The synthesis of fluorinated N-heterocyclic carbenes

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Abbreviations

1-Bu-2-MeIM	1-butyl-2-methylimidazole
1-HexIM	1-hexylimidazole
1-Pent-2-MeIM	1-pentyl-2-methylimidazole
1-PrIM	1-propylimidazole
1-OctIM	1-octylimidazole
Å	ångström(s)
°C	Degree Celsius
^{13}C	Carbon-13
Acac	acetyl acetonate
aq.	Aqueous
ATRP	Atom transfer radical polymerization
BDE	Bond dissociation energy
[bmim]$^+$	1-butyl-3-methylimidazolium cation
$CHCl_3$	chloroform
cm^{-1}	wavenumber(s)
cod	1,5-cyclooctadiene
Cp*	Pentamethylcyclopentadiene
dba	Dibenzylidene acetone/ dibenzalacetone
DCM	dichloromethane
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
[emim]$^+$	1-ethyl-3-methylimidazolium cation
eqv.	equivalent(s)
EtOAc	ethyl acetate
Et_2O	diethyl ether
EtOH	ethanol
G	Gram
H	hour(s)
^{1}H	proton-1
HOMO	highest occupied molecular orbital
Hz	Hertz
IAd	1,3-bis(adamantyl)imidazol-2-ylidene
I^{t}Bu	1,3-bis(tert-butyl)imidazol-2-ylidene
IL	Ionic liquid
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IpFMe	1-pentafluorobenzyl-3-methylimidazol-2-ylidene
I^{i}Pr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
IR	infrared spectroscopy
ITol	1,3-bis(4-methylphenyl)imidazol-2-ylidene
KO^{t}Bu	Potassium tert- butoxide
J	coupling constant value

L	litre(s)
LDA	lithium diisopropylamide
mCPBA	3-chloroperoxybenzoic acid/ meta-chloroperbenzoic acid
Me	Methyl group
MeOH	Methanol
Mes	Mesityl group
min	minutes(s)
Mol	mole(s)
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
OAc	Acetate
PCy_3	Tricyclohexylphosphine
PEG	Poly ethylene glycol
Ph	Phenyl group
PPh_3	Triphenyl phosphine
ppm	parts per million
RCM	ring closing metathesis
rt	room temperature
S_NAr	nucleophilic aromatic substitution
SIMes	1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SI^iPr	1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene
SITol	1,3-bis-(4-methylphenyl)imidazolin-2-ylidene
TfOH	Sulfonic acid
THF	Tetrahydrofuran
tht	tetrahydrothiophene
TLC	thin layer chromatography
TM	transition metal
$TMNO.2H_2O$	trimethylamine N-oxide dihydrate

Abstract

The synthesis of a number of imidazolium salts bearing fluorine-substituted aromatic systems has been reported. 1,3-bis(4-fluorophenyl)imidazolium chloride (**26**), 1,3-bis(2,4-difluorophenyl)imidazolium chloride (**27**) and 1,3-bis(2,4,5-trifluorophenyl)imidazolium chloride (**33**) were prepared via a one-pot condensation involving glyoxal, formaldehyde and the appropriate fluorinated primary amine. It was not possible to prepare and isolate 1,3-bis(pentafluorophenyl)imidazolium chloride in the same way. A series of imidazolium salts were synthesized in which one of the nitrogen substituents contained a polyfluorinated chain; these have been prepared via two different synthetic routes. In the first approach, imidazole was first reacted with polyfluoroalkyl halides ($C_8F_{17}C_2H_4I$ and $C_4F_9C_2H_4I$) to give 1-(polyfluoroalkyl)imidazoles (**37** and **38**). The second approach involved initial preparation of alkylated imidazoles (R = Pr, Hex, Bu, Oct) and polyfluoroalkyl triflates $R_FC_2H_4OSO_2CF_3$ (R_F = C_6F_{13}, C_8F_{17}) resulting in the formation of imidazolium (**46** - **49**) and methylimidazolium (**50** - **52**) salts bearing both fluorinated and non-fluorinated chains.

Whilst investigating the preparation and use of diaryliodonium salts for the synthesis of *N*-substituted imidazoles, the single crystal X-ray structure of bis(4-methylphenyl)iodonium triflate (**53**) was obtained and was found to contain a hydronium triflate, **53**.$H_5O_2^+OTf^-$.

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1.0 Introduction

1.1 Carbenes

The first description of carbene species was reported by Geuther and Hermann[1] in 1855 in which they suggested the formation of a divalent carbon intermediate called dichlorocarbene in the alkaline hydrolysis of chloroform.[2]

Now the term carbene is applied to molecules that have two non-bonding electrons on a neutral carbon centre. The unpaired electrons can be either in the same orbital with antiparallel spins (singlet state) or in two different orbitals with parallel spins (triplet state).[3]

1.2 Stabilization and reactivity of carbenes

1.2.1 Triplet Carbenes

Of the two types of carbene, triplet carbenes are generally the more stable form, even so they are still reactive; they can be trapped by oxygen to produce ketones via a ketone oxide intermediate. Moreover, triplet carbenes can rearrange and decompose by a number of different routes, including alkene dimerization, C-H insertion and cyclopropanation of alkenes ([2+1] cycloaddition). Initially thought to be stable only at low temperature (77 K), Tomioka et al.[4] managed to synthesize a triplet carbene which was stable in solution at ambient temperature for up to one week; this discovery came more than 30 years after Zimmerman[5] tried to isolate the same compound. Stabilisation of triplet carbenes can be achieved by delocalization of the unpaired elections in an aromatic network. [2]

1.2.2 Singlet Carbenes

Singlet carbenes are usually more reactive than triplet carbenes; the carbene multiplicity is found to be highly dependent on the electronegativity of both α- substituents. σ-electron withdrawing groups result in a preference of the singlet state by stabilising the occupied non-bonding orbital and increasing its s-character.[6] Singlet carbenes have been divided into five categories based on the mesomeric effects and stabilization of their α- groups: +M/+M, -M/-M, -M/+M, +M/-M and cyclopropylidenes.[2]

Carbenes can also be usefully classified based on their basicity. Factors such as substitution patterns, electronic properties of attached groups and the NCN bond angle can all influence the basic properties of a carbene (**Fig 1**).[3]

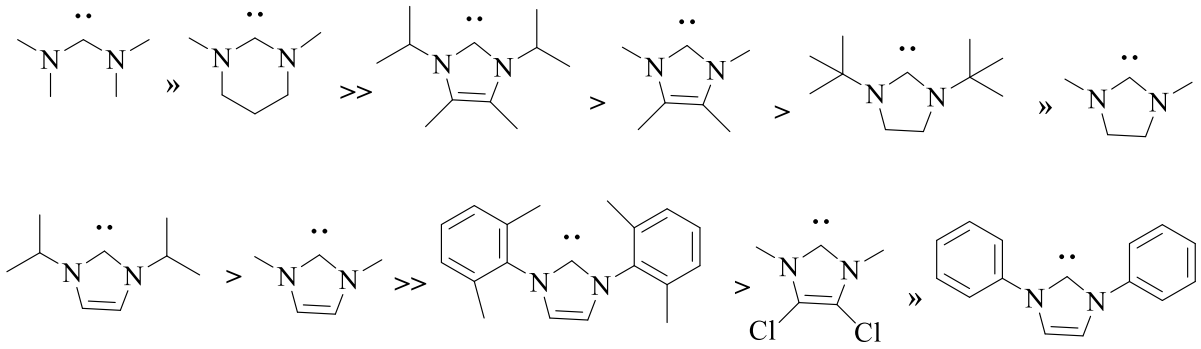
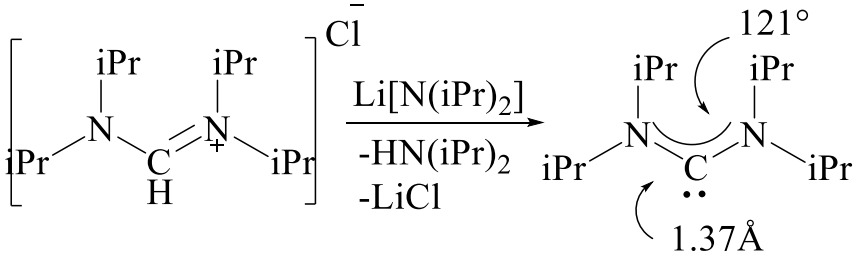


Fig1. Some carbenes ordered according to their basicity.

It is clear from the above structures that carbenes can be acyclic or heterocyclic in nature.

1.2.3 Acyclic Carbenes

These were discovered by Alder in 1996. Treatment of *N,N,N',N'*-tetraisopropyl formamidinium chloride with lithium diisopropyl amide (LDA) in THF yielded the bis(diisopropylamino) carbene (**1**) as the final product.(**Equation 1**)[7]



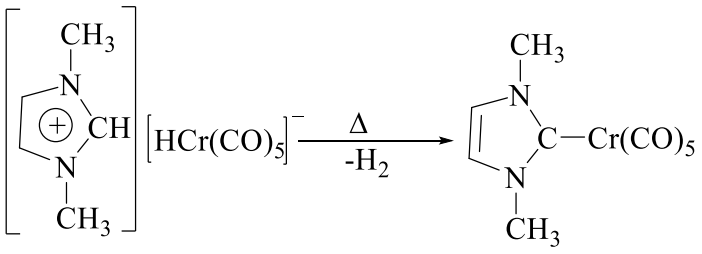
(**1**)

1

The first stable transition metal complexes of acyclic carbenes, such as $(CO)_5W(COCH_3(Ph))$ were reported by Fischer[8], in which the carbene carbon was characterized as electrophilic. Ten years later, Schrock[9] isolated nucleophilic carbenes with the reverse metal-carbon bond polarization.[3]

1.3 N-Heterocyclic Carbenes (NHCs)

Ofele and Wanzlick reported the preparation of the NHC-containing complexes **2** and **3** which were synthesized from imidazolium salts and their respective metal precursors (**Scheme 1**). Prior to their discovery in 1968, it was believed that N-heterocyclic carbenes would be limited to metal coordination compounds derived from azolium precursors. [7]



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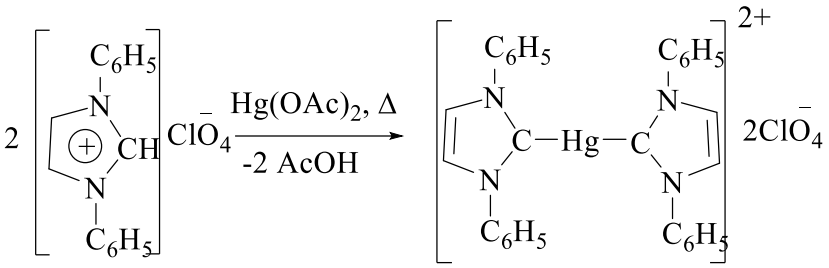
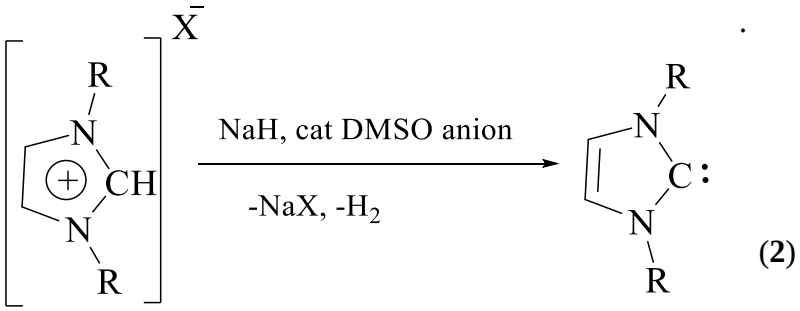


3

Scheme 1

There was a breakthrough in the field of organometallic NHC chemistry in 1991 when Arduengo isolated a free carbene.[10] Subsequently, Arduengo illustrated a general method for isolation of a free NHC by deprotonation of an imidazolium salt [equation **2**], the formation of which can be influenced by several factors such as the amount of NaH and KOtBu or DMSO anion.[7]

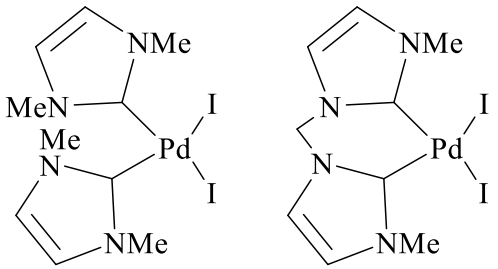


(2)

Metal complexes of NHCs have been demonstrated to be thermally stable and hydrolytically durable due to the presence of strong M-C bonds. These ligands have surpassed classic phosphines for their ease of preparation and low cost.[11] N-heterocyclic carbenes are now considered to be useful as ligands in catalytic reactions and NHCs have replaced classic phosphines in some reactions due to their wide application and stability.[7] The application of NHCs in organometallic chemistry includes a wide range of reactions such as polymerization, hydrogenation, hydrosilylation, hydroboration and allylic substitution.[12]

The majority of transition metal NHC complexes in catalysis have been used in olefin metathesis and palladium catalysed coupling reactions.[13-15] In order to improve the performance of NHCs in Heck type CC-coupling reactions, electron withdrawing substituents were introduced to the backbone of imidazolylidene ring.[16] NHCs can also be used in their own rights, for example as nucleophilic reagents and organocatalysts in different reactions such as the benzoin condensation.[17]

Herrmann[18] reported the use of complexes **4** and **5** in the Mizoroki-Heck reaction in 1995. It is assumed that the strong σ-donor ability of carbenes accelerates the oxidative addition of the aryl halide in the catalytic cycle due to the metal being more electron rich.[12]



4 **5**

Scheme 2. NHC complexes used in Mizoroki-Heck coupling reactions.

The metal-NHC bond is subject to the same decomposition reactions as alkyl complexes, since some characteristics of this bond e.g. length and polarization resembles that of metal-carbon bonds. To date some of the most popular reactions are based on NHCs possessing sterically demanding groups such as the mesityl group (Mes), which enhance reductive elimination due to the increase in the steric bulkiness of the metal centre.

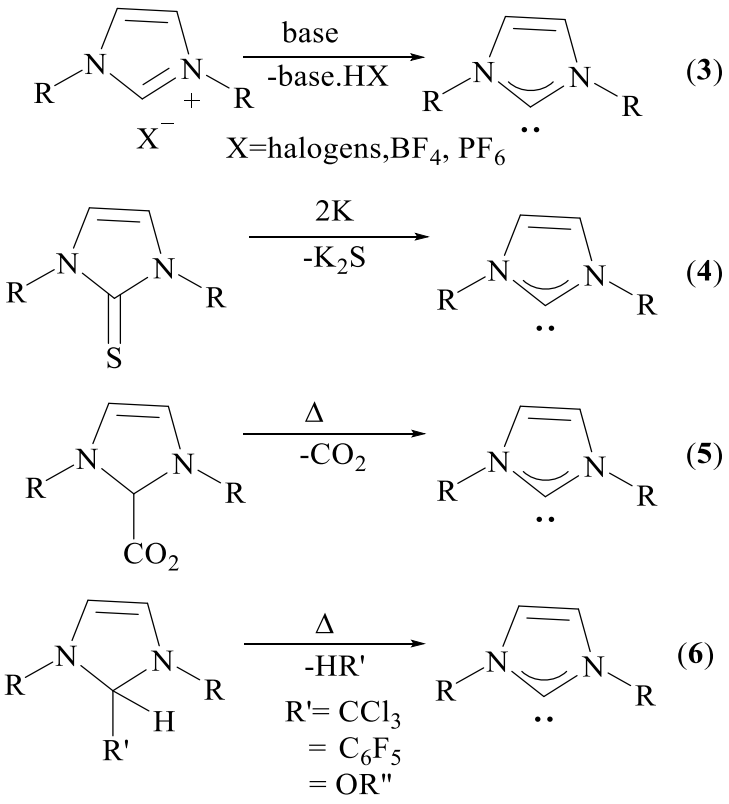
C-H activation of the substituents on the nitrogen of carbenes can lead to NHC decomposition. The latter is believed to be due to the increase in electron density on the metal centre and ligand bulkiness.[12]

Alder et al.[19] studied a series of cyclic NHCs (possessing 5, 6 and 7 membered rings) with variable alkyl substitutions on the N atoms. It was observed that by increasing the bulkiness of the alkyl substituents there was an increase in the stability of monomeric NHCs. However, this effect is less obvious in 5 membered NHCs due to the small N-C-N angle.[20]

1.4 Preparation of NHCs

Free carbenes can be formed by three different common methods: (**Scheme 3**)[21]

1. Deprotonation of imidazolium salts by a strong base. (**3**)[22]
2. Reduction of a thione with molten potassium. (**4**)
3. Thermal decomposition methods. (**5 and 6**)

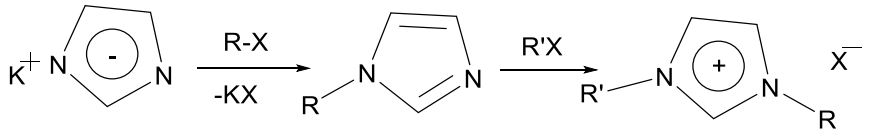


Scheme 3

The first of these methods is often preferred these days, which requires the synthesis of an *N*-substituted azolium salt, which can be achieved by two common synthetic approaches.

1. Nucleophilic substitution at the imidazole heterocycle.
2. Multi component reaction

In the first approach, the reaction of potassium imidazolide with an alkyl halide in toluene results in the formation of 1-alkylimidazole[23]. Alkylation at the 3 position of the heterocycle ring is then carried out by adding another equivalent of alkyl halide.[24]The only problem with this method is that only primary alkyl halides can be used to produce the imidazolium salts. (**Scheme 4**)[25]

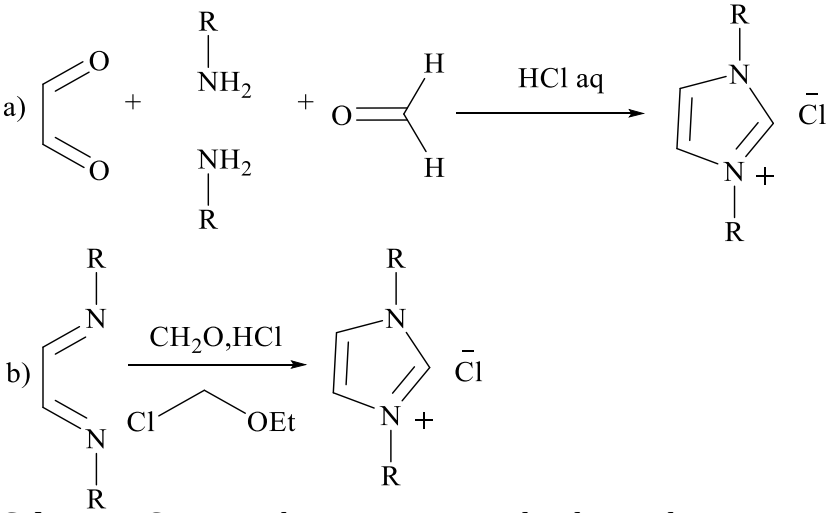


Scheme 4. Preparation of imidazolium salts from potassium imidazolide.

As an example of the second approach, Gridnev reported the synthesis of 1-alkylimidazole from a multi-component reaction using glyoxal, formaldehyde, amine and ammonium chloride followed by alkylation by an alkyl halide to obtain imidazolium salts.[25, 26]

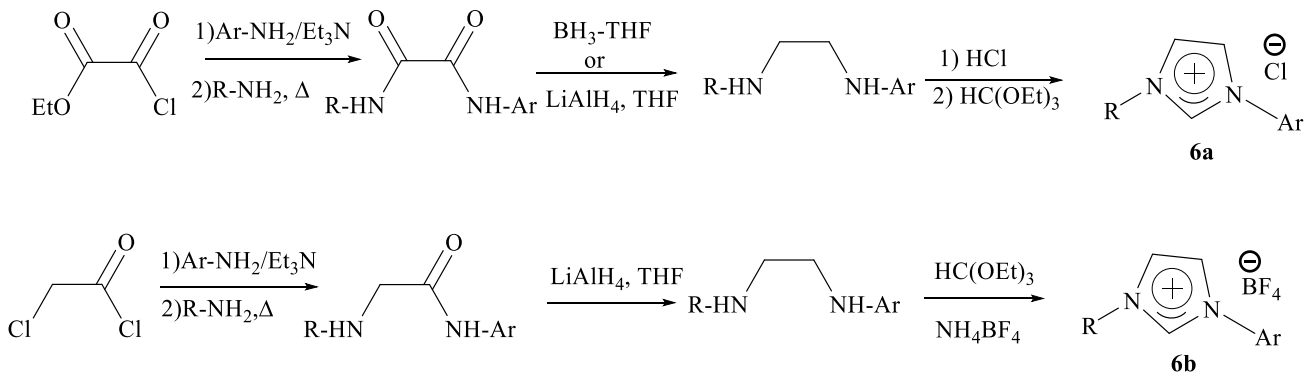
The synthesis of *N*,*N*-disubstituted symmetric imidazolium salts was described by Arduengo[27] in 1991 in which glyoxal was reacted with a 2:1 stoichiometric amount of an aromatic or aliphatic amine and paraformaldehyde in the presence of hydrochloric acid. (**Scheme 5a**)

However, a more pure product was obtained from a two-step reaction sequence using a diazadiene. (**Scheme 5b**)[28]



Scheme 5. Some synthetic routes to imidazolium salts

Dissymmetric imidazolinylidene salts can be obtained via the condensation of ethyl chlorooxoacetate with aniline, followed by amidation with an amine. Subsequent reduction and cyclization of the diamine with triethylorthoformate under acidic condition yielded the salt **6**. Kotschy[29] prepared the imidazolinylidene salts **6** using a similar approach in which chloroacetyl chloride was used as a starting material (**Scheme 6**)[30]



Scheme 6

Once the NHC has been prepared they can be used to make metal complexes. The synthesis of mercury bis-NHC complexes using mercury (II) diacetate was described by Wanzlick et al.[31] The method also proved successful for the preparation of palladium (II) and nickel (II) complexes in which the corresponding metal (II) diacetates and imidazolium or triazolium salts were used as the starting materials.[25]

1.5 M-C orbital interactions in TM-NHC complexes

Bonding of NHCs to transition metals (TM) can be considered to be composed of the following components**:**

1. σ donation from the NHC σ orbital to an appropriate TM orbital.
2. π-back donation from an occupied TM d_π orbital in to the NHC p orbital of π symmetry.
3. Delocalization of the NHC π system into an unoccupied TM-based orbital.[13]

The M-L π interaction has two parts:

M ⟶ L π* back bonding

L ⟶ M π donation

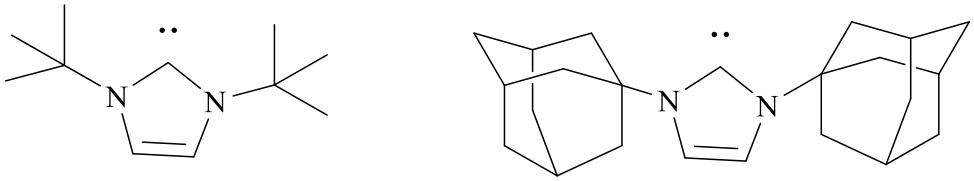
The M⟶L π* interaction forms as a result of the overlap between the π* orbital of the carbene and the HOMO orbital of the metal centre, while L⟶M π donation is between a metal d orbital and the occupied NHC π orbital of the carbene carbon.[21]

It was widely believed that the bonding properties of NHCs are similar to trialkylphosphines, with the high kinetic stability of NHC complexes being related to the strong carbene π donation.[13, 32]

1.5.1 Steric and electronic effects in NHC-metal bonding

The electronic stability of monomeric NHCs depends on the σ withdrawing characteristics of the N atoms and π donation into the carbene p_π orbital from the nitrogen π system. On the other hand, bulky substituents on the N atoms prevents NHCs from dimerization.[20]

Tolman[33] explained the steric and electronic impacts of phosphine metal bonding, however, less research has been done about the bonding of NHCs to transition metals. A few detailed studies have been undertaken; for instance, the unsaturated $Ni(CO)_2(NHC)$ complexes were prepared from the reaction of $Ni(CO)_4$ with ligands IAd and I^tBu in order to determine NHC- metal bond dissociation energy. These complexes also allowed direct comparison of steric properties of NHCs with phosphine ligands. (**Scheme 7**)[34, 35]



I^tBu IAd

Scheme 7

From the calculated data in table **1**, the weakest NHC metal bonds (10-12 kcal/mol) are reported for Cp*Ru(NHC)Cl complexes, while the BDE value is in the range of 40-45 kcal/mol for unsaturated $Ni(CO)_2(NHC)$. These data also indicate that NHC ligand coordination to a metal is generally more favourable than phosphines or CO. Moreover, the data suggests that steric properties such as the bulkiness of the substituents bound to aromatic rings and N atoms of NHC ligands, can influence BDE values.[35]

Entry	Complex	BDE of	BDE(experimental)	BDE(theoretical)
1	Cp*Ru(ITol)Cl	ITol	18.8[a]	26.2
2	Cp*Ru(SITol)Cl	SITol	-	27.5
3	Cp*Ru(IMes)Cl	IMes	15.6[a]	19.2
4	Cp*Ru(SIMes)Cl	SIMes	16.8[a]	19.2
5	Cp*Ru(I^{i}Pr)Cl	I^{i}Pr	11.1[a]	11.6
6	Cp*Ru(SI^{i}Pr)Cl	SI^{i}Pr	12.1[a]	10.9
7	Cp*Ru(IAd)Cl	IAd		1.8
8	Cp*Ru(PCy_3)Cl	PCy_3	10.5[a]	
9	$Ni(CO)_2$IMes	IMes		46.5
10	$Ni(CO)_2$SIMes	SIMes		47.7
11	$Ni(CO)_2$IAd	IAd	43[b]	46.5
12	$Ni(CO)_2$I^{t}Bu	I^{t}Bu	39[b]	44.3
13	$Ni(CO)_2PPh_3$	PPh_3		30.0
14	$Ni(CO)_3$IMes	IMes		41.1
15	$Ni(CO)_3$SIMes	SIMes		40.2
16	$Ni(CO)_3$IAd	IAd		20.4
17	$Ni(CO)_3$I^{t}Bu	I^{t}Bu		24.0
18	$Ni(CO)_3PPh_3$	PPh_3		26.7
19	$Ni(CO)_3$IMes	CO		28.3(27.2)[c]
20	$Ni(CO)_3$SIMes	CO		26.8(26.4)[c]
21	$Ni(CO)_3$IAd	CO		7.6(14.1)[c]
22	$Ni(CO)_3$I^{t}Bu	CO		13.3(15.6)[c]
23	$Ni(CO)_3PPh_3$	CO		30.4

Table 1. Bond dissociation energies, BDE, in a series of Ru and Ni complexes

BDE in kcal/mol.

