Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

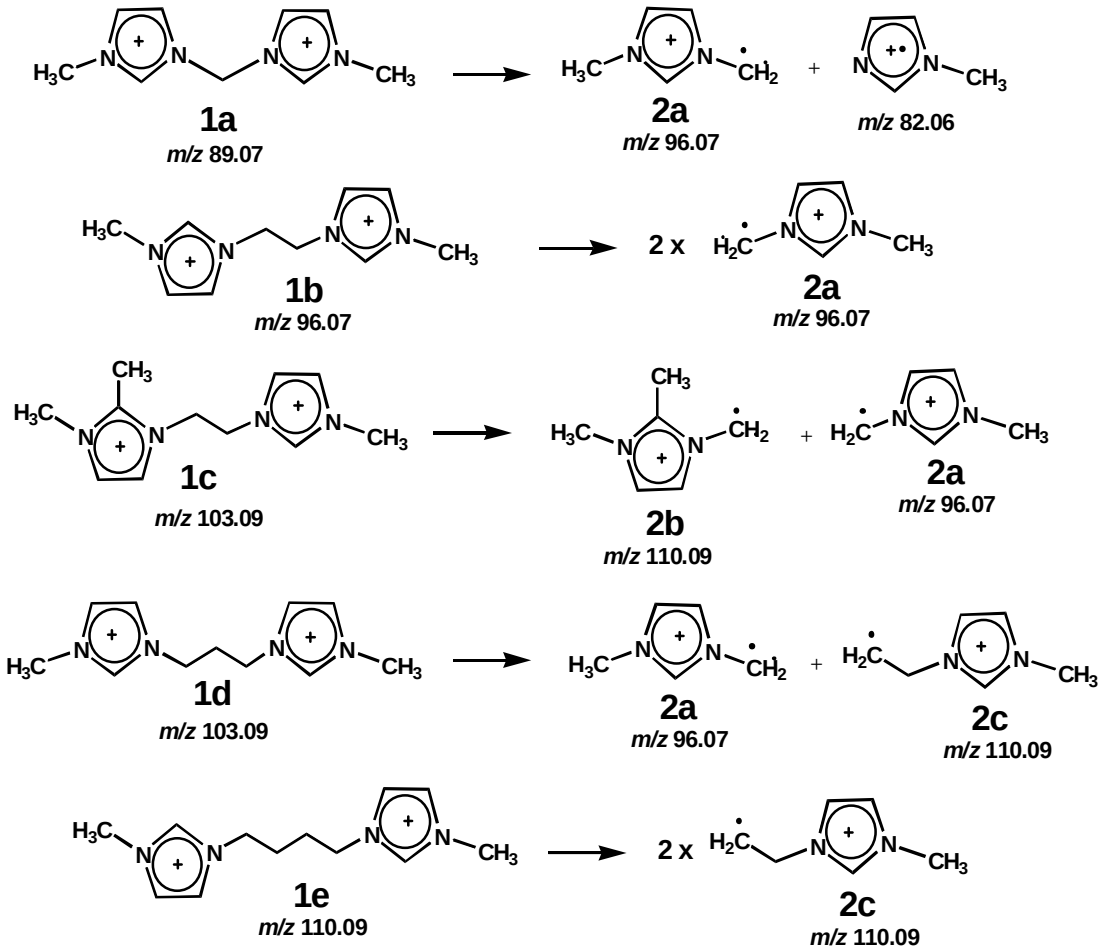
© Wiley-VCH 2007

69451 Weinheim, Germany

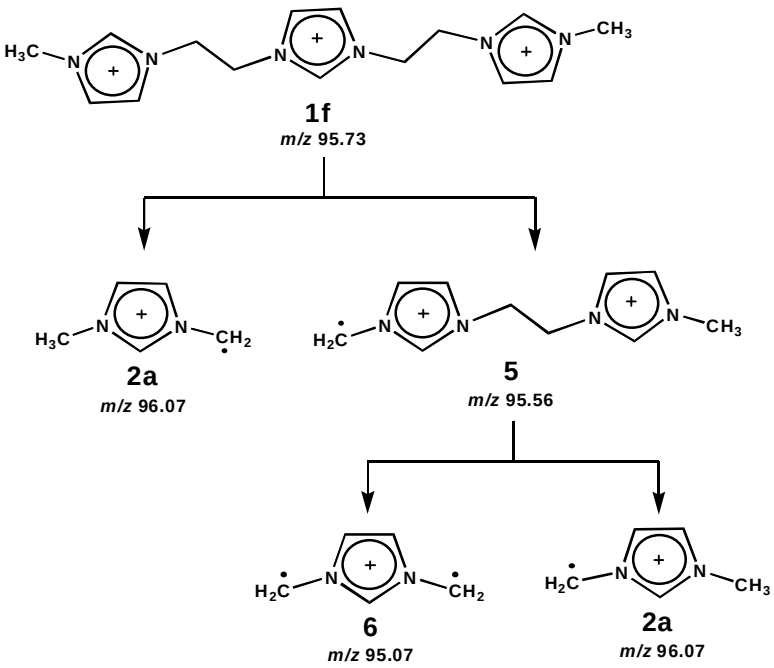
Multiply Charged (*Di*)-Radicals:

Fabiane M. Nachtigall,[1] Yuri Eberlim de Corilo,[1] Cláudia C. Cassol, Günter Ebeling, Nelson H. Morgon,[1] Jairton Dupont[2]* and Marcos N. Eberlin[1]*

