

Preparation of the alkynyl–hydride complexes $MH(C\equiv CR)\{PPh(OEt)_2\}_4$ of iron and ruthenium

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Received 2 August 1995

Abstract

The hydride $FeClHP_4$ [$P = PPh(OEt)_2$] was prepared by allowing the complex $[FeH(\eta^2-H_2)P_4]BPh_4$ to react with an excess of lithium chloride. Treatment of $FeClHP_4$ with lithium acetylide $Li[RC\equiv C]$ ($R = Ph, p\text{-tolyl}$ or $t\text{-Bu}$) gave the alkynyl–hydride $FeH(C\equiv CR)_4$ derivatives. Related ruthenium $RuH(C\equiv CR)_4$ complexes were also obtained by treating RuH_2P_4 with CF_3SO_3Me , followed by treatment with lithium acetylide. The characterization of the complexes by IR and 1H , ^{31}P and ^{13}C NMR spectroscopy is discussed, along with some studies on the protonation reactions of the alkynyl–hydride derivatives.

Keywords: Iron; Alkynyl compounds; Hydrides; Preparation; Protonation

1. Introduction

Transition-metal–alkynyl complexes [1] continue to attract interest, not only for their strict relationship with the vinylidene derivatives [2,3], of which they are common precursors to and reaction products of, but also for their potential applications in the materials science field [4,5]. Metal σ -acetylide derivatives may be, in fact, precursors of molecules containing a linear array and delocalizable Π -systems [4] or polymeric materials with the properties of non-linear optical materials or liquid crystals [5].

In this contest, a number of acetylide complexes have been prepared with cyclopentadienyl, arene ring and mono- and polydentate phosphines as supporting ligands [1–3] and their synthesis generally involves terminal alkynes, vinylidenes, or the use of alkali-metal acetylides.

Our interest in this field has been devoted to the use of monodentate phosphite ligands $P(OMe)_3$, $P(OEt)_3$ and $PPh(OEt)_2$ and has already led to the synthesis of new alkenyl, enynyl and acetylides complexes [6] of Fe, Ru, and Os. As part of these studies, we now report the synthesis and characterization of new alkynyl–hydride complexes of iron(II) and ruthenium(II) of the type

$MH(C\equiv CR)[PPh(OEt)_2]_4$ together with some results on their reactivity.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out under an appropriate atmosphere (argon, H_2) 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 $-20^\circ C$. All solvents used were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. Diethoxyphenyl phosphine was prepared by the method of Rabinowitz and Pellon [7]. Alkynes were Aldrich products, used without any further purification. Lithium acetylides $Li^+RC\equiv C^-$ ($R = Ph$ or $p\text{-tolyl}$) were prepared by reacting a slight excess of the appropriate acetylene (40 mmol) with lithium (35 mmol, 0.24 g) in 10 cm^3 of THF. Instead, tert-butyl acetylide $Li^+t\text{-BuC}\equiv C^-$ was prepared by adding to a solution of $t\text{-BuC}\equiv CH$ (10 mmol, 1.23 cm^3) in 10 cm^3 of THF cooled to $-80^\circ C$ a solution of $Li^+t\text{-Bu}$ 2.5 M in hexane (8 mmol, 3.2 cm^3). The reaction mixture was stirred for 20–30 min at $-80^\circ C$ and then used. Other reagents were purchased from commercial sources in the highest

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available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Model 683 or Digilab Bio-Rad FTS-40 spectrophotometer. NMR spectra (^1H , ^{13}C , ^{31}P) were obtained on a Bruker AC200 spectrometer at temperatures varying between -90 and $+30^\circ\text{C}$, unless otherwise stated. ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are reported with respect to 85% H_3PO_4 , with downfield shifts considered positive. The conductivity of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25°C was measured with a Radiometer CDM 83 instrument.

2.2. Synthesis of complexes

Hydride species FeH_2P_4 , $[\text{FeH}(\eta^2\text{-H}_2)\text{P}_4]\text{BPh}_4$ and RuH_2P_4 [$\text{P} = \text{PPh}(\text{OEt})_2$] were prepared by the methods previously reported [8].

