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Note

Structure and properties of protonated *N*-alkyl-2-aza[3]ferrocenophanes

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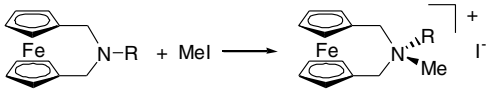
Abstract

Protonation of *N*-alkyl-2-aza[3]ferrocenophanes by HCl and NH_4PF_6 affords hexafluorophosphate salts having a trialkylammonium group. Structures of the protonated and unprotonated *N*-(*p*-methylbezyl)-2-aza[3]ferrocenophanes were determined by X-ray crystallography. Variable temperature $^{13}C\{^1H\}$ NMR spectra of the *N*-protonated *N*-hexyl-2-aza[3]ferrocenophane revealed inversion of the nitrogen of the 2-aza[3]ferrocenophane on the NMR time scale probably via partial deprotonation of the nitrogen atom. Cyclic voltammograms of the *N*-protonated compounds exhibited reversible redox peaks at higher potentials than those of the corresponding neutral ferrocenophanes.

Keywords: Ferrocene; Ferrocenophane; Protonation; Electrochemistry

1. Introduction

Ferrocene derivatives have received considerable attention because they undergo one-electron redox reaction reversibly at lower potentials than those of organic ligands [1]. Electrochemical properties of ferrocene are influenced by substituents of its cyclopentadienyl (Cp) ligands, and introduction of *N*-containing groups on the Cp ligand leads to not only change of the redox potential of the Fe center but also intramolecular electronic communication between the metal center and the ligand. Plenio et al. reported that the ferrocene derivatives with aminoalkyl substitutents showed the oxidation potential changing against the iron–nitrogen distances [2]. Kaifer et al. observed electrochemical communications between ferrocenyl groups separated by a $-CH_2N(C_6H_{13})CH_2-$ group and its disruption caused by protonation of the amino group [3]. We have prepared a series of *N*-alkyl- and *N*-aryl-2-aza[3]ferrocenophanes by using coupling reactions catalyzed by transition metal complexes and investigated electrochemical oxidation which is accompanied by electron transfer between Fe(III) and the nitrogen atoms of the oxidized species [4,5]. These chemical properties of *N*-alkyl- and *N*-aryl-2-aza[3]ferrocenophanes have been applied to regulation of equilibrium constants between *trans*- and *cis*-azobenzene contained in the molecule under photo-irradiation and formation of ferrocene-containing pseudorotaxanes induced by electrochemical oxidation [5,6]. *N*-alkyl-2-aza[3]ferrocenophanes undergo methylation at the nitrogen upon their reaction with MeI as shown in Eq. (1) [4b,4c]. Products of analogous *N*-protonation of the azaferrocenophanes have not been studied in detail, although they may be formed in an acidic solution of the compounds. In this paper we report preparation of cationic *N*-protonated 2-aza[3]ferrocenophanes as well as their dynamic behavior in solution and electrochemical properties



R = hexyl
= $(CH_2)_6OH$
= cyclohexyl
= $(CH_2)_4Ph$

(1)

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2. Results and discussion

2.1. Preparation and characterization of N-protonated 2-aza[3]ferrocenophanes

Reaction of HCl(aq) with *N*-(methylbezyl)-2-aza[3]ferrocenophane (**1**) forms [**1**-H](Cl), which is treated with NH_4PF_6 to form [**1**-H](PF_6) with a tertiaryammonium group as shown in Eq. (2). An analogous reaction with *N*-hexyl-2-aza[3]ferrocenophane (**2**) yields [**2**-H](PF_6). Fig. 1 depicts molecular structures of **1** and [**1**-H](PF_6) determined by X-ray crystallography. Selected bond distances and angles are listed in Table 1. In each compound, cyclopentadienyl ligands are in the eclipsed conformation similar to the structure of the previously reported [3]ferrocenophanes [4,5,7,8]. The N1–C11, N1–C12, N1–C13 bond distances of **1** (1.463(7), 1.463(6), 1.490(6) Å) are normal as the C–N distances of neutral compounds, while those of [**1**-H](PF_6) (1.53(2), 1.52(2), 1.53(2) Å) are in longer range than those of **1** probably due to positive charge at the nitrogen atom. *N*-methylated aza[3]ferrocenophanes also showed elongation of the N–C bonds (1.52–1.57 Å) [4c]. The C–N–C bond angles of **1** (109.2(3)–113.6(4)°) are similar to the corresponding angles of [**1**-H](PF_6) (110(2)–114(2)°) and slightly larger than those of *N*-methylated *N*-hexyl-aza[3]ferrocenophanes (103(1)–114(1)°) [4b,4c].

