C–H activation of diphenylphosphinoaryl-derivatives with dimethyltetrakis (trimethylphosphine)iron(II)

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ABSTRACT

Fe(CH$_3$)$_2$(PMe$_3$)$_4$ reacts with 1-(diphenylphosphino)naphthalene or benzyldiphenylphosphine within 4 h at 20 °C to give the novel metallated methyl iron complexes Fe(CH$_3$){P(C$_6$H$_5$)$_2$(C$_{10}$H$_6$)}(PMe$_3$)$_3$ (**1**) and Fe(CH$_3$){(C$_6$H$_4$)CH$_2$P(C$_6$H$_5$)$_2$}(PMe$_3$)$_3$ (**3**), respectively, via selective activation of the C–H bond of the pre-chelating ligands. The complexes are thermally unstable releasing metal through a reductive elimination of the aromatic backbone and leading to a C,C-coupling product that is regiospecifically methylated, namely 8-methyl(diphenylphosphino)naphthalene (**2**). Carbonylation (1 bar, 20 °C, 1 h) of complex **1** effects monosubstitution of a trimethylphosphine ligand *trans* to the metallated 8-C atom to afford Fe(CH$_3$){P(C$_6$H$_5$)$_2$(C$_{10}$H$_6$)}(CO)(PMe$_3$)$_2$ (**4**). The remaining methyl group in the parent complex **1** reacts with trimethylsilylethyne and *tert*-butylethyne affording the new complexes **5** and **6** bearing an alkynyl substituent *trans* to the diphenylphosphino anchoring group. The complexes **1** and **3**–**6** are diamagnetic and possess octahedral coordination geometry. All novel complexes were fully characterized by spectroscopic methods and by X-ray diffraction.

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1. Introduction

C–H activation of various organic substrates and cyclometalation reactions have been extensively studied for more than five decades finding applications in industrial processes. In particular activation of small molecules has become an important area of research in homogenous catalysis. Most cyclometalation reactions postulate a pre-coordination of heteroatoms N, P, or S when forming a metallacycle. Among the oldest C–H activation processes are those involving P-donor groups with electron-rich complexes of the late transition metals [1].

With regard to phosphorus ligands, such as triarylphosphines containing additional *ortho* alkyl- or aryl-substituents of the phenyl rings, have been successfully used for the preparation of cyclometallated transition metal complexes through C–H bond cleavage, which represents the initial step for the catalytic or stoichiometric functionalization of organic substrates.

It has been shown that many of these cyclometalation reactions are reversible (Scheme 1). However, with a methyl group in the starting complex the formation of a metallacycle is practically irreversible (D = donor atom, N, P or S) through elimination of methane, because methane has never been observed to cleave a Fe–C or Co–C bond which can occur with dihydrogen [2].

Recently we observed highly selective formations of four- (**A**), five- (**B**) and six-membered (**C**) metallacycles (Scheme 2) by C–H activation of aliphatic- and aromatic C–H bonds with methyl-cobalt(I) in reaction with various *ortho* substituted diphenylphosphino-aryl derivatives [3].

On the basis of the results with cobalt, we report an extension of our work with trimethylphosphine supported dimethyl–iron complexes, the preparation and reactivity of cyclometallated aryl-functionalized diphenylphosphino complexes of Fe(II) under very mild conditions.
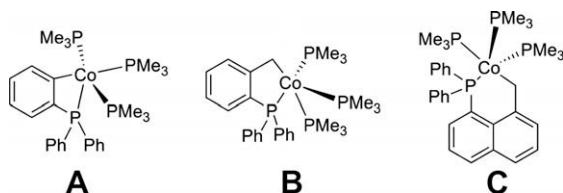
2. Results and discussion

Upon P-coordination of 1-diphenylphosphinonaphthalene as a pre-chelating reactant rotational orientations of *ortho* C–H bonds will be restricted, when compared with 2-diphenylphosphino-toluene [4]. Nevertheless, reaction with [Fe(CH$_3$)$_2$(PMe$_3$)$_4$] proceeds below 20 °C (Eq. (1)).
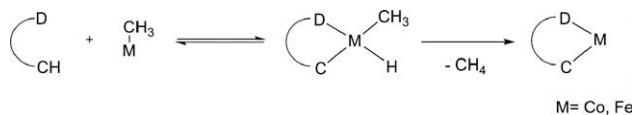
Scheme 1. C–H activation with methyl-iron and methyl-cobalt.

Scheme 2. Four-, five- and six-membered cobaltacycles.
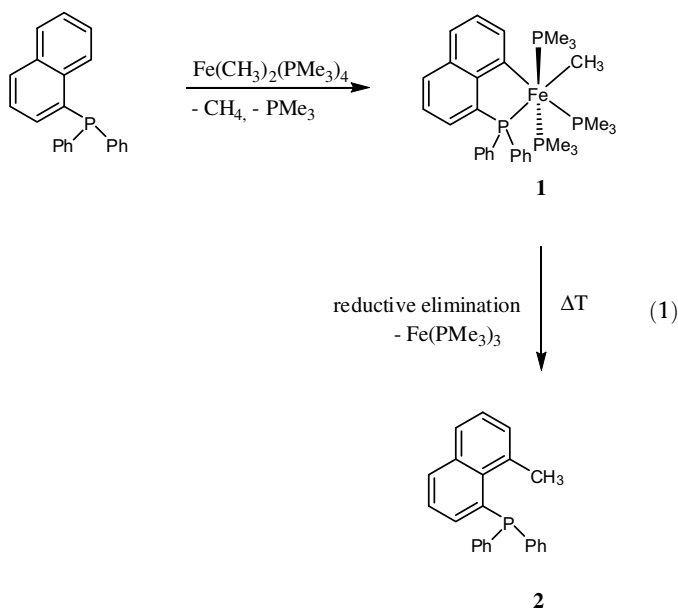
Red-orange crystals of **1**, melting with decomposition above 127 °C, were obtained from pentane solutions when cooling down to −27 °C. In the $^{31}P\{^1H\}$ NMR spectrum, the observed coordination chemical shift of $\delta = 75$ ppm is only compatible with the PPh$_2$-group ($\delta = 66.9$ ppm) as part of a five-membered ferracycle [5]. This configuration is confirmed in the molecular structure of **1**.

The iron atom is centered in an octahedron with a *meridional* arrangement of the trimethylphosphine ligands. The PPh$_2$-anchoring group and the methyl group (C32) are in *trans* configuration and the metallated carbon (C30) with the naphthyl-backbone and the P-anchoring group, forming a C30–Fe1–P4 bite angle of 83.99(12)°. The naphthyl backbone describes a slightly twisted conformation. If we define the naphthyl system as a plane, then the P4 donor atom of the PPh$_2$ anchoring group lies with 0.305 Å above this plane and the iron center Fe1 with 0.229 Å under this plane. It appears as a result of steric repulsion, originated by the spatial requirement of the phenylsubstituents, forcing a bending of the two *trans* disposed trimethylphosphine ligands [P2–Fe1–P3 = 159.84(5)°], towards the less space requiring methyl group C1. Similar distortions were previously observed from us with related cobalt complexes [3].

