

Lithiation and alkylation reactions of the tri-phosphaferrocenes, $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-C}_5\text{R}_5)]$, (R = H and Me): Crystal and molecular structures of the $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{Me}_5)_2$ dimer, $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{Me}_5)]$ and *cis*- $[\text{PtCl}_2(\text{PMe}_3)\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{H}_5)]$

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Abstract

Treatment of the 1,2,4-tri-phosphaferrocenes, $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-C}_5\text{R}_5)]$, (R = H; Me) with $^n\text{BuLi}$ leads to alkylation of one of the two adjacent ring phosphorus atoms to afford the corresponding lithium salts $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{R}_5)_2$ (R = H; Me). A single crystal X-ray diffraction study reveals that $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{Me}_5)_2$ exhibits an unusual dimeric structure in the solid state. Treatment of the lithium salts with MeI gives the monomeric zwitterion complexes $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{R}_5)]$, (R = H; Me). The molecular structure of $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{Me}_5)]$ and the platinum(II) complex *cis*- $[\text{PtCl}_2(\text{PMe}_3)\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{H}_5)]$ have also been determined by single crystal X-ray diffraction studies.

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1. Introduction

The preparation of ferrocene, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ was a landmark in the development of organo-transition metal chemistry [1–4]. Replacement of one or more CR fragments in the cyclopentadienyl ring systems by phosphorus in $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)_2]$, (R = H; R = Me) [5,6], gives a wide variety of poly-phosphaferrocene derivatives typified by $[\text{Fe}(\eta^5\text{-PC}_4\text{H}_2\text{R}_2)(\eta^5\text{-C}_5\text{H}_5)]$ (R = H; R = Me) [7,8], $[\text{Fe}(\eta^5\text{-PC}_4\text{H}_2\text{Me}_2)_2]$ [9], $[\text{Fe}(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)(\eta^5\text{-C}_5\text{R}_5)]$ (R = H [10]; R = Me [11]), $[\text{Fe}(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)_2]$ [12], $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-C}_5\text{R}_5)]$ (R = H [10]; R = Me [13]), $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{Ph}_2)(\eta^5\text{-C}_5\text{H}_2^t\text{Bu}_3)]$ [14], $[\text{Fe}(\eta^5\text{-P}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ [15], $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)]$ and $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)_2]$ [16].

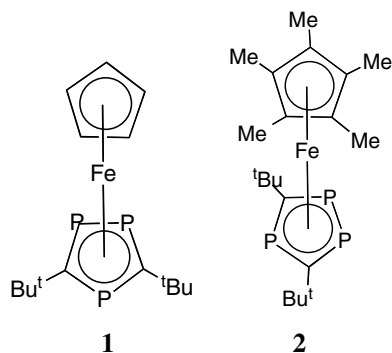
The presence of the lone pair electrons on each phosphorus ring atom gives an additional ligation propensity for these poly-phosphaferrocenes toward other transition metals, which is not available to the parent ferrocenes and this has been widely exploited [17,18]. More recently there has been considerable interest in using phosphametalloenes as ligands for a variety of catalytic processes and this rapidly developing area has recently been comprehensively reviewed [19,20].

The nature of the bonding in phosphaferrocenes and related phosphametalloenes containing the η^5 -ligated 3,5-ditertiarybutyl-1,2,4-triphospholyl ring system, has been explored by electrochemical measurements in solution and gas-phase photoelectron spectroscopic techniques, coupled with supportive DFT calculations [12,21,22]. These studies have established that replacement of CR fragments by P in the corresponding parent metallocene reduces the overall electron density at the metal centre.

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In this paper we report the first lithiation and alkylation reactions of the two 1,2,4-tri-phosphaferrocenes **1** and **2**.



2. Results and discussion

Treatment of $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{tBu}_2)(\eta^5\text{-C}_5\text{R}_5)]$ ($\text{R} = \text{H}$ **1**; $\text{R} = \text{Me}$ **2**) with 1 equiv. of $n\text{BuLi}$ in hexane at room temperature gave, respectively, the very air and moisture sensitive complexes $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{R}_5)$ ($\text{R} = \text{H}$ **3**; $\text{R} = \text{Me}$ **4**) via *exclusive* nucleophilic attack of the *n*-butyl anion at one of the phosphorus atoms of the adjacent pair in the $\text{P}_3\text{C}_2\text{tBu}_2$ ring (Scheme 1). The complex $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{H}_5)$ **3** is insoluble in hydrocarbon solvents or Et_2O , but is slightly soluble in co-ordinating solvents such as THF or pyridine, whereas $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{Me}_5)$ **4** exhibits some solubility in hydrocarbon solvents. Both complexes **3** and **4** were characterised by multi-nuclear NMR spectroscopy and in the case of **4** by a single crystal X-ray diffraction study, which showed an unusual dimeric structure in the solid-state (*vide infra*).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{H}_5)$ **3** in $\text{C}_5\text{D}_5\text{N}$ is entirely consistent with the specific single alkylation of one of the less sterically hindered phosphorus atoms of the $\text{P}_3\text{C}_2\text{tBu}_2$ ring. The spectrum showed the expected three distinct different phosphorus environments, the P^nBu resonance at -157.2 ppm, which is characteristic of a saturated P_A atom, occurs as a doublet of doublets with a large coupling (263.6 Hz) expected for a

one-bond $J(\text{P}_\text{A}\text{P}_\text{B})$ coupling, and a further small coupling (31.5 Hz) lying in the expected range for a two-bond $J(\text{P}_\text{A}\text{P}_\text{C})$ coupling. The unsaturated P_B atom directly attached to the P_A centre gave rise to a doublet of doublets pattern at 34.5 ppm with the same large coupling (263.6 Hz) and a further small coupling $J(\text{P}_\text{B}\text{P}_\text{C})$ (32.8 Hz). The remaining unsaturated P_C resonance occurs as a doublet of doublets centred at -49.1 ppm, with the expected couplings to P_A and P_B .