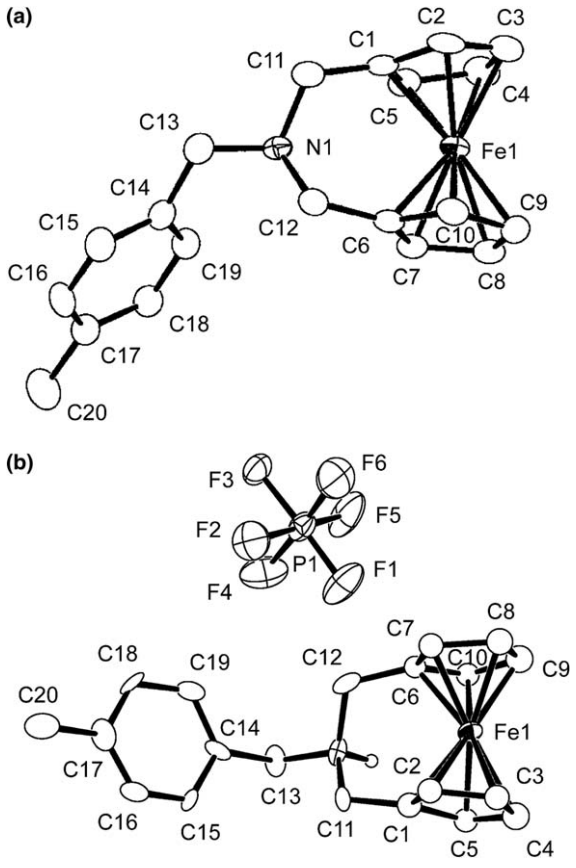
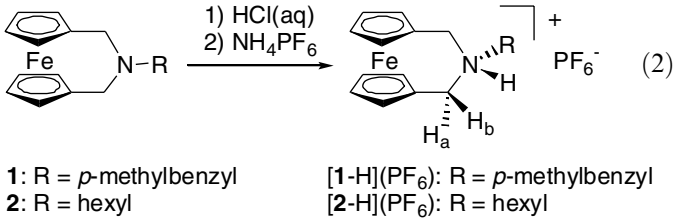


Fig. 1. Molecular structures of (a) **1** and (b) [**1**-H](PF_6).

Table 1
Selected bond distances, bond angles of **1** and [**1**-H](PF_6)

Compound	**1**	[**1**-H](PF_6)
Bond distances		
Fe1–C1	2.008(5)	2.02(2)
Fe1–C2	2.016(5)	2.03(2)
Fe1–C3	2.051(5)	2.04(2)
Fe1–C4	2.044(6)	2.03(2)
Fe1–C5	2.025(6)	2.03(2)
Fe1–C6	2.002(4)	1.98(2)
Fe1–C7	2.020(5)	2.05(2)
Fe1–C8	2.052(6)	2.04(2)
Fe1–C9	2.053(6)	2.04(2)
Fe1–C10	2.020(4)	2.07(2)
C1–C11	1.500(7)	1.50(2)
C6–C12	1.506(7)	1.53(2)
N1–C11	1.463(7)	1.53(2)
N1–C12	1.463(6)	1.52(2)
N1–C13	1.490(6)	1.53(2)
Bond angles		
C11–N1–C12	113.6(4)	114(2)
C11–N1–C13	110.4(4)	110(2)
C12–N1–C13	109.2(3)	112(2)

Dihedral angles between the cyclopentadienyl ligands of **1** and [**1**-H](PF_6) are 12.2(3)° and 11(1)°, respectively.



