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Photochemical replacement of benzene in the tetramethylcyclopentadienyl complex of iron, $[(\eta\text{-}C_5Me_4H)Fe(\eta\text{-}C_6H_6)]^+$

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Irradiation of the cation $[(\eta\text{-}C_5Me_4H)Fe(\eta\text{-}C_6H_6)]^+$ (**1**) and Bu^tNC with visible light in acetonitrile results in the displacement of the benzene ligand, giving $[(\eta\text{-}C_5Me_4H)Fe(Bu^tNC)_3]^+$ (**2**). Reactions of complex **1** with $P(OR)_3$ and dppe in MeCN yield the complexes $[(\eta\text{-}C_5Me_4H)Fe(MeCN)\{P(OR)_3\}_2]^+$ (R = Me (**3**) and Et (**4**)) and $[(\eta\text{-}C_5Me_4H)Fe(MeCN)(dppe)]^+$ (**5**) containing two Fe—P bonds. The same reactions in CH_2Cl_2 give the tris(phosphite) complexes $[(\eta\text{-}C_5Me_4H)Fe\{P(OR)_3\}_3]^+$ (**6**, **7**). A photochemical reaction of complex **1** with pentaphosphaferrocene $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$ yields the triple-decker cation $[(\eta\text{-}C_5Me_4H)Fe(\mu\text{-}\eta:\eta\text{-}cyclo\text{-}P_5)FeCp^*]^+$ (**8**) with a bridging pentaphospholyl ligand. Structures $[\mathbf{2}]PF_6$ and $[\mathbf{3}]PF_6$ were identified by X-ray diffraction.

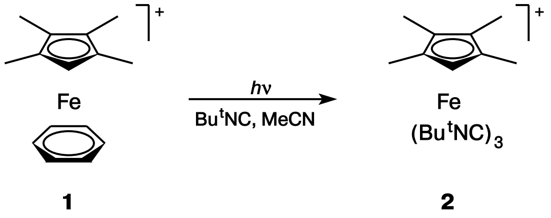
Key words: iron, sandwich compounds, triple-decker complexes.

It is known that the cationic iron complex $[CpFe(\eta\text{-}C_6H_6)]^+$ exchanges its benzene for other ligands upon irradiation with visible light.[1—4] This reaction was used to obtain a great number of organometallic compounds (*e.g.*, sandwich and triple-decker complexes) containing the fragment CpFe.[5—10] Unfortunately, this method is unsuitable for the pentamethylated analog $[Cp^*Fe(\eta\text{-}C_6H_6)]^+$,[11] which is probably due to the electronic and steric effects of five methyl groups. The present study deals with photochemical reactions of the tetramethylcyclopentadienyl complex of iron, $[(\eta\text{-}C_5Me_4H)Fe(\eta\text{-}C_6H_6)]^+$.

Results and Discussion

The electronic properties of the tetramethylcyclopentadienyl ligand (C_5Me_4H) are similar to those of pentamethylcyclopentadienyl. However, lack of one methyl group considerably reduces its steric volume in complexes with transition metals. A comparative study reveals that the cation $[(\eta\text{-}C_5Me_4H)Fe(\eta\text{-}C_6H_6)]^+$ (**1**) reacts with Bu^tNC in acetonitrile under irradiation with visible light at a rate of about three times higher than that for the pentamethylated analog $[Cp^*Fe(\eta\text{-}C_6H_6)]^+$. Starting from cation **1**, we obtained the tris(isocyanide) complex $[(\eta\text{-}C_5Me_4H)Fe(Bu^tNC)_3]^+$ (**2**) (Scheme 1);* the 83% conversion was achieved after 20 h.

