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Copper and palladium complexes with *N*-heterocyclic carbene ligands functionalised with carboxylate groups

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ABSTRACT

The new imidazolium salts functionalised with the trimethylsilyl ester group **1a**–**c**, were easily obtained by quaternisation of alkyl- or aryl-imidazoles with trimethylsilyl bromoacetate. Salt **1a** was isolated and fully characterised. It reacted with mesityl copper (Cu_5Mes_5) under trimethylsilyl abstraction to form the complex **2**. Methanolysis of **1a–c** gave good yields of the carboxylic acid functionalised imidazolium salts **3a**–**c**. Deprotonation of the latter in liquid ammonia led to the zwitterionic imidazolium carboxylates **4a**–**c**. Reaction of **4a** with (Cu_5Mes_5) gave solutions from which the insoluble polymeric **5a** crystallised slowly. Generation of the carboxylate-functionalised NHC *in situ* followed by reaction with $Pd(OOCCH_3)_2$ gave the new complex **6a** in which the NHC-carboxylate ligand is chelate bidentate.

1. Introduction

Ester, amide and carboxylate-functionalised *N*-heterocyclic carbene (NHC) ligands are interesting additions to the ever growing class of mixed donor ligands containing NHC and other 'classical' donor groups [1]. The combination of the soft, neutral strongly σ-donating NHC and the hard carboxylate, ester or amide donors may lead to new hemilabile metal complexes, or complexes with high solubility in polar solvents; formation of polymetallic assemblies by virtue of the excellent bridging properties of the carboxylate group and the stabilisation of higher metal oxidation states are further attractive features. Even though the electronically related ester- and carboxylate-functionalised phosphines have already been studied by various groups [2], amide, [–C(=O)NR_2], functionalised NHC complexes of Pd and Ni have only recently been reported [3]. Methyl imidazolium carboxylic acids and carboxylates have been studied as ionic liquids [4]. In this paper we report a mild and general high yielding synthesis of the carboxylic acid/carboxylate-functionalised imidazolium salts as precursors to NHC complexes. We also report the first examples of Pd(II) and Cu(I) complexes in which the ligand is bidentate NHC-carboxylate bound and bridging NHC and carboxylate bound giving rise to polymers. The compounds described in this paper are shown in Schemes 1–3.

2. Results and discussion

2.1. Synthesis of imidazolium salts

The quaternisation of alkyl- or aryl-imidazoles with $BrCH_2COOSiMe_3$ proceeds in good yields in dioxane at 80–90 °C (see Scheme 1). In one case the imidazolium salt [**1a**, R = DiPP] was isolated as moisture sensitive colourless powder and characterised by spectroscopic and analytical methods.

The imidazolium salts **1a–c**, were converted directly to the carboxylic acid functionalised imidazolium salts **3a–c** by methanolysis in CH_2Cl_2 under mild conditions. The carboxylic acid derivatives were air stable powders which were characterised spectroscopically and analytically. The structure of **3a** was also determined crystallographically (see Fig. 1). Metric data for this compound are listed in the caption and refinement parameters are given in Table 1.

Preliminary studies show that the imidazolium salts **1a–c** are convenient starting materials for further derivatisation. For example reaction with primary alkylamines leads cleanly to imidazolium amides in good yields.

The presence of two acidic sites in **3a–c** raised the question of the optimum conditions for the selective deprotonation at the imidazolium C2 and the carboxylic acid protons. The presence of the enolisable protons α-to the carboxylic acid may further complicate selective deprotonation methods. Attempts to deprotonate **3a–c** with one equivalent of $KN(SiMe_3)_2$ or $LiNPr^i_2$ led to intractable mixtures, possibly due to competing reactions at more than one sites. Reactions with triethylamine led to the zwitterionic imidazo-