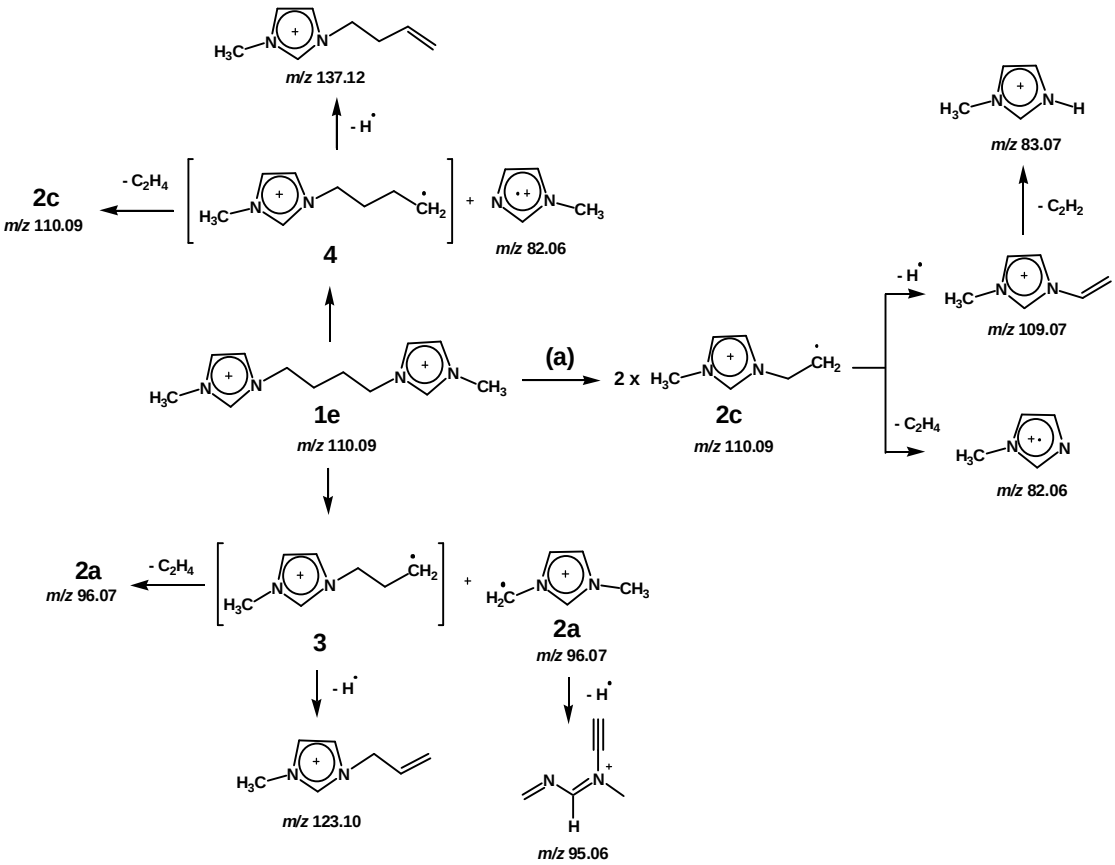
[1] ThoMSon Mass Spectrometry Laboratory Institute of Chemistry UNICAMP Campinas, SP, Brazil - 13083-970 E-mail: eberlin@iqm.unicamp.br [2]Laboratory of Molecular Catalysis Institute of Chemistry UFRGS Porto Alegre, RS, Brazil - 91501-970 E-mail: dupont@iq.ufrgs.br.



