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FULL PAPER

Biphasic hydroformylation in new molten salts—analogies and differences to organic solvents †

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New ionic compounds 1,2,3-trimethylimidazolium triflate (**1**) and 1-ethyl-2,3-dimethylimidazolium triflate (**2**) and (3-butylimidazole)triphenylboron (**4**) have been formed by alkylation and condensation reactions. An ion exchange reaction yielded the ionic compound 1-butyl-3-methylimidazolium tetraphenylborate (**3**). Molecular structures of all four compounds were determined by single crystal X-ray diffractometry. Utilizing two known rhodium complexes as catalyst precursors, compounds **1**, **2** and **4** were used as solvents for biphasic hydroformylation reactions of two long chain 1-olefins. The results were compared to reactivities in the conventional solvent toluene in which similar turnover numbers but a higher tendency towards isomerization and hydrogenation occurred.

Introduction

Within the last 15 years ionic liquids have experienced a renaissance, especially since these liquids, which consist of ion pairs, have found application as solvents in biphasic catalysis. With melting points above 100 °C, similar compounds are known as molten, fused or liquid organic salts. The first ionic liquid was synthesized in 1914,[1] however, it was only once the first reports of their use as reaction media for organic synthesis appeared that their importance became apparent to the broader scientific community.[2] Ionic liquids show a unique combination of properties including high polarity, low viscosity, high liquid temperature range, high thermal stability, immiscibility with certain organic solvents, wide tunability and no effective vapour pressure.[3] Typical components are 1-alkylpyridinium, 1,3-dialkylimidazolium, ammonium or phosphonium cations and halide, $AlCl_4^-$, PF_6^-, SbF_6^- or BF_4^- anions. Ionic liquids have been utilized in Friedel–Crafts reactions,[2,4] aromatic substitution,[5] acylative cleavage,[6] Heck reactions,[7] hydroesterification,[8] carbonylation,[9] dimerization,[10] polymerization,[11] and hydrogenation[12] in which often novel and unusual chemical reactivities were found.

Rhodium complexes show high catalytic activities for organic transformations and are widely used in combination with chiral phosphine, sulfide or cyclopentadienyl ligand systems in asymmetric catalysis.[13,14] We report here how our newly synthesized molten salts were used as solvents in catalytic reactions utilizing chiral and achiral catalyst precursors, thus improving the scope and potential enantiomeric excess in biphasic catalytic hydroformylation.[15]

Experimental

All reactions and manipulations were carried out under a dry argon atmosphere using standard Schlenk, vacuum-line and glovebox techniques. All solvents were dried and purified by conventional methods and were freshly distilled under argon before use. Melting points were measured by differential scanning calorimetry (2nd run) on a Du Pont 2100 apparatus at a heating/cooling rate of 10 °C per minute. Thermogravimetric analyses were performed on a Perkin Elmer Thermogravimetric Analyzer TGA 7. NMR spectra were recorded on a Varian VXR 300 spectrometer (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75.48 MHz; ^{19}F{^{1}H}, 283.65 MHz) or Varian INOVA 600 spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 150.87 MHz) at 25 °C. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Chemical shifts for ^{19}F{^{1}H} measurements are given relative to $CFCl_3$ in acetone. The IR spectra were recorded on a Perkin Elmer 1600 Series FTIR spectrometer. Mass spectra (FAB in 3-nitrobenzyl alcohol) were obtained using a Micromass (VG) instrument with 70SE magnet sector. Only characteristic fragments containing the isotopes of the highest abundance are listed. Elemental analyses were performed on a Fisons CHNS 1108 elemental analyser. 1-Butyl-3-methylimidazolium chloride[16] and (−)-(η^4-cycloocta-1,5-diene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I)[17] were prepared according to published procedures. 1-Butylimidazole and 1,2-dimethylimidazole (Aldrich) were dried over P_4O_{10} and distilled prior to use. Ammonium tetraphenylborate, ethyl trifluoromethanesulfonate, methyl trifluoromethanesulfonate, silver(I) oxide, and tris(triphenylphosphine)rhodium(I) chloride were used as purchased (Aldrich).

Syntheses

1,2,3-Trimethylimidazolium trifluoromethanesulfonate (1). To a solution of 1,2-dimethylimidazole (34.4 g, 357.8 mmol) in 1,1,1-trichloroethane (140 mL) was slowly added methyl trifluoromethanesulfonate (50.0 g, 304.7 mmol) at 0 °C. The white suspension was heated to 75 °C for 3 h, cooled and stirred for 8 h at 25 °C. After filtration through a d4-frit the residue was washed twice with 1,1,1-trichloroethane (80 mL). The solvent was removed under vacuum (10^{-2} mbar), leaving 69.5 g (88%) of a white solid, mp 129 °C (Found: C, 32.54; H, 4.13; N, 10.56; S, 12.06%. $C_7H_{11}N_2O_3SF_3$ requires C, 32.31; H, 4.26; N, 10.77; S, 12.32%; M 260.23); $\tilde{\nu}$/cm^{-1} 3150m, 1598m, 1555m, 1466m, 1418m, 1277s, 1161s, 1029s, 775s, 757s, 738s, 724w, 659s, 638s, 574s, 518s (KBr); δ_H (acetone-d_6, 300 MHz) 7.60 (s, 2 H, H^{4,5}), 3.95 (s, 6 H, H^{6,8}), 2.75 (s, 3 H, H^7); δ_C (acetone-d_6, 75.41 MHz) 137.6 (C^2), 114.4 (C^{4,5}), 113.7 (q, $^1J_{CF}$ = 323.3 Hz, CF_3), 26.5 (C^{6,8}), 0.6 (C^7); δ_F (acetone-d_6, 283.65 MHz) −78.1; *m*/*z* (FAB, positive ion) 111 (M^+, 100%); *m*/*z* (FAB, negative ion) 149 (M^-, 100%).