2.2.1. $\text{FeClH}[\text{PPh}(\text{OEt})_2]_4$ (1)

To a solution of $\text{FeH}_2[\text{PPh}(\text{OEt})_2]_4$ (3 mmol, 2.55 g) in 20 cm^3 of ethanol cooled to -80°C was added a solution of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (3 mmol, 0.43 cm^3 of 54% solution) and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of lithium chloride (45 mmol, 1.90 g) in 10 cm^3 of ethanol was added and the solution stirred until an orange solid began to precipitate out (1–2 h). The precipitation of the solid was completed by reducing the volume of the reaction mixture to about 10 cm^3 by evaporation and then cooling to 0°C . The solid obtained was filtered and crystallised from toluene (15 cm^3) and ethanol (10 cm^3); yield $\geq 60\%$.

Anal. Found: C, 54.05; H, 7.05; Cl, 4.20. $\text{C}_{40}\text{H}_{61}\text{ClFeO}_8\text{P}_4$. Calc.: C, 54.30; H, 6.95; Cl, 4.00%. M.p. 94°C (decomp.).

2.2.2. $\text{FeH}(\text{C}\equiv\text{CR})[\text{PPh}(\text{OEt})_2]_4$ (2) ($R = \text{Ph}(\mathbf{a})$, p -tolyl($\mathbf{b})$ or t -Bu($\mathbf{c})$)

An excess of the appropriate lithium acetylide $\text{Li}^+\text{C}\equiv\text{CR}^-$ (3 mmol, 1.2 cm^3 of 2.5 M solution; in THF) was added to a solution of $\text{FeClH}[\text{PPh}(\text{OEt})_2]_4$ (1 mmol, 0.88 g) in 15 cm^3 of THF. The reaction mixture was stirred for 30 min and then the solvent was removed under reduced pressure. The brown oil obtained was triturated at 0°C with 5 cm^3 of ethanol until a yellow solid precipitated out, which was filtered and purified by chromatography on silica gel. A typical purification involves a 40 cm column (diameter 3 cm) using hexane/diethylether (1:1) as eluent. The first eluted was evaporated to dryness, giving an oil which was treated with 10 cm^3 of ethanol and stirred until the yellow solid precipitated out; yield $\geq 60\%$.

Anal. Found: C, 60.55; H, 6.95. $\text{C}_{48}\text{H}_{66}\text{FeO}_8\text{P}_4$ (2a). Calc.: C, 60.65; H, 7.00%. M.p. 102°C (decomp.).

Anal. Found: C, 60.85; H, 7.00. $\text{C}_{49}\text{H}_{68}\text{FeO}_8\text{P}_4$ (2b). Calc.: C, 61.00; H, 7.10%.

Anal. Found: C, 59.10; H, 7.65. $\text{C}_{46}\text{H}_{70}\text{FeO}_8\text{P}_4$ (2c). Calc.: C, 59.35; H, 7.60%.

2.2.3. $\text{RuH}(\text{C}\equiv\text{CR})[\text{PPh}(\text{OEt})_2]_4$ (3) ($R = \text{Ph}(\mathbf{a})$ or p -tolyl($\mathbf{b})$)

Methyl triflate (1 mmol , 0.11 cm^3) was added to a solution of $\text{RuH}_2[\text{PPh}(\text{OEt})_2]_4$ (1 mmol , 0.90 g) in 20 cm^3 of diethyl ether and the reaction mixture stirred for 2 h. An excess of the appropriate lithium acetylide $\text{Li}^+\text{C}\equiv\text{CR}^-$ (3 mmol, 1.2 cm^3 of 2.5 M solution in THF) and 15 cm^3 of THF were added. After 2 h of stirring, the reaction mixture was evaporated to dryness and treated with 8 cm^3 of ethanol. A pale yellow solid slowly precipitated out, which was then filtered and crystallised from diethylether/ethanol (2:10 cm^3); yield $\geq 75\%$.

Anal. Found: C, 57.70; H, 6.70. $\text{C}_{48}\text{H}_{66}\text{O}_8\text{P}_4\text{Ru}$ (3a). Calc.: C, 57.90; H, 6.70%. M.p. 160°C (decomp.).

Anal. Found: C, 58.45; H, 6.70. $\text{C}_{49}\text{H}_{68}\text{O}_8\text{P}_4\text{Ru}$ (3b). Calc.: C, 58.25; H, 6.80%.

