Bis(alkynyl) and Alkynyl–Vinylidene Iron(II) Complexes with Monodentate Phosphite Ligands†

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The bis(alkynyl) derivatives $[Fe(C{\equiv}CR)_2L_4]$ [R = Ph, *p*-tolyl or Bu^t; L = $P(OMe)_3$, $P(OEt)_3$ or $PPh(OEt)_2$] were prepared and their protonation and methylation reactions with HBF_4 and CF_3SO_3Me afforded alkynyl–vinylidene cations $[Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}L_4]^+$ and $[Fe(C{\equiv}CR)\{{=}C{=}C(Me)R\}L_4]^+$, respectively. The aryldiazovinylidene $[Fe(C{\equiv}CR)\{{=}C{=}C(N{=}NC_6H_4Me\text{-}p)Ph\}\{P(OEt)_3\}_4]BPh_4$ was also prepared. The complexes were characterized by infrared and ^1H, ^{31}P and ^{13}C NMR spectra and the crystal structure of $[Fe(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4$ has been determined. The reactivity of the new vinylidene complexes was studied and showed the rearrangement in solution of the $[Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}L_4]^+$ cations to enynyl $[Fe(\eta^3\text{-}RC_3CHR)L_4]^+$ derivatives only in the case of L=$PPh(OEt)_2$. Deprotonation with base giving $[Fe(C{\equiv}CR)_2L_4]$ as well as substitution of the vinylidene ligand in $[Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}L_4]^+$ cations by CO and $CNC_6H_4Me\text{-}p$ giving $[Fe(C{\equiv}CR)(CO)\{P(OEt)_3\}_4]^+$ and $[Fe(C{\equiv}CR)(p\text{-}MeC_6H_4NC)\{P(OEt)_3\}_4]^+$ derivatives are also discussed.

Transition-metal vinylidene complexes are key species in the chemistry of two-carbon ligands[1] and continue to attract considerable interest.[1–3] This interest arises from different factors including the peculiar reactivity modes and structural properties which vinylidene compounds exhibit[1–3] and their good potential for use in organic synthesis.[4] It has also been suggested that vinylidene species play an important role in Fischer–Tropsch chemistry[5] and in acetylene polymerisation.[6]

Among the metal centres used to bind the C=CRR′ (R = alkyl or aryl, R′ = H or Me) unit, iron and ruthenium play a prominent role. However, a perusal of the literature shows that their vinylidene chemistry involves mainly complexes containing cyclopentadienyl[1,7] or an arene ring[8] as ancillary ligands. Iron vinylidene complexes have been described, only recently[2a,c,9] with only bidentate phosphine ligands of the type $[FeCl\{{=}C{=}C(H)R\}(L\text{–}L)_2]^+$ and $[Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}(L\text{–}L)_2]^+$ (R = Me, Pr^i or Ph; L–L = $Me_2PCH_2CH_2PMe_2$ or $Et_2PCH_2CH_2PEt_2$).

We recently began a study on the reactions of alkynes with phosphite-containing iron(II), ruthenium(II) and osmium(II) complexes which has already led to enynyl and acetylides complexes.[10] As part of these studies we report here the synthesis and characterisation of bis(acetylide) and acetylide–vinylidene iron(II) complexes with monodentate phosphite ligands together with a crystal structure determination and some reactivity studies of the new vinylidene compounds.

Experimental

General Comments.—All operations were performed under an inert atmosphere (argon), using standard Schlenk techniques or a Vacuum Atmosphere dry-box. All solvents 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;[11] trimethyl and triethyl phosphite were Ega Chemie products, purified by distillation under nitrogen. Alkynes were Aldrich products, used without any further purification. Lithium acetylides $Li^+RC{\equiv}C^-$ (R = Ph or *p*-tolyl) were prepared by treating a slight excess of the appropriate acetylene (40 mmol) with lithium (35 mmol, 0.24 g) in tetrahydrofuran (thf, 10 cm^3). The acetylide $Li^+Bu^tC{\equiv}C^-$, on the contrary was prepared by adding to a solution of $Bu^tC{\equiv}CH$ (10 mmol, 1.23 cm^3) in thf (10 cm^3) cooled to −80 °C a solution of LiBu^n (2.5 mol dm^{-3}, 8 mmol, 3.2 cm^3). The mixture was stirred for 20–30 min at −80 °C and then used. Diazonium salts were obtained in the usual way.[12] *p*-Tolyl isocyanide was prepared by the method of Ziehn and co-workers.[13] Other reagents were obtained from commercial sources in the highest available purity and used as received.

Infrared spectra were recorded on a Digilab Biorad FTS-40 spectrophotometer, NMR spectra (^1H, ^{13}C, ^{31}P) on a Bruker AC 200 spectrometer at temperatures between −90 and +34 °C, unless otherwise stated. Proton and ^{13}C spectra are referred to internal tetramethylsilane; $^{31}P\text{-}\{^1H\}$ with respect to 85% H_3PO_4, with downfield shifts considered as positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane or acetone at 25 °C were measured on a Radiometer CDM 83 instrument. Solution susceptibilities were determined by the Evans method.[14]

Synthesis of Complexes.—$[Fe(C{\equiv}CR)_2\{P(OMe)_3\}_4]$ (R = Ph **1a** *or p*-tolyl **1b**). Anhydrous iron(II) chloride (1.26 g, 10 mmol) was placed in a three-necked flask (100 cm^3) and an excess of trimethyl phosphite (5.6 cm^3, 45 mmol) added. The yellow suspension obtained was vigorously stirred for 2 h and then a solution of $Li^+C{\equiv}CR^-$ in thf added (20 mmol, 9.5 cm^3 of 2.1 mol dm^{-3} solution). The reaction mixture was treated with thf (20 cm^3), stirred for 1 h and then the solvent removed under reduced pressure. The oil obtained was dissolved in thf (10 cm^3) and chromatographed through a silica gel column (length 80 cm, diameter 5 cm) using hexane–thf (4:1) as eluent. The first yellow bond eluted was evaporated to dryness and the oil obtained triturated with methanol (10 cm^3). A yellow solid

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

slowly separated which was filtered off and dried under vacuum; yield $\geqslant 15\%$.