^{1}H NMR spectrum of [**1**-H](PF_6) is shown in Fig. 2(a). The NH hydrogen shows the signal at δ 7.15. The $C_5H_4CH_2$ hydrogens give two signals at δ 3.22 (H_a) and 4.19 (H_b) which were coupled with each other ($^2J = 14$ Hz) and with NH hydrogen ($^3J = 10$ and 2 Hz, respectively). Table 2 compares the observed ^3J values with the calculated ones by using the torsion angles obtained from X-ray crystallography based on Karplus equation [9,10]. H_a and H_b were assigned unequivocally to the signals of the *anti* and *syn* CH_2 hydrogens to the NH hydrogen, respectively, because the observed coupling constants are consistent with those calculated based on conformation of the crystal structure. $^{13}C\{^1H\}$ NMR spectrum of [**1**-H](PF_6) shows five signals for the C_5H_4 carbons while the corresponding carbons of **1** give three $^{13}C\{^1H\}$ NMR signals only (Fig. 2(b)) [4]. The nitrogen of **1** undergoes rapid inversion that renders a pair of the CH carbons magnetically equivalent as shown in Scheme 1(i). Five $^{13}C\{^1H\}$ NMR signals for the C_5H_4 ligands of [**2**-H](PF_6) were observed at 0 °C while the four of them undergo coalescence at higher temperature as shown in Fig. 3. Addition of HPF_6 to the solution retards the dynamic process, and the spectrum with equimolar HPF_6 exhibits five C_5H_4

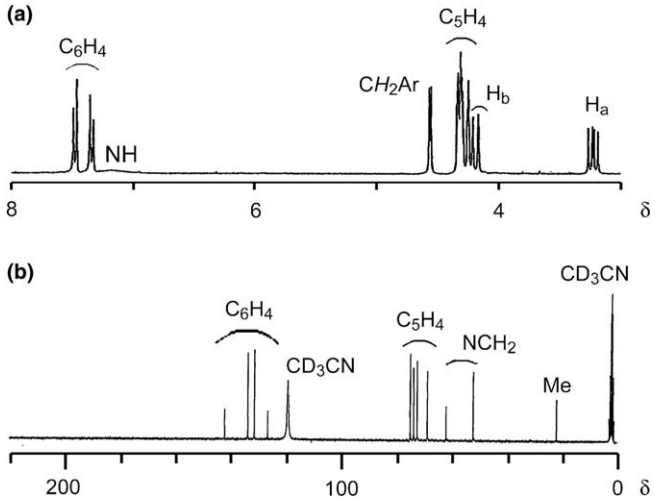
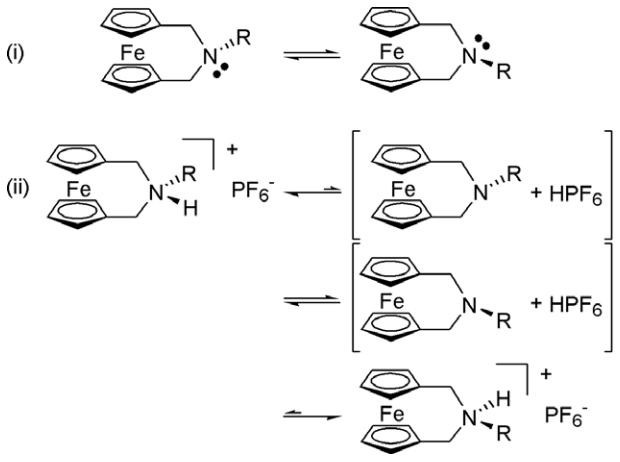


Fig. 2. (a) ^{1}H NMR (300 MHz) and (b) ^{13}C{^{1}H} NMR (75.5 MHz) spectra of [**1**-H](PF$_6$) in CD$_3$CN at 25 °C.

Table 2
Selected torsion angles of [**1**-H](PF$_6$) and coupling constants

	δ_H	^3J (found) (Hz)	^3J (calculated)[a] (Hz)	Torsion angles (°)	
H_a	3.24	10	8.7	H1–N1–C11–H10	167
			8.7	H1–N1–C12–H13	166
H_b	4.19	2	0.4	H1–N1–C11–H11	74
			0.2	H1–N1–C12–H12	76

[a] Calculated from Karplus equation using and the torsion angles determined by X-ray crystallography.



Scheme 1.

carbons signals even at 70 °C (Fig. 3(e)). These spectroscopic results indicate stereochemical inversion of the nitrogen of [**2**-H](PF$_6$) via partial formation of HPF$_6$ on the NMR time scale in solution. Scheme 1(ii) depicts a possible mechanism to account for inversion of trialkylammonium nitrogen of the molecule. Since direct inversion of the stereochemistry of the *N*-protonated 2-aza[3]ferrocenophanes is not plausible, partial formation of the neutral