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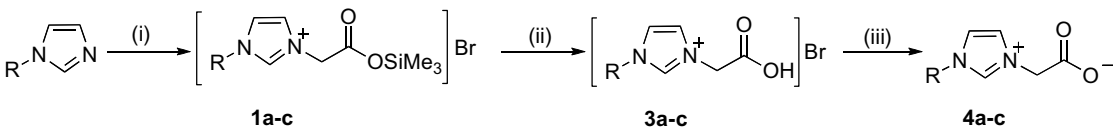
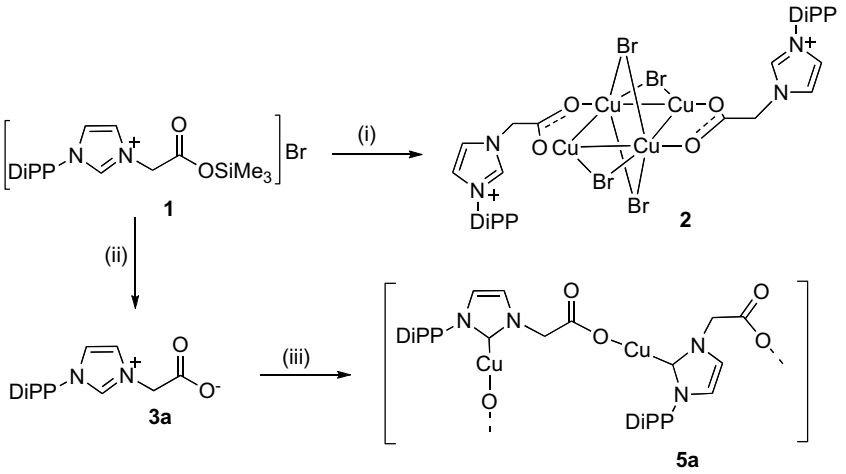
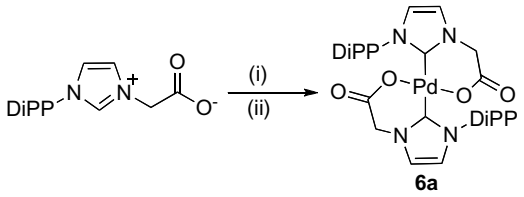


Scheme 1. The synthesis of trimethylsilylcarboxylate **1a–c**, carboxylic acid **3a–c** and carboxylate **4a–c** functionalised imidazolium salts (a: R = 2,6-di-isopropylphenyl, DiPP b: R = mesityl, c: R = *tert*-butyl). Reagents and conditions: (i) $BrCH_2COOSiMe_3$, dioxane, 80 °C (ii) methanol, CH_2Cl_2; (iii) liq. NH_3, then CH_2Cl_2.



Scheme 2. The synthesis of the copper complexes **2** and **5a**. Reagents and conditions: (i) $(CuMes)_5$ THF, RT; (ii) methanol, CH_2Cl_2; (iii) $(CuMes)_5$.



Scheme 3. The synthesis of the palladium complex **6a**. Reagents and conditions: (i) $LiNPr^i_2$ in THF; (ii) 0.5 equiv. $Pd(OOCCH_3)_2$ in THF.

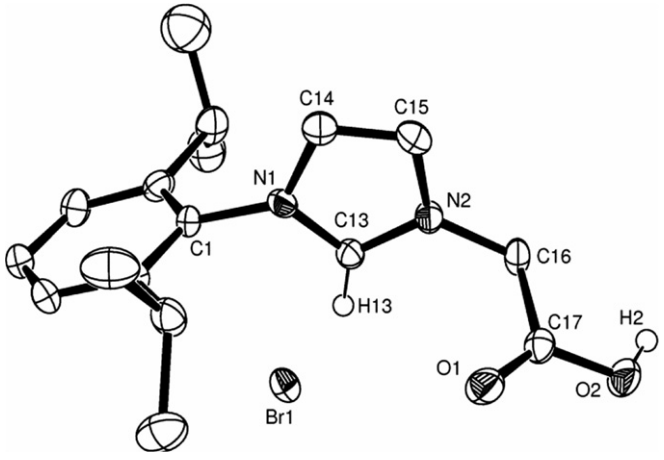


Fig. 1. ORTEP representation of the structure of **3a** showing 50% probability ellipsoids. H atoms (except imidazolium C-2) are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(13)–N(1) = 1.339(3); C(13)–N(2) = 1.329(3); C(17)–O(1) = 1.206(3); C(17)–O(2) = 1.320(3); N(2)–C(13)–N(1) = 108.6(2).

lium carboxylates (see Scheme 1) [4c], however, isolation of analytically pure samples was hampered by persistent contamination by triethylammonium hydrobromide. Clean and selective deprotonation of the carboxylic acid was accomplished by suspending the salts in liquid ammonia. After completion of the reaction and evaporation of the ammonia, the resulting colourless solid residue was extracted with CH_2Cl_2 giving pure zwitterionic **4a–c** after evaporation of the CH_2Cl_2. In this case the ammonium bromide was completely insoluble in dichloromethane and can be easily removed by filtration. The zwitterions were characterised by analytical and spectroscopic methods. In addition **4a** was characterised crystallographically (Fig. 2). Metric data for this compound are listed in the caption and refinement parameters are given in Table 1.

