



# Ionic Liquids

# Chiral and Redox-Active Room-Temperature Ionic Liquids Based on Ferrocene and L-Proline

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**Abstract:** The syntheses of room-temperature ionic liquids (RTILs) combining the naturally occurring amino acid L-proline and ferrocene (Fc) building blocks are reported. After quaternization of ({[(25)-*N*-methylpyrrolidine-2-yl]methyleneoxy}-carbonyl)ferrocene (**1**) with alkyl iodides and anion exchange, the resulting diastereomeric (15,25)- and (1*R*,25)-[(ferrocenyl-carbonyl)oxy]methylene-*N*,*N*-dialkylpyrrolidine-1-ium RTILs are redox-active and air- and water-stable. They are also thermally

Introduction

Since the discovery of salts with low melting points by Walden in 1914, a variety of low-melting salts, so-called ionic liquids (ILs), have been found and characterized.<sup>[1]</sup> As they consist most commonly of bulky organic cations and polyatomic inorganic anions, their various combinations offer a whole new branch of liquids. Owing to their strong Coulombic interactions, they are proposed as solvents for chemical syntheses, catalysis, and biocatalysis and in the fields of electrochemistry and analytics. Even their use as heat-transfer media or extractants has been discussed.<sup>[2]</sup> Through the introduction of a redox-active center in the cation or anion, the IL can act not only as a solvent but also as an electron donor or acceptor with possible applications in dye-sensitized solar cells,<sup>[3]</sup> supercapacitors, and batteries.<sup>[4]</sup> Examples from the literature for redox-active cations are ferrocene-based derivatives such as (ferrocenylmethyl)imidazolium room-temperature ionic liquids (RTILs) in which the oxidation state of the iron atom can be changed reversibly from Fe<sup>II</sup> to Fe<sup>III[5]</sup> or the viologen derivative 1-butyl-1'-heptyl-4,4'-bipyridinium bis(trifluoromethanesulfonyl)imide.<sup>[6]</sup> An example of a redox-active anion in an IL is SCN-, which was included in 1alkyl-3-methylpyridinium ILs, for example.<sup>[7]</sup> A typical synthesis route to ILs is the quaternization of nitrogen- or phosphoruscontaining heterocycles. Most commonly, imidazolium-based ILs are synthesized and already available industrially.<sup>[8]</sup> Although imidazolium-based ILs with chiral pyrrolidine side groups have been investigated for their catalytic activity in aldol reactions,<sup>[9]</sup> chirality in combination with redox activity in the same IL could lead to new applications in synthesis. Such ILs

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201600585. stable up to 263 °C. The electrochemical Fe<sup>II</sup>/Fe<sup>III</sup> potential is shifted to +0.28 V versus Fc/Fc<sup>+</sup>. Before anion exchange, several iodide derivatives were obtained as crystalline products, and their crystal structures are reported. According to the NMR spectroscopic data cation–anion aggregates are present in the non-coordinating solvent CDCl<sub>3</sub>. In contrast, in the polar solvent  $[D_6]$ dimethyl sulfoxide ( $[D_6]$ DMSO), the ion pairs are separated.

could serve as solvents and at the same time act as electron donors or acceptors and control the stereochemistry of the reaction.

ILs with a cationic pyrrolidinium unit are rather rare. However, L-proline is an interesting starting material, as it is a naturally occurring chiral amino acid. The first pyrrolidinium-based ILs were reported by MacFarlane et al. in 1999.<sup>[10]</sup>

Herein, we report the synthesis and characterization of pyrrolidinium ILs containing a ferrocenyl group as a redoxactive center. Although ferrocenoyl hydroxyproline derivatives have been reported,<sup>[11]</sup> to the best of our knowledge, this is the first time that RTILs have been prepared by linking ferrocene to a pyrrolidine ring through an ester bridge. These RTILs are formed by quaternization of the pyrrolidine ring with alkyl iodides and subsequent exchange of the iodide anion by bis(tri-fluoromethanesulfonyl)imide (NTf<sub>2</sub><sup>-</sup>).

## **Results and Discussion**

#### **Reaction Sequence**

The ferrocene (Fc) ester ({[(2S)-N-methylpyrrolidine-2-yl]methyleneoxy}carbonyl)ferrocene (1) was synthesized by reaction of [(2S)-1-methylpyrrolidine-2-yl]methanol and ferrocene monocarboxylic acid chloride, FcCOCl, in tetrahydrofuran (THF, 1). [(2*S*)-1-Methylpyrrolidine-2-yl]methanol Scheme was obtained from L-proline, formic acid, acetic anhydride, and LiAlH<sub>4</sub>.<sup>[12]</sup> FcCOCl<sup>[13]</sup> was formed by the reaction of FcCOOH<sup>[14,15]</sup> with oxalyl chloride in the presence of catalytic amounts of N,N-dimethylformamide (DMF). The N atom of the pyrrolidine ring was quaternized with alkyl iodides to give the desired (2S)-[(ferrocenylcarbonyl)oxy]methylene-N,N-dialkylpyrrolidine-1-ium iodides. To generate salts with lower melting points, anion exchange with NTf<sub>2</sub><sup>-</sup> was performed. The resulting





 $NTf_2^-$  salts **7–11** (Table 1) are liquids at room temp. and show good stability towards air, light, and moisture. Details concerning the product characterization are given in the Supporting Information.



R = Me (7), Et (1S2S-8) and (1R2S-8), Pr (1S2S-9) and (1R2S-9), Bu (1S2S-10) and (1R2S-10), Pen (1S2S-11) and (1R2S-11).

Scheme 1. Synthetic route to (2*S*)-2-[(ferrocenylcarbonyl)oxy]methylene-*N*,*N*-dialkylpyrrolidine-1-ium iodides **2–6** and  $NTf_2^-$  salts **7–11**. Compounds **3–6** and **8–11** were obtained as diastereomeric mixtures.

