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# Intramolecular nucleophilic attack on cationic iron(II) vinylidene complexes: synthesis and crystal structure of the alkenyl $[Fe(C{=}CMe^tBu)(\eta\text{-}C_5H_5)(Ph_2P)_2CH]$ containing an unprecedented bicyclopentane ring system

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## Abstract

Reaction between $[Fe({=}C{=}CMe^tBu)(\eta\text{-}C_5H_5)(dppm)][CF_3SO_3]$ (dppm = bis(diphenylphosphino) methane) and NaOMe at −20°C resulted in the deprotonation of dppm followed by the intramolecular nucleophilic attack of the methanide group on the vinylidene α-carbon to give $[Fe(C{=}CMe^tBu)(\eta\text{-}C_5H_5)\{(Ph_2P)_2CH\}]$. An X-ray single-crystal structure determination shows that the complex contains a novel 1-ferra-2,4-diphosphabicyclo[1.1.1]pentane ring system.

The chemistry of transition metal vinylidene complexes has undergone rapid expansion in the last few years [1] and several recent reports have shown the utility of these complexes in stoichiometric [2] and catalytic organic synthesis [3]. Vinylidene complexes have also been proposed as intermediates in the polymerization of alkynes [4] and in a variety of coupling reactions involving terminal alkynes, leading to the selective formation of new carbon–carbon bonds [5]. Their reactivity, which has been extensively studied both experimentally and theoretically [6], is dominated by nucleophilic additions to the α-carbon atom of the vinylidene group. Substituted vinylidene cationic complexes $[M{=}C{=}C(R^1)R^2]^+$ (M = $[Fe(\eta\text{-}C_5H_5)L_2]$ or $[Ru(\eta\text{-}C_5H_5)L_2]$) are especially prone to this type of addition and many nucleophiles both "hard" and "soft" add regioselectively to the carbon centre [7], such as water, alcohols and phosphines and anions such as methyl and phenyl

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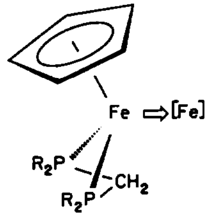
groups, hydride, phenylmercaptide and cyanide [8]. However, mono- and un-substituted vinylidene systems undergo a competitive deprotonation at $\beta$-carbon in the presence of typical bases. This reaction, which is the reverse of the vinylidene synthesis from the $\sigma$-acetylide complex, is not general and appears to depend on the basicity of the nucleophile [9*].

We have recently reported [10] that the cationic vinylidene iron(II) complex $[Fe(=C=CH_2)(\eta\text{-}C_5H_5)(dppm)]^+$ can be readily deprotonated to the acetylide $[Fe(C\equiv CH)(\eta\text{-}C_5H_5)(dppm)]$ by $KO^tBu$ or $LiN(SiMe_3)_2$ in THF. We have also described [11] the systematic synthesis of a series of vinylidene complexes $[Fe]^+=C=CR^1R^2$ in which the substitution on the vinylidene group, as well as different auxiliary ligands, enables their chemistry to be systematically explored. We describe here the reactions of monosubstituted vinylidene complexes ($R^1 = H$) with alkoxides, and the synthesis and characterization of the product obtained by the deprotonation of $[Fe(=C=CMe^tBu)(\eta\text{-}C_5H_5)(dppm)][CF_3SO_3]$(I).



R= Ph (dppm) or Me (dmpm)

$[Fe]^+=C=CR^1R^2$

*dppm*

$R^2 = H$; $R^1 = H, Ph, CO_2Me, CO_2Et, {}^tBu, CH_2OCH_3$

$R^2 = Me$; $R^1 = Ph, {}^tBu, CO_2Me, CH_2OCH_3$

$R^2 = I$; $R^1 = Ph, {}^tBu$

*dmpm*

$R^2 = Me$; $R^1 = CH_2OCH_3, {}^tBu$

A THF solution of the monosubstituted vinylidene complexes $[Fe(=C=CHR^1)(\eta\text{-}C_5H_5)(dppm)][BF_4]$ ($R^1 = Ph$ or ${}^tBu$) was treated with NaOMe for 1 h to give a solution from which crystalline solids were isolated, identified as the known [10] alkynyl complexes by NMR and IR spectroscopy (eq. 1). The use of $KO^tBu$ led to similar deprotonations.

