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Preliminary communication

Synthesis of the η^1 -phosphaalkyne complex *trans*-[FeH(P \equiv CBu^t)(dppe)₂][BF₄] and its conversion into a η^1 -fluorophosphaalkene complex. Crystal structure of *trans*-[FeH(PF=CHBu^t)(dppe)₂][FeCl₂F₂]

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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(η^1 -P \equiv CR)₂-(R'PCH₂CH₂PR'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 TIBF₄ led to the η^1 -phosphaalkyne complex *trans*-[FeH(η^1 -P \equiv CBu^t)(dppe)₂][BF₄], **1**, which was isolated as a yellow powder and identified by multinuclear NMR studies.

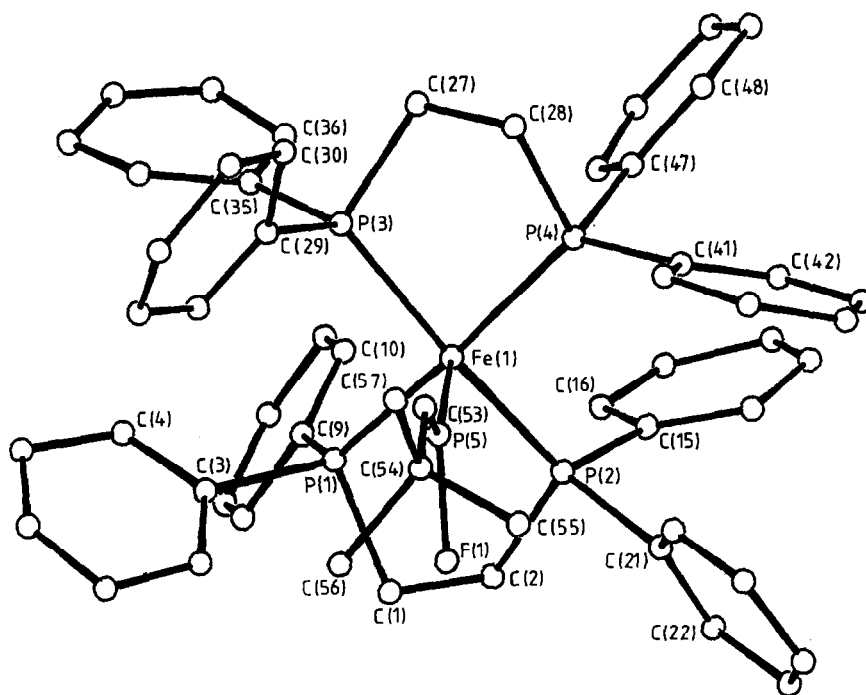


Fig. 1. Crystal structure of *trans*-[FeH(η^1 -PF=CHBu¹)(dppe)₂][FeCl₂F₂].

In the ¹H 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 phosphoalkyne-P nucleus.

Interestingly, attempted recrystallisation, of an impure sample of **1** from CH₂Cl₂ 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=CHBu¹)(dppe)₂][FeCl₂F₂], **2** (Fig. 1). Its formation presumably involves an hitherto unknown initial nucleophilic attack by fluoride ion on the η^1 -bonded phosphoalkyne, 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 phosphoalkene 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(PPh₃)₂{ η^1 -PF=C(SiMe₃)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 phosphoalkene 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 -phosphoalkene 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 $[\text{Fe}(\text{CO})_4\{\eta^1\text{-PN}(\text{SiMe}_3)_2\text{=C}(\text{SiMe}_3)_2\}]$ [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*- $[\text{RhCl}(\text{PPh}_3)_2\{\eta^1\text{-PX=C}(\text{SiMe}_3)_2\}]$ (X = F or Cl).

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