

# Preparations of novel half-sandwich iron carbonyl phosphine complexes: intramolecular link between the cyclopentadienyl and the phosphine ligand

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## Abstract

The novel iron half-sandwich complex ( $\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$ )Fe(CO)Cl (**4**), in which the ligating phosphine was connected to the cyclopentadienyl ring, was prepared by reacting the  $\text{LiC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$  (**2**) with  $\text{FeCl}_2$  followed by CO bubbling. Reaction of **4** with  $\text{sp}^-$ ,  $\text{sp}^2$ - and  $\text{sp}^3$ -hybridized carbon nucleophiles provided formal substitution product ( $\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$ )Fe(CO)R (**5**). Solid state structures of the methyl complex **5a**, phenylacetylide **5g** and trimethylsilylacetylide **5j** were characterized by single-crystal X-ray analyses.

**Keywords:** Iron; Alkyl; Alkyne; Cyclopentadienyl; Phosphine; Vinyl

## 1. Introduction

The chemistry of half-sandwich iron complexes that possesses the chiral [ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)$ ] fragment [1] have been studied extensively. For example, a variety of carbene complexes of this type have been synthesized and displayed cyclopropanation of alkenes [2]. Acyl ligands attached to the chiral [ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)$ ] fragment showed stereoselective reactions including alkylations [3], aldol reactions [4], Michael additions [5] and Diels–Alder reactions [6]. All the above-mentioned iron complexes contained four discrete ligands, namely a cyclopentadienyl, a carbon monoxide, a phosphine and an organic ligand. None of them linked to each other, forming a bidentate-type structure. Although half-sandwich iron complexes that contain a bisphosphine bidentate ligand have been reported, the iron complexes that contain a heterobidentate ligand of the type of cyclopentadienyl-phosphine bidentate are not known in the literature.

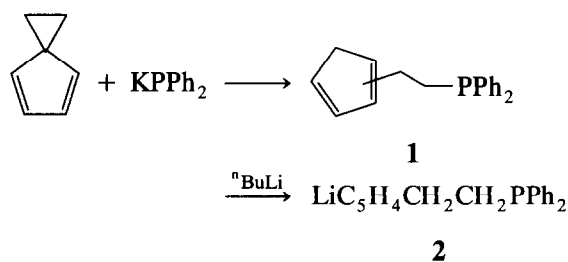
Cyclopentadienes with a ligating phosphine substituent have been used in the syntheses of manganese

[7], ruthenium [8] and cobalt [9] complexes. The molecular structure of the chelate ruthenium complex ( $\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$ )Ru(PPh<sub>3</sub>)Cl has been shown to have a very similar structure to that of the non-chelate complex ( $\eta^5\text{-C}_5\text{H}_5$ )Ru(PPh<sub>3</sub>)<sub>2</sub>Cl [10]. It is our intention to explore the chemistry of chelate iron complexes of this type and to investigate their variances with the non-chelate complexes. In this paper we report the synthesis of chelate iron complex ( $\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$ )Fe(CO)Cl (**4**) and a general procedure for the preparation of chelate compounds of the general formula of ( $\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$ )Fe(CO)R (R = organic residue). The solid state structures for which R = CH<sub>3</sub> (**5a**),  $\eta^1\text{-C}\equiv\text{CPh}$  (**5g**) and  $\eta^1\text{-C}\equiv\text{CSi}(\text{CH}_3)_3$  (**5j**) will be reported.

## 2. Results and discussion

The heterobifunctional ligand  $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{PPh}_2$  (**1**) is a good starting point for synthesizing such a class of compounds. It could be easily prepared by treatment of spiro [4.2]hepta-2,4-diene with potassium diphenylphosphide [11]. Compound **1** was isolated as 1:1 mixture of two regioisomers. Fortunately, deprotonation of **1** provided single lithiated compound **2** (Scheme 1).

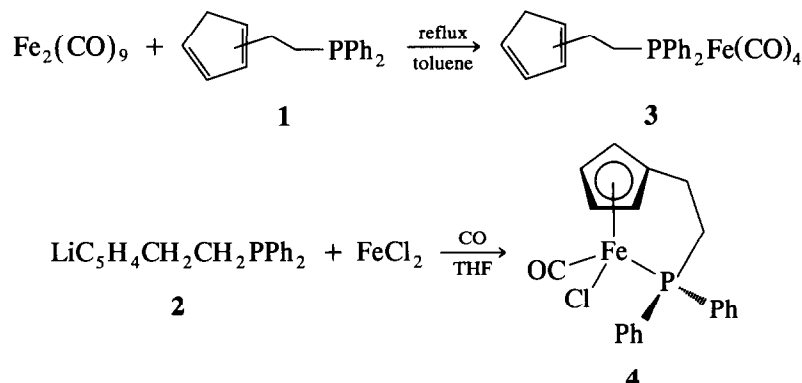
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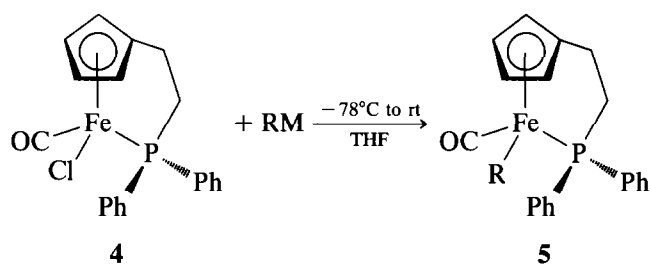
Scheme 1.

### 2.1. Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})\text{Cl}$ (**4**)

Previous methods for preparing non-chelate cyclopentadienyliron carbonyl trialkylphosphine halides required three steps, including the preparation of the cyclopentadienyliron dicarbonyl dimer followed by halogenation and carbonyl displacement with trialkylphosphines [12]. Preparation of the chelate complex **4** (Scheme 2) was originally designed to follow a procedure similar to that for preparing the non-chelate complex. However, in an attempt to synthesize the corresponding iron dimer by the standard procedure [13], only phosphine tetracarbonyliron (**3**) was isolated. Attention was then turned to the more direct one-pot methodology. Treatment of ferrous chloride with **2** in tetrahydrofuran (THF) followed by carbon monoxide bubbling provided chloride **4** with a 30–39% yield [14]. Examining the  $^{31}\text{P}$  NMR spectrum showed that the chemical shift of phosphorus moved from  $\delta = 15$  ppm of the free ligand to  $\delta = 71$  ppm, indicating that phosphorus was coordinated to the metal. A sharp absorption at  $1956\text{ cm}^{-1}$  in the infrared spectrum suggested a terminal CO group. In the  $^{13}\text{C}$  NMR spectrum, the resonance corresponding to the terminal CO displayed at  $\delta = 219.0$  ppm was split into a doublet ( $^2J_{\text{cp}} = 27.5$  Hz). This was due to the spin coupling by the ligated phosphorus atom which was only two bonds away. In the  $^1\text{H}$  NMR spectrum, only three Cp ring proton signals were observed ( $\delta = 5.77, 5.23$  and  $5.02$  ppm) in the normal Cp region. The fourth proton was observed



Scheme 2.



RM = (a)  $\text{CH}_3\text{MgCl}$ , 92%; (b)  $^n\text{BuLi}$ , 58%;  
 (c)  $\text{CH}_2=\text{CHCH}_2\text{MgCl}$ , 72%; (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ , 55%;  
 (e)  $\text{C}_6\text{H}_5\text{Li}$ , 45%; (f)  $\text{CH}_2=\text{CHMgBr}$ , 60%;  
 (g)  $\text{C}_6\text{H}_5\text{C}\equiv\text{CLi}$ , 87%; (h) cyclohexyl- $\text{C}\equiv\text{CLi}$ , 85%;  
 (i) *n*-pentyl- $\text{C}\equiv\text{CLi}$ , 75%; (j)  $(\text{CH}_3)_3\text{Si-C}\equiv\text{CLi}$ , 80%.

Scheme 3.

upfield at  $\delta = 2.88$  ppm. This result may arise from the shielding effect of one of the phenyl groups of phosphorus [8].

In principle, bifunctional compound **1** coordinated with iron would provide monomeric, dimeric and/or polymeric complexes. However, only one isomer was isolated. The structure was proposed as the monomeric **4** based on the highest fragmentation peak appeared in the mass spectrum at  $m/e = 368$ , which was assigned to the monomeric molecular ion minus CO. Related manganese [7], ruthenium [8] and cobalt [9] complexes were also reported as the monomeric form. Transformation of **4** into the corresponding alkyl derivatives and structural determination of **5a**, **5g** and **5j** by single-crystal diffraction analyses suggested that **4** was a monomeric structure (see below).

### 2.2. Preparations of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})\text{R}$ (**5**)

The conventional method for the preparation of alkylmetal complexes by reaction of alkyllithium or alkylmagnesium reagents with metal halides proved to be quite successful in our system. For example, **4** reacted with methylmagnesium chloride to give the methyl complex **5a** with an excellent yield (92%)

Table 1  
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in **5a**

<i>Bond lengths</i>			
Fe–P	2.1665(17)	Fe–C(1)	1.748(6)
Fe–C(2)	2.063(6)	Fe–C(3)	2.106(5)
P–C(9)	1.855(6)	C(1)–O(1)	1.110(8)
<i>Bond angles</i>			
P–Fe–C(1)	94.96(20)	Fe–P–C(11)	117.70(20)
P–Fe–C(2)	94.30(17)	Fe–P–C(21)	106.6(3)
P–Fe–C(3)	82.62(15)	C(9)–P–C(11)	103.0(3)
C(1)–Fe–C(2)	86.5(3)	C(9)–P–C(21)	106.6(3)
C(2)–Fe–C(6)	90.19(25)	C(11)–P–C(21)	100.6(3)
Fe–P–C(9)	104.40(19)	Fe–C(1)–O(1)	176.5(7)
<i>Torsion angles</i>			
P–Fe–C(3)–C(8)	–1.3(2)	C(9)–P–C(21)–C(26)	117.1(5)
Fe–P–C(11)–C(12)	–179.0(5)	C(7)–C(3)–C(4)–C(5)	–0.1(3)
C(9)–P–C(21)–C(22)	–2.6(3)	C(8)–C(3)–C(7)–C(6)	–171.8(7)
C(21)–P–C(9)–C(8)	–173.6(5)	P–C(9)–C(8)–H(8-1)	–75.9(5)
Fe–P–C(11)–C(16)	1.5(3)	P–C(9)–C(8)–H(8-2)	167.6(8)

(Scheme 3). For reactions of **4** with *n*-butyllithium, allylmagnesium chloride or benzylmagnesium chloride also provided the desired compounds respectively with reasonable yields (55–72%). Slight lower yields were obtained for the aryl complex **5e** (45%) and the vinyl complex **5f** (60%). Quite good yields were obtained for alkynyl complexes (**5g–5j**, 75–87%) [15]. Reactions were performed at  $-78^{\circ}\text{C}$  by adding organometal reagents to the dark-green THF solution of **4** followed by warming to room temperature. The terminal carbonyl stretchings of **5** appeared between 1900 and 1903  $\text{cm}^{-1}$  for alkyl complexes (**5a–5d**), 1918 and 1920  $\text{cm}^{-1}$  for olefinic complexes (**5e** and **5f**) and between 1944 and 1953  $\text{cm}^{-1}$  for acetylenic complexes (**5g–5i**). The chemical shifts of  $^{31}\text{P}$  appeared in the region between

$\delta = 83.0$  ppm and  $\delta = 96.1$  ppm. The  $^{31}\text{P}$  resonances of the alkyl complexes **5a–5d** displayed at the downfield side ( $\delta = 96.1$ – $93.6$  ppm) and the acetylenic complexes **5g–5i** showed at the upfield side ( $\delta = 82.3$ – $84.4$  ppm) while the olefinic complexes **5e** and **5f** appeared in between ( $\delta = 89.2$ – $90.9$  ppm).

