Inorganica Chimica Acta, *192* (1992) 211–217

Iron(II) complexes of naphthalenes. X-ray structure of [cyclopentadienyl–iron(II)–η^6-octamethylnaphthalene]PF_6

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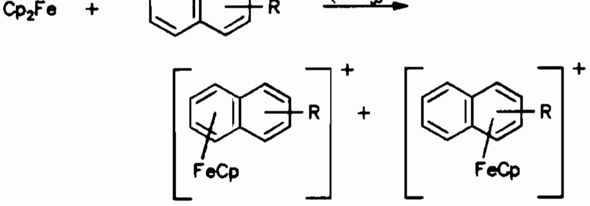
(Received June 18, 1991; revised October 21, 1991)

Abstract

Complex ions [cyclopentadienyl–Fe(methylnaphthalene)]$^+$ with 4 to 8 methyl substituents have been prepared from [CpFe(*o*-dichlorobenzene)]$^+$ by a photochemical ligand exchange. Complexation shifts have been determined for ^1H and ^{13}C resonances of the η^6-bonded naphthalenes. The X-ray structure of [CpFe(octamethylnaphthalene)]PF_6 0.5 acetone has been determined. Crystals are monoclinic, the space group *C*2/*c* with unit-cell dimensions $a = 10.689(4)$, $b = 22.391(5)$, $c = 20.550(4)$ Å, $\beta = 93.41(2)°$, $Z = 8$. The structure determination established a distorted molecular geometry of the octamethylnaphthalene that is different from the free arene and its $Cr(CO)_3$ complex.

Introduction

Iron(II) complexes of aromatics like [CpFe(arene)]$^+$ [1–3] have been recently studied by using polyaromatics with the goal focussed on their cathodic and $LiAlH_4$ reductions [4, 5]. The complexes of naphthalenes, [CpFe(naphthalene)]$^+$, attracted our attention because unsymmetrically substituted naphthalenes can be used to study the influence of different substitution patterns on their reactivity upon complexation. Such a study has been realized by the replacement of one of the cyclopentadienyl ligands of ferrocene by unsymmetrically substituted methyl- and dimethylnaphthalenes, yielding pairs of complex ions [6] (reaction (1)).



(1)

The influence of the substituents on the ratio of the two isomers implied a reaction mechanism involving an η^2-bonded intermediate of the associated naphthalene.

For highly substituted naphthalenes, distortions resulting from steric interaction may be expected. A X-ray crystal structure analysis of free octamethylnaphthalene (OMN) [7] and of its complex [(OMN)$Cr(CO)_3$] [8] confirmed similar distortions in both OMN units. Shorter metal–arene ring distances in the complexes of iron(II) [9] compared to those of chromium(0) [10] might produce a stronger interaction of a CpFe$^+$ unit with a highly substituted naphthalene.

Synthesis of complexes

The synthesis of [CpFe(arene)]$^+$ ions originates from a method introduced by Nesmeyanov *et al.* [11, 12] and Coffield *et al.* [13]. By this procedure complex ions [CpFe(naphthalene)]$^+$ have been prepared from ferrocene and methyl- as well as dimethylnaphthalenes by a ligand exchange reaction in the presence of $AlCl_3$ as catalyst [6] (reaction (1)). However, side-reactions occur and a part of the naphthalene is hydrogenated leading to at least 5–10% of complexes of tetralins [6, 12, 14]. Moreover, the methyl substituents of the naphthalenes are partially eliminated and shifted by $AlCl_3$ before the arene is bonded to the metal; this side reaction is very pronounced for 1,8-dimethylnaphthalene [6]. For OMN the exchange reaction with ferrocene and $AlCl_3$ resulted in a mixture of complex ions, for

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0020-1693/92/$5.00

which nine ^{1}H resonances of different Cp units (4.5–5.0 ppm) have been recorded.

A mild ligand exchange is achieved by photolysis of [CpFe(arene)]$^+$ ions [11, 15–17]. Starting with [CpFe(*p*-xylene)]$^+$ the exchange succeeded with hexamethylbenze [15], 2,2-paracyclophane [16] and 2,3-dimethylindol [17], but not with polyaromatics [2]. With OMN we obtained a trace of product; with other methyl-substituted naphthalenes there was no exchange reaction.

