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Preliminary communication

Synthesis of the η^1 -phosphaalkyne complex trans-[FeH(P=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 phosphoruscarbon 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=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=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=CBu^t.

Treatment of a solution of *trans*-[FeHCl(dppe)₂] in tetrahedrofuran with $P=CBu^{t}$ in the presence of TlBF₄ led to the η^{1} -phosphaalkyne complex *trans*-[FeH($\eta^{1}-P=CBu^{t}$)(dppe)₂][BF₄], 1, which was isolated as a yellow powder and identified by multinuclear NMR studies.

The ³¹P{¹H} NMR spectrum of 1 in CD₂Cl₂ exhibits the typical pattern expected for an [A₄X] 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=CBu¹)(dppe)₂], 3, which was obtained by displacement of N₂ from *trans*-[ReCl(N₂)(dppe)₂] *



(3)

In the ${}^{31}P-{}^{1}H$ coupled NMR spectrum of 1, the phosphaalkyne-P resonance changes into a doublet $({}^{2}J(PH)_{trans} = 54.5 \text{ Hz})$ of quintets. $(J(P^{A}P^{B}) = 36 \text{ Hz})$, 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 $({}^{2}J(PH)_{cis} = 46.4 \text{ Hz})$ in *trans*-[FeH(CNMe)(dppe)_2][BF_4] **.

^{*} 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 $2 < \theta < 22^{\circ}$ 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=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 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)][FeCl₂F₂], **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(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 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 phosphoal-kene [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 $[Fe(CO)_4\{\eta^1-PN(SiMe_3)_2=C(SiMe_3)_2\}]$ [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-PX=C(SiMe_3)_2}] (X = F or Cl).

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References

1 For a review see: J.F. Nixon, Chem. Rev., 88 (1988) 1327.

- 2 J.C.T.R. Buckett-St. Laurent, M.A. King, H.W. Kroto, J.F. Nixon and R.J. Suffolk, J. Chem. Soc., Chem. Commun., (1983) 155; O.J. Scherer, Angew. Chem., Int. Ed. Engl., 24 (1985) 924.
- 3 P.B. Hitchcock, M.J. Maah, J.F. Nixon, J.A. Zora, G.J. Leigh and M.A. Bakar, Angew. Chem., Int. Ed. Engl., 26 (1987) 414.
- 4 A.J.L. Pombeiro, in U. Schubert (Ed.), Advances in Metal Carbene Chemistry, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989.
- 5 A.J.L. Pombeiro, M.F.C.G. Silve, D.L. Hughes and R.L. Richards, Polyhedron, 8 (1989) 1972.
- 6 A.J.L. Pombeiro, J. Organomet. Chem., 358 (1988) 273.
- 7 P.B. Hitchcock, M.F. Meidine, J.F. Nixon, H. Wang, D. Gudat and E. Niecke, J. Organomet. Chem., 368 (1989) C29.
- 8 R.H. Neilson, R.J. Thorne, I. Vickoric and W.H. Watson, Organometallics, 3 (1984) 1132.