Reaction of the zwitterions **4a–c** with one equivalent of base $[KN(SiMe_3)_2$ or $LiNPr^i_2]$ gave intractable mixtures.

2.2. Complexes derived from imidazolium trimethylsilylcarboxylates

The presence of the trimethylsilyl protected carboxylic acid tethered to imidazolium group seemed attractive for the controlled synthesis of mononuclear and binuclear NHC complexes. However, it proved impossible to form selectively complexes in which the trimethylsilylcarboxylate functionality on the tether remained intact. In all cases desilylation took place even under strictly anhydrous conditions.

Reaction of **1a** with $(CuMes)_5$ [5] in THF for short reaction times followed by crystallisation by addition of ether gave moderate yields of complex **2**. Longer reaction times or work up or use of chlorinated solvents led to insoluble polymers. Complex **2** was characterised by elemental analysis and crystallography. Spectroscopic characterisation was hampered by its low solubility in common organic solvents. A diagram of the molecule is shown in Fig. 3; metric data for the complex are listed in the caption and refinement parameters are given in Table 1.

The complex comprises a tetranuclear copper cluster with four bridging bromides and two bridging acetates; the latter are tethered to non-coordinated imidazolium groups. Therefore, trimethylsilyl abstraction has taken place. The four copper atoms lie on the

Table 1
Summary of the crystal data, data collection and refinement for compounds **3a**, **4a**, **2**, **5a** and **6a**

	3a	**4a**	**2**	**5a**	**6a**
Chemical formula	$C_{17}H_{23}BrN_2O_2$	$C_{17}H_{22}N_2O_2$	$C_{34}H_{44}Br_4Cu_4N_4O_4$	$C_{18}H_{23}Cl_2CuN_2O_2$	$C_{18}H_{26}Cl_2N_2O_2Pd_{0.50}$
Formula weight	367.28	286.37	1146.53	433.82	426.52
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	*Cc*	$P2_1/c$	$P\bar{1}$	$P2_1/c$	*Pbca*
a (Å)	13.8480(3)	10.6375(6)	8.7491(4)	13.0427(5)	9.7822(3)
b (Å)	17.2330(6)	14.4475(11)	8.9462(3)	10.2452(4)	18.0772(8)
c (Å)	7.6383(3)	11.0317(8)	14.5575(6)	14.6127(6)	22.1400(9)
α (°)	90	90	74.445(2)	90	90
β (°)	92.497(2)	110.835(4)	82.423(2)	92.874(2)	90
γ (°)	90	90	65.198(2)	90	90
V (Å^3)	1821.09(10)	1584.54(19)	3978.8(2)	1950.17(13)	3915.1(3)
Z	4	2	1	4	8
T (K)	120(2)	120(2)	120(2)	120(2)	120(2)
No. data	9312	19204	20016	23051	22233
No. unique	3866	3620	4595	4462	4505
R_{int}	0.0262	0.1346	0.0587	0.0943	0.0990
Final $R(\|F\|)$ for	0.0277	0.0702	0.0393	0.0575	0.0661
Final $R(F^2)$	0.0622	0.1902	0.0807	0.1706	0.1677

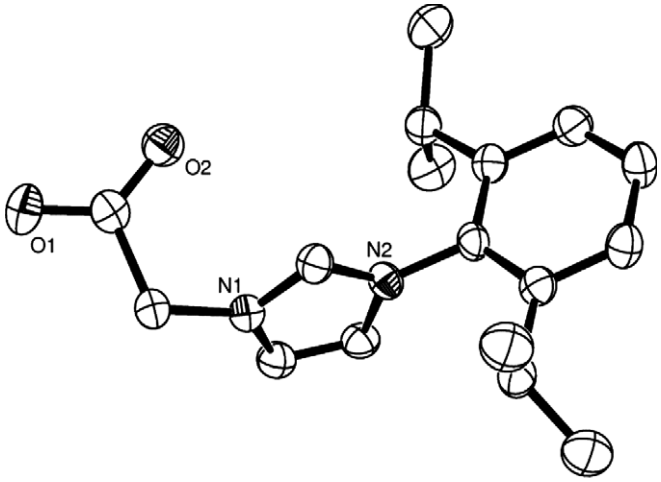


Fig. 2. ORTEP representation of the structure of **4a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C(5)–N(1) = 1.329(3); C(5)–N(2) = 1.336(3); N(1)–C(5)–N(2) = 108.5(2).