The ^1H NMR spectrum of **3** showed the expected two singlets at 1.79 and 1.53 for the different ^tBu groups and a singlet for the 5 equiv. protons of the C_5H_5 group at 4.48 ppm, with the expected relative intensity ratio 9:9:5, respectively. The mass spectrum of **3** exhibited a peak at 410 (80%) corresponding to the ion $[\text{Fe}(\text{P}_3\text{C}_2\text{tBu}_2)\text{C}_5\text{H}_5\text{BuH}]^+$.

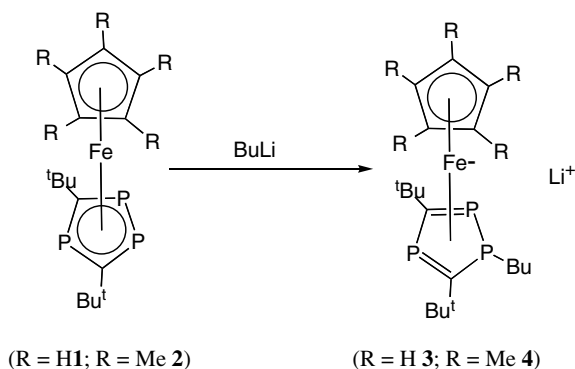
The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{Me}_5)$ **4** in $\text{C}_5\text{D}_5\text{N}$ are both similar to those of **3**, the $^{31}\text{P}\{^1\text{H}\}$ spectrum showing a doublet of doublets at -140.9 ppm for the saturated P_A with one large coupling (265.9 Hz) and a smaller coupling to P_C of 33.2 Hz. The two unsaturated P atoms P_B and P_C showed the expected doublet of doublets. $^{31}\text{P}\{^1\text{H}\}$ chemical shifts and coupling constants for **3** and **4** are summarised in Table 1.

The ^1H NMR spectrum of **4** shows two singlets for the ^tBu groups at 1.72 and 1.91 ppm, and a singlet for the methyl protons of the C_5Me_5 group at 2.23 ppm, with the expected relative intensity ratio 9:9:15. The mass spectrum of **4** contained a peak at *m/e* 480 corresponding to the ion $[\text{Fe}(\text{P}_3\text{C}_2\text{tBu}_2)\text{C}_5\text{Me}_5\text{BuH}]^+$.

The identity of **4** was confirmed by a single crystal X-ray diffraction study (see Fig. 1), which reveals an unusual dimeric structure in the solid state, consisting of two $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{P}^n\text{Bu})(\eta^5\text{-C}_5\text{Me}_5)$ units related by a centre of symmetry. Each lithium atom is bonded to the saturated P centre within its own unit as well as to the corresponding phosphorus centre of the second unit. The

Table 1
 $^{31}\text{P}\{^1\text{H}\}$ NMR data ($\text{C}_5\text{D}_5\text{N}$, 25 °C) for complexes **3** and **4**, chemical shifts in (ppm) and coupling constants in (Hz)

Complex	δP_A	δP_B	δP_C	$^1J(\text{P}_\text{A}\text{P}_\text{B})$	$^2J(\text{P}_\text{A}\text{P}_\text{C})$	$^2J(\text{P}_\text{B}\text{P}_\text{C})$
3	-157.2	34.5	-49.1	263.6	31.5	32.8
4	-140.9	34.3	-44.1	265.9	33.2	33.2



Scheme 1.

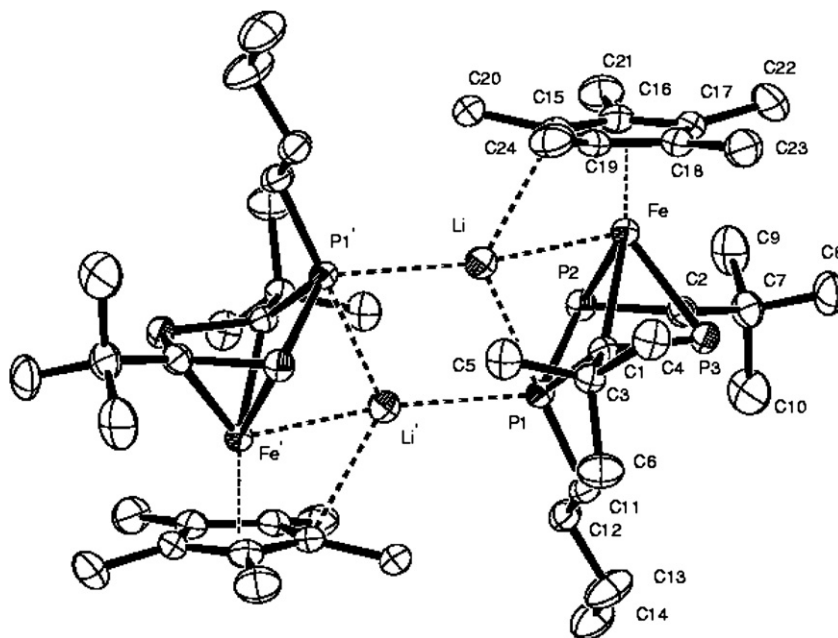


Fig. 1. Molecular structure of $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{Bu})(\eta^5\text{-C}_5\text{Me}_5)$ (**4**). Selected bond distances (Å) and angles (°): P(1)–C(1) 1.825(3), C(1)–P(3) 1.802(3), P(3)–C(2) 1.773(3), C(2)–P(2) 1.796(3), P(2)–P(1) 2.177(1), Fe–C(1) 2.198(3), Fe–P(2) 2.325(9), Fe–C(2) 2.113(3), Fe–P(3) 2.255(9), Fe–M(1) 1.729(3), Li–P(1) 2.599(5), Li–C(1) 2.535(6), Li–Fe 2.542(5), Li–Li' 3.003(11), P(1)–C(1)–P(3) 113.47(16), C(1)–P(3)–C(2) 95.82(16), P(3)–C(2)–P(2) 118.92(16), C(2)–P(2)–P(1) 94.32(10), P(2)–P(1)–C(1) 89.66(10), P(2)–P(1)–C(11) 107.05(11), C(11)–P(1)–Li 173.89(17), C(1)–P(1)–Li' 122.61(16), P(2)–P(1)–Li' 115.79(13).