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b107720a/

 DOI: 10.1039/b107720a

1-Ethyl-2,3-dimethylimidazolium trifluoromethanesulfonate (2). Similar to the preparation of **1**, reaction of 1,2-dimethylimidazole (15.5 g, 161.2 mmol) with ethyl trifluoromethanesulfonate (25.0 g, 140.3 mmol) in 1,1,1-trichloroethane (60 mL) gave after workup 30.9 g (80%) of a white solid, mp 113 °C (Found: C, 35.23; H, 4.90; N, 10.15; S, 11.47%. $C_8H_{13}N_2O_3SF_3$ requires C, 35.04; H, 4.78; N, 10.21; S, 11.69%; M 274.26); $\tilde{\nu}$/cm^{-1} 3146s, 2983m, 2296w, 1641w, 1594m, 1548m, 1456w, 1426m, 1392m, 1266s, 1227s, 1153s, 1088w, 1033s, 954m, 806m, 773s, 757m, 727m, 712w, 671m, 639s, 573s, 518s (KBr); δ_H (acetone-d_6, 300 MHz) 7.68 (d, ^3J = 2.1 Hz, 1 H, H$^{4/5}$), 7.63 (d, ^3J = 2.1 Hz, 1 H, H$^{4/5}$), 4.33 (q, ^3J = 7.4 Hz, 2 H, H^6), 3.94 (s, 3 H, H^9), 2.77 (s, 3 H, H^8), 1.47 (t, ^3J = 7.4 Hz, 3 H, H^7); δ_C (acetone-d_6, 75.41 MHz) 136.7 (C^2), 114.5 (C$^{4/5}$), 113.3 (q, $^1J_{CF}$ = 323.4 Hz, *C*F$_3$), 112.4 (C$^{4/5}$), 35.0 (C^6), 26.3 (C^9), 6.1 (C^7), 0.4 (C^8); δ_F (acetone-d_6, 283.65 MHz) −81.0; *m*/*z* (FAB, positive ion) 125 (M$^+$, 100%); *m*/*z* (FAB, negative ion) 149 (M$^-$, 100%).

1-Butyl-3-methylimidazolium tetraphenylborate (3). To ammonium tetraphenylborate (17.8 g, 52.8 mmol) was slowly added at 25 °C a suspension of silver(I) oxide (6.1 g, 26.4 mmol) in degassed H_2O (50 mL) under light protection. The grey mixture was stirred for 1 h and a solution of 1-butyl-3-methylimidazolium chloride (10.0 g, 57.3 mmol) in degassed H_2O (100 mL) was added. The suspension was stirred for 30 h and filtered using a d4-frit. After washing twice with degassed H_2O (50 mL), the solvent was removed under vacuum (10^{-2} mbar) and the remaining off-white solid was extracted with dichloromethane (50 mL). The organic fraction was dried with calcium chloride and the solvent was removed under vacuum (10^{-2} mbar) leaving 15.4 g (63%) of a white solid, mp 131 °C (decomp.) (Found: C, 83.75; H, 7.27; N, 6.00%. $C_{32}H_{35}N_2B$ requires C, 83.84; H, 7.69; N, 6.11%; M 458.45); $\tilde{\nu}$/cm^{-1} 3438m, 3162m, 3133m, 3100s, 3082s, 3051s, 2994m, 2954s, 2869m, 1941w, 1888w, 1824w, 1766w, 1678w, 1608w, 1579m, 1561s, 1479s, 1449m, 1426s, 1379m, 1338w, 1267m, 1248s, 1159s, 1143s, 1032m, 841s, 741s, 708s, 646m, 622m, 611s, 484m, 472w (KBr); δ_H (chloroform-d_1, 300 MHz) 7.53 (m, 8 H, C*H*(phenyl)^{ortho}), 6.97 (m, 8 H, C*H*(phenyl)^{meta}), 6.78 (m, 4 H, C*H*(phenyl)^{para}), 5.94 (t, ^3J = 2.0 Hz, 1 H, H^5), 5.76 (t, ^3J = 2.0 Hz, 1 H, H^4), 4.67 (s, 1 H, H^2), 3.15 (t, ^3J = 7.6 Hz, 2 H, H^6), 2.74 (s, 3H, H^{10}), 1.32 (m, 2 H, H^7), 1.14 (m, 2 H, H^8), 0.89 (t, ^3J = 7.2 Hz, 3 H, H^9); δ_C (chloroform-d_1, 75.41 MHz) 164.4 (q, $^1J_{CB}$ = 49.4 Hz, C(phenyl)^{ipso}), 135.9 (C(phenyl)^{ortho}), 134.9 (C^2), 126.1 (C(phenyl)^{meta}), 122.6 (C^5), 122.2 (C(phenyl)^{para}), 120.5 (C^4), 48.9 (C^6), 35.3 (C^{10}), 31.5 (C^7), 19.2 (C^8), 13.2 (C^9); *m*/*z* (FAB, positive ion) 139 (M$^+$, 100%); *m*/*z* (FAB, negative ion) 319 (M$^-$, 100%).

