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Generation of a bridging ethenyl ligand at a di-iron centre via carbon-phosphorus bond cleavage

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Abstract

UV irradiation of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) with diphenylvinylphosphine yields $[Fe_2(CO)_5(\mu\text{-}Ph_2PCH{=}CH_2)(\mu\text{-dppm})]$ (**2**) in which the vinylphosphine acts as a bridging four electron donor ligand to the di-iron centre. Thermolysis of **2** results in carbon-phosphorus bond cleavage giving the μ-alkenyl complex $[Fe_2(CO)_4(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ (**3**). The μ-ethenyl moiety in **3** is static at room temperature but at higher temperatures "windshield wiper" fluxionality is observed, a process conveniently monitored by ^{31}P NMR spectroscopy.

Introduction

The cleavage of phosphorus-element bonds is a potentially useful way of generating interesting organic and inorganic fragments at a metal centre. To this end we have been exploring the reactions of the di-iron complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) with a number of phosphorus containing ligands in order to generate new metal-element bonds and explore their reactivity [1-4]. It is well known that the ease of cleavage of the phosphorus-carbon bond varies considerably with hybridisation at carbon such that $P\text{-}C(sp) > P\text{-}C(sp^2) > P\text{-}C(sp^3)$ [5]. Thus, Carty and co-workers have extensively employed the facile $P\text{-}C(sp)$ cleavage of alkynyl phosphines in order to generate the alkynyl moiety at a variety of metal centres [6]. We have previously found that the oxidative-addition of phosphorus-carbon bonds to the di-iron complex **1** is a facile process which allows the synthesis of a number of new metal-carbon bonds [1-3]. Herein we describe the coordination of diphenylvinylphosphine to a di-iron centre followed by later phosphorus-carbon bond cleavage resulting in the generation of bridging ethenyl and diphenylphosphido moieties at the di-iron centre.

Experimental

General comments. All reactions were carried out under an N_2 atmosphere using predried solvents. NMR spectra were recorded on a Varian VXR 400 spectrometer.

IR spectra were recorded on a Perkin–Elmer 983 spectrometer. Column chromatography was carried out on columns of deactivated alumina (6% w/w water). Elemental analysis was performed within the chemistry department of University College. UV photolysis were carried out using a Hanovia medium pressure lamp. Diphenylvinylphosphine was purchased from Aldrich and used as supplied.

Synthesis of [$Fe_2(CO)_5(\mu$-$Ph_2PCH{=}CH_2)(\mu$-dppm)] (2)

Irradiation of a toluene solution (150 cm^3) of [$Fe_2(CO)_7(\mu$-dppm)] (**1**) (610 mg, 0.88 mmol) and diphenylvinylphosphine (186 mg, 0.88 mmol) whilst purging with N_2 resulted over 3 h in a colour change from red to yellow. Concentration of the solution to 30 cm^3 followed by addition of hexane resulted in the formation of a **2** as a yellow solid (420 mg, 56%). Anal. Found C, 62.60; H, 4.13; P, 10.97. $Fe_2C_{44}H_{35}O_5P_3$ calcd.: C, 62.26; H, 4.28; P, 10.97%. ^1H NMR ($CDCl_3$): δ 7.9–7.0 (30H, m, Ph), 4.01 (1H, dt, *J* 14.6, 9.3 Hz, PCH_2P), 3.36 (1H, ddd, *J* 14.6, 12.1, 9.3 Hz, H_c), 2.82 (1H, m, PCH_2P), 2.43 (1H, ddt, *J* 22.3, 8.6, 4.7 Hz, H_b), 2.16 (1H, ddd, *J* 38.1, 8.6, 4.7 Hz, H_a). ^{31}P NMR ($CDCl_3$) δ 65.8 (dd, *J* 92, 11 Hz, P_b), 62.7 (dd, *J* 92, 58 Hz, P_a), 31.3 (dd, *J* 58, 11 Hz, P_c) ppm. ^{13}C NMR ($CDCl_3$) δ 218.7 (br, 3CO), 213.1 (m, 2CO), 61.8 (d, *J* 23 Hz, CH), 47.0 (t, *J* 16 Hz, PCH_2P), 34.6 (br, CH_2). IR (CH_2Cl_2) 2008(m), 1981(m), 1942(s), 1931(s), 1870(m) cm^{-1}.

