[2-(N,N-Dimethylaminomethyl)ferrocenyl] as a ligand towards mercury

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Abstract

The diorganomercurial bis[2-(N,N-dimethylaminomethyl)ferrocenyl]mercury(II), $(FcN)_2Hg$ (**3**), can be obtained by the symmetrisation of the heteroleptic $(FcN)HgCl$ (**2**) with $Na_2S_2O_3$ or in the transmetallation reaction of **2** with $(FcN)Li$. By crystallisation only the crystals of *rac*-$(FcN)_2Hg$ were obtained. X-ray diffraction analysis revealed linear coordinated mercury atom with two η^1-bonded FcN ligands. Additionally, weak chelate interactions exist between mercury and nitrogen atoms of the $-CH_2NMe_2$ side chains. According to the ^{1}H-NMR findings, these interactions are not preserved in solution. Diorganomercurial **3** appears in solution as a mixture of two diastereomers with *rac/meso*-$(FcN)_2Hg$ ratio of 1:1. This diastereomeric ratio in solution remains constant within a wide temperature range and in different solvents. The NMR spectroscopic data of the heteroleptic organomercurials $[(FcN)HgCl]_2 \cdot H_2O$ (**1**) and $(FcN)HgCl$ (**2**) indicate the chelate-free structure of this compounds in solution within the studied temperature interval (-80 to 90 °C). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1-[2-(N,N-dimethylaminomethyl)ferrocenyl] ligand; Mercury; Diastereomeric ratio
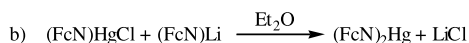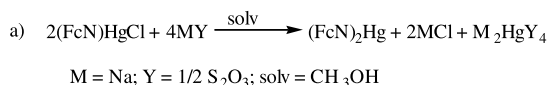
1. Introduction

Organomercurials of the type RHgCl and R_2Hg are often less reductive towards transition metal chlorides with d-metal atoms in higher oxidation states than lithium organyls, due to the decreasing polarity of the Hg–C bond, yielding the corresponding transition metal organometallics [1].

The heteroleptic [2-(N,N-dimethylaminomethyl)-ferrocenyl]mercury(II) chloride, (FcN)HgCl, was syn-

thesised previously by Slocum and Engelmann in 1970 [2], whereas its crystal structure was determined later on in 1985 by Kuz'mina et al. [3]. The homoleptic FcN-derivative is still unknown, although some unsuccessful efforts to synthesise this compound were done [4].

Mercury compounds are often good precursors for the synthesis of the organometallic compounds of transition metals. One can obtain for example $PhVOCl_2$ from a transmetallation of $VOCl_3$ and Ph_2Hg [5], or $MeWoCl_3$ from a transmetallation of $WOCl_4$ and Me_2Hg [6].

The aim of our study is the synthesis of the FcN-derivatives with less polar metal–carbon bonds than in (FcN)Li, which is still the most common organylating agent for the synthesis of transition metal FcN-derivatives, but often reflects a strong reducing effect towards the transition metal compounds [7]. Therefore, it was of importance to synthesise this homoleptic mercury–FcN-compound, to study its properties and its behaviour in solution. Additionally, it was also essential to investigate whether the homoleptic mercury derivative also

a) $2(FcN)HgCl + 4MY \xrightarrow{\text{solv}} (FcN)_2Hg + 2MCl + M_2HgY_4$

   $M = Na; Y = 1/2\ S_2O_3; \text{solv} = CH_3OH$

b) $(FcN)HgCl + (FcN)Li \xrightarrow{\text{Et}_2O} (FcN)_2Hg + LiCl$
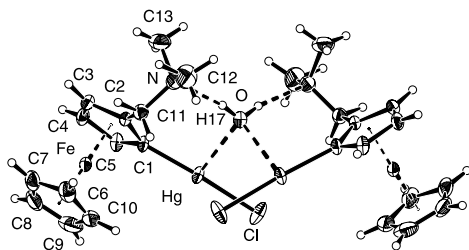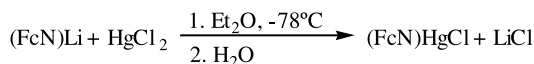
Scheme 1.