In the  $^1\text{H}$  NMR spectra, the chemical shifts of Cp protons of **5** appeared in the normal region ( $\delta = 4.78$ – $3.60$  ppm). Other protons were also displayed at their usual positions. However, it is worth noting that one of the protons on the carbon atom next to the Cp ring couples with the phosphorus to give the  $^3J$  coupling constant at about 33–39 Hz. The large coupling may result from their large dihedral angle of about  $167^{\circ}$  (Tables 1–3).

Table 2  
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in **5g**

<i>Bond distances</i>			
Fe–P	2.1859(17)	C(1)–O(1)	1.155(8)
Fe–C(1)	1.726(6)	C(2)–C(7)	1.501(9)
Fe–C(9)	1.919(6)	C(9)–C(10)	1.214(9)
P–C(8)	1.834(6)	C(10)–C(11)	1.418(8)
<i>Bond angles</i>			
P–Fe–C(1)	95.74(20)	P–Fe–C(31)	120.39(18)
P–Fe–C(2)	81.32(17)	C(8)–P–C(21)	103.3(3)
P–Fe–C(4)	146.01(20)	Fe–C(9)–C(10)	172.7(5)
P–Fe–C(9)	92.54(17)	C(9)–C(10)–C(11)	173.4(6)
C(1)–Fe–C(9)	87.0(3)	C(8)–P–C(31)	107.2(3)
Fe–P–C(8)	102.74(19)	C(21)–P–C(31)	103.0(2)
P–Fe–C(21)	118.45(19)	Fe–C(1)–O(1)	179.4(6)
<i>Torsion angles</i>			
C(1)–Fe–P–C(31)	–19.9(3)	Fe–P–C(21)–C(22)	–150.7(4)
C(3)–Fe–P–C(8)	0.4(2)	C(8)–P–C(31)–C(32)	21.4(3)
C(9)–Fe–P–C(8)	–173.7(3)	C(7)–C(2)–C(3)–C(4)	174.1(7)
P–Fe–C(2)–C(7)	10.1(2)	Fe–C(2)–C(7)–C(8)	18.7(2)
C(31)–P–C(8)–C(7)	175.1(5)	C(2)–C(3)–C(4)–C(5)	0.3(3)
Fe–P–C(21)–C(26)	30.2(3)	P–C(8)–C(7)–H(7-1)	80.1(5)
C(8)–P–C(31)–C(36)	–159.5(5)	P–C(8)–C(7)–H(7-2)	–166.2(7)

Table 3

Selected bond lengths (Å), bond angles (°) and torsion angles (°) in **5j**

Bond distances			
Fe(1)–P(1)	2.1725(19)	Si(1)–C(10)	1.810(7)
Fe(1)–C(1)	1.729(7)	C(1)–O(1)	1.154(9)
Fe(1)–C(9)	1.908(7)	C(9)–C(10)	1.211(10)
P(1)–Fe(1)–C(1)	94.25(21)	Fe(1)–P(1)–C(31)	120.64(22)
P(1)–Fe(1)–C(2)	82.58(23)	C(8)–P(1)–C(21)	107.3(3)
P(1)–Fe(1)–C(4)	144.48(25)	C(8)–P(1)–C(31)	102.8(3)
P(1)–Fe(1)–C(9)	93.72(18)	C(21)–P(1)–C(31)	102.3(3)
C(1)–Fe(1)–C(9)	87.3(3)	Fe(1)–C(1)–O(1)	179.1(6)
Fe(1)–P(1)–C(8)	102.69(25)	Fe(1)–C(9)–C(10)	175.7(5)
Fe(1)–P(1)–C(21)	119.33(21)	Si(1)–C(10)–C(9)	170.1(6)
C(3)–Fe(1)–P(1)–C(8)	–7.0(2)	C(2)–C(3)–C(4)–C(5)	–0.2(3)
C(6)–Fe(1)–P(1)–C(21)	179.6(2)	C(8)–P(1)–C(21)–C(22)	–4.9(3)
P(1)–Fe(1)–C(2)–C(7)	–4.0(3)	Fe(1)–P(1)–C(31)–C(32)	–2.0(2)
P(1)–Fe(1)–C(3)–C(4)	174.8(5)	C(6)–C(2)–C(3)–C(4)	0.2(3)
C(1)–Fe(1)–P(1)–C(21)	11.8(3)	C(7)–C(2)–C(3)–C(4)	–172.6(7)
C(4)–Fe(1)–P(1)–C(8)	–1.4(3)	C(7)–C(2)–C(6)–C(5)	172.7(7)
C(8)–P(1)–C(21)–C(26)	174.2(5)	P(1)–C(8)–C(7)–H(7-1)	–76.0(5)
Fe(1)–P(1)–C(31)–C(36)	175.4(4)	P(1)–C(8)–C(7)–H(7-2)	166.6(8)

### 2.3. Solid state structure of **5a**, **5g** and **5j**

Crystal structures of **5a**, **5g** and **5j** are quite similar to each other (Figs. 1–3). They are essentially piano-stool structures with a distorted three-legged nature. The angle between the carbonyl group and the organic group (about 87°; see Tables 1–3) is somewhat smaller than those of the other two angles, the phosphorus and the carbonyl group (about 95°) and the phosphorus and the organic group (about 94°). In the literature [16], a more flexible non-chelate ethyl complex ( $\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)-}$

$(\text{C}_2\text{H}_5)(\text{PPh}_3)$  (**6**) showed about equal angles (approximately 93°) between these three legs.

Iron-carbonyl had a linear geometry for all three complexes and iron-acetylene was also linear for **5g** and **5j**. The bond length of iron to the chelate phosphorus was 2.166 Å for **5a** (see Table 1), 2.186 Å for **5g** (see Table 2) and 2.172 Å for **5j** (see Table 3) compared with 2.186 Å for the non-chelate ethyl complex **6**. The Fe–P bond length of chelate **5a** was about 0.02 Å shorter than that of the non-chelate **6**. This suggests that the iron and phosphine bound more tightly for the

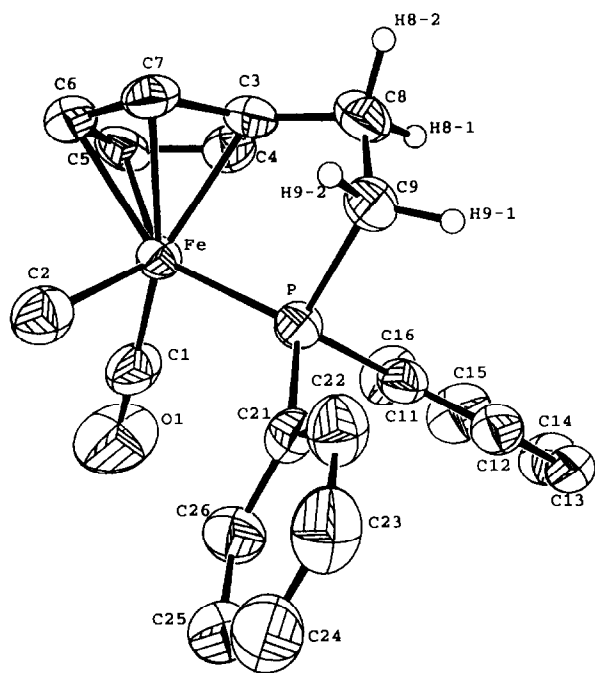


Fig. 1. ORTEP drawing of  $\eta^5\text{-}\eta^2\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2\text{Fe(CO)CH}_3$  (**5a**).

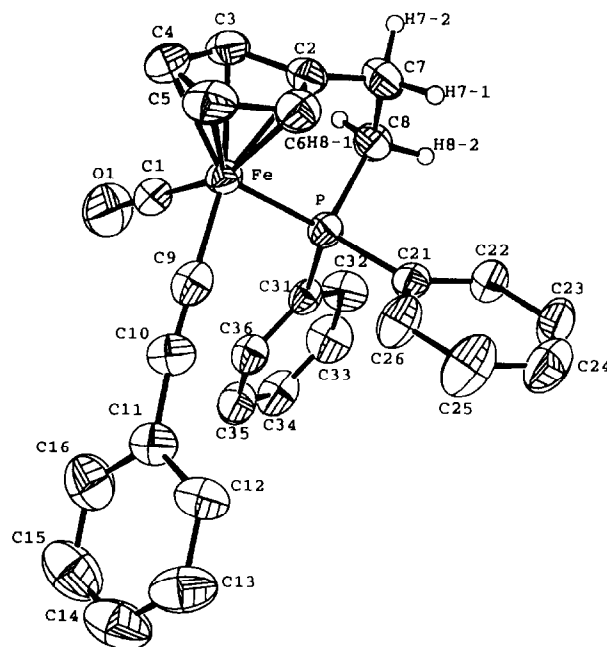


Fig. 2. ORTEP drawing of  $(\eta^5\text{-}\eta^2\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe(CO)(}\eta^1\text{-C}\equiv\text{CPh)}$  (**5g**).

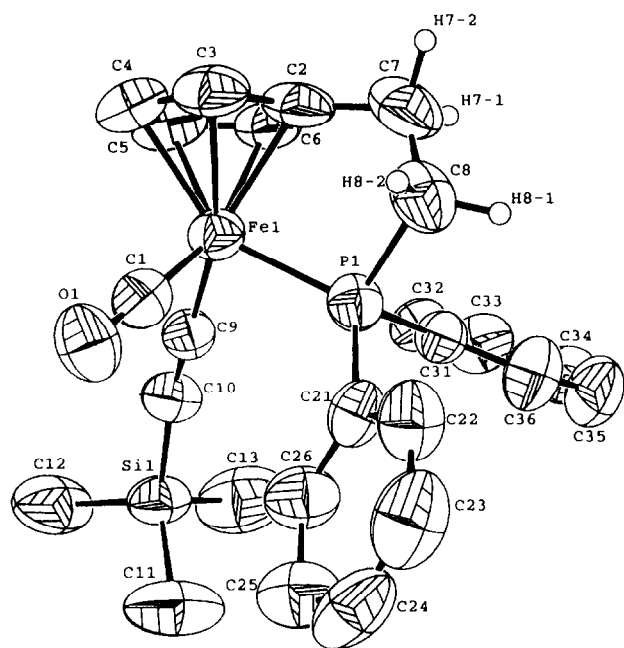


Fig. 3. ORTEP drawing of  $\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2\text{Fe}(\text{CO})(\eta^1\text{-C}\equiv\text{CSiMe}_3)$  (**5j**). There are two essentially similar independent molecules within the unit cell. Only one molecule is shown.

chelate complex than that for the non-chelate complex. Upon chelation, the side chain bent away from the cyclopentadienyl plane by  $9.2^\circ$  for **5a**,  $5.9^\circ$  for **5g** and  $7.4^\circ$  for **5j**. For both **5a** and **5j**, one of the phenyl plane was coplanar with the Fe–P bond and the other phenyl plane was coplanar with the P–C(9) bond for **5a** and P–C(8) bond for **5j**.

