ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 614–615 (2000) 158–167

Journal of Organometallic Chemistry

Transformation of cyclohexadiene on an Fe_3P frame: cluster complexes with hexadiene, cyclohexadiene and arene ligands

Hubert Wadepohl *, Stefan Gebert, Hans Pritzkow

Anorganisch-Chemisches Institut der Ruprecht-Karls-Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 3 April 2000

Dedicated to Prof. Sheldon Shore on the occasion of his 70th birthday.

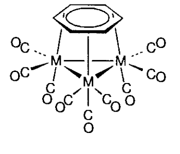
Abstract

UV photolysis of the phosphinidine-bridged cluster complex $[Fe_3(CO)_9(H)_2(P^tBu)]$ (**9**) in the presence of 1,3-cyclohexadiene gives the complex $[Fe_3(CO)_8(\eta^4\text{-1,3-cyclohexadiene})(\mu_3\text{-}P^tBu)]$ (**13**) in 20% yield. As a side-reaction, hydrogenolysis of cyclohexadiene occurs to give the complexes $[Fe_3(CO)_8(2\text{-}5\text{-}\eta\text{-2,4-hexadiene})(\mu_3\text{-}P^tBu)]$ (**14**) and $[Fe_3(CO)_8(1\text{-}4\text{-}\eta\text{-1,3-hexadiene})(\mu_3\text{-}P^tBu)]$ (**15**) in about 5% yield each. The crystal and molecular structures of **13**, **14** and **15** were determined. The (cyclo)hexadiene ligands are bonded to the Fe_3P clusters in the apical coordination mode; of the carbonyl ligands two are semi-bridging. The composition $[Fe_3(\mu_2\text{-}H)(CO)_7(\mu\text{-1-3-}\eta\text{:4,5-hexadienyl})(\mu_3\text{-}P^tBu)]$ (**16**) is tentatively assigned to a fourth product (2% yield), based on IR and NMR spectroscopic data. On heating to 80°C, a mixture of the complexes **14** and **15** is quantitatively converted into **16**. Complex **13** is also formed in lower yield (15%) from $[Fe_3(CO)_{10}(P^tBu)]$ (**10**) and 1,3-cyclohexadiene in a thermal reaction. UV irradiation of complex **13** in benzene solution gives $[Fe_3(CO)_7(\eta\text{-}C_6H_6)(\mu_3\text{-}P^tBu)]$ (**18a**) in low yield. In toluene, a 3:7 mixture of **18a** and $[Fe_3(CO)_7(\eta\text{-}C_6H_5Me)(\mu_3\text{-}P^tBu)]$ (**18b**) is obtained, proving the dehydrogenation of the cyclohexadiene ligand in **13** to give an η^6-benzene. The apical (η^6-) coordination of the toluene ligand in **18b** is confirmed by a crystal structure analysis, which also shows the presence of a face-capping carbonyl ligand. © 2000 Elsevier Science B.V. All rights reserved.

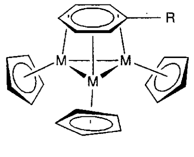
Keywords: Cyclohexadiene; Cluster complexes; Arene ligands

1. Introduction

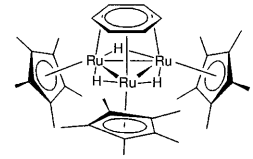
In recent years, multicentre metal bonding of arenes has developed into a flourishing area [1]. Not many years ago, this type of coordination was considered rather exotic. Naturally, it is unavailable for mononuclear complexes, and most likely to occur in metal cluster complexes. The face-capping (μ_3) coordination mode of an arene is now well established [2]. However, the known cluster complexes with face capping ligands are still restricted to a very few classes of compounds: (i) carbonyl metal clusters of ruthenium and osmium, mainly of nuclearity 3, 5 and 6, e.g. **1** [3] and **2** [4], (ii) trinuclear cyclopentadienyl metal clusters of cobalt and rhodium, e.g. **3** [5] and **4** [6], and (iii) most recently complexes with a $[(\eta\text{-}C_5Me_5)Ru(H)]_3$ frame, e.g. **5** [7]. The complexes **3** are still the only μ-arene clusters in the first transition metal series. In an early theoretical study, an analogous triiron carbonyl system, $[\{(CO)_3\text{-}Fe\}_3(\mu_3\text{-benzene})]$ (**6**) was considered unstable, based on extended Hückel molecular orbital calculations [8]. Judging from the remarkable stability of the tricobalt clusters of type **3** we felt that μ-arene clusters with an oligonuclear iron carbonyl frame might not be excessively labile and isolatable, provided that synthetic routes can be found.



1, M = Ru
2, M = Os



3, M = Co
4, M = Rh



5

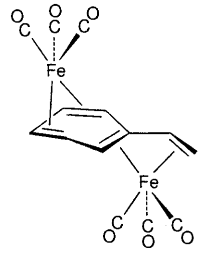
---

* Corresponding author. Tel.: +49-622-1544-827; fax: +49-622-1544-197.

E-mail address: bu9@ix.urz.uni-heidelberg.de (H. Wadepohl).

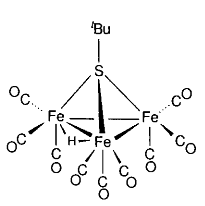
0022-328X/00/$ - see front matter
PII: S0022-328X(00)00573-8

During the syntheses of **3** and **4**, the metal cluster is assembled on the arene using reactive $(C_5R_5)M$ fragments (M = Co, Rh), which are generated in situ. Only rhodium is capable of attacking the arene ring directly [6,9]. In the case of cobalt, an unsaturated side chain has to provide a landing stage which actively assists in the metal complexation of the arene nucleus [5,10]. Both routes are not feasible for iron. On the one hand, the affinity of carbonyl iron fragments for an arene is too low to give stable products or intermediates [11]. On the other hand, reaction of alkenylbenzenes with carbonyl iron fragments stops at the dinuclear stage, with the products **7** not undergoing further reaction [12].

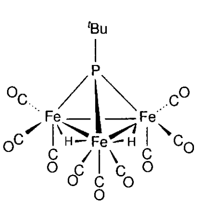


7

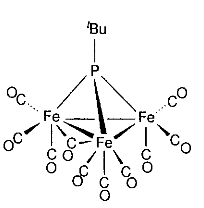
During the syntheses of **1** and **2**, a cyclohexadiene molecule is attached to a pre-formed trinuclear carbonyl metal cluster, and subsequently transformed into μ_3-cyclohexadienyl and finally μ_3-benzene. An analogous procedure seemed feasible for an iron cluster, but only if degradation of the metal cluster can be inhibited during the reaction. This essentially eliminates $[Fe_3(CO)_{12}]$ as a starting material, the chemistry of which is dominated by fragmentation processes [13]. Capping of a trinuclear iron cluster with a main group element substantially reduces its tendency to fragment. Such complexes should therefore be suitable precursors for the synthesis of arene iron clusters. Here we report on reactions of $[Fe_3(CO)_9(H)(S^tBu)]$ **8**, $[Fe_3(CO)_9(H)_2(P^tBu)]$ (**9**) and $[Fe_3(CO)_{10}(P^tBu)]$ (**10**) with cyclohexadiene.



8



9



10

2. Results and discussion

2.1. General

There is an important prerequisite for the facial coordination of an arene to a metal cluster: the topology of the potential coordination site must match the electronic *and* steric requirements of the facial ligand. Face-capping cyclohexadienyl and arene ligands are formally donating 5 and 6, respectively, electrons, which must be accommodated within the cluster complex. The geometric constraints of a carbocyclic ligand on a facial coordination site on the cluster 'surface' are considerably more severe than those on an apical site. Therefore, the presence of sterically demanding ligands on the metals that constitute the facial coordination site will be counterproductive.