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Fig. 1. Molecular structure of **1** with thermal ellipsoids at 50% probability level. H atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for [(FcN)HgCl]$_2 \cdot$H$_2$O (**1**)

Hg–C1	2.054(4)	C1–Hg–O	96.6(1)
Hg–Cl	2.345(1)	Cl–Hg–O	89.7(1)
Hg–O	2.642(3)	Hg–O–Hg′	92.8(2)
N–C11	1.475(6)	C2–C1–Hg	128.9(3)
N–C12	1.460(9)	C5–C1–Hg	123.2(3)
N–C13	1.459(8)	C2–C11–N	114.4(4)
Fe–C(1m) [a]	1.640(9)	C12–N–C11	109.9(5)
Fe–C(2m)	1.652(7)	C13–N–C11	110.0(5)
Hg···Hg′	4.180(5)	C13–N–C12	109.2(6)
		C1–Hg–Cl	172.2(1)

[a] Suffix 'm' denotes a centroid of the Cp ring.

$$(FcN)Li + HgCl_2 \xrightarrow[\text{2. H}_2\text{O}]{\text{1. Et}_2\text{O, -78°C}} (FcN)HgCl + LiCl$$

Scheme 2.

forms different diastereomers and if so, does an exchange between those diastereomers take place in solution, analogously to the already studied FcN-derivatives of magnesium [8], zinc [9] and lead [10].

2. Results and discussion

Two strategies for the synthesis of bis[2-(*N,N*-dimethylaminomethyl)ferrocenyl]mercury(II) were developed: a symmetrisation of the heteroleptic derivative (FcN)HgCl with different complexing agents, such as potassium cyanide, -iodide and -thiocyanate and sodium thiosulfate, and a transmetallation reaction between (FcN)HgCl and (FcN)Li. These synthetic pathways are shown in Scheme 1.

The synthesis of the heteroleptic precursor (FcN)HgCl proceeded according to Slocum et al. [2]. According to this method, (FcN)Li reacts with one equivalent of HgCl$_2$ in diethyl ether at room temperature. Afterwards, the reaction mixture is hydrolysed due to the better separation of LiCl formed in the reaction. From the diethyl ether phase, orange crystals were obtained. Surprisingly, elemental analysis and ¹H-NMR spectroscopy revealed a hydrate of formula [(FcN)HgCl]$_2 \cdot$H$_2$O (**1**). Most probably (FcN)HgCl

preferably crystallises as a hemi-hydrate in the presence of traces of water. The compound **1** is air-stable and well soluble in both polar and nonpolar solvents.

The X-ray diffraction analysis revealed that **1** crystallises in the monoclinic space group *C*2/*c* (Fig. 1). The most important bond lengths and angles are summarised in Table 1.

Before discussing the crystal structure of **1**, it is necessary to focus on the dual behaviour of mercury. One has to differentiate between the characteristic coordination, where the mercury–donor atom bond distance is within the sum of the appropriate covalent radii, and the effective coordination sphere, in which this distance is within the sum of the van der Waals radii. Grdenic proposed the value of 1.5–1.73 Å for the van der Waals radius of mercury, as this is half the distance between the mercury atoms in metallic mercury [11]. In more recent works, the van der Waals radius of mercury was extended to the range 1.7–2.0 Å [12].

The asymmetric unit of **1** consists of half the formal unit, in which the other half of the molecule is generated by the C_2-axis running through the oxygen atom of the water molecule. Thus, **1** consists of two (FcN)HgCl units interconnected via the water molecule, that is, through H···N hydrogen bonds between hydrogen atoms of the water and nitrogen atoms of the –CH$_2$NMe$_2$-groups of each FcN ligand. The H17···N hydrogen bond is 1.938(7) Å, the O–H17···N distance 2.745(5) Å and the angle O–H17···N 168.5(4)°.

The coordination at the mercury atom is linear (C1–Hg – Cl = 172.2(1)°) with one η^1-bonded FcN-group and one chlorine. The Hg–C1 bond length of 2.054(4) Å corresponds to a relatively short Hg–C bond [13,14]. The Hg–Cl bond is with 2.345 Å within the interval for Hg–Cl bonds [13,14].

An additional interaction between the mercury atoms and the oxygen from water is present in **1**, as seen in Fig. 1. This Hg–O distance (2.641(4) Å) is too large to be considered as a bond, but it can be described as a strong interaction (the sum of covalent radii for Hg and O is 2.38 Å, the sum of the van der Waals radii 2.90–3.13 Å). This Hg–O distance is comparable to the average value of 2.680 Å obtained statistically from different mercury hydrates [14].

The sum of angles around oxygen (ca 309°) deviates significantly from the corresponding ideal value for a tetrahedral coordination of 327°: the bond angles Hg–O–Hg′, Hg–O–H17 and H17–O–H17′ are 92.8(3), 102.3(3) and 112.9(6)°, respectively. The coordination geometry around nitrogen atoms is virtually tetrahedral with an average value of C–N–C bond angles of 110.8°.

Despite its interesting crystal structure, hydrate **1** possesses no preparative value, due to the hydrolytic decomposition of (FcN)Li during the transmetallation reaction with **1**, according to the Scheme 1b. Therefore, it was important to obtain the reactant (FcN)HgCl as

an anhydrous substance. The synthesis described above was modified by leaving out the hydrolysis (Scheme 2) and the reddish–brown crystals of anhydrous (FcN)HgCl (**2**) were obtained. The compound **2** was characterised by elemental analysis, NMR spectroscopy and X-ray diffraction analysis.

