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Review

Abnormal *N*-heterocyclic carbenes

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Contents

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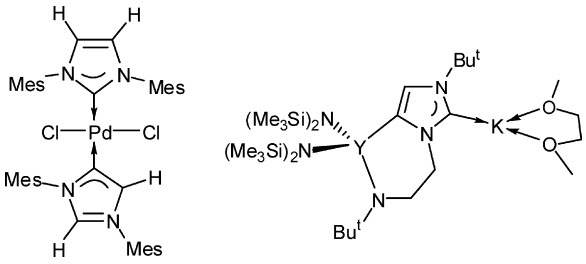
Abstract

Metal NHC complexes have been known for over 50 years, but only during the last 15 have they been studied as potential catalysts.

N-heterocyclic carbene (NHC) complexes are often more straightforward to make than the phosphine analogues with which they are often compared, are generally more stable, less odorous and on many occasions have been shown to be anywhere between 100 and 1000 times more effective.

For a decade it was assumed that NHCs always interacted with metal atoms in the same way. However, examples have now been found that exhibit unusual binding behaviour. It is important to understand why such abnormal binding occurs and what effects this could have on the catalytic properties of NHC complexes.



Keywords: Abnormal; Wrong; Carbene; NHC; Heterocyclic; Bond activation; Platinum; Palladium; Iridium; Lanthanide; Imidazolium

1. Introduction

N-heterocyclic carbenes (NHCs) have become of considerable importance in organometallic chemistry and homogeneous catalysis [1].

Although they are considered to behave like tertiary phosphines in many respects, NHCs exhibit stronger σ-donor properties [2]. Several advantages are gained in using NHCs rather than their phosphorus analogues; these include tighter binding (which limits decomposition reactions associated with ligand dissociation), greater thermal stability, and increased basicity. Additionally, NHC–metal complexes can usually be made *in situ* with high yields.

In the early years of the development of metal–NHC chemistry, a wide range of palladium and ruthenium complexes were isolated and studied as homogeneous catalysts, exemplified by complexes 1.0.1 and 1.0.2, Fig. 1 [2]. These, and similar late metal complexes were shown to be isolable from either the direct deprotonation of the imidazolium salt (exemplified by the reaction to make 1.0.1) [3] or by the addition of the already-formed NHC ligand.

After ruthenium catalysts containing one NHC group were discovered to be effective in alkene metathesis reactions, much work was undertaken to optimise the system [4]. Substitution of tricyclohexylphosphine with SIMes (**1.0.2**) was found to improve the activity of both ring-closing metathesis (RCM), and ring-opening metathesis polymerisation (ROMP), by 10^2 to 10^3 times. The E:Z selectivity of the reaction was also changed from being under kinetic control (in the phosphine systems) to thermodynamic control (**1.0.2**).

During the exploratory syntheses and the investigation of the catalytic activity of a range of systems in which a phosphine was replaced by a carbene ligand, the consensus was that all NHCs bind to metal centres in the same way. The free carbenes originally isolated always showed structures in which the singlet electron pair resides at C2, see Fig. 2, and it was considered that the presence of the adjacent nitrogen atoms stabilised both C2-centred free carbene and the M–C2$_{carbene}$ bond uniquely.

A wide variety of NHC structures were subsequently developed, most of which use simple synthetic organic chemical methodology. Both the electronic and steric properties may be controlled by modifying the carbon backbone or changing the functional groups that are bonded to the ring. In this way, specialized catalysts with specific solubility, electron-donor properties, etc. can be designed for use as less odorous, and more tuneable replacements for phosphine ligands.

The increasing use of metal *N*-heterocyclic carbene (NHC) complexes in homogeneous catalysis naturally generated many systems in which the carbene is made by an *in situ* deprotonation of an imidazolium salt, with the exact nature of the catalyst often remaining uninvestigated.

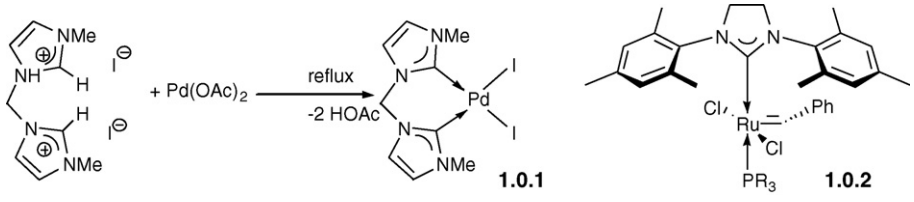


Fig. 1. Synthesis of a palladium(II) NHC precatalyst (**1.0.1**) LHS, and a ruthenium(II) precatalyst, (**1.0.2**) RHS, for Heck and alkene metathesis reactions, respectively.

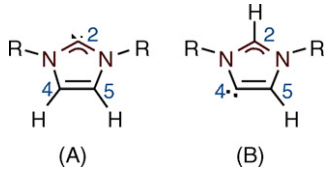


Fig. 2. A generic NHC showing the carbon labeling: (A) 'normal' carbene, and (B) abnormal carbene.

It is now clear that in some instances, the use of standard procedures to generate a metal carbene complex can actually result in the formation of abnormally bound carbenes—*i.e.* ligands bound through a backbone C4 or C5 carbon, as a result of an H migration from the backbone to C2, Fig. 2 [2].

With the increasing use of NHCs to enhance early metal catalyst systems [4], in which the NHC binds less strongly to the metal, the behaviour and occurrence of 'abnormally bound' carbene adducts may prove to be of widespread relevance across the periodic table, and of importance in homogeneous catalysis and small molecule reactivity.

The total number of complexes that exhibit abnormal binding is currently small, but the number and range of abnormally, or C4 or C5-bound complexes is increasing. The increasing use of *in situ* carbene generation in catalytic systems that are not rigorously characterised, suggests that there may be more examples than we are currently aware of. This review will cover the known examples from the d-and f-block. For the range of metals covered, we will also look at whether these complexes may be 'special cases', or whether the observation of the 'abnormal' carbene is symptomatic of a more general behaviour for the given metal.

2. Overview of metal NHC chemistry

2.1. Synthetic strategies to NHC metal complexes

The synthesis of a wide range of ligand precursors is relatively straightforward, and many are now commercially available [5]. However, the subsequent deprotonation of the NHC–metal complex is more challenging and can give unexpected results.

Many strategies have been employed to prepare NHC–metal complexes, dependant upon the metal centre of interest. NHCs can be introduced as imidazolium salts, as free carbenes or *via* transmetallation routes. Typical methods are given below [5].

2.1.1. Lappert method

Insertion of a metal into the C=C bond of bis(imidazolidin-2-ylidene)-based electron-rich olefins; successful for the synthesis of noble metal bis(carbene) adducts.

2.1.2. Proton abstraction

Generation of a free carbene by deprotonation of an imidazolium precursor with a strong base (e.g. NaH, Bu^tOK, Bu^nLi) prior to metallation.

2.1.3. Transmetallation from silver

Metal exchange starting with a silver–NHC complex (prepared by the direct reaction of the imidazolium precursor and Ag_2O).

2.1.4. In situ deprotonation

A strong or weak base (such as KH, Li(HMDS), $KOBu^t$, or NEt_3, NaOAc, Cs_2CO_3) is used to deprotonate an imidazolium salt *in situ*.

2.1.5. Oxidative addition

Oxidative addition of an imidazolium cation by activation of the C2–X (X = Me, I, H) bond at low valent or metal hydride precursors.

2.1.6. Direct metallation

Metallation of an imidazolium salt with a basic metal precursor such as $Pd(OAc)_2$ or $[Ir(COD)(OEt)]_2$.