Iron clusters with arene ligands are extremely rare [13]. To our knowledge, only one complex, $[Fe_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3\text{-}CCl)(\mu_3\text{-}CC(O)OEt)]$, has been structurally characterised [14]. A facial coordination site for the benzene ligand is not available in this bicapped triangular triiron cluster. A few triiron cluster complexes with a cyclohexadiene ligand have been reported [15,16]. In all cases, an apical η^4 coordination of the 1,3-cyclohexadiene ligand is attained.

2.2. Reaction of $[Fe_3(CO)_9(H)(S^tBu)]$ (8) with cyclohexadiene

The preparation and crystal structure of the cluster complex $[Fe_3(CO)_8(\eta^4\text{-cyclohexadiene})(\mu_3\text{-}S)]$ has been reported [15]. However, this complex was only obtained in very small yield from $[Fe_3(CO)_{12}]$, 1,3-cyclohexadiene and sulphur. The complexes $[Fe_3(CO)_9(H)(\mu_3\text{-}SR)]$ [17] were thought to be more readily accessible starting materials for the synthesis of organometallic complexes with an $Fe_3(\mu_3\text{-}S)$ frame. Under thermal or photochemical reaction conditions up to three carbonyl groups may be replaced by donor ligands EPh_3 (E = P, As, Sb) [18].

In the presence of 1,3-cyclohexadiene, the cluster complex $[Fe_3(CO)_9(H)(\mu_3\text{-}S^tBu)]$ (**8**) was stable in hexane solution for hours at 70°C. Only decomposition to mainly insoluble products was observed when **8** was heated in toluene–1,3-cyclohexadiene at 120°C. Addition of three equivalents of Me_3NO to a solution of **8** in dichloromethane in the presence of excess 1,3-cyclohexadiene led to a product which was insoluble in *n*-hexane. According to IR (ν_{CO}) and ^{1}H-NMR spectral data this product consisted of mainly the anion $[Fe_3(CO)_9(S^tBu)]^-$ (**11**) [18], the deprotonation product of **8**. Addition of trifluoroacetic acid regenerated the starting material **8**. Similar results were obtained when **8** in acetonitrile was first treated with three equivalents of Me_3NO, followed by addition of 1,3-cyclohexadiene. Complex **8** is known to be fairly acidic [18]. Deprotonation by Me_3NO is therefore not surprising. The negative charge of **11** reduces the elctrophilicity of the carbonyl ligands, and so effectively blocks further reaction with the aminoxide.

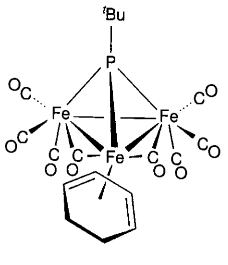
UV irradiation of **8** in *n*-hexane–1,3-cyclohexadiene, followed by chromatography on silica, gave three product fractions in very small yield. Using NMR spectroscopy, the presence of coordinated cycohexadiene was detected only in the second, purple fraction. The number of resonances could only be accounted for by at least two different substitution products. Attempts to further separate the material into pure compounds were unsuccessful.

*2.3. Reaction of $[Fe_3(CO)_9(H)_2(\mu_3\text{-}P^tBu)]$ (**9**) and $[Fe_3(CO)_{10}(\mu_3\text{-}P^tBu)]$ (**10**) with 1,3-cyclohexadiene*

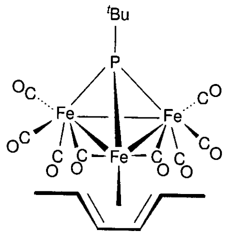
Under thermal reaction conditions, no substitution product of $[Fe_3(CO)_9(H)_2(\mu_3\text{-}P^tBu)]$ (**9**) [19] with 1,3-cyclohexadiene could be obtained. At temperatures up to 70°C no reaction took place even with a large excess of cyclohexadiene. At 100°C in toluene decomposition of the cluster was observed.

Chemical activation of **9** with Me_3NO (3.5 equivalents) in the presence of 1,3-cyclohexadiene also did not lead to substitution. The reaction product was insoluble in non-polar solvents. Using IR and ^{31}P-NMR spectroscopy, it was shown to mainly consist of the deprotonation product of **9**, $[Fe_3(CO)_9(H)(\mu_3\text{-}P^tBu)]^-$ (**12**). This assignment was confirmed by addition of CF_3COOH, which nearly quantitatively regenerated the starting material **9**. The anion **12** did not further react with Me_3NO.

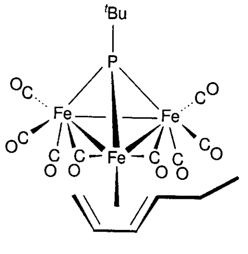
UV irradiation of **9** in the presence of 1,3-cyclohexadiene led to nearly complete consumption of the starting material within a few hours. Using medium pressure column chromatography, four Fe_3P cluster complexes could be isolated from the product mixture. The main product (21% yield) was the red complex $[Fe_3(CO)_8(\eta^4\text{-1,3-cyclohexadiene})(\mu_3\text{-}P^tBu)]$ **13**. Two further products, the purple complexes **14** and **15**, were isolated in about 5% yield each. These cluster complexes both contain an open chain hexadiene, functioning as a 2-5-η-2,4-hexadiene (complex **14**) and a 1-4-η-1,3-hexadiene (complex **15**) ligand, respectively. As no hexadiene was detected in the cyclohexadiene reagent, formation of **14** and **15** clearly results from hydrogenolysis of a carbon carbon bond of cyclohexadiene. An olive-green solid was isolated as the fourth product in about 2% yield. Structure **16** is tentatively assigned to this cluster on the basis of spectroscopic data (see below). This complex was generated in higher yield when the reaction mixture was heated to 80°C after photolysis. After about 1 h, the complexes **14** and **15** were completely converted into **16**, with **13** remaining unaffected.



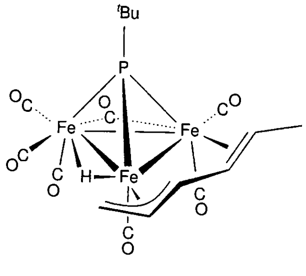
13



14



15



16

Heating $[Fe_3(CO)_{10}(\mu_3\text{-}P^tBu)]$ (**10**) [20] in the presence of 1,3-cyclohexadiene at 120°C for 6 h gave a 15% yield of the η^4-cyclohexadiene cluster complex **13**. In contrast to **9**, no reaction with cyclohexadiene was observed when **10** was irradiated with a mercury lamp in *n*-hexane or THF. Treatment of **10** with Me_3NO in the presence of 1,3-cyclohexadiene in methylene chloride, acetonitrile or THF only gave the anion **12**. This amounts to a substitution of a carbonyl by a hydride (H^-) ligand. An analogous reaction was observed when $[Os_6(CO)_{18}]$ was treated with Me_3NO in the absence of further ligands [21]. Substitution of CO by Me_3N, followed by transfer of a hydride from the coordinated amine and loss of $[Me_2NCH_2]^+$ was suggested as a mechanism [21].

