PERKIN 1

Preparation of tetraalkylformamidinium salts and related species as precursors to stable carbenes

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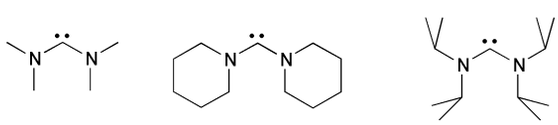
Methods are described for the preparation of a range of *N*,*N*,*N*′,*N*′-tetraalkylformamidinium and *N*,*N*-dialkyliminium ions **4**–**20** as anhydrous salts for use as precursors to diamino- and amino-carbenes. These methods include a novel method involving nucleophilic addition to formamides followed by trapping with electrophiles such as triflic anhydride, various methods of formamide activation, exchange reactions involving orthoesters and the transamination of amidinium salts, and alkylation methods.

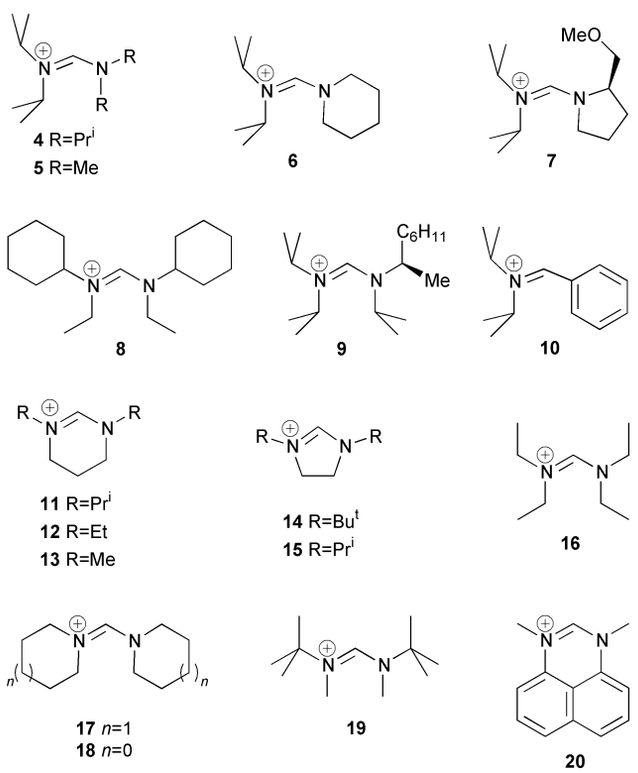
Introduction

We required a wide range of amidinium and iminium ions as precursors to stable carbenes.[1–7] We have been particularly interested in the preparation of carbenes where the carbene centre is not part of a ring such as **1**–**3** (we will use the term non-cyclic for these cases, even if there are rings elsewhere in the structure). Preparation of these carbenes is best achieved by deprotonation of per-alkylated and often sterically hindered formamidinium and iminium ions using non-nucleophilic amide bases,[8] and this therefore requires access to tetraalkylformamidinium and *N*,*N*-dialkyliminium ions as pure, anhydrous salts which are at least sparingly soluble in ether or hydrocarbon solvents.



1 **2** **3**

While the literature on preparative methods for amidinium and iminium salts is extensive,[9] we found many published methods to be ineffective, especially for the preparation of highly hindered tetraalkylated examples. We also found that literature methods of isolation were inadequate in many cases, as many salts of this type have been previously prepared only *in situ* and used without isolation. In this paper, we report reliable methods for making amidinium and iminium salts **4**–**20**.



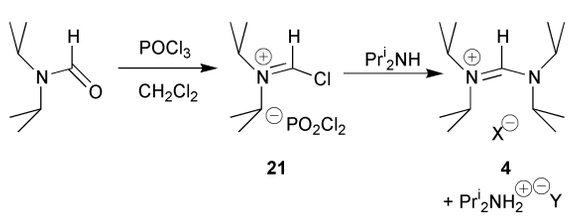
4 R=Pr^i
5 R=Me
6
7
8
9
10
11 R=Pr^i
12 R=Et
13 R=Me
14 R=Bu^t
15 R=Pr^i
16
17 *n*=1
18 *n*=0
19
20

Results and discussion

The methods discussed here can be divided into four broad categories: 1) formamide activation; 2) nucleophilic additions to formamides; 3) exchange reactions of orthoesters or amidinium salts; and 4) alkylation of amidines.

1 Formamide activation

The use of Vilsmeier–Haack chemistry to prepare *N*,*N*′-dialkyl- or *N*,*N*′,*N*′-trialkyl-amidinium salts is well established.[9,10] However the preparation of *N*,*N*,*N*′,*N*′-tetraalkylformamidinium salts by these methods is severely complicated by difficulties in isolating the desired salt from ammonium salt by-products. The crude product in these reactions is typically dark and intractable, and the isolation of the amidinium salt is complicated by the mixture of counterions present (*e.g.* $PO_2Cl_2^-$, as well as Cl^-), so that the salts form low melting waxy solids. Thus, we reported[4] the preparation of tetraisopropylformamidinium salt **4** (Scheme 1), using phosphorus



21 **4** + Pr$^i_2$NH$_2$ Y

Scheme 1

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Table 1 Yields of formamide activation reactions

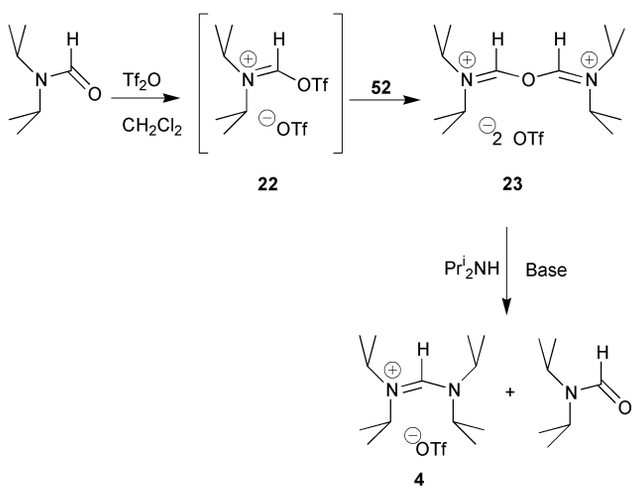
Salt	Preparative method and yields (%)		
	$POCl_3$	Tf_2O	Nucleophilic addition
4	66,[a] 75[b]	38	—
5	36[a]	—	—
6	62	—	52
7	77[b]	—	—
8	—	85	—
9	59[a]	16	—
10	—	—	37

[a] Aqueous NH_4PF_6 work-up. [b] Worked-up by aqueous $NaBF_4$ wash.

oxychloride, but in less than 25% yield after a difficult work-up.† A number of other tetraalkylformamidinium salts, **5**–**9**, have been successfully generated *via* the $POCl_3$–formamide activation method (Table 1), but in some cases, *e.g.* **8**, it proved impossible to isolate the salt in a satisfactory state of purity, even when NMR spectra indicated that the amidinium cation had been cleanly formed.

