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Stepwise reduction of a phosphaalkyne $P\equiv C$ bond to a phosphaalkene and a phosphine at the $FeH(dppe)_2$ centre. Crystal and molecular structure of the η^1-co-ordinated phosphaalkyne complex *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BPh_4]$

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Treatment of *trans*-$[FeH(Cl)(dppe)_2]$ **1** (dppe = $Ph_2PCH_2CH_2PPh_2$) in thf with $P\equiv CBu^t$, in the presence of $Tl[BF_4]$, gave the η^1-co-ordinated phosphaalkyne complex *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BF_4]$ **2a** which forms *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BPh_4]$ **2b** on reaction with $Na[BPh_4]$ or, upon reaction with HBF_4 in CH_2Cl_2, converts into the η^1-fluorophosphaalkene and the difluorophosphine complexes *trans*-$[FeH(\eta^1\text{-}PF{=}CHBu^t)(dppe)_2]A$ (A = BF_4 **3a** or $FeCl_2F_2$ **3b**) and *trans*-$[FeH(PF_2CH_2Bu^t)(dppe)_2][BF_4]$ **4**, respectively. The phosphine complex *trans*-$[FeH(PH_3)(dppe)_2][BF_4]$ **5a** was also formed in a reaction of **1** with $P\equiv CBu^t$ in the presence of $Tl[BF_4]$ and $[NH_4][BF_4]$ and converts into *trans*-$[FeH(PH_3)(dppe)_2][BPh_4]$ **5b** upon treatment with $Na[BPh_4]$. A single crystal structural study of **2b** showed that a shortening of the $P\equiv C$ triple bond from 1.542(2) to 1.512(5) Å results upon η^1 co-ordination of the phosphaalkyne, which represents the shortest P–C bond so far reported. The electrochemical P_L ligand parameter has been estimated for η^1-$P\equiv CBu^t$ and its net electron donor/acceptor ability is compared with those of related unsaturated ligands.

Introduction

Phosphaalkynes, $P\equiv CR$, have played an important role in the currently expanding area of main group element compounds containing multiple bonds.[1,2] They exhibit a rich inorganic and organometallic chemistry utilising both the triple bond and the phosphorus lone-pair electrons.[1,2] Particularly interesting is the observation[3] that, in spite of the presence of the latter, protonation occurs exclusively at the carbon centre, in accord with the known excess of electron density on the alkyne carbon.[4]

The co-ordination chemistry of phosphaalkynes has been dominated by η^2 ('side-on') interaction with transition metals in accord with the nature of the HOMO[1,2,5] which is of the $P\equiv C$ π type. Nevertheless, we showed previously[6–8] that certain complexes containing a narrow co-ordination site suitable only for ligation of linear molecules do bind phosphaalkynes in an η^1-'end-on' fashion. To date only one such complex has been structurally characterised, namely the bis(phosphaalkyne) molybdenum(0) complex *trans*-$[Mo(\eta^1\text{-}P\equiv CAd)_2(Et_2PCH_2CH_2PEt_2)_2]$ (Ad = adamantyl).[6] The related complexes of Re^I and Fe^{II}, *trans*-$[ReCl(\eta^1\text{-}P\equiv CBu^t)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[7] and *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BF_4]$,[8] are also known but they have not been structurally characterised because the $P\equiv C$ bond is activated. The former readily reacts with water to form the novel η^1-phosphinidene oxide complex *trans*-$[ReCl\{P(O)CH_2Bu^t\}(dppe)_2]$[7] and the latter affords the η^1-fluorophosphaalkene complex *trans*-$[FeH(\eta^1\text{-}PF{=}CHBu^t)(dppe)_2][FeCl_2F_2]$ by HF addition (presumably deriving from the BF_4^- anion) across the unco-ordinated $P\equiv C$ bond,[8] as we have described in a preliminary way.

