DOI: 10.1002/ejic.200600737

Thiocyanate Functionalised Ionic Liquids: Synthesis, Characterisation and Reactivity

Dongbin Zhao,[a] Zhaofu Fei,[a] Wee Han Ang,[a] Rosario Scopelliti,[a] and Paul J. Dyson*[a]

Keywords: Ionic liquids / Thiocyanate / Palladium complexes / Imidazolium salts

The reaction of chloromethyl thiocyanate with 1-methylimidazole affords the imidazolium salt, 1-thiocyanomethyl-3-methylimidazolium chloride, [C_1SCNmim]Cl (**1a**). Exchange of the chloride anion in **1a** by $[PF_6]^-$, $[BF_4]^-$, $[Tf_2N]^-$ or $[AuCl_4]^-$ affords salts **1b**, **1c**, **1d** and **1e**, respectively. Salts [C_1SCNmim][BF_4] (**1c**) and [C_1SCNmim][Tf_2N] (**1d**) melt below 100 °C and can therefore be classified as ionic liquids. The reaction of **1a** with $PdCl_2$ affords [C_1SCNmim]$_2$[$PdCl_4$] (**2a**), whereas **1c** reacts with $PdCl_2$ to form the complex [$PdCl_2${C_1SCNmim}$_2$][BF_4]$_2$ (**2c**). In the presence of HNO_3 both **1a** and **1c** react with $PdCl_2$ with the loss of HCN to form a sulfide-bridged palladium dimer [$PdCl_2${C_1Smim}]$_2$ (**3**). The structures of **1a**, **1e**, **2a** and **3** have been determined in the solid state by single-crystal X-ray diffraction.

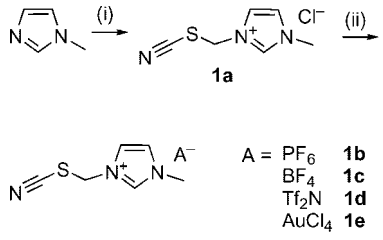
Introduction

Ionic liquids incorporating functional groups on the cation and/or anion have started to receive extensive attention as media for a wide range of applications, in particular in homogeneous and heterogeneous catalysis, but also in material science.[1] In certain instances, when a functional group is incorporated into an ionic liquid structure, highly specific properties are imparted to the liquid, and in such cases these functional ionic liquids are often referred to as task-specific ionic liquids.[2] Many different functional groups have already been incorporated onto ionic liquid cations, for example, alkenes,[3–5] alkynes,[6,7] amines,[8] amides,[9] ethers, alcohols,[10] acids,[11] thiols,[12–14] urea and thiourea,[2] fluorous chains,[15] glycidyl chains,[16] phosphoryl,[17] and ferrocenyl groups.[18] In addition, ionic liquids with functional anions have also been reported, for example, with transition metal carbonyl anions,[19,20] perfluoroalkyl-[21] and nitrile-functionalised[22] trifluoroborate anions, as well as numerous others.[23]

We have previously reported the synthesis, characterisation and reactivity of ionic liquids carrying the nitrile functionality based on both imidazolium[24] and pyridinium[25] cations. It was shown that the nitrile-functionalised ionic liquids were excellent solvents for conducting Suzuki and Stille coupling reactions employing $PdCl_2$ as a precatalyst.[26] While the nitrile group was shown to coordinate to the palladium(II) centre following dissolution in the ionic liquids, it was found that under the catalytic conditions palladium nanoparticles formed. Transmission electron microscopy (TEM) revealed the presence of nanoparticles with a typical diameter of 5 nm and the nanoparticles showed superior stability to those isolated from nonfunctionalised ionic liquids. Thus, we thought that it might be interesting to see if related thiocyanate ionic liquids could be prepared and used in a similar fashion and in this paper we describe the synthesis, characterisation and the reactivity of a series of imidazolium ionic liquids incorporating the thiocyanate functionality.

Results and Discussion

The synthetic route used to prepare the thiocyanate-functionalised imidazolium salts described herein is illustrated in Scheme 1. In the first step chloromethyl thiocyanate and 1-methylimidazole are stirred at 0 °C in acetone to afford the new imidazolium salt, [C_1SCNmim]Cl (**1a**). The product precipitates from the reaction and is obtained as a fine colourless microcrystalline material following filtration and washing.



Scheme 1. Synthesis of thiocyanate-functionalised imidazolium salts; Reagents and conditions: (i) $ClCH_2SCN$, acetone, 0 °C; (ii) HPF_6, Li[Tf_2N] or $HAuCl_4$ in water, $NaBF_4$ in acetone, room temp.

[a] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL),
1015 Lausanne, Switzerland
E-mail: paul.dyson@epfl.ch

Single crystals of **1a** suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound at room temperature. The structure of **1a** that corroborates the spectroscopic data obtained in solution (see below) is shown in Figure 1 with key bond parameters given in the caption. The imidazolium ring is almost perfectly planar, bond angles in the rings range from 106.7(2) to 107.6(2)° and distances from 1.331(3) to 1.379(3) Å. The –S–C≡N moiety is essentially linear with a C–N distance of 1.147(3) Å, which is in the expected range.

