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Allenylidene and derived alkynyl complexes of iron(II) with the $\{FeBr(Et_2PCH_2CH_2PEt_2)_2\}^+$ centre

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Dedicated to Professor E.O. Fischer on the occasion of his 85th birthday

Abstract

The allenylidene complexes *trans*-[FeBr{=C=C=C(R)Ph}(depe)$_2$][BPh$_4$] (depe = $Et_2PCH_2CH_2PEt_2$; R = Me **1**, Ph **2**) were obtained by treatment of a methanolic solution of *trans*-[FeBr$_2$(depe)$_2$] with the appropriate alkynol HC≡C–C(R)Ph(OH), in the presence of Na[BPh$_4$]. The methylallenylidene ligand in **1** undergoes reversible deprotonation (by NaOMe) to yield the enynyl (or ene–yne) complex of iron(II), *trans*-[FeBr{–C≡C–C(=CH$_2$)Ph}(depe)$_2$] **3**. The diphenylallenylidene ligand in **2** undergoes regioselective hydride γ-addition on reaction with K[B{CH(Me)Et}$_3$H] to afford the alkynyl complex *trans*-[FeBr{–C≡C–C(H)Ph$_2$}(depe)$_2$] **4**.

Keywords: Iron; Alkynols; Allenylidenes; Alkynyls; Enynyls; Propargyl alcohols

1. Introduction

The chemistry of allenylidene complexes, [M]=C=C=CR$_2$, is currently attracting great attention [1–4], being developed mainly after the Selegue [5] general synthetic method based on the dehydration of propargylic alcohols (alkynols), HC≡C–CR$_2$OH, by transition metal centres. The interest of allenylidene complexes does not arise only from the associated rich coordination chemistry, but also from their recognized significance in material science [6,7], in synthesis (e.g. towards metal-containing copolymers [3,8]) and in catalysis (e.g. ruthenium–allenylidene complexes as catalyst precursors for olefin metathesis [9–15] or as catalysts for various reactions of propargylic alcohols [16–20]).

However, allenylidene complexes of iron are still scarce [21–28] and in pursuit of our interest on the activation, by transition metal centres, of alkynes [29–35] and alkynols or derived alkenylcarbyne complexes [21,24,36–38], namely towards the formation of multiple metal-carbon bonded species, we have initiated the investigation of the coordination chemistry of alkynols at an iron(II) phosphinic centre. Hence, the cyclic allenylidene complex *trans*-[FeBr(=C=C=C$_6$H$_{10}$)(depe)$_2$][BPh$_4$] (depe = $Et_2PCH_2CH_2PEt_2$) and the η^2-alkyne complexes *trans*-[FeBr{η^2-HC≡C(CH$_2$)$_n$OH}(depe)$_2$][BPh$_4$] ($n = 1$ or 2) were obtained on reaction of *trans*-[FeBr$_2$(depe)$_2$], in the presence of Na[BPh$_4$], with the corresponding cyclic alkynol HC≡CC$_6$H$_{10}$OH or linear primary alkynols HC≡C(CH$_2$)$_n$OH, respectively (Scheme 1) [21]. The cyclic alkynol underwent dehydration to afford the ligated allenylidene, but the primary alkynols were stable towards dehydration allowing the isolation of η^2-alkyne complexes which commonly are postulated as intermediates in the formation of the allenylidene products.

In the work we now report we have extended the investigation to (i) tertiary alkynols HC≡C–C(R)PhOH and to (ii) the study of the effect of the nature of the organic R group (alkyl vs. aryl). Hence, both HC≡C–C(R)Ph(OH) (R = Me; Ph) are shown to undergo dehydration to yield the corresponding linear allenyli-

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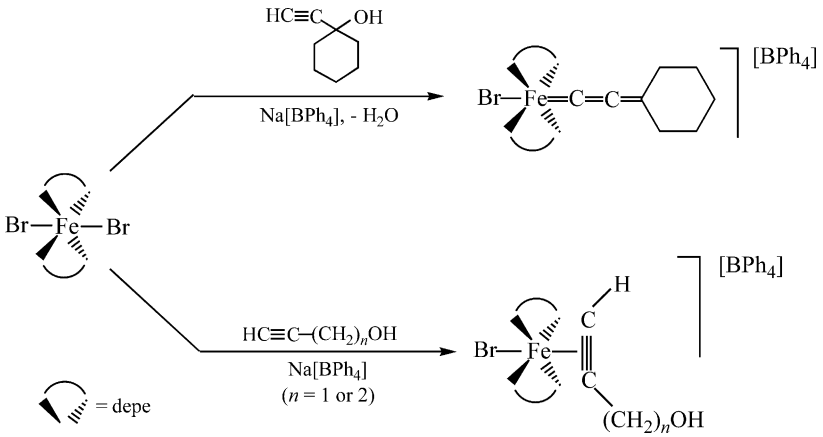


Scheme 1.

dene complexes *trans*-[FeBr{=C=C=C(R)Ph}(depe)$_2$]$^+$ which exhibit different further reactivities. In fact, the methylallenylidene ligand, =C=C=C(Me)Ph, exhibits acidic character to give the ligated –C≡C–C(=CH$_2$)Ph which, to our knowledge, provides the first example of an enynyl (or ene–yne) complex of iron to be reported. In contrast, the diarylallenylidene presents a γ-electrophilic behaviour to form the alkynyl group –C≡C–C(H)Ph$_2$ upon reaction with an hydridic reagent.

