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Preliminary communication

Synthesis of the η^1-phosphaalkyne complex *trans*-$[FeH(P\equiv CBu^t)(dppe)_2][BF_4]$ and its conversion into a η^1-fluorophosphaalkene complex. Crystal structure of *trans*-$[FeH(PF{=}CHBu^t)(dppe)_2][FeCl_2F_2]$

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Abstract

The first example of the transformation of an η^1-ligated phosphaalkyne metal complex to an η^1-phosphaalkene complex is reported.

The rapidly developing coordination chemistry of compounds with phosphorus–carbon multiple bonds constitutes a rich new field linking main-group element and transition metal chemistry [1].

A variety of ligating behaviour has already been established for such types of unsaturated organophosphorus compounds, but only a few examples are known of complexes containing η^1-ligated phosphaalkynes, ($P\equiv CR$), in agreement with the expected predominance of the η^2-type coordination indicated by photoelectron spectroscopic studies [2]. The first complexes of the type *trans*-$[M(\eta^1\text{-}P\equiv CR)_2(R'PCH_2CH_2PR'_2)_2]$ (M = Mo or W; R = Bu^t or adamantyl, R′ = alkyl or aryl), containing η^1-ligated phosphaalkynes have only recently been prepared and structurally characterised [3].

In related studies on a variety of unsaturated linear molecules, such as isocyanides, nitriles or alkyne-derived species [4–6], we have established an η^1-ligating mode at an axial position in octahedral transition metal complexes containing two *trans*-chelating diphosphine ligands. This result prompted us to investigate this type of binding site with the phosphaalkyne $P\equiv CBu^t$.

Treatment of a solution of *trans*-$[FeHCl(dppe)_2]$ in tetrahydrofuran with $P\equiv CBu^t$ in the presence of $TlBF_4$ led to the η^1-phosphaalkyne complex *trans*-$[FeH(\eta^1\text{-}P\equiv CBu^t)(dppe)_2][BF_4]$, **1**, which was isolated as a yellow powder and identified by multinuclear NMR studies.

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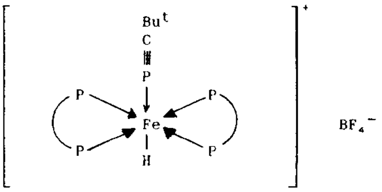
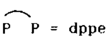
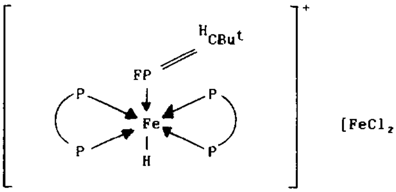
The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 exhibits the typical pattern expected for an $[A_4X]$ spin system, consisting of a quintet ($\delta_p = -154$ ppm rel. to $P(OMe)_3$), assigned to the phosphaalkyne phosphorus ($^2J(P^AP^B) = 36$ Hz) and a doublet with a four-fold intensity, ($\delta_p = -62.3$ ppm) due to the resonance of the dppe phosphorus nuclei. The same type of pattern is observed for the structurally related complex *trans*-[ReCl(η^1-P≡CBu^t)(dppe)$_2$], **3**, which was obtained by displacement of N_2 from *trans*-[ReCl(N_2)(dppe)$_2$] *



(1)





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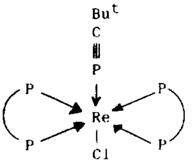

(3)

In the ^{31}P–^1H coupled NMR spectrum of **1**, the phosphaalkyne-P resonance changes into a doublet ($^2J(PH)_{trans} = 54.5$ Hz) of quintets. ($J(P^AP^B) = 36$ Hz), thus providing for the first time a value for the coupling constant between an *sp* hybridised phosphorus and a *trans*-hydride ligand. Surprisingly this value is only marginally higher than that for the *cis* phosphorus(dppe)–hydride coupling ($^2J(PH)_{cis} = 46.4$ Hz) in *trans*-[FeH(CNMe)(dppe)$_2$][BF$_4$] **.

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* The details of this reaction will be reported separately.

** M.A.N.D.A. Lemos and A.J.L. Pombeiro, unpublished.

*** *Crystal data:* $C_{57}H_{59}Cl_2F_3Fe_2P_5$, F.W. 1138.6, monoclinic, space group $P2_1/n$, a 11.114(12), b 23.652(11), c 24.045(8) Å, β 99.85(5)°, U 6227.3 Å, $Z = 4$, D_{calc} 1.21 g cm^{-3}, $F(000) = 2356$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 7.2$ cm^{-1}.

Data were collected on a crystal of dimensions ca $0.1 \times 0.1 \times 0.05$ mm using an Enraf-Nonius CAD4 diffractometer. Because diffraction was extremely weak, out of 7833 unique reflections measured for $2 < \theta < 22°$ and $+h+k \pm l$ only 2068 reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement and no correction was made for absorption. Most of the non-hydrogen atoms were located using the automated Patterson solution routines of SHELXS-86, and the remainder found on a difference map. The anion was originally thought to be $FeCl_4^-$ but it soon became apparent that two atoms were fluorines. Because of the limited data only the Fe atoms were assigned anisotropic thermal parameters. Refinement, with H atoms omitted, using a weighting scheme $w = 1/\sigma^2(F)$ converged at $R = 0.123$, $R' = 0.156$. A difference map showed an area of residual peaks of up to 1.3 e Å^{-3} not connected with the cation or anion, which we attributed to a disordered solvent molecule but it was not included in the model. Refinement used the SPD-plus program system run on a Microvax computer.