Scheme 1



Reactions of cation **1** with phosphites $P(OR)_3$ (R = Me, Et) in MeCN afford the bis(phosphite) complexes $[(\eta\text{-}C_5Me_4H)Fe(MeCN)\{P(OR)_3\}_2]^+$ (**3**, **4**) containing coordinated acetonitrile (Scheme 2). A similar reaction with $Ph_2P(CH_2)_2PPh_2$ (dppe) gives the cation $[(\eta\text{-}C_5Me_4H)Fe(MeCN)(dppe)]^+$ (**5**). Earlier,[3] the same pattern has been observed in reactions of the unsubstituted complex $[CpFe(\eta\text{-}C_6H_6)]^+$ with phosphines and phosphites. However, our recent investigations[12] have shown that the cyclohexadienyl complex $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ reacts with $P(OR)_3$ in acetonitrile to give the tris(phosphite) cations $[(\eta^5\text{-}C_6H_7)Fe\{P(OR)_3\}_3]^+$. The observed differences are probably associated with the higher lability of the Fe—N bond in the complex $[(\eta^5\text{-}C_6H_7)Fe(MeCN)\{P(OR)_3\}_2]^+$ compared to complexes **3**—**5**. Nevertheless, the tris(phosphite) complexes $[(\eta\text{-}C_5Me_4H)Fe\{P(OR)_3\}_3]^+$ (**6**, **7**) were obtained in CH_2Cl_2, which is a poorly coordinating ligand (Scheme 3).

Earlier,[6] it has been demonstrated that irradiation of the complex $[CpFe(\eta\text{-}C_6H_6)]^+$ with visible light in the

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* All the cationic complexes obtained were isolated as salts with the anion PF_6^- (the anions are omitted from the schemes).

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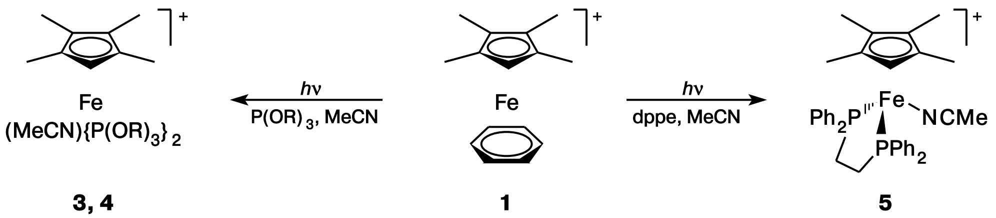
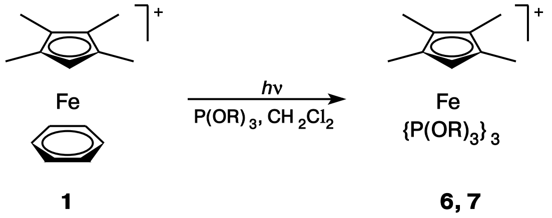
Scheme 2



R = Me (**3**), Et (**4**)

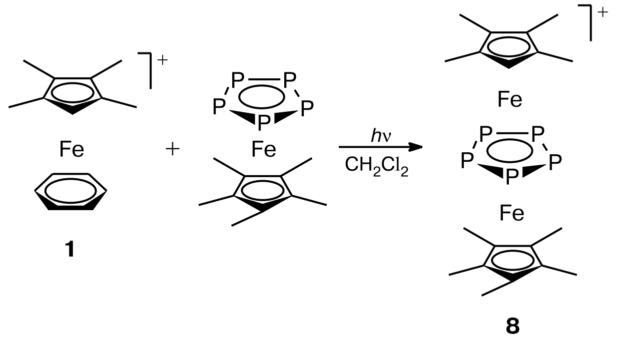
Scheme 3



R = Me (**6**), Et (**7**)

presence of pentaphosphaferrocene Cp*Fe(η-*cyclo*-P_5) gives the triple-decker cation [CpFe(μ-η:η-*cyclo*-P_5)-FeCp*]$^+$ with a bridging pentaphospholyl ligand. Using complex **1** in a similar reaction with Cp*Fe(η-*cyclo*-P_5) in CH_2Cl_2, we obtained the triple-decker cation [(η-C_5Me_4H)Fe(μ-η:η-*cyclo*-P_5)FeCp*]$^+$ (**8**) (Scheme 4). It should be noted that the synthesis of the related decamethylated complex [Cp*Fe(μ-η:η-*cyclo*-P_5)FeCp*]$^+$ involves the acetonitrile derivative [Cp*Fe(MeCN)$_3$]$^+$ (see Ref. 13), which is not easily accessible but is more reactive than the corresponding benzene complex.[9,14,15]

