Studies of the reactivity of *N*-heterocyclic carbenes with halogen and halide sources

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The reactivity of the *N*-heterocyclic carbene (NHC) 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, IMes, with a series of halide sources, including 1,1,1,2,2,2-hexachloroethane, 1,2-dibromoethane and dibromine, has been assessed. These result in the formation of the imidazolium species 1,3-bis(2,4,6-trimethylphenyl)-2-chloroimidazolium chloride, [IMesCl][Cl], 1,3-bis(2,4,6-trimethylphenyl)imidazolium bromide, [IMesH][Br] and 1,3-bis(2,4,6-trimethylphenyl)-2-bromoimidazolium bromide, [IMesBr][Br]. Treatment of IMes with 2.0 equiv. of carbon tetrabromide, CBr_4, in tetrahydrofuran or benzene yields the new NHC 1,3-bis(2,4,6-trimethylphenyl)-4,5-dibromoimidazol-2-ylidene, $IMesBr_2$. $IMesBr_2$ is indefinitely stable in air and has been characterised by XRD. The molecular and supramolecular structures of compounds [IMesBr][Br]·3MeCN, [IMesH][Br], [IMesCl][Cl]·MeCN and [IMesCl][AlCl$_4$], the latter formed from the addition of aluminium trichloride to [IMesCl][Cl], are discussed.

Introduction

The isolation of the first room temperature stable *N*-heterocyclic carbene (NHC) by Arduengo *et al.* in 1991[1] brought about a renaissance in the use of imidazol-2-ylidenes[2] for transition metal complex preparations, and the tailoring of such complexes to diverse catalytic processes.[3–6] Their activity in this respect has received considerable interest, most notably because of the recognised analogy between NHCs and nucleophilic tertiary phosphine ligands.[7] This analogy has also been exploited in the synthesis of an increasing number of exceptionally stable main group metal–carbene complexes.[8] In this area we have utilised the stabilising properties of monodentate NHCs to prepare a series of group 13 halide complexes,[9,10] including the first thallium (III) carbene adducts,[11] and remarkably stable group 13 hydride complexes, *e.g.* [InH$_3$(IMes)],[12] which does not decompose until 115 °C in the solid state and whose chemistry we are systematically studying.[13]

In recent years synthetic studies in our lab have yielded numerous imidazolium species from preparations employing NHCs.[14] Although we are acutely aware of the facility by which imidazolium salts form when water is present in the reaction of NHCs with group 13 halides, in most cases extensive efforts were made to rigorously exclude moisture and yet these salts formed in moderate to high yield. In these situations we have been content to presume that the acidic imidazolium protons originated from the solvent, whilst the counterions derived from the group 13 starting material used.[15] To expand upon this supposition and further define the reactivity of NHCs with halogen/halide containing reagents we herein report the preparation of several imidazolium and NHC compounds utilising IMes that elaborate upon the known reactivity of NHCs and corroborate the suggestion that imidazolium species need not derive from metal complex hydrolysis. In addition, the molecular structures of five IMes based compounds are discussed with particular emphasis on the supramolecular architecture of three imidazolium halide species.

Results and discussion

The reaction of diiodine with NHCs has been well documented,[16–18] however, reaction of the same carbenes with lighter dihalogens, or sources thereof, has been less prominent in the literature.[2] In 1997 Arduengo *et al.* reported the synthesis of IMesCl$_2$ (1,3-bis(2,4,6-trimethylphenyl)-4,5-dichloroimidazol-2-ylidene) and its reactivity with carbon tetrachloride to form 'mixed carbene dimers'.[19] The NHC IMesCl$_2$ possesses remarkable aerobic stability (*ca.* 2 days) in the solid state, however, since its publication few synthetic chemists have chosen to utilise the undoubted advantages this offers.[20] This may result from lesser donation relative to non-halogenated NHCs, however, studies conducted within our group have raised doubts as to the specificity of the preparation of IMesCl$_2$ detailed by Arduengo using IMes and two equivalents of carbon tetrachloride. In our hands this procedure has proved difficult to control stoichiometrically, leading to the random formation of unidentified imidazolium by-products (see section (ii)).

Reports from Kuhn *et al.* have identified the reaction of 1,2-dichloroethane with NHCs as a high yield route to 2-chloro-1,3-disubstituted imidazolium chloride salts.[21] The synthetic versatility of these reagents, *e.g.* 2-chloro-1,3-dimethylimidazolium chloride, given the acronym DMC, has been demonstrated by a wealth of studies from the group of Ishikawa.[22] These have highlighted the use of DMC as a dehydrating agent (comparable to the ubiquitous dicyclohexylcarbodiimide, DCC), a chlorination agent, oxidising agent, reducing agent and an active reagent in the rearrangement of ureas, carbamates, thiocarbamates and carboxamides.[22]

Given the bond energies of carbon–hydrogen and carbon–chlorine bonds (*ca.* 413 kJ mol^{-1} and 327 kJ mol^{-1})[23,24] it is somewhat surprising that solely 2-chloro chloride imidazolium products result from the reaction of 1,2-dichloroethane ($\{CH_2Cl\}_2$) with NHCs. The individual undertaking of this process appears even more unlikely when one considers the energetic advantage of HCl, and not Cl$_2$, 'elimination' from the chlorocarbon. Indeed, should hydrogen chloride or dichlorine be eliminated as intermediates in the formation of imidazolium species, which is not inconceivable given the high basicity of NHCs, the relative bond energies of each (H–Cl; 432.0 kJ mol^{-1}, Cl–Cl; 243.4 kJ mol^{-1})[23,24] suggest hydrogen chloride elimination would be preferred. Accordingly, it could be argued that a considerable quantity of imidazolium chloride (2-hydro in addition to 2-chloro) results from the syntheses listed by Kuhn *et al.*[21] Interestingly, by this premise, the over-all disparity in bond enthalpies would increase were the halide to be bromide, *i.e.* dibromine expulsion is less likely with respect to hydrogen bromide elimination than dichlorine elimination with respect to hydrogen chloride loss.[23,24] Conversely, it could also be argued that the barrier to 2-hydroimidazolium halide formation is greater than 2-haloimidazolium formation as a result of the superior strength of C–H bonds relative to weaker C–Cl and C–Br bonds (latter 290 kJ mol^{-1}).[23,24]

(i) Reaction of IMes with 1,1,1,2,2,2-hexachloroethane

In view of our failure to prepare IMesCl$_2$ using the procedure reported by Arduengo *et al.*,[19] the alternative preparation of reacting IMes with hexachloroethane (1:1) was proposed. Hexachloroethane is a colourless solid that freely sublimes under atmospheric pressure at ambient temperature, and can thus be purified with ease. However, the use of 1,2-dichloroethane ($\{CH_2Cl\}_2$) in the preparation of 2-chloroimidazolium reagents by Kuhn[21] and Ishikawa[22] suggested a similar 2-chloro IMes compound could result.