$[\mathrm{Fe(C{\equiv}CR)_2\{P(OEt)_3\}_4}]$ (R = Ph **2a**, *p*-tolyl **2b**, *or* Bu^t **2c**). These compounds were prepared as the related **1** by treating $\mathrm{FeCl_2}$ with an excess of $\mathrm{P(OEt)_3}$ and then with the appropriate lithium acetylide in thf. After chromatography, yellow solids were obtained by triturating the oil obtained with ethanol (10 cm^3): yields varied between 25 (**2a**) and 15% (**2b** and **2c**).

$[\mathrm{Fe(C{\equiv}CR)_2\{PPh(OEt)_2\}_4}]$ (R = Ph **3a** *or p*-tolyl **3b**). An excess of $\mathrm{PPh(OEt)_2}$ (5 mmol, 10 cm^3) was added to a suspension of anhydrous $\mathrm{FeCl_2}$ (1.26 g, 10 mmol) in thf (30 cm^3) and the mixture refluxed for 2 h. A solution of the appropriate acetylide in thf (20 mmol, 9.5 cm^3 of 2.1 mol dm^{-3} solution) was added and the mixture stirred for 2 h. Removal of the solvent under reduced pressure gave a brown oil which was triturated with ethanol (10 cm^3). A yellow solid separated after 2–3 h of stirring, which was dissolved in thf (5 cm^3) and chromatographed through a silica gel column (length 80 cm, diameter 5 cm) using hexane–thf (4:1) as eluent. The first band eluted was evaporated to dryness giving an oil which was treated with ethanol (10 cm^3) and stirred until a yellow solid separated (about 1 h); yield $\geqslant 20\%$.

$[\mathrm{Fe(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OMe)_3\}_4]BF_4}$ **4a**. To a solution of $[\mathrm{Fe(C{\equiv}CPh)_2\{P(OMe)_3\}_4}]$ **1a** (0.26 g, 0.34 mmol) in diethyl ether (10 cm^3) cooled to -80 °C was added a solution of $\mathrm{HBF_4{\cdot}Et_2O}$ (50 µl of 54% solution, 0.34 mmol). The mixture was brought to room temperature and stirred for 30 min. The solid which separated was filtered off and dried under vacuum; yield $\geqslant 80\%$.

$[\mathrm{Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}\{P(OEt)_3\}_4]BF_4}$ (R = Ph **5a**, *p*-tolyl **5b**, *or* Bu^t **5c**) *and* $[\mathrm{Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}\{PPh(OEt)_2\}_4]BF_4}$ (R = Ph **6a**, *or p*-tolyl **6b**). A slight excess of $\mathrm{HBF_4{\cdot}Et_2O}$ (52 µl of 54% solution, 0.36 mmol) was added to a solution of the appropriate bis(acetylide) $[\mathrm{Fe(C{\equiv}CR)_2L_4}]$ **2**,**3** (0.3 mmol) in diethyl ether (15 cm^3) cooled to -80 °C. The mixture was brought to 0 °C and stirred for about 1 h to complete precipitation of the complex. The green solid obtained was filtered off, washed with diethyl ether and dried under vacuum; yield $\geqslant 80\%$.

$[\mathrm{Fe(C{\equiv}CPh)\{{=}C{=}C(Me)Ph\}\{P(OMe)_3\}_4][CF_3SO_3]}$ **7a**. Methyl trifluoromethanesulfonate (33 µl, 0.3 mmol) was added to a solution of complex **1a** (0.15 g, 0.2 mmol) in diethyl ether (10 cm^3) cooled to -80 °C. The mixture was brought to room temperature and stirred for 30 min. A green oil separated which was vigorously stirred at 0 °C until a green solid formed; yield $\geqslant 70\%$.

$[\mathrm{Fe(C{\equiv}CR)\{{=}C{=}C(Me)R\}\{P(OEt)_3\}_4][CF_3SO_3]}$ (R = Ph **8a**, *p*-tolyl **8b**, *or* Bu^t **8c**). To a solution of the appropriate bis(acetylide) **2** (0.3 mmol) in diethyl ether (10 cm^3) cooled to -80 °C was added a slight excess of $\mathrm{CF_3SO_3Me}$ (44 µl, 0.4 mmol) and the mixture brought to room temperature. A green solid began to separate after 20–30 min which was then filtered off and dried under vacuum; yield $\geqslant 80\%$.

$[\mathrm{Fe(C{\equiv}CR)\{{=}C{=}C(Me)R\}\{PPh(OEt)_2\}_4][CF_3SO_3]}$ (R = Ph **9a** *or p*-tolyl **9b**). Attempts to prepare these complexes by treating the bis(acetylide) $[\mathrm{Fe(C{\equiv}CR)_2L_4}]$ **3** with $\mathrm{CF_3SO_3Me}$ failed because a green oil was always obtained which decomposed during crystallisation.

$[\mathrm{Fe(\eta^3\text{-}RC_3CHR)\{PPh(OEt)_2\}_4]BPh_4}$ (R = Ph **10a** *or p*-tolyl **10b**). A sample of the appropriate vinylidene $[\mathrm{Fe(C{\equiv}CR)\{{=}C{=}C(H)R\}\{PPh(OEt)_2\}_4]BF_4}$ (0.3 mmol) was dissolved in dichloromethane (10 cm^3) and the mixture stirred for 2 h at room temperature. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (5 cm^3) containing an excess of $\mathrm{NaBPh_4}$ (0.2 g, 0.6 mmol). By vigorously stirring the resulting solution at -10 °C, a yellow orange solid separated which was filtered off and collected; yield $\geqslant 80\%$. The compounds were characterised by comparison of their spectroscopic properties with those of previously[10a] reported complexes.

$[\mathrm{Fe(C{\equiv}CPh)(CO)\{P(OEt)_3\}_4]BPh_4}$ **11**. A solution of $[\mathrm{Fe(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4}$ (0.20 g, 0.2 mmol) in 1,2-dichloroethane (10 cm^3) was refluxed under CO for 6 h and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (5 cm^3) giving a brown solution from which a pale yellow solid was obtained by adding $\mathrm{NaBPh_4}$ (0.14 g, 0.4 mmol) in ethanol (5 cm^3). The product was crystallised from dichloromethane (3 cm^3)–ethanol (5 cm^3), and dried under vacuum; yield $\geqslant 70\%$.