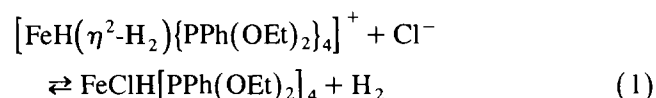
2.3. Protonation reactions

The reactions of the acetylide complexes $\text{MH}(\text{C}\equiv\text{CR})\text{P}_4$ (2 and 3) with the protic acids $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ or $\text{CF}_3\text{SO}_3\text{H}$ were carried out in different solvents such as CH_2Cl_2 , $\text{C}_2\text{H}_5\text{OH}$ or Et_2O operating under an atmosphere of H_2 or argon. The progress of the reactions can be followed by ^1H and ^{31}P NMR spectroscopy: in a typical experiment $30\text{ }\mu\text{mol}$ of the appropriate $\text{MH}(\text{C}\equiv\text{CR})\text{P}_4$ complex in 0.5 cm^3 of CD_2Cl_2 was placed in an NMR tube under the appropriate atmosphere, cooled to -80°C and $30\text{ }\mu\text{mol}$ of HBF_4 or $\text{CF}_3\text{SO}_3\text{H}$ was added. The spectra of these reaction mixtures were registered as the temperature increased, until 0°C was reached, and then for about 1 h at this temperature. However, the products of the protonation reaction can also be separated as solids and identified by IR and NMR spectroscopy. As an example, a solution of $\text{FeH}(\text{C}\equiv\text{CPh})\text{P}_4$ (0.4 mmol , 0.38 g) in 10 cm^3 of diethylether under H_2 (1 atm.) was cooled to -80°C and triflic acid (0.4 mmol , $35\text{ }\mu\text{l}$) was added. The reaction mixture was brought to 0°C and stirred until a solid began to separate out (30 min). After 2 h the solid was filtered, washed with diethylether and dried under vacuum; yield in $[\text{FeH}(\eta^2\text{-H}_2)\text{P}_4]\text{CF}_3\text{SO}_3 \geq 35\%$, in $[\text{Fe}(\text{C}\equiv\text{CPh})\{\text{C}=\text{C}(\text{H})\text{Ph}\}\text{P}_4]\text{CF}_3\text{SO}_3 \geq 30\%$. The protonation reaction can also be carried out in ethanol and the complexes formed separated by precipitation with an excess of NaBPh_4 ; yield in $[\text{FeH}(\eta^2\text{-H}_2)\text{P}_4]\text{BPh}_4 \geq 25\%$, in $[\text{Fe}(\text{C}\equiv\text{CPh})\{\text{C}=\text{C}(\text{H})\text{Ph}\}\text{P}_4]\text{BPh}_4 \geq 35\%$.

3. Results and discussion

The non-classical hydride cation $[\text{FeH}(\eta^2\text{-H}_2)\{\text{PPh}(\text{OEt})_2\}_4]^+$ reacts at room temperature with an excess of

LiCl to give the new species $\text{FeClH}[\text{PPh}(\text{OEt})_2]_4$ (**1**) according to



Owing to equilibrium (1), an excess of lithium chloride must be used to obtain good yields of the hydrido–chloro derivative. Some properties of the complex, which is a diamagnetic orange solid, rather instable in air, are reported in Table 1. The IR spectrum shows the $\nu(\text{Fe-H})$ band at 1960 cm^{-1} , while in the ^1H NMR the characteristic signal of the hydride appears at $+30^\circ\text{C}$ as a well-resolved quintet at -25.61 ppm with J_{PH} of 55 Hz. This quintet broadens as the temperature is lowered and at -80°C appears as a very broad multiplet.

The $^{31}\text{P}\{^1\text{H}\}$ NMR of **1** is temperature-dependent and the slightly broad signal observed at $+30^\circ\text{C}$ changes as the temperature is lowered and resolves into a complicated multiplet of the type shown in Fig. 1. This multiplet indicates the presence of inequivalent phosphorus nuclei and may suggest the existence of a geometry with the hydride and the chloride ligands in a mutually *cis* position. However, the ^{31}P spectra may also be interpreted on the basis of the presence of a