Reaction of solid hexachloroethane with a solution of IMes in acetonitrile results in the formation of a light yellow slurry that when sonicated for one day and extracted into fresh acetonitrile gives [IMesCl][Cl], (1), as solvent dependent colourless prisms (Scheme 1 (i)). (Crystallographic data for all compounds characterised by X-ray crystallography are listed in Table 1, POV-RAY diagrams with 20% ellipsoids included in
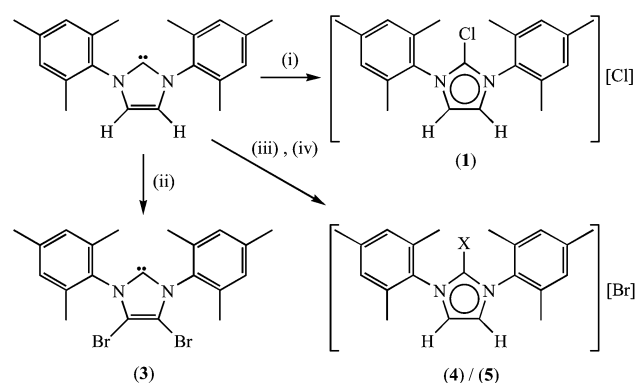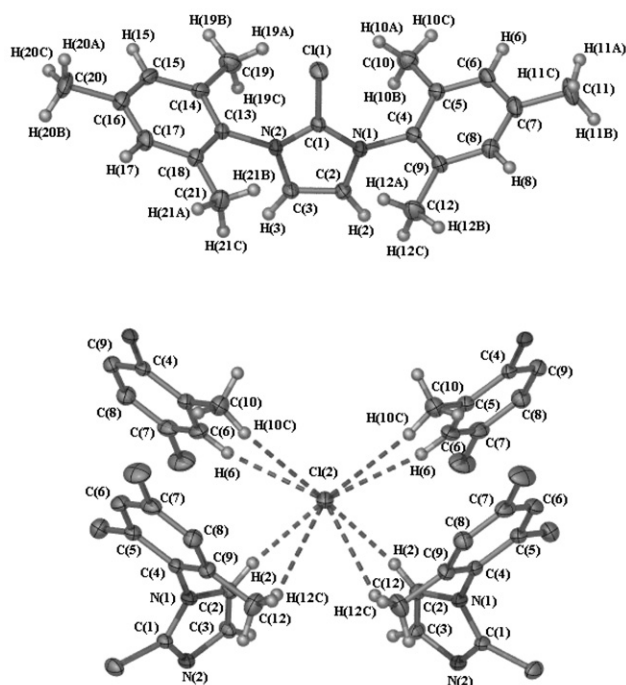

Scheme 1 *Reagents and conditions:* (i) MeCN, C$_2$Cl$_6$, −C$_4$Cl$_6$, (ii) THF, 2CBr$_4$, −2CHBr$_3$, (iii) THF, Br$_2$; X = Br, (iv) MeCN, $\{CH_2Br\}_2$, −C$_2$H$_4$ and C$_2$HBr; X = H and Br (54:46%).

Figs. 1–5, relevant bond lengths and angles listed in figure captions, esd's included except where hydrogens placed in calculated positions using the riding model.) The X-ray structure determination of (1) reveals a heavily disordered acetonitrile molecule of solvation and one unique ion pair (space group P2$_1$/m) within the asymmetric unit. The molecular structure of the [IMesCl] cation is shown in Fig. 1. Compound (1) bears a close structural similarity to the known compound 2-chloro-1,3-bis(2,4,6-trimethylphenyl)-4,5-dichloroimidazolium chloride, (2).[19] The carbenic carbon–chlorine bond of (1) displays a length of 1.677(5) Å, which compares well to that of (2) (1.683(4) Å),[19] whilst the internal N–C–N angle of the imidazolium heterocycle of (1) at 109.1(4)° is similar to that of (2) (109.9(2)°) and thus greater than the angle displayed by the 2-hydroimidazolium of [IMesH][Cl]·MeOH (108.7(4)°).[25] Unlike (2), compound (1) does not display any close contact of the chloride anion to the 2-position chlorine ((2); 3.144 Å, C–Cl–Cl angle of 173.06°).[19] In contrast, the chloride anion of (1) appears to interact in a regimented fashion with hydrogens upon the C(12), C(10) (both *ortho*-methylphenyl positions of IMes), C(6) (*meta*-aryl proton) and C(2) (hydrogen of C$_2$H$_2$ heterocycle backbone) atoms of proximal [IMesCl] cations within the crystal lattice (see Fig. 1). These occur with atomic distances within the combined van der Waals radii of the

Table 1 Summary of crystal data for compounds (1)·MeCN, (3), (4)·3MeCN, (5) and (6)

|	[IMesCl][Cl]·MeCN (1)·MeCN	[IMesBr$_2$] (3)	[IMesBr][Br]·3MeCN (4)·3MeCN	[IMesH][Br] (5)	[IMesCl][AlCl$_4$] (6)
Mol. formula	C$_{23}$H$_{27}$N$_3$Cl$_2$	C$_{21}$H$_{22}$N$_2$Br$_2$	C$_{27}$H$_{33}$N$_5$Br$_2$	C$_{21}$H$_{25}$N$_2$Br	C$_{84}$H$_{96}$N$_8$Al$_4$Cl$_{20}$
M	416.40	463.23	587.40	385.34	2034.61
T/K	296(2)	296(2)	296(2)	296(2)	296(2)
Space group	P2$_1$/m	P2$_1$/n	P2$_1$/c	P2$_1$	P$\bar{1}$
a/Å	10.242(4)	11.4179(12)	11.5086(15)	8.7182(9)	16.952(3)
b/Å	17.141(6)	14.8370(16)	19.474(3)	14.0483(15)	18.808(3)
c/Å	16.496(6)	13.4527(14)	13.6523(18)	16.2655(18)	19.068(3)
α/deg	90	90	90	90	63.838(3)
β/deg	100.767(8)	114.275(2)	101.511(2)	101.879(2)	88.463(3)
γ/deg	90	90	90	90	77.431(4)
V/Å^3	2844.9(17)	2077.5(4)	2998.2(7)	1949.5(4)	5309.0(15)
Z	4	4	4	4	2
D_c/g cm^{-3}	0.924	1.478	1.301	1.313	1.273
μ/mm^{-1}	0.235	3.908	2.726	2.113	0.590
Reflections collected	13171	9289	13454	8933	24829
Reflections unique	4215	2995	4298	5220	15142
Parameters varied	253	232	316	453	1069
R_{int}	0.0678	0.0905	0.0797	0.0486	0.0964
R_1	0.0764	0.0579	0.0480	0.0424	0.0689
wR_2	0.2052	0.1418	0.1132	0.0933	0.1540

Fig. 1 Molecular structure and anion coordination environment of [IMesCl][Cl]·MeCN, (**1**)·MeCN. Only relevant hydrogen atoms depicted for second illustration. Selected bond lengths (Å) and angles (°): C(1)–Cl(1) 1.677(5), N(1)–C(1) 1.325(5), N(2)–C(1) 1.329(5), C(2)–C(3) 1.339(6), N(1)–C(4) 1.448(6), N(2)–C(13) 1.462(5), H(2)···Cl(2)# 2.5593, H(12C)···Cl(2)# 3.2845, H(6)···Cl(2)# 2.8875, H(10C)···Cl(2)# 3.1224, C(2)···Cl(2)# 3.4575(50), C(12)···Cl(2)# 4.1302(67), C(6)···Cl(2)# 3.7872(56), C(10)···Cl(2)# 4.0076(55), Cl(1)–C(1)–N(1) 125.5(3), Cl(1)–C(1)–N(2) 125.4(3), N(1)–C(1)–N(2) 109.1(4), C(1)–N(1)–C(2) 107.7(4), N(1)–C(2)–C(3) 107.8(4), C(1)–N(2)–C(3) 108.6(4), N(2)–C(3)–C(2) 106.7(4), C(2)–H(2)···Cl(2)# 162.47, C(12)–H(12C)···Cl(2)# 148.02, C(6)–H(6)···Cl(2)# 163.16, C(10)–H(10C)···Cl(2)# 154.03, C(4) ring–imidazolium ring 76.48(15), C(13) ring–imidazolium ring 81.64(14), C(4) ring–C(13) ring 41.01(18).