The latter revealed the monoclinic space group $P2_1/c$, opposite to the results of Kuz'mina et al., whose crystals from a methanol solution crystallised in the monoclinic space group $P\bar{1}$. This polymorphism is most probably due to different crystallisation conditions. The $P2_1/c$ polymorph is described in the following text, whereas the parameter of the other polymorh are given in brackets for comparison. The molecular structure of **2** is shown in Fig. 2, the most important molecular parameters are listed in Table 2.

In the single crystal of **2** a centrosymmetric dimer is formed due to intermolecular Hg···N interactions, generating a ten-membered ring system. The mercury atoms are three-coordinated with one chlorine, one η^1-bonded FcN-group and one nitrogen of the second (FcN)HgCl molecule in a T-shape arrangement. Although both mercury atoms are situated one on the top of the other, the distance between these two atoms is too large (3.859(5) Å) to consider an interaction between them [11,12].
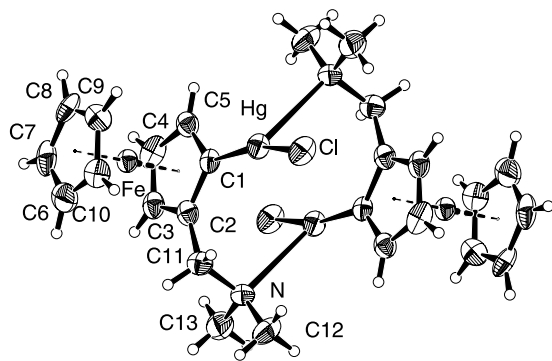

Fig. 2. Molecular structure of **2** with thermal ellipsoids at 50% probability level. H atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for (FcN)HgCl (**2**)

Hg–C1	2.063(9)	C1–Hg–Cl	164.2(3)
Hg–Cl	2.352(3)	C1–Hg···N′	100.4(1)
Hg···N′	2.780(4)	Cl–Hg···N′	94.7(6)
N–C11	1.487(13)	C2–C1–Hg	1.241(7)
N–C12	1.457(14)	C5–C1–Hg	1.283(8)
N–C13	1.473(15)	C2–C11–N	113.1(9)
Fe–C(1m) [a]	1.648(6)	C12–N–C11	109.5(9)
Fe–C(2m)	1.647(5)	C13–N–C11	109.9(8)
		C13–N–C12	109.8(10)

[a] Suffix 'm' denotes a centroid of the Cp ring.

The Hg–C1 bond length in **2** of 2.063(9) Å [2.042 Å] corresponds to those of 2.054(4) Å in **1** and of 2.065(7) Å in ferrocenophane [(FcN)Hg]$_2$ [15]. The Hg–Cl bond distance of 2.352(3) Å [2.323 Å] in **2** corresponds well to the bond lengths of 2.345(1) Å in **1** and 2.35(1) Å in Et$_2$NCH$_2$CH$_2$HgCl [16].

Both covalent bonds to mercury in **2** form a bond angle Cl–Hg–Cl of 164.2(3)° [169.4°]. The distortion from linearity is caused by the interaction of mercury with the nitrogen atom of the –CH$_2$NMe$_2$ side chain from a neighboured (FcN)HgCl molecule. The distance between the mercury and the nitrogen atom (2.780(4) Å [2.772 Å]) is significantly shorter than the sum of the corresponding van der Waals radii (3.00–3.23 Å) [11,12]. This intramolecular Hg···N interaction is comparable to those of 2.72(2) and 2.83 Å found in Et$_2$NCH$_2$CH$_2$HgCl [16] and methyl-2-mercaptopyrimidinatomercury(II), respectively [17]. The C1–Hg···N and Cl–Hg···N bond angles of 100.4(1) [99.9] and 94.7(6)° [90.2°], respectively, correspond to the planar T-shaped coordination around the mercury atom. The Cp-rings of the FcN ligands are ecliptically arranged. Each nitrogen atom possesses an ideal tetrahedral geometry.

The bonding relations in **2** are comparable to those in the FcN-derivative of gold(I) [(FcN)Au]$_2$ [18].

After successful synthesis of the heteroleptic reactant (FcN)HgCl (**2**), the preparation of the diorganomercurial (FcN)$_2$Hg followed as already described in Scheme 1. At first, a symmetrisation of **2** with different complexing agents was carried out (Scheme 1a). However, if the potassium compounds were used as complexing agents (KI, KCN and KSCN), no reaction was observed, despite of carrying out the reactions in refluxing acetone. The symmetrisation of **2** with Na$_2$S$_2$O$_3$ in refluxing methanol successfully yielded (FcN)$_2$Hg (**3**) in 75% yield.