*2.4. Molecular structures of $[Fe_3(CO)_8(\eta^4\text{-1,3-cyclohexadiene})(\mu_3\text{-}P^tBu)]$ (**13**), $[Fe_3(CO)_8(2\text{-}5\text{-}\eta\text{-2,4-hexadiene})(\mu_3\text{-}P^tBu)]$ (**14**) and $[Fe_3(CO)_8(1\text{-}4\text{-}\eta\text{-1,3-hexadiene})(\mu_3\text{-}P^tBu)]$ (**15**)*

Single crystal X-ray structure determinations were carried out for complexes **13**, **14** and **15**. Crystals of complex **14** were found to contain two independent molecules with similar structure. Unfortunately, owing to the poor crystallinity of **14**, the quality of the diffraction data did not allow a complete refinement of this structure. Hence, beyond the atomic connectivities no detailed statements about the structure of **14** can be made. The molecules of **13**, **14** and **15** are depicted in Figs. 1–3. Important bond lengths and angles are collected in Tables 1 and 2.

The molecules consist of pseudo-tetrahedral Fe$_3$P cluster cores. The (cyclo-)hexadiene ligand is coordinated to an iron atom (Fe(1)) in the η^4 bonding mode. Three terminal carbonyls are bonded to each of the two remaining iron atoms. The remaining two CO ligands bridge the two iron iron bonds involving Fe(1) in a very asymmetric fashion. They are closer to Fe(1) than to Fe(2) and Fe(3) (Tables 1 and 2). The phosphinidine group is slightly displaced from a position above the centre of the Fe$_3$ triangle, away from Fe(1). There is little variation in the iron–iron bond lengths, both within the same molecules and between **13** and **15** (range 2.638(3)–2.701(2)). Iron–iron and iron–phosphorus bond lengths compare well with those of other Fe$_3$ phosphinidine cluster complexes, e.g. [Fe$_3$(CO)$_{10}$(μ_3-P^{t}Bu)] (**7**) [20], [Fe$_3$(CO)$_9${P(OMe)$_3$}(μ_3-P^{t}Bu)] [20], [Fe$_3$(CO)$_9$(H)$_2$(μ_3-PPh)] [19], and [Fe$_3$(CO)$_9$(H)$_2$(μ_3-PSi^{i}Pr$_3$)] [22]. The coordinated η^4-1,3-diene part of the hexadiene ligands in **14** and **15** is approximately bisected by an approximate plane of symmetry, which passes through Fe(1), the phosphorus atom and the middle of the Fe(2)-Fe(3) bond. The open part of the diene system faces the phosphinidene. In **13**, the η^4-cyclohexadiene is rotated from an analogous position by about 133°, to minimize steric repulsions between the

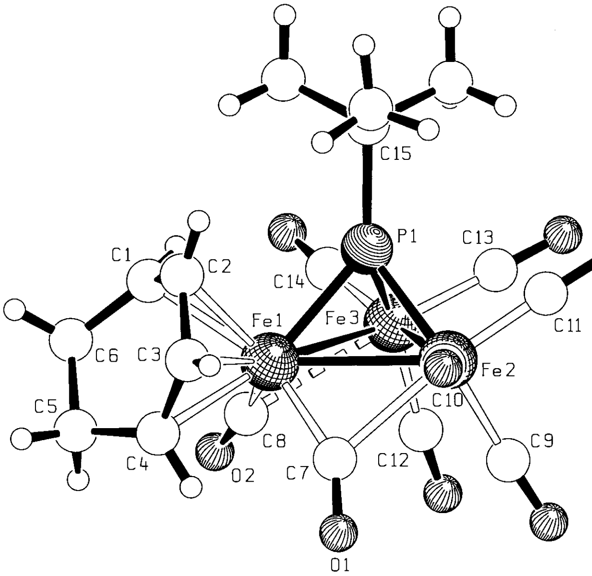


Fig. 1. Molecular structure of [Fe$_3$(CO)$_8$(η^4-1,3-cyclohexadiene)(μ_3-P^{t}Bu)] (**13**).

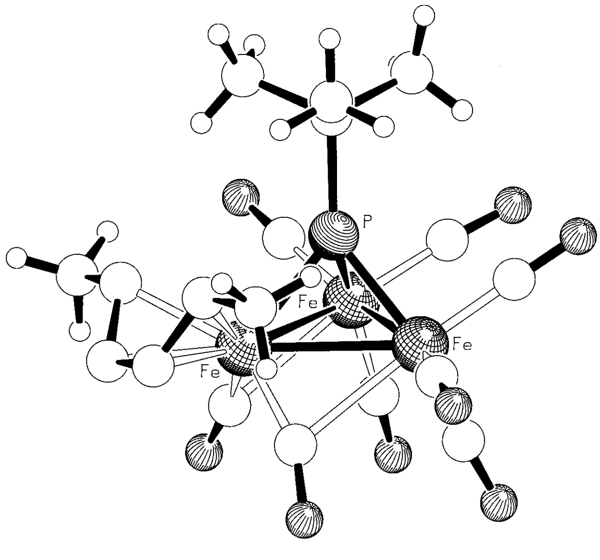


Fig. 2. Molecular structure of [Fe$_3$(CO)$_8$(2-5-η-2,4-hexadiene)(μ_3-P^{t}Bu)] (**14**).

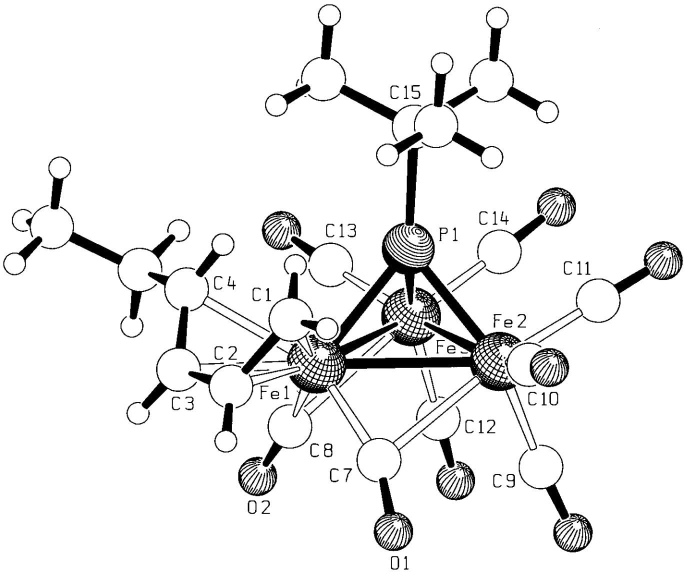


Fig. 3. Molecular structure of [Fe$_3$(CO)$_8$(1-4-η-1,3-hexadiene)(μ_3-P^{t}Bu)] (**15**).

Table 1

Selected bond lengths (Å) and angles (°) for [Fe$_3$(CO)$_8$(η^4-1,3-cyclohexadiene)(μ_3-P^{t}Bu)] (**13**) with e.s.d. values in parentheses

Fe1–Fe2	2.6814(15)	Fe1–Fe3	2.7009(18)
Fe2–Fe3	2.6805(15)	Fe1–P1	2.203(2)
Fe2–P1	2.1545(18)	Fe3–P1	2.137(2)
Fe1–C1	2.171(6)	Fe1–C2	2.071(6)
Fe1–C3	2.052(6)	Fe1–C4	2.161(6)
Fe1–C7	1.844(6)	Fe1–C8	1.790(7)
Fe2–C7	2.214(6)	Fe2–C9	1.816(7)
Fe2–C10	1.780(7)	Fe2–C11	1.745(7)
Fe3···C8	2.567	Fe3–C12	1.808(7)
Fe3–C13	1.751(8)	Fe3–C14	1.792(6)
C1–C2	1.419(9)	C1–C6	1.483(8)
C2–C3	1.423(8)	C3–C4	1.381(8)
C4–C5	1.501(9)	C5–C6	1.534(9)
Fe1–P1–C15	137.4(2)	Fe2–P1–C15	132.9(2)
Fe3–P1–C15	132.3(3)	Fe1–C7–O1	151.0(5)
Fe2–C7–O1	126.7(5)	Fe1–C8–O2	166.2(6)
Fe3–C8–O2	119.3(5)		

methylene groups and the bulky *tert*-butyl substituent on P (Fig. 1). The molecular structure of **13** is similar to those of $[Fe_3(CO)_8(\eta^4\text{-cyclohexadiene})(\mu_3\text{-NPh})]$ **17** [16] and $[Fe_3(CO)_8(\eta^4\text{-cyclohexadiene})(\mu_3\text{-S})]$ [15]. The somewhat shorter iron–iron bonds in **17** (average 2.55) can be explained by the smaller nitrogen atom of the μ_3-phenylimido ligand.