The Fe–C(sp^3) bond is very long [Fe–C32 = 2.114(4) Å], while the metallated carbon distance Fe–C(sp2) is shortened [Fe1–

C30 = 2.021(4) Å] when compared with average Fe–C bond distances. All other bond length show typical values of bond distances and the sum of internal angles (536.8°) in the five membered ring indicates less deviation from planarity. A multiplet arising from multiple phosphorus couplings at $\delta = -0.38$ ppm (3H) in the ^1H NMR spectrum at 293 K is attributable to the Fe–CH$_3$ group, and a broad multiplet at $\delta = 0.42$ ppm indicates a collapse of the $^2J_{(P,H)}$ coupling by reversible trimethylphosphine dissociation, whereas the aromatic hydrogen atoms (16H) resonate in the typical area of 6.45–7.83 ppm.

Cyclometallated iron complexes through C–H activation brought about with a diphenylphosphino group are very rare and only a few compounds have been identified by NMR spectra [6]. There is only one X-ray structure of a related complex known from literature which shows a cyclometallated phenyl(methyl)naphthylphosphine ferracycle with supporting cyclopentadienyl ligands which has not yet been fully characterized [7]. The broadening of signals in the NMR spectra of **1** (iron(II) in an octahedral coordination) when the sample is slightly warmed (40 °C), can be attributed to a partial reductive elimination in polar solvents, which leads to the new C,C-coupling product **2** and releasing a Fe(0) fragment and elemental iron (Eq. (1)). Concentrated ether solutions at 4 °C afford colourless crystals of **2** which were suitable for X-ray diffraction (Fig. 2).

The X-ray structure confirms what the NMR spectra indicated: formation of a newly assembled phosphine ligand which had already been prepared in a multistep reaction [8].

Most characteristic is the shift of the phosphorus nucleus in $^{31}P\{^1H\}$ NMR at 0.8 ppm as singlet and the introduced CH$_3$-group in 8-position of the naphthalene ring which appears in ^1H NMR as a doublet (3.12 ppm, $^5J_{P,H} = 4.2$ Hz) resonance indicating a coupling with the phosphorus nucleus also observed in the $^{13}C\{^1H\}$ NMR at $\delta = 27.5$ ppm as doublet with $^4J_{P,C} = 32.2$ Hz. The C–C distances and the C–P bond lengths (1.8379–1.8526 Å) are in the range reported for other arylphosphines. Ligand **2** shows a typical propeller-type conformation of two phenyl rings and a naphthyl

Fig. 1. Molecular structure of **1**. Selected distances [Å] and angles [°]: Fe1–C30 2.021(4), Fe1–C32 2.114(4), Fe1–P4 2.2192(11), Fe1–P2 2.2539(13), Fe1–P1 2.2629(13), Fe1–P3 2.3028 (11); C30–Fe1–P4 83.99(12), C30–Fe1–P1 173.24(13), P2–Fe1–P1 92.78(5), P4–Fe1–P3 93.54(4), P4–Fe1–P1 101.28(5), P2–Fe1–P3 159.84(5), P1–Fe1–P3 103.29(5), C32–Fe1–P2 90.62(13), C32–Fe1–P3 79.92(13), C32–Fe1–P1 81.73(12), C30–Fe1–C32 93.48(16).

Fig. 2. Molecular structure of **2**. Selected distances [Å] and angles [°]: P1–C1 1.8379(18), P1–C7 1.8403(18), P1–C13 1.8526(18), C15–C23 1.508(3), C14–C13 1.448(2), C14–C15 1.442(2), C13–C22 1.377(2), C14–C19 1.432(2), C15–C16 1.378(3); C1–P1–C7 101.66(8), C1–P1–C13 103.06(8), C7–P1–C13 100.01(8), C14–C15–C23 125.04(18).
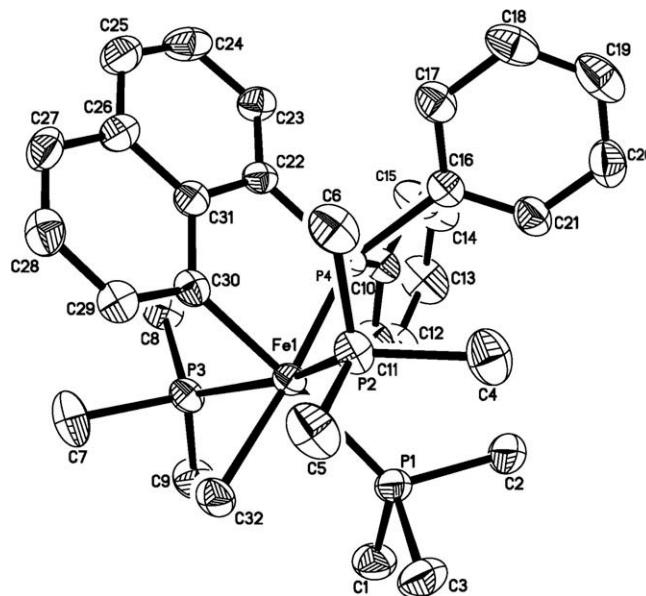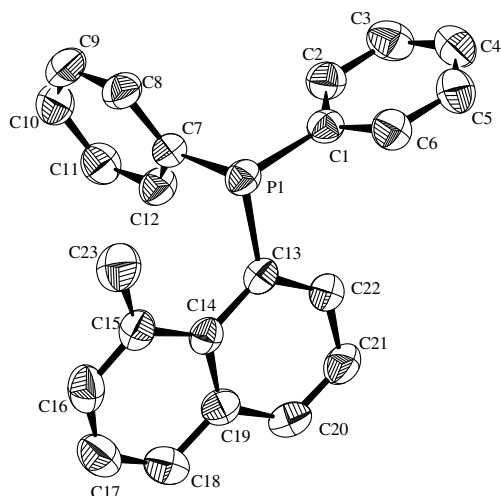

Fig. 3. Molecular structure of **3**. Selected distances [Å] and angles [°]: Fe01–C3 2.080(5), Fe01–C8 2.113(6), Fe01–P1 2.229(4), Fe01–P2 2.261(10), Fe01–P3 2.251(4), Fe01–P4 2.251(8), C1–C2 1.498(5), C2–C3 1.413(4); C3–Fe01–P1 80.30(7), C3–Fe01–P3 177.89(6), P1–Fe01–P2 99.62(3), P3–Fe01–P2 90.65(3), P4–Fe01–P2 164.00(3), P1–Fe01–P4 95.40(3), C8–Fe01–P2 82.65(8), C8–Fe01–P4 81.48(8).

ring bonded to the phosphorus atom, which can be also found in various tris-(aryl) substituted phosphine ligands in solid state [9].