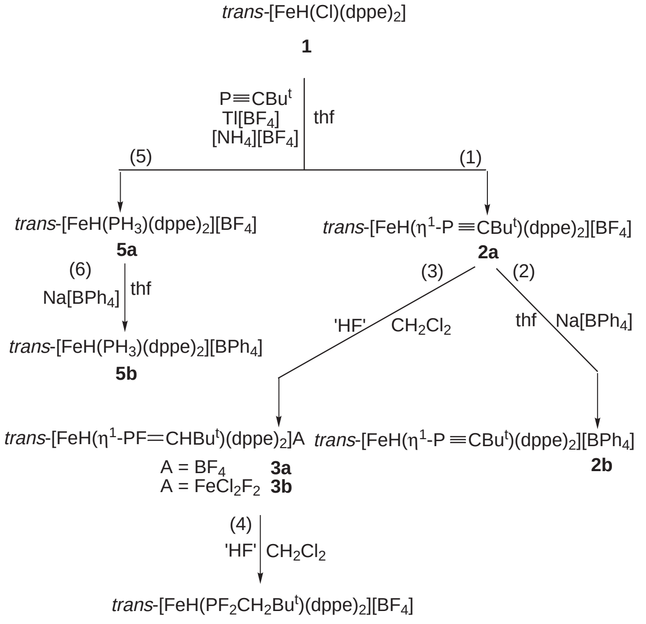
In contrast to the known elongation of the $P\equiv C$ triple bond observed in several η^2-transition metal phosphaalkyne complexes[1,2,5] to typical P=C double-bond lengths (*ca.* 1.67 Å), the $P\equiv C$ bond distance in the above zerovalent molybdenum complex [1.520(12) Å] was found to be comparable with that determined for $P\equiv CBu^t$ [1.542(2) Å],[4,9] within experimental error. It was therefore of special interest to see if η^1 co-ordination of a phosphaalkyne to a metal in a higher oxidation state might lead to further shortening of the $P\equiv C$ triple bond in view of the anticipated weaker effect of any d_π–π^* orbital interaction. We now report the preparation of the first stable η^1-phosphaalkyne iron(II) complex, *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BPh_4]$, and a single crystal X-ray diffraction study which establishes that η^1 co-ordination does indeed lead to an unprecedented further shortening of the $P\equiv C$ bond.

Moreover we describe in detail the further rare conversion of the η^1-phosphaalkyne ligand into a phosphaalkene (the η^1-fluorophosphaalkene $PF{=}CHBu^t$) and a derived fluorophosphine ($PF_2CH_2Bu^t$), as well as the first example of reduction of the phosphaalkyne to PH_3. A related transformation of a phosphaalkyne (whose complex, however, was not isolated) into a co-ordinated fluorophosphine ($PHFCH_2Bu^t$) has recently been achieved by others[10] in reactions of $P\equiv CBu^t$ with the ruthenium hydride complex $[RuH(Cl)(CO)(PPh_3)_3]$, and this prompted us to report our results in the iron system.

Results and discussion

η^1-Co-ordinated phosphaalkyne complexes

Reaction of the phosphaalkyne $P\equiv CBu^t$ with *trans*-$[FeH(Cl)(dppe)_2]$ **1** in thf, in the presence of $Tl[BF_4]$, yielded *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BF_4]$ **2a** [reaction (1), Scheme 1] which was isolated as a yellow powder (contaminated with the TlCl and $Tl[BF_4]$ salts). Complex **2a** was then treated, in thf, with $Na[BPh_4]$ to give *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BPh_4]$ **2b** which was isolated as a yellow crystalline solid (*ca.* 90%



Scheme 1

yield) upon recrystallisation from CH_2Cl_2–MeOH [reaction (2), Scheme 1].

In the ^{13}C-{^1H} NMR spectrum (CD_2Cl_2) of complex **2b** the P≡*C*Bu^t and P≡C*C*Me$_3$ resonances occur as doublets at δ 183.38 [J(CP) 140] and 39.28 [^2J(CP) 8 Hz], respectively. The former chemical shift is comparable with that of the unco-ordinated phosphaalkyne [δ 184.3 (C_6D_6)] and does not show the downfield shift typical of the η^2-(2e)-bonded phosphaalkyne, *e.g.* in [Pt(η^2-P≡CBu^t)(PPh$_3$)$_2$] [δ 242.0–239.5 (m)(C_6D_6)]^5, and in the recently described η^2-(4e)-bonded phosphaalkyne complex [Mo(η^5-C$_5$H$_5$)(η^2-P≡*C*Bu^t){η^2-(MeO)$_2$POBF$_2$OP(OMe)$_2$}] [δ 328.5, dt, J(PC) 114, ^2J(PC) 6.6 Hz].[11]

The ^{31}P-{^1H} NMR spectrum of complex **2a** shows a typical [A_4X] spin system consisting of a quintet [δ(P^X) −154 relative to P(OMe)$_3$, ^2J(P^{A}P^X) 36 Hz, P≡CBu^t] and a doublet, with the same coupling constant, of four-fold intensity [δ(P^A) −62.3, 2 dppe]. In the ^1H-undecoupled ^{31}P NMR spectrum the phosphaalkyne resonance splits into a doublet of quintets [^2J(P^{X}H)$_{trans}$ 54, ^2J(P^{A}P^X) 36 Hz] providing for the first time a value for the coupling constant between an sp-hybridised phosphorus and a *trans*-hydride ligand. Surprisingly this value was found to be only 8 Hz higher than that for the phosphorus (dppe)–hydride(*cis*) coupling [^2J(PH)$_{cis}$ 46 Hz][12] in *trans*-[FeH(CNMe)(dppe)$_2$][BF$_4$].