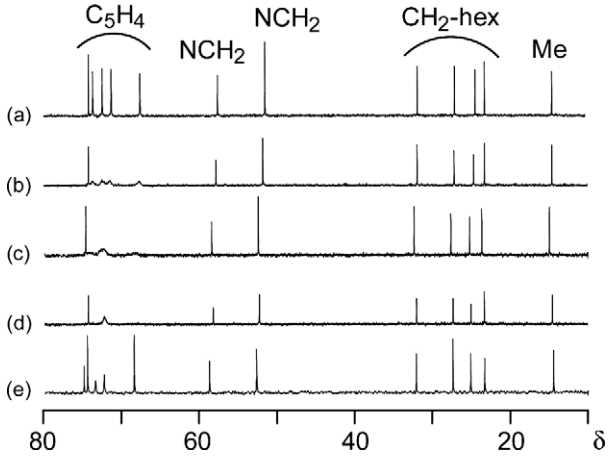


Fig. 3. ^{13}C{^{1}H} NMR spectra (100 MHz) of [**2**-H](PF$_6$) in CD$_3$CN at (a) 0 °C, (b) 25 °C, (c) 50 °C, (d) 70 °C, and (e) 70 °C (after the addition of 1 eq of HPF$_6$).

2-aza[3]ferrocenophanes via deprotonation of the nitrogen atom is reasonable for the formally conformational inversion of ammonium nitrogen. Comparison of Figs. 2(b) and 3 indicates that the inversion reaction of [**1**-H](PF$_6$) is slower than that of [**2**-H](PF$_6$). Previously inversion of amine was reported to be retarded by sterically bulky substitutents at nitrogen atom [11,12]. Slower inversion of [**1**-H](PF$_6$) than that of [**2**-H](PF$_6$) may be attributed to the steric reason in inversion of the amine, although rate-determining step of the total reaction lies in dissociation of HPF$_6$ from tertiaryammonium.

2.2. Electrochemical behavior of the 2-aza[3]ferrocenophanes

[**1**-H](PF$_6$) and [**2**-H](PF$_6$) undergo electrochemical oxidation at $E_{Ox} = +0.44$ V (vs. Ag$^+$/Ag) and +0.45 V, respectively. The redox potentials of neutral and cationic ferrocenophanes are summarized in Table 3. Fig. 4 depicts cyclic voltammograms of **2** and [**2**-H](PF$_6$) in MeCN. Two redox peaks of **2** are observed as shown in Fig. 4(a). Initial oxidation of **2** ($E_{1/2} = +0.05$ V) occurs at the Fe(II) center to form a Fe(III) species, while second oxidation ($E_{1/2} = +0.42$ V) is assigned to the further oxidation of the oxidized species that contains Fe(II) species formed by electron transfer from amine to the Fe(III) center in part [4].

Table 3
Redox potential of the 2-aza[3]ferrocenophanes[a]

Compound	$E_{1/2}$ (V)
1	+0.05
2	+0.03
[**1**-H](PF$_6$)	+0.40
[**2**-H](PF$_6$)	+0.40
Ferrocene	+0.04

[a] Electrochemical potentials are obtained by cyclic voltammogram (CV) in MeCN containing ^{n}Bu$_4$NPF$_6$ as the electrolyte. Potentials are referenced with Ag$^+$/Ag. Sweep rate: 0.10 V s^{-1}.

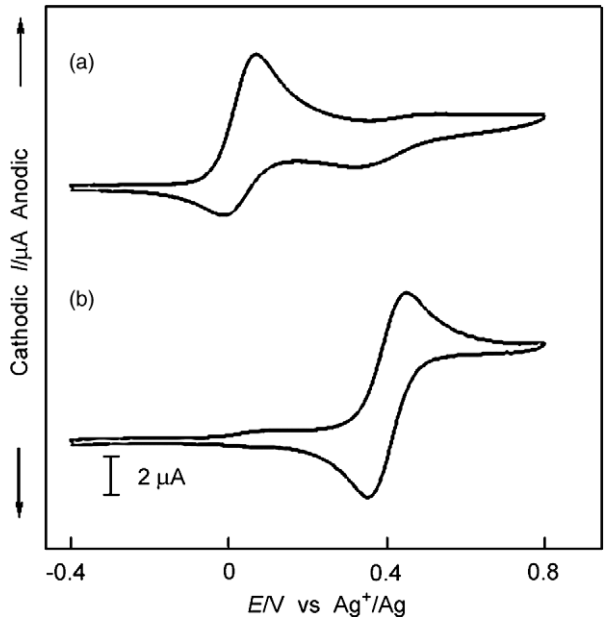


Fig. 4. Cyclic voltammograms in MeCN containing 0.10 M $^{n}Bu_4NPF_6$ at 25 °C. Sweep rate: 0.10 V s^{-1}. (a) **2**. (b) [**2**-H](PF_6) (1.0 mM).

