Reactivity of Iron(II) Non-classical Hydrides with Alkynes

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The complex $[FeH(\eta^2-H_2)\{PPh(OEt)_2\}_4]BPh_4$ reacts with terminal alkynes HC≡CR (R = *p*-tolyl, Bu^t or $SiMe_3$) to give the corresponding alkenes $H_2C=CHR$ and the butenynyl derivative $[Fe(\eta^3-RC_3CHR)\{PPh(OEt)_2\}_4]^+$. In contrast, the related complex $[FeH(\eta^2-H_2)\{P(OEt)_3\}_4]BPh_4$ reacts with terminal alkynes to yield alkenes and σ-acetylide $[Fe(C{\equiv}CR)\{P(OEt)_3\}_5]^+$ derivatives. Activated alkynes such as $HC{\equiv}CCO_2Me$ and $MeO_2CC{\equiv}CCO_2Me$ react with both $[FeH(\eta^2-H_2)L_4]BPh_4$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] to give vinyl derivatives $[Fe\{CH=CH(CO_2Me)\}L_4]^+$ and $[Fe\{C(CO_2Me)=CH(CO_2Me)\}L_4]^+$, respectively. The characterization of the complexes by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy is discussed.

There has been considerable interest in the reactions of transition-metal hydrides with alkynes,[1,2] not only because of the nature of the resulting products and the factors governing the reaction course, but also because these hydride compounds are potential catalysts for acetylene hydrogenation or polymerization. However, despite the large number of studies reported[2] on mono- and di-hydrides of several metals, very little is known about the reactivity of iron hydrides toward alkynes.[3]

In a previous paper[4] we reported the reactivity of ruthenium $[RuH(\eta^2-H_2)L_4]BF_4$ [L = $P(OMe)_3$, $P(OEt)_3$ or $PPh(OEt)_2$] toward alkynes, which allowed the synthesis of new organoruthenium compounds such as butenynyl and σ-vinyl derivatives. Catalytic reduction of alkyne to alkene under mild conditions was also observed. Now we have extended our studies to include the related iron complexes in order to determine whether non-classical iron hydrides show similar properties, and also for insight on the influence of phosphite ligands on the chemistry of acetylenes. The result of our investigations, which include the synthesis and characterization of new η^3-enynyl, σ-acetylyde and σ-vinyl iron complexes, are reported here.

Experimental

General Comments.—All operations were performed under an inert atmosphere (argon) by using standard Schlenk techniques or a Vacuum Atmosphere dry-box. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon;[5] triethyl phosphite was an Ega Chemie product purified by distillation under nitrogen. Acetylenes were Aldrich products used without further purification. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin Elmer model 683 spectrophotometer, NMR spectra (^1H, ^{13}C, ^{31}P) on Varian FT-80A and Bruker AC 200 spectrometers at temperatures between −85 and +34 °C, unless otherwise noted. Proton and ^{13}C spectra are referred to internal tetramethylsilane, $^{31}P-\{^1H\}$ with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in $MeNO_2$ at 25 °C were measured on a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[6]

Synthesis of Complexes.—Molecular hydrogen complexes $[FeH(\eta^2-H_2)L_4]BPh_4$ were prepared following the method previously reported.[7]

$[Fe(\eta^3-RC_3CHR)\{PPh(OEt)_2\}_4]BPh_4$ **1** (R = Bu^t **a**, $SiMe_3$ **b** or *p*-tolyl **c**). An excess of the appropriate alkyne (2.5 mmol) was added to a solution of $[FeH(\eta^2-H_2)\{PPh(OEt)_2\}_4]BPh_4$ (0.5 mmol, 0.59 g) in CH_2Cl_2 (15 cm^3) cooled to −80 °C. The reaction mixture was brought to 0 °C (in about 15 min) and then stirred for 2 h. Removal of the solvent at reduced pressure gave a green-brown oil which was treated with ethanol (10 cm^3). The resulting solution, after addition of an excess of $NaBPh_4$ (1 mmol, 0.34 g) in ethanol (5 cm^3), was slowly cooled to −10 to −20 °C until microcrystals of the product separated. These were recrystallized by dissolving the product in cold CH_2Cl_2 (5 cm^3) and, after filtration, adding ethanol (15 cm^3) at 0 °C until a solid separated; yields varied from 50 (**1b**) to 80% (**1a**).