2. Results and discussion

2.1. Synthesis and characterization

Treatment of a MeOH solution of *trans*-[FeBr$_2$(depe)$_2$], at 40 °C, in the presence of Na[BPh$_4$], with 2-phenyl-3-butyn-2-ol, HC≡CC(Me)Ph(OH) or 1,1-diphenyl-2-propyn-1-ol, HC≡CCPh$_2$(OH), leads to the formation of the allenylidene complexes *trans*-[FeBr{=C=C=C(R)Ph}(depe)$_2$][BPh$_4$] (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$; R = Me **1**, Ph **2**), respectively (Scheme 2, reactions 1 and 2), isolated as dark violet (**1**) or dark blue (**2**) solids, in ca. 80–50% yields. The complexes, as well as all the others discussed below, have been characterised by IR and multinuclear NMR spectroscopies, FAB$^+$MS spectrometry and elemental analysis.

In the IR spectra, the characteristic asymmetric stretching vibration ν(C=C=C) of the allenylidene ligand is observed as a strong intensity band at 1893 (**1**) or 1876 (**2**) cm^{-1}, in accord with the electronic nature of the R groups. These values are comparable with those known for related allenylidene iron species, such as [Fe(CO)$_2$(=C=C=CPh$_2$){P(OMe)$_3$}$_2$] (1868 cm^{-1}) [26] and [Fe(η^5-C$_5$H$_5$)(=C=C=CPh$_2$)(dppe)]$^+$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) (1926 cm^{-1}) [27], and fall in the range (1988–1870 cm^{-1} [3]) commonly observed for the allenylidene metal complexes.

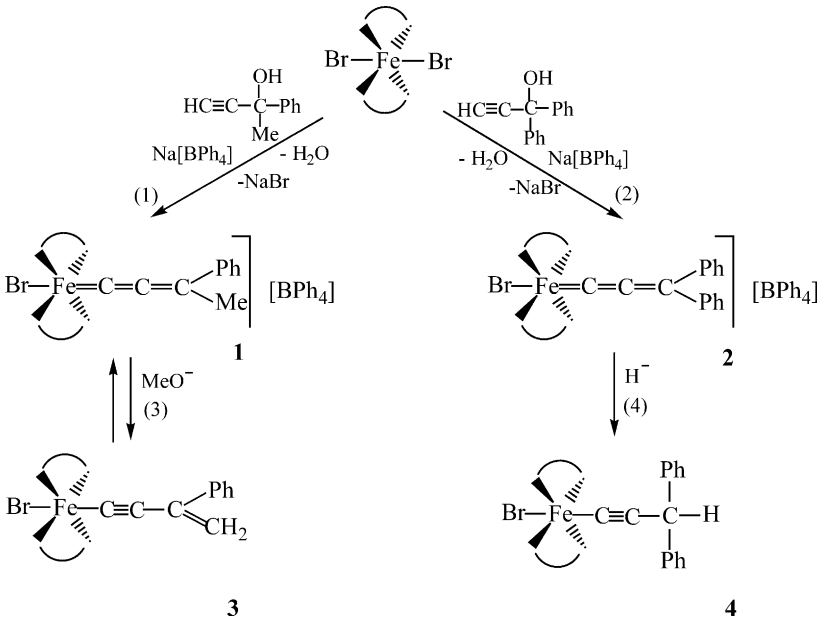
The *trans* geometry of these complexes is assigned on the basis of the singlet observed in their ^{31}P–{^{1}H}-NMR spectra. In the ^{13}C–{^{1}H}-NMR spectra the carbon atoms from the cumulenic chain are observed at δ 306.5 (**1**) and 305.5 (**2**) (qnt, $^2J_{CP}$ = 36 Hz, assigned to C$_\alpha$), 235.1 (**1**) and 244.9 (**2**) (qnt, $^4J_{CP}$ = 4 and 5 Hz, C$_\gamma$ with the lowest J_{CP} value, in comparison with those for C$_\alpha$ and C$_\beta$) and 148.5 (**1**) and 149.4 (**2**) ppm (qnt, $^3J_{CP}$ = 6 Hz, C$_\beta$). The allenylidene complexes [W(=C=C=CPh$_2$)(CO)$_5$] [39] (δ 302.5 (C_α) > δ 155.5 (C_γ) > δ 145.0 (C_β)) and [Mn(η^5-C$_5$H$_5$)(=C=C=CPh$_2$)(CO)$_2$] [40] (δ 304.5 (C_α) > δ 223.3 (C_γ) > δ 139.8 (C_β)) also display the same order of ^{13}C chemical shifts within the cumulenic carbon chain, although for most of the allenylidene complexes the order $C_\alpha > C_\beta > C_\gamma$ has been proposed [3] without given evidence.