As the chain length of the alkyl group R in the alkyl iodides increases, the quaternization yield decreases. This is due to the

decreasing reactivity of the alkyl halides with increasing alkyl chain length.<sup>[18]</sup> The yields and the 1S,2S/1R,2S product ratios are reported in Table 1. The diastereomeric ratios were determined by comparing the integrals of the <sup>1</sup>H NMR signals of the methyl groups of both diastereomers. The 1S,2S diastereomer is always the minor product in a ratio close to 43:57. Within the error of the <sup>1</sup>H NMR signal integration, only a slight preference for the 1R,2S diastereomer can be determined.

#### **Melting Points and Decomposition Processes**

The melting points and decomposition temperatures (beginning of weight loss) of **1–11** were determined by simultaneous thermal analysis (STA) and are summarized in Table 1. The volatile decomposition products were analyzed by mass spectrometry and gas-phase IR spectroscopy. The melting point of the methylated iodide **2** is 175 °C, whereas the glass transition temperature of **6** (R = pentyl) is below –25 °C and its decomposition temperature of 166 °C is slightly lower than those of the other iodides (184–194 °C). The change of the anion from I<sup>-</sup> to NTf<sub>2</sub><sup>-</sup> affects the melting points below –25 °C. Compounds **7–11** show the same decomposition behavior between 180 and 263 °C. With a liquid range from below –25 to 263 °C, **10** shows the highest thermal stability and the widest liquid range.

#### **Crystal Structures**

Single-crystal structure analyses were performed for the IL precursors FcCOCI, **2**, (1*S*,2*S*)-**3**, (1*R*,2*S*)-**4**, and (1*R*,2*S*)-**5** (Table 2). On the basis of their different crystal shapes, (1*S*,2*S*)-**3** and (1*R*,2*S*)-**3** (Figure 1) were separated manually, and the crystal structures of both diastereomers of **3** were determined. The chiral compounds crystallize in chiral space groups, monoclinic *P*2<sub>1</sub> for **2** (*Z* = 4) and (1*R*,2*S*)-**3** (*Z* = 2) and orthorhombic *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> for (1*S*,2*S*)-**3**, (1*R*,2*S*)-**4**, and (1*R*,2*S*)-**5** (*Z* = 4). Although the molecules are closely related, the free rotation of the pyrrolidinium ring around the C12–C13 bond, ring puckering, the orientation of the alkyl groups at the nitrogen atom, and the ori-

Table 1. Reaction yields of 1–11 and 15,25/18,25 ratios. The ratios were determined by integration of the signals of the methyl groups of <sup>1</sup>H NMR spectra of the compounds in CDCl<sub>3</sub> or [D<sub>6</sub>]DMSO. The melting points ( $T_m$ ), glass transition ( $T_g$ ), and decomposition ( $T_{dec}$ ) temperatures were determined by simultaneous thermal analysis (STA) experiments of the diastereomeric mixtures.

	R	Х	Yield <sup>[a]</sup> [%]	1 <i>S</i> ,2 <i>S</i> /1 <i>R</i> ,2 <i>S</i> ratio	$T_{\rm m}$ and $(T_{\rm g})$ [°C]	T <sub>dec</sub> [°C]
Ferrocene	-			_	173 <sup>[16]</sup>	>460 <sup>[17]</sup>
1	-		74	-	<r.t.< td=""><td>170</td></r.t.<>	170
2	methyl	1-	91	-	(155) <sup>[b]</sup> 175	194
3	ethyl	1-	94	45:55, 42:58 <sup>[c]</sup>	142	191
4	propyl	1-	62	_[d]	_[e]	190
5	butyl	1-	37	43:57	_[e]	184
6	pentyl	I-	30	45:55	(<-25)	166
7	methyl	$NTf_2^-$	64	-	(<-70)	180
8	ethyl	$NTf_2^-$	42	42:58 <sup>[c]</sup>	(<-25)	245
9	propyl	$NTf_2^-$	67	40:60	(<-25)	209
10	butyl	$NTf_2^-$	97	_[d]	(<-25)	263
11	pentyl	$NTf_2^-$	76	46:54	(<-25)	251

[a] The yield refers to the last step in the synthesis. [b] Phase transition. [c] In  $[D_6]DMSO$ . [d] The integrals of the <sup>1</sup>H NMR signals could not be analyzed because of overlap with other signals. [e] No melting point was observed before decomposition.