$[Fe(C{\equiv}CR)\{P(OEt)_3\}_5]BPh_4$ **2** (R = Bu^t **a**, $SiMe_3$ **b** or *p*-tolyl **c**). An excess of the appropriate alkyne (2.5 mmol) was added to a solution of $[FeH(\eta^2-H_2)\{P(OEt)_3\}_4]BPh_4$ (0.5 mmol, 0.52 g) in CH_2Cl_2 (10 cm^3) cooled to −80 °C and the reaction mixture, brought to room temperature, was stirred for about 2 h. The solvent was evaporated under reduced pressure, giving an oil which was treated with ethanol (10 cm^3) containing an excess of $NaBPh_4$ (1 mmol, 0.34 g). The resulting solution was vigorously stirred at 0 °C until a yellow solid separated, which was crystallized by slow cooling to −30 °C of its saturated solution in ethanol–dichloromethane (15 cm^3:3 cm^3); yield ⩾ 50%.

$[Fe\{CH=CH(CO_2Me)\}L_4]BPh_4$ [L = $PPh(OEt)_2$ **3** or $P(OEt)_3$ **4**]. Methyl propiolate (4 mmol, 0.35 cm^3) was added to a solution of the appropriate $[FeH(\eta^2-H_2)L_4]BPh_4$ derivative (0.8 mmol) in CH_2Cl_2 (20 cm^3), and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure, giving a brown oil which was triturated with ethanol (15 cm^3) containing an excess of $NaBPh_4$ (1 mmol, 0.34 g). After several hours of vigorous stirring an orange solid separated, which was crystallized by slow cooling to −30 °C of its saturated solution in ethanol–dichloromethane (15 cm^3:3 cm^3); yield ⩾ 40%.

$[Fe\{C(CO_2Me)=CH(CO_2Me)\}\{P(OEt)_3\}_4]BPh_4$ **5**. An excess of $MeO_2CC{\equiv}CCO_2Me$ (2.1 mmol, 0.26 cm^3) was added to a solution of $[FeH(\eta^2-H_2)\{P(OEt)_3\}_4]BPh_4$ (0.7 mmol, 0.74 g) in CH_2Cl_2 (15 cm^3) and the reaction mixture was stirred for 24 h. After removal of the solvent under reduced pressure, the oil obtained was triturated with ethanol (15 cm^3) containing an excess of $NaBPh_4$ (1 mmol, 0.34 g) to give an orange solid. This was crystallized by cooling to −30 °C the solution obtained by

