, 1P, P_C, $^2J_{P(C)-P(T)} = 24.8$), 49.1 (dd, 2P, P_T, $^2J_{P(T)-P(U)} = 35.3$ Hz), 61.0 (t, 1P, P_U).

$[Fe\{\eta^3\text{-}HC{\equiv}CC_6H_4C{\equiv}C{-}C{=}CH(C_6H_4)C{\equiv}CH\}L]^+$ 3. 1,4-Diethynylbenzene (10 mg, 80 μmol) was added to a stirred solution of FeH(Cl)L **6** (*ca.* 10 mg, 26 μmol) in methanol (5 ml), resulting in a change from yellow to red. On addition of sodium tetraphenylborate (20 mg, 60 μmol) in methanol (5 ml) a red precipitate formed. The crude product was isolated by filtration, washed with methanol (10 ml) and dried *in vacuo* to yield $[Fe\{\eta^3\text{-}HC{\equiv}CC_6H_4C{\equiv}C{-}C{=}CH(C_6H_4)C{\equiv}CH\}L]^+$ **3** (BPh_4 salt).

Major isomer **3a**. $^{31}P\text{-}\{^1H\}$ NMR (BPh_4 salt, 162 MHz, acetone-d_6, 300 K): δ 171.0 (t, 1P, P_C, $^2J_{P(C)-P(T)} = 26.7$, $^2J_{P(C)-P(U)} = 4.3$), 48.9 (dd, 2P, P_T, $^2J_{P(T)-P(U)} = 35.8$ Hz), 63.7 (t, 1P, P_U).

$^{31}P\text{-}\{^1H\}$ NMR (BPh_4 salt, 162 MHz, acetone-d_6, 233 K): δ 170.5 (t, 1P, P_C, $^2J_{P(C)-P(T)} = 25.3$, $^2J_{P(C)-P(U)} = 4.3$), 49.9 (dd, 2P, P_T, $^2J_{P(T)-P(U)} = 36.2$ Hz), 64.2 (t, 1P, P_U).

Minor isomer **3b**. $^{31}P\text{-}\{^1H\}$ NMR (BPh_4 salt, 162 MHz, acetone-d_6, 233 K): δ 163.7 (t, 1P, P_C, $^2J_{P(C)-P(T)} = 30.5$, $^2J_{P(C)-P(U)} = 12.8$), 55.5 (dd, 2P, P_T, $^2J_{P(T)-P(U)} = 36.2$ Hz), 78.7 (t, 1P, P_U).

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