Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 251 (2007) 841–859

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Structural and catalytic properties of chelating bis- and tris-*N*-heterocyclic carbenes

José A. Mata [a], Macarena Poyatos [b], Eduardo Peris [a,*]

[a] *Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, Av. Vicente Sos Baynat, s/n, 12071-Castellón, Spain*
[b] *Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06520-8107, USA*

Received 6 April 2006; accepted 13 June 2006
Available online 18 June 2006

Contents

Abstract

The use of polydentate NHC ligands has allowed the preparation of new compounds whose stability is entropically improved by the chelate effect. Chelate-*N*-heterocyclic ligands also provide interesting features that can allow fine tuning of topological properties such as steric hindrance, bite angles, chirality and fluxional behavior. In this manuscript, we have focused our attention in compounds with chelate-*N*-heterocyclic ligands in bidentate and tripod coordination forms. Special attention is paid to structural and catalytic properties.

Keywords: *N*-Heterocyclic carbenes; Chelate; Tripod; Catalysis

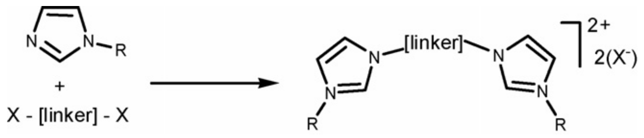
1. Introduction

N-Heterocyclic carbene ligands (NHCs), first reported by Ofele [1] and Wanzlick [2] and later isolated in the free state by Arduengo et al. [3], have emerged as an extremely useful class of ligands for transition-metal catalysis. It is well recognized that the replacement of phosphines by *N*-heterocyclic carbenes can provide complexes with enhanced catalytic performances and higher stability [4,5]. In the same context, the use of polydentate NHC ligands has allowed the preparation of new compounds whose stability is entropically improved by the chelate effect, extending this promising area [6,7]. Most of these poly-carbenes reported so far are bidentate and *pincer* (tridentate-*mer*) biscarbene ligands that were first coordinated to Pd and later on to other transition metals such as Rh, Ru and Ir [6,7]. Not only chelating bis-NHCs are yielding more stable metal complexes,

---

[*] Corresponding author. Tel.: +34 964 728243; fax: +34 964 728214.
E-mail address: eperis@qio.uji.es (E. Peris).

0010-8545/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2006.06.008



Scheme 1.

but they are also giving interesting features that can provide fine tuning of topological properties such as steric hindrance, bite angles, chirality and fluxional behavior.

In this review, we summarize the most relevant examples of chelate bis-*N*-heterocyclic carbene complexes reported to date, and we will discuss the main features regarding their synthetic, topological and catalytic properties. We have focused our attention in all those examples dealing with bis- and tris-carbene complexes in a bidentate and tripod (tridentate-*fac*) coordination shapes. Hybrid or mixed chelating ligands, and *pincer* coordinations have not been considered since these may be appearing in other manuscripts within this same special issue of *Coordination Chemistry Reviews*.

2. Chelate bis-*N*-heterocyclic carbene complexes

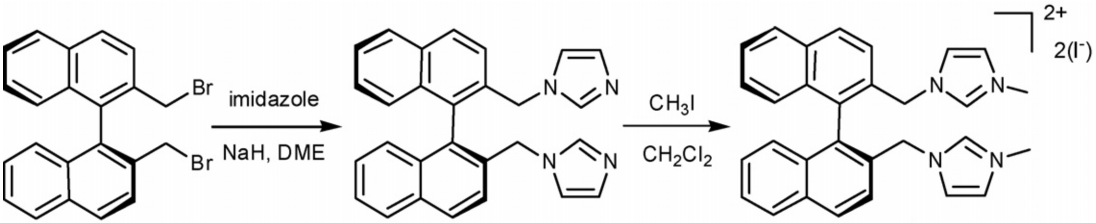
2.1. Synthesis of ligand precursors

Chelate biscarbene ligands have often been prepared from *N*-alkyl or -aryl imidazolium salts. The preparation of the imidazolium precursors is usually straightforward from commercial available products. For the preparation of bisimidazolium salts, a common method consists of the direct reaction between two equivalents of the corresponding *N*-alkylimidazole and one of the desired alkyl dihalide (Scheme 1) [8–10]. This methodology provides an easy modular route to the preparation of a large library of bidentate NHC precursors. These bis-NHC precursors can be easily modified by introducing changes in both the linker between the imidazole units and in the N-substituents.

Alternatively, these biscarbene precursors can be obtained by N-quaternisation of the imidazole ring at the 3-position with an alkyl halide, as shown in Scheme 2. In this example, nucleophilic substitution of the dibromomethyl compound with the anion of imidazole followed by quaternization with methyl iodide, gave the desired bisimidazolium salt **1** (Scheme 2) [11].

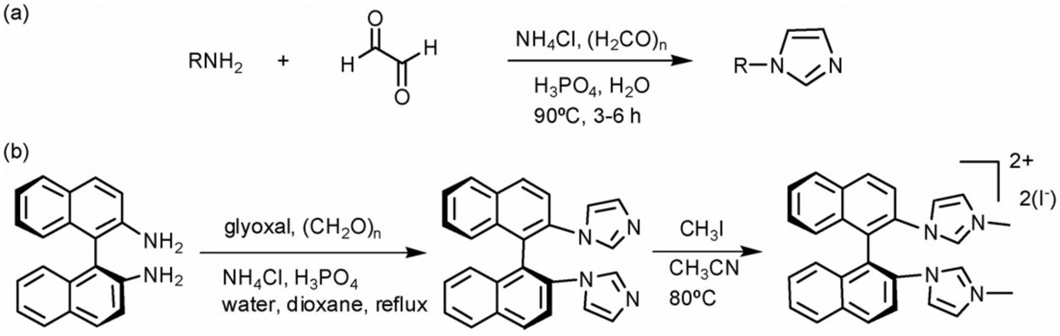
Other routes to bisimidazolium salts have been reported and employed in the design of chiral biscarbene complexes [12,13]. For example, the one-pot condensation strategy to obtain aliphatic amines [14] (Scheme 3a) was used in the synthesis of a new chiral bisimidazolium salt. The reaction of (*S*)-BINAM with glyoxal, paraformaldehyde and ammonium chloride, gave the neutral binaphthyl compound **2**, which was easily alkylated to afford the bisimidazolium salt **3** (Scheme 3b) [13].

While the properties of phosphines are well established by the Tolman map of electronic and steric effects [15], such systematic study is not yet available for *N*-heterocyclic carbenes. In general, it is difficult to modulate the electronic and steric effects of chelating biscarbene ligands, although several points can be considered. The wingtips (R_1) mainly modulate the steric properties of the ligand, with little effect on its electron-donating nature [16]. The linker (R_2) establishes a relationship between the azole ring orientation and the equatorial plane of the metal complex, and also affords a way to modulate the chelating bite angle [17]. The backbone (R_3) of the imidazole ring mainly contributes to the electronic properties of the ligand (Scheme 4) [18].



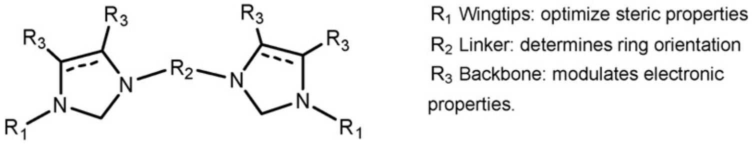
1

Scheme 2.



2 **3**

Scheme 3. (a) One-pot direct condensation to give imidazoles. (b) Synthesis of chiral bisimidazolium salt **3**.



Scheme 4.

2.2. Routes to chelate bis-N-heterocyclic carbene complexes

In the preparation of chelating *N*-heterocyclic carbene complexes several methods have proved to be efficient, and these have been reviewed [4,7,19–21]. Among the most widely used coordination methods are: (i) isolation of the free biscarbene; (ii) insertion of a metal into a C=C bond of electron rich olefins; (iii) *in situ* deprotonation of the bisimidazolium salts with a weak base, which can be either added to the reaction mixture (*e.g*. NaOAc, NEt_3, Cs_2CO_3) or be present as a ligand in the metal precursor (*e.g*. $Pd(OAc)_2$, $Rh_2(OAc)_4$); (iv) transmetallation from a silver(I) NHC complex prepared by treatment of the imidazolium salt with Ag_2O; (v) oxidative addition of the C2–H bond of an imidazolium cation.

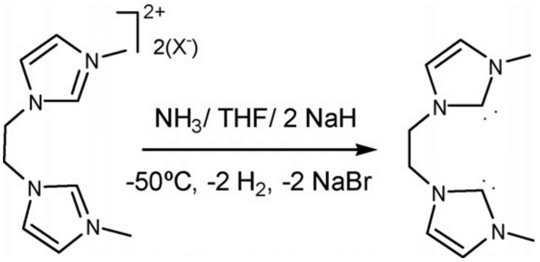
In this section, we briefly describe these synthetic procedures including some relevant examples, not aiming to give any comprehensive description.

(i) Isolation of free biscarbenes: Herrmann et al. synthesized the first bidentate free bisimidazolylidene ligand using the liquid-ammonia route in high yield (95%) (Scheme 5). Unfortunately, the free carbene is very sensitive to temperature and moisture [22]. Other routes, such as deprotonation of the corresponding imidazolium dibromides with $K[N(SiMe_3)_2]$ in THF, have been used to prepare similar ligands but in lower yields [23–25]. The free biscarbene ligands are generally less stable than the monocarbene analogues, and in general they are “extremely sensitive” to air.