The reactivity of 1-(diphenylphosphino)-8-methyl-naphthalene (**2**) was investigated with $Fe(CH_3)_2(PMe_3)_4$ under same reaction conditions as for complex **1**. We observed similar as for 2-diphenylphosphinotoluene and triphenylphosphine, no indication of an *ortho* metalation or sp^3-CH activation, that might produce four- or five-membered metallacycles, as previously shown by us with methyl cobalt complex $[Co(CH_3)(PMe_3)_4]$. Both complexes $[Co(CH_3)(PMe_3)_4]$ and $[Fe(CH_3)_2(PMe_3)_4]$ have the same set of trimethylphosphine ligands, except for the iron complex which carries an additional, labile methyl group in *cis* configuration of octahedral coordination. It appears that in a competition of cyclometalation versus reductive elimination, $[Fe(CH_3)_2(PMe_3)_4]$ releases ethane, when reacting with triphenylphosphine with a non optimum fit bite angle [Co: four-membered metallacycle = 71.5°] [3], when compared with the observed five membered metallacycle (**1**: 83.99(12°)).

From a steric point of view both pre-chelating ligands are similar, moreover 2-diphenylphosphinotoluene contains three alkylic C–H bonds for activation, when compared with one aromatic C–H bond in 8-diphenylphosphinonaphthalene. Secondly, aliphatic C–H bonds are weaker with (96–102 kcal/mol) than aromatic C–H bonds with (110 kcal/mol), but it is a common observation that the stronger aromatic C–H bond is activated in preference of the weaker aliphatic C–H bond due to higher energy of the metal–carbon(aryl) bond strength formed in the product complex [1]. This might explain why we don't observe C–H activation of the methyl substituent in 2-diphenylphosphinotoluene.

However, when formally inserting a methylene bridge in the pre-chelating phosphine, i.e. using benzyldiphenylphosphine, a cyclometalation is observed to arrive at the same ring size but with reversed ring positions as compared with 2-diphenylphosphinotoluene. After combining the reactants at −70 °C the mixture turned from red to red brown within 4 h (Eq. (2)).
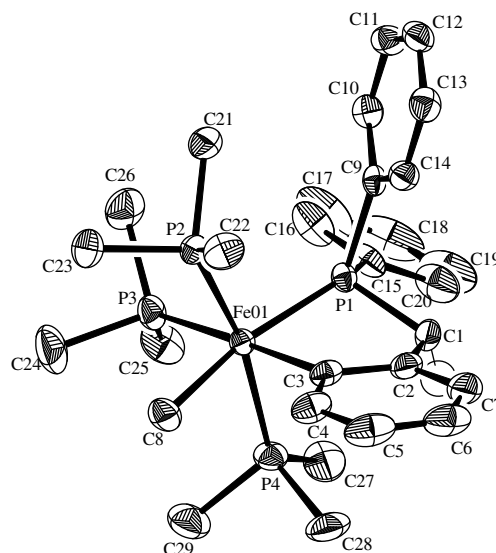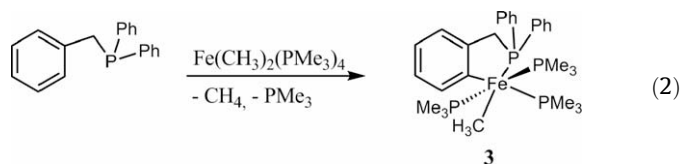

All volatile materials were removed in vacuum as soon as precipitation of the orange product **3** started. Extraction of the remaining solid with diethyl ether at 20 °C and cooling down the red-brown solution gave short orange rods in only moderate yield. Complex **3** is air-stable for some minutes but under argon decomposes above 52 °C.

The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at (δ = 72.3 ppm) with a large coordination shift (84 ppm) as compared to benzyldiphenylphosphine, indicating incorporation of the PPh_2 group in a five-membered metallacycle. Two sets of signals of anisochronic trimethylphosphine arise at 17.6 ppm and 10.0 ppm with a ratio of 2:1 consistent with a *meridional* arrangement. Slow decomposition in solution of **3** is observed in the $^{31}P\{^1H\}$ NMR, accompanied by line broadening and suppressing of the P,P-couplings when compared with the thermodynamic more stable mono carbonyl complex **4**. The most striking feature in the $^{13}C\{^1H\}$ NMR of **3** is a singlet resonance for the metallated aryl carbon at 178.1 ppm which is close to that for the related complex **1** (178.5 ppm).

The expected configuration is confirmed in the molecular structure of **3** (Fig. 3). All bond lengths in **3** are similar to those in the naphthyl derivative **1** (Fig. 1). In particular, the distances [Fe01–C3 = 2.080(5) Å and Fe01–C8 = 2.113(6) Å] fall in the range reported for Fe–C(sp^3) and Fe–C(sp^2) bonds (1.97–2.09 Å) [10,19]. Only *Kubas* reported a dimethyl–iron complex which contains Fe–C distances at 2.15 Å and 2.18 Å [20]. The approximation of octahedral geometry is less ideal than in **1**, and the sum of the internal angles in the five-membered ring (528.1°) is smaller than expected for planarity (540°) while this sum in **1** is 536.8°. The distortion of the five-membered metallacycle is a result of the methylene bridge in the ligand which causes angular strain and therefore directly influences the thermal stability (dec. > 52 °C) when compared with complex **1** (>123 °C dec.) with a better fit of its rigid naphthyl backbone.

Similar cyclometalation reactions by C–H activation in *ortho* position of benzyldiphenylphosphines have been previously described with Au [11], Ni [12], Co [13], Pt [14], and Pd [15]. Products with related pincer type ligands incorporating two benzylic phosphine anchoring groups have been shown in other laboratories to attain higher thermal stabilities [16].

3. Reaction with carbon monoxide

Carbonylated methyliron compounds, $[Fe(CH_3)_2(CO)_2(PMe_3)_2]$ or $[Fe(CH_3)I(CO)_2(PMe_3)_2]$ [17], are unreactive towards diphenyl(2-substituted phenyl)phosphines under similar conditions and fail to undergo cyclometalation involving a C–H activation of the prescribed type. However, CO ligands are smoothly introduced into metallacyclic product complexes. In solution under 1 bar of CO at 20 °C, **1** is smoothly transformed into the monocarbonyl complex **4** (Eq. (3).

(3)
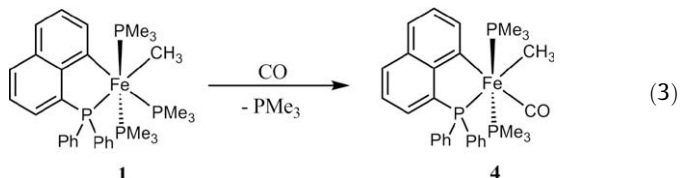
Yellow-orange crystals of **4** were obtained from pentane which are air-sensitive and decompose under argon above 161 °C. In the infrared spectra a strong ($\nu C{\equiv}O$) absorption is registered at 1872 cm^{-1} and clearly indicates a terminal carbon monoxide ligand [18]. In the ^{1}H NMR the loss of the *cis*-disposed trimethylphosphine resonance indicates substitution at this position. The ^{31}P{^{1}H} NMR spectrum contains a triplet ($\delta = 74.4$ ppm, PPh$_2$) and a doublet ($\delta = 15.9$ ppm, PMe$_3$), with couplings that suggest a five-membered ferracycle as part of an octahedral coordination with two *trans*-disposed PMe$_3$ ligands perpendicular to the ring plane and the (PPh$_2$)-donor group in *a cis*-position. The expected configuration is confirmed in the molecular structure of **4** (Fig. 4).