[a] Taken from [36]. [b] Taken from [34].[c] Calculated with a QM/MM approach, see [34].

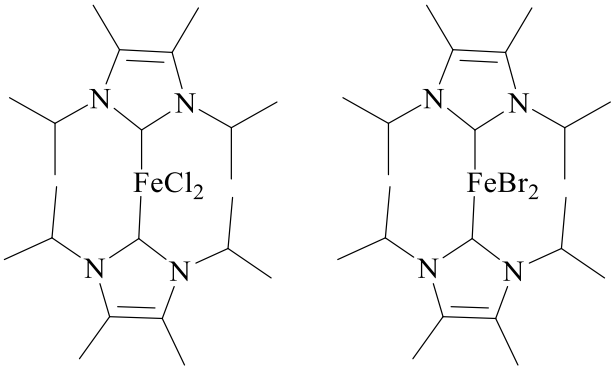
A series of triscarbene-nickel hydride complexes were synthesized by oxidative addition of electron-rich $(NHC)_2Ni$ to the carbene centre of imidazolium salts. The stability of the resulting (NHC) nickel-hydrides is attributed to the steric bulkiness and electronic properties of the carbene ligands. The influence of the "steric factor'' has also been deduced from the study of other nickel (0) complexes and their catalytic properties in C-C and C-F activation reactions.[3]

1.6 Metal-NHC Complexes

In the following sections a selection of metal-NHC complexes and their reactions and applications are given. Whilst deliberately not exhaustive, the aim is to illustrate the breadth of metals, complexes and applications that exist.

1.6.1 Iron-NHC complexes in polymerization reactions

The first application of NHCs in homogeneous iron catalysis was mentioned by the Grubbs[37] group in 2000 in which they reported the synthesis of two $[(I^iPrMe)_2FeX_2]$ complexes **7**,**8 (scheme 8**) and investigated their activity in atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate. The results were consistent with those in anionic polymerization and other ATRP metal-based systems. The high activity of those complexes was attributed to the electron-donating abilities of the NHC ligands.[38]



7 **8**

Scheme 8. $[(NHC)_2Fe]X_2$ complexes tested in atom transfer radical polymerization reactions

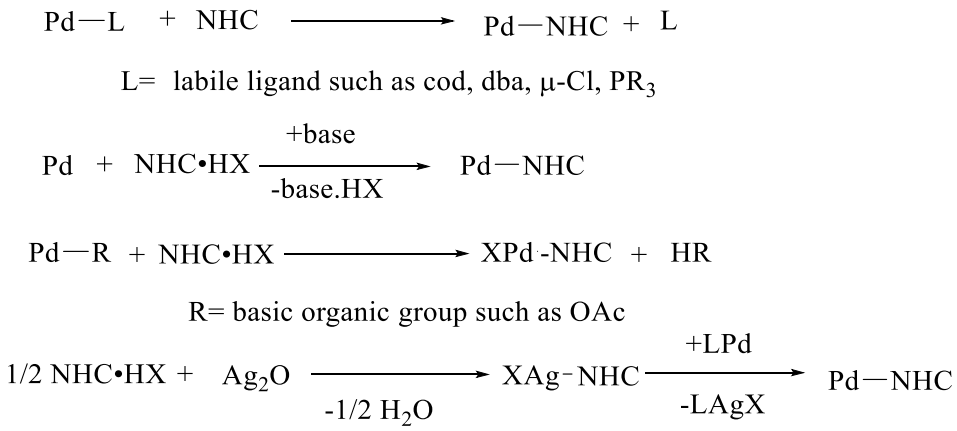
1.6.2 Palladium-NHC complexes

Palladium *N*-heterocyclic carbene complexes have the following benefits; Low toxicity, high dissociation energies for Pd-NHC bonds and easy preparation.[39]

Binuclear carbene complexes of palladium have been prepared using $Pd(OAc)_2$ and imidazolum salts in the presence of NaI and KO^tBu.[11, 40]

Most Pd-NHC complexes are formed via three methods:[21]

1. Substitution of a labile ligand with a free carbene; the final product can be obtained in a short time under an inert atmosphere.
2. *In situ* formation of the free carbene from an imidazolium salt and a suitable Pd source e.g. $[Pd(OAc)_2]$
3. Transmetallation from Ag complexes; [AgX(NHC)], which can be formed directly from Ag_2O and an imidazolium salt. Subsequent reaction of the complex with a suitable Pd source results in transmetallation of the NHC from Ag to Pd. The drawback of this method is the light sensitivity of the silver complex. (**Scheme 9**)

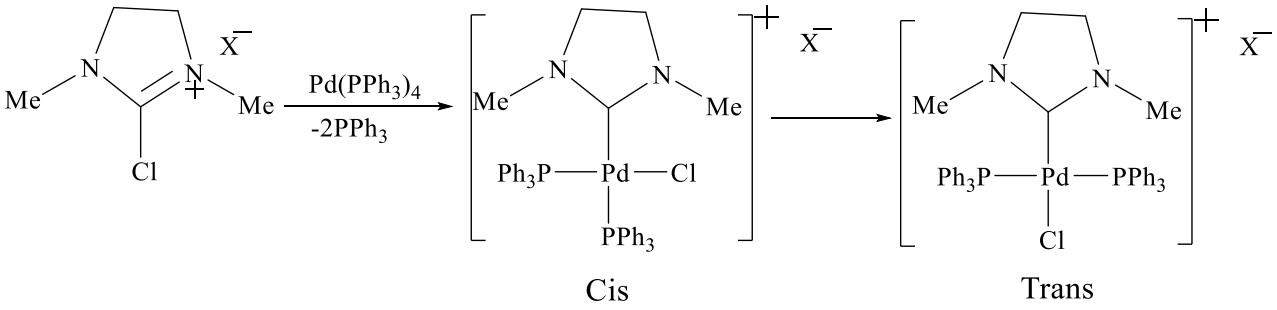


Scheme 9. Synthetic routes to Pd–NHC complexes.

Two approaches can be used in order to get a catalytically active species from coupling reactions with Pd.[41]

1. The treatment of Pd(0) with ancillary ligands results in the formation of an *in situ* catalyst.
2. The use of Pd (II) complexes as pre-catalysts.

(NHC)Pd(allyl)Cl was easily synthesized from the commercially available palladium allyl chloride dimer.[42] The palladium complex becomes less stable by substitution on the allyl moiety, which increases the steric bulk around the metal centre and decreases the back bonding donation from the metal to the olefin.[43] Pd-NHC complexes can also be prepared from oxidative addition of imidazolium chlorides. (**Scheme 10**)[12, 44]



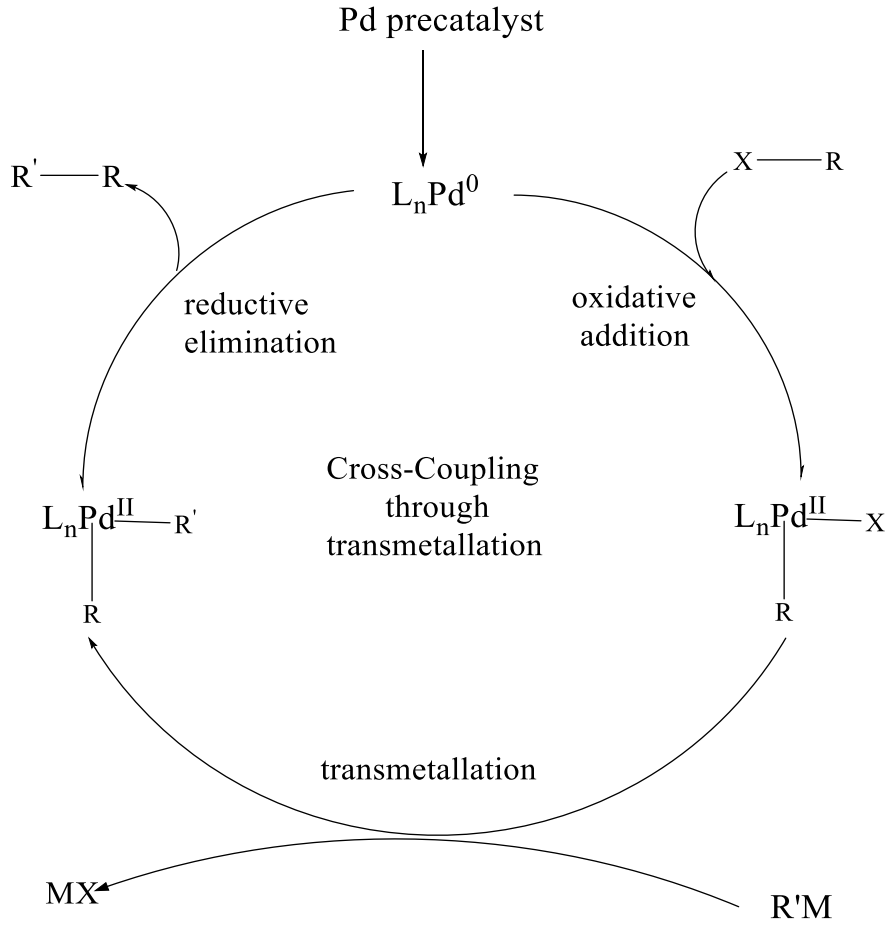
Scheme 10

Cis-chelating bidentate NHC complexes of palladium (II) are highly stable and have proven to be active precatalysts for cross coupling reactions.[45]

The Suzuki-Miyaura reaction is undoubtedly one of the best methods for C-C bond formation.[46] Palladium NHC complexes are excellent catalysts for this transformation, while nickel-complexes are less efficient. Further palladium NHC complexes have been used in various coupling reactions under oxidative conditions e.g. homocoupling of arylboronic acids[47] or terminal alkynes[48]. $Pd(NHC)_2$ catalysed coupling reactions of aryl chlorides with

aryl boronic acids at room temperature has been reported by Herrmann.[49] Such are the advantages of NHCs that many are now replacing phosphine analogues in palladium catalysed cross-coupling reactions.[21]

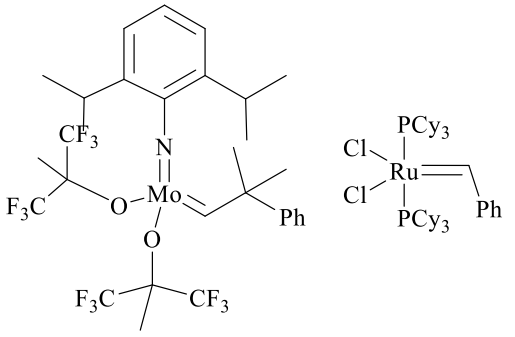
Cross-coupling through transmetallation proceeds by activation of a Pd pre-catalyst and consecutive oxidation addition and reduction elimination to generate the coupling product and reproduce the active Pd catalyst (**Scheme 11**). The formation of a stable Pd-NHC bond, which prevents catalyst decomposition, is one of the main advantages of using Pd-NHC complexes in this application.[21]



Scheme 11. Generalized cross-coupling mechanism

1.6.3 Ruthenium-NHC complexes

The role of NHCs in metal catalysed reactions came to attention after the synthesis of NHC-ruthenium complexes. Complexes **(11** and **12)** allowed the synthesis of carbocycles and heterocycles from their acyclic dienes which were impossible to obtain via Schrock's[50] or Grubbs'[51] catalyst **9** and **10**. (**Fig 2**)[3]



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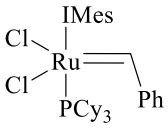

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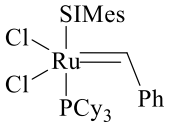
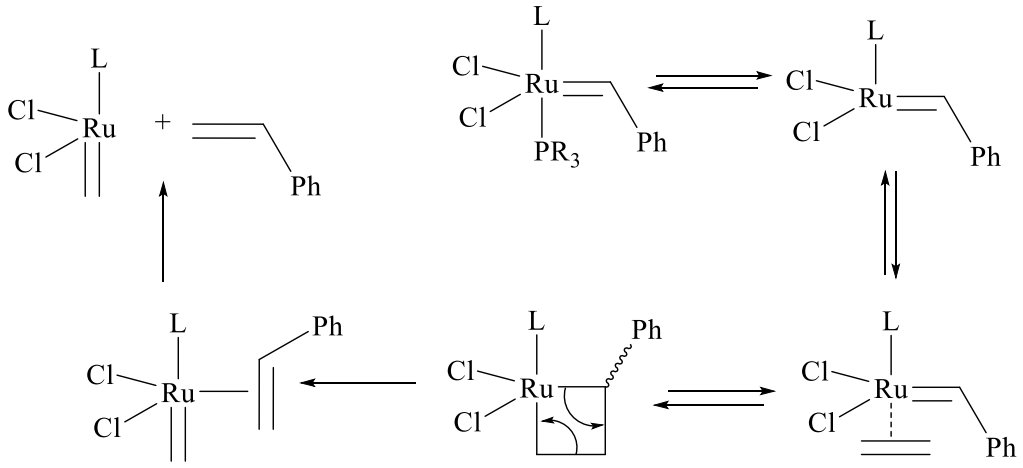


12

Fig 2. Pre-catalysts for olefin metathesis.

During the ruthenium catalysed olefin metathesis, phosphine dissociation and subsequent formation of an olefin π complex results in a metalacycle intermediate (**Scheme 12**). The presence of an NHC accelerates olefin coordination, lowers activation energy and stabilizes the metalacyclic intermediate which is believed to be the reason behind the faster reaction of complexes **11** and **12**. Of these two, **12** is more catalytically active than **11** in alkene metathesis which might be related to the donor ability of the NHC ligand.

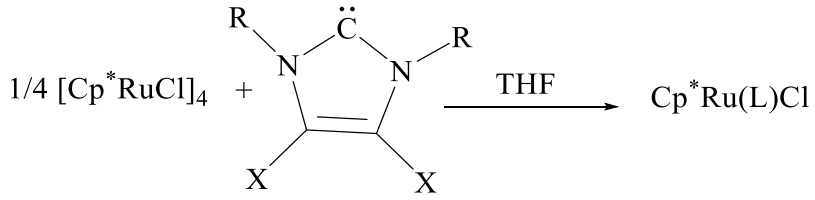
It has also been reported that the higher catalytic activity of ruthenium complexes containing saturated carbenes can be due to the increased basicity of the ligand;[52] however, there are only a limited number of reports regarding pK_b values of imidazol-2-ylidenes.[3]



Scheme 12. Mechanism for olefin metathesis

The reaction of $[Cp^*RuCl]_4$ [$Cp^*=\eta^5$-C_5Me_5] with carbene ligands (L) yields the coordinatively unsaturated $Cp^*Ru(L)Cl$ complexes (**13-17**) [L = 1,3-R_2-imidazol-2-ylidene [R

= cyclohexyl (ICy, **13**); 4-methylphenyl (ITol, **14**); 4-chlorophenyl(IpCl, **15**); adamantyl (IAd, **16**)] and 4,5-dichloro-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes-Cl, **17**)). (**Scheme 13**) The coordination of Cp* to carbene complexes was confirmed by ^{1}H NMR spectroscopy and an assessment of their steric bulk was made. [53]

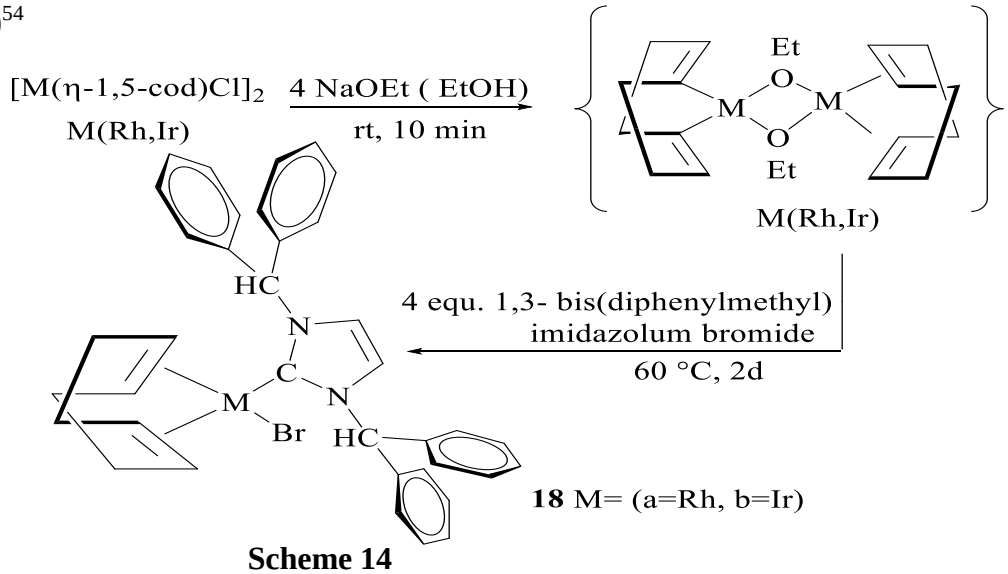


R	X	L	
cyclohexyl	H	ICy	**13**
4-methyl phenyl	H	ITol	**14**
4-chlorophenyl	H	IpCl	**15**
admantyl	H	IAd	**16**
2,4,6-trimethylphenyl	Cl	IMesCl	**17**

Scheme 13

1.6.4 Iridium and Rhodium-NHC complexes

In a one-pot synthesis of rhodium and iridium carbene complexes, *in situ* conversion of an organometallic halide reagent into an alkoxide, which deprotonates the *N*-heterocyclic azolium salt and simultaneous ligand replacement afforded the complexes (**18a, b**). (**Scheme 14**)[54]



Scheme 14

The basicity of NHC ligands was determined by comparison of the CO stretching frequency in the IR spectra of different [(NHC)M$(CO)_n$] complexes (M= Ir, Rh).[55] The CO frequency is dependent on the degree of the back donation from the metal centre. A very basic NHC ligand has relatively low CO stretching frequency due to strong σ-donation from the NHC to the metal centre and little π-back donation from the metal to the NHC ligand.[30]

1.6.5 Nickel-NHC complexes

The introduction of NHC ligands has increased the number of Ni-catalysed reactions remarkably. The catalytic activity of a number of previously studied complexes has been improved by replacing the phosphine or amine ligands of existing complexes with NHCs.

