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Reactions of cationic vinylidene complexes $[Fe\{=C=C(R^1)R^2\}(\eta\text{-}C_5H_5)(dppm)]^+$ [dppm = bis(diphenylphosphino)methane] with nucleophiles: stereoselective synthesis and crystal structure of the alkenyl complex (E)-$[Fe\{C(H)=C(Me)Ph\}(\eta\text{-}C_5H_5)(dppm)]$

M. Pilar Gamasa, José Gimeno, Elena Lastra,

Departamento de Quìmica Organometálica, Facultad de Quìmica, Universidad de Oviedo, E-33071 Oviedo (Spain)

Maurizio Lanfranchi and Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma (Italy)

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Abstract

The reactivity of the cationic vinylidene complexes $[Fe\{=C=C(R^1)R^2\}(\eta\text{-}C_5H_5)(dppm)]^+$ toward different nucleophiles has been investigated. Whereas the disubstituted complexes (R^1 = Me; R^2 = Ph or ^{t}Bu) are unreactive with water and methanol, the addition of the anion hydride proceeds stereoselectively to give the alkenyl E isomers. The structure of (E)-$[Fe\{C(H)=C(Me)Ph\}(\eta\text{-}C_5H_5)(dppm)]$ has been determined by an X-ray diffraction study. Nucleophilic additions to the unsubstituted complex ($R^1 = R^2$ = H) have also been examined.

The most significant reactions of vinylidene complexes are nucleophilic attacks at C_α. Although such processes, especially for systems of the type $[M\{=C=C(R^1)R^2\}(\eta\text{-}C_5H_5)L_2]^+$ (M = Fe or Ru), are well documented both theoretically [1] and experimentally [2], the influence of the metal auxiliary and the vinylidene substituents on the regio- and stereochemistry [2] has yet to be investigated in detail. For a particular metal auxiliary, it is well known that the overall rate of the reactions depends on the size of the substituents on the vinylidene group [3]. The relative size can also determine the stereochemistry of the nucleophilic addition, as shown recently by Davis *et al.* [4] in the reaction of NaCN with $[Ru\{=C=C(Me)Ph\}(\eta\text{-}C_5H_5)(PMe_3)_2]^+$ which leads with high stereoselectivity to the formation of (Z)-$[Ru\{C(CN)=C(Me)Ph\}(\eta\text{-}C_5H_5)(PMe_3)_2]$. We have recently

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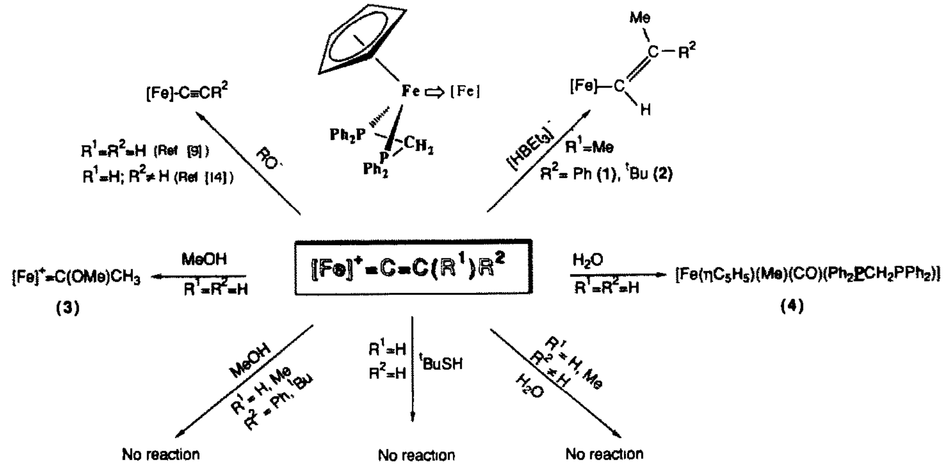
Correspondence to: Professor J. Gimeno, Departamento de Quìmica Organometálica, Facultad de Quìmica, Universidad de Oviedo, E-33071 Oviedo, Spain; or Professor A. Tiripicchio, Istituto di Chimica Generale ed Inorganica, Università di Parma, Viale delle Scienze 78, I-43100 Parma, Italy.