4. Reaction with alkynes

Using alkyne reactants, the interesting question arises as whether attack by the metal would proceed as a regioselective addition or promote ring opening through a subsequent reductive C,C-coupling reaction. When the reactants are combined at −70 °C,

the color instantly changes to yellow and an evolution of gas commences (Eq. (4)).

(4)

5: R = SiMe$_3$
6: R = *tert.*-Butyl
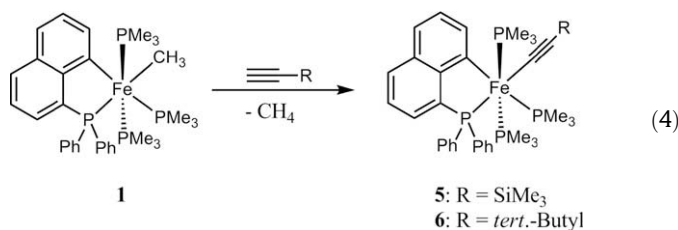
Under mild conditions the acidic *tert*-butylethyne and trimethylsilylacetylene smoothly substitute the methyl group from the parent complex **1**, affording orange yellow cubic crystals (from pentane at 4 °C). The lustrous yellow orange crystals of **5** and **6** have narrow melting ranges (**5**: 92–95 °C; **6**: 102–105 °C) and melt without decomposition. In solution both complexes are thermally more stable than complex **1**. Heating solutions of **5** and **6** does not induce reductive C,C-coupling reactions, but bis(alkinyl)tetrakis(trimethylphosphine)iron(II) complexes were identified as byproducts. Related bis(alkinyl)iron(II) complexes are described in the literature with supporting bis(dimethylphosphino)-ethane ligands [21].

The IR spectrum of **5** contains two conspicuous new bands which are assigned to the terminal alkinyl ligand and the deformation mode in the SiMe$_3$-group [**5**: $\nu = 1972$ (C${\equiv}$C), 829 cm^{-1} (δ SiMe3); **6**: $\nu = 2049$ (C${\equiv}$C) cm^{-1}]. The ^{31}P{^{1}H} NMR spectra of **5** and **6** in [d_6]-benzene at 298 K show a pattern of three resonances [**5**: $\delta = 4.4$ ppm, 9.8 ppm, 81.5 ppm; **6**: $\delta = 5.6$ ppm, 10.8 ppm, 78.5 ppm] with similar $^2J_{(PP)}$-couplings (28.5 Hz and 33.5 Hz), suggesting three P-donor functions in an octahedral coordination geometry, which is only in accord with a *meridional* configuration. Both solution structures of *mer*-**5** and *mer*-**6** were confirmed for the crystal by an X-ray diffraction analysis (Figs. 5 and 6).

In the molecular structure of **5** (Fig. 5) the iron atom attains an octahedral coordination by two *trans* PMe$_3$ groups (P4–Fe1–P2 = 159.59(5)°) a *cis* PMe$_3$ group (P3) opposite to the metallated carbon (C1) atom (C1–Fe1–P3 = 174.38(14)°), and the chelating phosphorus atom (P1) *trans* to the alkinyl group (C${\equiv}$CSiMe$_3$) with an angle of (C32–Fe1–P1 = 172.99(16)°). Bond angles are close to 90°, with the smallest being the bite angle of the five-membered
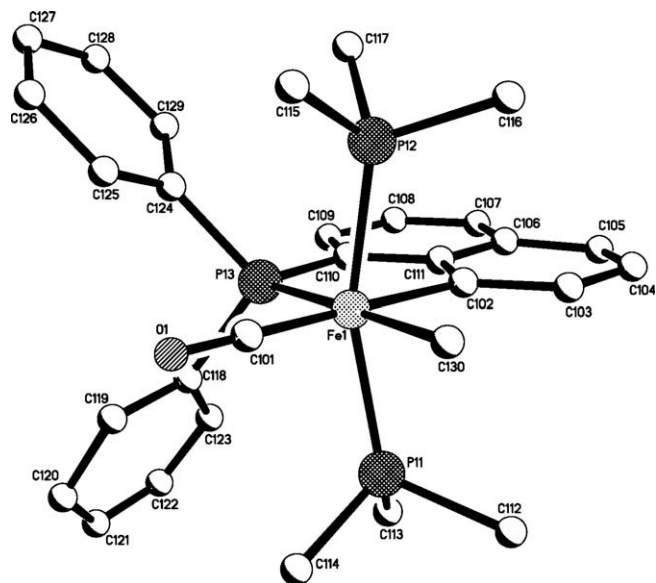
Fig. 4. Molecular structure of **4**. Selected distances [Å] and angles [°]: Fe1–C101 1.685(5), Fe1–C130 2.163(10), Fe1–C102 2.048(11), C101–O1 1.147(12), Fe1–P11 2.228(3), Fe1–P12 2.226(3), Fe1–P13 2.204(3), C110–C111 1.388(14), C102–C111 1.442(15); C102–Fe1–P13 82.8(4), C130–Fe1–P13 177.8(3), C101–Fe1–C102 177.6(6), P13–Fe1–P11 97.32(13), P13–Fe1–P12 97.22(13), P11–Fe1–P12 161.82(14), C102–Fe1–C130 99.4(4), C130–Fe1–P12 83.2(3), C102–Fe1–C130 99.4(4), O1–C101–Fe1 179.6(15).

