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Mono-, Bi- and Tridentate N-Heterocyclic Carbene Ligands for the Preparation of Transition-Metal-Based Homogeneous Catalysts

Rosa Corberán,[a] Elena Mas-Marzá,[b] and Eduardo Peris*[c]

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This microreview focuses on the preparation of homogeneous catalysts of group 8–11 metals containing N-heterocyclic carbene ligands. The current status of the design of mono-, bi- and tridentate NHC ligands is reviewed through the description of the authors' own work. The catalytic applications of such complexes include hydrogen-borrowing, C–C coupling, reduction of double bonds and C–H activation reactions.

Introduction

Due to their topological and coordination versatility, N-heterocyclic carbenes (NHCs) are an increasingly useful type of ligand for catalyst design. After the pioneering reports by Öfele and Wanzlick,[1] and the early studies by Lappert[2] on the coordination to late transition-metal complexes, NHC chemistry remained quiescent for more than twenty years, until Arduengo pointed out the idea that NHCs could be stable enough for crystallographic characterization.[3] In 1995, Herrmann took the story a step forward, with the use of NHCs in the preparation of the first NHC-based homogeneous catalysts.[4] Since then, many research groups have provided a large number of NHC-based catalysts for a wide variety of reactions, and many reviews covering aspects such as preparation,[5,6] stability,[7] stereoelectronic properties,[8] coordination strategies,[6,9] and catalytic applications[10–13] have been entirely devoted to this type of ligand.

In 2001, our group started a new line of research aiming to search for 'stable homogeneous catalysts' that could overcome the temperature threshold of traditional catalysts and may facilitate the activation of traditionally inert bonds. For this purpose, we decided to combine two stabilizing effects. First, the strength of the M–C bond when using N-heterocyclic carbenes, and second, the stabilizing chelate effect[14] provided by bidentate and tridentate ligands. Starting with the preparation of palladium pincer NHC complexes,[15] we then extended our studies to other metals such as Rh, Ir and Ru and designed a wide variety of ligands with different architectures. The easy access to NHC precursors, and their coordination capabilities, allowed us to design catalysts for a large number of catalytic applications. In this microreview, we aim to provide the reader with an overview of our most recent work in the field of NHC chemistry, with a detailed comparison to the work carried out by other groups. Some overlap with the already-existing related reviews is inevitable, but we will try to cover aspects not reported in previous published articles.

Chelating NHCs

Most of the poly-NHCs reported so far are bis(chelate) and *pincer* (tridentate-*mer*) bis(carbene) ligands. The design of *tripodal* chelating carbenes is a more recent development, and only a few examples are described in the literature.[12,16] Not only do chelating NHCs yield more stable metal complexes, but they also provide interesting features that can fine tune the topological properties such as steric hindrance, bite angles, chirality and fluxional behaviour. This may be the reason why the number of chelating NHC compounds has gradually increased over the last decade, and several reviews have appeared describing the most recent developments with regard to design, structural features and catalytic activity of complexes containing polydentate NHC ligands.[11,12,16–18]

Chelating Bis(NHC)s

The most relevant features of the structural and catalytic properties of metal complexes containing chelating bis(NHC)s have been described in a recent review.[12] As depicted in Scheme 1, the topological and electronic properties of such ligands can be modulated by introducing modifications in the wingtips, linkers and backbones.

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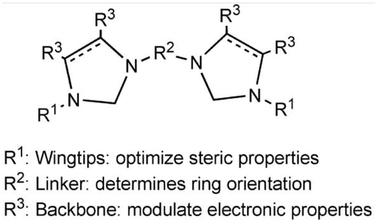
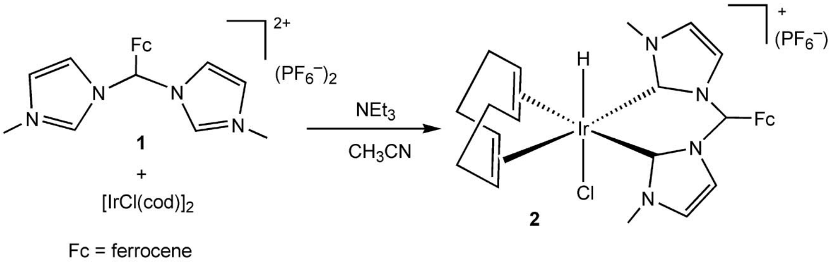
[a] Department of Chemistry, Merkert Chemistry Center, Boston College,
Chestnut Hill, Massachusetts 02467, USA
[b] Department of Chemistry, University of Bath,
Claverton Down, BA2 7AY, Bath, UK
[c] Departamento de Química Inorgánica y Orgánica, Universitat Jaume I,
Av. Vicente Sos Baynat s/n, Castellón, E-12071,
Fax: +34964728214
E-mail: eperis@qio.uji.es



Scheme 1.

It has been observed that the coordination of bis(imidazolylidene) ligands to $[RhCl(cod)]_2$ leads to Rh^I or Rh^{III} species, depending on the linker lengths between the azole rings. Long linkers favour the formation of square-planar Rh^I complexes, while short linkers afford pseudo-octahedral Rh^{III} species or dinuclear Rh^I species in which the ligand bridges the two metal centres.[19,20] The origin of this effect has been ascribed to the restricted rotation of the azole rings upon coordination and the different preferred orientation of these rings depending on the linker lengths.[20] A detailed study on the factors affecting the coordination of bischelating NHCs with a full explanation of the structural parameters derived was recently reported by Crabtree and co-workers.[21]

With regard to the coordination of the bis(NHC) ligands from their corresponding bis(imidazolium) precursors, an interesting consequence could be derived from the preparation of the first stable NHC–Ir^{III}–H complex (**2**, Scheme 2).[22] This species was obtained by direct oxidative addition of the imidazolium salt **1** to $[IrCl(cod)]_2$ in the presence of NEt_3. At this stage, it was postulated that, in the coordination of an imidazolium precursor by C2–H oxidative addition, a reductive elimination of HX (supported by a weak base) might follow the process (Scheme 3).[22] In



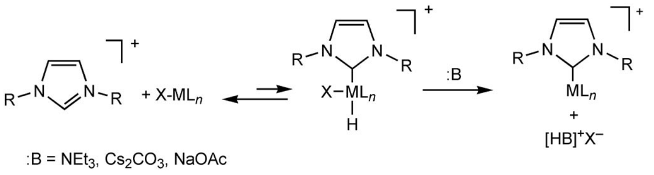
Scheme 2.

Rosa Corberán graduated in Chemistry in 2003 from the Universitat Jaume I (Castellón-Spain). She finished her PhD in Chemistry at the same university in 2008, under the supervision of Prof. Eduardo Peris. Her research was centred on the design of new transition-metal-based catalysts with N-heterocyclic carbene ligands. As a graduate student, she also spent six months in Prof. Antoine Baceiredo's group (Université Paul Sabatier, Toulouse) working on the synthesis of new homogeneous catalysts with carbodiphosphorane ligands. In October 2008, she joined Prof. Amir Hoveyda's group at Boston College as a postdoctoral associate.

Elena Mas-Marzá graduated in Chemistry from the Universitat Jaume I (Castellón-Spain) in 2002, where she also received her PhD in 2006, under the supervision of Prof. Eduardo Peris. Her research was centred on the design of catalysts with N-heterocyclic carbene ligands in new topologies and their catalytic applications. In 2007, she joined Prof. Antoni Llobet's group at the Institut Català d'Investigació Química (ICIQ) as a postdoctoral associate, where she worked on the study of ruthenium complexes for oxidation processes. In January 2008, she joined Mike Whittlesey's group at the University of Bath as a postdoctoral associate.

Eduardo Peris graduated in Chemistry in 1988 in Valencia. He received his PhD degree in Chemistry (1991) from the Universidad de Valencia, under the supervision of Prof. Pascual Lahuerta. In 1994, he joined Robert Crabtree's group at Yale University, where he stayed for two years, working on the determination of hydrogen bonding to metal hydrides (dihydrogen bond). In October 1995, he moved to the Universitat Jaume I (Castellón-Spain) as an Assistant Professor (1995–1997), Lecturer (1997–2007) and finally Professor of Inorganic Chemistry. At the Universitat Jaume I, he started a new research project related to the use of organometallic push–pull compounds with non-linear optical properties. The current interest of his group is the design of N-heterocyclic carbene based compounds for homogeneous catalysis and biomedical applications.

the particular case of compound **2**, it was initially proposed that the ferrocenyl fragment between the azole rings may sterically protect M–H from further reductive elimination of HCl, but further studies showed that this fragment was not necessary in order to obtain the NHC–Ir^{III}–H species.[23]



Scheme 3.

