

Di- and triphospha-ferrocenes: crystal and molecular structures  
of  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)]$  and of the adducts  
 $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{Mo}(\text{CO})_5]$   
and  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{W}(\text{CO})_5]$ <sup>1</sup>

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Abstract

Synthesis and structural studies of the iron ‘sandwich’ complex  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)]$  **1** are described. The lone pair electrons of the two adjacent phosphorus atoms of the  $\text{C}_2^t\text{Bu}_2\text{P}_3$  ring in the triphospha-ferrocene complex  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)]$  **2** can ligate to other metal centres. The results of single crystal X-ray structural studies of the molybdenum and tungsten pentacarbonyl  $\eta^1$ -complexes  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{M}(\text{CO})_5]$  (**4**: M = Mo, **5**: M = W) are discussed; they form an isostructural series with the previously reported chromium complex. The starting material **2** reacts with  $[(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\text{THF})]$  to form the adduct  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Me})]$  **6**. The phenyl-substituted di- and triphosphacyclopentadienides  $[\text{Na}(\text{DME})_3][\text{C}_3\text{Ph}_3\text{P}_2]$  and  $[\text{Na}(\text{DME})_3][\text{C}_2\text{Ph}_2\text{P}_3]$  (DME = 1,2-dimethoxyethane) react with ferrous chloride and  $\text{Li}[\text{C}_5\text{Me}_5]$  to give the ‘sandwich’ compounds  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_3\text{Ph}_3\text{P}_2)]$  **9** and  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{Ph}_2\text{P}_3)]$  **10**. The latter reacts with  $\text{W}(\text{CO})_5(\text{THF})$  to yield the  $\eta^1$ -complex  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{Ph}_2\text{P}_3)\text{W}(\text{CO})_5]$  **11**.

**Keywords:** Phosphorus; Iron; Molybdenum; Tungsten; Metallocenes; Fluxionality; X-ray diffraction

1. Introduction

Syntheses and structures of di-, tri-, penta- and hexaphosphorus analogues of ferrocene, hexaphosphorus analogues of chromocene and  $\eta^3$ -transition metal complexes involving the  $\text{C}_2^t\text{Bu}_2\text{P}_3$  ring system (**8b**) have been described [1–7]. Unlike their simple metallocene analogues, these complexes have further coordinating potential towards other transition metal centres by virtue of the availability of the ring phosphorus lone-pair electrons not already utilized in their  $\eta^3$ - or  $\eta^5$ -metal ligation. In a previous paper [8] the synthesis and structural characterization of four such compounds were described:  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)_2\text{Fe}(\text{CO})_4]$ ,  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)_2\text{W}(\text{CO})_5]$ ,  $[\text{Fe}(\eta^5\text{-C}_3^t\text{Bu}_3\text{P}_2)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{W}(\text{CO})_5]$  and  $[\text{Fe}(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)_2\text{Ru}_3(\text{CO})_{10}]$ . The

latter is of special interest since it represents the first example of interlinkage of both  $(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)$  ligated ring systems in hexaphospha-ferrocene complexes. Recently [9] we described the synthesis and structural characterization of the ruthenium compound  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{Ru}_3(\text{CO})_9]$  as a first example of a triphospha-ferrocene in which the two adjacent phosphorus atoms are coordinated to three transition metal centres involving side-on and end-on coordination. This mode of attachment can be regarded as  $\mu^3\text{-}\eta^2$ -ligation of a PP and PC multiple-bonded system to three metal centres.

Previously [10] we reported the synthesis and structural characterization of the tetrametallic complex  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{Ni}(\text{CO})_2]_2$  which represents the first example of intermolecular interlinkage of two of the original triphospha-ferrocene systems via two metal centres. Furthermore, the syntheses of  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{Fe}(\text{CO})_4]$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)\text{W}(\text{CO})_5]$  and  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^t\text{Bu}_2\text{P}_3)]$

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<sup>1</sup> Dedicated to Professor Marvin D. Rausch on the occasion of his 65th birthday.

Cr(CO)<sub>5</sub>] were described. The latter was characterized by an X-ray crystal structure determination.

In this paper we report on synthesis and structural characterization of the diphospha-ferrocene [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>3</sub><sup>t</sup>Bu<sub>3</sub>P<sub>2</sub>)] **1** and of the triphospha-ferrocenes [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)M(CO)<sub>5</sub>] (**4**: M = Mo, **5**: M = W), with a view to elucidating structural relationships within a series of related phospho-ferrocenes.

The synthesis of the manganese compound [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)Mn(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)] **6** is described. Furthermore, we report the synthesis of the novel phenyl-substituted di- and triphospha-ferrocenes [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>3</sub>Ph<sub>3</sub>P<sub>2</sub>)] **9** and [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>Ph<sub>2</sub>P<sub>3</sub>)] **10**. The latter reacts with W(CO)<sub>5</sub>-(THF) to yield the η<sup>1</sup>-complex [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub>Ph<sub>2</sub>P<sub>3</sub>)W(CO)<sub>5</sub>] **11**. The phenyl-substituted phospho-ferrocenes were characterized by <sup>1</sup>H-, <sup>13</sup>C- and <sup>31</sup>P-NMR spectroscopy.

## 2. Results and discussion

### 2.1. Synthesis of the diphospha-ferrocene [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>3</sub><sup>t</sup>Bu<sub>3</sub>P<sub>2</sub>)] **1**

We recently described the preparation of the triphospha-ferrocene [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)] **2** [9]. Treatment of ferrous chloride with a mixture of the solution of the anions [C<sub>3</sub><sup>t</sup>Bu<sub>3</sub>P<sub>2</sub>]<sup>-</sup> **7b**, [C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>]<sup>-</sup> **8b** and [C<sub>5</sub>Me<sub>5</sub>]<sup>-</sup> led to the formation of a 1:1 mixture of the triphospha-ferrocene **2** and the diphospha-ferrocene **1**. Decamethylferrocene and the earlier described penta- and hexaphospha-ferrocenes [1] are formed as by-products, which could easily be separated by column chromatography. The products **1** and **2**, which can be separated as a mixture from the other products by column chromatography, were obtained as red solids. Because both phosphorus atoms in **1** are sterically protected by the <sup>t</sup>Bu groups, treatment of the mixture of **1** and **2** with nickel tetracarbonyl leads only to the formation of the previously described iron nickel complex [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)Ni(CO)<sub>2</sub>]<sub>2</sub> [10]. **1** remains unchanged and can now be separated as red, air-stable, crystalline solid.