(3-Butylimidazole)triphenylboron (4). To a suspension of ammonium tetraphenylborate (17.6 g, 52.2 mmol) in acetonitrile (50 mL) was added 1-butylimidazole (15.0 mL, 114.1 mmol) at 20 °C. The white suspension was heated for 70 h to 81 °C while the system was continuously purged with argon. The mixture was filtered using a d4-frit and the residue was washed twice with acetonitrile (10 mL). The solvent was removed under vacuum (10^{-2} mbar) and the remaining solid was recrystallized from ethylacetate yielding 16.5 g (86%) of a white solid, mp 152 °C (Found: C, 81.60; H, 7.75; N, 7.49%. $C_{25}H_{27}N_2B$ requires C, 81.97; H, 7.43; N, 7.65%; M 366.31); $\tilde{\nu}$/cm^{-1} 3426m, 3145m, 3125s, 3062s, 3000s, 2966s, 2930s, 2877m, 1961w, 1889w, 1829w, 1775w, 1725w, 1644w, 1614m, 1586m, 1537s, 1484m, 1455s, 1428s, 1386w, 1361m, 1309w, 1261m, 1241m, 1162s, 1108s, 1069m, 1027m, 998m, 882w, 865m, 834s, 799m, 751s, 727s, 706s, 672s, 648s, 620m, 608m (KBr); δ_H (acetone-d_6, 600 MHz) 8.01 (t, ^4J = 1.5 Hz, 1 H, H^2), 7.39 (m, 1 H, H^5), 7.20 (m, 6 H, C*H*(phenyl)^{ortho}), 7.14 (m, 6 H, C*H*(phenyl)^{meta}), 7.07 (m, 3 H, C*H*(phenyl)^{para}), 7.02 (m, 1 H, H^4), 4.19 (t, ^3J = 7.6 Hz, 2 H, H^6), 1.84 (m, 2 H, H^7), 1.33 (m, 2 H, H^8), 0.93 (t, ^3J = 7.4 Hz, 3 H, H^9); δ_C (acetone-d_6, 150.87 MHz) 155.4 (m, C(phenyl)^{ipso}), 139.2 (C^2), 135.9 (C(phenyl)^{ortho}), 128.2 (C^4), 128.0 (C(phenyl)^{meta}), 125.9 (C(phenyl)^{para}), 121.5 (C^5), 49.5 (C^6), 33.9 (C^7), 20.7 (C^8), 14.3 (C^9); *m*/*z* (FAB, positive ion) 366 (M$^+$, 5%), 289 (M − phenyl, 100%).

General procedure for hydroformylation experiments

In a nitrogen glovebox the catalyst precursor (0.15 mmol), a magnetic stir bar and the solid reaction medium (5 g) or toluene (20 mL) were placed in a glass lined 300 ml stainless steel autoclave. The apparatus was sealed and 30 mmol of the freshly distilled substrate was added. The vessel was placed in a thermostatically controlled oil bath at the chosen temperature and charged with a 1 : 1 hydrogen/carbon monoxide mixture (Afrox) at 80 bar. After a reaction time of 6 h the apparatus was cooled, opened, and the organic layer decanted off. The now solid reaction medium was further extracted with chloroform (10 mL). A sample of the combined organic fractions was taken to determine the conversion and the linear : branched ratio by ^{1}H NMR. The reported results represent the average of experiments carried out in duplicate.

X-Ray structure determination

X-Ray structures were obtained for **1**, **2**, **3** and **4**, however, recently the structure of **3** was published by Dupont *et al.*[18] The details of the data collection and structure solution and refinement for **3** are, therefore, not included in this paper, although they have been deposited with the Cambridge Crystallographic Data Centre (CCDC deposition number 169679). However, in the previous publication the authors were not able to determine absolute structure, possibly as a result of twinning, since this was also found to be present in the current determination. In addition, and in contrast to the current determination, no disorder was observed. As shown in the discussion, disorder observed in a crystal structure is related to the melting point of that crystal, therefore it is of great importance. Details of the modelling of the disorder, as well as of the twinning in **3** are thus included in this paper, and the discussion refers to the current structural determination.