In the electron impact mass spectra of **13**–**15** the molecular ions are present with low intensity. Consecutive loss of all eight CO ligands is observed. Single resonances are found in the ^{31}P-NMR spectra in the region around $\delta = 500$, typical of μ_3-phosphinidine ligands. There is only little difference between the ^{31}P resonances of **14** ($\delta = 467.4$) and **15** ($\delta = 476.4$). The corresponding resonance for **13** is shifted to somewhat higher field ($\delta = 510.2$).

The ^{1}H- and ^{13}C-NMR spectral data for **13**–**15** in solution show a higher molecular symmetry on the NMR timescale than was found in the solid state. Only two multiplets are observed for the 'inner' and 'outer' CH groups, respectively, of the η^4-1,3-diene system in **13**, but two separate multiplets are detected for the methylene groups (due to *exo* and *endo* orientations of the methylene hydrogens). Only one hexadienyl methyl resonance ($\delta = 0.75$, $J_{HP} = 2.1$ Hz) is present in the proton spectrum of **14**, again indicating the approximate mirror symmetry of the coordination site of the η^4-2,4-hexadiene ligand.

2.5. Spectra and proposed structure of complex **16**

In the electron impact ionisation mass spectrum of compound **16**, the peak with highest *m*/*z* corresponds to the mass of $[\textbf{14}\text{-CO}]^+$ or $[\textbf{15}\text{-CO}]^+$, respectively. The presence of a total of seven CO ligands is indicated by their sequential loss in the mass spectrum. The IR (ν_{CO}) spectrum is dissimilar from those of **13**, **14** and **15**, and shows bands due to terminal and bridging carbonyl ligands. A ^{31}P-NMR resonance at $\delta = 515.9$ indicates the presence of a μ_3-phosphinidine ligand. The interpretation of the proton NMR data are is complicated by the overlap of several resonances. The most prominent feature in the ^{1}H-NMR spectrum is a dublet ($J_{PH} = 33$ Hz) at high field ($\delta = -27.2$), obviously due to a bridging hydride ligand. Apart from the strong resonance due to the *tert*-butyl group ($\delta = 1.95$), the rest of the spectrum consists of five multiplets in the range $4.3 \geq \delta \geq -2$. Likewise, a large number of ^{13}C-NMR resonances is observed. Not counting the *tert*-butyl and carbonyl signals, six resonances are present in the range $84 \geq \delta \geq 20$.

Table 2
Selected bond lengths (Å) and angles (°) for $[Fe_3(CO)_8(1\text{-}4\text{-}\eta\text{-}1,3\text{-hexadiene})(\mu_3\text{-P}^t\text{Bu})]$ (**15**) with e.s.d. values in parentheses

Fe1–Fe2	2.677(2)	Fe1–Fe3	2.700(3)
Fe2–Fe3	2.638(3)	Fe1–P1	2.677(2)
Fe2–P1	2.161(3)	Fe3–P1	2.161(3)
Fe1–C1	2.142(9)	Fe1–C2	2.042(9)
Fe1–C3	2.067(9)	Fe1–C4	2.209(9)
Fe1–C7	1.784(9)	Fe1–C8	1.800(9)
Fe2–C7	2.367(9)	Fe2–C9	1.797(9)
Fe2–C10	1.793(9)	Fe2–C11	1.748(9)
Fe3–C8	2.501(9)	Fe3–C12	1.803(9)
Fe3–C13	1.773(11)	Fe3–C14	1.743(10)
C1–C2	1.393(14)	C2–C3	1.402(14)
C3–C4	1.356(13)	C4–C5	1.494(13)
C5–C6	1.454(13)		
Fe1–P1–C15	136.7(3)	Fe2–P1–C15	132.0(3)
Fe3–P1–C15	135.2(3)	Fe1–C7–O1	159.7(8)
Fe1–C8–O2	163.1(8)	Fe2–C7–O1	121.2(7)
Fe3–C8–O2	121.1(7)		

Based on the mass and NMR spectroscopic data we assume that **16** is generated from **14** or **15** by loss of carbon monoxide, followed by intramolecular CH activation. The presence of a C_6 chain in **16** is corroborated by the results of a series of ^{1}H, ^{1}H double resonance experiments. The available data do not allow to assign a unique structure to **16**. We propose the presence of a bridging hexadienyl ligand, coordinated to an iron–iron edge of the Fe_3P cluster core in a 1-3-η^3:4,5-η^2 fashion. Most likely, the so-called 'S-conformation' [23] of the metal coordinated pentadienyl unit is attained. The 1-3-η^3:4,5-η^2 coordination of an unsaturated C_5 chain has been observed previously in the cluster complex $[Ru_5(CO)_{12}(H)(\mu_4\text{-S})(\mu_2\text{-}1,5\text{-}Me_2C_5H_5)]$ [24]. The closely related 1-3-η^3:3-5-η^3 coordination variant was found in a similar complex, $[Ru_6(CO)_{15}(H)(\mu_4\text{-S})(\mu_2\text{-}1,5\text{-}Me_2C_5H_5)]$ [24]. Based on electron bookkeeping rules, we favour the less symetrical 1-3-η^3:4,5-η^2 coordination for **16**. In such a structure, all of the iron atoms attain an 18 valence electron count.

2.6. Reactivity of $[Fe_3(CO)_8(\eta^4\text{-}1,3\text{-cyclohexadiene})(\mu_3\text{-P}^t\text{Bu})]$ (**13**)

The formation of the hydrido triiron cluster complex **16** from **14** and **15** shows that intramolecular CH activation is possible even in a cluster with first-row transition metals. Therefore, thermal transformation of the cyclohexadiene ligand in **13** into a cyclohexadienyl seemed feasible.

When **13** was heated in hexane at 70°C for several hours, the IR spectra indicated slow decomposition. Only a small amount of the complex $[Fe_3(CO)_9(H)_2(\mu_3\text{-P}^t\text{Bu})]$ (**9**) was isolated after workup. Decomposition of **13** was much faster in boiling toluene. As a product, the cluster complex $[Fe_3(CO)_9(\text{P}^t\text{Bu})_2]$ [25] was identified. This complex has been known to be the decomposition product of many phosphinidene-bridged iron clusters [26]. Addition of Me_3NO to a solution of **13** in methylene chloride at room temperature did not result in any changes in the ν_{CO} region of the IR spectrum. Heating

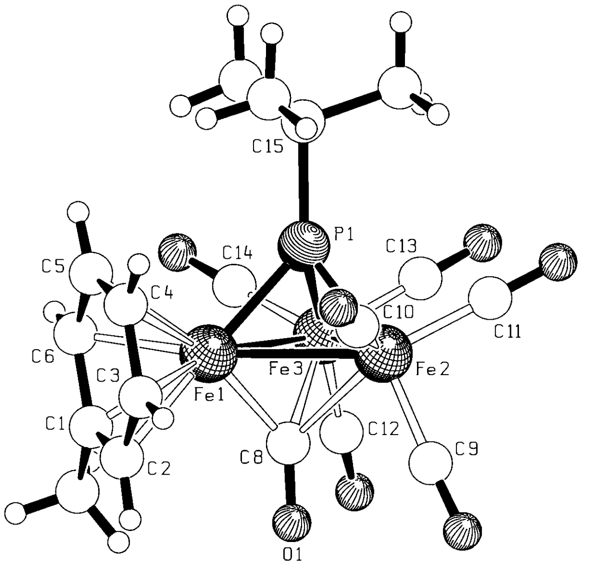
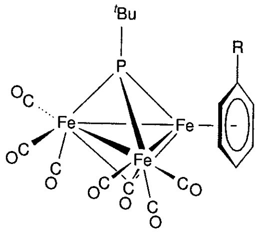


Fig. 4. Molecular structure of $[Fe_3(CO)_7(\eta\text{-}C_6H_5Me)(\mu_3\text{-}P^tBu)]$ (**18b**).

of the mixture to 40°C resulted in complete decomposition.

