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Direct *in situ* synthesis of cationic N-heterocyclic carbene iridium and rhodium complexes from neat ionic liquid: Application in catalytic dehydrogenation of cyclooctadiene

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ABSTRACT

A direct synthetic route to cationic N-heterocyclic carbene (NHC) complexes of rhodium and iridium from neat dialkyl-imidazolium ionic liquids (ILs) has been found. The method uses complexes bearing basic anionic ligands, [M(COD)(PPh_3)X], X = OEt, $MeCO_2$, which react with the inactivated imidazolium cation in the absence of external bases yielding one M-NHC moiety and the free protonated base. This new one-pot synthesis leaving pure, catalytically active IL solutions is faster, cleaner and more efficient than traditional syntheses of such NHC complexes. The observed reactivity also gives insight into NHC incorporation of rhodium and iridium catalyzed reactions performed in common dialkyl-imidazolium ILs.
The complexes synthesised in this manner are compared with their bis-phosphine analogues in terms of activity for catalytic dehydrogenation of 1,5-cyclooctadiene and 1,3-cyclooctadiene in neat [BMIM][NTf_2] as solvent. Even at high temperature, no ligand exchange reaction is observed with [(COD)M(PPh_3)$_2$][NTf_2] catalysts. As expected, the yields of all the reactions were low, iridium was much more active in C–H activation than rhodium and the NHC ligands were more stable than triphenylphosphine. For all catalysts, the isomerisation of 1,5-cyclooctadiene is the major reaction. However, the phosphine-NHC complex of iridium seems to be more selective for dehydrogenation than its bis-phosphine counterpart, which is more active in transfer-hydrogenation and less stable under the applied conditions. Different reaction conditions were tried in order to optimise selectivity for dehydrogenation over isomerisation and transfer-hydrogenation. Surprisingly, with 1,3-cyclooctadiene as substrate selectivity for dehydrogenation is much higher than with 1,5-cyclooctadiene for all catalysts.

1. Introduction

Selective C–H activation of saturated hydrocarbon units via dehydrogenation is still one of the "dream reactions" of catalysis [1,2]. The major problem of the dehydrogenation reaction is the very unfavourable thermodynamics [3,4]. Strategies to overcome this difficulty include: (i) the use of hydrogen acceptors [5], (ii) photochemical stimulation via UV–Vis irradiation [6], (iii) continuous removal of dihydrogen from the catalytic phase [7].

In recent years, much work on dehydrogenation has been carried out by the organometallic community; however, there is still no satisfactory solution. A number of transition metals have been successfully applied in C–H activation [4], but iridium intrinsically holds the highest potential for dehydrogenation activity [8]. Since N-heterocyclic carbene complexes of rhodium or iridium are less thermally sensitive than their alkylphosphine analogues [9,10], their use in catalytic hydrogenation has recently been tested [11]. [(COD)Ir(PCy_3)(NHC)]$^+$ was found to be even superior in terms of activity as well as stability to Crabtree's catalyst [(COD)Ir(PCy_3)(pyridine)]$^+$.

Much of the efforts so far concentrated on the design of more reactive catalysts, but little attention was paid to the particular difficulty of reaction engineering. Besides the problem of product separation and catalyst recovery (the "classical" drawbacks of homogeneous catalysis) [12], the lack of suitable solvents is still a severe limitation for C–H activation catalysts.

Ionic liquids (ILs) have been promoted as a novel class of solvents for synthesis and catalysis [13–15], since they combine a variety of advantages such as environmental friendliness (virtually no vapour pressure, easiness of recovery and recycling), physical

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robustness within a large temperature range and high solubilisation potential. In general, a significant advantage of using ionic liquids in homogeneous catalysis is the stabilization of organometallic catalysts by their weak coordinating effect. However, gases like dihydrogen show very low solubility in these media even at high pressure [16,17], and high temperature [18].

It has been shown that metallation of imidazolium salts can occur under mild conditions with certain transition metals to generate N-heterocyclic carbene (NHC) ligands [19–21]. These findings suggest that ionic liquids may act as reagents and not only as solvents in transition metal catalyzed reactions. Therefore, in several catalytic systems the difference of the activity in ionic liquids, compared with organic solvents, has been explained by a possible in situ formation of a NHC ligand. This ligand is coordinated to the metal centre and consequently the nature and the activity of the catalytic system are not only changed by solvent effects [22,23]. In particular, this formation of NHC ligands probably also plays an important role in the stabilization of iridium nanoparticles synthesised by reduction of $[Ir(COD)Cl]_2$ in imidazolium-ILs [24].

As the cationic complexes of Osborn and Schrock shown in Fig. 1, are active hydrogenation catalysts in organic as well in ionic liquid solvents [25,26], they have been tested in catalytic dehydrogenation of cyclooctadiene (COD) to cyclooctatriene (cotr) and cyclooctatetraene (cot) in dialkyl-imidazolium ionic liquids.

The facile coordination of the substrate to the catalyst should be an advantage for the dehydrogenation reaction: activation of pre-coordinated ligands in the proximity of the metal centre has a striking entropic advantage over oxidative addition of free substrate [27]. The activity, selectivity and stability of the classical bis-phosphine complexes will be compared with their mono-NHC analogues.

For the latter, a direct synthetic route from neat dialkyl-imidazolium ILs was found. The idea of the new approach to $[(COD)M(PR_3)NHC]^+$ complexes depicted in Fig. 2 was to try the reaction of complexes bearing basic ligands with uncoordinated imidazolium cations in the absence external bases or halides, but in the presence of 1 equiv. of the respective phosphine instead. The formation of the carbene ligand would be forced to occur on the metal and thus avoid the formation of a free carbene. A similar approach has been developed in the case of palladium, however it was not an *in situ* procedure [28]. ILs, being practically non volatile, open up the possibility of working in solution under reduced pressures even at high temperatures [29]. This property was exploited in evaporating the protonated base in order to drive the reaction to completion.

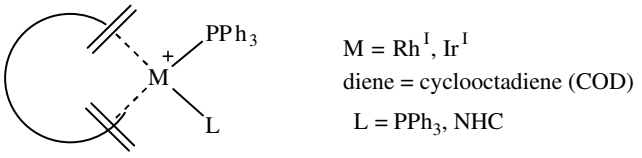

Fig. 1. Complexes used for catalytic isomerisation/dehydrogenating of cyclooctadienes.