In the ^1H NMR spectrum of complex **2a** or **2b** the hydride resonance is a sextet [overlapping doublet of quintets, ^2J(HP^A) ≈ ^2J(HP^X) 53 Hz] at δ −12.28.

The molecular structure of complex **2b** has been obtained by a single crystal X-ray diffraction study and is depicted in Fig. 1. Selected bond lengths and angles are listed in Table 1. It exhibits the expected octahedral-type co-ordination around the Fe^{II}, with the phosphaalkyne being *trans* to the hydride ligand. Of special interest is the observation that the P(1)–C(1) distance [1.512(5) Å] is the shortest yet recorded, indicating for the first time that η^1-ligated phosphaalkynes behave similarly to phosphaalkenes for which η^1 co-ordination is known[13] to result in a shorter P=C distance whereas significant lengthening of the P=C bond occurs in η^2-bonded complexes.

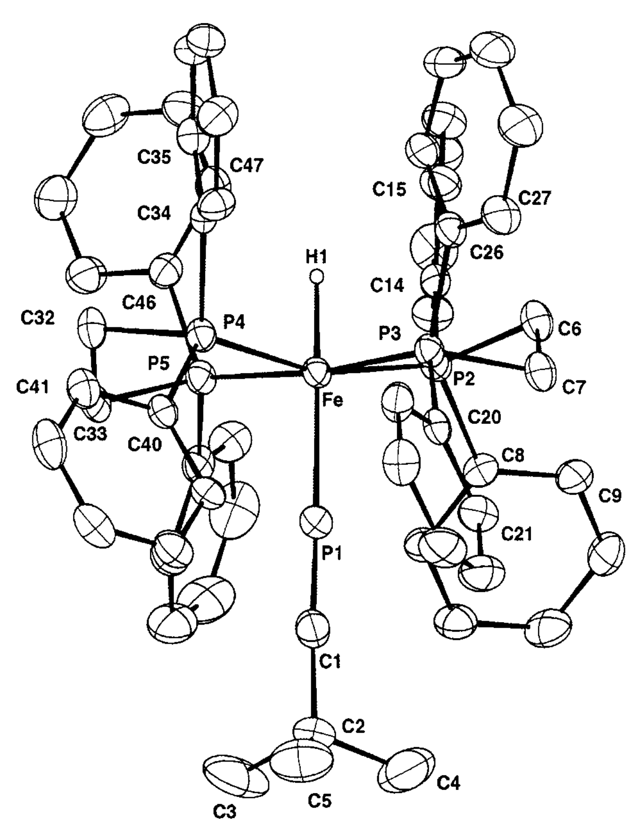


Fig. 1 Molecular structure of the complex cation of *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BPh$_4$] **2b**.

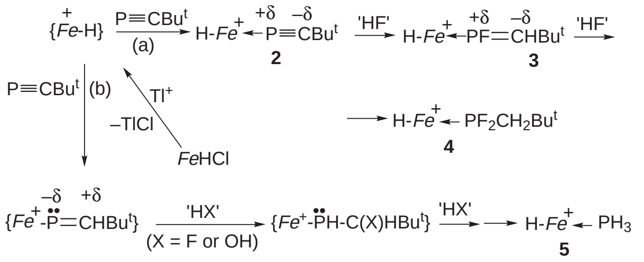
Table 1 Selected bond lengths (Å) and angles (°) for complex **2b**.

Fe–H(1)	1.37(4)	Fe–P(1)	2.148(2)
Fe–P(2)	2.286(2)	Fe–P(3)	2.274(2)
Fe–P(4)	2.275(2)	Fe–P(5)	2.267(2)
P(1)–C(1)	1.512(5)	C(1)–C(2)	1.482(7)
H(1)–Fe–P(1)	176(2)	H(1)–Fe–P(5)	85(2)
P(1)–Fe–P(5)	92.25(6)	H(1)–Fe–P(3)	90(2)
P(1)–Fe–P(3)	93.55(6)	P(5)–Fe–P(3)	173.88(6)
H(1)–Fe–P(4)	83(2)	P(1)–Fe–P(4)	99.01(6)
P(5)–Fe–P(4)	84.05(5)	P(3)–Fe–P(4)	93.11(5)
H(1)–Fe–P(2)	81(2)	P(1)–Fe–P(2)	97.09(6)
P(5)–Fe–P(2)	96.48(6)	P(3)–Fe–P(2)	84.74(5)
P(4)–Fe–P(2)	163.86(6)	C(1)–P(1)–Fe	177.9(2)

The shortening of the P≡C bond in complex **2b** can be rationalised by considering complexes containing the structurally related unsaturated isocyanides,[14] carbonyl,[14] organonitriles or dinitrogen ligands,[15] where the electron lone pair orbital involved in σ co-ordination to the metal has some antibonding character for the unsaturated bond. Theoretical studies at the MP2/6-311+G** level[4] on protonation of P≡CMe established that no linear P-protonated ion could be found but instead an unsymmetrical hydrogen-bridged structure is favoured. Related theoretical studies, currently underway, on the effect of adding H$^+$, Li$^+$ or Fe^{2+} ions to PC≡H will be the subject of a separate publication.[16]