UV irradiation of **13** in benzene for 12 h gave a 7% yield of the η^6-benzene cluster complex $[Fe_3(CO)_7(\eta\text{-}C_6H_6)(\mu_3\text{-}P^tBu)]$ (**18a**) after chromatographic workup. This complex was formed in lower yield when the irradiation of **13** was carried out in *n*-heptane solution. After irradiation of **13** in toluene a 3:7 mixture of **18a** and the toluene derivative $[Fe_3(CO)_7(\eta\text{-}C_6H_5CH_3)(\mu_3\text{-}P^tBu)]$ (**18b**) was isolated. Clearly, the η^4-cyclohexadiene ligand in **13** can be transformed into η^6-benzene during the photochemically induced reaction. As a competing process, substitution of the cyclohexadiene ligand by the aromatic solvent (benzene or toluene) takes place. For the reactions carried out in toluene it also appears likely that substitution of one η^6-arene in **18** for another is involved as well.



18a, R = H
18b, R = Me

*2.7. Structure and spectra of $[Fe_3(CO)_7(\eta\text{-}C_6H_5R)(\mu_3\text{-}P^tBu)]$ (**18a**) (R = H) and (**18b**) (R = CH_3)*

The cluster complex **18b** was always obtained as a non-separable mixture with **18a**. Repeated recrystallisation from *n*-hexane–toluene resulted in a few single crystals. The specimen which was selected for an X-ray crystal structure analysis was found to only contain complex **18b**. The molecular structure is shown in Fig. 4, important bond lengths and angles are collected in Table 3. There are two independent molecules with very

Table 3
Selected bond lengths (Å) and angles (°) for $[Fe_3(CO)_7(\eta\text{-}C_6H_5Me)(\mu_3\text{-}P^tBu)]$ (**18b**) with e.s.d. values in parentheses

Molecule 1		Molecule 2	
Fe1–Fe2	2.6294(12)	Fe4–Fe5	2.6297(12)
Fe1–Fe3	2.6395(12)	Fe4–Fe6	2.6384(11)
Fe2–Fe3	2.7141(11)	Fe5–Fe6	2.7177(12)
Fe1–P1	2.1559(12)	Fe4–P2	2.1529(12)
Fe2–P1	2.1644(12)	Fe5–P2	2.1704(11)
Fe3–P1	2.1653(12)	Fe6–P2	2.1665(12)
Fe1–C1···C6	2.115(3)···2.139(3)	Fe4–C19···C24	2.106(3)···2.137(3)
Fe1–C8	1.885(3)	Fe4–C26	1.887(3)
Fe2–C8	2.251(3)	Fe5–C26	2.172(3)
Fe2–C9	1.808(3)	Fe5–C27	1.808(3)
Fe2–C10	1.775(3)	Fe5–C28	1.774(3)
Fe2–C11	1.790(3)	Fe5–C29	1.788(3)
Fe3–C8	2.196(3)	Fe6–C26	2.229(3)
Fe3–C12	1.806(3)	Fe6–C30	1.797(3)
Fe3–C13	1.787(3)	Fe6–C31	1.782(3)
Fe3–C14	1.786(3)	Fe6–C32	1.782(3)
C–C (ring, η^6-toluene)	1.401(4)···1.418(4)	C–C (ring, η^6-toluene)	1.401(4)···1.412(4)
Fe1–P1–C15	136.06(9)	Fe4–P2–C33	136.97(10)
Fe2–P1–C15	134.34(9)	Fe5–P2–C33	133.33(10)
Fe3–P1–C15	133.75(10)	Fe6–P2–C33	133.90(10)
Fe1–C8–O1	140.5(2)	Fe4–C26–O8	139.5(2)
Fe2–C8–O1	128.8(2)	Fe5–C26–O8	130.3(2)
Fe3–C8–O1	129.7(2)	Fe6–C26–O8	128.0(2)

similar structures in the asymmetric unit. The Fe_3P cluster core consists of an isosceles triangle of iron atoms, capped by the μ_3-phosphinidene group. The toluene ligand is coordinated to an iron atom (Fe(1) and Fe(4), respectively) in the η^6-fashion. The iron–iron bonds originating from Fe(1)/Fe(4) are significantly shorter (average 2.63 Å) than the bond between the two $Fe(CO)_3$ groups (average 2.72 Å). A μ_3-CO ligand is capping the face of the Fe_3 triangle which is not occupied by the phosphinidene ligand. This carbonyl ligand is considerably closer to the Fe(η^6-toluene) than to the $Fe(CO)_3$ groups (averages over the two molecules: 1.89 Å versus 2.21 Å). Such an asymmetrically μ_3-bridging carbonyl ligand is also present in a related structure, viz. $[Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-NPh})]$ [27]. The toluene ligands in **18b** are bonded to Fe(1)/Fe(4) in the η^6-fashion; there is only little variation in length of their endocyclic carbon–carbon bonds (D_{CC}(average) = 1.41 Å). The orientation of the methyl group of this ligand with respect to the rest of the molecule minimises steric repulsions with the ^{t}BuP group.

3. Conclusion

The present work demonstrates that dehydrogenation of cyclohexadiene to form benzene can be brought about in the coordination sphere of a triiron cluster without disruption of the metal core. However, the efficiency of this process is low, compared to ruthenium and osmium clusters. This is not unexpected, due to the much lower CH-activating power of the metals in the first transition series [2c,28]. Furthermore, the benzene ligand does not become attached to the metal cluster in the facial coordination mode, but rather prefers an apical (η^6) coordination. Unfortunately, when complex **13** is generated from **9**, one CO and two hydrogen ligands are substituted by the cyclohexadiene, rather than two carbonyls. Hence, the number of carbonyls that remain in the Fe_3P cluster is too large to accomodate a facial carbocyclic ligand. In particular, there is not enough space in the arene complexes **18** for both a bridging CO and a face capping arene.

4. Experimental

4.1. General procedures

All operations were carried out under an atmosphere of purified nitrogen or argon (BASF R3-11 catalyst) using Schlenk techniques. Solvents were dried by conventional methods. Silica used as a stationary phase for column chromatography was heated to 180–200°C under vacuum for several days and then stored under nitrogen. Medium pressure liquid chromatography was carried out with a Büchi 680 system using silica (32–63 mm) as the stationary phase. An all-quartz Normag falling film UV reactor equipped with a Heraeus TQ 150 high pressure mercury lamp was used for photochemical reactions. Running tap water was employed as a coolant (10–15°C). The cluster complexes **8** [18], **9** [19] and **10** [20] were prepared according to literature procedures. NMR spectra were obtained on Bruker AC 200 (200.1 MHz for ^1H, 50.3 MHz for ^{13}C) and JEOL FX90Q (36 MHz for ^{31}P) instruments. ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to internal $SiMe_4$ or residual solvent peaks. ^{31}P spectra are referenced to external 85% H_3PO_4. Infrared spectra were recorded in CaF_2 cells with a Bruker IFS-28 Fourier transform spectrometer (optical resolution 0.5 cm^{-1}). Elemental analyses were performed by Mikroanalytisches Labor Beller, Göttingen.