### 2.2. Syntheses of the triphospha-ferrocenes [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)M(CO)<sub>5</sub>] (**4**: M = Mo, **5**: M = W)

In a previous paper [10] we described the preparation of the chromium and tungsten pentacarbonyl adducts [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)M(CO)<sub>5</sub>] (**3**: M = Cr, **5**: M = W) of which the chromium pentacarbonyl adduct **3** was structurally characterized.

We now present single crystal X-ray diffraction studies of **5** and the closely related molybdenum pentacar-

Table 1  
<sup>31</sup>P{<sup>1</sup>H}-NMR data<sup>a</sup> for **1–11**

Compound	δ( <sup>31</sup> P)	<sup>1</sup> J(PP) (Hz)	<sup>2</sup> J(PP) (Hz)	Ref.
<b>1</b> <sup>b</sup>	23.07(A)			
<b>2</b> <sup>b</sup>	38.10(A) 48.24(B)		44.9	[9]
<b>3</b> <sup>b,c</sup>	39.10(A) 16.41(B) 79.11(X)	404.3	35.6(AB) 49.4(AX)	[10]
<b>4</b> <sup>b,c</sup>	36.51(A) 14.27(B) 85.35(X)	487.2	35.2(AB) 47.9(AX)	
<b>5</b> <sup>b,c</sup>	35.93(A) 19.73(B) 25.45(X)	544.7	35.5(AB) 48.2(AX)	[10]
<b>6</b> <sup>b</sup>	36.35(A) 2.86(B) 140.95(X)	424.5	38.2(AB) 47.7(AX)	
<b>7a</b> <sup>d</sup>	188.95(A)			
<b>8a</b> <sup>d</sup>	274.41(A) 253.91(B)		43.8(AB)	
<b>9</b> <sup>b</sup>	14.67(A)			
<b>10</b> <sup>b</sup>	28.59(A) 51.44(B)		41.7(AB)	
<b>11</b> <sup>b</sup>	37.85(A) 21.73(B) 27.28(X)	521.7	35.8(AB) 47.2(AX)	

<sup>a</sup> Chemical shifts in ppm downfield from 85% H<sub>3</sub>PO<sub>4</sub> as an external standard.

<sup>b</sup> In CDCl<sub>3</sub>.

<sup>c</sup> At -35°C.

<sup>d</sup> In DME, C<sub>6</sub>D<sub>6</sub> capillary.

bonyl adduct [Fe(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(η<sup>5</sup>-C<sub>2</sub><sup>t</sup>Bu<sub>2</sub>P<sub>3</sub>)Mo(CO)<sub>5</sub>] **4** which has been synthesized by treatment of **2** with molybdenum hexacarbonyl in the presence of trimethylamine oxide. The iron–molybdenum complex **4** could be isolated as a brown, air-stable, crystalline solid which was characterized by microanalysis, mass spectrometry, IR spectroscopy and <sup>1</sup>H-, <sup>31</sup>P-, <sup>13</sup>C- and <sup>95</sup>Mo-NMR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of **4** represents an ABX spin system with values of chemical shifts and coupling constants lying in the same region as described for **3** and **5** [10] (see Table 1). Variable-temperature <sup>31</sup>P{<sup>1</sup>H}-NMR studies reveal that complex **4** is fluxional in solution as already described for **3** and **5** [10]. This fluxional process is best visualized as an intramolecular 1,2-shift of the metal pentacarbonyl moiety between the two directly bonded phosphorus atoms [10]. The 1,2-shift is responsible for line-broadening at room temperature, while at -35°C the <sup>31</sup>P-NMR spectrum of **4** exhibits the characteristic ABX pattern expected for the rigid structure.

### 2.3. Single crystal X-ray structural determination of **1**, **4** and **5**

A single crystal X-ray diffraction study of **1** established the molecular structure shown in Fig. 1. Bond

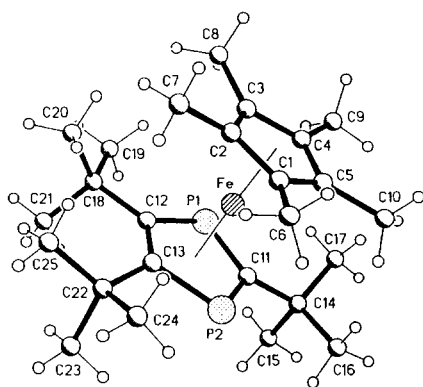


Fig. 1. Molecular structure of  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_3^1\text{Bu}_3\text{P}_2)]$  **1** showing the atom numbering scheme. Selected bond lengths and angles are: Fe–P1 2.2916(9), Fe–P2 2.2942(9), P1–C12 1.796(3), P1–C11 1.741(3), P2–C11 1.746(3), P2–C13 1.790(3), C12–C13 1.439(4) Å; P1–C11–P2 117.28(14), P1–C12–C13 115.5(2), C11–P2–C13 96.03(12), C12–C13–P2 115.3(2), C11–P1–C12 95.85(12)°.