The yields of photolysis of different complex ions [CpFe(arene)]$^+$ in the presence of phenanthroline distinctly depend on the basicity of the leaving arene [18]. The photolytic exchange reactions of methylnaphthalenes were successful with less basic arenes in the starting complexes. In particular, [CpFe(*o*-dichlorobenzene)]PF_6 was convenient, because the *Rf* values of the starting complex and of the products were sufficiently different for chromatographic separation.

The ratio of the isomers for the complexes formed from ferrocene with methylnaphthalenes and with unsymmetrically substituted dimethylnaphthalenes indicated an inhibition for methyl substituents in the 2- and 3-positions. The differences for the complexation of 1,2- and 1,3-dimethylnaphthalene implied an associative mechanism including an η^2-bonded intermediate for the entering naphthalene [6]. Ruiz and Astruc interpreted their results for the exchange reaction of the neutral complexes [CpFe(arene)] with phosphorus ligands by an associative reaction with an η^4-bonded intermediate of the leaving arene [19].

Starting from ferrocene and $AlCl_3$ for tetra- to octamethyl-substituted naphthalenes, only 1,2,3,4-tetramethylnaphthalene gave a successful exchange reaction. the ratio of 1:3 obtained for the pair of isomeric complexes **8** and **9** strongly favoured the unsubstituted ring being bonded to the iron. This is as expected for a kinetically controlled associative mechanism. Conversely, according to the Cp resonances of the two isomers (**8** 4.41 ppm; **9** 4.65 ppm), the tetrasubstituted part of this naphthalene (complex **8**) represents the better donor.

NMR spectra

The new complexes **6–15** have been characterized by ^{1}H and ^{13}C NMR spectra (400 MHz; see 'Experimental'). The complexation shifts have been determined by comparison with the spectra of the free arenes recorded in the same conditions.

The complexation shifts for methyl groups in a β-position (in the π-bonded ring as well as in the annelated ring) are independent of other substituents (H or CH_3) and their position; they only differ by $\leqslant 0.02$ ppm.

The complexation shifts of methyl groups in the α-position of the naphthalene are affected by methyl substituents in all the other positions on the ring (Table 1). The complexation shifts for **11**, **12** and **15**, calculated with the values observed for other complexes from Table 1, indicate a non-additivity of the effects. Therefore it is concluded that structural distortions may affect these shifts.

The ^{1}H resonances of aromatic protons of the naphthalene are also shifted by the complexation. As expected, protons of the π-bonded ring are shifted to higher field and protons in the annelated ring to lower field. The shifts of the β-protons are more pronounced than those of the α-protons [1–3].

In the unsubstituted naphthalene ring, which is π-bonded to the iron, the complexation shifts for the β-protons are not influenced by the methyl groups in the annelated ring (**1**, **3**, **5** and **9** with a mean value of 0.93 ± 0.02 ppm; Table 2).

TABLE 1. Complexation shifts for methyl groups in the 1,4-position of the complex ions [CpFe(subst. naphthalene)]$^+$

Substituted naphthalene	Complexes with their 1,4-dimethyl groups			
	No.	In the π-bonded ring (ppm)	No.	In the annelated ring (ppm)
1,4-dimethyl-[a]	**2**	0.45	**3**	0.16
1,4,6,7-tetramethyl-	**6**	0.42	**7**	0.16
1,4,5,8,-tetramethyl-	**10**	0.49	**10**	0.22
1,2,3,4-tetramethyl-	**8**	0.56	**9**	0.19
1,4,5,6,7,8-hexamethyl-	**11**	0.58	**12**	0.28
1,2,3,4,5,6,7,8-octamethyl-	**15**	0.65	**15**	0.32

[a] Ref. 6.

TABLE 2. Complexation shifts of aromatic protons for substituted naphthalenes (**1–5** from ref. 6). Substituents in the 1,2,3,4-positions are in the ring, which is π-bonded to the iron (values in ppm)

Compound no.	Naphthalene	π-Bonded ring		Annelated ring	
		α	β	α	β
1	not substituted	−0.47	−0.93	+0.23	+0.38
2	1,4-dimethyl-		−0.76	+0.29	+0.53
3	5,8-dimethyl-	−0.62	−0.94		+0.39
4	2,3-dimethyl-	−0.27		+0.27	+0.45
5	6,7-dimethyl-	−0.34	−0.94	+0.20	
6	2,3,5,8-tetramethyl-	−0.46			+0.42
7	1,4,6,7-tetramethyl-		−0.80	+0.24	
8	1,2,3,4-tetramethyl-			+0.37	+0.52
9	5,6,7,8-tetramethyl	−0.59	−0.91		
10	1,4,5,8-tetramethyl-		−0.64		+0.57
11	1,4,5,6,7,8-hexamethyl		−0.67		
12	1,2,3,4,5,8-hexamethyl-				+0.55

