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5. Non-Classical N-Heterocyclic Carbene Complexes

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Abstract

The expansion of the concept of N-heterocyclic carbenes as ligands for transition metals to mesoionic ligand systems has led to the discovery of a wide range of non-classical carbene-type ligands. These non-classical carbene-type ligands are characterised by a significantly lower heteroatom stabilisation of the (putative) free carbene, a situation that also affects the ligand donor properties and hence the reactivity of the coordinated metal centre. Based on the unique impact of non-classical carbene-type ligands, a number of attractive transition metal-catalysed processes have been disclosed in recent years, predominantly in the area of cross-coupling reactions, hydrogenations, and olefin metathesis.

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5.1 Introduction

The transition metal chemistry of N-heterocyclic carbenes is dominated by 2-imidazolylidenes and their derivatives including oxazoles, thiazoles, 1,2,4-triazoles, and pyrimidines, as well as related saturated systems.¹ These carbenes have found widespread application as strongly donating ligands in transition metal-catalysed reactions and also as organocatalysts in their own right.² They have become highly popular, last but not least because the free carbenes are stabilised by two adjacent heteroatoms which renders the carbene often sufficiently stable to be manipulated and isolated under ambient conditions. For example, free *N*,*N*-dimesitylimidazol-2-ylidene (IMes) is bottleable and commercially available.³

In contrast to these classical types of NHCs, isomers with less extensive heteroatom stabilisation, termed here 'non-classical carbenes', have initially received much less attention.⁴ Non-classical carbenes can contain just one, or even no heteroatom in positions α to the carbene carbon atom. Due to the lower number of heteroatoms adjacent to the carbene carbon, π stabilising effects are substantially diminished as compared to classical carbenes, which in turn reduces the stability of the free carbene. On the other hand, the electron-withdrawing inductive influence of the heteroatoms is significantly decreased. As a consequence, these non-classical carbenes are surmised to be stronger donors than their classical homologues.⁵ They have gained interest especially as ligands in transition metal complexes because of their distinct electronic properties, which open up new synthetic and catalytic opportunities.

This chapter focuses specifically on the catalytic applications of complexes comprising nonclassical carbene ligands, including work published until late 2009. General and synthetic aspects have been reviewed comprehensively elsewhere,⁴ and only a brief summary is given here. We use the term 'non-classical' as a general term for all NHC-type carbenes that are not stabilised by two adjacent heteroatoms.⁶ Hence, non-classical carbene ligands are for example derived from imidazolium, thiazolium, and oxazolium, 1,2,3-triazolium, pyrazolium, isothiazolium, pyridinium, and quinolinium salts, and they also include cyclic (alkyl)(amino)carbenes (CAAC) and (amino)(ylide)carbenes. Moreover, this definition also encompasses acyclic systems with reduced heteroatom stabilisation. Despite not belonging to the family of heterocyclic ligands, acyclic carbenes with reduced heteroatom stabilisation

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are chemically strongly related to the cyclic analogues and they have therefore been included in this chapter. The class of acyclic carbenes is of significant broadness and includes, amongst others,⁷ (alkyl)(amino)-, (amino)(aryl)-, and (amino)(silyl)carbenes.⁸ Different kinds of non-classical carbene complexes, including representative acyclic systems with reduced heteroatom stabilisation, are summarised in Figure 5.1.



Figure 5.1 Metal complexes comprising the classical imidazol-2-ylidene ligand (**A**) and representative non-classical carbene ligands (complexes **B**–**N**), including normal carbenes (**B**, **C**, **D**, **E**), abnormal carbenes (**F**, **G**, **H**, **I**), remote carbenes (**E**, **G**, **I**), cyclic (alkyl)(amino)carbenes (**J**), acyclic carbenes (**K**, **L**, **M**) and (amino)(ylide)carbenes (**N**, *cf*. refs 4, 7, and 8). Substituted nitrogen centres may be replaced by oxygen or sulphur. The M=C bond representation — while strongly overemphasizing the differences in the nature of the metal-carbon bond in these non-classical carbene complexes — has been used to accentuate normal and abnormal bonding.

Various terminologies have been used for specific subclasses of non-classical carbenes: 'normal' carbenes include all carbenes that can be represented by a neutral canonical resonance form and 'abnormal' carbenes those for which a valence bond representation requires the introduction of formal charges on some nuclei (for example C4-bound imidazolylidenes, Scheme 5.1).⁴ Carbenes with no heteroatom in the position α to the

carbene carbon atom are denoted 'remote' carbenes. Hence, remote carbenes can be either normal (**E**, Figure 5.1) or abnormal (**I**, Figure 5.1).

C-2 bound carbene



C-4 bound carbene



Scheme 5.1 The most relevant limiting resonance forms of C2- and C4-bound imidazolylidenes.

The nature of the metal-carbene bond and the degree of M–C_{carbene} π interaction may vary considerably within non-classical carbene complexes. For example in abnormal imidazol-4ylidenes, the question arises as to whether the contributions from mesoionic limiting resonance forms prevail, including a metal-bound vinylic M-C=C fragment and an intramolecularly stabilising cationic amidinium NCN unit.4 Recent crystallographic and computational analysis of an abnormal free carbene do not indicate substantial differences when compared to classical NHCs,⁹ thus supporting a similar bonding situation.¹⁰ Moreover evaluation of geometrical features from an X-ray structure determination of, and calculations on non-classical carbene rhodium(I) complexes comprising acyclic aminocarbene ligands reveal structural features that do not deviate significantly from Fischer-type carbene complexes. These studies illustrate the strong relationship of non-classical carbenes both to normal imidazolium-derived carbenes and to Fischer-type carbene ligands.¹¹ It should be noted that structural analyses based on NHC M-C_{carbene} bond lengths generally provide little insight for investigating the bond order, as the M-C bond is relatively insensitive to the carbene bonding mode. Spectroscopic analyses using ¹³C NMR techniques are also often inconclusive, since chemical shifts appear to be much more sensitive to substituent effects than to the carbene bonding mode. Recently, an approach using a diisopropyl benzimidazolin-2-ylidene (bimy) ancillary ligand as ¹³C NMR reporter group in complexes [(bimy)PdBr₂(carbene)] has been suggested as an alternative technique for measuring the donor properties of carbenes.¹² Preliminary data indicate that the probe may be at least as

sensitive as commonly used IR spectroscopy of carbonyl complexes, though further data may be required to make this method broadly applicable.