#### Table 2. Crystal-structure data of 2, (1R,2S)-3, (1S,2S)-3, (1R,2S)-4, and (1R,2S)-5.



	2	(1 <i>R</i> ,2 <i>S</i> )- <b>3</b>	(1 <i>S</i> ,2 <i>S</i> )- <b>3</b>	(1 <i>R</i> ,2 <i>S</i> )- <b>4</b>	(1 <i>R</i> ,2 <i>S</i> )- <b>5</b>
Color, habit	orange needles	orange plates	orange needles	orange needles	orange plates
Formula	C <sub>18</sub> H <sub>24</sub> FeINO <sub>2</sub>	C <sub>19</sub> H <sub>26</sub> FeINO <sub>2</sub>	C <sub>19</sub> H <sub>26</sub> FeINO <sub>2</sub>	C <sub>20</sub> H <sub>28</sub> FeINO <sub>2</sub>	$C_{21}H_{30}FeINO_2$
Formula weight [g/mol]	469.13	483.16	483.16	497.18	511.21
Temperature [K]	180	213	213	213	180
Diffractometer	STOE IPDS 2T	STOE IPDS I	STOE IPDS I	STOE IPDS I	STOE IPDS 2T
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group	P2 <sub>1</sub>	P2 <sub>1</sub>	P212121	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P212121
<i>a</i> [pm]	1191.7(2)	755.5(2)	834.2(1)	806.3(3)	819.76(8)
<i>b</i> [pm]	1245.2(2)	1255.4(2)	999.0(2)	1044.5(3)	1056.4(1)
<i>c</i> [pm]	1244.2(2)	1011.7(3)	2365.9(5)	2446.0(7)	2484.5(3)
β [°]	96.78(2)	94.72(2)	90	90	90
<i>V</i> [10 <sup>6</sup> pm <sup>3</sup> ]	1833.5(5)	956.2(4)	1971.6(7)	2060(1)	2151.6(4)
Ζ	4	2	4	4	4
Calcd. density [g/cm <sup>3</sup> ]	1.699	1.678	1.628	1.603	1.578
$\mu$ [mm <sup>-1</sup> ]	2.515	2.414	2.341	2.243	2.150
$\theta$ range [°]	1.0-24.0	2.3-28.0	1.6-25.0	1.6-22.5	1.0-25.0
Unique reflections (R <sub>int</sub> )	5652 (0.0564)	4414 (0.0531)	3461 (0.1662)	2694 (0.2046)	3728 (0.0514)
Reflections with $l > 2\sigma(l)$	3450	3576	1790	1186	2071
Parameters	419	219	194	128	237
$R_1 \left[ l > 2\sigma(l) \right]$	0.0422	0.0296	0.0538	0.0553	0.0353
$wR_2$ (all reflections)	0.0679	0.0546	0.1101	0.1028	0.0495
Flack parameter	-0.03(4)	-0.05(2)	-0.1(1)	-0.01(8)	0.02(4)
Largest difference peak and hole $[e \times 10^{-6} \text{ pm}^{-3}]$	0.59 and -0.45	0.87 and -0.43	1.22 and -0.50	0.60 and -0.69	0.62 and -0.37

entation of the ferrocene backbones lead to different conformations and to different packings in the unit cell (Figures 2 and S20–S24). The basic crystallographic data are listed in Table 2.



Figure 1. Crystals of the (15,25)-**3** and (1R,25)-**3** diastereomers (polarized light).

Although the cell parameters of the orthorhombic structures are similar, only (1R,2S)-4 and (1R,2S)-5 are isostructural. The unit cell of (1R,1S)-5 is slightly larger owing to the butyl group instead of the propyl group in (1R,2S)-4. As depicted in Figure 2, the orientation of the propyl and butyl groups in (1R,2S)-4 and (1R,2S)-5 with respect to the pyrrolidinium ring and ferrocenylester backbone are the same. This is in agreement with similar torsion angles for O2–C12–C13–N1 [–84(2)° in (1R,2S)-4 and -78.3(8)° in (1R,2S)-5] and C12–C13–N1–C18 [–80(2)° in (1R,2S)-4 and -87.1(8)° in (1R,2S)-5]. In (1S,2S)-3, the unit-cell parameters and the positions of the molecules in the unit cell are very similar to those of (1R,2S)-4 and (1R,2S)-5. However, the rotation of the pyrrolidinium group in (1S,2S)-3 around the C12–C13 bond results in torsion angles O2–C12–C13–N1 of 76(2)° and C12–C13–N1–C18 of –32(2)°. In the monoclinic structures of 2, which has two independent molecules per asymmetric unit, and (1R,2S)-**3**, these torsion angles are  $60(2)^{\circ}$  in **2** and  $58.2(6)^{\circ}$  in (1R,2S)-**3** for O2–C12–C13–N1 and -89(2) and  $-75(2)^{\circ}$  in **2** and  $-76.2(6)^{\circ}$  in (1R,2S)-**3** for C12–C13–N1–C18. For small substituents (R = Me, Et) at the N atom, the pyrrolidine N atom is orientated towards the unsubstituted ferrocene cyclopentadienyl ring. For the bulkier substituents such as R = Pr and Bu, the N atom points outwards (Figure 2).



Figure 2. Structures of the crystallographically independent [(ferrocenyl-carbonyl)oxy]methylene-*N*,*N*-dialkylpyrrolidine-1-ium cations of **2**, (1*S*,25)-**3**, (1*R*,25)-**3**, (1*R*,25)-**3**, (1*R*,25)-**3**, (1*R*,25)-**5**. The thermal displacement ellipsoids are shown at the 50 % probability level. The atom labeling follows the scheme shown for (1*R*,25)-**5**.

The main difference between the 1R,2S and 1S,2S diastereomers of **3** is the relative position of the bulkier alkyl group in relation to the ferrocene–ester part on the pyrrolidine ring; for all 1R,2S diastereomers, the longer alkyl group (ethyl, propyl, or





Table 3. Puckering parameters<sup>[21]</sup>  $q_2$  and  $\varphi_2$  as well as the  $z_j$  coordinates of the pyrrolidinium-ring-containing structures. The calculations were started with atom N1 followed by C13, C14, C15, and C16.