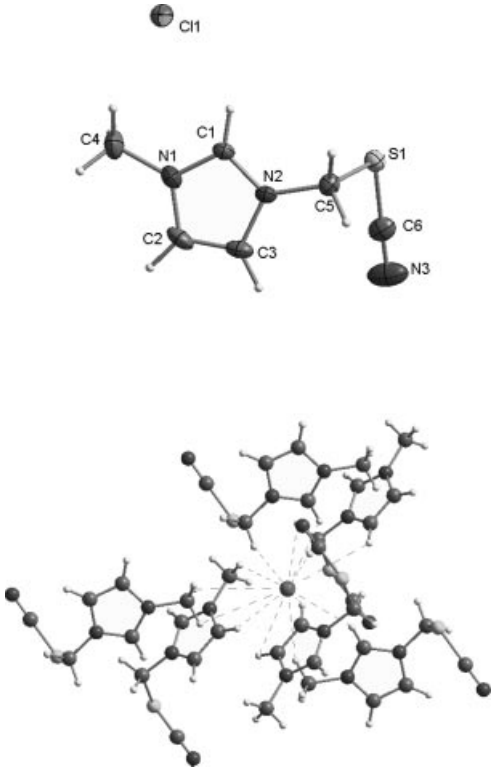


Figure 1. ORTEP representation of **1a** (top) and its packing diagram (bottom) indicating the positions of the imidazolium cations with respect to the chloride anion; atoms are represented by ellipsoids at the 50% probability level. Key bond lengths [Å] and angles [°]: C1–N1, 1.331(3); C1–N2, 1.338(3); N1–C4, 1.468(3); N2–C5, 1.453(3); C5–S1, 1.825(2); S1–C6, 1.704(3); C6–N3, 1.147(3); N1–C1–N2, 107.6(2); C1–N1–C4, 124.8(2); C1–N2–C5, 125.0(2); N2–S1–C6, 113.1(2); C5–S1–C6, 98.4(2); S1–C6–N3, 177.7(2).

The lattice of **1a** is characterised by extensive H bonding between the imidazolium cations and the chloride anion (see Figure 1 for **1a**), resulting in a compact structure held together by short contacts.

Subsequent reaction of **1a** with HPF_6, $NaBF_4$, $LiTf_2N$ [Tf_2N = bis(trifluoromethanesulfonyl)imide] or $HAuCl_4$ in water or acetone affords [C_1SCNmim][PF_6] (**1b**), [C_1SCNmim][BF_4] (**1c**), [C_1SCNmim][Tf_2N] (**1d**) and [C_1SCNmim][$AuCl_4$] (**1e**), respectively (see Scheme 1). Salts **1b**–**1e** are all solids at room temperature with melting points of 120, 78, 47 and 150 °C, respectively, and thus **1c** and **1d** can be considered as ionic liquids on the basis of the widely accepted definition.[26]

Salts **1a**–**1e** were characterised using electrospray ionisation mass spectrometry (ESI-MS) and IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The positive ion ESI mass spectra of **1a**–**1e** in methanol disclose a parent peak at *m*/*z* = 154 corresponding to the cation [C_1SCNmim]$^+$. In the negative ion mode intense peaks corresponding to the anticipated anions in **1a**–**1e** are observed. In keeping with previous observations, aggregates are also observed but dissipate when the spectra are recorded under high dilution conditions.[21]

The main feature in the IR spectra of **1a**–**1e** is the characteristic –S–C≡N vibrations. For **1a**, the stretching vibrations of C–S and C≡N bands are observed at 730 and 2159 cm^{-1}, respectively. For **1b**–**1e**, the C–S vibrations are essentially the same, however, the C≡N vibration shifts to higher wavenumbers, ca. 2169 cm^{-1}. The ^{1}H and ^{13}C NMR spectra of **1a**–**1e** in CD_3CN or [D_6]DMSO are as expected with little change in the spectra as the anion is varied. The proton at the 2-position in the imidazolium ring is observed at 9.05 pm for compound **1a** in D_2O solution. Compounds **1b**, **1c** and **1d** are poorly soluble in D_2O, the chemical shifts of the proton at the 2-position are 8.63, 8.72 and 8.78 ppm