Despite these formal ambiguities, non-classical variations of NHCs constitute an attractive class of ligands with great opportunities for catalysis and synthesis in general. This chapter aims to overview the most recent advances in using non-classical NHC ligands in transition metal-mediated catalysis and to illustrate the attractive prospects that emerge from these achievements.

5.2 Synthesis of Non-Classical Carbene Complexes

A variety of different methods have been used for the formation of classical NHC complexes, and most of these methods are also applicable to the synthesis of non-classical NHC metal systems. Most frequently used methods for metallating cyclic non-classical carbene precursors include direct metallation *via* C–H bond activation, and C–X bond¹³ as well as C–H bond oxidative addition.¹⁴ Less common are transmetallation protocols, first because the relevant metal carbene precursors, especially the Ag–carbene salts, have only limited stability.¹⁵ In addition, argentation suffers from a low regioselectivity, partially originating from the weak acidity of the proton to be removed. For example, exocyclic C–H bond activation has been observed in C2-methylated imidazolium salts, a reaction pathway that is successfully prevented when using C2-arylated imidazolium salts.¹⁶

Another key route towards metal carbene complexes involves the generation of the free carbene, either *in situ* or isolated, and subsequent metal coordination. While the stability of classical carbenes makes the free carbene route the method of choice for complex synthesis (and largely contributed to the enormous success of this class of ligands), the reduced heteroatom stabilisation in non-classical carbenes generally precludes the formation of free carbenes.¹⁷ Theoretical investigations using energy decomposition analyses have shown that for example 4-imidazolylidene is about 20 kcal mol⁻¹ less stable than its classical counterpart, 2-imidazolylidene.¹⁸

While free carbenes with low heteroatom stabilisation such as **1** (Figure 5.2) have been pioneered by Bertrand and co-workers as early as in the late 1980'ies,¹⁹ non-classical

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carbenes have remained elusive until recently. The isolation of the free (alkyl)(amino)carbene **2** has demonstrated that a single electron-active substituent is in fact sufficient for stabilising a carbene.²⁰ Building on this success and on the remote effect of oxygen atoms as π stabilisers, the first abnormal pyrazolylidene, **3**, has been crystallised, which may also be formulated with an allene resonance structure.²¹ Currently, a range of persistent carbenes are known that may find use as non-classical carbene ligands.⁶ Recent achievements include the stabilisation of an all-carbon four-membered ring allene,²² and, most relevant in the context of this chapter, the carbene **4** as the first abnormal 4-imidazolylidene that is stable at room temperature,⁹ indicating that the free carbene route may be more feasible than initially thought for metallating imidazolium salts at the abnormal position. The presence of aryl substituents on the imidazolium precursor presumably constitutes a critical parameter for ensuring sufficient stability of the free carbene.



Figure 5.2 Stable free carbenes with reduced heteroatom stabilisation.

Only a few cases are known where non-classical carbene bonding is competitive with classical carbene complex formation. When using imidazolium salts in which the normal position is sterically encumbered, in combination with iridium or osmium polyhydride precursors, abnormal carbenes are preferentially formed.²³ Calculations further attribute a pivotal role to the anion in the imidazolium salt precursor,^{23a} since C–H bond activation in the formation of abnormal carbene complexes has been computed to proceed *via* oxidative addition, which is favoured by non-coordinating anions. In contrast normal carbene complexation occurs through a heterolytic C–H bond cleavage (deprotonation) process, which is promoted by small coordinating anions that support the stabilisation of the dissociating proton. Preferential abnormal carbene formation has also been accomplished with $[IrCI(COD)]_2 (COD = 1,5-cyclooctadiene),²⁴ a precursor that shows a high affinity to olefins.$

Interestingly, abnormal imidazol-4-ylidene complexes have also been obtained *via* C–H activation starting from normal free imidazol-2-ylidene. Little mechanistic information is available and in most cases sterics have been reasoned to be responsible for the preferred abnormal metallation.²⁵ Although steric factors and counterion effects can, to some degree, promote abnormal carbene formation, in most cases protection of the C2-position by substitution with an alkyl- or aryl group is necessary to ensure the selective formation of the desired product. It must be noted however that in metallation reactions using iridium or silver precursors, exocyclic C(sp³)–H bond activation of C2-methylated imidazolium cations have been observed, thus yielding metal-alkyl complexes.¹⁵ In the light of these complications, protection of the C2 position with an aryl group may generally be more reliable.

Metal-mediated activation of the C–H bond in non-classical carbene precursors is often promoted by the presence of acetate as an additive (Scheme 5.2).^{26,27} The underlying principle is thought to be strongly related to electrophilic cyclometallations. Thus, the availability of two Lewis basic sites in close proximity — one for metal coordination and the second for proton abstraction — prearranges the reactants, thus favouring M–C bond formation either *via* agostic interactions or *via* a six-membered transition state involving hydrogen bonding. Generally, C–H bond activation for the synthesis of non-classical carbene complexes requires slightly more forcing conditions than the metallation of classical carbene precursors, which is in agreement with the different C–H bond strengths in the starting material.



Scheme 5.2 Metallation of triazolium salts using an acetate-containing metal precursor.