Data were collected on a Nonius Kappa CCD diffractometer[19] using monochomated Mo-Kα radiation (λ = 0.71073 Å). Refinement was based on F^2. All non-hydrogen atoms were refined anisotropically. H atoms could in many cases be identified from Fourier difference maps, but were placed in calculated positions using a riding model. Disorder was observed in the structures of **2**, **3** (this disorder had not been modelled in a previous structure determination[18]) and **4**. Each structure was dealt with in the same way: the positions of the disordered atoms were identified from the Fourier difference map; all atoms in the same disordered group were refined anisotropically with common site occupancies and the total site occupancy for the two disordered groups was constrained to 1; if necessary the ISOR, SADI and/or SIMU restraint commands were used to obtain sensible structures and displacement parameters. In addition to the large amount of static disorder there is also a considerable amount of dynamic disorder that is evidenced by large anisotropic displacement ellipsoids. Structures for both **2** and **3** were found to be twinned. The space group in **3** is non-centrosymmetric, and the Flack test[20] suggested the presence of a racemic twin. Refinement revealed a racemic twin ratio of 0.86 : 0.14. Identification of twinning in **2** was more complicated—systematic absences observed were not consistent with any space group, although the unit cell was found to have all angles approximately equal to 90°, and thus data were collected in *P*1. Careful inspection of the systematic absences and atomic positions identified from an initial direct methods solution revealed that the space group was $P2_1/c$ with twinning across a mirror plane perpendicular to the *c*-axis. In addition it was found that the asymmetric unit consisted of two chemically

Table 1 Crystal data and refinement for $[C_6H_{11}N_2{\cdot}CF_3SO_3]$ (**1**), $[C_7H_{13}N_2{\cdot}CF_3SO_3]_2$ (**2**), $[C_8H_{15}N_2{\cdot}BC_{24}H_{20}]$ (**3**) and $[C_{25}H_{27}N_2B]_2$ (**4**)

	1	**2**	**4**
Formula	$C_7H_{11}N_2F_3SO_3$	$C_{16}H_{26}N_4F_6S_2O_6$	$C_{50}H_{54}N_4B_2$
M	260.23	548.52	732.62
T/K	298(2)	172(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	6.8313(2)	15.722(1)	11.3171(10)
b/Å	14.4530(5)	8.615(1)	12.7981(10)
c/Å	11.3689(4)	18.081(1)	15.6049(10)
α/°	90	90	73.70(1)
β/°	96.503(2)	89.979(11)	74.38(1)
γ/°	90	90	77.22(1)
U/Å^3	1115.26(6)	2449.0(4)	2063.1(3)
Z	4	4	2
μ/mm^{-1}	0.327	0.302	0.068
Reflections collected/unique	5124/2524 [R_{int} = 0.020]	8798/4027 [R_{int} = 0.019]	11327/9087 [R_{int} = 0.016]
Data/restraints/parameters	2524/0/153	4027/12/428	9087/36/534
Reflections with $I > 2\sigma(I)$	1977	3411	6746
$R1(I > 2\sigma(I))$	0.043	0.039	0.050
$wR2$ (all data)	0.116	0.103	0.133

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1**, **2** and **4**

1		**2**		**4**	
Imidazole ring					
N(1)–C(2)	1.326(3)	N(1)–C(2)[a]	1.34(1)	N(1)–C(1)[a]	1.326(3)
N(2)–C(2)	1.324(3)	N(2)–C(2)[a]	1.32(3)	N(1)–C(2)[a]	1.381(2)
N(1)–C(5)	1.392(3)	N(1)–C(5)[a]	1.39(2)	N(2)–C(1)[a]	1.337(2)
N(2)–C(4)	1.391(3)	N(2)–C(4)[a]	1.39(2)	N(2)–C(3)[a]	1.373(3)
N(1)–C(6)	1.463(3)	N(1)–C(3)[a]	1.45(3)	B–N[a]	1.615(3)
				B–C[a]	1.632(3)
N(2)–C(3)	1.465(3)	N(2)–C(6)[a]	1.46(3)	N(2)–C(4)[a]	1.474(2)
C(2)–N(1)–C(5)	108.47(18)	C(2)–N(1)–C(5)[a]	108.5(6)	C(1)–N(1)–C(2)[a]	106.4(1)
C(2)–N(2)–C(4)	108.53(18)	N(2)–C(2)–N(1)[a]	107.9(5)	C(1)–N(2)–C(3)[a]	107.8(2)
N(2)–C(2)–N(1)	108.40(19)	C(2)–N(2)–C(4)[a]	109.1(6)	N(1)–C(1)–N(2)[a]	110.4(2)
				C(1)–N(1)–B[a]	129.8(1)
				C(2)–N(1)–B[a]	123.7(1)
				C–B–C[a]	111(3)
Anion					
S–O[a]	1.437(5)	S–O[a]	1.426(9)		
S(1)–C(7)	1.821(2)	S–C[a]	1.801(6)		
C–F[a]	1.329(3)	C–F[a]	1.32(1)		
O–S–O[a]	115.0(6)	O–S–O[a]	114.8(16)		
O–S–C[a]	103.20(1)	O–S–C[a]	103.3(4)		
F–C–F[a]	107.5(3)	F–C–F[a]	107.0(8)		
F–C–S[a]	111.3(1)	F–C–S[a]	111.8(7)		