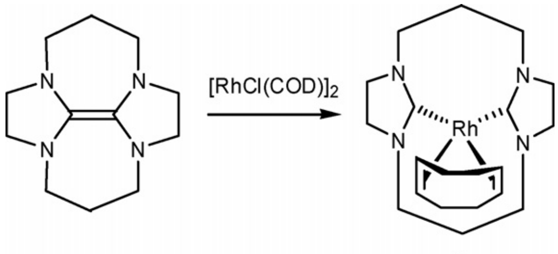
(ii) Insertion of a metal into a C=C bond of electron rich olefins: With the pioneering works of Lappert and co-workers [21,26,27], electron-rich olefins (enetetramines) were used as *N*-heterocyclic carbene precursors (carbenoids) in the synthesis of new carbene-transition metal adducts. Reaction of the electron-rich olefins with the corresponding metal complexes can provide mono-, bis-, tris- and even tetrakiscarbene complexes. All the NHC complexes obtained by this method are saturated NHCs. An extensive review about this type of reaction was published by Lappert in 1988 [27]. In the case of chelating biscarbenes, few examples can be found in the literature. For example, the transannularly bonded electron-rich olefin **4** reacts with $[RhCl(COD)]_2$ yielding the biscarbene-metal chelate complex **5** by insertion of the metal atom into the C=C bond (Scheme 6) [26]. A similar complex with a bis(benzimidazolinylidene) ligand was obtained by the same procedure by Thummel and co-workers in 1995 [28].

(iii) *In situ* deprotonation of azolium salt with a base: The *in situ* deprotonation of an azolium salt to produce the desired NHC has the advantage that the carbene does not have to be isolated, thus simplifying the reaction work-ups when the aim is the preparation of the metal complex. This avoids the handling of the free NHCs, which most of the times are air and moisture sensitive. Deprotonation can be carried out by means of an external base (NaH, *n*-BuLi, *t*-BuOK, etc.). In the case of chelating carbenes with linkers between the azole rings, some complications can appear since the linkers often contain acidic protons that may be deprotonated along with the cleavage of the biscarbene ligand. To circumvent this problem, weak bases such as NaOAc, Cs_2CO_3, NEt_3 or metal precursors containing basic ligands such as acetates, hydrides or alkoxides can be used. Scheme 7 shows an example of a chelate bis-NHC that is obtained by reaction of a bisimidazolium salt with palladium acetate [19].

(iv) Transmetallation from a silver NHC complex: Wang and Lin reported in 1998 this procedure to form palladium and gold NHC complexes [29]. In a typical reaction, an imidazolium salt is treated with silver oxide to provide a mono- or bis-NHC silver complex, as shown in Scheme 8. The silver NHC complex is stable enough to be isolated, or it can be used *in situ* to form the corresponding M-NHC complex after the addition of the corresponding metal precursor. In most cases transmetallation reactions can be carried out under aerobic conditions, and the process has been successful with a variety of metals such as Au, Cu, Ni, Pd, Pt, Rh, Ir

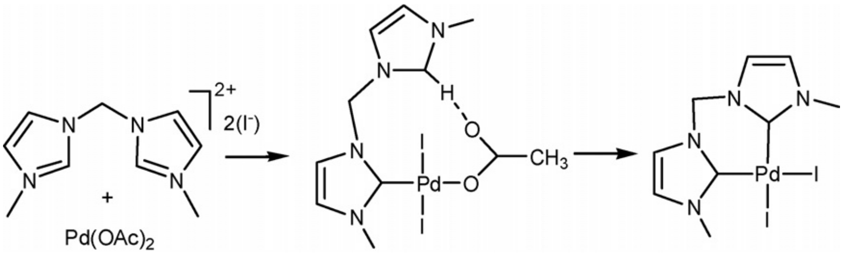


Scheme 5.

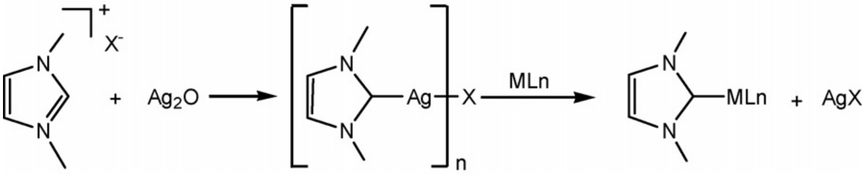


4 **5**

Scheme 6.



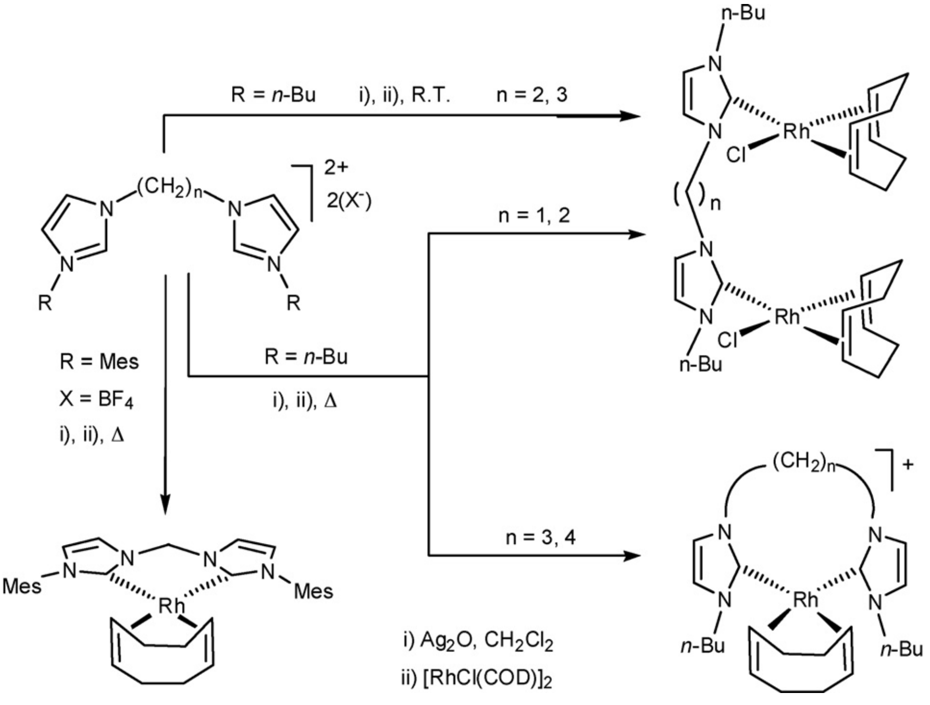
Scheme 7.



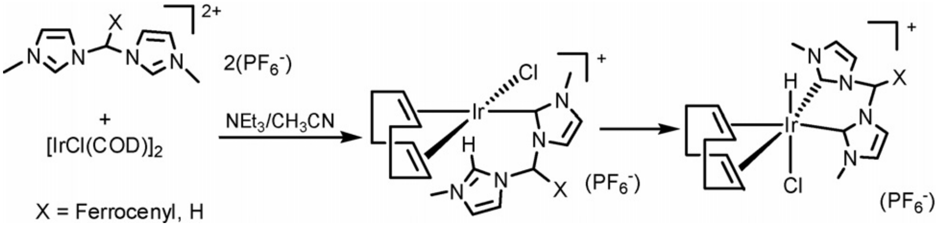
Scheme 8.

and Ru [30]. Sometimes the reaction conditions used for the transmetallation can afford different types of compounds. For example, the reaction of bisimidazolylidene complexes of silver with $[RhCl(COD)]_2$ can either yield dimetallic complexes of Rh(I) with a bridging bisimidazolylidene, or monometallic Rh(I) complexes with a chelate bis-NHC ligand, depending on the length of the linker between the azole rings and the reaction temperature [17]. The size of the N-substituents also contributes to the final geometry of the complex, as shown by the introduction of bulky mesityl groups that force the chelating coordination (Scheme 9) [31].

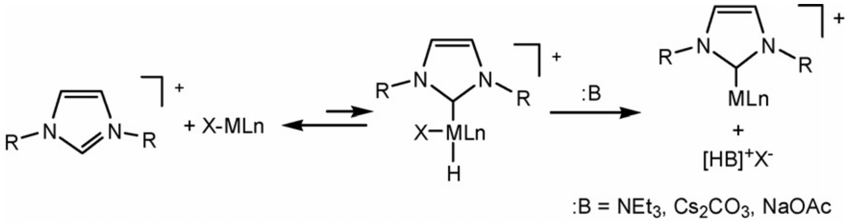
(v) Oxidative addition via C–H activation of an imidazolium salt: Direct oxidative addition of C2–H bonds of mono-imidazolium salts to low-valent transition metal compounds constitute a relatively recent method to afford NHC metal complexes [32,33]. In the case of chelating biscarbenes, only two examples of C2–H oxidative addition have unambiguously been described. The reaction of a ferrocenyl-bisimidazolium salt with $[IrCl(COD)]_2$ in the presence of NEt_3 provided the first evidence of the preparation of a stable bis-NHC-Ir^{III}-H complex by direct oxidative addition of the imidazolium salt [34]. Initially, it seemed that the ferrocenyl fragment may be sterically protecting the M–H from further reductive elimination, but later it was shown that this fragment was not necessary in order to obtain other desired NHC-Ir^{III}-H complexes (Scheme 10) [35]. The fact that the NHC-Ir^{III}-H species were obtained,



Scheme 9.



Scheme 10.

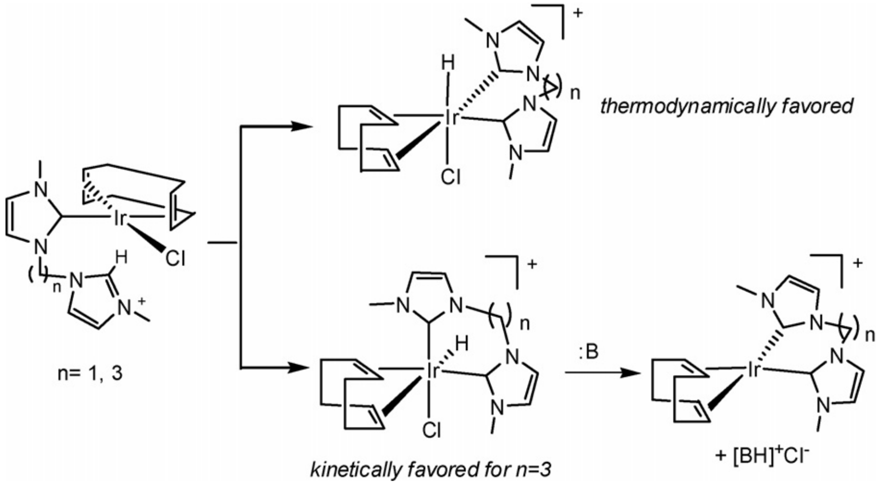


Scheme 11.