Table 1 Proton and phosphorus-31 NMR spectral data

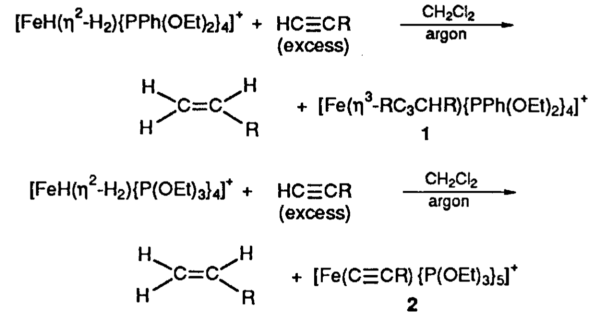
	^{1}H NMR^{b,c}			
Compound^a	δ	Assignment	Spin system	^{31}P-{^{1}H} NMR, δ^{b,d}
$[Fe(\eta^3\text{-}Bu^tC_3CHBu^t)\{PPh(OEt)_2\}_4]^+$	6.32 (m)	$C{\equiv}C{-}C{=}CH$		191 (m)^e
	3.61 (m)	$POC\mathit{H}_2CH_3$		
	1.28, 1.13 (s)	CMe_3		
	1.16 (t)	$POCH_2C\mathit{H}_3$		
$[Fe\{\eta^3\text{-}(Me_3Si)C_3CH(SiMe_3)\}\{PPh(OEt)_2\}_4]^+$	3.76 (m)	$POC\mathit{H}_2CH_3$		191 (m)^e
	1.24 (t)	$POCH_2C\mathit{H}_3$		
	0.34, 0.13 (s)	$SiMe_3$		
$[Fe\{\eta^3\text{-}(p\text{-}MeC_6H_4)C_3CH(C_6H_4Me\text{-}p)\}\{PPh(OEt)_2\}_4]^+$	3.63 (m)	$POC\mathit{H}_2CH_3$		190 (m)^e
	2.40, 2.33 (s)	$C\mathit{H}_3C_6H_4$		
	1.19 (t)	$POCH_2C\mathit{H}_3$		
$[Fe(C{\equiv}CCMe_3)\{P(OEt)_3\}_5]^+$	4.15 (m)^f	$POC\mathit{H}_2CH_3$	AB_4^{f}	δ_A 154.6, δ_B 151.2
	1.26 (t)	$POCH_2C\mathit{H}_3$		[J(AB) = 105.4]
	1.12 (s)	CMe_3		
$[Fe(C{\equiv}CSiMe_3)\{P(OEt)_3\}_5]^+$	4.24 (m)^f	$POC\mathit{H}_2CH_3$	AB_4^{f}	δ_A 152.7, δ_B 149.8
	1.32 (t)	$POCH_2C\mathit{H}_3$		[J(AB) = 105.5]
	0.04 (s)	$SiMe_3$		
$[Fe\{C{\equiv}C(C_6H_4Me\text{-}p)\}\{P(OEt)_3\}_5]^+$	4.11 (m)	$POC\mathit{H}_2CH_3$	AB_4	δ_A 154.1, δ_B 150.6
	2.27 (s)	$C\mathit{H}_3C_6H_4$		[J(AB) = 105.9]
	1.25 (t)	$POCH_2C\mathit{H}_3$		
$[Fe\{CH{=}CH(CO_2Me)\}\{PPh(OEt)_2\}_4]^+$	10.04 (m)	$C\mathit{H}{=}CH(CO_2Me)$	ABC_2	δ_A 106.8, δ_B 91.5, δ_C 85.4
	6.16 (m)	$CH{=}C\mathit{H}(CO_2Me)$		[J(AB) = 62.4, J(AC) = 113.3,
	3.95, 3.87 (m)	$POC\mathit{H}_2CH_3$		J(BC) = 61.8]
	3.77 (s)	CO_2Me		
	1.50, 1.28 (t)	$POCH_2C\mathit{H}_3$		
$[Fe\{CH{=}CH(CO_2Me)\}\{P(OEt)_3\}_4]^+$	10.75 (m)	$C\mathit{H}{=}CH(CO_2Me)$	ABC_2	δ_A 169.4, δ_B 159.7, δ_C 148.8
	6.44 (m)	$CH{=}C\mathit{H}(CO_2Me)$		[J(AB) = 79.6, J(AC) = 155.0,
	4.09 (m)	$POC\mathit{H}_2CH_3$		J(BC) = 84.0]
	3.82 (s)	CO_2Me		
	1.35, 1.30, 1.25 (t)	$POCH_2C\mathit{H}_3$		
$[Fe\{C(CO_2Me){=}CH(CO_2Me)\}\{P(OEt)_3\}_4]^+$	6.22 (m)	$={C}\mathit{H}(CO_2Me)$	ABC_2	δ_A 166.1, δ_B 157.5, δ_C 146.9
	4.14 (m)	$POC\mathit{H}_2CH_3$		[J(AB) = 104.4,
	3.83, 3.75 (s)	CO_2Me		J(AC) = 148.5,
	1.27, 1.25 (t)	$POCH_2C\mathit{H}_3$		J(BC) = 102.0]

[a] All compounds are BPh_4^- salts. [b] At room temperature in $(CD_3)_2CO$. [c] Phenyl-proton resonances are omitted. [d] Coupling constants in Hz; positive shift downfield from 85% H_3PO_4. [e] At −80 °C. [f] In CD_2Cl_2.

dissolving the solid in ethanol (10 cm^3) and enough dichloromethane (1–2 cm^3) to obtain a saturated solution at room temperature; yield ⩾ 45%.

Results and Discussion

The reaction of molecular hydrogen complexes $[FeH(\eta^2\text{-}H_2)L_4]BPh_4$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] with terminal alkynes $HC{\equiv}CR$ (R = p-tolyl, Bu^t or $SiMe_3$) is influenced by the nature of the phosphite ligands, as shown in Scheme 1. Under an inert atmosphere, alkenes (about 1.5 equivalents) are obtained in both cases, but while the butenynyl derivative **1** can be isolated in high yield with the $PPh(OEt)_2$ ligand, the acetylide compound **2** is obtained from the $[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$ starting complex. The formation of enynyl or acetylide iron(II) derivatives from this reaction by changing the nature of the phosphite contrasts with the results obtained in the case of ruthenium,[4] for which enynyl $[Ru(\eta^3\text{-}RC_3CHR)L_4]BPh_4$ complexes were always obtained with all the phosphites used. Furthermore, operating under a hydrogen atomosphere (1 atm, 101 325 Pa) at 20 °C, selective hydrogenation of alkyne to alkene (about 10 turnovers in 3 h) is also observed with both catalysts $[FeH(\eta^2\text{-}H_2)L_4]BPh_4$ [L = $P(OEt)_3$ or $PPh(OEt)_2$]. This catalytic hydrogenation, however, needs further investigation and will not be discussed here.