$[\mathrm{Fe(C{\equiv}CPh)\{{=}C{=}C(N_2C_6H_4Me\text{-}}p\mathrm{)Ph\}\{P(OEt)_3\}_4]BPh_4}$ **12**. Toluene-*p*-diazonium tetrafluoroborate (0.206 g, 1 mmol) and the bis(acetylide) $[\mathrm{Fe(C{\equiv}CPh)_2\{P(OEt)_3\}_4}]$ **2a** (0.92 g, 1 mmol) in equimolar amount, were placed in a three-necked flask (50 cm^3) and cooled to about -196 °C. Dichloromethane (20 cm^3) was then added and the mixture brought to room temperature and stirred for about 30 min. The solvent was evaporated under reduced pressure to give a red oil which was treated with ethanol (5 cm^3). Addition of $\mathrm{NaBPh_4}$ (0.7 g, 2 mmol) in ethanol (5 cm^3) to the resulting solution afforded a red solid which was filtered off and crystallised from dichloromethane (3 cm^3)–ethanol (7 cm^3); yield $\geqslant 70\%$.

Structure Analysis of $[\mathrm{Fe(C{\equiv}CPh)\{{=}C{=}C(H)Ph\}\{P(OEt)_3\}_4]BF_4}$ **5a**.—*Crystal data*. $M = 1010.54$, orthorhombic, space group $P2_12_12_1$, $a = 25.84(3)$, $b = 13.95(1)$, $c = 15.26(2)$ Å, $U = 5501$ Å^3, $Z = 4$, $D_c = 1.22$ g cm^{-3}, $F(000) = 2136$, $\mu(\text{Mo-K}\alpha) = 4.5$ cm^{-1}, crystal size 0.23 × 0.37 × 0.58 mm.

Lorentz, polarisation and absorption corrections were applied to 5384 intensity data collected by use of a Philips PW 1100 diffractometer and Mo-Kα radiation up to $2\theta_{\max} = 50°$. The structure was solved by direct methods and refined using full-matrix least-squares procedures in which only the iron and phosphorus atoms were refined anisotropically. Convergence occurred at a conventional *R* factor of 0.1359 for 1371 data and 274 variables. Programs used were SIR 92,[15] SHELXL 92[16] and PARST.[17] The X-ray analysis was rendered difficult by the weak diffracting power of the crystal, disorder problems involving the phosphite molecules and, above all, the tendency of the compound to twin. All attempts to select a crystal showing no sign of any twinning were unsuccessful. Three complete data sets with three different specimens were collected but none gave a satisfactory refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The bis(alkynyl) derivatives $[\mathrm{Fe(C{\equiv}CR)_2L_4}]$ **1**–**3** were synthesised by treating lithium acetylides with a phosphite containing iron(II) chloride solution (Scheme 1). The elemental analysis

$$\mathrm{FeCl_2} + \text{excess L} \xrightarrow[\text{THF}]{\mathrm{Li^+RC{\equiv}C^-}} [\mathrm{Fe(C{\equiv}CR)_2L_4}]$$

Scheme 1 L = $\mathrm{P(OMe)_3}$ **1**, $\mathrm{P(OEt)_3}$ **2**, $\mathrm{PPh(OEt)_2}$ **3**, R = Ph **a**, *p*-tolyl **b** or Bu^t **c**

and some spectroscopic properties of the complexes, which are air-stable yellow diamagnetic solids, are reported in Tables 1 and 2. The infrared spectra show only one medium-intensity $\nu(\mathrm{C{\equiv}C})$ band at 2060–2072 cm^{-1} (dichloromethane) in agreement with a mutually *trans* position of the two acetylide ligands. This arrangement (**I**) is confirmed by the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectra which display between -90 and $+30$ °C only one sharp singlet at δ 162.3–181.8. The ^{1}H and the ^{13}C NMR

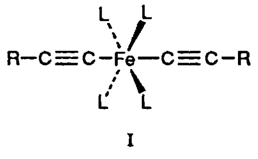

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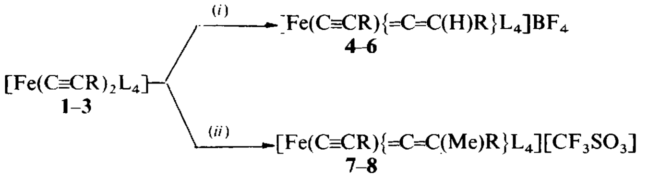
Table 1 Physical, analytical and selected IR data for the complexes