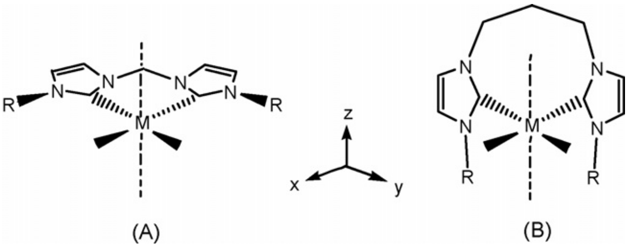
suggested that the role of the weak base (NEt_3 in this case) had to be reconsidered in order to explain the overall metallation process. The mechanism shown in Scheme 11 was proposed, suggesting a two-step process implying first the oxidative addition of the C2–H bond of the imidazolium salt and then the reductive elimination of HX supported by the weak base. A combined experimental and theoretical approach was also performed in order to find an unified mechanism for the metallation of a series of bisimidazolium salts with different lengths of the linker between the azolium rings [35]. The formation of the 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, since only the latter one would be ready to undergo the reductive elimination of HCl (Scheme 12). The *trans* products are the thermodynamically favored complexes, but in the case of the ligands with long linker lengths, the *cis* complexes are kinetically favored, thus providing the bis-NHC-Ir^{I} reductive elimination products [35]. Although the low number of chelate NHC complexes obtained by C2–H oxidative addition may suggest that this method should be considered as ‘marginal’, some other complexes obtained by the ‘deprotonation with a weak base’ method, may well be due to C2–H oxidative additions that have been masked in virtue of the process depicted in Scheme 11.

3. Properties of chelating bis-*N*-heterocyclic carbene complexes

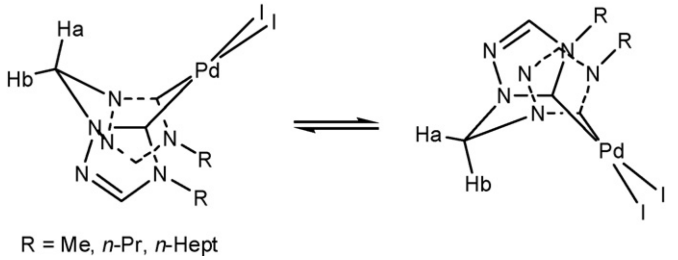
The steric profile of NHC ligands arises from the high anisotropy of the azole rings. NHCs are fan-shaped with a slim axis at right angles to the bulky azole ring plane. When free rotation around the metal–NHC bond is possible, the NHC is expected to orientate its slim axis to the bulky plane of the



Scheme 12.



Scheme 13. Linker length determines the orientation of the azole rings. Short linkers (A) display a conformation close to the *xy* plane. Long linkers (B) allow alignment of azole rings with the *z*-axis.



Scheme 14. Dynamic boat-to-boat inversion in methylene–chelating biscarbene palladium complexes.

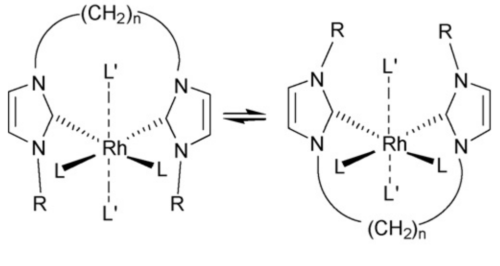
complex, thus minimizing the steric interference between the NHC and the coordination sphere about the metal. As an example, monodentate carbene complexes of d^8 square planar metals always have the plane of the NHC essentially perpendicular to the sterically crowded square plane of the complex [33,36]. The bulky NHC azole ring plane is generally directed towards the empty positions in the ±*z* direction, while the slim NHC angle lies in the *xy* plane of the complex. NMR spectroscopy indicates that the barriers for rotation around the metal–ligand bond can be rather high and depend on the steric congestion of the *cis* ligands [37]. In the case of chelate bis-NHC complexes the situation is different. In such compounds, rotation around the M–NHC bond would be expected to be restricted, so the bulky ligand axis might be forced into closer contact with the sterically crowded complex plane, depending on the linker length and rigidity. The effective steric size of the ligand might then vary as a result of the length of the linker and can affect the reactivity of the complex. The general principle is illustrated by diagrams A and B in Scheme 13. For short linkers, the NHC ligand tends to prefer a conformation with the azole rings in (or close to) the *xy* plane, while long linkers allow the azole rings to align more closely with the *z*-axis.

The smallest metallacycle formed in a chelating biscarbene complex is a six-membered ring as depicted in Scheme 13A. In the case of Pd(II) pseudo square planar complexes, the ^{1}H NMR spectrum shows a singlet multiplicity due to the resonances of the protons of the methylene linking group, indicating a fluxional rather than a locked behavior [38]. Scheme 14 illustrates the dynamic process for a square planar chelating bistriazolylidene palladium (II) complex. The free energy values ($\Delta G^{\neq}$) were determined by means of NMR spectroscopy ranging from 18 to 20 kcal/mol for the boat-to-boat inversion. A similar equilibrium has been recently described for analogue complexes bearing an alkyl chain functionalized with a hydroxyl group [39].

The behavior of complexes with longer linkers is different [17]. For these complexes, no inversion of the macrocyclic seven-, eight- or nine-membered rings was observed upon varying the temperature up to 100 °C, thus implying that these metallacycles are rigid (Scheme 15), and hence the linker $(CH_2)_n$ protons become diastereotopic. Comparison of different rhodium chelating biscarbene complexes show that the fluxional behavior is mainly decided by the size of the metallacycle rather than the nature of the co-ligands. Scheme 15 shows different examples of Rh(III) and Rh(I) complexes with an indication about the dynamic fluxional process at room temperature. Complexes with long linkers [$n = 2$–4, $(CH_2)_n$] show no interconversion at room temperature, independently of the bulkiness of the other co-ligands, geometry or oxidation state of the metal (entries 3–8). For the methylene-linked complexes (entries 1, 2) the boat-to-boat conversion takes place even at room temperature, independently of the size of the ancillary wingtips.

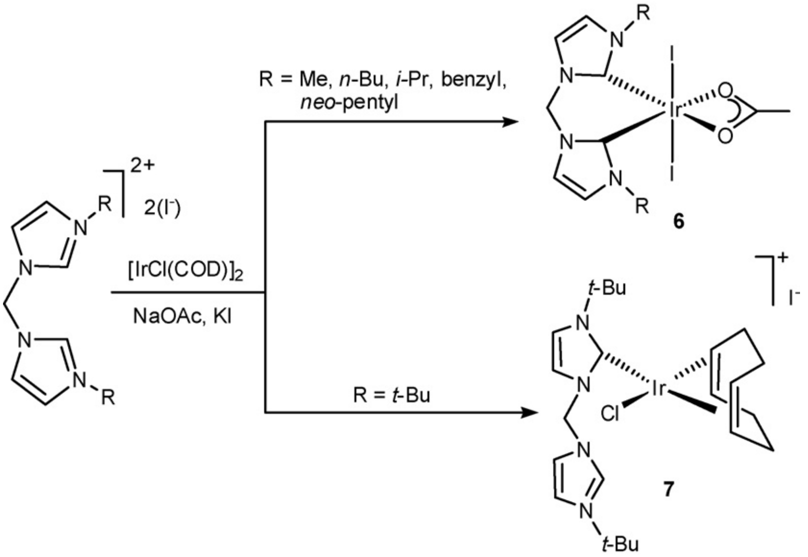
Iridium analogue complexes follow the same trend as rhodium. Crabtree and co-workers prepared a series of complexes with a methylene linker and different wingtips. In all cases, the methylene bridge is observed by ^{1}H NMR as a singlet, indicating the non rigidity of the complex. Changing the bulkiness of the wingtip groups, does not affect the conformation of the chelate biscarbene ligand. Interestingly, for the case of *tert*-butyl group, the chelate complex was not observed, instead a monocarbene complex was obtained (complex **7** in Scheme 16) [9].

We have seen how the linker length determines the orientation of the azole rings in chelating biscarbene complexes. This in turn, influences the dynamics of such systems. In order to



Entry	Linker	L	L'	Fluxional (R.T.)
1	$-CH_2-$	CH_3COO^-	I	yes
2	$-CH_2-$	CH_3CN	I	yes
3	*o*-phenylene	CH_3COO^-	I	no
4	$-(CH_2)_2-$	COD	-	no
5	$-(CH_2)_3-$	COD	-	no
6	$-(CH_2)_3-$	CO	-	no
7	$-(CH_2)_4-$	COD	-	no
8	$-(CH_2)_4-$	CO	-	no

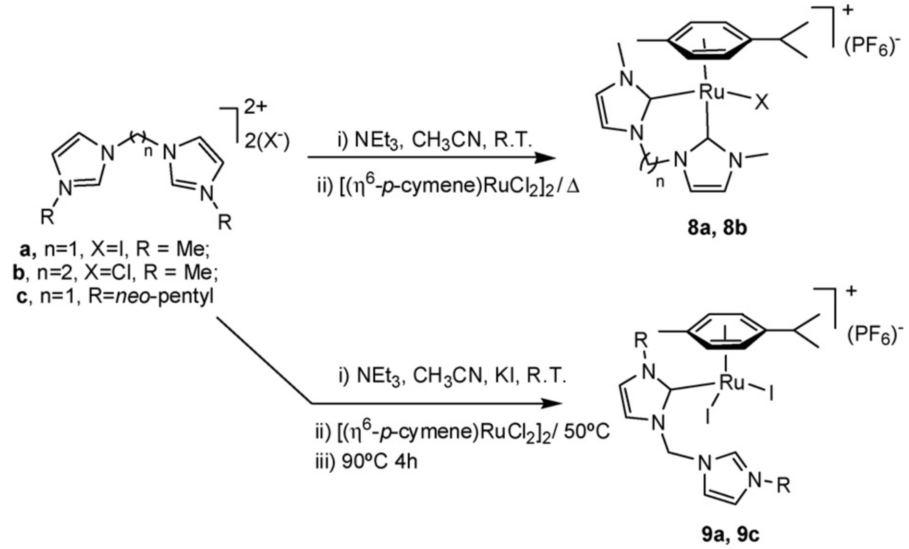
Scheme 15. Dynamic processes of chelating rhodium biscarbene complexes at room temperature.



