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Preparation of acetylide and propadienylidene complexes of iron(II)

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Abstract

Depending on the nature of the phosphine ligands, the reaction of phosphite-containing FeCl₂ solutions with propargylic alcohols $HC \equiv CCRR'(OH)$ affords propadienylidene [Fe(=C=C=CPh₂){P(OEt)₃}₅](BPh₄)₂ and [FeCl(=C=C=CPh₂){PPh(OEt)₂}₄]BPh₄ complexes and acetylide [Fe{C=CCRR'(OH)}{P(OEt)₃}BPh₄ derivatives (R = R' = Ph; R = Me, R' = Ph). In contrast, the reaction of phosphite-containing FeCl₂ solutions with terminal alkynes RC=CH affords mononuclear [Fe(C=CPh){P(OEt)₃}]BPh₄ and binuclear [Fe[P(OEt)₃]₅](µ-1,4-C=CC₆H₄C=C)](BPh₄)₂ acetylide derivatives. All the new complexes were characterised by IR and ¹H, ³¹P and ¹³C NMR data, and a geometry in solution was also established. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Iron; Acetylide; Vinylidene; Propadienylidene

1. Introduction

The chemistry of transition-metal allenylidene complexes [1] $[M]=C=C=CR_2$ continues to attract interest, both due to their potential usefulness in organic synthesis [2] and their interesting reactivity [3]. A number of complexes have been synthesised in recent years [1], generally by reacting propargylic alcohols with appropriate transition metal derivatives, and involving, as metal centres, the Cr and Fe triads, Mn, Re, Rh and Ir. Of these, ruthenium allenylidene constitutes the largest group; relatively few examples are reported for iron. In fact, apart from the cyclopentadienyl [CpFe(=C=C= CPh_2)(dppe)]BF₄ and [Cp*Fe{=C=C=C(OMe)Me}(dppe)]BPh₄ (dppe=Ph₂PCH₂CH₂PPh₂) species [4], only carbonyl complexes [5] of the type [Fe(=C=C= CRR')(CO)₂P₂][P = P(OMe)₃, PEt₃] and [Fe(=C=C= $CRR')(CO)_4$ are described.

We previously reported [6] the reactions of terminal alkynes with phosphite-containing iron(II) complexes which led to enynyl, acetylide and vinylidene complexes. We have now extended these studies to include propargylic alcohols. Both new propadienylidene and acetylide iron(II) complexes can be prepared, and the results of these investigations are reported here.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out under an inert atmosphere (Ar or N₂) using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes turned out to be quite air-stable and were stored at -25 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Anhydrous FeCl₂ was purchased from Chempur and used as received. Phenyldiethoxyphosphine (PPh(OEt)₂) was prepared by the method of Rabinowitz and Pellon [7]; triethylphosphite was an Aldrich product, purified by distillation under nitrogen. Alkynes PhC=CH and HC= $CCPh_2(OH), HC \equiv CCHPh(OH), HC \equiv CCH_2(OH), HC \equiv$ CCMePh(OH) were Aldrich products, used without further purification. 1,4-Diethynylbenzene was prepared following the method previously reported [8]. Other reagents were purchased from commercial sources in the highest available purity and used as received. IR spectra were recorded on Digilab Bio-Rad FTS-40 or Nicolet Magna 750 FT-IR spectrophotometers. NMR spectra (¹H, ¹³C, ³¹P) were obtained on a Bruker AC200 spectrometer at temperatures between -90 and +30 °C, unless otherwise stated. ¹H and ¹³C $\{^{1}H\}$ spectra are referred to internal tetramethylsilane; ${}^{31}P{}^{1}H$

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chemical shifts are reported with respect to 85% H₃PO₄, with downfield shifts considered positive. The SwaN-MR software package [9] was used to treat NMR data. The conductivity of 10^{-3} mol dm⁻³ solutions of the complexes in MeNO₂ at 25 °C was measured with a CDM 83 Radiometer.