[a] Average value.

equivalent but crystallographically independent ion pairs. All calculations were performed using SHELXL 97[21] within the WINGX package.[22] Details of the data collection and structure refinement are included in Table 1. Selected bond lengths and angles are given in Table 2. When a bond length or angle occurs more than once (*i.e.* for two chemically equivalent but crystallographically different molecules in an asymmetric unit), the average value is given. Average values for similar bonds (*e.g.* B–C bonds in $B(C_6H_5)_4$ anion) are also given. Figures were generated using Ortep3 for Windows; displacement ellipsoids are at the 50% probability level.[23]

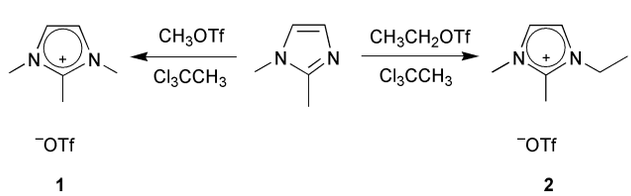
CCDC reference numbers 169677–169680.

See http://www.rsc.org/suppdata/dt/b1/b107720a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses of ionic compounds

The commonly used ionic liquids with 1,3-dialkylimidazolium cations can be deprotonated under basic conditions to form the corresponding carbene compounds.[24] To inhibit this degradation we synthesized two new compounds with alkyl substituents in the 2 position. Depending on the triflate used, compounds **1** and **2** were obtained by alkylation of 1,2-dimethylimidazole at 0 °C in analogy to a previously published procedure.[25] After work up the products were isolated as white solids in 88 and 80% yield (Scheme 1).



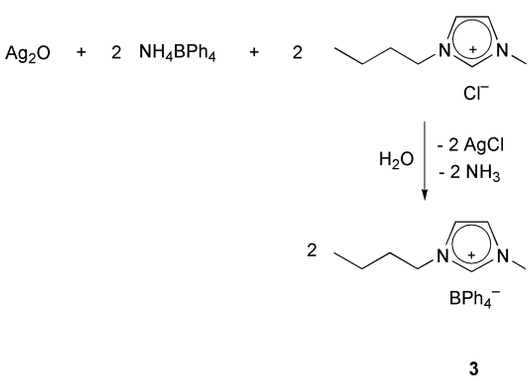
1 **2**

Scheme 1

The highly symmetrical compound **1** melts at 129 °C, while the unsymmetrical substituted compound, **2**, melts at 113 °C. Furthermore, **1** shows a liquid crystal phase formation at 48

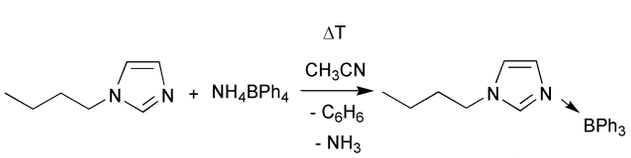
°C.[26] Their melting points are significantly higher than for the unsubstituted compounds 1,3-dimethylimidazolium triflate (39 °C) and 1-ethyl-3-methylimidazolium triflate (−9 °C). However, the melts decompose only at very high temperatures of 495 °C (**1**) and 450 °C (**2**) as shown by DSC and TGA measurements. The molten salts are, therefore, suitable reaction media for catalytic applications over a wide temperature range.

A different synthesis of compound **3** that contains the sterically demanding tetraphenylborate anion, was published after we finished this work.[18] Salt **3** was obtained by ion exchange between ammonium tetraphenylborate and 1-butyl-3-methylimidazolium chloride in the presence of silver(I) oxide in water. Formation of insoluble silver(I) chloride and volatile ammonia drives the reaction (Scheme 2). After work up the compound was isolated in 63% yield as a white solid, melting at 131 °C with degradation (DSC) and exhibiting an actual decomposition temperature of 270 °C (TGA).



Scheme 2

Much lower melting points (<50 °C) were reported for molten tetraalkylammonium tetraalkylborates (linear alkyls with 2, 4, 6, and 8 carbon atoms) which, however, were only stable at temperatures up to 100 °C.[27] Decomposition of **3** presumably occurs because the tetraphenylborate anion is not chemically inert and easily fragments by generating benzene. Furthermore, this fragmentation was observed during our attempted synthesis of 1-butylimidazolium tetraphenylborate. This compound was expected to have a lower melting point than **3**.[26] Reaction of ammonium tetraphenylborate and excess 1-butylimidazole gave the desired compound in solution. However, as coordinated acetonitrile had to be removed at high temperatures under vacuum, the salt decomposed and formed the coordination compound (3-butylimidazole)triphenylboron, **4**, in 86% yield (Scheme 3). Volatile benzene and ammonia were also produced.