Li–P distances of 2.559 and 2.656 Å are comparable to those reported for $[(\text{Ph}_2\text{P})_2\text{CHLi.TMEDA}]$ (2.582 Å) and $[\{\text{Me}_2\text{PCH}_2\text{Li}(\text{TMEDA})\}_2]$ (2.593 Å) [23,24].

The Li atom in **4** is also linked to the carbon atom directly bonded to the saturated P centre of the $\text{P}_3\text{C}_2'\text{Bu}_2$ ring and to the closest carbon centre of the C_5Me_5 ring, with bonding distances of 2.535 and of 2.589 Å respectively. These values are close to the average Li–C distances (2.536 Å) in the related complex $[\text{Li}(\text{TMEDA})][\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-COD})]$ [25]. Each lithium is also bonded to the Fe centre within its unit with a Li–Fe distance of 2.542(5) Å, which lies very close to that reported for both $[\text{Li}(\text{TMEDA})][\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-COD})]$ (2.530 Å) and $[\text{Li}(\text{TMEDA})][\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-C}_2\text{H}_2)]$ (2.532 Å). The Li–Li' distance (3.003(11) Å) is longer than the sum of the covalent radii of Li suggesting there is an insignificant metal–metal interaction.

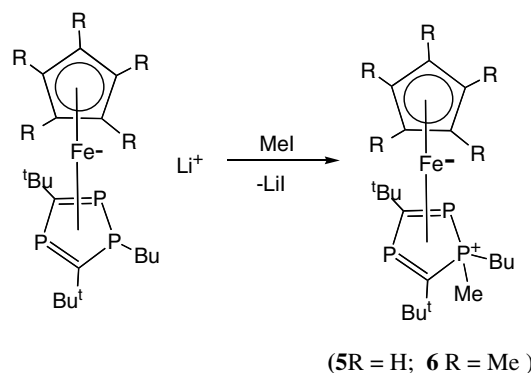
The $\text{P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{Bu}$ ring system in **4** may be regarded as acting as an overall four electron donor in which the Fe centre co-ordinates to the approximately planar P(2), C(2), P(3) and C(1) centres, with a mean Fe–C distance of 2.156 Å and Fe–P distance of 2.290 Å.

2.1. Reaction of $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{Bu})(\eta^5\text{-C}_5\text{R}_5)$ ($R = \text{H}$ or Me) with MeI

Treatment of $\text{LiFe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{Bu})(\eta^5\text{-C}_5\text{R}_5)$ ($R = \text{H}$ **3**; $R = \text{Me}$ **4**) with MeI in THF at room temperature gave the zwitterionic complexes $\text{Fe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{BuMe})(\eta^5\text{-C}_5\text{R}_5)$ ($R = \text{H}$ **5**, $R = \text{Me}$ **6**) respectively, by preferential electrophilic attack of MeI on the previously alkylated saturated phosphorus atom P_A of the $\text{P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{Bu}$ ring. (Scheme 2).

Both compounds **5** and **6** were fully characterized: (i) by multi-nuclear spectroscopy and (ii) by single crystal X-ray diffraction studies on **6** and the *cis*- $[\text{PtCl}_2(\text{PMe}_3)]$ adduct **7** of compound **5**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{P}''\text{BuMe})(\eta^5\text{-C}_5\text{H}_5)]$ **5** gave the expected [AMX] spin-system pattern of lines expected for the three distinctly different P environments. The quaternary P_A atom gave rise to a doublet of doublets at –175.2 ppm, with a large coupling (312.5 Hz) in the range expected for one bond P–P couplings and a small coupling (30.4 Hz) in the range of two-bond P–P couplings. P_B gave rise to a doublet of doublets centred at 44.4 ppm with the same large coupling to P_A (312.5 Hz) and smaller coupling to P_C (20.7 Hz). The P_C centre gave rise to a doublet of doublets pattern at –14.7 ppm with the expected two small couplings. The ^1H NMR spectrum of **5** showed two singlets at 1.48 and 1.02 ppm for the ^tBu groups,

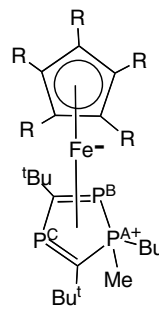


Scheme 2.

a multiplet at 1.74 ppm for the P_{Me} group, and a singlet for the five protons of the η⁵-C₅H₅ ring at 4.38 ppm with the relative intensity ratio 9:9:3:5. The mass spectrum showed peaks at 424 (40%) and 367 (100%) assigned to the molecular ions [Fe(C₅H₅)(P₃C₂^tBu₂)MeBu]⁺ and [Fe(C₅H₅)(P₃C₂^tBu₂-Me)]⁺, respectively.

The ³¹P{¹H} and ¹H NMR spectra of [Fe(η⁴-P₂C₂^tBu₂PBuMe)(η⁵-C₅Me₅)] **6** are very similar to their counterparts in **5**. The ³¹P{¹H} spectrum showed a doublet of doublets at -161.0 ppm for the quaternary P_A,

Table 2
³¹P{¹H} NMR data (C₆D₆, 25 °C) for complexes **5** and **6**, chemical shifts in ppm and coupling constants in Hz



