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Stepwise reduction of a phosphaalkyne P≡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(η^1-P≡CBu^t)(dppe)$_2$][BPh$_4$]

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Treatment of *trans*-[FeH(Cl)(dppe)$_2$] **1** (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) in thf with P≡CBu^t, in the presence of Tl[BF$_4$], gave the η^1-co-ordinated phosphaalkyne complex *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BF$_4$] **2a** which forms *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BPh$_4$] **2b** on reaction with Na[BPh$_4$] or, upon reaction with HBF$_4$ in CH$_2$Cl$_2$, converts into the η^1-fluorophosphaalkene and the difluorophosphine complexes *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$]A (A = BF$_4$ **3a** or FeCl$_2$F$_2$ **3b**) and *trans*-[FeH(PF$_2$CH$_2$Bu^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≡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≡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≡CBu^t and its net electron donor/acceptor ability is compared with those of related unsaturated ligands.

Introduction

Phosphaalkynes, P≡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≡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(η^1-P≡CAd)$_2$(Et$_2$PCH$_2$CH$_2$PEt$_2$)$_2$] (Ad = adamantyl).[6] The related complexes of Re^I and Fe^{II}, *trans*-[ReCl(η^1-P≡CBu^t)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$)[7] and *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BF$_4$],[8] are also known but they have not been structurally characterised because the P≡C bond is activated. The former readily reacts with water to form the novel η^1-phosphinidene oxide complex *trans*-[ReCl{P(O)CH$_2$Bu^t}(dppe)$_2$][7] and the latter affords the η^1-fluorophosphaalkene complex *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][FeCl$_2$F$_2$] by HF addition (presumably deriving from the BF$_4^-$ anion) across the unco-ordinated P≡C bond,[8] as we have described in a preliminary way.

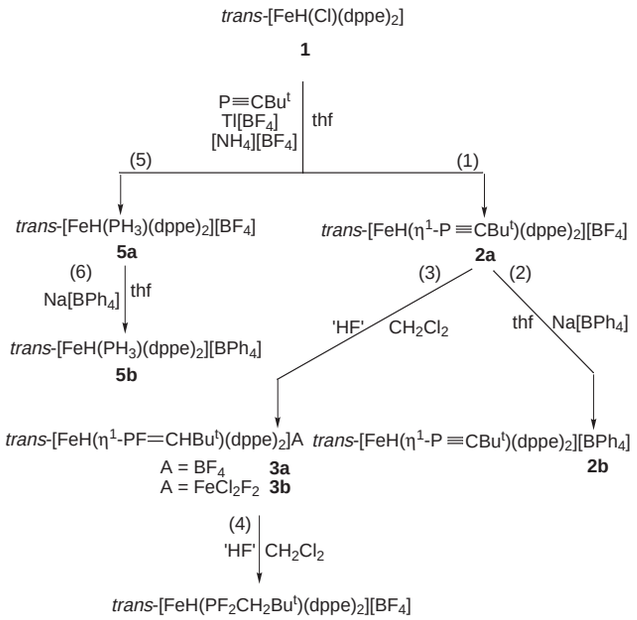
In contrast to the known elongation of the P≡C triple bond observed in several η^2-transition metal phosphaalkyne complexes[1,2,5] to typical P=C double-bond lengths (*ca.* 1.67 Å), the P≡C bond distance in the above zerovalent molybdenum complex [1.520(12) Å] was found to be comparable with that determined for P≡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≡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(η^1-P≡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≡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$_2$CH$_2$Bu^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$_2$Bu^t) has recently been achieved by others[10] in reactions of P≡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≡CBu^t with *trans*-[FeH(Cl)(dppe)$_2$] **1** in thf, in the presence of Tl[BF$_4$], yielded *trans*-[FeH(η^1-P≡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(η^1-P≡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_5H_5)(η^2-P≡*C*Bu^t){η^2-$(MeO)_2POBF_2OP(OMe)_2$}] [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 [$\delta(P^X)$ −154 relative to $P(OMe)_3$, $^2J(P^AP^X)$ 36 Hz, P≡CBu^t] and a doublet, with the same coupling constant, of four-fold intensity [$\delta(P^A)$ −62.3, 2 dppe]. In the ^1H-undecoupled ^{31}P NMR spectrum the phosphaalkyne resonance splits into a doublet of quintets [$^2J(P^XH)_{trans}$ 54, $^2J(P^AP^X)$ 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, $^2J(HP^A) \approx {}^2J(HP^X)$ 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.