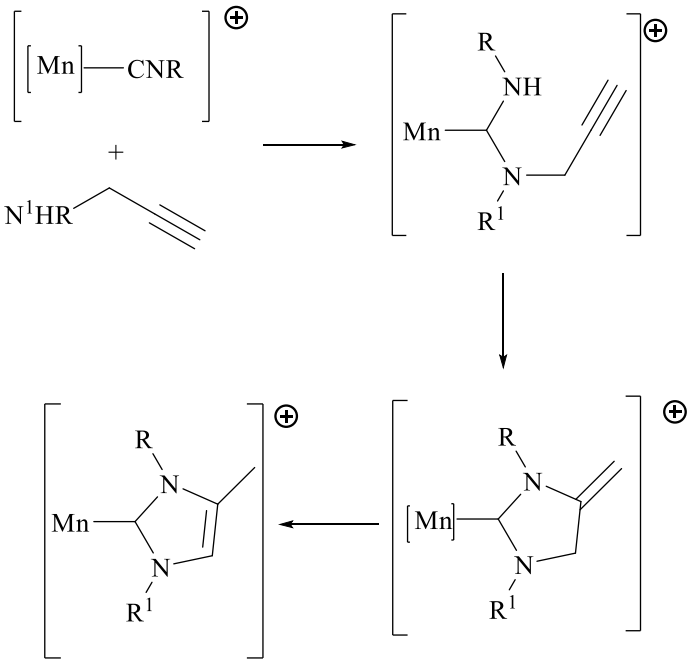
Nickle-NHC complexes can be prepared *in situ* from the reaction of a nickel source such as Ni $(cod)_2$ or Ni$(acac)_2$ with a free carbene or an imidazolium salt in the presence of a base.[30]

1.6.6 Copper-NHC complexes

The first bis-cationic NHC-copper complex was isolated by the reaction of a copper triflate salt with two equivalents of free carbene.[30, 56] While mono NHC copper (I) complexes have been prepared via alkylation of thiazoyl or imidazolyl cuprates.[57] The application of NHC-copper complexes in hydrosilylation of carbonyl compounds and conjugate addition of dialkylzinc reagents have been reported for a long time.[30]

1.6.7 Manganese-NHC complexes

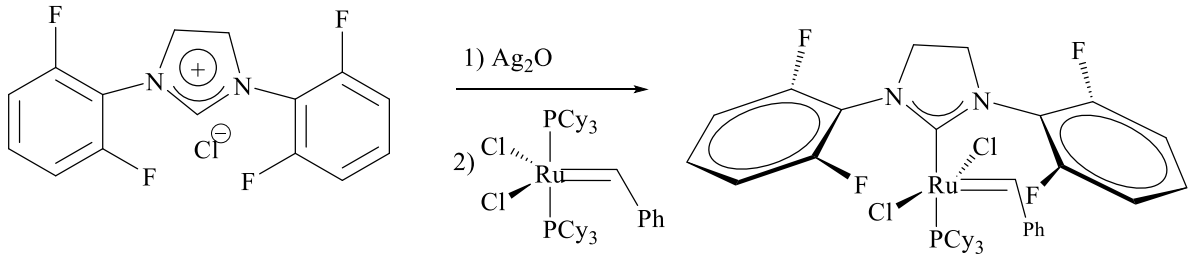
NHC containing complexes of manganese were one of the first classes of NHCs to be isolated.[58] No catalytic activity has been reported for manganese in oxidation states I, II and IV. However, NHC-manganese (III) complexes can be found in the literature.[59] Manganese NHC complexes have been formed by coupling of propargylamines (or alcohols) and isocyanides. (**Scheme 15**)[38]



Scheme 15

1.7 Fluorinated NHCs

Grubbs[60] prepared a ruthenium complex containing a fluorinated NHC by using the imidazolium salt **19** and silver oxide. Subsequent transmetallation of **19** resulted in complex **20**. **20** is a perfect catalyst for RCM reactions which is related to the presence of the fluorine-ruthenium interaction. These are rare, but were proposed to account for the greater stability of the catalyst based on reducing the likelihood of intermolecular C-H bond activation. This in turn may lead to decomposition of the ruthenium complex. (**Scheme 16**).[30]



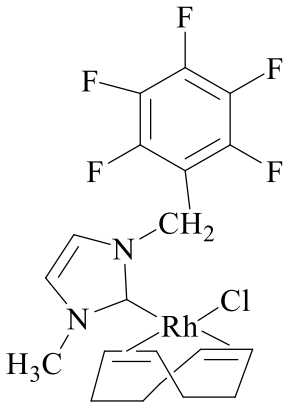
19 **20**

Scheme 16

1.7.1 Fluorinated NHC complexes of Iridium and Rhodium

Treatment of $[M(cod)Cl]_2$ (M= Rh, Ir) with the silver salt of the fluorinated NHC, 1-pentafluorobenzyl-3-methylimidazol-2-ylidene (IpFMe)[61] results in formation of the four-

coordinate complex Rh(IpFMe)(cod)Cl(**21**). Similarly, the iridium analogue of (**21**) Ir(IpF-Me)(cod)Br (**22**) is obtained by reaction of $[Ir(cod)(OMe)]_2$ with 1-pentafluorobenzyl-3-methylimidazolium bromide at ambient temperature (**Scheme 17**). The formation of **22** was confirmed by the down field singlet at 182.1 ppm in ^{13}C {^{1}H} NMR spectrum.[62]



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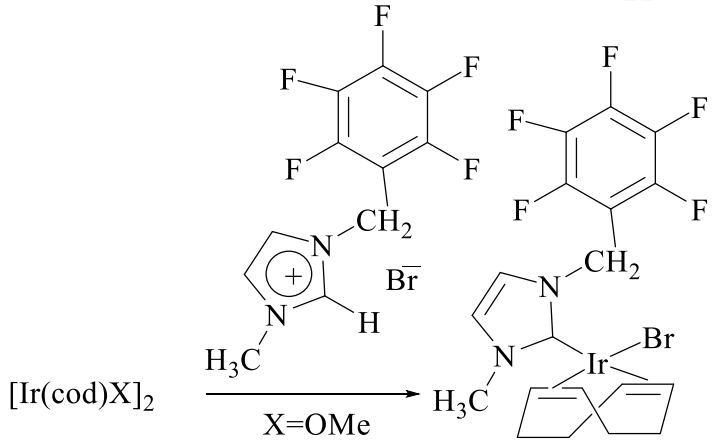
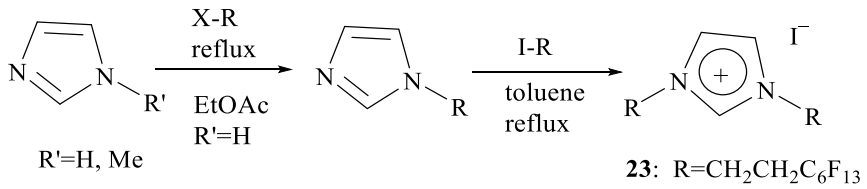


22

Scheme 17. Rh(IpFMe)(cod)Cl (**21**) and formation of Ir(IpFMe)(cod)Br (**22**)

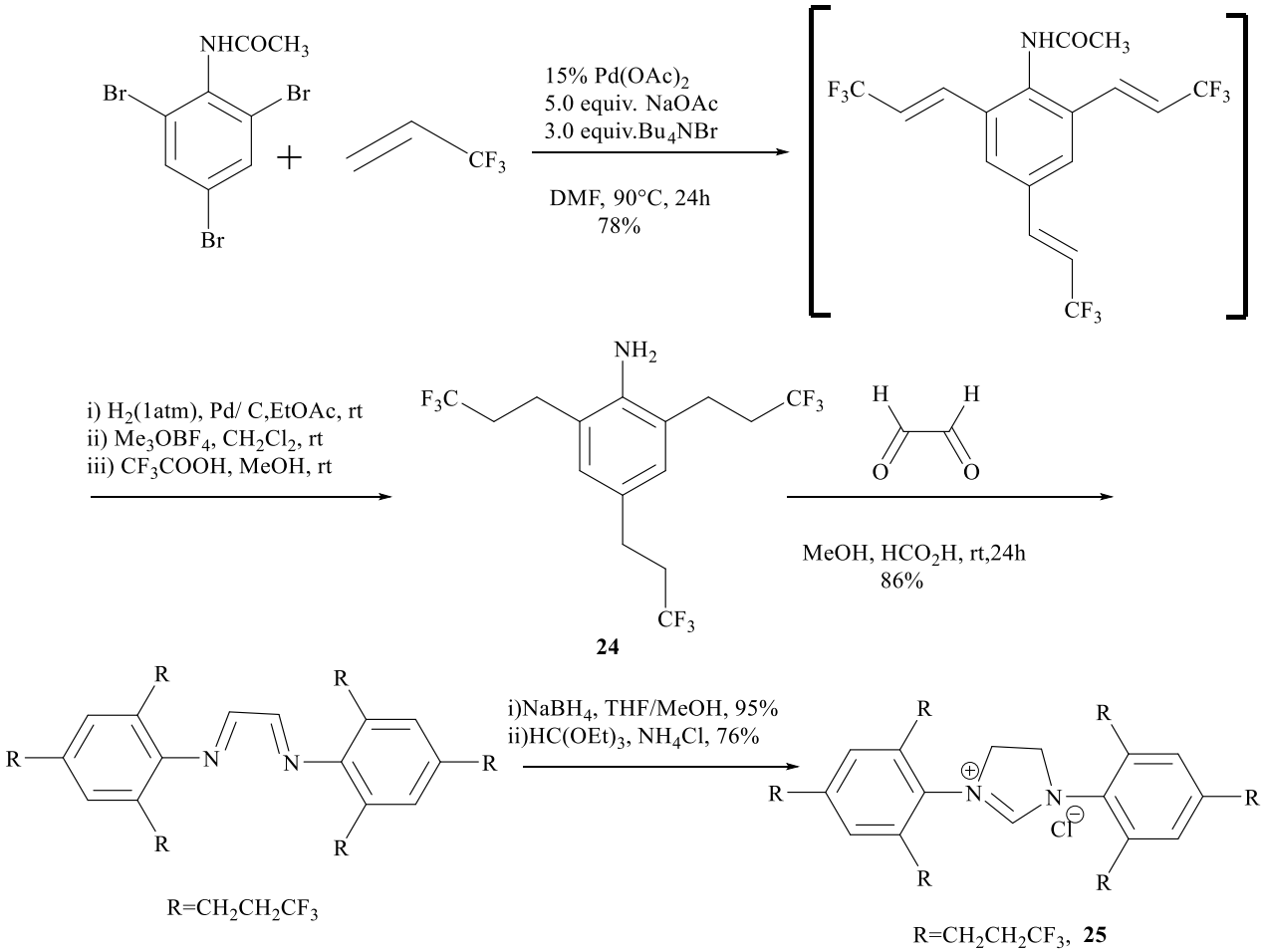
1.7.2 The synthesis of fluoroalkylated NHCs

Alkylation of imidazole with $ICH_2CH_2C_6F_{13}$ and consecutive quaternization of the fluoroalkylimidazole with the same iodide afforded the fluorous *N*,*N'*-difluoroalkyl substituted imidazolium salt (**23**).(**Scheme 18**)[11]



Scheme 18. Preparation of fluorous imidazolium salt **23**

The synthesis of trifluoropropyl NHCs was achieved from 2,4,6 tribromoaniline acetate in six steps. The latter compound reacted with 3,3,3-trifluoro-1-propene under Heck conditions and consecutive acidic hydrogenation and deprotection yielded 2,4,6-tri(trifluoromethylpropanyl)aniline (**24**). Treatment of **24** with glyoxal, followed by reduction by $NaBH_4$ and cyclization with $HC(OEt)_3$ gave the imidazolium salt (**25**). (**Scheme 19**)[39]



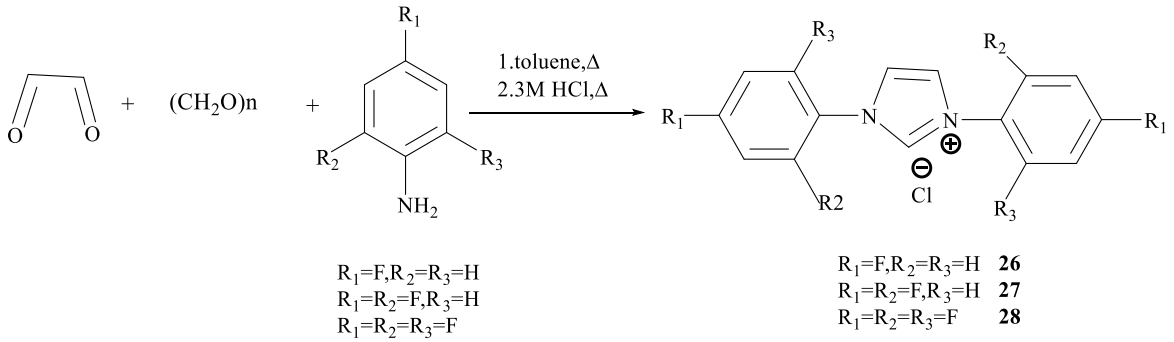
Scheme 19. Preparation of imidazolium salt **25**.

In order to investigate the effect of fluorine, a series of non-fluorinated analogues were prepared from salt **25**. It was observed that the reaction of non-fluorinated salts in the Suzuki-Miyaura reaction of p-chloroanisole and phenylboronic acids results in a lower yield of the coupling product.

The high reactivity of the catalyst generated from fluorine containing imidazolium salt **25** was suggested to be due to the presence of the electron withdrawing $CH_2CH_2CF_3$ group which enhances the dissociation of the NHC from $Pd(NHC)_2$ and results in an active monocarbene palladium species that undergoes reductive elimination to form the product.[39]

1.7.3 The synthesis of fluorinated N-aryl NHCs

The imidazolium salts *N,N'*-bisfluoroarylimidazolium chloride (**26**-**28)** were synthesized by a one-pot reaction of the fluorinated aniline, glyoxal and formaldehyde. Salts (**26**, **27**) can be used as ligands to prepare the bis-cyclometalated carbene carbonyl complexes of ruthenium and iridium. (**Scheme 20**)[63]



Scheme 20. Preparation of bisfluoroarylimidazolium salts

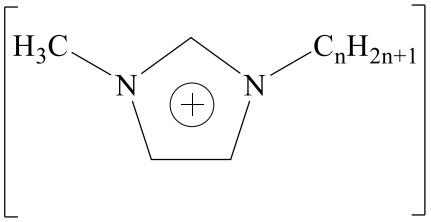
1.8 Ionic Liquids

In addition to acting as NHCs, imidazolium compounds can also form the basis of a series of ionic liquids, ILs. These are described as liquids that are composed only of cations and anions and have a melting point of 100°C or below. The early reports of ionic liquids goes back to 1914 when Walden[64] mentioned the first room temperature molten salt. He reported the formation of ethylammonium nitrate, $(C_2H_5NH_3)NO_3$, with a melting point of 12°C from

the reaction of ethylamine with concentrated nitric acid. Later, Hurley and Weir et al.[65] reported that room temperature ionic liquids could be obtained by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. In 1992 the first air and moisture stable imidazolium based ionic liquid with tetrafluoroborate or hexafluorophosphate as counter ions were reported by Wilkes and Zaworotko. These ionic liquids showed higher air stability than the chloroaluminate ones.[66]

Varma et al. suggested the synthesis of imidazolium-based ionic liquid using a household microwave oven. This quick, solventless method worked well for the preparation of imidazolium based ionic liquids containing long alkyl chain substituents in high yields.[67]

Ionic liquids based on the 1-alkyl-3-methylimidazolium cation with general structure shown below (**Scheme 21**) like the 1-ethyl-3-methylimidazolium $[emim]^+$ and 1-butyl-3-methylimidazolium $[bmim]^+$ are now among the most commonly used ILs.[68]



Scheme 21. Structure of 1-alkyl-3-methylimidazolium $[C_nmim]^+$ cation

Room temperature ionic liquids have widespread applications, including as solvents for a number of different reactions such as Friedel-Crafts[69], dimerization reactions of alkenes[70] and Diels-Alder[71] reactions.[72]

Ionic liquids are considered to be potential solvents for several other reactions for the following reasons:[73]

1. Colourless liquids with relatively low viscosity
2. Low vapour pressure under room temperature
3. Immiscible with numerous organic solvents
4. Stable to oxidation

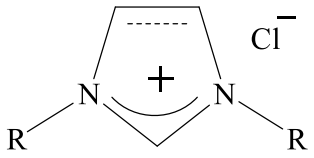
The viscosity of ionic liquids depends on their affinity to form hydrogen bonds and the strength of van der Waals interactions. Longer alkyl chain on the cation of imidazolium ionic liquids lead to high viscosity due to stronger van der Waals interaction while delocalized charge on the anion results in low viscosity. The conductivity of ionic liquids are influenced

by their viscosities, molecular weight, densities and ion size.[74] The low viscosity ionic liquid, [bmim]NTf_2 can be used as a reaction medium in Pd-catalyzed Mizoroki-Heck, Suzuki-Miyaura and Stille coupling reactions.[75] Based on a report by Ngo el al. introducing asymmetry in imidazolium –based cations result in a significant decrease in melting point.[76]

The acidic 2-H proton in imidazolium ionic liquids can be deprotonated in the presence of a base to from a carbene. These imidazolylidine carbenes can act as ligands to metals like palladium (II).[72] Therefore, several transition metal complexes of dialkylimidazol-2-ylidene have been synthesized based on this reaction in solvents such as THF.[77] The extensive application of imidazoles, especially imidazolium salts in different areas such as ionic liquids (ILs) as electrolytes and as carbene ligands for transition metal complexes, have increased in recent years. Liquid imidazolium salts have been used for industrial purposes due to their low volatility. However, there has been environmental concerns regarding the toxicity[78] and antiseptic properties[79] of these compounds. [80]

1.9 Project Aims

The aim of this project was to synthesise imidazolium salts, with the potential to act as both ionic liquids and as precursors of fluorinated NHCs (of general structure shown in **scheme 22**). These imidazolium systems were to be prepared in either step-wise or one-pot reactions involving glyoxal, formaldehyde and appropriate amines, and both symmetric and dissymmetric variations would be investigated, as would NHCs possessing fluoroaryl and fluoroalkyl chains.



R= alkyl, aryl, fluroaryl, etc.

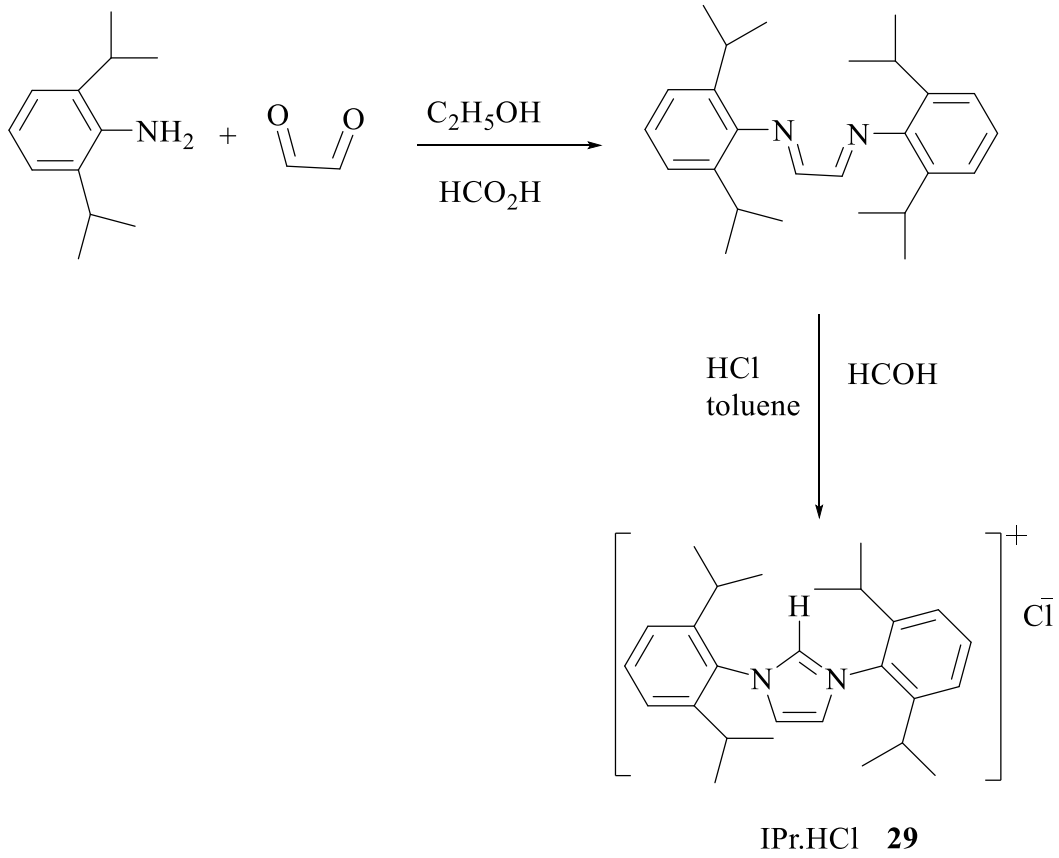
Scheme 22

2.0 Results and Discussions

As a starting point in this work the preparation of non-fluorinated imidazolium systems were investigated in order to ensure that good conversion and yields under appropriate reaction conditions could be achieved.

2.1 The synthesis of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride

This compound was prepared by a two step-reaction from glyoxal and 2,6-diisopropyl aniline in the presence of catalytic amount of formic acid to give the diazabutadiene (diimine) intermediate as a yellow solid in a moderate yield. Subsequent reaction of the latter compound with paraformaldehyde and HCl yielded the title compound, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr HCl) as an off white solid. The identity of the compound was confirmed by comparison with previously reported ^{1}H NMR spectra.[81] (**Scheme 23**)



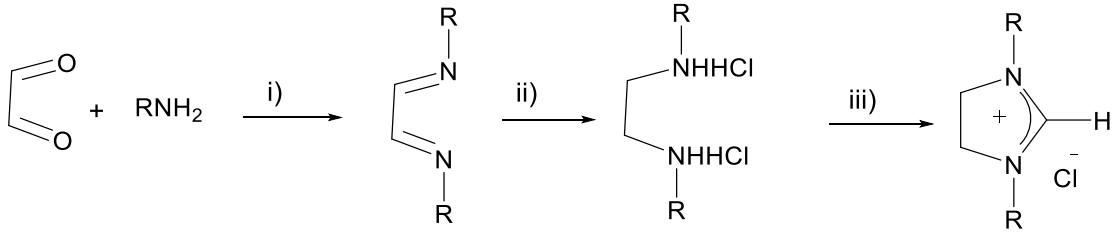
Scheme 23. Synthesis of the IPr.HCl

2.2 The synthesis of 1,3-diarylimidazolinium salts

The unsaturated imidazol-2-ylidenes containing small groups on the nitrogen centres, such as methyl are stable for a number of hours at room temperature. The introduction of sterically demanding substituents at the nitrogen atoms of the imidazolin-2-ylidene moiety prevents dimerization with formation of the electron rich olefin.[82]

These imidazolinium salts can be prepared in a three step sequence by using glyoxal and the desired amine. (**Scheme 24**)

I. Formation of the diimine
II. Reduction of the diimine to diamine hydrochloride
III. Cyclization of diamine moiety



R=(2,4,6-trimethylphenyl)
R=(2,6-diisopropylphenyl)

30 a,b **31 a,b** **32 a,b**

Scheme 24. Reagents and conditions: i) n-PrOH, 60-70°C, (**30a**:75%, **30b**:84%); ii) $NaBH_4$, THF, HCl, (**31a**:60%, **31b**:64%); iii) $HC(OEt)_3$, Δ, (**32a**:45%, **32b**:11%)

In order to prepare the 1,3-bis-(2,4,6-trimethylphenyl)imidazolinium chloride (**32a** R=Mes), 2,4,6-trimethyl aniline was reacted with glyoxal. The reaction mixture was stirred at room temperature for 16 hours followed by heating for 4h at 60 °C to give the glyoxal diimine (**30a**) as a yellow solid in 75% yield. Treatment of the diimine with sodium borohydride and subsequent addition of HCl resulted in the formation of the corresponding diamine dihydrochloride (**31a**). The formation of the latter compound was confirmed by the ^{1}H NMR spectrum with the appearance of a singlet at 3.91 ppm for four (NCH_2) hydrogens.

The cyclization reaction of **31a** using triethyl orthoformate afforded the imidazolinium salt (**32a**) as a high melting point white solid. **Fig 2.2.1** shows the ^{1}H NMR spectrum of **32a** as the desired product, rather than the triethyl orthoformate adduct of the desired NHC, which has been reported in some cases. Similarly, 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (**32b**) was prepared from glyoxal and 2,4,6-trimethylaniline. The reaction mixture was stirred at 70°C for one hour and glyoxal diimine (**30b**) precipitated by adding 20 ml of water. The obtained diimine was reacted with sodium borohydride and stirred at room temperature for 24 h followed by heating under reflux for 2 h. The corresponding diamine

dihydrochloride (**31b**) was afforded by addition of diluted HCl and was confirmed by comparison with the previously published data.[82] The cyclization reaction of the diamine dihydrochloride provided the imidazolinium salt (**32b**) on a small scale.

