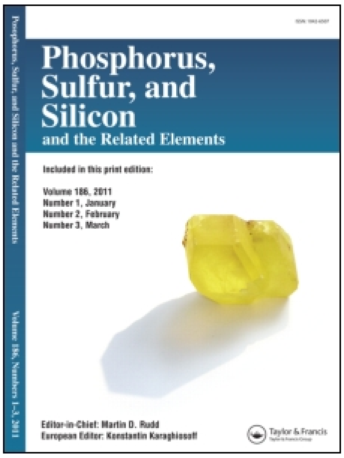


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Syntheses, Structure and Reactivity of η^1, η^3-1-Phosphaallyliron Complexes

F. Mercier[a]; F. Mathey[a]
[a] Laboratoire CNRS-SNPE, Thiais, (France)

To cite this Article Mercier, F. and Mathey, F.(1987) 'Syntheses, Structure and Reactivity of η^1, η^3-1-Phosphaallyliron Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 217 — 220
To link to this Article: DOI: 10.1080/03086648708080561
URL: http://dx.doi.org/10.1080/03086648708080561

Phosphorus and Sulfur, 1987, Vol. 30, pp. 217–220
Photocopying permitted by license only

SYNTHESES, STRUCTURE AND REACTIVITY OF η^1,η^3-1-PHOSPHAALLYL-IRON COMPLEXES

F. MERCIER and F. MATHEY

Laboratoire CNRS-SNPE, 2-8 rue H. Dunant, 94320 Thiais (France)

Abstract : Syntheses, structure and reactivity of η^1,η^3-phosphaallyliron complexes $[\eta^1P-(\eta^3-RP-CH=CHR')Fe(CO)(Cp)]W(CO)_5$.

Although the ubiquitous η^3-allyl ligand has been shown to play an important role in many transition metal mediated reactions, little is known about the chemistry of η^3-heteroallyl complexes :


a

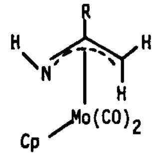

b

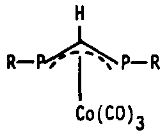

c


d

If we except three heteroallyl species containing nitrogens (1) which have been synthetized but not structurally characterized, two such compounds have been unambiguously characterized very recently. One is the η^3-1-azaallylmolybdenum complex (2) and the other is a tricarbonyl(1,3-diphosphaallyl)cobalt complex (3) :

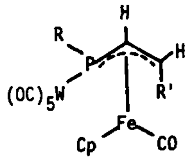
R = Ph,
4-C_6H_4-Me



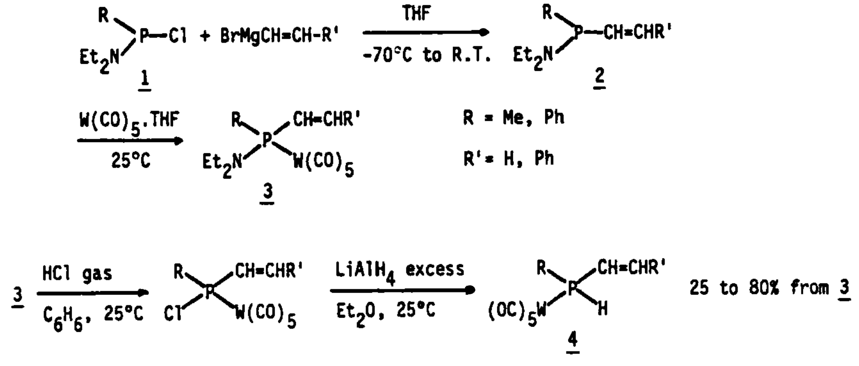


R = 2,4,6-tri-tert-butylphenyl

We wish to report hereafter on the synthesis of η^1,η^3-1-phosphaallyliron complexes belonging to the a type :

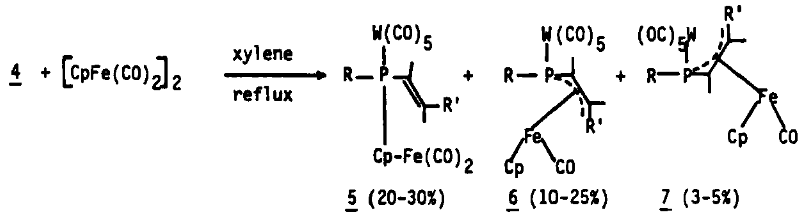


Such complexes could be formed from secondary vinylphosphines. However these molecules are particularly unstable because of the tendency of the P-H bond to add to the vinyl bond to give polymerized by-products. On the other hand, we have shown in preceding papers (4) that P-complexation with $W(CO)_5$ is a very powerful tool for stabilizing compounds with P-H bonds. We are not quite sure of the reasons of this stabilizing effect in the coordination sphere of tungsten but it could be due to an enhancement of the P-H bond strength disfavoring homolytic cleavage. Therefore quite stable and versatile vinyl complexes were prepared successfully in 3 steps from the corresponding vinyldiethylaminophosphines 2.



A similar scheme was used for the synthesis of stable divinylphosphines 4 (R=CH=CHR') from 1 (R=Cl) and two equivalents of vinyl magnesium bromide.