Oxidative addition provides an alternative method towards the synthesis of non-classical carbene complexes (Scheme 5.3),²⁸ and also avoids protection protocols in order to specifically inhibit normal carbene formation. This methodology has been well developed in recent years for the metallation of non-classical imidazolylidene, pyrazolylidene, and

pyridylidene ligand precursors as well as for CAACs and allows for installing various metals including molybdenum and the metals of the nickel–palladium–platinum triade.¹³



Scheme 5.3 Preparation of remote carbene complexes by oxidative addition of a quinolinium salt to a metal precursor.

Moreover, the carbene may be constructed directly in the metal coordination sphere, much like Fischer carbene complex synthesis. For example, the cycloaddition of alkynes to amino-functionalised Fischer carbene chromium complexes furnishes non-classical pyridylidene complexes, which have been demonstrated to be useful precursors for transmetallation to rhodium(I) and gold(I).²⁹

5.3 Reactivity and Stability

An elegant study by Cavell and co-workers has indicated that abnormal imidazolylidenes are more prone to reductive elimination than normal imidazolylidenes.¹⁴ In the presence of an alkene ligand the mixed dicarbene complex **11** undergoes reductive elimination of the 4-imidazolylidene exclusively (equation 5.1), thus yielding the platinum(0) diolefin complex **12** and the imidazolium salt **13**. No reductive elimination of the normally bound 2-imidazolylidene ligand was observed under these conditions.



Similar trends have been deduced in a complementary study using the palladium complexes **14** and **15** comprising sterically identical normal and abnormal bis(imidazolylidene) ligands (Scheme 5.4).³⁰ In the presence of chlorine, complex **14** is stable and does not appear to react, while the abnormal carbene complex decomposes to $[PdCI_4]^{2-}$ and a doubly chlorinated bisimidazolium dication **16**. This outcome has been explained by oxidative CI_2 addition to complex **15**, followed by reductive $C_{carbene}$ —CI bond formation. Obviously, this process is unfavourable with normally bound imidazolylidenes. It is worth noting that an analogue of complex **15** that lacks alkyl substituents at the C5 and C5' positions induces reductively cleaved has been rationalised by the enhanced electron donor properties of the non-classical carbene, which makes them more susceptible towards elimination processes. Evidently, steric factors can be ruled out in these systems.



Scheme 5.4 The reactivity of normal- and abnormal carbene palladium complexes towards chlorine.

The increased donor properties of non-classical carbenes relative to their classical analogues have been demonstrated both theoretically and experimentally. The complexes **14** and **15** were analysed by X-ray photoelectron spectroscopy.³⁰ Both the palladium 3d and 3p electron binding energies in the abnormal complex **15** are lower by 0.5 eV than in the normal complex **14**, which reflect the stronger donor capabilities of the abnormal carbene ligand. Furthermore, X-ray diffraction and infrared spectroscopic studies have been used to demonstrate the larger *trans* influence of abnormal carbenes as compared to their normal analogues.^{16,31}

The increased donor ability of abnormally bound imidazolylidenes increases the nucleophilicity of the metal centre. Abnormal NHC-palladium complexes have thus been found to show reactivity towards Lewis acids. When the abnormal NHC complex **15** is treated with AgBF₄, the adduct **18** is formed in addition to the expected halide abstraction (*cf*

formation of **17**, Scheme 5.5). Crystallographic analysis has revealed short Ag....Pd contacts of 2.8701(6) Å, suggesting a strong metal-metal interaction. Calculations indicate that the palladium centre acts as a Lewis base in this adduct, despite its formal dipositive charge. No such adduct formation has been observed with analogous normal NHC palladium complexes.



Scheme 5.5 The reactivity of normal- and abnormal carbene palladium complexes towards acids.

Adduct **18** may be considered as model intermediate for reactions of the palladium complex with other electrophiles. For example, strong Brønsted acids like HCI, which react only with the abnormal palladium complex **15** but not with its normal counterpart, induce C_{carbene}–Pd bond cleavage to yield the imidazolium salt **20**. The rates of this acidolysis are too fast to allow the detection of an intermediate similar to adduct **18**. Notably, the coordination of two abnormal carbenes inverts the electronic properties of the palladium centre. While palladium(II) is generally considered to be electrophilic, it is obviously nucleophilic in complex **15** and related species. This fact offers a plethora of new synthetic possibilities and unprecedented reactivity schemes, which cannot be accessed by using classical carbene or phosphine ligands.

5.4 Application in Catalysis

When considering that non-classical carbene ligands increase the electron density at the metal centre, catalytic processes that are rate-limited by an oxidative addition step should benefit particularly from this class of ligands. For example, enhanced catalytic activity may be expected for the transition metal-mediated activation of dihydrogen and aryl–halogen bonds. Taking into account these considerations and the fact that it is more difficult to find catalytically silent palladium than catalytically active species, not surprisingly, the largest body of catalysis using non-classical carbene metal complexes encompasses palladium-mediated cross-coupling reactions. In parallel, a number of attractive catalytic applications have been disclosed recently that comprise other transformations, including direct and transfer hydrogenation as well as alkylation reactions. A most recent study further suggests that non-classical NHC ligands may find use in rhodium-catalysed C–H bond activation processes.

5.4.1 Cross-Coupling Reactions

5.4.1.1 Mizoroki-Heck and Suzuki-Miyaura coupling

Several studies have reported on the catalytic activity of non-classical carbene palladium complexes in Mizoroki-Heck and in Suzuki-Miyaura coupling reactions (Scheme 5.6). Here, we have attempted to group them into three categories, including *i*) comparative studies between non-classical and classical carbene complex catalysts, *ii*) accounts comparing different types of non-classical carbene complexes, and *iii*) investigations that elucidate mechanistic details.