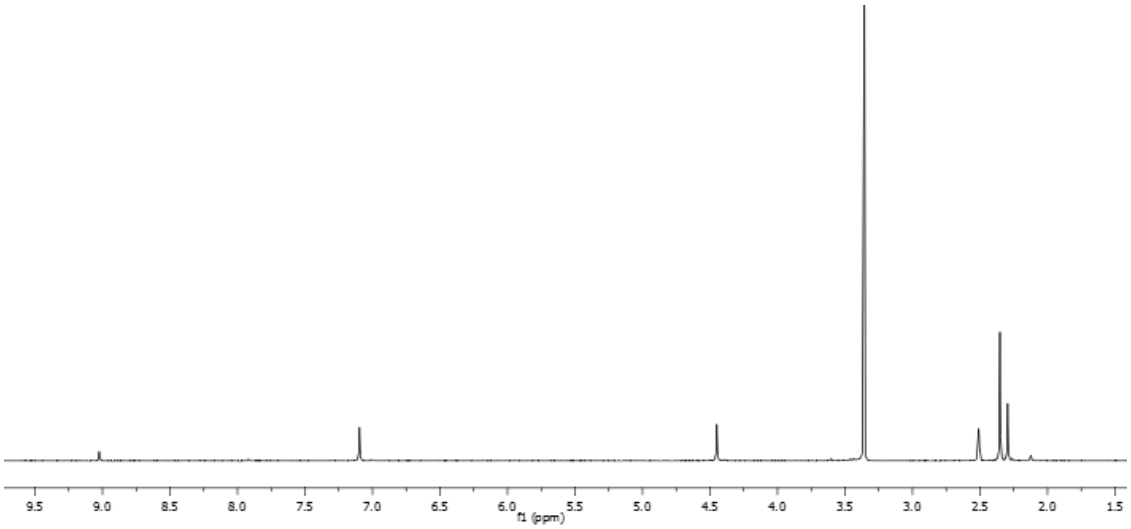


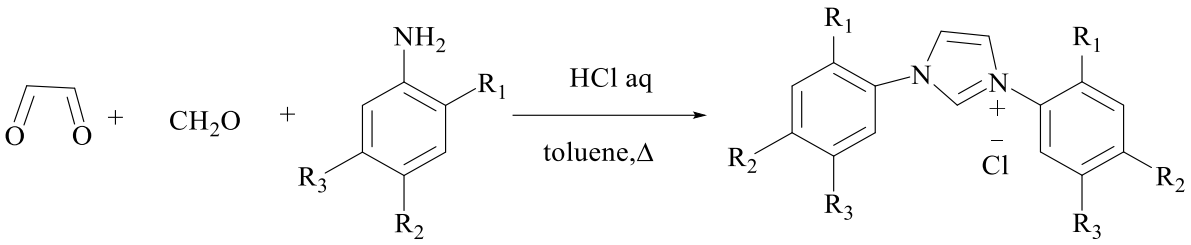
Fig 2.2.1. ^{1}H NMR spectrum of imidazolinium salt **32a**

2.3 The synthesis of *N,N'*-bisfluoroarylimidazolium chlorides

A one-pot condensation of 2,4-difluoroaniline with paraformaldehyde and glyoxal was carried out in refluxing toluene over 12 hours. Subsequently, the solvent was removed in vacuo and the dark slurry obtained was washed repeatedly with diethyl ether and THF. The desired 1,3-bis(2,4-difluorophenyl) imidazolium chloride **(27**) was obtained as an off white solid (20%) by recrystallization from diethyl ether and DMSO. Salts **26** and **27** were synthesized in a similar method described by Harding and Hope et al.[63]

The formation of the imidazolium salt (**27**) was confirmed by peaks at 10.20 ppm for the acidic NCHN proton and 8.45 ppm for the hydrogens of the back-bone in the ^{1}H NMR spectrum. A peak at 138.8 ppm in the ^{13}C NMR spectrum was assigned to the carbene carbon and the fluorine-bearing carbons appeared considerably deshielded in the ^{13}C NMR spectrum (δ~ 160 ppm) compared to the hydrogen bearing ones (δ~ 123 ppm). The spectrum also showed strong coupling to fluorine with $^{1}J_{CF}$ coupling constants of ca. 240 Hz. The 4-fluorophenyl and 2,4,5-trifluorophenyl analogues (**26**) and (**33**) were synthesized in a similar method from their respective fluorinated amines without any further need for purification. Both the NMR and elemental analysis figures suggested that water was present in the p-fluoro analogue (**26**).

A close match between the calculated and observed elemental analysis figures was obtained for a formulation of **26**.2H_2O. Scheme **25** shows the general method for preparing the *N,N'*-bisfluoroarylimidazolium salts



R_2=F, R_1=R_3=H
R_1=R_2=F, R_3=H
R_1=R_2=R_3=F

R_2=F, R_1=R_3=H **26**
R_1=R_2=F, R_3=H **27**
R_1=R_2=R_3=F **33**

Scheme 25. Preparation of imidazolium salts **26**, **27** and **33**.

The fluorine spectrum of the 1,3-bis(2,4-difluorophenyl) imidazolium chloride, **27**, showed two sets of doublets at -105.4 and -118.4 ppm, while the spectra for the trifluoro (**33**) and p-fluoro analogues (**26**) were much more complicated with three sets of doublet of doublets and an overlapping triplet of triplets respectively.

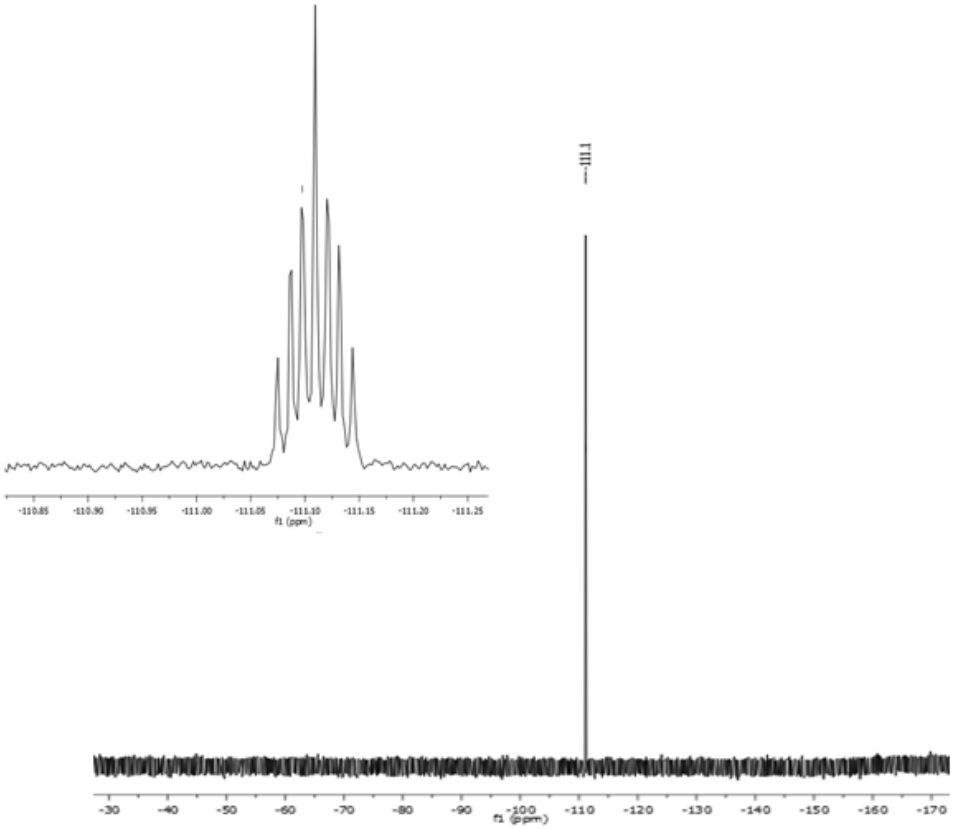


Fig 2.3.1. ^{19}F NMR spectrum of imidazolium salt **26**

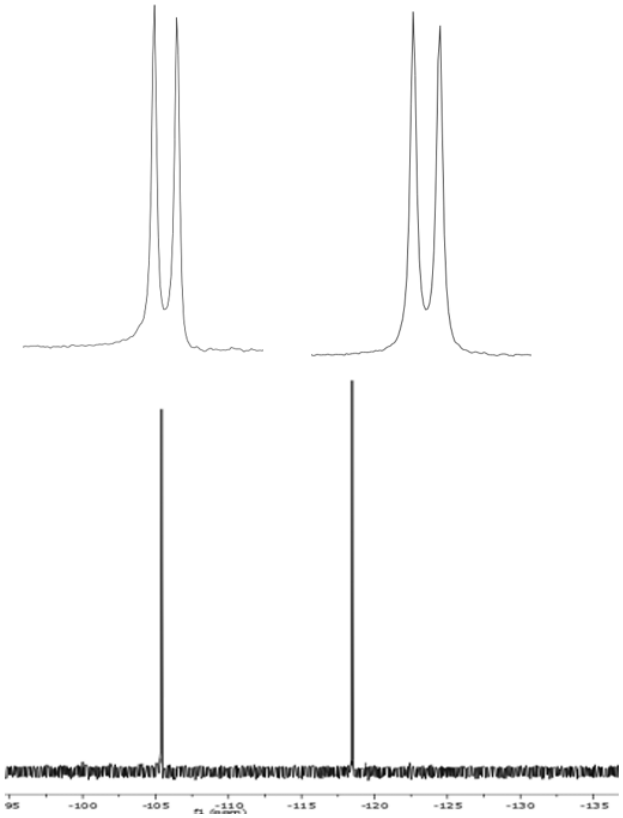


Fig 2.3.2. ^{19}F NMR spectrum of imidazolium salt **27**

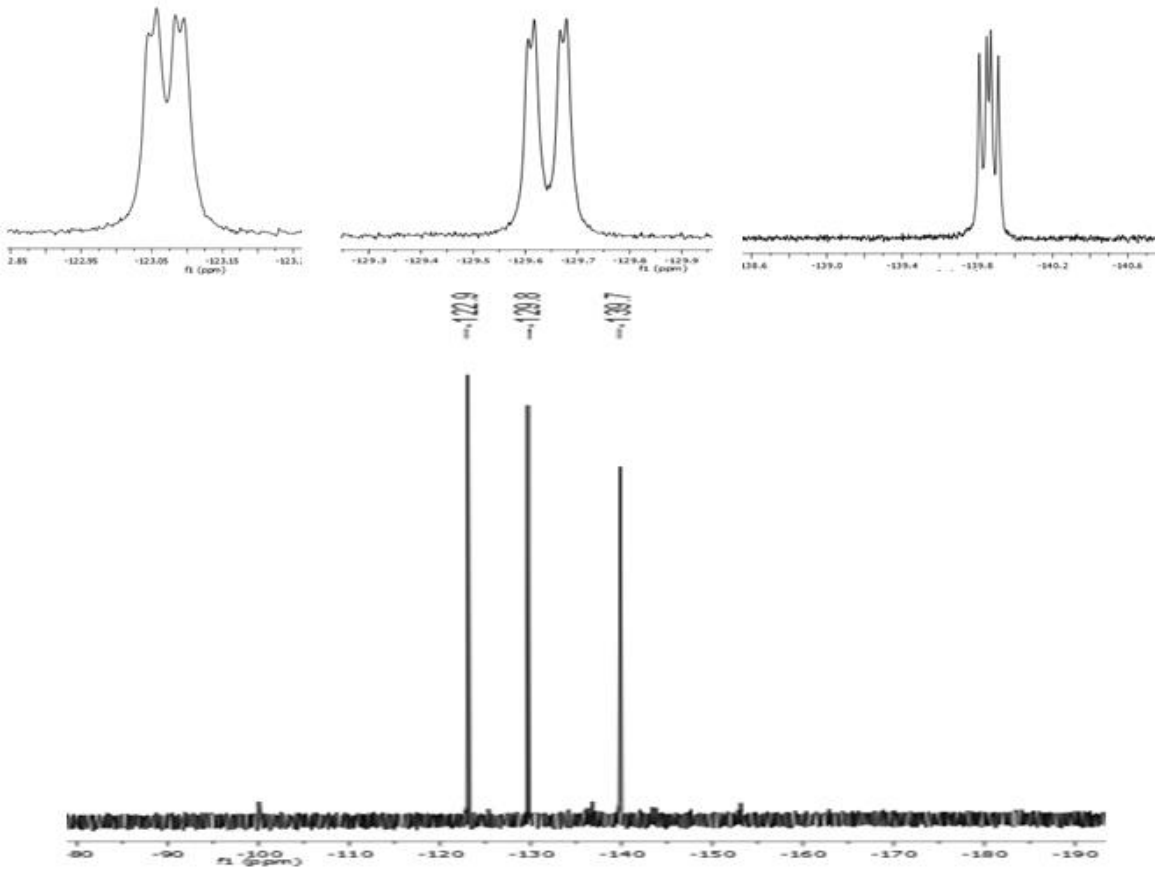
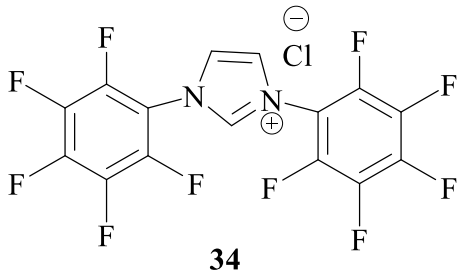


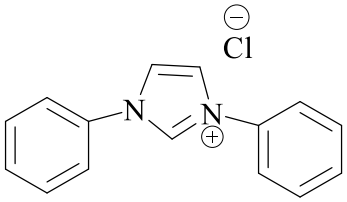
Fig 2.3.3. $^{19}F\{^{1}H\}$ NMR spectrum of imidazolium salt **33**

An attempt was made to synthesize 1,3-bis(pentafluorophenyl) imidazolium chloride (**34**) by treatment of pentafluoroaniline with glyoxal. The reaction mixture was heated for 12 hours at 100 °C and upon cooling to room temperature, two layers were formed. The top layer was extracted and concentrated in vacuo. It was washed with Et_2O/THF to give a dark orange coloured compound. However, based on the ^1H NMR data, the obtained compound was not pure. TLC of the product with toluene and $CHCl_3$ failed to show a clear spot as the compound moved with the solvent front; however, only one spot was observed in TLC with different solvents such as Et_2O, THF, DCM which suggests that there is only one compound, or two compounds which do not separate under these conditions, which would be in agreement with the ^1H NMR result. Unfortunately, the desired compound could not be isolated from this mixture, which can be attributed to incomplete reaction arising from the reduced nucleophilicity associated with an increase in the fluorine content.

Likewise, one pot condensation of aniline with glyoxal and paraformaldehyde failed to produce the 1,3-bis(diphenyl) imidazolium chloride (**35**). The instability of **35** may be due to the electronic effect of the phenyl rings on the imidazole nitrogens which make the adjacent centre unstable.[83]



34



35

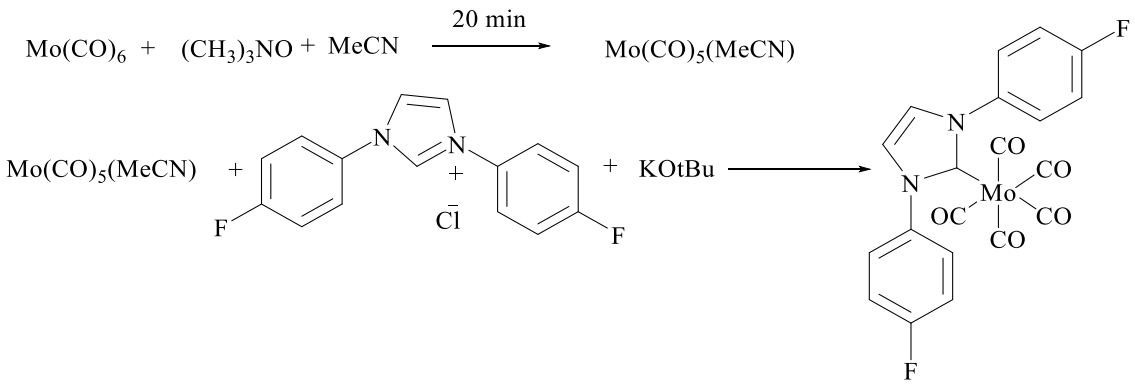
Scheme 26. Compounds which could not be successfully prepared from one-pot condensation of the appropriate aniline, glyoxal and paraformaldehyde.

2.4 Preparation of the molybdenum complex of imidazolium salt (26)

In order to investigate the influence of fluorine substitution on the aromatic rings of NHCs, the imidazolium salt (**26**) was used as a precursor for the synthesis of the 1,3-bis(4-fluorophenyl)imidazol-2-ylidene–pentacarbonyl molybdenum complex. A mixture of molybdenum hexacarbonyl and $TMNO.2H_2O$ was stirred at room temperature in MeCN to generate the $Mo(CO)_5(MeCN)$ intermediate. To this was added the free carbene generated *in situ* from potassium tert-butoxide and **26**. The resulting mixture was stirred for 24 h (**Scheme 27**). The ^1H NMR spectrum exhibited the loss of the NCHN resonance at 10.41 ppm suggesting coordination of the carbene ligand. Unfortunately the complex could not be purified by column chromatography. However, the IR spectrum recorded of the crude

product revealed a change in the carbonyl stretching region of the IR spectrum, with the single peak of $Mo(CO)_6$ at 1962 cm^{-1} being replaced with peaks at 1977 and 2086 cm^{-1}. The increase in the number of peaks suggests that the symmetry of the product is lower than that of $Mo(CO)_6$ and the position of absorptions show the expected shift compared to similar complexs. For instance, in $Mo(CO)_5$(IMes) the highest v(CO) band is observed at 2059 cm^{-1} and for $Mo(CO)_5$(IBz) at 2062 cm^{-1}. [84] The highest observed carbonyl stretch for **26**, at 2086 cm^{-1}, suggests that there is less back donation from the fluorinated NHC ligand than there is from the non-fluorinated NHCs which resulted in a higher frequency CO absorption.

By analysing the integrals of the peaks in the ^1H NMR spectrum, it was obvious that only 47% of the starting NHC was converted to the desired compound. This is confirmed by the fluorine NMR spectrum of the reaction mixture which indicated the existence of a second fluorine environment that can be assigned to the starting material.



Scheme 27. Preparation of the molybdenum complex

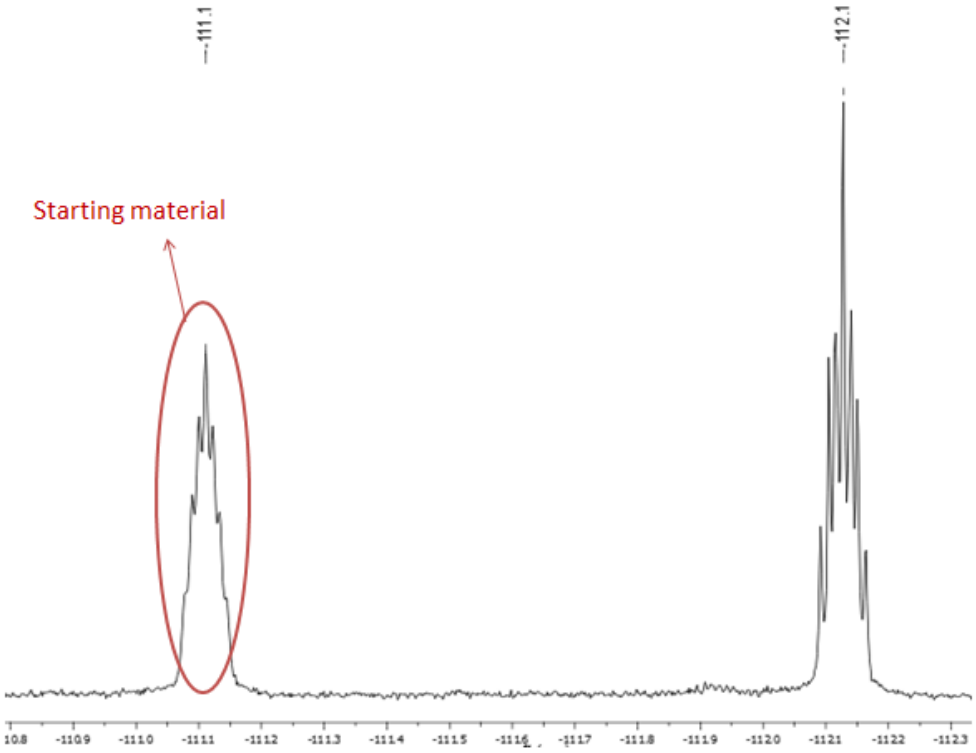
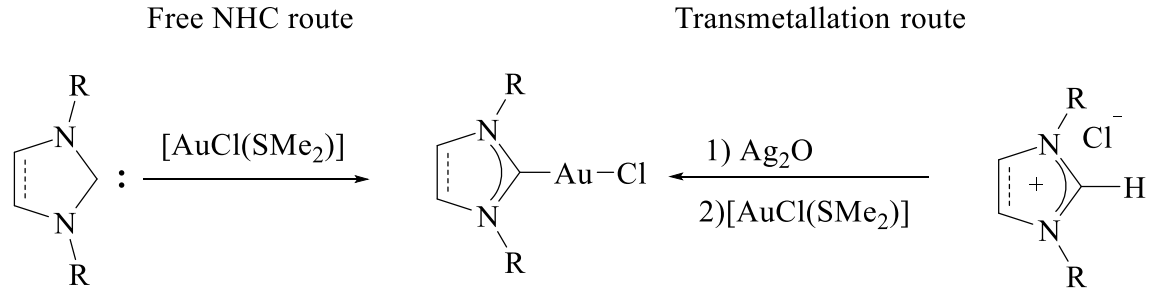


Fig 2.4.1.[19]F NMR spectrum after the preparation 1,3-bis(4-fluorophenyl)imidazol-2-ylidene–pentacarbonyl molybdenum complex

2.5 The synthesis of NHC-gold complex

Gold-NHC complexes can be used as catalysts in different reactions such as C-H activation, C-C coupling, polymerization, hydroamination etc. [AuCl(NHC)] (NHC= IPr, Mes) derivatives are precursors in gold (I) cationic and neutral complexes. The bulkiness of NHC ligands containing 2,6-diisopropylphenyl or mesityl groups in [AuCl(NHC)] complexes plays an important role in the formation of three-coordinate gold(I)-NHC complexes.[85a] These complexes can be formed in two synthetic routes involving the free NHC and transmetallation.[85b] (**Scheme 28**)

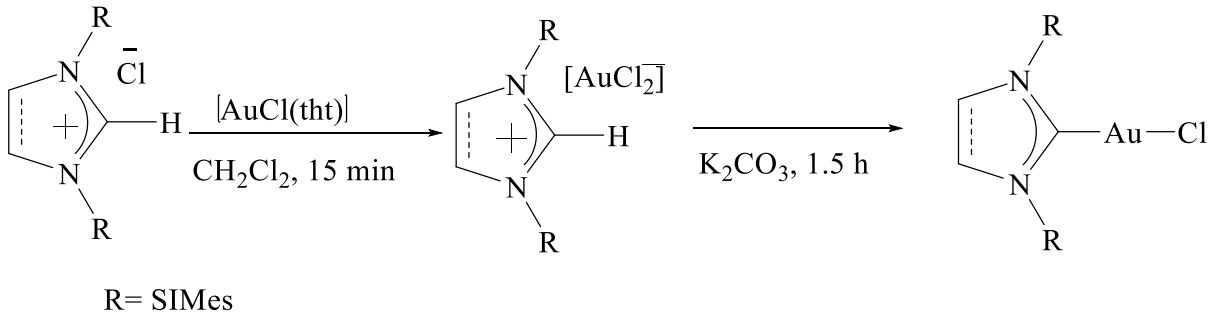


NHC=IPr(75%) and SIPr(81%), R=2,6-$^{i}Pr_2$-C_6H_3
NHC=IMes (51%) and SIMes(63%), R=2,4,3-Me_3-C_6H_2

Scheme 28. Preparative routes to gold(I)-NHC complexes

The above methods, however, suffer from a few drawbacks, such as the necessity of dried solvents and decomposition to metallic gold. In the transmetallation route, pure compound often cannot be obtained and requires further purification with activated carbon. Moreover, the Ag_2O reagent needs to be prepared fresh and the reaction is light sensitive.

[AuCl(NHC)] (NHC= SIMes) has been synthesized using the corresponding imidazolium salt and [AuCl(tht)] (tht=tetrahydrothiophene). The ligand substitution reaction yielded the $[NHC\text{-}H]^+[AuCl_2]^-$ intermediate. Subsequent deprotonation of the latter compound with a mild base like K_2CO_3 would give the desired [AuCl(NHC)] complex.[85b] When the same reaction was conducted in the lab, for unknown reasons it did not work and the [AuCl(NHC)] complex could not be isolated at the end. The formation of the intermediate compound was, however, confirmed by comparing the ^1H NMR data with the previously published work.

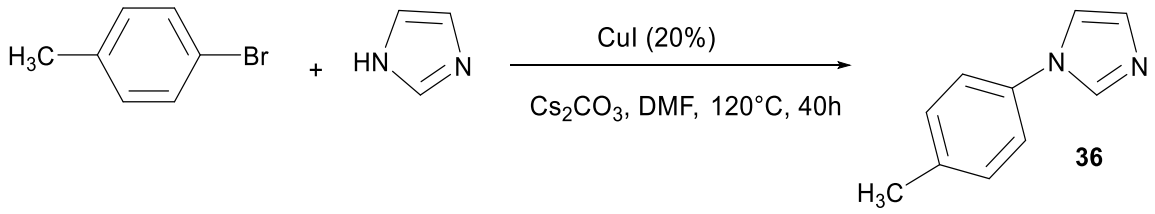


Scheme 29. Synthesis of an NHC- gold(I) complex.