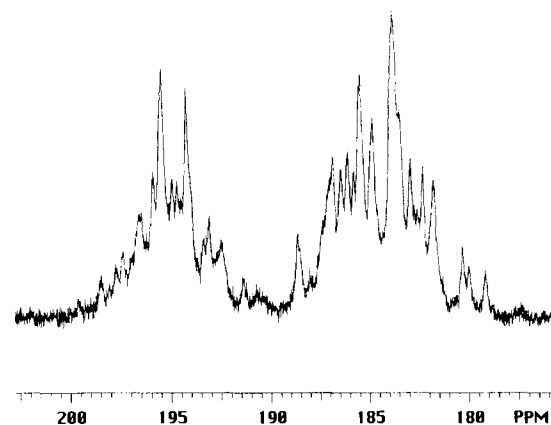


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $\text{FeClH}[\text{PPh}(\text{OEt})_2]_4$ (**1**) in CD_2Cl_2 at -80°C ; see text for details.

trans geometry, in which the phosphite ligands are made inequivalent by the different arrangement of the phenyl and ethoxy groups of one phosphite with respect to the other, i.e., for example, with the phenyl substituent lying on one side of an approximate plane of the four P atoms and the ethoxy groups on the other. A sketch of two possible isomers (**A** and **B**), with inequivalent phosphorus atoms, is shown in Fig. 2, for which an ABCD or an A_2B_2 ^{31}P pattern respectively is ex-

Table 1
Selected IR and NMR data for iron(II) and ruthenium(II) complexes

Compound	IR ^a		¹ H NMR ^{b,c}		³¹ P{ ¹ H} NMR ^{b,d}		¹³ C NMR ^{b,c}	
	ν (cm^{-1})	Assign	δ	Assign	Spin system	δ , J(Hz)	δ	Assign
1 $\text{FeClH}[\text{PPh}(\text{OEt})_2]_4$	1960 m	$\nu(\text{Fe-H})$	3.64 m ^e 1.05 t -25.61 qi ($J_{\text{PH}} = 55\text{ Hz}$)	CH_2 CH_3 FeH		187.8 br ^e		
2a $\text{FeH}(\text{C}\equiv\text{CPh})[\text{PPh}(\text{OEt})_2]_4$	2050 s	$\nu(\text{C}\equiv\text{C})$	3.7, 3.5 br ^e 1.06 t br -13.54 qi ($J_{\text{PH}} = 50\text{ Hz}$)	CH_2 CH_3 FeH		187 br ^e	119.4 qi br ^e 62.7 m 16.4 q	$\equiv\text{C-R}$ CH_2 CH_3
2b $\text{FeH}(\text{C}\equiv\text{C } p\text{-tolyl})[\text{PPh}(\text{OEt})_2]_4$	2060 s 1882 m	$\nu(\text{C}\equiv\text{C})$ $\nu(\text{Fe-H})$	3.7, 3.5 br ^f 2.29 s 1.08 t -13.54 qi ($J_{\text{PH}} = 50\text{ Hz}$)	CH_2 CH_3 <i>p</i> -tolyl CH_3 phos FeH		188 br ^f		
2c $\text{FeH}(\text{C}\equiv\text{C}^i\text{Bu})[\text{PPh}(\text{OEt})_2]_4$	2058 s	$\nu(\text{C}\equiv\text{C})$	3.8, 3.3 br ^g 1.33 s 1.03 t -14.97 qi ($J_{\text{PH}} = 50\text{ Hz}$)	CH_2 CH_3 ⁱ Bu CH_3 phos FeH		192 br ^g		
3a $\text{RuH}(\text{C}\equiv\text{CPh})[\text{PPh}(\text{OEt})_2]_4$	2062 s 1840 w	$\nu(\text{C}\equiv\text{C})$ $\nu(\text{Ru-H})$	3.77, 3.26 m ^h 0.99 t -9.25 qi ($J_{\text{PH}} = 22\text{ Hz}$)	CH_2 CH_3 RuH	A_4 ^h A_2B_2 ^{i,j}	166.8 s $\delta_{\text{A}} = 171.8$ $\delta_{\text{B}} = 167.9$ $J_{\text{AB}} = 54.2$	124.9 qi ^g ($^2J_{\text{CP}} = 18.4$) 115.5 qi, br 62.1 t 16.5 q	$\text{MC}\equiv$, $\text{C}\equiv\text{R}$ CH_2 CH_3
3b $\text{RuH}(\text{C}\equiv\text{C } p\text{-tolyl})[\text{PPh}(\text{OEt})_2]_4$	2065 s 1845 w	$\nu(\text{C}\equiv\text{C})$ $\nu(\text{Ru-H})$	3.76, 3.25 m ^g 2.33 s 0.97 t -9.30qi ($J_{\text{PH}} = 22\text{ Hz}$)	CH_2 CH_3 <i>p</i> -tolyl CH_3 phos RuH	A_4 ^g	166.8 s	115.3 qi, br 61.3 t 21.3 q 16.4 q	$\text{C}\equiv\text{R}$ CH_2 CH_3 <i>p</i> -tolyl CH_3 phos