	<i>q</i> <sub>2</sub> [Å]	$\varphi_2$ [°]	Conformation	Zj
<b>2</b> – mol I	0.37(1)	164(3)	<sup>5</sup> T <sub>1</sub>	$z_2 = 0.14(1), z_3 = -0.01(1), z_4 = -0.13(1), z_5 = 0.22(1)$
<b>2</b> – mol II	0.40(1)	192(2)	1 <sup>2</sup>	$z_2 = 0.232(9), z_3 = -0.13(1), z_4 = -0.03(1), z_5 = 0.17(1)$
(1 <i>S</i> ,2 <i>S</i> )- <b>3</b>	0.37(2)	18(3)	<sup>1</sup> T <sub>2</sub>	$z_2 = -0.22(1), z_3 = 0.14(1), z_4 = -0.00(1), z_5 = -0.14(1)$
(1 <i>R</i> ,2 <i>S</i> )- <b>3</b>	0.404(5)	177(1)	E1	$z_2 = 0.199(3), z_3 = -0.066(4), z_4 = -0.092(4), z_5 = 0.215(4)$
(1 <i>R</i> ,2 <i>S</i> )- <b>4</b>	0.36(2)	251(3)	E <sub>3</sub>	$z_2 = 0.19(1), z_3 = -0.23(1), z_4 = 0.18(1), z_5 = -0.07(1)$
(1 <i>R</i> ,2 <i>S</i> )- <b>5</b>	0.42(1)	250(1)	E <sub>3</sub>	$z_2 = 0.220(5), z_3 = -0.266(6), z_4 = 0.210(6), z_5 = -0.074(6)$

butyl) and the ferrocene–ester group are both arranged pseudoequatorially around the pyrrolidine ring (*trans* conformation). The only structure analysis of a 1*S*,2*S* diastereomer [(1*S*,2*S*)-**3**] shows a pseudoequatorial arrangement of the ethyl group and a pseudoaxial positioning of the ferrocene ester group (*cis* conformation). For steric reasons, free rotation around the C12–C13 bond is less likely in the 1*S*,2*S* diastereomer than in the 1*R*,2*S* diastereomer. The smaller methyl group (C17) makes rotation around the C12–C13 bond possible. This higher degree of rotational freedom might be a reason for the marginal preference for the formation of the 1*R*,2*S* diastereomers.

In all structures, the O1–C11–O2 group is in the plane of the substituted cyclopentadienyl ring consisting of atoms C6 to C10 and provides a rigid ferrocene–ester backbone. The C6–C11–O1 (124–128°), C6–C11–O2 (108–114°), and O2–C12–C13 angles (107–112°) are in the expected ranges and similar to those in FcCOOH<sup>[19]</sup> (C6–C11–O1: 122°; C6–C11–O2: 116°) and the ferrocene ester 3-{4-[(4-methoxyphenoxy)carbonyl]phenoxy}propyl ferrocenecarboxylate (C6–C11–O1: 125°; C6–C11–O2: 111°; O2–C12–C13: 110°).<sup>[20]</sup>

In the crystal structures of 2-5, the pyrrolidinium ring is in the twist [2, (15,25)-3] or envelope [(1R,25)-3, (1R,25)-4, and (1R,2S)-5] conformation. In Table 3, the Cremer–Pople puckering parameters for the five-membered pyrrolidinium rings are listed.<sup>[21]</sup> In the propyl and butyl derivatives (1R,2S)-4 and (1R,2S)-5, C14 is out of the plane in the envelope conformation, in contrast to the methyl (2) and ethyl [(15,25)-3, (1R,25)-3] derivatives, in which we observe twist [2, (15,25)-3] as well as envelope [E1 for (1R,2S)-3] conformations. The total puckering amplitudes  $q_2$  for these pyrrolidinium rings are between 0.36 and 0.42 Å, similar to the puckering amplitudes of other 2S pyrrolidinium rings with a quaternized N atom ( $q_2 = 0.36$  Å for CCDC-771076,  $q_2 = 0.37$  Å for CCDC-771077,  $q_2 = 0.41$  Å for CCDC-769510, and  $q_2 = 0.38$  Å for CCDC-769512).<sup>[21,22]</sup> Only (1*R*,2*S*)-**3** is close to the "pure envelope" conformation (with  $\varphi_2 = 0$  or 180°) and also fulfills the requirements for the z values, that is,  $z_2 = z_5$  and  $z_3 = z_4$ .<sup>[21]</sup> Although the energy barrier for the rotation of the cyclopentadienyl rings is low, the cyclopentadienyl rings of the ferrocenyl group in all crystal structures reported herein are eclipsed.

#### **X-ray Powder Diffraction**

The powder diffraction pattern of a mixture of the diastereomers (1S,2S)-**3** and (1R,2S)-**3** is shown in Figure 3 together with their simulated patterns from the single-crystal structure data. Clearly, the powder contains both diastereomers. The diastereomeric ratio of (15,25)-**3**/(1R,25)-**3** of 43(5):57(3), as determined by a Rietveld fit (Figure S5), fits well to the results of the NMR spectroscopy study (43:57, Table 1). Rietveld phase analyses could not be performed for the diastereomeric mixtures of **4** and **5** as no single crystals of the (1*S*,2*S*) diastereomers could be obtained. On the basis of the reflections that are different from those of the (1*R*,2*S*) diastereomer in the X-ray powder patterns (Figures S7 and S8), for example, at  $2\theta = 18.88$ , 20.68, and 24.36° for **4**, the fraction of the crystalline (1*S*,2*S*) diastereomer decreases from **3** to **5**. The temperature-dependent powder X-ray diffraction patterns of the manually separated diastereomers of **3** and their mixture are shown in Figure S6. In combination with the STA experiment (Figure S10), the melting point of this powder mixture was demonstrated to be ca. 140 °C.



Figure 3. X-ray powder diffraction pattern of the mixture of (15,25)-**3** and (1*R*,25)-**3** (top) in comparison with their simulated patterns from the singlecrystal structure data;  $\lambda$ (Cu- $K_{\alpha 1}$ ) = 154.060 pm. The high background intensity is due to fluorescence effects.