A combined experimental and theoretical approach was performed in order to find a unified mechanism for the metallation of a series of bis(imidazolium) salts with different lengths of the linker between the azole rings of the bis(carbene) ligand.[23] From these studies, it was concluded that metallation of the second imidazolium ring proceeds by C2–H oxidative addition, and consequently, that the final formation of bis(NHC)–Ir^{III}–H (short linker) or bis(NHC)–Ir^{I} (long linker) depends on whether the oxidative addition yields the *trans* (short linker) or *cis* (long linker) products, because only the latter can undergo reductive elimination of HCl (Scheme 4). The *trans* products are thermodynamically favoured, but with long linker lengths, the *cis* complexes are kinetically favoured and thus provide the bis(NHC)–Ir^{I} reductive elimination products.[23]

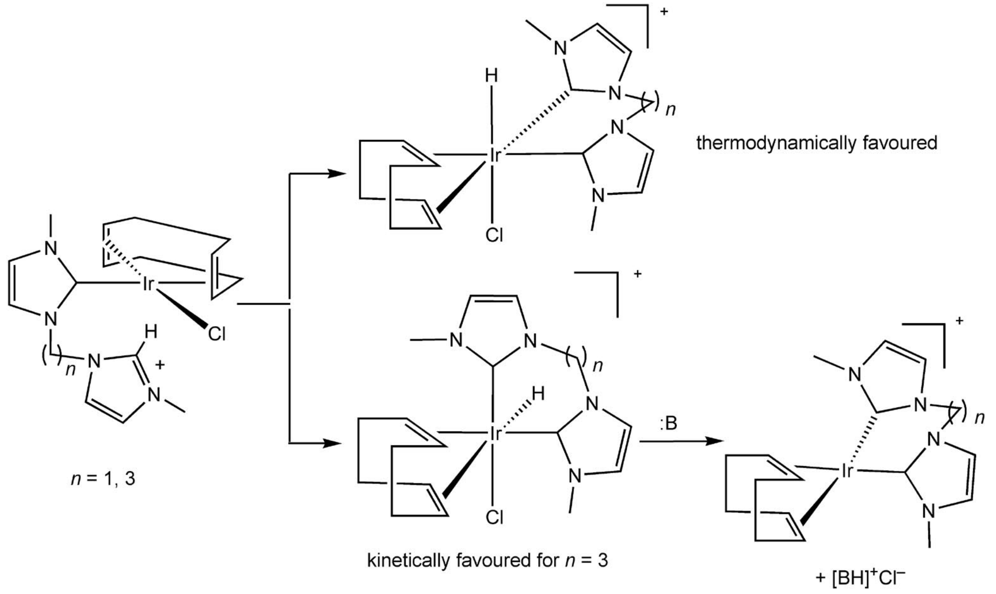
The coordination of bis(NHC)s was also extended to 'η^6-arene-Ru' complexes and leads to chelate or monometallic species. The type of species formed depends on linker lengths and the bulkiness of the wingtips.[24]

In order to influence the electronic properties of bis(NHC)s, substitution at the 4 and 5 positions of the azole ring was found to significantly modify the basicity of the carbene.[25] In this context, the introduction of chlorine substituents in the backbone of imidazolylidene reduces the σ-donor capability of the ligand.[26,27] This effect is shown to have important implications on the catalytic properties of the chelating bis(NHC)s compounds **4**–**7** (Scheme 5) when compared to the related nonchlorinated complexes,[27] as will be discussed later (vide infra).

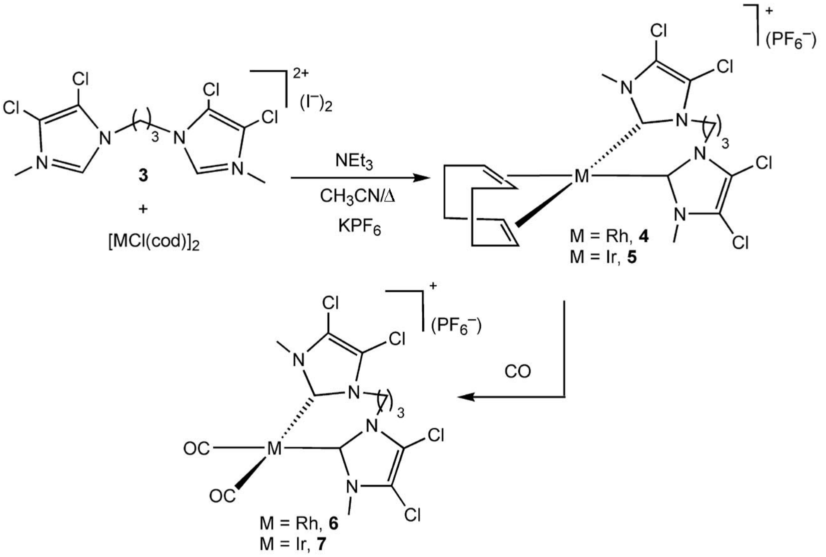
Abnormal carbenes (*a*NHC), NHC ligands bound to the metal centre through the backbone C4 or C5 carbon atom, were first reported by Crabtree and co-workers[28] and have been recently reviewed by Arnold.[29] In order to prepare abnormal NHC complexes, one of the most convenient methods is to block the imidazolium ligand precursors by substitution at the C2 position with alkyl or aryl groups.[30]

The use of bis(imidazolium) salts with C2–Me substituents was found to give unexpected results in the reactions with $[Cp^*IrCl_2]_2$. As depicted in Scheme 6, reaction of imidazolium precursor **8** (only one azolium ring blocked) with $[Cp^*IrCl_2]_2$ yielded compound **9**, in which the chelating bis(NHC) ligand is coordinated in both the abnormal and normal modes.[31]

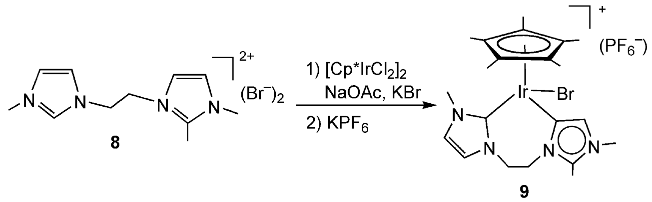
With the use of doubly C2–Me substituted bis(imidazolium) salts, it was found that the length of the linker between the azole rings clearly determines the outcome of the reaction (Scheme 7). Reaction of the methylene-bridged ligand **10** with $[Cp^*IrCl_2]_2$ afforded compound **11**, in which the bischelating ligand is coordinated as an *a*NHC and a metallated methylene group. In the case of the ethylene-bridged bis(imidazolium) **12**, the major product obtained was the expected chelating bis(*a*NHC), together with the chelating C2–Me activated compound and a new neutral species with a 1,2-dimethylimidazole ligand (compounds **13**, **14** and **15**, respectively).[31]



Scheme 4.



Scheme 5.

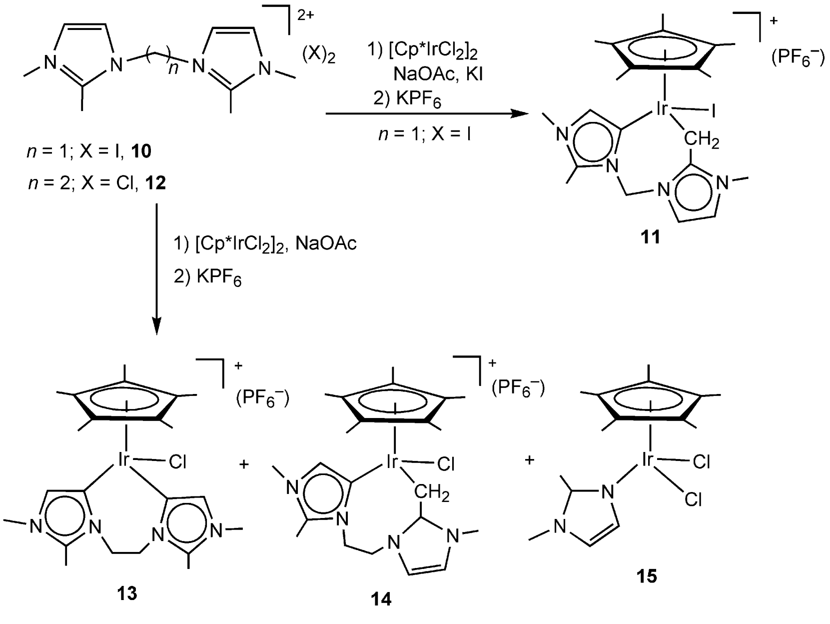


Scheme 6.