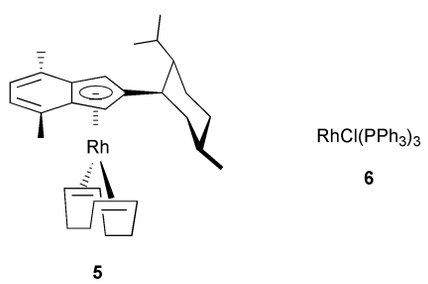


Scheme 3

Similar bond cleavages have been reported for alkylammonium salts of *N*-triphenylboron-*N*′-methylpiperazinium[28] and during the accidental synthesis of (3-methylimidazole)-triphenylboron starting from the cation $[ReO_2(1\text{-mim})_4]^+$ (mim = methylimidazole) and $Na[BPh_4]$.[29] Compound **4** melts without decomposition at 152 °C (DSC) with an eventual decomposition temperature of 280 °C (TGA). The melt is, therefore, suitable as a reaction medium. Imidazolium compound **3** with no substituent in the 2-position, can indeed be deprotonated under basic conditions by a methyllithium solution in diethyl ether to form the corresponding free carbene (carbene signal at 202 ppm in the $^{13}C\{^1H\}$ NMR in acetone-d_6 at 75.48 MHz). Pure crystalline compounds **1**–**4** although fairly stable in air, were handled under an inert atmosphere at all times. The high thermal stability of **1**–**3** was confirmed by mass spectrometry (FAB) as the molecular ions form the peaks of highest intensity. In the case of the covalent compound **4**, however, easy loss of a phenyl ring was detected.

Catalytic hydroformylation

The newly synthesized ionic compounds **1** and **2** as well as the new coordination compound **4** were used as solvents for biphasic hydroformylation reactions. The prochiral substrates 1-hexene and 1-dodecene were reacted with the chiral, stereomerically pure catalyst precursor (−)-(η^4-cycloocta-1,5-diene)-(2-menthyl-4,7-dimethylindenyl)rhodium(I),[17,30] **5**, and the achiral Wilkinson complex $[(PPh_3)_3RhCl]$, **6** (Scheme 4) at 140 or 155 °C. No Rh(0) deposition, that could have led to heterogeneous reactions, was observed. The results are compiled in Table 3. High olefin conversions of 68 to 100% were achieved at 80 bar CO/H_2 pressure after reaction times of 6 h. The turnover numbers are in the typical range for rhodium catalysts.[31] The Wilkinson catalyst, however, shows higher conversions than **5** and reactions in the melts of **1**, **2** and **4** occurred in general slower than in toluene. This is probably due to lower solubility and diffusion coefficients of the gases and the substrates in the molten reaction media.



Scheme 4

The actual yields of the corresponding linear and branched aldehydes are often also lower and vary between 38 and 100%. This is due to competing hydrogenation which transforms the olefins into the corresponding unreactive alkane in 0 to 60% yield. This hydrogenation rate is significantly higher than in the conventional solvent toluene in which less than 10% hydrogenation occurs. In previous articles on the use of ionic liquids in hydroformylation reactions, this increase was not mentioned. Only 1–2% byproducts were reported[32] even though hydrogenation and hydroformylation were catalyzed simultaneously by a rhodium catalyst in an ionic liquid.[33]

The observed linear/branched ratios varied between 1 : 0.4 and 1 : 2.2 and are unaffected by the nature of the solvent. Typical linear/branched ratios of 1 : 1 to 1 : 3 in toluene are mentioned in the literature.[34] In molten salts **1**, **2** and in toluene the tendency of catalyst precursor **6** to form the linear aldehyde is higher than that of **5**, which favours the branched products. In the covalent solvent (**4**) at increased temperature, however, both catalyst precursors favour the branched products as a dramatic increase in isomerization activity occurs.

In the case of 1-dodecene, for example, all six possible aldehydes are detectable and the 3- and higher aldehydes are formed in up to 44% yield. No essential reactivity change occurred when the covalent compound **4** was substituted for the molten salts **1** and **2**. However, only from the latter could the catalyst be recovered successfully in multicyclic reactions. In general, the tendency towards isomerization of the olefinic double bond to the thermodynamically more stable isomers is higher than in toluene, as ionic liquids are known to stabilize the necessary cationic intermediates.[33] The isomerizations under the current

Table 3 Hydroformylation in the presence of rhodium catalyst precursors[a]

Solvent	Catalyst	Substrate	*T*/°C	Conversion(%)	Yield of aldehyde(%)	Yield of alkane(%)	n : i[b]	Isomerisation[c](%)	*n*[d]
1	**5**	hexene	140	81	53	28	1 : 1.0	9	3
1	**5**	dodecene	140	82	60	22	1 : 1.4	23	4
1	**6**	hexene	140	91	66	25	1 : 0.6	5	3
1	**6**	dodecene	140	100	59	41	1 : 0.4	4	4
2	**5**	hexene	140	68	40	28	1 : 0.9	10	3
2	**5**	dodecene	140	89	51	38	1 : 2.1	35	3
2	**6**	hexene	140	96	82	14	1 : 0.5	2	3
2	**6**	dodecene	140	100	73	27	1 : 0.4	3	4
4	**5**	hexene	155	100	57	43	1 : 2.2	14	3
4	**5**	dodecene	155	98	38	60	1 : 1.3	44	4
4	**6**	hexene	155	99	58	41	1 : 1.8	28	3
4	**6**	dodecene	155	100	68	32	1 : 1.5	29	6
toluene	**5**	hexene	140	100	92	8	1 : 1.3	15	3
toluene	**5**	dodecene	140	100	94	6	1 : 0.9	9	4
toluene	**6**	hexene	140	100	90	10	1 : 0.6	5	3
toluene	**6**	dodecene	140	100	100	0	1 : 0.5	3	4