The dihedral angle of phosphorus and one of the protons next to the Cp ring was  $167.6^\circ$  for **5a**,  $-166.2^\circ$  for **5g** and  $166.6^\circ$  for **5j**. The large dihedral angle is in accordance with the large coupling constant (33–39 Hz) between the proton and phosphorus in the  $^1\text{H}$  NMR spectra.

### 3. Experimental section

All reactions were performed under an argon atmosphere with the use of Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Spiro[4.2]hepta-2,4-diene was prepared according to the literature procedure [11]. Potassium diphenylphosphide, methylmagnesium chloride, allylmagnesium chloride, benzylmagnesium chloride, phenyllithium, vinylmagnesium bromide and trimethylsilylacetylene were purchased from Aldrich. Iron(II) chloride tetrahydrate, *n*-butyllithium, phenylacetylene, cyclohexylacetylene and 1-heptyne were purchased from Merck. IR solution spectra were recorded on a Perkin–Elmer 882 IR spectrophotometer using 0.1 mm cells with  $\text{CaF}_2$  windows. Melting points were determined by using a

Yanaco model MP micromelting-point apparatus and were uncorrected.  $^1\text{H}$  NMR (300 MHz),  $^{13}\text{C}$  NMR (75 MHz) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz) were obtained with a Bruker AC-300 Fourier transform spectrophotometer. On the assignment of  $^1\text{H}$  and  $^{13}\text{C}$  NMR data, the carbon bound to the phosphorus was designated  $\text{C}_1$  and the hydrogen atoms on  $\text{C}_1$  were designated  $\text{H}_{1a}$  and  $\text{H}_{1b}$ . The next carbon atom was designated  $\text{C}_2$  and the hydrogen atoms on  $\text{C}_2$  were designated  $\text{H}_{2a}$  and  $\text{H}_{2b}$ . Elemental analyses were obtained on a Perkin–Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on a VG 70-250S mass spectrophotometer.

#### 3.1. Preparation of (2-diphenylphosphinoethyl)cyclopentadiene (**1**)

To a stirred solution of spiro[4.2]hepta-2,4-diene (1.76 g, 19.1 mmol) in THF (100 ml) was added a THF solution of potassium diphenylphosphide (0.5 M, 38.5 ml) at room temperature. The resulting orange solution was heated under reflux overnight. After cooling to room temperature, THF was evaporated under reduced pressure. Residues were dissolved with  $\text{CH}_2\text{Cl}_2$  (300 ml) followed by washing successively with 0.1 M solution of HCl (250 ml), saturated  $\text{NaHCO}_3$  solution (100 ml) and brine (200 ml). The  $\text{CH}_2\text{Cl}_2$  layer was concentrated. The orange liquid residue was then flash chromatographed [17] on silica gel using 5% EtOAc in hexane as eluent. Products (4.06 g (76%); two regioisomers) were collected at  $R_f = 0.50$  (thin layer chromatography (TLC); silica gel; 5% EtOAc in hexane) as a colorless liquid after removal of solvents.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-14.66$ ,  $-14.82$  ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.46–7.39 (4H, m, phenyl-H atoms), 7.33–7.29 (6H, m, phenyl-H atoms), 6.41–6.02 (3H, m, olefinic-H atoms), 2.92–2.85 (2H, m, ring methylene), 2.56–2.44 (2H, m), 2.32–2.24 (2H, m).

#### 3.2. Preparation of $\text{LiC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2$ (**2**)

To a stirred solution of **1** (4.06 g, 14.58 mmol) in THF (11 ml) at  $0^\circ\text{C}$  was added a hexane solution of  $^n\text{BuLi}$  (1.6 M, 9.2 ml) slowly over 15 min. The resulting orange solution was accounted for 0.6 M solution of **2** and ready for further reactions.

#### 3.3. Preparation of $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})\text{Cl}$ (**4**)

Greenish-yellow powders of iron(II) chloride tetrahydrate (7.5 g, 37.7 mmol) was placed in a 250 ml two-necked flask. Air was evacuated and filled with nitrogen. Benzene (150 ml) was added. A Dean–Stark trap and a refluxing condenser were connected. The mixture was then heated under reflux for azeotropic removal of water under nitrogen for 16 h. After cooling

to room temperature, benzene was removed as much as possible by using a syringe under a positive nitrogen stream. THF (140 ml) was then added. The suspension was cooled in a dry ice–acetone bath.

To the suspension was added a solution of **2** (15 ml  $\times$  0.6 M) over 5 min. After stirring for another 5 min, the cool bath was removed and CO was allowed to bubble through the resulting deep-purple solution by using a stainless needle for 2 h. The resulting dark green solution was filtered through Celite. The dark residue after removal of solvents was flash chromatographed on silica gel using 10% EtOAc in hexane to remove some of the unreacted ligand, followed by 50% EtOAc in hexane. The green band was collected and concentrated to provide 1.412 g (39%) of **4** as dark green solids. Melting point (m.p.), 75°C (decomposition). TLC (silica gel):  $R_f = 0.51$  (50% EtOAc in hexane). IR (THF):  $\nu$  1956  $\text{cm}^{-1}$ ,  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  71.2 ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.09–8.01 (2H, m, phenyl), 7.52–7.36 (8H, m, phenyl), 5.77–5.76 (1H, m, Cp–H), 5.23–5.22 (1H, m, Cp–H), 5.02–5.01 (1H, m, Cp–H), 3.45–3.33 (1H, m), 2.88–2.87 (1H, m, Cp–H), 2.85–2.73 (1H, m), 2.29–1.96 (2H, m) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  219.0 (CO,  $J_{\text{cp}} = 27.5$  Hz), 135.1 (C,  $J_{\text{cp}} = 42.4$  Hz, Ph), 133.5 (CH  $\times$  2,  $J_{\text{cp}} = 9.1$  Hz, Ph), 133.1 (C,  $J_{\text{cp}} = 31.7$  Hz, Ph), 130.9 (CH  $\times$  2,  $J_{\text{cp}} = 9.1$  Hz, Ph), 130.5 (CH, Ph), 130.2 (CH, Ph), 128.6 (CH  $\times$  2,  $J_{\text{cp}} = 12.8$  Hz, Ph), 128.4 (CH  $\times$  2,  $J_{\text{cp}} = 9.8$  Hz, Ph), 113.6 (C,  $J_{\text{cp}} = 6.7$  Hz, Cp), 96.8 (CH,  $J_{\text{cp}} = 3.7$  Hz, Cp), 84.0 (CH, Cp), 76.6 (CH, Cp), 61.6 (CH, Cp), 45.4 (CH<sub>2</sub>,  $J_{\text{cp}} = 31.0$  Hz, C<sub>1</sub>), 21.0 (CH<sub>2</sub>,  $J_{\text{cp}} = 6.5$  Hz, C<sub>2</sub>) ppm. Mass spectroscopy (MS) (fast atom bombardment (FAB),  $^{35}\text{Cl}^{56}\text{Fe}$ ): 368 (100, M<sup>+</sup> – CO), 333 (50, M<sup>+</sup> – CO – Cl). Anal. Found: C, 60.28; H, 4.62. C<sub>20</sub>H<sub>18</sub>ClOPFe Calc.: C, 60.56; H, 4.57%.

### 3.4. General procedure for the preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})\text{R}$ (**5a–5f**) (R = CH<sub>3</sub>, *n*-Bu, allyl, benzyl, Ph or vinyl)

Over a period of 3 min, a solution of alkylmetal reagent (methylmagnesium chloride, *n*-butyllithium, allylmagnesium chloride, benzylmagnesium chloride, phenyllithium or vinylmagnesium bromide) (1.5 mmol) was added to a stirred solution of **4** (521 mg, 1.31 mmol) in THF (15 ml) at  $-78^\circ\text{C}$ . After addition was complete, the cold bath was removed and the solution was stirred at room temperature for 20–30 min. The resulting orange–red solution was concentrated under reduced pressure. The residue was then dissolved with CH<sub>2</sub>Cl<sub>2</sub> (2 ml) and flash column chromatographed on neutral alumina (activity V) upon elution with 0–15% EtOAc in hexanes. The first orange band was collected and concentrated to provide the desired product with a 45–92% yield.

$(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})\text{CH}_3$  (**5a**): red crystalline (92%). M.p., 175–178°C. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  1900  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  96.4 ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.80–7.71 (2H, m, phenyl), 7.40–7.26 (8H, m, phenyl), 4.76 (1H, s, Cp–H), 4.40 (1H, s, Cp–H), 4.34 (1H, s, Cp–H), 4.22 (1H, s, Cp–H), 3.39–3.24 (1H, m, H<sub>1a</sub>), 3.01 (1H, tdd,  $J = 12.5, 5.8$  and 3.8 Hz, H<sub>1b</sub>), 2.40 (1H, dddd,  $J = 39.1, 13.6, 7.1$  and 3.8 Hz, H<sub>2a</sub>), 1.98–1.85 (1H, m, H<sub>2b</sub>),  $-0.46$  (3H, d,  $J = 6.6$  Hz, CH<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  222.5 (CO,  $J_{\text{cp}} = 27.2$  Hz), 136.4 (C,  $J_{\text{cp}} = 39.7$  Hz, Ph), 134.6 (C,  $J_{\text{cp}} = 35.0$  Hz, Ph), 133.1 (CH  $\times$  2,  $J_{\text{cp}} = 10.3$  Hz, Ph), 131.3 (CH  $\times$  2,  $J_{\text{cp}} = 8.3$  Hz, Ph), 129.7 (CH, Ph), 129.0 (CH, Ph), 128.1 (CH  $\times$  4,  $J_{\text{cp}} = 8.8$  Hz, Ph), 116.5 (C,  $J_{\text{cp}} = 7.5$  Hz, Cp), 86.9 (CH, Cp), 83.6 (CH, Cp), 78.5 (CH, Cp), 75.9 (CH, Cp), 46.1 (CH<sub>2</sub>,  $J_{\text{cp}} = 26.6$  Hz, C<sub>1</sub>), 21.7 (CH<sub>2</sub>,  $J_{\text{cp}} = 6.9$  Hz, C<sub>2</sub>),  $-21.7$  (CH<sub>3</sub>,  $J_{\text{cp}} = 18.3$  Hz) ppm. MS (FAB,  $^{56}\text{Fe}$ ): 376 (42, M<sup>+</sup>), 348 (100, M<sup>+</sup> – CO), 361 (10, M<sup>+</sup> – CH<sub>3</sub>), 333 (62, M<sup>+</sup> – CO – CH<sub>3</sub>). Anal. Found: C, 66.74; H, 5.71. C<sub>21</sub>H<sub>21</sub>OPFe Calc.: C, 67.04; H, 5.63%.