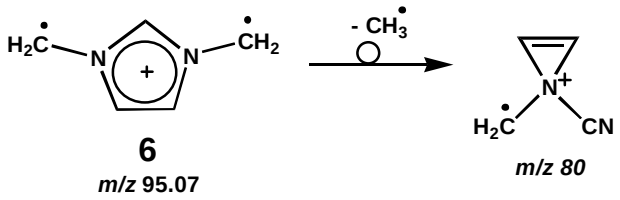
Scheme S1.



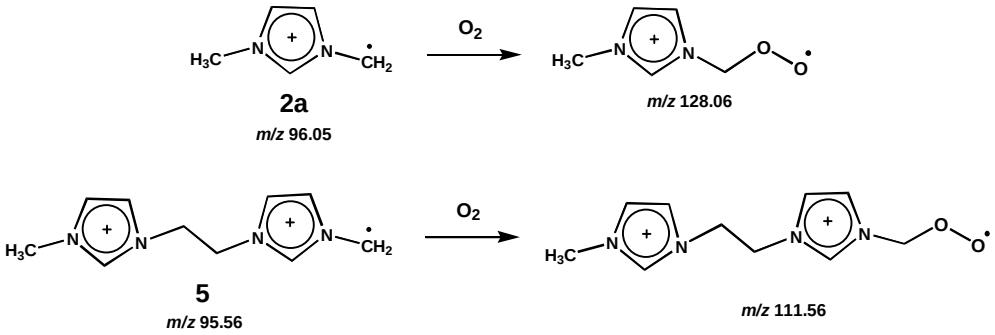
Scheme S2



Scheme S3.



Scheme S4.



Scheme S5.