All the other resonances of the allenylidene and depe ligands have also been assigned (see Section 4) in the ^{1}H-, ^{13}C–{^{1}H}- and ^{13}C-NMR spectra, including those of *ipso*-, *ortho*-, *meta*- and *para*- atoms of the phenyl rings.

Further, the FAB$^+$MS spectra of the complexes exhibit the molecular ion, [M]$^+$, and the corresponding fragments derived from the stepwise elimination of the bromide, [M−Br]$^+$, allenylidene, [M−C=C=CR$_2$]$^+$, or depe, [M−depe]$^+$, ligands.

2.2. Reactivity

The methylallenylidene complex **1** undergoes deprotonation by NaOMe which acts as a Brönsted base towards the methyl group of the allenylidene ligand yielding (Scheme 2, reaction 3) *trans*-[FeBr{–C≡C–C(=CH$_2$)Ph}(depe)$_2$] (**3**) that appears to be the first enynyl (or ene–yne) complex of iron to be reported. This compound is also obtained upon reaction of **1** with the hydridic reagent K-selectride, K[B{CH(Me)Et}$_3$H]. In its IR spectrum, ν(C≡C) and ν(C=C) appear as bands at 2020 (strong) and 1552 (medium) cm^{-1}, respectively, whereas in the ^{1}H-NMR spectrum the =CH_2 resonances occur as two doublets ($^2J_{HH}$ ca. 2 Hz) at δ ca. 5.4 and



Scheme 2.

5.1. These features are comparable with those quoted for the related complexes [Ru(η^5-C_5Me_5){–C≡C–C(=CH_2)Ph}(dippe)] (**a**, dippe = ^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$) (δ 5.3 and 5.0, each signal observed as a doublet with $^2J_{HH}$ ca. 2 Hz) [41] and [OsH(η^5-C_5H_5){–C≡C–C(=CH_2)Ph}(P^{i}Pr$_3$)$_2$][PF_6] (**b**, δ 5.4 and 5.0 as singlets) [43].

In the ^{13}C–{^{1}H}-NMR spectrum, the resonances of the –C≡C–C=CH_2 moiety in **3** appear as a quintet ($^2J_{CP}$ = 28 Hz, C_α) at δ 135.7, a quintet (J_{CP} = 2 Hz, C_β or C_γ) at δ 135.9, a multiplet (C_γ or C_β) at δ 122.9 and a quintet ($^5J_{CP}$ = 2 Hz, =CH_2) at δ 111.0 which, in the ^{13}C-NMR spectrum, splits into the expected triplet (J_{CH} = 158 Hz) of quintets. The δ (=CH_2) and the $^2J_{CP}$ (C_α) values are comparable with those displayed by complexes **a** (109.6 ppm, 21 Hz [41]) and **b** (117.3 ppm, 24 Hz [42]) which also present the other δ values for the enynyl group similar to those of **3** (with the exception of the much higher field C_α resonance quoted [42] for the Os(IV) complex **b**).

The *trans* geometry of complex **1** is assigned on the basis of the singlet resonance at δ 67.4 ppm rel. H_3PO_4, observed in the ^{31}P–{^{1}H}-NMR spectrum, whereas by FAB$^+$MS spectrometry its molecular ion was detected, $[M]^+$ (m/z = 675), as well as a fragmentation pattern initiated by the stepwise elimination of the bromide $[M-Br]^+$ (m/z = 596), the alkynyl [M–(–C≡C–C(=CH_2)Ph)]$^+$ (m/z = 547) or the depe $[M-depe]^+$ (m/z = 469) ligands.

The deprotonation of the methylallenylidene ligand in complexes **1** to give the enynyl product **3** is reversible since the latter undergoes protonation at the methylidene carbon, by reaction with HBF_4, in CH_2Cl_2, to regenerate the methylallenylidene species, forming the compound identical to **1** but with $[BF_4]^-$ as the counterion, as proved by the IR, ^{1}H- and ^{31}P–{^{1}H}-NMR spectra (they are identical for both compounds, except the data that concern the counterions). Regeneration of the allenylidene complex [Ru(η^5-C_5H_5){=C=C=C(C=CHCH=CHNMe)(CH_3)}(PPh_3)$_2$][PF_6] by protonation of the respective enynyl [Ru(η^5-C_5H_5){–C≡C–C(C=CHCH=CHNMe)(=CH_2)}(PPh_3)$_2$] with water has been reported by others [43]. The latter complex and the related enynyl Ru(II) complex **a** mentioned above were obtained by the same general method we have used in the preparation of **3** (deprotonation of the methyl group of a methylallenylidene complex), although by using LiBu [43] or KOBu^t [41], respectively, as the base. The enynyl complex [OsH(η^5-C_5H_5){–C≡C–C(=CH_2)Ph}(P^{i}Pr$_3$)$_2$][PF_6] was derived from the spontaneous conversion, in $CHCl_3$, of the hydride–hydroxyalkynyl compound [OsH(η^5-C_5H_5){–C≡C–C(CH_3)Ph(OH)}(P^{i}Pr$_3$)$_2$][PF_6] which resulted from treatment of [OsCl(η^5-C_5H_5)(P^{i}Pr$_3$)$_2$] with HC≡CC(CH_3)Ph(OH), in the presence of Tl[PF_6] [42].