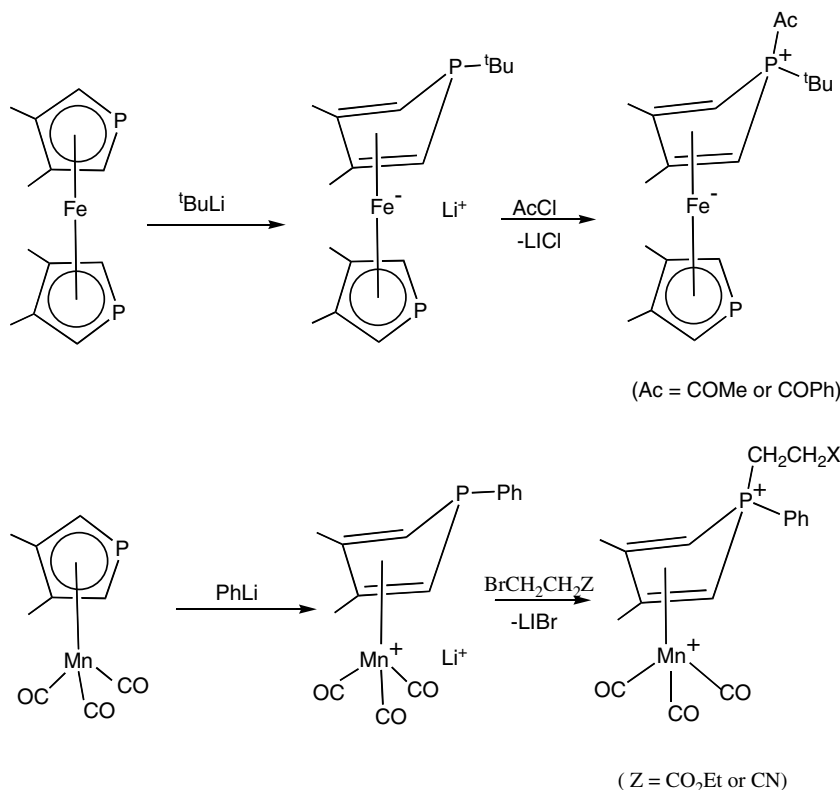
(R = H **5**; R = Me **6**)

Compound	δP _A	δP _B	δP _C	¹ J(P _A P _B)	² J(P _A P _C)	² J(P _B P _C)
5	-175.2	44.4	-14.8	312.5	30.4	20.7
6	-161.0	47.1	3.7	317	33	22

($J(P_A P_B) = 317$ Hz) and a smaller $J(P_A P_C)$ coupling of 33 Hz. The P_B atom, adjacent to the quaternary P_A, gave rise to the expected doublet of doublets at 47.1 ppm with one large coupling (317 Hz) and one small coupling (22 Hz). The P_C atom gave rise to a doublet of doublets at 3.7 ppm with the expected two further small couplings. The ¹H NMR spectrum of **6** showed two singlets at 1.61 and 1.18 ppm for the ^tBu groups, together with a singlet for the C₅Me₅ ring at 1.88 ppm and the expected doublet of doublets at 1.75 ppm for PCH₃ (²J(P_AH) = 10.8 Hz; ³J(P_BH) = 5.5 Hz). The mass spectrum showed peaks at 494 (75%) and 437 (100%) assigned to the ions [Fe(C₅Me₅)(P₃C₂^tBu₂)MeBu]⁺ and [Fe(C₅Me₅)(P₃C₂^tBu₂)Me]⁺, respectively. ³¹P chemical shift and coupling constant data for both **5** and **6** are summarised in Table 2.

Although similar zwitterionic complexes, of the 1,1'-diphosphaferrocene and the phosphacymantrene, shown below in Scheme 3, were previously reported by Mathey and co-workers [26–28], no structural details concerning the nature of the intermediate lithium compounds were reported.

In the present work, the structure of [Fe(η⁴-P₂C₂^tBu₂PⁿBuMe)(η⁵-C₅Me₅)] **6** was confirmed by a single crystal X-ray diffraction study, (Fig. 2), which reveals the P₂C₂^tBu₂PⁿBuMe ring to be acting as a 4-electron donor to the iron centre *via* the almost coplanar C(2)P(3)-C(1)P(2) centres. The average Fe–P and Fe–C bond distances of 2.28 and 2.16 Å respectively, are very similar to the corresponding values found in **4**. The Fe–P(1) distance



Scheme 3.