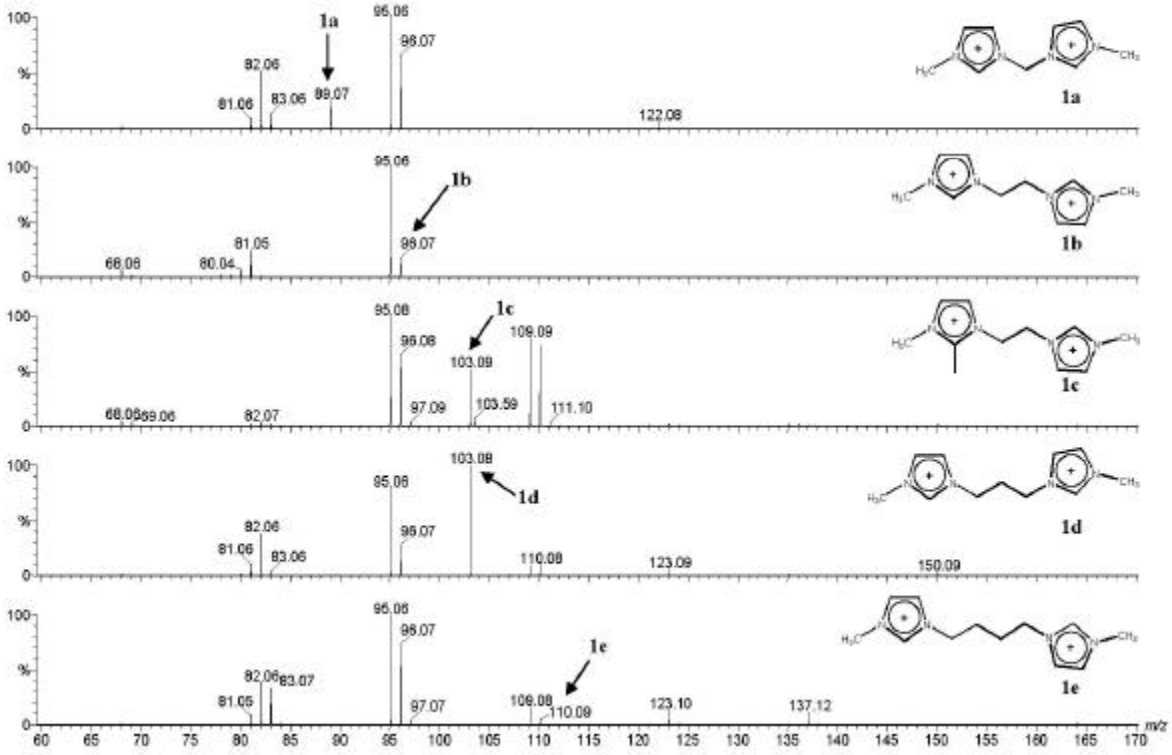


Figure S1. ESI-MS/MS for CID of the di-imidazolium ions **1a-e**.

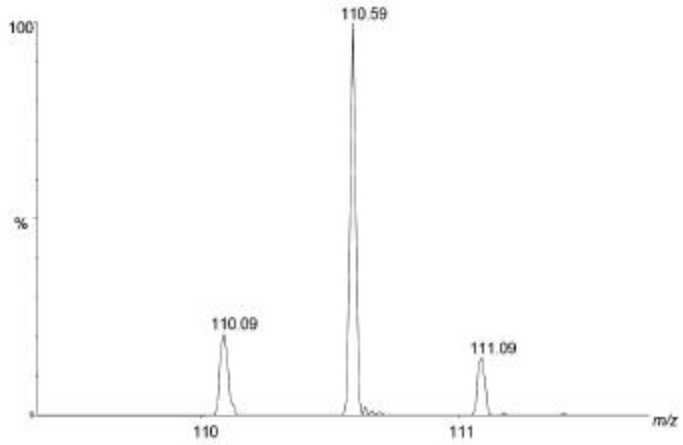


Figure S2. ESI-MS/MS for the ^{13}C isotopologue ion **1e** of *m/z* 110.59. Note that the "in-half" homolytic cleavage of the alkyl bridge is revealed by the formation of a pair of singly charged fragment ions of *m/z* 110.09 and 111.09 (^{13}C). Similar spectrum was collected for the ^{13}C isotopologue ion **1b** of *m/z* 96.59.

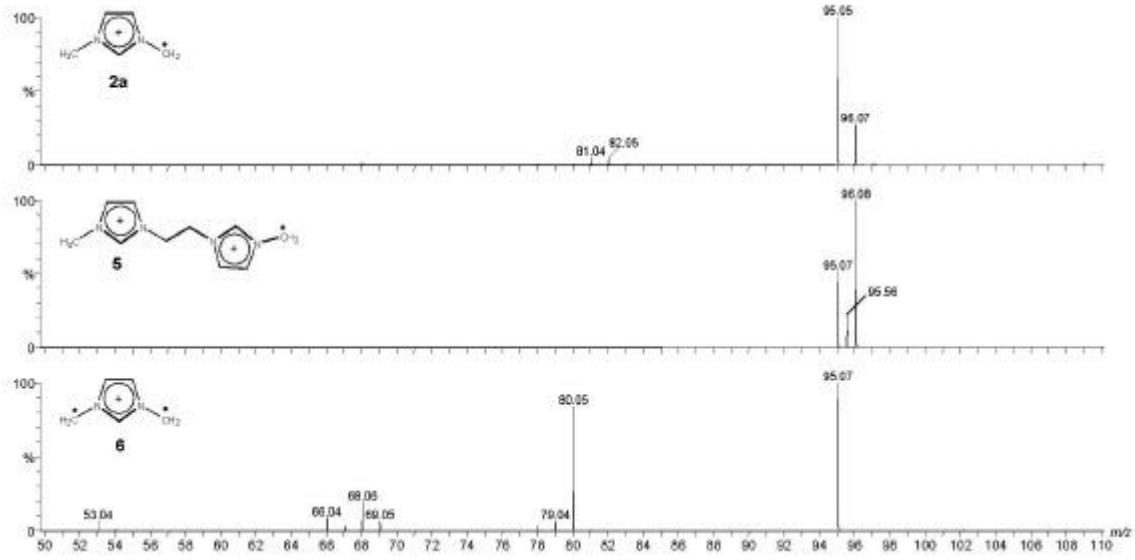
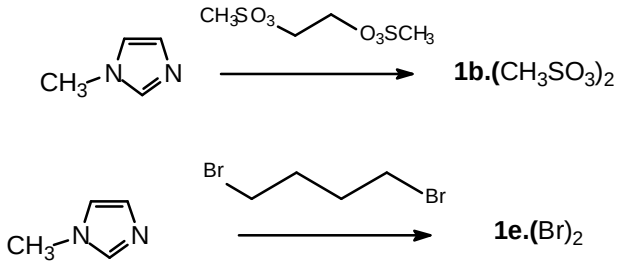