C–H···X hydrogen bound unit, with C–H–Cl angles of *ca.* 150° or greater. Unfortunately, the hydrogens at these positions were necessarily placed in calculated positions (riding model) to attain acceptable refinement, and therefore cannot unambiguously testify to the participation of these atoms in the hydrogen-bond anion coordination sphere proposed. In a similar vein, the disorder of the acetonitrile of solvation, which would presumably complete the coordination sphere of the anion, suggests a lack of absolute coordination of the chloride
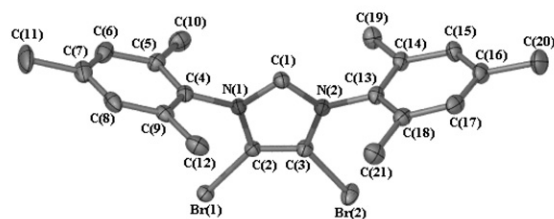
Fig. 2 Molecular structure of [IMesBr$_2$], (**3**). Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.375(8), C(1)–N(2) 1.365(8), N(1)–C(2) 1.388(7), N(2)–C(3) 1.382(7), C(2)–C(3) 1.331(8), C(2)–Br(1) 1.866(6), C(3)–Br(2) 1.866(6), N(1)–C(4) 1.456(8), N(2)–C(13) 1.430(8), N(1)–C(1)–N(2) 102.4(5), C(1)–N(1)–C(2) 112.5(5), N(1)–C(2)–C(3) 105.5(5), C(1)–N(2)–C(3) 111.5(5), N(2)–C(3)–C(2) 108.2(5), N(1)–C(2)–Br(1) 124.7(4), N(2)–C(3)–Br(2) 123.1(5), C(2)–C(3)–Br(2) 128.7(5), C(3)–C(2)–Br(1) 129.8(4), C(4) ring–imidazolium ring 84.69(18), C(13) ring–imidazolium ring 88.37(18), C(4) ring–C(13) ring 31.53(33).
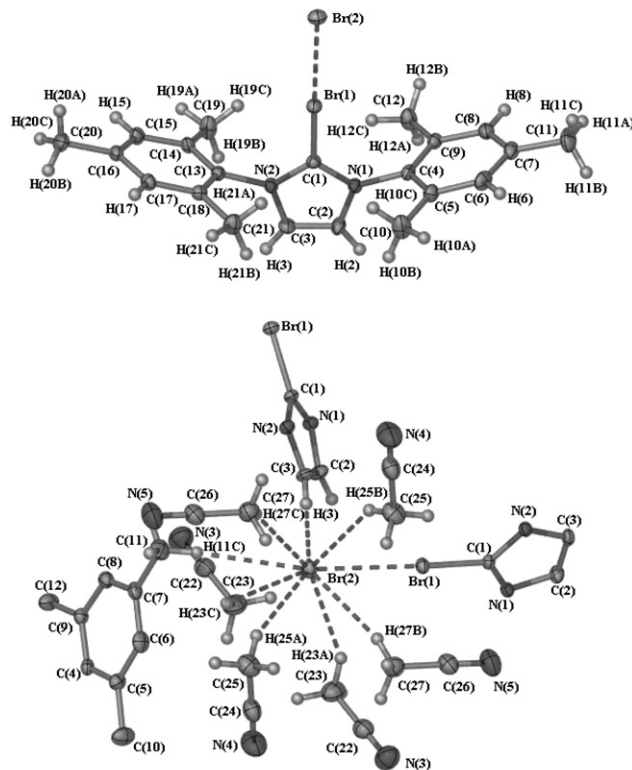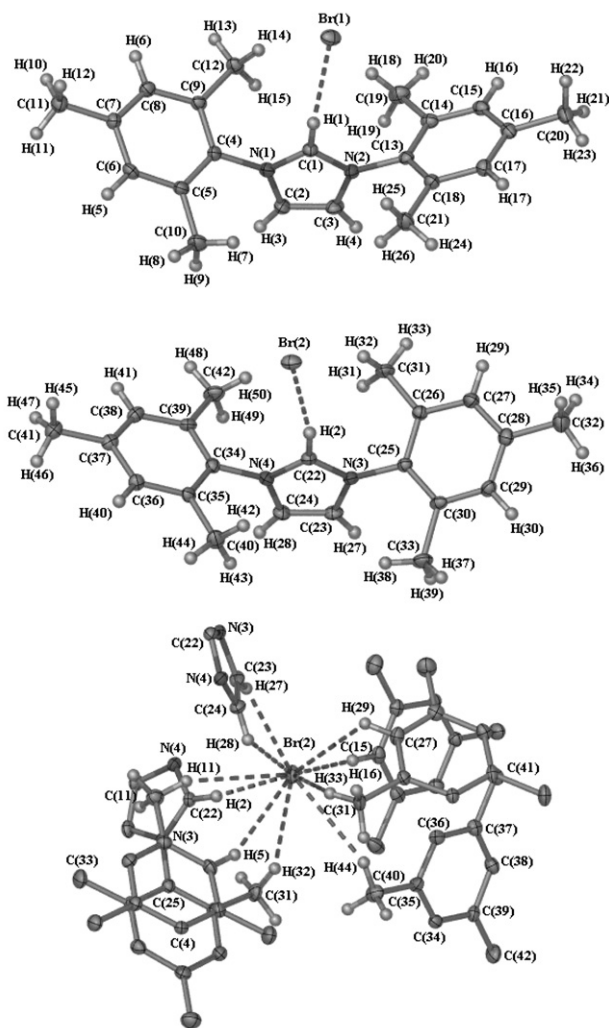
Fig. 3 Molecular structure and anion coordination environment of [IMesBr][Br]·3MeCN, (**4**)·3MeCN. Only relevant hydrogen atoms depicted for second illustration. Selected bond lengths (Å) and angles (°): Br(1)···Br(2) 3.1137(8), Br(1)–C(1) 1.861(4), C(1)–N(1) 1.326(6), C(1)–N(2) 1.349(6), N(1)–C(2) 1.383(6), N(2)–C(3) 1.381(6), C(2)–C(3) 1.326(7), N(1)–C(4) 1.449(6), N(2)–C(13) 1.456(6), H(27B)···Br(2) 2.9957, H(23A)···Br(2) 3.0025, H(25A)···Br(2) 3.0258, H(27C)···Br(2)# 3.0714, H(25B)···Br(2)# 2.9757, H(3)···Br(2)# 2.7062, H(23C)···Br(2)# 3.4430, H(11C)···Br(2)# 2.9503, C(27)···Br(2) 3.9560(74), C(23)···Br(2) 3.8625(77), C(25)···Br(2) 3.9515(81), C(27)–Br(2)# 3.9363(74), C(25)–Br(2)# 3.8115(72), C(3)–Br(2)# 3.6322(54), C(23)–Br(2)# 4.1054(81), C(11)–Br(2)# 3.9244(72), Br(2)···Br(1)–C(1) 176.66(14), Br(1)–C(1)–N(1) 125.5(3), Br(1)–C(1)–N(2) 126.0(4), N(1)–C(1)–N(2) 108.4(4), C(1)–N(1)–C(2) 108.0(4), C(1)–N(2)–C(3) 107.9(4), C(27)–H(27B)···Br(2) 166.78, C(23)–H(23A)···Br(2) 147.14, C(25)–H(25A)···Br(2) 157.99, C(27)–H(27C)···Br(2)# 147.92, C(25)–H(25B)···Br(2)# 143.89, C(3)–H(3)···Br(2)# 165.04, C(23)–H(23C)···Br(2)# 126.77, C(11)–H(11C)···Br(2)# 172.74, C(4) ring–imidazolium ring 85.39(15), C(13) ring–imidazolium ring 81.15(15), C(4) ring–C(13) ring 32.23(22).