lengths and angles in the  $[\text{Fe}(\eta^5\text{-C}_3^1\text{Bu}_3\text{P}_2)]$  moiety agree well with those of the sandwich compound  $[\text{Fe}(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)(\eta^5\text{-C}_3^1\text{Bu}_3\text{P}_2)]$  [1]. The observed PP and PC distances are very similar in both complexes. The diphosphacyclopentadienyl system reveals only negligible deviation from planarity (av. 0.006 Å). The distances between the iron atom and the centres of the cyclopentadienyl and diphosphacyclopentadienyl ring systems (1.710 and 1.683 Å) resemble those in similar compounds [9,10]. The  $\text{C}_5\text{Me}_5$  and  $\text{C}_3^1\text{Bu}_3\text{P}_2$  ring systems are essentially parallel (dihedral angle  $2.8^\circ$ ) and staggered (torsion angle C5–centre–centre–C11  $-26^\circ$ ). The molecular structures of the isostructural species **4** and **5** were confirmed by single crystal X-ray diffraction studies, indicating that the  $\text{C}_2^1\text{Bu}_2\text{P}_3$  ring is bonded in an  $\eta^5\text{-}\eta^1$ -fashion to the iron and molybdenum or tungsten atom respectively, with the iron atom sandwiched between the two five-membered rings (Fig. 2). The structures agree well with those of the closely related (and isostructural) chromium complex  $[\text{Fe}(\eta^5\text{-C}_5\text{-Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)\text{Cr}(\text{CO})_5]$  **3** [10]. The triphosphacyclopentadienyl rings in **4** and **5** show slight deviations of 0.015 Å (av.) from planarity. The observed iron–cyclopentadienyl ring centre distances of 1.719 Å and 1.716 Å in **4** and **5** and the iron–triphosphacyclopentadienyl ring distances of 1.664 Å and 1.663 Å are very similar to those of the corresponding chromium complex **3** [10]. The ring systems are parallel (dihedral angles ca.  $1.5^\circ$ ) and eclipsed (torsion angle C5–centre–centre–C11 ca.  $8^\circ$ ) in **4** and **5**. It is remarkable that the phosphorus–tungsten bond distance in **5** is shorter than the corresponding phosphorus–molybdenum bond distance in **4** (2.5263(12) Å and 2.5448(12) Å respectively]. The metal–carbon bond distances in trans-position to phosphorus are shorter by 4–6 pm than those trans to carbon.

#### 2.4. $^{95}\text{Mo}$ -NMR study of **4**

The  $^{95}\text{Mo}$ -NMR spectrum of **4** exhibits a broad signal at  $-1693$  ppm without any fine structure (line width 210 Hz). The values for  $^1J(^{95}\text{Mo}^31\text{P})$  couplings usually lie between 117 and 290 Hz [11]. No phosphorus–molybdenum coupling constant could be determined in the  $^{95}\text{Mo}$ -NMR spectrum of **4**, owing to the fast 1,2-shift of the  $\text{Mo}(\text{CO})_5$  fragment. Compound **4** represents a complex of the general type  $\text{Mo}(\text{CO})_5\text{L}$  and its  $\delta(^{95}\text{Mo})$  value of  $-1693$  ppm lies at higher frequency than the values for already known  $\text{PR}_3$  complexes of this kind. This indicates relatively high deshielding of the  $^{95}\text{Mo}$  nucleus, which could conceivably be attributed to the (minimal) distortion of the octahedral structure of the  $\text{Mo}(\text{CO})_5$  fragment caused by the neighbouring  $^1\text{Bu}$  groups of the triphosphacyclopentadienyl ring. A similar deshielding for steric reasons is observed for the compounds  $\text{Mo}(\text{CO})_5(\text{P}^1\text{Bu}_3)$  ( $\delta(^{95}\text{Mo}) = -1711$ ) and  $\text{Mo}(\text{CO})_5(\text{PPh}_3)$  ( $\delta(^{95}\text{Mo}) = -1745$ ) [12].

#### 2.5. Synthesis of lithium and sodium diphosphollides and triphosphollides

The reaction of [phenyl(trimethylsilyloxy)methylidene](trimethylsilyl)phosphine **13** with sodium afforded

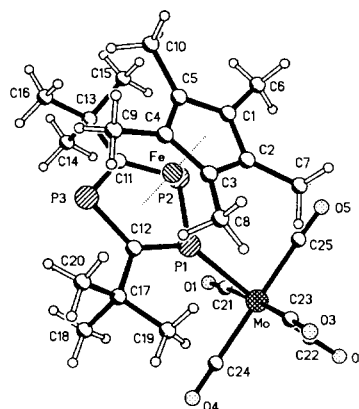
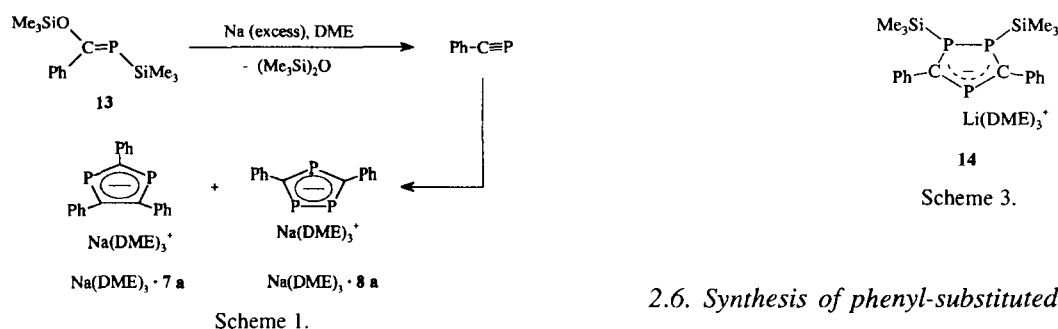


Fig. 2. Molecular structures of the isostructural complexes  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)\text{M}(\text{CO})_5]$  (**4**: M = Mo, **5**: M = W) showing the atom numbering scheme. Selected bond lengths and angles are: **4**: Fe–P1 2.3311(12), Fe–P2 2.3492(14), Fe–P3 2.3149(13), P1–P2 2.107(2), P1–C12 1.760(4), P3–C11 1.759(4), P2–C11 1.766(4), P3–C12 1.768(4), P1–Mo 2.5448(12), Mo–C21 2.041(4), Mo–C22 2.002(4) Å; P2–C11–P3 122.5(2), P1–C12–P3 118.7(2), P2–P1–C12 101.97(13), P1–P2–C11 97.18(13), C11–P3–C12 99.6(2), Mo–P1–C12 139.92(13), P2–P1–Mo 116.63(5), P1–Mo–C21 87.51(12), P1–Mo–C22 174.51(14), P1–Mo–C23 92.95(11), P1–Mo–C24 94.36(12), P1–Mo–C25 88.65(12)°. **5**: Fe–P1 2.3267(12), Fe–P2 2.3479(12), Fe–P3 2.3157(12), P1–P2 2.1069(14), P1–C12 1.754(4), P3–C11 1.755(4), P2–C11 1.764(4), P3–C12 1.764(4), P1–W 2.5263(12), W–C21 2.032(4), W–C22 2.000(4) Å; P2–C11–P3 122.7(2), P1–C12–P3 118.7(2), P2–P1–C12 102.09(13), P1–P2–C11 96.84(13), C11–P3–C12 99.5(2), W–P1–C12 139.61(13), P2–P1–W 116.95(5), P1–W–C21 87.08(12), P1–W–C22 174.58(14), P1–W–C23 92.78(11), P1–W–C24 94.32(12), P1–W–C25 88.51(13)°.