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

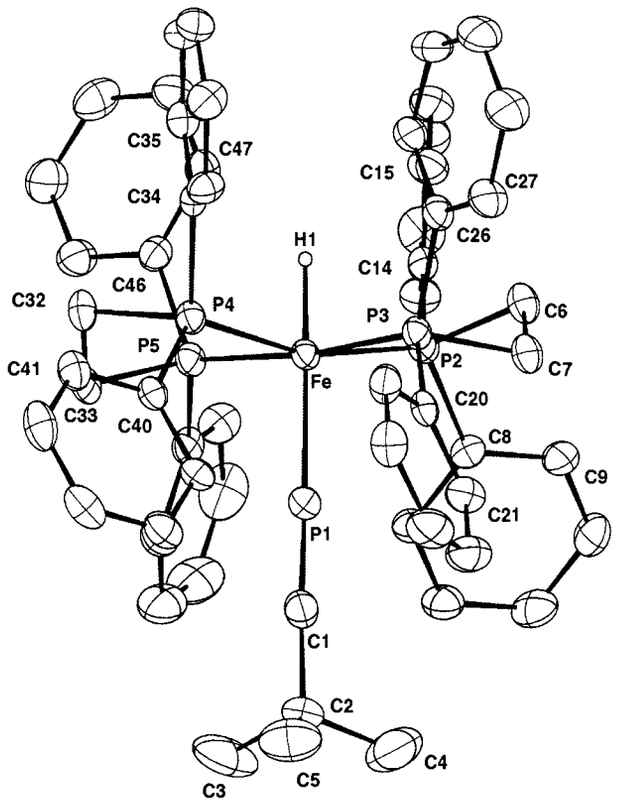


Fig. 1 Molecular structure of the complex cation of *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BPh_4] **2b**.

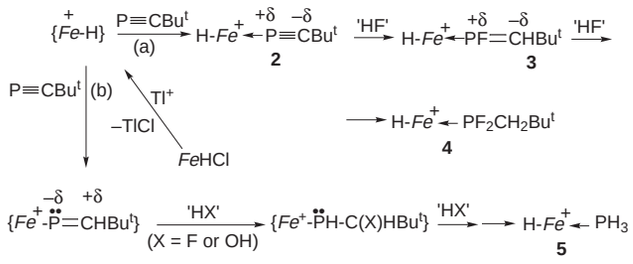
Table 1 Selected bond lengths (Å) and angles (°) for complex **2b**.

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)

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)$_2$][$FeCl_2F_2$] (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)($Me_2PCH_2CH_2PMe_2$)$_2$][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_2Cl_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 $E^o = 1.00$ 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

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

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_2Cl_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($PF_2CH_2Bu^t$)(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)$_2$][$FeCl_2F_2$] **3b** which was isolated as red crystals upon prolonged attempted recrystallization of **2a**, from CH_2Cl_2–Et_2O, 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_4XY] spin system (Y = F nucleus) consisting of a doublet of quintets centred at $\delta(P^X)$ 177.6 relative to P(OMe)$_3$ [1P, $^1J(P^XF)$ 985, $^2J(P^XP^A)$ 38 Hz, PF=CHBu^t] and a doublet at $\delta(P^A)$ −61.7 [4P, $^2J(P^XP^A)$ 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 $CFCl_3$, $^1J(P^XF)$ 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 [$^2J(HP^X) \approx {}^2J(HP^A)$ 53 Hz] centred at δ −9.4.

In the ^{31}P-{^{1}H} NMR spectrum ([A_4XY_2] spin system) of the difluorophosphine complex **4** the *P*$F_2CH_2Bu^t$ resonance appears as a triplet [$^1J(P^XF)$ 1067 Hz] of quintets [$^2J(P^XP^A)$ 34 Hz] at δ 137.5. The $^1J(P^XF)$ 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 [$J(P^AP^X)$ 29 Hz] at $\delta(P^X)$ −232.9 which, in the ^{1}H-undecoupled spectrum, transforms into a quartet [with a large constant, $^1J(P^XH)$ 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_3H], 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*←P̈=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_2O) to generate *Fe*–P̈H–C(X)HBu^t which, upon β-H elimination, rearrangement (in the case of HX = H_2O, involving conversion of the enol *Fe*–P̈H-C(OH)Bu^t into the keto form H–*Fe*←PH_2COBu^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 $[Ru(PHFCH_2Bu^t)Cl(CO)(PPh_3)_2(CNR)]^+$ 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 $P{\equiv}CBu^t$[29] were prepared by published methods, and $HBF_4{\cdot}Et_2O$ (Aldrich) was commercially available.