2.1.7. Thermal elimination of H–X from the C2 position

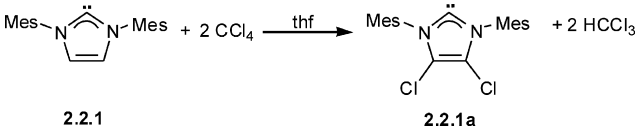
It has been demonstrated that a 2,2-functionalised *N*,*N*′-dialkylimidazole, more easily described as an NHC-alcohol or -chloroform adduct can be described as "protected" form of the NHC ligand. For example $[H(CCl_3)C\{NArCH_2\}_2]$ or $[H(C_6F_5)C\{NArCH_2\}_2]$ can be heated to afford $HCCl_3$ or HC_6F_5, and the carbene $C\{NArCH_2\}_2$.

To the best of our knowledge, there are no examples of abnormally bound carbenes formed from the Lappert method (Section 2.1.1), addition into an electron rich alkene, from the direct reaction of a free, monodentate NHC with a metal complex, (Section 2.1.2), or from the relatively new thermolysis route (Section 2.1.7).

2.2. General reactivity of the NHC backbone CH groups

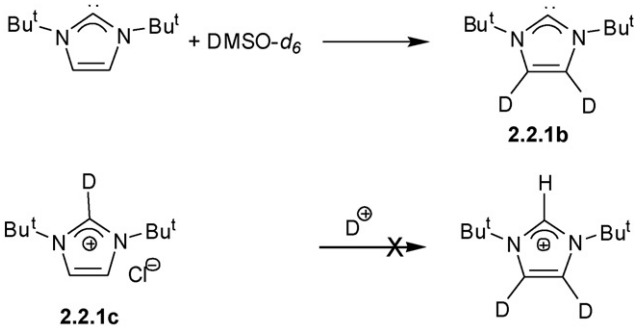
Prior to the observations of NHC backbone metallation, it was known that the C4 and C5 CH groups of the imidazole-2-ylidene are acidic. These backbone CH reactions are exemplified by the replacement of both C4 and C5 hydrogen atoms by halogen or deuterium atoms.

Chlorination of the backbone is readily achieved for carbenes with simple hydrocarbyl *N*-substituents. For example, the carbene 1,3-dimesitylimidazol-2-ylidene 2.2.1 reacts with carbon tetrachloride in THF at room temperature over 20 min to produce 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene (**2.2.1a**) and chloroform, Eq. (2.1) [6]. The chlorinated NHC is significantly more stable than its precursor, remaining inert to the chloroform produced in the reaction, and unchanged in air for up to 2 days in the solid state, or overnight in benzene solution:



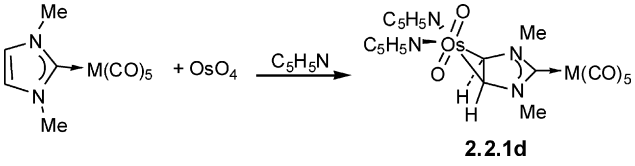
(2.1)

The aromatic ring protons in *N*,*N*′-di-*tert*-butylimidazol-2-ylidenes also undergo rapid deuterium–hydrogen exchange in DMSO-d_6, D_2O, or CD_3OD [7]. The mechanism is suggested to be different to that for the chlorination above, since the carbenium salt (**2.2.1c**) is not deuterated under the reaction conditions that lead to rapid H:D exchange for the carbene, Scheme 1.



Scheme 1. Deuteration of C4 and C5ofthe NHC.

In one instance the NHC backbone has also been osmylated [8]. Treatment of an ether solution of complexes $[M(CO)_5(C\{NMeCH\}_2)]$ (M = Cr, Mo, W) with osmium tetraoxide in the presence of pyridine affords the bimetallic complexes (**2.2.1d**) (M = Cr, Mo, W) in about 80% yields as air-stable, brown powders which were characterised by single crystal X-ray diffraction, Eq. (2.2). The oxy functionalization does not significantly influence the metal–carbene bond:



(2.2)

3. Syntheses and structures of abnormally bound NHC complexes

A Scifinder search (see Section 5) for M-[C{N(R)CH}$_2$] or M-[C{N(R)CH$_2$}$_2$]-containing compounds returns approximately 1700 characterised compounds. Over 900 of these are structurally characterised, normally bound metal–NHC containing compounds. Of these, only a few abnormal NHC–metal complexes have been structurally characterised. Listed below are all the known examples of abnormal *N*-heterocyclic carbene complexes, their syntheses and structures.

3.1. Iron

Compound (**3.1.1b**) was formed by reacting $[FeCl_2(tmeda)]_2$ (tmeda = tetramethylethylenediamine) with a 2,6-pyridyldicarbene (C–N–C) pincer ligand (2,6-bis(3-(4-*t*-butyl-2,6-dimethylphenyl)imidazol-2-ylidene-1-yl)pyridine) in THF, Fig. 3 [9].

The paramagnetic $[FeCl_4]^{2-}$ counterion caused broadening of the resonances in the NMR spectra and anion exchange with BPh_4^- was needed to achieve interpretable spectra. Compound (**3.1.1b**) was also analysed by X-ray diffraction. A similar structure is believed to be obtained for (**3.1.1a**) although it has not been fully characterised.

$[Ru(C–N–C)_2]^{2+}$ has been characterised and is normally bound (the *N*-functional groups are the less bulky *n*-butyl)

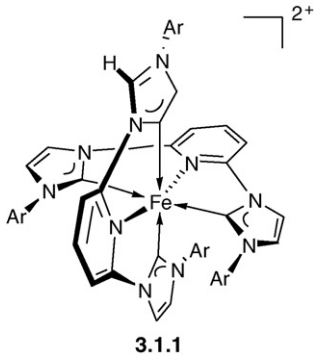
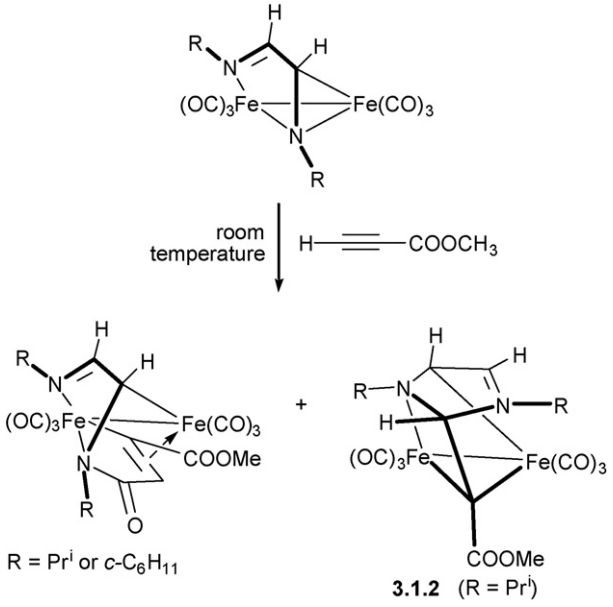


Fig. 3. The structure of the crowded $[Fe(C–N–C)(C–N–C^*)]^{2+}$ complex [Ar = 2,6-$Pr^i_2C_6H_3$, a; 2,6-Me_2-4-$Bu^tC_6H_2$, b].

[10]. The similarities in ionic radius and coordination environment indicates a steric driving force for the formation of $[Fe(C–N–C)(C–N–C^*)]^{2+}$ over $[Fe(C–N–C)_2]^{2+}$.

The structures of these compounds suggest strong parallels with the work of Meyer on NHC–Cu(I) complexes (**3.1.1**). Fe(II) is a soft cation and the complex is formed from the free NHC ligand (rather than an imidazolium salt). Additionally C4 binding is suggested to occur to relieve steric strain in the product; its synthesis involves exchange of basic ligands on the metal centre for NHCs (although tmeda is significantly more basic than MeCN).

It is notable that in 1986, di-iron–α-di-imine complexes were reported to react with terminal alkynes, such as methyl propynoate, to afford unusual products in which one C atom of the alkyne had inserted into the diazabutadiene ligand to afford a 6π electron heterocyclic ligand, reminiscent of an NHC, (**3.1.2**) Scheme 2 [11]. The *iso*-propyl derivative was structurally characterised. The heterocycle bridges the two metals, binding to one Fe centre through an azadiene N atom, and the other through the adjacent 'backbone' carbon of the azadiene backbone.