2.2. Synthesis of complexes

2.2.1. $[Fe(=C=C=CPh_2) \{P(OEt)_3\}_5](BPh_4)_2$ (1) and $[Fe\{C=CCPh_2(OH)\} \{P(OEt)_3\}_5](BPh_4)_3$ (3a)

Anhydrous FeCl₂ (0.126 g, 1 mmol) and an excess of $P(OEt)_3$ (1 cm³, 6 mmol) were placed in a three-necked flask (25 cm³). The suspension was stirred for 1 h and then 10 cm³ of EtOH and a solution of HC= $CCPh_2(OH)$ (0.208 g, 1 mmol) in 2 cm³ of EtOH were added. The reaction mixture was stirred for 2 h, treated with an excess of NEt₃ (0.28 cm³, 2 mmol), and stirred for a further 2 h. The solvent was removed under reduced pressure, giving an oil which was treated with EtOH (4 cm³) containing an excess of NaBPh₄ (0.68 g, 2 mmol). A dark-pink solid, containing both compounds 1 and 3a, slowly separated out, and was filtered and crystallised fractionally. Typical separation involved the slow cooling to -25 °C of a saturated solution of the mixture of compounds in EtOH (5 cm³) and enough CH_2Cl_2 to dissolve the solid at room temperature (r.t.). The first solid separated was acetylide 3a, with yield: \geq 15%; propadienylidene 1 was obtained with yield: \geq 40%.

Anal. Calc. for $C_{93}H_{125}B_2FeO_{15}P_5$ (1): C, 65.1; H, 7.3. Found: C, 65.2; H, 7.2%. $\Lambda_M = 121.4 \text{ S cm}^2 \text{ mol}^{-1}$.

Anal. Calc. for $C_{69}H_{106}BFeO_{16}P_5$ (**3a**): C, 58.7; H, 7.6. Found: C, 58.9; H, 7.5%. $\Lambda_M = 56.7 \text{ S cm}^2 \text{ mol}^{-1}$.

2.2.2. $[FeCl(=C=C=CPh_2) \{PPh(OEt)_2\}_4]BPh_4(2)$

A suspension of anhydrous FeCl₂ (0.126 g, 1 mmol) in an excess of PPh(OEt)₂ (1.2 cm³, 6 mmol) was stirred for 1 h and then a solution of HC=CCPh₂(OH) (0.208 g, 1 mmol) in 10 cm³ of EtOH was added. The reaction mixture was stirred for 2 h and then an excess of NEt₃ (0.28 cm³, 2 mmol) was added. After 2 h of stirring, the solvent was evaporated to dryness, giving an oil which was treated with EtOH (4 cm³) containing an excess of NaBPh₄ (0.68 g, 2 mmol). A dark-pink solid separated out, and was filtered and crystallised from CH₂Cl₂ (2 cm³) and EtOH (5 cm³); yield: $\geq 55\%$.

Anal. Calc. for C₇₉H₉₀BFeClO₈P₄: C, 68.1; H, 6.5; Cl, 2.5. Found: C, 68.0; H, 6.3; Cl, 2.7%. $\Lambda_{\rm M} = 51.3$ S cm² mol⁻¹.

2.2.3. $[Fe\{C \equiv CCMePh(OH)\}\{P(OEt)_3\}_5]BPh_4(3b)$

Anhydrous FeCl₂ (0.126 g, 1 mmol) and an excess of $P(OEt)_3$ (1 cm³, 6 mmol) were placed in a three-necked flask (25 cm³). The suspension was stirred for 1 h and then EtOH (10 cm³) and HC=CCMePh(OH) (0.15 g, 1

mmol) were added. The reaction mixture was stirred for 2 h and an excess of NEt₃ (1.4 cm³, 10 mmol) was added. After 2 h of stirring at r.t., the solvent was removed under reduced pressure, giving a brown oil which was treated with EtOH containing an excess of NaBPh₄ (0.68 g, 2 mmol). A brown solid slowly separated out from the resulting solution, which was filtered and crystallised from CH₂Cl₂ (2 cm³) and EtOH (5 cm³); yield: \geq 30%.

Anal. Calc. for $C_{64}H_{104}BFeO_{16}P_5$: C, 56.9; H, 7.8. Found: C, 57.2; H, 8.0%. $\Lambda_M = 50.4$ S cm² mol⁻¹.