2.6 *N*-Arylation of imidazole

Copper (I) iodide can be used as a catalyst in the arylation reaction of nitrogen containing heterocycles such as imidazoles with aryl and hetroaryl halides. The procedure is highly efficient and a variety of functional groups can be tolerated on the aryl halide.[86] It was hoped that in this way fluorinated groups might be introduced.

In order to prepare 1-(4-methylphenyl)imidazole (**36**), imidazole was reacted with 4-bromotoluene and a catalytic amount of CuI under N_2. The reaction mixture was heated at 120°C for 40h followed by filtration through silica gel and washing with ethyl acetate to give the desired product. (**Scheme 30**)



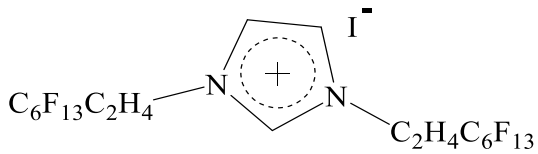
Scheme 30.Synthesis of 1-(4-methylphenyl)imidazole

Alternatively, the synthesis of compound **36** is reported in a similar method by using poly (ethylene glycol) (PEG) as a recyclable catalyst. PEG is an environmentally friendly compound which is less toxic and easily degradable.[87]Unfortunately, however, the compound was only obtained on a small scale when the same reaction was conducted in the lab.

Instead of using the method above for preparing NHCs containing fluoroalkyl fragments an alternative method was investigated. This was based on *N*-alkylation of imidazole, followed by a second *N*-alkylation with a fluoroalkyl triflate to generate a non-symmetrically-substituted NHC.

2.7 The synthesis of 1-(polyfluoroalkyl)imidazoles

Some NHCs bearing polyfluorinated chains are already known, for example, metal complexes containing fluorous tails can be used in fluorous biphase catalysis or for recovering the catalyst by fluorous solid phase extraction.[88] The application of imidazolium salt **23** bearing linear fluorous chains and its palladium NHC complex has been reported by Xu et al. in 2000.[11]

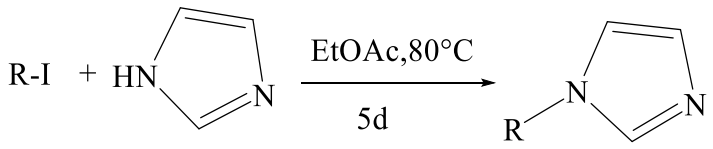


Scheme 31. Imidazolium salt **23**

Generally polyfluoroalkylated imidazoles can be prepared from the reaction of imidazole with a polyfluoroalkyl halide or triflate. Imidazole being used in excess to neutralize the acid formed during the reaction.[88]

Polyfluoroalkylimidazole **37** was prepared from the commercially available 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl iodide as an alkylating reagent

and imidazole. The alkylation process proceeded by stirring the reaction mixture at 80°C for 5 days followed by extraction with water and ethyl acetate to afford the desired compound **37**. The ^{1}H and ^{19}F NMR data for the compound was in agreement with that reported by Cvacka and Kvicala et al.[88]



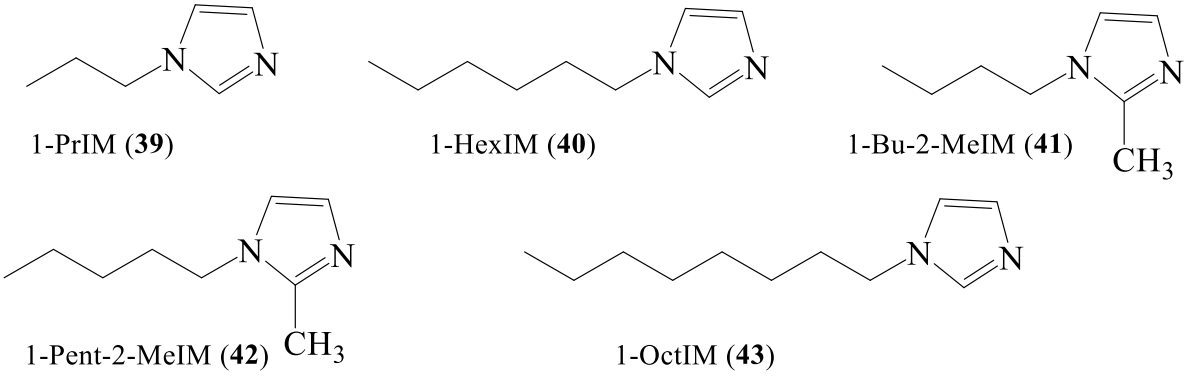
R= $C_8F_{17}C_2H_4$ (**37**)
R=$C_4F_9C_2H_4$ (**38**)

Scheme 32. Preparation of 1-(polyfluoroalkyl)imidazoles **37** and **38**

Likewise, compound **38** was obtained by a similar method in a sealed tube using the appropriate polyfluoroalkyl halide and imidazole. The formation of the desired compound was confirmed by ^{1}H NMR spectroscopy in which the peaks showed the expected chemical shift and integrals compare to **37**. Peaks at 7.65 (s), 7.11 (s), 6.99 (s), 4.33 (m) and 2.62 (m) ppm were assigned to the product.

2.8 The synthesis of *N*-alkylated–substituted imidazoles

Alkylimidazoles **39**-**43** were prepared from alkylation of the appropriate imidazoles with an alkyl bromide or iodide in DMF in the presence of potassium tert-butoxide and subsequent extraction with ethyl acetate. The extracts were washed with brine and dried by anhydrous magnesium sulfate. The removal of the solvent under vacuum afforded the desired *N*-alkylimidazoles. Alkylimidazoles (**39**, **41**-**43**) were obtained without further need for purification, however; 1-hexylimidazole (1-HexIM, **40**) required purification by column chromatography using ethyl acetate and hexane in 1:1 ratio as eluent. The spectroscopic analysis of all compounds were compatible with the data previously published.[89]



Scheme 33. Alkylimidazoles (**39**)-(**43**)

Unfortunately, this method failed to give 1-octylimidazole. However, success was achieved when a mixture of imidazole with 1-iodooctane in acetonitrile was heated to 80°C for 12 hours. After cooling to room temperature, the solvent was removed and the residue obtained was extracted with dichloromethane (DCM) and washed with water to afford 1-octylimidazole as a yellow liquid. The presence of singlet peaks at 7.34, 6.93, 6.79 ppm and multiplets at 1.65, 1.16, 0.78 ppm for the corresponding hydrogens confirmed the formation of the compound.

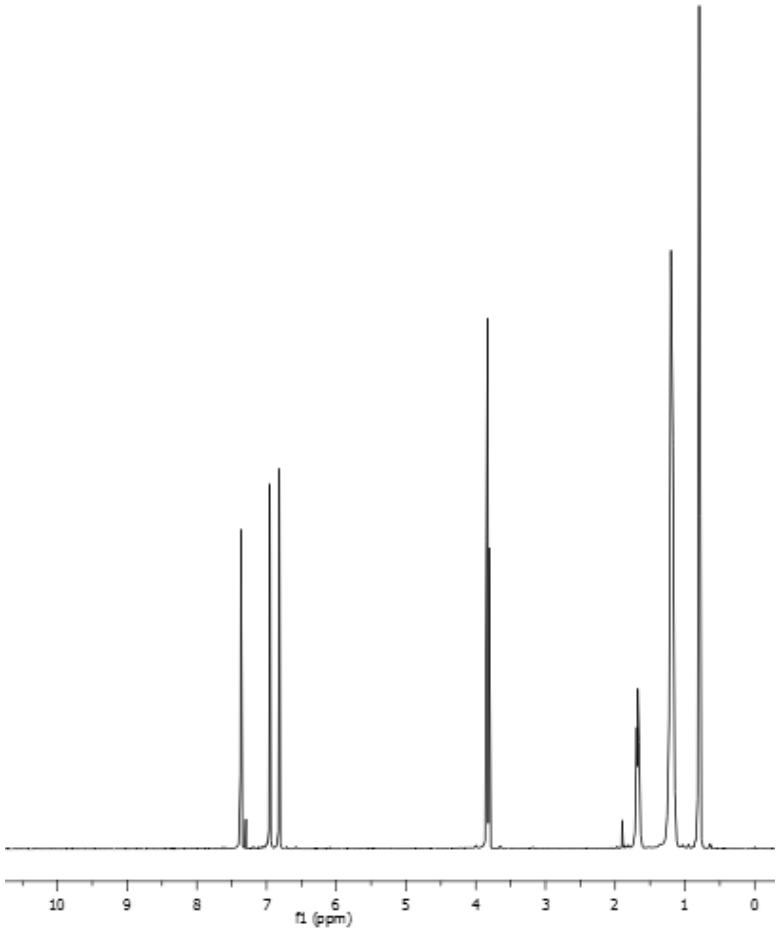
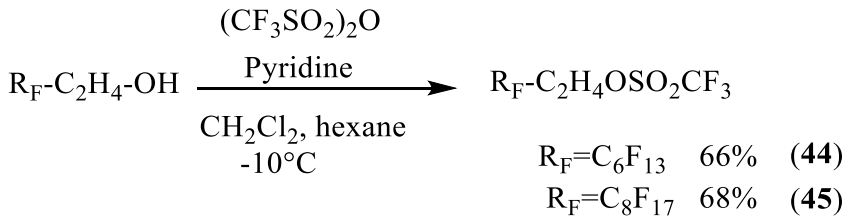


Fig 2.8.1. ^{1}H NMR spectrum of 1-octylimidazole

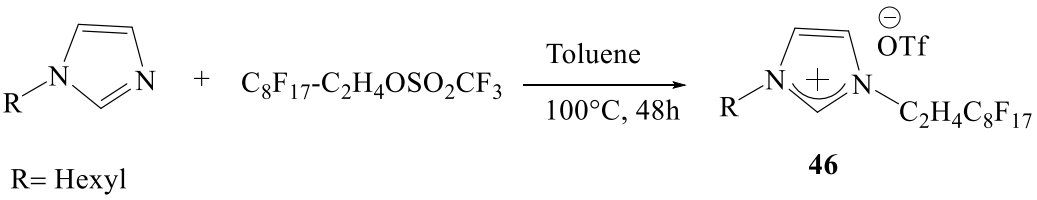
2.9 The synthesis of polyfluoroalkylated imidazolium salts

These were prepared by reaction of alkylated imidazole with polyfluorinated triflates which were in turn synthesized from commercially available fluoroalcohols and triflic anhydride according to the modified procedure developed by Fife et al.[90] in good yields.[91]



Scheme 34. Preparation of fluorinated triflates **44** and **45**

The reaction of 1-hexylimidazole with the fluorinated triflate $C_8F_{17}C_2H_4OSO_2CF_3$ was carried out by stirring the reaction mixture at 100°C for 48 hours. Upon cooling to room temperature, the product was obtained as white crystals. The ^{1}H NMR spectrum showed peaks at 9.28 (m), 7.90 (t) and 7.82 (t) which are characteristic of the protons on the imidazolium ring. At 4.57 and 4.18 ppm multiplets were observed for CH_2 groups of the fluorinated chain, while the signals for the non-fluorinated chain appeared between 3.0 and 0.84 ppm. Salts **46** and **47** share quite similar ^{1}H NMR patterns, whilst their ^{19}F NMR spectra are also similar, except for the relative intensity of the peak observed at ca. -121 ppm, which reflects the different fluorinated chain lengths.



Scheme 35. Formation of imidazolium salt **46**

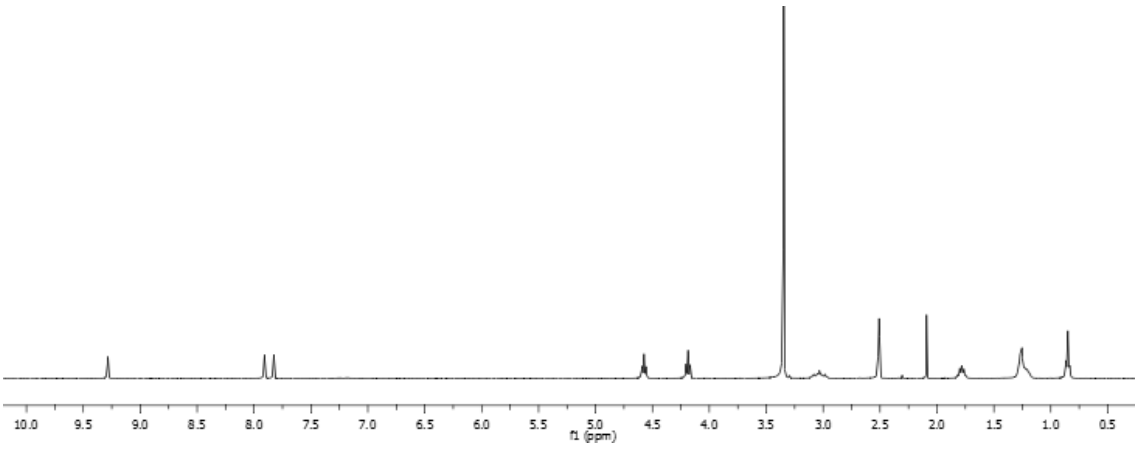


Fig 2.9.1. ^{1}H NMR spectrum of imidazolium salt **46**

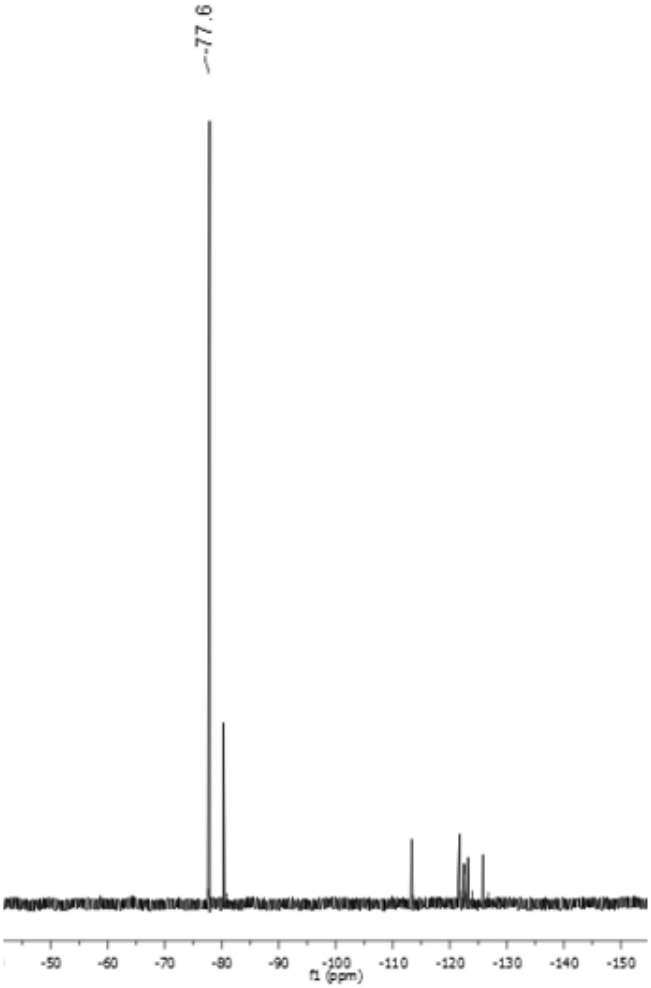
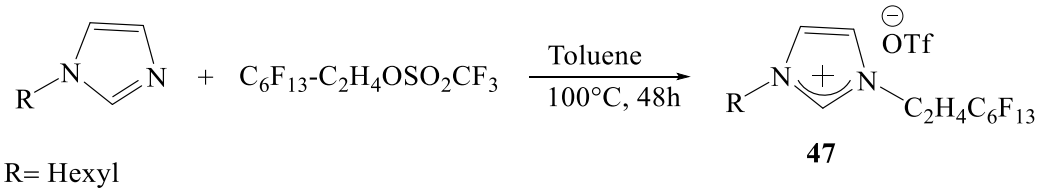


Fig 2.9.2. $^{19}F\{^{1}H\}$NMR spectrum of imidazolium salt **46**

Alkylation of 1-hexylimidazole with the polyfluorinated triflate, $C_6F_{13}C_2H_4OSO_2CF_3$ resulted in the formation of the desired imidazolium salt **47**. The reaction proceeded smoothly by stirring the reaction mixture at 100°C for 48 hours. Subsequently, the solvent was removed in vacuum and the crude product was dissolved in a small amount of ethyl acetate. Imidazolium salt **47** was obtained as a viscous oil by addition of an excess amount of hexane to the mixture. The ^{1}H NMR data showed a singlet peak at 9.28 ppm and two triplet peaks due to coupling of the backbone hydrogens at 7.89 and 7.81 ppm. The peaks for the CH_2 groups appeared as multiplets at 4.56, 4.18, 3.02, 1.77 and 1.25 ppm while the peak at 0.83 ppm was assigned to the terminal CH_3 group.

The ^{19}F $\{^{1}H\}$ NMR spectrum showed a singlet at -77.8 for the CF_3 group of the triflate counter ion and a triplet at -80.2 ppm for the CF_3 group of the fluorinated chain and five sets of multiplets each corresponding to two fluorines for the five CF_2 groups of the fluorinated chain.



R= Hexyl

47

Scheme 36. Formation of imidazolium salt **47**

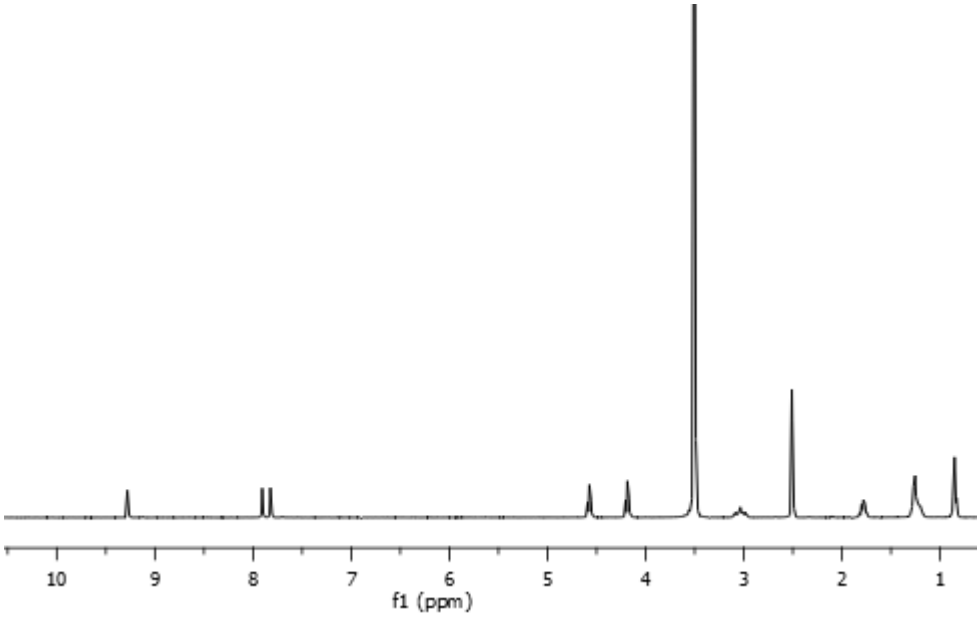
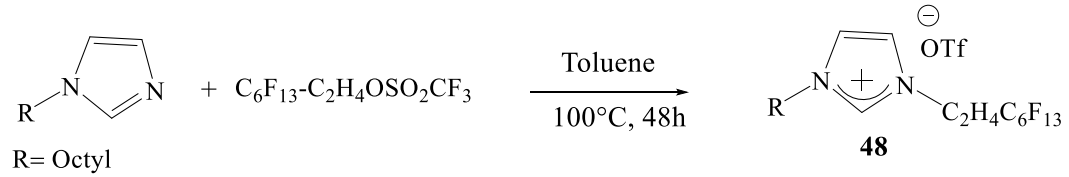


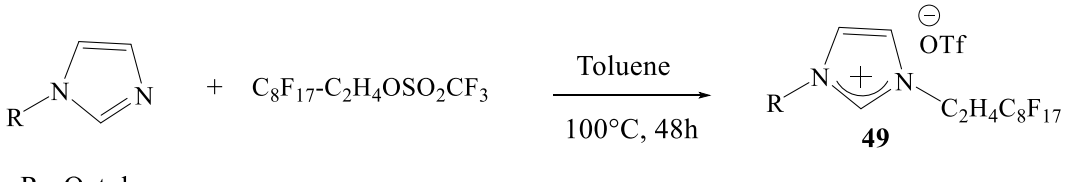
Fig 2.9.3. ^{1}HNMR spectrum of imidazolium salt **47**

The same method was employed in the synthesis of imidazolium salts **48** and **49** from 1-octylimidazole and fluorinated triflates **44** and **45** in which the oily crude products were dissolved in a small amount of EtOAc and precipitated with 10 fold excess of hexane. The = obtained oils were decanted and dried under reduced pressure.



R= Octyl

48



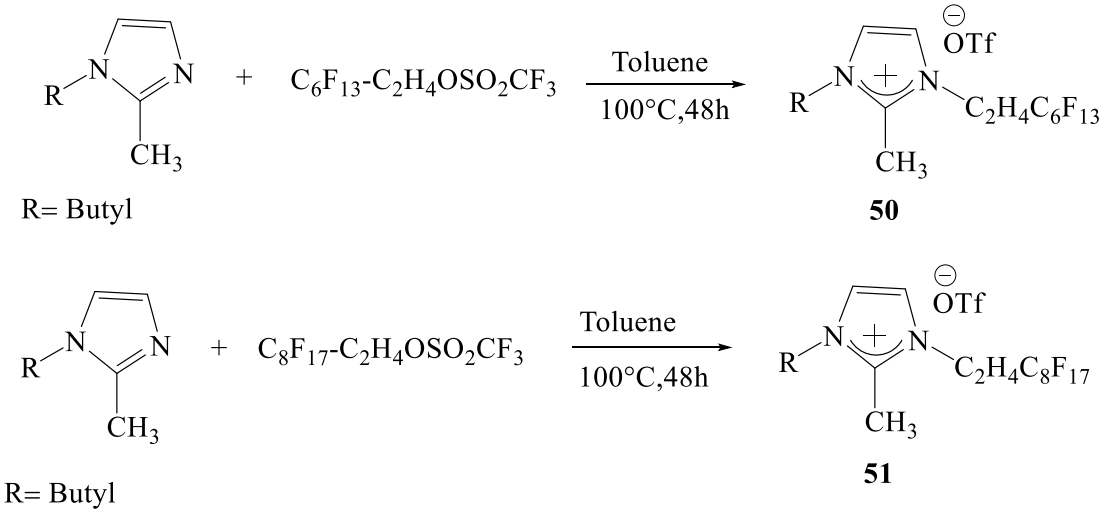
R= Octyl

49

Scheme 37. Formation of imidazolium salts **48** and **49**

The observation of peaks at 9.30 (1H) and triplets at 7.91 and 7.82 ppm, due to coupling of the backbone hydrogens in the ^{1}H NMR spectrum of salt **48** confirmed the formation of the desired compound. The hydrogens for the octyl chain and ethylene spacer of the fluorous ponytail appeared as multiplets at 4.56 (2H), 4.18 (2H), 3.02 (2H), 1.77 (2H), 1.25 (6H) and 0.83(3H) ppm. The ^{1}H NMR spectrum of salt **49** was almost identical to that of salt **48** while the integrals of the peaks varied in ^{19}F NMR spectrum of **49** because of the increase in fluorous ponytail length.