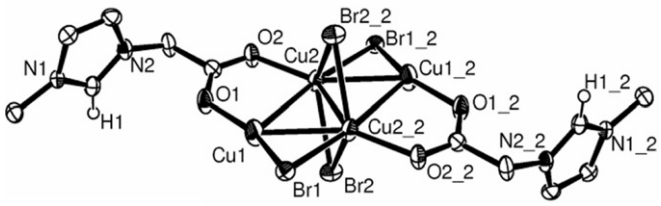


Fig. 3. ORTEP representation of the structure of **2** showing 50% probability ellipsoids. H atoms (except imidazolium C-2) are omitted for clarity. Selected bondlengths (Å) and angles (°) with estimated standard deviations: Cu(1)–Cu(2)#1 = 2.5601(7); Cu(1)–Cu(2) = 2.8298(7); Cu(2)–Cu(2)#1 = 2.6425(10); Br(1)–Cu(1) = 2.2931(7); Br(1)–Cu(2)#1 = 2.5553(6); Br(2)–Cu(2) = 2.4607(7); Cu(1)–O(1) = 1.911(3); Cu(2)–O(2) = 2.022(3); Br(1)–Cu(1) = 2.2931(7); Br(1)–Cu(2)#1 = 2.5553(6).

same plane in a rhomboidal arrangement bridged unsymmetrically by μ^4-bromides. The Cu–Cu distances in the Cu_4 plane are 2.8298(7) Å (between the acetate bridged Cu atoms) and 2.5601(7) Å (between the Br bridged Cu atoms). Complexes containing analogous Cu(I) halide clusters are very rare. A $[Cu_4(\mu^4\text{-}I)_2(\mu^2\text{-}I)_2(\mu^2\text{-dppm})_2]$, dppm = bis-diphenylphosphinomethane, complex[6a] and $[Cu_4(\mu^4\text{-}I)_2(\mu^2\text{-}I)_2(\mu^2\text{-PP})_2]$, PP = 2-diphenylphosphino-phosphinine)[6c] have been structurally characterised. $[Cu_4(\mu^4\text{-}Cl)_2(\mu^2\text{-}Cl)_2[\mu^2\text{-}(P_5Ph_5)]_2]$ [6b] has also recently been isolated and structurally characterised. Complex **2** is the first example without phosphorus donor ligands that adopts this geometry.

2.3. NHC complexes of copper(I) and palladium (II)

Alkanolysis of $(CuMes)_5$ by the zwitterion **4a** under carefully controlled conditions (see Section 3) gave yellow solutions, from which the insoluble polymeric complex **5a** was obtained. The characterisation of **5a** was carried out by analytical and crystallographic methods. A diagram of the polymeric repeat unit is shown in Fig. 4; metric data are listed in the caption of the figure. Fig. 5 gives a view of the polymeric chain in which the coordination sphere of the copper atoms can be seen. Refinement parameters are given in Table 1.

The Cu(I) centres in **5a** adopt an almost linear geometry (*ca* 177.2°); they are coordinated to the $C2_{NHC}$ of one polymer repeat unit and one oxygen atom of the κ^1-carboxylate of the following repeat unit. In this way a zig-zag polymeric organometallic chain is obtained. The bond lengths Cu–C_{NHC} (1.859(4) Å) and Cu–$O_{acetate}$ (1.864(3) Å) are very similar. Polymeric Cu(I) pyridine functionalised NHC complexes have been previously reported [7]. The lower

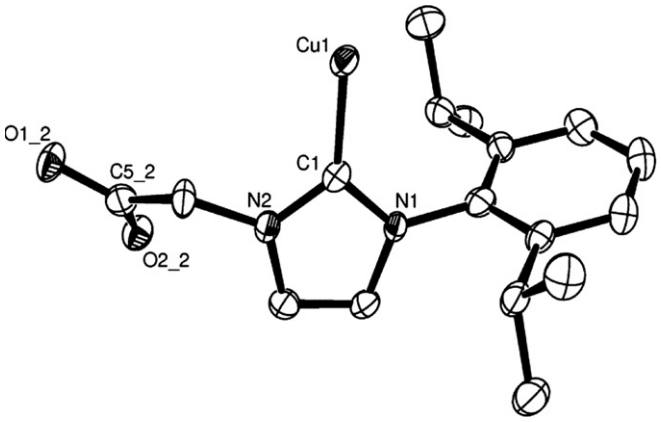


Fig. 4. ORTEP representation of the structure of the repeat unit of the polymer **5a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C(1)–N(2) = 1.356(5); C(1)–N(1) = 1.364(5); C(1)–Cu(1) = 1.859(4); O(1)–Cu(1) = 1.864(3); N(2)–C(1)–N(1) = 103.2(3).