$(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_3$  (**5b**): orange–red liquid (58%). TLC (silica gel):  $R_f = 0.62$  (decomposition) (10% EtOAc in hexane). IR (THF):  $\nu$  1903  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  94.6 ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.73–7.65 (2H, m), 7.40–7.25 (8H, m), 4.68–4.66 (1H, m, Cp–H), 4.46–4.44 (1H, m, Cp–H), 4.38–4.36 (1H, m, Cp–H), 4.24–4.22 (1H, m, Cp–H), 3.23 (1H, dddd,  $J = 13.2, 10.7, 7.0$  and 6.1 Hz, H<sub>1a</sub>), 2.95 (1H, dddd,  $J = 13.2, 11.4, 6.1$  and 4.3 Hz, H<sub>1b</sub>), 2.34 (1H, dddd,  $J = 35.7, 13.7, 7.0$  and 4.3 Hz, H<sub>2a</sub>), 1.89 (1H, tdd,  $J = 13.7, 10.6$  and 6.1 Hz, H<sub>2b</sub>), 1.28–0.84 (5H, m), 0.64 (3H, t,  $J = 7.2$  Hz), 0.46–0.35 (1H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  222.7 (CO,  $J_{\text{cp}} = 27.7$  Hz), 136.6 (C,  $J_{\text{cp}} = 40.0$  Hz, Ph), 134.6 (C,  $J_{\text{cp}} = 32.3$  Hz, Ph), 133.0 (CH  $\times$  2,  $J_{\text{cp}} = 10.0$  Hz, Ph), 131.5 (CH  $\times$  2,  $J_{\text{cp}} = 8.5$  Hz, Ph), 129.6 (CH, Ph), 129.1 (CH, Ph), 128.1 (CH  $\times$  2,  $J_{\text{cp}} = 3.7$  Hz, Ph), 128.0 (CH  $\times$  2,  $J_{\text{cp}} = 2.9$  Hz, Ph), 116.0 (C,  $J_{\text{cp}} = 7.7$  Hz, Cp), 88.2 (CH,  $J_{\text{cp}} = 3.6$  Hz, Cp), 82.6 (CH, Cp), 77.6 (CH, Cp), 76.6 (CH, Cp), 46.3 (CH<sub>2</sub>,  $J_{\text{cp}} = 27.1$  Hz, C<sub>1</sub>), 41.3 (CH<sub>2</sub>,  $J_{\text{cp}} = 3.1$  Hz), 28.3 (CH<sub>2</sub>), 21.8 (CH<sub>2</sub>,  $J_{\text{cp}} = 7.4$  Hz, C<sub>2</sub>), 13.8 (CH<sub>3</sub>), 3.8 (CH<sub>2</sub>,  $J_{\text{cp}} = 16.2$  Hz) ppm. MS (FAB,  $^{56}\text{Fe}$ ): 418 (14, M<sup>+</sup>), 390 (25, M<sup>+</sup> – CO), 361 (10, M<sup>+</sup> – Bu), 333 (100, M<sup>+</sup> – CO – Bu). Anal. Found: C, 68.65; H, 6.68. C<sub>24</sub>H<sub>27</sub>OPFe Calc.: C, 68.91; H, 6.51%.

$(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Fe}(\text{CO})(\eta^1\text{-CH}_2\text{CH=CH}_2)$  (**5c**): orange solid (72%). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  1904  $\text{cm}^{-1}$ . IR (THF):  $\nu$  1901  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  93.6 ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.75–7.68 (2H, m, phenyl), 7.42–7.24 (8H, m, phenyl), 5.96–5.76 (1H, m), 4.74–4.72 (1H, m, Cp–H), 4.45 (1H, dd,  $J = 16.9$  and 2.7 Hz), 4.39–4.37 (1H, m, Cp–H), 4.25 (1H, dd,

$J = 9.8$  and  $2.7$  Hz), 4.12–4.10 (1H, m, Cp–H), 4.09–4.07 (1H, m, Cp–H), 3.29 (1H, dddd,  $J = 13.1$ , 11.0, 7.1 and 6.1 Hz, H<sub>1a</sub>), 2.99 (1H, dddd,  $J = 13.1$ , 11.6, 5.9 and 4.0 Hz, H<sub>1b</sub>), 2.39 (1H, dddd,  $J = 37.0$ , 13.7, 7.1 and 4.0 Hz, H<sub>2a</sub>), 1.89 (1H, tdd,  $J = 13.7$ , 11.0 and 5.9 Hz, H<sub>2b</sub>), 1.63 (1H, td,  $J = 8.2$  and 4.9 Hz), 1.01 (1H, q,  $J = 8.2$  Hz) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  222.1 (CO,  $J_{\text{cp}} = 27.2$  Hz), 152.0 (CH,  $J_{\text{cp}} = 4.0$  Hz), 136.2 (C,  $J_{\text{cp}} = 40.6$  Hz, Ph), 134.3 (C,  $J_{\text{cp}} = 33.4$  Hz, Ph), 133.0 (CH  $\times$  2,  $J_{\text{cp}} = 10.4$  Hz, Ph), 131.3 (CH  $\times$  2,  $J_{\text{cp}} = 8.9$  Hz, Ph), 129.8 (CH, Ph), 129.3 (CH, Ph), 128.3 (CH  $\times$  2,  $J_{\text{cp}} = 10.6$  Hz, Ph), 128.2 (CH  $\times$  2,  $J_{\text{cp}} = 10.7$  Hz, Ph), 116.4 (C,  $J_{\text{cp}} = 7.9$  Hz, Cp), 101.4 (CH<sub>2</sub>), 92.0 (CH, Cp), 84.3 (CH, Cp), 78.5 (CH, Cp), 74.6 (CH, Cp), 46.1 (CH<sub>2</sub>,  $J_{\text{cp}} = 27.3$  Hz, C<sub>1</sub>), 21.7 (CH<sub>2</sub>,  $J_{\text{cp}} = 7.4$  Hz, C<sub>2</sub>), 6.1 (CH<sub>2</sub>,  $J_{\text{cp}} = 14.0$  Hz). MS (FAB, <sup>56</sup>Fe): 403 (42, M<sup>+</sup> + 1), 361 (95, M<sup>+</sup> – allyl), 333 (100, M<sup>+</sup> – CO – allyl). Anal. Found: C, 68.25; H, 5.82. C<sub>23</sub>H<sub>23</sub>OPFe Calc.: C, 68.68; H, 5.76%.

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)CH<sub>2</sub>Ph (**5d**): orange crystalline (55%). M.p., 152–155°C. TLC (silica gel):  $R_f = 0.48$  (decomposition) (10% EtOAc in hexane). IR (THF):  $\nu$  1903 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  94.1 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.81–7.74 (2H, m), 7.43–7.40 (3H, m), 7.36–7.28 (5H, m), 7.03–6.97 (4H, m), 6.84–6.78 (1H, m), 4.63–4.61 (1H, m, Cp–H), 4.49–4.47 (1H, m, Cp–H), 3.93–3.91 (1H, m, Cp–H), 3.62–3.60 (1H, m, Cp–H), 3.37 (1H, dddd,  $J = 13.2$ , 10.9, 7.3 and 6.4 Hz, H<sub>1a</sub>), 3.08 (1H, dddd,  $J = 13.2$ , 11.8, 5.8 and 4.1 Hz, H<sub>1b</sub>), 2.42 (1H, dddd,  $J = 36.5$ , 13.7, 7.3 and 4.1 Hz, H<sub>2a</sub>), 2.11 (1H, dd,  $J = 8.2$  and 6.3 Hz, benzyl–H<sub>a</sub>), 1.90 (1H, tdd,  $J = 13.7$ , 10.9 and 5.8 Hz, H<sub>2b</sub>), 1.32 (1H, t,  $J = 8.2$  Hz, benzyl–H<sub>b</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  222.6 (CO,  $J_{\text{cp}} = 27.1$  Hz), 158.0 (C), 135.9 (C,  $J_{\text{cp}} = 41.3$  Hz, Ph), 134.1 (C,  $J_{\text{cp}} = 33.8$  Hz, Ph), 133.1 (CH  $\times$  2,  $J_{\text{cp}} = 10.0$  Hz, Ph), 131.3 (CH  $\times$  2,  $J_{\text{cp}} = 8.6$  Hz, Ph), 130.0 (CH, Ph), 129.3 (CH, Ph), 128.3 (CH  $\times$  2,  $J_{\text{cp}} = 8.5$  Hz, Ph), 128.2 (CH  $\times$  2,  $J_{\text{cp}} = 8.6$  Hz, Ph), 127.5 (CH  $\times$  2, Ph'), 126.7 (CH  $\times$  2, Ph'), 121.1 (CH, Ph'), 116.6 (C,  $J_{\text{cp}} = 7.8$  Hz, Cp), 89.7 (CH, Cp), 85.5 (CH, Cp), 80.8 (CH, Cp), 74.2 (CH, Cp), 46.1 (CH<sub>2</sub>,  $J_{\text{cp}} = 26.8$  Hz, C<sub>1</sub>), 21.6 (CH<sub>2</sub>,  $J_{\text{cp}} = 7.0$  Hz, C<sub>2</sub>), 7.6 (CH<sub>2</sub>,  $J_{\text{cp}} = 14.1$  Hz) ppm. MS (FAB, <sup>56</sup>Fe): 452 (8, M<sup>+</sup>), 424 (41, M<sup>+</sup> – CO), 361 (26, M<sup>+</sup> – benzyl), 333 (100, M<sup>+</sup> – CO – benzyl). Anal. Found: C, 71.45; H, 5.52. C<sub>27</sub>H<sub>25</sub>OPFe Calc.: C, 71.70; H, 5.57%.

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)( $\eta^1$ -Ph) (**5e**): orange liquid (45%) IR (THF):  $\nu$  1918 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  89.2 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.62–7.55 (2H, m), 7.39–7.36 (3H, m), 7.25–7.18 (3H, m), 7.12–7.05 (4H, m), 6.58–6.55 (3H, m), 4.78 (1H, s, Cp–H), 4.68 (1H, s, Cp–H), 4.54 (1H, s, Cp–H), 4.28 (1H, s, Cp–H), 3.43–3.31 (1H, m, H<sub>1a</sub>), 3.10–2.98

(1H, m, H<sub>1b</sub>), 2.44 (1H, dddd,  $J = 33.1$ , 13.3, 6.6 and 6.1 Hz, H<sub>2a</sub>), 2.09 (1H, tdd,  $J = 13.3$ , 9.7 and 6.6 Hz, H<sub>2b</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  222.0 (CO,  $J_{\text{cp}} = 27.5$  Hz), 158.6 (C,  $J_{\text{cp}} = 23.8$  Hz, Ph'), 145.9 (CH  $\times$  2, Ph'), 136.3 (C,  $J_{\text{cp}} = 40.4$  Hz, Ph), 133.6 (C,  $J_{\text{cp}} = 36.3$  Hz, Ph), 132.4 (CH  $\times$  2,  $J_{\text{cp}} = 11.4$  Hz, Ph), 132.3 (CH  $\times$  2,  $J_{\text{cp}} = 9.8$  Hz, Ph), 129.7 (CH, Ph), 129.1 (CH, Ph), 128.2 (CH  $\times$  2,  $J_{\text{cp}} = 9.3$  Hz, Ph), 127.7 (CH  $\times$  2,  $J_{\text{cp}} = 8.9$  Hz, Ph), 125.7 (CH  $\times$  2, Ph'), 120.2 (CH, Ph'), 119.4 (C,  $J_{\text{cp}} = 7.0$  Hz, Cp), 92.0 (CH, Cp), 82.6 (CH, Cp), 77.2 (CH, Cp), 75.0 (CH, Cp), 46.8 (CH<sub>2</sub>,  $J_{\text{cp}} = 27.4$  Hz, C<sub>1</sub>), 21.7 (CH<sub>2</sub>,  $J_{\text{cp}} = 6.3$  Hz, C<sub>2</sub>) ppm. MS (FAB, <sup>56</sup>Fe): 438 (20, M<sup>+</sup>), 410 (100, M<sup>+</sup> – CO), 361 (8, M<sup>+</sup> – phenyl), 333 (78, M<sup>+</sup> – CO – phenyl). Anal. Found: C, 70.89; H, 5.35. C<sub>26</sub>H<sub>23</sub>OPFe Calc.: C, 71.25; H, 5.29%.