Scheme 1.

described [5] the synthesis of cationic vinylidene complexes of the type $[Fe]^+{=}C{=}C(R^1)R^2$ ($[Fe] = Fe(\eta\text{-}C_5H_5)(L\text{-}L)$; L–L = bis(diphenylphosphino)-methane (dppm) or bis(dimethylphosphino)methane (dmpm)) in which the substituents R^1 and R^2 are groups with different steric and electronic properties. This has enabled us to explore their reactivity systematically. We describe here the nucleophilic addition of hydride to the vinylidene complexes $[Fe\{{=}C{=}C(R)Me\}(\eta\text{-}C_5H_5)(dppm)]^+$ ($R = Ph$ or ${}^tBu$) which proceeds stereoselectively to give the alkenyl complexes (E)-$[Fe\{C(H){=}C(Me)R\}(\eta\text{-}C_5H_5)(dppm)]$. We have also examined the reactivity of the unsubstituted vinylidene complex $[Fe({=}C{=}CH_2)(\eta\text{-}C_5H_5)(dppm)]^+$ toward typical nucleophiles such as water, methanol, and t-butylthiol, and the behaviour of the corresponding mono- and di-substituted derivatives, which in contrast are unreactive to the same reagents. The results are summarized in Scheme 1.

A solution of $Li[HBEt_3]$ in hexane was added to a solution of $[Fe\{{=}C{=}C(R)Me\}(\eta\text{-}C_5H_5)(dppm)]^+$ ($R = Ph$ or ${}^tBu$) in tetrahydrofuran (THF) at −20°C. After warming to room temperature and removal of the solvent the crude residue was extracted with diethyl ether to give complexes **1** (75%) and **2** (70%) as red crystalline solids.

The complexes were chemically and spectroscopically characterized [6*] as alkenyl derivatives. Significantly, the proton NMR spectrum of **2** shows the hydrogen vinylic resonance as a triplet at δ 6.72 ppm (${}^3J(PH) = 8.9$ Hz). ${}^{13}C\{{}^1H\}$ NMR spectra of **1** and **2** show the expected signals of the alkenyl α-carbon atom (δ 155.0 and 140.7 ppm, respectively) along with singlet resonances (δ 25.4 and 20.55 ppm, respectively) assigned to the methyl groups. The appearance of singlet signals is in accord with a *cis* arrangement of the metal auxiliary [Fe] and the methyl groups about the carbon–carbon double bond, for which a P–C coupling is not to be expected [7]. To confirm the configuration of the alkenyl group, the crystal structure of the pentane solvate of **1** was determined by an X-ray diffraction study [8*]. The structure is shown in Fig. 1 together with the most significant bond

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

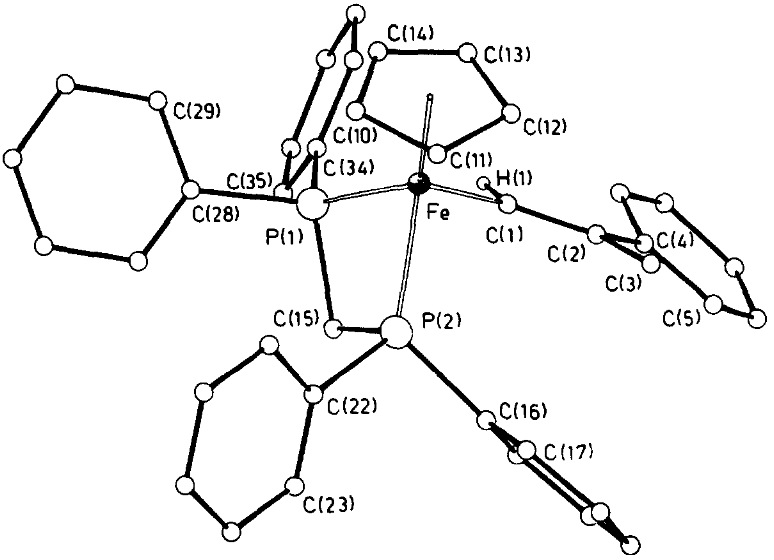
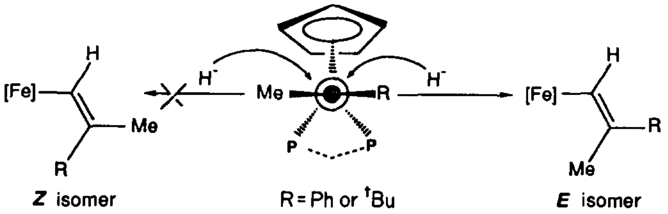