Many tetraalkylformamidinium salts are hydrolysed quite rapidly in contact with water, although this is less of a problem with hindered cations. A useful alternative for hindered salts is to dissolve the product mixture in cold water and immediately add an aqueous solution of ammonium hexafluorophosphate. Amidinium hexafluorophosphate salts usually precipitate from the aqueous mixture, while other species (*e.g.* ammonium ions) remain in solution.[11]

As alternatives to $POCl_3$, oxalyl and thionyl chloride were found to be insufficiently electrophilic for our purposes, however trifluoromethanesulfonic (triflic) anhydride has been shown to be effective in related processes by ourselves[7] and by Sforza *et al.*[12] Activation of a secondary formamide with triflic anhydride forms a monotriflate species, such as **22** (Scheme 2),



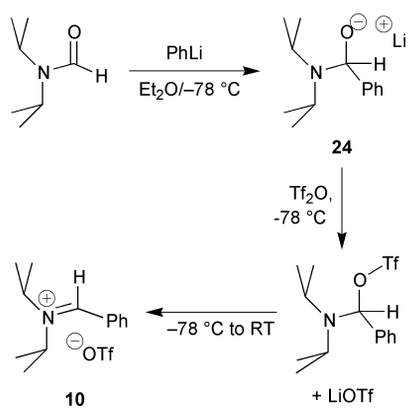
Scheme 2

analogous to the chloroiminium salt **21** in Scheme 1. It has been shown however[13,14] that the monotriflate species then reacts with a second molecule of formamide to generate a dication, such as **23**, which precipitates from even relatively polar solutions. We confirmed the identity of the precipitate formed upon slow addition of Tf_2O to a cooled dichloromethane solution of diisopropylformamide as the dication **23**. Reaction of this mixture with diisopropylamine gives reasonable yields of the tetraisopropylformamidinium salt **4** but also regenerates one equivalent of the original formamide (Scheme 2), suggesting that the dication is also the active electrophile in solution.‡ Other hindered salts, such as **8** and **9**, were prepared in a similar manner (Table 1).

Product mixtures from Tf_2O reactions are usually colourless crystalline solids as opposed to the dark intractable tar typically formed in the corresponding $POCl_3$ reactions. Careful recrystallisation of the amidinium triflate away from the ammonium salt side-products is now sometimes possible, for example, in the case of salt **4**, but this generally gives low isolated yields, and precipitation of the hexafluorophosphate salt from aqueous solutions, as described above, remains the most reliable method of purification if the salt is sufficiently stable.

2 Nucleophilic addition to formamides

As the removal of the ammonium salt by-products is the fundamental obstacle to isolation of tetraalkylformamidinium salts, methods of preparing the amidinium or iminium salts without an organic salt impurity were investigated. A solution of diisopropylformamide in diethyl ether§ was treated firstly with phenyllithium and then with triflic anhydride at −78 °C to trap the resultant lithium alkoxide **24** (Scheme 3). As



Scheme 3

the reaction mixture warms to room temperature, triflate is eliminated to give the extremely hygroscopic iminium salt **10** which precipitates from solution and was isolated in reasonable yield (Table 1). Attempts to use bulky aryllithium reagents, such as mesityllithium, were less successful—the products were observed by ^1H NMR, but in mixtures (*ca.* 25% impurities) from which they could not be easily isolated. This novel methodology has been successfully employed during the preparation of the highly hindered C_3-symmetric amine (*R*,*R*,*R*)-tris(1-phenylethyl)amine.[15]

Reaction of lithium diisopropylamide (LDA) with benzaldehyde, with subsequent trapping by oxalyl chloride, also gave phenyliminium salt **10** in the same manner. The corresponding reaction to generate formamidinium salts by reaction of lithium amides with formamides also proved to be a viable method for the one case to which it was applied. The preparation of formamidinium salt **6** by reaction of lithium piperidide and diisopropylformamide with subsequent trapping by Tf_2O proceeds in reasonable yield (52%, see Table 1).

3 Exchange reactions of orthoesters or amidinium salts

Orthoester exchange. Saba *et al.* reported the synthesis of cyclic amidinium salts by treatment of suitable diamines with

† In this earlier report an accurate elemental analysis of the salt **4**·**X** was never achieved due to the mixture of counterions.

‡ Crossover studies showed that the monocation and dication are in equilibrium in solution.

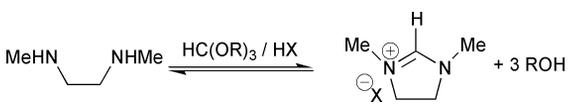
§ It is interesting to note that this reaction does not proceed in tetrahydrofuran—even when rigorously dried. An intractable polymeric solid precipitates upon addition of the trapping agent (Tf_2O, $Cl(CO)_2Cl$, or $SOCl_2$)—the nature of this substance is unclear, although presumed to be polymerised solvent.

Table 2 Yields of exchange reactions[a]

Salt	Preparative method and yields (%)		
	Orthoester exchange	Oxonium salt exchange	Amidine exchange
11	83[b]	59	—
12	56[b]	—	—
13	48[b]	—	—
14	60[c]	98	66,[d] 65[e]
15	33[b]	—	—
17	—	62	68[e]
18	—	88	—

[a] Yields not optimised. [b] NH_4^+ salts used as acid source. [c] Ethereal HBF_4 used as acid source. [d] Amidinium acetate used. [e] Tetramethylformamidinium chloride used.

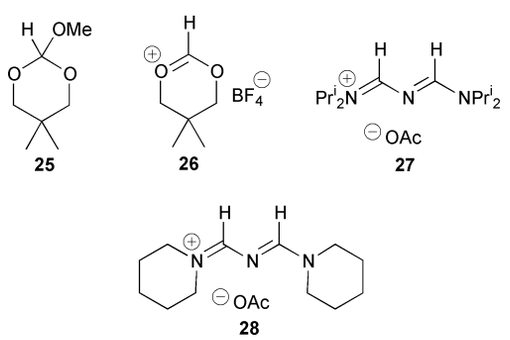
an orthoester (as solvent) in the presence of an acid (an example is shown in Scheme 4).[16] Reaction of trimethyl orthoformate with an acid and *N*,*N*′-dialkylated diamines proceeded



Scheme 4

in generally high yields in our hands (Table 2). We also found that it was possible to prepare the 2-^{13}C-labelled amidinium salt **11** from ^{13}C-labelled triethyl orthoformate using just one equivalent of orthoester and ethanol as solvent. The reaction rate was significantly decreased, but the subsequent isolation was actually easier.

Application of this method to the synthesis of non-cyclic tetraalkylformamidinium salts proved less useful. Reaction of 2 equivalents of a secondary monoamine with trimethyl orthoformate under the same conditions resulted in methylation of half of the added amine and elimination of the corresponding formamide. Attempts to prevent this by using triethyl orthoformate, where alkylation should be slower, also proved unsuccessful.



Cyclic orthoester **25**,[17] in which any S_N2 alkylation reaction would have to occur at a hindered neopentyl-like centre, should avoid this side-reaction. In fact, we found it more convenient to prepare and isolate the corresponding oxonium salt **26** immediately before reaction with the amine, although its extreme sensitivity to hydrolysis makes careful handling essential. Reaction of secondary diamines with oxonium salt **26** is an efficient method of generating cyclic salts such as **11** and **14** (Table 2). It has also proved effective in the synthesis of relatively unhindered non-cyclic tetraalkylformamidinium ions such as **16**–**18**. Attempts to generate the sterically hindered salt **4** by reaction of diisopropylamine with the oxonium ion **26** were unsuccessful, presumably due to the reluctance of a second molecule of amine to attack the highly hindered intermediate oxyiminium salt.