Scheme 4



The structures of the complexes [**2**]PF_6 and [**3**]PF_6 were examined by X-ray diffraction. The structures of cations **2** and **3** are shown in Figs 1 and 2; selected bond lengths are given in Tables 1 and 2. The distance Fe...C_5Me_4H in cation **3** (1.730 Å) is close to the corresponding distance in the neutral complex (η-C_5Me_4H)-Fe(CO)(PPh_3)I (1.737 Å),[16] while in tris(isocyanide) complex **2**, this distance is somewhat shorter (1.713 Å). The Fe—C(Bu^tNC) bonds in cation **2** (on average, 1.838 Å) are shorter than those in the related complexes [(η^5-C_6H_7)-Fe(Bu^tNC)$_3$]$^+$ (on average, 1.854 Å)[17] and [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)Fe(Bu^tNC)$_3$]$^+$ (on average, 1.847 Å).[18] The bonds Fe—P (on average, 2.154 Å) and Fe—N (1.912 Å) in cation **3** are also shorter than those in [CpFe(MeCN){P(OMe)$_3$}$_2$]$^+$ (on average, Fe—P, 2.179 Å; Fe—N, 1.924 Å).[19] The stronger coordination of the σ-ligands to the Fe atom in the tetramethylcyclopenta-

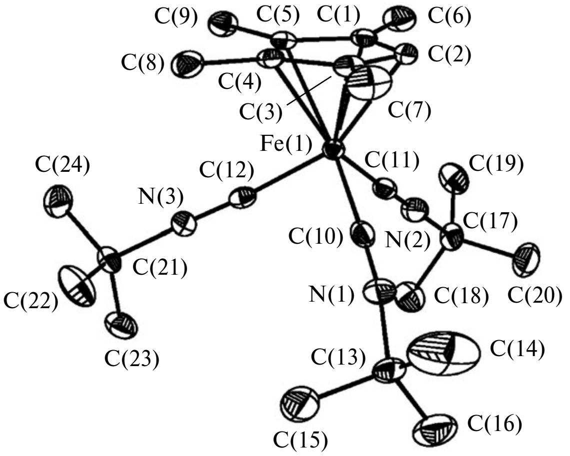


Fig. 1. Structure of cation **2** with atomic thermal displacement ellipsoids (p = 50%). The hydrogen atoms are omitted.

Table 1. Selected bond lengths (d) in cation **2**

Bond	d/Å	Bond	d/Å
Fe(1)—C(1)	2.101(2)	Fe(1)—C(11)	1.841(2)
Fe(1)—C(2)	2.082(2)	Fe(1)—C(12)	1.836(2)
Fe(1)—C(3)	2.105(2)	C(10)—N(1)	1.161(3)
Fe(1)—C(4)	2.095(2)	C(11)—N(2)	1.158(3)
Fe(1)—C(5)	2.100(2)	C(12)—N(3)	1.161(3)
Fe(1)—C(10)	1.837(2)		

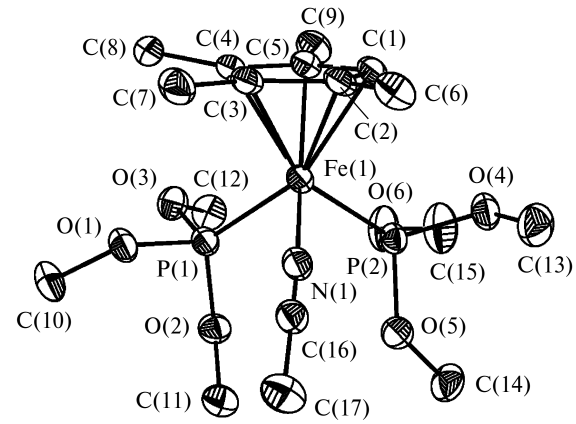


Fig. 2. Structure of cation **3** with atomic thermal displacement ellipsoids (*p* = 50%). The hydrogen atoms are omitted.