These features are different when the β-protons in the π-bonded ring are next to methyl groups (in α-position) in the same ring as in complex **2**. For this pattern of substitution in the π-bonded ring, methyl groups in the annelated ring affect the complexation shift of the β-protons (in 2,3-position). For methyl groups in the α-position of the annelated ring (5,8-dimethyl substituents as in **10**) and for methyl groups in the β-position of the annelated ring (6,7-dimethyl substituents as in **7**) the effects compared to **2** are the inverse. From the complexation shifts of the complex ions **2**, **7** and **10** an estimated value of -0.68 ppm results for complex **11**; this is in good agreement with the experimental value of -0.67 ppm.

Alterations of the complexation shifts are lower for α-protons of the π-bonded naphthalene ring, but the substituent effects are different for the β-protons. For α-protons in an unsubstituted ring alterations do appear in the presence of methyl groups in the annelated ring. The effects for methyl groups in the 5,8-position (**1** and **3** as well as **4** and **6**) are the opposite with respect to those recorded for methyl groups in the 6,7-positions (**1** and **5**). For **9** a complexation shift of -0.48 ppm is derived using the values of the complexes **1**, **3** and **5**. This does not agree well with the measured value of -0.59 ppm.

These results discussed above indicate that some of the effects observed for the complexation shifts, like irregularities and non-additivities for methyl groups and protons in the α-position, may be attributed to different distortions of the naphthalene ligand in the complexes studied.

It has been observed that the ^{13}C resonances of the cyclopentadienyl ligand in the series $[\mathrm{CpFe(CH_3)}_n\mathrm{C_6H}_{6-n}]^+$ are shifted down field with the increasing number of methyl groups and fall in the range of 75.63 ppm for $[\mathrm{CpFeC_6H_6}]^+$ to 77.35 ppm for $[\mathrm{CpFe(CH_3)_6C_6}]^+$ [20]. When some further electron delocalization in the arene ligand is allowed, these resonances are still higher, i.e. 77.9 ppm for $[\mathrm{CpFe(diphenyl)}]^+$ and 78.4 ppm for $[\mathrm{CpFe(fluorene)}]^+$ [21]. Finally, in our methyl-substituted naphthalene complexes, the lowest fields are observed for ^{13}C resonances of their Cp ligand: 78.75 ppm for $[\mathrm{CpFe(1,4,5,8\text{-}tetramethylnaphthalene)}]^+$ (**10**) and 78.80 ppm for $[\mathrm{CpFe(OMN)}]^+$ (**15**). Although the differences of these resonances are rather small, the trends observed are consistent with both an electron delocalization (benzene, diphenyl, naphthalene) and a donor strength (methyl substituents).

The complexation shifts for ^{13}C resonances of the aromatic carbon atoms in $[\mathrm{CpFe(methylnaphthalene)}]^+$ ions are observed in the range -29.55 to -37.98 ppm for the atoms in the π-bonded ring (Table 3). Note, that the lowest complexation shift (in absolute value and upfield) is observed for the α-positions (C6 and C9 atoms from Fig. 1) in $[\mathrm{CpFe(OMN)}]^+$. For the annelated ring these complexation shifts are much smaller, as expected, and fall in the range of -0.5 to $+12.2$ ppm. It is worth noting, that the methyl carbon atoms at the naphthalene ligand are little affected by complexation as shown by their small values of the complexation shifts (-1.90 to $+3.66$ ppm).

TABLE 3. Complexation shifts of the ^{13}C resonances for some selected C atoms of $[\mathrm{CpFe(naphthalene)}]^+$ and related complexes $[\mathrm{CpFe(arene)}]^+$ [20, 21].