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)( $\eta^1$ -CH=CH<sub>2</sub>) (**5f**): orange liquid (60%). IR (THF): 1920 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  90.0 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.62–7.33 (11H, m, phenyls and vinyl–H), 5.62 (1H, ddd,  $J = 9.8$ , 4.8 and 2.3 Hz, vinyl–H), 5.13 (1H, dt,  $J = 17.6$  and 2.3 Hz, vinyl–H), 4.77–4.75 (1H, m, Cp–H), 4.60–4.58 (1H, m, Cp–H), 4.53–4.51 (1H, m, Cp–H), 4.21–4.19 (1H, m, Cp–H), 3.22 (1H, tdd,  $J = 13.1$ , 8.2 and 6.6 Hz, H<sub>1a</sub>), 3.05 (1H, tdd,  $J = 13.1$ , 10.0 and 6.8 Hz, H<sub>1b</sub>), 2.34–2.00 (2H, m, H<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  221.2 (CO,  $J_{\text{cp}} = 26.8$  Hz), 155.6 (CH,  $J_{\text{cp}} = 25.2$  Hz, vinyl–C) 136.0 (C,  $J_{\text{cp}} = 40.1$  Hz, Ph), 134.1 (C,  $J_{\text{cp}} = 36.3$  Hz, Ph), 132.6 (CH  $\times$  2,  $J_{\text{cp}} = 8.5$  Hz, Ph), 132.2 (CH  $\times$  2,  $J_{\text{cp}} = 9.5$  Hz, Ph), 129.8 (CH, Ph), 129.5 (CH, Ph), 128.2 (CH  $\times$  2,  $J_{\text{cp}} = 11.2$  Hz, Ph), 128.0 (CH  $\times$  2,  $J_{\text{cp}} = 10.3$  Hz, Ph), 126.4 (CH<sub>2</sub>, vinyl–C), 118.6 (C, Cp), 88.8 (CH, Cp), 82.6 (CH, Cp), 79.2 (CH, Cp), 75.0 (CH, Cp), 47.2 (CH<sub>2</sub>,  $J_{\text{cp}} = 27.8$  Hz, C<sub>1</sub>), 21.4 (CH<sub>2</sub>, C<sub>2</sub>) ppm. MS (FAB, <sup>56</sup>Fe): 388 (24, M<sup>+</sup>), 361 (38, M<sup>+</sup> – vinyl), 333 (100, M<sup>+</sup> – vinyl – CO). Anal. Found: C, 67.78; H, 5.45. C<sub>22</sub>H<sub>21</sub>OPFe Calc.: C, 68.06; H, 5.45%.

**3.5. General procedure for the preparation of ( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)R (**5g–5j**) (R =  $\eta^1$ -C $\equiv$ CPh,  $\eta^1$ -C $\equiv$ C-cyclohexyl,  $\eta^1$ -C $\equiv$ C-*n*-pentyl,  $\eta^1$ -C $\equiv$ CSiMe<sub>3</sub>)**

A solution of *n*-butyllithium in hexane (1.3 M  $\times$  2.0 ml) was added to a stirred solution of acetylenic compound (phenylacetylene, cyclohexylacetylene, 1-heptyne or trimethylsilylacetylene) (2.6 mmol) in THF (10 ml) at –78°C over 5 min. After having been stirred for 10 min, a deep-green solution of **4** (874 mg, 2.2 mmol) in THF (20 ml) was added over 5 min. The cool bath was then removed and the solution was allowed to stir at room temperature for 30 min. The resulting deep-red solution was concentrated under reduced pressure. The residue was dissolved with CH<sub>2</sub>Cl<sub>2</sub> (2 ml) and then

chromatographed on neutral alumina (activity V) upon elution with 0–10% EtOAc in hexane. The orange band was collected and concentrated to provide the desired product with a 78–87% yield.

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)( $\eta^1$ -C≡CPh) (**5g**): red crystal (87%). M.p., 147–149°C. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2083m (acetylene), 1953s (CO) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  84.4 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.05–7.98 (2H, m), 7.66–7.59 (2H, m), 7.40–7.33 (6H, m), 7.09–7.00 (4H, m), 6.98–6.92 (1H, m), 5.03–5.01 (1H, m, Cp), 4.91–4.89 (1H, m, Cp), 4.86–4.84 (1H, m, Cp), 4.19–4.17 (1H, m, Cp), 3.31 (1H, dddd,  $J$  = 13.0, 10.3, 6.2 and 5.5 Hz, H<sub>1a</sub>), 3.11 (1H, dddd,  $J$  = 13.0, 9.4, 8.5 and 7.1 Hz, H<sub>1b</sub>), 2.24 (1H, dddd,  $J$  = 37.8, 13.8, 7.1 and 5.5 Hz, H<sub>2a</sub>), 2.13 (1H, tdd,  $J$  = 13.8, 9.4 and 6.2 Hz, H<sub>2b</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  218.3 (CO,  $J_{cp}$  = 25.5 Hz), 135.7 (C,  $J_{cp}$  = 42 Hz, Ph), 134.2 (C,  $J_{cp}$  = 38.7 Hz, Ph), 133.1 (CH × 2,  $J_{cp}$  = 9.2 Hz, Ph), 131.1 (CH × 2,  $J_{cp}$  = 9.1 Hz, Ph), 130.9 (CH × 2), 129.9 (CH × 2), 129.1 (C), 128.4 (CH × 2,  $J_{cp}$  = 9.5 Hz, Ph), 128.0 (CH × 2,  $J_{cp}$  = 9.7 Hz, Ph), 127.4 (CH × 2, Ph'), 123.7 (CH, Ph'), 117.9 (C × 2), 108.7 (C,  $J_{cp}$  = 33.7 Hz), 87.9 (CH, Cp), 82.3 (CH, Cp), 78.8 (CH, Cp), 73.6 (CH, Cp), 46.8 (CH<sub>2</sub>,  $J_{cp}$  = 29.1 Hz, C<sub>1</sub>), 21.0 (CH<sub>2</sub>, C<sub>2</sub>) ppm. MS (FAB, <sup>56</sup>Fe): 462 (30, M<sup>+</sup>), 434 (100,

M<sup>+</sup> – CO), 361 (16, M<sup>+</sup> – PhCC), 333 (52, M<sup>+</sup> – CO – PhCC). Anal. Found: C, 72.78; H, 5.10. C<sub>28</sub>H<sub>23</sub>OPFe. Calc.: C, 72.74; H, 5.01%.

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)( $\eta^1$ -C≡C-C<sub>6</sub>H<sub>11</sub>) (**5h**): orange liquid (85%). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2093w (acetylene), 1944s (CO) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  83.0 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.16–8.09 (2H, m, Ph), 7.66–7.59 (2H, m, Ph), 7.42–7.35 (6H, m, Ph), 4.94 (1H, Cp), 4.82 (1H, Cp), 4.76 (1H, Cp), 4.07 (1H, Cp), 3.27 (1H, dddd,  $J$  = 13.0, 10.2, 5.9 and 4.2 Hz, H<sub>1a</sub>), 3.03 (1H, dddd,  $J$  = 13.0, 10.8, 7.5 and 7.3 Hz, H<sub>1b</sub>), 2.41–2.31 (1H, m), 2.23 (1H, dddd,  $J$  = 36.2, 13.6, 7.3 and 4.2 Hz, H<sub>2a</sub>), 2.02 (1H, tdd,  $J$  = 13.6, 10.8 and 5.9 Hz, H<sub>2b</sub>), 1.78–1.10 (10H, m) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  218.8 (CO,  $J_{cp}$  = 26.6 Hz), 136.0 (C,  $J_{cp}$  = 41.6 Hz, Ph), 134.5 (C,  $J_{cp}$  = 36.9 Hz, Ph), 133.5 (CH × 2,  $J_{cp}$  = 8.7 Hz, Ph), 130.9 (CH × 2,  $J_{cp}$  = 8.4 Hz, Ph), 129.8 (CH, Ph), 129.6 (CH, Ph), 128.1 (CH × 2,  $J_{cp}$  = 8.9 Hz, Ph), 127.7 (CH × 2,  $J_{cp}$  = 9.1 Hz, Ph), 121.6 (C, acetylene), 117.0 (C, Cp), 88.4 (CH, Cp), 83.7 (C,  $J_{cp}$  = 35.7 Hz, acetylene), 82.0 (CH, Cp), 78.0 (CH, Cp), 72.7 (CH, Cp), 46.8 (CH<sub>2</sub>,  $J_{cp}$  = 29.1 Hz, C<sub>1</sub>), 34.9 (CH<sub>2</sub> × 2), 32.8 (CH), 26.1 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub> × 2), 20.7 (CH<sub>2</sub>, C<sub>2</sub>) ppm. MS (FAB, <sup>56</sup>Fe): 468 (7, M<sup>+</sup>), 441 (80, M<sup>+</sup> + 1 – CO), 361 (15, M<sup>+</sup> –

Table 4  
Crystal data and details of the structure determination of **5a**, **5g** and **5j**