Table 2. Selected bond lengths (*d*) in cation **3**

Bond	*d*/Å	Bond	*d*/Å
Fe(1)—C(1)	2.097(2)	Fe(1)—N(1)	1.912(2)
Fe(1)—C(2)	2.120(3)	Fe(1)—P(1)	2.1516(8)
Fe(1)—C(3)	2.118(3)	Fe(1)—P(2)	2.1553(7)
Fe(1)—C(4)	2.134(3)	C(16)—N(1)	1.126(3)
Fe(1)—C(5)	2.102(3)		

dienyl complexes is probably due to the stronger electron-donating properties of the C_5Me_4H ligand compared to Cp, C_6H_7, and 9-SMe_2-7,8-$C_2B_9H_{10}$.

Thus, we discovered that complex **1** can exchange its benzene molecule for other ligands when exposed to visible light, which makes this complex a convenient synthetic equivalent of the cation $[(\eta\text{-}C_5Me_4H)Fe]^+$.

Experimental

Reactions were carried out under argon in dry solvents prepared according to standard procedures. Reaction products were isolated in air. The starting complex Cp*Fe(η-*cyclo*-P_5) was prepared as described earlier.[9] The complex $[(\eta\text{-}C_5Me_4H)Fe(CO)_2]_2$ was synthesized by analogy with $[Cp^*Fe(CO)_2]_2$; octane was used as a solvent instead of 2,2,5-trimethylhexane.[20] Irradiation was carried out in a Schlenk tube 15 mm in diameter with mercury luminescent lamps (total power 650 W) at 5—10 °C. The Schlenk tube and the lamps were immersed in an appropriate vessel lined with aluminum foil and cooled with running water. ^1H and ^{31}P NMR spectra were recorded on a Bruker Avance-400 instrument (400.13 and 161.98 MHz, respectively).

[(η-Tetramethylcyclopentadienyl)(η-benzene)iron] hexafluorophosphate, $[(\eta\text{-}C_5Me_4H)Fe(\eta\text{-}C_6H_6)]PF_6$ ([1]PF_6). A solution of Br_2 (0.6 g, 3.8 mmol) in CH_2Cl_2 was added dropwise to a solution of $[(\eta\text{-}C_5Me_4H)Fe(CO)_2]_2$ (1.7 g, 3.6 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1 h and concentrated. Dry $AlCl_3$ (5 g, 37.5 mmol) and benzene (20 mL) were added to the residue. The reaction mixture was stirred at room temperature for 16 h and then refluxed for 5 h. On cooling to 0 °C, it was carefully hydrolyzed with water. The aqueous layer was separated and filtered. The product was precipitated by adding aqueous NH_4PF_6. The resulting yellow precipitate was filtered off, washed with water, and dried *in vacuo*. The crude product was reprecipitated from acetone with ether to give the complex [**1**]PF_6 (2.65 g, 91%) as a yellow solid. Found (%): C, 44.74; H, 4.53. $C_{15}H_{19}F_6FeP$. Calculated (%): C, 45.03; H, 4.79. ^1H NMR (acetone-d_6), δ: 2.01 (s, 6 H, $C_5\underline{Me_4}H$); 2.02 (s, 6 H, $C_5\underline{Me_4}H$); 5.00 (s, 1 H, $C_5Me_4\underline{H}$); 6.17 (s, 6 H, C_6H_6).

[(η-Tetramethylcyclopentadienyl)tris(*tert*-butyl isocyanide)-iron] hexafluorophosphate, $[(\eta\text{-}C_5Me_4H)Fe(Bu^tNC)_3]PF_6$ ([2]PF_6). A solution of the complex [**1**]PF_6 (150 mg, 0.37 mmol) and Bu^tNC (0.3 mL) in acetonitrile (10 mL) was irradiated for 24 h. The solvent was removed *in vacuo*. The residue was dissolved in a small amount (2—3 mL) of CH_2Cl_2 and separated by column chromatography (column 10×1 cm, Al_2O_3). The collected yellow fraction was concentrated to ~2 mL and diluted successively with ether (10 mL) and light petroleum (10 mL). The resulting precipitate was filtered off, washed with ether, and dried *in vacuo* to give the complex [**2**]PF_6 (75 mg, 35%) as a yellow solid. Found (%): C, 50.35; H, 7.13; N, 7.31. $C_{24}H_{40}F_6FeN_3P$. Calculated (%): C, 50.45; H, 7.06; N. 7.35. ^1H NMR (acetone-d_6), δ: 1.55 (s, 27 H, Bu^t); 1.82 (s, 6 H, $C_5\underline{Me_4}H$); 1.84 (s, 6 H, $C_5\underline{Me_4}H$); 4.41 (s, 1 H, $C_5Me_4\underline{H}$).