Scheme 16. The steric properties of the wingtips show reactivity differences on metalation of chelating biscarbenes.

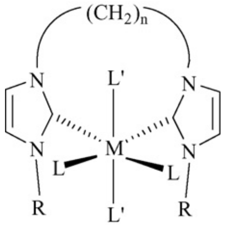
quantify the orientation of the azole rings, the α angle is defined as the average angle between the two imidazolium ring planes and the *xy* plane of the metal complex [17]. Representative data of chelating biscarbene complexes are summarized in Table 1. Examination of models and crystal structures suggests that the α angle is mainly dependent on the length of the linker, although the geometry and size of the wingtips also have some influence. For the shortest linker ($n = 1$, n is defining the length of the linker as the number of methylene units in $(CH_2)_n$), square-planar complexes of Pd(II), Ni(II) and Rh(I) show a relatively large α angle (entries 1–12) due to the absence of apical ligands. In contrast, Rh(III) and Ir(III) octahedral complexes show a small α angle (entries 13–17) due to the presence of bulky ligands in the $\pm z$ direction. The smallest α angle found is for the Rh(III) acetate complex with the bulkiest nortricyclyl group ($\alpha = 11.9°$, entry 17). For the $n = 2$ case, α is larger, with a maximum value of 70° (entries 18–21). Increasing the linker length to $n = 3$ or 4 shows that the bulky NHC azole ring planes are directed towards the $\pm z$ direction, with α close to 90° (entries 22–24). An exception is found in the case of a rigid linker as *o*-phenylene where the α angle is abnormally small for a $n = 2$ ($\alpha = 33.4°$, entry 20). In a similar way, the bite angles tend to approach an ideal angle of 90°, as the length of the linker increases. Both α value and the bite angles are a measure of the flexibility of the chelating bis-NHC ligands.

The reactivity of biscarbene ruthenium(II)–arene complexes with bisimidazolium salts was also studied [52]. The reaction of methylene- and ethylene-bridged bisimidazolium salts with $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ in the presence of NEt_3 resulted in the substitution of one of the halogen ligands from the coordination



Scheme 17.

Table 1
Representative literature structural data on chelating biscarbenes



Entry	M	Linker *n*	Wingtips R	L	L′	Bite angle C–M–C (°)	α (°)[a]	Reference
1	Pd(II)	1	CH_3	I, I	–	83.7	48.6	[40]
2	Ni(II)	1	CH_3	Biscarbene	–	86.6	42.5	[41]
3	Pd(II)	1	CH_3	I, I	–	83.2	47.3	[42]
4	Pd(II)	1	CH_2CH_2OH	I, I	–	83.6	45.5	[43]
5	Ni(II)	1	*t*-Bu	Cl, PMe_3	–	84.9	57.5	[23]
6	Pd(II)	1	*t*-Bu	Biscarbene	–	83.4	56.8	[23]
7	Pd(II)	1	CH_3	CH_3CN, CH_3CN	–	84.1	40.2	[44]
8	Pd(II)	1	*t*-Bu	I, I	–	83.4	56.4	[45]
9	Pd(II)	1	CH_3	Biscarbene	–	81.8	41.5	[46]
10	W(0)	1	CH_3	CO, PPh_3	CO, CO	79.5	30.9	[47]
11	Rh(I)	1	CH_3	COD	–	83.2	45.7	[48]
12	Rh(I)	1	CH_3	CO, CO	–	83.5	45.0	[48]
13	Rh(III)	1	*n*-Bu	CH_3COO^-	I, I	87.3	19.7	[49]
14	Rh(III)	1	CH_3	CH_3CN, CH_3CN	I, I	87.8	26.3	[49]
15	Ir(III)	1	*i*-Pr	CH_3COO^-	I, I	86.4	19.5	[9]
16	Ir(III)	1	*neo*-pentyl	CH_3COO^-	I, I	87.2	21.6	[9]
17	Rh(III)	1	*n*-Bu	CH_3COO^-	I, ntc[b]	86.2	11.9	[50]
18	Pd(II)	2	*t*-Bu	CH_3, CH_3	–	88.1	65.2	[25]
19	Ni(II)	2	*t*-Bu	Cl, $PPMe_3$	–	88.4	70.3	[23]
20	Rh(III)	*o*-Phenylene	*n*-Bu	CH_3COO^-	I, I	92.2	33.4	[8]
21	Rh(I)	2	*n*-Bu	COD	–	84.0	63.0	[17]
22	Rh(I)	3	*n*-Bu	COD	–	87.6	78.0	[17]
23	Rh(I)	4	*n*-Bu	CO, CO	–	91.0	84.3	[17]
24	Rh(I)	*o*-Xylylene	CH_3	COD	–	90.6	86.6	[51]
25	Ir(III)	1	CH_3	COD	H, Cl	84.6	40.2	[35]
26	Ir(I)	3	*n*-Bu	COD	–	84.6	90.5	[35]
27	Ir(I)	4	CH_3	COD	–	94	90.0	[35]

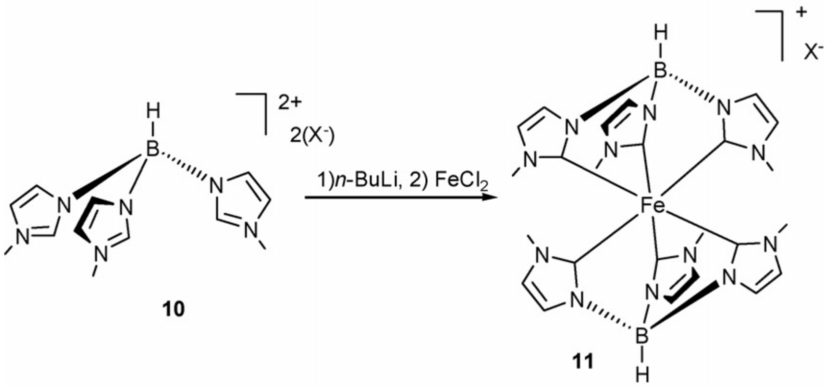
[a] Average of the dihedral angles evaluated using $N'–C_{carbene}–M–C_{carbene}$.

[b] ntc = nortricyclyl. CCDC holds the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or data_request@ccdc.cam.ac.uk). Applications of the Cambridge Structural Database in organic chemistry and crystal chemistry. F.H. Allen, W.D.S. Motherwell. Acta Cryst. B 58 (2002) 407–422.

sphere of the Ru atom and coordination of the bisimidazol-2-ylidene ligand, as outlined in Scheme 17. It was concluded that steric reasons (mainly the length of linkers bridging the imidazole rings) determine both, reactivity and synthetic problems to the final products. The reaction products are determined by the length of the biscarbene-linker, thus providing good yields for the biscarbene complex with a methylene linker (**8a**) and low yields for the ethylene-bridged one (**8b**). The reaction failed for the propylene-bridged bisimidazolium salt. For these complexes the *p*-cymene ligand is highly sterically demanding, forcing the azole rings to orientate the slim angle axis in the bulky plane of the complex. For the propylene-bridged ligand, a similar effect would force the azole rings to dispose far from their natural orientation (orthogonal to the coordination plane) thus yielding an unstable structure. For the imidazolium salt containing the sterically demanding *neo*-pentyl groups, the only reaction product, which we could isolate was the monocarbene complex labeled as **9c** (Scheme 17). This compound did not evolve to the corresponding chelate biscarbene complex, even under harsher reaction conditions such as addition of an excess of NEt_3 or use of a stronger base such as NaH or *t*-BuOK [52].

4. Tripod coordination of bis-*N*-heterocyclic carbene complexes

The use of poly-dentate NHC ligands allows the preparation of compounds with improved stability and interesting topological properties. Whereas there are many studies describing the coordination of *pincer* (tridentate-*mer*) *N*-heterocyclic carbene ligands [6], the use of poly-carbene ligands with tripod (tridentate-*fac*) geometry is still scarce. Most of the phosphine-free tripod ligands reported so far are N-donors, such as tris(pyrazolyl)borates [53], triamidoamines [54] and trisoxazolines [55]. The design of NHC ligands with a tripod coordination



Scheme 18.

is important because the *fac* tricoordinate geometry should determine the catalytic properties of the metal complex, especially when the stability of the ligand–metal bond is high, and the catalytic activity of the complex must rely on the lability of the other co-ligands, and the relative geometry of the potential vacant sites.

Fehlhammer and co-workers obtained the first chelating tris-*N*-heterocyclic-carbene complex in 1996 (**11** in Scheme 18), with a triscarbene ligand similar to Trofimenko's trispyrazolyl borate. Interestingly, the same imidazolium precursor coordinates to lithium after reaction with *n*-BuLi, providing a dimetallic complex with two triscarbene ligands [56]. The same ligand precursor, **10**, was later coordinated to Co(III), giving an hexacarbene complex similar to **11** [57].