of (**1**)·MeCN. This debases the argument for a rigid hydrogen bound geometry about the chloride. Irrespective, it remains that according to the criteria of Schuster, Zundel and Sandorfy,[26] the putative H···Cl contact distances of the hydrogens at the C(2) and C(6) positions are within the van der Waals approach of H···Cl, *i.e.* < 2.80–3.00 Å[27] (*e.g.* C(2) position hydrogen, contact distance 2.5593 Å), and are therefore by definition C–H···Cl hydrogen bonds.

The molecular structure of (**1**) makes a contribution to the field of anion coordination chemistry that has been, until recently, one of the least studied areas of supramolecular chemistry.[28] This has occurred despite the fundamental role anion coordination plays in many chemical and biological processes.[29–31] These processes include the binding and transport of biologically important anions,[32] catalysis of organic reactions[32] and synthesis of receptors for the clean-up of anionic pollutants.[29,33]

(ii) Reaction of IMes with carbon tetrabromide

The failure of the reaction detailed in section (i) to yield IMesCl$_2$ prompts questions concerning how our lack of

Fig. 4 Molecular structure both unique cation pairs and single anion (Br(2)) coordination sphere of [IMesH][Br], (**5**). Only relevant hydrogen atoms depicted for second illustration. Selected bond lengths (Å) and angles (°), those of second anion (Br(1)) coordination sphere in parentheses (closest analogue): Br(1)···H(1) 2.53(4), Br(2)···H(2) 2.49(5), H(1)–C(1) 0.96(4), H(2)–C(22) 1.01(5), C(1)–N(1) 1.329(8), C(1)–N(2) 1.330(7), N(1)–C(2) 1.403(8), N(2)–C(3) 1.381(7), C(2)–C(3) 1.336(8), C(22)–N(3) 1.318(7), C(22)–N(4) 1.321(7), N(3)–C(23) 1.396(7), N(4)–C(24) 1.374(7), C(23)–C(24) 1.319(9), C(1)···Br(1) 3.463(6), C(22)···Br(2) 3.475(6), H(16)···Br(2)# 3.1409 (3.1549), H(5)···Br(2)# 3.1780 (3.3485), H(32)···Br(2) 3.2795 (3.1850), H(29)···Br(2)# 3.2730 (3.1144), H(27)···Br(2)# 2.8248, H(28)···Br(2)# 3.3783 (2.7415), H(11)···Br(2)# 3.1456 (3.1101), H(33)···Br(2)# 3.4616 (3.3901), H(44)···Br(2)# 3.2254 (3.0637), C(22)···Br(2) 3.4712(60) (3.4632(62)), C(15)···Br(2)# 4.0360(63) (3.9294(64)), C(6)···Br(2)# 4.0519(56) (4.2063(58)), C(31)···Br(2) 4.1704(73) (4.0965(67)), C(27)···Br(2)# 3.7991(66) (4.0040(59)), C(23)···Br(2)# 3.5263(63), C(24)···Br(2)# 3.7850(62) (3.5825(59)), C(11)···Br(2)# 4.0423(67) (4.0338(78)), C(31)···Br(2)# 4.2320(70) (4.2708(68)), C(40)···Br(2)# 3.9649(70) (3.9870(68)), Br(1)···H(1)– C(1) 163(3), N(1)–C(1)–N(2) 108.5(5), Br(2)···H(2)–C(22) 166(4), N(3)–C(22)–N(4) 109.3(5), C(15)–H(16)···Br(2)# 162.10 (138.92), C(6)–H(5)···Br(2)# 157.31 (154.38), C(31)–H(32)···Br(2)# 155.20 (159.17), C(27)–H(29)···Br(2)# 117.97 (160.71), C(23)– H(27)···Br(2)# 133.10, C(24)–H(28)···Br(2)# 109.02 (150.86), C(11)– H(11)···Br(2)# 156.16 (161.94), C(31)–H(33)···Br(2)# 138.86 (153.51), C(40)–H(44)···Br(2)# 135.22 (161.82), C(4) ring–imidazolium ring 69.34(25), C(13) ring–imidazolium ring 85.55(19), C(4) ring–C(13) ring 45.27(21), C(25) ring–imidazolium ring 62.51(21), C(34) ring–imidazolium ring 88.46(17), C(25) ring–C(34) ring 47.45(21).
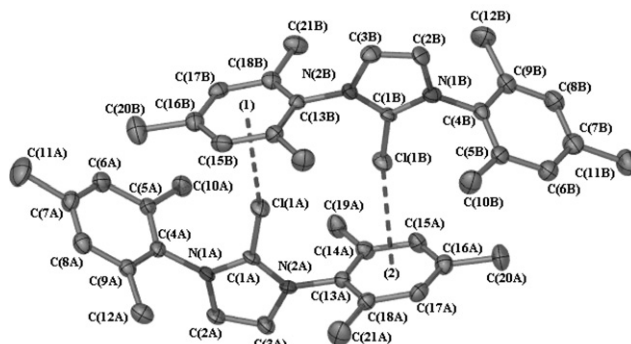
Fig. 5 Molecular structure of the cation dimer of [IMesCl][AlCl₄], (**6**). All hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°), mean of unlocked cations in parentheses: Cl(1A)···(1) 3.2768(197), Cl(1B)···(2) 3.4681(201), Cl(1A)–C(1A) 1.659(8), Cl(1B)–C(1B) 1.671(8) (1.676), C(1A)–N(1A) 1.325(9), C(1A)–N(2A) 1.338(9), N(1A)–C(2A) 1.399(9), N(2A)–C(3A) 1.393(9), C(2A)– C(3A) 1.334(10), C(1B)–N(1B) 1.325(9), C(1B)–N(2B) 1.331(9) (1.323), N(1B)–C(2B) 1.391(10), N(2B)–C(3B) 1.380(9) (1.378), C(2B)–C(3B) 1.326(11) (1.335), N(1A)–C(4A) 1.464(10), N(2A)– C(13A) 1.448(10), N(1B)–C(4B) 1.433(10), N(2B)–C(13B) 1.422(10) (1.456), (1)···Cl(1A)–C(1A) 166.06(64), (2)···Cl(1B)–C(1B) 166.31(59), Cl(1A)–C(1A)–N(1A) 124.4(7), Cl(1A)–C(1A)–N(2A) 125.5(7), Cl(1B)–C(1B)–N(1B) 124.5(8), Cl(1B)–C(1B)–N(2B) 124.5(8) (125.73), N(1A)–C(1A)–N(2A) 110.1(7), N(1B)–C(1B)– N(2B) 111.0(7) (110.4), C(4A) ring–imidazolium ring 74.97(27), C(13A) ring–imidazolium ring 88.69(27), C(4A) ring–C(13A) ring 39.85(27), C(4B) ring–imidazolium ring 74.45(29), C(13B) ring–imidazolium ring 85.25(28) (83.71), C(4B) ring–C(13B) ring 38.71(28) (44.30).