Comparative study of the photochemical exchange of benzene for Bu^tNC in the complexes [1]PF_6 and $[Cp^*Fe(\eta\text{-}C_6H_6)]PF_6$. A mixture of [**1**]$PF_6$ (20 mg, 0.05 mmol), $[Cp^*Fe(\eta\text{-}C_6H_6)]PF_6$ (21 mg, 0.05 mmol), and Bu^tNC (0.2 mL) was dissolved in acetonitrile (2 mL). The resulting solution was irradiated for 10 h. The solvent was removed *in vacuo* and the residue was reprecipitated from acetone with light petroleum. The yellow precipitate (42 mg) was dissolved in acetone-d_6. According to ^1H NMR data, the conversion was 75% for [**1**]PF_6 and 25% for $[Cp^*Fe(\eta\text{-}C_6H_6)]PF_6$. $\underline{[Cp^*Fe(Bu^tNC)_3]PF_6}$. ^1H NMR (acetone-d_6), δ: 1.55 (s, 27 H, Bu^t); 1.82 (s, 15 H, Cp*).

[(η-Tetramethylcyclopentadienyl)(acetonitrile)bis(trialkyl phosphite)iron] hexafluorophosphate, $[(\eta\text{-}C_5Me_4H)Fe(MeCN)\{P(OR)_3\}_2]PF_6$ ([3]PF_6 and [4]PF_6). A solution of the complex [**1**]PF_6 (150 mg, 0.37 mmol) and $P(OR)_3$ (0.2 mL) in acetonitrile (10 mL) was irradiated for 20 h. The products were isolated as described for the complex [**2**]PF_6.

Complex [**3**]PF_6 (R = Me), yield 151 mg (66%), orange solid. Found (%): C, 33.20; H, 5.62; N, 2.21. $C_{17}H_{34}F_6FeNO_6P_3$. Calculated (%): C, 33.40; H, 5.61; N. 2.29. ^1H NMR (acetone-d_6), δ: 1.51 (s, 6 H, $C_5\underline{Me_4}H$); 1.71 (s, 6 H, $C_5\underline{Me_4}H$); 2.56 (s, 3 H, MeCN); 3.80 (t, 18 H, $P(OMe)_3$, $J_{H,P}$ = 5 Hz); 4.38 (s, 1 H, $C_5Me_4\underline{H}$). ^{31}P NMR (acetone-d_6), δ: −144.3 (sept, 1 P, PF_6^-, $J_{P,F}$ = 707 Hz); 175.6 (s, 2 P, $P(OMe)_3$).

Complex [**4**]PF_6 (R = Et), yield 57 mg (22%), orange solid. Found (%): C, 39.71; H, 6.76; N, 1.96. $C_{23}H_{46}F_6FeNO_6P_3$. Calculated (%): C, 39.72; H, 6.67; N. 2.01. ^1H NMR (acetone-d_6), δ: 1.34 (t, 18 H, $P(OEt)_3$, $J_{H,H}$ = 10 Hz); 1.51 (s, 6 H, $C_5\underline{Me_4}H$); 1.71 (s, 6 H, $C_5\underline{Me_4}H$); 2.54 (s, 3 H, MeCN); 4.16 (m, 12 H, $P(OEt)_3$); 4.37 (s, 1 H, $C_5Me_4\underline{H}$). ^{31}P NMR (acetone-d_6), δ: −143.8 (sept, 1 P, PF_6^-, $J_{P,F}$ = 707 Hz); 170.9 (s, 2 P, $P(OEt)_3$).

