Versatile Methods for the Synthesis of Si(OR)3-Functionalised Imidazolium Salts, Potential Precursors for Heterogeneous NHC Catalysts and Composite Materials

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Abstract: Versatile methodologies for the synthesis of N-alkyl and N-aryl, and alkoxysilyl-functionalised mono- and bis-imidazolium salts are discussed. Such salts could find applications for heterogeneous N-heterocyclic catalysts and sol-gel materials. Key words: ionic liquids, carbenes, supported catalysis, imidazolium salts, alkoxysilyl

Imidazolium salts attract considerable interest because their unique physical and chemical properties allow them to fulfil different functions in chemistry. Firstly, they can be used as alternative reaction media owing to their ability to dissolve a large range of organic and inorganic compounds. 1 The main advantages they have over organic solvents are that they have a negligible vapour pressure, they are able to dissolve a large range of organic and inorganic compounds,1 and they can be used as alternative reaction media owing to their ability to dissolve a large range of organic and inorganic compounds.1 The main advantages they have over organic solvents are that they have a negligible vapour pressure, they can increase reactions rates and selectivity, and they can immobilise starting materials and/or catalyst precursors. The latter point allows easy separation of the products and reuse of the salts, as they can thus be recycled together with the compounds that they are hosting. These advantages account for the large number of organic reactions performed in such solvents, be they stoichiometric (for example Biginelly,2 Wittig,3 Balz–Shiemann4 and Diels–Alder5 reactions, Friedel–Crafts acylation and alkylation,6 N- or O-regioselective alkylation,7 nucleophilic displacement,8 alkylation of alcohols,9 reduction of aldehydes,10 cycloadditions11), transition-metal catalysed (hydroformylation,12 carbonylation,13 alkylic alkylation,14 cross coupling,15 Heck coupling,16 hydrogenation,17 esterification,18 polymerisation,19 olefin metathesis20) or biocatalytic (for instance lipase-catalysed transesterification, alcoholysis, ammoniolysis and perhydrolysis).21

The second major use of imidazolium salts is in the formation of N-heterocyclic carbenes (NHCs) via deprotonation of the 2-carbon.22 The usefulness of NHCs as ligands for organometallic catalysis has been demonstrated in a wide range of reactions, for instance cross coupling and Heck reactions,23 furan formation,24 cyclopropanation,25 hydroboration,26 hydrogenation,27 copolymerisation,28 and metathesis reactions.29 More recently, attention has turned to immobilised NHC complexes which combine high catalytic activity and selectivity with potential recyclability. For this purpose, different immobilisation techniques are used, for instance immobilisation in a liquid phase,30 on polymeric31 or mineral32 supports [for example using Si(OEt)3-functionalised imidazolodinylidene ruthenium complexes].32c

To this end, we were interested in developing alkoxysilyl-modified imidazolium salts of the type 1 that could be subsequently immobilised on oxide and ceramic supports by either grafting or by sol-gel processing of the molecular precursor without a substrate (Scheme 1). The syntheses of precursors of the type 1 are reported below.

![Scheme 1](image)

The synthetic pathway chosen is based on the synthesis of an alkoxysilyl N-functionalised imidazole that can then be reacted with alkyl halides in order to obtain imidazolium salts of the type 1. For this purpose, N-(3-propyltrimethoxysilyl)imidazole (2a) was synthesised by reaction of sodium imidazole with 3-iodopropytrimethoxysilane (Scheme 2).

Two equivalents of 2a were then reacted with diiodomethane or 1,3-diodopropane, leading to the bisimidazolium salts 3a and 3b, respectively, in high yields. No solvent is required to perform these latter reactions. The same synthetic pathway was applied to the synthesis of 1,1'-di(3-propyltrimethoxysilyl)-3,3'-m-dibromoimidazolium dibromide (4), obtained by the reaction of 2a with a,a'-dibromo-m-xylene. In this case, the reaction can also be performed without a solvent, however, purification of the product by washing proves to be difficult, probably due to the viscosity of the oil. The use of toluene as a sol-
vent and for purification by washing proved to be beneficial since clean compound 4 could then be obtained (NMR evidence) although some toluene (ca. 20%) remained for this contamination, as even after a long period of time in vacuo, the toluene could not be fully removed.

For comparison, 3a was also synthesised by the reaction of N,N’-dimidazolylmethane (5) with 3-iodopropyltrimethoxysilane. This alkylating reagent was also used to synthesise the monoimidazolium salts (Scheme 3).