Scheme 2. Alkyne insertion into a diazabutadiene ligand to form a bridging NHC analogue.

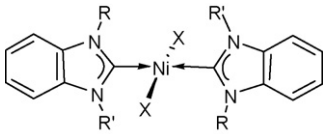


Fig. 4. Nickel benzimidazol-2-ylidene complexes.

3.2. Ruthenium

Ruthenium NHC complexes are widely studied and well known as catalysts for a range of important reactions, discussed in other articles in this issue. Despite this interest, no abnormally bound NHC complexes have been characterised.

3.3. Osmium

Osmium NHC complexes are extremely rare. The complexes [(η^6-*p*-cymene)OsCl(=CHPh)(NHC)]OTf (NHC = 1,3-bis(2,6-diisopropylphenyl)-imidazolylidene) and IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene) have been studied as initiators for olefin CM, RCM, and ROMP reactions [12].

3.4. Cobalt

There are only 19 structurally characterised normal cobalt–NHC complexes. The cobalt adducts are all paramagnetic making NMR spectroscopic studies of the complexes difficult. NMR spectroscopy is one of the major ways to identify if an NHC is normally or abnormally bound, thus there is a severe limit on the rate at which studies on such complexes can be undertaken.

3.5. Rhodium

Benzimidazole analogues of NHCs can be used to obviate chemistry at the NHC backbone (*vide infra*), for example the nickel complexes based on (**3.5.1**), Fig. 4 [13].

However, other fused imidazole-based ligands are also accessible, and provide some interesting Rh(I) chemistry.

The NHC salt (**3.5.2**) was added to a slurry of $[Rh(COD)Cl]_2$ and $KN(SiMe_3)_2$ in THF and stirred overnight. The resultant mix was purified by column chromatography to yield (**3.5.3**) (39%), Eq. (3.1). The compound was characterised by ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction [10]:

(3.1)

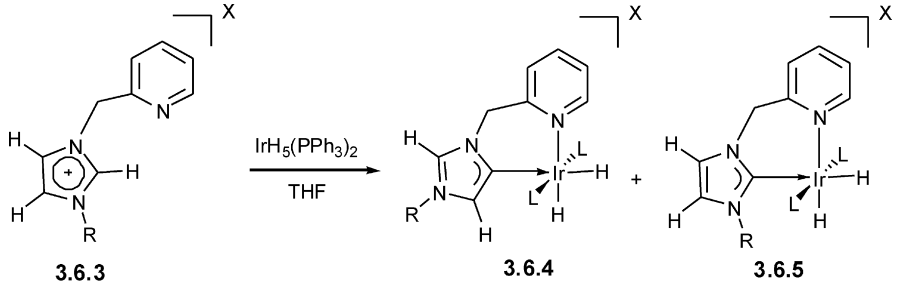
The Rh(I) analogue of compound (**3.5.3**), where the *N*-alkyl functional group is isopropyl rather than mesityl could not be formed *via* transmetallation from a silver carbene reagent. This result is unexpected since the C2 bound analogue of (**3.5.3**) can be formed by both routes: either deprotonation of a NHC salt or transmetallation with the silver carbene complex.

3.6. Iridium

Thanks mainly to the work of Crabtree and co-workers, abnormal NHC complexes of iridium and the conditions required for their formation are among the most understood. There is significant interest in iridium as it is an especially reactive metal in homogeneous catalytic transformations, and shows so many examples of C–C and C–H alkane activation chemistry. Work in the field is limited by the high cost of the metal.

Silver–NHC complexes were reacted with $[Ir(COD)Cl]_2$ (COD = cycloocta-1,5-diene) in dichloromethane to yield the abnormally bound carbenes (**3.6.1**) and (**3.6.2**), Scheme 3 [14]. The structures were examined by ^1H and ^{13}C NMR spectroscopy, and compound (**3.6.1**) was analysed by single crystal X-ray diffraction.

Treatment of (**3.6.3a–c**) with $IrH_5(PPh_3)_2$ in refluxing THF for 2 h gave (**3.6.4a–c**) in almost quantitative yields, Eq. (3.2) [15]. The NHC complex was C5 bound rather than C2 bound as expected. The structure was deduced by ^1H and ^{13}C NMR spectroscopy and confirmed by single crystal X-ray diffraction (of (**3.64a** and **b**)):



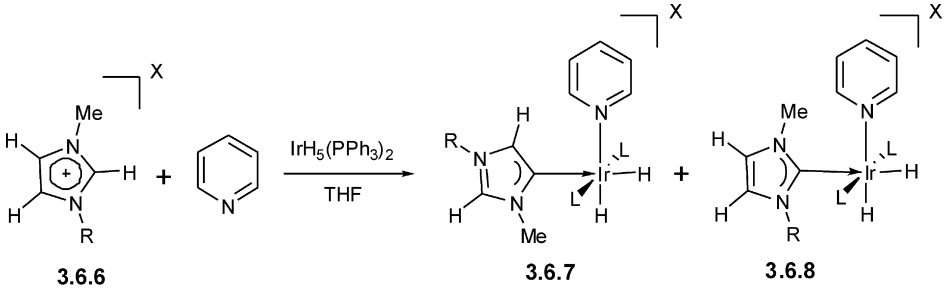
[X=BF_4; L = PPh_3; R= mesityl, **a**; Pr^i, **b**; Bu^n, **c**; Me, **d**] (3.2)

This reaction need not be undertaken in air- or moisture-free conditions. Compounds (**3.6.4a–c**) are colourless solids that are stable toward air and moisture after recrystallisation to purify from THF/pentane.

Large *N*-functional groups (R) such as *iso*-propyl lead to exclusive formation of the abnormal C4 bound isomer. In the

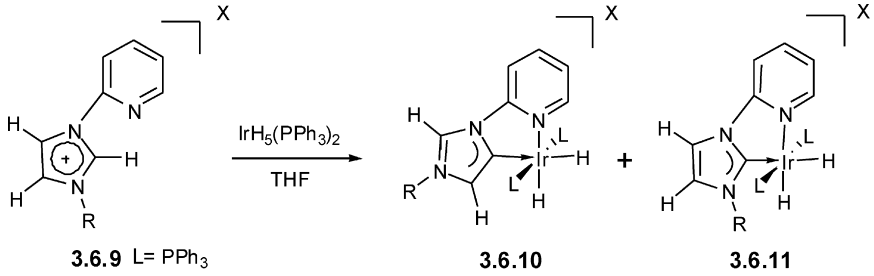
case of (**3.6.3d**) (R = Me) both isomers are formed in a ratio of ca. 55:45 abnormal:normal (**3.6.4d**:**3.6.5d**). The ratio was determined by integration of the NMR spectra of the mixtures, since the similar solubilities of the compounds prevented their separation.