The diphenylallenylidene ligand in complex **2** undergoes regioselective hydride addition to the C_γ atom upon treatment with K-selectride, leading to the formation of the neutral alkynyl complex *trans*-[FeBr{–C≡C–C(H)Ph$_2$}(depe)$_2$] (**4**) (Scheme 2, reaction 4). This reaction contrasts with that occurring with the methylallenylidene complex **1** which on treatment with the hydridic reagent undergoes deprotonation to give **3**. Hence, the Brönsted acidity of **1** overcomes its conceivable electrophilic behaviour.

Complex **4** exhibits in the IR spectrum a medium intensity ν(C≡C) vibration at 2057 cm^{-1}, whereas the presence of the proton at the acetylenic chain C≡C–

C(*H*)Ph_2 is accounted for by the singlet resonance observed at δ 4.91 in the ^{1}H-NMR spectrum. This chemical shift is similar to those observed for the related Ru(II) complexes *trans*-[RuCl{–C≡C–C(H)Ph_2}L_2] (δ 4.3 or 4.8 for L = $Ph_2PCH_2PPh_2$ [44] or dppe [45]). In the ^{13}C–{^{1}H}-NMR spectrum of **4**, the C_α, C_β and C_γ resonances of the alkynyl ligand appear at much higher fields, δ 113.5 (qnt, $^2J_{CP}$ = 28 Hz), 118.2 (m) and 47.7 (m), respectively, compared with the allenylidene precursor **2**. In the ^{13}C-NMR spectrum, the C_γ signal splits into the expected doublet (J_{CH} = 127 Hz).

These δ values are comparable with those reported for *trans*-[RuCl{–C≡C–C(H)Ph_2}L_2]: δ 103.1 (qnt, $^2J_{CP}$ = 16 Hz, C_α), 109.0 (s, C_β) and 48.1 (s, C_γ), for L = $Ph_2PCH_2PPh_2$ [44]; δ 105.4 (qnt, $^2J_{CP}$ = 16 Hz, C_α), 111.4 (s, C_β) and 49.2 (s, C_γ), for L = dppe [45]. These Ru(II) complexes where also obtained from γ-addition of hydride to the respective allenylidene compounds upon reaction with $NaBH_4$. The alkynyl complex [Re{–C≡C–C(H)Ph_2}$(CO)_2$(triphos)] (triphos = MeC(CH_2-PPh_2)$_3$) [46] was synthesised similarly by using $LiHBEt_3$ as the hydride source. Our alkynyl complex **4** appears to correspond to the first example of this type of reaction at an iron(II) centre.

The FAB$^+$MS spectrum of complex **4** shows the molecular ion, $[M]^+$ (m/z = 738), which by loss of H, Br, –C≡C–C(H)Ph_2 or depe leads to the corresponding fragments with m/z = 737, 659, 547 and 532.

3. Final comments

This work shows that a phosphinic iron(II) centre can stabilize allenylidene ligands conveniently prepared from tertiary alkynols to give stable $[Fe]^+$=C=C=CR_2 complexes that are readily obtained from reactions of the alkynols with *trans*-[$FeBr_2$(depe)$_2$] which presents one labile bromide ligand. The π-electron releasing ability of the binding *trans*-{FeBr(depe)$_2$}$^+$ site has a stabilizing role of the π-electron acceptor allenylidene ligand whose reactivity is strongly dependent on the nature (alkyl or aryl) of the organic R group. Although the diarylallenylidene $[Fe]^+$=C=C=CPh_2 behaves as a γ-electrophile and undergoes regioselective addition of an anionic nucleophile (H^-) to yield an alkynyl derivative, [Fe]–C≡C–C(H)Ph_2, the methylallenylidene species $[Fe]^+$=C=C=C(CH_3)Ph behaves as a Brönsted acid. The latter reaction appears to be particularly promising in providing an easy entry to enynyl species, [Fe]–C≡C–C(=CH_2)Ph, with an extra (ene) functional site (apart from the ynyl one) available for further reactivity which deserves to be explored.