2.2.4. $[Fe(C \equiv CPh) \{P(OEt)_3\}_5]BPh_4(3c)$

Anhydrous FeCl₂ (0.63 g, 5 mmol) and an excess of $P(OEt)_3$ (5.0 cm³, 30 mmol) were placed in a threenecked flask (50 cm³), and the resulting suspension was stirred for about 1 h. EtOH (15 cm³) and then an excess of the appropriate alkyne (15 mmol) were added and the reaction mixture refluxed for 15 min. The solvent was removed under reduced pressure, giving an oil which was treated with EtOH (4 cm³) containing an excess of NaBPh₄ (3.42 g, 10 mmol). A yellow solid slowly separated out, and was filtered and crystallised from CH₂Cl₂ (2 cm³) and EtOH (5 cm³); yield: $\geq 35\%$.

Anal. Calc. for $C_{62}H_{100}BFeO_{15}P_5$: C, 57.0; H, 7.7. Found: C, 56.8; H, 7.8%. $\Lambda_M = 58.5 \text{ s cm}^2 \text{ mol}^{-1}$.

2.2.5. $[{Fe[P(OEt)_3]_5}_2(\mu-1,4-C \equiv CC_6H_4C \equiv C)](BPh_4)_2(4)$

An excess of P(OEt)₃ (1.0 cm³, 6 mmol) was added to 0.126 g (1 mmol) of anhydrous $FeCl_2$ in a 25-cm³ threenecked flask and the resulting suspension stirred for 1 h. Tetrahydrofurane (10 cm³) and a solution of 1,4-HC= $CC_6H_4C \equiv CH$ (63 mg, 0.5 mmol) in 3 cm³ in THF were added and, after 2 h of stirring, an excess of NEt₃ (1.4 cm³, 10 mmol) was further added. The reaction mixture was stirred for 3 h and then the solvent evaporated to dryness under reduced pressure, giving a brown oil which was treated with 4 cm³ of EtOH. The addition to the resulting solution of an excess of NaBPh₄ (0.68 g, 2 mmol) in 2 cm^3 of EtOH caused the separation of an orange-brown solid, which was filtered and crystallised from CH₂Cl₂ (2 cm³) and EtOH (5 cm³); yield: $\geq 25\%$. Anal. Calc. for C₁₁₈H₁₉₄B₂Fe₂O₃₀P₁₀: C, 55.9; H, 7.7. Found: C, 56.1; H, 7.8%. $\Lambda_{\rm M} = 124.5 \text{ S cm}^2 \text{ mol}^{-1}$.

3. Results and discussion

Propadienylidene complexes $[Fe(=C=C=CPh_2)-{P(OEt)_3}_5](BPh_4)_2$ (1) and $[FeCl(=C=C=CPh_2)-{PPh(OEt)_2}_4]BPh_4$ (2) were prepared by allowing iron(II) chloride solutions containing an excess of phosphite to react with propargylic alcohol, as shown in Scheme 1.



The reaction depends on the nature of the phosphite, affording pentakis complex 1 with $P(OEt)_3$, or chloroderivative 2 with $PPh(OEt)_2$. Furthermore, a mixture of propadienylidene 1 and acetylide 3a (ratio 2.7:1) forms in the case of Eq. (1), and these were separated by fractional crystallisation. The formation of both complexes 1 and 3a is not surprising, as propargylic alcohol probably tautomerises on the iron centre (Scheme 2), giving a hydroxy-vinylidene [A] which, in the presence of NEt₃, can either lose H₂O to give propadienylidene 1 or undergo deprotonation, affording the new acetylide 3a (Scheme 2).

Phosphite-containing FeCl₂ solutions in ethanol probably contain a mixture of phosphite complexes of the type $[FeClP_5]^+$, $FeCl_2P_4$ and $[FeP_6]^{2+}$, analogous to those observed in THF as solvent [10], with the pentakis species predominating in the case of P(OEt)₃. Treatment of these solutions with HC=CCPh₂OH may afford intermediates of type [**A**], whose reaction with NEt₃ gives final species **1** and **3a**. In contrast, in the case of PPh(OEt)₂, a hydroxy-vinylidene of the type



Scheme 2. $[Fe]^+ = [FeClP_5]^+$.