Fig. 5. Molecular structure of **5**. Selected distances [Å] and angles [°]: Fe1–C1 2.005(5), Fe1–C32 1.921(4), Fe1–P1 2.2396(12), Fe1–P2 2.2649(14), Fe1–P3 2.2821(15), Fe1–P4 2.2986(13), C32–C33 1.210(6), C33–Si1 1.799(5); C1–Fe1–P1 83.99(12), C1–Fe1–P3 174.38(14), C1–Fe1–P2 83.89(14), P1–Fe1–P2 96.19(5), C32–Fe1–P4 79.04(15), P1–Fe1–P3 100.11(5), C32–Fe1–P1 172.99(16), C1–Fe1–P4 79.65(13), P1–Fe1–P4 94.01(5), P2–Fe–P4 159.59(5), P3–Fe1–P4 103.75(6).
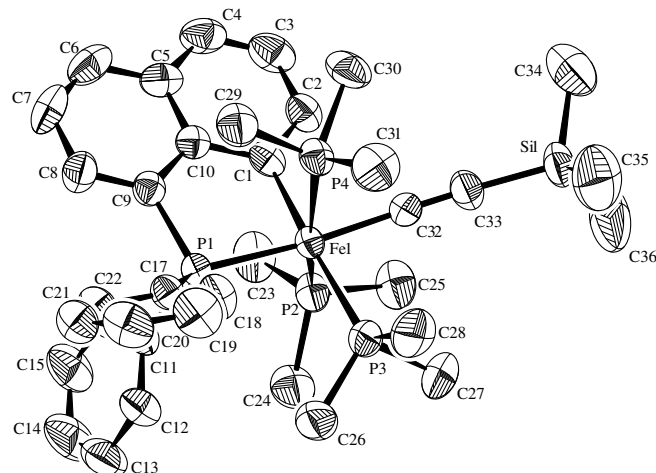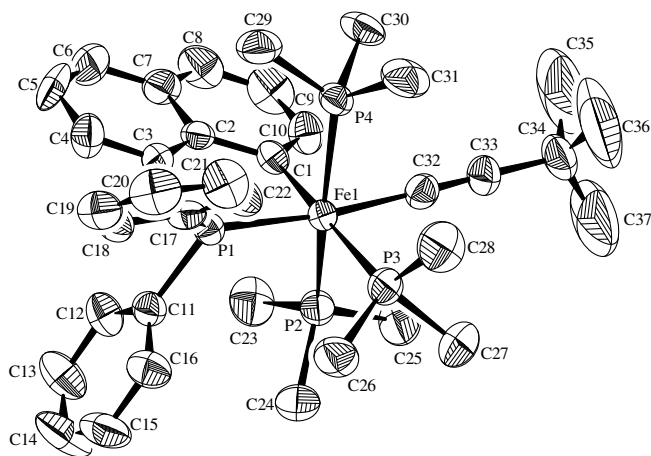
Fig. 6. Molecular structure of **6**. Selected distances [Å] and angles [°]: Fe1–C1 2.024(6), Fe1–C32 1.961(6), Fe1–P1 2.2269(17), Fe1–P2 2.2657(18), Fe1–P3 2.2826(18), Fe1–P4 2.2906(17), C32–C33 1.198(9), C33–C34 1.464(9), C1–C2 1.437(8), C2–C3 1.421(9); C1–Fe1–P1 83.56(17), C1–Fe1–P3 174.41(18), P1–Fe1–P2 96.13(6), C32–Fe–P3 82.46(19), P2–Fe1–P3 91.99(7), P1–Fe1–P3 100.25(7), C32–Fe1–P4 79.0(2), C1–Fe1–P4 80.22(17), P1–Fe1–P4 94.30(6), P2–Fe1–P4 159.53(7), P3–Fe1–P4 103.4(7).

chelate ring (C1–Fe1–P1 = 83.99(12)°). The sum of internal angles is 537°, indicating considerable relaxation of the metallacycle towards planarity. The Fe–P bond lengths from (2.23–2.29 Å) fall within the range observed for other Fe(II) complexes containing PMe₃ groups [22]. The complex contains two different Fe–C bonds with sp-and sp² hybridization with (1.921(4) and 2.005(5) Å), which are consistent with literature reports. When compared to the parent complex **1** the shortened Fe–C1 bond length is due to the electron-withdrawing influence of the alkynyl group.

From the reaction of **1** with *tert*-butylethyne, pentane solutions afforded shiny orange red crystals of **6**. An X-ray diffraction study reveals that complex **6** attains a molecular structure (Fig. 6) that is closely related with that of complex **5**.

The coordination geometry (Fig. 6) shows an octahedrally surrounded iron atom bearing the *tert*-butylethynyl substituent in the position of the former methyl group (*trans* to the PPh₂-group). The bite angle C1–Fe1–P1 = 83.56(17)° almost matches that in **5** (83.99(12)°), while no influence of the bulky *tert*-butyl group is recognized, when comparing the bite angle with that of the parent complex **1** (83.99(8)°). The triple bonds in **6** with C32–C33 = 1.198(9) Å and in **5** (1.210 Å) are similar with a proposed cumulene-type coordination of a related iron-complex (1.196 Å and 1.210 Å) but in our case with no significant deviation from linearity along the axis FeCCSi, that is believed to indicate such type of coordination [23]. The Fe–P and Fe–C distances fall in the usual ranges of bond lengths in trimethylphosphine stabilized iron(II) complexes.

5. Conclusions

Reactions of diphenylphosphino substituted aryl compounds with Fe(CH₃)₂(PMe₃)₄ achieve cyclometalation by C–H activation of aromatic C–H bonds under mild conditions (−70 °C) forming novel five-membered iron(II) metallacyles **1** and **3**. At the present stage of our investigation, our attempts to induce similar reactions in the case of triphenylphosphine by an *ortho* metalation resulting in four-membered metallacycles remained unsuccessful, probably due to the fact that a reductive elimination of the two methyl groups in the starting complex is favoured by an irreversible release of ethane. Indeed, in such cases, we do observe the formation

of Fe(PMe₃)₄ as a prevailing side reaction and other byproducts which could not be identified. This can be also understood as an elusive *ortho*-metallated intermediate, which demetalates by reductive C,C-coupling affording the newly assembled ligand **2**. Besides, we should consider that C–H bond activation in aromatic hydrocarbons is favoured over aliphatic ones due to kinetic and thermodynamic reasons, which might explain that we do not observe C–H activation of the methyl substituent in 2-diphenylphosphinotoluene. Carbon monoxide smoothly substitutes selectively one trimethylphosphine ligand *trans* to the PPh₂-group (in complex **4**) but no insertion products are observed. The attached methyl group in the cyclometallated complex **1** can be easily substituted by an acidic alkyne which increases the thermodynamic stability of the product complexes **5** and **6**.

6. Experimental

General procedures and materials: Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Literature methods were used in the preparation of trimethylsilylethyne and *tert*-butylethyne [24], 1-diphenylphosphinonaphthalene [25], benzyldiphenyl-phosphine [26], 2-diphenylphosphinotoluene [27], dimethyltetrakis(trimethyl-phosphine)eisen(II) [28]. Other chemicals were used as purchased. Infrared spectra (4000–400 cm⁻¹), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker Avance 300 and on a Bruker DRX 500 spectrometer. ¹³C{¹H} and ³¹P{¹H} NMR resonances were obtained with broadband proton decoupling. Elemental analyses were carried out at Kolbe Microanalytical Laboratory, Mülheim/Ruhr (Germany) and on an Elementar Vario EL III. Melting points were measured in capillaries sealed under argon and are uncorrected.