#### **Cyclic Voltammetry Studies**

The Fe<sup>II</sup>/Fe<sup>III</sup> redox potential in ferrocene derivatives is influenced by the substituents of the cyclopentadienyl rings. For example, the electron-releasing substituent in *tert*-butyl ferrocene shifts the redox potential to -0.061 V versus Fc/Fc<sup>+</sup>, whereas ferrocene carbaldehyde with an electron-withdrawing substituent shows its redox activity at +0.415 V versus Fc/Fc<sup>+</sup> [high-speed channel electrode with a Pt mesh counter and a silver wire quasireference electrode, (Bu<sub>4</sub>N)ClO<sub>4</sub> as supporting electrolyte in acetonitrile at 21 °C].<sup>[23]</sup>



The formal potentials  $E_{f.Fc}^{0}$  in acetonitrile versus a Ag/AgNO<sub>3</sub> electrode are summarized in Table 4. The biggest shift relative to the potential of ferrocene ( $E_{f,Fc}^0 = 0$  V) was observed for FcCOCI ( $E_{fc}^{0} = +0.40$  V, Figure S25) owing to the electron-withdrawing properties of the carboxylic acid chloride group. Ferrocene monocarboxylic acid and the synthesized esters have similar  $E_{fc}^{0}$  values in the range +0.24 to +0.28 V. The quaternization of the N atom and the type of anion do not influence the electrochemical potential of the ferrocenyl group significantly (Figure 4). In the iodide salts 2–6, the iodide anions are also redoxactive. The cyclic voltammogram of tetra-n-butylammonium iodide (TBAI) shows two peaks at  $E_{f,Fc}^{0}$  (I1) = -0.18 V and  $E^{0}_{f,Fc}$  (I2) = +0.22 V. These peaks originate in the reactions given in Equations (1) and (3).<sup>[26,31]</sup> In **2–6** with the combination of iodide and the ferrocenyl group, the I2 and Fc peaks overlap to form one single peak. However, interactions between iodine and ferrocene species leading to modified electrochemical properties have been reported.<sup>[32,33]</sup> In this work, shifts of the redox potentials owing to interactions between the iodine atom

Table 4. Formal potentials  $E^{0}_{f,Fc}$  in acetonitrile referenced to Fc/Fc<sup>+</sup>. For **2–6**, the second peak pair 12 overlaps with the ferrocene peak and, therefore, could not be analyzed separately (marked as 12+Fc). The estimated uncertainty of these measurements is ca.  $\pm 0.02$  V.

	Anion	E <sup>0</sup> <sub>f,Fc</sub> [V]	Literature values [V]
Ferrocene	-	0	
Cobaltocene	$PF_6^-$	-1.33	-1.33 <sup>[a,b]</sup>
TBAI	I-	-0.18 (I1), 0.22 (I2)	-0.10 (I1), 0.22 (I2), <sup>[c]</sup> -0.13 (I1), 0.17 (I2) <sup>[d]</sup>
FcCOOH	-	0.24	0.17 <sup>[28]</sup> , 0.25 <sup>[29]</sup>
FcCOCI	-	0.40	
1	-	0.27	
2–6	I <sup>_</sup>	-0.18 (I1), 0.27 (I2+Fc)	
7–11	$NTf_2^-$	0.28	

[a] Ref.<sup>[24]</sup>; in CH<sub>2</sub>Cl<sub>2</sub>. [b] Ref.<sup>[25]</sup>; in MeCN. [c] Ref.<sup>[26]</sup>; calculated according to ref.<sup>[30]</sup> from 0.01  $\times$  Ag/AgNO<sub>3</sub>  $\rightarrow$  Fc/Fc<sup>+</sup> -0.09 V. [d] Ref.<sup>[27]</sup>; calculated according to ref.<sup>[30]</sup> from saturated calomel electrode (SCE)  $\rightarrow$  Fc/Fc<sup>+</sup> -0.38 V.



and the ferrocenyl units, as observed in CV experiments of substituted ferrocenium triiodides in ILs,<sup>[33]</sup> were not observed; the Fc/Fc<sup>+</sup> formal potentials of the iodides **2–6** are the same as those of the NTf<sub>2</sub><sup>-</sup> salts **7–11** (Table 4).

(3)

Peak pair I1:  $3 \downarrow = 1_3 + 2 e^-$  (1)

 $|^{-} + |_2 \rightleftharpoons |_3^{-}$  (2)

Peak pair I2:  $I_3^- \rightleftharpoons 3/2 I_2 + e^-$ 



Figure 4. Cyclic voltammograms ( $E^0_{f,Fc}$ ) of TBAI (-0.18, +0.22 V), **1** (+0.27 V), **3** (-0.18 V, +0.27 V), and **8** (+0.28 V) in acetonitrile; scan rate 0.1 V/s. The cyclic voltammograms of **2**, **4**, **5**, and **6** are similar to that of **3**. The NTf<sub>2</sub><sup>-</sup> RTILs **7**, **9**, **10**, and **11** show the same electrochemical behavior as **8**. Conditions for all CV experiments: 1 mmol/L analyte, 0.1 mol/L TBAPF<sub>6</sub> versus a Ag/ AgNO<sub>3</sub> electrode ([AgNO<sub>3</sub>] = 0.01 mol/L, 0.1 mol/L tetra-*n*-butylammonium perchlorate; scan rate 0.1 V/s) with a Pt-wire counter electrode (d = 0.5 mm) and a Pt-disc working electrode (A = 0.0222 cm<sup>2</sup>, r = 0.8 mm), 23 °C.

#### **NMR Spectroscopy Studies**

The carbon atoms C13, C16, C17, and C18 (see atom-labeling scheme in Figure 2) and the attached protons are expected to

Table 5. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts [ppm] of atoms at the 13-, 16-, 17-, and 18-positions of 2–11 in CDCl<sub>3</sub> and [D<sub>6</sub>]DMSO (in parentheses).