moimidazol-2-ylidene (IMesBr₂ (**3**)). We have observed that the slow addition of carbon tetrachloride to tetrahydrofuran solutions of IMes frequently results in precipitation of imidazolium salts. These can be separated by filtration to yield solutions rich in IMesCl₂ and the IMes precursor, however, problems arise in the separation of the two NHCs, which is complicated by the similar solubility of both species in common laboratory solvents. It was hoped that a 4,5-dibrominated system would obviate imidazolium separation. The drop-wise addition of carbon tetrabromide in tetrahydrofuran over extended periods (*ca.* 30 minutes) to solutions of IMes led to far greater control of the halogenation process, *i.e.* without precipitation of imidazolium salts (Scheme 1 (ii)). Compound (**3**) was crystallised from toluene as solvent free colourless plates in high yield (*ca.* 80%).

The enhanced stability of (**3**) relative to IMes is evidenced by its tolerance of bromoform in solution; a stoichiometric preparation of (**3**) in *deutero*-benzene clearly displaying the generation of two equivalents of bromoform (by ^{1}H NMR spectrum integration). Similarly, the carbene IMesCl₂ also proves unreactive to the chloroform that is formed concomitantly during the analogous CCl₄ preparative procedure.[19] Compound (**3**) is remarkably stable to air, tolerating exposure for periods in excess of 3 months without observeable decomposition (^{1}H NMR). This places (**3**) with IMesCl₂ in terms of aerobic stability, although the aerobic stability of IMesCl₂ beyond 2 days was not reported.[19] Presumably the electronegativities of chlorine and bromine play a major role in this stability enhancement (2.8 and 2.7, respectively, Allred & Rochow scale),[34] as do the larger covalent radii of bromine and chlorine with respect to hydrogen (Br; 1.14, Cl; 0.99, H; 0.30 Å).[35] Compound (**3**) possesses a thermal robustness comparable to IMesCl₂ (176 °C dec., IMesCl₂ 180–182 °C dec.),[19] whilst the ^{1}H NMR spectrum of (**3**) shows resonances at 2.06, 2.08 and 6.72 ppm for the *para*-, *ortho*-methyl and *meta*-aromatic ring protons respectively. This compares to 2.09, 2.12 and 6.75 ppm for the analogous signals of IMesCl₂ (also C₆D₆).[19] The carbenic carbon resonance of (**3**) occurs at 221.2 ppm in its

control during the preparation of IMesCl₂ can be addressed. To counteract this it was proposed that carbon tetrabromide be employed instead of carbon tetrachloride in an effort to prepare the new carbene 1,3-bis(2,4,6-trimethylphenyl)-4,5-dibro-

^{13}C NMR (C_6D_6) spectrum, which is similar to that of related NHCs (IMesCl$_2$ 219.9 ppm C_6D_6,[19] IMes 219.8 ppm d_8-THF).[36]

The molecular structure of compound (**3**) is illustrated in Fig. 2. Like (**1**), (**3**) displays one unique molecule per asymmetric unit, and crystallises in the monoclinic space group $P2_1/n$. The heterocyclic geometry of (**3**) is close to that of the solid-state structure of IMesCl$_2$. The N–C–N angle of 102.4(5)° is slightly greater than that of IMesCl$_2$ (101.9(2)),[19] but the nitrogen–carbenic carbon bond lengths of 1.365(8) and 1.375(8) Å are almost identical to those of the 4,5-chloro carbene (1.364(2) Å). The influence of the bromo-substituents upon the C$_2$ backbone (1.331(8) Å) is indistinguishable from the effect of the 4,5-chloro substituents, which render the C–C bond 1.330(4) Å.[19] This means overall there is no apparent heterocyclic modification that the 4,5-position halo substituents induce that would indicate the enhancement in stability incurred by their inclusion (IMes 4,5-C–C bond 1.331(5) Å).[19,36] However, the dihedral angles of the imidazole heterocycle to the phenyl rings of (**3**) of 84.69(18) and 88.37(18)° suggest limited rotational freedom about the exocyclic C–N bonds. This is a greater restriction than IMes and IMesCl$_2$, which exhibit analogous angles of 80.25, 71.48 (IMes) and 81.35° (IMesCl$_2$), and therefore infers that the rotational hindrance of compound (**3**) about these bonds is borne out of 4,5-carbon bromine substituents inciting near orthogonal ring to ring torsion angles.

The formation of bromoform from the stoichiometric treatment of IMes with CBr$_4$ suggests that (**3**) forms *via* the reaction path suggested by Arduengo *et al.* for the synthesis of IMesCl$_2$.[19] As per the synthesis of IMesCl$_2$, the inability of ^{1}H NMR spectroscopy studies to identify these intermediates indicates that the reaction sequence is accelerated from the initial IMes halogenation step onwards. This is consistent with a strong σ-inductive effect for the ring bromides, which increase the acidity of ring protons, driving the process to complete formation of (**3**).

(iii)   Reaction of IMes with dibromine

The reaction of IMes and 1,3-disubstituted-4,5-dimethylimidazol-2-ylidenes with diiodine leads to the formation of linear carbenic carbon–iodine–iodine species, or 2-iodoimidazolium I$_3^-$, I$_5^-$ or I$_7^-$ ionic compounds.[16–18] To our knowledge the reaction of NHCs with dibromine has not been reported, which is surprising given the precedent for formation of carbenic carbon–halogen–halogen bonds seen for both dichlorine and diiodine.[16–18,21,22]

Tetrahydrofuran solutions of IMes readily react with dibromine at ambient temperature to produce 2-bromo-1,3-bis(2,4,6-trimethylphenyl) imidazolium bromide, (**4**), as a precipitate (Scheme 1 (iii)). Compound (**4**) can be purified by crystallisation from acetonitrile to give the trisacetonitrile solvate (by ^{1}H NMR). Crystals of (**4**)·3MeCN show no sign of solvent loss even when placed under vacuum. The molecular structure of (**4**)·3MeCN, which crystallises in the triclinic space group $P2_1/c$, is shown in Fig. 3. Like compound (**1**), a coordination sphere for the bromide ion of (**4**)·3MeCN can be identified that describes a regular array of hydrogen bonds and close bromine–bromine contacts. These furnish the central bromide anion with no less than eight interactions within the van der Waals approach of H···Br or Br···Br.[34] Frustratingly, the hydrogens of (**4**)·3MeCN were necessarily refined in calculated positions (riding model), however, unlike (**1**)·MeCN the acetonitrile molecules in the solvated structure of (**4**) are structurally well behaved (no disorder). Six acetonitrile C–H bonds appear in close contact with each individual bromide anion. These augment two putative close hydrogen contacts that derive from the C(11) (*para*-methyl of mesityl group upon proximal [IMesBr] cation) and C(3) (carbon of C$_2$H$_2$ unit upon adjacent