Synthesis of [$Fe_2(CO)_4(\mu$-$CH{=}CH_2)(\mu$-$PPh_2)(\mu$-dppm)] (3)

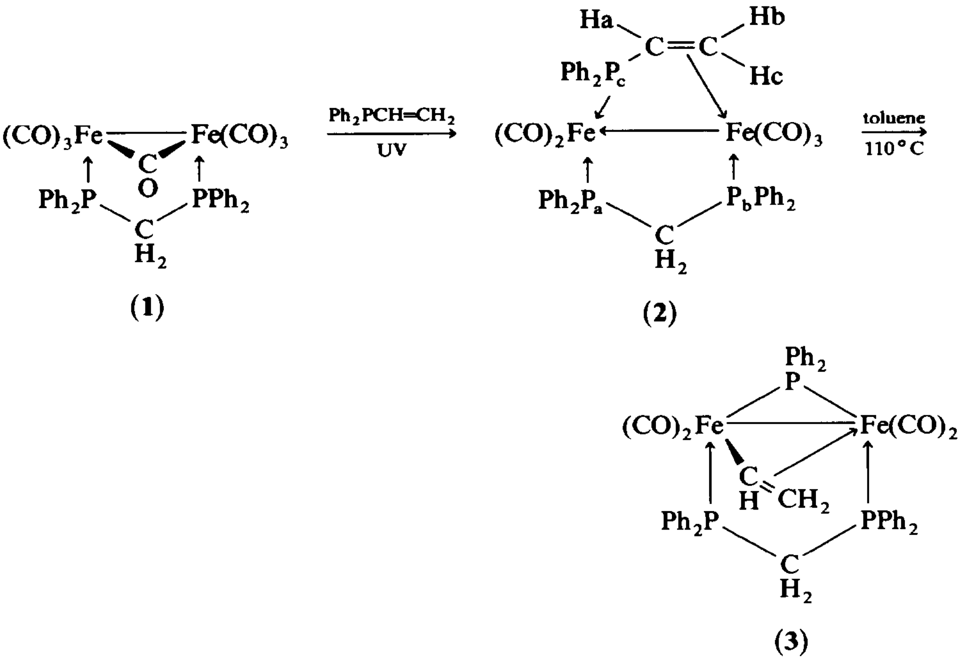
Thermolysis of a toluene solution (40 cm^3) of **2** (200 mg, 0.24 mmol) for 4 h resulted in a colour change from yellow to orange. After removal of solvent, chromatography eluting with hexane–diethyl ether (4 : 1) afforded an orange band which provided **3** (160 mg, 77%) as an orange powder. Crystallisation from a dichloromethane–hexane solution at $-20\,^\circ C$ gave orange crystalline **3** which contained half a molecule of CH_2Cl_2 as shown by ^1H NMR spectroscopy. Anal. Found C, 61.18; H, 4.44; P, 10.41. $Fe_2C_{43}H_{35}O_4P_3(1/2CH_2Cl_2)$ calcd.: C, 60.52; H, 4.17; P, 10.78%. ^1H NMR ($CDCl_3$) δ 8.3–6.5 (30H, m, Ph), 6.32 (1H, m, H_a), 3.80 (1H, ddt, *J* 2.6, 4.3, 9.0 Hz, PCH_2P), 2.69 (1H, dt, *J* 18.0, 9.0 Hz, PCH_2P) 2.59 (1H quin, *J* 5.9 Hz, H_c), 2.38 (1H, t, *J* 10.7 Hz, H_b). ^{31}P NMR ($CDCl_3$) (293 K) δ 202.1 (dd, *J* 91, 81 Hz, μ-PPh_2), 84.2 (dd, *J* 81, 65 Hz, PPh_2), 72.1 (dd, *J* 91, 65 Hz, PPh_2) ppm. ^{13}C NMR ($CDCl_3$)δ 219.9 (dd, *J* 28, 22 Hz, CO), 219.3 (d, *J* 10 Hz, CO), 219.2 (dd, *J* 10, 5 Hz, CO), 213.9 (t, *J* 19 Hz, CO), 155.1 (t, *J* 23 Hz C_α), 142 –127 (m, Ph), 74.7 (dd, *J* 17, 5 Hz, C_β), 40.2 (dd, *J* 45, 28 Hz, PCH_2P) ppm. IR (CH_2Cl_2) 1979(m), 1947 (s), 1915(m), 1899(m) cm^{-1}.