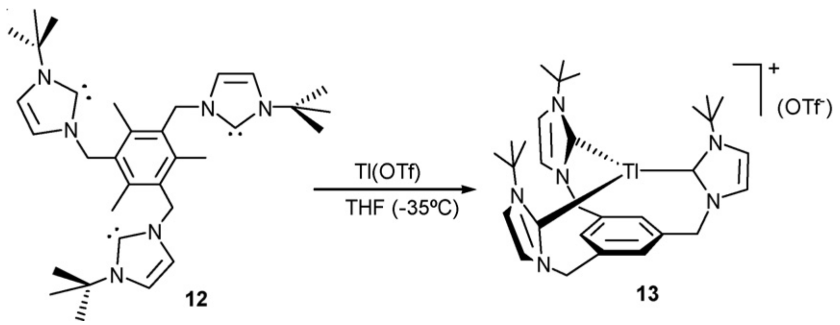
In 1994, the stable triscarbene 1,3,5-[tris(3-*tert*-butylimidazole-2-ylidene)methyl]-2,4,6-trimethylbenzene (timtmb$^{t\mathrm{Bu}}$, **12**) was described [58]. Although it fitted the topological requirements to coordinate in the tripod form, its big cavity allowed coordination only to large metal ions, such as thallium(I) (**13**, Scheme 19) [59].

In the design of new triscarbene ligands with a tripod coordination the group of Meyer and co-workers has provided very interesting examples. The preparation of the ligand 1,1,1-[tris(3-alkylimidazole-2-ylidene)methyl]ethane (TIME^R) afforded the preparation of complexes with group 11 metals [60,61] and then with Ir and Rh (Scheme 20) [62]. The helicoidal silver complex **14** was used in most cases as a carbene-transfer agent to provide the other metal complexes. Unfortunately, bi- and trimetallic complexes were obtained in all cases, instead of mononuclear compounds in which the ligand would presumably coordinate in a tripod fashion.

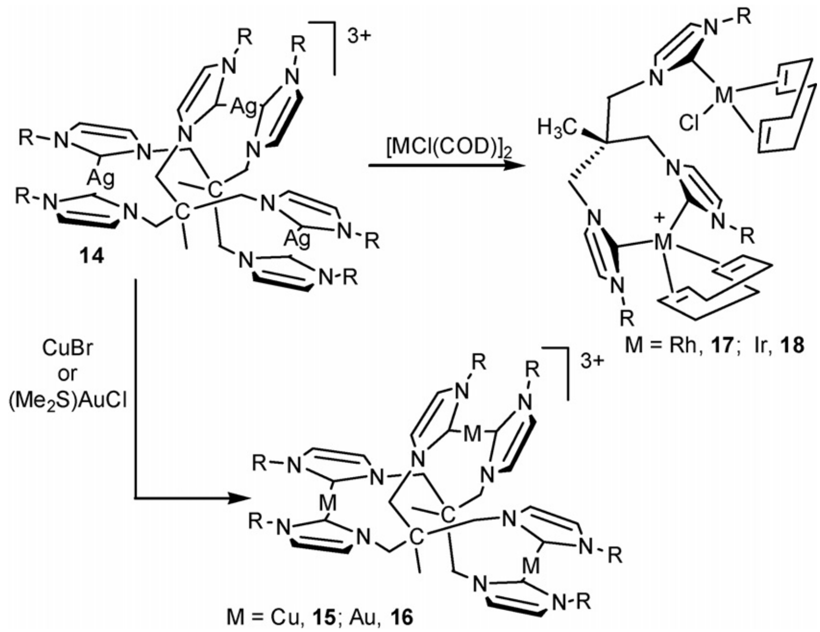
The introduction of a central nitrogen atom yields new triscarbene ligands that coordinate in an N-anchored tripod form. The tetradentate-tris-NHC ligand tris[2-(3-alkylmethylimidazole-2-ylidene)ethyl]amine (TIMEN^R, **19**, Scheme 21) can be obtained by deprotonation of the corresponding trisimidazolium salt $[H_3TIMEN^R](PF_6)_3$. This ligand, has afforded complexes with Co [63], Ni [64] and Cu [60]. Scheme 21 shows the preparation of the Cu(I) complex **20** [60]. This type of tripod-shaped ligands has been reviewed by Meyer and Hu [65]. Attempts to coordinate these *N*-anchored ligands to Rh(I) and Ir(I) gave trinuclear compounds rather than the desired tripod compounds [66].

In 2003, we described a CCO tripod ligand, which combines two NHC groups and a phenoxy unit [67]. In the presence of a weak base such as NEt$_3$, the imidazolium precursor (2-hydroxyphenyl)bis-(3-methylimidazolium-l-yl)methane diiodide (**21**) reacted with [RhCl(COD)]$_2$ in refluxing CH$_3$CN to give the Rh(III) complex **22** (Scheme 22). The substitution of the phenyl ring by a pyridine affords the biscarbene precursor (2-pyridine)bis(3-methylimidazolium-l-yl)methane diiodide, **23** in Scheme 22, which can potentially coordinate in a CCN tripod form. However, all the attempts to coordinate this pre-ligand in the tripod form were unsuccessful [68].

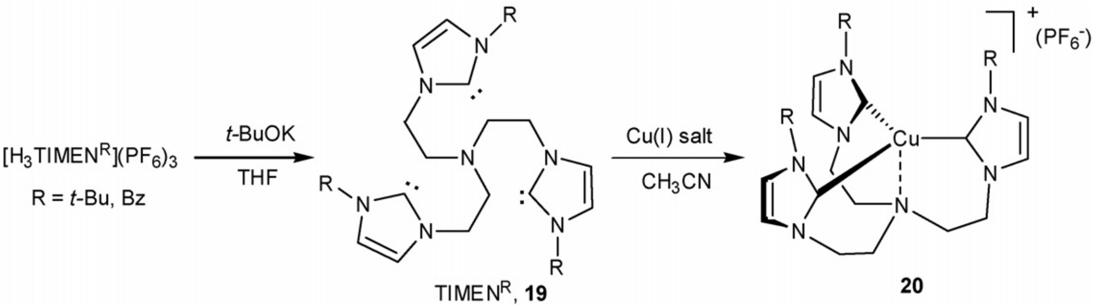
Another example of CCO tripodal coordination was reported by Arnold and Scarisbrick recently [69]. In this case, the coordi-



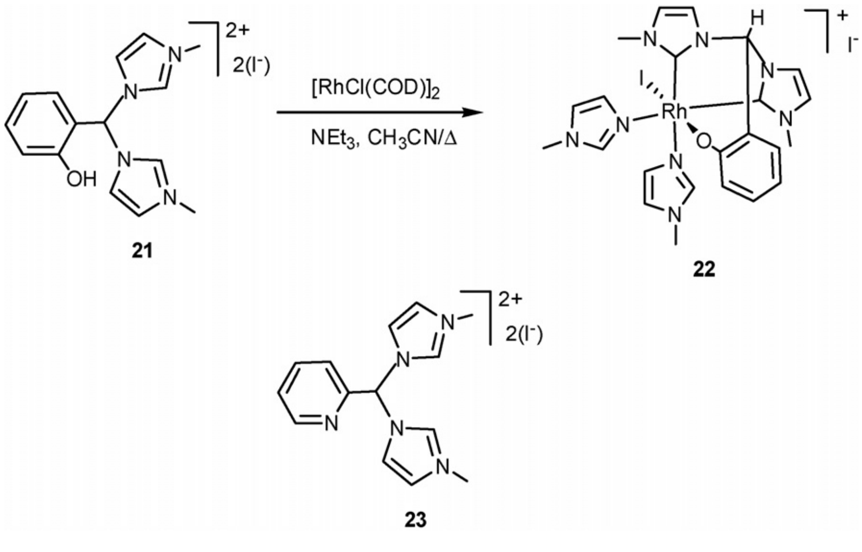
Scheme 19.



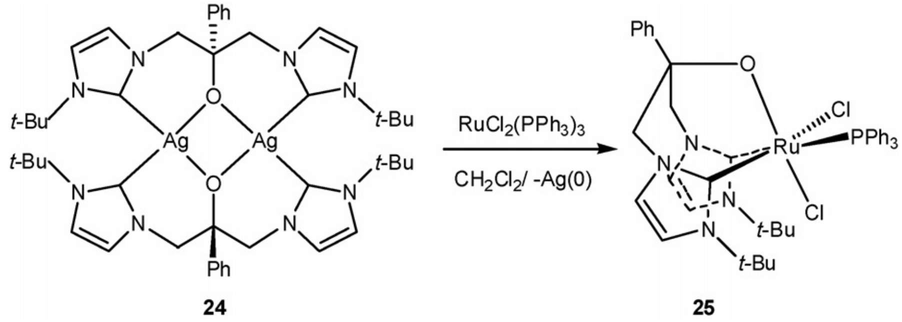
Scheme 20.



Scheme 21.



Scheme 22.



Scheme 23.

nation of the ligand precursor was achieved via transmetallation from a silver NHC complex. The reaction between complex **24** and $RuCl_2(PPh_3)_3$ afforded a tripod Ru(III) complex (**25**, Scheme 23) and a dark precipitate of silver metal, which confirms that Ru(II) has been oxidized by the silver(I) NHC compound.

5. Chiral chelate biscarbene compounds

Given the potential application in homogeneous catalysis, the design of chiral NHC ligands for use in asymmetric catalysis has been an area of significant interest. Herrmann et al. developed the first examples of chiral NHC ligands in 1996 [70]. These were obtained by introducing N-substituents containing a centre of chirality and successfully coordinated to Rh(I). The new catalysts obtained gave good activity but moderate enantioselectivities (32% e.e.) in the hydrosilylation of acetophenone [70]. A few years later, Burgess and co-workers were able to obtain the first complexes giving high enantioselectivities using bidentate oxazoline-imidazolylidene ligands [71]. Since then, the area has grown dramatically and several chiral NHC-based complexes have been described and reviewed [72]. Regarding bis-NHC complexes, most of the chiral complexes possess a C_2-symmetry, and these are reviewed here.