[IMesBr] cation) atoms (2.9503 and 2.7062 Å respectively, van der Waals approach of H···Br < 3.15 Å, therefore both examples of C–H···Br hydrogen bonds), and a bromine–bromide contact of 3.1137(8) Å, with a C–Br–Br angle of 176.66(14)°. This last contact is within the van der Waals approach of Br···Br (4.0 Å)[34] but considerably distended with respect to the bromine–bromine bond of dibromine (2.28 Å).[27] As per NHC complexes of diiodine,[16–18] (**4**) can be thought of as a transition state model for the nucleophilic attack of a base upon Br$_2$.

A rigid coordination sphere for (**4**)·3MeCN is given credence by the non-lability of solvent molecules. These participate in an elaborate hydrogen-bond network that secures their position within the crystal lattice (see Fig. 3). Hydrogen bonding in NHC based structures has been observed before in the extensive chain propagation of [{IMes}$_2$H][PF$_6$] and other inorganic salts.[25] However, the degree of three-dimensional hydrogen bonding described by the solid state motifs of (**4**)·3MeCN is unusually pronounced. The tendency of the proton in the 2-position of imidazolium cations to participate as a site for hydrogen bonding has been well documented.[25] In general, it is found that anions that can function as H-bond acceptors are positioned in the crystal lattice such that a near linear C–H–X arrangement is generated. As seen in (**1**), the lack of a proton in the 2-position of (**4**), and perhaps the inductive effect of the 2-halo substituent (ring protons of increased acidity), leads to the generation of H-bonds to the halide anion from hydrogens at the 4,5-positions of the heterocycle, as well as significant interaction of the hydrogens bonded to the mesityl substituent with proximal anions. Accordingly, the supramolecular architecture of (**4**)·3MeCN provides the structural archive with an example that displays an unprecedented, or as yet unrecognised, degree of hydrogen bound anion–solvent molecule interaction within the crystal lattice.

(iv)   Reaction of IMes with 1,2-dibromoethane

The reaction of NHCs with 1,2-dichloroethane for the preparation of 2-chloroimidazolium chloride species by the groups of Kuhn and Ishikawa purportedly leads to the formation of solely 2-chloro chloride reagents, *e.g.* DMC.[21,22] Given the minor energetic disparity involved in formation of 2-chloroimidazolium salts with respect to 2-hydro species, as alluded to above, and the calculably smaller barrier to breaking C–X bonds (X = Cl or Br) it was proposed that the reaction of 1,2-dibromoethane (1.0 molar equivalents) with IMes be undertaken and monitored by ^{1}H NMR spectroscopy. This was deemed worthwhile as generation of 2-hydroimidazolium bromide from this reaction would make the formation of analogous 2-hydroimidazolium species from 1,2-dichloroethane reactions difficult to refute. The preparation was conducted using *ca.* 0.15 mmol of IMes in d_3-acetonitrile (*ca.* 1.0 cm^3). After stirring for two hours, characterisation by ^{1}H NMR spectroscopy identified (**4**) and two unknown compounds, one consistent with a symmetrical IMes based species (in 46:54 ratio with (**4**)), and another that was later identified as vinyl bromide. The formation of vinyl bromide testifies to the '*quasi*-elimination' of HBr from 1,2-dibromoethane, as does the subsequent isolation of [IMesH][Br], (**5**), see Scheme 1 (iv), and suggests that 1,1,2,2-tetrachloroethylene is the by-product in the synthesis of (**1**). On this evidence the formation of 2-hydroimidazolium salts using 1,2-dichloroethane occurs, contrary to the reports of Kuhn *et al.*[21]

Compound (**5**) was fractionally crystallised from acetonitrile (monoclinic, space group $P2_1$) in preference to its co-product (**4**). The molecular structures of the two distinct [IMesH][Br] units of (**5**) are shown in Fig. 4. The unit cell of (**5**) contains eight ion pairs, which describe two unique hydrogen bound bromide coordination architectures (only Br(2) shown in Fig. 4). The 2-position hydrogens of the imidazolium heterocycles

were located and refined isotropically to give reliable H···Br contact distances of 2.49(5) and 2.53(4) Å. These are within the van der Waals contacts for a H···Br hydrogen bond (2.95–3.15 Å).[27] The mean geometry within the heterocycles of (5) is similar to that of the imidazolium ring of [IMesH][Cl]·MeOH.[25] The mean interring N–C–N angle of 108.9° is in agreement with this statement (108.7(4)°) as are the mean carbenic carbon–nitrogen and C_2H_2 C–C bond lengths of 1.325 and 1.328 Å (1.326 and 1.353(6) Å, respectively). Like (4)·3MeCN, the structure of (5) describes coordination of the bromide anions by hydrogen bonds; these are those of the imidazolium 2-position hydrogen and C_2H_2 backbone hydrogens (for Br(1) only H(4) and not H(3)). This is augmented by lesser contacts that can be considered as borderline on the basis of van der Waals radii (see Fig. 4), although, as for the hydrogens within the structures of (1)·MeCN and (4)·3MeCN, the placement of these atoms has been calculated employing the riding model. None-the-less, the 4,5-position donor carbon is a prominent feature of all three supramolecular structures (1)·MeCN, (4)·3MeCN and (5).

Interestingly, whilst undertaking the ^{1}H NMR spectroscopic study detailed above, the fast deuterium labelling of the 4,5-postions of IMes was observed by the rapid loss of signals attributable to these protons after dissolution of IMes in d_3-acetonitrile. Recently, further reports detailing the analogous deuterium labelling of NHCs and imidazolium salts have come forward,[37,38] the latter relying upon palladium–carbon and palladium–alumina catalysts.[38] >From these it is evident that *deuterated* solvents that contain activated/acidic positions, *e.g.* CD_3OD, $(CD_3)CO$ and CD_3CN, are capable of initiating rapid hydrogen/deuterium exchange at the acidic 4,5-positions of NHCs and other imidazole based heterocycles. For NHCs this results as a consequence of their high Lewis basicity, which promotes the lability of D^+ at acidic/activated positions within the deuterated medium.