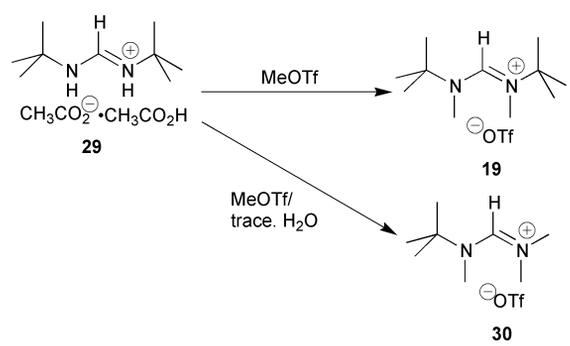
Transamination of amidinium salts. The elimination of ammonia from amidinium acetate by exchange with a secondary amine, might also be expected to afford tetraalkylamidinium salts. As with orthoesters, the formation of cyclic salts, such as **14**, by this method was successful (Table 2). However, the corresponding reaction with diisopropylamine or piperidine gave 1,1,5,5-tetraisopropyl-1,3,5-triazapenta-1,3-dienium acetate **27** and 1-(piperidinium-1-yl-idene)-3-(piperidin-1-yl)-2-azapropene acetate **28** respectively—confirmed by NMR spectroscopy and X-ray crystallography after conversion to the corresponding hexafluorophosphate salts. 1,1,5,5-Tetramethyl-1,3,5-triazapenta-1,3-dienium chloride ("Gold's reagent"), a dimethylamino analogue of these compounds, has been previously reported[18] (prepared from cyanuric chloride and *N*,*N*-dimethylformamide) and was shown to be a general β-dimethylaminomethylenating agent.[19] The synthetic utility of **27** and **28** in this sense is currently under examination.

To avoid this side reaction, amidinium acetate was replaced by an anhydrous solution of *N*,*N*,*N*′,*N*′-tetramethylformamidinium chloride. Reaction with piperidine under reflux gave the desired tetraalkylamidinium salt **17** in good yield.[10] However, the corresponding reaction with diisopropylamine did not form **4**, but stopped at the unsymmetrical *N*,*N*-diisopropyl-*N*′,*N*′-dimethylformamidinium salt **5**.

In general, the preparation of cyclic or unhindered non-cyclic examples such as **11**–**18** by these exchange reactions works well, but hindered non-cyclic tetraalkylamidinium salts cannot be made by these methods.

4 Alkylation of amidines

Stepwise alkylation is an obvious route to tetraalkylamidinium salts, but the final alkylation is limited by problems with elimination (except for methylations) and with low reactivity (methyl triflate is therefore the reagent of choice). *N*,*N*′-Di-*tert*-butyl-*N*,*N*′-dimethylamidinium triflate salt **19** was prepared by dimethylating di-*tert*-butylamidinium acetate **29** using methyl triflate as shown in Scheme 5 in 73% yield.[20] It was a surprise to



Scheme 5

find that trace quantities of water were sufficient to cause elimination of isobutene, resulting in the isolation of [(*tert*-butylmethylamino)methylidene]dimethylammonium triflate **30**·OTf. The perimidinium salt **20** was also prepared by quaternisation of 1*H*-perimidine[21] with methyl triflate in reasonable yield (73%). We have previously reported the application of alkylation to be useful in the synthesis of some iminium salts.[7]

Conclusions

We have developed a range of methods to prepare a variety of tetraalkylformamidinium salts and related compounds for application to the preparation of novel diaminocarbenes. For cyclic or unhindered tetraalkylformamidinium salts, the alkylation and exchange/transamination methods allow straightforward preparation of high purity material with relatively little

Table 3 Summary of single crystal X-ray diffraction data

Compound	**4**·OTf	**6**·PF_6	**12**·PF_6	**17**·BF_4	**23**·OTf	**28**·PF_6
Formula	$C_{14}H_{29}F_3N_2O_3S$	$C_{12}H_{25}F_6N_2P$	$C_8H_{17}F_6N_2P$	$C_{11}H_{21}BF_4N_2$	$C_{16}H_{30}F_6N_2O_7S_2$	$C_{12}H_{22}F_6N_3P$
Formula weight	362.45	342.31	286.21	268.11	540.54	353.30
Crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	*Pbcn*	*Pbca*	$Pca2_1$
a/Å	8.996(2)	9.610(2)	8.1410	18.086(3)	11.322(1)	12.094(2)
b/Å	9.238(2)	12.226(3)	11.230(1)	9.734(1)	17.900(2)	16.099(1)
c/Å	11.992(2)	14.090(2)	14.131(2)	7.642(2)	24.468(4)	16.456(1)
α/°	90.02(2)	90	90	90	90	90
β/°	91.36(2)	90	101.22(1)	90	90	90
γ/°	112.50(2)	90	90	90	90	90
V/Å^3	920.4(3)	1655.3(6)	1267.2(3)	1345.46(4)	4958.5(12)	3204.05(6)
Z	2	4	4	4	8	8
μ/mm^{-1}	0.218	0.220	0.272	0.116	0.297	0.232
Temperature/K	173	293.2	293.2	173	173	173
Measured reflections	5877	1109	3051	7836	2689	19842
Independent reflections	4034	1109	2212	1532	2194	6988
R_{int}	0.0175	Not calc.	0.0117	0.0255	0.0345	0.0402
R	0.0572	0.0593	0.0509	0.0525	0.0472	0.0398

isolation required. For highly hindered salts such as **4**, **8** and **9**, which are of particular interest in diaminocarbene chemistry, the formamide activation and aqueous hexafluorophosphate isolation techniques can be used. Nucleophilic addition/electrophile trapping offers a useful alternative, and merits further development. It is applicable to the preparation of iminium as well as these hindered formamidinium salts and removes the necessity for complex isolation procedures other than recrystallisation from anhydrous solvents.

Experimental

Instrumentation

NMR spectra were recorded using standard pulse sequences on JEOL JNM-LA300 or JEOL JNM-GX400 spectrometers. Coupling constants are quoted in hertz (Hz). Mass spectra (FAB and EI) were measured on a Fisons VG Analytical Autospec spectrometer. Melting points were determined on a Kofler hotstage electrothermal capillary apparatus and are uncorrected. Elemental combustion analyses were measured using a Perkin-Elmer 240C elemental analyser.

General notes

All procedures were performed under an inert atmosphere unless otherwise specified. All solvents and reagents were rigorously dried by using standard techniques and stored under an inert atmosphere. All glassware was oven-dried at 140 °C before use. Amidinium and iminium salts were generally stored under anhydrous conditions in a vacuum desiccator (over P_2O_5), a vacuum oven (80 °C, 20 mmHg) or a nitrogen atmosphere glove box.

Crystal structure analyses. Many of the details of the structure analyses of **4**·OTf, **6**·PF_6, **12**·PF_6, **17**·BF_4, **23**·OTf, and **28**·PF_6 are presented in Table 3. Data collection was carried out at low temperature on Bruker P4 or SMART diffractometers. Data collection for **23**·OTf was incomplete due to crystal decomposition. In **28**·PF_6 the two independent formula units are nearly, but not exactly, related by a centre of inversion. Attempted refinement in the likely alternative space groups (*Pbca* and *Pbcm*) was unsuccessful. The indeterminate value of the absolute structure parameter (0.56(8)) may imply some inversion twinning.

Full details of the structure determinations are available. CCDC reference numbers 155803–155808. See http://www.rsc.org/suppdata/p1/b1/b104110j/ for crystallographic files in .cif or other electronic format.

Aqueous counter-ion conversion to hexafluorophosphate. A reaction mixture (2–4 g) containing the desired product was dissolved in ice-cold distilled water or dilute acid (*ca.* 25 cm^3, 0.5 M) and added to a cooled aqueous solution (*ca.* 25 cm^3) of ammonium hexafluorophosphate (*ca.* 2 equivalents). The resulting precipitate was filtered and washed first with cold water (*ca.* 2 × 10 cm^3) and then diethyl ether (*ca.* 10 cm^3).