Attempted carbonylation of 3

Subjecting a toluene solution (20 cm^3) of **3** (100 mg, 0.12 mmol) to 50 atm of carbon monoxide for 2 d resulted only in the quantitative recovery of starting material.

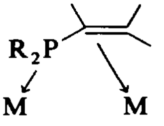
Results and discussion

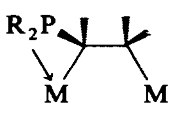
Photolysis of a toluene solution of [$Fe_2(CO)_6(\mu$-$CO)(\mu$-dppm)] (**1**) and diphenylvinyl phosphine led to the isolation of [$Fe_2(CO)_5(\mu$-$Ph_2PCH{=}CH_2)(\mu$-dppm)] (**2**) in 56% yield. Complex **2** is a yellow crystalline solid which while moderately air stable in the solid state, decomposes rapidly when solutions are exposed to air. The



(1) (2) (3)

coordination of both the phosphorus and vinyl moieties of the diphenylvinylphosphine ligand was clearly shown by ^{1}H NMR spectroscopy. Thus, the vinylic protons are all shifted to high field (with respect to the uncoordinated ligand) being observed at δ 2.16(5.94) H_a, 2.43(5.66) H_b, and 3.36(6.68) H_c. The coordination of diphenylvinylphosphine bridging two metal centres is relatively rare, being only recently reported [7–10]. It may be formally represented as a bridging η^1-P, η^2-(C=C) vinylphosphine (**A**) or alternatively, as a η^1-P, μ-(C=C) substituted olefin (**B**). In both these representations, the ligand acts as a net 4-electron donor to the dimetal centre. In crystallographically characterised examples, [7,8] representation **A** clearly predominates, as shown by the absence of a bonding interaction between the central carbon atom and the phosphorus bound metal centre. It is, however, noteworthy that for the heavier congeners of the iron triad, diosmacyclobutane complexes such as $[Os_2(CO)_8(\mu\text{-}H_2CCH_2)]$ are known [11], while at related di-iron centres examples of three-membered Fe–P–C metalla-


(A)


(B)

cycles have also been characterised [2,12]. In the absence of X-ray crystallographic data in this instance, the two forms cannot easily be differentiated. However, the high field ^{13}C NMR shift (δ -25.2 ppm) of the carbon atoms of the Os_2C_2 ring of $[Os_2(CO)_8(\mu\text{-}H_2CCH_2)]$ [13], compared with relatively low field resonances at δ 61.8 (d, J 23 Hz) and 34.6 (br) assigned to CH and CH_2, respectively in **2**, lead us to prefer the bridging vinylphosphine representation **A**, the adoption of which necessitates a donor-acceptor interaction between the metal centres.

The bridging vinylphosphine ligand in **2** is static at room temperature as evidenced by ^{31}P NMR spectroscopy which shows three distinct doublet of doublets at 65.8 (P_B), 62.7 (P_A), and 31.3 (P_c) ppm, the latter being attributed to the vinylphosphine ligand. The static nature of the diphenylvinylphosphine ligand contrasts with the behaviour found for this ligand at a dipalladium centre in which rapid room temperature fluxionality is observed [8].