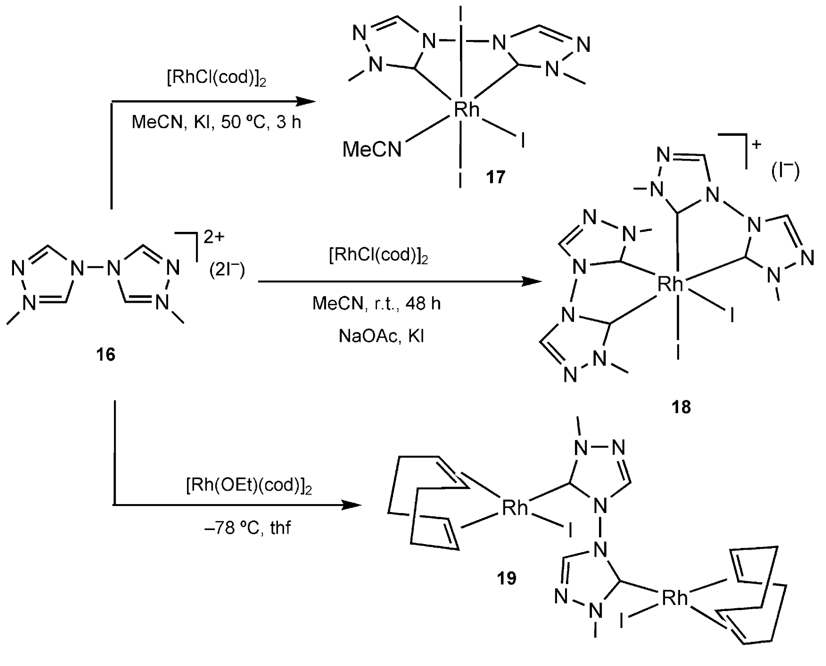
The triazolium salt **16** constitutes the only example of a bis(NHC) ligand with a direct N–N bond linking the azolium rings (Scheme 8). Precursor **16** presents a wide chemical versatility and was recently coordinated to Rh, Ru and Pd.[32,33] For the coordination of **16** to Rh, different products were obtained, depending on the conditions employed (**17**, **18** and **19**, Scheme 8).[32,33]

Interestingly, the reaction of **16** with $[Rh(OAc)(CO)_2]_2$ yielded the dirhodium(II) species **20** (Scheme 9). Compound **20** constitutes the first example of a dirhodium(II) species containing an NHC ligand.[32]

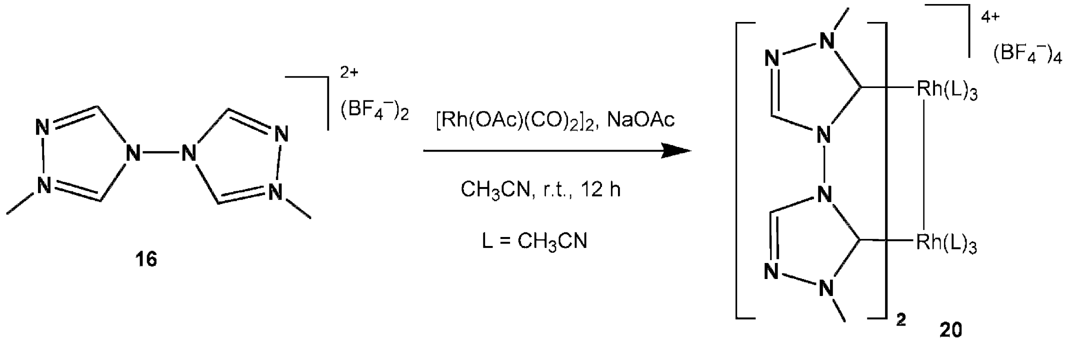
The coordination of **16** was also extended to Ru^{II} and Pd^{II}, which led to monometallic and dimetallic compounds.[33] Scheme 10 shows the coordination of **16** to Ru.



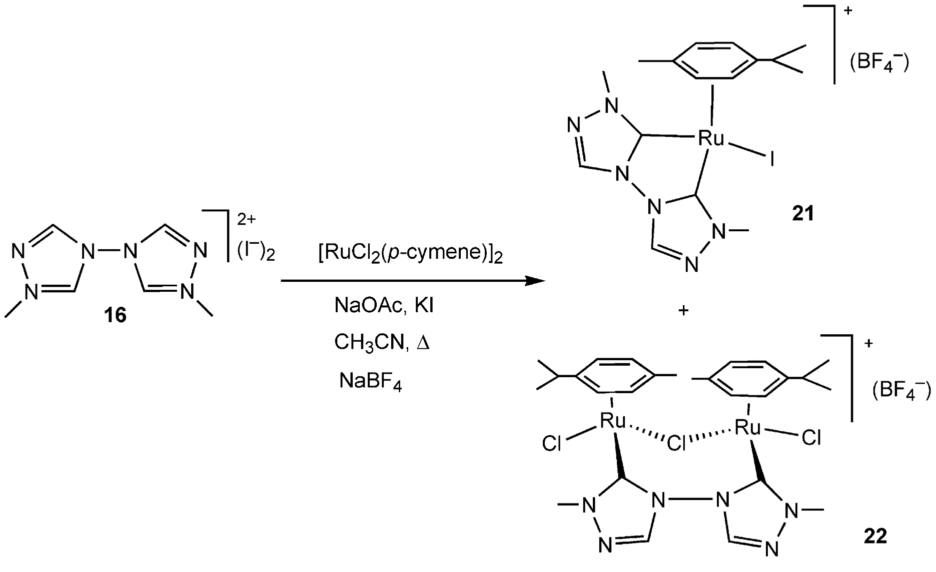
Scheme 7.



Scheme 8.



Scheme 9.

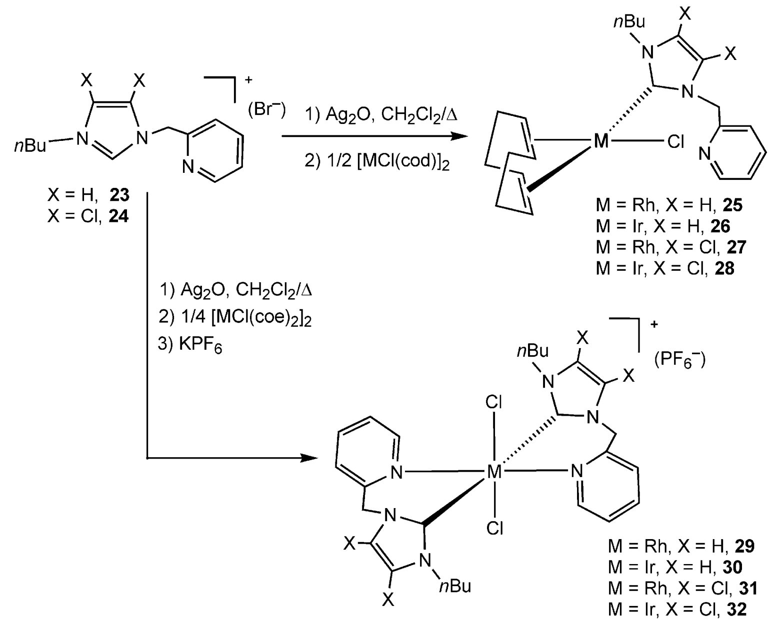


Scheme 10.

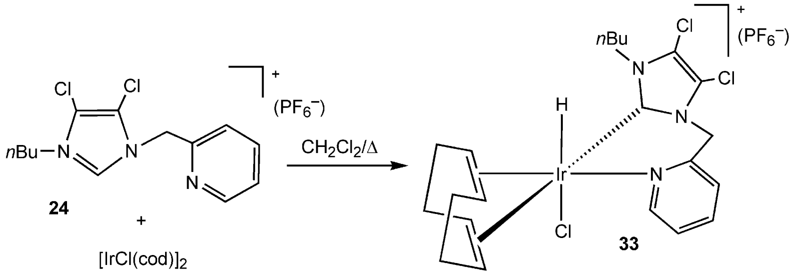
Chelating Functionalized NHCs

Cavell and co-workers have recently reviewed the latest advances in homogeneous catalysis with donor-functionalized NHC complexes.[13]

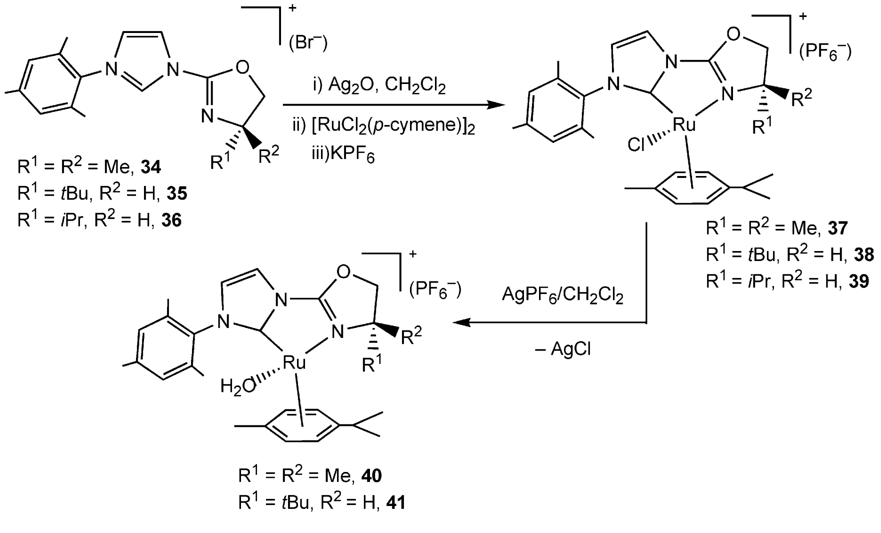
Pyridine–imidazolylidene ligands (pyridine–NHCs) have provided a large diversity of coordination modes.[28,34] For the coordination of precursors **23** and **24** to Rh and Ir, the type of coordination obtained seems to be clearly influ-



Scheme 11.