Scheme 1

The complexes $[Fe(\eta^3\text{-}RC_3CHR)\{PPh(OEt)_2\}_4]BPh_4$ are green or orange solids, diamagnetic, stable in the solid state and in deoxygenated polar organic solutions, in which they behave as 1:1 electrolytes (Tables 1 and 2).[8] At room temperature the ^{31}P-{^{1}H} NMR spectra of compounds **1** show a singlet, but as the temperature is lowered a change is observed until a non-symmetrical multiplet appears at −80 °C. However, even at this temperature the spectra are still broad enough to prevent the assignment of the parameters δ and J to an ABC_2 system. Besides the signal of the phosphite ligand and the BPh_4^- anion, the ^{1}H NMR spectra of **1** show two singlets for the methyl protons of the substituent R (p-tolyl, Bu^t or $SiMe_3$) indicating the existence of non-equivalent groups. A doublet of multiplets at δ 6.32 is also present for $[Fe(\eta^3\text{-}Bu^tC_3CHBu^t)\{PPh(OEt)_2\}_4]^+$ **1a** and may be attributed to the vinyl proton of the η^3-RC_3CHR ligands. In the ^{13}C NMR spectra of **1a** (Table 3) two vinyl-carbon signals occur, one as a multiplet at δ 147.7 attributed to C_γ, and one as a doublet of multiplets at δ 143.6 ($^1J_{CH}$ = 162.8 Hz) due to C_δ. Two signals are also observed at δ 32.7 and 30.2 for the methyl carbon of the Bu^t group.

These data do not allow us to define the formulation and geometry of the complex unambiguously. However, the

Table 2 Physical, analytical and selected IR data for the complexes

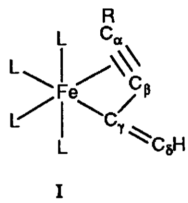
Compound[a]	M.p./°C (decomp.)	Λ_M[b]/S cm^2 mol^{-1}	Analysis[c] (%) C	H	IR[d]/cm^{-1}
1a $[Fe(\eta^3\text{-}Bu^tC_3CHBu^t)\{PPh(OEt)_2\}_4]^+$	116	97.8[e]	68.35 (68.55)	7.50 (7.50)	—
1b $[Fe\{\eta^3\text{-}(Me_3Si)C_3CH(SiMe_3)\}\{PPh(OEt)_2\}_4]^+$	108	55.7	64.95 (65.20)	7.25 (7.30)	1610m ν(C=C)
1c $[Fe\{\eta^3\text{-}(p\text{-}MeC_6H_4)C_3CH(C_6H_4Me\text{-}p)\}\{PPh(OEt)_2\}_4]^+$	50	56.9	69.95 (70.30)	7.05 (7.00)	—
2a $[Fe(C{\equiv}CCMe_3)\{P(OEt)_3\}_5]^+$	130	52.8	55.75 (56.00)	8.30 (8.15)	2085w ν(C≡C)[f] [2085w]
2b $[Fe(C{\equiv}CSiMe_3)\{P(OEt)_3\}_5]^+$	108	53.6	54.10 (54.40)	7.95 (8.05)	2010m ν(C≡C) [2016m]
2c $[Fe\{C{\equiv}C(C_6H_4Me\text{-}p)\}\{P(OEt)_3\}_5]^+$	130	53.0	56.90 (57.30)	7.80 (7.80)	2095w ν(C≡C)[g] [2095w]
3 $[Fe\{CH{=}CH(CO_2Me)\}\{PPh(OEt)_2\}_4]^+$	132	54.2	70.60 (70.95)	4.55 (4.70)	1573m ν(C=O)
4 $[Fe\{CH{=}CH(CO_2Me)\}\{P(OEt)_3\}_4]^+$	138	56.4	55.40 (55.55)	7.60 (7.60)	1575m ν(C=O)
5 $[Fe\{C(CO_2Me){=}CH(CO_2Me)\}\{P(OEt)_3\}_4]^+$	115	57.3	54.70 (54.85)	7.60 (7.40)	1712m ν(C=O) 1591s ν(C=O)

[a] All compounds are BPh_4^- salts. [b] In nitromethane solution (10^{-3} mol dm^{-3}) at 25 °C, except for **1a**. [c] Calculated values in parentheses. [d] In KBr, except for values in square brackets (CH_2Cl_2). [e] In acetone solution (10^{-3} mol dm^{-3}) at 25 °C. [f] At 2086 cm^{-1} in Nujol mull. [g] At 2097 cm^{-1} in Nujol mull.