Scheme 5.6 General reaction schemes of the Mizoroki-Heck and Suzuki-Miyaura coupling reactions.

In a number of cases palladium-catalysed cross-coupling reactions have served as tool to demonstrate the beneficial effect of non-classical carbene ligands in catalysis when

compared to classical, 2-imidazolylidenes. For example, the catalytic activity of the normal/abnormal dicarbene complex **21** is much higher than that of its normal/normal analogue **22**, both in the Heck coupling of bromobenzene with butyl acrylate, as well as in the Suzuki coupling of aryl chloride with arylboronic acid (Figure 5.3).³² It is interesting to note that *in situ* formation of the catalyst from the dimesityl imidazolium salt and [Pd(OAc)₂] in the presence of a base ensues catalytic activity that is similar to that of complex **21**. This result suggests the formation of complex **21**, at least in minor quantities, even though stoichiometric reactions under catalytic conditions afford the catalytically less active complex **22**.



Figure 5.3 Catalysts used in Mizoroki-Heck and Suzuki-Miyaura coupling reactions; general reaction conditions for Mizoroki-Heck: 2 mol % catalyst loading, 120°C, 2 equiv. CsCO₃, *N*,*N*-dimethylacetamide (DMA); general reaction conditions for Suzuki-Miyaura: 2 mol % catalyst loading, 80°C, 2 equiv. CsCO₃, dioxane).

A complex closely related to **21** (R = 2,6-(*i*-Pr)₂-Ph) performs considerably worse than both classical 2-imidazolylidene complexes and mixtures of $[Pd(OAc)_2]$ and imidazolium salts, when used as catalysts in intramolecular arylation (equation 5.2).³³ In this case, the abnormal binding mode has apparently a detrimental effect on the catalytic activity.



The catalytic activity of the 2-pyrazolinylidene complex **23a** (Figure 5.4) in the Heck coupling of aryl bromides with styrene is twice that of its normal 2-imidazolylidene analogue.^{13f} In addition, the 2-pyrazolinylidene complex requires a shorter induction period than its 2-imidazolylidene counterpart. The catalytic activity of the catalyst has been slightly increased

by increasing the steric bulk around the metal centre, which has been achieved by modifying the *ortho*-positioned nitrogen substituent from a methyl to a phenyl group (**23b**).



Figure 5.4 Catalysts used in Mizoroki-Heck coupling reactions (1 mol % catalyst loading, 130°C, 1.5 equiv. NaOAc, DMA).

The performance of complex **24** comprising a quinolinylidene as a remote carbene ligand (Figure 5.5) has been compared to that of simple 2-imidazolylidene and phosphine containing palladium catalysts in the Heck coupling of activated and non-activated aryl bromides with butyl acrylate.³⁴ The remote carbene complex shows much higher activity in the reactions. Superior catalytic activity of **24** has also been observed in the Suzuki coupling of a deactivated aryl bromide with phenylboronic acid. Since the complexes are structurally very different, purely electronic comparisons are difficult. Nevertheless, the non-classical carbene ligand appears to have a beneficial effect on the catalytic performance of the complex.



Figure 5.5 Catalyst used in Mizoroki-Heck (145°C, 1.5 equiv. NaOAc, DMA) and Suzuki-Miyaura (130°C, 1.5 equiv. K_2CO_3 , xylene) coupling reactions. ^a 150°C, 0.2 equiv. $[R_4N]Br$.

In some cases, the catalytic performance is improved upon abstraction of metal-bound halides. Such improvement is illustrated by the enhanced activity that is achieved upon halide abstraction in complex **25** to yield the cationic complex **26** (Figure 5.6).³⁵



Figure 5.6 Catalysts used in Suzuki-Miyaura coupling reactions (phenylboronic acid, 1 mol % catalyst loading, 1.5 equiv. K_2CO_3 , H_2O). ^a RT. ^b 80°C, 1.5 equiv [(*n*-Bu)₄N]Br.

Acyclic aminocarbenes have not been used widely thus far as ligands for transition metal catalysts. The (amino)(aryl)carbene complexes **27** and **28** are rare examples that have been tested for catalysis, and they show moderate activity in the Suzuki-coupling of aryl iodides and bromides with phenylboronic acid (Figure 5.7).³⁶



Figure 5.7 Catalysts used in Suzuki-Miyaura coupling reactions (1 mol % catalyst loading, 66°C, K₂CO₃, THF).

Even though the different applied conditions do not allow for comparing the non-classical carbene complexes, these few examples noted above demonstrate the potential of non-classical carbenes as spectator ligands in cross-coupling catalysts. Further improvements may be accomplished by adapting some of the principles developed for classical carbene complexes. For example, the introduction of sterically demanding substituents in the *ortho* position, perhaps paired with coordinatively labile ligands *trans* to the non-classical carbene may be beneficial.³⁷

Raubenheimer and co-workers have compared the catalytic activity of structurally related 2-, 3- and 4-pyridylidene complexes in Suzuki coupling involving activated aryl chlorides as substrates.³⁸ Complex **31**, a normal remote carbene complex, gives the highest product yields (Figure 5.8), followed by complex **30**, an abnormal remote carbene complex, while the normal carbene complex **29** shows the lowest performance. Even though the differences are relatively small, these studies suggest that the reduction of the inductive effect exerted by the nitrogen atom has some influence on the activity of the catalyst.