^a In KBr pellets. ^b At room temperature. ^c Phenyl resonances are omitted. ^d Positive shift downfield from 85% H_3PO_4 . ^e In $\text{CD}_3\text{C}_6\text{D}_5$. ^f In C_6D_6 . ^g In CD_2Cl_2 . ^h In CDCl_3 . ⁱ In $(\text{CD}_3)_2\text{CO}$. ^j At -80°C .

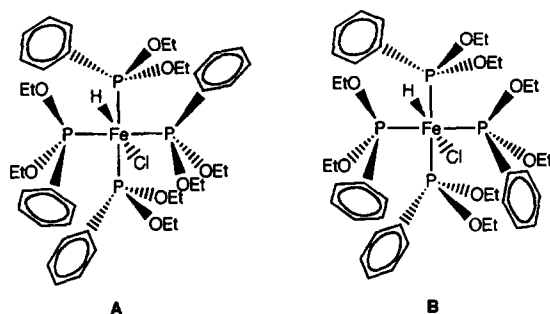
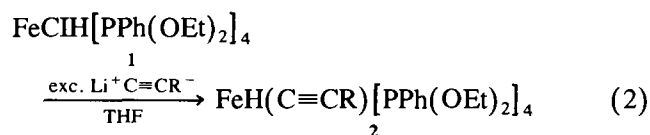


Fig. 2. Two of the possible isomers with inequivalent phosphorus atoms for $\text{FeClH}[\text{PPh}(\text{OEt})_2]_4$.

pected. By superimposing the ^{31}P multiplets of the possible isomers present in the solution, a spectrum of the type in Fig. 1 may be expected for **1**.

An example of inequivalent phosphorus atoms in octahedral complexes containing four PPhMe_2 ligands in a plane has recently been reported [9] for $\text{trans}[\text{IrCl}_2(\text{PPhMe}_2)_4]\text{ClO}_4$. Taking into account that the chemical shift of the hydride in **1** occurs at a very low frequency (-25.61 ppm) as compared with the value generally observed in complexes in which the hydride is *trans* to a phosphite ligand [10], we find that a *trans* octahedral geometry is possible for our complex.

The chloride ligand in **1** is labile and can be substituted by molecular hydrogen (at 1 atm. and 20°C) to give back the $[\text{FeH}(\eta^2\text{-H}_2)\text{P}_4]^+$ complex, as shown in Eq. (1). In the presence of lithium ethylate (Li^+EtO^-) or lithium hydroxide in ethanol, however, the hydride FeH_2P_4 is obtained in almost quantitative yield. More interesting is the reaction with lithium acetylides, which allows the facile synthesis of the alkynyl–hydride complexes $\text{FeH}(\text{C}\equiv\text{CR})[\text{PPh}(\text{OEt})_2]_4$ (**2**) according to



$\text{R} = \text{Ph}$ (**a**), *p*-tolyl (**b**) or ^tBu (**c**)

Complexes **2** can be isolated in good yields as air-stable, yellow diamagnetic solids, moderately soluble in polar and non-polar organic solvents, where they behave as non-electrolytes. Their formulation is supported by elemental analyses and IR and NMR spectra, reported in Table 1. In particular, the infrared spectra of **2** show the $\nu(\text{C}\equiv\text{C})$ band of the acetylide ligand at $2060\text{--}2050$ cm^{-1} and, in the case of **2b**, also the $\nu(\text{Fe}\text{--}\text{H})$ is observed as a medium intensity band at