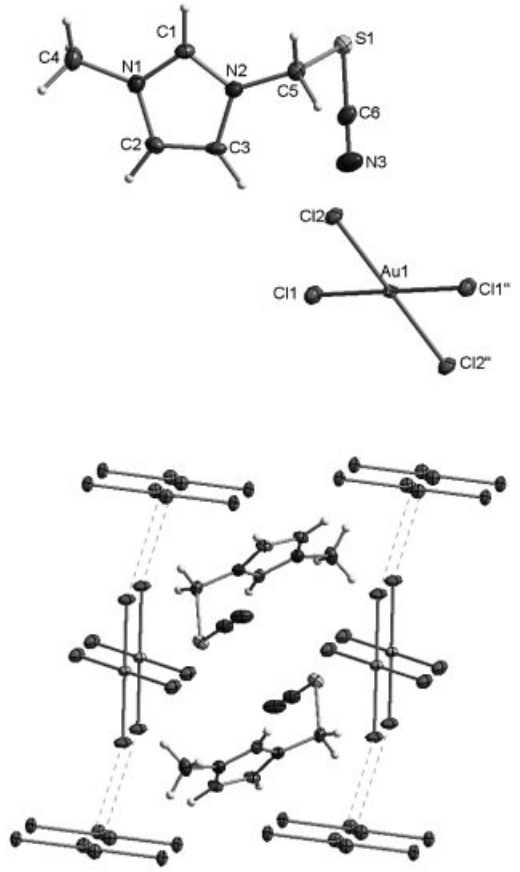


Figure 2. ORTEP representation of **1e** (top) and its packing diagram (bottom); atoms are represented by ellipsoids at the 50% probability level. Key bond lengths [Å] and angles [°]: C1–N1, 1.329(4); C1–N2, 1.334(4); N1–C4, 1.472(4); N2–C5, 1.453(4); C5–S1, 1.840(3); S1–C6, 1.698(3); C6–N3, 1.149(4); Au1–Cl_{ave}, 2.290(2); N1–C1–N2, 108.0(3); C1–N1–C4, 125.5(3); C1–N2–C5, 125.0(3); N2–S1–C6, 112.3(2); C5–S1–C6, 96.6(2); S1–C6–N3, 177.9(3).

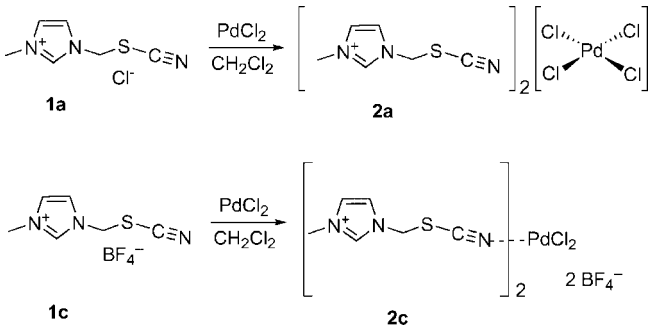
in CD_3CN, respectively. The other ring protons have chemical shifts between 7.4 and 7.6 ppm. The $-CH_3$ and $-CH_2-$ protons exhibit peaks at ca. 5.70 and 3.90 ppm, respectively, and these values differ only slightly as the anion varies from **1a** to **1d**.

Single crystals of the $AuCl_4^-$ **1e** compound suitable for X-ray crystallographic analyses were obtained from aqueous solutions by slow evaporation. The structure of **1e** is shown in Figure 2 and key bond parameters are given in the caption. The solid-state structures of the related salts $[C_2mim][AuCl_4]$ and $[C_4mim][AuCl_4]$ have previously been reported[27] and the crystal structure of complex **1e** is very similar to these earlier reported salts, i.e. forming a pseudo-rhombic structure with the imidazolium cation encased within a box composed of the $[AuCl_4]^-$ anions. In addition, the Au–Cl bond lengths within the square planar $[AuCl_4]^-$ anion and the intermolecular $Cl\cdots AuCl_4$ distance [3.445(1) Å] are comparable to those in $[C_2mim][AuCl_4]$ and $[C_4mim][AuCl_4]$ [3.356(3) and 3.452(3) Å, respectively].

Reactivity of the Thiocyanate-Functionalised Ionic Liquids with Palladium(II) Chloride

A dichloromethane solution of **1a** was treated with 0.5 equiv. $PdCl_2$, affording $[C_1SCNmim]_2[PdCl_4]$ (**2a**) as shown in Scheme 2. The reaction requires several days to reach completion, presumably because of the low solubility of **1a** and $PdCl_2$ in this solvent. Related compounds containing the $[PdCl_4]^{2-}$ with other imidazolium cations have previously been reported.[26,28] In contrast to the chloride salt, the tetrafluoroborate salt (**1c**) reacts with $PdCl_2$ in dichloromethane at room temperature to form $[PdCl_2\{C_1SCNmim\}_2][BF_4]_2$ (**2c**).

Both of the palladium compounds have been characterised by ^1H and ^{13}C NMR spectroscopy, although this provided only limited information. A comparison of their IR spectra was, however, very informative; the stretching vibration of the C≡N group remains essentially unchanged in **2a**, relative to the imidazolium precursor **1a**, whereas in **2c**, the $\upsilon_{C\equiv N}$ stretching band is observed at a higher wavenumber, 2219 cm^{-1}, indicating coordination of the nitrile



Scheme 2. Synthesis of complexes **2a** and **2c**.

group to the palladium(II) centre. Single crystals of **2a** suitable for X-ray diffraction analysis were grown from aqueous solution by slow evaporation and the structure of **2a** is shown in Figure 3, and key bond parameters are given in the caption. Indeed, the CN moieties do not interact with the Pd centre, instead the S atoms of the thiocyanate moiety are directed towards the Pd centre with a Pd···S distance of 3.513(1) Å. A common feature of square-planar Pd^{II} and Pt^{II} complexes in the solid state is long interactions in the axial positions so as to form pseudo-octahedral structures.[29]