The Fe–P (phosphaalkyne) distance, Fe–P(1) 2.148(2) Å, can be compared to that of the related Fe–P (phosphaalkene) complex *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][FeCl$_2$F$_2$] (see below), 2.112(12) Å,[8] both being shorter than the Fe–P (dppe) bond length [average 2.276(2) Å] presumably reflecting the smaller sp and sp^2 radii of phosphorus. The Fe–H(1) distance, 1.37(4) Å, is comparable with that of *trans*-[FeH(N$_2$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$][BPh$_4$], 1.32(2) Å,[17] and [FeH(N$_2$)(dppe)$_2$]Br, 1.53(9) Å,[18] but shorter than the expected value, 1.53 Å, based on the sum of the iron and hydrogen covalent radii.

Complex **2a** undergoes a single electron non-reversible anodic wave at $E^{ox}_{p/2} \approx 1.13$ V *vs.* SCE (measured at 200 mV s^{-1}), as evidenced by cyclic voltammetry at a platinum-wire electrode, in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$, which, by digital simulation, is shown to involve a quasi-reversible redox process[19] ($k_{het} = 5 \times 10^{-5}$ cm s^{-1}), at E° = 1.00 V. This value approaches that reported (1.04 V)[20] for the analogous



Scheme 2 (a) Nucleophilic attack route at the phosphaalkyne P. (b) Postulated phosphaalkyne insertion (hydrometallation) followed by electrophilic attack route. *Fe* = Fe(dppe)$_2$.

carbonyl complex *trans*-[FeH(CO)(dppe)$_2$]$^+$, thus indicating that the η^1-phosphaalkyne ligand behaves as a *net* π-electron acceptor minus σ-electron donor comparable to CO. Its electrochemical P_L value can be estimated as *ca.* −0.04 V from the known[20] eqn. (1), in which E_s is the electron-richness of the

$$E^{ox} = E_s + \beta P_L \qquad (1)$$

metal site {FeH(dppe)$_2$}$^+$ (*i.e.* the oxidation potential of its carbonyl complex, 1.04 V) and β the polarisability (1.0) of this site.[20] Since the η^1-phosphaalkyne is not believed to be a strong π acceptor (see above), in contrast to CO (with $P_L = 0$) which is effective in both π acceptance and σ donation, the similarity of the P_L values for these two ligands indicates that the former behaves neither as a strong σ donor nor as an efficient π acceptor. In comparison with acetonitrile ($P_L = -0.58$ V)[20] or isocyanides (*e.g.* CNMe with $P_L = -0.43$ V),[20] η^1-P≡CBu^t is a weaker net electron donor (stronger net electron acceptor).

Phosphaalkene and phosphine complexes

A CH$_2$Cl$_2$ solution of *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BF$_4$] **2a** was treated with HBF$_4$ and the reaction yielded a mixture of the η^1-fluorophosphaalkene complex *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][BF$_4$] **3a** and the difluorophosphine complex *trans*-[FeH(PF$_2$CH$_2$Bu^t)(dppe)$_2$][BF$_4$] **4** [reactions (3) and (4), Scheme 1], isolated as orangish yellow crystals and thin yellow needles, respectively. These products, formed upon a sequential addition of two HF groups across the P≡C bond of the η^1-phosphaalkyne ligand [Scheme 2(a)], have been characterised mainly by NMR spectroscopy and, in the case of **3a**, by a single X-ray diffraction study[8] of the analogous *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][FeCl$_2$F$_2$] **3b** which was isolated as red crystals upon prolonged attempted recrystallization of **2a**, from CH$_2$Cl$_2$–Et$_2$O, in the presence of [NH$_4$][BF$_4$]–Tl[BF$_4$]. As observed for the η^1-phosphaalkyne ligand in **2b**, the P=C bond length in the η^1-phosphaalkene complex **3b** [1.66(4) Å] is shorter than that known[21] for a free phosphaalkene, in contrast with the expected elongation of such a bond upon η^2 co-ordination to a metal due to π-back donation from a metal d filled orbital to a π* orbital of the η^2-P=C (phosphaalkene) or η^2-P≡C (phosphaalkyne) bond. The bond lengths and angles within the phosphaalkene ligand of **3b** are comparable to those reported[22] for *trans*-[RhCl{η^1-PF=C(SiMe$_3$)$_2$}(PPh$_3$)$_2$], but the Fe–P (fluorophosphaalkene) bond distance, 2.112(12) Å, in **3b** is shorter than those found for the tetracarbonyliron complexes [Fe(CO)$_4${η^1-PN(SiMe$_3$)$_2$=C(SiMe$_3$)$_2$}][23] and [Fe(CO)$_4${η^1-PR=CPh(SiMe$_3$)}][24] (R = 2,4,6-tri-*tert*-butylphenyl), 2.208(2) and 2.263(1) Å, respectively.