	R	X-	13		16		17		18	
			1H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C
1	-	-	2.64	64.2	2.35, 3.17	57.6	2.53	41.4	-	-
2	methyl	I-	4.53-4.74 (4.06)	74.0 (72.6)	4.12-4.31 (3.69)	68.2 (66.7)	3.68 (3.30)	53.5 (51.9)	3.33 (3.06)	47.1 (45.3)
(1 <i>S</i> ,2 <i>S</i> )- <b>3</b>	ethyl	I-	4.94 (4.14)	75.0 (73.8)	3.79, 4.03 (3.50, 3.71)	63.3 (61.3)	3.49 (3.18)	49.6 (47.9)	3.49, 3.79 (3.36)	53.0 (51.2)
(1 <i>R</i> ,2 <i>S</i> )- <b>3</b>	ethyl	I-	4.64 (4.08)	73.1 (71.8)	3.89, 4.09 (3.61)	64.8 (63.1)	3.20 (3.00)	44.4 (42.3)	3.89 (3.45, 3.71)	60.4 (59.0)
(1 <i>S</i> ,2 <i>S</i> )- <b>4</b>	propyl	I-	4.79	75.2	3.83-4.01, 4.19	64.0	3.54	50.3	3.30, 3.46	59.0
(1 <i>R</i> ,2 <i>S</i> )- <b>4</b>	propyl	I-	4.66	73.5	3.83-4.01, 4.19	65.4	3.22	44.8	3.64-3.83	66.4
(1 <i>S</i> ,2 <i>S</i> )- <b>5</b>	butyl	I-	4.83	75.0	3.77-3.97, 4.23	63.5	3.50	50.2	3.22-3.44	57.4
(1 <i>R</i> ,2 <i>S</i> )- <b>5</b>	butyl	I-	4.63	73.6	3.77-3.97, 4.23	65.5	3.17	44.7	3.60–3.77, 3.77–3.97	64.9
(1 <i>S</i> ,2 <i>S</i> )- <b>6</b>	pentyl	I-	4.73	75.0	3.80	63.8	3.45	50.2	3.24, 3.41	57.7
(1 <i>R</i> ,2 <i>S</i> )- <b>6</b>	pentyl	I-	4.55	73.5	3.86, 4.13	65.0/ 65.3 <sup>[a]</sup>	3.15	44.4	3.68	65.0/ 65.3 <sup>[a]</sup>
7	methyl	$NTf_2^-$	4.07 (4.06)	74.1 (72.7)	3.71 (3.68)	68.5 (66.8)	3.32 (3.29)	53.5 (51.9)	3.06 (3.06)	46.1 (45.3)
(1 <i>S</i> ,2 <i>S</i> )- <b>8</b>	ethyl	$NTf_2^-$	4.14 (4.11)	75.2 (73.7)	3.25-3.81 (3.60)	62.9 (61.8)	3.16 (3.17)	49.3 (47.7)	3.25–3.81 (3.39, 3.70)	52.4 (51.8)
(1 <i>R</i> ,2 <i>S</i> )- <b>8</b>	ethyl	$NTf_2^-$	4.07 (4.07)	73.1 (71.6)	3.25-3.81 (3.60)	60.7 (63.7)	2.97 (3.00)	43.0 (42.0)	3.25–3.81 (3.39, 3.70)	64.5 (59.6)
(1 <i>S</i> ,2 <i>S</i> )- <b>9</b>	propyl	$NTf_2^-$	4.09-4.25	75.2	3.57-3.80	63.6	3.05-3.27	49.9	3.05-3.27	58.7
(1 <i>R</i> ,2 <i>S</i> )- <b>9</b>	propyl	$NTf_2^-$	4.09-4.25	73.4	3.57-3.80	64.9	2.99	43.6	3.33, 3.51	66.7
(1 <i>S</i> ,2 <i>S</i> )- <b>10</b>	butyl	$NTf_2^-$	4.22	75.3	3.42-3.83	63.8	3.19	50.1	3.06-3.39	57.3
(1 <i>R</i> ,2 <i>S</i> )- <b>10</b>	butyl	$NTf_2^-$	4.22	73.6	3.42-3.83	65.5	2.98	43.5	3.42-3.83	65.5
(1 <i>S</i> ,2 <i>S</i> )- <b>11</b>	pentyl	$NTf_2^-$	4.16	75.2	3.46-3.78	63.6	3.20	49.9	3.16	57.4
(1 <i>R</i> ,2 <i>S</i> )- <b>11</b>	pentyl	$NTf_2^-$	4.11	73.4	3.46–3.78	65.0	2.99	43.4	3.31, 3.46–3.78	65.6

[a] These signals could not be assigned unambiguously because of their proximity.



be influenced mostly by the newly created stereocenter at the quaternized N atom. With the help of 2D NMR spectroscopy [<sup>1</sup>H–<sup>1</sup>H COSY, heteronuclear single quantum coherence (HSQC), and HMBC], it is possible to distinguish between the 1R,2S and 15,25 diastereomers. The NMR spectra of manually separated crystals of the diastereomers (15,25)-3 and (1R,25)-3 were recorded (Figures S17-S19). The chemical shifts of C13 and C17 are characteristic of the different diastereomers (Table 5). The chemical shift of atom C13 of the (1R,2S) diastereomer in CDCl<sub>3</sub> is 73 ppm, and that of the (15,25) diastereomer is 75 ppm. For C17, the signals of the (15,25) diastereomer are in the range  $\delta$  = 49.3-52.9 ppm, and those of the (1R,2S) diastereomers are at  $\delta$  = 43.0–44.8 ppm. The <sup>1</sup>H NMR spectra of **1** and both diastereomers of 3 are presented in Figures S2 and S4. Atoms H7-H10 were assigned in accordance with the study by Richards et al.<sup>[34]</sup>