$$[Fe(=C=CHR^1)(\eta\text{-}C_5H_5)(dppm)]^+ + OMe^- \rightarrow [Fe(C\equiv CR^1)(\eta\text{-}C_5H_5)(dppm)] + MeOH \qquad (1)$$

Although the disubstituted vinylidene complex (I) was found to react similarly, the deprotonation takes place on one of the dppm methylene hydrogen atoms. Thus, the treatment of a THF solution of I with NaOMe at room temperature led to a red solution from which complex II was isolated in 75% yield as a red air-stable crystalline solid (eq. 2) [12*]. No products arising from the nucleophilic attack of the anion methoxide on the vinylidene $\alpha$ carbon could be detected.

$$[Fe(=C=CMe^tBu)(\eta\text{-}C_5H_5)(dppm)]^+ + OMe^- \rightarrow \underset{(II)}{[Fe(C_2Me^tBu)(\eta\text{-}C_5H_5)(Ph_2P)_2CH]} + MeOH \qquad (2)$$

The IR spectrum (Nujol mull), which does not show the absorptions typical of $\nu$(C–F) and $\nu(SO_3)$, and the conductivity (in $Me_2CO$) indicate that II is a neutral

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* Reference number with asterisk indicates a note in the list of references.

complex. This is confirmed by the FAB mass spectrum which shows the presence of the parent ion $[M^+ + 1]$ 601. The $^{31}P\{^1H\}$ NMR spectrum in $C_6D_6$ exhibits a singlet resonance at $\delta$ 14.62 ppm, indicating that the two phosphorus atoms are chemically equivalent. The $^1H$ and $^{13}C$ NMR spectra [12*] exhibit the expected resonances for the cyclopentadienyl, aromatic, methyl and t-butyl protons. The signals are shifted to higher fields relative to the corresponding resonances in the vinylidene precursor complex I [11], reflecting the neutral character of the new compound II (*i.e.* $\delta(C_5H_5)$ $^1H$ NMR 4.6, *vs.* 5.2; $^{13}C$ NMR: 70.2, *vs.* 85.5 ppm). Significantly, the $^{13}C$ NMR spectrum is very informative since it shows the disappearance of the typical low field vinylidene $\alpha$-carbon resonance ($\delta$ 365.5t ppm). This seems to suggest a loss of the *sp* character of the $\alpha$-carbon atom, pointing to an intramolecular addition of the methanide carbon atom to the $\alpha$-carbon of the vinylidene group. To confirm this and to establish the stereochemistry of the resulting metallacycle, the structure of II was determined by X-ray diffraction * (Fig. 1).

The complex II consists of monomeric molecules in which the iron atom is bound to a cyclopentadienyl ring (in a typical symmetric $\eta^5$-fashion), a vinylic carbon and the two phosphorus atoms from the deprotonated dppm ligand, showing a coordination sphere consistent with a "pseudo-octahedral" structure. The most remarkable feature is the presence of an unprecedented 1-ferra-2,4-diphosphabicyclo[1.1.1]pentane ring formed by the nucleophilic attack of the dppm methanide group on the $\alpha$-carbon (C1) of the former vinylidene system. This is a new bonding mode in the extensive coordination chemistry of groups derived from dppm [13]. A related 1-ferra-2,5-diphosphabicyclo[2.1.1]hexane ring has also been reported [14]. The bicyclic system consisting of three four-membered rings is highly strained as illustrated by the internal angles: C(1)–Fe–P(1) 65.8(4)°, C(1)–Fe–P(2) 68.0(4)°, Fe–P(1)–C(2) 82.4(4)°, Fe–P(2)–C(2) 83.1(4)°, Fe–C(1)–C(2) 92.4(7)°, P(1)–C(2)–C(1) 83.7(8)°, P(2)–C(2)–C(1) 86.8(7)°, P(1)–C(2)–P(2) 91.4(6)°, P(1)–Fe–P(2) 74.9(2)°. The last two angles, as well as the bonding distances in the chelate deprotonated dppm ring, are typical of the small bite dppm ligand, and comparable to that found in $[Fe(C{\equiv}CPh)(\eta\text{-}C_5H_5)(dppm)]$ [10] and $[Fe({=}C{=}CMePh)(\eta\text{-}C_5H_5)(dppm)]^+$ [11]. Although the Fe–C(1) bond length is about 0.07 Å longer than that in the analogous vinyl complex $[Fe((E)\text{-}C(H){=}C(Me)Ph)(\eta\text{-}C_5H_5)(dppm)]$ [15] (1.987 Å), the distance is typical of Fe–C($sp^2$) bonds [16*]. The exocyclic C(1)–C(3) double bond has a length typical of an alkenyl group, 1.35(2) Å, and is coplanar with its substituents (C(2), C(4) and C(5) atoms), as expected for