The ^{31}P-{^{1}H} NMR spectrum of complex **3a** displays a pattern of lines typical of an [A$_4$XY] spin system (Y = F nucleus) consisting of a doublet of quintets centred at δ(P^X) 177.6 relative to P(OMe)$_3$ [1P, ^1J(P^{X}F) 985, ^2J(P^{X}P^A) 38 Hz, PF=CHBu^t] and a doublet at δ(P^A) −61.7 [4P, ^2J(P^{X}P^A) 38 Hz, dppe]. The considerable downfield shift of the co-ordinated phosphaalkene P in complex **3a** with respect to the phosphaalkyne P in **2** conceivably reflects the change in hybridisation of the phosphorus atom from an sp to an sp^2 mode. Although the ^1J(PF) value in complex **3a** is higher than those observed[25] in the η^2-fluorophosphaalkene complexes [Ni(PBu$_3$)$_2${η^2-PF=C(SiMe$_3$)$_2$}] [^1J(PF) 872 Hz] and [Pt(PPh$_3$)$_2${η^2-PF=C(SiMe$_3$)$_2$}] [^1J(PF) 907 Hz], it is somewhat lower than the similar coupling found[22] in *trans*-[RhCl{η^1-PF=C(SiMe$_3$)$_2$}(PPh$_3$)$_2$] [^1J(PF) 1127 Hz]. The value ^1J(PF) is confirmed by the ^{19}F NMR spectrum of **3a** in which the fluorine nucleus (Y) resonates as a doublet of doublets due to coupling to *P*F=CHBu^t and to the *trans*-hydride [δ_F −55.0 relative to CFCl$_3$, ^1J(P^{X}F) 985, ^3J(FH) 15 Hz]. The ^{1}H NMR spectrum reveals the hydride proton resonance as a doublet [^3J(HF) *ca.* 10 Hz] of sextets [^2J(HP^X) ≈ ^2J(HP^A) 53 Hz] centred at δ −9.4.

In the ^{31}P-{^{1}H} NMR spectrum ([A$_4$XY$_2$] spin system) of the difluorophosphine complex **4** the *P*F$_2$CH$_2$Bu^t resonance appears as a triplet [^1J(P^{X}F) 1067 Hz] of quintets [^2J(P^{X}P^A) 34 Hz] at δ 137.5. The ^1J(P^{X}F) value, which has been confirmed by ^{19}F NMR, is significantly higher than the corresponding one [^1J(PF) 844 Hz] reported[10] for [Ru(PHFCH$_2$Bu^t)Cl(CO)(CNC$_6$H$_3$Me$_2$-2,6)(PPh$_3$)$_2$][BF$_4$]. The presence of two electronegative fluorine atoms in **4** may be a contributing factor.

In addition to the η^1-bonded phosphaalkyne complex **2a**, another unexpected product, **5a**, was formed in the reaction of *trans*-[FeH(Cl)(dppe)$_2$] with Tl[BF$_4$]–[NH$_4$][BF$_4$] in thf. It was isolated upon working up (see Experimental section) of the mother-liquor separated from **2a**, as a yellow microcrystalline solid, and is formulated as the phosphine complex *trans*-[FeH(PH$_3$)(dppe)$_2$][BF$_4$] **5a** on the basis of NMR spectroscopic evidence. On treatment with Na[BPh$_4$], in MeOH, **5a** converts into *trans*-[FeH(PH$_3$)(dppe)$_2$][BPh$_4$] **5b** [reaction (6), Scheme 1]. The ^{31}P-{^{1}H} NMR spectrum shows a quintet [J(P^{A}P^X) 29 Hz] at δ(P^X) −232.9 which, in the ^{1}H-undecoupled spectrum, transforms into a quartet [with a large constant, ^1J(P^{X}H) 320 Hz] of broad sextets, being assigned to co-ordinated PH$_3$. In the ^{1}H NMR spectrum the PH$_3$ protons appear as the expected doublet [^1J(HP^X) 320 Hz] of quintets [^3J(HP^A) 5 Hz] centred at δ 3.2.