In Table 5, the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of atoms C13, C16, C17, C18 and the attached protons of 1-11 are summarized. The assignment of atoms H17/C17 (trans to the ferrocenyl-ester part) and H18/C18 (cis position) of 2 and 7 is in accordance with studies by Faure et al. and Blunden and Crabb et al.<sup>[35]</sup> The difference of 0.29-0.35 ppm between the <sup>1</sup>H signals of the methyl protons H17 of the 1S,2S and 1R,2S diastereomers as well as that for the dimethyl compounds 2 and 7 between methyl protons H17 and H18 fits well to  $\Delta \delta = 0.3$  ppm for the diastereotopic methyl groups in N,N-dimethyl-2-methylpyrrolidine-1-ium iodides.[36] In reports about N-alkyl-N-methyl-2-organylpyrrolidinium iodides (with alkyl = methyl, ethyl and organyl = methyl, phenyl), the signal of the methyl group trans to the organyl group is observed at higher  $\delta$  values than that for the cis position.[37] These results are consistent with those from our investigation.

In Figures 5 and 6, the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of **1**– **11** in  $CDCl_3$  are visualized. For the <sup>1</sup>H NMR chemical shifts, it is clear that the change from the neutral molecule **1** to the quaternary ammonium salts **2** or **7** causes downfield shifts by ca. 1 ppm for H16 and H17 and ca. 2 ppm for H13. The influence of the chain length of the alkyl substituents decreases with increasing alkyl chain length.

Chloroform as a non-coordinating and relatively apolar solvent leads to a closer anion-cation contact in solution; therefore, the type of anion in the IL influences the chemical shifts of some <sup>1</sup>H and <sup>13</sup>C nuclei in the cation. In the iodide salts, the <sup>1</sup>H NMR signals are shifted downfield relative to those of the NTf<sub>2</sub><sup>-</sup> salts; a significant difference in the chemical shifts of 13-H, 16-H, 17-H, and 18-H exists between the iodide salt 2 and the NTf<sub>2</sub><sup>-</sup> salt **7** in CDCl<sub>3</sub>. This chemical-shift difference between the iodide and NTf<sub>2</sub><sup>-</sup> salts is observed for all 13-H and 16-H atoms of 3-11. The 17-H signals of the 15,25 iodide diastereomers ( $\delta$  = 3.45 and 3.54 ppm) and the 1*R*,25 NTf<sub>2</sub><sup>-</sup> diastereomers ( $\delta \approx 2.9$  ppm) are separated clearly from those of the 1R,2S I<sup>-</sup> and 1S,2S NTf<sub>2</sub><sup>-</sup> diastereomers, which overlap. Owing to peak overlap for 18-H, the assignment to distinct diastereomers is possible only for the 1R,2S diastereomers of the iodides. An explanation might be the localization of the negative charge at only one atom for the iodide versus its distribution over the NTf<sub>2</sub><sup>-</sup> anion and its proximity to the cation. As shown in Fig-





Figure 5. <sup>1</sup>H NMR chemical shifts for 13-H, 16-H, 17-H, and 18-H of the neutral compound **1**, the iodide salts **2–6**, and the  $NTf_2^-$  salts **7–11** in  $CDCI_3$ .



Figure 6. <sup>13</sup>C NMR chemical shifts for C13, C16, C17, and C18 of the neutral compound **1**, the iodide salts **2–6**, and  $NTf_2^-$  salts **7–11** in CDCl<sub>3</sub>.

ures 5 and 6, the type of anion makes no difference to the chemical shift of C13. The only influence on C13 is the stereochemical configuration. In contrast, the chemical shifts of C16, C17, and C18 show not only differences between the 15,25 and 1R,2S diastereomers but also partly between the two different anions. In contrast, the NMR spectra of the compounds in [D<sub>6</sub>]DMSO show a different behavior: the ions are solvated, and the chemical shifts are independent of the nature of the anions. Howarth et al. reported similar observations for ferrocenylimidazolium salts. They discovered C-H···X hydrogen bonds of 1,3di(ferrocenylmethyl)imidazolium salts in CDCl<sub>3</sub> with Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>,  $NO_3^-$ ,  $HSO_4^-$ , and  $PF_6^-$  anions.<sup>[38]</sup> On the basis of the work by Howarth et al. and Dupont et al., the differences are attributed to the presence of a contact ion pair structure in CDCl<sub>3</sub> in contrast to solvent-separated ions in [D<sub>6</sub>]DMSO.<sup>[39]</sup> For the NTf<sub>2</sub>salts, the <sup>19</sup>F NMR chemical shift of -79.2 ppm is in agreement with values reported previously.[40]

### Conclusions

The syntheses of a series of six new RTILs based on ferrocene units coupled to a pyrrolidinium ring through an ester bridge





are reported. One RTIL has an iodide anion, and the other five have NTf<sub>2</sub><sup>-</sup> anions. The quaternization of the chiral pyrrolidine units with alkyl iodides results in diastereomeric mixtures, and the two diastereomers 1*S*,2*S* and 1*R*,2*S* are obtained in product ratios of 43:57 according to NMR spectroscopic data and 43(5):57(3) according to PXRD experiments for (1*S*,2*S*)-**3** and (1*R*,2*S*)-**3**. Thus, there is only a slight preference for the 1*R*,2*S* diastereomer.

In their NMR spectra, both diastereomers differ in their chemical shifts; the <sup>13</sup>C atoms C13 (2*S* stereocenter) and C17 (methyl group attached to the 1*S*/1*R* stereocenter) of the 1*S*,2*S* diastereomers are more deshielded than those in the 1*R*,2*S* diastereomers. The NMR spectra of the compounds in CDCl<sub>3</sub> show different chemical shifts for the cation depending on the anion,  $I^-$  or NTf<sub>2</sub><sup>-</sup>. In the more polar solvent [D<sub>6</sub>]DMSO, this effect vanishes. Therefore, a contact ion pair structure in CDCl<sub>3</sub> is proposed in contrast to solvent-separated ions in [D<sub>6</sub>]DMSO.