Fig. 1. A view of the complex (E)-[Fe{C(H)=C(Me)Ph}(η-C_5H_5)(dppm)] (1) with the most important bond lengths (Å) and angles (deg): Fe–P(1) 2.150(4), Fe–P(2) 2.176(4), Fe–C(1) 1.987(14), Fe–CE 1.68(2) (CE is the centroid of the cyclopentadienyl ring), C(1)–C(2) 1.36(2), C(2)–C(3) 1.50(2), C(2)–C(4) 1.49(2); P(1)–Fe–P(2) 74.4(2), P(1)–Fe–C(1) 86.7(4), P(2)–Fe–C(1) 85.5(4), CE–Fe–C(1) 124.5(8), CE–Fe–P(1) 129.4(8), CE–Fe–P(2) 138.1(7), Fe–C(1)–C(2) 133(1), C(1)–C(2)–C(3) 125(1), C(1)–C(2)–C(4) 120(1), C(3)–C(2)–C(4) 115(1).

distances and angles. The geometry of the Fe(η-C_5H_5)(dppm) moiety is similar to those found in other structures [5,9] and the Fe–C(1) bond length, 1.987(14) Å, is in the range found by typical Fe–C(sp^2) bonds [10,11]. The alkenyl complex adopts the E configuration and the vinyl group orientation deviates remarkably from right-angles to the plane containing Fe–C(1)–CE (CE is the centroid of the cyclopentadienyl ring which should be preferred according to theoretical calculations [1]. The dihedral angle between this plane and Fe–C(1)–C(2) is 68(1)°. Analogous iron alkenyl complexes also show alkenyl moiety deviations from the right-angle position *e.g.* [Fe{σ-C(CO_2Et)=CMe_2}(η-C_5H_5)(CO)(PPh_3)] (82.8(2)°) [10], (Z)-[Fe{C(Me)=C(Ph)Me}(η-C_5H_5)(CO){P$(OPh)_3$}] (59.3(1)°) [11]. The Fe-C(1)–H(1)–C(2)–C(3)–C(4) moiety is planar, with the phenyl group tilted by 25.9(4)°.

Since the reaction only leads to the formation of the E isomer, nucleophilic addition (*syn* to the phenyl or ^{t}Bu group, the bulkier vinylidene substituents) presumably proceeds without any steric obstruction.