Figure 5.8 Catalysts used in Suzuki-Miyaura coupling reactions (0.1 mol % catalyst loading, 130°C, 2.2 equiv. $K_2CO_3,\,DMA).$

In a similar study, the catalytic activity of the classical carbene complex **32** and its abnormal thiazolylidene analogues **33** and **34** (Figure 5.9), obtained by oxidative addition, has been tested in the Suzuki coupling of activated aryl bromides.³⁸ At 70°C and under inert reaction conditions, the catalytic activity decreased in the order **32** > **33** > **34**. The abnormal thiazolylidene complexes were thus less active than their normal counterpart. It is worth noting that the steric impact of the ligand in the normal carbene complex **32** and in the abnormal system **33** is quite similar, differing only by the absence and presence, respectively, of a hydrogen atom in the *ortho* position. Further tuning of the ligands' nitrogen substituents may give more insight into the effects of the abnormal binding mode on the catalysts' activity. In particular, complex **34** is much less affected by steric modifications than complexes **32** and **33**.



Figure 5.9 Catalysts used in Suzuki-Miyaura coupling reactions (0.1 mol % catalyst loading, 130°C, 2.2 equiv. K_2CO_3 , DMA).

Mechanistic insights on non-classical carbene palladium-catalysed reactions have been obtained from some kinetic measurements. For example, time-dependent analysis of the conversions obtained with the quinolylidene complex **24** and with the pyridylidene complexes

29–31 indicates no induction period,^{34,38} thus pointing to a homogeneous mode of action. In agreement with this assumption, no palladium black formation has been noticed in any of the catalytic runs. In most other cases, however, no mechanistic analyses have been reported and both homogeneous and heterogeneous working modes of the catalysts need to be considered. This ambiguity is exemplified by the chelating pyridylidene palladium complex **35** (Figure 5.10), which shows catalytic activity in Suzuki-type coupling that is comparable to that of in situ prepared systems of [Pd(OAc)₂] in pyridinium salt ionic liquids.³⁹ This similarity evokes the hypothesis that the catalytically active species is the same in both processes. Whether this is a palladium aggregate stabilised by pyridinium salts or a pyridylidene-palladium complex obtained from C–H bond activation in the ionic liquid remains to be established. Poisoning tests using mercury(0) do not affect the catalytic activity of complex **35**, suggesting a homogeneous process that involves a well-defined, molecular active site.⁴⁰ It should be noted, however, that the mercury test has not been validated for C–C bond forming reactions, and a systematic study may be required to make this test also reliable for cross-coupling catalysis.



Figure 5.10 Catalyst used in Suzuki-Miyaura coupling reactions (phenylboronic acid, 5 mol % catalyst loading, 100°C, 2 equiv. K_2CO_3 , DMSO).

When using the pyridylidene complex **37** or the dimeric compounds **36** in Heck-coupling (Figure 5.11), sigmoidal kinetics have been measured.⁴¹ Furthermore, essentially no effect has been noted upon exchanging the donor group E of the carbene chelate, or upon changing the catalyst precursor from the polymeric pyridylidene system **37** to the dimeric complex **36**, comprising a palladium centre as highly labile substituent at the nitrogen. These findings altogether and the required high reaction temperatures suggest a heterogeneous process, which is in this case reinforced by the mercury test. Conversions abruptly stop upon addition of mercury(0) to catalytic runs.



Figure 5.11 Catalysts used in Mizoroki-Heck coupling reactions (styrene, 0.2 mol % catalyst loading, 140°C, 1.1 equiv. K_2CO_3 , DMA).

The abnormal or remote binding mode of the carbene ligand does not always have as pronounced an effect on the catalytic activity of the catalyst as in the examples mentioned above. The 4-imidazolylidene chelate complex **38** (Figure 5.12) has been tested as catalyst in the Heck coupling of aryl bromides with styrene.^{13c} In this instance, the activity of the abnormal complex is comparable to that of similar classical 2-imidazolylidene complexes.⁴² The forcing conditions necessary to obtain catalytic conversion (140°C) and the absence of any conversions with less activated substrates raises the question of whether the catalysis is in fact homogeneous or whether heterogeneous pathways are followed, implying initial decomposition of the carbene complexes. Since conversions drop significantly in reactions performed in the presence of excess mercury(0), again a heterogeneous mode of action of the catalyst may be indicated. In line with this hypothesis, the carbene complex **21** (R = 2,6-(*i*-Pr)₂-Ph) featuring a similar abnormal imidazolylidene ligand produces mixtures of palladium black and imidazolium salt during catalytic arylation experiments.³³



Figure 5.12 Catalyst used in Mizoroki-Heck coupling reactions (general reaction conditions: 0.5 mol % catalyst loading, 140°C, 1.1 equiv. NaOAc, DMA).

An indirect hint toward ligand dissociation may be deduced from catalytic runs that have been carried out with the normal 2-pyridylidene palladium complex **39** (Figure 5.13).⁴³ Heck-coupling results have been noted to be unspectacular and the catalyst does not display better activity than $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone). Again, formation of colloidal palladium

from molecular palladium(0) species may need to be taken into account, thus making the carbene ligand inefficient for tailoring selectivity in product formation.



Figure 5.13 Palladium pyridylidene complex used as catalyst for Heck-type coupling.

5.4.1.2 Kumada-Corriu coupling

The nickel(II) complexes 40-43 containing non-classical 2- and 4-guinolinylidene ligands display catalytic activity in Kumada-Corriu-type cross-coupling involving aryl chlorides and Grignard reagents (Scheme 5.7).44 Their catalytic activity was compared to that of 2- and 4pyridylidene, 2-imidazolylidene, a phosphane-containing complex and the most active catalyst system known to date, consisting of an *in situ* formed catalyst from IMes·HBF₄ and Ni(acac)₂ (acac = acetylacetonato). Remarkably, the catalytic activity of the quinolinylidene complex **42c** compared well with that of the benchmark system and at higher catalyst loadings, even deactivated aryl chlorides could be converted. Time-dependent monitoring of the conversion with various quinolinylidene catalysts does not reveal any induction period, which is in line with fast formation of the catalytically active species and with a homogeneous mode of action. Complex 42c displayed the highest catalytic activity and best product selectivity, but other than that no obvious correlation has been observed between the catalytic performance and the type of carbene ligand (e.g. remote vs non-remote). The pyridinylidene- and quinolinylidene systems all gave better conversions than the simple imidazolylidene and phosphine systems. While these results may suggest that the stronger donor power of nonclassical carbene ligands and hence the higher electron density at the nickel centre may enhance the catalytic performance, it should be noted that the steric properties of these systems are quite different. In particular the absence and presence of shielding ortho substituents in the carbene ligand may affect the catalytic activity substantially (cf palladiummediated cross-coupling in the previous section).