Substituted naphthalene/arene	Complex no.	Complexation shift (ppm)	
		C6 and C9	C10 and C11
Octamethyl-	15	−29.55	−33.71
1,4,5,6,7,8-Hexamethyl-	11	−37.98	−35.95
1,4,5,8-Tetramethyl-	10	−36.09	−36.38
Fluorene		−35.6	−36.1
Hexamethylbenzene		−34.2	
Diphenyl			−37.3

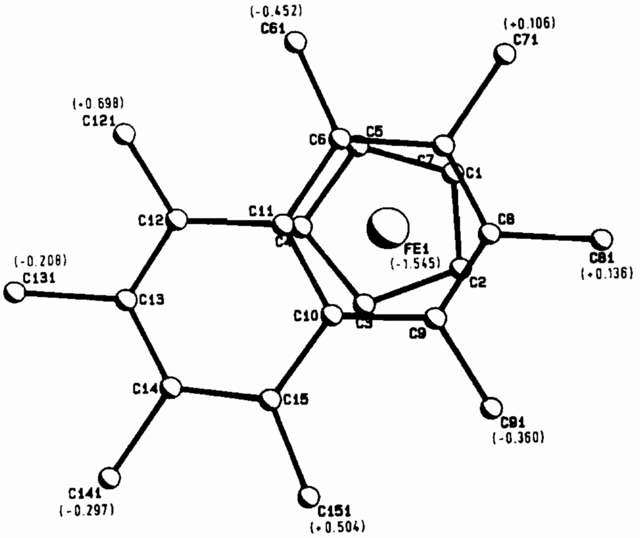


Fig. 1. Representation of the cation [cyclopentadienyl–Fe(octamethylnaphthalene)]$^+$ with the numbering of the C atoms. The values in parentheses illustrate the distortions of the methyl groups. Indicated are the distances (Å) below (−) or above (+) the least-squares plane described by the ring carbon atoms C6–C15. The estimated standard deviations vary from 0.009–0.011 Å.

X-ray structure of [CpFe(octamethylnaphthalene)PF$_6$ 0.5 acetone

The structure of **15** is built up of $[\mathrm{CpFe(OMN)}]^+$ cations, $\mathrm{PF_6}^-$ anions and acetone molecules. Selected interatomic distances are given in Table 4.

TABLE 4. Selected interatomic distances (Å) in [cyclopentadienyl–Fe(octamethylnaphthalene)]PF_6

Fe–C1	2.030(9)	Fe–C6	2.050(8)	C6–C7	1.43(1)
Fe–C2	2.024(9)	Fe–C7	2.093(7)	C7–C8	1.38(1)
Fe–C3	2.022(8)	Fe–C8	2.133(7)	C8–C9	1.44(1)
Fe–C4	2.014(9)	Fe–C9	2.036(8)	C9–C10	1.45(2)
Fe–C5	2.060(1)	Fe–C10	2.129(7)	C6–C11	1.47(1)
		Fe–C11	2.142(6)	C10–C11	1.41(1)
				C11–C12	1.46(2)
				C12–C13	1.36(1)
				C13–C14	1.40(1)
				C14–C15	1.38(1)
				C10–C15	1.47(2)

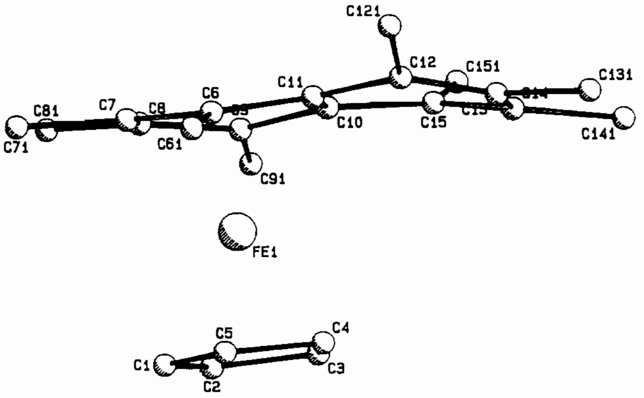
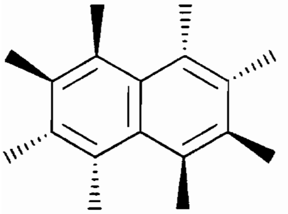


Fig. 2. Molecular structure of the [cyclopentadienyl–Fe(octamethylnaphthalene)]$^+$ cation.

In the complex cation (Fig. 1) the mean Fe–C(Cp) bond length of 2.030 Å is the same as in ferrocene (2.033 Å [22]) and other [CpFe(arene)]$^+$ ions, for example [CpFe(perylene)]$^+$ 2.04 Å [4] or [CpFe(*para*-cyclophane)]$^+$ 2.056 Å [23].