2. Results and discussion

The target structure of rhodium and iridium complexes that is supposed to react with the imidazolium cation to give the desired $[(COD)M(PR_3)(NHC)]^+$ complexes is $[(COD)M(base)(PR_3)]$. The bases used for instance were acetate ($MeCO_2$), 2,4-pentanedioate (acac) and ethoxide (OEt); chloride was also included for the sake of comparison. Known synthetic pathways to these complexes are summarised in Fig. 2 [30–32].

While some of the complexes of general formula $[(COD)M(base)(PR_3)]$ were difficult to obtain in acceptable yields from organic solvents, the respective base bridged dimers could easily be synthesised in high purity for all cases investigated. Therefore, in all following activation experiments the target complex was formed *in situ* by mixing 1 equiv. of the respective dimer with 2 equiv. of PPh_3 in a 40-fold excess of $[BMIM][NTf_2]$ as solvent. From the many possible weakly coordinating anions, the bistriflamide (NTf_2^-) was chosen for the preparation of the ionic liquid used. These BTA-based ILs exhibit low viscosities, high thermal stabilities and offer synthetic advantages such as hydrophobicity of the resulting salts.

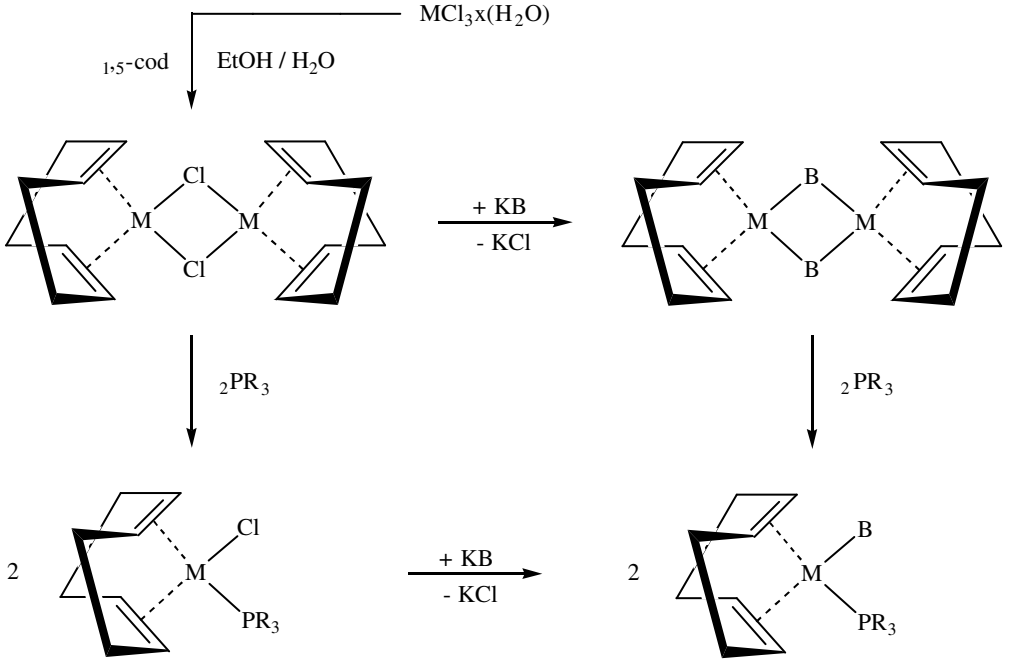

Fig. 2. Synthetic routes to $[(COD)M(B)(PR_3)]$ for M = Rh^I, Ir^I and B = anionic base (30–32).

This is an important feature for organometallic synthesis and catalysis in ILs as the IL can be extracted with deionised water to become essentially free from halides and other ionic impurities. Moreover, satisfying dryness of BTA-based ILs is easy to achieve by heating in vacuum.

Activation was tried by heating and under UV–Vis irradiation at 30 °C, both reactions being carried out *in vacuo* in order irreversibly to remove any protonated base. In no case did photolysis lead to the formation of NHC complexes according to the NMR spectra of the mixtures.

The [(COD)M(PPh_3)Cl] complexes showed different reactivity for rhodium and iridium. [(COD)Ir(PPh_3)Cl] was stable in solution up to 120 °C *in vacuo*, higher temperatures resulted in decomposition to a metallic mirror. [(COD)Rh(PPh_3)Cl] stays unchanged at moderate temperatures (up to 80 °C), but above 100 °C an orange solid precipitated from the IL. NMR analysis revealed that it was pure $[(COD)RhCl]_2$, and no traces of a NHC complex could be found in solution.

The corresponding [(COD)M(PPh_3)(acac)] complexes did not behave in such a clean manner. Although indication of NHC formation was seen, the reaction did not go to completion upon further or longer heating. Instead, decomposition was observed. In all other successful cases the respective NHC complex remained stable upon heating to at least 140 °C *in vacuum*.

In the case of the acetate and ethoxide precursors, upon heating, the initial slurry suddenly became a clear homogeneous solution with characteristic colouration (deep orange in the case of rhodium, purple for iridium) above a certain temperature. Bubbling was also observed, indicating liberation of an evaporable species. In the ^{1}H NMR spectrum of these solutions new signals appeared close to those from the protons in 4/5 position, and of the N-methyl and the N-methylene group (approx. 0.5 ppm upfield) of the imidazolium salt, indicating the presence of an altered imidazolium species. Interestingly, the ^{31}P NMR spectra show only one single compound with a chemical shift very similar to $[(COD)M(PPh_3)_2]^+$. In the case of rhodium, a $^1J_{PRh}$ coupling of 156 Hz proves phosphine coordination to the metal. In the ^{13}C NMR spectra, all peaks from PPh_3 and COD can be observed as well as the carbon signals of the imidazolium ion. Finally, one new quaternary signal at 176.23 ppm appears as a doublet of doublet ($^1J_{CRh}$ = 47.3 Hz, $^2J_{CP}$ = 16 Hz, NCN) and at 173.39 ppm as a doublet (2JCP = 9.8 Hz), for the rhodium and iridium complexes, respectively. ^{1}H NMR confirms the presence of the coordinated diene; all these data are indicate that $[(COD)M(PPh_3)NHC]^+$ complexes were formed *quantitatively*.

Table 1 sums up the thermal activation results.

For the sake of complete characterisation, isolation of the successfully formed NHC complexes from the IL was tried. Interestingly, it was found that the *in situ* formed NHC complexes showed a very high affinity to the parent IL and could not be a 100% separated from it. Extraction or crystallisation with the help of organic solvents failed. Even column chromatography over silica gel only yielded a concentrated oil of the respective complex in some IL. Dilution of the oil with chloroform and layering with hexanes finally resulted in crystallisation of some pure material in the case of iridium. The X-ray structure confirmed the successful formation of [(COD)Ir(PPh_3)NHC][NTf_2], Fig. 3.