Given these syntheses, work was undertaken to prepare analogues where the abnormal NHC was monodentate, to determine if chelation is necessary for C5 binding [11]. The simple imidazolium salts (**3.6.6a** and **b**) were reacted with pyridine and $IrH_5(PPh_3)_2$ under the same conditions to give a good yield of (**3.6.7a** and **b**), Eq. (3.3). The C5-bound NHC complexes have the least sterically hindered of the three imidazole carbon atoms selectively bound to iridium. Although compound (**3.6.7**) is less stable than the tethered analogue (**3.6.4**), chelation is not required for abnormal binding to occur:



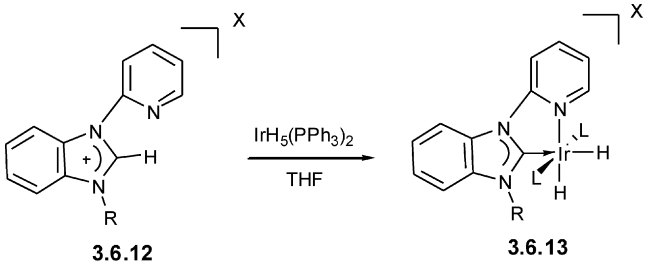
[X=BF_4; L = PPh_3; R=Pr^i, **a**; Bu^n, **b**] (3.3)

The imidazolium salts (**3.6.9**) also react with $IrH_5(PPh_3)_2$, like their methylene-linked analogues (**3.6.3**) [15]. Under identical reaction conditions the products are the abnormal NHC complexes (**3.6.10**). The reaction of the bulky (**3.6.9a**) is substantially slower and does not result in full conversion to (**3.6.10a**), Eq. (3.4). After recrystallisation, (**3.6.10b–d**) were obtained as colourless, high-melting (>200 °C) solids. Most notably for R = Me, the compound (**3.6.11d**) was not seen; unlike its methylene-linked analogue, only the abnormal NHC was observed:



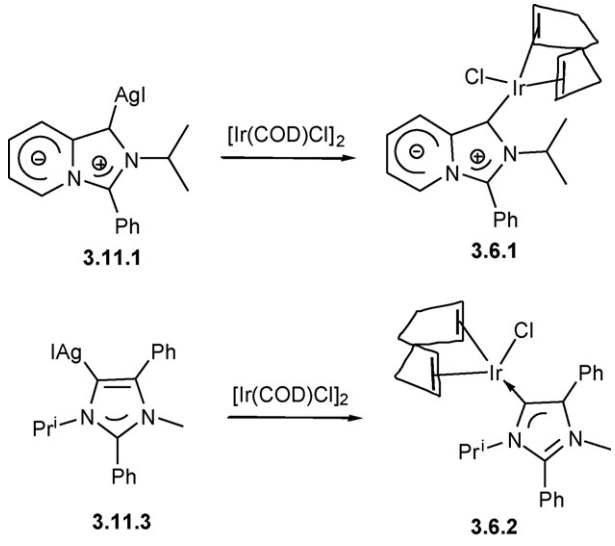
[X=BF_4; L = PPh_3; R= mesityl, **a**; Pr^i, **b**; Bu^n, **c**; Me, **d**] (3.4)

If the C4 and C5 positions are blocked to prevent abnormal binding, the C2 bound complex can form under conditions that would normally result in the abnormal carbene. The reaction of $IrH_5(PPh_3)_2$ with the benzimidazolium salt (**3.6.12**), under the same conditions that formed (**3.6.10**) (refluxing THF, 2 h), yields the C2-bound complex (**3.6.13**) (Eq. (3.5)). An X-ray diffraction crystallographic study on compound (**3.6.13**) revealed unambiguously that it was normally bound:

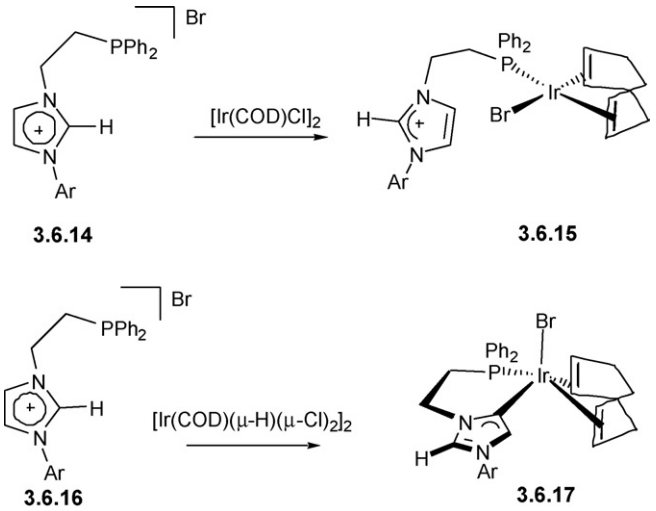


L = PPh_3, X = Br, BF_4, R = Pr^i. (3.5)

Attempts to prepare analogous tethered compounds (using phosphine instead of pyridine) were of limited success [16]. Reaction of $[Ir(COD)Cl]_2$ with phosphine tethered NHCs gen-



Scheme 3. Formation of abnormally bound iridium NHC complexes by transmetallation.



Scheme 4. Attempts to generate phosphine-tethered NHC Ir complexes. Ar = 2,6-Pr^{i}_{2}–C_6H_3.

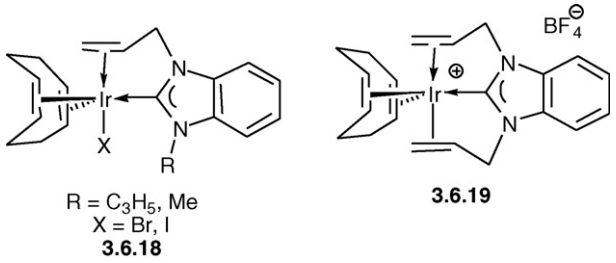


Fig. 5. Benzannelated iridium carbene complexes.

erated *in situ* gave intractable solids and reaction of compound (**3.6.14**) with $[Ir(COD)Cl]_2$ gave the imidazolium functionalised phosphine complex of iridium (**3.6.15**), Scheme 4. However, the reaction of $[Ir(COD)(\mu\text{-}H)(\mu\text{-}Cl)_2]_2$ with (**3.6.16**) generated *in situ* gave (after work up) an orange crystalline compound (**3.6.17**). The structure of (**3.6.17**) was determined by X-ray crystallography.

Interestingly, an excellent catalyst for catalytic transfer hydrogenation reactions of ketones has been made using a benzannelated NHC complex of Ir, Fig. 5 [17]. This ensures that only the C2-bound carbene complexes are generated.

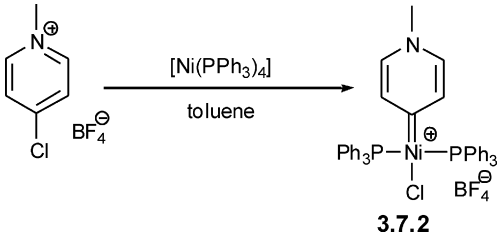
3.7. Nickel

$[Ni(1,5\text{-}COD)_2]$ was reacted with an excess of 1,3-bis-*tert*-butylimidazol-2-ylidene in THF in a sealed Schlenk tube (ungreased) over a 2-week reaction period, which resulted in the formation of a deep blue, crystalline compound (**3.7.1**), Fig. 6 [18]. The structure was analysed by ^{1}H and ^{13}C NMR spectroscopy and resolved using X-ray crystallography.

Studies of this system suggest that (**3.7.1**) is formed *via* H–C bond activation of one of the *tert*-butyl groups on the NHC, followed by migration of a proton to a cyclooctadiene (COD) ligand and elimination of isobutene. The reaction fails in the dark and requires 1,5-COD to isomerise to 1,3-COD (presumably a reaction initiated by sunlight).

This reaction is unusual as it demonstrated the first example of *N*-alkyl bond cleavage in an NHC compound.