Compound	M.p./°C (decomp.)	Λ_M[a]/ S cm^2 mol^{-1}	Analysis[b] (%) C	H	IR[c] (cm^{-1})
1a $[Fe(CCPh)_2\{P(OMe)_3\}_4]$	123		44.45 (44.60)	6.20 (6.15)	2065s (2064s)
1b $[Fe(CCC_6H_4Me\text{-}p)_2\{P(OMe)_3\}_4]$	96		46.20 (46.05)	6.40 (6.45)	2074s (2072s)
2a $[Fe(CCPh)_2\{P(OEt)_3\}_4]$	141		52.20 (52.05)	7.65 (7.65)	2069s (2063s)
2b $[Fe(CCC_6H_4Me\text{-}p)_2\{P(OEt)_3\}_4]$	129		52.90 (53.05)	7.95 (7.85)	2068s (2064s)
2c $[Fe(CCBu^t)_2\{P(OEt)_3\}_4]$	120		48.80 (49.00)	8.80 (8.90)	2077s (2072s)
3a $[Fe(CCPh)_2\{PPh(OEt)_2\}_4]$	122		64.15 (64.00)	6.70 (6.70)	2058s (2060s)
3b $[Fe(CCC_6H_4Me\text{-}p)_2\{PPh(OEt)_2\}_4]$	117		64.45 (64.55)	6.95 (6.90)	2067s (2061s)
4a $[Fe(CCPh)\{CC(H)Ph\}\{P(OMe)_3\}_4]BF_4$	91	87.9	40.05 (39.95)	5.50 (5.65)	2108s, 1655s, 1630m
5a $[Fe(CCPh)\{CC(H)Ph\}\{P(OEt)_3\}_4]BF_4$	126	88.0	47.40 (47.55)	7.15 (7.10)	2105s, 1658s, 1645s
5b $[Fe(CCC_6H_4Me\text{-}p)\{CC(H)C_6H_4Me\text{-}p\}\{P(OEt)_3\}_4]BF_4$	104	84.0	48.65 (48.55)	7.15 (7.30)	2103s, 1644s
5c $[Fe(CCBu^t\{CC(H)Bu^t\}\{P(OEt)_3\}_4]BF_4$		89.6	44.60 (44.55)	8.15 (8.20)	2092s, 1678s, 1652s
6a $[Fe(CCPh)\{CC(H)Ph\}\{PPh(OEt)_2\}_4]BF_4$	101	90.0	58.85 (59.05)	6.15 (6.30)	2098s, 1653m, 1629s
6b $[Fe(CCC_6H_4Me\text{-}p)\{CC(H)C_6H_4Me\text{-}p\}\{PPh(OEt)_2\}_4]BF_4$		86.5	59.55 (59.70)	6.55 (6.50)	2098s, 1640s
7a $[Fe(CCPh)\{CC(Me)Ph\}\{P(OMe)_3\}_4][CF_3SO_3]$	109	82.7	39.00 (39.25)	5.35 (5.40)	2104s, 1650 (sh), 1632s
8a $[Fe(CCPh)\{CC(Me)Ph\}\{P(OEt)_3\}_4][CF_3SO_3]$	108	83.6	46.35 (46.40)	6.90 (6.75)	2100s, 1627s
8b $[Fe(CCC_6H_4Me\text{-}p)\{CC(Me)C_6H_4Me\text{-}p\}\{P(OEt)_3\}_4][CF_3SO_3]$	108	82.3	47.25 (47.40)	7.15 (6.95)	2105s, 1666m, 1631s
8c $[Fe(CCBu^t)\{CC(Me)Bu^t\}\{P(OEt)_3\}_4][CF_3SO_3]$	95	80.3	43.45 (43.60)	7.70 (7.80)	2095m, 1653s
11 $[Fe(CCPh)(CO)\{P(OEt)_3\}_4]BPh_4$	164	57.6	58.45 (58.55)	7.40 (7.35)	2105m, 1990s ν(CO)[d]
12 $[Fe(CCPh)\{CC(N_2C_6H_4Me\text{-}p)Ph\}\{P(OEt)_3\}_4]BPh_4$[e]	96	54.3	62.50 (62.65)	7.20 (7.20)	2108m

[a] In nitromethane solution (10^{-3} mol dm^{-3}) at 25 °C. [b] Calculated values in parentheses. [c] In Nujol mull or CH_2Cl_2 (in parentheses). [d] At 2106m and 1990s cm^{-1} in dichloromethane solution. [e] N, 1.95 (2.05)%.



Scheme 2 L = $P(OMe)_3$ **4**, **7**; $P(OEt)_3$ **5**, **8**; $PPh(OEt)_2$ **6**; R = Ph **a** *p*-tolyl **b** or Bu^t **c**. (*i*) $HBF_4{\cdot}Et_2O$; (*ii*) CF_3SO_3Me

spectra also confirmed the formulation proposed, showing the characteristic signals of the phosphite and acetylide ligands. In particular, the methyl groups of the *p*-tolyl and of the Bu^t substituent appear as singlets in the ^1H NMR spectra at δ 2.12–2.17 (**1b**, **2b**, **3b**) and at 1.33 (**2c**) respectively, while in the ^{13}C spectra the sp-hybridised C_α and C_β carbons of the acetylide moieties appear as quintets at δ 120.6–128.4 with $^2J_{CP}$ 40 Hz for the former and at δ 130.9–131.7 ($^3J_{CP}$ = 2 Hz) for the latter. Bis(acetylide) complexes have recently been reported with bidentate phosphine ligands[2a,9,18] and show similar spectroscopic properties with ν(C≡C) bands only slightly lower than those of our derivatives **1–3**.

Complexes **1–3** react with HBF_4 or CF_3SO_3Me in diethyl ether to give the corresponding vinylidene derivatives **4–8** (Scheme 2) which can be isolated and characterised (Tables 1, 2). All complexes are green diamagnetic air-stable solids and in solutions of polar organic solvents they behave as 1 : 1 electrolytes.[19] Their IR spectra show a medium-intensity band at 2092–2108 cm^{-1} due to ν(C≡C) of the alkynyl ligand and one or two medium-intensity bands at 1678–1627 cm^{-1} attributed to ν(C=C) of the vinylidene ligands.[1–3] In the ^1H NMR spectra the characteristic vinyl proton of the =C=(H)R ligand in **4–6** appears as a quintet at δ 4.66–6.13 owing to coupling with the four P atoms of the phosphite ligands (J_{PH} = 6–7 Hz), whereas for the methylvinylidenes **7** and **8** the signal of the CH_3 group is a quintet too, but at δ 1.82–2.19. However, strong support for the formulation of the complexes as alkynyl-vinylidene came from the proton-coupled ^{13}C NMR spectra which show the characteristic highly deshielded Fe=C= carbene carbon resonance as a quintet of doublets for the vinylidene (**5a**) at δ 380.2 ($^2J_{CP}$ = 40 $^2J_{CH}$ = 5.5 Hz) and as a quintet of quartets at δ 386.2–382.9 ($^2J_{CP}$ = 40, $^3J_{CH}$ = 4 Hz) for the methylvinylidene derivatives (**7a** and **8b**). Furthermore, the vinylic =C(H)R carbon resonances are observed in the ^{13}C spectra as a doublet of multiplets at δ 119.5 with $^1J_{CH}$ = 152 Hz for **5a** and as a complicated multiplet at δ 125.7 for **8b**. Finally, the C_α ethynyl carbons of the $RC\equiv C^-$ ligand appear as quintets at δ 109.8–99.8 ($^2J_{CP}$ = 50 Hz), while the methyl carbon atom of the =C=C(Me)R fragment in **7a** and **8b** is a quartet of multiplets at δ 11.1–11.8 with typical $^1J_{CH}$ of 123 Hz.