Table 1
Activation results of [BMIM][NTf_2] for heating with the respective complex in vacuo

Precursor	Reactivity with [BMIM][NTf_2]
[(COD)Rh (PPh_3)Cl]	Dimerisation to $[Rh(cod)Cl]_2$ above 100 °C
[(COD)Rh(PPh_3)OAc]	Quant. NHC-formation above 80 °C
[(COD)Ir(PPh_3)OAc]	Quant. NHC-formation above 100 °C
[(COD)Rh(PPh_3)acac]	Some NHC-formation above 50 °C
[(COD)Ir(PPh_3)acac]	Some NHC-formation above 60 °C
[(COD)Rh(PPh_3)OEt]	Quant. NHC-formation above 50 °C
[(COD)Ir(PPh_3)OEt]	Quant. NHC-formation above 60 °C

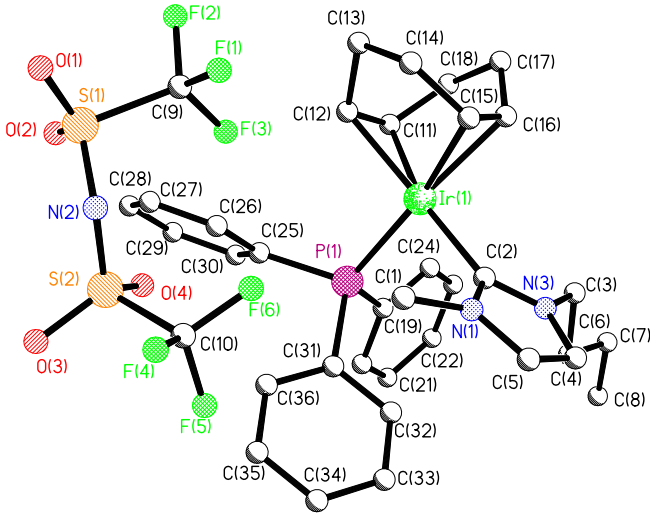

Fig. 3. X-ray crystal structure of [(COD)Ir(PPh_3)NHC][NTf_2] (hydrogen atoms are omitted for clarity).

The metal–carbene bond length of 2.053(6) Å suggests a single rather than a double bond, consistent with there being little π-backbonding from the metal. The Ir–C bond lengths to the COD ligand are not statistically variant while the C–N bond lengths within the imidazolium ring support a high degree of delocalisation. In general, the data are consistent with similar complexes reported in the literature [33] (see Tables 2 and 3).

The phosphine–NHC complexes were also analysed by electrospray ionisation (ESI) mass spectrometry [34]. All negative spectra (ESI^-) only showed one peak at m/z = 280 arising from the bistriflamide counter anion and in (ESI^+) $[(COD)Ir(PPh_3)NHC]^+$ gave rise to signals at m/z = 699.24 and 701.24 in the ratio expected for (^{191}Ir/^{193}Ir = 37: 63), see supporting information.

An important observation, which led us to investigate the activity of these complexes in dehydrogenation reactions, was that, in the observed fragmentation of all $[(COD)M(PPh_3)L]^+$ complexes (L = NHC or PPh_3), there is a progressive loss of 2 mass units (up to a total of 4) on increasing the cone voltage. This could be interpreted as dehydrogenation after the phosphine ligand has dissociated from the complex. Most probably, COD is dehydrogenated to cyclooctatriene (cotr) and cyclooctatetraene (cot), affording $[M(cot)L]^+$ (L = NHC or PPh_3). This observation has also been made before for some tungsten and molybdenum carbonyl complexes of COD and cotr [35]. However, loss of hydride from other ligands, such as phosphines or NHC is also possible to some extent. Both ligands are known to undergo metallation reactions [36].

Table 2
Selected bonds lengths (Å) and angles (°) with estimated standard deviations

Ir(1)–C(2)	2.053(6)	C(11)–Ir(1)–C(2)–N(3)	−3.5(11)
Ir(1)–C(11)	2.198(6)	C(12)–Ir(1)–C(2)–N(3)	−148.3(6)
Ir(1)–C(12)	2.215(6)	C(11)–Ir(1)–C(2)–N(1)	170.8(6)
Ir(1)–C(15)	2.200(6)	C(12)–Ir(1)–C(2)–N(1)	26.0(10)
Ir(1)–C(16)	2.222(14) Å	C(15)–Ir(1)–C(2)–N(3)	−102.8(6)
C(2)–N(1)	1.345(8)	C(16)–Ir(1)–C(2)–N(3)	−66.2(6)
C(2)–N(3)	1.354(8)	P(1)–Ir(1)–C(2)–N(3)	96.5(5)
N(3)–C(4)	1.378(8)		
N(1)–C(5)	1.384(8)		
C(4)–C(5)	1.345(9)		
Ir(1)–P(1)	2.3177(16)		

Table 3
Crystal data and structure refinement for [(COD)Ir(PPh$_3$)NHC][NTf$_2$]

Formula	$C_{36}H_{41}F_6IrN_3O_4PS_2$
Formula weight	981.01
Crystal size (mm)	0.10 × 0.03 × 0.01
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.1476(16)
b (Å)	12.644(2)
c (Å)	15.919(3)
α (°)	85.442(15)
β (°)	76.826(13)
γ (°)	75.861(12)
Volume (Å^3)	1927.9(6)
Z	2
D_{calc} (Mg/m^3)	1.690
Reflections collected	12 357
Independent reflections [R_{int}]	6825 [0.0926]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0551$, $wR_2 = 0.1366$
R indices (all data)	$R_1 = 0.0569$, $wR_2 = 0.1391$
Goodness-of-fit on F^2	1.015
Absorption coefficient (mm^{-1})	3.684
$F(000)$	976
θ Range for data collection (°)	3.96–25.38
Maximim and minimum transmission	1.0000 and 0.8656
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6825/0/445
Largest difference in peak and hole (e Å^{-3})	2.597 and −2.094

Considering that iridium is generally more active in C–H activation and forms stronger metal–ligand bonds than rhodium, the results summarised in Table 1 suggest that pre-dissociation of one of the ligands is needed before the imidazolium is attacked. As no external base is present in the medium, the formation of the NHC ligand must occur on the metal, and no free carbene should be present during the reaction. The d^8 metal centre must be involved directly in the observed C–H activation by forming an NHC ligand from an uncoordinated, common dialkyl–imidazolium IL under pH neutral conditions. Possible routes of formation are described in Fig. 4.