The ethylene spacer containing fluorous chains were attached in a similar method mentioned above, using 1-butyl-2-methylimidazole (1-Bu-2MeIM, **41**) and the triflates **44** and **45** (**scheme 38**). However, the work up of the reactions were different in that the imidazolium salt **51** was obtained as a viscous oil by removing the solvent directly from reaction mixture and drying under reduced pressure.



Scheme 38. Formation of imidazolium salts **50** and **51**

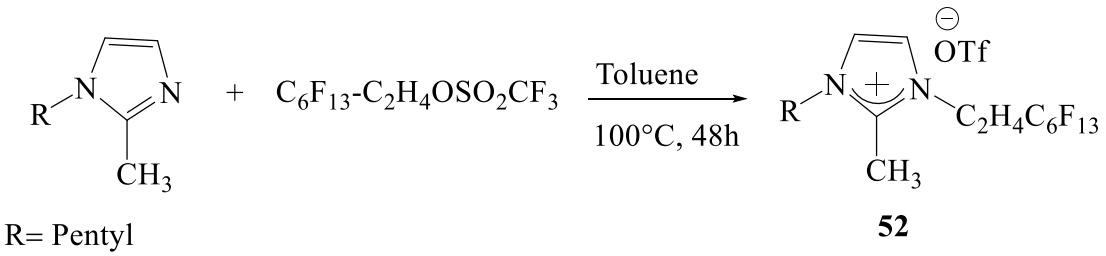
The ^{1}H NMR spectrum of salt **50** showed multiplets at 7.79 (1H) and 7.72 (1H) ppm for the backbone. The peaks for the CH_2 groups appeared at 4.48, 4.13, 2.93, 1.69 and 1.28 ppm as multiplets. Moreover, there was a distinctive singlet peak for the CH_3 group attached to the C2 carbon at 2.65 ppm. All the peaks were shifted in the ^{1}H NMR spectrum of salt **51** in which the peaks for the backbone hydrogens appeared at 7.0 and 6.72 ppm, while multiplets at 3.84, 3.66 and 1.62 ppm correspond to the CH_2 groups and the peaks for the methyl groups attached to C2 carbon and the butyl chain appeared as a singlet and multiplet at 2.29 and 0.88 ppm respectively.

Unfortunately, the reaction of the 1-propylimidazole (1-PrIM, **39**) with the shorter chain fluorinated triflate, $C_6F_{13}C_2H_4OSO_2CF_3$ gave a mixture of the starting material and product.

Based on ^{1}H NMR data, the peaks at 9.28 (1H), 7.91 (1H), 7.82 (1H), 4.57 (t, 2H), 4.15 (t, 2H), 3.03 (m, 2H), 1.81 (m, 2H) and 0.84 (m, 3H) are assigned to the product.

In order to prepare the polyfluoroalkyl imidazolium salt **52**, 1-pentyl -2-methylimidazole was reacted with the polyfluorinated triflate $C_8F_{17}C_2H_4OSO_2CF_3$. The reaction mixture was stirred at 100 °C for 48 hours. After evaporating the solvent, the crude oil was dissolved in EtOAc and precipitated with an excess amount of hexane.

The ^{1}H NMR spectrum exhibited two multiplets for the backbone hydrogens at 7.80 and 7.74 ppm. The peaks at 4.50, 4.14, 2.95 and 1.67 ppm were assigned to CH_2 groups of the polyfluoroalkyl and pentyl substituents respectively. Sadly, one of the peaks for a methyl group was over-shadowed by those of some residual solvent, which was difficult to completely remove due to the viscosity of the obtained oil, hence its position could not be distinguished clearly. Even after drying the final product under vacuum for an hour, traces of the solvents could be found in the ^{1}H NMR spectrum.



Scheme 39. Formation of imidazolium salt (**52**)

Surprisingly, the reaction of 1-pentyl-2-methylimidazole (1-pent-2-MeIM, **42**) with the long chain fluorinated triflate in a similar method, failed to give exclusively the title compound. However, the peaks at 7.79 (1H), 7.72 (1H), 4.48 (4H), 2.26 (3H), 2.61 (2H), 1.75 (4H) and 0.84 ppm were assumed to be from the compound.

2.10 X-ray crystallography of diaryliodonium salt (53)

Diaryliodonium salts have been used for the direct quaternization of *N*-substituted imidazoles by using a copper catalyst to obtain aryl imidazolium salts in relatively high yields. The mentioned method can be used for synthesis of this class of compounds with a wide range of functional groups.[92]

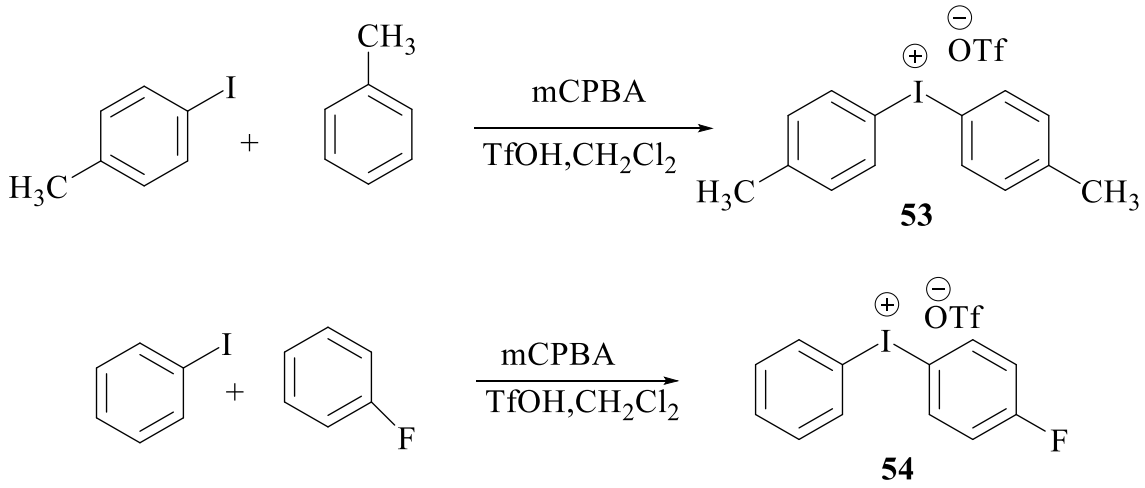
Diaryliodonium salts can be prepared in a 2-3 step procedure by oxidation of an aryl iodide to give an iodine (III) compound and subsequent ligand exchange. In many cases anion exchange is also necessary due to its impact on solubility and reactivity of the iodonium salts. Non-nucleophilic anions like triflate or tetrafluoroborate have proven to be more effective than halide anions in many cases.

Symmetrical iodonium salts can be obtained from pre-formed inorganic iodine(III) compounds while diaryliodonium salts can also be synthesized in a one-pot reaction involving oxidation and ligand exchange of iodoarenes and arenes. However, problems with the mentioned methods have limited the use of diaryliodonium salts in organic chemistry.

The one-pot synthesis of diaryliodonium salts was carried out using an aryl iodide with a commercially available oxidant in the presence of an arene and an acid. Trifluoromethane sulfonic acid (TfOH) and boron trifluoride are the optimized reagents for this procedure without the need for an anion exchange step.[93]

Diaryliodonium triflates **53** and **54** were prepared from their corresponding aryl iodides (4-iodotoluene and iodobenzene) and arenes (toluene, fluorobenzene) respectively, followed by drop wise addition of TfOH. The final compounds were isolated by cooling down the reaction mixture to complete the precipitation. The NMR data of both compounds were comparable with the previously published work. The multiplet peaks in the ^{1}H NMR spectrum of the salt **54** at 8.32, 8.24, 7.69, 7.54, 7.42 ppm indicated the formation of the title compound. The ^{19}F NMR spectrum of the compound showed a singlet at -77ppm for the triflate counter ion and a set of triplet of triplets at -106 ppm for the fluorine coupling to two pairs of hydrogens. The ^{1}H NMR spectrum of diaryliodonium salt **53** exhibited a doublet (8.09 ppm, ortho-CH), multiplet (7.32 ppm, meta-CH) and a singlet (2.33 ppm, CH_3x2).

The structure of salt **53** was also confirmed by single crystal X-ray crystallographic analysis. Crystals, suitable for X-ray diffraction work of **53** were obtained directly following their synthesis. Unfortunately, the same did not occur for **54**. The crystal structure of **53** is shown in **Fig 2.10.2** and selected bond lengths and angles are listed in **Table 2**.



Scheme 40. Desired diaryliodonium triflates **53** and **54**

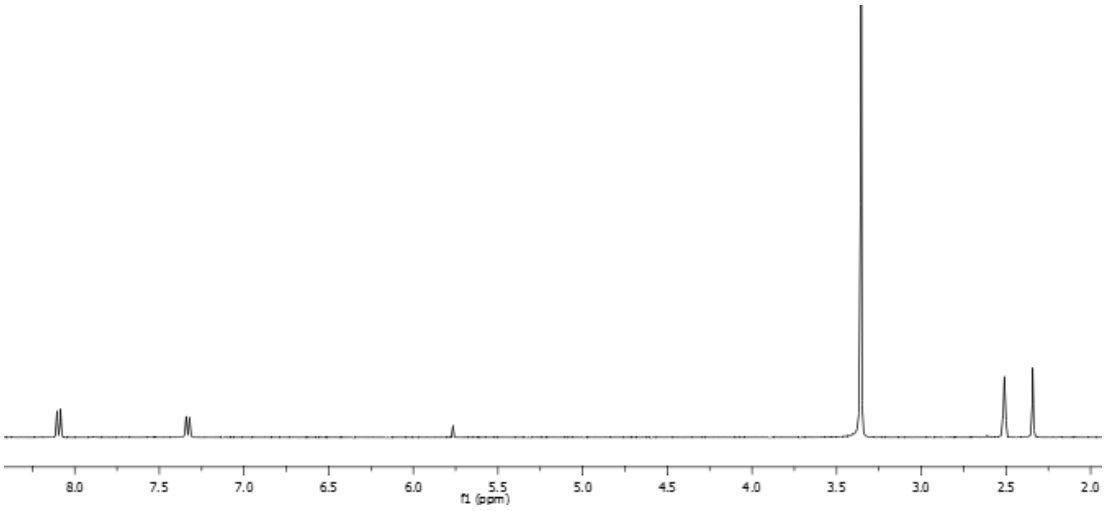


Fig 2.10.1. ^{1}H NMR spectrum of diaryliodonium triflate **53**

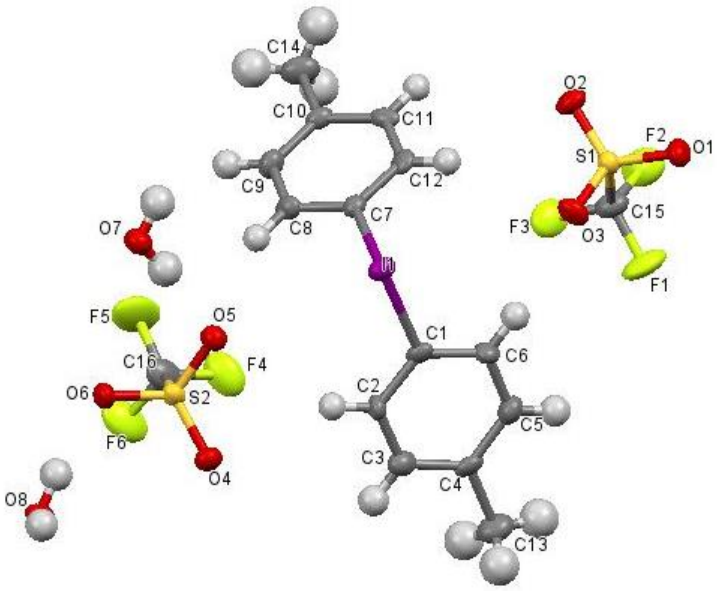


Fig 2.10.2.Crystal structure of diaryliodonium triflate **53**

As shown in **Fig 2.10.2**, the crystal structure confirms the presence of the diaryliodonium triflate. However, there are two, rather than one, triflate counter ions. Close inspection of the distances shows a short O7…O8 length of 2.392(5) Å, which is approximately 0.65 Å less than the sum of the van der Waals radii, suggesting that the two water molecules are linked by a proton to generate a hydronium ion, which accounts for the presence of the additional triflate counter ion. Thus the crystal structure is of **53**.$H_5O_2^+OTf^-$

Table 2.Selective geometric parameters (Å, º) for diaryliodonium triflate **53**

C1—I1—C7	99.11 (16)	I1—C7	2.103 (4)
O3—S1—O2	115.0 (2)	I1—C1	2.107 (4)
O1—S1—O2	115.2 (2)	C2—C1—I1	118.0 (3)
O1—S1—O3	114.1 (2)	C6—C1—I1	119.5 (4)
C15—S1—O2	102.9 (2)	C6—C1—C2	122.5 (4)
C15—S1—O3	103.3 (2)	C8—C7—I1	119.9 (3)
C12—C7—I1	117.8 (3)	C9—C8—C7	118.4 (5)

The C-C and C-H bond lengths are unexceptional. The two C-I bond distances of 2.103 (4) and 2.107 (4) Å are similar to that observed in related systems, such as Ph_2I^+ BF_4^-(C-I) = 2.12 Å. The C-I-C angle is 99.11(16)°, which is less than the ideal tetrahedral angle, but similar to that found in Ph_2I^+ BF_4^- (96.5)°.

3.0 Conclusion

A series of imidazolium salts were prepared successfully in either step-wise or one-pot reactions from glyoxal, formaldehyde and primary amines. The imidazolium salts IPr.HCl, SIPr.HCl and SIMes.HCl were obtained in a step-wise procedure based on previously published synthetic methods.

The synthesis of *N*,*N*'-bisfluoroarylimidazolium chlorides, **26**, **27** and **33** were achieved via a one-pot reaction over 12 hours. The target compounds were obtained by the removal of solvent under reduced pressure and subsequently washed with diethyl ether and THF. The desired 1,3-bis(2,4-difluorophenyl)imidazolium chloride, **27**, was obtained on a small scale by recrystallization from diethyl ether and DMSO. However, the 4-fluorophenyl (**26**) and 2,4,5-trifluorophenyl (**33**) analogues were obtained without further need for purification. In all cases the formation of the target compounds was confirmed by spectroscopy. This includes the observation of the peaks assigned to the acidic proton of imidazolium ring in the ^{1}H NMR spectra between 10.20 and 10.49 ppm. Imidazolium salts **26** and **33** illustrated complicated patterns in the ^{19}F NMR spectra with an overlapping triplet of triplets and multiple sets of doublets. Even though one-pot condensation to give the above imidazolium salts was successful, the reaction to form the imidazolium chloride bearing five fluorines on the phenyl rings failed to give the title compound exclusively by the same method. Imidazolium salt **26** was used as a precursor to prepare a fluorinated-NHC molybdenum complex; the reaction of molybdenum hexacarbonyl with the free carbene generated from the NHC in the presence of potassium tert-butoxide yielded the metal complex. Sadly, only 47% of the starting NHC was converted to the product and the obtained compound could not be isolated pure even after column chromatography. However, a shift in the carbonyl stretching frequency and change in the number of CO stretches observed in the IR spectrum of the crude product suggested the product has a lower symmetry than the starting material.

Alkylation of imidazole was carried out with alkyl halides in a method described by Smiglak and Hines et al.[89] However, an alternative method was applied for the preparation of fluoroalkylated imidazoles **37** and **38**, by reacting imidazole with polyfluoroalkyl halides. The reaction mixtures were stirred at 80°C for 5 days and subsequently extracted to give the desired compounds. The formation of both compounds were confirmed by ^{1}H NMR and ^{19}F NMR spectroscopy.

Fluorinated ponytails were attached to the alkylated imidazole ring using polyfluoroalkyl triflates. The reaction proceeded smoothly by stirring the reaction mixture for 48 hours followed by the addition of ethyl acetate and hexane to precipitate the products. This resulted

in the preparation of imidazolium salts containing both polyfluorinated and non-fluorinated chains. Polyfluorinated imidazolium salt **23** bears structural resemblance to fluorinated imidazolium salts investigated and prepared for this project.

Finally, diaryliodonium salt **53** and **54** were obtained in a one-pot reaction from arenes and aryl iodides with 2-3 equivalents of TfOH. Although these were not ultimately used in the formation of imidazolium salts, the structure of salt **53** was obtained by X-ray crystallographic analysis. The data related to the crystal is provided in the result and discussion part of the report.

4.0 Experimental Procedures

General procedures

All chemical structures were drawn using Chem Draw Ultra v 15.0.

Chromatography

Column chromatography was performed using silica gel (Sigma-Aldrich) 40-63 μm 60 Å. The solvent systems are specified in individual experiments.

Infra-red spectroscopy

IR spectra were recorded on a Bruker Alpha-P spectrometer fitted with an ATR attachment. Absorption maxima are reported in wave numbers (cm^{-1}).

Nuclear Magnetic Resonance

^{1}H NMR spectra were recorded using a Bruker Avance 400 spectrometer. Chemical shifts are reported in parts per million to the nearest 0.01 ppm and referenced to the residual non-deuterated solvent peak. Multiplicity of the peaks were assigned as followed; s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or as a combination of these.

^{13}C NMR spectra were recorded using a Bruker Avance (100.6 MHz) spectrometer.

^{19}F NMR spectra were recorded using a Bruker Avance (376.5 MHz) spectrometer.

Room temperature refers to 20-25 °C.

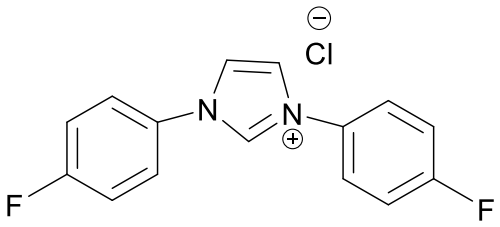
All the chemicals were handled in accordance with safety instructions.

Elemental analyses were performed by the Microanalytical service, The University of Manchester, Manchester, UK.

Crystallography

X-ray diffraction data was collected on an Oxford Xcalibur Sapphire 2 diffractometer using Mo Kα radiation (λ = 071073 Å) and corrected for Lorentz, polarisation and absorption using the multi-scan methods, with full-matrix least-squares refinement of F^2 using the Olex2 programme.

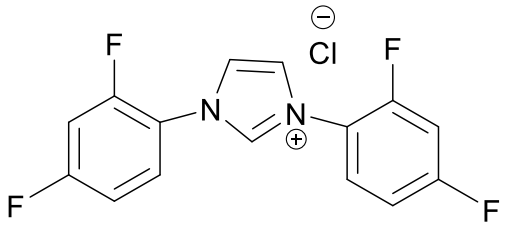
4.1 1,3-Bis(4-difluorophenyl)imidazolium Chloride (26)



To a stirred solution of 4-fluoroanaline (4.3 g, 38.7 mmol) in toluene (17 ml) was added paraformaldehyde (0.58 g, 19.3 mmol). The resulting mixture was heated to 100˚C and then cooled to 40˚C before glyoxal (2.80 g, 19.3 mmol, 40 % aqueous solution) was added. The mixture was stirred for 5 minutes, then HCl (6.45 ml, 3 M) was added dropwise. The mixture was heated to 100˚C for 12 h. After cooling to room temperature, it was concentrated in vacuo. The title compound was afforded as a solid by washing with Et_2O and THF (4.9 g, 86%). The characterisation data was in agreement with the literature.[63]

^{1}H NMR (400 MHz; DMSO) 10.41 (s, 1H, NCHN), 8.57 (br s, 2H, NCHCHN), 8.01 (m, 4H, Ar-H), 7.61 (m, 4H, Ar-H); ^{13}C{^{1}H} NMR (100.6 MHz; DMSO) 161.5 (d, $^1J_{CF}$ 245.0 Hz, Ph-C), 135.3 (s, NHCN), 131.6 (d, $^4J_{CF}$ 2.5 Hz, Ph-C), 125.1 (d, $^3J_{CF}$ 10.0 Hz, Ph-C), 122.5 (s, NCHCHN), 117.4 (d, $^2J_{CF}$ 23.0 Hz, Ph-C); ^{19}F NMR (376 MHz; DMSO) -111.1 (tt, J 8.7, 4.7 Hz, 4-CF); Calc. for $C_{15}H_{11}ClF_2N_2$ (26.2H_2O) : C, 54.81; H, 4.6; N, 8.52; Cl, 10.78. Found: C, 55.73; H, 4.32; N, 8.18; Cl, 10.62%

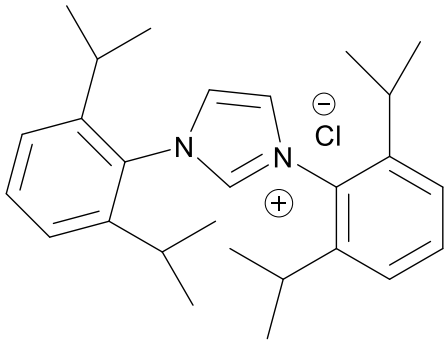
4.2 1,3-Bis(2,4-difluorophenyl)imidazolium Chloride (27)



To a stirred solution of 2,4-difluoroanaline (5 g, 38.7 mmol) in toluene (20 ml) was added paraformaldehyde (0.58 g, 19.3 mmol). The reaction mixture was heated to 100˚ C and then cooled to 40˚C. Glyoxal was added (2.80 g, 19.3 mol, 40 % aqueous solution) and the resulting solution was stirred for 5 minutes before HCl (6.45 ml, 3 M) was added dropwise. It was again heated to 100˚C for 12 h followed by cooling to room temperature. The mixture was concentrated in vacuo to give a dark slurry which was washed with Et_2O and THF. The final product (**27**) was obtained as an off-white powder by recrystallization from DMSO/Et_2O (1.27 g, 20%). The characterisation data was in agreement with the literature.[63]

^{1}H NMR (400 MHz; DMSO) 10.20 (s, 1H, NCHN), 8.45(s, 2H, NCHCHN), 8.10 (td, J 8.9 5.2 Hz, 2H, ArH), 7.83 (ddd, J 11.1 8.8 2.7 Hz, 2H, Ar-H), 7.48-7.51 (m, 2H, Ar-H); ^{13}C{^{1}H} (100.6 MHz; DMSO) 160.3 (dd, $^1J_{CF}$ 240.0 11.5 Hz, Ph-C), 152.3 (dd, J_{CF} 242.0 15.6, Ph-C), 138.8 (N_2C), 128.7 (d, J 10.2 Hz), 123.9 (d, J 2.3 Hz, NCH), 119.3 (dd, J_{CF} 3.9 7.5 Hz, Ph-C), 112.8 (dd, J 19.5 3.8 Hz, Ph-C), 105.9 (dd, J 23.1 4.1 Hz, Ph-C); ^{19}F{^{1}H} NMR (376 MHz; DMSO) -105.4 (d, J_{FF} 8.0 Hz, 2F, 4-CF), -118.4 (d, J_{FF} 8.0 Hz, 2F, 2-CF); Calc. for $C_{15}H_9ClF_4N_2$: C, 54.81; H, 2.76; N, 8.52; Cl; 10.79. Found: C, 43.15; H, 5.28; N, 5.49; Cl, 7.43%.

4.3 1,3-Bis(2,6-diisopropylphenyl)imidazolium Chloride (29)

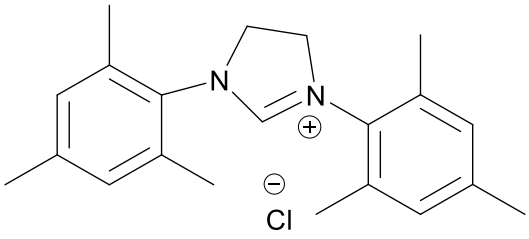


A round bottom flask was loaded with 2,6-diisopropylaniline (10.0 g, 56 mmol), glyoxal (4.0 g, 28 mmol, 40 % in water) and absolute ethanol (50 ml). A few drops of formic acid were added as catalyst. The reaction mixture was stirred for two days and a yellow solid was collected by filtration and was subsequently washed with cold methanol to give the intermediate compound, bis (2,6-dispropylphenyl) diazabutadiene[81] in 61% yield.