Scheme 2

Scheme 3

The compounds 3-iodopropyltrimethoxysilane and 2a were reacted neat in order to obtain the salt 6a, which bears two alkoxysilyl functions. The same strategy was applied to an N-alkyl and an N-arylimidazole, namely N-methylimidazole (2b) and 4’-(imidazol-1-yl)acetophenone (2c) leading to 1-(3-propyltrimethoxysilane)-3-methylimidazolium iodide (6b) and 1-(4-acetylphenyl)-3-(3-propyltrimethoxysilane)imidazolium iodide (6c), respectively.

All the new compounds were obtained in high yields (73–99%) and characterised by 1H and 13C NMR spectroscopy, chemical ionization HRMS (High-Resolution Mass Spectrometry) and electrospary ionization mass spectrometry. The latter experiments (ESI+ mode) were performed with methanol solutions of the salts. In the case of 2a, strong peaks corresponding to [M + Na]+ and [M + H]+ were observed. With respect to the monoimidazolium salts, intense peaks indicative of the parent ion [M – I]+ were present, whilst for the bisimidazolium salts, peaks corresponding to [M – X]+ (X = I, Br) and [M – 2 I]+ (for 3a and 3b) or [M – 2 Br]+ (for 4) were observed. The most notable feature in the 1H NMR spectra of imidazolium salts is the characteristic resonance for the acidic hydrogen in the 2-position of the 5-membered ring. For compounds 3, 4 and 6, in CDCl3, the signals corresponding to the 2-hydrogen are found between 10.86 (for 6c) and 9.82 ppm (for 3b and 6b). Interestingly, while such peaks are often reported as singlets, we observe either broad singlets (6b and 6c), a triplet (6a) or doublets of doublets (3a, 3b and 4). A doublet is observed for H-4 and H-5 of 6a (\(J_{HH} = 1.7\) Hz) while doublets of doublets are observed for all of the other non-symmetrical imidazolium salts, with coupling constants of 1.8 Hz (6c), 1.7 Hz (6b) and 1.6 Hz (3a, 3b and 4). Selective decoupling 1H NMR experiments proved the multiplicity to be due to coupling between the acidic hydrogen in the 2-position with those in 4- and 5-positions. This was also confirmed by H-D exchange experiments performed in CD3OD. Thus, in the 1H NMR spectrum of compound 3b, the doublets of doublets in CDCl3 for H-4 and H-5 are replaced by doublets when run in CD3OD, after standing, with a concomitant loss of the H-2 signal. Further H-D exchange experiments were performed on 4 and 6c and showed again that H-2 undergoes facile exchange with deuterium when the salts are dissolved in CD3OD.

In summary, we have developed two different and versatile routes for the synthesis of trialkoxysilyl-functiona-

bled mono- and bis-imidazolium salts. Given the potential diversity of salts obtained by these attractive methods, tuning of the imidazolium cation can be easily achieved, which is of great interest for the development of composite materials and heterogenised NHC catalysts. Studies concerning both subjects are currently being carried out by our groups and will be reported elsewhere.

All procedures were performed under an atmosphere of dry N2 using modified Schlenk line techniques. All solvents were dried over appropriate reagents and freshly distilled prior to use. N,N’-Dimidazolylmethane (5) was prepared according to a literature procedure. The following chemicals were commercially available: 3-iodopropyltrimethoxysilane, sodium imidazolate (90% purity, taken into account for adjusting the stoichiometry of the reaction), diiodomethane, 1,3-diiodopropane, \(a, a’,dibromo-m-xylene\), N-methylimidazole (2b) and 4’-(imidazol-1-yl)acetophenone (2c), 3-iodopropyltrimethoxysilane, sodium imidazolate and 4’-(imidazol-1-yl)acetophenone (2c) were used as received whilst N-methylimidazole (2b), diiodomethane, 1,3-diiodopropane were distilled and \(a, a’,dibromo-m-xylene\) was sublimed prior to use. Unless otherwise stated, no solvent was used for the syntheses. NMR spectra were recorded on a Bruker AC 200F spectrometer. Experiments run in CD3OD were recorded after 5 h. Mass spectra (MeOH solutions) were recorded on a Waters QZ4000 spectrometer operating in ESI mode. High-resolution mass spectra (MeOH solutions) were recorded on a Finnigan MAT95 spectrometer operating in CI mode.