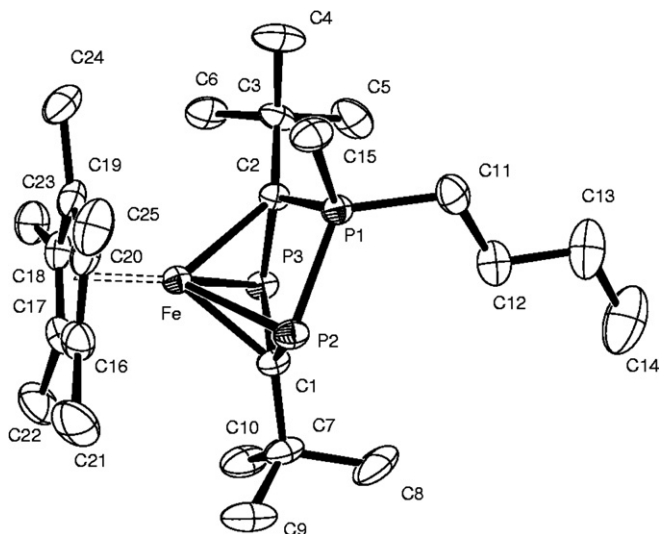


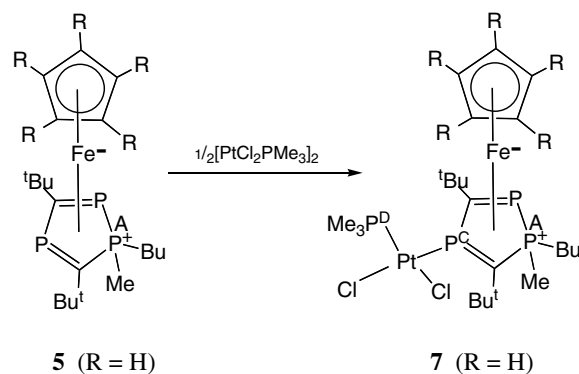
Fig. 2. Molecular structure of $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2'\text{Bu}_2\text{P}'\text{BuMe})(\eta^5\text{-C}_5\text{Me}_5)]$ (**6**). Selected bond distances (Å) and angles ($^\circ$): P(1)–C(2) 1.765(3), P(1)–C(11) 1.832(3), P(1)–C(15) 1.815(3), P(2)–P(1) 2.1253(10), P(2)–C(1) 1.794(3), C(1)–P(3) 1.767(3), P(3)–C(2) 1.790(3), Fe–P(2) 2.3003(8), Fe–C(1) 2.107(3), Fe–P(3) 2.2652(9), Fe–C(2) 2.210(3), Fe–M(1) 1.716(3). P(2)–P(1)–C(2) 97.57(9), C(15)–P(1)–C(11) 100.77(15), C(11)–P(1)–P(2) 117.93(11), C(15)–P(1)–P(2) 106.99(11), C(2)–P(1)–C(11) 119.48(14), C(15)–P(1)–C(2) 114.23(14), P(1)–C(2)–P(3) 114.64(15), C(2)–P(3)–C(1) 98.27(13), P(3)–C(1)–P(2) 120.23(16), C(1)–P(2)–P(1) 94.62(10).

in **6** (2.839 Å) lies outside of the usual range of Fe–P bond distances, but is shorter than the corresponding Fe–P(1) distance in **4** by 0.268 Å, which perhaps might indicate an electrostatic interaction between the quaternary P(1) and the negative charge of the iron centre.

The structure of **5** was also confirmed by a single crystal X-ray experiment on its Pt(II) adduct *cis*-[PtCl₂(PMe₃)₂]{Fe(η⁴-P₂C_{2'}Bu₂PBuMe)(η⁵-C₅H₅)} **7**, which was obtained by treatment of **5** with half an equivalent of [(PtCl₂(PMe₃)₂)]₂ in CHCl₃ at room temperature (see Scheme 4).

The structure of the complex *cis*-[PtCl₂(PMe₃)₂]{Fe(η⁴-P₂C_{2'}Bu₂PBuMe)(η⁵-C₅H₅)} **7** in solution was established by multi-nuclear NMR spectroscopy. The ³¹P{¹H} NMR spectrum of **7** showed the expected four distinct phosphorus environments. The quaternary P_A gave rise to a doublet of doublets at –187.6 ppm, with a large coupling to the adjacent P_B (290.3 Hz) and a small coupling to the P_C (40.1 Hz). P_B exhibited a doublet of doublets of doublets with the same large coupling (290.3 Hz) and a small coupling to the P_C atom (6.9 Hz) as well as an observable smaller four bond coupling (3.1 Hz) with the P^D of the *cis*-PMe₃ ligand. P_C gave an eight-line multiplet with the expected large ¹⁹⁵Pt satellites. The 8-line pattern is attributed to coupling of the P_C atom to the quaternary P_A (40.2 Hz); coupling to P_B (6.9 Hz) and coupling to P_D (28.7 Hz). The P_D resonance gave rise to a doublet of doublets with the expected ¹⁹⁵Pt satellites.

Confirmation of the above assignments came from the ¹⁹⁵Pt{¹H} NMR spectrum of **7** which showed a doublet of doublets of doublets at –4436.8 ppm with large splitting of 3561 and 3868 Hz, corresponding to coupling to P_D and



Scheme 4.

P_C, respectively, and further small splitting (25.7 Hz) by coupling to P_B. The observation that both ¹J(PtP) coupling constants in **7** are greater than 3000 Hz and ²J(P_CP_D) coupling is very small suggests that the square planar complex has a *cis*-configuration. The ³¹P{¹H} NMR data for **7** are given in Table 3.

The ¹H NMR spectrum of **7** showed two singlets at 1.38 and 1.17 of equal intensity for the non-equivalent ^tBu groups, while the five protons of η⁵-C₅H₅ exhibited a singlet at 4.45 ppm. The Me group attached to the quaternary P_A showed a doublet of doublets at 2.08 ppm, with a coupling to the quaternary P_A (10.59 Hz) in the range expected and a small coupling to P_B (6.4 Hz). The resonance of the PMe₃ protons exhibited a doublet at 1.90 ppm, (²J(PCH) = 11.7 Hz), together with ¹⁹⁵Pt satellites. The FAB mass spectrum of **7** showed a peak at *m/e* 766 (55%) for the ion [PtCl₂(PMe₃)₂]{Fe(P₂C_{2'}Bu₂PBuMe)(C₅H₅)} ⁺.

The molecular structure of **7** was determined by a single crystal X-ray diffraction study and is shown in Fig. 3. As

Table 3

³¹P{¹H} NMR data (CDCl₃, 25 °C) for **7** (chemical shifts in ppm and coupling constants in Hz)

(7, R = H)			
δP _A	–187.5	² J(P _C P _D)	28.6
δP _B	56.8	¹ J(P _D Pt)	3561
δP _C	62.3	¹ J(P _C Pt)	3868
δP _D	–19.4	³ J(P _B Pt)	25.7
¹ J(P _A P _B)	290.2	² J(P _A H _{Me})	10.6
² J(P _A P _C)	40.1	³ J(P _B H _{Me})	6.4
² J(P _B P _C)	6.9	² J(P _D H _{PMe})	11.7
⁴ J(P _B P _D)	3.1		

anticipated, the Pt(II) centre is co-ordinated to P_C and with a *cis*-geometry of the two chlorine atoms, in agreement with both the ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR spectra. The platinum is in a pseudo square-planar environment, with the Pt–P and Pt–Cl bond lengths in **7** being very similar to those found for **3**. The C(1), P(2), C(2) and P(3) centres form a four co-ordinate, four electron donor to the Fe centre. The mean Fe–P, Fe–C, P–C and P–P bond distances are very similar to their counterparts in **3**. Although the Fe–P(1) distance of 2.878 Å lies outside the normal range of Fe–P bond lengths, an electrostatic interaction between the quaternary P(1) and the negative charge on the iron centre cannot be precluded.