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* Crystal data: Crystals of the complex were obtained by slow diffusion of $Et_2O$ into a hexane solution of II. $C_{37}H_{38}P_2Fe$, $M_r = 601.51$, monoclinic, space group $P2_1/c$, $a = 14.693(9)$ Å, $b = 13.159(6)$ Å, $c = 17.602(7)$ Å, $\beta = 113.68(1)°$, $V = 3117(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.28$ g/cm$^3$, T = 200 K; crystal dimensions $0.20 \times 0.17 \times 0.10$ mm$^3$. Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å) graphite monochromated; 5953 reflections measured on an Enraf–Nonius CAD4 ($\omega$–$2\theta$ scan technique), range $0 < \theta < 25$ and $-17 \le h \le 17$, $0 \le k \le 15$, $0 \le l \le 21$; 5473 unique reflections ($R_{int} = 0.059$, averaging double measured) and 1351 observed with $I > 3\sigma(I)$. Semiempirical and empirical absorption corrections were applied; $\mu = 6.07$ cm$^{-1}$. The structure was solved by Patterson interpretation (SHELX 86) and anisotropically refined (SHELX 76) to a final $R = 0.059$, $R_w = 0.057$. (217 parameters and $w = 1/(\sigma^2(F_o) + 0.0008\ F_o^2)$; maximum shift/error 0.03, $\rho_{max} = 0.56$ e/Å$^3$; $\rho_{min} = -0.035$ e/Å$^3$. All calculations were made on a MicroVax-3400 at the Scientific Computer Center of the University of Oviedo.

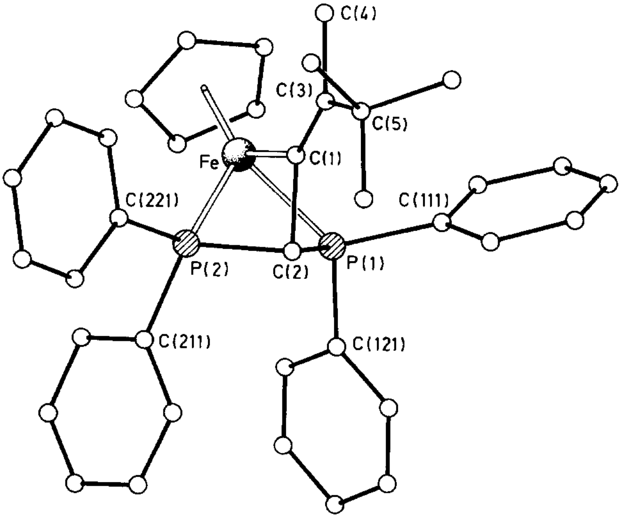
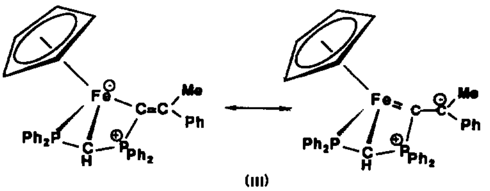