Compound **3** can also be synthesised in the transmetallation reaction of **2** with (FcN)Li in a 1:1 ratio in diethyl ether. In this way orange crystals of (FcN)$_2$Hg were obtained in 91% yield.

Diorganomercurial **3** is air-stable and well-soluble in all common solvents. The ^{1}H- and ^{13}C-NMR data of **3** in CDCl$_3$ at 23 °C show that it appears in solution as a mixture of diastereomers in the ratio of 1:1 (see Scheme 3).

From a saturated solution of **3** single crystals of the *rac*-diastereomer **3a** were obtained and characterised by X-ray crystallography. The *rac*-(FcN)$_2$Hg possesses a set of either *R*- or *S*-configured FcN ligands. Therefore, it is assumed that in the other diastereomer **3b** one of the ligands is *R*- and the other one *S*-configured (*mes*o-(FcN)$_2$Hg). The molecular structure of **3a** is shown in Fig. 3. Selected bond lengths and angles of **3a** are given in Table 3.

$(R, R)/(S, S)$-$(FcN)_2Hg$ $(R, S)/(S, R)$-$(FcN)_2Hg$
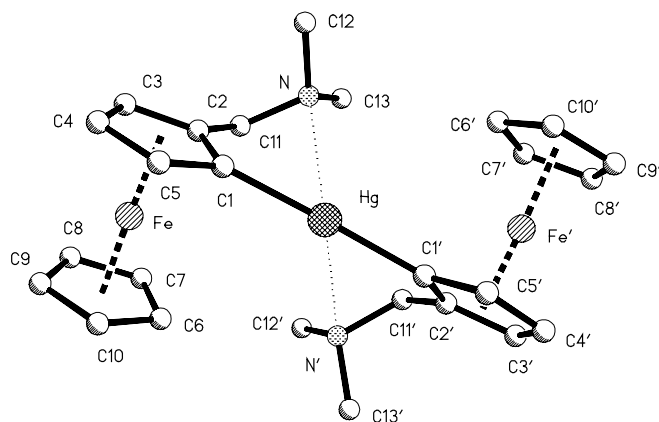
3a   **3b**
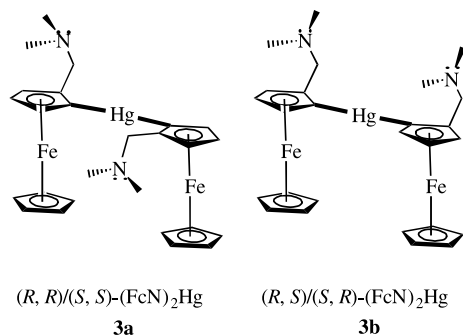
Scheme 3.

Fig. 3. Molecular structure of **3a** (*rac*-diastereomer) with thermal ellipsoids at 50% probability level. H atoms are omitted for clarity. To all atoms of the second FcN ligand a ′ sign is assigned, since both FcN groups, although not symmetrically related, are of the equal connectivity.

Table 3
Selected bond lengths (Å) and angles (°) for *rac*-$(FcN)_2Hg$ (**3a**)

Bond lengths			
Hg–C1	2.046(5)	Fe–C(1m) [a]	1.653(6)
Hg–C1′	2.047(5)	Fe–C(2m)	1.652(6)
Hg···N	3.308(5)	Fe′–C(1′m)	1.649(7)
Hg···N′	3.415(4)	Fe′–C(2′m)	1.651(7)
N′–C11	1.461(6)	N′–C11′	1.462(6)
N–C12	1.456(8)	N′–C12′	1.462(6)
N–C13	1.456(8)	N′–C13′	1.452(6)
Bond angles			
C1–Hg–C1′	177.1(2)	C5–C1–Hg	130.7(4)
C2–C1–Hg	122.8(4)	C5′–C1′–Hg	130.9(4)
C2′–C1′–Hg	123.1(3)	C11–N–C12	110.9(5)
C12–N–C13	109.8(5)	C11–N–C13	109.8(4)
C11′–N′–C12′	109.7(4)	C11′–N′–C13′	110.3(4)
		C12′–N′–C13′	109.1(4)

[a] Suffix 'm' denotes a centroid of the Cp ring.

The asymmetric unit of **3a** consists of one formal unit. One approximate C_2-axis runs through the mercury atom, which is almost perfectly linearly coordinated (C1–Hg–C1′ = 177.05(19)°). The Hg–C1 and Hg–C1′ bond lengths of 2.046(5) and 2.047(5) Å, re-

spectively, are almost identical and correspond well to the Hg–C distances of 2.054(4) Å in **1** and 2.063(9) Å in **2**. The distances between mercury and the nitrogen atoms of the each FcN ligand (3.308(5) and 3.415(4) Å) are slightly larger than the sum of the corresponding van der Waals radii, and are therefore considered as very weak interactions. It is to be expected that such weak coordinations are not preserved in solution.