To a solution of bis (2,6-dispropylphenyl) diazabutadiene (5.0 g, 13.2 mmol) in toluene (100 ml) was added paraformaldehyde (0.4 g, 13.2 mmol). The reaction mixture was heated to 100˚C until most of the solid paraformaldehyde was dissolved. It was cooled to 40˚C followed by addition of HCl (3.3 ml, 4 M in dioxane). The mixture was heated to 70 ˚C for 5 h and was subsequently stirred for 36 h at room temperature. The off-white solid was collected by filtration and washed with THF to afford the title compound (2.80 g, 50%). The characterisation data was in agreement with the literature.[81]

^{1}H NMR (400 MHz; DMSO) 10.21 (s, 1H, NCHN), 8.57 (d, J 1.5 Hz, 2H, NCHCHN), 7.68 (m, 2H, 4-CH), 7.52 (d, J 7.8 Hz, 4H, 3-CH), 2.34 (sep, J 6.9 Hz, 4H, C<u>H</u>(CH_3)$_2$), 1.26 (d, J 6.8 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.15 (d, J 6.9 Hz, 12H, CH(C<u>H</u>$_3$)$_2$); ^{13}C{^{1}H} (100.6 MHz, DMSO) 145.2, 137.1, 132.7, 130.5, 126.6, 124.8, 28.9, 24.2, 23.6; Calc. for $C_{27}H_{37}ClN_2$: C, 76.30; H, 5.77; N, 6.57; Cl, 8.34. Found: C, 73.40; H, 8.61; N, 6.21; Cl, 8.59%

4.4 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium Chloride (32a)



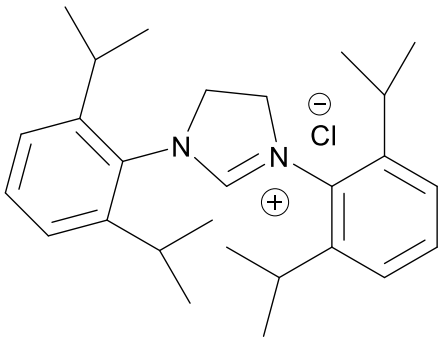
To a solution of 2,4,6-timethylaniline (6.76 g, 50 mmol) in n-propanol (30 ml) were added 3.6 g of glyoxal (40 % aqueous solution, 25 mmol), n-propanol (10 ml) and water (5 ml). The reaction mixture was stirred at room temperature for 16 h and then for 4 h at 60˚C. A yellow solid precipitated out by addition of 20 ml of water. The solid was obtained by filtration and dried in vacuo to give the glyoxal-bis-(2,4,6-trimethylphenyl)imine in 75% yield.

A mixture of 2.0 g (6.83 mmol) of the imine in THF (27 ml) was treated with sodium borohydride (1.06 g, 28.0 mmol) at 0˚C. The mixture was stirred at room temperature for 16 h and was heated subsequently for 2 h under reflux. To the resulting mixture was added 20 ml of ice-water and hydrochloric acid (20 ml, 3 M) to precipitate a colourless solid. The intermediate compound, bis(2,4,6-trimethylphenylamine)ethane dihydrochloride (**31a**) was obtained by filtration and dried in vacuo.(1.5 g, 60%)

A mixture of **31a** (1.0 g, 2.70 mmol), 8.93 ml of triethylorthoformate and two drops of formic acid was heated in a distillation apparatus until there was no more ethanol left to be distilled. The temperature of reaction mixture reached 130˚C and was subsequently cooled to room temperature. The solid title compound was collected by filtration and dried in vacuo (0.42 g, 45%). The characterisation data was in agreement with the literature.[82]

^{1}H NMR (400 MHz; DMSO) 9.02 (s, 1H, NCHN), 7.09 (s, 4H, 3-CH), 4.44 (s, 4H, NCH_2), 2.34 (s, 12H, 2-CH_3), 2.29 (s, 6H, 4-CH_3); ^{13}C{^{1}H} (100.6 MHz, DMSO) 161.1 (N<u>C</u>HN), 139.2 (4-C), 135.8 (1-C), 131.3 (ipso-C), 129.9 (3-C), 51.4 (N<u>C</u>H_2), 21.0 (4-CH_3), 17.6 (2-CH_3); Calc. for $C_{21}H_{29}ClN_2$: C, 73.56; H, 7.94; N, 8.17; Cl, 10.34. Found: C, 70.71; H, 8.17; N, 7.77; Cl, 5.23%

4.5 1,3-Bis(2,6-diisopropylphenyl)imidazolinium Chloride (32b)



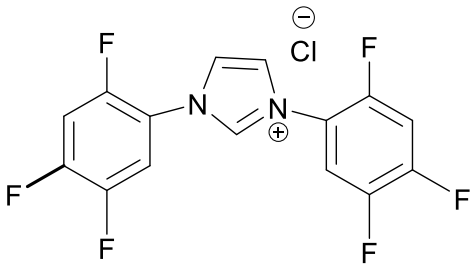
To a mixture of 2,6-diisopropylaniline (4.92 g, 28 mmol) in n-propanol (20 ml) were added glyoxal (1.81 g, 12.5 mmol, 40% aqueous solution), n-propanol (2 ml) and water (5 ml). After one hour stirring at 70°C, 20 ml of water was added. The resulting precipitate was obtained by filtration and dried in vacuo. (3.95 g, 84%)

To the solution obtained glyoxal-bis-(2,6-diisopropyl phenyl)imine (1.95 g, 5.17 mmol) in THF (21 ml) was added sodium borohydride (0.82 g, 21.81 mmol) at 0°C. The resulting mixture was stirred for 24 h at room temperature and subsequently refluxed for 2 h. To the reaction mixture was added ice-water (21 ml) and then HCl (21 ml, 3M). The intermediate compound (**31b**) was collected by filtration and dried in vacuo. (1.50 g, 64%).

A mixture of *N*,*N*-bis(2,6-diisophenylamino)ethane dihydrochloride (**31b**) (1.50 g, 3.30 mmol), triethyl orthoformate (19 ml) and two drops of formic acid were refluxed for 45 h. Upon cooling to room temperature, a solid formed which was collected by filtration and dried in vacuo (0.15 g, 11%). The characterisation data was in agreement with the literature.[82]

^{1}H NMR (400 MHz; DMSO) 9.48 (s, 1H, NCHN), 7.55 (m, 2H, Ar-CH), 7.42 (d, J 7.8 Hz, 4H, Ar-CH), 4.54 (s, 4H, NCH_2), 3.08 (sept, J 6.9 Hz, 4H, $C\underline{H}(CH_3)_2$), 1.35 (d, J 6.7 Hz, 12H, $CH(C\underline{H}_3)_2$, 1.19 (d, J 6.9 Hz, 12H, $CH(C\underline{H}_3)_2$); $^{13}C\{^{1}H\}$ (100.6 MHz, DMSO) 161.1 (NCHN), 146.6 (2-C), 131.5 (4-C), 130.3 (ipso-C), 125.3 (3-C), 54.1 (C-4,5), 28.7 ($\underline{C}H(CH_3)_2$), 25.4 ($CH(\underline{C}H_3)_2$), 23.7 ($CH(\underline{C}H_3)_2$); Calc. for $C_{27}H_{39}ClN_2$: C, 75.94; H, 9.20; N, 6.56; Cl, 8.30. Found: C, 70.02; H, 8.43; N, 6.07; Cl, 11.48%

4.6 1,3-Bis(2,4,5-trifluorophenyl)imidazolium Chloride (33)

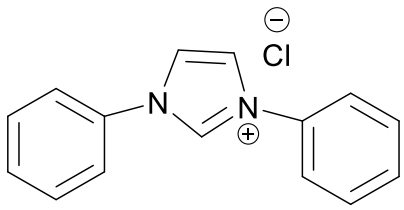


To a stirred solution of 2,4,5-trifluoroanaline (5.7 g, 38.7 mmol) in toluene (23 ml) was added paraformaldehyde (0.58 g, 19.3 mmol). The mixture heated to 100˚C until all the reagents were dissolved. It was cooled to 40˚C and glyoxal was added (2.80 g, 19.3 mmol, 40% aqueous solution). The mixture was stirred for an additional 5 minutes before HCl (6.45 ml, 3 M) was added slowly. It was heated to 100˚C for 12 h and cooled to room temperature. The resulting mixture was concentrated in vacuo to give a dark slurry which was washed with Et_2O and THF repeatedly to afford the final compound. (3.16 g, 45%)

^{1}H NMR (400 MHz; DMSO) 10.49 (s, 1H, NCHN), 8.50 (m, 4H, NCHCHN and Ar-H), 8.15 (m, 2H, Ar-H); $^{13}C\{^{1}H\}$ (100.6 MHz; DMSO) 139.3 (s, NCHN), 123.7 (d, J 23.3 Hz, NCHCHN), 116.3 (d, J_{CF} 24.0 Hz, Ph-C), 107.9 (dd, J_{CF} 25.8 22.5 Hz, Ph-C). Signals for quaternary carbons were not detected.

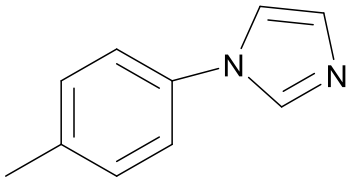
$^{19}F\{^{1}H\}$ NMR (376 Hz; DMSO) -122.9 (dd, J_{FF} 14.7 4.4 Hz), -129.8 (dd, J_{FF} 23.3 4.3 Hz), -139.7 (dd, J_{FF} 22.9 14.8 Hz);Calc. for $C_{15}H_7ClF_6N_2$: C, 49.41; H, 1.93; N, 7.68; Cl, 9.72. Found: C, 49.45; H, 2.38; N, 7.50; Cl, 6.40%

4.7 1,3-Bis(diphenyl)imidazolium Chloride (35)



To a stirred solution of aniline (3.60 g, 38.7 mmol) in toluene (15 ml) was added paraformaldehyde (0.58 g, 19.3 mmol). The resulting mixture was heated to 100˚C and then cooled to 40˚C before glyoxal (2.80 g, 19.3 mmol, 40% aqueous solution) was added. The reaction mixture was stirred for an additional 5 minutes before HCl (6.45 ml, 3 M) was added dropwise. It was heated to 100˚C for 12 h and again cooled to room temperature. The solvent was removed in vacuo to give a dark slurry. Unfortunately the final compound could not be isolated after the slurry was washed with Et_2O and THF.

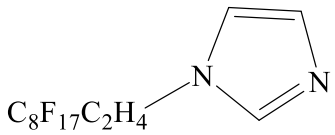
4.8 1-(4-methylphenyl)imidazole (36)



A mixture of copper (I) iodide (0.11 g, 0.57 mmol), caesium carbonate (1.95 g, 6.0 mmol), imidazole (0.28 g, 4.1 mmol), 4-bromotoluene (0.51 g, 3.0 mmol) in DMF (6 ml) was prepared in a sealed tube under N_2. The tube was evacuated twice and filled with N_2. The reaction mixture was stirred for 30 minutes at room temperature and then heated to 120˚C for 40 h. It was cooled to room temperature and diluted with 9 ml of ethyl acetate. The mixture was filtered through silica gel and washed with 60 ml of ethyl acetate. The resulting residue was concentrated in vacuo to give the desired compound as an oil (**36**) (0.28 g, 59%). The characterisation data was in agreement with the literature.[86]

^{1}H NMR (400 MHz; $CDCl_3$) 7.81 (s, 1H, NCHN), 7.12 (m, 5H, NCHCHN and Ar-H), 6.84 (m, 1H, Ar-H), 2.19 (s, 3H, CH_3); $^{13}C\{^1H\}$ (100.6 MHz; $CDCl_3$) 137.3, 136.6, 134.9, 130.6, 130.4, 118.7, 20.7

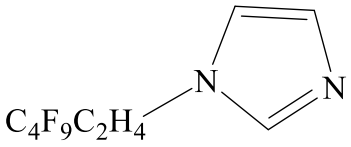
4.9 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)imidazole (37)



A mixture of 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (0.5 g, 0.87 mmol) and imidazole (0.14 g, 2.05 mmol) in 40 ml of ethyl acetate was stirred for 5 days at 80 °C. The mixture was extracted with water (2×30 ml)/ EtOAc (20 ml) and dried with magnesium sulfate. The final product was obtained as an oil by removing the solvent in vacuo (0.25 g, 56%). The characterisation data was in agreement with the literature.[88]

^{1}H NMR (400 MHz; $CDCl_3$) 7.56 (s, 1H), 7.12 (s, 1H), 6.97 (s, 1H), 4.32 (m, 2H), 2,61 (m, 2H); ^{13}CNMR (100.6 MHz; $CDCl_3$) 137.0, 129.6, 119.1, 108-118 (m), 39.1, 32.9 (m); ^{19}F NMR (376 MHz; $CDCl_3$) -80.6 (t, J_{FF} 10.1 Hz, 3F), -114.4 (bs, 2F), -121.8 (bs, 2F), -122.3 (bs, 4F), -122.6 (bs, 2F), -123.3 (bs, 2F), -126.0 (bs, 2F)

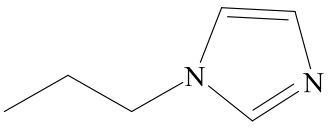
4.10 1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)imidazole (38)



A mixture of 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodohexane (0.30 g, 0.82 mmol) and imidazole (0.14 g, 2.05 mmol) in 40 ml of ethyl acetate was stirred for 5 days at 80 °C. The mixture was extracted with water (2×30 ml)/ EtOAc (20 ml) and dried with magnesium sulfate. The final product was obtained as an oil by removing the solvent in vacuo. (0.08 g, 32%)

^{1}H NMR (400 MHz; $CDCl_3$) 7.65 (s, 1H), 7.11 (s, 1H), 6.99 (s, 1H), 4.33 (m, 2H), 2.62 (m, 2H); ^{13}CNMR (100.6 MHz; $CDCl_3$) 129.5, 121.4, 108.7-119, 39.2, 26.6; ^{19}F NMR (376 MHz; $CDCl_3$) -81.0 (m, 3F), -114.4 (m, 2F), -124.6 (m, 2F), -126.0 (m, 2F)

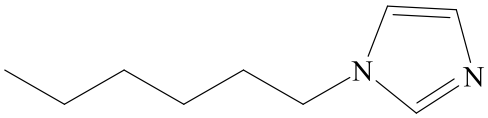
4.11 1-Propylimidazole (1-PrIM) (39)



Imidazole (3.40 g, 50 mmol) was dissolved in DMF (10 ml). Potassium tert-butoxide (6.7 g, 60 mmol) was added at 0-5 °C followed by addition of 1-iodopropane (12.23 g, 72 mmol). The reaction mixture was stirred at ambient temperature overnight. After addition of water (20 ml), the solution was extracted with ethyl acetate (3×40 ml). The extract was washed with brine and dried with anhydrous magnesium sulfate. The final compound was obtained as an oil by removing the solvent in vacuo (2.50 g, 45%). The characterisation data was in agreement with the literature.[89]

^{1}H NMR (400 MHz; $CDCl_3$) 7.35 (s, 1H), 6.93 (s, 1H), 6.81 (s, 1H), 3.77 (m, 2H), 1.69 (m, 2H), 0.82 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz; $CDCl_3$) 137.0 (2-C), 129.1(4-C), 118.7 (5-C), 48.5, 24.3,10.9; Calc. for $C_6H_{10}N_2$: C, 64.43; H, 9.15; N,25.43. Found: C, 60.87; H, 8.84; N, 24.33%

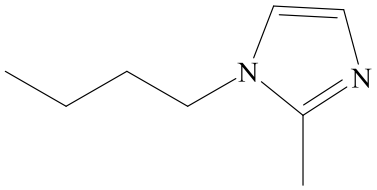
4.12 1-Hexylimidazole (1-HexIM) (40)



To a solution of imidazole (3.40 g, 50 mmol) in DMF (10 ml) was added potassium tert-butoxide (6.7 g, 60 mmol) at 0-5 °C followed by addition of 1-iodohexane (15.26 g, 72 mmol). The reaction mixture was stirred at ambient temperature overnight. After addition of water (20 ml), the solution was extracted with ethyl acetate (3×40 ml). The extract was washed with brine and dried with anhydrous magnesium sulfate. The solvent was removed in vacuo and the obtained residue was purified by column chromatography (eluent: ethyl acetate/ hexane) to give the title compound as an oil (2.3 g, 30%). The characterisation data was in agreement with the literature.[89]

^{1}H NMR (400 MHz; $CDCl_3$) 7.35 (s, 1H), 6.93 (s, 1H), 6.80 (s, 1H), 3.81 (m, 2H), 1.65 (m, 2H), 1.15 (m, 6H), 0.78 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz; $CDCl_3$) 137.0 (2-C), 129.2 (4-C), 118.7 (5-C), 47.0, 31.1, 31.0, 26.1, 22.4, 14.1; Calc. for $C_9H_{16}N_2$: C, 71.01; H, 10.59; N, 18.40. Found: C, 67.92; H, 10.57; N, 17.35%

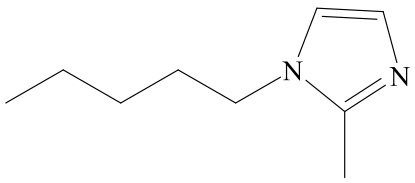
4.13 1-Butyl-2-methylimidazole (1-Bu-2-MeIM) (41)



To a solution of 2-methylimidazole (4.10 g, 50 mmol) in DMF (10 ml) was added potassium tert-butoxide (6.7 g, 60 mmol) at 0-5 °C followed by addition of 1-iodobutane (13.2 g, 72 mmol). The reaction mixture was stirred at ambient temperature overnight. After addition of water (20 ml), the solution was extracted with ethyl acetate (3×40 ml). The extract was washed with brine and dried with anhydrous magnesium sulfate. The final compound was obtained as an oil by removing the solvent in vacuo (2.5 g, 36%). The characterisation data was in agreement with the literature.[89]

^{1}H NMR (400 MHz; $CDCl_3$) 6.76 (m, 1H), 6.70 (m, 1H), 3.71 (t, J 7.2 Hz, 2H), 2.26 (s, 3H), 1.59 (m, 2H), 1.22 (m, 2H), 0.84 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz; $CDCl_3$) 143.9 (2-C), 126.5 (4-C), 118.7 (5-C), 45.4, 32.5, 19.4, 13.7, 13.3; Calc. for $C_8H_{14}N_2$: C, 69.53; H, 10.21; N, 20.26. Found: C, 64.80; H, 10.06; N, 18.90%

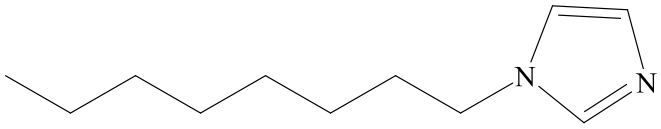
4.14 1-Pentyl-2-methylimidazole (1-Pent-2-MeIM) (42)



To a solution of 2-methylimidazole (4.10 g, 50 mmol) in DMF (10 ml) was added potassium tert-butoxide (6.7 g, 60 mmol) at 0-5°C followed by addition of 1-bromopentane (10.87 g, 72 mmol). The reaction was stirred at ambient temperature overnight. After addition of water (20 ml), the solution was extracted with ethyl acetate (3×40 ml). The extract was washed with brine and dried with anhydrous magnesium sulfate. The final product was obtained as an oil by removing the solvent in vacuo (3.87 g, 50%). The characterisation data was in agreement with the literature.[89]

^{1}H NMR (400 MHz; $CDCl_3$) 6.42 (m, 1H), 6.37 (m, 1H), 3.37 (m, 2H), 1.92 (s, 3H), 1.27 (m, 2H), 0.88 (m, 4H), 0.46 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz; $CDCl_3$) 143.7 (2-C), 126.2 (4-C), 118.6 (5-C), 45.5, 30.8, 29.1, 22.2, 13.7, 13.4; Calc. for $C_9H_{16}N_2$: C, 71.01; H, 10.59; N, 18.40. Found: C, 66.01; H, 10.64; N, 16.88%

4.15 1-Octylimidazole (43)



Imidazole (1.00 g, 14.7 mmol) was added to an over saturated solution of potassium hydroxide (2.00 g) in acetonitrile (10 ml) and was stirred for 2 hours at ambient temperature. 1-iodooctane (1.76 g, 7.3 mmol) was added drop wise and the mixture was heated up to 80 °C for 12 hours. After cooling to room temperature, the solvent was removed in vacuo. Water (10 ml) and DCM (20 ml) were added and the solution was stirred for 10 minutes at room temperature. The organic layer was separated, washed with water (3×10 ml) and dried with magnesium sulfate. The final compound obtained as a yellow liquid by removing the solvent in vacuo (0.72 g, 54%). The characterisation data was in agreement with the literature.[94]

^{1}H NMR (400 MHz; $CDCl_3$) 7.34 (s, 1H), 6.93 (s, 1H), 6.79 (s, 1H), 3.80 (t, J 7.2 Hz, 2H), 1.65 (m, 2H), 1.16 (m, 10H), 0.78 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100.6 MHz; $CDCl_3$) 137.1 (2-C), 129.2 (4-C), 118.7 (5-C), 47.1, 31.8, 31.0, 29.5, 29.2, 26.5, 22.6, 14.2; Calc. for $C_{11}H_{20}N_2$: C, 73.29; H, 11.18; N, 15.53. Found: C, 71.03; H, 11.40; N, 15.48%

4.16 2-(perfluorohexyl)ethyl triflate (44)

4.17 2-(perfluorooctyl)ethyl triflate (45)

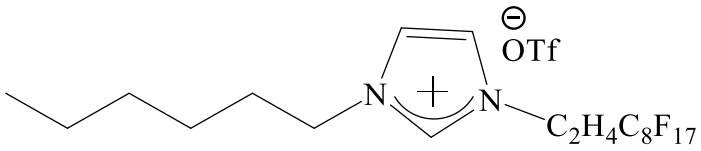
The flask was charged with dry DCM (20 ml), cooled to -10 °C and triflic anhydride (1.50 g, 5.3 mmol) was added. After 5 minutes, a mixture of 2-(perfluorohexyl) ethanol (1.92 g, 5.3 mmol), dry hexane (25 ml), dry pyridine (0.39 g, 5.0 mmol) and dry DCM (25 ml) was slowly added. The mixture was stirred and cooled for 40 minutes, followed by removal of the salts by filtration. The crude triflate was purified via a short column of silica (eluent: CH_2Cl_2). The final compound was obtained by removal of the solvents in vacuo (1.75 g, 66%). The characterisation data was in agreement with the literature.[91]

^{1}H NMR (400 MHz; $CDCl_3$) 4.79 (m, 2H), 2.69 (m, 2H); ^{19}F{^{1}H}NMR (376 MHz; $CDCl_3$) -75.1 (s, 3F), -81.3 (m, 3F), -114.0 (m, 2F), -122.2 (m, 2F), -123.3 (m, 2F), -123.8 (m, 2F), -126.5 (m, 2F)

The triflate (**45**) was afforded from the same method mentioned above by using 2-(perfluorooctyl) ethanol (2.45 g, 5.3 mmol). (2.17 g, 68%)

^{1}H NMR (400 MHz; $CDCl_3$) 4.80 (m, 2H), 2.69 (m, 2H); ^{19}F{^{1}H}NMR (376 MHz; $CDCl_3$) -74.7 (s, 3F), -80.9 (m, 3F), -113.6 (m, 2F), -121.7 (m, 2F), -121.9 (m, 4F), -122.8 (m, 2F), -123.5 (m, 2F), -126.2 (m, 2F)

4.18 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-3-hexylimidazolium triflate (46)