6.1. Methyl[8-(diphenylphosphanyl)naphthyl-C¹,P]tris(trimethylphosphine)iron(II) (**1**)

1-(Diphenylphosphanyl)naphthalene (710 mg, 2.27 mmol) in 50 mL of THF at −70 °C was combined with FeMe₂(PMe₃)₄ (895 mg, 2.27 mmol) in 50 mL of THF. During warm-up a gas evolution was observed and the mixture turned red brown and was kept stirring for further 4 h at 20 °C. The volatiles were removed in vacuo and the remaining residue was extracted with three 80 mL portions of pentane. At −27 °C the solution afforded dark red rhombic crystals of **1**. Yield 1040 mg (75%); m.p. 127–129 °C. IR (Nujol): v = 1578 w (v C≡C) cm⁻¹. ¹H NMR (500 MHz, [D₈]THF, 293 K, ppm): δ = −0.38 (m(br), 3H, Fe-CH₃), 0.42 (m(br), 27H, PCH₃), 6.45–7.83 (m, 16H, Ar-H) ppm. ¹³C{¹H} NMR (125 MHz, [D₈]THF, 293 K, ppm): δ = −4.5 (m, Fe-CH₃), 13.8 (m, PCH₃), 17.7 (m, PCH₃), 117.8 (s, CH), 122.6 (s, CH), 122.6 (s, CH), 125.8 (s, CH), 127.4 (s, CH), 128.7 (s, CH), 132.3 (s, C), 133.3 (s, C), 134.0 (s, CH), 142.9 (s, CH), 178.1 (s, Fe-C) ppm. ³¹P{¹H} NMR (200 MHz, [D₈]THF, 293 K, ppm): δ = 7.91 (dd, ²J_{P,P} = 107.3 Hz, ²J_{P,P} = 73.8 Hz, 1P, PCH₃), 30.5 (d, ²J_{P,P} = 73.8 Hz, 2P, PCH₃), 66.9 (d, ²J_{P,P} = 107.3 Hz, 1P, PPh₂) ppm. Anal. Calc. for C₃₂H₃₆FeP₄ (610.5): C, 62.95; H, 7.60. Found: C, 62.84; H, 7.75%.

6.2. [1-(Diphenylphosphino)-8-methyl-naphthalene] (**2**)

After combining 1-(diphenylphosphino)naphthalene (710 mg, 2.27 mmol) with FeMe₂(PMe₃)₄ (895 mg, 2.27 mmol) in 50 mL of THF, the reaction mixture was slightly warmed to 40 °C. After 4 h, 10 ml of 2 N NH₄Cl solution was added and the organic phase separated. THF was removed in vacuo and the remaining oil residue taken up in 50 ml ether which afforded white cubic crystals of **2** when cooled to 4 °C. (274 mg, 37%); m.p. 126–128 °C. ¹H

NMR (300 MHz, [d_6]acetone, 293 K, ppm): δ = 3.12 (d, $^5J_{P,H}$ = 4.2 Hz, 3H, CH$_3$), 7.15 (ddd, $^3J_{H,H}$ = 6.4, $^3J_{P,H}$ = 5.0, $^4J_{H,H}$ = 1.5 Hz, 1H, CH), 7.23–7.29 (m, 6H, CH), 7.31–7.32 (m, 1H, CH), 7.34–7.38 (m, 6H, CH), 7.73 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, CH), 7.82 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.4 Hz, 1H, CH) ppm. ^{13}C{^{1}H} NMR (125 MHz, [d_6]acetone, 293 K, ppm): δ = 27.5 (d, $^4J_{P,C}$ = 32.2 Hz, CH$_3$), 125.1 (s, CH), 125.9 (s, CH), 126.6 (d, $^2J_{P,C}$ = 16.3 Hz, C), 128.5 (s, CH), 129.2 (d, $^2J_{P,C}$ = 16.5 Hz, CH), 131.3 (s, CH), 131.9 (s, CH), 132.2 (m, CH), 134.6 (d, $^1J_{P,C}$ = 20.4 Hz, CH), 135.2 (d, $^1J_{P,C}$ = 29.3 Hz, C), 135.8 (s, CH), 136.1 (s, C), 136.4 (s, C), 139.1 (d, $^2J_{P,C}$ = 14.0 Hz, C) ppm. ^{31}P{^{1}H} NMR (200 MHz, [d_6]acetone, 293 K, ppm): δ = 0.8 (s, 1P) ppm. Anal. Calc. for C$_{23}$H$_{29}$P (326.4): C, 84.64; H, 5.87. Found: C, 83.95; H, 6.22%.

6.3. Methyl[2-(diphenylphosphanyl)benzyl-C,P]tris(trimethylphosphine)iron(II) (3)

Benzyldiphenylphosphine (679 mg, 2.45 mmol) in 50 mL of THF were combined at −70 °C with FeMe$_2$(PMe$_3$)$_4$ (963 mg, 2.45 mmol) in 50 mL of diethyl ether effecting a change of color from brown to orange red. After warm-up the mixture was kept stirring at 20 °C for 4 h, and then the volatiles were removed in vacuo to give a light orange red solid. This was dissolved in 50 mL of diethyl ether and crystallized at 4 °C to give orange red sticks which were suitable for X-ray diffraction. Yield 323 mg (23%); m.p. 50 °C (dec.). IR (Nujol): v = 1584 w (v C=C), 1565 w (v FeC=C) cm^{-1}, 945 vs (ρ_1 PCH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, [D$_8$]THF, 293 K, ppm): δ = −0.46 (s(br), 3H, Fe-CH$_3$), 0.45 (s(br), 18H, PCH$_3$), 0.65 (s(br), 9H, PCH$_3$), 1.82 (m, 2H, PCH$_2$), 6.53–7.60 (m, 14H, Ar-H) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_8$]THF, 293 K, ppm): δ = 4.1 (m, Fe-CH$_3$), 14.2 (m, PCH$_3$), 18.5 (m, PCH$_3$), 49.8 (d, $^1J_{P,C}$ = 26.9 Hz, PCH$_2$), 119.7 (s, CH), 121.5 (s, CH), 121.9 (s, CH), 127.3 (m, CH), 127.5 (s, CH), 132.9 (d, $^2J_{P,C}$ = 12.8 Hz, CH), 142.1 (s, C), 143.7 (s, C), 144.9 (s, CH), 180.5 (s, FeC) ppm. ^{31}P{^{1}H} NMR (200 MHz, [D$_8$]THF, 293 K, ppm): δ = 10.0 (s(br), 1P, PCH$_3$), 17.6 (s(br), 2P, PCH$_3$), 72.3 (s(br), 1P, PPh$_2$) ppm. Anal. Calc. for C$_{29}$H$_{46}$FeP$_4$ · 0.5C$_5$H$_{12}$ (610.46): C, 61.97; H, 8.59; P, 20.29. Found: C, 61.80; H, 8.67; P, 20.60%.