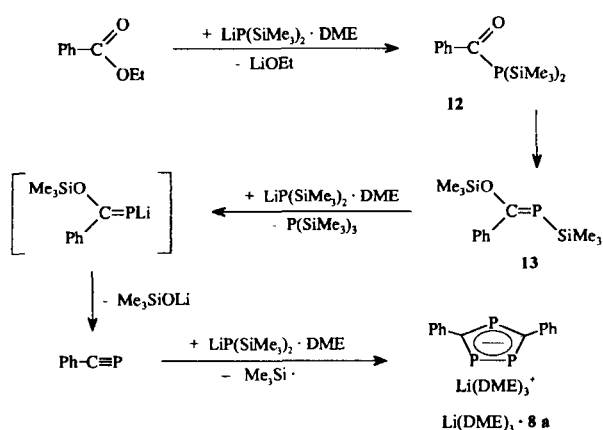
the phenyl-substituted di- and triphosphollides **7a** and **8a** in 1:1 molar ratio (Scheme 1).

Phenylmethyldynephosphine  $\text{Ph-C}\equiv\text{P}$  could be detected as an intermediate by  $^{31}\text{P}$ -NMR spectroscopy. It belongs to the class of phosphalkynes that are unstable at room temperature, with a half-life of 7 min [13,14].

Conversion of the lithium phosphide  $\text{LiP}(\text{SiMe}_3)_2 \cdot \text{DME}$  with ethyl benzoate in a 1:2 molar ratio gave the triphosphollide **8a** with  $[\text{Li}(\text{DME})_3]^+$  as counterion. The di- and triphosphollides **7a** and **8a** were characterized by their  $^{31}\text{P}$ -NMR spectra, which resemble those of the  $^t\text{Bu}$  analogues [15]. The following mechanism can be proposed for the formation of **7a** (Scheme 2).

The intermediates **12** and **13** could be detected by  $^{31}\text{P}$ -NMR spectroscopy. Becker and Hübler [16] described the analogous reaction of  $\text{LiP}(\text{SiMe}_3)_2 \cdot \text{DME}$  with ethylbenzoate in a 1:1 molar ratio and obtained the triphosphollide **14** in which two trimethylsilyl groups are still bonded to phosphorus (Scheme 3).

Compound **14** could be isolated in reasonable yield and was structurally characterized [15]. We could not detect **14**, using a different molar ratio of lithium phosphide/ethyl benzoate as described by Becker and Hübler. **14** is probably formed as intermediate and is then converted rapidly into **7a** with loss of two trimethylsilyl groups.



## 2.6. Synthesis of phenyl-substituted phospho-ferrocenes

Treatment of a mixture of  $[\text{Li}(\text{DME})_3]^+[\text{C}_2\text{Ph}_2\text{P}_3]^-$  and  $\text{Li}[\text{C}_5\text{Me}_5]$  with ferrous chloride yields the phenyl-substituted phospho-ferrocene **10** in low yield.

Compound **10** could be separated by column chromatography and was obtained as a red solid, which was characterized by  $^{31}\text{P}$ -,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy and mass spectrometry (Tables 1 and 2). Its  $\{^1\text{H}\}^{31}\text{P}$ -NMR spectrum represents an  $\text{AB}_2$  spin system and resembles that of the  $^t\text{Bu}$  analogue **2** (see Table 1). Complex **10** was also obtained together with the diphospho-ferrocene **9** by treatment of  $\text{Li}[\text{C}_5\text{Me}_5]$  and a mixture of  $[\text{Na}(\text{DME})_3]^+[\text{C}_3\text{Ph}_3\text{P}_2]^-$  and  $[\text{Na}(\text{DME})_3]^+[\text{C}_2\text{Ph}_2\text{P}_3]^-$  with ferrous chloride. Compounds **9** and **10** can be separated as a mixture by column chromatography and were obtained as red solids and characterized by their  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR spectra. A further separation by column chromatography was not possible. Because both phosphorus atoms are sterically protected by the phenyl groups, treatment of the mixture of **9** and

Table 2  
 $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data<sup>a</sup> for **1**, **4**, **6**, **10** and **11**

Complex	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
<b>1</b>	1.17 (s, 9H, $\text{P}_2\text{CMe}_3$ )	13.16 (s, $\text{C}_5\text{Me}_5$ )
	1.53 (s, 18 H, $\text{CMe}_3$ )	36.31 (m, $\text{CMe}_3$ )
	1.92 (s, 15 H, $\text{C}_5\text{Me}_5$ )	37.23 (m, $\text{CMe}_3$ )
<b>4</b>		83.72 (s, $\text{C}_5\text{Me}_5$ )
	1.43 (s, 18 H, $\text{CMe}_3$ )	12.69 (s, $\text{C}_5\text{Me}_5$ )
	1.89 (s, 15 H, $\text{C}_5\text{Me}_5$ )	36.15 (m, $\text{CMe}_3$ )
		38.78 (m, $\text{CMe}_3$ )
		88.22 (s, $\text{C}_5\text{Me}_5$ )
<b>6</b>		205.06 (s, CO)
	1.42 (s, 18 H, $\text{CMe}_3$ )	12.53 (s, $\text{C}_5\text{Me}_5$ )
	1.92 (s, 15 H, $\text{C}_5\text{Me}_5$ )	13.64 (s, $\text{C}_5\text{H}_4\text{Me}$ )
	2.38 (s, 3 H, $\text{C}_5\text{H}_4\text{Me}$ )	35.82 (m, $\text{CMe}_3$ )
	4.44 (s, 4 H, $\text{C}_5\text{H}_4\text{Me}$ )	38.26 (m, $\text{CMe}_3$ )
<b>10</b>		82.92 (m, $\text{C}_5\text{H}_4\text{Me}$ )
		87.69 (s, $\text{C}_5\text{Me}_5$ )
		202.47 (s, CO)
	1.87 (s, 15 H, $\text{C}_5\text{Me}_5$ )	12.80 (s, $\text{C}_5\text{Me}_5$ )
	6.82–7.32 (m, 10 H, $\text{C}_6\text{H}_5$ )	87.67 (s, $\text{C}_5\text{Me}_5$ )
<b>11</b>		142.7–150.2 (m, $\text{C}_6\text{H}_5$ )
	1.75 (s, 15 H, $\text{C}_5\text{Me}_5$ )	13.75 (s, $\text{C}_5\text{Me}_5$ )
	7.13–7.25 (m, 10 H, $\text{C}_6\text{H}_5$ )	88.25 (s, $\text{C}_5\text{Me}_5$ )
		138.8–148.5 (m, $\text{C}_6\text{H}_5$ )
	202.6 (s, CO)	

<sup>a</sup> In  $\text{CDCl}_3$ ; chemical shifts in ppm downfield from  $\text{SiMe}_4$ ; s = singlet, m = multiplet.