In the temperature range between +30 and −70 °C the ^{31}P-{^1H} NMR spectra of all the vinylidene complexes are sharp singlets at δ 137.9–161.3, suggesting the existence in solution of a *trans* geometry analogous to that observed in the solid state (see below). However, as the temperature is lowered below −70 °C the singlet observed in the ^{31}P spectra broadens and at −90 °C an A_2B_2 multiplet appears (Fig. 1), which can be simulated with the parameters reported in Table 2. This behaviour may be explained on the basis of a restricted rotation of the phosphite ligands as the temperature is lowered,[20] which may cause a distortion of the molecule to minimise the phosphorus and vinylidene group interactions. In this way a distorted *trans*-octahedral geometry (**II**) similar to that found in the solid state seems to be present at very low temperature in solution. For such a geometry, in which two phosphorus atoms are closer to the acetylide ligands (P_A) and the other two closer to the vinylidene group (P_B), an A_2B_2 spectrum is expected, as previously observed in the *trans* [RuH(Cl)(L-L)$_2$] complex[21] with inequivalent phosphorus atoms [L-L = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane]. These observations demonstrate the analogy between the solid-state (see below) and solution structure of these complexes.

Although the X-ray results for complex **5a** do not allow for a detailed discussion especially of the bonding parameters of the lighter atoms, some of which are quite unrealistic, a few general observations can be made, as the basic features of the structure are clear. The crystal structure consists of [Fe(C≡CPh){=C=C(H)Ph}{P(OEt)$_3$}$_4$]$^+$ cations and BF_4^- anions separated by normal contacts. An ORTEP[22] view of the cationic complex which emphasises the metal environment is shown in Fig. 2 together with the main bond distances and angles (atomic coordinates are in Table 3). The iron atom is surrounded by the four P atoms from the phosphite molecules and two C atoms from the vinylidene and acetylide groups in a somewhat distorted-octahedral array. Of the three co-ordination planes, the set formed by the four P atoms shows a

Table 2 Proton, ^{31}P and ^{13}C NMR spectral data

	^{1}H[a,b]		^{31}P-{^{1}H}[a,c]	^{13}C[a,d]		
Compound	δ	Assignment	δ	δ	Assignment	J/Hz
1a[e]	3.87 (m)	$\mathrm{P(OCH_3)}$	165.0 (s)	130.9 (qnt, br)	C_β acetylide	
				120.6 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 40
				53.6 (t)	$\mathrm{CH_3}$ phosphite	
1b[e]	3.84 (m)	$\mathrm{P(OCH_3)}$	163.9 (s)			
	2.24 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$				
2a[e]	4.19 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	162.3 (s)	131.7 (qnt)	C_β acetylide	$^{3}J_{CP}$ = 2
	0.99 (t)	$\mathrm{POCH_2C}H_3$		123.9 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 40
				61.8 (t)	$\mathrm{CH_2}$ phosphite	
				16.8 (q)	$\mathrm{CH_3}$ phosphite	
2b[e]	4.50 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	162.5 (s)			
	2.12 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$				
	1.30 (t)	$\mathrm{POCH_2C}H_3$				
2c[e]	4.47 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	163.4 (s)			
	1.33 (s)	$\mathrm{C(CH_3)_3}$				
	1.32 (t)	$\mathrm{POCH_2C}H_3$				
3a[e]	3.74 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	181.8 (s)	128.4 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 40
	1.05 (t)	$\mathrm{POCH_2C}H_3$		62.8 (t)	$\mathrm{CH_2}$ phosphite	
				16.6 (q)	$\mathrm{CH_3}$ phosphite	
3b[e]	3.76 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	181.7 (s)			
	2.17 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$				
	1.07 (t)	$\mathrm{POCH_2C}H_3$				
4a	6.13 (qnt) (J_{PH} = 6)	$\mathrm{CC}(H)\mathrm{Ph}$	141.9 (s)			
	3.87 (m)	$\mathrm{P(OCH_3)}$				
5a	5.99 (qnt) (J_{PH} = 7)	$\mathrm{CC}(H)\mathrm{Ph}$	138.0 (s)	380.2 (qnt of d)	C_α vinylidene	$^{2}J_{CP}$ = 40, $^{2}J_{CH}$ = 5.5
	4.24 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	[f] δ_A 143.5, δ_B 137.1	119.5 (d of m)	C_β vinylidene	$^{1}J_{CH}$ = 152
	1.28 (t)	$\mathrm{POCH_2C}H_3$	J_{AB} = 129.0	102.9 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 50
				64.0 (t of m)	$\mathrm{CH_2}$ phosphite	
				15.7 (q of m)	$\mathrm{CH_3}$ phosphite	
5b	5.97 (qnt) (J_{PH} = 7)	$\mathrm{CC}(H)\mathrm{C_6H_4Me}$	137.9 (s)			
	4.24 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$				
	2.32 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$				
	1.29 (t)	$\mathrm{POCH_2C}H_3$				
5c	4.66 (qnt) (J_{PH} = 7)	$\mathrm{CC}(H)\mathrm{Bu^t}$	139.6 (s)			
	4.18 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$				
	1.29 (t)	$\mathrm{POCH_2C}H_3$				
	1.15 (s)	$\mathrm{C(CH_3)_3}$				
	1.14 (s)	$\mathrm{C(CH_3)_3}$				
6a[g]	5.84 (br)	$\mathrm{CC}(H)\mathrm{Ph}$	161.3 (s)	378 (br)	C_α vinylidene	
	3.62 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		109.8 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 50
	1.16 (t)	$\mathrm{POCH_2C}H_3$		64.7 (m)	$\mathrm{CH_2}$ phosphite	
				16.3 (q of m)	$\mathrm{CH_3}$ phosphite	
6b[g]	5.95 (br)	$\mathrm{CC}(H)\mathrm{C_6H_4Me}$	154.0 (s)			
	3.70 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$				
	2.34 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$				
	1.18 (t)	$\mathrm{POCH_2C}H_3$				
7a	3.82 (m)	$\mathrm{P(OCH_3)}$	142.8 (s)	386.2 (qnt of q)	C_α vinylidene	$^{2}J_{CP}$ = 40, $^{3}J_{CH}$ = 4
	2.17 (qnt,br)	$\mathrm{CC(C}H_3\mathrm{)Ph}$		99.8 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 50
				55.0 (m)	$\mathrm{CH_3}$ phosphite	
				11.1 (q of m)	$\mathrm{CH_3}$ vinylidene	
8a	4.16 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	138.5 (s)			
	2.18 (qnt)	$\mathrm{CC(C}H_3\mathrm{)Ph}$	[f] δ_A 142.5, δ_B 137.6			
	1.23 (t)	$\mathrm{POCH_2C}H_3$	J_{AB} = 128.7			
8b	4.19 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	138.7 (s)	382.9 (qnt of q)	C_α vinylidene	$^{2}J_{CP}$ = 40, $^{3}J_{CH}$ = 4
	2.33 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$	[f] δ_A 143.0, δ_B 137.7	125.7 (m)	C_β vinylidene	
	2.31 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$	J_{AB} = 128.3	100.8 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 50
	2.19 (qnt)	$\mathrm{CC(C}H_3\mathrm{)C_6H_4Me}$		63.9 (t of m)	$\mathrm{CH_2}$ phosphite	
	1.25 (t)	$\mathrm{POCH_2C}H_3$		21.4, 21.1 (q)	$\mathrm{CH_3}$ *p*-tolyl	
				16.4 (q of m)	$\mathrm{CH_3}$ phosphite	
8c				11.8 (q of m)	$\mathrm{CH_3}$ vinylidene	
	4.20 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	139.9 (s)			
	1.82 (m)	$\mathrm{CC(C}H_3\mathrm{)Bu^t}$				
	1.30 (t)	$\mathrm{POCH_2C}H_3$				
11[g,h]	1.17 (s)	$\mathrm{C(CH_3)_3}$				
	4.34 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	146.4 (s)			
	1.34 (t)	$\mathrm{POCH_2C}H_3$	[f] δ_A 151.7, δ_B 143.3			
12[g,h]			J_{AB} = 120.0			
	4.33 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	134.8 (s)	386.2 (qnt)	C_α vinylidene	$^{2}J_{CP}$ = 40
	2.36 (s)	$\mathrm{C}H_3\mathrm{C_6H_4}$		101.5 (qnt)	C_α acetylide	$^{2}J_{CP}$ = 50
	1.28 (t)	$\mathrm{POCH_2C}H_3$		64.7 (m)	$\mathrm{CH_2}$ phosphite	
				21.2 (q)	$\mathrm{CH_3\ N_2C_6H_4Me}$-*p*	
				16.3 (m)	$\mathrm{CH_3}$ phosphite	