The synthesized RTILs based on ferrocene, pyrrolidinium, and  $NTf_2^-$  show thermal stability up to 263 °C (**10**). Of the iodide derivatives, only the pentyl compound **6** is liquid at room temp. The decomposition of the iodide ILs starts between 166 and 194 °C. We are aware that the compounds might remain liquid even below their melting point because of hindered crystallization. For **6–11**, we could not observe the formation of a solid.

The single-crystal structure analyses of the IL precursors FcCOCI, **2**, (1S,2S)-**3**, (1R,2S)-**3**, (1R,2S)-**4**, and (1R,2S)-**5** reveals that their crystal structures are closely related. However, only (1R,2S)-**4** and (1R,2S)-**5** are isostructural. The pyrrolidine ring appears in the twist [**2** and (1S,2S)-**3**] or envelope conformation [(1R,2S)-**3**, (1R,2S)-**4**, and (1R,2S)-**5**]. The main difference between the structures of the 1R,2S and 1S,2S diastereomers in the crystalline state is the arrangement of the longer alkyl chain (e.g., ethyl, propyl, and butyl) in relation to the ferrocenyl–ester group. For 1R,2S, both groups are arranged pseudoequatorially (*trans* conformation) around the pyrrolidinium ring, whereas the ethyl group is pseudoequatorial and the ferrocenyl–ester group is pseudoexial (*cis* conformation) for 1S,2S.

Cyclic voltammetry studies show  $Fe^{II} / Fe^{III}$  redox potentials of ca. +0.28 V versus  $Fc/Fc^+$  for the [(ferrocenylcarbonyl)oxy]methylene-*N*,*N*-dialkylpyrrolidine-1-ium salts. This potential is independent of alkyl chain length and type of anion. Therefore, the chemical behavior can be changed by further anion exchange and adapted to special needs, but the redox potential will remain the same.

## **Experimental Section**

Ferrocene monocarboxylic acid chloride<sup>[13]</sup> and [(25)-1-methylpyrrolidine-2-yl]methanol<sup>[12]</sup> were prepared according to literature procedures.

CCDC 1452807 (for **2**), 1452808 [for (1R,2S)-**3**], 1452809 [for (1S,2S)-**3**], 1452810 [for (1R,2S)-**4**], 1452811 [for (1R,2S)-**5**], and 1452812 (for FcCOCI) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

({[(25)-N-Methylpyrrolidine-2-yl]methyleneoxy}carbonyl)ferrocene (1): Ferrocene monocarboxylic acid chloride (0.965 g, 3.9 mmol) was dissolved in THF (25 mL). [(25)-1-Methylpyrrolidine-2-yl]methanol (0.5 mL) was added, and the solution was heated under reflux for 1 h. A yellow solid precipitated from the red solution. The organic phase was cooled to room temp., and water (40 mL) was added. After deprotonation with NaOH pellets (0.5 g), **1** was extracted three times with Et<sub>2</sub>O (10 mL each). The combined organic phases were dried with MgSO<sub>4</sub>, and the solvent was removed under reduced pressure to leave **1** as an orange oil, yield 1.03 g (74 %).

**lodides 2–6:** Compound **1** (0.70 g, 2.0 mmol) was dissolved in an excess of alkyl iodide (2 mL), and the mixture was stirred at room temp. for 1 h. After 3 h at 70 °C, a yellow precipitate (**2–5**) or red oil (**6**) was separated, washed with Et<sub>2</sub>O, and dried. Single crystals were obtained by recrystallization from MeOH/Et<sub>2</sub>O (1:1) at -22 °C.

**Bis(trifluoromethylsulfonyl)imides 7–11:** The syntheses of the NTf<sub>2</sub><sup>-</sup> salts were performed by a literature procedure.<sup>[43r]</sup> LiNTf<sub>2</sub> (2 mmol) dissolved in water (10 mL) was added to the iodide salt (**2–6**, 1 mmol) in water (10 mL). Immediately, a yellow emulsion formed, and an orange-brown oil separated from the aqueous phase after a few seconds. The suspension was stirred for a further 16 h at room temp. The oil was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The combined organic phases were dried with MgSO<sub>4</sub>, and the CH<sub>2</sub>Cl<sub>2</sub> was removed under reduced pressure. The resulting red oils were dried at 10<sup>-2</sup> mbar and 40–50 °C for 2 h.

**Supporting Information** (see footnote on the first page of this article): Details on the synthetic procedures and characterization of 1–11; crystal structure data of FcCOCl, **2**, (1*S*,2*S*)-**3**, (1*R*,2*S*)-**3**, (1*R*,2*S*)-**4**, and (1*R*,2*S*)-**5**; NMR spectra of **1**, (1*S*,2*S*)-**3**, and (1*R*,2*S*)-**3**; (temperature-dependent) X-ray powder diffraction patterns of **2**–**5**; Rietveld refinement of the mixture of (1*S*,2*S*)-**3** and (1*R*,2*S*)-**3**; STA data of **1**–**11**; IR spectra of **1**–**3**, **7**, and **8**.

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## lonic Liquids

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- ☐ Chiral and Redox-Active Room-Temperature Ionic Liquids Based on Ferrocene and ∟-Proline



The syntheses of the first ferroceneand pyrrolidinium-based room-temperature ionic liquids (RTILs) linked through ester bridges are reported. The RTILs are reversibly redox-active through the Fe<sup>II</sup> metal center as well as chiral and thermally stable up to 263  $^{\circ}$ C.

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