Table 3 Carbon-13 NMR spectral data for selected iron compounds[a]

Compound[b]	δ	Assignment[c]	Coupling constant/Hz
$[Fe(\eta^3\text{-}Bu^tC_3CHBu^t)\{PPh(OEt)_2\}_4]^{+\,d}$	147.7 (m)	C_γ	
	143.6 (dm)	C_δ	162.8 ($^1J_{CH}$)
	121.5 (dm)	C_α or C_β	15.4 ($^1J_{CH}$)
	64.6 (m)	CH_2 of phosphite	
	37.5 (m)	*C*Me$_3$	
	37.4 (m)	*C*Me$_3$	
	32.7 (qm)	C*Me*$_3$	
	30.2 (qm)	C*Me*$_3$	
	16.3 (m)	CH_3 of phosphite	
$[Fe(C{\equiv}CCMe_3)\{P(OEt)_3\}_5]^{+\,d}$	125.1 (m)	*C*≡CCMe$_3$	12.0 (*trans*-$^2J_{CP}$)
	79.6 (m)	C≡*C*CMe$_3$	
	62.9 (m)		
	61.9 (m)	CH_2 of phosphite	
	32.4 (qm)	C*Me*$_3$	130.7 ($^1J_{CH}$)
	30.5 (m)	*C*Me$_3$	
	16.2 (m)	CH_3 of phosphite	
$[Fe\{CH{=}CH(CO_2Me)\}\{P(OEt)_3\}_4]^{+\,e}$	232.6 (m)	C_α	
	181.5 (m)	C=O	14.3 (*trans*-$^2J_{CP}$)
	124.1 (dm)	C_β	169.0 ($^1J_{CH}$)
	62.4 (m)	CH_2 of phosphite	
	53.7 (qm)	OMe	147.7 ($^1J_{CH}$)
	16.3 (m)	CH_3 of phosphite	
$[Fe\{C(CO_2Me){=}CH(CO_2Me)\}\{P(OEt)_3\}_4]^{+\,e}$	221.4 (m)	C_α	
	181.1 (dm)	C=O	13.1 (*trans*-$^2J_{CP}$)
	177.9 (m)	C=O	
	125.3 (dm)	C_β	168.9 ($^1J_{CH}$)
	62.7 (m)	CH_2 of phosphite	
	53.9 (qm)	OMe	148.1 ($^1J_{CH}$)
	50.9 (qm)	OMe	145.6 ($^1J_{CH}$)
	16.1 (m)	CH_3 of phosphite	

[a] All phenyl-carbon resonances are omitted. [b] All compounds are BPh_4^- salts. [c] For assignments see geometries I–V. [d] In CD_2Cl_2. [e] In $(CD_3)_2CO$.



I

related ruthenium derivatives[4] $[Ru(\eta^3\text{-}RC_3CHR)L_4]^+$, the X-ray crystal structure of which is known, show very similar spectroscopic properties and it is therefore plausible to propose a type I butenynyl structure for the iron complex too. In order to confirm such a formulation, we attempted to liberate and identify the RC≡C–CH=CHR organic compound by protonation with acetylacetone (Hacac); the anion acac$^-$ should also allow the FeL_4 fragment to be trapped.

Monitoring the progress of the reaction between $[Fe(\eta^3\text{-}Bu^tC_3CHBu^t)\{PPh(OEt)_2\}_4]BPh_4$ and Hacac at 50 °C by ^1H NMR spectroscopy, we observed the disappearance of the multiplets at δ 6.32 (vinyl protons) and the two singlets at δ 1.28 and δ 1.13 (CH_3 of Bu^t), and the parallel appearance of two doublets at δ 5.71 and 5.33 (AB quartet, J_{AB} = 11.9 Hz) and a singlet at δ 1.86 (CH_3 of Bu^t), attributed to (*Z*)-Bu^{t}C≡C–CH=CHBu^t formed by protonation of the η^3-Bu^{t}C$_3$-CHBu^t ligand with acetylacetone. Furthermore, the corresponding spectra taken during the reaction between $[Fe\{\eta^3\text{-}(p\text{-}MeC_6H_4)C_3CH(C_6H_4Me\text{-}p)\}\{PPh(OEt)_2\}_4]^+$ and Hacac show the appearance of the same signals as those observed in