The reaction between P≡CBu^t and the starting hydride-chloride complex **1** in thf, in the presence of Tl[BF$_4$]–[NH$_4$][BF$_4$], was monitored by ^{31}P-{^{1}H} and ^{1}H NMR which showed the initial formation of only the η^1-phosphaalkyne **2a** and the PH$_3$ **5a** complexes. The former was the major product and did not convert into the latter. Moreover, no reaction was found between **2a** and hydrogen gas (bubbled through the thf solution) or Li[BEt$_3$H], and attack by HBF$_4$ led to complexes **3** and **4** as discussed above. The formation of the PH$_3$ complex **5a** is intriguing and appears to follow a distinct pathway to the one that leads to the η^1-P≡CBu^t complex **2a**. The mechanism conceivably involves the formation of the postulated phosphaalkenyl *Fe*←$\ddot{\text{P}}$=CHBu^t [*Fe* = Fe(dppe)$_2$] intermediate containing a nucleophilic phosphorus centre. It could undergo subsequent protonation at P and nucleophilic attack at C (by 'HX' = 'HF' or H$_2$O) to generate *Fe*–$\ddot{\text{P}}$H–C(X)HBu^t which, upon β-H elimination, rearrangement (in the case of HX = H$_2$O, involving conversion of the enol *Fe*–$\ddot{\text{P}}$H-C(OH)Bu^t into the keto form H–*Fe*←PH$_2$COBu^t) and further 'HX' addition would lead to the final hydrido PH$_3$ complex **5a** [Scheme 2(b)]. The corresponding organic products however were not detected. Such a phosphaalkenyl intermediate would be formed by hydrometallation of P≡CBu^t, a type of reaction known[10] for [RuH(Cl)(CO)(PPh$_3$)$_3$] which gives [Ru(η^1-P=CHBu^t)Cl(CO)(PPh$_3$)$_2$(CNR)] (R = C$_6$H$_3$Me$_2$-2,6) on treatment with CNR, and, more recently, also observed by us[26] in the addition of [ZrH(Cl)(η^5-C$_5$H$_5$)$_2$] to the η^2-ligated phosphaalkyne in [Pt(η^2-P≡CBu^t)(dppe)]. These observations are closely related to the insertion reactions we have previously observed[27] for an alk-1-yne, HC≡CCO$_2$Me, into the Fe–H bond of *trans*-[FeH(Cl)(dppe)$_2$] **1** to give a vinyl product, by using similar experimental conditions to those in this work. A precedent for the conversion of a phosphaalkenyl into a phosphine ligand has also been reported[10] for the above phosphaalkenylruthenium complex which is converted into the fluorophosphine compound [Ru(PHFCH$_2$Bu^t)Cl(CO)(PPh$_3$)$_2$(CNR)]$^+$ by protonation at the phosphaalkenyl phosphorus followed by nucleophilic addition of 'HF' (K[HF$_2$] or [NBu$^n_4$]F).

Experimental

All the manipulations and reactions were carried out in the absence of air using standard inert gas flow and vacuum techniques. Solvents were purified by standard procedures; *trans*-[FeH(Cl)(dppe)$_2$][28] and P≡CBu^t[29] were prepared by published methods, and HBF$_4$·Et$_2$O (Aldrich) was commercially available.

Infrared measurements were carried out on a Perkin-Elmer 683 spectrophotometer; ^{1}H, ^{31}P, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Unity 300 or a Bruker 360 MHz spectrometer.

The electrochemical experiments were performed on an EG & G PAR 173 potentiostat and an EG & G PARC 175 universal programmer. A two-compartment three-electrode cell, with a platinum-wire working electrode, probed by a Luggin capillary connected to a silver wire pseudo-reference electrode and a platinum auxiliary electrode, was employed. The potentials were measured in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$ by using the ferrocene–ferrocenium redox couple ($E^{\text{ox}}_{\frac{1}{2}} = 0.545$ V *vs.* SCE) as internal reference. The method of digital simulation has been described[30] previously. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sxt = sextet, m = complex multiplet, br = broad, dd = doublet of doublets, dqnt = doublet of quintets, dsxt = doublet of sextets, tqnt = triplet of quintets.

Preparations

***trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BF$_4$] 2a and *trans*-[FeH(PH$_3$)(dppe)$_2$]A (A = BF$_4$ 5a or BPh$_4$ 5b).** A thf (15 cm^3) solution of *trans*-[FeH(Cl)(dppe)$_2$] (330 mg, 0.371 mmol) was treated with a 1 : 1 mixture of P≡CBu^t (0.751 mmol) plus (Me$_3$Si)$_2$O and Tl[BF$_4$] (75 mg, 0.475 mmol) containing a smaller amount of [NH$_4$][BF$_4$]. The mixture changed from dark red to yellow and was stirred for *ca.* 24 h. The yellow solid which precipitated was then filtered off, washed with thf and dried *in vacuo*. Extraction with CH$_2$Cl$_2$ immediately followed by filtration, addition of Et$_2$O and cooling at *ca.* −15 °C led to the formation of yellowish orange crystals of complex **2a** which were filtered off and dried *in vacuo* (*ca.* 65% yield). Prolonged recrystallisation of crude **2a** resulted in its conversion into other species (see below), but simple replacement of the counter ion [BF$_4$]$^-$ to give **2b** occurs upon treatment with Na[BPh$_4$] in thf–MeOH.