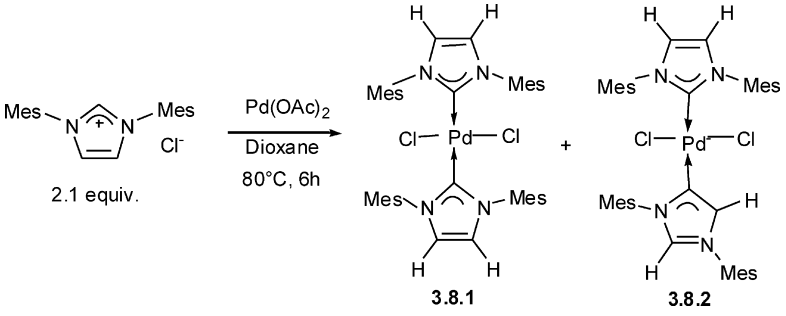
Very recently, a new class of *N*-heterocycles have been demonstrated to forma carbenic-type bond to nickel(0). The oxidative substitution of $Ni(PPh_3)_4$ with methylated chloropyridines or chloroquinolines, Eq. (3.6), forms a *N*-methyl-1,4-dihydropyridinylidene-type carbene adduct of Ni(II) [19]. The ligands can behave as both NHCs (carbene carbon next to N, examples of which have been seen before) and rNHCs (designated remote NHCs) (carbene carbon removed from N). The latter, (**3.7.2**), in Eq. (**3.6**), is designated a remote carbene complex, and theoretical studies suggest that they form significantly stronger bonds – mainly of an electrostatic nature – with the metal:



(3.6)

3.8. Palladium

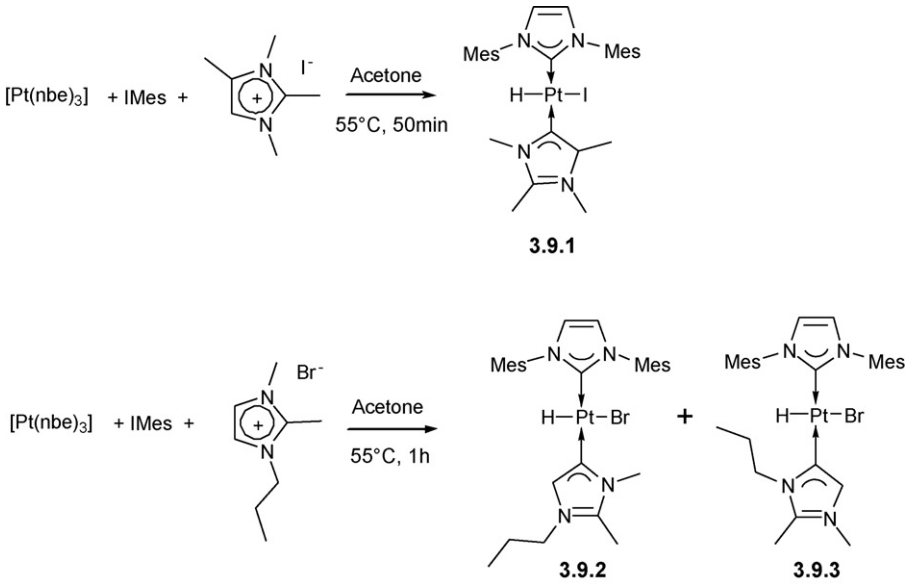
Two equivalents of IMes·HCl (*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolium chloride) and 1 equiv. of palladium (II) acetate were heated in dioxane, at 80 °C for 6 h, to yield a single palladium-containing product (**3.8.2**), Eq. (3.7) [20]:



(3.7)

The reaction was repeated under various conditions, as summarised in Table 1. The structure of (**3.8.1**) and (**3.8.2**) were deduce confirmed by single crystal X-ray diffraction.

The effect of adding a base to the reaction mixture gives clues to the mechanistic details. The mechanism has not been unambiguously established, but it appears that the formation



Scheme 5. Oxidative addition to a Pt(0) centre at C4 and C5 in imidazolium salts, nbe = norbornene.

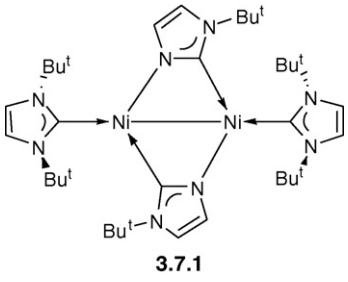


Fig. 6. The unusual nickel complex (**3.7.1**) formed at 25 °C in sunlight.

of a mono NHC–Pd complex is followed by insertion into the C(5)–H bond of a second NHC salt.

The related unusual C(2)–C(4) complex was also obtained with IPr·HCl (*N*,*N*′-bis(2,6-diisopropylphenyl)imidazolium chloride). The different alternatives for the atom through which the NHC group binds to the metal centre leads to significant differences in the catalytic behaviour of the complex. Compound (**3.8.2**) is a much better catalyst for Suzuki–Miyaura and Heck cross-coupling reactions than (**3.8.1**).

The ability to generate NHCs *in situ* is a very powerful tool but it has been shown that an *in situ* generated catalyst may not be the same as a pre-made NHC–metal complex [20]. This is an important consideration when designing a synthesis, as changing the components of the system could alter the structure of a catalyst generated *in situ*. The binding mode of the NHC to a metal such as Pd has been shown to have a substantial effect on the catalytic behaviour of the NHC–metal complex.

Table 1
The effect of reaction conditions on the product mixture for the synthesis of normal and abnormally bound palladium NHC complexes, from ref. [20]

Conditions	Yield of **3.8.1**	Yield of **3.8.2**	Other products
$Pd(OAc)_2$	<1%	74%	
$Pd(OAc)_2$ and Cs_2CO_3	Inseparable mix	Not seen	$(IMes)_2Pd(OAc)_2$
$Pd(Cl)_2$ and Cs_2CO_3	68%	<1%	
$Pd(OAc)_2$ and dimethylaniline	–	Major product	

The reactivity of (**3.8.1**) and (**3.8.2**) were studied for the Suzuki–Miyaura[1] and Heck cross coupling reactions and compared with the *in situ* formed catalyst (from $Pd(OAc)_2$ (1 equiv.) and IMesHCl (2 equiv.)).

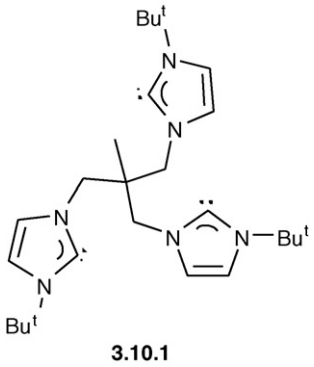
The normally bound complex (**3.8.1**) proved to be inactive for both coupling reactions whilst the unusual complex (one normally bound, one abnormally bound) (**3.8.2**) proved effective in both reactions (and had a higher isolated yield for the Heck reaction than the *in situ* catalyst).

3.9. Platinum

Complexes (**3.9.1**–**3.9.3**) were prepared in one-pot reactions. [Pt(norbornene)$_3$], IMes (bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene) and the desired C2 blocked NHC were mixed together in a molar ratio of 1:1:1.8 (Scheme 5) [21].

The products were obtained by washing the crude residues with *n*-hexane and extracting with THF. The products were analysed by ^{1}H and ^{13}C NMR spectroscopy and crystals of (**3.9.3**) were characterised using single-crystal X-ray diffraction analysis. Analysis of the proton NMR spectra showed that the isomers (**3.9.2**) and (**3.9.3**) are formed in a 3:1 ratio. It is most probable that this is a result of steric factors. The reaction is proposed to proceed *via* formation of a [Pt(IMes)(norbornene)$_2$] complex, which then undergoes oxidative addition of the C4/C5–H bond of the imidazolium salt.

[1] *Note*: Mono NHC–metal complexes are known to be much better catalysts for the Suzuki–Miyaura reaction.



3.10.1

Fig. 7. The free TIME$^{t\text{-BU}}$ ligand.

3.10. Copper

The reaction of 1 equiv. of [1,1,1-tris(3-*tert*-butylimidazol-2-ylidene)methyl]ethane (TIME$^{t\text{-Bu}}$, (**3.10.1**)) with [$(CH_3CN)_4Cu$][PF_6] in acetonitrile yields the copper complex (**3.10.2**) as an off-white powder in high yield (∼70%) Fig. 7 [22]. The structure was analysed using X-ray crystallography and the assignments were consistent with the ^{1}H and ^{13}C NMR spectra obtained. One of the three C2-carbenes has undergone a proton migration, to bind as a C4-carbene, generating a di-C2-carbene, C4-carbene complex.

Examining the ORTEP structure for (**3.10.2**), Fig. 8, it is clear why one of the NHC groups coordinates *via* C4. If it were to coordinate *via* C2 the *tert*-butyl group would impinge on one of the other NHC rings. The *tert*-butyl groups also prevent the formation of [(TIME$^{t\text{-Bu}}$)Cu](PF_6) since even with all the NHC groups binding *via* C4, it would be difficult to fit the chelate ligands around the copper centre.