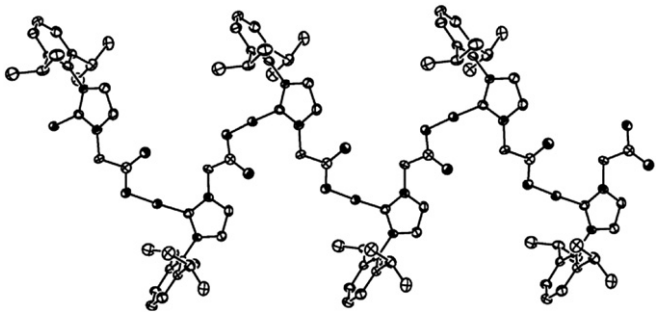


Fig. 5. View of the structure of the polymer **5a**.

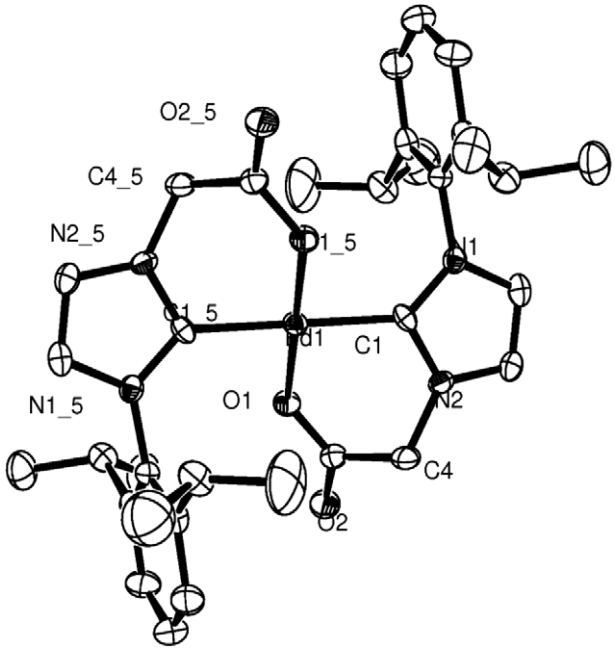


Fig. 6. ORTEP representation of the structure of **6a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd(1)–O(1) = 2.013(3); Pd(1)–C(1) = 2.014(5); O(1)#1–Pd(1)–C(1)# 1 = 87.44(18); O(1)–Pd(1)–C(1)#1 = 92.56(18); O(1)#1–Pd(1)–C(1) = 92.56(18).

solubility of the polymers obtained here may be due to longer chain lengths. Once crystallised, the air and moisture sensitive **5a** could not be redissolved in dichloromethane and decomposed by attempted dissolution in polar non-protic solvents.

The reaction of $Pd(OAc)_2$ with two equivalents of the NHC ligand generated *in situ* at lower temperatures from **4a** and one equivalent $LiNPr^i_2$ in THF gave after workup low to moderate yields of **6a** in the form of off-white crystals. The structure of **6a** was confirmed crystallographically (see Fig. 6).

The complex comprises a square planar Pd centre with two κ^2 ligands arranged such as the NHC and carboxylate donors are mutually *trans*. The Pd–C_{NHC} (2.014(5) Å) and Pd–$O_{acetate}$ (2.013(3) Å) bond distances are within the expected range [8]. The six membered chelate rings adopt a boat conformation.

The solid-state structure of **6a** is maintained in solutions in non-polar solvents as suggested by the ^{1}H NMR spectroscopy. The diastereotopic isopropyl methyls of the DiPP substituent of the NHC functional group appear as two doublets at δ 1.05 and 1.27, while the methine protons as one septet at δ 2.32. The protons α to the coordinated carboxylates appear as a broad singlet at δ 3.27.

Palladium carboxylates with monodentate or bidentate NHC ligands have been described especially with relevance to C–H activation [9]. Complex **6a** is the first example where the NHC and the carboxylate functional groups are part of the same chelate providing additional stabilisation.

3. Conclusions

The Cu(I) and Pd(II) complexes with the new carboxylate-functionalised NHC ligands reveal two different coordination modes of the ligand: chelating bidentate and bridging two different metal centres. In the latter case organometallic linear polymeric copper (I) structures have been observed. The presence of hard (COO^-) and a strong σ-donor (NHC) on the same coordination sphere may favour the stabilisation of higher oxidation states of various metals or promote hemilabile behaviour which are areas of future investigation in our group.