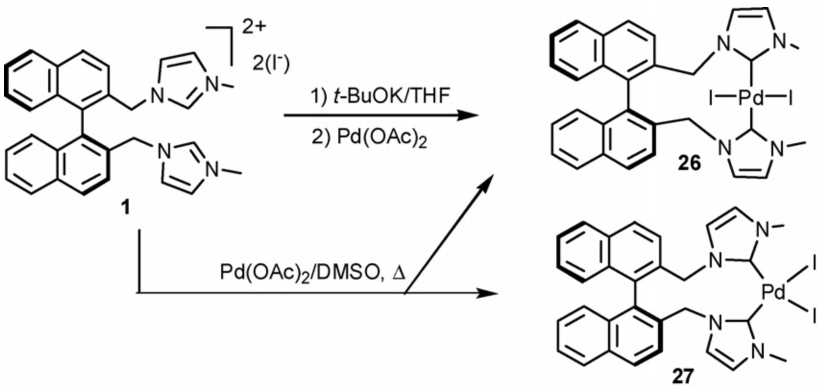
In 2000, RajanBabu described the first chelate *N*-heterocyclic biscarbene ligand with a 2,2′-binaphtyl backbone and its coordination to Pd(II) and Ni(II) [11]. Depending on the deprotonation method used, the coordination to Pd(II) of the binaphtyl bisimidazolium salt, **1** (Scheme 2), gave different compounds. The *in situ* deprotonation of the salt with *t*-BuOK followed by reaction with $Pd(OAc)_2$, gave the *trans* isomer, **26**, while direct reaction of the salt with the metal complex in DMSO at reflux gave a mixture of the *cis*-(**27**) and *trans* isomers (Scheme 24). Either the direct reaction of **1** with $Ni(acac)_2$ or the reaction of the preformed free ligand with $(Ph_3P)_2NiCl_2$ gave the *trans* isomer.

A more rigid biscarbene ligand has been described and successfully coordinated to rhodium by Shi and co-workers [73]. As depicted in Scheme 25, the reaction of the imidazolium precursor **28** with $[RhCl(COD)]_2$ in the presence of a weak base such as NaOAc and an excess of KI, gave hexacoordinate Rh(III) complex **29**.

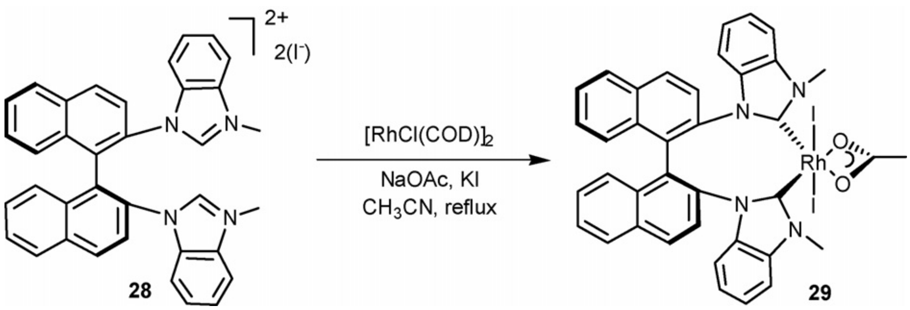
Another methodology to develop chiral-NHC ligands consists of the use of a *trans*-cyclohexadiamine backbone, which bridges both carbene units. Imidazolium salt **30** (Scheme 26) was coordinated to Pd(II) by transmetallation from a silver NHC complex, but unfortunately there are no reports of its catalytic activity [74].

Using the same strategy, a new C_2-symmetric biscarbene ligand was obtained. The chiral bisimidazolium salt **32** reacted with Ag_2O affording the dinuclear compound **33**, which reacts with $PdCl_2(CH_3CN)_2$ to provide the chiral palladium complex **34** (Scheme 27) [12].

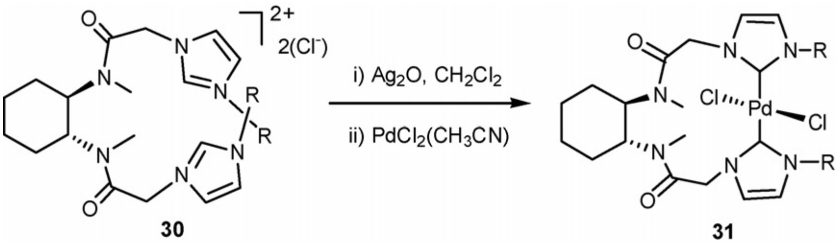
Harrison and co-workers prepared a series of chiral NHC complexes introducing different chiral backbones between the carbene units. They reported the synthesis and structure of *cis*/*trans*-benzimidazole-2-ylidene Pd(II) complexes based on a *trans*-2,2′-dimethyl-1,3-dioxalane backbone. The *cis*-biscarbene palladium(II) complex **35** (Scheme 28) was



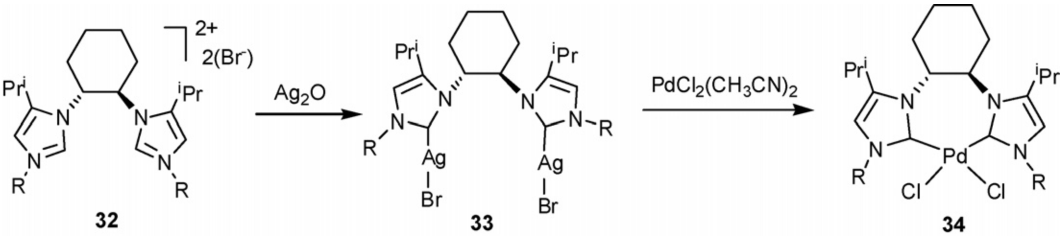
Scheme 24.



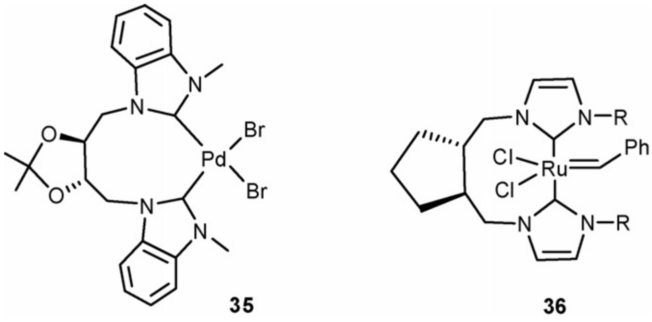
Scheme 25.



Scheme 26.



Scheme 27.



Scheme 28.

obtained by reaction of the bis-benzimidazolium precursor with Pd(OAc)$_2$ in hot DMSO [75]. The same group described the air-stable NHC chelating ruthenium alkylidene complex **36** (Scheme 28), with a chiral cyclopentane backbone, which can potentially be an effective catalyst in asymmetric metathesis reactions [76].

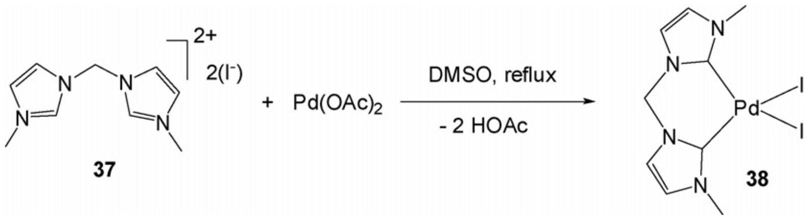
6. Catalytic applications

Several catalytic applications of NHC-based complexes have been described showing the great versatility of this kind of ligands, and these have been reviewed recently [4,6,77]. Here, we present a more detailed account of the catalytic applications of chelate biscarbene complexes. In general, biscarbene complexes present some advantages; the strong M–C$_{\text{carbene}}$ bond, together with the chelate effect, enhance their stability, thus preventing degradation of the catalyst allowing the use of harsher reaction conditions in most cases.

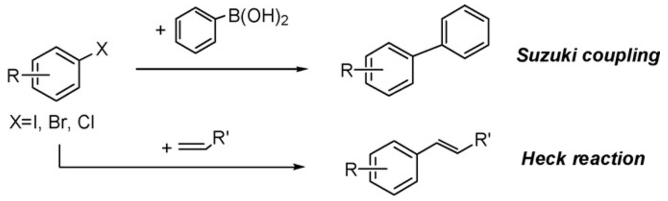
6.1. Heck and related C–C bond formation reactions

Bis(*N*-alkylimidazolium) salts were first coordinated to Pd, allowing the preparation of a new family of very efficient catalysts in C–C coupling reactions. The first chelating biscarbene complex used in catalysis was described by Herrmann et al. in 1995 [5]. The reaction of the ligand precursor **37** with Pd(OAc)$_2$ in DMSO at reflux, with the loss of two equivalents of acetic acid, afforded the Pd(II) complex **38** (Scheme 29) [78]. As a result of the exceptionally stable M–C$_{\text{carbene}}$ bond formed and the chelation of the biscarbene ligand, this compound displayed extraordinary stability to heat, air, and moisture.

Compound **38** was tested as a catalyst in the Heck reaction and Suzuki coupling (Scheme 30) at temperatures of up to 140 °C. High activities were achieved in the Heck coupling of bromoarenes, even when low catalyst loadings (0.1–1 mol%)



Scheme 29.