[a] At room temperature in $\mathrm{CD_2Cl_2}$, J in Hz. [b] Phenyl-proton resonances are omitted. [c] Positive shift downfield from 85% $\mathrm{H_3PO_4}$, spin system A_4 except where indicated. [d] All phenyl-carbon resonances omitted. [e] Proton and ^{31}P-{^{1}H} in $\mathrm{C_6D_6}$. [f] At −80 °C, spin system A_2B_2. [g] At −10 °C. [h] In $\mathrm{(CD_3)_2CO}$.

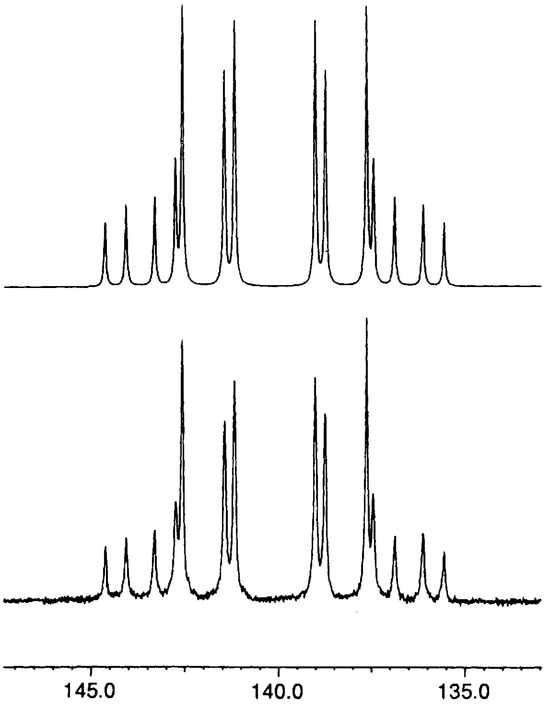
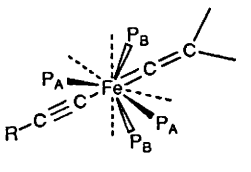


Fig. 1 Observed (bottom) and calculated (upper traces) $^{31}P-\{^1H\}$ NMR spectra of $[Fe(C\equiv CPh)\{=C=C(Me)Ph\}\{P(OEt)_3\}_4][CF_3SO_3]$ **8a** in CD_2Cl_2 at −80 °C. The simulated spectra were obtained with the parameters reported in Table 2. See text for discussion



II

significant degree of tetrahedral distortion as previously found for the closely related structure of the ruthenium derivative[23] $[Ru(C\equiv CPh)\{=C=C(Me)Ph\}\{P(OEt)_3\}_4][CF_3SO_3]$ while the other two sets are essentially planar. The iron–phosphorus distances agree with those found for mutually *trans*-co-ordinated phosphites in six-co-ordinate iron(II) complexes.[24] The iron–vinylidene carbon distance of 1.75 Å lies within the range of lengths observed in mononuclear vinylidene complexes,[1,25] whereas the iron–acetylide carbon distance of 2.04 Å is rather long when compared with those found in mononuclear σ-bonded acetylide iron(II) complexes.[9b,18,26] The reason for this lengthening could be a structural *trans* effect produced by the vinylidene ligand.