Infrared measurements were carried out on a Perkin-Elmer 683 spectrophotometer; ^1H, ^{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_2Cl_2 by using the ferrocene–ferrocenium redox couple ($E^{ox}_{\frac{1}{2}}$ = 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(η¹-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 $P{\equiv}CBu^t$ (0.751 mmol) plus $(Me_3Si)_2O$ 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_2Cl_2 immediately followed by filtration, addition of Et_2O 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 $P{\equiv}CBu^t$, separated from the crude complex **2a**, was taken to dryness and extraction with CH_2Cl_2 (5 cm^3) followed by filtration and addition of Et_2O (8 cm^3) resulted in the formation of an oily precipitate. The solution was filtered and, on addition of Et_2O on the following day, *trans*-$[FeH(PH_3)(dppe)_2][BF_4]$ **5a** precipitated as a yellow solid which was washed with Et_2O and dried *in vacuo* (*ca.* 10% yield).

Complex **2a** (Found: C, 65.2; H, 5.6. $C_{57}H_{58}BF_4FeP_5$ requires C, 65.8; H, 5.6%): ^1H NMR (CD_2Cl_2) δ −12.28 [1 H, sxt, $^2J(HP^A) \approx {}^2J(HP^X)$ 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-{^1H} NMR (CD_2Cl_2) δ −154.0 [1P, qnt, $^2J(P^AP^X)$ 36, P≡CBu^t] and −62.3 [4P, d, $^2J(P^AP^X)$ 36 Hz, dppe]; ^{31}P NMR (CD_2Cl_2) δ −154.0 [1P, dqnt, $^2J(P^XH)$ 54, $^2J(P^AP^X)$ 36, P≡CBu^t] and −62.3 [4P, t, $^2J(P^AH)$ *ca.* 44 Hz, dppe].

Complex **5a** (Found: C, 53.4; H, 5.0. $C_{52}H_{52}BF_4FeP_5{\cdot}3CH_2Cl_2$ requires C, 53.7; H, 4.4%); ^1H NMR (CD_2Cl_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-{^1H} NMR (CD_2Cl_2) δ −232.9 [1P, qnt, $^2J(P^XP^A)$ 29, PH_3] and −56.9 [4P, d, $^2J(P^AP^X)$ 29 Hz, dppe]; ^{31}P NMR (CD_2Cl_2) δ −232.9 [1P, qsxt, br, $^1J(P^XH)$ 320 Hz, PH_3] and −56.9 (4P, t, br, dppe).

Complex **5b**: identical ^1H and ^{31}P NMR spectra to those of **5a** (with the additional ^1H resonances due to BPh_4^-).

***trans*-[FeH(η¹-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_2Cl_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 ^1H and ^{31}P NMR spectra identical to those of **2a** (with the additional ^1H resonances due to the BPh_4^- counter ion). ^{13}C-{^1H} NMR (CD_2Cl_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(η¹-PF=CHBu^t)(dppe)$_2$][BF$_4$] 3a and *trans*-[FeH(PF$_2$CH$_2$Bu^t)(dppe)$_2$][BF$_4$] 4.** Unrecrystallised *trans*-$[FeH(\eta^1\text{-}P{\equiv}CBu^t)(dppe)_2][BF_4]$ **2a** (192 mg, *ca.* 0.18 mmol) was dissolved in CH_2Cl_2 (30 cm^3) and the solution filtered to eliminate traces of contaminant thallium salts. A 1:100 Et_2O diluted solution (3.5 cm^3) of commercial $[Et_2OH][BF_4]$ (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_2O 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_2O, dried *in vacuo* and separated mechanically.

Complex **3a** (Found: C, 57.8; H, 5.8. $C_{57}H_{58}BF_5P_5{\cdot}2CH_2Cl_2$ requires C, 57.5; H, 5.1%): ^1H NMR (CD_2Cl_2) δ −9.4 [1 H, dsxt, $^2J(HP^A) \approx {}^2J(HP^X)$ 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-{^1H} NMR (CD_2Cl_2) δ −61.7 [4P, d, $^2J(P^AP^X)$ 38, dppe] and 177.6 [1P, dqnt, $^1J(P^XF)$ 985, $^2J(P^XP^A)$ 38 Hz, PF]; ^{19}F NMR (CD_2Cl_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**: ^1H NMR (CD_2Cl_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-{^1H} NMR (CD_2Cl_2) δ −63.3 [4P, d, $^2J(P^AP^X)$ 34, dppe] and 137.5 [1P, tqnt, $^1J(P^XF)$ 1067, $^2J(P^XP^A)$ 34 Hz, $PF_2CH_2Bu^t$]; ^{19}F NMR (CD_2Cl_2) δ −149.5 (4F, s, BF_4) and −39.3 [2F, d, $^1J(FP)$ 1067 Hz, $PF_2CH_2Bu^t$].

***trans*-[FeH(η¹-PF=CHBu^t)(dppe)$_2$][FeCl$_2$F$_2$] 3b.** This complex was obtained upon prolonged attempted recrystallisation, from CH_2Cl_2–Et_2O, of *trans*-$[FeH(\eta^1\text{-}P{\equiv}CBu^t)(dppe)_2][BF_4]$ **2a** contaminated with $Tl[BF_4]$–$[NH_4][BF_4]$. Crude **2a** (0.208 g, *ca.* 0.183 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and the remaining solid was filtered off. Concentration of the filtered solution followed by addition of Et_2O 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_2Cl_2–Et_2O (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.