[**2**-H](PF_6) exhibits the redox between ferrocene and ferrocenium cations only ($E_{1/2} = +0.40$ V) because the ammonium group does not cause electrochemical and chemical oxidation at all. A small oxidation peak at +0.09 V is probably due to neutral ferrocenophane **2** formed partly in the solution. The higher potentials of the redox of ferrocene group are ascribed to a static charge of the ammonium cation. An analogous shift of the potential of oxidation and reduction of the Fe center is observed also between **1** ($E_{1/2} = +0.05$ V) and [**1**-H](PF_6) ($E_{1/2} = +0.40$ V) [4c].

In summary, we report the synthesis of cationic *N*-alkyl-2-aza[3]ferrocenophanes which undergo inversion at nitrogen atom in solution. The structural change of [**1**-H](PF_6) was slower than that of [**2**-H](PF_6). The obtained cationic ferrocenophanes exhibit reversible oxidation and reduction of the Fe(II) center at higher potentials than those of the corresponding neutral aza[3]ferrocenophanes.

3. Experimental

3.1. General

Compounds **1** and **2** were prepared according to the literature method [4]. HPF_6 (60 wt% solution in water) was purchased from ACROS ORGANICS. The other chemicals were commercially available. NMR spectra (^1H, $^{13}C\{^1H\}$) were recorded on a Varian MERCURY300 and JEOL EX-400 spectrometer. The chemical shifts were referenced with respect to CD_2HCN (δ 1.93) for ^1H and CD_3CN (δ 1.30) for ^{13}C as internal standards. Electrospray ionization mass spectrometry (ESIMS) was recorded on a ThermoQuest Finnigan LCQ Duo. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder. Cyclic voltammetry (CV) was measured in MeCN solution containing 0.1 M $^{n}Bu_4NPF_6$ with ALS Electrochemical Analyzer Model-600A. The measurement was carried out in a standard one-compartment cell under inert gas equipped with Ag^+/Ag reference electrode, a platinum-wire counter electrode and a platinum-disk working electrode (ID: 1.6 mm).

3.2. Preparation of [1-H](PF_6)

A suspension of **1** (315 mg, 0.95 mmol) in 6 N HCl (50 mL) was stirred for 24 h at room temperature. Evaporation of the solvent gave [**1**-H](Cl) which was washed with water. To a suspension of [**1**-H](Cl) in acetone (50 mL) was added NH_4PF_6 (1.60 g, 9.8 mmol), and the mixture was stirred for 4 h at room temperature. The precipitate was removed by filtration. Evaporation of the filtrate gave an orange solid which was washed with water and dried in vacuo to give [**1**-H](PF_6) as a yellow solid (370 mg, 0.78 mmol, 82%). Anal. Calcd. for $C_{20}H_{22}NF_6FeP + 0.5H_2O$: C, 49.41; H, 4.77; N, 2.88. Found: C, 49.34; H, 4.65; N, 2.78%. ^1H NMR (300 MHz, CD_3CN, 25 °C): δ 2.40 (s, 3H, Me), 3.22 (dd, 2H, NCH_2, $J = 14$, 10 Hz), 4,19 (dd, 2H, NCH_2, $J = 14$, 2 Hz), 4.24–4.26 (2H, C_5H_4), 4.30–4.35 (6H, C_5H_4), 4.57 (d, 2H, NCH_2, $J = 4$ Hz), 7.15 (br, 1H, NH), 7.34 (d, 2H, C_6H_4, $J = 8$ Hz), 7.48 (d, 2H, C_6H_4, $J = 8$ Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN, 25 °C): δ 21.3 (Me), 51.4 ($C_5H_4CH_2$), 61.2 ($C_6H_4CH_2$), 68.0 (C_5H_4), 71.7 (C_5H_4), 73.0 (C_5H_4), 74.2 (C_5H_4), 74.3 (C_5H_4), 125.9 (C_6H_4), 130.7 (C_6H_4), 133.1 (C_6H_4), 141.5 (C_6H_4). ESIMS (MeCN): $m/z = 332$ $[M - PF_6]^+$.