4. Experimental

4.1. General methods

Elemental analyses were carried out by the microanalytical laboratory at London Metropolitan University. All manipulations were performed under nitrogen in a Braun glove box or using standard Schlenk techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior use. The light petroleum used throughout had a b.p. 40–60 °C.

The starting materials $BrCH_2COOSiMe_3$, Bu^t-imidazole, mesityl-imidazole, 2,6-diisopropylphenyl-imidazole and Cu_5Mes_5 were prepared according to literature procedures [10,11,5]. NMR data were recorded on Bruker AV-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^{1}H), respectively. The spectra were referenced internally using the signal from the residual protio-solvent (^{1}H) or the signals of the solvent (^{13}C).

4.1.1. 3-(2,6-Di-isopropylphenyl)-1-(O-trimethylsilyl-acetato)-imidazolium bromide (**1a**)

A solution of *O*-trimethylsilyl-bromoacetate (2.75 g, 0.013 mol) and 2,6-di-isopropylphenyl-imidazol (3 g, 0.013 mol) in dioxane (50 mL) was heated at 80 °C for 8 h. After cooling the reaction mixture to room temperature, the volatiles were removed under reduced pressure and the residue was washed with ether and dried under vacuum to give the product as a colourless moisture sensitive solid. Yield: 3.80 g, 67%. ^{1}H NMR ($CDCl_3$): δ 10.35 (s, 1H, C2–H imidazolium), 7.90 and 7.18 (s, 1H each, imidazolium backbone), 7.48 (t, 1H, DiPP), 7.32 (d, 2H, DiPP), 5.46 (s, 2H, CH_2 linker), 2.35 [sept, 2H, C*H*(CH_3)$_2$], 1.12 and 1.23 [d, 6H each, CH(C*H*$_3$)$_2$], 0.32 [s, 9H, OSi(CH_3)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 0.30 [OSi(CH_3)$_3$], 24.49 and 24.71 [CH(CH_3)$_2$], 29.21 [CH(CH_3)$_2$], 52.36 (CH_2), 124.92, 125.25, 130.78, 132.45, 140.08 and 146.17 (all aromatic), 166.66 (C-2 imidazolium). Calc. for $C_{20}H_{31}N_2SiO_2Br$: C, 54.66; H, 7.11; N, 6.37. Found: C, 53.80; H, 6.95; N, 6.22%.

4.1.2. General method for the synthesis of the carboxylic acid functionalised imidazolium salts ***3a–c***

Under N_2, trimethylsilyl bromoacetate (1 mmol) and dioxane (ca. 20 mL) were added to a preweighted ampoule. The imidazole (1 mmol) was then added to the solution, the ampoule was evacuated partially, sealed and heated to 90 °C overnight. On cooling a white or yellow precipitate emerged. This was dissolved in dichloromethane (100 mL) and methanol (ca. 2 mL) was added to the solution dropwise with stirring. After the completion of the addition and stirring for 0.5 h the volatiles were removed under reduced pressure leaving a creamy white solid, which was washed

with ether and dried under vacuum to afford analytically and spectroscopically pure imidazolium bromides.

*4.1.3. [3-(2,6-Di-isopropylphenyl)-(1-acetic acid)]-imidazolium bromide (**3a**)*

Prepared as above from (2,6-di-isopropylphenyl)-imidazole. Yield: 0.30 g, ca. 78%. Calc. for $C_{17}H_{23}N_2O_2Br$: C, 55.59; H, 7.11; N, 7.63. Found: C, 55.50; H, 6.04; N, 7.59%. ^{1}H NMR (DMSO-d_6): δ 9.63 (1H, s, imidazolium), 8.12 and 8.10 (1H each, s, imidazol backbone), 7.62 (t, J = 8.1 Hz, 1H, DiPP), 7.44 (d, J = 8.0 Hz, 2H, DiPP), 5.32 (s, 2H, CH_2 linker), 2.29 (septet, J = 6.8 Hz, 2H, Pr^i), 1.14 (dd, J = 6.9 Hz, 12H, Pr^i). ^{13}C{^{1}H} NMR (DMSO-d_6): 166.92 (COO), 144.11 (aromatic), 138.27 (aromatic), 130.56 (aromatic), 129.53(aromatic), 123.62 (aromatic), 123.46 (aromatic), 49.27 (CH_2), 27.06 (Pr^i), 22.84 (Pr^i), 22.74 (Pr^i). IR (Nujol, cm^{-1}), 1735 (C=O). MS (ES$^+$) 287.3 (M−Br).