The bis(acetylide)iron(II) complexes also react with other electrophilic reagents such as arenediazonium cations to give, for example, the diazovinylidene derivative $[Fe(C\equiv CPh)[=C=C(N=NC_6H_4Me\text{-}p)Ph\}\{P(OEt)_3\}_4]BPh_4$ **12** (Scheme 3) which can be isolated and characterised (Tables 1,2). The IR spectrum of **12** shows a ν(C≡C) band at 2108 cm^{-1}, while in the ^1H NMR spectrum the signal of the methyl substituent of $N_2C_6H_4Me\text{-}p$ appears as a singlet at δ 2.36. However, diagnostic for the formulation of vinylidene derivatives is the presence of a highly dishielded carbene-carbon atom observed as a quintet at δ 386.2 with $^2J_{CP}$ = 40 Hz. Also C_α of the acetylide ligand appears as a quintet at δ 101.5 ($^2J_{CP}$ = 50 Hz) in the ^{13}C NMR spectrum while the methyl group of the $N_2C_6H_4Me\text{-}p$ substituent appears at δ 21.2 as a quartet (in the proton-coupled spectrum). The $^{31}P-\{^1H\}$ NMR spectrum of **12** is a sharp singlet at δ 134.8 until −70 °C, but at lower temperature it broadens giving an A_2B_2 multiplet at −90 °C. On this evidence, distorted *trans* geometries in solution, similar to that of the other vinylidenes **6–8** can reasonably be proposed for this derivative.

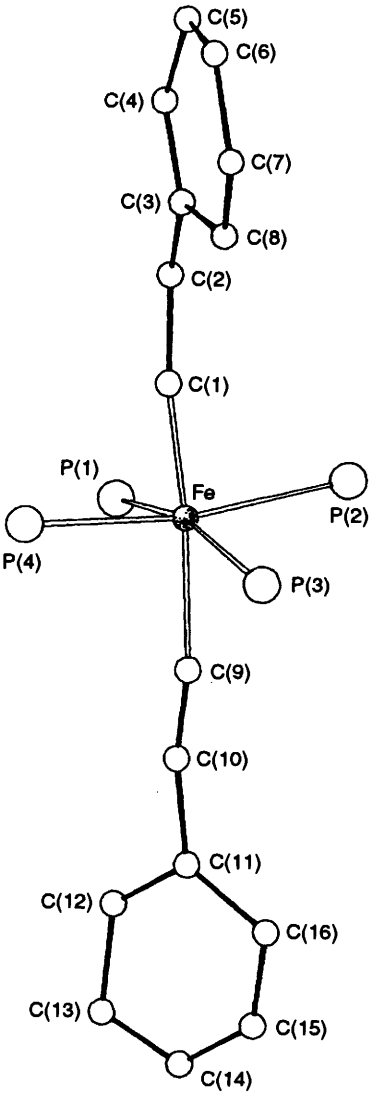


Fig. 2 Perspective view of the cationic complex $[Fe(C\equiv CPh)\{=C=C(H)Ph\}\{P(OEt)_3\}_4]^+$. Radii are arbitrary and OEt groups are omitted. Selected bond distances (Å) and angles (°): Fe–P(1) 2.22(1), Fe–P(2) 2.34(2), Fe–P(3) 2.20(1), Fe–P(4) 2.16(2) Fe–C(1) 1.75(4) and Fe–C(9) 2.04(4); P(1)–Fe–P(3) 162.2(5), P(2)–Fe–P(4) 169.4(8), C(1)–Fe–C(9) 174(2), Fe–C(1)–C(2) 146(4) and Fe–C(9)–C(10) 159(4)

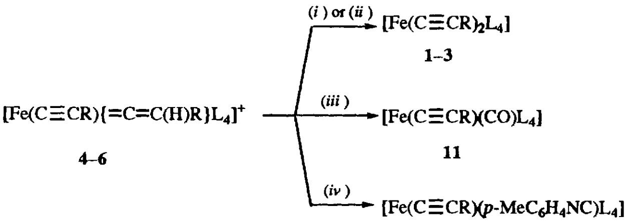
$$[Fe(C\equiv CPh)_2L_4] \xrightarrow{p\text{-}MeC_6H_4N_2^+} [Fe(C\equiv CPh)\{=C=C(N=NC_6H_4Me\text{-}p)Ph\}L_4]^+ \quad \mathbf{12}$$

Scheme 3 L = $P(OEt)_3$

Reactivity.—All the vinylidene and methylvinylidene complexes are stable in solution except the $PPh(OEt)_2$ derivatives $[Fe(C\equiv CR)\{=C=C(H)R\}\{PPh(OEt)_2\}_4]^+$ **6** which react in solution to afford the enynyl cations $[Fe(\eta^3\text{-}RC_3CHR)\{PPh(OEt)_2\}_4]^+$. The reaction is rather rapid at room temperature and therefore the spectroscopic data for **6** were obtained at about −10 °C. The formation of enynyl