The coordination sphere of mercury in **3a** corresponds to that in the diorganomercurial ($C_6H_4CH_2$-$NMe_2)_2Hg$, where linearly coordinated mercury atom (Hg–C = 2.10(2) Å) forms additional interactions with nitrogen atoms of the –CH_2NMe_2 side chains [19]. The authors describe these Hg–N distances of 2.89(1) Å as strong chelate interactions. This confirms that the distances between mercury and nitrogen atoms present weak interactions.

The bonding of the mercury atom to the cylopentadienyl ring causes a distortion around the α-carbon atoms in **3a**. The C2–C1–Hg and C2′–C1′–Hg angles inside the Cp rings (122.8(4) and 123.1(3)°, respectively) are therefore smaller than the angles outside the Cp rings C5–C1–Hg and C5′–C1′–Hg (130.7(4) and 130.9(4)°, respectively).

The chemical shifts in the ^1H- and ^{13}C-NMR spectra of the organomercurials $[(FcN)HgCl]_2 \cdot H_2O$ (**1**), $(FcN)HgCl$ (**2**) and $(FcN)_2Hg$ (**3**) are virtually identical and in accordance with those of other comparable FcN-derivatives, such as $(FcN)_2Mg(solv)$ [8], $(FcN)_2Zn$ [9], $(FcN)ZnCl$ [9] and $(FcN)_2Pb$ [10]. Furthermore, the

Table 4
^1H-NMR data (δ, ppm, $CDCl_3$, 23 °C) for $[(FcN)HgCl]_2 \cdot H_2O$ (**1**), $(FcN)HgCl$ (**2**) and $(FcN)_2Hg$ (**3**)

	NMe_2	CH_2N	CpFe	C_5H_3
1 [a]	2.34 (s, 6H)	3.04 (d, 1H, J = 14)	4.23 (s, 5H)	4.03 (s, 1H)
		3.55 (d, 1H, J = 14)		4.25 (s, 1H)
				4.29 (s, 1H)
2	2.24 (s, 6H)	3.05 (d, 1H, J = 14)	4.11 (s, 5H)	4.04 (s, 1H)
		3.56 (d, 1H, J = 14)		4.26 (s, 1H)
				4.30 (s, 1H)
3 [b]	2.23 (s, 12H)	3.23 (d, 2H, J = 13)	4.15 (s, 10H)	4.02 (s, 2H)
	2.15 (s, 12H)	3.46 (d, 2H, J = 13)	4.25 (s, 10H)	4.03 (s, 2H)
		3.24 (d, 2H, J = 13)		4.30 (s, 2H)
		3.47 (d, 2H, J = 13)		4.31 (s, 2H)
				4.41 (s, 2H)
				4.42 (s, 2H)

[a] Signal from water at 1.67 ppm.
[b] A differentiation between *rac*- and *meso*-$(FcN)_2Hg$ not possible.

Table 5
^{13}C NMR data (δ, ppm, CDCl$_3$, 23 °C) for (FcN)HgCl (**2**) and (FcN)$_2$Hg (**3**)

	NMe$_2$	CH$_2$N	CpFe	C$_5$H$_3$	C$_5$H$_3$–CH$_2$N	Hg–C$_5$H$_3$
2	45.3	59.3 ($^3J_{C,Hg}$ 33 Hz)	69.3	68.7 ($J_{C,Hg}$ 160 Hz)	90.5 ($^2J_{C,Hg}$ 140 Hz)	84.9 ($^1J_{C,Hg}$ 975 Hz)
				69.6 ($J_{C,Hg}$ 203 Hz)		
				71.9 ($J_{C,Hg}$ 249 Hz)		
3 [a]	45.3 45.4	61.5 ($^3J_{C,Hg}$ 25 Hz)	68.1	70.4 ($J_{C,Hg}$ 109 Hz)	91.0 ($^2J_{C,Hg}$ 90 Hz)	104.1 ($^1J_{C,Hg}$ 1355 Hz)
		61.7 ($^3J_{C,Hg}$ 25 Hz)	68.2	72.0 ($J_{C,Hg}$ 79 Hz)	91.2 ($^2J_{C,Hg}$ 90 Hz)	104.4 ($^1J_{C,Hg}$ 1355 Hz)
				74.6 ($J_{C,Hg}$ 133 Hz)		
				70.5 ($J_{C,Hg}$ 109 Hz)		
				72.1 ($J_{C,Hg}$ 78 Hz)		
				74.7 ($J_{C,Hg}$ 133 Hz)		

[a] A differentiation between *rac*- and *meso*-(FcN)$_2$Hg not possible.