In octamethylnaphthalene (OMN) as well as in its complex [(OMN)Cr$(CO)_3$], the distortion concerning the eight methyl groups is analogous [7, 8]; they deviate in pairs from the plane formed by the naphthalene rings (structure I) as has been established earlier for octachloronaphthalene [24].



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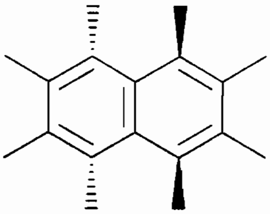

II

For the complex [CpFe(OMN)]$^+$ (**15**) we have ascertained another type of distortion for the methyl groups (structure II and Fig. 2). The deviations are less pronounced than in [(OMN)Cr$(CO)_3$]; consequently, the twist about the central C10–C11 bond, measured as the dihedral angle between the C9/C10/C11/C15 and the C6/C10/C11/C12 planes, is only 3.8(7)° for [CpFe(OMN)]$^+$ compared to 19.3° in [(OMN)Cr$(CO)_3$] [8].

The deformations of the naphthalene ring in the cation [CpFe(OMN)]$^+$ are described by deviations of the carbon atoms C6 through C15 from their best least-squares plane: C6 −0.111, C7 −0.043, C8 +0.042, C9 −0.060, C10 +0.069, C11 +0.070, C12 +0.163, C13 −0.082, C14 −0.141 and C15 +0.093 Å with e.s.d.s equal to 0.006–0.008 Å. These deviations occur on the same side (over (+) and below (−)) of the plane as those of the corresponding methyl carbon atoms C61 up to C151 (Fig. 1). As a consequence of these distortions, the Fe–C6 and Fe–C9 distances (mean value 2.043 Å) are shorter than the other four Fe–C distances (mean value 2.124 Å, Table 4). In [(OMN)Cr$(CO)_3$] the Cr–C distances to the π-bonded part of the naphthalene are longer: Cr–C10 and Cr–C11 2.32 Å, the other four Cr–C distances 2.20 Å.

The mean C–C bond lengths in both parts of the naphthalene in [CpFe(OMN)]$^+$ are equal to 1.430 and 1.413 Å, and they are the same as in [(OMN)Cr$(CO)_3$] (1.430 and 1.417 Å). The central bond C10–C11 in [CpFe(OMN)]$^+$ (1.41 Å) is a little shorter than in the free octamethylnaphthalene (1.423 Å, [7]); for [(OMN)Cr$(CO)_3$] this central bond is longer (1.440 Å) [8].

For [CpFe(OMN)]$^+$ the angle C6/C11/C12 is 119.9°, compared to 121.5° in naphthalene [25]. For the uncomplexed OMN and its Cr$(CO)_3$ complex this angle is enlarged to about 124° [7, 8].

The shapes of the HOMO and the LUMO in free naphthalene are mostly composed of the C6 and C9 (as well as the C12 and C15) atomic orbitals [26]. The distortion of the ring (Fig. 2) assures shorter Fe–C6 and Fe–C9 distances (Table 4) and a better overlap of the naphthalene HOMO with the LUMO frontier orbitals of the iron(II) (d_{xz}, d_{yz}) [4]. On the other hand the occupied d_{z^2}-orbital may interact favorably with the LUMO of the naphthalene.

A presumed difference in the bonding of the OMN complexes with chromium(0) and iron(II) may be due to better acceptor properties and the smaller size of iron(II) compared to chromium(0).

Experimental

[CpFe(naphthalene)]PF_6 [6], [CpFe(*o*-dichlorobenzene)]PF_6 [27], octamethyl- and 1,2,3,4,5,8-hexamethylnaphthalene [28], 1,2,3,4-tetramethylnaphthalene [29], and 1,4,5,8-, 1,4,5,7- and 1,4,6,7-tetramethylnaphthalene [30] were prepared according to literature methods. CH_2Cl_2 was dried using P_4O_{10}, distilled and saturated with argon.

The ^1H and ^{13}C NMR spectra were recorded in d_6-acetone with a 400 MHz spectrometer from Bruker. The resonances, which have been underlined in the following text, have been assigned to the π-bonded ring of the naphthalene.