3.3. Preparation of [2-H](PF_6)

A suspension of **2** (308 mg, 0.99 mmol) in 6 N HCl (50 mL) was stirred for 12 h at room temperature. An extra portion of 6 N HCl (50 mL) and acetone (10 mL) was added to the reaction mixture and the mixture was stirred for further 3 days. Evaporation of the solvent gave [**2**-H](Cl) which was washed with water. To a suspension of [**2**-H](Cl) in acetone (50 mL) was added NH_4PF_6 (1.60 g, 9.8 mmol), and the mixture was stirred for 4 h at room temperature. The precipitate was removed by filtration. Evaporation of the filtrate gave a solid which was washed with water and dried in vacuo to give [**2**-H](PF_6) as a yellow solid (372 mg, 0.72 mmol, 72%). Anal. Calcd. for $C_{18}H_{26}NF_6FeP$: C, 47.29; H, 5.73; N, 3.06. Found: C, 47.55; H, 5.74; N, 3.01%. ^1H NMR (300 MHz, CD_3CN, 25 °C): δ 0.93 (t, 3H, CH_3, $J = 7$ Hz), 1.35–1.40 (6H, CH_2), 1.88 (m, 2H, CH_2) 3.35-3.40 (4H, $C_5H_4CH_2$, NCH_2CH_2), 4.10 (d, 2H, $CpCH_2$, $J = 14$ Hz), 4.29–4.32 (6H, C_5H_4), 4.42 (br, 2H, C_5H_4), 6.70 (br, 1H, NH). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN, 25 °C): δ 12.9 (Me), 21.8 (CH_2), 23.1 (CH_2), 25.7 (CH_2), 30.6 (CH_2), 50.6 (NCH_2), 56.8 (NCH_2), 66.8 (br, C_5H_4), 70.6 (br, C_5H_4), 71.7 (br, C_5H_4), 73.0 (br, C_5H_4), 73.5 (C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 0 °C): δ 14.2 (Me), 22.9

Table 4
Crystal data and details of structure refinement of **1** and [**1**-H](PF$_6$)

Compound	**1**	[**1**-H](PF$_6$)
Formula	$C_{20}H_{21}FeN$	$C_{20}H_{22}FeNPF_6$
Molecular weight	331.24	477.21
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	18.633(6)	12.850(5)
b (Å)	7.432(2)	16.360(7)
c (Å)	23.417(6)	9.425(3)
β (°)	95.86(2)	93.27(3)
V (Å^3)	3326(2)	1978(1)
Z	8	4
F(000)	1392.00	976.00
D_c (g cm^{-1})	1.364	1.602
Crystal size (mm)	$1.30 \times 1.20 \times 1.00$	$0.20 \times 0.10 \times 0.05$
Unique reflections	7402	4740
Used reflections	3354 [$I \geqslant 2.0\sigma(I)$]	910 [$I \geqslant 3.0\sigma(I)$]
Number of variables	439	234
R	0.052 [$I \geqslant 2.0\sigma(I)$]	0.072 [$I \geqslant 3.0\sigma(I)$]
R_w	0.060 [$I \geqslant 2.0\sigma(I)$]	0.089 [$I \geqslant 3.0\sigma(I)$]
Goodness-of-fit	1.00	1.03

(CH_2), 24.2 (CH_2), 26.8 (CH_2), 31.7 (CH_2), 51.6 (NCH_2), 57.8 (NCH_2), 67.8 (C_5H_4), 71.6 (C_5H_4), 72.7 (C_5H_4), 74.0 (C_5H_4), 74.5 (C_5H_4-*ipso*).

3.4. X-ray structure analyses

Crystals of **1** and [**1**-H](PF$_6$) suitable for X-ray diffraction study were obtained by recrystallization from $CHCl_3$/MeOH and MeCN/Et_2O, respectively, and mounted in glass capillary tubes. All measurements of **1** and [**1**-H](PF$_6$) were made on Rigaku AFC5R diffractometer and Rigaku AFC7R diffractometer, respectively, with graphite monochromated Mo Kα radiation. Calculations were carried out by using a program package CRYSTAL STRUCTURE™ for Windows [13]. Crystal data and detailed results of refinement are summarized in Table 4. For [**1**-H](PF$_6$), the cyclopentadienyl ligands of C1–C10 were refined isotropically. All hydrogen atoms were included at calculated positions with fixed thermal parameters.

4. Supplementary material

Crystallographic data for the crystal structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 603405 and 603406 for **1** and [**1**-H](PF$_6$), respectively. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Acknowledgments

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