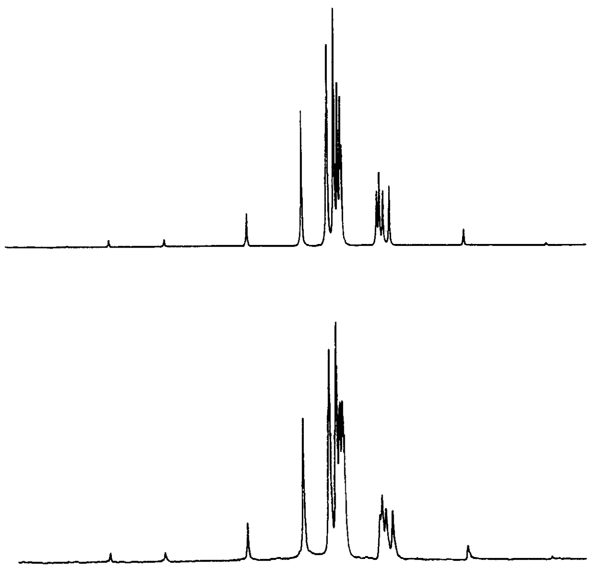
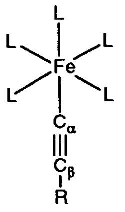


Fig. 1 Observed (bottom) and calculated (top) 32.203 MHz ^{31}P-{^{1}H} NMR spectra of $[Fe\{C{\equiv}C(C_6H_4Me\text{-}p)\}\{P(OEt)_3\}_5]BPh_4$ **2c** in CD_2Cl_2 at 30 °C. The simulated spectrum was obtained with the following parameters: spin system AB_4, δ_A 154.1, δ_B 150.6, J_{AB} = 105.9 Hz



II

Table 4 Infrared data (cm^{-1}) for iron acetylide complexes

Compound	ν(C≡C)[a]	Ref.
$[Fe(C{\equiv}CBu^t)L_5]^+$	2085	This work
$[Fe\{C{\equiv}C(C_6H_4Me\text{-}p)\}L_5]^+$	2097	This work
$[FeCl(C{\equiv}CPh)(dmpe)]$	2044	11(*a*)
$[Fe(C{\equiv}CPh)_2(dmpe)]$	2037	11(*b*)
$[Fe(C{\equiv}CBu^t)_2(dmpe)]$	2059	11(*b*)
$[FeH(C{\equiv}CBu^t)(dmpe)]$	2060[b]	12
$[Fe(C{\equiv}CPh)_2(depe)]$	2035	11(*b*)

L = $P(OEt)_3$, dmpe = $Me_2PCH_2CH_2PMe_2$, depe = $Et_2PCH_2CH_2PEt_2$.

[a] In Nujol mull. [b] In C_6D_6.

the reaction with Hacac of the related $[Ru\{\eta^3\text{-}(p\text{-}MeC_6H_4)\text{-}C_3CH(C_6H_4Me\text{-}p)\}L_4]^+$ derivative,[4] *i.e.* two doublets at δ 6.65 and 5.84 (AB quartet, J_{AB} = 11.9 Hz) and a singlet at δ 2.35 attributed to (*Z*)-(p-MeC_6H_4)C≡C–CH=CH(C_6H_4Me-p). On the basis of these data, therefore, the presence of the butenynyl ligands in compounds **1** seems to be confirmed. The NMR spectra (^{1}H and ^{31}P) also revealed the formation of $[Fe(acac)L_4]^+$, which was unstable and was not isolated. Enynyl complexes have precedents for Ru,[2b,4] Os,[9] W,[10] and also for iron[3b] in $[Fe\{\eta^3\text{-}C(CHPh)C_2Ph\}(dmpe)]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) in which the phosphine ligand is bidentate.

The acetylide derivatives $[Fe(C{\equiv}CR)\{P(OEt)_3\}_5]BPh_4$ are yellow, diamagnetic compounds, air-stable both as solids and in solutions of polar organic solvents, and 1:1 electrolytes.[8] In the IR spectra, the ν(C≡C) of the acetylide ligand appears at 2010–2095 cm^{-1}, and in the ^{1}H NMR spectra only one singlet for the methyl protons of the substituent R (p-tolyl, Bu^t or $SiMe_3$) is observed. Two multiplets at δ 125.1 (J_{CP} = 12.0 Hz) and 79.6 appear for the C_α and C_β carbon atoms of the acetylide ligand in the ^{13}C NMR spectrum of $[Fe(C{\equiv}CBu^t)\{P(OEt)_3\}_5]^+$ **2a**, whereas the signals for the substituent Bu^t appear at δ 32.4 (qm, $^1J_{CH}$ = 130.7 Hz) for the methyl carbon atom and at δ 30.5 for the quaternary carbon atom, respectively. Moreover, in the temperature range −80 to +30 °C, the ^{31}P-{^{1}H} NMR spectrum appears as AB_4 multiplets which can be simulated with the parameters reported in Fig. 1, consistent with the proposed formulation **II**.