Scheme 5.7 Kumada-Corriu coupling reactions (general reaction conditions: 1 mol % catalyst loading, RT, THF).

5.4.1.3 Hydroamination and Buchwald-Hartwig amination

The CAAC gold complex **44a** catalyses the amination of terminal and internal alkynes (Scheme 5.8).⁴⁵ When using ammonia or a primary amine as substrate, imines are the major product. For ammonia fixation, the reaction has also been successfully carried out using the preformed ammonia complex **44b** as catalyst.^{45b} At elevated temperatures (> 130°C) two acetylenes are coupled to ammonia, which provides an interesting synthetic approach to substituted pyrroles starting from diynes. Secondary amines undergo similar hydroamination of acetylenes and afford enamines in good yields.^{45c} Remarkably, the gold carbene complex **44a** also catalyses the coupling of enamines to terminal acetylenes, a reaction that produces substituted allenes.^{45a} Based on these results, Bertrand and co-workers have developed a one-pot procedure for the formation of allenes from terminal alkynes by using tetrahydroisoquinoline as sacrificial secondary amine.^{45c} This process yields 1,3-disubstituted allenes as final product. Unlike these species, terminal, *i.e.* 1,1-disubstituted allenes are efficiently hydroaminated in the presence of primary or secondary amines and catalytic amounts of complex **44a** (equation 5.3).^{45d}



Scheme 5.8 Hydroamination reactions catalysed by **44a** and **b** (general reaction conditions: 5 mol % catalyst loading, > 70° C, $C_{6}D_{6}$). R, R'' = alkyl, aryl; R', R'' = H, alkyl, aryl.

The catalytic C–N bond formation process has been postulated to involve a gold(III) intermediate, which is supposed to be readily accessible owing to the strong donor properties of the non-classical carbene spectator ligand.

Furthermore, the acyclic (amino)(aryl)carbene palladium complex **27** (*cf* Figure 5.7) gives high conversions in the coupling of aryl bromides with morpholine at ambient temperature. For pyridyl chloride substrates, elevated temperatures (70 °C) are required in order to achieve an appreciable 73% yield.³⁶

5.4.1.4 Ketone α -arylation

The palladium complexes **45–47** containing cyclic (alkyl)(amino)carbene ligands (Figure 5.14) as well as the acyclic (amino)(aryl)carbene complex **48** (Figure 5.15) have been investigated in the room temperature α -arylation of propiophenone (equation 5.4) with sterically hindered, non-activated aryl chlorides.⁴⁶ Complex **47** shows superior activity, which has been rationalised by the steric bulk of the *ortho*-positioned cyclohexyl moiety. The substituted cyclohexyl group is flexible and bulky, thus destabilizing *cis*-coordinating ligands and, in contrast to the unsubstituted cyclohexyl fragment in **46**, resistant towards engaging in stabilising agostic interactions with the palladium centre. This situation pronounces the coordinative unsaturation at the metal centre, thus rendering it particularly reactive. Complex **47** favourably competes with the most active phosphane-based systems known to date.

Notably, the (alkyl)(amino)carbene ligands exhibit strong donor properties, determined to be far stronger than that of electron rich phosphines and normal imidazolylidenes by infrared spectroscopic analysis of the carbonyl derivatives of analogous complexes comprising a [RhCl(CO)₂] unit.



Figure 5.14 Catalysts used in α -arylation reactions (general reaction conditions used: 0.5 mol % catalyst loading, 1.1 equiv. *t*-BuONa, THF). ^a Reactions performed at 50°C.



Figure 5.15 Catalyst used in α -arylation reactions (general reaction conditions: 2 mol % catalyst loading, RT, 1.1 equiv. *t*-BuOK, THF).

Despite being less activating than the cyclic (alkyl)(amino)carbene complexes, the (amino)(aryl)carbene ligand in **48** is of considerable interest in its own rights.⁴⁶ Due to its strong topological relationship with Buchwald's biaryl phosphine, this carbene ligand may become a useful ligand for a wide range of metal-mediated coupling reactions.

5.4.2 Hydrogenation and Hydrosilylation Reactions

5.4.2.1 Direct hydrogenation

The abnormal 4-imidazolylidene complex **50** has been found to catalyse the hydrogenation of cyclooctene as a model olefin substrate at ambient temperature and atmospheric H₂ pressure (Scheme 5.9).⁴⁷ Its normal analogue **49** shows a far lower catalytic activity. The higher activity of the abnormal carbene complex has been explained in terms of higher electron density at palladium in **50** due to stronger *o*-donation of the abnormal carbene. Consequently, activation of dihydrogen *via* an oxidative addition mechanism is expected to be favoured. Notably, while the dicationic bissolvento complex **50** displays catalytic activity, its neutral analogue **15** is inactive, perhaps because of the lower tendency of **15** to coordinate a substrate molecule. Consistent with this model, strongly coordinating solvents such as MeCN, DMF, and DMSO have a detrimental effect on catalyst performance, and polar solvents with weak coordination ability such as alcohols have been found to work best.



Scheme 5.9 Hydrogenation reactions catalysed by 49 and 50 (general reaction conditions: 1 bar H₂, RT, EtOH).