The thiocyanate group is relatively reactive and the cleavage of the carbon–sulfur bond can occur in both acidic and basic media[30] such that the resulting mercaptan anion can potentially coordinate to a metal centre. Accordingly, the reaction of **1a** or **1c** with $PdCl_2$ in 20% HNO_3 solution slowly affords orange-red crystals, which were characterised as $[PdCl_2\{C_1Smim\}]_2$ (**3**) by X-ray crystallographic analysis. The structure of **3** is shown in Figure 4, with key bond parameters given in the caption, and contains a mercaptoimidazolium zwitterion as a ligand. In keeping with other related Pd^{II} complexes[31] the geometry around the Pd centres is distorted square planar with the mercapto-S atoms functioning as a bidentate-bridging ligand. The dimer complex contains numerous intramolecular H-bonding interactions between the chloro atoms and the H atoms on the imidazolium moiety.

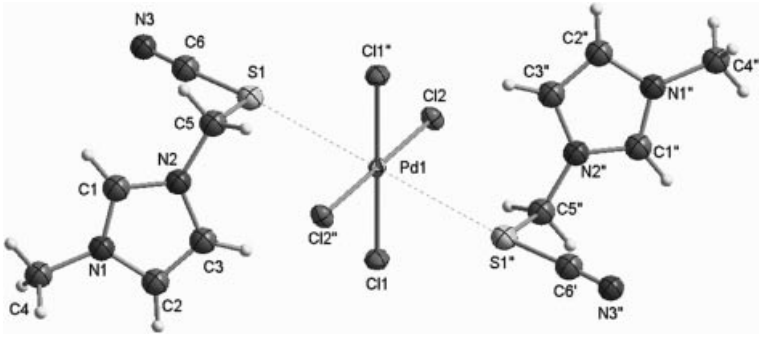


Figure 3. ORTEP representation of **2a**; atoms are represented by ellipsoids at the 50% probability level. The dotted lines (for visual purposes only) show the alignment of the thiocynate bonds towards Pd1. Key bond lengths [Å] and angles [°]: C1–N1, 1.319(4); C1–N2, 1.345(4); N1–C4, 1.464(14); N2–C5, 1.453(4); C5–S1, 1.818(3); S1–C6, 1.699(4); C6–N3, 1.141(4); Pd1–Cl_{ave}, 2.31; N1–C1–N2, 108.6(3); C1–N1–C4, 125.7(3); C1–N2–C5, 125.1(3); N2–S1–C6, 113.9(2); C5–S1–C6, 98.3(2); S1–C6–N3, 177.3(3).

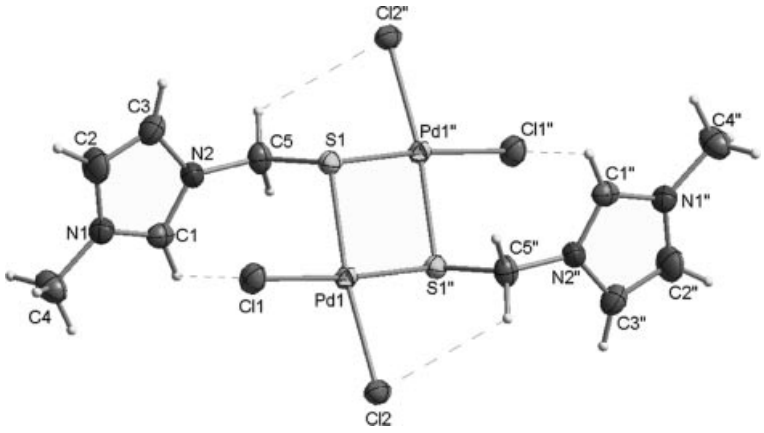


Figure 4. ORTEP representation of **3**; atoms are represented by ellipsoids at the 50% probability level. Key bond lengths [Å] and angles [°]: C1–N1, 1.331(14); C1–N2, 1.334(14); N1–C4, 1.474(14); N2–C5, 1.471(13); C5–S1, 1.828(11); Pd1–Cl_{ave}, 2.346(3); N1–C1–N2, 107.7(9); C1–N1–C4, 123.6(9); C1–N2–C5, 126.0(9); N2–S1–C6, 113.7(7).

Concluding Remarks

In the present study, a series of thiocyanate-functionalised imidazolium salts were prepared, two of which can be classified as ionic liquids. According to the nature of the anion, viz. coordinating or noncoordinating, the salts react differently with palladium(II) chloride. However, in the presence of nitric acid cleavage of the C–S bond is induced and the same palladium dimer is formed irrespective of the type of anion present. Since none of the thiocyanate-functionalised imidazolium salts are liquid at room temperature, and the C–S bond is susceptible to cleavage, it was decided not to use them for palladium-catalysed reactions.