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

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References

1 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus*: *The Carbon Copy*, Wiley, New York, 1998, p. 366; J. F. Nixon, *Coord. Chem. Rev.*, 1995, **145**, 201; *Chem. Soc. Rev.*, 1995, 319; *Chem. Ind.*, 1993, 404; *Endeavour*, 1991, **15**, 49; *Chem. Rev.*, 1988, **88**, 1327.
2 M. Regitz, *J. Heterocycl. Chem.*, 1994, **31**, 663; *Proc. 4th Symp. Org. Synth. via Organometallics*, *Aachen*; 1992, 93, *Chem. Rev.*, 1990, **90**, 191; *Heteroatom Chemistry*, ed. E. Block, VCH, New York, 1990, p. 295; M. Regitz and P. Binger, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, eds. M. Regitz and O. J. Scherer, Georg Thieme, Stuttgart, 1990, ch. 2.
3 K. K. Laali, B. Geissler, M. Regitz and J. J. Houser, *J. Org. Chem.*, 1995, **60**, 6362.
4 M. Y. Antipin, A. N. Chernega, K. A. Lysenko, Y. T. Struchkov and J. F. Nixon, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 505.
5 J. C. T. R. Burckett-St. Laurent, M. A. King, H. W. Kroto, J. F. Nixon and R. J. Suffolk, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 755.
6 P. B. Hitchcock, M. J. Maah, J. F. Nixon, J. A. Zora, G. J. Leigh and M. A. Bakar, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 474.
7 P. B. Hitchcock, J. A. Johnson, M. A. N. D. A. Lemos, M. F. Meidine, J. F. Nixon and A. J. L. Pombeiro, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 645.
8 P. B. Hitchcock, M. A. N. D. A. Lemos, M. F. Meidine, J. F. Nixon and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1991, **402**, C23.
9 A. N. Chernega, M. Yu. Antipin, Y. T. Struchkov, M. F. Meidine and J. F. Nixon, *Heteroatom Chem.*, 1991, **2**, 665.
10 R. B. Bedford, D. E. Hibbs, A. F. Hill, M. B. Hursthouse, K. M. A. Malik and C. Jones, *Chem. Commun.*, 1996, 1895; R. B. Bedford, A. F. Hill and C. Jones, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 547.
11 G. Brauers, M. Green, C. Jones and J. F. Nixon, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1125.
12 M. A. Baptista, M. A. N. D. A. Lemos, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1992, **424**, 49.
13 P. B. Hitchcock, M. F. Meidine, J. F. Nixon, H. Wang, D. Gudat and E. Niecke, *J. Organomet. Chem.*, 1989, **368**, C29.
14 A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, 1975, **14**, 247.
15 K. G. Caulton, R. L. Dekock and R. F. Fenske, *J. Am. Chem. Soc.*, 1970, **92**, 515.
16 T. Vespremi and J. F. Nixon, unpublished work.
17 A. Hills, D. L. Hughes, M. Jimenez-Tenorio, G. J. Leigh and A. T. Rowley, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3041.
18 G. A. Ghilhardi, S. Midollini, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, 1981, **205**, 193.
19 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, pp. 224–227.
20 J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett and D. R. Stanley, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 2032.
21 T. A. Van der Knaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam and M. Konijn, *Tetrahedron*, 1984, **40**, 765.
22 P. B. Hitchcock, M. F. Meidine, J. F. Nixon, H. Wang, D. Gudat and E. Niecke, *J. Organomet. Chem.*, 1989, **368**, C29.
23 R. H. Neilson, R. J. Thomas, I. Vickovic and W. H. Watson, *Organometallics*, 1984, **3**, 1132.
24 R. Appel, C. Cassar, M. Immenkeppel and F. Knoch, *Angew. Chem.*, *Int. Ed. Engl.*, 1984, **23**, 895.
25 D. Gudat, M. F. Meidine, J. F. Nixon and E. Niecke, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1206.
26 M. H. A. Benvenutti, N. Cenac and J. F. Nixon, *Chem. Commun.*, 1997, 1327.
27 S. S. P. Almeida, M. T. Duarte, L. M. D. Ribeiro, F. Gormley, A. M. Galvão, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1996, **524**, 63.
28 P. Giannoccaro and A. Sacco, *Inorg. Synth.*, 1997, **17**, 69.
29 T. Allspach, M. Regitz, G. Becker and W. Becker, *Synthesis*, 1986, 31.
30 M. A. N. D. A. Lemos and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1992, **438**, 159.
31 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1985.
32 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

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