Preliminary mechanistic investigations suggest that the catalytic activity is associated with the formation of particles in the 100-500 nm range. It is thus conceivable that the activation of the catalytically active species occurs through a mechanism that is strongly related to the oxidative addition – reductive elimination cycle described for the reaction of **15** with Cl₂, thus affording an imidazolium salt and a palladium polyhydride species, which may aggregate to the hydrogenation-active species. In such a model, the abnormal carbene ligand has the role of a mediator, as only in abnormal carbene complexes, reductive elimination and hence

catalyst activation takes place, while normal carbene palladium complexes may be less active as a consequence of their pronounced stability towards reductive elimination reactions.

5.4.2.2 Transfer Hydrogenation

The related biscarbene complexes of rhodium(III) **51–53**, prepared by NaOAc-assisted double C–H bond activation with RhCl₃, show catalytic activity in the transfer hydrogenation of ketones (Scheme 5.10).⁴⁸ When using *i*-PrOH as hydrogen source, conversions were good, while their normal counterparts were essentially inactive. Not unexpectedly, the substitution pattern on the heterocyclic nitrogen atoms does not influence the catalytic activity significantly. Electronic differences appear to be more relevant. For example, exchanging the iodide spectator ligands for chlorides as in complex **52b** increases the catalytic activity by a factor of three, reflected by the TOF₅₀ ~ 300 h⁻¹ for **52b** as opposed to TOF₅₀ ~ 100 h⁻¹ for **52a**. A more electron-rich metal centre is believed to accelerate the product release step in the catalytic cycle, which may also account for the significant increase in catalytic activity when switching from normal carbene ligands to stronger σ -donating abnormal carbenes.



Scheme 5.10 Transfer hydrogenation reactions catalysed by **51**, **52** and **53** (general reaction conditions: 0.1 equiv. KOH, 82° C).

Due to the microscopic reversibility of transfer hydrogenation, this reaction is particularly suitable for involvement in cascade processes. For example, β -alkylation of secondary alcohols with primary alcohols has been demonstrated (Scheme 5.11), including first the dehydrogenation of the alcohols followed by aldol condensation, which is catalysed by the base typically used in transfer hydrogenations.⁴⁹ Subsequent re-hydrogenation of the aldol condensation product provides the β -alkylated alcohol.



Scheme 5.11 Reaction sequence for the cascade process leading to transition metal catalysed β -alkylation of secondary alcohols with primary alcohols.

The normal and abnormal imidazolylidene and the non-classical, normal 2-pyrazolylidene ruthenium complexes **54–57** have been investigated as catalysts in such β -alkylations (Figure 5.16).⁵⁰ In line with the results mentioned above, the non-classical carbene complexes perform better than the classical imidazolylidene complex **54**. The 2-pyrazolylidene complexes **56**, and especially the biscarbene complex **57**, show the highest catalytic activity, while the abnormal imidazolylidene complex **55** affords comparable conversions but requires longer reaction times.



Figure 5.16 Catalysts used in β -alkylations (general reaction conditions: 1 mol % catalyst loading, 110°C, toluene).

These ruthenium complexes have also been investigated as catalysts for the dimerisation of phenylacetylene (Scheme 5.12).⁵⁰ The trimerisation of acetylene is typically a competitive process and when compared to $[RuCl_2(p-cymene)]_2$ the catalysts **54–57** afford higher yields of the dimerisation product. However, the obtained results do not allow a clear distinction between the effects of the different types and bonding modes of the carbene ligands.



Scheme 5.12 Dimerisation of phenylacetylene (general reaction conditions: 5 mol % catalyst loading, 0.25 equiv. NEt_3, 70°C, CH_3CN).

5.4.2.3 Hydrosilylation

The rhodium(I) isoquinolinylidene complexes **61a-c** have been used as catalysts in the hydrosilylation of acetophenone (Scheme 5.13).⁵¹ The carbene ligands have been modified by introducing an electron withdrawing NO₂ substituent and electron donating OMe group, respectively, at the conjugated benzene ring. Displacing the COD ligand in these complexes by CO has allowed for analysis of the donor ability of the ligands by infrared spectroscopy. Not surprisingly, the methoxy-substituted ligand is the most basic in this series, and the nitrosubstituted ligand slightly less basic than the unsubstituted ligand. These results indicate that fine-tuning of the electronic properties of the carbene ligands *via* aryl substitution is efficient.



Scheme 5.13 The hydrosilylation of acetophenone catalysed by 61 (general reaction conditions used: 0.5 mol % catalyst loading, RT).

The catalytic activity of the slightly more electron-rich complex **61a** is higher than that of **61b**. Further increase of the electron density on the metal centre promotes, however, undesired reactions as catalysis using complex **61c** produces a complex mixture within minutes.

The performance of normal and abnormal carbene complexes as *in situ* formed hydrosilylation catalysts was investigated by using [Pt(nbe)₃] (nbe = norbornene) and the imidazolium salts **62** and **63** containing a unprotected and a methyl-protected C2 position, respectively (Scheme 5.14).⁵² Styrene is converted in good yields, while ketones appear to be only moderately appropriate substrates. Interestingly, the different imidazolium salts and hence presumably the different carbene bonding mode has a pronounced influence on the product selectivity. The normal carbene precursor **62** induces the predominant formation of the branched hydrosilylation product **64**. In contrast, the abnormal carbene precursor **63** affords the substitution product **65** resulting from dehyrogenative hydrosilylation. The different selectivity in C–Si bond formation and the propensity of the [Pt(nbe)₃]/abnormal carbene precursor towards dehydrogenation point to fundamentally different modes of action and hold great promise for further catalytic transformation of olefins with non-classical carbene metal complexes.



Scheme 5.14 Hydrosilylation reactions catalysed by *in situ* generated catalysts (general reaction conditions: 120°C, toluene).