**10** with  $[\text{W}(\text{CO})_5(\text{THF})]$  leads only to the formation of the red, air-stable complex  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{Ph}_2\text{P}_3)\text{W}(\text{CO})_5]$  **11** and unchanged **9**. Both compounds could easily be separated by column chromatography and their structures were elucidated by their  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR spectra. Compounds **9**, **10** and **11** were further characterized by their mass spectra.

The  $\{^1\text{H}\}^{31}\text{P}$ -NMR spectrum of **9** shows a singlet at 14.67 ppm, while the spectrum of **11** exhibits the expected ABX spin system. Chemical shifts and coupling constants resemble those of the  $\text{M}(\text{CO})_5$  adducts of the corresponding  $^1\text{Bu}$  analogues (see Table 1).

### 3. Experimental details

#### 3.1. General procedures

All experiments were performed in an oxygen-free atmosphere of nitrogen using conventional Schlenk techniques. Solvents were purified and dried according to the usual methods [17]. "In vacuo" (i.v.) refers to a pressure of 0.05 Torr at 25°C. The sodium salts, involving the anions  $[\text{C}_3^1\text{Bu}_3\text{P}_2]^-$  **7b** and  $[\text{C}_2^1\text{Bu}_2\text{P}_3]^-$  **8b**, were made from  $^1\text{BuCP}$  [15,18];  $\text{W}(\text{CO})_5(\text{THF})$  [19],  $\text{Mo}(\text{CO})_5(\text{NMe}_3)$  [20,21],  $[\text{Mn}(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{THF})]$  [19],  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)]$  [9],  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)\text{Cr}(\text{CO})_5]$  [10] and  $[\text{LiP}(\text{SiMe}_3)_2(\text{THF})_2]$  [22] were prepared according to literature procedures; all other starting materials were commercially available. IR spectra were obtained using a Nicolet 320 FT-IR spectrometer. The irradiations were performed by use of a mercury medium-pressure lamp (Heraeus, Original Hanau, type TQ 150). NMR spectra were recorded on a Bruker AC 200 instrument ( $^1\text{H}$ : 200.1 MHz,  $^{13}\text{C}$ : 50.3 MHz,  $^{31}\text{P}$ : 81.0 MHz). Positive shifts are to lower field. Mass spectra were obtained using a Finnigan spectrometer MAT 8430. The elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen and Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig.  $^{95}\text{Mo}$ -NMR spectra were recorded at ambient temperature on a Bruker WH 400 (26.08 MHz, field strength 9.3956 T); a 2 M aqueous solution of  $\text{K}_2\text{MoO}_4$  of pH 11 was used as a standard.

#### 3.2. Synthesis of $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_3^1\text{Bu}_3\text{P}_2)]$ **1**

To a solution of a 1:1 mixture of 475 mg  $[\text{Na}(\text{DME})_3][\text{C}_3^1\text{Bu}_3\text{P}_2]$  and  $[\text{Na}(\text{DME})_3][\text{C}_2^1\text{Bu}_2\text{P}_3]$  in 10 ml DME was added  $\text{Li}[\text{C}_5\text{Me}_5]$  (175 mg, 1.23 mmol) with stirring. Ferrous chloride (180 mg, 1.42 mmol) was added to the dark brown reaction mixture, which turned black after 5 min of stirring. The mixture

was stirred for 16 h at room temperature and the solvent then removed i.v. The black residue was extracted with *n*-hexane and fractionated by column chromatography (silica gel/*n*-hexane), affording the known green complexes  $[\text{Fe}(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)_2]$  and  $[\text{Fe}(\eta^5\text{-C}_3^1\text{Bu}_3\text{P}_2)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)]$  [1], decamethylferrocene and a red solid mixture of **1** and **2**. To a solution of this mixture in 5 ml of dichloromethane, nickel tetracarbonyl (2.60 g, 15.23 mmol), diluted with 5 ml of dichloromethane, was added dropwise at 0°C with stirring. Carbon monoxide was released immediately and stirring was continued for 4 h at room temperature. After removal of the volatile material i.v., the black residue was extracted with *n*-hexane and column chromatography (silica gel/*n*-hexane) afforded the known complex  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)\text{Ni}(\text{CO})_2]_2$  [10] and **1**. Pale red crystals of **1** suitable for X-ray analysis were obtained after recrystallization from *n*-hexane.

110 mg (0.24 mmol, 28%); m.p. 167°C (dec.). Anal. Found: C, 64.97; H, 9.43.  $\text{C}_{25}\text{H}_{42}\text{FeP}_2$  (460.40). Calc.: C, 65.22; H, 9.19%. Mass spectrum (EI, 70 eV)  $m/z$  (%): 460 (2)  $[\text{M}]^+$ , 326 (100)  $[\text{M}-\text{C}_5\text{Me}_5]^+$ , 156 (4)  $[\text{FePC}^1\text{Bu}]^+$ , 57 (6)  $[^1\text{Bu}]^+$ .

#### 3.3. Synthesis of $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)\text{Mo}(\text{CO})_5]$ **4**

To a solution of  $\text{Mo}(\text{CO})_6$  (0.29 g, 1.10 mmol) in 15 ml acetonitrile was added a solution of 0.13 g (1.17 mmol) of trimethylamine-*N*-oxide dihydrate in 2 ml of methanol. After stirring for 30 min at room temperature, a solution of **2** (460 mg, 1.09 mmol) in 10 ml of *n*-hexane was added to this mixture. The reaction mixture was refluxed for 45 min leading to a deep brown solution. After removal of the volatile material i.v., the black residue was extracted with *n*-hexane and was separated by column chromatography (silica gel/*n*-hexane). Deep brown crystals of **4** suitable for X-ray analysis were obtained after recrystallization from *n*-hexane.