Experimental Section

1-Methylimidazole, 1-chloromethyl thiocyanate, HPF_6, $NaBF_4$, $LiTf_2N$ and $HAuCl_4$ were obtained commercially and used as received. The synthesis of **1a** was performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques in solvents dried using the appropriate reagents and distilled prior to use. All other compounds were made without precautions to exclude air or moisture. IR spectra were recorded with a Perkin–Elmer FT-IR 2000 system. NMR spectra were measured with a Bruker DMX 400, using $SiMe_4$ as the external standard for the ^1H NMR spectra at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded with a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument on samples diluted in solvents (methanol, water or DMSO). Samples were infused directly into the source at 5 μL min^{-1} using a syringe pump and the spray voltage was set at 5 kV and the capillary temperature at 50 °C.[32] Elemental analysis was carried out at the Institute of Chemical Science and Engineering at the EPFL.

Synthesis of [C_1SCNmim]Cl (1a): A solution of 1-methylimidazole (8.21 g, 0.10 mol) and $ClCH_2SCN$ (12.9 g, 0.12 mol) in acetone (20 mL) was stirred at room temp. for 1 h during which time a white precipitate formed. The precipitate was washed with THF (3 × 30 mL) and dried under vacuum for 24 h. Yield: 18.6 g, 98%. M.p. 145 °C. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a saturated acetonitrile solution of the compound at room temp. ESI-MS (H_2O) (*m*/*z*) positive ion: 154 [C_1SCNmim], negative ion: 35 [Cl]. ^1H NMR (D_2O): δ = 9.05 (s, 1 H), 7.69 (s, 1 H), 7.54 (s, 1 H), 5.85 (s, 2 H), 3.92 (s, 3 H) ppm. ^{13}C NMR (D_2O): δ = 136.98, 124.32, 122.60, 111.62, 50.43, 36.36 ppm. IR (neat): $\tilde{\nu}$ = 3134, 3064 (υ_{C-H} aromatic), 2980, 2920, 2848, 2821 (υ_{C-H} aliphatic), 2159 ($\upsilon_{C\equiv N}$), 1731 ($\upsilon_{C=N}$), 730 (υ_{C-S}) cm^{-1}. $C_6H_8ClN_3S$ (189.66): calcd. C 38.00, H 4.25, N 22.15; found C 37.97, H 4.26, N 22.18.

Synthesis of [C_1SCNmim]PF_6 (1b): HPF_6 (8.03 g, 60 wt.-%, 0.033 mol) was added to a solution of **1a** (5.7 g, 0.03 mol) in water (50 mL) at room temp. After 10 min the white solid that had formed was collected by filtration and washed with ice water (3 × 15 mL), and then dried under vacuum. Yield: 8.07 g, 90%. M.p. 120 °C. ESI-MS (methanol) (*m*/*z*) positive ion: 154 [C_1SCNmim], negative ion: 145 [PF_6]. ^1H NMR (CD_3CN): δ = 8.63 (s, 1 H), 7.60 (s, 1 H), 7.47 (s, 1 H), 5.63 (s, 2 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (CD_3CN): δ = 136.74, 124.99, 122.28, 109.79, 50.34, 36.55 ppm. IR (neat): $\tilde{\nu}$ = 3167, 3125, 3106 (υ_{C-H} aromatic), 2987, 2938 (υ_{C-H} aliphatic), 2169 ($\upsilon_{C\equiv N}$), 1713 ($\upsilon_{C=N}$), 726 (υ_{C-S}) cm^{-1}. $C_6H_8PF_6N_3S$ (299.18): calcd. C 24.09, H 2.70, N 14.05; found C 23.97, H 2.65, N 14.08.

Synthesis of [C_1SCNmim]BF_4 (1c): A mixture of **1a** (5.7 g, 0.03 mol) and $NaBF_4$ (3.62 g, 0.033 mol) in acetone (50 mL) was stirred at room temp. for 48 h. After filtration and removal of the solvent the resulting colourless solid was washed with THF and diethyl ether to give the product. Yield: 6.7 g, 93%. M.p. 78 °C. ESI-MS (H_2O) (*m*/*z*) positive ion: 154 [C_1SCNmim], negative ion: 87 [BF_4]. ^1H NMR (CD_3CN): δ = 8.78 (s, 1 H), 7.64 (s, 1 H), 7.50 (s, 1 H), 5.70 (s, 2 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (CD_3CN): δ = 136.93, 124.98, 122.33, 109.90, 50.33, 36.47 ppm. IR: (neat): $\tilde{\nu}$ = 3156, 3117, 3093 (υ_{C-H} aromatic), 2989, 2901 (υ_{C-H} aliphatic), 2169 ($\upsilon_{C\equiv N}$), 1713 ($\upsilon_{C=N}$), 727 (υ_{C-S}) cm^{-1}. $C_6H_8BF_4N_3S$ (241.02): calcd. C 29.90, H 3.35, N 17.43; found C 29.93, H 3.32, N 17.38.