Having in our hands stable complexes of secondary vinylphosphines, we then centered our efforts on the preparation of η^3-phosphaallyliron complexes. The reaction of complexes 4 with $[CpFe(CO)_2]_2$ in boiling xylene afforded the η^1,η^3-phosphaallyliron complexes 6 and 7 among other products.



The products distribution was found to depend critically on the temperature conditions and substituents used. Thus, when R = Ph, Me R'= H, we noted the formation of saturated complexes

$$[CpFe(CO)_2]\,[P(R)(Et)]\,[W(CO)_5]$$

the proportions of which increased when increasing the temperature up to 130°C. Complex 5 has the classical 3-electron μ-phosphido structure. It can be seen as a η^1 (σ)heteroallyl complex intermediate which can then thermally give the η^3-heteroallyliron complex after losing CO. This CO displacement reaction can also be achieved by a brief irradiation in CH_2Cl_2 solution to give a 80% overall yield of a mixture of 6 and 7 (ratio 1/3).

The η^3-heteroallyl structure of complexes 6 (R = R'= Ph) was demonstrated by a single crystal X-ray diffraction study. The results are illustrated in Fig. 1. The short P-C(vinyl) bond of 6 (1.761(5) Å) is quite similar to those found in various η^5-phosphapentadienyl complexes (5), and in the recently described 1,3-diphosphaallylcobalt complex (2).

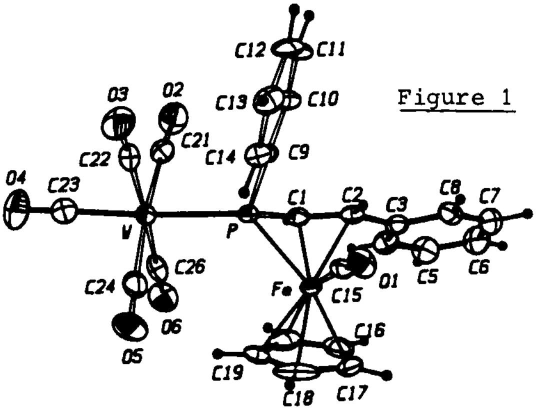


Figure 1

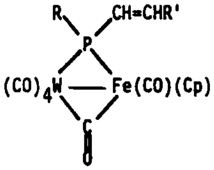
Complex 6 (R = Ph, R'= H) was also analyzed by crystal X-ray diffraction but we were unable to get good enough crystals to obtain reliable bond distances and angles. Nevertheless, the collected data gave us valuable informations concerning the stereochemistry of the compound. The overall structure is similar to that of 6 (R = R'= Ph) where the W atom and H_C are syn (W-P-C-H_C dihedral angle ca 6.6°) and Fe-CO unit is pointing towards the opposite direction to C-H_C.

On the basis of ^1H NMR spectra, we postulate that in complexes 7 H_C is probably anti to W and located close to the Fe-CO unit. This stereochemistry explains why H_C resonates at lower field than in 6 and why no coupling is observed between H_C and P.

Other complexes were completely characterized by elemental analyses, NMR, IR and mass spectroscopy.

At room temperature in solution, an equilibrium between 6 and 7 appears to take place favoring the formation of 6 (which is the thermodynamic product). Of course there is an important question concerning how does interconversion, between 6 and 7, take place and if the mechanism is involving or not an η^1-heteroallyl intermediate. Our first approach to this problem was to study the reactivity of the η^3 species. Indeed, if the $6 \rightleftarrows 7$ equilibration involves an $\eta^3 \rightarrow \eta^1$ allyl conversion with the release of a free coordination site on the metal, this one could be occupied by an external ligand.

We have therefore begun to investigate the reaction of these complexes with various reagents. By thermolysis or photolysis of the syn isomer 6, we do not observed any new complexes with weak two-electron donors (, PhCH=CHPh, THF...). When using strong donors like PR^2_3 (R^2= OMe, Ph), the reactions proceed and give new compounds such as $\left[CpFe(CO)_2\right]\left[P(R)(CH{=}CHR')\right]\left[W(CO)_4(PR^2_3)\right]$. But these compounds do not result from an intermolecular displacement of the vinyl unit by the phosphane. They result from an addition of the phosphane to an unstable complex which is intermediately formed. This latter complex, which is briefly observed during the photolysis of 5, is similar to the complexes described recently by King (6).



References

(1) H.R. Keable, M. Kilner, J. Chem. Soc. Dalton Trans. (1972), 153 ;
T. Inglis, M. Kilner, T. Reynoldson, E.E. Robertson, ibid (1975) 924 et 930
P.F. Dos Santos Filho and U. Schuchardt, J. Organometal. Chem. (1984), 263, 385
(2) M. Green, R.J. Mercer, C.E. Morton, A.G. Orpen, Angew. Chem. Int. Ed. Engl. 24 (1985) 422
(3) R. Appel, W. Schuhn, F. Knoch, Angew. Chem. Int. Ed. Engl. 24 (1985) 420
(4) F. Mercier, F. Mathey, Tetrahedron Letters, 26 (1985) 1717
(5) F. Mathey, J. Fischer, J.H. Nelson, Structure and Bonding 55 (1983) 153 ;
F. Nief and J. Fischer, Organometallics, (1986), 5, 877
(6) R.B. King, W.K. Fu, E.M. Holt, Inorg. Chem. (1985), 24, 3095