[(η-Tetramethylcyclopentadienyl)(acetonitrile){1,2-bis(diphenylphosphino)ethane}iron] hexafluorophosphate, $[(\eta\text{-}C_5Me_4H)Fe(MeCN)(dppe)]PF_6$ ([5]PF_6). A solution of the complex [**1**]PF_6 (150 mg, 0.37 mmol) and dppe (148 mL) in acetonitrile

(10 mL) was irradiated for 20 h. The product was isolated as described for the complex [**2**]PF_6. The yield of the complex [**5**]PF_6 was 91 mg (32%), red solid. Found (%): C, 57.15; H, 5.11; N, 1.48. $C_{37}H_{40}F_6FeNP_3 \cdot 0.25CH_2Cl_2$. Calculated (%): C, 57.16; H, 5.22; N, 1.79. ^{1}H NMR (acetone-d_6), δ: 1.32 (s, 6 H, C_5Me_4H); 1.51 (s, 6 H, $C_5\underline{Me_4}H$); 2.29 (m, 2 H, CH_2); 2.46 (m, 2 H, CH_2); 3.90 (s, 1 H, $C_5Me_4\underline{H}$); 7.60 (m, 16 H, Ph); 7.76 (m, 4 H, Ph). ^{31}P NMR (acetone-d_6), δ: −144.2 (sept, 1 P, PF_6^-, $J_{P,F}$ = 707 Hz); 91.2 (s, 2 P, dppe).

[(η-Tetramethylcyclopentadienyl)tris(trialkyl phosphite)iron] hexafluorophosphate, [(η-C_5Me_4H)Fe{P(OR)$_3$}$_3$]PF_6 ([6]PF_6 and [7]PF_6). A solution of the complex [**1**]PF_6 (150 mg, 0.37 mmol) and $P(OR)_3$ (0.2 mL) in CH_2Cl_2 (10 mL) was irradiated for 24 h. The products were isolated as described for the complex [**2**]PF_6.

Complex [**6**]PF_6 (R = Me), yield 29 mg (11%), red solid. Found (%): C, 29.64; H, 5.36. $C_{18}H_{40}F_6FeO_9P_4 \cdot CH_2Cl_2$. Calculated (%): C, 29.29; H, 5.43. ^{1}H NMR (acetone-d_6), δ: 1.66 (s, 6 H, $C_5\underline{Me_4}H$); 1.73 (s, 6 H, $C_5\underline{Me_4}H$); 3.80 (s, 27 H, $P(OMe)_3$); 3.35 (s, 1 H, $C_5Me_4\underline{H}$). ^{31}P NMR (acetone-d_6), δ: −144.3 (sept, 1 P, PF_6^-, $J_{P,F}$ = 708 Hz); 173.5 (s, 3 P, $P(OMe)_3$).

Complex [**7**]PF_6 (R = Et), yield 86 mg (28%), red solid. Found (%): C, 36.75; H, 6.53. $C_{27}H_{58}F_6FeO_9P_4 \cdot CH_2Cl_2$. Calculated (%): C, 37.14; H, 6.68. ^{1}H NMR (acetone-d_6), δ: 1.34 (t, 27 H, $P(OEt)_3$, $J_{H,H}$ = 7 Hz); 1.68 (s, 6 H, $C_5\underline{Me_4}H$); 1.77 (s, 6 H, $C_5\underline{Me_4}H$); 4.18 (m, 18 H, $P(OEt)_3$); 3.30 (s, 1 H, $C_5Me_4\underline{H}$). ^{31}P NMR (acetone-d_6), δ: −144.3 (sept, 1 P, PF_6^-, $J_{P,F}$ = = 708 Hz); 168.6 (s, 3 P, $P(OEt)_3$).