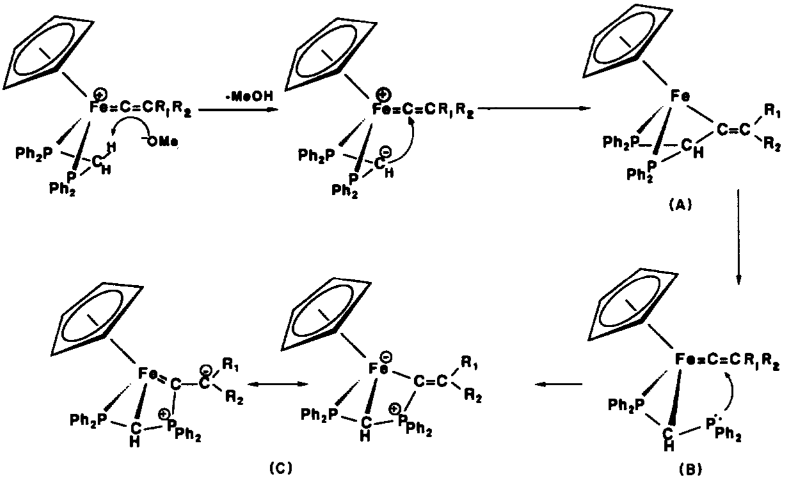
Fig. 1. PLUTO drawing of the complex II with principal bond lengths (Å) and angles (deg): Fe–M*, 1.684(18) (M* is the centroid of the cyclopentadienyl ring); Fe–P(1), 2.164(4); Fe–P(2), 2.150(5); Fe–C(1), 2.06(1); C(1)–C(2), 1.59(2); C(1)–C(3), 1.35(2); P(2)–Fe(1)–C(1), 68.0(4); P(1)–Fe–C(1), 65.8(4); P(1)–Fe–P(2), 74.9(2); Fe–P(1)–C(2), 82.4(4); Fe–P(2)–C(2), 83.1(4); Fe–C(1)–C(2), 92.4(7); P(2)–C(2)–C(1), 86.8(7); P(1)–C(2)–C(1), 83.7(8); P(1)–C(2)–P(2), 91.4(6); C(2)–C(1)–C(3), 130.1(12); Fe–C(1)–C(3), 137.3(10).

the $sp^2$ character of C(1) and C(3). The alkenyl complex adopts the E configuration, which is known to be thermodynamically the more stable isomer [17].

Treatment of the analogous vinylidene complex $[Fe(=C=CMePh)(\eta\text{-}C_5H_5)(dppm)][CF_3SO_3]$ with NaOMe under the same conditions proceeds in a different way. It leads to a complex formulated as $[Fe(C_2(Me)Ph)(\eta\text{-}C_5H_5)(Ph_2P)_2CH]$ (III), on the base of IR and NMR spectroscopy, and mass spectrometry [18*]. Although the complex was not isolated in analytical purity, apparently a deprotonation of dppm has also taken place. However the $^1H$ and $^{31}P$ NMR spectra at room temperature indicate that a metallacycle is not present. Significantly, the phosphorus NMR spectrum shows doublets at $\delta$ 68.9 and 1.1 ppm, typical of an AB system, revealing the chemical inequivalence of the phosphorus atoms. The uncommonly large value of the coupling constant ($^2J$(P–P) 106.5 Hz), similar to that found in phosphonium salts and phosphorus ilydes [19], seems to suggest the formation of an ilyde metallacycle complex containing the ring system 1-ferra-3,5-diphosphabicyclo[2.1.0]pentane.



(III)



Scheme 1.

When the mixture is allowed to react at 0°C for 1 h, an air-sensitive solid is obtained, identified by NMR spectroscopy as a mixture of the complex III and the metallacycle analogous to II, $[Fe(C{=}CMePh)(\eta\text{-}C_5H_5)\{(Ph_2P)_2CH\}]$ (IV), in a molar ratio of *ca.* 1:10 [20*]. The $^{31}P\{^1H\}$ NMR spectra of this mixture between 0 and 25°C show the gradual disappearance of the singlet resonance assigned to the equivalent phosphorus atoms of IV, and growth of the doublets characteristic of III. After 2 h at room temperature the spectrum reveals an almost quantitative transformation of IV to III.

The reaction of the vinylidene complex $[Fe({=}C{=}CMeCH_2OMe)(\eta\text{-}C_5H_5)(dppm)]^+$ with $MeO^-$ at different temperatures has also been studied by $^{31}P\{^1H\}$ NMR spectroscopy, revealing a transformation similar to that discussed above. However, a new transient species is detected. A singlet at $\delta$ 17.90 ppm and an AB spin system at $\delta$ 67.63d and 0.86d ppm ($^2J$(P–P) 107 Hz), together with two additional doublets at $\delta$ 15.98 and −19.31 ppm ($^2J$(P–P) 158.2 Hz) are observed. The ratios of components are clearly dependent on the reaction conditions. At room temperature and after 1 h of reaction the spectrum shows preponderance of the AB system, with minor intensities due to the other signals (molar ratio *ca.* 10:1:1).