4.2. Preparation of *$[Fe_3(CO)_8(\eta^4\text{-}1,3\text{-cyclohexadiene})(\mu_3\text{-}P^tBu)]$ (**13**), $Fe_3(CO)_8(2\text{-}5\text{-}\eta\text{-}2,4\text{-hexadiene})(\mu_3\text{-}P^tBu)]$ (**14**) and $Fe_3(CO)_8(1\text{-}4\text{-}\eta\text{-}1,3\text{-hexadiene})(\mu_3\text{-}P^tBu)]$ (**15**)*

A solution of 1.3 g (2.55 mmol) of $[Fe_3(CO)_9(H)_2(\mu_3\text{-}P^tBu)]$ (**9**) and 2 ml (20.8 mmol) of 1,3-cyclohexadiene in 150 ml of toluene was irradiated at ambient temperature for 20 h. After filtration, solvent was removed from the reaction mixture under reduced pressure. The residue was chromatographed on silica (3 × 25 cm). A reddish fraction (mainly **9**) was washed from the column with *n*-hexane. With *n*-hexane–toluene (9:1) an olive–green fraction was obtained, to give 30 mg (2.1%) of complex **16** as brown needles after removal of solvent and recrystallisation from little *n*-hexane. A red–purple fraction was collected next, which was further separated into three components using MPLC on silica (5 × 50 cm, *n*-hexane). Three product fractions were collected to give the complexes **13** (300 mg, 21%, red–brown solid), **15** (50 mg, 3.5%, purple solid) and **14** (60 mg, 4.2%, purple solid) after removal of solvent. The products were recrystallised from *n*-hexane at 0°C.

4.2.1. Complex **13**

IR (ν_{CO}, cm^{-1}, in *n*-hexane): 2062 (s), 2019 (vs), 1998 (s), 1979 (s), 1962 (m), 1930 (w), 1851 (w). ^1H-NMR (in C_6D_6): $\delta = 1.18$ (m, 2H, CH_2-*endo*), 1.39 (d, $J_{PH} = 17.3$ Hz, 9H, ^{t}Bu), 1.65 (m, 2H, CH_2-*exo*), 3.31 (m, 2H, CH), 4.47 (m, 2H, CH). $^{13}C\{^1H\}$-NMR (in C_6D_6): $\delta = 23.3$ (CH_2), 31.9 (d, $J_{PH} = 2$ Hz, CH_3), 46.1 (d, $J_{PH} = 7.5$ Hz, CMe_3), 80.8 (d, $J_{PH} = 2$ Hz, CH), 81.6 (CH), 212.0 (CO), 233.2 (d, $J_{PH} = 2$ Hz, CO). $^{31}P\{^1H\}$-NMR (C_6D_6) $\delta = 510.2$. EI-MS: $m/z = 560$ (6%, M^+), 504 (7, $[M\text{-}2\ CO]^+$), 474 (4, $[M\text{-}3\ CO\text{-}2\ H]^+$, 446 (4, $[M\text{-}4\ CO\text{-}2\ H]^+$), 418 (40, $[M\text{-}5\ CO\text{-}2\ H]^+$), 362 (12, $[M\text{-}7\ CO\text{-}2\ H]^+$), 334 (9, $[M\text{-}8\ CO\text{-}2\ H]^+$), 278 (24,

[M-8 CO-H-^{t}Bu]$^+$), 200 (42, [Fe$_3$PH]$^+$), 79 (100, [C$_6$H$_7$]$^+$). Anal. Calc. for $C_{18}H_{17}Fe_3O_8P$ (559.846): C, 38.62; H, 3.06; P, 5.53; Found: C, 38.81; H, 3.11; P, 5.50%.

4.2.2. Complex **14**

IR (ν_{CO}, cm^{-1}, in n-hexane): 2059 (s), 2013 (vs), 1994 (s), 1971 (s), 1957 (m), 1923 (w), 1895 (w). ^{1}H-NMR (in C$_6$D$_6$): $\delta = 0.75$ (m, 8H, CH$_3$ + CH), 1.53 (d, $J_{PH} = 17.7$ Hz, 9H, ^{t}Bu), 4.66 (d, 2H, CH). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): $\delta = 467.4$. EI-MS: $m/z = 562$ (8%, M^+), 534 (11, [M-CO]$^+$), 506 (26, [M-2 CO]$^+$, 478 (11, [M-3 CO]$^+$), 450 (13, [M-4 CO]$^+$), 422 (60, [M-5 CO]$^+$), 392 (24, [M-6 CO-2 H]$^+$), 364 (26, [M-7 CO-2 H]$^+$), 336 (28, [M-8 CO-2 H]$^+$), 280 (33, [M-8 CO-H-^{t}Bu]$^+$), 199 (47, [Fe$_3$P]$^+$), 82 (22, [C$_6$H$_{10}$]$^+$), 67 (41, [C$_6$H$_{10}$-CH$_3$]$^+$).

4.2.3. Complex **15**

IR (ν_{CO}, cm^{-1}, in n-hexane): 2060 (s), 2014 (vs), 1995 (s), 1973 (s), 1959 (m), 1916 (w), 1899 (w). ^{1}H-NMR (in C$_6$D$_6$): $\delta = -0.06$ (m, 1H, CH$_{endo}$), 0.59 (t, 3H, CH$_3$), 0.82 (m, 2H, CH$_2$), 1.03 (m, 1H, CH$_{exo}$), 1.50 (d, $J_{PH} = 17.8$ Hz, 9H, ^{t}Bu), 4.59 (m, 1H, CH), 4.95 (m, 1H, CH). ^{13}C{^{1}H}-NMR (in C$_6$D$_6$): $\delta = 16.7$ (CH$_2$CH$_3$), 26.5(CH$_2$CH$_3$), 33.1 (d, $J_{PH} = 2$ Hz,CCH$_3$), 44.3 (d, $J_{PH} = 3$ Hz, CMe$_3$), 74.8 (CH), 77.2 (d, $J_{PH} = 2$ Hz, CH), 85.6 (CH), 91.3 (CH), carbonyl carbons were not detected. ^{31}P{^{1}H}-NMR (C$_6$D$_6$) $\delta = 476.4$. EI-MS: $m/z = 562$ (1%, M^+), 534 (1, [M-CO]$^+$), 506 (3, [M-2 CO]$^+$, 478 (1, [M-3 CO]$^+$), 450 (1, [M-4 CO]$^+$), 422 (6, [M-5 CO]$^+$), 392 (3, [M-6 CO-2 H]$^+$), 364 (4, [M-7 CO-2 H]$^+$), 336 (4, [M-8 CO-2 H]$^+$), 280 (5, [M-8 CO-H-^{t}Bu]$^+$), 199 (9, [Fe$_3$P]$^+$), 82 (51, [C$_6$H$_{10}$]$^+$), 67 (100, [C$_6$H$_{10}$-CH$_3$]$^+$).