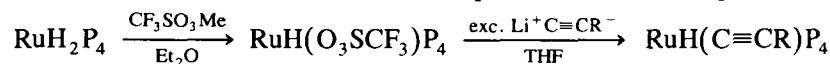
1882 cm^{-1} . Apart from the signals of the phosphite ligands, the ^1H NMR spectra show the singlet of the methyl group of the *p*-tolyl or ^tBu substituent of the acetylide ligand and a quintet between -13.54 and -14.97 with J_{PH} of 50 Hz attributed to the hydride ligand. This quintet broadens in all the compounds **2** as the temperature is lowered and at -90°C appears as a broad hump. Also, the ^{31}P NMR spectra are temperature-dependent and the slightly broad signal that appears at room temperature at $187\text{--}192$ ppm is split into a complicated multiplet with lowering of the sample temperature. Also, in this case, we cannot unambiguously assign a stereochemistry to the complexes, because the ^{31}P multiplet present at low temperature may be consistent with either a *cis* geometry or a *trans* one (**1**), with inequivalent P atoms due to the arrangement of the substituents of the phosphite ligands, as proposed for the hydride compound **1**. The ^{13}C spectra also confirm the formulation proposed for complexes **2**, showing in the spectra of **2a** the characteristic signals of the phosphite ligands and the $\text{C}\beta$ carbon atom of the acetylide ligand at 119.4 ppm. The signal of $\text{C}\alpha$, on the contrary, cannot be assigned, owing to the masking of the signal probably due to the phenyl carbon atoms.

The related hydrido–acetylide complexes of ruthenium, $\text{RuH}(\text{C}\equiv\text{CR})[\text{PPh}(\text{OEt})_2]_4$ (**3**), can also be prepared, but following a different pathway which involves the reaction of the dihydride RuH_2P_4 with an equimolar amount of methyl triflate in diethylether, followed by treatment with an excess of lithium acetylide in THF, as shown in Scheme 1.

The reaction between the hydride $\text{RuH}_2[\text{PPh}(\text{OEt})_2]_4$ and an equimolar amount of $\text{CF}_3\text{SO}_3\text{CH}_3$ proceeds with gas evolution (CH_4 by ^1H NMR) and probable formation of the triflate complex $\text{RuH}(\eta^1\text{-O}_3\text{SCF}_3)[\text{PPh}(\text{OEt})_2]_4$, as observed in the related $\text{RuH}_2[\text{P}(\text{OEt})_3]_4$ and $\text{OsH}_2[\text{P}(\text{OEt})_3]_4$ complexes [11,6c]. The further reaction with lithium acetylide gives the $\text{RuH}(\text{C}\equiv\text{CR})\text{P}_4$ derivatives **3** as final products.

The new ruthenium acetylide complexes are white, air-stable solids, moderately soluble in polar and non-polar organic solvents and non-electrolytes. Some spectroscopic properties are reported in Table 1.

The infrared spectra show the $\nu(\text{C}\equiv\text{C})$ of the acetylide ligand as a medium intensity band at 2062 (**3a**) and 2065 (**3b**) cm^{-1} , whereas the stretch of the $\text{Ru}\text{--}\text{H}$ bond appears as a weak absorption at 1840 and 1845 cm^{-1} for **3a** and **3b** respectively. The ^1H NMR spectra confirm the presence of the hydride ligand,



3

$\text{P} = \text{PPh}(\text{OEt})_2$; $\text{R} = \text{Ph}$ **a** or *p*-tolyl **b**.

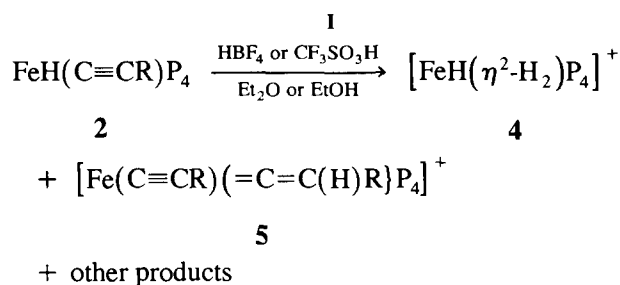
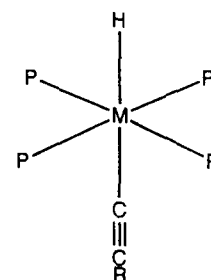
Scheme 1.

showing a sharp quintet at -9.25 to -9.30 ppm with J_{PH} of 22 Hz. Furthermore, the ^{13}C NMR spectra show the signals of the carbon atoms of the acetylide ligand as quintets, owing to the coupling with the four phosphorus atoms of the phosphite ligands. The $\text{C}\alpha$ appears at 124.9 ppm (**3a**) with a large $^2J_{\text{CP}}$ coupling constant of 18.4 Hz, while the $\text{C}\beta$ appears at 115.5 ppm (**3a**) and 115.3 ppm (**3b**) as a slighter broad quintet with a very low value of $^3J_{\text{CP}} (< 1 \text{ Hz})$.