3. Conclusions

Treatment of the tri-phosphaferrocenes [Fe(η⁵-P₃C₂^tBu₂)(η⁵-C₅R₅)] (R = H **1**; Me **2**) with 1 equiv. of ⁿBuLi in hexane at room temperature gave, respectively, LiFe(η⁴-P₂C₂^tBu₂PⁿBu)(η⁵-C₅R₅) (R = H **3**; R = Me **4**) *via* exclusive nucleophilic attack of the n-butyl anion at one of the phosphorus atoms of the adjacent pair in the P₃C₂^tBu₂ ring. The solid-state structure of the lithium salt is an unusual dimer. The neutral zwitterionic compounds Fe(η⁴-P₂C₂^tBu₂PⁿBuMe)(η⁵-C₅R₅), which are formed

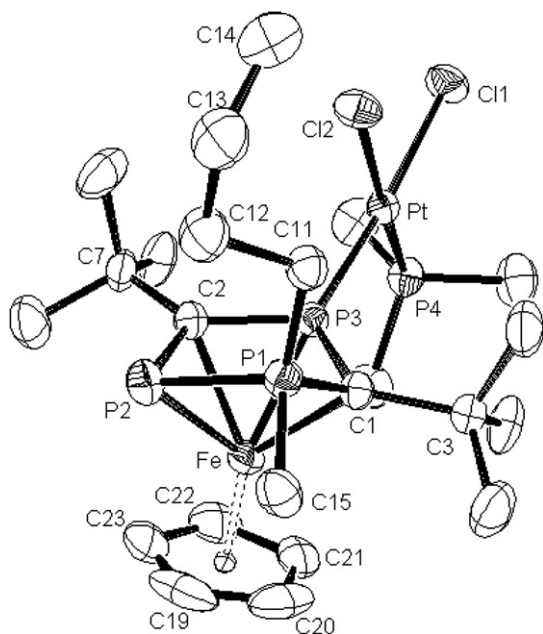


Fig. 3. Molecular structure of *cis*-[PtCl₂(PMe₃)](Fe(η⁴-P₂C₂^tBu₂PⁿBuMe)(η⁵-C₅H₅)) (**7**). Selected bond distances (Å) and angles (°): P(1)–C(1) 1.761(6), P(1)–C(11) 1.824(6), P(1)–C(15) 1.809(6), P(1)–P(2) 2.140(2), P(2)–C(2) 1.762(6), C(2)–P(3) 1.757(5), P(3)–C(1) 1.780(5), Fe–C(1) 2.155(5), Fe–C(2) 2.098(6), Fe–P(2) 2.3196(18), Fe–P(3) 2.1899(16), Fe–M(1) 1.701(6), Pt–P(4) 2.2380(15), Pt–P(3) 2.2434(15), Pt–Cl(1) 2.3628(15), Pt–Cl(2) 2.36743(14), C(1)–P(1)–P(2) 96.09(18), C(11)–P(1)–C(15) 104.9(3), P(1)–P(2)–C(2) 95.57(18), P(2)–C(2)–P(3) 117.9(3), C(2)–P(3)–C(1) 100.5(3), P(3)–C(1)–P(1) 111.8(3), P(3)–Pt–P(4) 100.32(6), P(3)–Pt–Cl(1) 173.74(5), P(3)–Pt–Cl(2) 85.34(5), P(4)–Pt–Cl(1) 85.65(6), P(4)–Pt–Cl(2) 173.98(6).

from the lithium salts by treatment with MeI, can act as ligands towards Pt(II) centres.

4. Experimental

Many of the compounds are air- and/or moisture-sensitive and all manipulations were carried out under rigorously anhydrous and oxygen-free conditions using standard high vacuum Schlenk line techniques or in an inert atmosphere. Glassware and Schlenk tubes were flame dried before used. THF and hexane were pre-dried over a sodium wire and distilled over sodium-potassium alloy under a blanket of dry dinitrogen before use. Chloroform and dichloromethane were dried over calcium hydride before distillation under dinitrogen. NMR solvents were purified by refluxing over a suitable drying agent, and vacuum-transferred into ampoules.

³¹P and ¹H NMR spectra were acquired on a Bruker Avance 300DPX spectrometer operating at 300 MHz for ¹H measurements, and 121.49 MHz for ³¹P measurements. ¹H NMR spectra are referenced to the residual proton chemical shift of the internal deuterated solvent (which in turn is referenced to TMS). ³¹P NMR spectra are referenced to H₃PO₄ (87% H₃PO₄ in D₂O as an external standard). All spectra were recorded at room temperature. Mass spectra (EI and FAB) were recorded by Dr. A. Abdul-Sada at the University of Sussex. Single crystal X-ray diffraction studies were carried out using the Enraf Nonius KAPPACCD diffractometer.

The following compounds were prepared according to literature procedures: [Fe(η⁶-C₆H₅-Me)(η⁵-C₅H₅)](PF₆), [Fe(η⁵-P₃C₂^tBu₂)(η⁵-C₅H₅)], [Fe(η⁵-P₃C₂^tBu₂)(η⁵-C₅Me₅)] [29–31], [{PtCl₂(PMe₃)₂]₂ [32,33].

4.1. Synthesis of LiFe(η⁴-P₂C₂^tBu₂PⁿBu)(η⁵-C₅H₅) (**3**)

A solution of [Fe(η⁵-P₃C₂^tBu₂)(η⁵-C₅H₅)] (0.40 g, 1.13 mmol) and ⁿBuLi (0.072 g, 1.13 mmol) was stirred overnight in hexane (15 ml) at room temperature. A powdery precipitate was obtained which was filtered off and washed with hexane (5 ml) and dried *in vacuo* to give LiFe(η⁴-P₃C₂^tBu₂)(η⁵-C₅H₅) as a beige powder (0.28 g, 60%).