4.2.4. Complex **16**

IR (ν_{CO}, cm^{-1}, in n-hexane): 2042 (s), 2012 (vs), 1989 (vs), 1972 (m), 1961 (m), 1936 (br,w). ^{1}H-NMR (in C$_6$D$_6$): $\delta = -27.16$ (d, $J_{PH} = 33$ Hz, 1H, FeHFe), $-$1.95 (t, 1H, CH), 1.84 (d, 3H, CH$_3$), 1.95 (d, $J_{PH} = 18.2$ Hz, 9H, ^{t}Bu), 2.7 (m, 3H, CH), 3.80 (m, 1H, CH), 4.28 (d, 1H, CH). ^{13}C{^{1}H}-NMR (in C$_6$D$_6$): $\delta = 20.4$ (CH$_3$), 32.5 (d, $J_{PH} = 4$ Hz, CCH$_3$), 36.9 (CH), 45.8 (d, $J_{PH} = 3$ Hz, CMe$_3$), 60.0 (CH), 75.5 (CH), 76.3 (CH), 83.6 (CH), 212.6 (CO). ^{31}P{^{1}H}-NMR (C$_6$D$_6$) $\delta = 515.9$. EI-MS: $m/z = 534$ (1%, M^+), 506 (6, [M-CO]$^+$), 478 (4, [M-2 CO]$^+$, 450 (2, [M-3 CO]$^+$), 422 (12, [M-4 CO]$^+$), 392 (8, [M-5 CO-2 H]$^+$), 364 (9, [M-6 CO-2 H]$^+$), 336 (10, [M-7 CO-2 H]$^+$), 280 (11, [M-7 CO-H-^{t}Bu]$^+$), 199 (18, [Fe$_3$P]$^+$), 82 (10, [C$_6$H$_{10}$]$^+$), 67 (23, [C$_6$H$_{10}$-CH$_3$]$^+$).

*4.3. Conversion of Fe$_3$(CO)$_8$(2-5-η-2,4-hexadiene)-(μ_3-P^{t}Bu)] (**14**) and Fe$_3$(CO)$_8$(1-4-η-1,3-hexadiene)-(μ_3-P^{t}Bu)] (**15**) into complex **16***

An approx. 5:1:1 mixture of the complexes **13**, **14** and **15** (360 mg) was heated in n-hexane at 80°C for 1 h. IR analysis of the reaction mixture indicated complete conversion of **14** and **15** into **16**. The product **16** (50 mg) was separated from unreacted **13** (300 mg) by column chromatography on silica (3 × 25 cm; n-hexane–toluene, 9:1).

*4.4. Preparation of [Fe$_3$(CO)$_8$(η^4-1,3-cyclohexadiene)(μ_3-P^{t}Bu)] (**13**) from [Fe$_3$(CO)$_{10}$(P^{t}Bu)] (**10**) and 1,3-cyclohexadiene*

A toluene solution (50 ml) of **10** (200 mg, 0.4 mmol) and 1,3-cyclohexadiene (0.5 ml, 5.2 mmol) was heated to 120°C for 6 h. Solvent was removed under vacuum to give an oily residue, which was chromatographed on silica (3 × 25 cm). A reddish band was washed from the column with n-hexane–toluene (9:1). With n-hexane–toluene (1:1) a dark-red fraction was obtained, to give **13** (30 mg, 14%) as dark-red crystals after removal of the solvent under vacuum and recrystallisation from n-hexane.

*4.5. Photolysis of [Fe$_3$(CO)$_8$(η^4-1,3-cyclohexadiene)(μ_3-P^{t}Bu)] (**13**). Preparation of [Fe$_3$(CO)$_7$(η^6-C$_6$H$_5$R)(μ_3-P^{t}Bu)] (**18a**) (R = H) and **18b** (R = Me)*

A solution of **13** (150 mg, 0.3 mmol) was irradiated with a mercury lamp for 12 h. Solvent was removed under vacuum and the residue chromatographed on silica (3 × 25 cm). Unreacted **13** was washed from the column with n-hexane–toluene (1:1). With toluene a brown fraction was obtained which gave the product(s) **18** as brown platelets after removal of solvent and recrystallisation from n-hexane/toluene.

4.5.1. Photolysis in benzene solution

Following the above procedure 10 mg (7%) of **18a** was obtained.

Complex **18a**: IR (ν_{CO}, cm^{-1}, in n-hexane): 2051 (vs), 2011 (s), 1989 (s), 1975 (m), 1959 (s), 1946 (m). ^{1}H-NMR (in C$_6$D$_6$): $\delta = 1.57$ (d, $J_{PH} = 17.3$ Hz, 9H, ^{t}Bu), 4.81 (d, $J_{PH} = 0.7$ Hz, 6H, C$_6$H$_6$). ^{13}C{^{1}H}-NMR (in C$_6$D$_6$): $\delta = 31.8$ (CCH$_3$), 42.0 (CMe$_3$), 92.1 (C$_6$H$_6$), 215.0 (CO). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): $\delta = 525.7$. EI-MS: $m/z = 530$ (2%, M^+), 502 (9, [M-CO]$^+$), 418 (23, [M-4 CO]$^+$), 390 (7, [M-5 CO]$^+$), 362 (3, [M-6 CO]$^+$), 334 (12, [M-7 CO]$^+$), 278 (23, [M-7 CO-C$_4$H$_8$]$^+$), 199 (51, [Fe$_3$P]$^+$), 78 (82, [C$_6$H$_6$]$^+$).

4.5.2. Photolysis in toluene solution

Following the above procedure 30 mg of an unseparable 30:70 mixture of **18a** and **18b** was obtained.

Complex **18b**: IR (ν_{CO}, cm^{-1}, in n-hexane): 2051 (vs), 2011 (s), 1989 (s), 1975 (m), 1959 (s), 1946 (m). ^{1}H-NMR (in C$_6$D$_6$): $\delta = 1.62$ (d, $J_{PH} = 17.3$ Hz, 9H, ^{t}Bu),

Table 4
Details of the crystal structure determinations of $[Fe_3(CO)_8(\eta^4\text{-1,3-cyclohexadiene})(\mu_3\text{-}P^tBu)]$ (**13**), $[Fe_3(CO)_8(\text{1-4-}\eta\text{-1,3-hexadiene})(\mu_3\text{-}P^tBu)]$ (**15**) and $[Fe_3(CO)_7(\eta\text{-}C_6H_5Me)(\mu_3\text{-}P^tBu)]$ (**18b**)

	13	**15**	**18b**
Formula	$C_{18}H_{17}Fe_3O_8P$	$C_{18}H_{19}Fe_3O_8P$	$C_{18}H_{17}Fe_3O_7P$
Crystal system	Tetragonal	Triclinic	Triclinic
Space group	$P4_12_12$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.255(6)	8.803(6)	8.729(4)
b (Å)		9.601(6)	15.495(8)
c (Å)	34.666(17)	13.879(10)	15.589(8)
α (°)	90	88.46(6)	95.01(2)
β (°)	90	78.06(6)	100.57(2)
γ (°)	90	84.69(5)	90.10(2)
V (Å^3)	4391(4)	1146.2(13)	2064.5(18)
Z	8	2	4
M_r	559.84	561.85	543.84
D_{calc} (g cm^{-3})	1.649	1.628	1.750
F_{000}	2256	568	1096
μ(Mo–K$_\alpha$) (mm^{-1})	2.07	1.98	2.19
X-radiation, λ (Å)	Mo–K$_\alpha$, graphite-monochromated, 0.71069		
Data collection temperature (°C)	Ambient	Ambient	-70
2θ Range (°)	3–54	3–50	3–50
h, k, l-Range	$-10 \le h \le 14,\ -7 \le k \le 10,\ -30 \le l \le 44$	$-10 \le h \le 10,\ -11 \le k \le 11,\ 0 \le l \le 16$	$-10 \le h \le 10,\ -18 \le k \le 18,\ 0 \le l \le 18$
Reflections measured			
Unique	3446	4040	7272
Observed	2677	2126	6146
Parameters refined	278	280	535
R-values			
R (observed reflections)	0.040	0.061	0.027
wR_2 (all reflections)	0.082	0.133	0.062
$w = 1/[\sigma^2(F) + (AP)^2 + BP]$			
A, B	0.0213, 4.35	0.04, 0.5	0.0266, 1.05
P	$\max((F_o^2, 0) + 2F_c^2))/3$		
GoF	1.081	1.012	1.009
Largest difference peak and hole (e Å^{-3})	0.46/−0.37	0.42/−0.41	0.29/−0.31

1.78 (s, 3H, $PhCH_3$), 4.68 (m, 3H, toluene), 4.80 (m, 2H, toluene). $^{31}P\{^1H\}$-NMR (C_6D_6) $\delta = 525.8$.