Synthesis of [C_1SCNmim][Tf_2N] (1d): $LiTf_2N$ (8.61 g, 0.03 mol) was added to a solution of **1a** (5.7 g, 0.03 mol) in water (50 mL) at room temp. After 10 min the pale yellow liquid that had formed was collected by decantation and washed with ice water (3 × 15 mL) and then dried under vacuum. The liquid slowly crystallised from water at room temp. Yield: 11.60 g, 89%. M.p. 47 °C. ESI-MS (methanol) (*m*/*z*) positive ion: 154 [C_1SCNmim], negative ion: 280 [Tf_2N]. ^1H NMR (CD_3CN): δ = 8.72 (s, 1 H), 7.60 (s, 1 H), 7.48 (s, 1 H), 5.72 (s, 2 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (CD_3CN): δ = 136.65, 124.97, 122.29, 109.66, 50.34, 36.49 ppm. IR: (neat): $\tilde{\nu}$ = 3145, 3112, 3091 (υ_{C-H} aromatic), 2988, 2901 (υ_{C-H} aliphatic), 2168 ($\upsilon_{C\equiv N}$), 1718

($\upsilon_{C=N}$), 731 (υ_{C-S}) cm^{-1}. $C_8H_8F_6N_4O_4S_3$ (434.36): calcd. C 22.12, H 1.86, N 12.90, found C 22.15, H 1.87, N 12.87.

Synthesis of $[C_1SCNmim]AuCl_4$ (1e): A mixture of $HAuCl_4$ (340 mg, 1.0 mmol) and **1a** (378 mg, 1.00 mmol) in water (10 mL) was stirred at room temp. for 10 min. The resulting suspension was heated to 100 °C to give a clear solution. After cooling to room temp. the resulting orange crystals were collected by filtration and dried under vacuum to give the product. Yield: 335 mg, 68%. M.p. 150 °C. ESI-MS (H_2O) (*m*/*z*) positive ion: 154 [$C_1SCNmim$], negative ion: 337 [$AuCl_4$]. ^1H NMR ([D$_6$]DMSO): δ = 9.76 (s, 1 H), 7.93 (s, 1 H), 7.85 (s, 1 H), 6.06 (s, 2 H), 3.94 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.70, 125.19, 122.75, 111.82, 50.99, 36.80 ppm. IR: (neat): $\tilde{\nu}$ = 3135, 3111 (υ_{C-H} aromatic), 2977, 2901 (υ_{C-H} aliphatic), 2169 ($\upsilon_{C\equiv N}$), 1714 ($\upsilon_{C=N}$), 729 (υ_{C-S}) cm^{-1}. $C_6H_8AuCl_4N_3S$ (492.98): calcd. C 14.62, H 1.64, N 8.52; found C 14.64, H 1.68, N 8.57.

Synthesis of $[C_1SCNmim]_2PdCl_4$ (2a): A mixture of $PdCl_2$ (177 mg, 1.0 mmol) and **1a** (378 mg, 2.00 mmol) in acetonitrile (5 mL) was stirred at room temp. for 7 d. After removal of the solvent the resulting orange solid was washed with dichloromethane (2 × 2 mL), and dried under vacuum to give the product. Yield: 549 mg, 99%. M.p. 146 °C. ESI-MS (DMSO) (*m*/*z*) positive ion: 154 [$C_1SCNmim$], negative ion: 124, 1/2 $[PdCl_4]^{2-}$. ^1H NMR ([D$_6$]-DMSO): δ = 9.76 (s, 1 H), 7.93 (s, 1 H), 7.85 (s, 1 H), 6.06 (s, 2 H), 3.94 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.70, 125.19, 122.75, 111.82, 50.99, 36.80 ppm. IR: (neat): $\tilde{\nu}$ = 3139, 3116, 3088 (υ_{C-H} aromatic), 2989, 2911 (υ_{C-H} aliphatic), 2168 ($\upsilon_{C\equiv N}$), 1718 ($\upsilon_{C=N}$), 734 (υ_{C-S}) cm^{-1}. $C_{12}H_{16}Cl_4N_6PdS_2$ (556.63): calcd. C 25.89, H 2.90, N 15.10;. found C 25.91, H 2.88, N 15.17.

Synthesis of $[C_1SCNmim]_2PdCl_2[BF_4]_2$ (2c): A mixture of $PdCl_2$ (177 mg, 1.0 mmol) and **1c** (482 mg, 2.00 mmol) in dichloromethane (5 mL) was stirred at room temperature for 7 d. After removal of the solvent the resulting orange solid was washed with dichloromethane (2 × 2 mL), and dried under vacuum to give the product. Yield: 652 mg, 99%. M.p. 144 °C. ESI-MS (DMSO) (*m*/*z*) positive ion: 154 [$C_1SCNmim$]. ^1H NMR ([D$_6$]DMSO): δ = 9.25 (s, 1 H), 7.83 (s, 1 H), 7.77 (s, 1 H), 5.91 (s, 2 H), 3.91 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.38, 125.20, 122.89, 111.71, 50.71, 36.71 ppm. IR: (neat): $\tilde{\nu}$ = 3144, 3109, 3084 (υ_{C-H} aromatic), 2911 (υ_{C-H} aliphatic), 2219 ($\upsilon_{C\equiv N}$) cm^{-1}. $C_{12}H_{16}B_2Cl_2F_8N_6PdS_2$ (659.37): calcd. C 21.86, H 2.45, N 12.75; found C 21.89, H 2.47, N 12.70.