4. Experimental

4.1. General procedures

All the manipulations and reactions were carried out in the absence of air using standard inert-gas flow and high-vacuum techniques. Solvents were purified and dried by standard methods and freshly distilled under dinitrogen. The complex *trans*-[$FeBr_2$(depe)$_2$] was prepared by a published method [47,48] and the alkynols were used as purchased from Aldrich. The IR spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets, and the NMR spectra (run in CD_2Cl_2 unless stated otherwise) on a Varian UNITY 300 spectrometer at room temperature (r.t.). ^{1}H, ^{13}C, ^{13}C–{^{1}H} and ^{31}P–{^{1}H} chemical shifts (δ) are reported in ppm relative to TMS and H_3PO_4, respectively. In the ^{13}C-NMR data, assignments and coupling constants common to the ^{13}C–{^{1}H}-NMR spectra are not repeated. Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; qnt = quintet; dq = doublet of quartet; dd = doublet of doublets; dt = doublet of triplets; dm = doublet of multiplets; tqnt = triplet of quintets; tm = triplet of multiplets; qqnt = quartet of quintets; m = multiplet; b = broad. C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (ca. 1.28 × 10^{-15} J) Xe atoms. Nominal molecular masses were calculated using the isotopes ^{56}Fe and ^{79}Br. However, further complexity due to addition (from matrix) or loss of hydrogen was usually not taken into account. Mass calibration for data system acquisition was achieved using CsI.

4.2. Syntheses

4.2.1. Allenylidene complexes *trans*-[FeBr{=C=C=C(*R*)Ph}(depe)$_2$][BPh_4] (*R* = *Me* **1**, *Ph* **2**)

To a stirred solution of *trans*-[$FeBr_2$(depe)$_2$] (0.20 g, 0.318 mmol) in MeOH (50 cm^3), under dinitrogen and at r.t., was added an excess (molar ratio 2:1) of a methanolic solution of the appropriate alkynol (0.636 mmol in 10 ml). The solution was stirred at 40 °C during ca. 3–4 h and along this time its colour changed, from pale green to violet or dark blue, in the reactions with HC≡CC(Me)Ph(OH) or HC≡CCPh_2(OH), respectively. Addition of a MeOH solution (10 cm^3) of Na[BPh_4] (0.120 g, 0.350 mmol) led to the precipitation of the allenylidene complexes **1** or **2**, respectively. These compounds were separated by filtration, recrystallized from CH_2Cl_2–Et_2O and dried in vacuo. Yield: 79% (0.25 g) **1**, 81% (0.272 g) **2**.

(**1**): Anal. Calc. for $C_{54}H_{76}BBrFeP_4$: C, 64.7; H, 7.8. Found: C, 64.5; H, 8.0%. IR (KBr, cm^{-1}): ν(C=C=C) 1893 (s). ^{1}H-NMR: δ 7.93 (d, $J_{HH} = 7.8$ Hz, 2H, H_o from C=C=CMe(C_6H_5)), 7.76 (t, $J_{HH} = 7.5$ Hz, 1H, H_p from C=C=CMe(C_6H_5)), 7.34 (m, 10H, H_m from C=C=CMe(C_6H_5) and H_o from BPh_4^-), 7.04 (t, $J = 7.2$ Hz, 8H, H_m from $B(C_6H_5)_4^-$), 6.89 (t, $J_{HH} = 6.9$ Hz, 4H, H_p from BPh_4^-), 2.46 (dq, $J_{HP} = 15.6$, $J_{HH} = 7.8$ Hz, 4H, $\frac{1}{4}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 2.15 (m, 4H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 1.91 (m, 4H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 1.76 (dq, $J_{HP} = 15.2$, $J_{HH} = 7.6$ Hz, 4H, $\frac{1}{4}$(CH_3CH_2)$_2$PCH$_2$CH$_2$P-(CH_2CH_3)$_2$), 1.72–1.59 (m, 11H, $\frac{1}{2}$(CH_3CH_2)$_2$PCH$_2$-CH$_2$P(CH_2CH_3)$_2$ and C=C=C(CH_3)Ph), 1.20 (m, 12H, $\frac{1}{2}$(CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 1.12 (m, 12H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$). ^{31}P–{^{1}H}-NMR: δ 55.3 ppm (s). ^{13}C–{^{1}H}-NMR: δ 306.5 (qnt, $^2J_{CP} =$ 36 Hz, C_α), 235.1 (qnt, $^4J_{CP} = 4$ Hz, C_γ), 164.3 (q, $^1J_{CB} = 49$ Hz, C_i from BPh_4^-), 148.5 (qnt, $^3J_{CP} = 6$ Hz, C_β), 143.3 (qnt, $J_{CP} = 3$ Hz, C_i from (C=C=CMe*Ph*), 136.2 (s, C_m from BPh_4^-), 131.6 (s, C_p from C=C=CMe*Ph*), 130.1 (s, C_o from C=C=CMe*Ph*), 126.8 (s, C_m from C=C=CMe*Ph*), 125.8 (q, $^2J_{CB} = 3$ Hz, C_o from BPh_4^-), 121.9 (s, C_p from BPh_4^-), 33.1 (qnt, $J_{CP} =$ 3 Hz, C=C=C(CH_3)Ph), 22.4 (qnt, $J_{CP} = 6$ Hz, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 20.3 (qnt, $J_{CP} =$ 11 Hz, (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 19.9 (qnt, $J_{CP} = 5$ Hz, $\frac{1}{2}$(CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 9.8 (s, $\frac{1}{2}$(CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 9.4 (s, $\frac{1}{2}$(CH_3-CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$). ^{13}C-NMR: δ 306.5 (qnt), 235.1 (qnt), 164.3 (q), 148.5 (m), 143.3 (m), 136.2 (dt, $^1J_{CH} = 153$, $^2J_{CH} = 7$ Hz), 131.6 (dt, $^1J_{CH} =$ 162, $^2J_{CH} = 7$ Hz), 130.1 (dd, $^1J_{CH} = 161$, $^2J_{CH} = 7$ Hz), 126.8 (dt, $^1J_{CH} = 158$, $^2J_{CH} = 6$ Hz), 125.8 (dm, $^1J_{CH} =$ 152 Hz), 121.9 (dt, $^1J_{CH} = 157$, $^2J_{CH} = 8$ Hz), 33.1 (qqnt, $^1J_{CH} = 130$ Hz), 22.4 (tm, $^1J_{CH} = 128$ Hz), 20.3 (m), 19.9 (tm, $^1J_{CH} = 130$ Hz), 9.8 (q, $^1J_{CH} = 128$ Hz), 9.4 (tm, $^1J_{CH} = 128$ Hz). FAB$^+$MS (*m*/*z*): 675 [M]$^+$, 596 [M−Br]$^+$, 547 [M−(=C=C=C(Me)Ph)]$^+$, 469 [M−depe]$^+$, 341 [M−depe−(=C=C=C(Me)Ph)]$^+$.