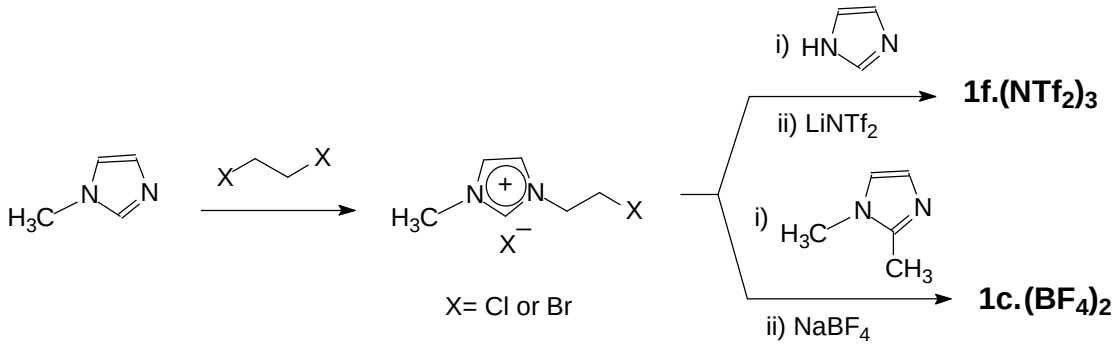
Figure S3. ESI-MS/MS for CID of the three types of charged radicals, that is: a) **2a** of *m/z* 96.07, b) **5** of *m/z* 95.56 and c) **6** of *m/z* 95.07 formed by dissociation of the *tri*-imidazolium ion **1f**.

General Remarks. Solvents were dried with suitable drying agents and distilled under argon prior to use. Chemicals were purchased from commercial sources (Acros or Aldrich) and used without further purification. NMR spectra were recorded on a Varian Inova 300. Infrared spectra were performed on a Bomem B-102 spectrometer. The calorimetric experiments were carried out on a 12 000 PL-DSC equipment with a heating rate of 10 ^{0}C/min. Bis (3-methylimidazolium-1-yl) methane di(iodide) **1a.(I)$_2$** and 1-methyl 3-(2-bromoethyl) imidazolium bromide were prepared, respectively, according to reported procedures.[i,ii] All the other imidazolium salts were prepared using a slightly modified procedure.[iii] 1,2-bis (3-methylimidazolium-1-yl) ethane di(methanesulfonate) **1b.(CH_3SO_3)$_2$** and 1,4-bis (3-methylimidazolium-1-yl) butane dibromide **1e.(Br)$_2$** were prepared in good yields by the reaction of two equivalents of 1-methylimidazole with ethylene di(methanesulfonate)[iv] and 1,4-dibromobutane, respectively (Scheme S6).



Scheme S6.

A mixture of 1,2-dimethylimidazole and 1-methyl 3-(2-chloroethyl) imidazolium chloride (easily prepared by the reaction of methylimidazole with a large excess of 1,2-dichloroethane) in acetonitrile heated to reflux for 4 h furnished 1-[2-(3-methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium dichloride. This salt, by simple anion metathesis with sodium tetrafluoroborate in water, yielded 1-[2-(3-methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium di(tetrafluoroborate) **1c.$(BF_4)_2$** in good yield (Scheme 2). The reaction of imidazole with equimolar amounts of 1-methyl 3-(2-bromoethyl) imidazolium bromide in acetonitrile at 60 °C for 48 h afforded 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tribromide which, by reaction with lithium trifluoromethanesulfonyl imidate, yielded the desired 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tri(trifluoromethanesulfonyl imidate) **1f.$(NTf_2)_3$** as a pale yellow greasy solid (Scheme S7).