(v) Reaction of [IMesCl][Cl] with aluminium trichloride

Owing to the incomplete structure refinement of (1)·MeCN (50% of MeCN disorder could not be modelled, removed using 'SQUEEZE' program, see Experimental) the generation of the tetrachloroaluminate salt of (1) was deemed a worthy synthetic target in evaluating the subsequent coordination sphere of the 2-chloro atom and the suprastructural ramifications of inorganic anion inclusion as per the [{IMes}$_2$H][PF$_6$] study of ref. 25. The addition of pre-sublimed aluminium trichloride to an acetonitrile solution of (1) led to the formation of [IMesCl][AlCl$_4$], (6). Compound (6) was crystallised from the concentrated reaction mixture to yield solvent free (6) as small colourless rods in moderate yield (61%). An X-ray structure determination of (6) revealed an apparent lack of anion–cation interactions when compared to (1)·MeCN, (4)·3MeCN, and (5), however, of the four ion pairs per asymmetric unit (triclinic, space group $P\bar{1}$), one pair of IMesCl cations combine to form a bound cation–cation unit (see Fig. 5). This unit is bound by aromatic substituent π-electron donation to the electronically unsaturated 2-chloroimidazolium moiety. The remaining ions appear discrete without apparent inter-atom contacts. There is considerable interest in X–H···π interactions, not only from structural and theoretical standpoints, but also because of the recognition of this type of interaction in peptide and protein structure[39] as well as large supramolecular architectures.[40] To our knowledge, the locked 2-chloro cations in the molecular structure of (6) are unprecedented in the structural catalogue of imidazolium salts. The metrical parameters for the cation dimer are close to those listed for (1)·MeCN. For example, the N–C–N angle of (1) is 109.1(4)°, whilst the π-donation observed for the locked cation pair of (6) increases the mean cation locked N–C–N angle to 110.6°. The carbenic carbon to chlorine bonds of the cation

pair; ave. 1.665 Å, are shorter than those of the unpaired cations (mean 1.675 Å) and that of (1) (1.677(5) Å). This presumably results from the donation of the π-(mesityl) group to the C–Cl bond.

Experimental

IMes was prepared by a literature procedure.[36] 1,1,1,2,2,2-Hexachloroethane, carbon tetrabromide and dibromine were purchased from Aldrich and used as received. 1,2-Dibromoethane was purchased from Aldrich and freeze–thaw degassed prior to use. Aluminium trichloride was obtained from Aldrich and doubly sublimed prior to use. The solvents tetrahydrofuran and toluene were predried by storage over sodium wire, and in the case of acetonitrile over granular calcium hydride and P_2O_5. All solvents were then refluxed over the drying agent under an atmosphere of high purity argon or dinitrogen for 12 hours prior to collection, and freeze–thaw degassed prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BZH 300/52 spectrometer with a Varian console (300 MHz, 75.46 MHz) in C_6D_6 or CD_3CN and referenced to the residual ^{1}H or ^{13}C resonances of the solvent used. Infrared spectra were undertaken as Nujol mulls on sodium chloride plates and recorded on a Nicolet Nexus FTIR spectrophotometer between 4000 and 400 cm^{-1}. Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses for compounds (1)·MeCN, (3), (4)·3MeCN and (5) were conducted at the University of Otago, P.O. Box 56, Dunedin, New Zealand. Microanalyses for (6) were repeatedly low in carbon, hydrogen and nitrogen due to contamination with aluminium trichloride.

[IMesCl][Cl]·MeCN, (1)·MeCN

IMes (0.30 g, 0.99 mmol) and 1,1,1,2,2,2-hexachloroethane (0.25 g, 1.05 mmol) were combined in a Schlenk flask and solvated with acetonitrile (30 cm^3). The resulting amber solution was sonicated for 24 h. Removal of volatiles *in vacuo* gave a light brown solid that was washed with toluene (*ca.* 15 cm^3) and extracted into acetonitrile (*ca.* 5 cm^3). This was concentrated *in vacuo* and placed at −30 °C to yield the title compound as solvent dependent colourless blocks (0.38 g, 92%), mp (decomp). 306 °C. ^{1}H NMR (300 MHz, CD$_3$CN, 300 K): δ 1.93 [s, 3H, CH$_3$CN], 2.07 [s, 12H, *o*-CH$_3$], 2.36 [s, 6H, *p*-CH$_3$], 7.18 [s, 4H, *m*-CH], 7.99 [s, 2H, C$_2$H$_2$]. ^{13}C NMR (75.5 MHz, CD$_3$CN, 300 K): δ 16.9 [s, *o*-CH$_3$], 20.6 [s, *p*-CH$_3$], 125.8 [s, C$_2$H$_2$], 130.1 [s, *m*-C], 135.0 [s, *o*-CCH$_3$], 135.7 [s, NC(Cl)N] 141.4 [s, *ipso*-C], 142.7 [s, *p*-CCH$_3$]. MS APCI: m/z (%) 340 [[IMesCl]$^+$, 100]. IR (Nujol) v/cm^{-1}: 866 (m), 917 (m sh), 1030 (m), 1153 (m), 1296 (s), 1327 (s), 1547 (m), 1593 (m). Anal. Calc. for C$_{23}$H$_{27}$N$_3$Cl$_2$: C, 66.34; H, 6.54; N, 10.09. Found: C, 66.24; H, 6.45; N, 10.39%.

[IMesBr$_2$], (3)

A solution of carbon tetrabromide (1.09 g, 3.29 mmol) in THF (10 cm^3) was added dropwise to a solution of IMes (0.50 g, 1.64 mmol), also in THF (10 cm^3), over a period of *ca.* 30 mins. The resulting brown solution was stirred for 3 h. Subsequent removal of volatiles *in vacuo* gave a dark brown residue that was extracted into toluene (10 cm^3), concentrated, filtered and the filtrate placed at −30 °C to yield the title compound as colourless plates (0.61 g, 80%), mp (decomp) 176 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 300 K): δ 2.06 [s, 6H, *p*-CH$_3$], 2.08 [s, 12H, *o*-CH$_3$], 6.72 [s, 4H, *m*-CH]. ^{13}C NMR (75.5 MHz, C$_6$D$_6$, 300 K): δ 18.0 [s, *o*-CH$_3$], 21.1 [s, *p*-CH$_3$], 107.0 [s, C$_2$H$_2$], 129.1 [s, *m*-C], 135.8 [s, *o*-CCH$_3$], 136.8 [s, *ipso*-C],

138.3 [s, *p*-C*C*H$_3$], 221.2 [s, NCN]. MS APCI: *m/z* (%) 305 [[IMesH]$^+$, 100], 382 [(M-Br)$^+$, 33], 463 [MH$^+$, 54]. IR (Nujol) v/cm^{-1}: 856 (m sh), 886 (w), 933 (m), 974 (m), 1035 (m), 1096 (w sh), 1132 (w), 1204 (m), 1230 (m), 1250 (s sh), 1609 (m sh), 1706 (w sh), 1721 (w sh), 1757 (w sh). Anal. Calc. for C$_{21}$H$_{22}$N$_2$Br$_2$: C, 54.57; H, 4.80; N, 6.06. Found: C, 54.83; H, 4.55; N, 6.16%.