 $[FeCl{PPh(OEt)_2}_4{=C=C(H)C(OH)Ph_2}]^+$ may form, yielding chloropropadienylidene **2** by treatment with NEt₃. However, an acetylide complex of the type $[FeCl{C=CCPh_2(OH)}{PPh(OEt)_2}_4]$ may also form by treatment with NEt₃, but in this case probably in low yield, and this prevents its separation as a solid.

The reactions with $HC \equiv CPh_2(OH)$ were also studied in the presence of Brønsted acid (HBF₄, CF₃SO₃H), but no evidence of formatione of propadienylidene complexes was detected. This result is rather surprising, because an acid is generally used to promote the loss of H_2O in hydroxy-vinylidene species to give the =C=C= CPh_2 ligand while, in our case, only in the presence of NEt₃ the propadienylidene species **1**, **2** were isolated. Probably, the hydroxy-vinylidene bound to an iron fragment containing phosphites as ancillary ligands requires NEt₃ to give propadienylidene, and the results show as both acid and basic media can promote the loss of H_2O in the reaction of propargylic alcohol.

Propargylic alcohols different from $HC = CCPh_2(OH)$, of the type HC = CCPhMe(OH), $HC = CCH_2(OH)$, or HC = CCHPh(OH), also react with phosphite-containing $FeCl_2$ solutions, but afford mixtures of products whose IR spectra exclude the presence of propadienylidene ligands. However, in the case of HC = CCMePh(OH), a pale-yellow solid was isolated, which was characterised as the acetylide $[Fe{C=CCMePh(OH)}{P(OEt)_3}_5]BPh_4$ (**3b**) derivative (Scheme 3).

These results on the reactivity of propargylic alcohols with phosphite-containing iron(II) solutions indicate that the nature of both the phosphite ligand and the acetylene play an important role in determining the reaction course and the stoichiometry of the final products. In fact, only with the diphenyl HC= CCPh₂(OH) species can propadienylidene complexes **1** and **2** be prepared, containing the pentakis(phosphite) FeP₅ fragment in the case of P(OEt)₃ (**1**); with the bulkier PPh(OEt)₂ ligand, chloro-species [FeClP₄(=C= C=CPh₂)]⁺ (**2**) was obtained. Acetylide species **3** can also be prepared, but only in the case of the compound with P(OEt)₃ ligand do solid samples result.

Good analytical data were obtained for propadienylidene complexes 1 and 2, which are purple solids stable in air and in solution of polar organic solvents, where they behave as 2:1 (1) or 1:1 (2) electrolytes [11].



Scheme 3.

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Table 1											
IR	and	NMR	data	for	iron	complexes					