Scheme S7.

Synthesis of 1,2-bis (3-methylimidazolium-1-yl) ethane di(methanesulfonate) 1b.$(CH_3SO_3)_2$. Ethylene di(methanesulfonate) (3.80 g, 17.2 mmol) was mixed with 1-methylimidazole (2.80 g, 34.4 mmol) and the reaction mixture was kept at 60 °C for 48 h. The resulting solid was crushed under acetone, filtered, washed with small portions of acetone and dried under reduced pressure, leaving the desired 1,2-bis (3-methylimidazolium-1-yl) ethane di(methanesulfonate) **1b.$(CH_3SO_3)_2$** as colorless crystals (5.89 g, 88 % yield). Melting point: 177.3 °C. ^{1}H NMR (dmso d_6) (ppm) d: 9.13 (s, 2H, CH imidazolium); 7.72 (t, 2H, *J* = 1.8 Hz, CH imidazolium); 7.14 (s, 2H, *J* = 1.8 Hz, CH imidazolium); 4.71 (s, 4H, NCH_2CH_2N); 3.85 (s, 6H, NCH_3); 2.36 (s, 6H, CH_3SO_3). ^{13}C NMR (dmso d_6) (ppm) d: 137.4, 123.9 and 122.4 (CH imidazolium); 48.4 (NCH_2CH_2N) 37.6 (NCH_3); 35.9 (CH_3SO_3).

Synthesis of 1-methyl 3-(2-chloroethyl) imidazolium chloride. A mixture of 1-methylimidazole (10.0 g, 122 mmol) and 1,2-dichloroethane (50.0 g, 505 mmol) was heated to reflux for 3 h. The oily precipitate was separated, washed with ethyl acetate (30 mL) and dissolved in a mixture of isopropanol (10 mL) and acetone (30 mL). This solution was kept in a freezer overnight, to ensure the crystallization of the byproduct 1,2-bis (3-methylimidazolium-1-yl) ethane dichloride. The remaining solution was separated from the crystals and was evaporated, giving the desired 1-methyl 3-(2-chloroethyl) imidazolium chloride

as pale amber oil, sufficiently pure for further work (7.80 g, 35 % yield). ^{1}H NMR (dmso d_6) (ppm) d: 9.63 (s, 1H, CH imidazolium); 8.00 (s, 1H, CH imidazolium); 7,86 (s, 1H, CH imidazolium); 4.61 (t, 2H, J= 5.5 Hz, CH_2Cl); 4,13 (t, 2H, J= 5.5 Hz, NCH_2); 3.91 (s, 3H, NCH_3).

Synthesis of 1-[2-(3-methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium dichloride. A mixture of 1,2-dimethylimidazole (5.07 g, 52.8 mmol) and 1-methyl 3-(2-chloroethyl) imidazolium chloride (9.56 g, 52.8 mmol) was dissolved in acetonitrile (50 mL) and heated to reflux for 4 h. The resulting white precipitate of 1-[2-(3-methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium dichloride was filtered off, washed with cold acetonitrile(2 x 10 mL) and dried under reduced pressure (10.95 g, 75 % yield). ^{1}H NMR (dmso d_6) (ppm) d: 9.56 (s, 1H, CH imidazolium); 7.95 (s, 1H, CH imidazolium); 7.76 (s, 1H, CH imidazolium); 7.65 (br s, 1H, CH imidazolium); 7.57 (br s, 1H, CH imidazolium); 4.72 (m, 4H, NCH_2CH_2N); 3.86 (s, 3H, NCH_3); 3.76 (s, 3H, NCH_3); 2.65 (s, 3H, CH_3). ^{13}C NMR (dmso d_6) (ppm) d: 145.3 (C quat. imidazolium); 137.7, 123.6, 122.7, 122.5 and 121.0 (CH imidazolium); 47.6 and 47.0 (NCH_2CH_2N); 35.9 and 34.9 (NCH_3); 9.6 (CH_3).