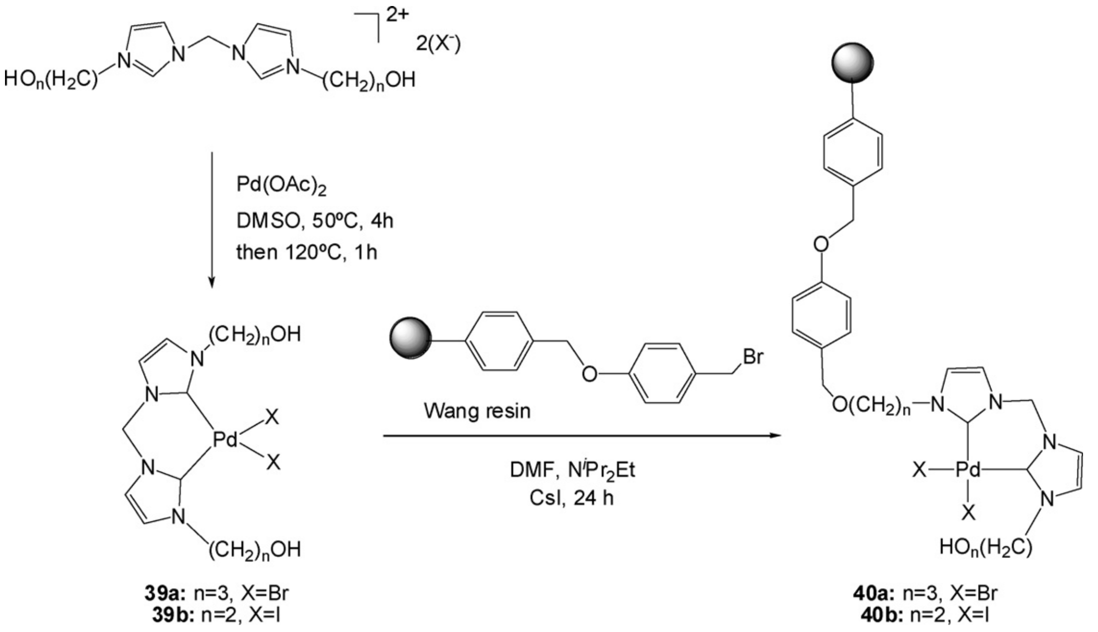


Scheme 30.

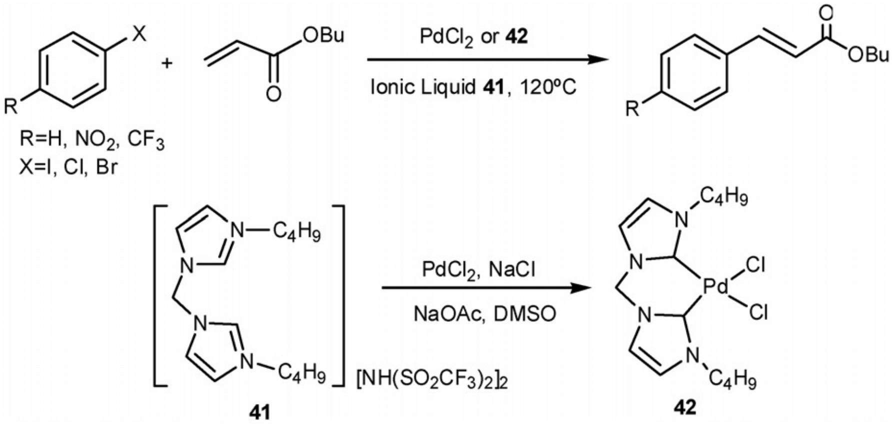
were used. However, only moderate activity was observed in the case of chloroarenes. Compound **38** was also active for the Suzuki coupling of a wide variety of bromoarenes and also one acceptor-substituted chloroarene, 4-chloroacetophenone. Although the catalytic activity displayed by compound **38** is comparable to other phosphine-based analogue complexes, its greater stability allows the reactions to be carried out at higher temperatures so that reaction rates can be enhanced [78].

The high stability of related chelate palladium compounds was also applied in the preparation of polymer-supported catalysts [43]. As depicted in Scheme 31, the biscarbene palladium(II) dihalide complexes **39** were attached to a *p*-bromomethylphenyl functionalized polystyrene (Wang resin) through an ether linkage. Solid-state ^{13}C NMR spectra of the palladium-loaded polymers **40** confirmed the presence of the carbene ligand system. The biscarbene complexes **39** and their heterogeneous counterparts, **40**, showed excellent activities in the Heck reaction. The high stability of these complexes allowed performing the reactions in the presence of air, at temperatures of up to 170 °C. After optimization of the reaction conditions, separation, and washing of the solids, the supported catalysts could be reused under the same reaction conditions. For example, in the case of the coupling of *p*-bromobenzene and styrene, the heterogeneous catalyst **40a** could be reused 15 times without detectable loss of activity.

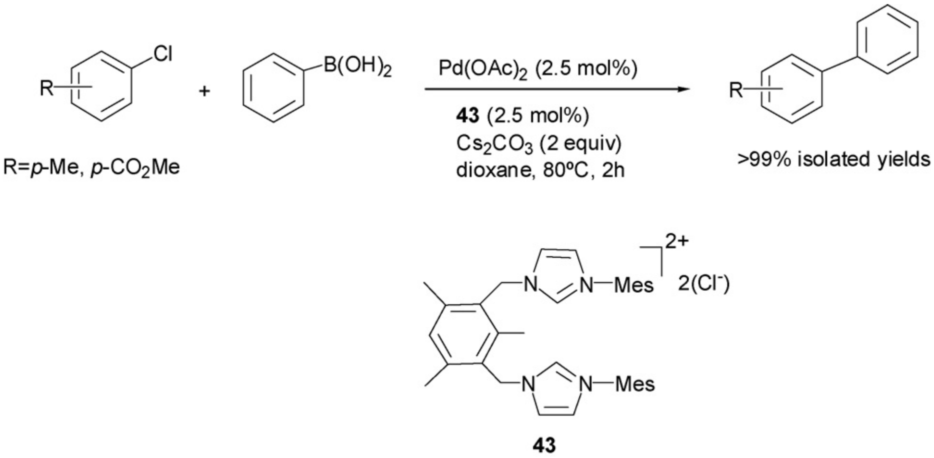
Another interesting example dealing with recyclable catalysts was recently reported by Shreeve and co-workers [79]. In this case, imidazolium-based ionic liquids were used as reaction media and also applied in Pd-catalyzed cross-coupling reactions. Because of its low melting point (−51 °C) and its high thermal decomposition point (412 °C), the bisimidazolium salt **41** (Scheme 32) falls into the ionic liquid class. The Heck reactions of aromatic halides with butyl acrylate were evaluated. Either $PdCl_2$ or complex **42** (1 mol% loading) were used with ionic liquid **41** as solvent and at 120 °C (Scheme 32). Although moderate results were obtained in the coupling of bromoarenes (up to 70% yield), the recovered ionic liquid could be reused three times without significant loss of activity and the yield slightly increased when the isolated complex **42** was used. Unfortunately, both catalytic systems failed in the activation of chloroarenes.



Scheme 31.



Scheme 32.

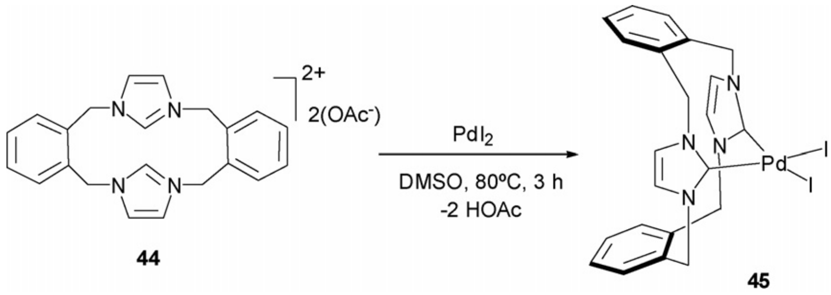


Scheme 33.

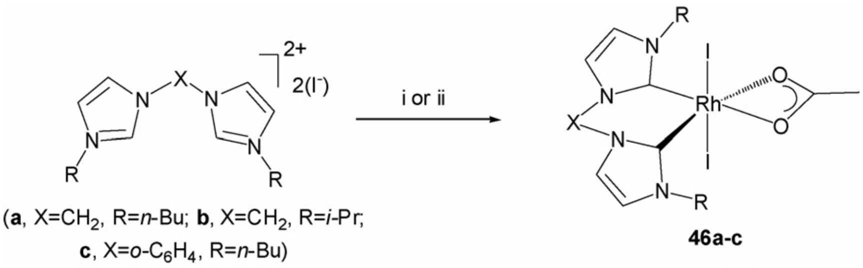
Trudell and co-workers also studied the activity of different palladium biscarbene complexes as catalysts for Suzuki cross-coupling reactions of aryl chlorides with arylboronic acids [80]. Remarkably, the Pd(OAc)$_2$/**43** catalyst system was found to be highly efficient in coupling a wide variety of aryl chlorides. Both electron-donating and electron-withdrawing substituents were well tolerated by the catalytic system and afforded the desired bis-aryl products in excellent yields (Scheme 33).

More rigid biscarbene metal complexes were described and successfully applied in cross-coupling reactions [81]. These complexes, derived from imidazolium-linked *ortho*-cyclophane salts, showed extraordinary stability to air and heat resulting from the increased rigidity imposed by the cyclophane skeleton. Palladium–cyclophane complex **45** (Scheme 34) was tested under standard Heck conditions and showed good activities (TONs of up to 7×10^6) in the coupling of iodobenzene and butyl acrylate to give the corresponding *trans*-stilbene. Moderate results were obtained in the coupling of activated bromoarenes with alkenes.

A series of palladium ethylene-linked biscarbene complexes was described by Lee et al. [82]. Their activity in Suzuki coupling reactions was studied and compared to that

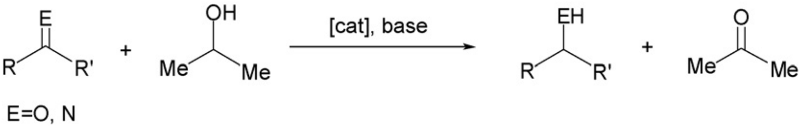


Scheme 34.



46a-c

Scheme 35. Synthetic routes: (i) $[RhCl(COD)]_2$, NaOAc, KI, refluxing EtCN; (ii) $[Rh(OAc)_2]_2$, refluxing CH_3CN.



Scheme 36.

shown by their methylene-linked analogues. For the coupling of electron-deficient bromoarenes with phenylboronic acid, ethylene-bridged complexes displayed better activities than the methylene-bridged ones. Both ethylene and methylene linked biscarbene complexes showed high activity in the Heck coupling reactions between styrene and aryl halides. The two complexes were able to activate aryl chlorides, although long reaction times (24 h) and high catalyst loadings (3 mol%) were required [82].