	Compound	IR ^a		¹ H NMR ^{b,c}		Spin system	$^{31}P\{^{1}H\}$ NMR ^{b,d}	$^{13}C{^{1}H} NMR^{b,e}$	
		\overline{v} (cm ⁻¹)	Assgnt	δ	Assgnt		δ (J Hz)	δ (J Hz)	Assgnt
1	$[Fe(=C=C=CPh_2){P(OEt)_3}_5]-(BPh_4)_2$	1950 m	v(C=C=C)	4.04 (m) 1.40 (t) 1.24 (t)	POCH ₂ CH ₃ POCH ₂ CH ₃	AB ₄	$\delta_{A} 139.9$ $\delta_{B} 138.4$ $J_{AB} = 119.3$	320.0 (m, br) 230.3 (m, br) 148.4 (s) 63.2 (s, br) 16.1 (s, br)	C_{α} C_{β} C_{γ} $POCH_2CH_3$ $POCH_2CH_3$
2	$\label{eq:constraint} \begin{split} & [FeCl(=C=C=CPh_2)\{PPh(OEt)_2\}_4]\text{-}\\ & BPh_4 \end{split}$	1918 m	v(C=C=C)	3.62 (br) 1.12 (br)	POCH ₂ CH ₃ POCH ₂ CH ₃	$\begin{array}{c}A_4\\A_2B_2\end{array}{}^f$	156 (br) δ_{A} 169.3 δ_{B} 157.6 $J_{AB} = 73.0$	319.7 (qnt) $J_{CP} = 27$ 239.7 (s, br) 152.5 (s) 64.9 (s, br) 16.1 (s, br)	C_{α} C_{β} C_{γ} $POCH_{2}CH_{3}$ $POCH_{2}CH_{3}$
3a	[Fe{C=CCPh ₂ (OH)}{P(OEt) ₃ } ₅]- BPh ₄	2091 m	v(C≡C)	4.20 (m) 1.40 (t) 1.37 (t)	POCH ₂ CH ₃ POCH ₂ CH ₃	AB ₄	$\delta_{A} 154.8$ $\delta_{B} 152.3$ $J_{AB} = 107.2$	120.1 (m) 103.1 (m) 75.5 (s) 63.2 (s, br) 62.4 (d) 16.1 (s, br)	C_{β} C_{α} C_{γ} POCH ₂ CH ₃ POCH ₂ CH ₂
3b	Fe{C=CCMePh(OH)}{P(OEt) ₃ } ₅]- BPh ₄	2074 m	v(C≡C)	8.65 (br) ^g 4.26 (m) 4.14 (m) 1.34 (t) 1.29 (t)	OH POCH ₂ CH ₃ POCH ₂ CH ₃	AB ₄ ^g	$\delta_{A} \ 155.5$ $\delta_{B} \ 152.7$ $J_{AB} = 106.5$	119.2 (m) g $110.3 (m)$ $63.0 (s, br)$ $62.1 (d)$ $46.9 (s)$ $16.2 (s)$ $8.87 (s)$	C_{β} C_{α} $POCH_{2}CH_{3}$ C_{γ} $POCH_{2}CH_{3}$ $C(CH_{3})$
3c	[Fe(C=CPh){P(OEt) ₃ } ₅]BPh ₄	2089 m	ν(C≡C)	4.31 (br) ^g 4.16 (br) 1.34 (t, br)	POCH ₂ CH ₃ POCH ₂ CH ₃	AB ₄ ^g	δ_{A} 154.8 δ_{B} 151.5 $J_{AB} = 105.8$	119.0 (m) 108.7 (m) [AB ₄ X system: δ_X 108.7 $J_{AX} = -22.25$ $J_{BX} = 47.3$] 62.7 (s, br) 61.6 (d) 15.9 (s, br)	C_{β} C_{α} POCH ₂ CH ₃
4	$[\{Fe[P(OEt)_3]_5\}_2(\mu-1,4-C=CC_6H_4C=C)](BPh_4)_2$	2085 m	<i>v</i> (C≡C)	4.29 (m) 1.33 (t, br)	POCH ₂ CH ₃ POCH ₂ CH ₃	AB ₄	$\delta_{A} 155.2 \\ \delta_{B} 152.3 \\ J_{AB} = 106.5$	13.9 (S, Dr)	POCH ₂ CH ₃

^a In KBr pellets.

^b In CD_2Cl_2 at 25 °C.

^c Phenyl proton resonances are omitted.

^d Positive shift downfield from 85% H₃PO₄.

^e Phenyl carbon resonances are omitted.

^g In (CD₃)₂CO.

The IR and NMR data (Table 1) support the proposed formulation and allow a geometry in solution to be established. The IR spectra show a mediumintensity band at 1950 cm⁻¹ for 1 and 1918 cm⁻¹ for 2, attributed to the $v_{(C=C=C)}$ of the propadienylidene ligand. However, support for the presence of the $=C_{\alpha}=C_{\beta}=C_{\gamma}Ph_2$ group in the complexes comes from the $^{13}C\{^{1}H\}$ NMR spectra, which show the characteristic highly deshielded C_{α} carbon resonance at 320.0 ppm for 1 and 319.7 ppm for 2. The spectra also reveal the signals due to the C_{β} and C_{γ} of the propadienylidene ligand at 239.7–230.3 and 152.5–148.4 ppm, respectively.