[CpFe(octamethylnaphthalene)]PF$_6$ (15)

A 100 ml tube with a screw cap and a teflon sealing was charged with 330 mg (0.8 mmol) [CpFe(*o*-dichlorobenzene)]PF_6, 432 mg (1.8 mmol) octamethylnaphthalene and 100 ml CH_2Cl_2. The solution was irradiated by a 100 W incandescent lamp. The colour of the solution turned from yellow to red. At the end of the reaction time (90 min) the solution was cooled, 5 g of silica gel added and the CH_2Cl_2 removed. The products together with the silica gel were placed on the top of a column (diameter 2 cm, length 30 cm), which had been filled up to 10 cm with silica gel. Elution with 100 ml of diethyl ether removed octamethylnaphthalene and some ferrocene. The mixture eluted with CH_2Cl_2/acetone (3:1) was re-chromatographed to separate the product from the unreacted starting complex. 120 mg (26.5%) of [CpFe(octamethylnaphthalene)]PF_6 was isolated as a red product, m.p. 161–165 °C (dec.). *Anal.* Calc. for $C_{23}H_{29}FePF_6$: C, 54.56; H, 5.77. Found: C, 54.32; H, 5.60%.

^1H NMR: 4.46 (s, Cp, 5H); 3.08 (s, $\underline{\alpha\text{-CH}_3}$, 6H); 2.66 (s, $\underline{\beta\text{-CH}_3}$, 6H); 2.75 (s, αCH_3, 6H); 2.42 (s, $\beta\text{-CH}_3$, 6H). ^{13}C NMR: 78.80 (Cp); 17.93, 17.57, 23.75, 22.66 (methyl groups); 142.06 (C13, C14), 132.70 (C12, C15), $\underline{101.54}$ (C6, C9), $\underline{100.39}$ (C10, C11), $\underline{93.94}$ (C7, C8).

[CpFe(1,4,5,8-tetramethylnaphthalene)]PF$_6$ (10)

Red solid (22%), m.p. 179 °C (dec.) *Anal.* Calc. for $C_{19}H_{21}FePF_6$: C, 50.69; H, 4.70. Found: C, 50.68; H, 4.84%.

^1H NMR: 4.70 (s, Cp, 5H); 3.25 (s, $\underline{\alpha\text{-CH}_3}$, 6H); 2.98 (s, $\alpha\text{-CH}_3$, 6H); 6.34 (s, $\underline{\beta\text{-H}}$, 2H); 7.55 (s, β-H, 2H). ^{13}C NMR: 78.75 (Cp); 26.24 and 26.03 (methyl groups); 138.97 (C13, C14); 134.71 (C12, C15), $\underline{99.18}$ (C10, C11), $\underline{97.89}$ (C6, C9), $\underline{91.87}$ (C7, C8).

[CpFe(1,2,3,4-tetramethylnaphthalene)]PF$_6$ (8 and 9)

Red product (18%), m.p. 184 °C (dec.); the ratio of the two isomers 51/49. *Anal.* Calc. for $C_{19}H_{21}FePF_6$: C, 50.69; H, 4.70. Found: C, 50.36; H, 4.44%.

^1H NMR of **8**: 4.41 (s, Cp, 5H); 3.10 (s, $\underline{\alpha\text{-CH}_3}$, 6H); 2.71 (s, $\underline{\beta\text{-CH}_3}$, 6H); 8.34 (m, α-H, 2H); 7.89 (m, β-H, 2H). ^1H NMR of **9**: 4.65 (s, Cp, 5H); 2.73 (s, $\alpha\text{-CH}_3$, 6H); 2.47 (s, $\beta\text{-CH}_3$, 6H); 7.38 (m, $\underline{\alpha\text{-H}}$, 2H); 6.46 (m, $\underline{\beta\text{-H}}$, 2H).

[CpFe(1,4,6,7-tetramethylnaphthalene)]PF$_6$ (6 and 7)

Red solid (27%), m.p. 187 °C (dec.); the ratio of the two isomers 23/77. *Anal.* Calc. for $C_{19}H_{21}FePF_6$: C, 50.69; H, 4.70. Found: C, 50.69; H, 4.74%.

^1H NMR of **7**: 4.51 (s, Cp, 5H); 3.00 (s, $\underline{\alpha\text{-CH}_3}$, 6H); 2.52 (s, $\beta\text{-CH}_3$, 6H); 6.28 (s, $\underline{\beta\text{-H}}$, 2H); 7.98 (s, α-H, 2H). ^1H NMR of **6**: 4.58 (s, Cp, 5H); 2.74 (s, $\alpha\text{-CH}_3$, 6H); 2.68 (s, $\underline{\beta\text{-CH}_3}$, 6H); 7.28 (s, $\underline{\alpha\text{-H}}$, 2H); 7.50 (s, β-H, 2H).