In the temperature range between $+30$ and -70°C the $^31\text{P}\{^1\text{H}\}$ NMR spectra of complexes **3a** and **3b** are sharp singlets at about 166 ppm, but at lower temperatures the signals broaden and appear, at -90°C , as well-resolved A_2B_2 multiplets, simulable with the parameters reported in Table 1.

These results may be explained on the base of the existence in solution of a *trans* octahedral geometry (**I**) in which the inequivalence of the P nuclei at low temperature may be due to a restricted rotation of the phosphite ligands, which makes these ligands two-by-two magnetically equivalent. This restricted rotation may, in fact, induce a different arrangement of the substituents of the P atoms of each phosphite $\text{PPh}(\text{OEt})_2$ ligand resulting, in this case, in the presence at low temperature of the rotamer with two-by-two magnetically equivalent phosphite ligands (A_2B_2 spectra).

We have also studied the reactivity of these acetylide complexes towards $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and $\text{CF}_3\text{SO}_3\text{H}$ in order to verify whether protonation takes place at the acetylide ($\text{RC}\equiv\text{C}^-$) ligand affording a vinylidene [2,3] or a II -alkyne [3f,m] complex, or at the hydride ligand giving an acetylide–dihydrogen [12] derivative of the type $[\text{M}(\text{C}\equiv\text{CR})(\eta^2-\text{H}_2)\text{P}_4]^+$. The protonation reaction of **2** has been carried out with both HBF_4 and $\text{CF}_3\text{SO}_3\text{H}$ in different solvents and operating under an argon or an hydrogen atmosphere, at low or room temperature. The results show that, in every case, the main products of the reaction are the hydrido–dihydrogen complex $[\text{FeH}(\eta^2-\text{H}_2)\text{P}_4]^+$ (**4**) [10c] and the alkynyl–vinylidene derivative $[\text{Fe}(\text{C}\equiv\text{CR})\{\text{C}=\text{C}(\text{H})\text{R}\}\text{P}_4]^+$ (**5**) [13],

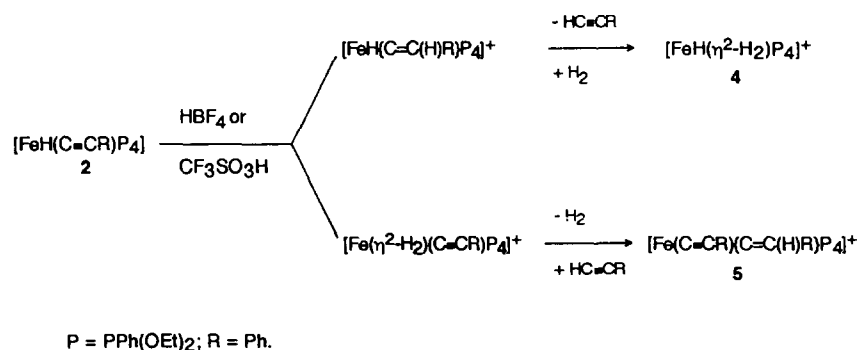


Scheme 2.

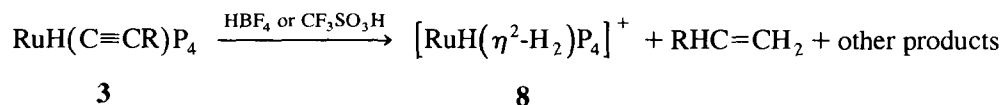
which can be isolated as solids and characterised (Scheme 2).

Also other products (probably from decomposition), which were not identified, are present in the reaction mixture and in the final solid obtained. However, no spectroscopic (IR and NMR) evidence was obtained of the formation of neither other $\eta^2-\text{H}_2$ or other vinylidene complexes, except **4** and **5**.