Scheme 12.



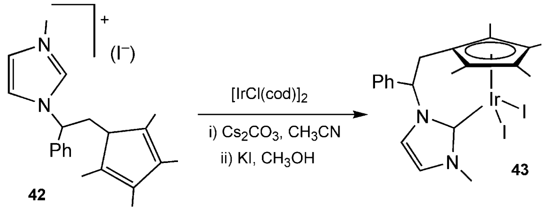
Scheme 13.

enced by the method of activation used and the metallic precursor employed (Scheme 11).[35]

An interesting result was achieved by direct reaction of $[IrCl(cod)]_2$ with **24** in the absence of a weak base. In this reaction, compound **33** was obtained by C2–H oxidative addition of the imidazolium salt, which is triggered by the chelate effect of the pyridine–NHC ligand (Scheme 12).[35]

With the use of oxazoline–imidazolylidene ligands (oxazoline–NHCs), a series of Ru,[36] Pd[37] and Rh[37] chelate complexes were obtained. Scheme 13 shows the transmetallation of the oxazoline–NHC precursors **34**–**36** from a silver carbene to $[RuCl_2(p\text{-cymene})]_2$; the half-sandwich Ru^{II} compounds **37**–**39** were obtained. Abstraction of the chlorido ligands in **37** and **38** furnished the dicationic aqua species **40** and **41**, respectively.[36]

In a very recent example, an unprecedented chelating Cp* ligand functionalized with a pendant NHC was coordinated to $[IrCl(cod)]_2$ (Scheme 14). The chiral Ir^{III} complex **43** was obtained as a racemic mixture of two possible enantiomers.[38] Related η^6-arene-NHC chelating ligands have also been coordinated to Ru by Cetinkaya and co-workers.[39]

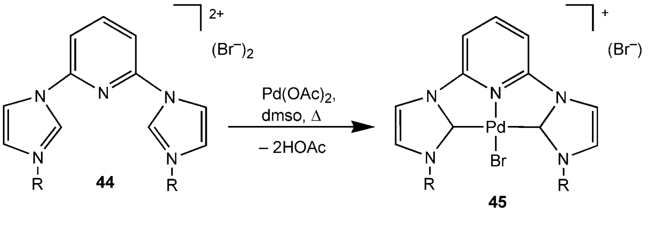


Scheme 14.

Pincer NHCs

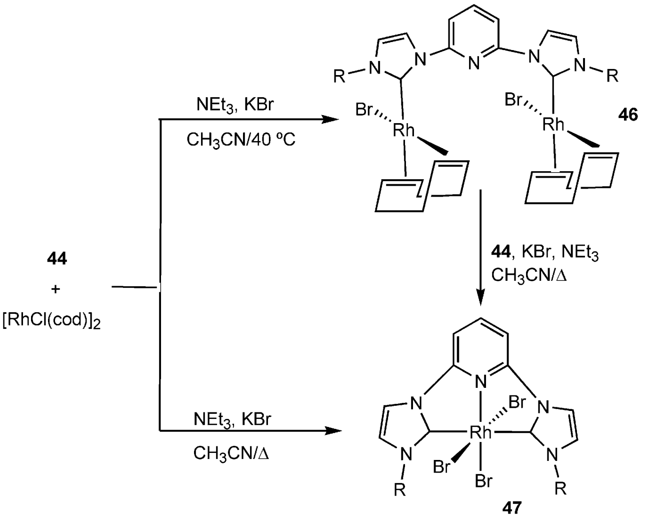
Pincer carbene complexes have appeared as an interesting family of ligands in the design of homogeneous catalysts. Thus far in the literature, there are numerous examples of this type of ligand incorporating one or more NHC units. All these examples, as well as their coordination across the periodic table, were reviewed recently by Danopoulos.[18]

The first example of a pincer NHC complex was described in 2001.[15] The reaction of the imidazolium salt **44** with $Pd(OAc)_2$ in dmso afforded the Pd^{II} species **45** with a rigid CNC ligand (Scheme 15).



Scheme 15.

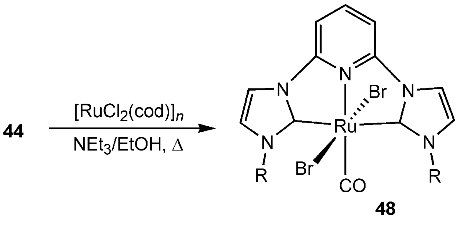
The coordination of **44** was soon extended to other transition metals. The reaction of **44** with $[RhCl(cod)]_2$, in the presence of a weak base, led to the formation of two types of complexes, depending on the reaction temperature. When the reaction was performed at 40 °C, the dimetallic Rh^I species **46** (Scheme 16) was obtained, in which the ligand bridges the two metal centres. In contrast, when the reaction was carried out in refluxing CH_3CN, a pseudo-octahedral Rh^{III} complex with the ligand in a *mer* disposition could be isolated (**47**, Scheme 16). Interestingly, the dimetallic species was converted into the monometallic complex by heating it to reflux in CH_3CN with 1 equiv. **44** in the presence of a weak base.[40]



Scheme 16.

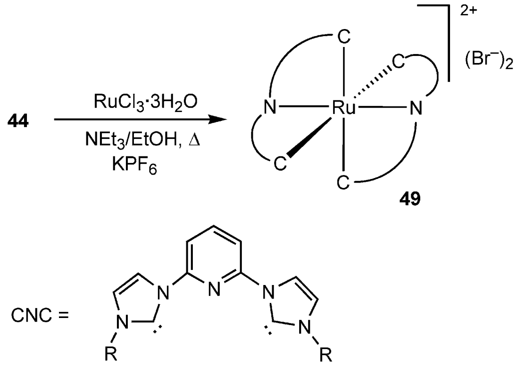
More recent studies by Haynes and Danopoulos demonstrated that the CNC pincer ligand **44** can be coordinated to Rh^I in a *mer* disposition to afford square-planar monometallic species. These complexes easily undergo oxidative addition reactions of C–halide bonds to form octahedral Rh^{III} species, but are resistant towards less polar bonds.[41]

The coordination of the CNC pincer ligand was also extended to Ru. Precursor **44** was treated with $[RuCl_2(cod)]_n$ in the presence of NEt_3 in EtOH to yield the pseudo-octahedral Ru^{II} complex **48**, as shown in Scheme 17.[42] It was proposed that the CO ligand was produced by decarbonylation of EtOH used as solvent. The generation of a CO ligand has also been observed in the synthesis of other Ru^{II} complexes in EtOH.[43]



Scheme 17.

Reaction of $RuCl_3{\cdot}nH_2O$ with **44** under similar reaction conditions gave a bis(pincer)–Ru^{II} complex (**49**, Scheme 18).



Scheme 18.

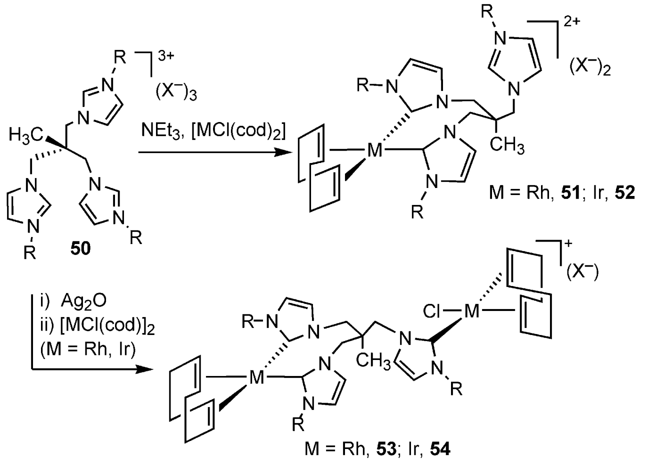
Tripodal NHCs

Despite the fact that the number of poly-NHC ligands is continuously increasing, the design of such ligands with a *tripodal* (*fac*) topology is restricted to a few examples. The design of ligands with a *tripodal* coordination has a major significance because the *fac* geometry should determine the catalytic properties of the complex, especially in the cases of NHC-based complexes, where the stability of the ligand–metal bond is high, and the catalytic activity of the complex must rely on the relative disposition of the potential vacant sites.