[(η-Tetramethylcyclopentadienyl)iron](μ-η:η-pentaphospholyl)[(η-pentamethylcyclopentadienyl)iron] hexafluorophosphate, [(η-C_5Me_4H)Fe(μ-η:η-cyclo-P_5)FeCp*]PF_6 ([8]PF_6). Dichloromethane (10 mL) was added to a mixture of the complex [**1**]PF_6 (40 mg, 0.10 mmol) and pentaphosphaferrocene Cp*Fe(η-*cyclo*-P_5) (40 mg, 0.12 mmol). The reaction mixture was irradiated for 15 h, concentrated to ~2 mL, and separated by column chromatography (column 10×1 cm, silica gel, CH_2Cl_2—Me_2CO (10 : 1)). The collected dark gray fraction was concentrated *in vacuo* and the residue was reprecipitated from CH_2Cl_2 with light petroleum. The yield of the complex [**8**]PF_6

Table 3. Crystallographic parameters and the data collection and refinement statistics for the complexes [**2**]PF_6 and [**3**]PF_6

Parameter	[**2**]PF_6	[**3**]PF_6
Molecular formula	$C_{24}H_{40}F_6FeN_3P$	$C_{17}H_{34}F_6FeNO_6P_3$
M	571.41	611.21
Crystal system	Orthorhombic	Triclinic
Space group	*Pccn*	$P\bar{1}$
a/Å	17.424(2)	8.8447(6)
b/Å	20.025(2)	11.6752(8)
c/Å	17.018(2)	12.7336(9)
α/deg	—	96.5340(10)
β/deg	—	91.0170(10)
γ/deg	—	93.9150(10)
V/Å^3	5937.9(12)	1302.90(16)
Z	8	2
d_{calc}/g cm^{-3}	1.278	1.558
Crystal size/mm	0.45×0.35×0.20	0.40×0.30×0.15
Crystal color and shape	Yellow plates	Red plates
Diffractometer	Bruker APEX II	Bruker SMART
Radiation	Mo-*K*α (λ = 0.71073)	
μ/mm^{-1}	0.616	0.838
Absorption correction	APEX2	SADABS
Temperature/K	100(2)	120(2)
Scan mode	ω	φ and ω
$2\theta_{max}$/deg	52.00	52.00
Number of measured reflections	54895	11309
Number of independent reflections (R_{int})	5829 (0.0959)	5072 (0.0185)
R_1 (on *F* for reflections with $I > 2\sigma(I)$)	0.0348 (4115 reflections)	0.0426 (4274 reflections)
wR_2 (on F^2 for all reflections)	0.0859	0.1063
Number of parameters refined	329	318
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$	
a	0.0383	0.0510
b	1.3603	2.0650
GOOF	1.021	0.996
F(000)	2400	632
Residual electron density, (d_{max}/d_{min})/e Å^{-3}	0.363/−0.293	1.156/−0.408

was 23 mg (34%), green solid. Found (%): C, 34.22; H, 4.20. $C_{19}H_{28}F_6Fe_2P_6$. Calculated (%): C, 34.16; H, 4.23. ^1H NMR (acetone-d_6), δ: 1.22 (s, 15 H, Cp*); 1.30 (s, 6 H, $C_5\underline{Me_4}H$); 3.41 (s, 1 H, $C_5Me_4\underline{H}$). ^{31}P NMR (acetone-d_6), δ: −144.2 (sept, 1 P, PF_6^-, $J_{P,F}$ = 707 Hz); −24.2 (s, 5 P, *cyclo*-P_5).

X-ray diffraction study of the complexes [2]PF_6 and [3]PF_6. Single crystals of [**2**]PF_6 and [**3**]PF_6 were grown by slow diffusion in a two-phase system consisting of a solution of the complex in CH_2Cl_2 and a mixture of Et_2O and light petroleum. Crystallographic parameters and the data collection and refinement statistics are given in Table 3. The structures were solved by the direct methods. All non-hydrogen atoms were located from difference electron-density maps and refined anisotropically on F^2_{hkl}; all hydrogen atoms were located geometrically and and refined using a riding model with $U(H) = n \cdot U(C)$, where $U(C)$ is the equivalent thermal parameter of the C atom bearing the H atom; n = 1.2 and 1.5 for the CH and Me groups, respectively. All calculations were performed with the SHELXTL PLUS 5 program package (see Ref. 21). The atomic coordinates, thermal parameters, and comprehensive data on the geometrical parameters of the complexes [**2**]PF_6 and [**3**]PF_6 have been deposited with the Cambridge Crystallographic Data Center (Nos 736 452 and 736 453, respectively).

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