410 mg (0.62 mmol, 57%); m.p. 114°C; Anal. Found: C, 44.84; H, 5.16.  $\text{C}_{25}\text{H}_{33}\text{FeMoO}_5\text{P}_3$  (658.25). Calc.: C, 45.62; H, 5.05%. IR  $\tilde{\nu}$  (CO): (*n*-hexane) 2073 (m), 1988 (s), 1947 (s)  $\text{cm}^{-1}$ . Mass spectrum (EI, 70 eV)  $m/z$  (%): 660 (1.5)  $[\text{M}]^+$ , 604 (2.0)  $[\text{M}-2\text{CO}]^+$ , 576 (1.0)  $[\text{M}-3\text{CO}]^+$ , 520 (4.5)  $[\text{M}-5\text{CO}]^+$ , 422 (100)  $[\text{M}-\text{Mo}(\text{CO})_5]^+$ , 57 (4)  $[^1\text{Bu}]^+$ .

#### 3.4. Synthesis of $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2^1\text{Bu}_2\text{P}_3)\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2]$ **6**

$[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{THF})]$  was prepared by irradiation of a solution of  $[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3]$  in 10 ml THF for 5 h. To the resulting solution was added a solution of **2** (720 mg, 1.71 mmol) in 10 ml of THF, and the dark brown reaction mixture was stirred for 16

h at room temperature. After removal of the volatile material i.v., the brown residue was extracted with *n*-hexane and fractionated by column chromatography (silica gel/*n*-hexane). Complex **6** was obtained as a deep brown solid after recrystallization from *n*-hexane.

870 mg (1.42 mmol, 83%); m.p. 141°C (dec.); C<sub>28</sub>H<sub>40</sub>FeMnO<sub>2</sub>P<sub>3</sub> (612.33); IR  $\tilde{\nu}$  (CO): (*n*-hexane) 1972 (s), 2011 (vs) cm<sup>-1</sup>. Mass spectrum (EI, 70 eV) *m/z* (%): 612 (12) [M]<sup>+</sup>, 556 (100) [M-2CO]<sup>+</sup>, 422 (26) [2]<sup>+</sup>, 284 (22) [2-<sup>t</sup>Bu<sub>2</sub>C<sub>2</sub>]<sup>+</sup>, 253 (6) [2-<sup>t</sup>Bu<sub>2</sub>C<sub>2</sub>P]<sup>+</sup>, 133 (6) [MnC<sub>5</sub>H<sub>4</sub>Me]<sup>+</sup>, 79 (5) [C<sub>5</sub>H<sub>4</sub>Me]<sup>+</sup>.

### 3.5. Synthesis of [C<sub>2</sub>Ph<sub>2</sub>P<sub>3</sub>]<sup>-</sup> **8a**

A solution of [LiP(SiMe<sub>3</sub>)<sub>2</sub>(THF)<sub>2</sub>] (13.1 g, 40 mmol) in 50 ml of DME was cooled to -30°C and a solution of C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>Et (12.01 g, 80 mmol) in 10 ml of DME was added dropwise within 40 min. The reaction mixture was allowed to warm up to room temperature, this was accompanied by a colour change from yellow to red. The intermediates **12** and **13** could be detected by <sup>31</sup>P-NMR spectroscopy (**12**: δ -172.40, **13**: δ 135.20).

Stirring was continued for 16 h at room temperature, leading to a deep green solution. The volatile materials were removed i.v. and the red-green residue was washed three times with *n*-hexane and dried i.v. The lithium salt of **8a** was obtained as a red-brown oil which could not be crystallized and was characterized by its <sup>31</sup>P-NMR spectrum (see Table 1). 16.67 g (30.34 mmol, 76%).

### 3.6. Synthesis of [C<sub>3</sub>Ph<sub>3</sub>P<sub>2</sub>]<sup>-</sup> **7a** and [C<sub>2</sub>Ph<sub>2</sub>P<sub>3</sub>]<sup>-</sup> **8a**

A piece of freshly cut sodium (0.40 g, 17.40 mmol) was added at room temperature to a solution of the phosphalkene **13** (2.25 g, 7.97 mmol) in 10 ml of DME with stirring. An exothermic reaction took place, accompanied by a colour change to red within 30 min. After 10 min of stirring the phosphalkyne Ph-C≡P could be detected by <sup>31</sup>P-NMR spectroscopy (δ -31.8 ppm) in solution. Stirring was continued for 16 h at room temperature, unreacted sodium was removed and the volatile material was removed i.v. The brown residue was washed three times with *n*-hexane and dried i.v.

Table 3  
Crystallographic data for compounds **1**, **4**, **5**

	Compound		
	<b>1</b>	<b>4</b>	<b>5</b>
Formula	C <sub>25</sub> H <sub>42</sub> FeP <sub>2</sub>	C <sub>25</sub> H <sub>33</sub> FeMoO <sub>5</sub> P <sub>3</sub>	C <sub>25</sub> H <sub>33</sub> FeO <sub>5</sub> P <sub>3</sub> W
<i>M<sub>r</sub></i>	460.38	658.21	746.12
Crystal habit	red prism	red tablet	red prism
Crystal size (mm <sup>3</sup> )	0.85 × 0.45 × 0.3	0.6 × 0.4 × 0.05	0.6 × 0.3 × 0.25
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (°C)	-130	-130	-130
Cell constants			
<i>a</i> (Å)	10.972(3)	9.587(4)	9.569(3)
<i>b</i> (Å)	14.277(5)	15.077(5)	15.049(5)
<i>c</i> (Å)	16.060(4)	19.955(5)	19.892(6)
β (°)	102.73(2)	90.23(3)	90.39(3)
<i>V</i> (Å <sup>3</sup> )	2453.9	2884	2865
<i>Z</i>	4	4	4
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.246	1.516	1.730
<i>F</i> (000)	992	1344	1472
μ (mm <sup>-1</sup> )	0.75	1.14	4.7
Transmissions	no abs. corr.	0.75–0.96	0.68–0.95
2θ <sub>max</sub> (°)	55	55	55
No. of reflections			
measured	7840	9038	7696
independent	5216	6634	6612
<i>R</i> <sub>int</sub>	0.048	0.042	0.026
<i>wR</i> ( <i>F</i> <sup>2</sup> , all reflections)	0.140	0.105	0.064
<i>R</i> ( <i>F</i> , <i>F</i> > 4σ( <i>F</i> ))	0.050	0.046	0.029
No. of parameters	267	327	327
No. of restraints	0	0	188
<i>S</i>	1.03	1.05	1.06
Max. Δ/σ	0.001	0.014	0.001
Max. Δρ (eÅ <sup>-3</sup> )	0.77	0.68	0.92