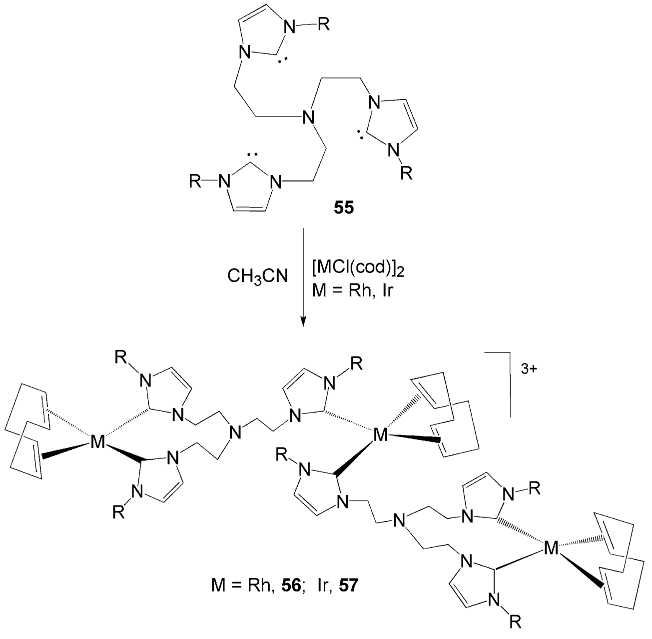
Several groups have described the synthesis and coordination of new tris- and bis(NHC) ligands designed in order to afford a tripodal coordination; unfortunately, in not all cases was this coordination achieved. The design and coordination of tripodal carbene ligands has been recently summarized in two reviews.[12,16]

In 2003, the group of Meyer and co-workers reported the synthesis of the tris(carbene) ligand precursor **50** (Scheme 19), as well as its coordination to group 11 metals.[44] Although **50** apparently presents the topological requirements to coordinate in a *fac* disposition, bi- and trimetallic species were instead formed in all cases. The coordination of **50** was then extended to Rh and Ir. Depending on the coordination strategies to $[MCl(cod)]_2$ (M = Rh, Ir), two different types of complexes were obtained. In the presence of a weak base, such as NEt_3, mononuclear Rh^I and Ir^I species were formed, where only two of the NHC units are coordinated and the third azole ring remains out of the coordination sphere of the metal (**51** and **52**, respectively, Scheme 19). On the other hand, transmetallation of **50** from a silver carbene afforded dimetallic Rh and Ir complexes (**53** and **54**, respectively, Scheme 19), in which the ligand bridges two metal fragments and is coordinated in a bischelating manner to one of the metal centres.[45]

Coordination of the N-anchored tris(carbene) ligand **55** (Scheme 20) afforded Co,[46] Ni,[47] Cu[16,48] and, more recently, Fe[49] complexes, in which the ligand is coordinated in a *tripodal* tri- or tetradentate form. The coordination of **55** to Rh and Ir was attempted, and in all cases, trinuclear compounds in which two ligands bridge three metal centres were obtained (**56** and **57**), as shown in Scheme 20.[50]

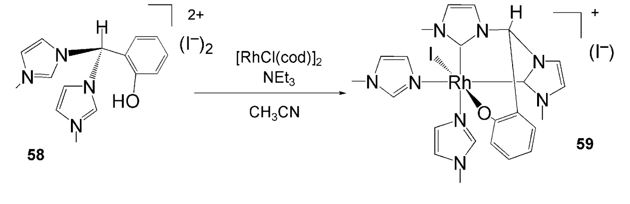


Scheme 19.

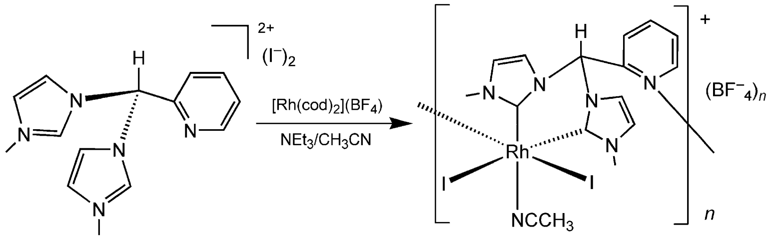


Scheme 20.

In order to achieve a *fac* coordination of an NHC ligand, other functionalized bis(NHC) ligands were obtained, in which the third coordination site is a heteroatom, such as O or N. The imidazolium salt **58** (Scheme 21) combines two



Scheme 21.



60 **61**

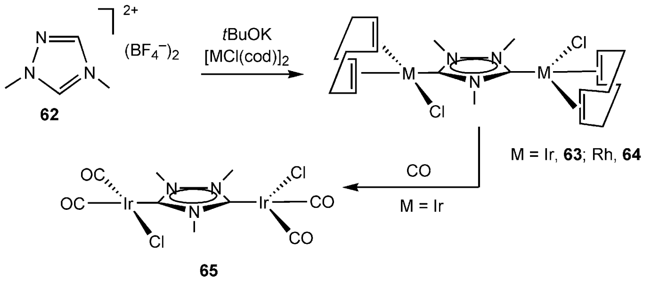
Scheme 22.

NHC groups and a phenoxy unit. In the presence of NEt_3, **58** reacted with $[RhCl(cod)]_2$ to afford the Rh^{III} complex **59** (Scheme 21), which constitutes the only example of a Rh compound with an NHC in a tripodal disposition.[51]

Substitution of the phenoxy unit by a pyridine ring failed when the ligand was coordinated in a tripodal manner. Precursor **60** coordinated to $[Rh(cod)_2]BF_4$ to yield the Rh^{III} polymeric species **61** displayed in Scheme 22.[52]

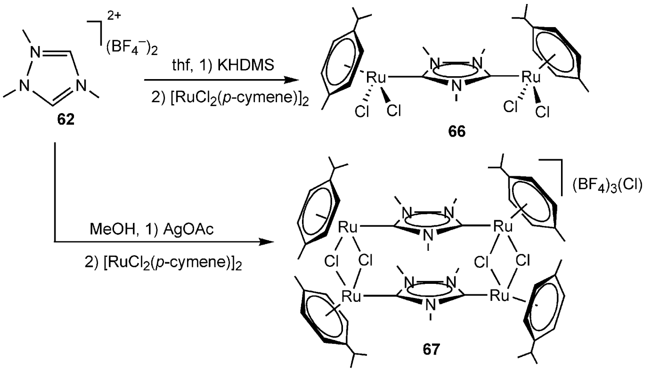
Dicarbenes in a Facially Opposed Coordination: *Janus-Head*-Type Ligands

The straightforward preparation of NHC precursors has allowed the design of carbene ligands with different topologies. In this sense, Bielawski and co-workers described a series of benzobis(imidazolylidene)s that show facially-opposed coordination abilities to two metallic fragments (*Janus-head*-type ligands).[53] We recently showed that 1,2,4-trimethyltriazolium tetrafluoroborate **62** (Scheme 23) can be used for the synthesis of dinuclear homo- and heterometallic compounds.[54,55] As shown in Scheme 23, **62** reacted with $[MCl(cod)]_2$ (M = Ir, Rh) in the presence of *t*BuOK to give the dinuclear compounds **63** and **64**, respectively.[54] These compounds consist of two metallic centres bridged by the azole ring. Compound **63** readily reacted with CO to yield the tetracarbonylated species **65** (Scheme 23). From the IR spectrum of **65**, it was concluded that the triazol–diylidene ligand displays a lower electron-donating ability than other known NHCs.



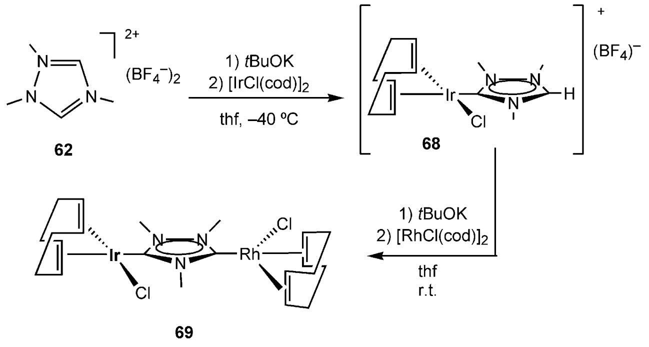
Scheme 23.

The coordination of **62** was also extended to Ir^{III} and Ru^{II}, which led to dimetallic and tetrametallic compounds.[55,56] Scheme 24 shows the coordination of **62** to Ru.



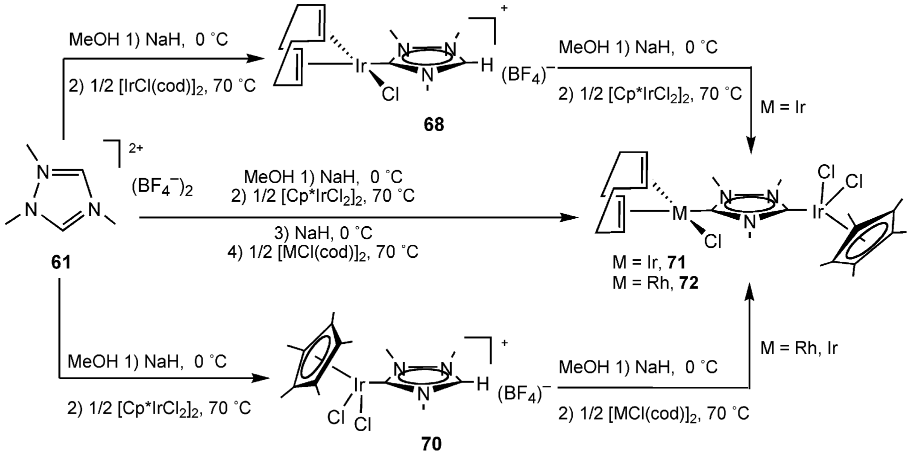
Scheme 24.