As disclosed in the beginning, pathway **(F)** over hexacoordinated 18 electron complexes should give Ir–NHC complexes more readily than with rhodium. Considering the observed phosphine dissociation in the case of [(COD)Rh(PPh$_3$)Cl] and high electrostatic repulsion of the imidazolium ion to a cationic species, pathway (**E**) seems to be the most probable. Therefore, the formation of a neutral 14 electron complex bearing a basic ligand would be responsible for the formation of a NHC Ligand from a neat dialkyl–imidazolium ionic liquid. In this case, the ligand strength of both the base and the phosphine determine the equilibrium (**A**)–(**C**)–(**D**). Reaction (**B**) might also take place, but is not thought to lead to NHC formation; the pK_a values of all bases are too low to deprotonate the imidazolium ion. The suggested reaction pathway also explains the reported reaction time of 3 days for the traditional synthesis of such complexes from [(COD)M(OEt)]$_2$ with imi-

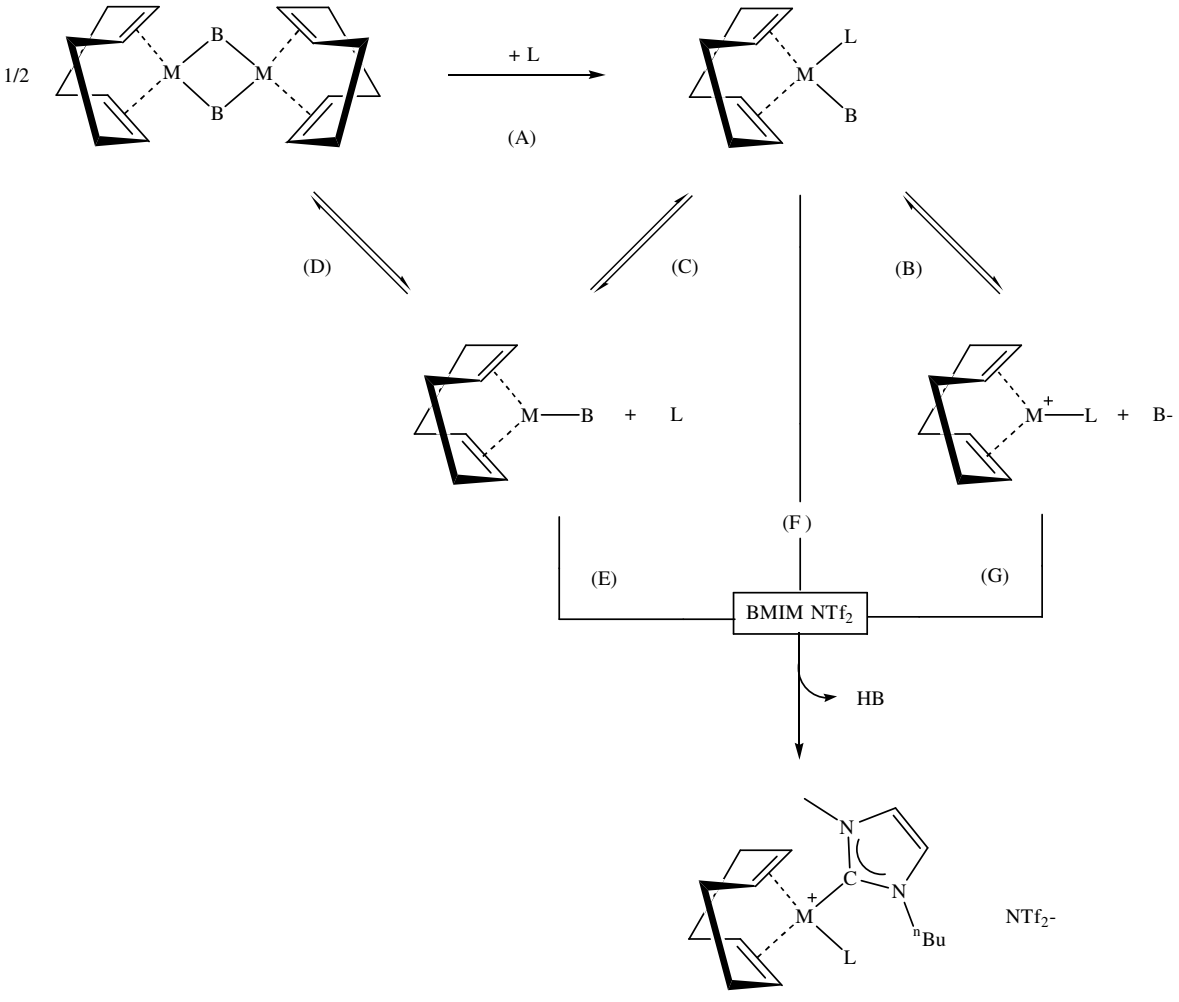

Fig. 4. Potential pathways of NHC formation.

dazolium halides in organic solvents [10,37]. In this case, halide bridged dimers would reform and thus only with a large excess of ethoxide the reaction proceeds slowly. When one equivalent of a neutral donor ligand reversibly creates the 14 electron fragment, the reaction proceeds within minutes under vacuum.

3. Catalysis

[(COD)Rh(PPh_3)$_2$][NTf_2] was found to be poorly soluble in pure, dry [BMIM][NTf_2]. Slow heating gave an orange homogeneous solution above 80 °C which contained only 34% of the initial complex and numerous side products. Therefore, the Rh–NHC complexes were barely active in dehydrogenation catalysis, and therefore only the case of iridium is discussed in the following. The iridium bis-phosphine complex was even less soluble, but more stable, however. At 100 °C, the complex reversibly dissolved in neat [BMIM][NTf_2] to give a deep purple solution showing unchanged [(COD)Ir(PPh_3)$_2$][NTf_2] which slowly recrystallised from the IL upon cooling to room temperature. The *in situ* generated NHC complexes were entirely soluble in the respective IL, and thermally more stable.

Solubility of the substrate determined at 25 °C by ^{1}H NMR shows 15 mol% of 1,5-COD in saturated [BMIM][NTf_2]. This amount is sufficient for homogeneous catalysis to occur, but still allows biphasic reaction engineering for the sake of product separation and catalyst recovery.