General procedures for preparing formamidinium and iminium salts. 1. Formamide activation

1.1 Phosphorus oxychloride. Typically a solution of a *N*,*N*-dialkylformamide (*ca.* 10 g) in anhydrous dichloromethane (40 cm^3) was added to a solution of phosphorus oxychloride (1 equivalent) in dry dichloromethane (100 cm^3; −78 °C). The reaction mixture was allowed to warm to room temperature and stirred under nitrogen for 2 h. The solution was then cooled to 0 °C and a mixture of the appropriate secondary amine (1 equivalent) and a tertiary amine base (typically triethylamine or diisopropylethylamine, 1 equivalent) in dichloromethane (50 cm^3) was slowly added. The reaction mixture was again allowed to warm slowly to room temperature and stirred for 2 h.

1.2 Triflic anhydride. Typically a solution of a *N*,*N*-dialkylformamide (2.5 g) in dry dichloromethane (10 cm^3), was added to a solution of triflic anhydride (0.5 equivalents) in anhydrous dichloromethane (30 cm^3; −78 °C) under a nitrogen atmosphere. After stirring at room temperature for 1 h, a mixture of *N*,*N*-dialkylamine (0.5 equivalents) and diisopropylethylamine (0.5 equivalents) in dichloromethane (10 cm^3) was then added dropwise to the suspension of the resultant dication at 0 °C. The solution was allowed to warm to room temperature and stirred for an hour.

2. Nucleophilic addition to formamides

Typically a solution of a *N*,*N*-dialkylformamide (1 g) in diethyl ether (10 cm^3) at −78 °C was slowly treated with an alkyllithium reagent (diluted in alkane solvent, 1 equivalent) or lithium amide (1 equivalent, prepared from the appropriate secondary amine and *n*-BuLi in diethyl ether). The mixture was stirred at −78 °C for 30 minutes, followed by a further 30 minutes at room temperature. The solution was then cooled to −78 °C before an ethereal solution of triflic anhydride (*ca.* 1.5 equivalents), or other trapping reagent *e.g.* oxalyl or thionyl chloride, was added dropwise with vigorous stirring. The solution was stirred for a further 10 minutes before being allowed to warm to room temperature. During warming, a white precipitate appeared (also significant gas evolution was observed if oxalyl

chloride was used). Once the reaction was complete, the solid was isolated by filtration under an inert atmosphere.

3. Exchange reactions

3.1 Exchange with trialkyl orthoformates.[15] Typically a mixture of an *N*,*N*′-dialkyldiamine (3.0 g), trimethyl or triethyl orthoformate (15 cm^3) and a suitable ammonium salt (*ca*. 1.5 equivalents) was heated under nitrogen at 120 °C, until no more alcohol was distilled (2–4 h). The excess orthoformate was then distilled from the reaction mixture under reduced pressure before work-up.

Alternatively, reaction of a diamine with 1 equivalent of orthoformate and a slight excess of ammonium salt in refluxing ethanol for 12–18 hours afforded reaction products with comparable yields, but that were more easily isolated.

3.2 Oxonium ion reaction. A solution of a *N*,*N*-dialkylamine (2 equivalents) or *N*,*N*′-dialkyldiamine (1 equivalent) in anhydrous dichloromethane (5 cm^3) was added dropwise to a stirred suspension of the freshly prepared oxonium salt **26**·BF_4 (4 g, see below for preparation) in dry dichloromethane (45 cm^3; −78 °C) under nitrogen. The reaction was allowed to warm to room temperature and stirred overnight. The resulting yellow–orange solution was then poured into ether and the product precipitated as an off-white powder, which was isolated by filtration.

5,5-Dimethyl-5,6-dihydro-4H-1,3-dioxinium tetrafluoroborate, ***26***·BF_4. The oxonium salt **26** was prepared using a modification of literature procedures[16,22] in rigorously dry conditions and under a nitrogen atmosphere. A solution of ethereal tetrafluoroboric acid (5.3 cm^3, 38.4 mmol) in dry dichloromethane (5 cm^3) was added dropwise to a stirred solution of dioxane **25**[16] (5.53 g, 37.9 mmol) in dichloromethane (45 cm^3; −78 °C). This was allowed to warm to room temperature and was stirred for 30 min. Dry diethyl ether (10 cm^3) was added, the solution cooled to −78 °C and the resulting crystals (which were almost transparent in solution) were filtered under nitrogen. The precipitate was then recrystallised at least twice from nitromethane (5 cm^3) with dichloromethane (50 cm^3) and diethyl ether (10 cm^3). Cooling to −78 °C ensured full precipitation of the oxonium salt **26**·BF_4 as fine, highly hygroscopic, colourless flakes (7.38 g, 96%); δ_H(400 MHz; CD_3NO_2) 1.29 (6 H, s, 2 × CH_3), 4.89 (4 H, s, 2 × CH_2) and 9.16 (1 H, s, OCHO); δ_C(100 MHz; CD_3NO_2) 21.0, 30.4, 83.5 and 176.6.

3.3 Amidine and formamidinium exchange. Typically, a solution of an *N*,*N*′-dialkyldiamine (*ca*. 2–3 g) or *N*,*N*-dialkylamine (*ca*. 2–3 g) and amidinium acetate or tetramethylformamidinium chloride (1 equivalent, see below for purification) in anhydrous ethanol (2 cm^3) was heated at 100 °C for 4 h under nitrogen with stirring. The gas flow from the reaction was bubbled through dilute aqueous acid solution to neutralise the ammonia/dimethylamine evolved.

Purification of N,N,N′,N′-tetramethylformamidinium chloride. A quantity of the salt was dissolved in dichloromethane and anhydrous sodium sulfate added. The solution was filtered and the filtrate treated with equal quantities of acetone and THF to precipitate all salts. The resulting colourless solid was redissolved in dichloromethane and acetone and any trace of insoluble material removed by filtration. THF was added to the filtrate and the resulting precipitate collected by filtration. The hygroscopic salt was stored under an inert atmosphere as a colourless crystalline powder. Mp 146–147 °C (lit.[23] 152–154 °C).

Diisopropylaminomethylidene(diisopropyl)ammonium hexafluorophosphate, ***4***·PF_6**.** Salt **4**·PF_6 was prepared from *N*,*N*-diisopropylformamide, phosphorus oxychloride, diisopropylamine and diisopropylethylamine using procedure 1.1 and hexafluorophosphate anion exchange as described in the General notes. The resultant solid was recrystallised from hot acetone–chloroform as colourless needles (66%); mp 326–326.5 °C (decomp.) (Found: C, 43.7; H, 7.9; N, 7.7. $C_{13}H_{29}F_6N_2P$ requires C, 43.6; H, 8.2; N, 7.8%); δ_H(300 MHz; $(CD_3)_2CO$) 1.46 (24 H, d, *J* 7, 8 × CH_3), 4.11–4.49 (4 H, br m, 4 × CH) and 7.66 (1 H, s, NCHN); δ_C(100 MHz; $(CD_3)_2CO$) 19.7–25.0 (br), 49.6–55.9 (br) and 152.3; *m*/*z* (FAB) 213 (M^+, 100%), 169 (10) and 133 (6).