Table 4, which reports IR data for some iron(II) acetylides, shows that our $[Fe(C{\equiv}CR)L_5]^+$ derivatives are the only cationic compounds and that their ν(C≡C) values are the highest observed. This seems to suggest a less conjugative interaction of C≡C with the metal in our case, as compared with other neutral complexes.

Activated alkynes such as $HC{\equiv}CCO_2Me$ and $MeO_2CC{\equiv}CCO_2Me$ react with both molecular hydrogen complexes at room temperature under argon to give the corresponding alkene and vinyl complexes $[Fe\{CH{=}CH(CO_2Me)\}L_4]BPh_4$ and $[Fe\{C(CO_2Me){=}CH(CO_2Me)\}L_4]BPh_4$, as shown in Scheme 2. It may be noted that the IR spectroscopy in

$$[FeH(\eta^2\text{-}H_2)\{PPh(OEt)_2\}_4]^+ + \underset{\text{(excess)}}{RC{\equiv}CCO_2Me} \xrightarrow[\text{argon}]{CH_2Cl_2} RCH{=}CH(CO_2Me) + \underset{\mathbf{3\text{–}5}}{[Fe\{CR{=}CH(CO_2Me)\}L_4]^+}$$

Scheme 2 R = H, L = $PPh(OEt)_2$ **3** or $P(OEt)_3$ **4**; R = CO_2Me, L = $P(OEt)_3$ **5**. For R = CO_2Me, the alkene is obtained as a mixture of (*E*) and (*Z*) isomers in about 1:1 ratio

the reaction between $[FeH(\eta^2\text{-}H_2)\{P(OEt)_3\}_4]^+$ and $HC{\equiv}CCO_2Me$ also shows the formation of an alkynyl derivative with a ν(C≡C) band at 2090 cm^{-1} and ν(CO) absorption of the CO_2Me group at 1705 cm^{-1}. However, this complex, formulated as $[Fe(C{\equiv}CCO_2Me)L_5]^+$ by analogy with **2**, is only present in small quantities (1–2%).

Complexes **3**–**5** are yellow-orange solids, stable, diamagnetic and 1:1 electrolytes.[8] The IR spectra of the methyl propiolate derivatives $[Fe\{CH{=}CH(CO_2Me)\}L_4]^+$ show a medium-strong band at 1573–1575 cm^{-1}, attributable to the ν(CO) of a co-ordinated carbonyl group of the chelated vinyl ligand. In the temperature range −80 to +30 °C the ^{31}P-{^{1}H} NMR spectra consist of a multiplet which can easily be simulated using an ABC_2 model. Apart from the proton signals of the phosphites and BPh_4^-, the ^{1}H NMR spectra show only one singlet at δ 3.77 (**3**) and 3.82 (**4**), attributed to the methyl protons of the $CH{=}CHCO_2Me$ ligand, and two multiplets at δ 10.04–10.75 and 6.16–6.44, attributed to the vinyl protons of the same ligand. The multiplicity of these signals is due to the coupling of each proton with the others and with the phosphorus nuclei of the phosphite ligands, as revealed by computer simulation using an ABC_2XY model (X = H_α, Y = H_β) with the parameters in Fig. 2. The value of 8.50 Hz for $J(H_\alpha H_\beta)$ is consistent with the mutually *cis* position of the two vinyl protons. Lastly, apart from the signals of the phosphite and phenyl carbon atoms, the ^{13}C NMR spectra show two multiplets at δ 232.6 and 124.1 ($^1J_{CH}$ = 169 Hz), attributed to the two C_α and C_β vinyl carbons, respectively. Furthermore, the carbonyl carbon atom is a multiplet at δ 181.5, with $J(CP_{trans})$ 14.3 Hz, whereas the methyl carbon atom of the OMe group appears at δ 53.7 ($^1J_{CH}$ = 147.7 Hz). On this basis, it is plausible to assign type **III** geometry to the complex, in which the metal is co-ordinated to four phosphorus atoms and one chelated vinyl ligand.

The dimethyl ester complex $[Fe\{C(CO_2Me){=}CH(CO_2Me)\}L_4]^+$ was isolated as a solid **5** with the $P(OEt)_3$ ligand, while in the case of $PPh(OEt)_2$ only an oily compound was obtained, the IR and NMR data for which confirmed its formulation as a vinyl derivative. The IR spectrum of **5** shows two ν(CO) bands