5.4.3 Olefin Metathesis

Cyclic (alkyl)(amino)carbenes have been explored as ligands in ruthenium- catalysed olefin metathesis.^{53,54} The carbene ruthenium complexes **67–69** (Figure 5.17) have been prepared *via* free carbenes and are air- and moisture-stable. Complexes **67** and **68** afford di- and tri-substituted olefins in high yield (Scheme 5.15). Analysis of the steric situation around the

ruthenium centre and in particular of the Ru– $C_{carbene}$ bond, which is shorter in the CAAC complexes than in 2nd generation metathesis catalysts comprising classical carbene ligands, has suggested that steric bulk at the carbene ligand may reduce reaction rates. Slower olefin conversion may originate from a limited flexibility in the four-membered metallacycle intermediate, especially when using substituted olefin substrates. Hence, using sterically less demanding carbenes such as in **69** increases the catalytic metathesis activity to a level that compares favourably with the activity of commercially available 2nd and 3rd generation Grubbs' catalysts. Yet, tetra-substituted olefins have not been accessible with this class of carbene ligands thus far.



Figure 5.17 Catalysts used in olefin metathesis reactions.



Scheme 5.15 Ring-closing metathesis reactions catalysed by **67**, **68** and **69** (general reaction conditions: R' = H, 5 mol % catalyst loading, C_6D_6 ; R' = Me, 1 mol % catalyst loading, C_6D_6).

The kinetic selectivity of the CAAC-based catalysts was investigated by probing the E/Z diastereoselectivity in the cross metathesis of *cis*-1,4-diaceto-2-butene with allylbenzene (equation 5.5).⁵⁵ Compared to the commercially available Grubbs' catalysts, **67-69** afforded lower E/Z ratios (3:1 at 70% conversion, ~ 2:1 at < 60% conversion). The activity of **69** is significantly higher than that of the more sterically hindered catalysts **67** and **68**.



Catalysts **67–69** also displayed high selectivities for the formation of terminal olefins in the ethenolysis of methyl oleate (Scheme 5.16). At low catalyst loadings (10 ppm) **69** achieved the highest TONs (35 000) reported to date.



Scheme 5.16 Ethenolysis of methyl oleate catalysed by **67** – **68** (general reaction conditions: 0.01 mol % catalyst loading, 40°C, 10 bar ethylene).

5.4.4 Bond Activation

The activation of strong bonds such as H–H and in particular of C–H bonds has thus far been achieved only in stoichiometric reactions and catalytic processes need yet to be developed. In this context, it is interesting to note that recently, the intramolecular activation of an unactivated alkyl-type C–H bond has been achieved under remarkably mild conditions by a rhodium centre coordinated to abnormal imidazolylidene ligands (equation 5.6).⁵⁶ The formed complex **71** comprises a unique *C*,*C*,*C*-tridentate facially coordinating dicarbene ligand, which is expected to be strongly donating because of the presence of two abnormal carbene and one anionic alkyl ligand. Studies using the analogous imidazolium salt **70** (R' = H) predisposed to normal carbene bonding indicate that the C–H bond activation leading to complex **71** is not a mere consequence of a constrained ligand geometry but a direct consequence of the electron density at the rhodium centre due to different carbene bonding modes. While the reaction is not catalytic, reversible C_{alkvl} –H bond cleavage has been

suggested based on isotope labelling studies. Such behaviour may useful for catalytic activation of C_{alkyl} -H bonds.



5.5 Conclusions

The achievements described in this chapter provide unambiguous evidence that non-classical carbenes can have a remarkable influence on the catalytic activity and the selectivity of transition metal complexes. This influence may in most cases be attributed to the increased σ -donor capacity of these ligands. The performance of the catalyst can be further improved by tailoring the steric bulk of the non-classical carbene ligand as well as by adjusting its donor capacity by incorporating electron-withdrawing and electron-donating groups on the ligand. Care may still be required when assigning the true nature of the catalytically active species. The determination of the mechanism by poisoning experiments and kinetics is not always straightforward and especially in cross-coupling and hydrogenation catalysis, some results have been contradictory.

The unique donor properties and versatile synthetic accessibility of non-classical carbenes make this class of ligands highly attractive in transition metal chemistry in general and in metal-mediated catalysis in particular. Despite the short time that has elapsed since the discovery of this class of ligands, numerous catalytic applications have been disclosed. Specifically various remarkable reactivity patterns have been identified, including the activation of typically unreactive C–H bonds. Based on the potential to further develop, modify and optimise non-classical carbenes, and with the perspective of generating a range of bottleable non-classical free carbenes, it is highly likely that this class of ligands will have a major impact on catalysis.

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5.6 References

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- This definition of 'non-classical carbenes' is in agreement with previous proposals (cf. 6 references 4 and 5). Worth noting, it also includes most Fischer-type carbene ligands, which are often acyclic and stabilized only by one heteroatom, typically an oxygen, sometimes also a sulphur or a nitrogen atom. The catalytic activity of Fischer carbenes is guite limited, last but not least because of the synthetic constraints connected to Fischer carbene preparation, including for example the use of catalytically less active molybdenum, tungsten, or chromium. While generally, it may be appropriate to use more specific terms (e.g. normal, abnormal, remote, or cyclic, acyclic, see ref. 4), we have used here for pragmatic reasons the more inclusive definition of 'non-classical' carbenes, as it allows for discussing chemically strongly related acyclic carbene metal complexes. Despite of the intrinsic relationship between Fischer-type carbene complexes and the non-classical carbene complexes discussed here, different styles of formulae representation have emerged, including a single bond between the metal and the carbene-type carbon in NHC-type systems, as opposed to double bond representation in Fischer-type and in most acyclic carbene complexes. These distinct representations undoubtedly overemphasize the (only minor) bonding mode differences.
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