Supplementary Information: Experimental details and tables of viscosity and microanalytical data

Experimental

General considerations

All operations were performed using standard Schlenk techniques with a dinitrogen atmosphere in order to reduce exposure to water. ^{1}H-, ^{13}C{^{1}H}-NMR spectra were collected on a Varian Unity-300 operating at 300 and 75 MHz respectively, or on a Varian INOVA-500 operating at 500 and 126 MHz respectively, in $CDCl_3$, referenced to residual solvent peaks. DSC was performed on a TA Q100: Samples of mass 0.5–10 mg were sealed in an aluminium pan and placed in the furnace with a 50 mL/min nitrogen stream; the temperature was raised at 10 °C/min. Viscosities were measured on an Anton Parr AMVn falling-ball viscometer or a Brookfield-Wells cone-and-plate viscometer operating at 0.005 – 0.2 s^{-1} rotation speed range. TGA data were collected on dried samples using a TA Instruments SDT Q600 at 10 °C/min after further drying at 100 °C for one hour in the instrument. Electrospray mass spectrometry was carried out on a Micromass LCT, with samples dissolved in acetonitrile. Water contents were determined by Karl Fischer titration using a Metrohm 831 KF coulometer. Chloride contents were determined by potentiometry using a Radiometer PHM64 Research pH meter with a Thermoscientific Orion 9617BNWP ionplus sure-flow chloride-selective electrode. Cyclic voltammetry was carried out at 100 mV/s on a AutolabEco Chemie, with associated GPES software, under a dinitrogen atmosphere, using a platinum (1 mm diameter) working electrode, platinum wire counter electrode and a silver reference electrode. Mircoanalysis was performed by Campbell Microanalytical Laboratory, Dunedin. Pentachlorocyclopropane was prepared from sodium trichloroacetate and trichloroethylene.[1] AgDCA was prepared from $AgNO_3$ and NaDCA. The amines were obtained commercially and distilled from KOH prior to use. CH_2Cl_2, $CHCl_3$, CH_3CN, toluene and acetone were used as supplied unless otherwise noted. NaDCA, HBF_4(aq), benzylchloride and 2-naphthol were used as obtained commercially. A commercially-obtained sample of LiTFSA was kindly provided by Prof. Ken Marsh. Sodium-β-naphthoxide was prepared from 2-naphthol according to a literature method.[2]

General Syntheses

Pentachlorocyclopropane was added to freshly distilled CH_2Cl_2 (from CaH_2). This was stirred at 0 °C under a dinitrogen atmosphere. A 7–8 fold excess of amine was added over 1 h and the solution stirred at 0 °C for a further 4 h and then at ambient temperature for 18 h, before heating to reflux (65 °C) for 5 h. The solution, usually yellow/orange in colour, was then placed under vacuum to remove the solvent.

The order of addition of pentachlorocyclopropane and amine can be reversed and, in some reactions, this resulted in products that were less coloured. In some reactions, four equivalents of the secondary amine was replaced by triethylamine. This modification may be useful if the secondary ammonium salt byproduct is hard to separate.

Removal of the secondary ammonium salts was carried out in several ways. Four options are outlined below. For some reactions, it was advantageous to use a combination of methods, which were selected depending on the solubilities of the species involved.

(i) The triaminocyclopropenium salt was extracted from an aqueous solution using chloroform or dichloromethane. The organic solvent was removed under vacuum.

(ii) A 1:2 mixture of acetonitrile:toluene was added to the dried triaminocyclopropenium and secondary ammonium salts. The solution was cooled in the freezer to precipitate out the secondary ammonium salt, which was then filtered off.

(iii) Dichloromethane was removed *in vacuo*. Acetone was added to precipitate the secondary ammonium salt, which was then filtered from the solution comprising the triaminocyclopropenium salt.

