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Preliminary communication

Different modes of hydrogen migration in reactions of diphosphaallene, ArP=C=PAr (Ar = $2,4,6\text{-}Bu^t_3C_6H_2$) with $[W(CO)_5(THF)]$ and $[Fe_3(CO)_{12}]$. Crystal and molecular structure of $[Fe_2(CO)_6(ArP{=}CH\overline{PCH_2(CMe_2)C}_6H_2Bu^t_2)]$

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Abstract

Rearrangement of ArP=C=PAr (Ar = $2,4,6\text{-}Bu^t_3C_6H_2$) involving hydrogen migration from carbon to phosphorus occurs on heating with $[W(CO)_5(THF)]$, but with $[Fe_3(CO)_{12}]$ an unusual carbon to carbon hydrogen migration results.

There is considerable current interest in the coordination chemistry of novel organophosphorus compounds derived from alkenes, alkynes and cyclic or acyclic polyalkenes by replacement of a CH entity by P or a CH_2 species by a PR fragment [1].

A variety of metal complexes of phospha-alkene [2], phospha-alkyne [2,3], diphospha-cyclobutadiene [4,5], η^3-phospha-allyl [6] and η^3-diphospha-allyl [7] ligands have been reported. Previously [8,9] we reported the first examples of η^2-diphosphaallene complexes of the type $[M(PR_3)_2(ArP{=}C{=}PAr)]$, (M = Pd, Pt; R = Et, Ph; Ar = $2,4,6\text{-}Bu^t_3C_6H_2$).

We now describe two different kinds of hydrogen migration reaction undergone by the diphosphaallene ArP=C=PAr (I) [10] in the coordination sphere of a transition metal. The diphosphaallenetungsten pentacarbonyl complex (II) [14**] which was prepared by treatment of (I) with $[W(CO)_5(THF)]$, [11] undergoes a hydrogen migration from carbon to phosphorus on heating in refluxing toluene for

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** This and other references marked with asterisks indicate notes occurring in the list of references.

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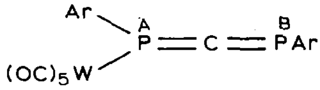
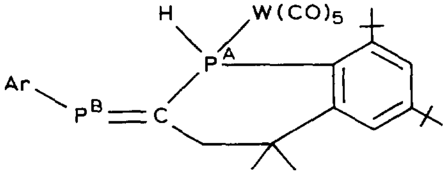
3 h. to afford the carbon–carbon coupled tetrahydro-1-phospha-naphthalene complex (III) [15*].



(II)



(III)

On the other hand I reacts with $[Fe_3(CO)_{12}]$ to give two products IV and V, in roughly equal amounts, both containing two non-equivalent phosphorus atoms [16 *]. Although the structure of V is not yet established, a single crystal X-ray diffraction study of IV [17 *] reveals the molecular structure shown in Fig. 1 which arises from an unexpected hydrogen migration from carbon to carbon within the diphosphaallene ligand.

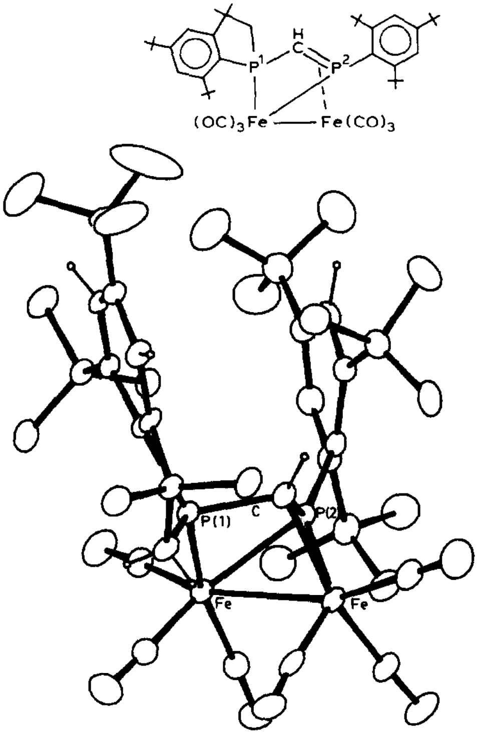
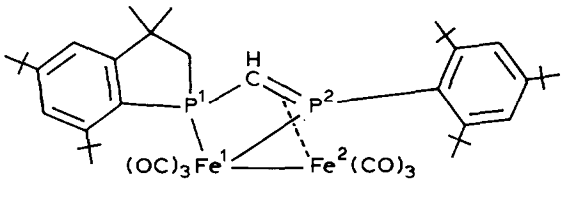


Fig. 1. Molecular structure of $[Fe_2(CO)_6\{ArP{=}CH\overline{PCH_2C(Me_2)C}_6H_2{}^tBu_2\}]$. Selected bond lengths are: Fe(1)–Fe(2) 2.738(1) P(1)–C 1.771(7); P(2)-C 1.783(6); Fe(1)–P(1) 2.295(2); Fe(2)-P(2) 2.171(2) Fe(1)–P(2) 2.313(2) Å.



(IV)

The structure of IV reveals that Fe(1) is bonded via two phosphorus lone pairs while Fe(2) is interacting solely with the P=C π system suggesting that Fe(1) donates a pair of electrons to Fe(2) to form the iron–iron bond [12]. We cannot at present rule out the possibility that the hydrogen migrates from carbon to carbon via phosphorus and the role of the metal in these diphosphaallene rearrangements is being studied further. Interestingly we have recently observed a double hydrogen migration from carbon to carbon to afford the ligated diphosphane ligand $Bu^t_2\overline{C_6H_2(CMe_2)CH_2P}CH_2\overline{PCH_2(CMe_2)C}H_2Bu^t_2$ as its $[W(CO)_4]$ complex [13].

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14 ^{31}P NMR data (shifts (ppm) are relative to 85% phosphoric acid, positive values to high frequency). II: $\delta(P_A)+151.9$; $\delta(P_B)+132.8$; $^2J(P^AP^B)$ 39 Hz; $^1J(P^BW)$ 273 Hz.
15 III: $\delta(P^A)$ 7.4 ppm (J(PH), 329.6 Hz); $\delta(P^B)$ 261.4 ppm, $J(P^AP^B)$ 48.8 Hz. $J(P^AW)$ 234.6 Hz.
16 IV: $\delta(P^1)+13.5$ ppm; $\delta(P^2)+56.7$ ppm; $J(P^1P^2)$ 46.4 Hz, ν(CO) 2040, 2005, 1975, 1965, 1940 cm^{-1} (hexane). Satisfactory elemental analysis.
V: $\delta(P^1)-13.6$ ppm, $\delta(P^2)+171.4$ ppm, $J(P^1P^2)$ 41.5 Hz. ν(CO) 2045, 2010, 1990, 1975, 1965 cm^{-1} (hexane).
17 *Crystal data*: $C_{43}H_{58}O_6P_2Fe_2 . C_8H_{10}$, $M = 950.8$, monoclinic, space group $P2_1/c$, a 20.098(7). b 10.675(5), c 26.141(30) Å, β 111.78(7)^0, U 5208.0 Å^3, $Z = 4$, $D_c = 1.21$ g cm^{-3}. The structure was solved by heavy atom methods and refined to $R = 0.051$, using 3742 unique reflections with $|F^2| > \sigma|F^2|$ measured on an Enraf–Nonius CAD 4 diffractometer.