Compound	<b>5a</b>	<b>5g</b>	<b>5j</b>
Formula	C <sub>21</sub> H <sub>21</sub> OPFe	C <sub>28</sub> H <sub>23</sub> OPFe	C <sub>50</sub> H <sub>54</sub> O <sub>2</sub> P <sub>2</sub> Si <sub>2</sub> Fe <sub>2</sub>
Molecular weight	376.22	462.31	916.80
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1
<i>a</i> (Å)	7.9227(10)	9.8499(23)	11.3917(13)
<i>b</i> (Å)	14.8015(20)	12.3835(19)	11.8482(16)
<i>c</i> (Å)	15.3754(10)	18.546(4)	19.579(4)
$\alpha$ (°)	90	90	98.832(14)
$\beta$ (°)	90	97.398(19)	90.147(13)
$\gamma$ (°)	90	90	113.342(11)
Cell volume (Å <sup>3</sup> )	1803.0(4)	2243.3(8)	2391.7(7)
<i>Z</i> ; <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	4; 1.386	4; 1.369	2; 1.274
<i>F</i> (000)	784	960	960
Crystal size (mm)	0.31 × 0.19 × 0.19	0.31 × 0.11 × 0.06	0.44 × 0.30 × 0.28
Scan range (°)	1.20 + 0.77 tan $\theta$	0.70 + 0.35 tan $\theta$	0.75 + 0.35 tan $\theta$
2 $\theta$ range (°)	4–45	4–45	4–45
<i>h</i> , <i>k</i> , <i>l</i> range	(0; 9), (0; 17), (0; 18)	(–10; 10), (0; 13), (0; 19)	(0; 12), (–12; 12), (–21; 21)
$\mu$ (cm <sup>-1</sup> )	9.256	7.575	7.565
Number of collected reflections	1837	3125	6618
Number of unique reflections	1837	2925	6239
Number of reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	1371	1651	3962
Number of refined parameters	219	280	524
Weighting scheme	1/ $\sigma^2$ ( <i>F</i> )	1/ $\sigma^2$ ( <i>F</i> )	1/ $\sigma^2$ ( <i>F</i> )
Final <i>R</i> , final <i>R</i> <sub>w</sub>	0.034; 0.037	0.037; 0.037	0.044; 0.054
Goodness of fit	1.54	1.30	2.21
Maximum shift/ $\sigma$ ratio	0.001	0.003	0.166
Minimum, maximum differences (e Å <sup>-3</sup> )	–0.280; 0.450	–0.210; 0.220	–0.200; 0.600



Table 5  
Atomic coordinates and  $B_{\text{iso}}$  of **5a**

Atom	x	y	z	$B_{\text{iso}}$ ( $\text{\AA}^2$ )
Fe	0.28248(9)	0.99707(6)	0.19377(5)	2.55(3)
P	0.24251(21)	0.85690(9)	0.22872(10)	2.74(6)
O(1)	0.6412(6)	0.9813(4)	0.1820(4)	8.2(4)
C(1)	0.5023(8)	0.9885(4)	0.1891(5)	4.4(3)
C(2)	0.2844(9)	0.9723(4)	0.0617(4)	4.4(3)
C(3)	0.0739(7)	1.0173(4)	0.2764(4)	3.1(2)
C(4)	0.2138(8)	1.0657(3)	0.3092(4)	3.5(3)
C(5)	0.2616(9)	1.1283(4)	0.2447(4)	3.6(3)
C(6)	0.1569(8)	1.1195(4)	0.1725(4)	3.9(3)
C(7)	0.0384(7)	1.0513(4)	0.1925(4)	3.5(3)
C(8)	-0.0087(8)	0.9356(4)	0.3184(4)	4.0(3)
C(9)	0.0183(8)	0.8520(4)	0.2633(4)	3.7(3)
C(11)	0.3560(8)	0.8130(4)	0.3241(4)	3.2(3)
C(12)	0.3383(8)	0.7237(4)	0.3493(4)	3.5(3)
C(13)	0.4235(9)	0.6906(4)	0.4206(4)	4.1(3)
C(14)	0.5261(10)	0.7460(5)	0.4686(4)	4.6(3)
C(15)	0.5437(12)	0.8349(5)	0.4436(5)	5.2(4)
C(16)	0.4600(9)	0.8683(4)	0.3729(4)	4.3(3)
C(21)	0.2733(8)	0.7651(3)	0.1527(4)	3.1(2)
C(22)	0.1495(9)	0.7033(4)	0.1307(4)	4.4(3)
C(23)	0.1832(11)	0.6353(5)	0.0708(5)	5.4(4)
C(24)	0.3361(13)	0.6268(6)	0.0328(5)	6.1(5)
C(25)	0.4628(13)	0.6879(5)	0.0537(5)	5.3(4)
C(26)	0.4301(8)	0.7559(4)	0.1133(4)	4.0(3)

Table 6  
Atomic coordinates and  $B_{\text{iso}}$  of **5g**

Atom	x	y	z	$B_{\text{iso}}$ ( $\text{\AA}^2$ )
Fe	0.23559(8)	0.49436(7)	0.10057(4)	2.77(3)
P	0.42241(15)	0.46176(11)	0.17447(8)	2.74(6)
O(1)	0.3405(6)	0.4205(4)	-0.0288(2)	6.7(3)
C(1)	0.2988(6)	0.4507(5)	0.0230(3)	3.8(3)
C(2)	0.2579(6)	0.6450(4)	0.1518(3)	3.4(3)
C(3)	0.2333(7)	0.6587(4)	0.0753(3)	4.1(3)
C(4)	0.1042(7)	0.6142(5)	0.0495(3)	4.7(3)
C(5)	0.0482(6)	0.5731(5)	0.1105(4)	4.4(3)
C(6)	0.1422(7)	0.5908(5)	0.1730(3)	3.9(3)
C(7)	0.3875(7)	0.6712(5)	0.2005(3)	4.3(3)
C(8)	0.5032(6)	0.5952(4)	0.1853(3)	3.5(3)
C(9)	0.1685(6)	0.3501(5)	0.1097(3)	3.4(3)
C(10)	0.1397(6)	0.2551(5)	0.1130(3)	3.5(3)
C(11)	0.1218(6)	0.1422(5)	0.1206(3)	3.5(3)
C(12)	0.0845(6)	0.0969(5)	0.1832(3)	4.2(3)
C(13)	0.0677(7)	-0.0138(6)	0.1896(4)	5.6(4)
C(14)	0.0921(8)	-0.0805(6)	0.1342(5)	6.3(5)
C(15)	0.1296(8)	-0.0398(7)	0.0724(5)	6.7(5)
C(16)	0.1447(7)	0.0720(6)	0.0650(4)	5.5(4)
C(21)	0.4064(6)	0.4212(4)	0.2686(3)	2.9(3)
C(22)	0.5093(7)	0.4460(5)	0.3250(3)	4.1(3)
C(23)	0.4971(8)	0.4116(6)	0.3951(3)	5.2(4)
C(24)	0.3841(9)	0.3545(6)	0.4099(3)	5.5(4)
C(25)	0.2834(7)	0.3310(6)	0.3546(4)	5.7(4)
C(26)	0.2929(6)	0.3646(6)	0.2841(3)	4.4(3)
C(31)	0.5499(6)	0.3687(4)	0.1485(3)	2.8(3)
C(32)	0.6889(6)	0.3902(5)	0.1624(4)	4.3(3)
C(33)	0.7850(6)	0.3171(6)	0.1429(4)	5.1(4)
C(34)	0.7425(7)	0.2224(6)	0.1100(3)	4.5(3)
C(35)	0.6049(7)	0.1983(5)	0.0952(3)	4.1(3)
C(36)	0.5096(6)	0.2719(5)	0.1145(3)	3.4(3)

$\text{C}_8\text{H}_{11}$ ), 333 (100,  $\text{M}^+ - \text{CO} - \text{C}_8\text{H}_{11}$ ). Anal. Found: C, 71.62; H, 6.29.  $\text{C}_{28}\text{H}_{29}\text{OPFe}$  Calc.: C, 71.80; H, 6.24%.

Table 7  
Atomic coordinates and  $B_{\text{iso}}$  of **5j**

Atom	x	y	z	$B_{\text{iso}}$ ( $\text{\AA}^2$ )
Fe(1)	0.46806(8)	0.74320(8)	0.41467(4)	4.51(5)
Fe(2)	0.20068(8)	0.24620(9)	0.08738(4)	4.86(5)
Si(1)	0.87101(18)	0.68596(18)	0.40027(11)	5.83(12)
Si(2)	0.63517(18)	0.25758(18)	0.08945(11)	5.72(12)
P(1)	0.51964(16)	0.84773(15)	0.32954(8)	4.68(10)
P(2)	0.14774(16)	0.14027(19)	0.17233(9)	5.66(11)
O(1)	0.6140(5)	0.9534(4)	0.5195(2)	6.8(3)
O(41)	0.1454(5)	0.0323(5)	-0.0198(3)	7.3(3)
C(1)	0.5558(6)	0.8699(6)	0.4772(4)	5.0(4)
C(2)	0.2838(6)	0.6811(7)	0.3672(4)	6.2(4)
C(3)	0.2855(6)	0.7318(7)	0.4379(4)	6.1(4)
C(4)	0.3211(7)	0.6613(7)	0.4780(4)	6.5(4)
C(5)	0.3418(6)	0.5662(6)	0.4339(5)	6.5(4)
C(6)	0.3188(6)	0.5777(7)	0.3654(4)	5.9(4)
C(7)	0.2653(7)	0.7356(8)	0.3048(4)	7.5(5)
C(8)	0.3709(7)	0.8637(7)	0.3073(3)	6.3(5)
C(9)	0.6148(6)	0.7033(5)	0.4103(3)	4.5(4)
C(10)	0.7130(7)	0.6864(6)	0.4087(3)	5.5(4)
C(11)	0.9904(7)	0.8463(7)	0.4013(5)	9.9(6)
C(12)	0.9171(8)	0.6198(8)	0.4687(5)	10.6(7)
C(13)	0.8741(9)	0.5874(9)	0.3176(5)	11.6(7)
C(21)	0.6469(7)	1.0030(6)	0.3443(3)	5.0(4)
C(22)	0.6290(8)	1.1087(7)	0.3337(4)	6.5(5)
C(23)	0.7301(12)	1.2223(8)	0.3457(4)	8.1(7)
C(24)	0.8485(10)	1.2347(7)	0.3676(4)	7.6(6)
C(25)	0.8680(7)	1.1319(8)	0.3795(4)	7.4(5)
C(26)	0.7662(7)	1.0162(6)	0.3679(4)	6.3(5)
C(31)	0.5560(6)	0.7783(6)	0.2464(3)	4.5(3)
C(32)	0.5557(6)	0.6604(6)	0.2361(3)	5.3(4)
C(33)	0.5748(7)	0.6064(6)	0.1716(4)	6.6(5)
C(34)	0.5952(7)	0.6700(8)	0.1176(4)	7.2(5)
C(35)	0.5984(8)	0.7872(9)	0.1268(4)	7.8(6)
C(36)	0.5798(7)	0.8429(6)	0.1911(4)	6.6(5)
C(41)	0.1645(6)	0.1163(7)	0.0232(4)	5.2(4)
C(42)	0.0954(8)	0.3391(8)	0.1382(4)	6.9(6)
C(43)	0.0444(7)	0.2924(7)	0.0694(4)	7.0(5)
C(44)	0.1439(8)	0.3495(7)	0.0266(4)	6.6(5)
C(45)	0.2554(8)	0.4288(7)	0.0677(5)	6.9(5)
C(46)	0.2246(8)	0.4240(7)	0.1375(4)	6.9(5)
C(47)	0.0293(9)	0.2957(11)	0.2013(5)	9.9(8)
C(48)	0.0005(7)	0.1589(11)	0.1977(4)	9.3(7)
C(49)	0.3724(6)	0.2599(5)	0.0881(3)	4.4(4)
C(50)	0.4799(6)	0.2637(6)	0.0862(3)	5.1(4)
C(51)	0.7726(16)	0.4088(15)	0.1091(10)	5.1(4)
C(51')	0.7575(17)	0.3871(16)	0.0566(10)	6.1(4)
C(51'')	0.7554(30)	0.3994(28)	0.1539(17)	5.0(7)
C(52)	0.6415(14)	0.1272(14)	0.1235(8)	7.3(4)
C(52')	0.6308(20)	0.1043(18)	0.0427(11)	11.6(6)
C(53)	0.6639(22)	0.2398(20)	0.1830(11)	13.3(7)
C(53')	0.6779(18)	0.2242(17)	-0.0088(10)	10.4(5)
C(61)	0.2478(6)	0.1968(6)	0.2536(3)	4.9(4)
C(62)	0.3659(6)	0.2953(6)	0.2603(3)	5.3(4)
C(63)	0.4377(7)	0.3377(6)	0.3238(4)	6.0(4)
C(64)	0.3891(9)	0.2817(8)	0.3798(4)	6.8(5)
C(65)	0.2736(9)	0.1828(8)	0.3735(4)	7.3(6)
C(66)	0.2035(7)	0.1418(7)	0.3112(4)	6.8(5)