Thermolysis of **2** in toluene results in phosphorus-carbon bond cleavage yielding the μ-ethenyl complex $[Fe_2(CO)_4(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)(\mu\text{-dppm})]$ (**3**) in 77% yield. The phosphorus-carbon bond cleavage process is clearly shown by ^{31}P NMR spectroscopy, the signal at 202.1 ppm being characteristic of a diphenylphosphido moiety bridging a metal-metal bond [14]. The observation of three well-resolved doublet of doublet of doublets also indicates that at room temperature the μ-ethenyl ligand is static, while the large J(PP) coupling constants of 91 and 81 Hz to the

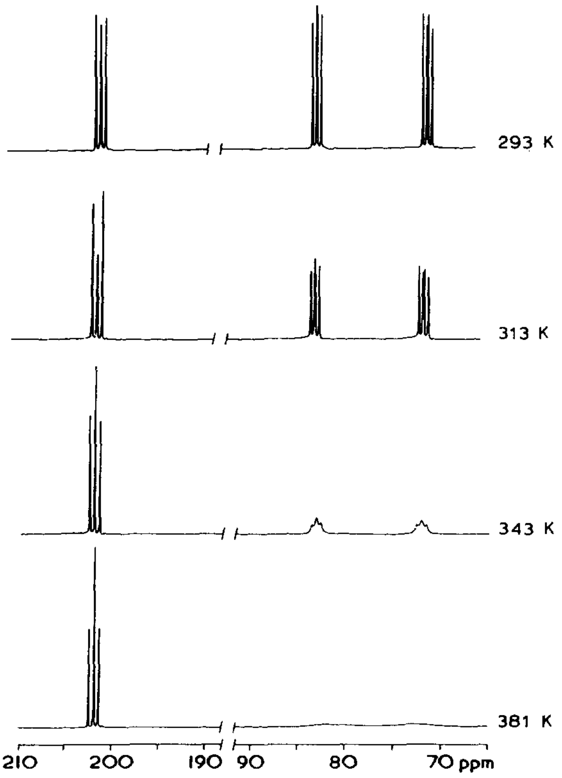


Fig. 1. Variable temperature ^{31}P NMR spectrum of **3** in toluene-d_8.

phosphido moiety indicate that the diphosphine phosphorus atoms are each *trans*- to this group. At higher temperatures the ethenyl ligand exhibits fluxionality, a process which is conveniently monitored by ^{31}P NMR spectroscopy (Fig. 1). At 108°C resonances due to the diphosphine ligand approach (but do not reach) coalescence, from which a limiting activation energy of 67.5($\pm$0.5) kJ mol^{-1} can be deduced. These observations are attributed to the well-known " windshield wiper" fluxionality of bridging alkenyl ligands [15]. It is noteworthy that the synthesis of the related unsubstituted μ-ethenyl complex $[Fe_2(CO)_6(\mu\text{-}CH{=}CH_2)(\mu\text{-}PPh_2)]$ has recently been described [16], via addition of Ph_2PCl to the μ-ethenyl complex $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)][PPh_4]$. No details of the fluxionality of this molecule are given.

The conversion of a vinylphosphine to μ-alkenyl and μ-phosphido moieties via carbon–phosphorus bond cleavage is similar to the reactivity previously reported for vinylsulphides upon reaction with tri-iron dodecacarbonyl, however, in this latter instance precoordination of the vinyl ligand prior to oxidative carbon–element bond cleavage was not observed [17]. Interestingly, in a related complex namely, $[Mo_2(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me){=}CHMe\}(\eta\text{-}C_5H_5)_2][BF_4]$ [7], the bridging vinylphosphine ligand is formed as a result of carbon–phosphorus bond formation between a bridging phosphido ligand and an alkenyl moiety which suggests that the transformation of **2** to **3** may be reversible. Exposure of **3** to high pressures of carbon monoxide did not, however, result in carbon–phosphorus bond formation, indeed **3** was recovered quantitatively.

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