[a] Reaction conditions as described in the Experimental section (6 h, 80 bar CO/H_2). [b] n : i = n-aldehyde : all iso-aldehydes. [c] Amount of 3- and higher aldehydes/amount of all aldehydes × 100. [d] Number of different aldehydes formed.

conditions are still less predominant than in the most successful synthetically applied isomerizations in toluene with up to 92% conversion.[35,36]

Isomerized 1-dodecene can give rise to six different aldehydes of which five are chiral. Isomerized 1-hexene can be converted into three different aldehydes of which two are chiral. Due to the high reaction temperatures, kinetic discrimination of the diastereomorphic catalytic transition states is low, resulting in low selectivity and enantiomeric excess. Therefore, no attempts were made to separate the different isomers or to determine enantiomeric purity of the products.

Structural studies

Colourless crystals of **1**, **2**, **3**, and **4** suitable for single crystal X-ray diffraction analysis were obtained by recrystallization from acetonitrile (**1**) or ethylacetate (**2**–**4**) at room temperature (**1**–**3**) or −78 °C (**4**). The molecular structures of molten salts **1**, **2**, and **3** (Figs. 1–3) consist of ion pairs with the cation being an imidazole with varying substituents, while the anion is either triflate (**1**, **2**) or tetraphenylborate (**3**). The covalent compound **4** (Fig. 4) consists of a triphenylboron functionalized imidazole.

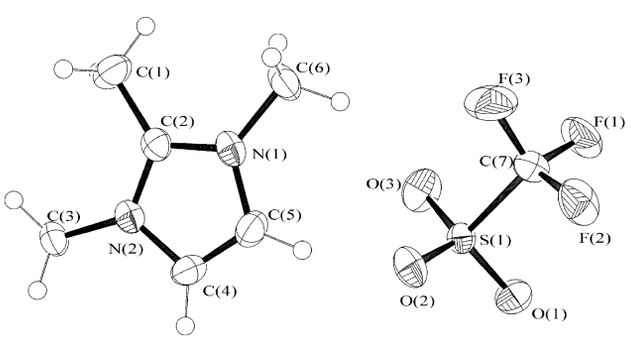


Fig. 1 Molecular structure of complex **1** showing the numbering scheme.

Conformational disorder was observed in the butyl chains of **3** (ratio 0.82 : 0.18) and **4** (ratio 0.62 : 0.38), while in **2** the entire imidazole ring is disordered (ratio 0.57 : 0.43). Very low peaks of electron density indicating a very small amount of disorder in the imidazole ring were also observed in the Fourier difference map of **1**, although the disorder could not be successfully modelled. Selected bond lengths and angles (Table 2) compare well with values found in the structures of (3-methylimidazole)triphenylboron,[29] 3-borane-1,4,5-trimethylimidazole,[37] lithium triethyl(1,4,5-trimethylimidazolyl)borate,[38] polymeric

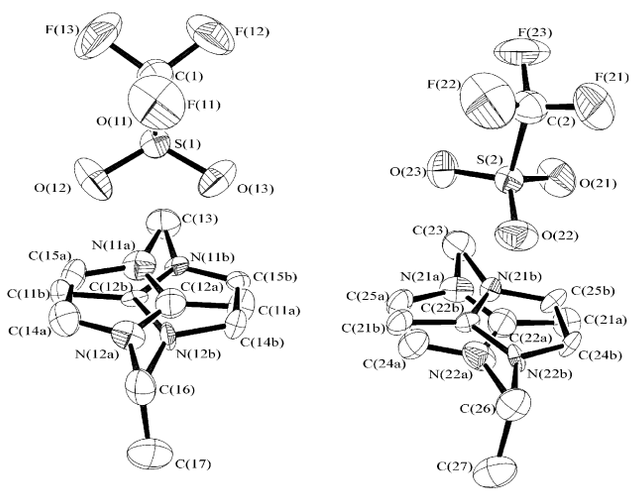


Fig. 2 Molecular structure of complex **2** showing the numbering scheme and disordered conformations. Hydrogen atoms have been omitted for clarity.