The result of this steric effect is interesting. The copper ions are in a more or less idealised trigonal planar coordination, coordinatively unsaturated, and with a partially shielded cavity between them about 5 Å deep; this should be ideal for subsequent small molecule activation reactions.

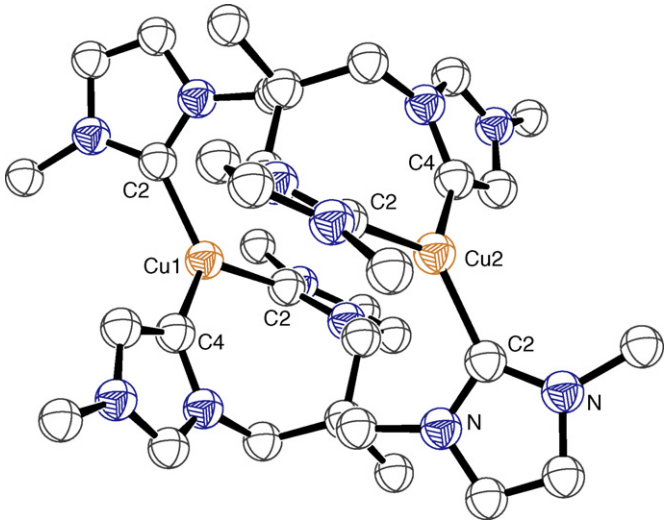


Fig. 8. Thermal ellipsoid drawing of the molecular structure of complex (**3.10.2**) [(TIME$^{t\text{-Bu}}$)$_2$$Cu_2$]($PF_6$)$_2$·4DMSO. Hydrogen atoms, *tert*-butyl methyl groups, anions, and solvent molecules are omitted for clarity, thermal ellipsoids at 50% probability.

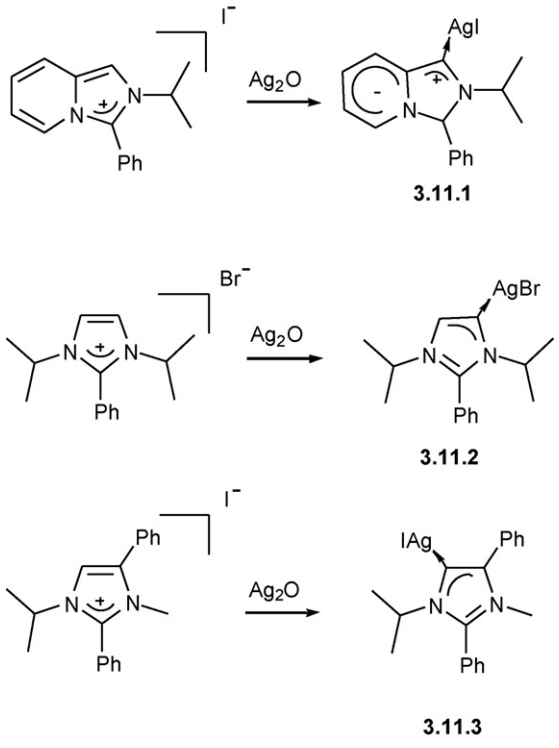
3.11. Silver

The imidazolium salts were reacted with silver oxide in dichloromethane to yield the abnormally bound carbenes (**3.11.1**–**3.11.3**), Scheme 6 [14]. The structures were determined by ^{1}H and ^{13}C NMR spectroscopy. The complexes drawn are representative of possible structures as silver–NHC complexes can exchange ligands in solution, resulting in solid state structures ranging fromXAg(NHC) to [Ag(NHC)$_2$][AgX_2].

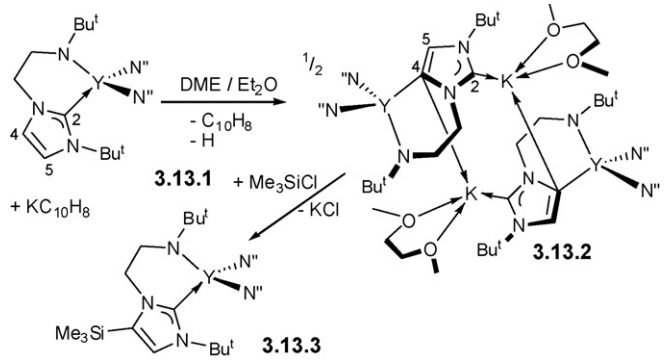
The silver structures shown were prepared as transmetallation agents. Compound (**3.11.1**) can be used to form an abnormally bound Ir(I) complex (complex (**3.6.1**)) but will not transmetallate with Rh(I).[14]. Compounds (**3.11.2**) and (**3.11.3**) both decompose rapidly, and addition of [Ir(COD)Cl]$_2$ only gives the transmetallation product for (**3.11.3**) [14(b)].

3.12. Gold

Gold is observed to form linear, two-coordinate complexes. Possibly due in part to the ease in which gold is precipitated out of solutions of its complexes, only thirty gold NHC complexes have been structurally characterised; all are normally bound. Production of an abnormally bound gold NHC complex by transmetallation with a silver carbene complex should be straightforward, but presumably would provide no additional insight into the scope of abnormal binding.



Scheme 6. Addition of silver to C2 protected NHC salts.



Scheme 7. Deprotonation of yttrium-bound NHCs at the backbone carbon atoms.

3.13. Yttrium and samarium

We have been studying the lanthanide chemistry of NHCs, using *N*-alkyl functionalized amido, and alkoxide substituents to stabilize σ-bound complexes such as (**3.13.1**) in Scheme 7 [23]. Trivalent f-element cations have recently begun to show a rich small molecule activation chemistry when substituted 6π-heterecycles such as pyrroles and aromatic solvents are used to stabilize low-oxidation state and unusual f-block complexes [24].

Treatment of the colorless amido carbene complex $Y(L)N''_2$ (**3.13.1**), with potassium naphthalenide in a DME/diethyl ether mixture at −78 °C affords a dark red solution upon warming to room temperature, from which a colorless crystalline solid (**3.13.2**) can be isolated in good yield, Scheme 7. Complex (**3.13.2**) is characterized as the bimetallic dimer $[N''_2Y(L)K(DME)]_2$ [25]. To the best of our knowledge, this is the first instance of a negatively charged, carbon–bridged NHC complex. The ^{13}C NMR resonances for C2 and C4 are observed at 199.2 and 167.5 ppm, respectively, in (**3.13.2**). These compare with a shift of 185.8 ppm for the C2 carbene carbon in (**3.13.1**), and 208.4 ppm for the potassium–NHC complex [$KOCMe_2CH_2$(1-C{NCHCHNPr^i})] [26]. The $^1J_{YC}$ coupling constant of 62 Hz is also the largest reported to date, and in line with those observed for the 2-metallated thiophene and furan, and terphenyl complexes $Y(C_5Me_5)_2(2\text{-}SC_4H_3)(THF)_n$ (E = S, $n = 1$, E = O, $n = 2$) and $Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)_2(2\text{-}SC_4H_3)(THF)$, and $Y(dmp)Cl_2(THF)_3$ (dmp = 2,6-dimesitylphenyl) [27].

The solid state structure, Fig. 9, is dimeric: the Y–C4 distance of 2.447(2) Å in (**3.13.2**) is significantly shorter than the Y-C2 distance in (**3.13.1**) of 2.501(5) Å, and is at the short end of the Y–C single σ-bond range [28]. The NHC is bound normally, *via* C2 to K, with a very short K–C2 distance of 2.954(2) Å.

The anionic nature of this bridging carbene opens up the possibility of quenching the deprotonated NHC group with other electrophiles and metal cations. A simple test reaction between complex (**3.13.2**) and Me_3SiCl in d_8-THF affords $Y(L')N''_2$ (**3.13.3**) in quantitative yield, and KCl, in which the NHC has reverted to C2-binding at the metal centre.