Remarkably, **62** could also be coordinated to two different metallic fragments to afford the heterobimetallic complex **69** (Scheme 25).[54] The formation of compound **69** was thought to proceed via a nonisolated monometallated species **68**, as shown in Scheme 25.



Scheme 25.

Following an alternative reaction pathway, the monometallated compound **68** and a related Ir^{III} species **70** (Scheme 26) could be isolated and used as synthons for the preparation of several hetero-dimetallic complexes.[55]



Scheme 26.

Mono NHCs

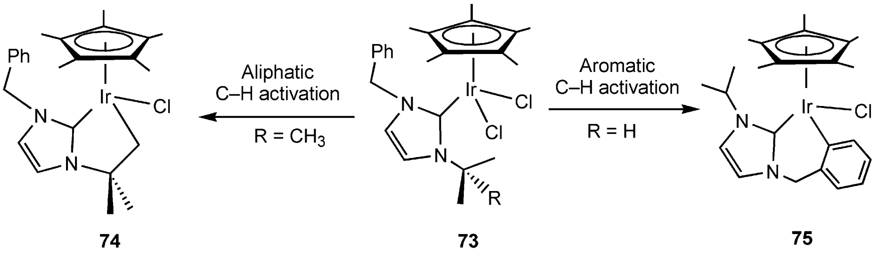
Inter- and intramolecular C–H activation abilities of ‘Cp*Ir(PR$_3$)’ complexes were extensively studied by Bergman and co-workers.[57,58] The replacement of the phosphane ligands by NHCs has provided new aspects for the C–H activation processes. The ability of Cp*Ir(NHC) complexes to undergo intramolecular C–H activation was initially reported by Herrmann[59] and Yamaguchi.[60] In other studies, aromatic and aliphatic intramolecular C–H activation of NHCs was shown to be a highly favourable process, when the NHC ligand contained the appropriate aliphatic or aromatic N substituents.[61–64] In the cases where both aliphatic and aromatic C–H activation were possible, as in the case depicted in Scheme 27, steric factors seem to determine the selectivity of the reaction.[62]

For the outcome of this reaction, it seems that the steric hindrance of the reaction products determines the selectivity of the process, as shown in Scheme 28. In this sense, the formation of the aliphatic C–H activation product (**74**, Scheme 27) is explained by the highly unstable structure that would be formed if aromatic C–H activation was produced for the *t*Bu-substituted NHC (central structure in Scheme 28). For the *i*Pr analogue, aromatic C–H activation produces a more relieved structure, because the *i*Pr group can orientate its small hydrogen atoms towards the methyl groups of the Cp* ring (left in Scheme 28).

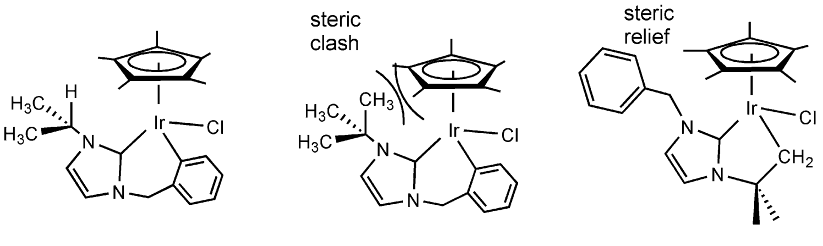
Catalytic Properties

Hydrogen-Borrowing Processes

The search for efficient catalysts for ‘hydrogen-borrowing’ strategies is very challenging. It can provide easy access to a wide variety of highly valuable organic molecules that have environmental benefits.[65] With regard to these processes, we have focused our interest on three cata-

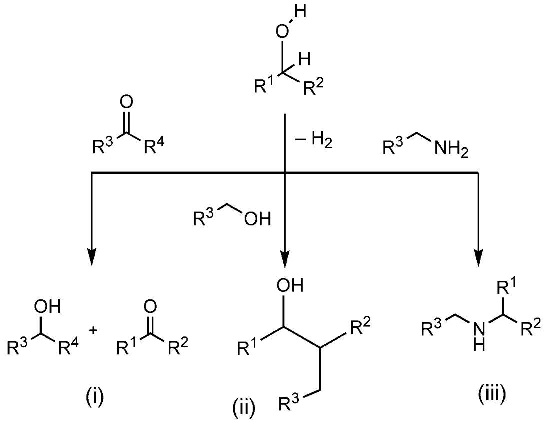


Scheme 27.



Scheme 28.

lytic reactions (Scheme 29): namely, (i) transfer hydrogenation, (ii) β-alkylation of secondary alcohols and (iii) N-alkylation of primary amines with alcohols.

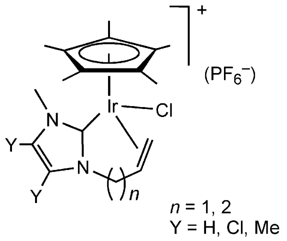


Scheme 29.

Transfer Hydrogenation

Hydrogen-transfer processes that involve the use of Rh, Ir and Ru NHC complexes probably constitute the most extensively studied processes for this family of compounds.[11–13] The results obtained with the Ru pincer catalyst **48** (Scheme 17)[42] are among the best in terms of catalytic activity, higher than those with other phosphane and amine pincer complexes of Ru.[66] Another significant example is the tripodal Rh^{III} complex **59** (Scheme 21), whose catalytic activity in transfer hydrogenation is one of the highest reported for a Rh catalyst.[51]

The catalytic activity of Cp*Ir^{III} complexes in the Oppenauer-type oxidation of alcohols is considerably enhanced by the introduction of N-heterocyclic carbene ligands.[67] The coordination of hemilabile ligands of the type N-alkenylimidazol-2-ylidene yielded a new family of transfer-hydrogenation catalysts (Scheme 30), although only moderate activities were found for these complexes.[64]

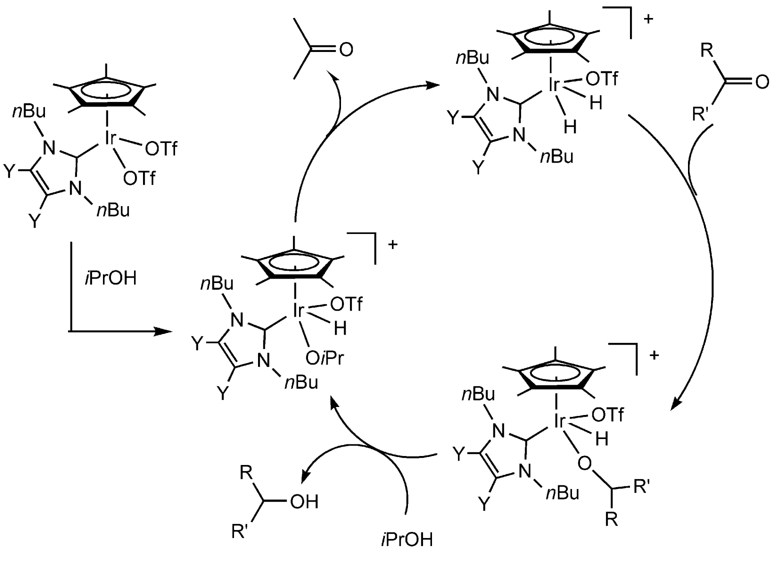


Scheme 30.

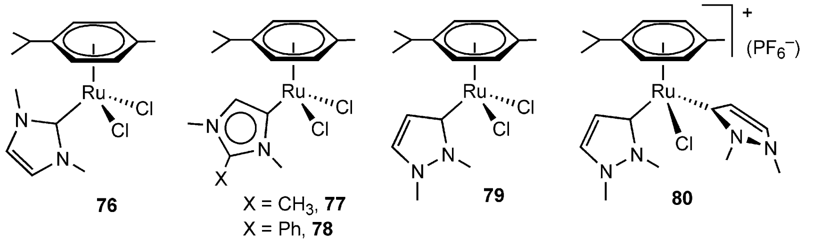
Interestingly, it has recently been found that for the enhancement of the catalytic activity of Cp*Ir^{III} complexes with monodentate NHC ligands, the addition of an external base is not required.[68] It has been proposed that these catalysts may operate through a hydridic mechanism that is based on the oxidative addition of the O–H bond of *i*PrOH to generate a "Cp*Ir^{V}(NHC)H(O*i*Pr)" intermediate, as shown in Scheme 31. The advantages thereof allowed the synthesis of chiral acetates through catalytic transfer hydrogenation/enzymatic dynamic kinetic resolution of aldehydes.[68]

β-Alkylation of Secondary Alcohols with Primary Alcohols

The catalytic β-alkylation of secondary alcohols with primary alcohols has important benefits relative to the traditional multistep processes, especially when the economical benefits of a high-yielding one-pot procedure and the use of an environmentally friendly process are considered. Ru[69] and Ir[70] catalysts have been used in this catalytic reaction.



Scheme 31.



Scheme 32.