(iv) Dichloromethane was removed *in vacuo*. Aqueous NaOH was added to convert the secondary ammonium salt to the amine which was then removed by washing with petroleum ether or diethyl ether. The aqueous solution was then neutralized with HCl before removing the water *in vacuo*. Addition of acetone precipitated NaCl, which was filtered off. NaCl could also be removed by washing a chloroform or dichloromethane solution of the triaminocyclopropenium salt with water.

Tris(dimethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NMe_2)_3]NTf_2$

$[C_3(NMe_2)_3]Cl$ (3.5 g, 17.2 mmol) was stirred with $LiNTf_2$ (15.0 g, 52.3 mmol) in H_2O (200 mL). The product was extracted with dichloromethane/diethyl ether mix (200 mL, 1:3), washed with H_2O (3 x 100 mL) and dried *in vacuo* to yield colourless crystals (1.5 g, 19.5%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NMe_2)_3]Cl$ with an additional peak at 119.8 ppm in the ^{13}C NMR spectrum due to NTf_2.

Tris(diethylamino)cyclopropenium chloride, $[C_3(NEt_2)_3]Cl$

C_3Cl_5H (66.7g, 311 mmol) and $HNEt_2$ (213 g, 2910 mmol) gave an orange liquid (77.0 g, 86.0% yield), that slowly solidified after separation from diethylammonium chloride using options (iii), (iv) and then (i). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.36 (q, $^3J_{HH} = 7.3$ Hz, 12H, NCH_2), 1.22 (t, $^3J_{HH} = 7.4$ Hz, 18H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 115.99 (C_3), 47.07 (CH_2), 14.24 (CH_3). ES-MS^+: m/z 252 (100%, M^+).

Tris(diethylamino)cyclopropenium tetrafluoroborate, $[C_3(NEt_2)_3]BF_4$

$[C_3(NEt_2)_3]Cl$ (5.77 g, 20.1 mmol) was stirred with aqueous HBF_4 (11 mL, 35%, 60 mmol) in H_2O (50 mL). The product was extracted with dichloromethane (50 mL) and washed again with aqueous HBF_4 (11 mL, 35%, 60 mmol). The product was then washed with H_2O (3x 50 mL), until the pH was neutral, and dried *in vacuo*, yielding an orange liquid (5.3 g, 78.4%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_3]Cl$.

Tris(diethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_3]NTf_2$

$[C_3(NEt_2)_3]Cl$ (7.30 g, 25.4 mmol) was stirred with $LiNTf_2$ (21.8 g, 76.0 mmol) in H_2O (200 mL). The product was extracted with chloroform (200 mL), washed with H_2O (3 x 200 mL) and dried *in vacuo* to yield an orange liquid (11.5 g, 85.2%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_3]Cl$ with an additional peak at 119.8 ppm in the ^{13}C NMR spectrum due to NTf_2.

Tris(dipropylamino)cyclopropenium chloride, $[C_3(NPr_2)_3]Cl$

$HNPr_2$ (88.6 g, 0.875 mol) was dissolved in CH_2Cl_2 (250 mL) and cooled to 0 °C. C_3Cl_5H (25.0 g, 0.117 mol) was added dropwise and the solution stirred overnight. The solution was refluxed for 3 h, before CH_2Cl_2 and excess amine was removed *in vacuo*. Acetone (200 mL) was added and the $[H_2NPr_2]Cl$ precipitate were filtered off. After removal of acetone under vacuum, the residual $[H_2NPr_2]Cl$ was removed by washing a CH_2Cl_2 solution (250 mL) with H_2O (3 x 150 mL). Removal of CH_2Cl_2 *in vacuo* yielded an orange liquid which solidified overnight (36.9 g, 84.9%). ^1H NMR (500 MHz, $CDCl_3$): δ 3.25 (t, $^3J_{HH} = 8.0$ Hz, 12H, NCH_2), 1.65 (m, 12H, NCH_2CH_2), 0.92 (t, $^3J_{HH} = 7.3$ Hz, 18H, $NCH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 115.98 (C_3), 52.22 (NCH_2), 21.81 (NCH_2CH_2), 10.52 (CH_3). ES-MS^+: m/z 336 (100%, M^+).