The deprotonation of the backbone is also effective for the Sm(III) analogue of (**3.13.1**); work with this and other strongly paramagnetic metals may allow access to carbene-bridged bimetallic lanthanide complexes, which have previously been predicted to display unusual magnetic behaviour.

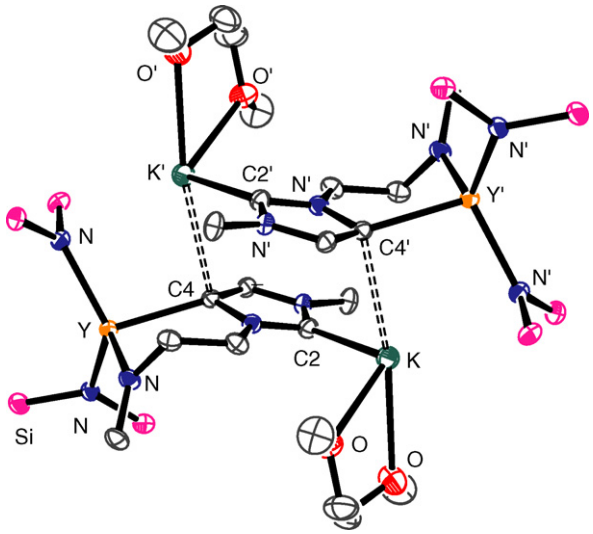


Fig. 9. Thermal ellipsoid drawing of the molecular structure of complex (**3.13.2**). Hydrogen atoms, *tert*-butyl and trimethylsilyl methyl groups, and solvent molecules are omitted for clarity, thermal ellipsoids at 50% probability.

4. Factors affecting abnormal binding

The factors discussed below are mainly for the formation of NHC Ir(III) complexes from iridium hydrides, since this is the most studied system where abnormal binding occurs. The other examples of abnormal binding are still mostly attributed to steric factors and the use of blocking groups during the syntheses.

4.1. Steric factors

In the abnormal NHC complexes of Fe, Cu, Ir and Pd, formation of the abnormal carbene is favoured as it lowers the steric strain at the metal centre. By varying the size of the *N*-functional groups on the NHC and the length of any tether, it is possible to control whether abnormal binding will occur or not [15].

Many analogies have been made between tertiary phosphines and NHCs due to their similar bulk and σ-donor properties. Molecular modelling studies have shown that the sterically very bulky phosphine ligand P^tBu_3 is closest to IPr (*N*,*N*′-bis(2,6-di-*iso*-propylphenyl)imidazolium). PPh_3 is best compared to ICy (*N*,*N*′-bis(*cyclo*-hexyl)imidazolium.

I^{t}Bu (*N*,*N*′-bis(*tert*-butyl)imidazolium) and IAd (*N*,*N*′-bis(adamantyl)imidazolium) are much bulkier than P^tBu_3, although the cone angle is less symmetrical [29]. This wider range of available sizes should allow for better tuning of NHC–metal complexes in catalysis.

4.2. Electronic effects

The idea that NHC ligands should be considered as simple σ-donors and poor π-acceptors is still under debate, although the largest estimate of the contribution to the metal carbene bond provided by backbonding is about 20% [2,22].

Synthesis of abnormal NHCs and their normal analogues with metals containing carbonyl ligands has enabled investigation of the relative electron donating power of the two binding modes. Examining the differences in ν(CO) stretching frequency by IR spectroscopy it can be seen abnormally bound NHCs are more electron donating than normal (C2-bound) NHCs [14].

Theoretical calculations on the remote NHC–nickel complexes also suggest that the metal carbene binding is more favourable in the *para*-bound pyridinylidene form (**3.7.2**), rather than the *ortho*-bound pyridinylidene, which would place the carbene next to the nitrogen atom, and that the bonding is primarily electrostatic in nature [19].

There appears to be two signals in the NMR spectra of NHC complexes that are diagnostic of abnormal carbene binding [15]. There is a large shift difference in the ^{1}H NMR spectra between the two heterocyclic protons (>3 ppm for C2 and C5 in abnormal cartenes compared to <1 ppm for C4 and C5 in normal NHCs) and the ^{13}C spectra shows a large difference in chemical shift of the metal bound carbene ($\delta \sim 140$ ppm in abnormal carbenes versus $\delta \sim 170$ ppm in normal cases).

4.3. Thermodynamic considerations

Density functional theory calculations have predicted that the free abnormal carbene should lie about 84 kJ mol^{-1} higher in energy than the free normal C2 carbene [15]. Given the observations surrounding the formation of abnormal carbene complexes from iridium hydrides this suggests therefore that the reaction is kinetic in nature. Until a system can be found in which the binding mode can be reversibly changed, from C2 to C4(5) and *vice versa*, the thermodynamics cannot be determined.

4.4. Kinetic factors

Quantum and molecular modelling calculations of the formation of the normal complex (**3.6.5**) and the abnormal complex (**3.6.4**) (Fig. 8b) have shown that the two isomers are essentially isoenergetic [17] The anion is hydrogen bonded to the C5 C–H bond in (**3.6.5**) and to the C2 C–H in (**3.6.4**). Without the ion pairing contribution the abnormal isomer (**3.6.4**) is 42 kJ mol^{-1} higher in energy than (**3.6.5**) highlighting the importance of the anion in this system (**4.5**). This has led to the conclusion that the abnormal carbene complex is the product of direct metallation assisted by counter ion effects.

The very different NMR spectroscopy characteristics (both ^{1}H and ^{13}C), of the normally and abnormally bound complexes, allow definite spectroscopic identification of the isomers. Whilst the isomers can not be interconverted under neutral conditions, even after changing anions, **3.6.5** can be converted to (**3.6.4**) (R = ^{n}Bu, ^{i}Pr) using HBF_4/CH_2Cl_2. This would indicate that the product ratio (Fig. 8b) is kinetic in origin.

4.5. Choice of anion

The counterion of the NHC salt used in the formation of NHC–Ir complexes from $[IrH_5(PPh_3)_2]$ has an effect on the ratio of the products in the reaction [30]. Until detailed studies are made of other systems where abnormal binding occurs, it is not possible to say whether this is a general trend or not.

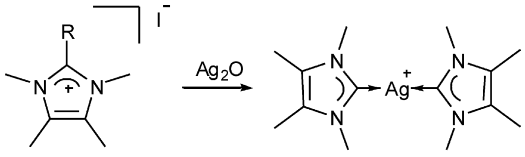
Table 2
The effect of anion on formation of a abnormal carbene

R Group	Anion (X)	Abnormal (**3.6.4**)	Normal (**3.6.5**)
Me	Br	9	91
Me	BF_4	55	45
Me	PF_6	50	50
Me	SbF_6	89	11
Pr^i	Br	16	84
Pr^i	BF_4	100	0

The reaction that generates (**3.6.4** and **3.6.5**) is under kinetic control and the product ratio is determined by the ion present during the synthesis, Table 2. Any subsequent ion exchange has no effect. The trend with change in anion seems to indicate that abnormal binding is favoured in NHC salts, where the anion has a greater affinity forthe acidic C2 hydrogen.

4.6. Blocking groups

The use of abnormally bound NHC silver complexes for transmetallation greatly increases the chance of being able to design abnormally bound complexes of metals such as Pd, Au, Rh, Ir, and Cu. Work by Crabtree and coworkers has shown that blocking the C2 position with a bulky group such as ^{i}Pr or Ph is necessary to prevent silver cleaving the C–R group (thus forcing silver to bind *via* C4/C5), Eq. (4.1) and Table 3 [31]:



4.6.1 4.6.2 (4.1)

The cleavage of the R group proceeds *via* a redox process indicated by the formation of a silver mirror on the wall of the reaction vessel (this is not observed in the normal metallation of 2H-imidazolium salts). The complete mechanism for the formation of (**4.6.2**) has been deduced, requiring 4 equiv. of silver for oxidation, and 1 equiv. for complex formation.