The resulting red–brown oily product, which could not be crystallized, proved to be an equimolar mixture of The sodium salts of **7a** and **8a** according to the integration of the resonance signals of the  $^{31}\text{P}$ -NMR spectrum (Table 1). 1.90 g (40%).

### 3.7. Synthesis of $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_3\text{Ph}_3\text{P}_2)]$ **9** and $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{Ph}_2\text{P}_3)]$ **10**

$\text{FeCl}_2$  (1.0 g, 7.89 mmol) was added to a solution of  $\text{Li}(\text{C}_5\text{Me}_5)$  (1.05 g, 7.39 mmol) containing  $[\text{Li}(\text{DME})_3]\text{-}[\text{C}_2\text{Ph}_2\text{P}_3]$  (3.30 g, 6.02 mmol) or a mixture of  $[\text{Na}(\text{DME})_3][\text{C}_2\text{Ph}_2\text{P}_3]$  and  $[\text{Na}(\text{DME})_3][\text{C}_3\text{Ph}_3\text{P}_2]$  (3.50 g, 5.90 mmol) in DME. The mixture turned black within 30 min and was stirred at room temperature for 16 h, the solvent was removed and the residue was extracted with *n*-hexane. The extract was subjected to column chromatography (silica gel/*n*-hexane) to give orange–brown crystals of **10** and a mixture of **9** and **10** respectively.

**10**: 135 mg (292 mmol, 5%); m.p. 112°C;  $\text{C}_{24}\text{H}_{25}\text{FeP}_3$  (462.23). Mass spectrum (EI, 70 eV)  $m/z$  (%): 520 (20) [**9**] $^+$ , 462 (85) [**10**] $^+$ , 342 (8) [**10**-PhCP] $^+$ , 209 (11) [**10**-Ph $_2$ C $_2$ P] $^+$ , 178 (7) [**10**-Ph $_2$ C $_2$ ] $^+$ .

Table 4

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound **1**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Fe	586.1(3)	7475.2(2)	2197.7(2)	14.8(1)
P(1)	1592.9(6)	6339.9(5)	3102.6(4)	19.3(2)
P(2)	1626.4(6)	8416.1(5)	3281.9(4)	19.1(2)
C(1)	-113(3)	8411(2)	1206(2)	23.6(6)
C(2)	-1025(3)	7709(2)	1226(2)	24.9(6)
C(3)	-497(2)	6821(2)	1108(2)	22.5(5)
C(4)	744(2)	6983(2)	1003(2)	22.9(5)
C(5)	978(3)	7962(2)	1061(2)	25.1(6)
C(6)	-319(4)	9446(2)	1186(2)	43.3(9)
C(7)	-2377(3)	7897(3)	1211(2)	40.2(8)
C(8)	-1157(4)	5911(3)	949(2)	39.5(8)
C(9)	1538(3)	6233(3)	744(2)	39.2(8)
C(10)	2077(3)	8470(3)	872(2)	41.3(9)
C(11)	2397(2)	7391(2)	3101(2)	18.4(5)
C(12)	210(2)	6851(2)	3336(2)	17.3(5)
C(13)	228(2)	7854(2)	3423(2)	17.7(5)
C(14)	3800(2)	7396(2)	3086(2)	24.7(6)
C(15)	4485(3)	7062(3)	3973(2)	33.3(7)
C(16)	4275(3)	8377(3)	2950(2)	37.9(8)
C(17)	4115(3)	6736(3)	2414(2)	34.1(7)
C(18)	-752(3)	6123(2)	3518(2)	26.0(6)
C(19)	-368(3)	5117(2)	3342(2)	34.8(7)
C(20)	-2085(3)	6250(3)	2969(2)	35.2(7)
C(21)	-737(3)	6149(3)	4471(2)	33.1(7)
C(22)	-627(2)	8545(2)	3789(2)	23.7(6)
C(23)	-62(3)	6826(2)	4756(2)	29.5(6)
C(24)	-581(3)	9528(2)	3404(2)	33.6(7)
C(25)	-2025(3)	8327(3)	3667(2)	35.4(7)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 5

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound **4**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Mo	7281.6(3)	3493.8(2)	4378.6(2)	20.1(1)
Fe	5227.3(5)	3996.0(4)	2304.4(3)	15.4(1)
P(1)	6417.9(9)	3301.7(6)	3179.8(5)	16.5(2)
P(2)	7657.7(10)	3862.5(7)	2420.3(5)	18.6(2)
P(3)	5429.2(10)	2598.6(7)	1834.0(5)	20.1(2)
O(1)	10233(3)	2798(3)	3894(2)	49.0(9)
O(2)	8545(4)	3889(3)	5802(2)	51.8(10)
O(3)	4270(3)	4048(2)	4912(2)	35.7(7)
O(4)	6786(4)	1485(2)	4794(2)	47.6(9)
O(5)	8257(4)	5465(2)	4028(2)	49.8(10)
C(1)	5119(4)	5372(2)	2189(2)	23.5(9)
C(2)	4406(4)	5118(2)	2778(2)	19.7(8)
C(3)	3288(4)	4548(3)	2586(2)	21.7(8)
C(4)	3335(4)	4432(3)	1882(2)	28.2(9)
C(5)	4454(5)	4959(3)	1635(2)	32.1(10)
C(6)	6267(5)	6055(3)	2162(3)	50.4(15)
C(7)	4651(5)	5492(3)	3457(2)	34.6(11)
C(8)	2119(4)	4282(3)	3044(3)	42.1(12)
C(9)	2304(6)	3935(4)	1456(3)	57(2)
C(10)	4656(7)	5183(4)	910(2)	67(2)
C(11)	6866(4)	3312(2)	1737(2)	18.3(8)
C(12)	5241(4)	2648(2)	2714(2)	19.0(8)
C(13)	7563(4)	3368(3)	1042(2)	24.8(9)
C(14)	8735(4)	2676(3)	1058(2)	33.1(10)
C(15)	8215(5)	4281(3)	908(2)	37.6(11)
C(16)	6556(5)	3124(4)	471(2)	37.8(11)
C(17)	4161(4)	2022(3)	3029(2)	20.2(8)
C(18)	4886(4)	1114(3)	3100(3)	35.6(11)
C(19)	3686(4)	2317(3)	3724(2)	28.1(9)
C(20)	2877(4)	1899(3)	2577(2)	29.3(9)
C(21)	9183(4)	3063(3)	4058(2)	30.2(10)
C(22)	8092(5)	3730(3)	5287(2)	32.8(10)
C(23)	5352(4)	3866(3)	4718(2)	24.2(8)
C(24)	6912(4)	2207(3)	4640(2)	29.6(10)
C(25)	7864(4)	4771(3)	4140(2)	30.2(10)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### 3.8. Synthesis of $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{Ph}_2\text{P}_3)\text{W}(\text{CO})_5]$ **11**