The formation of the two complexes **4** and **5** is rather surprising and may be explained on the basis of the possible protonation of the acetylide or the hydride ligand in the $\text{FeH}(\text{C}\equiv\text{CR})\text{P}_4$ derivative (Scheme 3), affording in one case the hydrogen–acetylide intermediate $[\text{Fe}(\eta^2-\text{H}_2)(\text{C}\equiv\text{CR})\text{P}_4]^+$ and in the other the vinylidene–hydride intermediate $[\text{FeH}\{\text{C}=\text{C}(\text{H})\text{R}\}\text{P}_4]^+$. Although these complexes were not identified, there are good precedents for them, such as the hydrogen–acetylide $[\text{Ru}(\eta^2-\text{H}_2)(\text{C}\equiv\text{CPh})(\text{dippe})]\text{BPh}_4$ derivative [dippe = 1,2-bis(diisopropylphosphino)ethane] [14] obtained as solid and characterized. Fur-



Scheme 3.



Scheme 4.

thermore, the protonation of metal acetylides is easy and generally takes place to C β -carbon atoms [2,3] giving vinylidene derivatives, even if the formation of an η^2 -alkyne $[\text{FeH}(\eta^2\text{-HC}\equiv\text{CR})\text{P}_4]^+$ cannot be excluded. However, in both these proposed intermediates the new ligand formed by protonation, i.e. $\eta^2\text{-H}_2$ in $[\text{Fe}(\eta^2\text{-H}_2)(\text{C}\equiv\text{CR})\text{P}_4]^+$ and the vinylidene $\text{C}=\text{C}(\text{H})\text{R}$ in $[\text{FeH}(\text{C}=\text{C}(\text{H})\text{R})\text{P}_4]^+$, must result in a very labile ligand which may easily be substituted by H_2 in the case of compound $[\text{FeH}(\text{C}=\text{C}(\text{H})\text{R})\text{P}_4]^+$, giving **4** and probably the free alkyne $\text{HC}\equiv\text{CR}$ obtained by rearrangement [15] of the vinylidene $\text{C}=\text{C}(\text{H})\text{R}$ ligand. In complex $[\text{Fe}(\eta^2\text{-H}_2)(\text{C}\equiv\text{CR})\text{P}_4]^+$, by substitution of the $\eta^2\text{-H}_2$ ligand with a free alkyne, the final complex **5** can also be formed after rearrangement of the alkyne $\text{HC}\equiv\text{CR}$ to the vinylidene ligand.

The final products of the reactions, **4** and **5**, seem therefore to be formed from the initial protonation intermediates $[\text{FeH}(\text{C}=\text{C}(\text{H})\text{R})\text{P}_4]^+$ and $[\text{Fe}(\eta^2\text{-H}_2)(\text{C}\equiv\text{CR})\text{P}_4]^+$ by reciprocal exchange of the H_2 and the $\text{C}=\text{C}(\text{H})\text{R}$ ligands. The instability of these protonated compounds and of the final derivatives [10,13] may also explain the formation of other compounds or decomposition products, which were always present in the reaction mixture and were not identified.

The protonation of the ruthenium complexes **3** carried out under an atmosphere of H_2 with HBF_4 or $\text{CF}_3\text{SO}_3\text{H}$ affords the molecular hydrogen complex $[\text{RuH}(\eta^2\text{-H}_2)\text{P}_4]^+$ (**8**) [16] and the appropriate alkene $\text{RHC}\equiv\text{CH}_2$, together with products not characterised (Scheme 4).

Instead, under argon, only a small amount of the alkene and unidentified products were obtained. As in the case of iron, these results may be interpreted on the basis of a protonation of both the hydride and acetylide ligands, affording the unstable $[\text{Ru}(\eta^2\text{-H}_2)(\text{C}\equiv\text{CR})\text{P}_4]^+$ and $[\text{RuH}(\text{C}=\text{C}(\text{H})\text{R})\text{P}_4]^+$ derivatives. However, the substitution of the vinylidene ligand with H_2 can give the compound $[\text{RuH}(\eta^2\text{-H}_2)\text{P}_4]^+$ and free alkyne, which is reported [6a] to be easily reduced to an alkene in mild conditions (1 atm, 20°C) in the presence of the same $[\text{RuH}(\eta^2\text{-H}_2)\text{P}_4]^+$ as catalyst. In this case, therefore, the formation of vinylidene-acetylide complexes seems to be excluded, resulting predominantly in the alkene reduction.

Acknowledgements

The financial support of Ministero dell'Università e della Ricerca Scientifica e Tecnologica, Rome, is grate-

fully acknowledged. We thank Daniela Baldan for technical assistance.

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