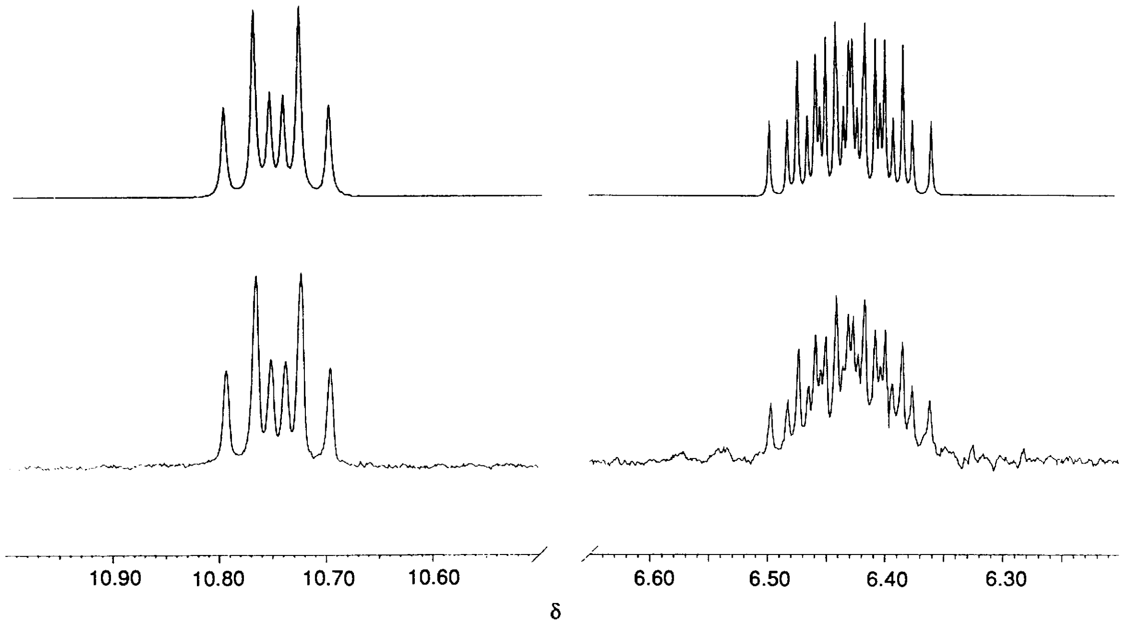
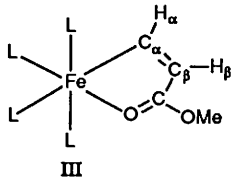
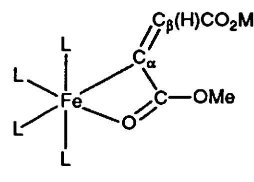


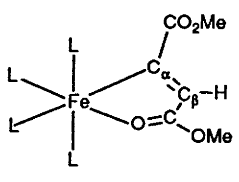
Fig. 2 Observed (bottom) and calculated (top) 200 MHz ^{1}H NMR spectra of the vinyl protons of $[Fe\{CH{=}CH(CO_2Me)\}\{P(OEt)_3\}_4]BPh_4$ **4** in $(CD_3)_2CO$ at 25 °C. The simulated spectrum was obtained with the following parameters: spin system ABC_2XY ($X = H_\alpha$, $Y = H_\beta$), δ_A 169.4, δ_B 159.7, δ_C 148.8, δ_X 10.75, δ_Y 6.43, $J_{AB} = 79.6$, $J_{AC} = 155.0$, $J_{AX} = 5.59$, $J_{AY} = 2.92$, $J_{BC} = 84.0$, $J_{BX} = 5.58$, $J_{BY} = 6.37$, $J_{CX} = 0.1$, $J_{CY} = 4.68$, $J_{XY} = 8.50$ Hz



III



IV



V

at 1591 and 1712 cm^{-1}, attributable to one co-ordinated carbonyl group and to one free CO_2Me substituent, respectively. Between −80 and +30 °C the $^{31}P\text{-}\{^1H\}$ NMR spectrum showed an ABC_2 multiplet, in agreement with two equivalent and two non-equivalent phosphorus groups. Apart from the signal of the phosphite ligands, the ^{1}H NMR spectrum displayed a multiplet at δ 6.22, due to the vinyl proton, and two singlets at δ 3.83 and 3.75 attributed to the methyl protons of two non-equivalent CO_2Me substituents. Two signals for the non-equivalent CO_2Me groups were also observed in the ^{13}C NMR spectra at δ 181.1 and 177.9 (CO group) and 53.9 and 50.9 (methyl carbon). Furthermore, the multiplet at δ 221.4 was attributed to the C_α carbenoid carbon atom, whereas the doublet of multiplets at δ 125.3 with $^1J_{CH} = 168.9$ Hz was assigned to the C_β vinyl atom. According to these data, it is reasonable to propose a cyclic structure for our complex, in which the carbonyl oxygen atom of one of the ester groups co-ordinates to iron in a structure of type **IV** or **V**

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