(**2**): Anal. Calc. for $C_{59}H_{78}BBrFeP_4$: C, 65.6; H, 7.7. Found: C, 66.0; H, 8.1%. IR (KBr, cm^{-1}): ν(C=C=C) 1876 (s). ^{1}H-NMR: δ 7.72 (t, $J_{HH} = 7.2$ Hz, 2H, H_p from C=C=C*Ph*$_2$), 7.62 (d, $J_{HH} = 7.8$ Hz, 4H, H_o from C=C=C*Ph*$_2$), 7.37 (t, $J_{HH} = 7.8$ Hz, 4H, H_m from C=C=C*Ph*$_2$), 7.33 (m, 8H, H_o from BPh_4^-), 7.03 (t, $J_{HH} = 7.2$ Hz, 8H, H_m from BPh_4^-), 6.88 (t, $J_{HH} = 7.1$ Hz, 4H, H_p from BPh_4^-), 2.43 (dq, $J_{HP} = 14.4$, $J_{HH} = 7.2$ Hz, 4H, $\frac{1}{4}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 2.09 (m, 4H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 1.86 (m, 4H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 1.68 (dq, $J_{HP} =$ 15.2, $J_{HH} = 7.6$ Hz, 8H, $\frac{1}{2}$(CH_3CH_2)$_2$PCH$_2$CH$_2$P-(CH_2CH_3)$_2$), 1.50 (dq, $J_{HP} = 15.2$, $J_{HH} = 7.6$ Hz, 4H, $\frac{1}{4}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$, 1.17 (m, 12H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 1.02 (m, 12H, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$). ^{31}P–{^{1}H}-NMR: δ 54.1 ppm (s). ^{13}C–{^{1}H}-NMR: δ 305.5 (qnt, $^2J_{CP} =$ 36 Hz, C_α), 244.9 (qnt, $^4J_{CP} = 5$ Hz, C_γ), 164.3 (q, $^1J_{CB} = 49$ Hz, C_i from BPh_4^-), 149.4 (qnt, $^3J_{CP} = 6$ Hz, C_β), 146.3 (qnt, $J_{CP} = 4$ Hz, C_i from C=C=C*Ph*$_2$), 136.2 (s, C_m from BPh_4^-), 130.5 (s, C_p from C=C=C*Ph*$_2$), 129.7 (s, C_o from C=C=C*Ph*$_2$), 128.0 (s, C_m from C=C=C*Ph*$_2$), 125.8 (q, $^2J_{CB} = 2$ Hz, C_o from BPh_4^-), 122.0 (s, C_p from BPh_4^-), 22.5 (qnt, $J_{CP} = 6$ Hz, $\frac{1}{2}$(CH_3-CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 20.2 (qnt, $J_{CP} = 11$ Hz, (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 19.9 (qnt, $J_{CP} = 6$ Hz, $\frac{1}{2}$(CH_3CH_2)$_2$PCH_2CH_2P(CH_2CH_3)$_2$), 9.9 (s, $\frac{1}{2}$ (CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 9.3 (s, $\frac{1}{2}$(CH_3-CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$). ^{13}C-NMR: δ 305.5 (qnt), 244.9 (qnt), 164.3 (q), 149.4 (m), 146.3 (m), 136.2 (dt, $^1J_{CH} = 153$, $^2J_{CH} = 7$ Hz), 130.5 (dt, $^1J_{CH} =$ 160, $^2J_{CH} = 7$ Hz), 129.7 (dd, $^1J_{CH} = 163$, $^2J_{CH} = 7$ Hz), 128.0 (dt, $^1J_{CH} = 162$, $^2J_{CH} = 6$ Hz), 125.8 (dm, $^1J_{CH} =$ 154 Hz), 122.0 (dt, $^1J_{CH} = 156$, $^2J_{CH} = 8$ Hz), 22.5 (tm, $^1J_{CH} = 130$ Hz), 20.2 (m), 19.9 (tm, $^1J_{CH} = 130$ Hz), 9.9 (q, $^1J_{CH} = 128$ Hz), 9.3 (q, $^1J_{CH} = 129$ Hz). FAB$^+$MS (*m*/*z*): 737 [M]$^+$, 658 [M−Br]$^+$, 547 [M−(=C=C=CPh$_2$)]$^+$, 531 [M−depe]$^+$, 341 [M−depe−(=C=C=CPh$_2$)]$^+$.