Diisopropylaminomethylidene(diisopropyl)ammonium tetrafluoroborate, ***4***·BF_4**.** Formamidinium salt **4**·BF_4 was also prepared by method 1.1 as described above. The reaction mixture was washed with aqueous sodium hydroxide solution (2.0 M) and saturated sodium tetrafluoroborate and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate before filtration and removal of solvent *in vacuo*. The product was dissolved in acetone and precipitated with a mixture of ether and pentane (4 : 1). The resultant solid was isolated by filtration and was purified by crystallisation from acetone–diethyl ether to afford colourless crystals (75%); mp 311–312 °C (Found: C, 52.1; H, 9.8; N, 9.1. $C_{13}H_{29}BF_4N_2$ requires C, 52.0; H, 9.7; N, 9.3%). Spectroscopic details were in agreement with the corresponding hexafluorophosphate salt above.

Diisopropylaminomethylidene(diisopropyl)ammonium trifluoromethanesulfonate, ***4***·**OTf.** Salt **4**·OTf was prepared from *N*,*N*-diisopropylformamide, triflic anhydride and diisopropylamine using procedure 1.2. The pale yellow reaction mixture was poured into diethyl ether. The colourless precipitate was collected by filtration, then shaken with a mixture of distilled water and ethyl acetate and the crude product was recovered as a solid floating at the interface of the two solutions. Subsequent recrystallisation from acetone–ethyl acetate gave the salt **4**·OTf as colourless needles (38%); mp 323–325 °C (decomp.) (Found: C, 46.5; H, 8.0; N, 7.6. $C_{14}H_{29}F_3N_2O_3S$ requires C, 46.4; H, 8.1; N, 7.7%). Spectroscopic details were in agreement with the corresponding hexafluorophosphate salt above. Crystals of sufficient quality for single crystal X-ray diffraction studies (Table 3) were obtained by diffusion of diethyl ether into an acetone solution of **4**·OTf.

Dimethylaminomethylidene(diisopropyl)ammonium hexafluorophosphate, ***5***·PF_6**.** Salt **5**·PF_6 was prepared from *N*,*N*-dimethylformamide, phosphorus oxychloride, diisopropylamine and diisopropylethylamine using procedure 1.1 and hexafluorophosphate anion exchange as described in the General notes. The formamidinium hexafluorophosphate **5**·PF_6 separated as a brown oil which was dissolved in ethyl acetate–acetone and heated with activated charcoal. After filtration and removal of the solvent *in vacuo* the resulting solid was recrystallised from hot ethyl acetate to afford colourless flakes (36%); mp 179–181 °C (Found: C, 35.5; H, 7.2; N, 9.2. $C_9H_{21}F_6N_2P$ requires C, 35.8; H, 7.0; N, 9.3%); δ_H(300 MHz; $(CD_3)_2CO$) 1.40 (12 H, d, *J* 7, 4 × CH_3), 3.41 (6 H, br s, 2 × CH_3), 3.81–4.36 (1 H, br m, CH), 4.41–5.01 (1 H, br s, CH) and 7.84 (1 H, s, NCHN); δ_C(100 MHz; $(CD_3)_2CO$) 19.3–25.4 (br), 41.3, 47.2, 48.6–53.0 (br) and 155.2; *m*/*z* (FAB) 157 (M^+, 100%) and 113.

Dimethylaminomethylidene(diisopropyl)ammonium tetrafluoroborate, ***5***·BF_4**.** Salt **5**·BF_4 was prepared from the corresponding hexafluorophosphate salt **5**·PF_6 by ion exchange chromatography. The tetrafluoroborate salt **5**·BF_4 was recrystallised by evaporation of acetone (*ca*. 5–10%) from hot ethyl acetate to afford colourless needles; mp 97–98 °C (Found: C, 44.45; H, 8.45; N, 11.4. $C_9H_{21}BF_4N_2$ requires C, 44.3; H, 8.7; N, 11.5%). Spectroscopic details were in agreement with the corresponding hexafluorophosphate salt above.

Diisopropyl(piperidin-1-ylmethylidene)ammonium hexafluorophosphate, ***6***·PF_6**.** Salt **6**·PF_6 was prepared from *N*,*N*-

diisopropylformamide, phosphorus oxychloride, piperidine and diisopropylethylamine using procedure 1.1 and hexafluorophosphate anion exchange as described in the General notes. Salt **6**·PF_6 was recrystallised from hot acetone–chloroform to afford colourless needles (62%); mp 209–210 °C; δ_H(400 MHz; $CDCl_3$) 1.38 (12 H, d, *J* 7, 4 × CH_3), 1.76 (6 H, br m, 3 × CH_2), 3.69 (4 H, m, 2 × CH_2), 4.02 (2 H, br m, 2 × CH) and 8.15 (1 H, s, NCHN); δ_C(100 MHz; $CDCl_3$) 22.3 (br), 22.9, 25.9, 50.5, 54.5 and 152.8.

Diisopropyl(piperidin-1-ylmethylidene)ammonium salt **6**·PF_6 was also prepared from formylpiperidine, lithium diisopropylamide (prepared in diethyl ether from diisopropylamine and *n*-BuLi) and triflic anhydride using procedure 2 and hexafluorophosphate anion exchange as described in the General notes. Physical and spectroscopic details were identical to the sample prepared above (52%). Crystals of sufficient quality for single crystal X-ray diffraction studies (Table 3) were obtained by diffusion of diethyl ether into an acetone solution of **6**·PF_6.

(*S*)-(+)-Diisopropyl(2-methoxymethylpyrrolidin-1-ylmethylidene)ammonium tetrafluoroborate, 7·BF_4. Formamidinium salt **7**·BF_4 was prepared from (*S*)-(−)-1-formyl-2-(methoxymethyl)pyrrolidine, phosphorus oxychloride and diisopropylamine using procedure 1.1. Dichloromethane was added to the reaction mixture and the solution was re-cooled in ice and washed with aqueous sodium hydroxide (2.0 M) and a saturated aqueous solution of sodium tetrafluoroborate. The aqueous washings were extracted with dichloromethane before being dried over anhydrous magnesium sulfate, filtered and the solvent removed *in vacuo*. The crude product, an orange oil, was then purified by column chromatography (10 : 1, CH_2Cl_2–MeOH). After removing traces of solvent, heating and cooling of the resultant oil allowed crystallisation of salt **7**·BF_4 as a low melting solid (77%); mp 50–51 °C; $[\alpha]_D^{20}$ +108.7 (Found: C, 49.7; H, 8.8; N, 9.3. $C_{13}H_{27}BF_4N_2O$ requires C, 49.65; H, 8.7; N, 8.9%); δ_H(300 MHz; $CDCl_3$) 1.36 (6 H, d, *J* 7, 2 × CH_3), 1.38 (6 H, d, *J* 7, 2 × CH_3), 1.65 (1 H, m, ring CH), 2.15 (3 H, m, ring CH + CH_2), 3.37 (3 H, s, OCH_3), 3.41–3.54 (2 H, m, CH_2O), 3.82 (1 H, septet, *J* 7, CH), 3.90, 3.82–3.84 (2 H, m, CH_2), 4.25 (1 H, m, CH), 4.62 (1 H, septet, *J* 7, CH) and 7.75 (1 H, s, NCHN); δ_C(75.5 MHz; $CDCl_3$) 24.4, 22.5, 20.6, 20.3, 25.7, 25.0, 49.0, 50.6, 58.6, 65.3, 74.1 and 151.4. *m*/*z* (EI) 227 (M^+, 55%).