NMR spectra of the compounds **1** and **2** in CDCl$_3$ at 23 °C are virtually identical and correspond to a (FcN)HgCl molecule. The ^{1}H-NMR data of all three compounds **1**, **2** and **3** are given in Table 4.

The ^{1}H-NMR chemical shifts of **1** and **2** are within the expected interval for FcN compounds. Both dimethylamino groups are magnetically equivalent, even at low temperatures (-80 °C), pointing to an unhindered inversion at the nitrogen atoms. This means that the intermolecular Hg···N interactions in **1**, as well as the intramolecular Hg···N chelate interactions in **2** are not preserved in solution. The methylene protons are split into an AB-spin system.

The ^{1}H-NMR data of (FcN)$_2$Hg show the presence of two diastereomers, *rac*- and *meso*-(FcN)$_2$Hg, in the ratio 1:1. Because of the presence of a C_2-axis in the former and an inversion centre in the latter diastereomer, in each diastereomer only one set of signals for both FcN groups appears. It was not possible to assign the signal sets to the appropriate diastereomer, due to their equal intensities. In the ^{1}H-NMR spectrum of **3** in CDCl$_3$ at 23 °C (Table 4) both NMe$_2$ substituients are magnetically equivalent, resulting in only one signal for both methyl groups. The methylene protons show a typical splitting pattern of a AB-spin system. The ^{1}H-NMR spectra of **3** remain unaltered within the temperature interval from -80 to 90 °C. The diastereomeric *rac*/*meso*-(FcN)$_2$Hg ratio of 1:1 remains unchanged in the given temperature interval. However, a possibility of an eventual exchange between the diastereomers **3a** and **3b** in solution cannot be ruled out, similarly to (FcN)$_2$Mg(OEt)$_2$ [8], (FcN)$_2$Zn [9] and (FcN)$_2$Pb [10]. A plausible explanation for this statistic diastereomeric distribution may be found in the geometric properties. Presumably the formation of both diastereomers is equally likely due to the linear geometry at the mercury atom. Since both –CH$_2$NMe$_2$ side chains are fairly apart from each other, both diastereomers will have nearly the same stability.

In the ^{13}C-NMR spectra of **2** and **3** almost all signals are accompanied by satellites due to ^{13}C–^{199}Hg coupling (see Table 5).

The chemical shift of the α-carbon atom in **2** appears at 84.9 ppm with a coupling constant $^1J_{C,Hg}$ of 975 Hz. The signal of the quaternary carbon atom bonded to the –CH$_2$NMe$_2$ side chain is shifted towards low field at 90.5 ppm and exhibits a coupling constant $^2J_{C,Hg}$ of 140 Hz. Further couplings were observed for the signal of the methylene group at 59.3 ppm ($^3J_{C,Hg} = 32$ Hz), as well as for the remaining signals of the disubstituted Cp ring at 68.7 ppm ($J_{C,Hg} = 160$ Hz), 69.6 ppm ($J_{C,Hg} = 203$ Hz) and 71.9 ppm ($J_{C,Hg} = 249$ Hz). The methyl signal of the dimethylamino groups is not attended by satellites. This is an additional indication, that the chelate structure of **2** is not preserved in solution.

In the ^{13}C NMR spectrum of **3** each diastereomer has only one set of signals for both FcN groups. Due to the ^{13}C–^{199}Hg coupling all the signals are attended by satellites, except for those of the methyl groups, similarly to **2**.

The signal of the α-carbon atom of each diastereomer appears at 104.1 and 104.4 ppm, respectively, and possesses a coupling constant $^1J_{C,Hg}$ of 1355 Hz each. This coupling constant has the same order of magnitude as the direct $^1J_{C,Hg}$ couplings of 1190 Hz in Ph$_2$Hg [20] and 1124.8 Hz in (2-Me-C$_6$H$_4$)$_2$Hg [20b,21]. The signal of the quaternary carbon atom bonded to the –CH$_2$NMe$_2$ side chain is shifted towards low field at 91.0 and 91.1 ppm for each diastereomer, respectively, and exhibits a coupling constant $^2J_{C,Hg}$ of 90 Hz each. This coupling in **3** resembles that of 67 Hz for the carbon atom in the 2-position to the mercury atom in (2-Me-C$_6$H$_4$)$_2$Hg [20b,21]. Additional couplings were found for the remaining signals of the C$_5$H$_3$-ring at 70.4 and 70.5 ppm ($J_{C,Hg} = 109$ Hz each), 72.0 and 72.1 ppm ($J_{C,Hg} = 79$ Hz each), 74.6 and 74.7 ppm ($J_{C,Hg} = 133$ Hz each). The signal of the methylene group for each diastereomer at 61.5 and 61.7 ppm, respectively, couples with the ^{199}Hg-nucleus with $^3J_{C,Hg} = 25$ Hz each, consistent with the corresponding values in **2**. The

coupling constants in **2** and **3** (32 and 25 Hz, respectively) are significantly smaller than the corresponding couplings of 101 Hz in organomercurial (2-Me$_2$NCH$_2$C$_6$H$_4$)HgCl [22] and 63 Hz in diorganomercurial (2-Me$_2$NCH$_2$C$_6$H$_4$)$_2$Hg [19], in which chelate structures, preserved in solution, were proven.