N-(3-Propyltrimethoxysilane)imidazole (2a)

3-Iodopropyltrimethoxysilane (9.79 mL, 50.0 mmol) was added to a stirred suspension of sodium imidazolate (5.005 g, 50.0 mmol) in THF (100 mL). The reaction mixture was heated at 66 °C for 13 h with exclusion of light and then allowed to cool to r.t. The solvent was removed in vacuo; CH2Cl2 (15 mL) was added and the solution was filtered. After removal of the solvent in vacuo, the resultant oil

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was purified by fractional distillation under reduced pressure. The product was obtained as a colourless oil (8.4 g, 73%).

1H NMR (200.13 MHz, CDCl3): δ = 7.40 (br s, 1 H, NCHN), 6.98 (dd, 1 H, J = 1.1 Hz, CH), 6.85 (dd, 1 H, J = 1.1 Hz, CH), 3.86 (m, 2 H, NCH2), 3.49 (s, 9 H, 3 OCH3), 1.81 (m, 2 H, CH2CH2CH2), 0.51 (m, 2 H, SiCH2).

13C NMR (50.32 MHz, CDCl3): δ = 139.7 (NCHN), 128.9 (CH), 118.3 (CH), 50.1 (OCH3), 48.6 (NCH2), 24.2 (CH2CH2CH2), 5.6 (SiCH2).


HRMS (CI): m/z calcd for C12H11N2O3Si: ([M + H]⁺, 247.2330; found: 247.2290).

1,1'-Di-(3-propyltrimethoxysilane)-3,3'-methyleneimidazolium Dibromide (3b)

1,3-Diodopropene (0.23 mL, 1.99 mmol) was added to N-(3-propyltrimethoxysilane)imidazole (2a: 0.915 g, 3.97 mmol). The reaction mixture was heated at 110 °C for 14 h with exclusion of light and then allowed to cool to r.t. The crude product was washed with toluene (3 × 10 mL) and dried in vacuo. The imidazolium salt was obtained as a colourless solid (1.047 g, 75%).

Method A: 1,3-Diiodopropane (0.23 mL, 1.99 mmol) was added to N-(3-propyltrimethoxysilane)imidazole (2a: 0.915 g, 3.97 mmol). The reaction mixture was heated at 110 °C for 14 h with exclusion of light and then allowed to cool to r.t. The crude product was washed with toluene (3 × 10 mL) and dried in vacuo. The imidazolium salt was obtained as a colourless solid (1.047 g, 75%).

Method B: 3-Iodopropyltrimethoxysilane (1.00 mL, 5.11 mmol) was added to a solution of N,N'-diamidazolymethane (5: 0.378 g, 2.55 mmol) in toluene (5 mL). The reaction mixture was heated at 100 °C (external temperature) for 15 h with exclusion of light and then allowed to cool to r.t. The crude product was washed with toluene (3 × 15 mL) and dried in vacuo. The imidazolium salt was obtained as a colourless solid (1.645 g, 89%).

1H NMR (200.13 MHz, CDCl3): δ = 10.81 (dd, 1 H, J = 1.6 Hz, NCHN), 9.00 (dd, 2 H, J = 1.6 Hz, CH), 7.75 (s, 2 H, NCHN), 7.47 (dd, 2 H, J = 1.6 Hz, CH), 4.30 (t, 4 H, J = 7.4 Hz, NCH3), 3.58 (s, 18 H, OCH3), 2.06 (m, 4 H, CH2CH2CH2), 0.68 (m, 4 H, SiCH2).

13C NMR (50.32 MHz, CDCl3): δ = 137.2 (NCHN), 123.1 (CH), 122.65 (NCHN), 106.8 (NCHN), 52.4 (NCH2), 24.2 (CH2CH2CH2), 5.9 (SiCH2).

HRMS (CI): m/z calcd for C6H10N2O3Si: ([M + H]⁺, 231.1165; found: 231.1164).

MS (ESI): m/z (%) = 253 ([M + Na]⁺, 80), 231 ([M + H]⁺, 100).

1,1'-Di-(3-propyltrimethoxysilane)-3,3'-methyleneimidazolium Dichloride (4)

N-(3-Propyltrimethoxysilane)imidazole (2a: 0.457 g, 1.99 mmol) was added to a solution of a,a'-dibromo-m-xylene (0.262 g, 0.99 mmol) in toluene (3 mL). The reaction mixture was heated at 100 °C (external temperature) with exclusion of light for 16 h. The mixture was allowed to cool to r.t. and the supernatant solution was removed with a pipette. The resultant oil was washed with toluene (3 × 5 mL) and dried in vacuo. The product was obtained as a colourless oil in quantitative yield.