In the temperature range +20 to -80 °C, the ${}^{31}P{}^{1}H{}$ NMR spectrum of the $[Fe(=C=C=CPh_2)P_5]^{2+}$ cation 1 appears as an AB₄ multiplet, in agreement with geometry (I). In contrast, the ${}^{31}P$ spectrum of the related complex $[FeCl(=C=C=CPh_2)P_4]^+$ (2) is temperature-

^f At -70 °C.

dependent and the sharp singlet which appears at + 20 °C changes as temperature falls and resolves into an A₂B₂ multiplet at -50 °C.

These results are difficult to interpret, because octahedral geometry with the halogenide and propadienylidene ligands in a mutually *cis* position should give an ABC₂- or AB₂C-type multiplet, whereas, in *trans* geometry, a sharp singlet is expected. However, the presence of inequivalent phosphorus *nuclei* at low temperature for **2** may also be interpreted on the basis of *trans* geometry (II), in which the four PPh(OEt)₂ phosphite ligands are made inequivalent by the different arrangement of the phenyl and ethoxy groups of one phosphite with respect to the other.

Examples of inequivalent phosphorus *nuclei* in octahedral complexes containing four PPh(OEt)₂ ligands in a plane have recently been reported for FeHCl[P-Ph(OEt)₂]₄ [6c], MnH(CO)[PPh(OEt)₂]₄ [12] and [Re-Cl(ArN₂){PPh(OEt)₂}₄]⁺ [13]. These precedents support the hypothesis of the existence, for **2**, of *trans* geometry in which restricted rotation around the Fe–P bond at low temperature makes the phosphite ligands 'two-by-two' inequivalent in the complex.

The IR spectra of acetylide complexes **3a** and **3b** show the $v_{(C=C)}$ of the acetylide ligand as a medium-intensity band at 2091 cm⁻¹ for **3a** and 2074 cm⁻¹ for **3b**. The ¹³C{¹H} NMR spectra also confirm the presence of the acetylide ligand in both complexes showing the characteristic C_{α} and C_{β} carbon signals at 110.3–103.1 and 120.1–119.2 ppm, respectively (Table 1). They also show the signals of the C_{γ} carbon atoms at 46.9 (**3b**) and 75.5 ppm (**3a**), and the proton NMR spectrum of **3b** displays a broad signal at 8.65 ppm, attributed to the OH group of the C=CCMePh(OH) ligand. Lastly, an AB₄ multiplet is present for both complexes in the ³¹P spectra, in agreement with the proposed formulation.

The results obtained with propargylic alcohols prompted us to extend study to other terminal alkynes. The results are summarised in Scheme 4 and show the formation of pentakis(phosphite) acetylide complexes **3c** and **4**. However, while the mononuclear complexes **3** had previously been prepared by us (except **3c**) following a different method [6], the dinuclear [{FeP₅}₂(μ -4,4'-C=CC₆H₄C=C)]²⁺ (**4**) is new, and was isolated as a pale-yellow solid and characterised.

The formation of acetylide in these reactions is not surprising, and probably involves deprotonation of a vinylidene =C=C(H)R intermediate of the type [Fe{= C=C(H)R}P₄]²⁺. Such a vinylidene ligand probably formes by a 1,2-hydrogen shift of a coordinate η^2 -alkyne group [14–16]. Deprotonation by NEt₃ or an excess of phosphite of the vinylidene intermediate gives the final acetylide derivative.

Analytical and spectroscopic data (Table 1) support the formulation of acetylide complexes **3c** and **4**.



The IR spectra of both mononuclear (3c) and binuclear (4) acetylide complexes show only one medium intensity band, at 2089 and 2085 cm⁻¹, respectively, due to the $v_{C=C}$ of the acetylide ligand. The ¹³C{¹H} NMR spectra of 3c also confirm the presence of the RC=C group, showing the characteristic signals of the C_{α} and C_{β} carbon atoms. Lastly, in the temperature range +30 to -80 °C, the ³¹P spectra of both complexes 3c and 4 appear as AB₄ multiplets, in agreement with the presence of a pentakis(phosphite) fragment in these acetylide derivatives.

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