³¹P{¹H} NMR (121.49 MHz) (C₅D₅N, 25 °C): δP_A = –157.2 (dd, ¹J(P_AP_B) = 263.6 Hz, ²J(P_AP_C) = 31.5 Hz), δP_B = 34.5 (dd, ²J(P_BP_C) = 32.8 Hz), δP_C = –49.1 (dd). ¹H (300 MHz): δH(^tBu) = 1.79 (s, 9H), δH(ⁿBu) = 1.53 (s, 9H), δH(C₅H₅) = 4.48 (s, 5H) ppm.

4.2. Synthesis of LiFe(η⁴-P₂C₂^tBu₂PⁿBu)(η⁵-C₅Me₅) (**4**)

A solution of [Fe(η⁵-P₃C₂^tBu₂)(η⁵-C₅R₅)] (0.30 g, 0.71 mmol) and ⁿBuLi (0.045 g, 0.71 mmol) was stirred overnight in hexane (15 ml) at room temperature. A powdery precipitate was obtained, which was filtered off and washed with hexane (5 ml) and dried *in vacuo* to afford a pinkish-brown powder (0.24 g, 70%).

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz) ($\text{C}_5\text{D}_5\text{N}$, 25 °C): $\delta\text{P}_\text{A} = -140.9$ (dd, $^1J(\text{P}_\text{A}\text{P}_\text{B}) = 265.95$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{C}) = 33.27$ Hz), $\delta\text{P}_\text{B} = 34.3$ (dd, $^2J(\text{P}_\text{B}\text{P}_\text{C}) = 33.28$ Hz), $\delta\text{P}_\text{C} = -44.1$ (dd). ^1H NMR (300 MHz): $\delta\text{H}(\text{tBu}) = 1.72$ (s, 9H), $\delta\text{H}(\text{tBu}) = 1.91$ (s, 9H), $\delta\text{H}(\text{Me}) = 2.23$ (s, 15H) ppm.

Crystal data for **4**: $\text{C}_{48}\text{H}_{84}\text{Fe}_2\text{Li}_2\text{P}_6$, $M = 972.55$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.1069(3)$, $b = 22.4884(8)$, $c = 12.6230(4)$ Å, $\beta = 91.078(2)$, $V = 2584.73(15)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 1.25$ Mg m⁻³, $\mu = 0.78$ mm⁻¹, $\lambda = 0.71073$ Å, $F(000) = 1040$, crystal size $0.15 \times 0.10 \times 0.10$ mm, 14,821 measured reflections, 3567 independent reflections ($R_{\text{int}} = 0.063$), 3007 reflections with $I > 2\sigma(I)$, final indices $R_1 = 0.036$, $wR_2 = 0.077$ for $I > 2\sigma(I)$, $R_1 = 0.048$, $wR_2 = 0.082$ for all data. Data collection: KappaCCD. Program package WINGX. Refinement using SHELXL-97.

4.3. Synthesis of $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBuMe})(\eta^5\text{-C}_5\text{H}_5)]$ (**5**)

A solution of $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-C}_5\text{H}_5)]$ (0.40 g, 1.13 mmol) in hexane (10 ml) and $^n\text{BuLi}$ (0.072 g, 1.13 mmol) in hexane was stirred overnight at room temperature. $[\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBu})(\eta^5\text{-C}_5\text{H}_5)]$ was obtained as a beige powder after the solution was filtered off. The resulting powder was dissolved in THF (10 ml), MeI (0.16 g, 1.13 mmol) was added, the mixture was stirred overnight, solvent was then removed and the product was extracted with hexane. $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBuMe})(\eta^5\text{-C}_5\text{H}_5)]$ was obtained as an oil and could not be crystallised.

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz) (C_6D_6 , 25 °C), $\delta\text{P}_\text{A} = -175.2$ (dd, $^1J(\text{P}_\text{A}\text{P}_\text{B}) = 312.5$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{C}) = 30.4$ Hz) $\delta\text{P}_\text{B} = 44.4$ (dd, $^2J(\text{P}_\text{B}\text{P}_\text{C}) = 20.7$ Hz), $\delta\text{P}_\text{C} = -14.8$ (dd). ^1H NMR (300 MHz): $\delta\text{H}(\text{tBu}) = 1.02$ (9H), $\delta\text{H}(\text{tBu}) = 1.48$ (s, 9H), $\delta\text{H}(\text{C}_5\text{H}_5) = 4.38$ (s, 5H), $\delta\text{H}(\text{Me}) = 1.74$ ppm. MS (EI), m/z : 424 (35%, $[\text{M}]^+$), 367 (100%, $[\text{M}-\text{Bu}]^+$).

4.4. Synthesis of $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{Me}_5)]$ (**6**)

A solution of $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^5\text{-C}_5\text{Me}_5)]$ (0.30 g, 0.71 mmol) in hexane (10 ml) and BuLi (0.045 g, 0.71 mmol) in hexane was stirred overnight at room temperature. $[\text{LiFe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBu})(\eta^5\text{-C}_5\text{Me}_5)]$ was obtained as a beige powder after the solution was filtered off. The resulting powder was dissolved in THF (10 ml), MeI (0.1 g, 0.71 mmol) was added, the mixture was stirred overnight, solvent was then removed and the product was extracted with hexane. $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{H}_5)]$ was crystallized from hexane at -35 °C to afford dark red crystals. (m.p. 150 °C, 0.14 g, 40%). $\text{C}_{25}\text{H}_{45}\text{P}_3\text{Fe}$ requires: C, 60.74; H, 9.17. Found: C, 60.74; H, 9.54%.