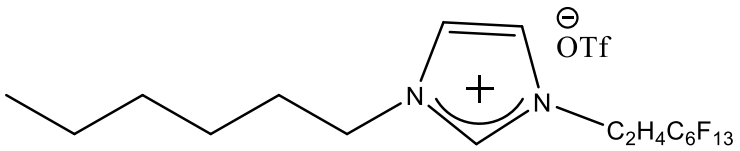


A mixture of 1-hexylimidazole (**40**) (0.077 g, 0.51 mmol) and triflate **45** (0.31 g, 0.51 mmol) in 4 ml of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After cooling to room temperature, white crystals dropped out of solution. The obtained crystals were decanted and dried in vacuo. (0.15 g, 40%)

^{1}H NMR (400 MHz; DMSO) 9.28 (m, 1H), 7.90 (t, J 1.8 Hz, 1H), 7.82 (t, J 1.8 Hz, 1H), 4.57 (t, J 6.9 Hz, 2H), 4.18 (t, J 7.0 Hz, 2H), 3.01 (m, 2H), 1.78 (m, 2H), 1.24 (m, 6H), 0.84 (m, 3H); ^{13}C NMR (100.6 MHz; DMSO) 135.1, 122.0, 121.8, 48.9, 29.8, 28.5, 24.4, 21.2, 12.3. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H}NMR (376 MHz; DMSO) -77.6 (s, 3F), -80.9 (t, J 10.1 Hz, 3F), -113.2 (m, 2F), -121.5 (bs, 2F), -121.7 (bs, 4F), -122.5 (bs, 2F), -123.1 (bs, 2F), -125.7 (bs, 2F);Calc. for $C_{20}H_{21}F_{20}N_2O_3S$: C, 33.04; H, 3.04; N, 3.67; S, 4.19. Found: C, 32.53; H, 2.73; N, 3.84; S, 4.08%

4.19 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-hexylimidazolium triflate (47)

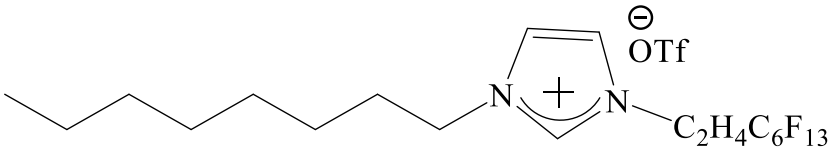


A mixture of 1-hexylimidazole (**40**) (0.11 g, 0.74 mmol) and triflate **44** (0.37 g, 0.74 mmol) in 4 ml of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After removing toluene on a rotary vacuum evaporator, the crude residue was dissolved in 2 ml of ethyl acetate and precipitated with 20 ml of hexane. The final oily product was decanted and dried in vacuo. (0.2 g, 41%)

^{1}H NMR (400 MHz; DMSO) 9.28 (s, 1H), 7.89 (t, J 1.8 Hz, 1H), 7.81 (t, J 1.8 Hz, 1H), 4.56 (m, 2H), 4.18 (m, 2H), 3.02 (m, 2H), 1.77 (m, 2H), 1.25 (m, 6H), 0.83 (m, 3H); ^{13}C NMR (100.6 MHz; DMSO) 136.5, 122.6, 122.4, 48.9, 30.3, 29.1, 24.9, 21.7, 13.4. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H}NMR (376 MHz; DMSO) -77.8 (s, 3F), -80.2 (t, J 9.9 Hz, 3F), -113.3 (m, 2F), -121.6 (m, 2F), -122.6 (m, 2F), -123.2 (m, 2F), -125.8 (m, 2F)

4.20 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-octylimidazolium triflate (48)

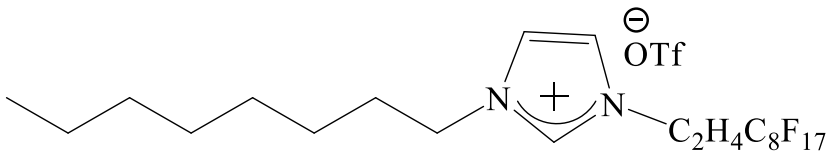


A mixture of 1-octylimidazole (**43**) (0.28 g, 1.59 mmol) and triflate **44** (0.79 g, 1.59 mmol) in 10 ml of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After removing toluene on a rotary vacuum evaporator, the crude residue was dissolved in 2 ml of ethyl acetate and precipitated with 20 ml of hexane. The obtained viscous oil was decanted and dried in vacuo. (0.45 g, 42%)

^{1}H NMR (400 MHz; DMSO) 9.30 (m, 1H), 7.91 (t, J 1.8 Hz, 1H), 7.82 (t, J 1.8 Hz, 1H), 4.56 (t, J 7.1 Hz, 2H), 4.18 (t, J 7.0 Hz, 2H), 3.02 (m, 2H), 1.77 (m, 2H), 1.25 (m,10H), 0.83 (m, 3H); ^{13}C NMR (100.6 MHz; DMSO) 137.7, 123.1, 122.9, 49.4, 31.5, 28.9, 28.7, 25.8, 22.4, 21.2, 14.1. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H}NMR (376 MHz; DMSO) -78.3 (s, 3F), -81.1 (m, 3F), -113.8 (m, 2F), -122.1 (m, 2F), -123.1 (m, 2F), -123.6 (m, 2F), -126.1 (m, 2F)

4.21 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-3-octylimidazolium triflate (49)

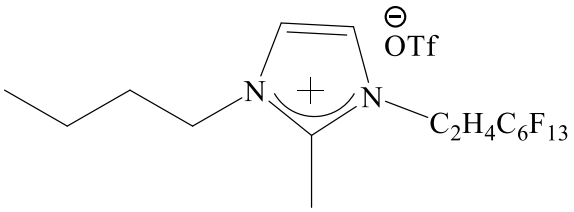


A mixture of octylimidazole (**43**) (0.15 g, 0.85 mmol) and triflate **45** (0.51 g, 0.85 mmol) in 7 ml of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After removing toluene on a rotary vacuum evaporator, the crude residue was dissolved in 2 ml of ethyl acetate and precipitated with 20 ml of hexane. The obtained viscous oil was decanted and dried in vacuo. (0.30 g, 45%)

^{1}H NMR (400 MHz; DMSO) 9.29 (m, 1H), 7.91 (t, J 1.8 Hz, 1H), 7.82 (t, J 1.8 Hz, 1H), 4.57 (t, J 6.8 Hz, 2H), 4.19 (t, J 7.0 Hz, 2H), 3.01 (m, 2H), 1.77 (m, 2H), 1.22 (m, 10H), 0.84 (m, 3H); ^{13}C NMR (100.6 MHz; DMSO) 137.1, 125.7, 123.1, 49.4, 31.5, 28.9, 28.7, 25.7, 22.4, 21.4, 14.1. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H}NMR (376 MHz; DMSO) -78.0 (s, 3F), -80.9 (m, 3F), -113.7 (bs, 2F), -121.8 (bs, 2F), -122.1 (bs, 4F), -122.9 (bs, 2F), -123.5 (bs, 2F), -126.3 (bs, 2F)

4.22 1-(3,3,4,4,5,5,6,6,7,7,8,8,8,-tridecafluorooctyl)-2-methyl-3-butylimidazolium triflate (50)

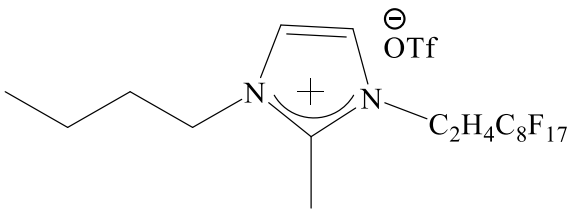


A mixture of 1-butyl-2-methylimidazole (**41**) (0.19 g, 1.39 mmol) and triflate **44** (0.69 g, 1.39 mmol) in 7 mL of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After removing toluene on a rotary vacuum evaporator, the crude residue was dissolved in 2 ml of ethyl acetate and precipitated with 20 ml of hexane. The obtained viscous oil was decanted and dried in vacuo. (0.35 g, 40%)

^{1}HNMR (400 MHz; DMSO) 7.79 (m, 1H), 7.72 (m, 1H), 4.48 (m, 2H), 4.13 (t, J 7.3 Hz, 2H), 2.93 (m, 2H), 2.65 (s, 3H), 1.69 (m, 2H), 1.28 (m, 2H), 0.88 (m. 3H)); ^{13}C NMR (100.6 MHz; DMSO) 125.7, 122.7, 47.8, 31.5, 19.2, 13.7, 9.6. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H} NMR (376 MHz; DMSO) -78.1 (s, 3F), -80.8 (m, 3F), -113.4 (bs, 2F), -122.1 (bs,2F), -123.0 (bs, 2F), -123.3 (m, 2F), -126.3 (m, 2F)

4.23 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-2-methyl-3-butylimidazolium triflate (51)

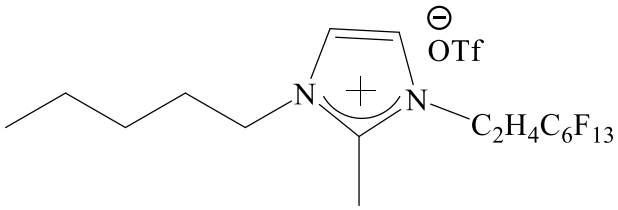


A mixture of 1-butyl-2-methylimidazole (**41**) (0.045 g, 0.33 mmol) and triflate **45** (0.2 g, 0.33 mmol) in 5 ml of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After cooling to room temperature, the solvent was removed in vacuo. The final product was obtained as a viscous oil. (0.095 g, 40%)

^{1}HNMR (400 MHz; DMSO) 7.0 (d, J 1.3 Hz, 1H), 6.72 (m, 1H), 3.84 (t, J 7.3 Hz, 2H), 3.66 (m, 2H), 2.29 (s, 3H), 1.62 (m, 2H), 1.26 (m, 4H), 0.88 (m, 3H); ^{13}C NMR (100.6 MHz; DMSO) 125.7, 122.0, 45.1, 31.4, 22.3, 19.6, 14.4. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H} NMR (376 MHz; DMSO) -77.9 (s, 3F), -80.3 (m, 3F), -113.2 (bs, 2F), -121.7 (bs,2F), -121.9 (bs, 4F), -122.6 (bs, 2F), -123.0 (m, 2F), -125.9 (m, 2F)

4.24 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2-methyl-3-pentylimidazolium triflate (52)

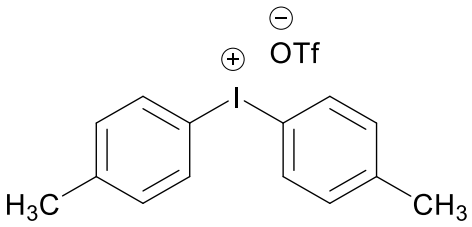


A mixture of 1-pentyl-2-methylimidazole (**42**) (0.2 g, 1.31 mmol) and triflate **44** (0.65, 1.31 mmol) in 7 ml of toluene was stirred for 48 hours in a Schlenk flask at 100 °C. After removing toluene on a rotary vacuum evaporator, the crude residue was dissolved in 2 ml of ethyl acetate and precipitated with 20 mL of hexane. The obtained viscous oil was decanted and dried in vacuo. (0.25 g, 30%)

^{1}H NMR (400 MHz; DMSO) 7.80 (m, 1H), 7.74 (m, 1H), 4.50 (t, J 7.1 Hz, 2H), 4.14 (t, J 7.1 Hz, 2H), 2.95 (m, 2H), 2.65 (m, 3H), 1.67 (m, 4H), 0.87 (m, 3H); ^{13}C NMR (100.6 MHz; DMSO) 121.9, 121.7, 31.4, 29.9, 22.5, 22.1, 21.0, 14.2. Signals for the fluorinated chain were not detected.

^{19}F{^{1}H} NMR (376 MHz; DMSO) -78.0 (s, 3F), -80.6 (m, 3F), -113.4 (bs, 2F), -121.9 (bs, 2F), -122.9 (bs, 2F), -123.2 (bs, 2F), -126.1 (bs, 2F)

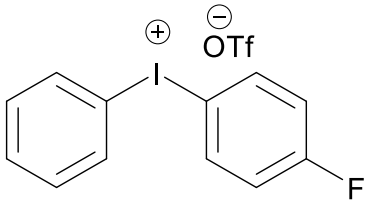
4.25 Bis(4-methylphenyl)iodonium triflate (53)



m-Chloroperbenzoic acid [65% active oxidant] (0.66 g, 2.4 mmol) and 4-iodotoluene (0.5 g, 2.3 mmol) were dissolved in CH_2Cl_2 (10 ml) in a sealed tube. Toluene (0.23 g, 2.6 mmol) and trifilic acid (0.4 ml, 4.53 mmol) were added to the mentioned mixture, resulting in a coloured solution. The reaction mixture was stirred for 10 minutes at ambient temperature and concentrated in vacuo. Et_2O (10 ml) was added to the mixture and it was stirred at room temperature for an additional 10 min before putting in a fridge for 3 hours to complete precipitation. The diaryliodonium salt (**53**) was obtained as an off-white solid by filtering off the precipitate and drying in vacuo (0.32 g, 30%). The characterisation data was in agreement with the literature.[93]

^{1}H NMR (400 MHz; DMSO) 8.09 (d, J 8.3 Hz, 4H, ortho-CH), 7.32 (m, 4H, meta-CH), 2.33 (s, 6H, 2x CH_3); $^{13}C\{^1H\}$ (100.6 MHz; DMSO) 142.3, 135.4, 132.7, 121.0 (q, J 321.1 Hz, $CF_3SO_3^-$), 113.5, 21.3; Calc. for $C_{15}H_{14}F_3IO_3S$: C, 39.33; H, 3.08; I, 29.70; S, 6.98. Found: C, 39.61; H, 3.02; I, 27.08; S, 6.84%

4.26 (4-fluorophenyl)(phenyl)iodonium triflate (54)



m-Chloroperbenzoic acid [65% active oxidant] (0.19 g, 0.74 mmol) and iodobenzene (0.14 g, 0.69 mmol) were dissolved in DCM (3 ml) in a sealed tube. Fluorobenzene (0.074 g, 0.78 mmol) and trifilic acid (0.18 ml, 2.03 mmol) were added to the mixture, resulting in a coloured solution. The reaction mixture was stirred for 1 h at room temperature and subsequently concentrated in vacuo. Et_2O (3 ml) was added to the mixture and it was stirred at room temperature for an additional 10 minutes. In order to complete precipitation, the flask was stored in a fridge for 3 hours before filtering off the diaryliodonium salt (**54**) as an off-white solid (0.12 g, 40%). The characterisation data was in agreement with the literature.[93]

^{1}H NMR (400 MHz; DMSO) 8.32 (dd, J 9.1 5.1, 2H, Ar-H), 8.24 (m, 2H, Ar-H), 7.69 (m, 1H, Ar-H), 7.54 (m, 2H, Ar-H), 7.42 (m, 2H, Ar-H); ^{13}C{^{1}H} (100.6 MHz; DMSO) 138.1, 135.0, 131.7, 130.7, 123.4, 120.8, 119.0, 110.2; ^{19}F NMR (376 MHz; DMSO) -77.7 (s, 3F, $CF_3SO_3^-$), -106.6 (tt, J 8.9 5.2 Hz); Calc. for $C_{13}H_9F_4IO_3S$: C, 34.85; H, 2.02; I, 28.32; S, 7.14. Found: C, 34.38; H, 2.07; I, 27.46; S, 6.86%

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Appendix 1

Crystal data of **53**

Table 3

Crystal data	
Chemical formula	$0.4(C_{14}H_{14}I)\cdot 0.8(CF_3O_3S)\cdot 0.8(H_2O)$
M_r	257.34
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, *b*, *c* (Å)	10.5461 (6), 11.3111 (8), 11.5604 (8)
α, β, γ (°)	70.910 (6), 71.651 (6), 74.920 (5)
V (Å^3)	1217.78 (15)
Z	5
Radiation type	Mo *K*α
μ (mm^{-1})	1.57
Crystal size (mm)	0.13 × 0.08 × 0.04
Data collection	
Diffractometer	Xcalibur, Sapphire2, large Be window diffractometer
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.28a (release 18-03-2013 CrysAlis171 .NET) (compiled Mar 18 2013,11:47:30) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.473, 1.000
No. of measured, independent and observed [$I \geq 2u(I)$] reflections	8527, 5339, 4073
R_{int}	0.050
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.673
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.100, 1.00

No. of reflections	5339
No. of parameters	305
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.46, -1.94

Table 4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.02645 (3)	0.24328 (3)	0.49389 (3)	0.02636 (11)
S1	0.19132 (12)	0.46937 (11)	0.72985 (11)	0.0243 (3)
S2	0.12598 (12)	-0.00243 (11)	0.19130 (11)	0.0244 (3)
O5	0.0599 (3)	0.1034 (3)	0.2459 (3)	0.0300 (8)
O8	0.0560 (3)	-0.2417 (3)	0.0812 (3)	0.0294 (8)
H8a	0.052 (4)	-0.1658 (17)	0.082 (5)	0.0442 (12)*
H8b	-0.019 (2)	-0.266 (4)	0.124 (4)	0.0442 (12)*
O4	0.1634 (3)	-0.1190 (3)	0.2806 (3)	0.0316 (8)
O2	0.1806 (3)	0.5814 (3)	0.6270 (3)	0.0329 (8)
O3	0.1244 (3)	0.3707 (3)	0.7341 (3)	0.0337 (8)
F1	0.4000 (3)	0.2925 (3)	0.7750 (3)	0.0573 (10)
O6	0.0614 (4)	-0.0131 (3)	0.1023 (3)	0.0340 (9)
O1	0.1692 (4)	0.4919 (3)	0.8507 (3)	0.0380 (9)
F3	0.4064 (3)	0.3736 (3)	0.5795 (3)	0.0545 (9)
F2	0.4467 (3)	0.4797 (3)	0.6838 (4)	0.0617 (10)
O7	-0.1259 (4)	0.2687 (3)	0.1279 (3)	0.0341 (8)
H7a	-0.145 (5)	0.3424 (19)	0.140 (5)	0.0512 (13)*
H7b	-0.066 (4)	0.223 (3)	0.167 (4)	0.0512 (13)*
F4	0.3601 (3)	0.0542 (4)	0.1632 (4)	0.0622 (10)
F6	0.3585 (3)	-0.0411 (4)	0.0290 (3)	0.0679 (11)
F5	0.2667 (4)	0.1555 (3)	0.0100 (3)	0.0748 (12)
C4	0.3787 (5)	-0.1008 (4)	0.6338 (4)	0.0268 (11)
C3	0.3182 (5)	-0.1045 (5)	0.5449 (5)	0.0334 (12)
H3	0.3453 (5)	-0.1745 (5)	0.5118 (5)	0.0400 (15)*
C7	0.1473 (4)	0.3676 (4)	0.3508 (4)	0.0215 (10)
C10	0.2964 (4)	0.5402 (4)	0.1652 (4)	0.0237 (11)
C8	0.1807 (4)	0.3616 (4)	0.2269 (4)	0.0257 (11)

H8	0.1533 (4)	0.3008 (4)	0.2064 (4)	0.0308 (13)*
C11	0.2599 (4)	0.5432 (4)	0.2903 (5)	0.0257 (11)
H11	0.2859 (4)	0.6044 (4)	0.3115 (5)	0.0308 (13)*
C1	0.1812 (4)	0.0966 (4)	0.5531 (4)	0.0231 (10)
C15	0.3704 (5)	0.4007 (5)	0.6898 (5)	0.0362 (13)
C5	0.3393 (5)	0.0051 (5)	0.6801 (5)	0.0337 (12)
H5	0.3807 (5)	0.0096 (5)	0.7383 (5)	0.0405 (15)*
C2	0.2181 (5)	-0.0064 (4)	0.5040 (4)	0.0266 (11)
H2	0.1772 (5)	-0.0103 (4)	0.4452 (4)	0.0319 (13)*
C6	0.2391 (5)	0.1052 (4)	0.6414 (5)	0.0288 (11)
H6	0.2120 (5)	0.1755 (4)	0.6739 (5)	0.0346 (14)*
C13	0.4867 (5)	-0.2102 (5)	0.6776 (5)	0.0436 (15)
H13a	0.4455 (8)	-0.2828 (12)	0.729 (3)	0.065 (2)*
H13b	0.553 (2)	-0.231 (2)	0.6053 (5)	0.065 (2)*
H13c	0.530 (3)	-0.1858 (13)	0.726 (3)	0.065 (2)*
C14	0.3792 (5)	0.6341 (5)	0.0634 (5)	0.0424 (15)
H14a	0.344 (2)	0.7175 (8)	0.076 (2)	0.064 (2)*
H14b	0.4721 (9)	0.610 (2)	0.068 (2)	0.064 (2)*
H14c	0.374 (3)	0.634 (3)	-0.0182 (5)	0.064 (2)*
C12	0.1855 (4)	0.4570 (4)	0.3845 (5)	0.0264 (11)
H12	0.1619 (4)	0.4592 (4)	0.4685 (5)	0.0317 (13)*
C9	0.2556 (5)	0.4481 (5)	0.1344 (5)	0.0302 (12)
H9	0.2792 (5)	0.4452 (5)	0.0507 (5)	0.0362 (14)*
C16	0.2869 (6)	0.0440 (6)	0.0922 (5)	0.0453 (15)

Table 5. Geometric parameters (Å, º)

I1—C7	2.103 (4)	F5—C16	1.320 (6)
I1—C1	2.107 (4)	C4—C3	1.385 (7)
S1—O2	1.434 (3)	C4—C5	1.383 (7)
S1—O3	1.449 (3)	C4—C13	1.518 (6)
S1—O1	1.438 (3)	C3—C2	1.390 (6)
S1—C15	1.819 (5)	C7—C8	1.383 (6)
S2—O5	1.449 (3)	C7—C12	1.380 (6)
S2—O4	1.434 (3)	C10—C11	1.384 (6)
S2—O6	1.450 (3)	C10—C14	1.514 (6)

S2—C16	1.821 (6)	C10—C9	1.403 (6)
F1—C15	1.331 (5)	C8—C9	1.383 (6)
F3—C15	1.324 (6)	C11—C12	1.386 (6)
F2—C15	1.322 (6)	C1—C2	1.373 (6)
F4—C16	1.338 (7)	C1—C6	1.382 (6)
F6—C16	1.329 (6)	C5—C6	1.395 (6)
C1—I1—C7	99.11 (16)	C9—C8—C7	118.4 (5)
O3—S1—O2	115.0 (2)	C12—C11—C10	121.3 (4)
O1—S1—O2	115.2 (2)	C2—C1—I1	118.0 (3)
O1—S1—O3	114.1 (2)	C6—C1—I1	119.5 (4)
C15—S1—O2	102.9 (2)	C6—C1—C2	122.5 (4)
C15—S1—O3	103.3 (2)	F1—C15—S1	111.7 (4)
C15—S1—O1	104.2 (2)	F3—C15—S1	111.3 (4)
O4—S2—O5	114.3 (2)	F3—C15—F1	106.6 (5)
O6—S2—O5	113.8 (2)	F2—C15—S1	110.9 (4)
O6—S2—O4	115.5 (2)	F2—C15—F1	107.8 (4)
C16—S2—O5	103.1 (2)	F2—C15—F3	108.4 (5)
C16—S2—O4	104.5 (3)	C6—C5—C4	121.5 (5)
C16—S2—O6	103.7 (2)	C1—C2—C3	118.1 (4)
C5—C4—C3	118.5 (4)	C5—C6—C1	117.8 (5)
C13—C4—C3	120.3 (5)	C11—C12—C7	118.4 (5)
C13—C4—C5	121.2 (5)	C8—C9—C10	120.9 (5)
C2—C3—C4	121.6 (5)	F4—C16—S2	110.3 (4)
C8—C7—I1	119.9 (3)	F6—C16—S2	110.9 (4)
C12—C7—I1	117.8 (3)	F6—C16—F4	108.6 (5)
C12—C7—C8	122.3 (4)	F5—C16—S2	110.7 (4)
C14—C10—C11	120.7 (4)	F5—C16—F4	107.6 (5)
C9—C10—C11	118.7 (4)	F5—C16—F6	108.6 (5)