All values for conversion, selectivity and turnover numbers were calculated from GC–MS analysis (see Table 4, Fig. 5). All C_8H_{12} compounds other than the starting material were considered as isomerisation products, C_8H_{12-x} as dehydrogenation products and C_8H_{12+x} as hydrogenation products. Apart from additional solvent, no other compounds were found in the organic fraction after catalysis. The main isomerisation occurred from 1,5- through 1,4- to 1,3-cyclooctadiene, although traces of saturated tricyclic and other C_8H_{12} hydrocarbons could also be observed (named as "other" in the following).

Liquid–liquid biphasic catalysis was attempted for dehydrogenation reactions at 140 and 160 °C. A clear, colourless organic phase remained separated on top of the highly coloured IL phase containing the catalyst. The mixture was stirred vigorously for several hours under ambient pressure of nitrogen while a bubbler allowed potential gas evolution. At the end a clear, colourless organic phase could be recovered, suggesting the highly coloured catalyst is essentially insoluble in the substrate.

At both 140 and 160 °C, the reaction with [(COD)Ir(PPh_3)$_2$][NTf_2] went to full conversion. [(COD)Ir(PPh_3)NHC][NTf_2] demonstrated much lower activity than the bis-phosphine complex. The main product using either catalyst was 1,3-COD. Although it seems as if more hydrogenation than dehydrogenation occurred, the number of dehydrogenated double bonds has to be taken into account. As no H_2 was added to the system, transfer-hydrogenation must have taken place. In direct comparison, the NHC complex is 20 times less active in terms of transfer-hydrogenation compared to the bis-phosphine catalyst. The ^{31}P NMR spectrum shows that the NHC catalyst was more stable, over 80% remained in the final solution, compared with 70% for the bis-phosphine complex, Table 4, Fig. 5.

All 1,5-COD had been consumed after 2 h at 160 °C with [Ir(COD)(PPh_3)$_2$][NTf_2]. Interestingly, less hydrogenation than dehydrogenation was found for the first time, indicating some true dehydrogenation with liberation of H_2. Approximately four turnovers of transfer-hydrogenation and one turnover of dehydrogenation occurred in 2 h. It seems as if the reaction with the NHC complex is less rapid than with the bis-phosphine catalyst, the, selectivity to dehydrogenation over transfer-hydrogenation looks better: roughly 1.5 turnovers of dehydrogenation and 0.2 turnovers of transfer-hydrogenation took place within 2 h. The catalyst is sufficiently stable: 72% of the initial complex remained (^{31}P NMR), and the ^{1}H and ^{13}C NMR still showed the presence of the NHC ligand.

Comparing the results at 160 °C with the reaction at 140 °C, it seems as if refluxing the substrate on the IL phase containing the catalysts does indeed help H_2 to evolve from the reaction medium. Interestingly, the NHC complex of iridium looks more active in dehydrogenation than in transfer-hydrogenation: the opposite behaviour to its bis-phosphine analogue. This, on the other hand, suggests that the stronger donor facilitates dehydrogenation.

In order to test whether dehydrogenation only occurs during isomerisation, the main isomerisation product 1,3-cyclooctadiene was employed as substrate under identical conditions. After 2 h, the iridium bis-phosphine catalyst yielded 6.8% conversion with an interesting product distribution. Transfer-hydrogenation seems to be suppressed. The isomerisation back to 1,4- and even 1,5-COD was observed with a yield of 2%. One new isomerisation product, bicyclo[3.3.0]oct-2-ene, was found with 4% yield, which remarkably requires a π–σ C–C bond rearrangement. Dehydrogenation occurred with 1.1% conversion corresponding to 1.5 turnovers within 2 h. The iridium NHC catalyst behaved similarly with slightly lower activity, Table 5.

Table 4
Product distribution from 1,5-COD after 5 h at 140° C or 2 h at 160° C in the presence of [(COD)Ir(PPh_3)$_2$][NTf_2] or [(COD)Ir(PPh_3)NHC][NTf_2], with a molar ratio COD/Cat 100:1

[(COD)Ir(PPh_3)$_2$][NTf_2]	[(COD)Ir(PPh_3)NHC][NTf_2]	[(COD)Ir(PPh_3)$_2$][NTf_2]	[(COD)Ir(PPh_3)NHC][NTf_2]
140 °C (5 h)	140 °C (5 h)	160 °C (2 h)	160 °C (2 h)
1,5-COD	1,5-COD	1,5-COD	1,5-COD
Conv. 100%	Conv. 84.5%	Conv. 100%	Conv. 96%
Isomerisation			
Conv. 83.9%	Conv. 79.4%	Conv. 91.9%	Conv. 94.4%
Selectivity			
3.5% 1,4-COD	67.0% 1,4-COD	10.9% 1,4-COD	11.5% 1,4-COD
71.3% 1,3-COD	26.4% 1,3-COD	62.1% 1,3-COD	86.9% 1,3-COD
9.1% other	6.0% other	18.9% other	0% other
Dehydrogenation			
Conv. 5.3%	Conv. 0.3%	Conv. 4.3%	Conv. 1.4%
Selectivity			
1% cotr	0.3% cotr	1.3% cotr	1.2% cotr
3.6% xylenes	0% xylenes	2.4% xylenes	0% xylenes
0.7% styrene or cot	0% styrene or cot	0.6% styrene or cot	0.2% styrene or cot
Hydrogenation			
Conv. 10.8%	Conv. 0.3%	Conv. 3.8%	Conv. 0.2%