Tris(dipropylamino)cyclopropenium tetrafluoroborate, $[C_3(NPr_2)_3]BF_4$

$[C_3(NPr_2)_3]Cl$ (7.49 g, 20.1 mmol) was dissolved in water (20 mL). HBF_4 (35%, 10 mL) was added to the solution, stirred and the $[C_3(NPr_2)_3]BF_4$ was then extracted with chloroform. HBF_4 (35%, 10 mL) was added to the chloroform extract, stirred and washed with 20 mL of water. The previous step was repeated. The resulting solution was washed with water until the pH was neutral. The solvent was removed under vacuum and the product formed a white solid (7.96 g, 93%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NPr_2)_3]Cl$.

Tris(dipropylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NPr_2)_3]NTf_2$

Metathesis to the NTf_2 salt was carried out by mixing $[C_3(NPr_2)_3]Cl$ (17.5 g, 47.1 mmol) with 3 equivalents of $LiNTf_2$ in H_2O (100 mL), followed by addition of $CHCl_3$ (100 mL) and washing with H_2O (3 x 100 mL). Removal of $CHCl_3$ *in vacuo* yielded an orange liquid (24 g, 83 %). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NPr_2)_3]Cl$ with an additional peak in the ^{13}C NMR due to NTf_2. Water content: 100 ppm.

Tris(dibutylamino)cyclopropenium chloride, $[C_3(NBu_2)_3]Cl$

C_3Cl_5H (25.0g, 117 mmol) and $HNBu_2$ (123 g, 950 mmol) gave a light brown liquid (50.8 g, 95.5% yield) that slowly solidified. The product was separated from dibutylammonium chloride using option (iii) and then (i) with dichloromethane. This was followed by washing with petroleum ether (4 x 50 mL) to remove residual amine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.27 (t, $^3J_{HH}$ = 7.91 Hz, 12H, NCH_2), 1.57 (m, 12H, NCH_2CH_2), 1.29 (m, 12H, $NCH_2CH_2CH_2$), 0.91 (t, $^3J_{HH}$ = 7.03 Hz, 18H, CH_3). ^{13}C NMR (75MHz, $CDCl_3$): δ 116.2 (C_3), 52.6 (NCH_2), 30.7 (NCH_2CH_2), 19.6 ($NCH_2CH_2CH_2$), 13.5 (CH_3). ES-MS$^+$: m/z 420 (100%, M^+).

Tris(dibutylamino)cyclopropenium tetrafluoroborate, $[C_3(NBu_2)_3]BF_4$

$[C_3(NBu_2)_3]Cl$ (6.17 g, 13.6 mmol) was stirred with HBF_4 (20 mL, 35%, 110 mmol) in H_2O (50 mL). The product was extracted with dichloromethane (75 mL) and washed again with HBF_4 (20 mL, 35%, 110 mmol). The organic layer was then washed with H_2O (3 x 50 mL) until the pH was neutral and dried *in vacuo* to yield an orange liquid (4.13 g, 79.6%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(NBu_2)_3]Cl$.

Tris(dibutylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NBu_2)_3]NTf_2$

$[C_3(NBu_2)_3]Cl$ (10.74 g, 23.6 mmol) was stirred with aqueous $LiNTf_2$ (7.8 g, 27.2 mmol) in water (100 mL). The product was extracted with dichloromethane (40 mL) and washed with H_2O (2 x 40 mL). Additional aqueous $LiNTf_2$ (7.7 g, 26.8 mmol) was added, and the solution was then washed with H_2O (3x 30 mL) and dried *in vacuo* to yield an orange liquid (12.9 g, 78.0%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(NBu_2)_3]Cl$ with an additional peak in the ^{13}C NMR due to NTf_2.