4.2.2. *Alkynyl complex trans-[FeBr{−C≡C−C(=CH$_2$)Ph}(depe)$_2$] (**3**)*

To a solution containing the allenylidene compound *trans*-[FeBr{=C=C=C(Me)Ph}(depe)$_2$][BPh_4] (0.20 g, 0.201 mmol) in CH_2Cl_2 (40 ml) was added NaOMe in a fivefold molar amount (0.054 g, 0.999 mmol). The solution was stirred, at r.t. and under dinitrogen, for 1 h 30 min and its colour changed from violet to dark orange. The solvent was removed in vacuo yielding an orange oily residue. Extraction with Et_2O followed by filtration, concentration and cooling at ca. −20 °C resulted in the precipitation of **3** as a dark orange solid. This precipitate was isolated by filtration and dried in vacuo. Yield: 55% (0.075 g).

(**3**): Anal. Calc. for $C_{30}H_{55}BrFeP_4$: C, 54.0; H, 8.3. Found: C, 54.0; H, 8.0%. IR (KBr, cm^{-1}): ν(C≡C) 2020 (s), ν(C=C) 1552 (m). ^{1}H-NMR (C_6D_6): δ 7.69 (d, $J =$ 7.2 Hz, 2H, H_o from −C≡C−C(=CH$_2$)(C_6H_5)), 7.17 (t, $J = 7.4$ Hz, 1H, H_p from −C≡C−C(=CH$_2$)(C_6H_5)), 7.10 (m, 2H, H_m from −C≡C−C(=CH$_2$)(C_6H_5)), 5.35 (d, $^2J = 2.1$ Hz, 1H, −C≡C−C(=CH_2)Ph), 5.07 (d, $^2J = 1.8$ Hz, 1H, −C≡C−C(=CH_2)Ph), 2.53 (dq, $J_{HP} = 14.8$ and $J = 7.4$ Hz, 4H, $\frac{1}{4}$(CH_3CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 2.41 (dq, $J_{HP} = 15.0$ and $J = 7.5$ Hz, 4H, $\frac{1}{4}$(CH_3-CH_2)$_2$PCH$_2$CH$_2$P(CH_2CH_3)$_2$), 1.80–1.58 (m, 16H, $\frac{1}{2}$

$(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.08 (m, 24H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$). $^{31}P-\{^1H\}$-NMR (C_6D_6): δ 67.4 ppm (s). $^{13}C-\{^1H\}$-NMR (C_6D_6): δ 143.1 (m, C_i from $-C\equiv C-C(=CH_2)(C_6H_5)$), 135.9 (qnt, $J_{CP}=2$ Hz, C_β or C_γ), 135.7 (qnt, $^2J_{CP}=28$ Hz, C_α), 129.0 (s, C_p from $-C\equiv C-C(=CH_2)(C_6H_5)$), 128.6 (s, C_o from $-C\equiv C-C(=CH_2)(C_6H_5)$), 127.6 (s, C_m from $-C\equiv C-C(=CH_2)(C_6H_5)$), 123.0 (m, C_γ or C_β), 111.0 (qnt, $^5J_{CP}=2$ Hz, $-C\equiv C-C(=CH_2)Ph$), 21.7 (qnt, $J_{CP}=11$ Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 21.4 (qnt, $J_{CP}=5$ Hz, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 21.2 (qnt, $J_{CP}=4$ Hz, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 10.9 (qnt, $J_{CP}=2$ Hz, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 10.4 (qnt, $J_{CP}=2$ Hz, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$). ^{13}C-NMR (C_6D_6): δ 143.1 (m), 135.9 (m), 135.7 (qnt), 129.0 (dm, $^1J_{CH}=158$ Hz), 128.6 (dd, $^1J_{CH}=158$, $^2J_{CH}=7$ Hz), 127.6 (dt, $^1J_{CH}=164$, $^2J_{CH}=8$ Hz), 123.0 (m), 111.0 (tqnt, $^1J_{CH}=158$ Hz, $-C\equiv C-C(=CH_2)Ph$), 21.7, 21.4 and 21.2 (tm, $^1J_{CH}=127$ Hz), 10.9 (qm, $^1J_{CH}=127$ Hz), 10.4 (qm, $^1J_{CH}=127$ Hz). FAB^+MS (m/z): 675 $[M]^+$, 596 $[M-Br]^+$, 547 $[M-(-C\equiv C-C(=CH_2)Ph)]^+$, 469 $[M-depe]^+$, 341 $[M-depe-(-C\equiv C-C(=CH_2)Ph)]^+$.