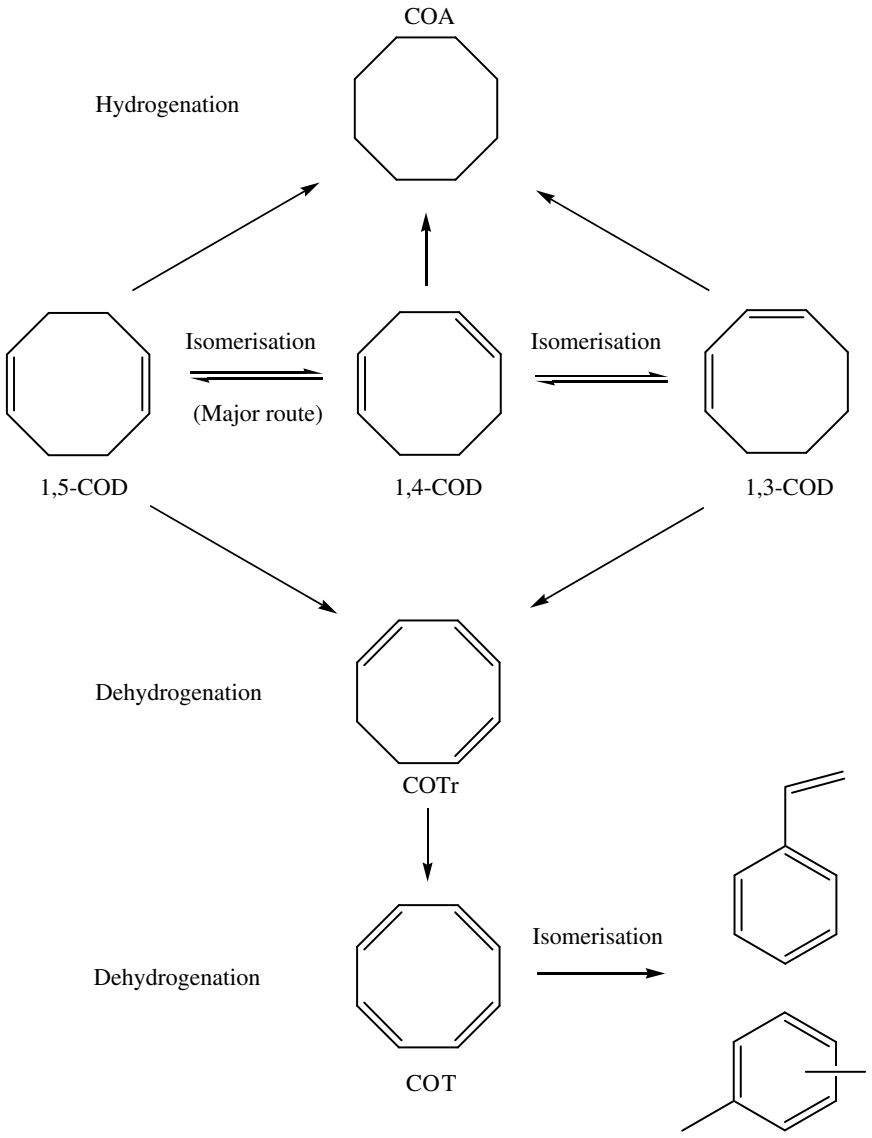

Fig. 5. Possible reaction sequence of 1,5-COD in the presence of $[(COD)Ir(PPh_3)_2][NTf_2]$ or $[(COD)Ir(PPh_3)NHC][NTf_2]$.

Table 5
Product distribution from $[(COD)Ir(PPh_3)_2][NTf_2]$ (upper table) and $[(COD)Ir(PPh_3)$-$NHC][NTf_2]$ (lower table) with 1,3-COD after 2 h at 160 °C with a molar ratio COD/Cat 100:1

Catalyst	Product	Conversion (%)
$[(COD)Ir(PPh_3)_2][NTf_2]$	Isomerisation	6.8
	Dehydrogenation	1.1
	Hydrogenation	0
$[(COD)Ir(PPh_3)](NHC)[NTf_2]]$	Isomerisation	6.4
	Dehydrogenation	0.5
	Hydrogenation	0

4. Conclusion

The direct route to NHC complexes of rhodium and iridium from dialkyl-imidazolium ILs allows easy access to the corresponding complexes. This one-pot synthesis does not necessitate any workup or purification and gives catalytically active IL solutions.

The application of the complexes $[(COD)Ir(PPh_3)_2][NTf_2]$ and $[(COD)Ir(PPh_3)NHC][NTf_2]$ in dehydrogenation catalysis was successfully demonstrated. Activity in the range of a few turnovers per hour looks reasonable when compared with other systems for catalytic dehydrogenation.

When one phosphine ligand is replaced by a more highly donating NHC ligand in the iridium complex, lower isomerisation as well as lower transfer-hydrogenation activity is observed. However, the catalyst is more stable and more selective; less side products are formed. Importantly, the NHC ligand is stable throughout the reaction; no wingtip-metallation or transalkylation was observed. The IL seems to prevent irreversible loss of the ligand, probably by acting as a reservoir. The fact that typically 70–80% can be recovered in the NMR regardless of the reaction time might be due to oxidation originating from the transfer of the catalyst solution, and does not necessarily reflect degradation through catalysis.

When the main isomerisation product, 1,3-cyclooctadiene, is used as substrate, no transfer-hydrogenation occurs but, besides some isomerisation, dehydrogenation occurs exclusively. Although overall activity is low, selectivity to dehydrogenation is much higher.

5. Experimental

All experiments were carried out under nitrogen atmosphere using Schlenk techniques. The inert gas was dried and deoxygen-

ated through a chromium(II)/silica glass column. Air stable substances (solid complexes and IL) were weighed quickly in air. All fittings were equipped with Teflon QuickFit™ seals; grease was not used in contact with chemicals.

Solvents were dried with suitable drying agents, distilled under nitrogen and stored over vacuum heated molecular sieves 4 Å. All chemicals were purchased from commercial sources including Aldrich, Acros, Strem and ABCR. Unless otherwise specified, the reagents were used as received. Gases were supplied from BOC Gases, UK.

Melting points were measured on a Gallenkamp Melting Point Apparatus using glass capillaries. Elemental analyses were conducted by the Analytical Service of the School of Chemistry, University of St Andrews on a Carlo Erba CHNS analyser.

Mass spectrometry was performed on a Micromass LCT high performance orthogonal acceleration reflection TOF mass spectrometer using a Z-flow atmospheric pressure ionisation source for electrosprayed samples. Measurements were conducted by the Mass Spectrometry Facility of the Biomolecular Science Department of the University of St Andrews.

Gas chromatographic analyses were carried out on a Hewlett Packard 5890 series gas chromatograph equipped with both flame ionisation detector (GC-FID) for quantitative analysis and a mass selective detector (GC–MS) for qualitative analysis. A fused silica column Supelco MDN-35 (35% phenyl- and 65% methyl-polysiloxane, 30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) was used with a flow rate of 1.0 ml/min. The temperature was held at 40 °C for 8 min and then raised to 200 °C at a heating rate of 20 °C/min.

NMR spectra were recorded on a Bruker Avance 300 or a Bruker Avance II 400 spectrometer at 300 K unless otherwise stated. ^{1}H and ^{13}C spectra were referred internally to deuterated solvents; chemical shifts are relative to Me_4Si. ^{19}F spectra were calibrated with the help of an internal Bruker reference program using proton solvent signals. ^{31}P spectra used external 85% H_3PO_4 as standard.