6.4. Methyl[8-(diphenylphosphanyl)naphthyl-C^1,P]carbonylbis(trimethylphosphine)iron(II) (4)

A sample of 1 (324 mg, 1.28 mmol) in 40 mL of THF was kept stirring under 1 bar of CO for 1 h to become a light red solution. The volatiles were removed in vacuo and the solid residue was extracted with three 70 mL portions of pentane. Crystallization at −27 °C afforded orange rods of 4, which were suitable for X-ray diffraction. Yield 241 mg (81%); m.p. 161–164 °C (dec.). IR (Nujol): v = 1872 cm^{-1} vs (v C=O), 1578 m (v C=C); 935 vs (ρ_1 PCH$_3$) cm^{-1}. ^{1}H NMR (500 MHz, [D$_8$]THF, 293 K, ppm): δ = −0.82 (dt, $^3J_{P,H}$ = 11.0 Hz, $^3J_{P,H}$ = 1.2 Hz, 3H, Fe-CH$_3$), 0.45 (t', |$^2J_{P,H}$ + $^4J_{P,H}$| = 7.1 Hz, 18H, PCH$_3$), 7.23–7.25 (m, 3H, Ar-H), 7.29–7.33 (m, 5H, Ar-H), 7.46 (td, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H, Ar-H); 7.65 (dt, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, Ar-H), 7.97 (dt, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 0.9 Hz, 2H, Ar-H), 8.11–8.15 (m, 3H, Ar-H), 8.32 (dt, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 0.9 Hz, 1H, Ar-H) ppm. ^{13}C{^{1}H} NMR (125 MHz, [D$_8$]THF, 293 K, ppm): δ = −0.21 (dt, $^2J_{P,C}$ = 20.0 Hz, $^2J_{P,C}$ = 7.5 Hz, Fe-CH$_3$), 15.8 (t', |$^1J_{P,C}$ + $^3J_{P,C}$| = 24.9 Hz, PCH$_3$), 122.5 (s, CH), 123.8 (d, $^4J_{P,C}$ = 5.0 Hz, CH), 125.4 (s, CH), 128.9 (d, $^1J_{P,C}$ = 30.1 Hz, CH), 129.2 (s, CH), 129.6 (s, C), 132.4 (d, $^3J_{P,C}$ = 10.2 Hz, CH), 132.9 (s, C), 133.3 (d, $^3J_{P,C}$ = 7.5 Hz, C), 135.4 (s, C), 138.3 (d, $^4J_{P,C}$ = 5.0 Hz, CH), 143.3 (d, $^1J_{P,C}$ = 31.3 Hz, CH), 154.6 (d, $^1J_{P,C}$ = 42.5 Hz, CH), 173.9 (s, CH), 180.4 (d, $^1J_{P,C}$ = 8.7 Hz, Fe-C), 221.8 (t, $^2J_{P,C}$ = 17.7 Hz, Fe-CO) ppm. ^{31}P{^{1}H} NMR (200 MHz, [D$_8$]THF, 293 K, ppm): δ = 15.9 (d, $^2J_{P,P}$ = 28.8 Hz, 2P, PCH$_3$); 74.4 (t, $^2J_{P,P}$ = 28.8 Hz, 1P, PPh$_2$) ppm. Anal. Calc. for

C$_{30}$H$_{37}$FeOP$_3$ (562.4): C, 64.07; H, 6.63; P, 16.52. Found: C, 63.85; H, 7.06; P, 16.37%.

6.5. Trimethylsilylethynyl[8-(diphenylphosphanyl)naphthyl-C^1,P]tris(trimethylphosphine)iron(II) (5)

Trimethylsilylethyne (140 mg, 1.42 mmol) in 50 mL of THF were combined at −70 °C with a sample of 1 (870 mg, 1.42 mmol) in 50 mL of THF effecting a change of color from red to orange. After warm-up the mixture was kept stirring at 20 °C for 16 h, and then the volatiles were removed in vacuo to give orange solid. This was dissolved in 50 mL of pentane and crystallized at −20 °C to give yellow crystals which were suitable for X-ray diffraction. Yield 404 mg (41%); m.p. 103–105 °C (dec.). IR (Nujol): v = 1972 cm^{-1} vs (v C≡C), 1587 m (v C=C), 1534 m (v FeC=C), 946 vs (ρ_1 PCH$_3$), 829 s (δ SiMe$_3$) cm^{-1}. ^{1}H NMR (300 MHz, [d_6]benzene, 293 K, ppm): δ = 0.50 (s, 9H, SiMe$_3$), 0.63 (t', |$^2J_{P,H}$ + $^4J_{P,H}$| = 7.8 Hz, 18H, PCH$_3$), 1.48 (d, $^2J_{P,H}$ = 3.7 Hz, 9H, PCH$_3$), 6.87–6.91 (m, 6H, Ar-H), 6.94 (m, 1H, Ar-H), 7.22 (m, 1H, Ar-H), 7.36 (m, 4H, Ar-H), 7.72 (m, 2H, Ar-H), 9.11 (m, 2H, Ar-H) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, [d_6]benzene, 293 K, ppm): δ = 1.5 (s, SiCH$_3$), 15.1 (m, PCH$_3$), 18.1–18.5 (m, PCH$_3$), 115.6 (s, CH), 117.3 (s, Fe-C≡C), 120.6 (s, CH), 125.4 (m, CH), 125.6 (s, CH), 126.2 (s, CH), 127.0 (s, CH), 127.3 (s, CH), 133.5 (d, $^1J_{P,C}$ = 18.2 Hz, C), 132.1 (s, CH), 138.5 (s, Fe-C≡C), 141.8 (d, $^2J_{P,C}$ = 11.9 Hz, C), 147.1 (s, C), 193.4 (m, Fe-C) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [d_6]benzene, 293 K, ppm): δ = 4.4 (d, $^2J_{P,P}$ = 28.5 Hz, 1P, PCH$_3$), 9.8 (dd, $^2J_{P,P}$ = 28.5 Hz, $^2J_{P,P}$ = 33.5 Hz, 2P, PCH$_3$), 81.5 (d, $^2J_{P,P}$ = 33.5 Hz, 1P, PPh$_2$) ppm. Anal. Calc. for C$_{36}$H$_{52}$FeP$_4$Si (692.6): C, 62.43; H, 7.57. Found: C, 62.01; H, 8.11%.

6.6. tert-Butylethynyl[8-(diphenylphosphanyl)naphthyl-C^1,P]tris(trimethylphosphine)iron(II) (6)