Table 3 Atomic coordinates (× 10^4) for complex **5a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Fe	8 708(2)	2 858(4)	10 138(5)	C(15)	10 593(51)	−564(112)	9 706(94)
P(1)	8 138(5)	1 671(8)	10 200(11)	C(16)	10 275(35)	318(63)	9 624(53)
P(2)	8 620(8)	2 987(13)	8 616(13)	C(17)	7 024(29)	1 583(51)	9 873(60)
P(3)	9 426(4)	3 673(8)	9 927(11)	C(18)	6 666(28)	2 219(54)	10 177(57)
P(4)	8 704(7)	2 979(16)	11 550(11)	C(19)	7 948(33)	254(65)	8 986(57)
O(1)	7 546(11)	2 038(21)	10 298(20)	C(20)	8 305(36)	−510(71)	8 482(52)
O(2)	8 083(14)	1 081(26)	9 376(23)	C(21)	8 424(55)	251(103)	10 819(92)
O(3)	8 218(14)	989(26)	11 072(22)	C(22)	8 012(28)	−385(53)	11 663(42)
O(4)	7 983(15)	2 853(29)	8 419(26)	C(23)	7 943(25)	2 701(51)	7 596(47)
O(5)	8 688(26)	3 879(54)	8 189(41)	C(24)	7 354(47)	3 310(108)	7 632(77)
O(6)	9 080(25)	2 186(58)	8 166(49)	C(25)	9 138(35)	4 379(67)	7 365(58)
O(7)	9 362(11)	4 778(21)	9 796(23)	C(26)	8 767(31)	5 479(63)	7 269(49)
O(8)	9 759(15)	3 566(29)	10 726(25)	C(27)	9 026(43)	1 965(94)	7 536(77)
O(9)	9 787(19)	3 426(34)	9 114(28)	C(28)	9 380(39)	1 305(76)	7 107(60)
O(10)	8 130(16)	2 887(33)	11 919(25)	C(29)	9 716(24)	5 528(42)	10 026(55)
O(11)	8 831(15)	4 047(31)	11 917(23)	C(30)	9 484(17)	6 475(30)	9 592(30)
O(12)	8 983(28)	2 383(61)	12 014(44)	C(31)	10 116(30)	2 854(61)	10 985(47)
C(1)	8 240(17)	3 756(28)	10 287(31)	C(32)	10 534(28)	3 351(58)	11 848(41)
C(2)	7 814(21)	4 294(39)	9 893(45)	C(33)	10 197(41)	3 669(72)	8 852(64)
C(3)	7 742(18)	5 374(31)	10 212(35)	C(34)	10 544(31)	3 237(63)	8 285(48)
C(4)	7 249(20)	5 759(38)	10 206(38)	C(35)	7 913(32)	3 206(63)	12 889(49)
C(5)	7 182(30)	6 770(49)	10 071(52)	C(36)	7 391(38)	2 985(85)	12 714(60)
C(6)	7 620(29)	7 324(53)	9 944(57)	C(37)	8 676(37)	4 786(72)	12 153(56)
C(7)	8 101(22)	6 921(41)	10 298(38)	C(38)	9 066(28)	5 490(56)	12 497(44)
C(8)	8 219(24)	5 958(44)	10 280(41)	C(39)	9 028(28)	1 565(58)	12 635(46)
C(9)	9 200(16)	1 723(30)	10 012(36)	C(40)	9 535(29)	1 334(56)	12 895(47)
C(10)	9 473(14)	1 117(26)	10 209(29)	B	1 373(18)	5 851(32)	113(40)
C(11)	9 810(22)	280(39)	10 007(47)	F(1)	1 746(17)	5 731(32)	708(27)
C(12)	9 731(27)	−459(50)	10 553(42)	F(2)	1 743(19)	5 816(37)	−501(32)
C(13)	10 102(29)	−1 271(53)	10 615(45)	F(3)	1 151(13)	6 652(25)	−190(27)
C(14)	10 448(24)	−1 279(42)	10 237(45)	F(4)	1 139(17)	5 062(34)	−189(33)



Scheme 4 L = $P(OMe)_3$, $P(OEt)_3$ or $PPh(OEt)_2$; base = NEt_3, $PhNH_2$ or $PhNHNH_2$. (*i*) Base; (*ii*) BH_4^- or $BHEt_3^-$; (*iii*) CO^-; (*iv*) *p*-MeC_6H_4NC

complexes from alkynyl–vinylidene compounds was previously observed[2a,c] for related derivatives of the type $[Fe(C{\equiv}CR)\{=C=C(H)R\}(L\text{–}L)_2]^+$ (L–L = $Me_2PCH_2CH_2PMe_2$ or $Et_2PCH_2CH_2PEt_2$) and a possible mechanism[2a] of reaction was also proposed. It therefore seems almost an exception the stability of the alkynyl–vinylidenes **4** and **5** instead of their reactivity to give enynyl derivatives as final products. However, $[Fe(\eta^3\text{-}RC_3CHR)L_4]^+$ complexes were previously obtained[10a] by us from the reaction of $[FeH(\eta^2\text{-}H_2)L_4]^+$ species with terminal alkynes, but only with L = $PPh(OEt)_2$ and $[Fe(C{\equiv}CR)L_5]^+$ were the only reaction products with L = $P(OEt)_3$. The influence of the phosphite ligand seems therefore to be analogous in the two reactions, which allow enynyl complexes to be obtained only with $PPh(OEt)_2$.

Some data on the reactivity of the vinylidene derivatives are summarised in Scheme 4. Deprotonation of complexes **4**–**6** is easy and affords the corresponding bis(alkynyl) derivatives **1**–**3**. The reaction proceeds at room temperature not only with amine or hydrazine as base, but also with $NaBH_4$ or $NaBHEt_3$ used in an attempt to reduce[7d,e] the $=C=C(H)R$ moiety to the alkenyl group $-CH=C(H)R$. More interestingly, also the related methylvinylidenes $[Fe(C{\equiv}CR)\{=C=C(Me)R\}L_4]^+$ **7** and **8** react with $NaBH_4$ to give the bis(alkynyl) derivatives $[Fe(C{\equiv}CR)_2L_4]$. These reactions indicated that, in contrast with what was previously found in other iron complexes,[7d,e,i] our vinylidene fragments $=C=C(H)R$ do not add hydrides as anionic nucleophiles to give vinyl complexes but the treatment with BH_4^- results in a deprotonation or demethylation reaction giving bis(acetylides) as final products.

The vinylidene ligand $=C=C(H)R$ in complexes **4**–**6** can also be substituted by CO and *p*-MeC_6H_4NC giving new acetylide complexes which, in the case of the carbonyl, can be isolated as a solid, whereas only oily products were obtained with isocyanides. As an example we describe here the derivative $[Fe(C{\equiv}CPh)(CO)\{P(OEt)_3\}_4]BPh_4$ **11** the IR spectrum of which shows ν(C≡C) at 2105 cm^{-1} and ν(CO) at 1990 cm^{-1} (Table 1). The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits a behaviour similar to those of the vinylidene precursors, showing between +30 and −60 °C a singlet near δ 146, which changes as the temperature is lowered further, giving an A_2B_2 multiplet at −80 °C. A distorted *trans* geometry analogous to that proposed for the vinylidene precursor **5** therefore seems to be present also for **11**.

We also attempted to prepare carbene complexes by treating our vinylidene derivatives with amines or alcohols, but no significant results were obtained. A deprotonation reaction occurs on treatment with amines whereas only decomposition was observed over a long reaction time with alcohols.

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