[CpFe(1,4,5,7-tetramethylnaphthalene)]PF$_6$ (13 and 14)

Red solid (47%), m.p. 163 °C (dec.); ratio of the isomers 67/33. *Anal.* Calc. for $C_{19}H_{21}FePF_6$: C, 50.69; H, 4.70. Found: C, 50.75; H, 4.64%.

^1H NMR of **13**: 4.62 (s, Cp, 5H); 3.25 (s, $\underline{\alpha\text{-CH}_3}$ peri to $\alpha\text{-CH}_3$, 3H); 3.01 (s, $\underline{\alpha\text{-CH}_3}$, 3H); 3.04 (s, $\alpha\text{-CH}_3$, 3H); 2.50 (d, $J=0.75$ Hz, $\underline{\beta\text{-CH}_3}$, 3H); 6.39 and 6.25 (d–d, $J=6.40$ Hz, $\underline{\beta\text{-H}}$, 2H); 7.85 (s, α-H, 1H); 7.59 (s, β-H, 1H). ^1H NMR of **14**: 4.65 (s, Cp, 5H); 3.28 (s, $\underline{\alpha\text{-CH}_3}$, 3H); 2.61 (s, $\underline{\beta\text{-CH}_3}$, 3H); 2.98 (s, $\alpha\text{-CH}_3$ peri to $\underline{\alpha\text{-CH}_3}$, 3H); 2.76 (s, $\alpha\text{-CH}_3$, 3H); 7.25 (d, $J=0.94$ Hz, $\underline{\alpha\text{-H}}$, 1H); 6.42 (s, $\underline{\beta\text{-H}}$, 1H); 7.56 and 7.51 (d–d, $J=7.02$ Hz, β-H, 2H).

[CpFe(1,2,3,4,5,8-hexamethylnaphthalene)]PF$_6$ (11 and 12)

Red solid (12%), m.p. 175 °C (dec.); ratio of the isomers 82/18. *Anal.* Calc. for $C_{21}H_{31}FePF_6$: C, 52.08; H, 6.45. Found: C, 53.76; H, 6.19%.

^1H NMR of **12**: 4.56 (s, Cp, 5H); 3.16 (s, $\underline{\alpha\text{-CH}_3}$, 6H); 2.69 (s, $\underline{\beta\text{-CH}_3}$, 6H); 2.93 (s, $\alpha\text{-CH}_3$, 6H); 7.53 (s, β-H, 2H). ^1H NMR of **11**: 4.53 (s, Cp, 5H); 3.23 (s, $\underline{\alpha\text{-CH}_3}$, 6H); 2.78 (s, $\alpha\text{-CH}_3$, 6H); 2.45 (s, $\beta\text{-CH}_3$, 6H); 6.31 (s, $\underline{\beta\text{-H}}$, 2H). ^{13}C NMR of **11**: 78.87 (Cp); 142.67 (C13, C14), 133.66 (C12, C15), $\underline{99.87}$ (C10, C11), $\underline{94.51}$ (C6, C9), $\underline{91.25}$ (C7, C8); 26.75 $\underline{\text{(methyl groups)}}$, 22.26, 18.11 (methyl groups).

Crystallographic studies

Crystals of [CpFe(OMN)]PF_6 0.5 acetone were isolated from a solution of 50 mg of complex **15** in 1 ml acetone, which had been layered with 10 ml pentane. The red crystals were washed with ether.

A red crystal having approximate dimensions 0.4×0.3×0.12 mm was mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined and refined from 25 randomly selected reflections (CAD4 routines). The crystal data are: monoclinic, space group *C2/c*, $a=10.689(4)$, $b=22.391(5)$, $c=20.549(4)$ Å, $\beta=93.41(2)°$, $V=4909.6$ Å^3, $Z=8$, $D_x=1.448$ g cm^{-3}, $\mu=7.35$ cm^{-1}. Intensities were measured with filtered Mo Kα radiation, $\lambda=0.71073$ Å, ω–2θ scan, $2°<\theta<25°$. Data reduction, decay and ab-

TABLE 5. Positional parameters and their estimated standard deviations for **15**