Synthesis of 1-[2-(3-methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium di(tetrafluoroborate) 1c.$(BF_4)_2$. 1-[2-(3-Methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium dichloride (5.00 g, 18.0 mmol) was dissolved in water (20 mL) and sodium tetrafluoroborate (3.0 g, 27.2 mmol) was added. The resulting mixture was stirred at room temperature for 1h. The water was evaporated under reduced pressure and the residue was extracted with methylene chloride (2 x 20 mL). The combined organic extract was filtered through a short pad of basic alumina and the solvent was evaporated under reduced pressure, leaving the desired 1-[2-(3-methylimidazolium-1-yl)-ethyl] 2,3-dimethyl imidazolium di(tetrafluoroborate) **1c.$(BF_4)_2$** as a pale yellow solid (5,30g, 77 % yield). Melting point: 114.7 °C. ^{1}H NMR (dmso d_6) (ppm) d: 9.05 (s, 1H, CH imidazolium); 7.71 (s, 1H, CH imidazolium); 7.66 (s, 1H, CH imidazolium); 7.59 (br s, 1H, CH imidazolium); 7.36 (br s, 1H, CH imidazolium); 4.60 (s, 4H, NCH_2CH_2N); 3.84 (s, 3H, NCH_3); 3.74 (s, 3H, NCH_3); 2.54 (s, 3H, CH_3). ^{13}C NMR (dmso d_6) (ppm) d: 145.2 (C quat. imidazolium); 137.3, 123.9, 122.7, 122.6 and 121.0 (CH imidazolium); 47.8 and 47.1 (NCH_2CH_2N); 36.0 and 34.9 (NCH_3); 9.2 (CH_3).

Synthesis of 1,3-bis (3-methylimidazolium-1-yl) propane dibromide 1d.$(Br)_2$.

1,3-Dibromopropane (2.02 g, 10.0 mmol) was mixed with 1-methylimidazole (1.64 g, 20.0 mmol) and the reaction mixture was kept at room temperature for 48 h. The resulting solid was crushed under acetone, filtered, washed with small portions of acetone and dried under reduced pressure, leaving the desired 1,3-bis (3-methylimidazolium-1-yl) propane di(bromide) **1d.$(Br)_2$** as pale amber crystals (2.56 g, 70 % yield). Melting point: 158.9 °C. ^{1}H NMR (D_2O) (ppm) d: 8.94 (br s, 2H, CH imidazolium); 7.67 (t, 2H, J = 1.9 Hz, CH imidazolium); 7.60 (s, 2H, J = 1.9 Hz, CH imidazolium); 4.47 (t, 4H, J = 7.2 Hz, NCH_2); 4.04 (s, 6H, NCH_3); 2.66 (quintet, 2H, J = 7.2 Hz, CH_2). ^{13}C NMR (D_2O) (ppm) d: 136.4, 124.1 and 122.4 (CH imidazolium); 46.6 (NCH_2); 36.5 (NCH_3); 30.0 (CH_2).

Synthesis of 1,4-bis (3-methylimidazolium-1-yl) butane dibromide 1e.$(Br)_2$. 1,4-Dibromobutane (10.79 g, 50.0 mmol) was mixed with 1-methylimidazole (8.16 g, 99.5 mmol) and the reaction mixture was kept at room temperature for 48 h. The resulting dark solid was crushed under acetone, filtered, washed with small portions of acetone and dried under reduced pressure, leaving the desired 1,4-bis (3-methylimidazolium-1-yl) butane di(bromide) **1c.$(Br)_2$** as light brown crystals (14.62 g, 77 % yield). Melting point: 127.9 °C. ^{1}H NMR (D_2O) (ppm) d: 8.59 (s, 2H, CH imidazolium); 7.33 (t, 2H, *J* = 1.8 Hz, CH imidazolium); 7.29 (s, 2H, *J* = 1.8 Hz, CH imidazolium); 4.10 (t, 4H, *J* = 4.9 Hz, NCH_2); 3.74 (s, 6H, NCH_3); 1.76 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) (ppm) d: 136.8, 129.1 and 118.6 (CH imidazolium); 46.6 (NCH_2); 30.6 (NCH_3); 25.8 (CH_2).