Synthesis of 3: **1a** or **1c** (0.2 mmol) was added to an aqueous solution of $PdCl_2$ in 20% HNO_3 (20 mmol L^{-1}, 10 mL) at room temp. After 5 d red crystals precipitated from the solution, which were collected by filtration. Yield: 11 mg, 9%. M.p. 137 °C. ^1H NMR ([D$_6$]DMSO): δ = 9.76 (s, 1 H), 7.88 (s, 1 H), 7.83 (s, 1 H), 3.94 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.81, 122.90, 121.66, 110.81, 35.97 ppm. IR: (neat): $\tilde{\nu}$ = 3158, 3117, 3066 (υ_{C-H} aromatic), 2911 (υ_{C-H} aliphatic), 733 (υ_{C-S}) cm^{-1}. $C_{10}H_{16}C_{l4}N_4Pd_2S_2$ (610.99): calcd. C 19.66, H 2.64, N 9.17; found C 19.66, H 2.67, N 9.14.

Structural Characterisation in the Solid State: Relevant details about the structure refinements are compiled in Table 1 and selected bond lengths and angles are given in the figure captions. For **1a**, **2a** and **3** the data collection was performed with a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD at 140(2) K and data reduction was performed using CrysAlis RED.[33] For **1e** data collection was carried out with a Bruker Nonius APEX II CCD at 100(2) K and data reduction was performed using EVALCCD. Structure solution was carried out using SiR92,[34] and refined by full-matrix least-squares refinement (against F^2) using SHELXTL software.[35] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in their geometrically generated positions and refined using the riding model. Empirical absorption corrections were applied for **1a**, **2a** and **3** using DELABS[36] and **1e** using SADABS,[35] and graphical representations of the structures were made with the program Diamond.[37]

Table 1. Crystallographic data.

Compound	**1a**	**1e**	**2a**	**3**
Formula	$C_6H_8ClN_3S$	$C_6H_8Cl_4AuN_3S$	$C_{12}H_{16}Cl_4N_6PdS_2$	$C_{10}H_{16}Cl_4N_4Pd_2S_2$
M_r [g mol^{-1}]	189.66	492.98	556.63	610.99
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a [Å]	8.2923(9)	7.7347(6)	9.0699(6)	11.2276(14)
b [Å]	11.2624(12)	8.0004(4)	11.9124(8)	7.6512(9)
c [Å]	9.9957(11)	11.2628(7)	9.5890(6)	11.5705(10)
α [°]	90	101.023(5)	90	90
β [°]	105.032(10)	91.615(6)	105.032(10)	104.606(10)
γ [°]	90	106.686(5)	90	90
Volume [Å^3]	901.57(17)	652.72(7)	101.077(5)	961.84(18)
Z	4	2	2	2
D_{calcd} [g cm^{-3}]	1.397	2.508	1.818	2.110
μ [mm^{-1}]	0.596	12.219	1.653	2.641
F(000)	392	456	552	592
Temperature [K]	140(2)	100(2)	140(2)	140(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Measured reflections	5108	12330	6001	5643
Unique reflns	1512	2964	1698	1634
Unique reflns [$I > 2\sigma(I)$]	1191	2550	1404	1196
No. of data / restraints / parameters	1512 / 0 / 101	2964 / 0 / 140	1698 / 0 / 116	1634 / 0 / 101
R[a] [$I > 2\sigma(I)$]	0.0286	0.0171	0.0252	0.0577
wR_2[a] (all data)	0.0688	0.0362	0.0555	0.1641
GoF[b]	0.965	1.112	0.977	1.133

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. [b] GoF = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ where n is the number of data and p is the number of parameters refined.

Acknowledgments

We thank Ecole Polytechnique Fédérale de Lausanne (EPFL) and the Swiss National Science Foundation for financial support.

[1] a) J. H. Davis Jr., *Chem. Lett.* **2004**, *33*, 1072; b) S.-G. Lee, *Chem. Commun.* **2006**, 1049; c) Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *12*, 2122; d) H. Xue, R. Verma, J. M. Shreeve, *J. Fluorine Chem.* **2006**, *127*, 159.

[2] A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis Jr., R. D. Rogers, *Chem. Commun.* **2001**, 135.

[3] B. K. M. Chan, N.-H. Chang, M. R. Grimmett, *Austr. J. Chem.* **1977**, *30*, 2005.

[4] W. Chen, F. Liu, *J. Organomet. Chem.* **2003**, *673*, 5.

[5] M. Sorm, S. Nespurek, *Acta Polym.* **1985**, *36*, 433.