On the basis of these experiments, we suggest that the formation of these metallacycle derivatives may occur by the pathway shown in Scheme 1. Complex (B), with an uncoordinated phosphorus atom, and which is observed only in the apparently slower reaction with the vinylidene complex $[Fe({=}C{=}CMeCH_2OMe)(\eta\text{-}C_5H_5)(dppm)]^+$, is consistent with the high field signal shown by the phosphorus NMR spectra ($\delta$ −19.31 ppm), typical of the monodentate dppm complexes [10]. Attempts to grow suitable crystals for X-ray structural determination have been unsuccessful. Further studies, exploring the chemical and dynamic relationships between these metallacycles, are in progress.

A full list of atomic parameters, bond lengths, and bond angles has been deposited with the Cambridge Crystallographic Data Centre.

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12 Under anaerobic and anhydrous conditions, a solution of $[Fe(=C=CMe^tBu)(\eta\text{-}C_5H_5)(dppm)][BF_4]$ (0.3 g; 0.4 mmol) in THF (20 mL) was treated at −20°C with an equimolar amount of NaOMe (prepared *in situ* from MeOH (5 mL) and NaH (0.4 mmol) after evaporating the excess of methanol) and the mixture was stirred at room temperature for 1 h. After evaporating to dryness, the resulting solid residue was extracted with diethyl ether and the solution filtered through an Alox 1 column (2×1 cm). Partial concentration of the red solution and cooling gave II as a red crystalline solid (0.18 g; 75% yield). Anal. Found: C, 74.8; H, 6.6. $C_{37}H_{38}P_2Fe$ calcd.: C, 74.0; H, 6.4%. $^1H$ NMR (300 MHz, $C_6D_6$, 23°C): $\delta$ 0.74 (s, 9H, $^tBu$), 2.40 (t, 3H, Me; $^3J(P\text{–}H)$ 8.0 Hz), 4.63 (s, 5H, $C_5H_5$), 5.72 (t, 1 H, CH $(PPh_2)_2$; $^2J(P\text{–}H)$ 3.8 Hz), 6.8–8.1 (m, 20H, $PPh_2$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 23°C): $\delta$ 14.62 (s) ppm. $^{13}C$ NMR (75.4 MHz, $C_6D_6$, 23°C): $\delta$ 25.54 (s, $CMe_3$), 28.52 (m, $CH_3$), 31.01 (s, $(CH_3)_3$), 64.46 (t, $CHPPh_2$; $J(PC)$ 23.8 Hz), 70.23 (s, $C_5H_5$), 127.2–135.8 (m, $PPh_2$) ppm.

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Organometallics, 2 (1983) 101; (b) $[Fe(C(CO_2Et)=CMe_2)(\eta\text{-}C_5H_5)(CO)(PPh_3)]$ (2.030(2) Å) D.L. Reger, P.J. McElliot, E. Mintz, N.G. Cherles, E.A.K. Griffith and E.L. Amma, Organometallics, 1 (1982) 443. (c) D.L. Reger and K.A. Belmore, J. Am. Chem. Soc., 105 (1983) 5710.

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18 Complex III: Air sensitive brown yellow solid. Soluble in diethylether and benzene. Solutions of III decompose slowly at room temperature. $^1$H NMR (300 MHz, toluene-$d_8$, 23°C): $\delta$ 1.75 (s, 3H, $CH_3$), 4.27 (s, 5H, $C_5H_5$), 5.55, 5.77, 6.29, 6.65 (m, 5H, Ph), 6.95–8.07 (m, 20H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-$d_8$, 23°C): $\delta$ 1.1 (d, $^2J$(PP) 106.6 Hz), 68.9 (d, $^2J$(PP) 106.6 Hz) ppm.

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20 Complex IV: $^1$H NMR (300 MHz, toluene-$d_8$, 0°C): $\delta$ 1.81 (t, 3H, $CH_3$; $^5J$(P–H) 7.2 Hz), 4.09 (s, 5H, $C_5H_5$), 5.26 (t, 1H, CH $(PPh_2)_2$; $^3J$(P–H) 3.6 Hz), 6.7–7.6 (m, 25H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-$d_8$, 0°C): $\delta$ 17.6 (s) ppm.