This contrasts with the additions of methyl and PPh_3 to the similar iron asymmetric vinylidene complexes $[Fe\{=C=C(R)Ph\}(\eta\text{-}C_5H_5)(CO)(PPh_3)]^+$, for which the thermodynamically less stable *Z* isomers (*syn* addition to the smaller substituent of the vinylidene group) are obtained, *i.e.* (*Z*)-$[Fe\{C(Nu)=C(R)Ph\}(\eta\text{-}C_5H_5)(CO)(PPh_3)]^+$ (R = H; Nu = PPh_3) [12], (R = Me; Nu = Me, 93 and 7% of the *Z* and *E* isomers, respectively) [13]. This seems to indicate that nucleophilic attack proceeds by thermodynamic control to give a stereoselective addition, due to the relatively small size of the hydride. The influence of the substituents on the ability of the vinylidene group to undergo nucleophilic additions is clearly shown by the behaviour toward typical nucleophiles [14*]. Thus, whilst mono- and di-substituted vinylidene complexes $[Fe]^+=C=C(R^1)R^2$ (R^1 = H; R^2 = Ph or ${}^tBu$. R^1 = Me; R^2 = Ph or ${}^tBu$) (see Scheme 1) are stable in refluxing methanol or in the presence of water, the unsubstituted derivative $R^1 = R^2 = H$ undergoes the expected transformations to give the methoxycarbene complexes **3** and **4**, respectively. The latter monocarbonyl complex is probably formed by the deprotonation of the unstable hydroxycarbene complex $[Fe]^+=C(OH)CH_3$, initially formed, followed by a migratory deinsertion of the methyl group. This process has also been described for the analogous ruthenium complex $[Ru\{=C=C(H)Ph\}(\eta\text{-}C_5H_5)(PPh_3)_2]^+$ [15]. However, no reaction is observed with t-butylthiol, which is a stronger nucleophile than methanol, after refluxing a solution in tetrahydrofuran for 2 h, indicating steric restrictions of nucleophilic attack due to the bulky size of the thiol. The influence on the metal of the chelating small-bite dppm is also evident since the analogous complex $[Fe\{=C=CH_2\}(\eta\text{-}C_5H_5)(dppe)]^+$ is unreactive toward alcohols and water [16].

Although at present a systematic study of the reactivity has not been completed, these results reveal that nucleophilic attack on a vinylidene system can be properly controlled by a careful selection of the steric and electronic properties of the metal-containing moiety as well as of the vinylidene substituents.

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6 Key spectroscopic data for the compounds **1** and **2**. Compound **1**: ${}^1H$ NMR (C_6D_6): δ 1.59 (s, 3H, CH_3), 3.25 (m, 1H, CH_aP), 3.86 (m, 1H, CH_bP), 4.42 (s, 5H, C_5H_5), 6.9–7.5 (m, 20H, Ph_2P) ppm; ${}^{31}P\{{}^1H\}$ NMR δ 46.43 s ppm; ${}^{13}C\{{}^1H\}$ NMR δ 25.4 (s, CH_3), 44.75 (m, CH_2P), 76.6 (s, C_5H_5), 124–132 (m, Ph_2P), 155 (m, FeC_α) ppm. Compound **2**: ${}^1H$ NMR (C_6D_6): δ 1.03 (s, 9H, ${}^tBu$), 1.38 (s, 3H, CH_3), 3.20 (m, 1H, CH_aP), 3.89 (m, 1H, CH_bP), 4.42 (s, 5H, C_5H_5), 6.72 (t, ${}^3J$(P–H) 8.9 Hz, FeCH), 7.0–7.4 (m, 20H, Ph_2P) ppm; ${}^{31}P\{{}^1H\}$ NMR δ 46.45 s ppm; ${}^{13}C\{{}^1H\}$ NMR δ 20.55 (s, CH_3),

28.5 (s, CMe_3), 31.1 (s, $(CH_3)_3$), 43.5 (t, J(C–P) 21 Hz, CH_2P), 76.45 (s, C_5H_5), 127–132 (m, Ph_2P), 140.7 (m, FeC_α) ppm.

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8 Crystal data for the pentane solvate of **1**, $C_{39}H_{36}FeP_2\cdot\frac{1}{2}C_5H_{12}$, $M = 658.58$, monoclinic, space group $P2_1/n$, $a = 9.756(4)$, $b = 18.014(6)$, $c = 20.199(6)$ Å, $\beta = 99.02(2)°$, $V = 3506(2)$ Å^3, $Z = 4$, $D_c = 1.248$ g cm^{-3}, $F(000) = 1388$, niobium-filtered Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu = 5.45$ cm^{-1}. The intensity data were collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 4914 Unique reflections were measured, with θ in the range 3–23°; 1577 having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms excepting the carbon atoms of the dppm ligand. In the final ΔF map a pentane molecule of solvation close to a symmetry centre was found disordered and distributed in two positions with equal occupancy factor. All hydrogen atoms, excepting H(1) which was clearly localized and refined isotropically, were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atoms. The R and R_w values were 0.0651 and 0.0738. Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

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