Table 7 (continued)

Atom	x	y	z	$B_{iso}$ ( $\text{\AA}^2$ )
C(71)	0.1135(9)	-0.0255(7)	0.1592(4)	7.1(5)
C(72)	0.2111(10)	-0.0606(9)	0.1422(5)	9.3(7)
C(73)	0.1905(14)	-0.1855(12)	0.1354(6)	13.1(9)
C(74)	0.0760(21)	-0.2701(17)	0.1438(10)	16.5(16)
C(75)	-0.0228(15)	-0.2422(20)	0.1580(9)	15.6(13)
C(76)	-0.0057(10)	-0.1148(11)	0.1680(4)	10.5(6)

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)( $\eta^1$ -C≡C-C<sub>5</sub>H<sub>11</sub>) (**5i**): orange liquid (75%). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2099w (acetylene), 1944s (CO) cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  83.5 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.08–8.01 (2H, m, Ph), 7.64–7.57 (2H, m, Ph), 7.40–7.29 (6H, m, Ph), 4.95–4.94 (1H, m, Cp), 4.85–4.84 (1H, m, Cp), 4.77–4.76 (1H, m, Cp), 4.08–4.07 (1H, m, Cp), 3.33–3.22 (1H, m, H<sub>1a</sub>), 3.09–2.99 (1H, m, H<sub>1b</sub>), 2.29–2.01 (4H, m, H<sub>2</sub> + acetylenic-CH<sub>2</sub>), 1.30–1.16 (5H, m), 0.91–0.81 (1H, m), 0.76 (3H, t,  $J = 7.0$  Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  218.9 (CO,  $J_{cp} = 26.2$  Hz), 135.9 (C,  $J_{cp} = 41.5$  Hz, Ph), 134.5 (C,  $J_{cp} = 37.4$  Hz, Ph), 133.5 (CH × 2,  $J_{cp} = 9.0$  Hz, Ph), 131.1 (CH × 2,  $J_{cp} = 9.0$  Hz, Ph), 129.8 (CH × 2, Ph), 128.3 (CH × 2,  $J_{cp} = 9.4$  Hz, Ph), 127.8 (CH × 2,  $J_{cp} = 9.5$  Hz, Ph), 117.3 (C,  $J_{cp} = 6.8$  Hz, Cp), 116.5 (C, acetylene), 88.3 (CH, Cp), 84.8 (C,  $J_{cp} = 35.6$  Hz, acetylene), 81.7 (CH, Cp), 78.1 (CH, Cp), 72.8 (CH, Cp), 46.9 (CH<sub>2</sub>,  $J_{cp} = 29.4$  Hz, C<sub>1</sub>), 31.2 (CH<sub>2</sub>), 30.7 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 20.9 (CH<sub>2</sub>,  $J_{cp} = 6.3$  Hz, C<sub>2</sub>), 14.0 (CH<sub>3</sub>) ppm. MS

Table 8

Anisotropic thermal parameters of **5a**

Atom	$u_{11}$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Fe	2.55(3)	3.37(3)	3.75(4)	-0.18(5)	-0.02(3)	0.10(5)
P	3.00(8)	3.53(7)	3.86(7)	-0.34(7)	-0.09(8)	0.07(7)
O(1)	3.5(3)	10.1(5)	17.5(6)	-0.6(3)	-1.4(3)	2.2(5)
C(1)	4.5(3)	4.0(3)	8.4(5)	0.0(3)	0.4(3)	1.3(4)
C(2)	5.5(4)	4.5(4)	6.5(4)	-0.1(3)	-0.1(4)	0.0(3)
C(3)	3.3(3)	4.5(4)	4.1(3)	0.8(3)	0.4(3)	-0.7(3)
C(4)	4.5(3)	4.3(3)	4.4(3)	0.5(3)	-0.4(4)	-0.6(3)
C(5)	4.3(4)	3.8(3)	5.7(4)	-0.3(3)	1.7(4)	-1.4(3)
C(6)	5.2(4)	3.8(3)	5.7(4)	1.1(3)	1.0(3)	0.4(3)
C(7)	3.0(3)	4.2(3)	6.0(4)	0.9(3)	-0.1(3)	0.1(3)
C(8)	3.5(3)	5.9(4)	5.7(4)	-0.1(3)	1.3(3)	0.0(3)
C(9)	3.2(3)	5.0(3)	5.8(4)	-0.6(3)	0.4(3)	0.7(3)
C(11)	3.3(3)	5.0(3)	4.0(4)	0.7(3)	0.2(3)	0.2(3)
C(12)	4.7(4)	3.9(3)	4.6(4)	0.1(3)	0.5(3)	-0.2(3)
C(13)	5.9(4)	4.8(4)	4.8(4)	1.7(3)	1.2(4)	1.1(3)
C(14)	6.3(5)	6.7(4)	4.4(4)	1.9(4)	-0.7(4)	0.3(4)
C(15)	7.3(6)	6.8(5)	5.6(5)	0.8(5)	-2.1(5)	-0.7(4)
C(16)	5.7(4)	5.1(4)	5.4(4)	-0.3(4)	-1.6(4)	-0.1(3)
C(21)	4.6(3)	3.6(3)	3.7(3)	0.2(3)	-0.4(3)	0.4(2)
C(22)	6.4(4)	4.6(4)	5.8(4)	-1.1(3)	0.1(4)	0.0(4)
C(23)	9.5(6)	5.2(4)	5.8(5)	-1.9(4)	-0.7(5)	-0.6(4)
C(24)	11.9(8)	5.9(5)	5.5(5)	0.6(5)	0.7(5)	-0.6(4)
C(25)	8.3(7)	5.6(4)	6.4(5)	1.4(5)	1.3(5)	0.4(4)
C(26)	5.0(4)	5.3(4)	4.8(4)	0.2(3)	0.1(3)	-0.7(3)

(FAB, <sup>56</sup>Fe): 456 (8, M<sup>+</sup>), 428 (38, M<sup>+</sup> - CO), 361 (11, M<sup>+</sup> - C<sub>7</sub>H<sub>11</sub>), 333 (100, M<sup>+</sup> - CO - C<sub>7</sub>H<sub>11</sub>). Anal. Found: C, 70.69; H, 6.62, C<sub>27</sub>H<sub>29</sub>OPFe Calc.: C, 71.06; H, 6.40%.

( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)( $\eta^1$ -C≡CSiMe<sub>3</sub>) (**5j**): red crystal (80%). M.p., 135–137°C. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2008m, 1951s, 1603w cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  82.3 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.15–8.08 (2H, m, Ph), 7.65–7.58 (2H, m, Ph), 7.44–7.34 (6H, m, Ph), 5.00–4.98 (1H, m, Cp), 4.84–4.82 (1H, m, Cp), 4.78–4.76 (1H, m, Cp), 4.14–4.12 (1H, m, Cp), 3.26 (1H, dddd,  $J = 13.0, 11.2, 5.8$  and  $3.7$  Hz, H<sub>1a</sub>), 3.04 (1H, ddt,  $J = 13.0, 11.3$  and  $7.4$  Hz, H<sub>1b</sub>), 2.27 (1H, dddd,  $J = 37.8, 13.7, 7.4$  and  $3.7$  Hz, H<sub>2a</sub>), 2.02 (1H, tdd,  $J = 13.7, 11.3$  and  $5.8$  Hz, H<sub>2b</sub>), 0.17 (3H, s, Si(CH<sub>3</sub>)<sub>a</sub>), -0.05 (6H, s, Si(CH<sub>3</sub>)<sub>b and c</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  218.1 (CO,  $J_{cp} = 25.1$  Hz), 135.8 (C,  $J_{cp} = 43.0$  Hz, Ph), 134.4 (C,  $J_{cp} = 32.2$  Hz, acetylene), 134.1 (C,  $J_{cp} = 37.8$  Hz, Ph), 133.6 (CH × 2,  $J_{cp} = 9.4$  Hz, Ph), 130.9 (CH × 2,  $J_{cp} = 8.7$  Hz, Ph), 130.1 (CH, Ph), 129.9 (CH, Ph), 128.3 (CH × 2,  $J_{cp} = 9.6$  Hz, Ph), 128.0 (CH × 2,  $J_{cp} = 9.6$  Hz, Ph), 125.1 (C, acetylene), 117.6 (C,  $J_{cp} = 6.9$  Hz, Cp), 88.4 (CH, Cp), 82.1