Tris(dibutylamino)cyclopropenium dicyanoamide, $[C_3(NBu_2)_3]DCA$

$[C_3(NBu_2)_3]Cl$ (6.00 g, 13.2 mmol) was stirred with AgDCA (7.8 g, 27.2 mmol) in H_2O (100 mL). Dichloromethane (150 mL) was added to form a separate layer containing the traiminocyclopropenium salt. A fine filter was used to remove solid AgCl and the solution was washed with H_2O (2 x 100 mL). The organic layer was concentrated and filtered again. It was then dried *in vacuo* to yield a yellow liquid (5.06 g, 79.0%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(NBu_2)_3]Cl$ with an additional peak in the ^{13}C NMR due to DCA.

Tris(dibutylamino)cyclopropenium trifluoromethanesulfonate, $[C_3(NBu_2)_3]OTf$

$[C_3(NBu_2)_3]Cl$ (6.00 g, 13.2 mmol) was stirred with LiOTf (2.25 g, 14.5 mmol) in H_2O (100 mL). The product was extracted with dichloromethane (75 mL), washed with H_2O (5 x 100 mL), and dried *in vacuo* to yield a yellow solid (5.95 g, 79.4%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(NBu_2)_3]Cl$ with an additional peak in the ^{13}C NMR due to OTf.

Tris(butylmethylamino)cyclopropenium chloride, $[C_3(NBuMe)_3]Cl$

C_3Cl_5H (25.0 g, 117 mmol) and $HNBuMe_2$ (81.0 g, 929 mmol) gave a light yellow liquid (35.0 g, 90.9% yield) after separation of butylmethylammonium chloride using option (iii) then (i) with chloroform. It was then washed with diethyl ether (2 x 100 mL) and petroleum ether (2 x 75 mL) to remove residual amine. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.29 (t, $^{3}J_{HH}$ = 7.8 Hz, 6H, NCH_2), 3.12 (s, 9H, NCH_3), 1.56 (m, 6H, NCH_2CH_2), 1.27 (m, 6H, $NCH_2CH_2CH_2$), 0.88 (t, $^{3}J_{HH}$ = 7.5 Hz, 9H, CH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 116.75 (C_3), 55.32 (NCH_2), 40.18 (NCH_3), 29.89 (NCH_2CH_2), 19.71 ($NCH_2CH_2CH_2$), 13.64 (CH_2CH_3).

Tris(butylmethylamino)cyclopropenium tetrafluoroborate, $[C_3(NBuMe)_3]BF_4$

$[C_3(NBuMe)_3]Cl$ (2.02 g, 6.13 mmol) was stirred with HBF_4 (1.3 mL, 35%, 7.23 mmol) in H_2O (15 mL). The product was extracted with chloroform (3 x 10 mL), and washed twice more with HBF_4 (1.3 mL, 35%, 7.23 mmol) in H_2O (15 mL). It was then washed with H_2O (3 x 30 mL) until the pH was neutral and was dried *in vacuo* to yield a brown liquid (2.19 g, 93.9%). ^{1}H, ^{13}C NMR and MS^+ as for $[C_3(NBuMe)_3]Cl$.

Tris(butylmethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NBuMe)_3]NTf_2$

$[C_3(NBuMe)_3]Cl$ (3.00 g, 9.10 mmol) was stirred with $LiNTf_2$ (5.00 g, 17.4 mmol) in H_2O (100 mL). The product was extracted with chloroform (50 mL), washed with H_2O (3 x 50 mL) and was dried *in vacuo* to yield a yellow liquid (3.90 g, 74.6%). ^{1}H, ^{13}C NMR and MS^+ as for $[C_3(NBuMe)_3]Cl$ with an additional peak in the ^{13}C NMR due to NTf_2.