4.2.3. Alkynyl complex trans-[FeBr{−C≡C−C(H)Ph$_2$}(depe)$_2$] (4)

To a stirred CH_2Cl_2 (30 ml) solution of the allenylidene complex *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$ (0.20 g, 0.189 mmol) was added a slight excess of $K[B\{CH(Me)Et\}_3H]$ (208 μl of a 1 M THF solution) and the system was left with stirring at r.t. and under dinitrogen for ca. 30 min. The colour changed from dark blue to dark orange. The solvent was removed in vacuo yielding an oily residue. Extraction with Et_2O followed by filtration, concentration and cooling at ca. −18 °C led to the precipitation of **4** as an orange solid which was separated by filtration and dried in vacuo. Yield: 60% (0.080 g).

(**4**): Anal. Calc. for $C_{35}H_{59}BrFeP_4$: C, 55.0; H, 7.9. Found: C, 55.0; H, 8.5%. IR (KBr, cm^{-1}): ν(C≡C) 2057 (m). ^1H-NMR (C_6D_6): δ 7.23–7.09 (m, 10H, H_o,H_m and H_p from $-C\equiv C-C(H)(C_6H_5)_2$), 4.91 (s,b, 1H, $-C\equiv C-C(H)Ph_2$), 2.36 (dq, $J_{HP}=15.2$, $J_{HH}=7.6$ Hz, 4H, $\frac{1}{4}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 2.26 (dq, $J_{HP}=15.2$, $J_{HH}=7.6$ Hz, 4H, $\frac{1}{4}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.90 (m, 8H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.79 (dq, $J_{HP}=15.2$, $J_{HH}=7.6$ Hz, 4H, $\frac{1}{4}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.64 (dq, $J_{HP}=14.8$, $J_{HH}=7.4$ Hz, 4H, $\frac{1}{4}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.20 (m, 12H, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.13 (m, 12H, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$). $^{31}P-\{^1H\}$-NMR (C_6D_6): δ 70.3 ppm (s). $^{13}C-\{^1H\}$-NMR: δ 146.5 (s,b, C_i from $-C\equiv C-C(H)(C_6H_5)_2$), 128.2 (s, C_o or C_m from $-C\equiv C-C(H)(C_6H_5)_2$), 128.2 (s, C_m or C_o from $-C\equiv C-C(H)(C_6H_5)_2$), 125.7 (s, C_p from $-C\equiv C-C(H)(C_6H_5)_2$), 118.2 (m, C_β), 113.5 (qnt, $^2J_{CP}=28$ Hz, C_α), 47.7 (m, C_γ), 20.9 (qnt, $J_{CP}=12$ Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 20.4–20.0 (m, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 10.2 (s, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 9.7 (s, $\frac{1}{2}(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$). ^{13}C-NMR: δ 146.5 (m), 128.2 (d,b, $^1J_{CH}=159$ Hz), 128.2 (d,b, $^1J_{CH}=159$ Hz), 125.7 (dt, $^1J_{CH}=160$, $^2J_{CH}=6$ Hz), 118.2 (m), 113.5 (qnt), 47.7 (dm, $^1J_{CH}=127$ Hz), 20.9 (tm, $^1J_{CH}=132$ Hz), 20.4–20.0 (m), 10.2 (q, $^1J_{CH}=126$ Hz), 9.7 (q, $^1J_{CH}=126$ Hz). FAB^+MS (m/z): 738 $[M]^+$, 737 $[M-H]^+$, 659 $[M-Br]^+$, 547 $[M-(-C\equiv C-C(H)Ph_2)]^+$, 532 $[M-depe]^+$, 341 $[M-depe-(-C\equiv C-C(H)Ph_2)]^+$.

4.2.4. Reaction of trans-[FeBr{−C≡C−C(=CH$_2$)Ph}(depe)$_2$] (3) with HBF$_4$

To a solution of the enynyl complex *trans*-$[FeBr\{-C\equiv C-C(=CH_2)Ph\}(depe)_2]$ (**3**) (0.060 g, 0.089 mmol) in CH_2Cl_2 (20 ml) was added a slight excess (1.2:1) of HBF_4 (0.107 mmol, ca. 15 μl of a 54% solution in Et_2O). The colour of the solution changed immediately from dark orange to violet. It was concentrated and addition of Et_2O (ca. 10 cm^3) led to the precipitation of the allenylidene complex **1**, although with $[BF_4]^-$ as the counterion, as a violet solid which was isolated by filtration and dried in vacuo. IR, ^1H and $^{31}P-\{^1H\}$-NMR (spectra identical to those of **1**, except the features concerning the different counterions) confirmed the formulation.

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