Table 9

Anisotropic thermal parameters of **5g**

Atom	$u_{11}$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Fe	3.59(4)	3.42(4)	3.53(4)	0.51(5)	0.43(3)	0.19(4)
P	3.31(9)	3.64(9)	3.49(9)	0.20(7)	0.46(7)	0.14(7)
O(1)	12.2(5)	8.9(4)	4.9(3)	2.3(3)	2.7(3)	-0.7(3)
C(1)	6.0(4)	4.4(4)	4.1(4)	0.2(3)	-0.1(3)	0.4(3)
C(2)	5.4(4)	3.1(3)	4.5(4)	0.4(3)	0.8(3)	-0.3(3)
C(3)	7.6(5)	3.5(4)	4.6(4)	0.8(4)	0.8(4)	0.7(3)
C(4)	6.5(5)	4.7(4)	6.2(5)	2.2(4)	-1.4(4)	0.2(3)
C(5)	3.3(4)	5.0(4)	8.4(5)	1.2(3)	0.5(4)	0.3(4)
C(6)	5.2(4)	4.9(4)	4.8(4)	1.4(3)	1.4(3)	-0.2(3)
C(7)	7.8(5)	3.7(4)	4.9(4)	-0.6(4)	0.7(4)	-0.7(3)
C(8)	4.6(4)	3.9(4)	4.7(4)	-0.8(3)	0.0(3)	0.1(3)
C(9)	3.0(4)	5.6(4)	4.3(4)	0.9(3)	0.6(3)	0.3(3)
C(10)	2.6(4)	4.5(4)	6.4(4)	-0.3(3)	0.7(3)	0.7(3)
C(11)	2.6(4)	4.6(4)	6.1(4)	-0.2(3)	0.9(3)	0.3(3)
C(12)	4.6(4)	4.0(4)	7.7(5)	-0.1(3)	1.3(4)	0.0(3)
C(13)	5.5(5)	5.7(5)	10.4(6)	0.3(4)	2.1(4)	2.1(5)
C(14)	5.7(5)	4.8(5)	13.6(8)	0.3(4)	1.2(5)	-0.6(5)
C(15)	7.3(6)	7.1(6)	11.2(7)	0.3(5)	1.9(5)	-3.4(5)
C(16)	6.9(6)	7.5(6)	6.7(5)	-0.7(5)	1.5(4)	-1.2(4)
C(21)	3.8(4)	3.7(3)	3.6(3)	1.0(3)	0.6(3)	0.0(3)
C(22)	6.1(4)	5.3(4)	3.8(4)	0.4(4)	0.1(3)	0.3(3)
C(23)	8.2(6)	7.6(5)	3.7(4)	1.7(4)	-0.7(4)	0.3(4)
C(24)	8.1(6)	8.8(6)	4.3(4)	2.7(5)	1.8(4)	1.5(4)
C(25)	5.0(5)	11.3(6)	5.8(5)	0.1(4)	1.8(4)	2.5(4)
C(26)	4.1(4)	8.6(5)	4.2(4)	0.3(4)	0.8(3)	1.3(4)
C(31)	3.6(4)	4.4(3)	2.8(3)	0.7(3)	0.8(3)	0.4(3)
C(32)	3.1(4)	5.4(4)	7.9(5)	0.1(3)	0.7(3)	0.1(4)
C(33)	3.4(4)	8.4(5)	7.6(5)	0.7(4)	0.9(4)	0.2(4)
C(34)	4.8(5)	7.6(5)	4.8(4)	3.0(4)	1.6(3)	0.5(4)
C(35)	5.7(5)	5.7(4)	4.3(4)	1.8(4)	0.6(3)	-0.2(3)
C(36)	3.6(4)	5.1(4)	4.2(4)	0.7(3)	0.5(3)	0.1(3)

Table 10  
Anisotropic thermal parameters of **5j**

Atom	$u_{11}$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Fe(1)	5.09(6)	6.06(6)	5.98(6)	2.36(5)	1.04(5)	0.66(5)
Fe(2)	4.97(6)	8.41(7)	5.34(6)	3.09(5)	-0.50(5)	0.74(5)
Si(1)	5.29(12)	7.21(13)	10.13(16)	2.54(11)	1.27(11)	2.70(12)
Si(2)	5.55(12)	7.67(14)	9.27(15)	3.15(11)	0.29(11)	2.26(11)
P(1)	6.14(12)	6.51(11)	5.85(11)	3.36(10)	0.49(9)	0.86(9)
P(2)	4.68(11)	10.44(15)	5.61(12)	2.16(11)	-0.05(9)	1.55(10)
O(1)	10.4(4)	7.4(3)	7.7(3)	3.7(3)	-1.4(3)	-0.3(3)
O(41)	7.8(4)	10.2(4)	8.1(4)	2.9(3)	0.1(3)	-1.6(3)
C(1)	6.6(5)	6.5(5)	6.8(5)	3.2(4)	1.1(4)	1.7(4)
C(2)	3.8(4)	9.5(6)	9.6(6)	2.7(4)	0.9(4)	-0.1(5)
C(3)	5.0(4)	8.4(5)	9.4(6)	3.1(4)	2.1(4)	-0.4(5)
C(4)	6.8(5)	8.3(5)	9.3(6)	2.4(4)	3.5(4)	2.3(5)
C(5)	6.1(5)	6.1(5)	11.6(7)	1.6(4)	3.1(5)	1.7(5)
C(6)	4.9(4)	8.1(5)	8.2(6)	1.9(4)	1.4(4)	-0.3(4)
C(7)	6.4(5)	12.7(7)	9.9(6)	5.1(5)	-0.9(5)	0.3(5)
C(8)	8.3(5)	9.7(6)	8.0(5)	6.0(5)	-0.1(4)	0.7(4)
C(9)	5.8(4)	5.5(4)	6.0(4)	2.2(4)	0.5(3)	1.0(3)
C(10)	5.7(5)	6.6(4)	8.4(5)	2.3(4)	0.4(4)	1.5(4)
C(11)	6.7(5)	7.5(5)	23.4(11)	2.3(5)	1.6(6)	4.5(6)
C(12)	7.5(6)	13.9(8)	20.2(10)	3.5(5)	-0.7(6)	9.0(7)
C(13)	11.8(8)	13.4(8)	18.0(10)	5.0(7)	6.0(7)	0.2(7)
C(21)	8.3(5)	6.1(4)	5.2(4)	3.4(4)	1.4(4)	1.0(3)
C(22)	10.8(6)	6.9(5)	7.4(5)	4.1(5)	0.2(4)	1.2(4)
C(23)	15.4(9)	7.4(6)	9.4(7)	5.6(7)	2.1(7)	2.3(5)
C(24)	12.8(8)	5.3(5)	8.6(6)	1.3(6)	4.2(6)	1.0(4)
C(25)	7.7(6)	7.7(6)	11.2(7)	2.1(5)	1.6(5)	0.3(5)
C(26)	7.3(5)	6.3(5)	10.5(6)	2.5(4)	1.2(5)	1.6(4)
C(31)	5.8(4)	6.1(4)	5.2(4)	2.4(3)	0.6(3)	0.6(3)
C(32)	6.8(5)	6.5(5)	7.0(5)	2.8(4)	1.6(4)	1.4(4)
C(33)	9.1(6)	7.3(5)	8.4(6)	3.4(4)	2.1(5)	-0.4(5)
C(34)	7.9(6)	10.3(7)	7.8(6)	3.1(5)	1.9(4)	-0.7(5)
C(35)	11.0(7)	12.8(7)	6.4(5)	5.1(6)	2.5(5)	2.8(5)
C(36)	11.5(6)	8.1(5)	6.7(5)	5.2(5)	2.0(5)	1.9(4)
C(41)	4.8(4)	8.3(5)	6.5(5)	2.2(4)	0.0(4)	1.4(4)
C(42)	7.6(6)	13.4(7)	7.8(6)	7.3(6)	-0.2(5)	0.2(5)
C(43)	6.6(5)	12.0(7)	8.9(6)	4.8(5)	-1.4(5)	1.4(5)
C(44)	9.3(6)	10.2(6)	7.3(5)	5.7(5)	-1.7(5)	1.4(5)
C(45)	8.8(6)	8.2(5)	10.0(6)	4.2(5)	-0.5(5)	1.6(5)
C(46)	8.0(6)	9.7(6)	9.7(7)	5.7(5)	-2.2(5)	-1.3(5)
C(47)	9.9(7)	22.9(12)	9.0(7)	11.5(9)	1.7(5)	1.4(8)
C(48)	5.3(5)	22.9(11)	7.3(6)	5.4(7)	1.6(4)	4.3(7)
C(49)	5.3(4)	6.6(4)	4.7(4)	2.3(4)	0.1(3)	0.7(3)
C(50)	5.2(4)	7.7(5)	6.6(4)	2.9(4)	0.3(3)	1.2(4)
C(51)	6.5(5)					
C(51')	7.7(5)					
C(51'')	6.3(9)					
C(52)	9.3(5)					
C(52')	14.7(7)					
C(53)	16.8(8)					
C(53')	13.2(6)					
C(61)	5.6(4)	8.3(5)	5.3(4)	3.2(4)	0.3(3)	1.5(4)
C(62)	6.4(5)	7.9(5)	6.0(4)	3.0(4)	-0.4(4)	0.8(4)
C(63)	7.1(5)	7.8(5)	7.6(5)	2.9(4)	-1.9(4)	0.5(4)
C(64)	11.2(7)	9.8(6)	6.1(5)	6.1(6)	-2.7(5)	-0.4(5)
C(65)	10.4(7)	11.8(7)	6.2(5)	4.8(6)	-0.4(5)	2.7(5)
C(66)	7.3(5)	10.9(6)	7.1(5)	2.6(5)	-0.4(4)	2.5(5)
C(71)	8.8(6)	7.9(6)	6.6(5)	-1.1(5)	-2.6(5)	2.6(4)
C(72)	12.6(9)	7.5(7)	12.9(8)	2.1(6)	-3.2(7)	1.3(5)
C(73)	20.7(14)	9.2(8)	17.5(11)	4.5(9)	-9.2(10)	0.2(8)
C(74)	28.3(26)	9.2(10)	16.0(14)	-2.6(16)	-14.7(19)	3.7(9)
C(75)	17.2(15)	16.5(18)	12.5(10)	-9.0(14)	-6.7(12)	8.2(11)
C(76)	10.9(8)	13.4(8)	9.5(7)	-2.6(7)	-3.7(6)	4.5(6)

(CH,Cp), 78.7 (CH, Cp), 73.4 (CH,Cp), 46.9 (CH<sub>2</sub>,  $J_{\text{cp}} = 29.2$  Hz, C<sub>1</sub>), 20.7 (CH<sub>2</sub>,  $J_{\text{cp}} = 6.4$  Hz, C<sub>2</sub>), 1.6 (CH<sub>3</sub> × 2), -0.1 (CH<sub>3</sub>) ppm. MS (FAB, <sup>56</sup>Fe): 458 (6%, M<sup>+</sup>), 430 (48, M<sup>+</sup> - CO), 333 (100, M<sup>+</sup> - CO - C<sub>2</sub>SiMe<sub>3</sub>). Anal. Found: C, 65.62; H, 5.92. C<sub>25</sub>H<sub>27</sub>OPSiFe Calc.: C, 65.50; H, 5.94%.

**3.6. Crystal structure of ( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)-Fe(CO)CH<sub>3</sub> (**5a**), ( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe(CO)-( $\eta^1$ -C≡CPh) (**5g**) and ( $\eta^5$ : $\eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)-Fe(CO)4-( $\eta^1$ -C≡CSiMe<sub>3</sub>) (**5j**)**

A single crystal of **5a** was grown in a 1:10 solution of dichloromethane and *n*-hexane at 5°C. The single crystal of **5g** was grown in a 1:15 solution of dichloromethane and *n*-hexane at 5°C and **5j** was grown in a 1:50 solution of dichloromethane and *n*-hexane at -20°C. Diffraction measurements of **5a**, **5g** and **5j** were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) in the  $\theta$ -2 $\theta$  scan mode. Unit-cell dimensions were obtained by least-squares refinement with use of 25 centered reflections in the range of  $19.20^\circ < 2\theta < 36.58^\circ$  for **5a**,  $14.96^\circ < 2\theta < 28.94^\circ$  for **5g** and  $14.96^\circ < 2\theta < 34.08^\circ$  for **5j**. All structures were refined by the full-matrix least-squares method. Dihedral angles of H-C-C-P were calculated using standard methylene bond angle and 0.95 Å for H-C bond length. Other crystal data and refinement details are listed in Table 4. Atomic coordinates and  $B_{\text{iso}}$  and anisotropic thermal parameters of non-hydrogen atoms of **5a**, **5g** and **5j** are listed in Tables 5–10.

#### 4. Supplementary material available

Lists of crystal data and refinement details, atomic coordinates and  $B_{\text{iso}}$ , bond lengths and angles and torsion angles of **5a**, **5g** and **5j** are available from T.-F.W.

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