tert-Butylethyne (91 mg, 1.11 mmol) in 50 mL of pentane were combined at −70 °C with a sample of 1 (680 mg, 1.11 mmol) in 50 mL of diethyl ether. After warm up the mixture was kept stirring at 20 °C for 16 h, and then the volatiles were removed in vacuo to give an orange solid. This was dissolved in 50 mL of diethyl ether/pentane (1:1) and crystallized at −20 °C to give orange rhombic crystals which were suitable for X-ray diffraction. Yield 233 mg (31%); m.p. 92–95 °C (dec.). IR (Nujol): v = 2049 vs (v C≡C), 1590 m (v C=C), 1533 m (v FeC=C), 942 vs (ρ_1 PCH$_3$) cm^{-1}. ^{1}H NMR (300 MHz, [d_6]benzene, 293 K, ppm): δ = 0.63 (s(br), 18H, PCH$_3$), 1.12 (s, 9H, CMe$_3$), 1.45 (d, $^2J_{P,H}$ = 4.1 Hz, 9H, PCH$_3$), 6.78 (m, 6H, Ar-H), 6.84 (m, 1H, Ar-H), 7.73 (m, 5H, Ar-H), 7.85 (m, 1H, Ar-H), 7.90 (m, 1H, Ar-H), 8.58 (m, 2H, Ar-H) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, [d_6]benzene, 293 K, ppm): δ = 14.8 (m, PCH$_3$), 17.7 (m, PCH$_3$), 31.7 (s, CCH$_3$), 34.9 (s, CCH$_3$), 110.9 (s, Fe-C≡C), 117.6 (s, CH), 120.1 (s, Fe-C≡C), 122.4 (s, CH), 123.1 (d, $^3J_{P,C}$ = 6.1 Hz, CH), 125.6 (s, CH), 126.2 (d, $^3J_{P,C}$ = 7.3 Hz, CH), 126.4 (s, CH), 127.2 (s, CH), 131.6 (d, $^1J_{P,C}$ = 19.2 Hz, C), 132.1 (d, $^2J_{P,C}$ = 12.0 Hz, CH), 139.8 (d, $^2J_{P,C}$ = 10.2 Hz, C), 145.3 (m, C), 189.2 (m, Fe-C) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, [d_6]benzene, 293 K, ppm): δ = 5.6 (d, $^2J_{P,P}$ = 30.5 Hz, 1P, PCH$_3$), 10.8 (dd, $^2J_{P,P}$ = 30.5 Hz, $^2J_{P,P}$ = 34.1 Hz, 2P, PCH$_3$), 78.5 (d, $^2J_{P,P}$ = 34.1 Hz, 1P, PPh$_2$) ppm. Anal. Calc. for C$_{37}$H$_{52}$FeP$_4$ (676.5): C, 65.69; H, 7.75. Found: C, 65.78; H, 8.50%.

6.7. Crystal structure analysis

Data collections were performed on a STOE IPDSII image plate detector and on a Bruker AXS SMART APEX diffractometer using Mo K$_\alpha$ radiation (λ = 0.71019 Å). Details of the crystal structure are given in Table 1. Data collection [29]: Stoe X-AREA, Bruker SMART. Data reduction [29]: Stoe X-RED, Bruker SAINT. The struc-

Table 1
Crystal data for compounds **1–6**

	1	2	3	4	5	6
Empirical formula	$C_{32}H_{46}FeP_4$	$C_{23}H_{19}P$	$C_{29}H_{46}FeP_4 \cdot 0.5C_5H_{12}$	$C_{30}H_{37}FeOP_3$	$C_{36}H_{52}FeP_4Si$	$C_{37}H_{52}FeP_4$
Molecular mass	647.48	326.25	610.46	562.36	692.60	676.52
Crystal size (mm)	$0.50 \times 0.30 \times 0.20$	$0.13 \times 0.10 \times 0.08$	$0.42 \times 0.21 \times 0.15$	$0.22 \times 0.20 \times 0.05$	$0.25 \times 0.25 \times 0.20$	$0.35 \times 0.20 \times 0.17$
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P21/c$	$P21/c$	$P21/c$	Cc	Cc
a (Å)	10.0702(19)	10.535(4)	18.9534(16)	18.696(5)	13.5257(11)	13.206(2)
b (Å)	10.1194(19)	15.970(6)	10.2773(8)	9.136(3)	14.6871(13)	15.087(3)
c (Å)	17.705(3)	10.826(4)	18.4165(2)	34.559(8)	19.850(2)	19.480(4)
α (°)	77.361(4)	90	90	90	90	90
β (°)	81.376(4)	106.858(6)	113.997(8)	106.450(12)	109.568(3)	108.834(7)
γ (°)	74.921(4)	90	90	90	90	90
V (Å³)	1691.5(5)	1743.1(11)	3277.3(5)	5661(3)	3715.5(6)	3673.4(12)
Z	2	4	4	8	4	4
$D_{calcd.}$ (g/cm³)	1.271	1.244	1.237	1.320	1.238	1.223
μ (Mo Kα) (mm^{-1})	0.658	0.158	0.674	0.724	0.634	0.608
Temperature (K)	298(2)	273(2)	193(2)	293(2)	273(2)	273(2)
Θ-Range (°)	$1.18 \leqslant \Theta \leqslant 26.37$	$2.02 \leqslant \Theta \leqslant 25.05$	$2.32 \leqslant \Theta \leqslant 26.05$	$1.14 \leqslant \Theta \leqslant 28.08$	$2.12 \leqslant \Theta \leqslant 24.99$	$2.12 \leqslant \Theta \leqslant 25.00$
h	$-12 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 11$	$-23 \leqslant h \leqslant 23$	$-24 \leqslant h \leqslant 24$	$-16 \leqslant h \leqslant 16$	$-15 \leqslant h \leqslant 15$
k	$-12 \leqslant k \leqslant 12$	$-19 \leqslant k \leqslant 14$	$-12 \leqslant k \leqslant 12$	$-11 \leqslant k \leqslant 12$	$-17 \leqslant k \leqslant 15$	$-17 \leqslant k \leqslant 17$
l	$-22 \leqslant l \leqslant 22$	$-12 \leqslant l \leqslant 12$	$-22 \leqslant l \leqslant 22$	$-43 \leqslant l \leqslant 45$	$-23 \leqslant l \leqslant 23$	$-23 \leqslant l \leqslant 22$
No. of reflection measured	15246	9052	31421	45735	20334	16879
No. of unique data [$R_{(int)}$]	6906[0.1214]	3084[0.025]	6423[0.0546]	13743[0.236]	6096[0.0606]	6280[0.065]
Parameters	345	218	364	632	391	391
Restraints	0	0	7	0	2	20
Goodness of fit (GoF) on F^2	0.856	1.034	0.881	0.882	1.032	0.872
R_1 [$I \geqslant 2\sigma (I)$]	0.0589	0.0355	0.0355	0.1076	0.0466	0.0538
wR_2 (all data)	0.1489	0.0951	0.0803	0.2763	0.1148	0.1545

tures were solved by direct methods using SHELXS-97 [30], and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [30]. For **1** it was not possible to refine the heavily disordered enclosed Et_2O solvent molecule. Accordingly, the data was treated with the SQUEEZE facility of PLATON [31], which resulted in smooth refinement. For **4** the structure was of marginal quality ($R_1 = 0.1076$) and should be understood as proof of connectivity only. Hydrogen atoms on C were placed at idealized positions (C–H = 0.93 Å, 0.96 Å for methyl groups) and were allowed to ride on the parent atom [$U_{iso}(H) = 1.2U(C)$ for CH groups and $U_{iso}(H) = 1.5U(C)$ for methyl groups].

Acknowledgments

Appendix A. Supplementary data

CCDC 681744, 681482, 681479, 681745, 681481 and 681480 contains the supplementary crystallographic data for (**1**), (**2**), (**3**), (**4**), (**5**) and (**6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.08.017.

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