***N*,*N*′-Dicyclohexyl-*N*,*N*′-diethylformamidinium trifluoromethanesulfonate, 8·OTf.** Salt **8**·OTf was prepared from *N*-cyclohexyl-*N*-ethylformamide, triflic anhydride and *N*-cyclohexyl-*N*-ethylamine using procedure 1.2. The solution was stirred at room temperature for 1 h before being poured into diethyl ether giving a yellow oil. The oil was partitioned between diethyl ether and water, with the ethereal fraction being dried over anhydrous magnesium sulfate before filtration and removal of the solvent *in vacuo*. The residue was recrystallised from ethyl acetate and ether (85%) as fine colourless flakes; mp 65–66 °C (Found: C, 52.6; H, 8.3; N, 6.8. $C_{18}H_{33}F_3N_2O_3S$ requires C, 52.2; H, 8.0; N, 6.8%); δ_H(300 MHz; $CDCl_3$) 1.26 (6 H, br t, *J* 7, 2 × CH_3), 1.03–1.98 (20 H, br m, 10 × CH_2), 3.48 (4 H, br q, *J* 7, 2 × CH_2), 3.66 (2 H, br s, 2 × CH) and 7.94 (1 H, br s, NCHN); δ_C(75 MHz; $CDCl_3$) 15.6, 24.7, 25.2, 31.8, 41.0, 68.1, 122.9 (q, *J* 321) and 153.7; *m*/*z* (FAB) 265 (M^+, 100%), 236 (3), 213 (5), 182 (3) and 138 (6).

(*R*)-(−)-{[(1-Cyclohexylethyl)isopropylamino]methylidene}-diisopropylammonium trifluoromethanesulfonate 9·OTf. Formamidinium salt **9**·OTf was prepared from *N*-isopropyl-*N*-(*R*)-(−)-1-cyclohexylethylformamide, triflic anhydride and diisopropylamine by procedure 1.2 as described above. Once the reaction was complete, dichloromethane was added and the reaction mixture was washed with sodium hydroxide solution (2.0 M) and distilled water. The aqueous layer was extracted with dichloromethane and the combined organic washings dried with anhydrous magnesium sulfate. Most of the solvent was removed *in vacuo* and then the crude product was separated as an orange oil by the addition of diethyl ether and *n*-pentane. The oil was dissolved in water and filtered. The filtrate was concentrated to afford **9**·OTf as a colourless solid (16%); mp 165–170 °C. $[\alpha]_D^{20}$ −24.5 (Found: C, 51.9; H, 8.8; N, 6.6; S, 7.5. $C_{19}H_{37}F_3N_2O_3S$ requires C, 53.0; H, 8.7; N, 6.5; S, 7.45%) (NMR spectra were run at elevated temperatures to simplify interpretation) δ_H(300 MHz; DMSO, 60 °C) 0.80–1.30 (5 H, br m, 2 × CH_2 and 1 × CH), 1.30–1.39 (21 H, 7 × CH_3), 1.50–1.78 (6 H, br m, 3 × CH_2), 3.53 (1 H, br dq, *J* 7, 1 × CH), 4.09 (3 H, br septet, *J* 7, 3 × CH) and 7.48 (1 H, s, NCHN); δ_C(75.5 MHz; DMSO, 60 °C) 20.33, 21.0 (br), 25.40, 25.47, 29.05, 30.09, 53.6 and 152.32; *m*/*z* (FAB) 281 (M^+, 100%).

(*R*)-(−)-{[(1-Cyclohexylethyl)isopropylamino]methylidene}-diisopropylammonium tetrafluoroborate 9·BF_4. Formamidinium salt **9**·BF_4 was prepared from *N*-isopropyl-*N*-(*R*)-(−)-1-cyclohexylethylformamide, phosphorus oxychloride and diisopropylamine by procedure 1.1 as described above. After the reaction was complete, dichloromethane was added and the reaction mixture was washed with sodium hydroxide solution (2.0 M) and saturated sodium tetrafluoroborate solution. The aqueous washings were extracted with dichloromethane and the combined organic fractions were dried over anhydrous magnesium sulfate and filtered. Most of the solvent was removed *in vacuo* before the crude product was precipitated as an orange oil by the addition of *n*-pentane. The product was purified by column chromatography (10 : 1, CH_2Cl_2–MeOH), to yield a tacky yellow oil. After removing traces of solvent, repeated heating, cooling and removal of solid allowed isolation. This procedure yielded the salt **9**·BF_4 as a pale yellow solid (59%). Spectroscopic details were in agreement with those of **9**·OTf as prepared above.

Benzylidenediisopropylammonium chloride 10·Cl. Iminium salt **10**·Cl was prepared from *N*,*N*-diisopropylformamide, phenyllithium and oxalyl chloride in diethyl ether using procedure 2 as described above. The easily hydrolysed solid product was isolated by filtration under N_2 and washed with Et_2O (37%); mp 225–230 °C (decomp.); δ_H(400 MHz; CD_3OD) 1.58 (6 H, d, *J* 7, 2 × CH_3), 1.64 (6 H, d, *J* 7, 2 × CH_3), 4.63 (1 H, septet, *J* 7, CH), 5.14 (1 H, septet, *J* 7, CH), 7.70–7.90 (5 H, m, 5 × ArH) and 9.18 (1 H, s, NCHN); δ_C(75 MHz; CD_3OD) 20.6, 24.7, 56.9, 59.1, 129.0, 131.1, 133.0, 136.6 and 173.1.

1,3-Diisopropyl-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate, 11·BF_4. Salt **11**·BF_4 was prepared from *N*,*N*′-diisopropylpropane-1,3-diamine, ammonium tetrafluoroborate and triethyl orthoformate using procedure 3.1. The product mixture was dissolved in acetonitrile and the insoluble ammonium salt was removed by filtration. The acetonitrile was removed under vacuum and the residue recrystallised by evaporation of acetone (*ca*. 5–10%) from hot ethyl acetate to give fine colourless needles (83%); mp 144–145 °C (Found: C, 47.2; H, 8.4; N, 10.8. $C_{10}H_{21}BF_4N_2$ requires C, 46.9; H, 8.3; N, 10.9%); δ_H(400 MHz; $(CD_3)_2CO$) 1.34 (12 H, d, *J* 7, 4 × CH_3), 2.14 (2 H, quin, *J* 6, CH_2), 3.51 (4 H, t, *J* 6, 2 × CH_2), 4.01 (2 H, septet, *J* 7, 2 × CH) and 8.27 (1 H, s, NCHN); δ_C(100 MHz; $(CD_3)_2CO$) 19.8, 20.1, 39.7, 57.4 and 151.7; *m*/*z* (FAB) 169 (M^+, 100%) and 126 (3).¶

Formamidinium salt **11**·BF_4 was also prepared by reaction of *N*,*N*′-diisopropylpropane-1,3-diamine with freshly prepared oxonium salt **26**·BF_4 using procedure 3.2. The resulting precipitate was recrystallised using the method above to give the formamidinium salt **11**·BF_4 (59%) as fine colourless needles. Spectroscopic details were in agreement with the product isolated above.

¶ Single crystal X-ray structure previously reported.[15]

1,3-Diethyl-3,4,5,6-tetrahydropyrimidin-1-ium hexafluorophosphate, 12·PF$_6$. Salt **12**·PF$_6$ was prepared from *N*,*N*′-diethylpropane-1,3-diamine, ammonium tetrafluoroborate and triethyl orthoformate using procedure 3.1 and hexafluorophosphate anion exchange as described in the General notes. The desired formamidinium hexafluorophosphate salt **12**·PF$_6$ was recrystallised by evaporation of acetone (*ca*. 5–10%) from hot ethyl acetate to give colourless prisms (56%); mp 87–88 °C (Found: C, 33.8; H, 6.2; N, 9.8. $C_8H_{17}F_6N_2P$ requires C, 33.6; H, 6.0; N, 9.8%); δ_H(300 MHz; $(CD_3)_2CO$) 1.30 (6 H, t, *J* 7, 2 × CH_3), 2.18 (2 H, quin, *J* 6, CH_2), 3.52 (4 H, t, *J* 6, 2 × CH_2), 3.59 (4 H, q, *J* 7, 2 × CH_2) and 8.18 (1 H, s, NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 13.4, 19.6, 43.1, 50.9 and 153.1; *m*/*z* (FAB) 141 (M^+, 100%) and 112 (4). Crystals of sufficient quality for single crystal X-ray diffraction studies (Table 3) were obtained by cooling (−30 °C) an acetone–ethyl acetate solution of **12**·PF$_6$.