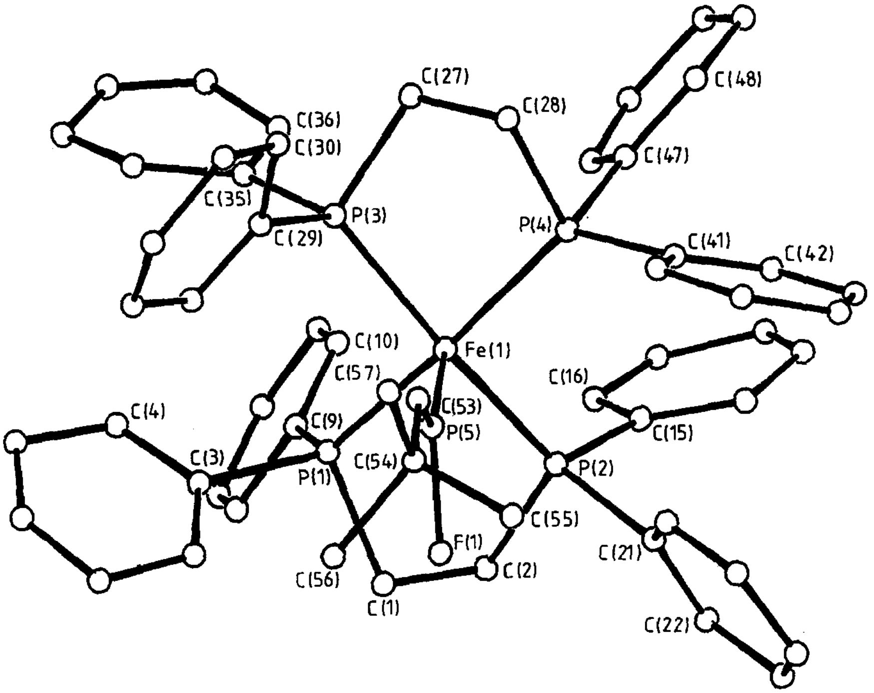

Fig. 1. Crystal structure of *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$][FeCl$_2$F$_2$].

In the ^{1}H NMR spectrum of **1**, the hydride resonance occurs as a sextet ($\delta = -12.2$ ppm; overlapping doublet of quintets), as a result of coupling with the four equivalent dppe-phosphorus nuclei and the phosphaalkyne-P nucleus.

Interestingly, attempted recrystallisation, of an impure sample of **1** from CH_2Cl_2 led to the isolation of a red crystalline solid which was structurally characterised by a single-crystal X-ray diffraction study *** as the η^1-fluorophosphaalkene complex *trans*-[FeH(η^1-PF=CHBu^t)(dppe)$_2$)][FeCl$_2$F$_2$], **2** (Fig. 1). Its formation presumably involves an hitherto unknown initial nucleophilic attack by fluoride ion on the η^1-bonded phosphaalkyne, which is probably activated by coordination to the Fe^{II} atom. Addition reactions across the η^1-ligated P≡C triple bond could provide a new synthetic route to a variety of η^1-ligated phosphaalkene metal complexes, and this is currently under study.

The P=C (1.66(4) Å) and the P–F (1.61(3) Å) bond distances in **2** as well as the Fe–P=C (141(2)°) and Fe–P–F (117(1)°) bond angles within the ligated fluorophosphaalkene, are comparable with the corresponding data for the related fluorophosphaalkene complex *trans*-[RhCl(PPh$_3$)$_2${η^1-PF=C(SiMe$_3$)$_2$}] (1.633(10) Å, 1.608(6) Å, 141.1(3)° and 113.8(3)°, respectively) [7]. As observed in other systems, the P=C bond length for η^1-coordinated phosphaalkene ligands is shorter than P=C distances reported for the η^2-binding mode [7] (1.69 to 1.83 Å). The latter usually exhibit a P=C bond lengthening on coordination consistent with population of the P=C π^* orbital by metal *d*-electrons, whereas in η^1-phosphaalkene complexes the P=C distance is comparable or even slightly shorter than that in the free phosphoalkene [1].

The Fe–P(fluorophosphaalkene) bond length of 2.112(12) Å in complex **2** is considerably shorter than that observed for the tetracarbonyl iron compound $[Fe(CO)_4\{\eta^1\text{-}PN(SiMe_3)_2{=}C(SiMe_3)_2\}]$ [8], and the Fe–P(diphos) bond lengths (2.302(12) and 2.268(11) Å). A short metal–P bond length has also been reported by us [7] for the other known η^1-ligated halogenophosphaalkene complexes *trans*-$[RhCl(PPh_3)_2\{\eta^1\text{-}PX{=}C(SiMe_3)_2\}]$ (X = F or Cl).

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