The ^{13}C chemical shifts of the α-carbon atoms in the homoleptic (FcN)$_2$Hg (**3**) are shifted downfield compared with the heteroleptic reactant **2**. The chemical shifts of the remaining carbon atoms in **3** correspond to those in **2**.

Redox behaviour of **3** was examined by electrochemical techniques (Fig. 4). At low scan it undergoes a single-stepped two-electron oxidation at $E^{\circ\prime} = +0.3$ V. With the progressive increase of the scan rate from 0.02 to 2.00 V/s the peak-current-ratio remains constant and equal 1 ($i_{pc}/i_{pa} = 1$). In contrast, the peak difference increases with increasing scan rate (from 90 mV at 0.02 V/s to 350 mV at 2.00 V/s), indicating transient chemical reversibility.

3. Experimental

3.1. General procedures

All manipulations were carried out by using standard Schlenk techniques under an inert Ar atmosphere. All solvents were dried by standard procedures and distilled under Ar prior to use. (FcN)Li was prepared by previously described method [23]. HgCl$_2$ and Na$_2$S$_2$O$_3$ were purchased commercially and used as received. ^{1}H- and ^{13}C-NMR data were recorded on a Varian 300 MHz
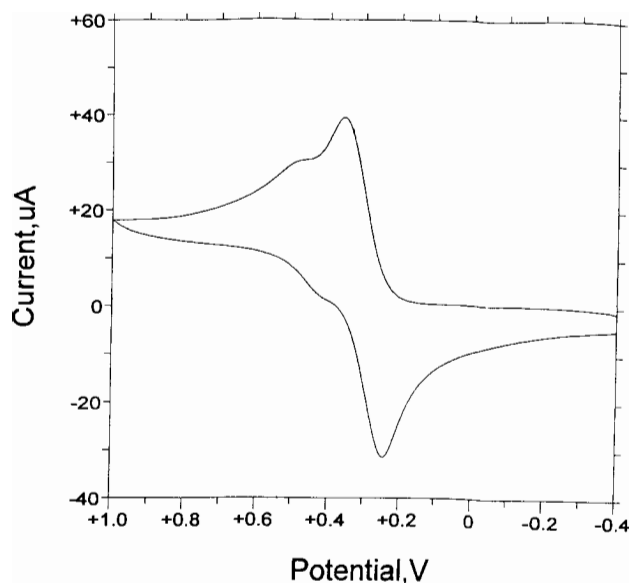
instrument and referenced to the deuterated solvent.

Materials and apparatus for electrochemistry have been described elsewhere (three-electrode-cell, platinum disk as a working electrode, platinum spiral as a counter electrode) [24]. The potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions (CH$_2$Cl$_2$ solution containing [NBu$_4$][PF$_6$] as a supporting electrolyte (0.2 mol/l) the one-electron oxidation of FcN occurs at $E^{\circ\prime} = +0.38$ V.

3.2. Synthesis of [(FcN)HgCl]$_2$·H$_2$O (*1*)

A suspension of (FcN)Li (1.57 g, 6.3 mmol) in Et$_2$O (50 ml) cooled to -78 °C was added to a cooled, rapidly stirred suspension of HgCl$_2$ (1.70 g, 6.3 mmol) in Et$_2$O (100 ml). The reaction mixture was stirred for 1 h and then allowed to warm up to room temperature (r.t.). After stirring for 2 days the reaction mixture was hydrolysed with water (50 ml) and stirred for further 3 h. The ether phase was separated and the water phase extracted three times with 20 ml ether. The ether phases were collected and dried over anhyd. MgSO$_4$. MgSO$_4$ was filtered off, the ether solution reduced to the volume of 10 ml in vacuum and stored at 7 °C to give reddish–brown crystals of **1**. Yield: 2.65 g, 80%. Anal. Calc. for C$_{26}$H$_{32}$Cl$_2$Fe$_2$Hg$_2$N$_2$O: C, 32.10; H, 3.52; N, 2.88; Cl, 7.29. Found: C, 32.9; H, 3.48; N, 2.90; Cl, 7.31%.