Atom	x	y	z	B (Å^2)
Fe	0.25445(9)	0.39536(4)	0.92130(5)	3.48(2)
P	0.2388(2)	0.4713(1)	0.6574(1)	5.14(5)
F1	0.1225(5)	0.4514(3)	0.6964(3)	9.1(2)
F2	0.3186(9)	0.4241(4)	0.6942(4)	15.7(3)
F3	0.1577(7)	0.5206(3)	0.6221(3)	10.2(2)
F4	0.1951(8)	0.4298(3)	0.5999(3)	11.2(2)
F5	0.3506(5)	0.4921(5)	0.6195(3)	12.5(3)
F6	0.2721(8)	0.5171(4)	0.7141(3)	11.8(3)
C1	0.194(1)	0.4642(4)	0.8632(5)	6.5(3)
C2	0.148(1)	0.4701(4)	0.9209(8)	7.7(3)
C3	0.252(2)	0.4751(4)	0.9675(4)	8.2(4)
C4	0.358(1)	0.4706(4)	0.9295(8)	7.7(3)
C5	0.314(1)	0.4649(4)	0.8652(5)	6.5(3)
C7	0.2172(8)	0.3185(3)	0.8654(4)	4.7(2)
C71	0.174(1)	0.3099(4)	0.7921(4)	6.7(3)
C8	0.1301(7)	0.3210(3)	0.9116(4)	4.7(2)
C81	−0.0108(8)	0.3126(4)	0.8928(5)	7.1(3)
C9	0.1666(7)	0.3359(4)	0.9781(4)	4.6(2)
C91	0.0648(6)	0.3554(4)	1.0229(5)	6.5(3)
C10	0.2984(7)	0.3344(3)	0.9988(3)	3.6(2)
C11	0.3879(7)	0.3280(3)	0.9514(3)	3.5(2)
C6	0.3480(7)	0.3253(3)	0.8822(4)	4.1(2)
C61	0.4354(9)	0.3332(4)	0.8273(4)	6.2(2)
C12	0.5203(7)	0.3279(3)	0.9713(4)	4.7(2)
C121	0.6205(8)	0.2983(4)	0.9299(5)	6.5(2)
C13	0.5568(9)	0.3485(4)	1.0316(5)	5.9(2)
C131	0.6984(8)	0.3582(4)	1.0500(6)	8.0(3)
C14	0.469(1)	0.3575(3)	1.0787(4)	5.5(2)
C141	0.511(1)	0.3758(5)	1.1506(5)	8.4(3)
C15	0.3439(9)	0.3440(3)	1.0666(4)	5.0(2)
C151	0.261(1)	0.3333(4)	1.1237(4)	7.1(3)
OA	0.461(2)	0.198(1)	0.733(1)	14.5(7)*
CA1	0.500	0.1465(8)	0.750	8.2(4)*
CA21	0.428(2)	0.098(1)	0.704(1)	7.9(6)*
CA22	0.406(3)	0.129(1)	0.701(1)	9.7(7)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the from of the isotropic equivalent displacement parameter defined as: $(4/3)\ [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

sorption (Ψ scan) corrections were performed with the Enraf-Nonius SDP library and all other calculations (structure determination and refinement) were carried out by use of the SHELX 76 program package with neutral scattering factors.

A total of 2429 reflections with $I > 2.5\sigma(I)$ was used in the structure determination and refinement. The cyclopentadienyl hydrogen atoms were placed in calculated positions and ridden on the carbon atoms bearing them. Because of the rather high values of residuals R, no attempt was made to locate the hydrogen atoms of the methyl groups (OMN) and of the acetone molecule. In the earlier steps of refinement the acetone molecule was placed in ordered position on a two-fold axis. However, the temperature parameters of the oxygen atom and of the methyl carbon atoms were abnormally high and the carbonyl C−O bond length too short. Refinement of this molecule in disordered position with the central carbon atom kept on the special position gave reasonable values of both the temperature and the geometrical parameters; final $R = 0.067$, $R_w = 0.074$ with $w^{-1} = \sigma^2(F) + 0.0036(F)^2$, $GOF = 1.261$. Final atomic coordinates are given in Table 5.

Supplementary material

Tables of anisotropic temperature factors, least-squares planes, full interatomic distances and angles as well as a listing of observed and calculated structure factors may be obtained from author M.M.K.

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