*4.1.4. [3-(Mesityl)-(1-acetic acid)]-imidazolium bromide (**3b**)*

Prepared as above from mesityl-imidazole. Yield: 0.22 g, 65%. Calc. for $C_{14}H_{17}N_2O_2Br$: C, 51.70; H, 5.27; N, 8.61. Found: C, 51.37; H, 5.12; N, 8.07%. ^{1}H NMR (DMSO-d_6): δ 9.51 (1H, s, imidazolium), 8.07 and 7.94 (1H each, t, J = 2.1 Hz, imidazol backbone), 7.14 (2, 2H, mes), 5.29 (s, 2H, CH_2 linker), 2.32 (s, 3H, *p*-Me), 2.01 (s, 6H, *o*-Me). ^{13}C{^{1}H} NMR (DMSO-d_6): 168.04 (COO), 140.46 (aromatic), 138.74 (aromatic), 134.38 (aromatic), 131.22 (aromatic), 129.24 (aromatic), 124.43 (aromatic), 50.27 (CH_2), 20.56 (Me), 16.79 (Me). IR (Nujol, cm^{-1}): 1718 (C=O). MS (ES$^+$) 245.3 (M−Br).

4.1.5. [3-(tert-Butyl)-(1-acetic acid)]-imidazolium bromide (3c)

Prepared as above from *tert*-butyl-imidazole. Yield: 0.15 g 56%. Calc. for $C_{14}H_{17}N_2O_2Br$: C, 41.08; H, 5.76; N, 10.66. Found: C, 40.85; H, 5.52; N, 10.10%. NMR (DMSO-d_6): δ 9.50 (1H, s, imidazolium), 8.08 and 7.83 (1H each, t, J = 1.8 Hz, imidazol backbone), 5.15 (s, 2H, CH_2 linker), 1.58 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR (DMSO-d_6): 167.87 (COO), 135.52 (aromatic), 131.22 (aromatic), 123.92 (aromatic), 59.57 (CH_2), 49.50 (Bu^t) 29.50 (Bu^t). IR (Nujol, cm^{-1}): 1718 (C=O). MS (ES$^+$) 245.3 (M−Br).

*4.1.6. General synthesis of the zwitterions **4a–c***

The imidazolium salt (1 mmol) was added to a flask and cooled to −78 °C. Liquid ammonia (ca. 50 mL) was condensed into the flask whilst stirring with a stir bar. After 15 min the flask was removed from the cooling bath and the ammonia was allowed to evaporate. The resulting residue was extracted into dichloromethane (3 × 50 mL). The dichloromethane extracts were combined and the volatiles were removed under vacuum. The solid residue was dried azeotropically with toluene.

*4.1.7. [3-(2,6-Di-isopropylphenyl)-(1-α-acetate)]-imidazolium (**4a**)*

White solid prepared as above from **3a**. Yield: 82%.

Calc. for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.17; H, 7.32; N, 9.33%. NMR (DMSO-d_6): δ 9.37 (1H, s, imidazolium), 7.93 (2H each, s, imidazol backbone), 7.61 (t, J = 7.8 Hz, 1H, DiPP), 7.44 (d, J = 7.5 Hz, 2H, DiPP), 4.65 (s, 2H, CH_2 linker), 2.50 (septet, J = 1.8 Hz, 2H, Pr^i), 1.15 (d, J = 1.9 Hz, 12H, Pr^i). ^{13}C{^{1}H} NMR (chloroform-*d*): δ 238.98, 172.37, 146.01, 139.03, 132.00, 130.73, 124.87, 122.08, 28.84, 24.65, 12.52. IR (Nujol, cm^{-1}), 1637 (C=O). MS (ES$^+$) 287.3 (M+H)$^+$.

*4.1.8. [3-(Mesityl)-(1-α-acetate)]-imidazolium (**4b**)*

White solid prepared as above from **3b**. Yield: 42%.

Calc. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.47; H, 6.23; N, 11.01%. ^{1}H NMR (chloroform-*d*): δ 9.59 (1H, s, imidazolium), 7.15 (2H imidazol backbone), 6.92 (2, 2H, mes), 5.38 (s, 2H, CH_2 linker), 2.27 (s, 3H, *p*-Me), 2.02 (s, 6H, *o*-Me). ^{13}C{^{1}H} NMR (chloroform-*d*): 197.43, 172.97, 157.77, 149.81, 144.86, 140.24, 134.14, 50.25, 20.06, 16.66. IR (Nujol, cm^{-1}): 1715 (C=O). MS (ES$^+$) 244.3 (M+H)$^+$.