The mother-liquor in the above reaction of *trans*-[FeH(Cl)(dppe)$_2$] with P≡CBu^t, separated from the crude complex **2a**, was taken to dryness and extraction with CH$_2$Cl$_2$ (5 cm^3) followed by filtration and addition of Et$_2$O (8 cm^3) resulted in the formation of an oily precipitate. The solution was filtered and, on addition of Et$_2$O on the following day, *trans*-[FeH(PH$_3$)(dppe)$_2$][BF$_4$] **5a** precipitated as a yellow solid which was washed with Et$_2$O and dried *in vacuo* (*ca.* 10% yield).

Complex **2a** (Found: C, 65.2; H, 5.6. C$_{57}$H$_{58}$BF$_4$FeP$_5$ requires C, 65.8; H, 5.6%): ^{1}H NMR (CD$_2$Cl$_2$) δ -12.28 [1 H, sxt, ^2J(HP^A) ≈ ^2J(HP^X) 53 Hz, FeH], 1.24 (9 H, s, Bu^t), 2.1–2.6 (8 H, m, CH$_2$ of dppe) and 7.1–7.4 (40 H, m, Ph); ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$) δ -154.0 [1P, qnt, ^2J(P^{A}P^X) 36, P≡CBu^t] and -62.3 [4P, d, ^2J(P^{A}P^X) 36 Hz, dppe]; ^{31}P NMR (CD$_2$Cl$_2$) δ -154.0 [1P, dqnt, ^2J(P^{X}H) 54, ^2J(P^{A}P^X) 36, P≡CBu^t] and -62.3 [4P, t, ^2J(P^{A}H) *ca.* 44 Hz, dppe].

Complex **5a** (Found: C, 53.4; H, 5.0. C$_{52}$H$_{52}$BF$_4$FeP$_5$·3CH$_2$Cl$_2$ requires C, 53.7; H, 4.4%); ^{1}H NMR (CD$_2$Cl$_2$) δ -11.0 [1 H, dqnt, ^2J(HP^X) 48, ^2J(HP^A) 19, FeH], 2.1–2.5 (8 H, m, CH$_2$ of dppe), 3.20 [3 H, dqnt, ^1J(HP^X) 320, ^3J(HP^A) 5 Hz, PH$_3$] and 6.5–7.6 (40 H, m, Ph); ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$) δ -232.9 [1P, qnt, ^2J(P^{X}P^A) 29, PH$_3$] and -56.9 [4P, d, ^2J(P^{A}P^X) 29 Hz, dppe]; ^{31}P NMR (CD$_2$Cl$_2$) δ -232.9 [1P, qsxt, br, ^1J(P^{X}H) 320 Hz, PH$_3$] and -56.9 (4P, t, br, dppe).

Complex **5b**: identical ^{1}H and ^{31}P NMR spectra to those of **5a** (with the additional ^{1}H resonances due to BPh$_4^-$).

***trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BPh$_4$] 2b.** To a mixture of complex **2a** (0.116 g, 0.11 mmol) with Na[BPh$_4$] (0.096 g, 0.28 mmol), was added thf (50 cm^3), the system stirred for 24 h and then taken to dryness *in vacuo*. The yellow residue was extracted by CH$_2$Cl$_2$ (10 cm^3) and the solution filtered. The filtrate was reduced in volume to *ca.* 2 cm^3 and MeOH (20 cm^3) was carefully placed on top so that two liquid layers were formed. The system stood overnight and yellow crystals of **2b** deposited. The mother-liquor was decanted and the crystals dried *in vacuo* (0.13 g, 91% yield). One of them was analysed by X-ray diffraction. Complex **2b** presents ^{1}H and ^{31}P NMR spectra identical to those of **2a** (with the additional ^{1}H resonances due to the BPh$_4^-$ counter ion). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 183.38 [d, J(CP) 140, P≡*C*Bu^t], 164.43 [1 : 1 : 1 : 1 q, J(BC) 49, BC], 135.13–120.90 (m, Ph), 39.28 [d, ^2J(PC) 8, P≡C*C*(CH$_3$)$_3$], 32.49 [qnt, virtual J(CP) 12 Hz, CH$_2$ of dppe], 30.69 (s), 30.55 (s) and 29.87 (s) [P≡CC(*C*H$_3$)$_3$].

***trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][BF$_4$] 3a and *trans*-[FeH(PF$_2$CH$_2$Bu^t)(dppe)$_2$][BF$_4$] 4.** Unrecrystallised *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BF$_4$] **2a** (192 mg, *ca.* 0.18 mmol) was dissolved in CH$_2$Cl$_2$ (30 cm^3) and the solution filtered to eliminate traces of contaminant thallium salts. A 1 : 100 Et$_2$O diluted solution (3.5 cm^3) of commercial [Et$_2$OH][BF$_4$] (85%, d = 1.15 g cm^{-3}) (0.213 mmol of acid) was then added dropwise, with stirring, under argon. After *ca.* 24 h the solution was concentrated *in vacuo* to *ca.* 10 cm^3 and Et$_2$O was added. Complexes **3a** and **4** precipitated as orangish yellow parallelepipedic crystals (*ca.* 40% yield) and as agglomerates of thin yellow needles (*ca.* 25% yield), respectively. They were filtered off, washed with Et$_2$O, dried *in vacuo* and separated mechanically.

Complex **3a** (Found: C, 57.8; H, 5.8. C$_{57}$H$_{58}$BF$_5$P$_5$·2CH$_2$Cl$_2$ requires C, 57.5; H, 5.1%): ^{1}H NMR (CD$_2$Cl$_2$) δ -9.4 [1 H, dsxt, ^2J(HP^A) ≈ ^2J(*H*P^X) 53, ^3J(HF) 12 Hz, FeH], 2.0–2.5 (8 H, m, CH$_2$ of dppe) and 6.5–7.5 (40 H, m, Ph); ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$) δ -61.7 [4P, d, ^2J(P^{A}P^X) 38, dppe] and 177.6 [1P, dqnt, ^1J(P^{X}F) 985, ^2J(P^{X}P^A) 38 Hz, PF]; ^{19}F NMR (CD$_2$Cl$_2$) δ -149.5 (4F, s, BF$_4$) and -55.0 [1F, dd, ^1J(FP) 985, ^3J(FH) 15 Hz, PF=CHBu^t].

Complex **4**: ^{1}H NMR (CD$_2$Cl$_2$) δ -10.4 (1 H, m, FeH), 2.0–2.5 (8 H, m, CH$_2$ of dppe), 2.85 (2 H, m, PC*H*$_2$Bu^t) and 6.5–7.5 (40 H, m, Ph); ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$) δ -63.3 [4P, d, ^2J(P^{A}P^X) 34, dppe] and 137.5 [1P, tqnt, ^1J(P^{X}F) 1067, ^2J(P^{X}P^A) 34 Hz, PF$_2$CH$_2$Bu^t]; ^{19}F NMR (CD$_2$Cl$_2$) δ -149.5 (4F, s, BF$_4$) and -39.3 [2F, d, ^1J(FP) 1067 Hz, PF$_2$CH$_2$Bu^t].

***trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][FeCl$_2$F$_2$] 3b.** This complex was obtained upon prolonged attempted recrystallisation, from CH$_2$Cl$_2$–Et$_2$O, of *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BF$_4$] **2a** contaminated with Tl[BF$_4$]–[NH$_4$][BF$_4$]. Crude **2a** (0.208 g, *ca.* 0.183 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) and the remaining solid was filtered off. Concentration of the filtered solution followed by addition of Et$_2$O led to the formation of a yellow solid of the recrystallised starting complex **2a**. The solution was filtered again, and the yellow powder which precipitated in very low amount was isolated by filtration (3 d after the beginning of the recrystallisation of crude **2a**), washed with CH$_2$Cl$_2$–Et$_2$O (1 : 3) and dried *in vacuo*; this product was shown to be the phosphine complex **5a** which was contaminating the crude sample of **2a**.

The filtered solution was again concentrated and Et_2O added until a precipitate started to be formed. It was filtered and a solid precipitated slowly as a mixture of yellow and red crystals which were filtered off (6 d after the beginning of the recrystallisation of crude **2a**), washed with CH_2Cl_2–Et_2O (1 : 3) and dried *in vacuo* (*ca.* 15% yield). As shown by an X-ray analysis, the red crystals were of complex **3b**.

X-Ray crystallography

Crystal data. $C_{81}H_{78}BFeP_5$ **2b**, $M = 1272.9$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.186(3)$, $b = 17.812(4)$, $c = 34.237(9)$ Å, $\beta = 98.86(2)°$, $U = 6740(3)$ Å^3, $Z = 4$, $D_c = 1.25$ Mg m^{-3}, crystal dimensions 0.3 × 0.3 × 0.2 mm, $F(000) = 2680$, Mo-Kα radiation, $\lambda = 0.71073$ Å, μ(Mo-Kα) 0.39 mm^{-1}. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer in the ω–2θ mode; of the total 9876 reflections measured, 6224 were considered observed, final indices $[I > 2\sigma(I)]$ $R1 = 0.053$, $wR2 = 0.102$. The structure was solved by direct methods using SHELXS 86[31] and refined by full-matrix least squares using SHELXL 93.[32] All non-hydrogen atoms were anisotropically refined except for the hydride H atom which was located on a difference map and freely refined isotropic.

CCDC reference number 186/1094.

See http://www.rsc.org/suppdata/dt/1998/3319/ for crystallographic files in .cif format.

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