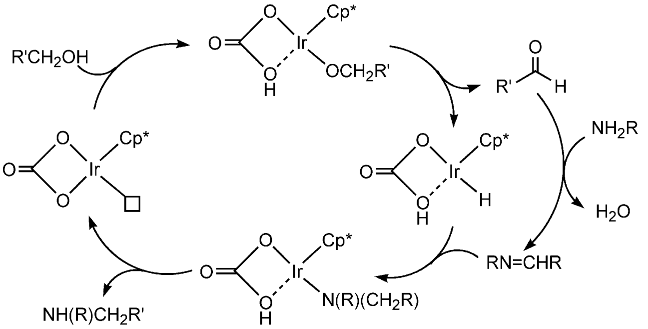
The first example of a Ru–NHC complex used in this reaction was reported in 2007.[56] The dimetallic and tetrametallic Ru^{II} compounds **66** and **67** (Scheme 24) are very active toward this catalytic transformation, especially relative to previously reported species.[69] Since the two metallic centres are connected by the triazol–diylidene ligand, it was pointed out that some cooperativity may enhance the catalytic performance of the compounds. Further, a series of Ru–(mono-NHC) compounds with improved catalytic properties was recently reported (Scheme 32).[71] An interesting feature of this work is that the different types of NHC ligands lead to different activities according to their basicity. In this sense, the more basic pyrazolylidene ligand enhances the catalytic behaviour of the compound in such a way that compound **79** (Scheme 32) is among the most efficient Ru catalysts for this type of reaction.

The unprecedented Ir^{III} compound with a Cp*-functionalized NHC ligand (compound **43**, Scheme 14) was tested in the catalytic β-alkylation of secondary alcohols with primary alcohols. The results showed high activities and good selectivities for the production of the alcohols.[38]

Amination of Alcohols

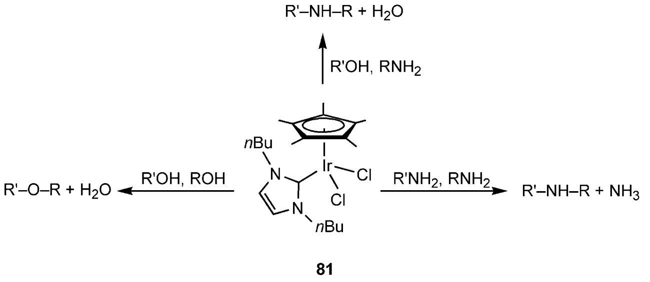
The metal-mediated alkylation of amines with primary alcohols is an important, fundamental reaction in synthetic organic chemistry that has been the focus of increasing interest for the preparation of molecules with pharmaceutical applications. For this reaction, only a few examples of Ru[72,73] and Ir[74,75] catalysts have been reported, such as $RuCl_2(PPh_3)_3$,[76] $RuClCp(PPh_3)_2$,[77] and, in a remarkable example, $Ru_3(CO)_{12}$ in combination with tri-*o*-tolylphosphane.[72,78]

The iridium catalyst $[Cp^*IrCl_2]_2$ was shown by Fujita, Yamaguchi and co-workers to be an efficient catalyst for the N-alkylation of amines with alcohols.[74,79] DFT calculations carried out on this system show that the addition of carbonate, which may coordinate to the metallic centre, lowers the energy barriers of many steps.[80] The proposed mechanism for this catalytic reaction in the presence of K_2CO_3 is shown in Scheme 33.



Scheme 33.

Compound **43** (Scheme 14) constitutes the first example of an Ir–NHC complex tested for this catalytic reaction, and shows activities that are comparable to those provided by other Ir catalysts.[38] In a very recent contribution, it was shown that compound **81** (Scheme 34) is a very versatile catalyst that can be used in several C–O and C–N coupling reactions involving alcohols and amines.[81] The catalytic performance of **81** is based on its great activity towards the hydrogen-borrowing processes.

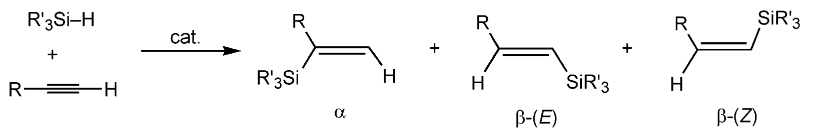


Scheme 34.

Hydrosilylation

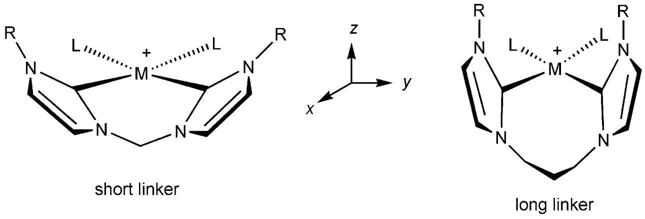
The hydrosilylation of multiple bonds represents a useful class of catalytic processes for the functionalization of organic molecules. Vinylsilanes, which are widely used as intermediates for organic synthesis, can be efficiently prepared by transition-metal-catalyzed addition of silanes to alkynes (Scheme 35).[82] Most of the recent efforts in the study of this reaction involve the design of efficient catalysts to enable the preparation of α, β-(*E*) or β-(*Z*) isomers independently (Scheme 35).

A vast number of Rh^I- and Ir^I–NHC complexes have shown activity for this reaction.[12,13] An interesting hypothesis that has been pointed out is the high dependence of the catalytic properties of bis(NHC) complexes of Rh and Ir on the length of the linker between the two azole rings.[19,20,50] As shown in Scheme 36, longer linkers favour the orientation



Scheme 35.

of the azole rings perpendicular to the coordination plane of the molecule, hence sterically hindering the z axis and disfavouring the oxidative addition of the silane.[20]

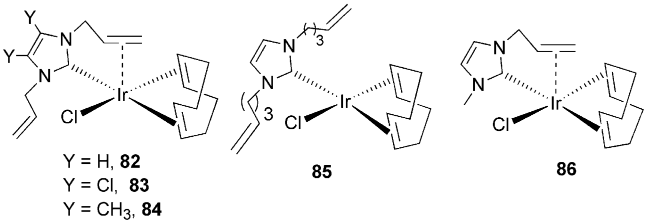


Scheme 36.

According to this, it has been found that Rh^{I}–bis(carbene) complexes with propylene linkers (*long linker*) are completely inactive for catalytic hydrosilylation reactions.[27] However, the introduction of chlorine substituents in the 4 and 5 positions of the imidazolylidene rings (compounds **4**–**7**, Scheme 5) clearly enhance the activity of the compounds under the same conditions. It was pointed out that, in the absence of significant steric differences, the lower basicity of the chlorinated bis(NHC) ligand may favour the labilization of the cod or CO ligands, which thus provides the required coordination vacant site to start the catalytic cycle.

Taking advantage of the lower activity of Ir^{I} compounds than that of their Rh^{I} counterparts, a mechanistic study on alkyne hydrosilylation was performed with mass spectrometry (MS).[83] The complexes used for this study were the Ir^{I} compounds **26** and **28** depicted in Scheme 11. Remarkably, all the expected intermediates for this catalytic reaction could be detected by MS under real catalytic conditions for the first time. As previously reported,[84] the presence of excess alkyne was found to favour the reaction that proceeds by the silylation mechanism, which yields the alkene and the corresponding alkynylsilane.

Ir^{I} complexes with N-alkenyl NHC ligands (compounds **82**–**86**, Scheme 37) were found to be very selective towards the formation of the β isomers, with a clear preference for the (*Z*)-vinylsilanes, which in some cases were obtained as the only products. These selectivities represent the highest reported to date for Ir complexes.[85]



Scheme 37.

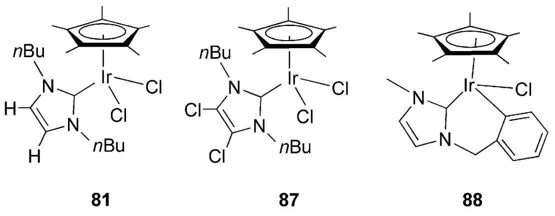
H/D Exchange

Deuterium-labelled compounds can be used in a wide range of applications, e.g. in biologically active systems, as solvents for NMR spectroscopy, and for the study of reaction mechanisms.[86]

The Cp*Ir^{III} complexes with phosphane ligands described by Bergman showed excellent results in catalytic H/D exchange (Scheme 38), in that they can activate a wide range of organic molecules with a variety of deuterium sources.[58,87] It was observed that substitution of the phosphane ligands by NHCs results in an improvement of the catalytic performance. A parallel study of the catalytic performance of compounds **81**, **87**, **88** (Scheme 39) and [Cp*IrCl$_2$(PMe$_3$)] for H/D exchange reactions was carried out.[61] The catalytic results showed that NHC species display higher activities and stabilities than the related phosphane complex in the deuteration of a wide set of organic substrates. Both the decrease in the basicity and the chelating coordination of the NHC ligand strongly affect the activity of the complex; the best performance is achieved with compound **81** (Scheme 39).

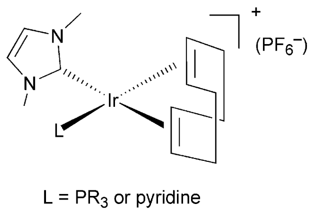
$$\text{R–H} \xrightarrow{\text{cat., D source}} \text{R–D}$$

Scheme 38.