*4.1.9. [3-(tert-Butyl)-(1-α-acetate)]-imidazolium (**4c**)*

Yellow oil prepared as above from **3c**. Yield 58%.

Calc. for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.77; N, 15.37. Found: C, 59.43; H, 7.32; N, 15.31. NMR (DMSO-d_6): δ 9.19 (1H, s, imidazolium), 7.87 and 7.62 (1H each, t, J = 1.8 Hz, imidazol backbone), 4.42 (s, 2H, CH_2 linker), 1.57 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR (DMSO-d_6): 165.87, 134.59, 130.14, 125.34, 118.70, 52.76, 49.50, 29.09. IR (Nujol, cm^{-1}): 1621 (C=O). MS (ES$^+$) 182.3 (M+H)$^+$.

*4.1.10. Synthesis of the copper cluster **2***

In the glove box 0.30 g (0.71 mmol) of 1a and 0.25 g (0.30 mmol) of $(CuMes)_5$ were placed in a Schlenk tube and mixed. To the solid mixture THF (30 mL) was added and stirred at room temperature for 1 h. After this time the reaction mixture was layered with ether. Colourless air sensitive crystals appeared after 1 day that were collected and dried. The crystals decomposed in chlorinared, protic or donor solvents which made the acquisition of NMR data impossible. Characterisation was carried out analytically and crystallographically. Calc. for $C_{34}H_{44}N_4O_4Cu_4Br_4$: C, 35.62; H, 3.87; N, 4.89. Found: C, 35.03; H, 3.55; N, 4.41.

*4.1.11. Synthesis of the copper polymer **5a***

In the glove box 0.30 g (1 mmol) of **4a** and 0.19 g (0.20 mmol) of $(CuMes)_5$ were placed in a Schlenk tube and mixed. THF (50 mL) was added and the solution became yellow to yellow-green within 1 h. At this stage the THF was removed under reduced pressure and the solid residue was crystallised by layering dichloromethane solutions with light petroleum. Longer THF contact times lead to the precipitation of white powder and should be avoided. Once the crystalline **5a** was obtained it cannot be dissolved in any solvent without decomposition, therefore the acquisition of NMR data was not possible.

Characterisation was carried out analytically and crystallographically. Calc. for $C_{17}N_2H_{19}O_2Cu.CH_2Cl_2$: C, 50.06; H, 4.90; N, 6.49. Found: C, 50.82; H, 5.15; N, 7.01%.

*4.1.12. Synthesis of the palladium complex **6a***

To a THF suspension of **4a** (0.43 g, 1.5 mmol) at −78 °C was added a pre-cooled solution of LiNPr$^i_2$ in THF (0.16 g, 1.5 mmol) followed by a solution of palladium acetate in the same solvent (0.15 g, 0.67 mmol in 10 mL). The cold reaction mixture was allowed to reach room temperature slowly and stirred overnight. Evaporation of the volatiles under reduced pressure, extraction of the solid residue in dichloromethane, filtration and layering with ether gave off-white air stable crystals. Yield 35%. Calc. for $C_{36}H_{52}O_4N_4Pd$: C, 50.67; H, 6.14; N, 6.57. Found: C, 50.02; H, 5.93; N, 6.22.

^{1}H NMR (dichloromethane-d_2): δ 8.25 and 8.10 (1H each, s, imidazol backbone), 7.65 (t, 1H, DiPP), 7.45 (d, 2H, DiPP), 3.27 (s, 2H, CH_2 linker), 2.32 (septet, 2H, Pr^i), 1.27 and 1.05 (dd, 12H, Pr^i).

4.2. Crystallography

A summary of the crystal data, data collection and refinement for compounds **3a**, **4a**, **2**, **5a** and **6a** are given in Table 1.

All data sets were collected on a Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo Ka radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were COLLECT, SCALEPACK, and DENZO [12]. The crystals were mounted on a glass fiber with silicon grease from Fomblin vacuum oil. All solutions and

refinements were performed using the WINGX package [13] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model.

5. Supplementary material

CCDC 689233, 689234, 689235, 689236 and 68923 contain the supplementary crystallographic data for **3a**, **4a**, **2**, **5a** and **6a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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