1,3-Dimethyl-3,4,5,6-tetrahydropyrimidinium iodide, 13·I. Salt **13**·I, previously reported by Alici *et al*.,[24] was prepared in 48% yield from *N*,*N*′-dimethylpropane-1,3-diamine, ammonium iodide and triethyl orthoformate using procedure 3.1. δ_H(400 MHz; $(CD_3)_2CO$) 2.21 (2 H, quin, *J* 6, CH_2), 3.33 (6 H, s, 2 × CH_3), 3.50 (4 H, t, *J* 6, 2 × CH_2) and 8.75 (1 H, s, NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 19.5, 42.1, 45.2 and 154.4; *m*/*z* (FAB) 353 ($2M^+I^-$, 5%) and 113 (M^+, 100).

1,3-Di-*tert*-butyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate, 14·BF$_4$. Salt **14**·BF$_4$ was prepared from *N*,*N*′-di-*tert*-butylethylenediamine, ethereal tetrafluoroboric acid and triethyl orthoformate using procedure 3.1. The reaction product was recrystallised from hot ethyl acetate to give colourless flakes (60%); mp 298–299 °C (lit.[24] 277 °C) (Found: C, 49.0; H, 8.5; N, 10.2. $C_{11}H_{23}BF_4N_2$ requires C, 48.9; H, 8.6; N, 10.4%); δ_H(300 MHz; $(CD_3)_2CO$) 1.46 (18 H, s, 6 × CH_3), 4.16 (4 H, s, 2 × CH_2) and 8.24 (1 H, s, NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 27.9, 46.1, 57.4 and 153.7; *m*/*z* (FAB) 183 (M^+, 100%), 127 (9) and 111 (15).

Formamidinium salt **14**·BF$_4$ was also prepared from *N*,*N*′-di-*tert*-butylethylenediamine and freshly prepared oxonium salt **26**·BF$_4$ using procedure 3.3. The resulting colourless precipitate was gathered by filtration (98%). Spectroscopic details were in agreement with the product isolated above.

1,3-Di-*tert*-butyl-4,5-dihydro-3*H*-imidazol-1-ium hexafluorophosphate, 14·PF$_6$. Salt **14**·PF$_6$ was prepared from di-*tert*-butylethylenediamine and amidinium acetate using procedure 3.3 and hexafluorophosphate anion exchange as described in the General notes. The desired formamidinium salt **14**·PF$_6$ was recrystallised by evaporation of acetone (*ca*. 5–10%) from a hot ethyl acetate solution to give colourless prisms (66%); mp 317–318 °C (Found: C, 40.3; H, 7.1; N, 8.4. $C_{11}H_{23}F_6N_2P$ requires C, 40.25; H, 7.1; N, 8.5%). Spectroscopic details were in agreement with the corresponding tetrafluoroborate salt above.

1,3-Diisopropyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate, 15·BF$_4$.[15] Salt **15**·BF$_4$ was prepared from *N*,*N*′-diisopropylethylenediamine, ammonium tetrafluoroborate and triethyl orthoformate using procedure 3.1. After filtration to remove the insoluble ammonium salt, the reaction mixture was recrystallised by evaporation of dichloromethane (~5–10%) from an ethyl acetate solution to give colourless flakes (33%); mp 144.5–146.5 °C (lit.[15] 152–153 °C); δ_H(300 MHz; $(CD_3)_2CO$) 1.41 (12 H, d, *J* 7, 4 × CH_3), 3.90 (4 H, s, 2 × CH_2), 4.03 (2 H, septet, *J* 7, 2 × CH) and 8.10 (1 H, s, NCHN).

Diethylaminomethylidene(diethyl)ammonium tetrafluoroborate, 16·BF$_4$. Salt **16**·BF$_4$ was prepared from *N*,*N*-diethylamine and freshly prepared oxonium salt **26**·BF$_4$ using procedure 3.2. The resulting colourless precipitate was gathered by filtration. δ_H(400 MHz; $CDCl_3$) 1.36 (12 H, t, *J* 7, 4 × CH_3), 3.56 (8 H, q, *J* 7, 4 × CH_2) and 7.69 (1 H, s, NCHN). Subsequent recrystallisation and filtration resulted in the colourless solid turning to a viscous oil (^{1}H NMR of the decomposition product indicated that salt **16**·BF$_4$ was rapidly hydrolysed to the corresponding diethylammonium salt and diethylformamide).

Piperidin-1-ylmethylidenepiperidinium tetrafluoroborate, 17·BF$_4$. Salt **17**·BF$_4$ was prepared from piperidine and freshly prepared oxonium salt **26**·BF$_4$ using procedure 3.2. The precipitate was recrystallised from hot ethyl acetate, affording the formamidinium salt **17**·BF$_4$ as fine colourless flakes (62%); mp 199–200 °C (Found: C, 49.4; H, 8.0; N, 10.4. $C_{11}H_{21}BF_4N_2$ requires C, 49.3; H, 7.9; N, 10.45%); δ_H(300 MHz; $CDCl_3$) 1.73 (12 H, br s, 6 × CH_2), 3.62 (8 H, br s, 4 × CH_2) and 7.67 (1 H, s, NCHN); δ_C(100 MHz; ($CDCl_3$) 23.0, 25.7, 49.1 (br), 54.6 (br) and 153.7; *m*/*z* (FAB) 181 (M^+, 100%). Crystals of sufficient quality for single crystal X-ray diffraction studies (Table 3) were obtained by diffusion of ether into an acetone solution of **17**·BF$_4$.

Piperidin-1-ylmethylidenepiperidinium hexafluorophosphate, 17·PF$_6$. Salt **17**·PF$_6$ was prepared from piperidine and *N*,*N*,*N*′,*N*′-tetramethylformamidinium chloride using procedure 3.2 and hexafluorophosphate anion exchange as described in the General notes The resultant solid was recrystallised by evaporation of acetone (*ca*. 5–10%) from hot ethyl acetate to give colourless needles (68%). Spectroscopic details were in agreement with those of the corresponding BF$_4$ salt above.

Pyrrolidin-1-ylmethylidenepyrrolidinium hexafluorophosphate, 18·PF$_6$. Salt **18**·PF$_6$ was prepared from pyrrolidine and freshly prepared oxonium salt **26**·BF$_4$ in CH_2Cl_2, using procedure 3.2 and hexafluorophosphate anion exchange as described in the General notes. The resultant solid was recrystallised by evaporation of acetone (*ca*. 5–10%) from hot ethyl acetate to give colourless needles (88%); mp 210–211 °C (Found: C, 36.2; H, 5.6; N, 9.2. $C_9H_{17}F_6N_2P$ requires C, 36.25; H, 5.75; N, 9.4%); δ_H(300 MHz; $(CD_3)_2CO$) 1.96 (4 H, quin, *J* 7, 2 × CH_2), 2.09 (4 H, quin, *J* 7, 2 × CH_2), 3.81 (4 H, br t, *J* 7, 2 × CH_2), 4.06 (4 H, br t, *J* 7, 2 × CH_2) and 8.22 (1 H, s, NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 24.7, 26.6, 49.1, 55.0 and 152.4; *m*/*z* (FAB) 153 (M^+, 100%) and 111 (7).