Scheme 39.

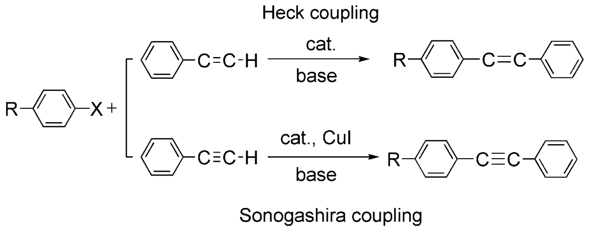
Recent significant examples in this catalytic reaction involve the use of a series of Ir^{I}–NHC complexes (Scheme 40) for the deuteration of aromatic substrates with D$_2$ gas.[88]



Scheme 40.

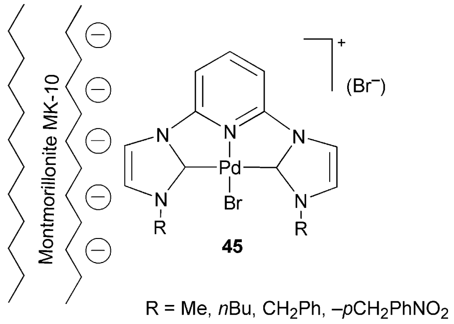
Heck and Related C–C Bond Formation Reactions

The use of Pd–NHC complexes in Heck C–C coupling reactions (Scheme 41) constitutes the earliest catalytic application reported for N-heterocyclic carbene ligands.[4] The high stability shown by this class of compounds together with their easy accessibility prompted the development of heterogenized catalysts for the design of recyclable systems. Some approaches to support[89] and heterogenize Pd catalytic systems involved immobilization of Pd catalysts on polymers,[90] modified mesoporous silica gel[91] or modified silica gel.[92]



Scheme 41.

Pd–CNC-pincer complexes (Scheme 15)[15] were used in the design of recyclable C–C coupling catalysts (Scheme 42).[93] The catalysts were immobilized onto montmorillonite K-10 and bentonite by solvent impregnation, and the activities in the Heck reaction compare well with their homogeneous counterparts, which shows that the activity of the catalyst is preserved upon immobilization.

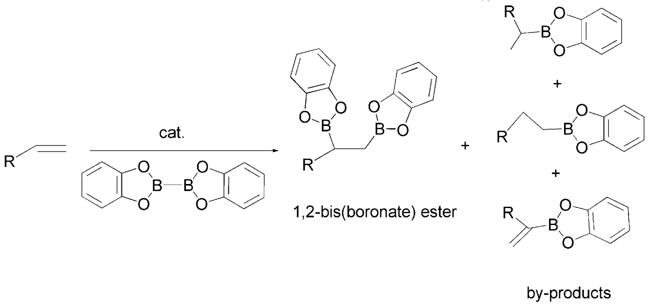


Scheme 42.

Similar heterogenized catalytic systems were tested in the Sonogashira coupling of aryl halides with phenylacetylene (Scheme 41).[94] The activities of the immobilized systems are higher than that of previously reported Pd–carbene catalysts[95] or Pd-immobilized catalytic systems[96] for the coupling of the same substrates.

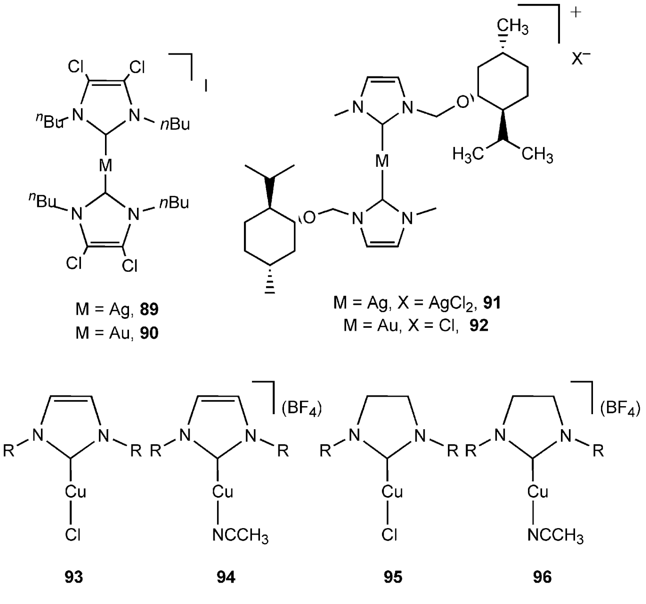
Alkene Diboration

One of the main challenges in the catalytic diboration of alkenes is the design of proper catalysts that selectively provide 1,2-bis(boronate) esters, whilst avoiding the generation of undesired hydroborated products (Scheme 43).[97]



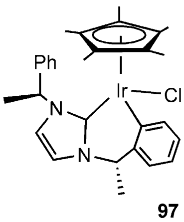
Scheme 43.

In 1995, Marder and co-workers reported that the use of Au^I-based catalysts could avoid undesired β-elimination side reactions, thus enhancing the chemoselectivity of the diboration.[98] From this seminal work, the introduction of NHC ligands in the coordination sphere of group 11 metals (Cu, Ag, Au, Scheme 44) was found to improve the performances of the catalytic systems both in terms of conversions and chemoselectivities.[99]



Scheme 44.

Group 10 metal catalysts with N-heterocyclic carbene ligands have also been recently applied in this catalytic reaction.[100] Mechanistic studies on alkene diboration with Pd^{II}–NHC complexes showed that, for these systems, the reaction proceeds through a base-mediated heterolytic cleavage of the B–B bond of the diborane rather than through oxidative addition to the metallic centre.[101] As a consequence, an excess of the diboron reagent is needed for the chemoselective 1,2-diboration, because only one of the borane units is transferred to the alkene. A similar mechanism was found for a chiral Ir^{III}–NHC catalyst (compound **97**, Scheme 45).[63]



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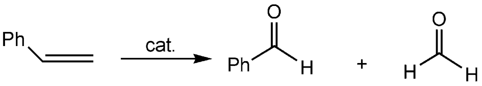
Scheme 45.

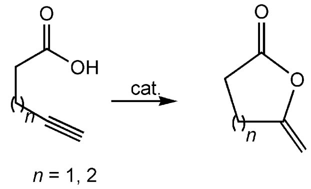
Other Catalytic Reactions

In addition to the reactions already discussed, other catalytic applications of NHC complexes have been reported in the last years. For example, compound **48** (Scheme 17) was used as a catalyst in the oxidative cleavage of alkenes to aldehydes (Scheme 46).[42] The reactions are highly selective and, remarkably, no side products from overoxidation reactions were observed, nor from the presence of epoxidation or diolization processes.



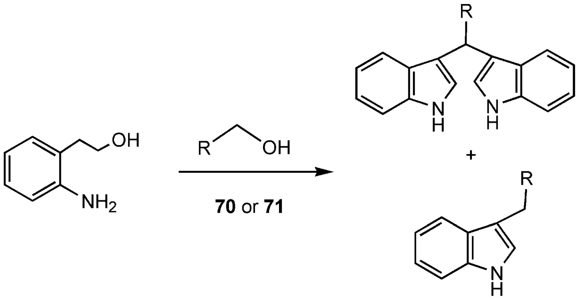
Scheme 46.

Several Rh^I- and Ir^I–NHC complexes were tested in the catalytic cyclization of alkynoic acids to yield the corresponding exocyclic enolic lactones (Scheme 47),[27,35,50,54] which show similar and even higher activities than those of complexes reported before.[102] The high catalytic activity shown by dimetallic Rh^I and Ir^I complexes with a triazol–diylidene ligand (Scheme 23) is remarkable.[54] Again, it has been observed for this catalytic reaction that the activity of the Rh^I and Ir^I catalysts containing bis(carbene) ligands with Cl substituents on the imidazole backbone (Scheme 5) is higher than that of the analogous species with unsubstituted NHC backbones.[27]



Scheme 47.

An important field in which N-heterocyclic carbenes are beginning to play a role is tandem catalysis. The heterobimetallic triazol–diylidene-based compounds **71** and **72** (Scheme 26) were successfully employed as tandem catalysts[54,55] in the synthesis of substituted bis(indole)s by catalytic cyclization of 2-aminophenethyl alcohol and subsequent indole functionalization with a series of primary alcohols (Scheme 48). The catalysts proved to be very active in the overall process, and a controlled tuning of the selectivity of the process could be achieved by changing the amount of the primary alcohol added in the second step of the reaction so that either the bis(indolyl)methane or the 3-alkylated indole could be obtained as the unique products of the reaction.



Scheme 48.

Conclusions

N-Heterocyclic carbenes are an extremely versatile class of ligands from both the topological and coordinative points of view. The design of NHC-based homogeneous catalysts is a straightforward task, which continuously allows the development of new products with enhanced catalytic activities and that are, in some cases, capable of performing new organic transformations. At first NHCs were known to mimic phosphane chemistry, but we are now sure that NHCs have found their own place in chemistry research, and still many new applications of complexes containing this type of ligands are to come.

Acknowledgments

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