Benzylation of sodium-β-naphthoxide. Sodium-β-naphthoxide (0.210 g, 1.26 mmol) was dissolved in $[C_3(NBu_2)_3]BF_4$ (1.71 g, 3.3 mmol) over 1 h. Benzylchloride (0.160 g, 1.25 mmol) was added and the solution stirred at 25 °C for 24 h. Addition of 10 mL of 1:2 water/ethanol dissolves the ionic liquid and precipitates the organic products. Analysis was done using ^{1}H-NMR spectroscopy to determine the product ratio.

References

1. C. Gluek, V. Poignee, H. Schwager, Synthesis, 1987, **3**, 260.
2. N. Kornblum, P. J. Berrigan, W. J. le Noble, *J. Am. Chem. Soc.*, 1963, **85**, 1141.

Table 1S. Viscosity data (cP) with water (ppm) and chloride (ppm) contents of the samples

Salt	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	H_2O	Cl^-
$[C_3(NEt_2)_3]BF_4$	206	115	69	44	29	21	15.5	37.3	2010
$[C_3(NEt_2)_3]NTf_2$	95	60	40	27.5	19.5	15	11.5	195.5	166
$[C_3(NPr_2)_3]NTf_2$	220	127	78.5	50	32	22.5	16.5	100.0	135
$[C_3(NBu_2)_3]Cl$	–	–	–	1450	675	345	190	12500	–
$[C_3(NBu_2)_3]BF_4$	–	545	275	153	90	57	37.5	109.6	429
$[C_3(NBu_2)_3]OTf$	–	–	–	39	25	17	11.5	278	916
$[C_3(NBu_2)_3]DCA$	293	160	95	61	41	29	21.5	180.7	100
$[C_3(NBu_2)_3]NTf_2$	230	135	84	55	38	27	19	64	377
$[C_3(NBuMe)_3]BF_4$	360	185	102	61	40	28	20.5	120.4	304
$[C_3(NBuMe)_3]NTf_2$	105	61	42	26	19.5	13.5	9.0	188.4	350

Table 2S. Microanalytical data (calcd/exptl)

Compound	C	H	N	Cl
$[C_3(NMe_2)_3]NTf_2$	29.46	4.05	12.49	
	29.58	4.10	12.28	
$[C_3(NEt_2)_3]Cl.1.6H_2O$	56.89	10.57	13.27	11.19
	56.96	10.12	12.66	11.93
$[C_3(NEt_2)_3]BF_4$	53.11	8.91	12.39	
	52.91	9.10	12.36	
$[C_3(NEt_2)_3]NTf_2$	38.34	5.68	10.52	
	38.80	5.81	10.60	
$[C_3(NPr_2)_3]Cl.2H_2O$	61.81	11.36	10.30	8.69
	62.01	10.77	8.93	9.56
$[C_3(NPr_2)_3]BF_4$	59.57	10.00	9.92	
	59.85	10.25	10.05	
$[C_3(NPr_2)_3]NTf_2$	44.79	6.86	9.08	
	44.95	6.99	9.11	
$[C_3(NBu_2)_3]Cl.0.72H_2O$	69.12	11.91	8.96	7.55
	69.09	11.38	9.06	7.99
$[C_3(NBu_2)_3]BF_4$	63.89	10.72	8.28	
	63.88	10.50	8.14	
$[C_3(NBu_2)_3]OTf$	59.02	9.55	7.37	
	59.33	9.83	7.41	
$[C_3(NBu_2)_3]DCA.0.4H_2O$	70.51	11.18	17.01	
	70.31	11.20	17.28	
$[C_3(NBu_2)_3]NTf_2$	49.70	7.77	7.99	
	49.43	7.92	8.07	
$[C_3(NBuMe)_3]Cl.1.24H_2O$	61.37	10.87	11.93	
	61.32	10.94	11.99	
$[C_3(NBuMe)_3]BF_40.19H_2O$	56.20	9.53	10.92	
	56.18	9.36	11.00	
$[C_3(NBuMe)_3]NTf_2$	41.80	6.31	9.75	
	41.52	6.30	9.88	