The ability to cleave C–R bonds at the C2 position is not unique to silver. There is initial data on cleavage of a C–R bond at C2 by Rh(I) in a 2-methyl imidazolium salt [14b] and by Pd(0) in 2-substituted imidazolium salts [32,33].

Whilst blocking at C2 is not necessary to form abnormal complexes for many metals, substitution at the C2 position with

Table 3
Cleavage of blocking group on C2-protected NHCs in Eq. (4.1)

R group on **4.6.1**	Yield of **4.6.2**
Me	>90%
$PhCH_2$	>90%
Et	<50%
Pr^i	No reaction
Ph	No reaction

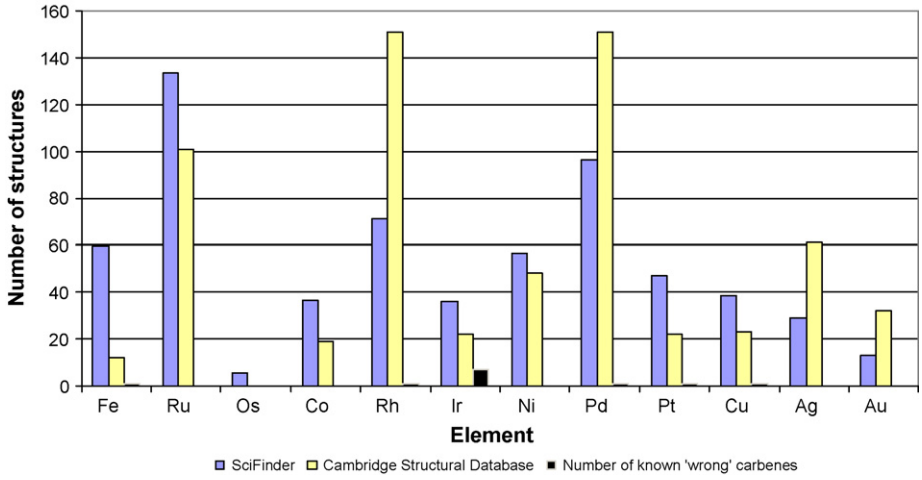


Fig. 10. Results of structural search. The number of structurally characterised NHC complexes that exhibit normal binding for the elements Fe–Au.

blocking groups such as benzene can be used to encourage the formation of the desired complex.

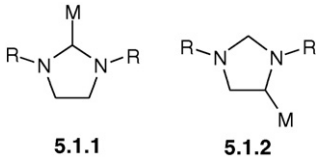
4.7. Choice of base

Studies of the structure of NHC–palladium complexes have revealed that the metallation site on the imidazolium salt is strongly influenced by the presence of base (Table 1) [20]. This has implications for the formation of NHC–metal catalysts *in situ*. The basic/acidic nature of the system will dictate if the abnormal or normal complex forms, and thus the catalytic activity of the reaction (abnormally bound have been shown to have different catalytic activities to normally bound NHCs, *vide supra*).

5. Analysis of abnormal carbene prevalence

A structural database search was conducted to get an approximate measure of the relative abundance of abnormal NHC complexes in the second half of the d-block, Fig. 10. It is notable that iridium has the greatest prevalence of abnormally bound carbene chemistry in a relatively small number of complexes. A high number of ruthenium and palladium complexes have been reported, although the structurally characterised carbene complexes are most numerous for rhodium and palladium. It remains unclear as to whether the large number of homogeneous catalysts derived from these metal carbene adducts are all genuinely C2-bound, both before, and during the catalytic chemistry.

The generic structure used for searches are shown in Fig. 11.



5.1.1 **5.1.2**

Fig. 11. Structural searches used (M = metal, Fe–Au; R = carbon containing group). The use of the program ConQuest to search the Cambridge structural database for (**5.2.1**) and (**5.2.2**) returned 642 normal and 4 abnormal structures, respectively [34] but we have also included some recently reported examples, yet to appear in the database [35]. A SciFinder Scholar search for structure (**5.1.1**) returned more than 4000 structures up to 2005 [21].

6. Conclusion

The number of papers on NHCs published each year is increasing rapidly (last year ~150 papers were published). This review has shown that abnormal binding accounts for approximately 2% of structurally characterised NHC–metal complexes. Given these factors it is likely that more examples of abnormal binding will be discovered, which, we hope, will give access to more asymmetric, and/or better catalysts, and other heterobimetallic complexes with perhaps interesting magnetic or electronic properties. To date, the targeted synthesis of abnormally bound NHC complexes should be most effective *via* transmetallation syntheses, the use of blocking groups, and from metal hydride reagents.

The formation of abnormally bound indium complexes from iridium hydrides at the moment are most prevalent. There are a vast number of metal hydrides; extension of this abnormal chemistry to other metals through hydride complexes would be interesting.

Many of the other examples of abnormal binding appear to be a result of steric factors. Understanding why abnormal binding occurs is fundamental, since this alternative binding mode further extends the versatility of NHCs as ligands.

NMR spectroscopy is a key tool for characterising the binding mode of NHC complexes. Identifying the structure of NHC complexes with paramagnetic metals takes much longer since the NMR spectra are strongly shifted, and often broadened to baseline, particularly for the 3d and 4f metals. Perhaps the simple ring deuteriation chemistry of the NHCs described in Section 2 may allow ^{2}H NMR spectroscopy to be used as a screening method for abnormal binding, as the deuterium NMR spectrum of a paramagnetic complex can often prove easy to interpret in place of the ^{1}H NMR spectrum [36].

It may be unwise to assume NHCs bind *via* the C2-atom for a complex or a catalyst in which the NHC is generated *in situ*, or indeed for a reaction in which additional bases are added to a metal carbene complex. It should also be mentioned in this context that potassium and sodium bases will often mediate the migration of one of the *N*-hydrocarbyl substituents from N to C2, resulting in N-bound, metal–imidazole adducts rather than metal carbenes [26,37].

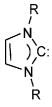
Some systematic studies need to be carried out to identify for a particular NHC or metal what binding modes are possible. Forcing abnormal binding to occur, in complexes that are currently effective catalysts, would allow evaluation of abnormal binding as a way to further optimise NHC catalyst systems.

The study of NHC–metal complexes is still an emerging discipline with many potentially important applications in synthetic organic chemistry. Many advantages of using *N*-heterocyclic carbenes as accelerating and directing donor ligands for early metal homogeneous catalysts, and as replacement for phosphines in late metal-based homogeneous catalysts, are reported each month. It seems reasonable to assume that the abnormal binding chemistry of NHCs will soon be well-understood and predictable, and exploited in new generations of homogeneous catalysts.

Acknowledgments

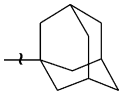
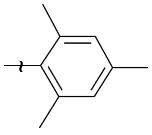
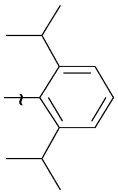
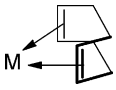
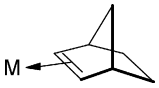
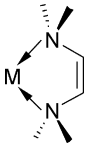
We thank the EPSRC, the Nuffield Foundation, the Leverhulme Foundation, the Royal Society, and the University of Nottingham for support.

Appendix A



NHC = N-Heterocyclic Carbene (imidazol-2-ylidene)

An S prefix to the abbreviation indicates that the NHC backbone is saturated

Abbreviation	Structure (R, R′ = for NHCs drawn)	Name
IAd		*N*,*N*′-bis(adamantyl)imidazolium
I*t*Bu		*N*,*N*′-bis(tert-butyl)imidazolium
ICy		*N*,*N*′-bis(cyclohexyl)imidazolium
IMes		*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolium
IPr		*N*,*N*′-bis(2,6-diisopropylphenyl)imidazolium
COD		Cycloocta-1,5-diene
nbe		Norbornene
tmeda		Tetramethylethylenediamine
N″	$N(SiMe_3)_2$	Hexamethyldisilazide, HMDS

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