X-ray crystallography was performed at 93 K using a Rigaku MM007 rotating anode generator/confocal optics and a Mercury CCD detector Mo Kα radiation ($\lambda = 0.71071$ Å). A full hemisphere of data were collected, corrected for Lorentz polarisation and absorption. Structure solution and refinement used SHELXTL.

Synthesis of 1-^{n}butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide; di-μ-chloro-bis(η^4-1,5-cyclooctadiene)-dirhodium(I), di-μ-chloro-bis(η^4-1,5-cyclooctadiene)diiridium(I); di-μ-acetato-bis(η^4-1,5-cyclooctadiene)dirhodium(I); di-μ-acetato-bis(η^4-1,5-cyclooctadiene)- diiridium(I); η^4-1,5-cyclooctadiene-μ-2,4-pentanedionato-rhodium(I): μ-2,4-pentanedionato-η^4-1,5-cyclooctadiene-iridium(I); bis(η^4-1,5-cyclooctadiene)di-μ-ethanoatodirhodium(I); bis(η^4-1,5-cyclooctadiene)di-μ-ethanoato-diiridium(I); chloro -η^4-1,5-cyclooctadienetriphenylphosphinerhodium(I) were carried out as described in the literature [30–32,38].

5.1. η^4-1,5-Cyclooctadienebis(triphenylphosphine)rhodium(I) bis{(trifluoromethyl)sulfonyl}amide

The complex, di-μ-chlorobis(η^4-1,5-cyclooctadiene)dirhodium(I) (100 mg, 0.203 mmol) was dissolved in dichloromethane (2 ml) to give an orange solution. A solution of lithium bis{(trifluoromethyl)sulfonyl}amide (120 mg, 0.418 mmol) in deionised water (2 ml) was added. Under vigorous stirring triphenylphosphine (400 mg, 1.53 mmol) was added to the emulsion, and the mixture was stirred for 2 h at room temperature. After phase separation, the water layer was removed with a syringe and the organic phase washed with water (2 ml × 3). The deep orange solution was reduced to half the volume with a stream of nitrogen and isopropanol (2 ml) was slowly added until an orange solid began to precipitate. Crystallisation was completed by addition of hexanes (2 ml) and the solid was collected on a frit and washed with hexanes. Drying *in vacuum* yielded of an orange microcrystalline solid (327 mg, 0.322 mmol, 79%). The product is soluble in acetone, ether and alcohols but insoluble in hexanes and water. M.p. = 144 °C (dec.).

^{1}H NMR ($CDCl_3$): $\delta = 7.44–7.27$ (m, 30H, phenyl), 4.55 (bs, 4H, COD_{vinyl}), 2.53 (m, 4H, COD_{allyl} inner), 2.24 (qua, $^{3}J_{HH} = 8.9$ Hz, 4H, COD_{allyl} outer). ^{13}C NMR ($CDCl_3$): $\delta = 134.04$, 130.51, 128.72 and 128.67 (m, phenyl), 99.18 (s, COD_{vinyl}), 30.64 (s, COD_{allyl}). ^{19}F NMR ($CDCl_3$): $\delta = -78.55$ (s, $N(SO_2CF_3)_2$). ^{31}P NMR ($CDCl_3$): $\delta = 26.31$ (d, $^{1}J_{PRh} = 145$ Hz, PPh_3).

ESI^{+}MS: 735.30 ($[Rh(COD)(PPh_3)]^{+}$); 473.16 $[Rh(COD)(PPh_3)]^{+}$; 471.16 $[Rh(C_8H_{10})(PPh_3)]^{+}$; 469.13 $[Rh(C_8H_8)(PPh_3)]^{+}$. Anal. Calc. for $C_{46}H_{42}F_6NO_4P_2RhS_2$ requires C, 54.4; H, 4.1; N, 1.4. Found: C, 54.4; H, 3.6; N, 1.4%.

5.2. η^4-1,5-Cyclooctadienbis(triphenylphosphine) iridium(I) bis{(trifluoromethyl)sulfonyl}amide

The complex was synthesised following the same procedure as for the rhodium analogue using. di-μ-chloro-bis(η^4-1,5-cyclooctadiene)diiridium(I) (100 mg, 0.149 mmol), lithium bis{(trifluoromethyl)sulfonyl}amide (100 mg, 0.348 mmol) and triphenylphosphine (400 mg, 1.53 mmol) to give the pure product as a purple powder (270 mg, 0.244 mmol, 84%). The solubility behaviour is similar to that of the rhodium complex. M.p. = 164 °C (dec.).

^{1}H NMR ($CDCl_3$): $\delta = 7.45–7.27$ (m, 30H, phenyl), 4.19 (bs, 4H, COD_{vinyl}), 2.35 (m, 4H, COD_{allyl} inner), 1.97 (qua, $^{3}J_{HH} = 8.6$ Hz, 4H, COD_{allyl} outer).^{13}C NMR ($CDCl_3$): $\delta = 134.24$, 131.37, 129.45 and 128.70 (m, phenyl), 87.17 (s, COD_{vinyl}), 31.09 (s, COD_{allyl}).^{19}F NMR ($CDCl_3$): $\delta = -78.59$ (s, $N(SO_2CF_3)_2$).^{31}P NMR ($CDCl_3$): $\delta = 17.41$ (s, PPh_3).

ESI^{+}MS. ($^{193}Ir/^{191}Ir = 63$: 37): 825.35, 823.36 ($[Ir(C_8H_{10})(PPh_3)_2]^{+}$); 561.21, 559.23 $[Ir(C_8H_{10})(PPh_3)]^{+}$; 557.19, 555.20 $[Ir(C_8H_8)(PPh_3)]^{+}$. Found: C 47.6, H 3.3, N 1.5; $C_{46}H_{42}F_6IrNO_4P_2S_2$ requires C 50.0, H 3.8, N 1.3.

5.3. Synthesis of N-Heterocyclic carbene complexes from neat [BMIM][NTf_2]

Pure [BMIM][NTf_2] was dried and degassed by heating to 100 °C *in vacuo* over night prior to use. Neat [BMIM][NTf_2] (1 g, 2.385 mmol) was mixed with the respective dimer (30–40 mg, 0.0596 mmol) to give a $BMIM^{+}$ to metal ratio of 20, equivalent to a metal concentration of 0.085 mol dm^{-3}. Triphenylphosphine (31 mg, 0.119 mmol) was added and the mixture was stirred *in vacuo* for several hours while being heated stepwise. As soon as a homogeneous solution was obtained, it was placed in an NMR tube together with a fused capillary of C_6D_6. The solution was analysed by NMR spectroscopy and heated further *in vacuum*.