3.3. Synthesis of (FcN)HgCl (*2*)

A suspension of (FcN)Li (1.57 g, 6.3 mmol) in Et$_2$O (50 ml) cooled at -78 °C was added to a cooled, rapidly stirred suspension of HgCl$_2$ (1.70 g, 6.3 mmol) in a mixture of Et$_2$O (75 ml) and *n*-pentane (75 ml). The reaction mixture was stirred for 1 h and then allowed to warm up to r.t. After stirring for 2 days, the solvent mixture was removed under reduced pressure, and the orange residue extracted with *n*-pentane (20 ml). The solution was reduced to incipient crystallisation and stored at 7 °C to give reddish–brown crystals of **2**. Yield: 2.68 g, 80%.

Anal. Calc. for C$_{13}$H$_{16}$ClFeHgN: C, 32.35; H, 3.35; N, 2.91; Cl, 7.42. Found: C, 32.12; H, 3.29; N, 2.95; Cl, 7.39%.

3.4. Synthesis of (FcN)$_2$Hg (*3*)

(a) To a solution of **2** (3.1 g, 6.3 mmol) in MeOH (100 ml) at 25 °C an excess of Na$_2$S$_2$O$_3$ (1.19 g, 7.6 mmol) was added. The reaction mixture was refluxed for 24 h, the solvent removed under reduced pressure and the residue extracted with *n*-pentane (10 ml). After cooling the *n*-pentane solution at -30 °C the orange crystals of **3** were obtained. Yield: 3.23 g, 75%.

Fig. 4. Cyclic voltammogram recorded at a platinum electrode in CH$_2$Cl$_2$ solution containing **3** (1.1×10^{-3} mol/l) and [NBu$_4$][PF$_6$] (0.2 mol/l).

Table 6
Crystallographic data for **1**, **2** and **3a**

	1	**2**	**3a**
Empirical formula	$C_{26}H_{34}Cl_2Fe_2Hg_2N_2O$	$C_{13}H_{16}ClFeHgN$	$C_{26}H_{32}Fe_2HgN_2$
Molecular mass	974.33	478.16	684.33
Dimensions (mm)	$0.41 \times 0.25 \times 0.21$	$0.43 \times 0.27 \times 0.23$	$0.51 \times 0.48 \times 0.10$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$C2/c$
a (Å)	27.580(6)	9.6489(12)	32.5539(6)
b (Å)	8.682(2)	8.0343(11)	8.0261(3)
c (Å)	12.492(3)	17.6496(12)	18.5419(3)
β (°)	92.95(3)	97.640(9)	92.645(3)
V (Å³)	2987.5(11)	1356.1(3)	4839.5(2)
Z	4	4	8
D_{calc} (g/ml)	2.166	2.342	1.880
T (K)	173(2)	173(2)	173(2)
μ (mm^{-1})	11.398	12.550	7.528
θ_{max} (°)	26.04	25.00	28.33
Reflections	10121	2291	15756
Unique reflections	2873	2291	5994
Structure determination	Direct methods	Direct methods	Direct methods
Refinement	F^2 in SHELXL	F^2 in SHELXL	F^2 in SHELXL
Parameters refined	207	155	284
$R_1[I>2\sigma(I)]$	0.0238	0.0448	0.0379
wR_2 (all data)	0.0536	0.1312	0.0822
Goodness-of-fit (an F^2)	1.075	1.108	0.962

(b) To a solution of **2** (3.1 g, 6.3 mmol) in Et$_2$O (200 ml) cooled at -78 °C a cooled suspension of (FcN)Li (1.57 g, 6.3 mmol) in Et$_2$O (50 ml) was added with vigorous stirring. After 1 h stirring the reaction mixture was allowed to warm up to r.t., and stirred for further 2 days. The solvent was removed under reduced pressure and the orange residue extracted with *n*-pentane (20 ml). The *n*-pentane solution was stored at 7 °C to give orange crystals of **3**. Yield: 3.91 g, 91%.

Anal. Calc. for $C_{26}H_{32}Fe_2Hg_2N_2$: C, 45.61; H, 4.71; N, 4.08. Found: C, 45.83; H, 4.64; N, 4.10%.

3.5. X-ray structure analysis of **1**, **2** and **3a**

Crystal and numerical data of the structure determinations are given in Table 6. A single crystal was mounted on a glass fibre and then transferred to the diffractometer in a stream of a cold gas (Stoe STADI IV-diffractometer for **1**, Bruker AXS Smart CCD System with LT-2 low-temperature-adapter for **2** and **3a**). Monochromatic Mo–K$_\alpha$ radiation ($\lambda = 71.073$ ppm) was used. Data were corrected for Lorentz and polarisation effects. Absorption correction (multi-scan

method SADABS) was employed. The structures were solved by direct methods using the SHELXS programme and refined by full-matrix least-squares against F^2 with SHELXL-97 [25]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found in difference Fourier maps and refined isotropically.

4. Supplementary material

Crystallographic data (excluding structure factors) for the reported structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 114067 (**1**), 114068 (**2**) and 146613 (**3a**). Copies of data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336093; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)

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