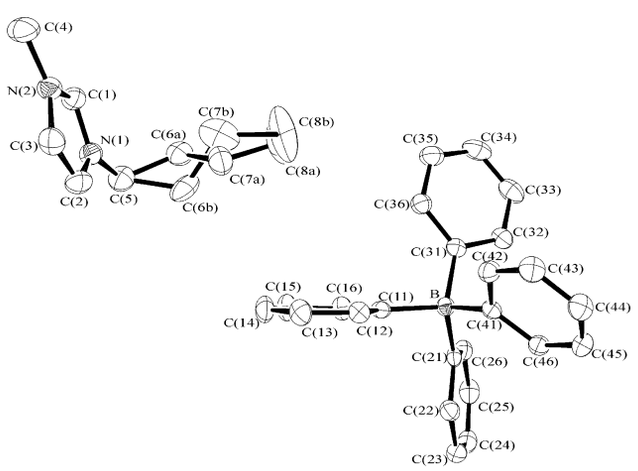


Fig. 3 Molecular structure of complex **3** showing the numbering scheme and disordered conformation. Hydrogen atoms have been omitted for clarity.

1-imidazolediphenylboranes[39] and the previously published structure of **3**.[18]

Crystal packing of **1** consists of tightly packed channels of alternating cation–anion pairs connected by hydrogen bonding between a triflate oxygen and a hydrogen of an imidazole

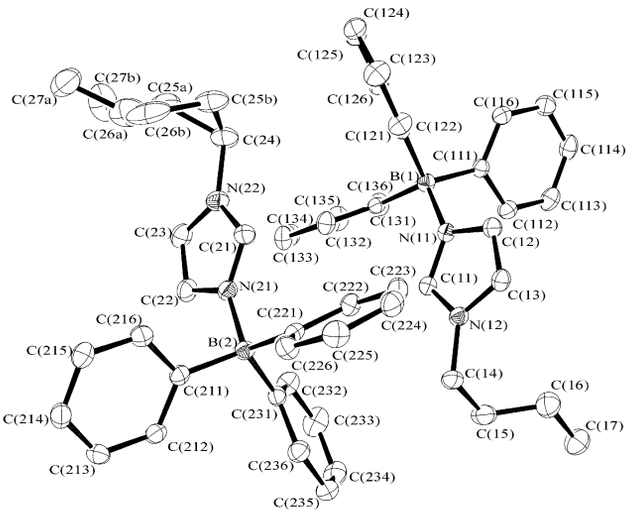


Fig. 4 Molecular structure of complex **4** showing the numbering scheme and disordered conformation. Hydrogen atoms have been omitted for clarity.

carbon. Although alternating rows of cations and anions are also observed in **2** the channel structure is not as clear as in **1** as a result of the different orientations of the two crystallographically independent molecules in the asymmetric unit. Hydrogen-bonding occurs between methyl hydrogens and triflate oxygens as well as between hydrogens on the terminal carbon of the ethyl chain and triflate fluorines. Packing in **3** consists of an interconnecting network of cations and anions linked by C–H $\cdots$ π interactions from imidazole hydrogens to phenyl rings and *vice-versa* as well as hydrogens on the butyl chains to phenyl rings. Similar C–H $\cdots$ π interactions are also observed in **4**, although the resulting interconnecting network of molecules is more tightly packed than in **3**.

Two opposing effects are observed in the crystal and molecular structures of **1**–**4** that have an influence on their melting points, namely hydrogen bonding (or similar non-bonded interactions such as C–H $\cdots$ π interactions) and disorder. Intermolecular interactions increase the order of the system by organising the crystal framework and thus raise the melting point, while disorder is associated with a lowering of the melting point.

The disorder can be interpreted as an indicator of poor packing efficiency, and is related to the fact that low symmetry is accepted as being the most important factor in achieving low melting *N*,*N*′-dialkylimidazolium salts.[26b] In **2** a large amount of disorder and very little hydrogen bonding is found. In addition the molecular structure is less symmetrical than **1**, and it thus has the lower melting point (113 °C). **1** has little discernable disorder and is highly symmetrical, and even though very little hydrogen bonding occurs, an increased melting point of 129 °C is observed. Although **3** exhibits disorder in the butyl chain along with low symmetry, widespread hydrogen bonding gives rise to the higher decomposition temperature of 131 °C. The highest melting point of 152 °C observed for **4**, can be ascribed to the large number of non-bonded interactions, although disorder of the butyl chain also occurs.

Conclusion

Alkylation reactions of 1,2-dimethylimidazole with the corresponding alkyl triflates yielded the new molten salts 1,2,3-trimethylimidazolium triflate and 1-ethyl-2,3-dimethylimidazolium triflate. The ion exchange reaction between $AgBPh_4$ and 1-butyl-3-methylimidazolium chloride provided a convenient entry into ionic compounds with bulky tetraphenylborate counter ions. The low thermal stability of tetraphenylborate anions was detected during the attempted synthesis of 1-butylimidazolium tetraphenylborate, yielding selectively (3-butylimidazole)triphenylboron.

X-Ray diffraction analyses revealed disorder in the molecular structures and hydrogen-bonding (or other intermolecular interaction) in the crystal structures of **1**, **2**, **3**, and **4**. These opposing structural influences accounted for the variation in measured melting temperatures.

The molten salts **1**, **2** and the covalent compound **4** were successfully used as reaction media for biphasic rhodium catalysed hydroformylation reactions of 1-olefins. High conversions with varying linear/branched ratios were observed. In comparison to the conventional solvent toluene, similar turnover numbers but a higher tendency towards isomerization and hydrogenation occurred.

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