4.6. Crystal structure determinations

Single crystals were grown from *n*-hexane solutions at 0°C (complexes **14** and **15**) or by temperature programmed slow cooling (25–0°C, 1°C h^{-1}) (complexes **13** and **18b**). Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer and corrected for Lorentz, polarisation and absorption effects (Table 4). A semi-empirical absorption correction was applied (ψ-scans).

The structures were solved by direct methods, and refined by full-matrix least-squares based on F^2 using all measured unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input in calculated positions.

The calculations were performed using the programs SHELXS-86 and SHELXL-97 [29]. Graphical representations were drawn with SCHAKAL-92 [30].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 144808 for compound **13,** CCDC no. 144809 for compound **15** and CCDC no. 144810 for compound **18b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The award of a Heisenberg Fellowship to H.W. is gratefully acknowledged.

References

[1] (a) H. Wadepohl, Angew. Chem. 104 (1992) 253. (b) H. Wadepohl, Comments Inorg. Chem. 15 (1994) 369.

[2] (a) D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, Chem. Rev. 94 (1994) 1585. (b) H. Wadepohl, S. Gebert, Coord. Chem. Rev. 143 (1995) 535. (c) H. Wadepohl, A. Metz, Chapter 1.15, in: P. Braunstein, L.A. Oro, P.R. Raithby (Hrsg.), Metal Clusters in Chemistry, Vol. 1, Wiley-VCH, 1999.

[3] B.F.G. Johnson, J. Lewis, M. Martinelli, A.H. Wright, D. Braga, F. Grepioni, J. Chem. Soc. Chem. Commun. (1990) 364.

[4] M.P. Gomez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby, A.H. Wright, J. Chem. Soc. Chem. Commun. (1985) 1682.

[5] H. Wadepohl, K. Büchner, H. Pritzkow, Angew. Chem. 99 (1987) 1294.

[6] J. Müller, P. Escarpa Gaede, K Quiao, Angew. Chem. 105 (1993) 1809.

[7] A. Inagaki, Y. Takaya, T. Takemori, H. Suzuki, J. Am. Chem. Soc. 119 (1997) 625.

[8] B.E.R. Schilling, R. Hoffmann, J. Am. Chem. Soc. 101 (1979) 3456.

[9] (a) J. Müller, Ha Kwang, O. Lettau, R. Schubert, Z. Anorg. Allg. Chem. 624 (1998) 1192. (b) J. Müller, C. Hirsch, Ke Quiao, Ha Kwang, Z. Anorg. Allg. Chem. 622 (1996) 1441.

[10] (a) H. Wadepohl, K. Büchner, H. Pritzkow, Organometallics 8 (1989) 2745. (b) H. Wadepohl, K. Büchner, M. Herrmann, H. Pritzkow, Organometallics 10 (1991) 861. (c) H. Wadepohl, T. Borchert, K. Büchner, H. Pritzkow, Chem. Ber. 126 (1993) 1615. (d) H. Wadepohl, T. Borchert, K. Büchner, M. Herrmann, F.-J. Paffen, H. Pritzkow, Organometallics 14 (1995) 3817. (e) H. Wadepohl, K. Büchner, M. Herrmann, A. Metz, H. Pritzkow, J. Organomet. Chem. 571 (1998) 267. (f) H. Wadepohl, K. Büchner, M. Herrmann, H. Pritzkow, J. Organomet. Chem. 573 (1998) 22.

[11] E.A. Koerner v. Gustorf, The Organic Chemistry of Iron, Academic Press, New York, 1978, p. 1981.

[12] (a) Rae Victor, R. Ben-Shoshan, S. Sarel, Tetrahedron Lett. 49 (1970) 4253, 4257. (b) Rae Victor, R. Ben-Shoshan, S. Sarel, J. Chem. Soc. Chem. Commun. (1970) 1680. (c) Rae Victor, R. Ben-Shoshan, S. Sarel, J. Org. Chem. 37 (1972) 1930.

[13] Gmelin Handbook of Inorganic Chemistry, 8th ed., Vol. Fe, Part C7, Springer, Heidelberg, 1986.

[14] D. Lentz, H. Michael, Inorg. Chem. 28 (1989) 3396.

[15] (a) N.A. Parpiev, M.T. Toshev, Kh. B. Dustov, G.G. Aleksandrov, A.I. Nekhaev, S.D. Alekseeva, B.I. Kolobkov, Dokl. Akad. Nauk Uzbekskoi SSR (1988) 47. (b) A.I. Nekhaev, S.D. Alekseeva, B.I. Kolobkov, G.G. Aleksandrov, M.T. Toshev, H.B. Dustov, J. Organomet. Chem. 401 (1991) 75.

[16] J.-S. Song, S.-H. Han, S.T. Nguyen, G.L. Geoffroy, A.L. Rheingold, Organometallics 9 (1990) 2386.

[17] J.A. Beer, R.J. Haines, J. Organomet. Chem. 24 (1970) 757.

[18] A. Winter, L. Zsolnai, G. Huttner, Chem. Ber. 115 (1982) 1286.

[19] G. Huttner, J. Schneider, G. Mohr, J. v. Seyerl, J. Organomet. Chem. 191 (1980) 161.

[20] K. Knoll, G. Huttner, L. Zsolnai, I. Jibril, M. Wasiucionek, J. Organomet. Chem. 294 (1985) 91.

[21] B.F.J. Johnson, J. Lewis, M. Pearsall, L.G. Scott, J. Organomet. Chem. 402 (1991) C27.

[22] D.L. Sunick, P.S. White, C.K. Schauer, Organometallics 12 (1993) 245.

[23] L. Stahl, J.P. Hutchinson, D.R. Wilson, R.D. Ernst, J. Am. Chem. Soc. 107 (1985) 5016.

[24] R.D. Adams, J.E. Babin, M. Tasi, T.A. Wolfe, J. Am. Chem. Soc. 110 (1988) 7093.

[25] H. Vahrenkamp, E.J. Wucherer, D. Wolters, Chem. Ber. 116 (1983) 1219.

[26] H. Lang, Ph.D. Dissertation, Konstanz, 1985.

[27] A. Basu, S. Bhaduri, H. Khwaja, P.G. Jones, K. Meyer-Bäse, G.M. Sheldrick, J. Chem. Soc. Dalton Trans. (1986) 2501.

[28] H. Wadepohl, T. Borchert, H. Pritzkow, Chem. Ber./Recueil 130 (1997) 593.

[29] (a) G.M. Sheldrick, SHELXS-86, Acta Crystallogr. Sect. A 46 (1990) 467. (b) G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.

[30] E. Keller, SCHAKAL-92, University of Freiburg, 1992.