Synhthesis of 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tribromide. Imidazole (2.80 g, 41.5 mmol) was mixed with 1-methyl 3-(2-bromoethyl) imidazolium bromide (11.20 g, 41.5 mmol) in acetonitrile (20 mL) and the reaction mixture was heated to 60 °C under stirring for 48 h. The solvent was evaporated under reduced pressure and the resulting white precipitate was dissolved in a minimum amount of hot methanol. Hot isopropanol was added until the appearance of the first sign of turbidity and then the solution was kept in a refrigerator overnight to ensure crystallization. The resulting colorless crystals of 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tribromide were filtered, washed with cold isopropanol and dried under reduced pressure (1,75 g, 16% yield). Melting point: 258 °C ^{1}H NMR (dmso d_6) (ppm) d: 9.21 (s, 1H, CH imidazolium); 9.15 (s, 2H, CH imidazolium); 7.72 (s, 2H, CH imidazolium); 7.68 (s, 2H, CH imidazolium); 7.65 (s, 2H, CH imidazolium); 4.71 (s, 8H, NCH_2CH_2N); 3.85 (s, 6H, NCH_3). ^{13}C NMR (dmso d_6) (ppm) d: 124.6, 123.5 and 123.1 (CH imidazolium); 49.3 and 48.8 (NCH_2CH_2N); 36.7 (NCH_3); (the two types of NCN imidazolium carbons have not been observed; however, these are observable in the ^{13}C NMR spectrum of derivative **1f.$(NTf_2)_3$**).

Synthesis of 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tri(trifluoromethanesulfonyl imidate) 1f.$(NTf_2)_3$. A solution of lithium trifluoromethanesulfonyl imidate (4.48 g, 15.6 mmol) in water (75 mL) was added to a solution of 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tribromide (2.74 g, 5.20 mmol) in water (75 mL). The resulting mixture was stirred for 3h. and then extracted with ethyl acetate (2x 30 mL). The combined extract was dried with magnesium sulfate and the solvent was evaporated under reduced pressure, leaving the desired 1,3-bis [2-(3-methylimidazolium-1-yl)-ethyl] imidazolium tri(trifluoromethanesulfonyl imidate) **1f.$(NTf_2)_3$** as a pale yellow greasy solid (4.51 g, 77 % yield). An analytical sample was obtained by recrystallization with isopropanol / methanol. Melting point: 82.7 °C ^{1}H NMR (dmso d_6) (ppm) d: 8.98 (s, 2H, CH imidazolium); 8.93 (br s, 1H, CH imidazolium); 7.72 (br s, 2H, CH imidazolium); 7.63 (s, 2H, CH imidazolium); 7.54 (br s, 2H, CH imidazolium); 4.65 (s, 8H, NCH_2CH_2N); 3.86 (s, 6H, NCH_3). ^{13}C NMR (dmso d_6) (ppm) d: 137.9, 137.8, 124.6, 123.6 and 123.0 (CH imidazolium); 122.0 (q, $^1J_{CF}$ = 322 Hz, $N(SO_2CF_3)_2$); 49.4 and 49.1 (NCH_2CH_2N); 36.6 (NCH_3).

Theoretical calculations. Further comments:

The high concentration of spin density on the α-methylene groups of ions **1a-f** corroborates their expected distonic natures with charge and spin sites apart from each other. These high spin concentrations show the ions to display high *mono*- or *di*-radical character on the α-methylene groups whereas the charge is confined (as long as covalent bond formalism is considered) within their aromatic imidazolium ion rings.

For ions **1a-f** (some optimized structures shown in Figure 3), major bond angles (ca 111.9^{o}) and lengths (ca 1.54 A) are calculated at the B3LYP/6-31G(d,p) level to fall within average values for an unstrained alkyl chain (for butane for instance, a and ß). This result indicates that intramolecular repulsion of the two (or three) positively charged imidazolium ion rings causes negligible stretching of the alkyl chain.

[i] Liu, Q.; van Rantwijk, F.; Sheldon, R. A.; *J. Chem. Technol. Biotechnol.*; 2006, *81*, 401.

[ii] Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P.; *Organometallics*; **2005**, *24*, 4241.

[iii] Cassol, C. C.; Ebeling, G.; Ferrera, B.; Dupont, J.; *Adv. Synth. Catal.*; **2006**, *348*, 243.

[iv] Sekera, V. C.; Marvel,C. S.; *J. Am. Chem. Soc.*; **1933**, *55*, 345.