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz) (C_6D_6 , 25 °C): $\delta\text{P}_\text{A} = -161.0$ (dd, $^1J(\text{P}_\text{A}\text{P}_\text{B}) = 317$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{C}) = 33$ Hz), $\delta\text{P}_\text{B} = 47.16$ (dd, $^2J(\text{P}_\text{B}\text{P}_\text{C}) = 22$ Hz), $\delta\text{P}_\text{C} = 3.69$ (dd). ^1H NMR (300 MHz): $\delta\text{H}(\text{tBu}) = 1.61$ (s, 9H), $\delta\text{H}(\text{tBu}) = 1.18$ (s, 9H), $\delta\text{H}(\text{Cp}^*) = 1.88$ (s, 15H), $\delta\text{H}(\text{Me}) = 1.75$ ppm (dd,

$^2J(\text{P}_\text{A}\text{H}_{\text{Me}}) = 10.8$ Hz, $^3J(\text{P}_\text{B}\text{H}_{\text{Me}}) = 5.51$ Hz). MS (EI), m/z : 494 (80%, M^+), 437 (100%, $[\text{M}-\text{Bu}]^+$).

Crystal data for **6**: $\text{C}_{25}\text{H}_{45}\text{FeP}_3$, $M = 494.37$, monoclinic, space group $C2/c$, $a = 20.2376(3)$, $b = 18.2117(3)$, $c = 15.6793(3)$ Å, $\beta = 112.459(1)$, $V = 5340.48(16)$ Å³, $T = 173(2)$ K, $Z = 8$, $D_c = 1.23$ Mg m⁻³, $\mu = 0.75$ mm⁻¹, $\lambda = 0.71073$ Å, $F(000) = 2128$, crystal size $0.40 \times 0.30 \times 0.15$ mm, 32,337 measured reflections, 5036 independent reflections ($R_{\text{int}} = 0.084$), 3563 reflections with $I > 2\sigma(I)$, final indices $R_1 = 0.047$, $wR_2 = 0.082$ for $I > 2\sigma(I)$, $R_1 = 0.085$, $wR_2 = 0.093$ for all data. Data collection: KappaCCD. Program package WINGX. Refinement using SHELXL-97.

4.5. Synthesis of $[\text{PtCl}_2(\text{PMe}_3)\{\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{H}_5)\}]$ (**7**)

A mixture of $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{P}^n\text{BuMe})(\eta^5\text{-C}_5\text{H}_5)]$ (0.2 g, 0.47 mmol) and $[\{\text{PtCl}_2\text{PMe}_3\}_2]$ (0.16 g, 0.24 mmol) in CHCl_3 (10 ml) was stirred at room temperature overnight. $[\text{PtCl}_2(\text{PMe}_3)\{\text{Fe}(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2\text{PBuMe})(\eta^5\text{-C}_5\text{H}_5)\}]$ was obtained as a pale orange powder after removing the solvent *in vacuo* and washing with hexane. The product could be crystallised from a mixture of CH_2Cl_2 and hexane at -35 °C to afford dark red crystals (m.p. 157 °C, 0.18 g, 50%). $\text{C}_{24}\text{H}_{46}\text{P}_4\text{Cl}_4\text{FePt}$ requires: C, 33.86; H, 5.45. Found: C, 33.04; H, 5.34%.

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz) (CDCl_3 , 25 °C): $\delta\text{P}_\text{A} = -187.6$ (dd, $^1J(\text{P}_\text{A}\text{P}_\text{B}) = 290.2$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{C}) = 40.1$ Hz), $\delta\text{P}_\text{B} = 56.87$ (ddd, $^2J(\text{P}_\text{B}\text{P}_\text{C}) = 6.9$ Hz, $^4J(\text{P}_\text{B}\text{P}_\text{D}) = 3.1$ Hz), $\delta\text{P}_\text{C} = 62.3$ (ddd, $^2J(\text{P}_\text{C}\text{P}_\text{D}) = 28.6$ Hz), $\text{P}_\text{D} = -19.5$. $^{195}\text{Pt}\{^1\text{H}\}$ (107.35 MHz):

$\delta\text{Pt} = -4436.8$ (ddd, $^1J(\text{P}_\text{D}\text{Pt}) = 3560.6$ Hz, $^1J(\text{P}_\text{C}\text{Pt}) = 3867.6$ Hz, $^3J(\text{P}_\text{B}\text{Pt}) = 25.7$ Hz). ^1H NMR (300 MHz): $\delta\text{H}(\text{tBu}) = 1.38$ (s, 9H), $\delta\text{H}(\text{tBu}) = 1.17$ (s, 9H), $\delta\text{H}(\text{C}_5\text{H}_5) = 4.45$ (s, 5H), $\delta\text{H}(\text{PMe}_3) = 1.9$ (d, $^2J(\text{HP}_\text{D}) = 11.7$ Hz), $\delta\text{H}(\text{Me}) = 2.08$ (dd, $^2J(\text{HP}_\text{A}) = 10.6$ Hz, $^3J(\text{HP}_\text{B}) = 6.4$ Hz) ppm. MS (EI), m/z : 766 (45%, $[\text{M}]^+$).

Crystal data for **7**: $\text{C}_{23}\text{H}_{44}\text{Cl}_{12}\text{FeP}_4\text{Pt} \cdot \text{CH}_2\text{Cl}_2$, $M = 851.23$, monoclinic, space group $P2_1/c$, $a = 16.2862(6)$, $b = 11.7011(6)$, $c = 19.0319(7)$ Å, $\beta = 112.540(2)$, $V = 3349.8(2)$ Å³, $T = 173(2)$ K, $Z = 4$, $D_c = 1.69$ Mg m⁻³, $\mu = 5.13$ mm⁻¹, $\lambda = 0.71073$ Å, $F(000) = 1688$, crystal size $0.4 \times 0.2 \times 0.1$ mm, 18,237 measured reflections, 7939 independent reflections ($R_{\text{int}} = 0.055$), 6406 reflections with $I > 2\sigma(I)$, Final indices $R_1 = 0.043$, $wR_2 = 0.098$ for $I > 2\sigma(I)$, $R_1 = 0.060$, $wR_2 = 0.107$ for all data. Data collection: KappaCCD. Program package WINGX. Refinement using SHELXL-97. There is a poorly defined molecule of dichloromethane solvate for which two alternative orientations were refined with distance constraints (SADI).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.062](https://doi.org/10.1016/j.jorganchem.2007.11.062).

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