[6] H. Schottenberger, K. Wurst, U. E. I. Horvath, S. Cronje, J. Lukasser, J. Polin, J. M. McKenzie, H. G. Raubenheimer, *Dalton Trans.* **2003**, 4275.

[7] Z. Fei, D. Zhao, R. Scopelliti, P. J. Dyson, *Organometallics* **2004**, *23*, 1622.

[8] W. A. Herrmann, C. Köcher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627.

[9] K.-M. Lee, Y.-T. Lee, I. J. B. Lin, *J. Mater. Chem.* **2003**, *13*, 1079.

[10] a) L. C. Branco, J. N. Rosa, J. J. Moura Ramos, C. A. M. Afonso, *Chem. Eur. J.* **2002**, *8*, 3671; b) A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, *Inorg. Chem.* **2004**, *43*, 3447.

[11] a) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis Jr., *J. Am. Chem. Soc.* **2002**, *124*, 5962; b) J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, *Chem. Commun.* **2003**, 28; c) N. Brausch, A. Metlen, P. Wasserscheid, *Chem. Commun.* **2004**, 1552; d) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *Chem. Eur. J.* **2004**, *10*, 4886; e) D. Li, F. Shi, J. Peng, S. Guo, Y. Deng, *J. Org. Chem.* **2004**, *69*, 3582.

[12] K.-S. Kim, D. Demberelnyamba, H. Lee, *Langmuir* **2004**, *20*, 556.

[13] H. Itoh, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **2004**, *126*, 3026.

[14] C. Baleizao, B. Gigante, H. Garcia, A. Corma, *Tetrahedron Lett.* **2003**, *44*, 6813.

[15] a) T. L. Merrigan, E. D. Bates, S. C. Dorman, J. H. Davis Jr, *Chem. Commun.* **2000**, 2051; b) Y. R. Mirzaei, H. Xue, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 361.

[16] D. Demberelnyamba, S. J. Yoon, H. Lee, *Chem. Lett.* **2004**, *33*, 560.

[17] Z. Mu, W. Liu, S. Zhang, F. Zhou, *Chem. Lett.* **2004**, *33*, 524.

[18] Y. Gao, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 3406.

[19] R. J. C. Brown, P. J. Dyson, D. J. Ellis, T. Welton, *Chem. Commun.* **2001**, 1862.

[20] P. J. Dyson, J. S. McIndoe, D. Zhao, *Chem. Commun.* **2003**, 508.

[21] Z.-B. Zhou, M. Takeda, M. Ue, *J. Flourine Chem.* **2004**, *125*, 471.

[22] D. Zhao, Z. Fei, C. A. Ohlin, G. Laurenczy, P. J. Dyson, *Chem. Commun.* **2004**, 2500.

[23] a) H. S. Kim, Y. J. Kim, J. Y. Bae, S. J. Kim, M. S. Lah, C. S. Chin, *Organometallics* **2003**, *22*, 2498; b) P. Wasserscheid, A. Bösmann, C. Bolm, *Chem. Commun.* **2002**, 200; c) J. Levillain, G. Dubant, I. Abrunhosa, M. Gulea, A.-C. Gaumont, *Chem. Commun.* **2003**, 2914.

[24] D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197.

[25] a) D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, P. J. Dyson, *J. Am. Chem. Soc.* **2004**, *126*, 15876; b) C. Chiappe, D. Pieraccini, D. Zhao, Z. Fei, P. J. Dyson, *Adv. Synth. Catal.* **2006**, *348*, 68.

[26] P. Wasserscheid, T. Welton (Ed.), *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, Germany, **2002**, p. 1.

[27] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, N. Winterton, *Inorg. Chem.* **1999**, *28*, 5637.

[28] D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, G. Laurenczy, P. J. Dyson, *Helv. Chim. Acta* **2005**, *88*, 665.

[29] For example see, a) E. C. Alyea, G. Ferguson, S. Kannan, *Chem. Commun.* **1998**, 345; b) P. W. Dyer, P. J. Dyson, S. L. James, P. Suman, J. E. Davies, C. M. Martin, *Chem. Commun.* **1998**, 1375.

[30] D. S. Tarbell, D. P. Harnish, *Chem. Rev.* **1951**, *49*, 1.

[31] a) J. Sola, R. Yanez, *J. Chem. Soc., Dalton Trans.* **1986**, 2021; b) T. Boschi, B. Crociani, L. Toniolo, U. Belluco, *Inorg. Chem.* **1970**, *9*, 532.

[32] P. J. Dyson, J. S. McIndoe, *Inorg. Chim. Acta* **2003**, *354*, 68.

[33] Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, **2002**.

[34] A. Altomare, M. C. Burla, G. Camalli, G. Cascarano, C. Giacovazzo, A. Gualiardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[35] G. M. Sheldrick, University of Göttingen, Germany, **1997**; Bruker AXS, Inc., Madison, Wisconsin, 53719, USA, **1997**.

[36] DELABS, N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

[37] *Diamond 3.0a*, Crystal Impact GbR, Bonn, Germany.

Received: August 7, 2006
Published Online: November 17, 2006