[IMesBr][Br]·3MeCN, (4)·3MeCN

Dibromine (0.36g, 0.116 cm^3, 2.25 mmol) was added added dropwise to a stirred solution of IMes in THF (30 cm^3) at room temperature. A colourless precipitate formed upon addition. After 3 hours stirring this was isolated by filtration, washed with toluene (10 cm^3) and extracted into acetonitrile (*ca.* 5 cm^3). Placement at −30 °C overnight yielded the title product as large clear colourless hexagonal rods (1.13 g, 85%), mp (decomp). 296 °C, solvent loss at 102 °C. ^{1}H NMR (300 MHz, CD$_3$CN, 300 K): δ 1.93 [s, 9H, C*H$_3$*CN], 2.04 [s, 12H, *o*-CH$_3$], 2.37 [s, 6H, *p*-CH$_3$], 7.19 [s, 4H, *m*-CH], 7.85 [s, 2H, C$_2$H$_2$]. ^{13}C NMR (75.5 MHz, CD$_3$CN, 300 K): δ 17.6 [s, *o*-CH$_3$], 21.2 [s, *p*-CH$_3$], 126.4 [s, NC(Br)CN], 127.2 [s, C$_2$H$_2$], 130.7 [s, *m*-C], 131.3 [s, *ipso*-C], 135.6 [s, *o*-*C*CH$_3$], 143.1 [s, *p*-*C*CH$_3$,]. MS APCI: *m/z* (%) 383 [[IMesBr]$^+$, 100]. IR (Nujol) v/cm^{-1}: 697 (m sh), 784 (m), 843 (m sh), 912 (w), 933 (w), 1040 (m), 1235 (s sh), 1557 (w), 1603 (w). Anal. Calc. for C$_{27}$H$_{33}$N$_5$Br$_2$: C, 55.21; H, 5.66; N, 11.92. Found: C, 55.01; H, 5.72; N, 11.69%.

[IMesH][Br], (5)

1,2-Dibromoethane (0.16 cm^3, 1.85 mmol) was added dropwise to a solution of IMes (0.56 g, 1.84 mmol) in acetonitrile (30 cm^3) at −30 °C. The amber solution was stirred overnight. Removal of volatiles *in vacuo* gave light red–orange solid that was washed with toluene (*ca.* 10 cm^3) and extracted into acetonitrile (*ca.* 10 cm^3) giving a bright red solution. This was concentrated *in vacuo* and placed at −30 °C to fractionally crystallise (5) as cubic orange tinted colourless blocks (0.30 g, 42%) mp 308 °C. ^{1}H NMR (300 MHz, CD$_3$CN, 300 K): δ 2.13 [s, 12H, *o*-CH$_3$], 2.35 [s, 6H, *p*-CH$_3$], 7.14 [s, 4H, *m*-CH], 7.75 [s, 2H, C$_2$H$_2$], 9.49 [br s, 1H, NC(H)N]. ^{13}C NMR (75.5 MHz, CD$_3$CN, 300 K): δ 17.6 [s, *o*-CH$_3$], 21.1 [s, *p*-CH$_3$], 125.4 [s, C$_2$H$_2$], 130.2 [s, *m*-C], 135.3 [s, *o*-*C*CH$_3$], 138.7 [s, *p*-*C*CH$_3$], 142.1 [s, *ipso*-C], 152.2 [s, NC(H)N]. MS APCI: *m/z* (%) 305 [[IMesH]$^+$, 100]. IR (Nujol) v/cm^{-1}: 682 (w), 764 (m), 861 (s), 938 (m), 963 (s), 1040 (s), 1102 (w), 1168 (m), 1224 (s), 1296 (m), 1322 (m), 1537 (s), 1603 (m). Anal. Calc. for C$_{21}$H$_{25}$N$_2$Br$_1$: C, 65.46; H, 6.54; N, 7.27. Found: C, 65.79; H, 6.53; N, 7.89%.

Subsequent attempts to isolate the second compound yielded a mixture of the imidazolium bromide and a second species. This second product analysed spectroscopically (^{1}H and ^{13}C NMR) as [IMesBr][Br] (see below), which was confirmed *via* an X-ray structure determination after fractional recrystallisation.

[IMesCl][AlCl$_4$], (6)

A solution of (1) (0.46 g, 1.23 mmol), prepared *via in vacuo* drying of its mono-acetonitrile solvate, in acetonitrile (15 cm^3) was added to a cooled (0 °C) solution of AlCl$_3$ (0.16 g, 1.20 mmol) in acetonitrile (15 cm^3). The resultant yellow solution was then warmed to room temperature and stirred overnight. Subsequent concentration *in vacuo*, filtration and placement at −30 °C yielded the title compound as small colourless rods (0.37 g, 61%), mp (decomp) 258 °C. ^{1}H NMR (300 MHz, CD$_3$CN, 300 K): δ 2.32 [s, 12H, *o*-CH$_3$], 2.47 [s, 6H, *p*-CH$_3$], 6.96 [s, 4H, *m*-CH], 7.42 [s, 2H, C$_2$H$_2$]. ^{13}C NMR (75.5 MHz, CD$_3$CN, 300 K): δ 14.0 [s, *o*-CH$_3$], 17.9

[s, *p*-CH$_3$], 122.4 [s, C$_2$H$_2$], 127.1 [s, *m*-C], 131.8 [s, *o*-*C*CH$_3$], 133.8 [s, NC(Cl)N], 138.7 [s, *ipso*-C], 139.7 [s, *p*-*C*CH$_3$]. MS APCI: *m/z* (%) 340 [[IMesCl]$^+$, 100]. IR (Nujol) v/cm^{-1}: 774 (w), 846 (w), 938 (s), 974 (m), 1040 (m), 1158 (m), 1230 (m), 1311 (s).

X-Ray diffraction data

For compounds (1)·MeCN, (3), (4)·3MeCN, (5),(6) hemispheres of data were collected (capillary sealed specimens) at room temperature on a Bruker SMART CCD diffractometer using the omega scan mode. Data sets were corrected for absorption using the program SADABS.[41] The structures were solved using direct methods and refined on F^2 using SHELXL97-2[42] and X-SEED[43] as an interface. All non-hydrogen atoms were located and were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined, except for compound (5) where H(1) and H(2) were found and refined isotropically. For compound (1)·MeCN, one acetonitrile molecule was disordered over four sites (0.5 occupancy on a mirror plane, *i.e.* 0.25 occupancy). The disorder of this molecule could not be successfully modelled. To simplify the refinement, the disordered solvent molecule was removed from the unit cell using the 'SQUEEZE' program (Platon). Crystal data; a summary of data collection and positional parameters appears in Table 1, selected bond lengths and angles appear in figure captions.

CCDC reference numbers 185383–185387. See http://www.rsc.org/suppdata/nj/b2/b204422f/ for crystallographic data in CIF or other electronic format.

Conclusion

In conclusion, the formation of what appear to be persistent hydrogen bonded anion coordination geometries by (1), (4) and (5) when crystallised from acetonitrile makes a worthy contribution to the ever-growing field of anion supramolecular chemistry.[28,29,33] All three compounds, and (6), display solid-state motifs that have either not been recognised or are unprecedented in the structural chemistry of imidazolium salts. The preparation of (3) heralds the synthesis of a completely air-stable NHC that we hope will be exploited rigorously in future synthetic studies.[11] These reactivity patterns are of interest to inorganic and organic synthesis alike because of increased understanding of unintended imidazolium salt formation and the identification of alternative paths to formation other than metal complex hydrolysis. Compounds (1), (4), (5) and (6) are also extremely topical given the current surfeit of imidazolium based ionic liquids popularised by 'green' preparative methodologies.[44]

Acknowledgements

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