A solution of  $\text{W}(\text{CO})_5(\text{THF})$  prepared from  $\text{W}(\text{CO})_6$  (250 mg, 0.71 mmol) in 15 ml of THF was added to a solution of **9** (220 mg, 0.48 mmol) in THF (5 ml). After stirring at room temperature for 5 h the volatile material was removed i.v. The orange–brown residue was extracted with *n*-hexane and fractionated by column chromatography (silica gel/*n*-hexane). After the removal of the solvent and recrystallization from *n*-hexane, **11** was obtained as a brown solid.

235 mg (0.30 mmol, 62%); m.p. 117°C (dec.);  $\text{C}_{29}\text{H}_{25}\text{FeO}_5\text{P}_3\text{W}$  (786.13); IR  $\tilde{\nu}$  (CO): (*n*-hexane) 2069 (vs), 1982 (s), 1945 (vs)  $\text{cm}^{-1}$ . Mass spectrum (EI, 70 eV)  $m/z$  (%): 786 (18) [**M**] $^+$ , 730 (72) [**M**-2CO] $^+$ , 674 (6) [**M**-4CO] $^+$ , 462 (33) [**M**-W(CO) $_5$ ] $^+$ .

Table 6

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for compound 5

	x	y	z	$U_{\text{eq}}$
W	7286.9(2)	3499.4(1)	4378.2(1)	19.3(1)
Fe	5230.9(5)	3999.0(3)	2308.2(2)	14.8(1)
P(1)	6433.8(9)	3304.9(6)	3182.5(5)	15.8(2)
P(2)	7666.5(9)	3867.3(6)	2419.0(5)	18.4(2)
P(3)	5429.4(10)	2596.5(6)	1839.4(5)	19.6(2)
O(1)	10233(3)	2800(3)	3887(2)	49.1(9)
O(2)	8556(4)	3902(3)	5805(2)	51.3(10)
O(3)	4280(3)	4054(2)	4908(2)	33.6(7)
O(4)	6769(4)	1490(2)	4789(2)	49.7(9)
O(5)	8243(3)	5467(2)	4018(2)	49.3(9)
C(1)	5126(4)	5380(3)	2193(2)	25.8(8)
C(2)	4399(4)	5118(2)	2782(2)	19.1(7)
C(3)	3280(4)	4545(2)	2587(2)	22.0(8)
C(4)	3347(4)	4432(3)	1880(2)	29.8(9)
C(5)	4457(5)	4960(3)	1636(2)	31.8(10)
C(6)	6258(5)	6060(3)	2173(3)	52(2)
C(7)	4634(5)	5492(3)	3467(2)	34.6(10)
C(8)	2121(4)	4282(3)	3044(3)	41.3(12)
C(9)	2307(6)	3931(4)	1457(3)	58(2)
C(10)	4654(7)	5183(4)	909(2)	71(2)
C(11)	6859(4)	3314(2)	1738(2)	18.7(7)
C(12)	5251(4)	2653(2)	2720(2)	17.3(7)
C(13)	7556(4)	3364(3)	1038(2)	24.5(8)
C(14)	8730(4)	2676(3)	1054(2)	33.0(10)
C(15)	8217(5)	4273(3)	900(2)	35.3(10)
C(16)	6548(5)	3118(4)	472(2)	38.2(11)
C(17)	4163(4)	2020(2)	3041(2)	20.1(7)
C(18)	4893(5)	1113(3)	3117(3)	35.9(10)
C(19)	3680(4)	2321(3)	3733(2)	27.7(9)
C(20)	2880(4)	1895(3)	2584(2)	30.7(9)
C(21)	9180(4)	3069(3)	4056(2)	28.7(9)
C(22)	8097(4)	3733(3)	5291(2)	32.2(10)
C(23)	5356(4)	3869(3)	4710(2)	22.1(8)
C(24)	6919(4)	2213(3)	4640(2)	29.3(9)
C(25)	7861(4)	4776(3)	4137(2)	30.9(9)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### 3.9. X-ray structure determination of 1, 4 and 5

Crystal data are presented in Table 3.

Data collection: data were collected with Mo K $\alpha$  radiation on a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low temperature attachment. Cell constants were refined from  $\pm \omega$  values of ca. 50 reflections in the  $2\theta$  range 20–23°. For 4 and 5 an absorption correction based on  $\psi$ -scans was applied.

Structure solution: direct methods (1), heavy-atom method (4), 5 isostructural with 4.

Structure refinement: anisotropic refinement on  $F^2$  (program SHELXL-93, G.M. Sheldrick, University of Göttingen), H atoms with rigid methyl groups, weighting scheme  $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$ , where  $3P = (2F_c^2 + F_o^2)$  and  $a$  and  $b$  are constants optimized by the program. Final atomic coordinates are presented in Tables 4, 5 and 6.

Full details have been deposited at the Fachinforma-

tionszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. This material can be obtained on citing the complete literature reference and the depository number CSD 401822 (1), 401824 (4), 401823 (5).

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