1H NMR (200.13 MHz, CDCl3): δ = 10.46 (dd, 2 H, J = 1.6 Hz, NCHN), 8.28 (dd, 2 H, J = 1.6 Hz, NCH), 8.16 (br s, 1 H, CCHC), 7.66 (dd, 2 H, J = 7.7, 1.3 Hz, CHCHC), 7.31 (dd, 2 H, J = 1.6 Hz, NCH), 7.19 (t, 1 H, J = 7.7 Hz, CHCHC), 5.66 (s, 4 H, NCH3), 4.30 (t, 4 H, J = 7.2 Hz, NCH2CH3), 3.56 (s, 18 H, OCH3), 2.00 (m, 4 H, CH2CH2CH2), 0.63 (m, 4 H, SiCH2).

13C NMR (50.32 MHz, CDCl3): δ = 136.0 (NCHN), 134.4 (C), 130.0 (CCHC), 129.6 (CHCHC), 129.5 (CHCHC), 123.1 (NCH), 121.5 (NCH), 51.9 (NCH3), 51.4 (NCH2CH3), 50.2 (OCH3), 23.6 (CH2CH2CH2), 5.5 (SiCH2).

HRMS (CI): m/z calcd for C31H19N2O3Si: ([M + 2 Br]⁺, 564.2979; found: 564.2785).

1,3,5-Tris-(3-propyltrimethoxysilane)imidazolium Iodide (6a)

3-Iodopropyltrimethoxysilane (0.40 mL, 2.04 mmol) was added to N-(3-propyltrimethoxysilane)imidazole (2a: 0.457 g, 1.99 mmol). The reaction mixture was heated at 110 °C for 17 h with exclusion of light and then allowed to cool to r.t. The crude product was washed with toluene (3 × 10 mL) and dried in vacuo. The imidazolium salt was obtained as a yellow oil in quantitative yield.

1H NMR (200.13 MHz, CDCl3): δ = 10.13 (br t, 1 H, J = 1.7 Hz, NCHN), 7.41 (d, 2 H, J = 1.7 Hz, CH), 4.56 (t, 4 H, J = 7.3 Hz, NCH3), 3.56 (s, 18 H, OCH3), 2.02 (m, 4 H, CH2CH2CH2), 0.64 (m, 4 H, SiCH3).

13C NMR (50.32 MHz, CDCl3): δ = 135.0 (NCHN), 121.75 (CHCH), 50.8 (NCH3), 49.8 (OCH3), 23.2 (CH2CH2CH2), 4.9 (SiCH3).

HRMS (CI): m/z calcd for C31H19N2O3Si: ([M + I]⁺, 393.1879; found: 393.1877.)
1H NMR (200.13 MHz, CDCl3): δ = 10.86 (br s, 1 H, NCHN), 8.16 (AA’BB’ spin system, dm, 2 H, aromatic), 7.91–7.97 (m, 3 H, aromatic and imidazolium protons), 7.45 (t, 2 H, NCH), 3.59 (s, 9 H, 3 OCH3), 2.14 (m, 2 H, CH2C=C, 0.74 (m, 2 H, SiCH3).

13C NMR (50.32 MHz, CDCl3): δ = 139.1 (CHCH), 135.4 (CHCH), 134.9 (C=O), 131.8 (C=O), 128.3 (CHCH), 127.4 (CHCH), 120.5 (NCH), 52.4 (NCH), 50.8 (OCH3), 26.8 (CH3), 24.1 (CH3CH2CH3), 5.9 (SiCH3).

HRMS (CI): m/z calcd for C8H12INO3Si ([M – I]–): 245.1321; found: 245.1321.

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1-(4-Acetylphenyl)-3-(3-propyltrimethoxysilane)imidazolium Iodide (6c)

3-Iodopropyltrimethoxysilane (1.00 mL, 5.11 mmol) was added to a solution of 4’-imidazol-1-y acetophenone (2c; 0.951 g, 5.11 mmol) in toluene (10 mL). The reaction mixture was heated at 100 °C (external temperature) with exclusion of light for 18 h. The mixture was allowed to cool to r.t. and the supernatant solution was removed with a pipette. The resultant solid was washed with toluene (3 x 10 mL) and dried in vacuo. The product was obtained as a colourless solid (1.871 g, 77%).

HRMS (CI): m/z calcd for C10H21N2O3Si ([M – I]: 245.1323; found: 245.1323.

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