Experiments attempting photochemical activation employed the same mixture of the respective complex with two equivalents of phosphine in neat [BMIM][NTf_2] which was transferred into an EPR tube made of quartz. A fused capillary of C_6D_6 was added and the solution was exposed to UV irradiation for 8 h at 30 °C while being *in vacuo* and analysed by NMR.

5.4. 1-^{n}Butyl-3-methylimidazolin-2-ylidene-η^4-1, 5-cyclooctadienetriphenylphosphinerhodium(I) bis{(trifluoromethyl)sulfonyl}amide

^{1}H NMR: $\delta = 7.48–7.35$ (m, 15H, phenyl), 7.07 and 6.99 (bs, 2H, NC*H*C*H*N), 4.85 (bd, 2H, COD_{vinyl} *trans* PPh_3), 4.2* (m, COD_{vinyl} 9i NHC), 4.1* (m, NCH_2R), 3.59 (s, 3H, NCH_3), 2.66–2.12 (m, 4H, COD_{allyl}), 1.90** (qui, $^{3}J_{HH} = 7.4$ Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.38**

(se, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.95** (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$).

^{13}C NMR: δ = 176.23 (dd, $^1J_{CRh}$ = 47.3 Hz, $^2J_{CP}$ = 16 Hz, NCN), 133.67 (d, $^2J_{CP}$ = 11.4 Hz, *ortho*-C phenyl), 131.54 (s, *para*-C phenyl), 131.03 (d, $^1J_{CP}$ = 23.9 Hz, α-C phenyl), 129.05 (d, $^3J_{CP}$ = 8.7 Hz, *meta*-C phenyl), 124.38 and 121.97 (s, NCHCHN), 120.13** (qua, $^1J_{CF}$ = 321 Hz, $N(SO_2CF_3)_2$), 97.06 (vt, $^1J_{CRh}$ = 9.4 Hz, $^2J_{CP}$ = 7.9 Hz, COD_{vinyl} *trans* PPh_3), 96.04 (vt, $^1J_{CRh}$ = 9.9 Hz, $^2J_{CP}$ = 8.9 Hz, COD_{vinyl} *trans* PPh_3), 94.60 and 94.01 (d, $^1J_{CRh}$ = 7.4 Hz, COD_{vinyl} *trans* NHC), 50.68 (s, NCH_2R), 37.15 (s, NCH_3), 31.91 (s, $NCH_2CH_2CH_2CH_3$), 30.73 (d, $^1J_{CRh}$ = 38.5 Hz, COD_{allyl} *trans* PPh_3), 29.20 (d, $^1J_{CRh}$ = 40.4 Hz, COD_{allyl} *trans* NHC), 19.94 (s, $NCH_2CH_2CH_2CH_3$), 13.14 (s, $NCH_2CH_2CH_2CH_3$).

^{31}P NMR: δ = 25.37 (d, $^1J_{PRh}$ = 156 Hz, PPh_3). [* Identified through C–H correlation spectra, peaks partly or completely overlapped with strong solvents signals of BMIM NTf_2. **Common signals for both the solvent and the complex.]

ESI$^+$MS: 611.16 ($[Rh(COD)(PPh_3)(NHC)]^+$); 349.09 ($[Rh(COD)(NHC)]^+$); 239.0 $[Rh(NHC)]^+$.

5.5. 1-^{n}Butyl-3-methylimidazolin-2-ylidene- η^4-1, 5-cyclooctadienetriphenylphosphineiridium(I) bis{(trifluoromethyl)sulfonyl}amide

^{1}H NMR: δ = 7.48–7.31 (m, 15H, phenyl), 7.07 and 6.97 (bs, 2H, NCHCHN), 4.46 (bs, 2H, COD_{vinyl} *trans* PPh_3), 4.1* (m, NCH_2R), 4.0* (m, COD_{vinyl} *trans* NHC), 3.47 (s, 3H, NCH_3), 2.65–2.05 (m, 4H, COD_{allyl}), 1.89** (qui, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.37** (se, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.94** (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{36}H_{41}F_6IrN_3O_4PS_2$ requires: C, 46.7; H, 4.2; N, 4.3. Found: C, 44.2; H, 4.1; N, 4.1%.

^{13}C NMR: δ = 173.39 (d, $^2J_{CP}$ = 9.8 Hz, NCN), 133.85 (d, $^2J_{CP}$ = 10.2 Hz, *ortho*-C phenyl), 131.23 (s, *para*-C phenyl), 130.56 (d, $^1J_{CP}$ = 50.4 Hz, α-C phenyl), 129.07 (d, $^3J_{CP}$ = 9.1 Hz, meta-C phenyl), 124.01 and 121.72 (s, NCHCHN), 120.13** (qua, $^1J_{CF}$ = 321 Hz, $N(SO_2CF_3)_2$), 86.82 (d, $^2J_{CP}$ = 11.7 Hz, COD_{vinyl} *trans* PPh_3), 85.78 (d, $^2J_{CP}$ = 12.1 Hz, COD_{vinyl} *trans* PPh_3), 80.05 and 79.56 (s, COD_{vinyl} *trans* NHC), 50.47 (s, NCH_2R), 36.87 (s, NCH_3), 30.24 (s, COD_{allyl} *trans* PPh_3), 29.66 (s, COD_{allyl} *trans* NHC), 31.74 (s, $NCH_2CH_2CH_2CH_3$), 19.89 (s, $NCH_2CH_2CH_2CH_3$), 13.09 (s, $NCH_2CH_2CH_2CH_3$).

^{31}P NMR: δ = 18.15 (s, PPh_3). [*Identified through C–H correlation spectra, peaks partly or completely overlapped with strong solvents signals of BMIM NTf_2. ** Common signals for both the solvent and the complex.]

ESI$^+$MS (^{193}Ir/ ^{191}Ir = 63: 37) 701.26, 699.26 $[Ir(COD)(PPh_3)(NHC)]^+$, 433.14, 435.14 $[Ir(C_8H_{10})(NHC)]^+$; 431.12, 429.10 $[Ir(C_8H_8)(NHC)]^+$. The complex was fully characterised by X-ray diffraction studies.

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Appendix A. Supplementary material

CCDC 279579 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.017.

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