***tert*-Butyl[(*tert*-butylmethylamino)methylidene]methylammonium trifluoromethanesulfonate, 19·OTf.** Methyl trifluoromethanesulfonate was added dropwise to a solution of *N*,*N*′-di-*tert*-butyl-*N*-methylformamidine (prepared by the method of Nivard *et al*.[20]) in acetonitrile and allowed to stir overnight at room temperature. The solvent was removed and the resulting yellow solid was recrystallised from ethyl acetate giving colourless flakes **19**·OTf (73%); mp 111–112 °C (Found: C, 43.2; H, 7.9; N, 8.4. $C_{12}H_{25}F_3N_2O_3S$ requires C, 43.1; H, 7.5; N, 8.4%); δ_H(300 MHz; $CDCl_3$) 1.48 (18 H, s, 6 × CH_3), 3.31 (6 H, s, 2 × CH_3) and 7.80 (1 H, s, NCHN); δ_C(75 MHz; $CDCl_3$) 28.1, 34.5, 62.8, 120.7 (q, *J* 320) and 153.4; *m*/*z* (FAB) 185 (M^+, 100%) and 128 (5).

Formamidinium salt **19**·PF$_6$ was prepared from the corresponding triflate salt, prepared above, using the anion exchange method described in the General notes. The resultant solid was recrystallised by evaporation of acetone (*ca*. 5–10%) from ethyl acetate to give colourless prisms; mp 222–223 °C (Found: C, 40.2; H, 7.8; N, 8.4. $C_{11}H_{25}N_2F_6P$ requires C, 40.0; H, 7.6; N, 8.5%); δ_H(300 MHz; $(CD_3)_2CO$) 1.53 (18 H, s, 6 × CH_3), 3.43 (6 H, s, 2 × CH_3) and 8.12 (1 H, s, NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 28.2, 35.2, 62.3 and 155.8; *m*/*z* (FAB) 185 (M^+, 100%).

1,3-Dimethyl-1*H*-perimidin-1-ium trifluoromethanesulfonate, 20·OTf. 1*H*-Perimidine (0.50 g, 2.98 mmol) was prepared by the literature method of Sachs,[21] and treated with methyl triflate (0.70 cm^3, 6.19 mmol) and 2,6-di-*tert*-butylpyridine (0.7 cm^3, 3.02 mmol) in dichloromethane (300 cm^3). The mixture was stirred overnight at room temperature. The solvent was removed and the yellow solid dissolved in the minimum amount of saturated bicarbonate solution, washed with diethyl ether and extracted into dichloromethane. The solvent was removed to give **20**·OTf, which was recrystallised as yellow needles from ethanol (73% yield); mp 275–276 °C (Found: C, 48.7; H, 3.7; N, 8.1. $C_{14}H_{13}F_3N_2O_3S$ requires C, 48.55; H, 3.8; N, 8.1%); δ_H(300 MHz; $CDCl_3$) 3.72 (6 H, s, 2 × CH_3), 6.84 (2 H, br dd, *J* 7 and 1, 2 × ArH), 7.49 (2 H, br dd, *J* 8 and 7, 2 × ArH), 7.58 (2 H, br dd, *J* 8 and 1, 2 × ArH) and 9.28 (1 H, s, NCHN); δ_C(75 MHz; CD_3OD) 39.7, 109.1, 121.9 (q, *J* 318), 122.2, 125.5, 129.6, 134.2, 136.1 and 154.5; *m*/*z* (FAB) 197 (M^+, 100%), 182 (19) and 133 (31).

1,1,5,5-Tetraisopropyl-1,5-diazonia-3-oxapenta-1,4-dienyl bis(trifluoromethanesulfonate), 23·OTf. Dication **23**·OTf was prepared by the addition of triflic anhydride (100 μL, 0.594 mmol) to a solution of *N*,*N*-diisopropylformamide (68 μL, 0.593 mmol) in d_3-nitromethane (0.867 g), at −78 °C in dry conditions under nitrogen. The solution was then allowed to warm to room temperature and the extremely hygroscopic solid precipitate was isolated by filtration. δ_H(400 MHz; CD_3NO_2) 1.59 (12 H, d, *J* 7, 4 × CH_3), 1.67 (12 H, d, *J* 7, 4 × CH_3), 4.58 (2 H, septet, *J* 7, 2 × CH), 4.87 (2H, septet, *J* 7, 2 × CH) and 9.46 (2 H, br s, 2 × NCHO); δ_C(75 MHz; CD_3NO_2) 19.6, 22.7, 58.1, 59.3, 121.2 (q, *J* 318) and 162.8. Crystals of sufficient quality for single crystal X-ray diffraction studies (Table 3) were obtained by cooling a dichloromethane–nitromethane solution of **23**·OTf to −30 °C.

1,1,5,5-Tetraisopropyl-1,3,5-triazapenta-1,3-dienium hexafluorophosphate, 27·PF_6. Salt **27**·PF_6 was prepared from diisopropylamine and amidinium acetate using procedure 3.3. The solvent was removed and the product was isolated as the hexafluorophosphate salt as described in the General notes. The hexafluorophosphate salt **27**·PF_6 was recrystallised from acetone–diethyl ether (2.25 g, 24%) to afford colourless prisms; mp 173–174 °C (Found: C, 43.7; H, 8.1; N, 10.85. $C_{14}H_{30}F_6N_3P$ requires C, 43.6; H, 7.85; N, 10.9%); δ_H(300 MHz; $(CD_3)_2CO$) 1.41 (12 H, d, *J* 7, 4 × CH_3), 1.42 (12 H, d, *J* 7, 4 × CH_3), 4.11 (2 H, septet, *J* 7, 2 × CH), 4.83 (2 H, septet, *J* 7, 2 × CH) and 8.59 (2 H, s, 2 × NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 19.9, 23.1, 50.8, 52.3 and 166.2; *m*/*z* (FAB) 240 (M^+, 100%), 225 (3), 196 (11), 182 (6), 154 (5) and 129 (14).

1-(Piperidinium-1-ylidene)-3-(piperidin-1-yl)-2-azapropene hexafluorophosphate 28·PF_6. Salt **28**·PF_6 was prepared from piperidine and amidinium acetate using procedure 3.3 and hexafluorophosphate anion exchange as described in the General notes. The hexafluorophosphate salt was recrystallised from dichloromethane–diethyl ether (63%) as thick colourless needles; mp 106–107 °C (Found: C, 41.05; H, 6.2; N, 11.8. $C_{12}H_{22}F_6N_3P$ requires C, 40.8; H, 6.3; N, 11.9%); δ_H(300 MHz; $(CD_3)_2CO$) 1.66–1.84 (12 H, br m, 6 × CH_2), 3.77 (4 H, br t, *J* 5, 2 × CH_2), 3.96 (4 H, br t, *J* 5, 2 × CH_2) and 8.49 (2 H, s, 2 × NCHN); δ_C(75 MHz; $(CD_3)_2CO$) 24.4, 26.2, 27.3, 46.5, 53.8 and 165.7; *m*/*z* (FAB) 208 (M^+, 100%) and 124 (4). Crystals of sufficient quality for single crystal X-ray diffraction studies (Table 3) were obtained by diffusion of diethyl ether into an acetone solution of the title compound to −30 °C.

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