6.2. *Transfer hydrogenation*

The extension of the coordination of biscarbene ligands to Rh and Ir has afforded the preparation of new complexes that are highly active in a wide variety of interesting catalytic reactions. We described the synthesis of the first chelate biscarbene complex of rhodium in 2002 [8]. The reaction of various bisimidazolium salts with $[RhCl(COD)]_2$ and NaOAc in refluxing EtCN or with $[Rh(OAc)_2]_2$ in refluxing CH_3CN, afforded the air stable Rh(III) complexes **46a–c**, as shown in Scheme 35 [8,49].

Complex **46b** was tested in transfer hydrogenation of ketones and imines in *i*-PrOH (Scheme 36), showing good activities. The hydrogenation of aromatic ketones was faster than for aliphatic ketones. N-substituted benzylidene imines were also converted to the corresponding amines but the rates were significantly slower than for ketones.

Using the same direct metallation protocol, the analogous air stable Ir(III) complexes were obtained (complexes **6** in Scheme 16) [9]. The biscarbene iridium complexes performed better as hydrogen transfer catalysts than their Rh(III) analogues. By far the most efficient catalyst is the *neo*-pentyl complex, which hydrogenates benzophenone almost quantitatively in only 4 min, with a turn over frequency at 50% conversion of $5 \times 10^4\,h^{-1}$. The activity of this complex is comparable to the most active ketone transfer hydrogenation catalysts described to date [83].

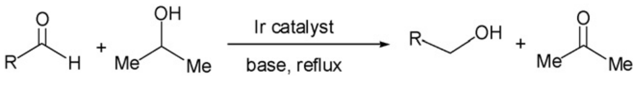
Similar *neo*-pentyl substituted iridium complexes have been successfully employed in hydrogen transfer of aldehydes using alkali-metal carbonates as co-catalysts (Scheme 37) [84]. The best results were obtained using K_2CO_3 as co-catalyst; for example, 2-naphthaldehyde was hydrogenated almost quantitatively in 20 min using a catalyst loading of 0.1 mol%.

Rhodium(III)–tripod complex **22** (Scheme 22) is highly active in ketone and imine transfer hydrogenation. In this case, aryl and alkyl ketones were converted to the corresponding alcohols in good yields after 2 h with catalyst loadings of 0.1 mol%. Noteworthy, lower catalyst loading of **22**, such as 10^{-3} mol%, still are efficient enough to catalyse the reduction of ketones in high yields. Turn over numbers of 50.000–70.000 were achieved in these latter conditions for the hydrogenation of benzophenone and cyclohexanone. These rates are considerably higher than those of the related biscarbene complexes **46** and are among the highest reported for this reaction using a rhodium catalyst. Imines were also hydrogenated to the corresponding amines, although the reactions were slower.

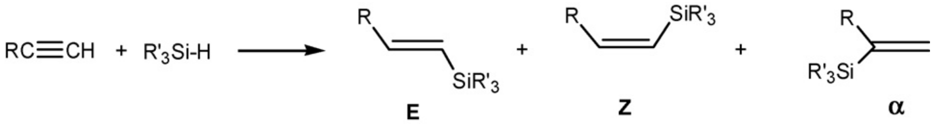
6.3. *Hydrosilylation of terminal alkynes*

The hydrosilylation of terminal alkynes (Scheme 38) represents a useful class of catalytic processes to functionalize organic molecules. Most recent efforts in the study of catalytic hydrosilylation concern to the design of new and efficient catalysts, which enable the preparation of both (*Z*)- and (*E*)-alkenylsilanes independently.

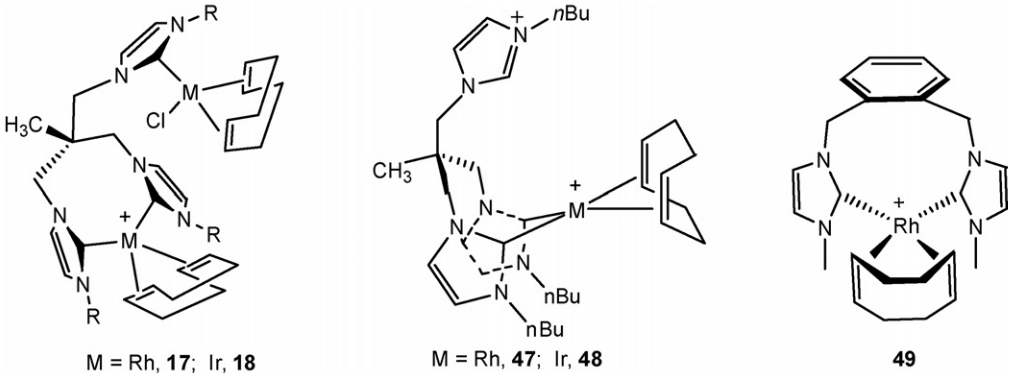
In this context, cationic Rh(I) complexes **17** (Scheme 21), **47** and **49** (Scheme 39) and Ir(I) complexes **18** (Scheme 21) and **48** (Scheme 39) reported by our group, were tested in this reaction since they display both the structural and the chemical requirements for this catalytic process [51,62]. The reactions were performed using phenylacetylene and 1-hexyne as substrates and different silanes such as $HSiMe_2Ph$ or $HSi(OEt)_3$. It is noteworthy that all the reactions were carried out without any special attention to exclude air, since the catalysts proved to be



Scheme 37.



Scheme 38.



Scheme 39.

fairly stable under oxygen-containing atmospheres, even at high temperatures.

For all the reactions studied, all the catalysts used gave mixtures of the *E*, *Z* and *α* isomers. In many metal-catalyzed hydrosilylations, the regioselectivity is capriciously affected by factors such as the type of alkynes and silanes, catalyst, solvent and temperature. However, it has been reported that cationic rhodium complexes catalyze the hydrosilylation of alkynes to give *E* vinylsilanes as the major products, while neutral ones tend to preferentially yield *Z* isomers [85]. For the cationic rhodium(I) complexes **17** and **47** [62], the opposite tendency was observed, the *Z* isomer was the major product in all cases studied, although the selectivity was not very high. For the cationic complex **49**, the tendency to yield the *E* isomer was observed and a higher selectivity was obtained when $HSiMe_2Ph$ was used instead of $HSi(OEt)_3$. Rhodium(I) complexes **17** and **47** were much more active than their iridium(I) analogues, **18** and **48**. The dimetallic complexes **17** and **18** showed higher activities than the monometallic complexes, **47** and **48**, probably indicating that the catalytic active site in the former ones is located in the cationic monocarbenic metal fragment of the bimetallic compound [62].

The mononuclear cationic complex **49** also displayed good activities in the hydrosilylation of styrene with $HSi(OEt)_3$ and $HSiMe_2Ph$ [51]. Catalyst loadings of 1 mol% gave quantitative conversions after 72 h at 60 °C, although, again, the selectivities were low.

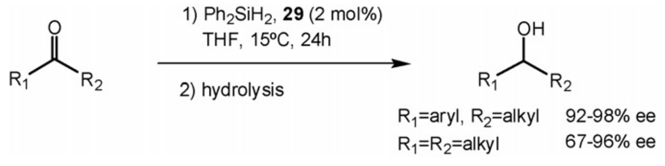
6.4. Asymmetric catalysis with chiral chelate biscarbene complexes

As shown in Section 5, several examples of chiral chelate biscarbene complexes have been described in the last decade. However, only a few of them have been successfully tested in asymmetric transformations. Rhodium(III) compound **29** (Scheme 25), containing a binaphthyl as chiral unit, is the first example of a chiral biscarbene ligand acting as efficient stereodirecting element [73]. It was tested in asymmetric hydrosilylation of ketones (Scheme 40) showing good to excellent yields and enantioselectivities (92–98% e.e.) for aryl alkyl ketones and moderate to excellent enantioselectivities for dialkyl ketones (67–96% e.e.).

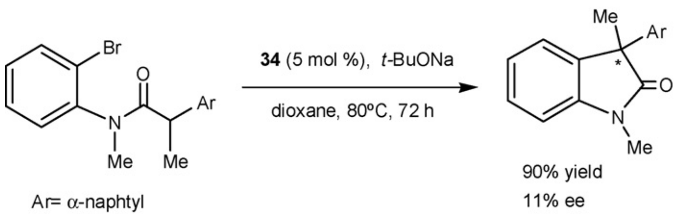
Palladium (II) complex **34** (Scheme 27) containing a *trans*-cyclohexadiamine backbone [12], was tested in asymmetric intramolecular cyclisation of amides to form oxindoles (Scheme 41), showing good activity (90% yield) but very poor enantioselectivity (11% e.e.). This process had been previously reported by Hartwig and co-workers [86].

6.5. Other catalytic reactions

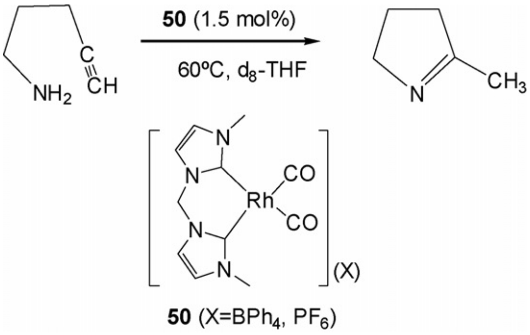
In addition to the reactions already mentioned, several other catalytic applications of chelate biscarbene complexes have been



Scheme 40.



Scheme 41.

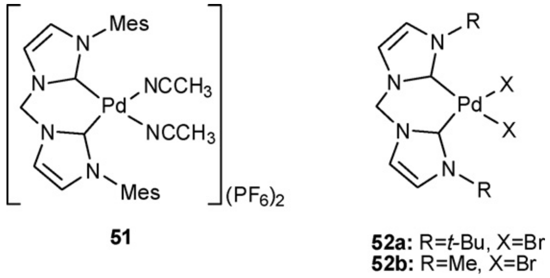


Scheme 42.

explored. For example, mononuclear rhodium(I) biscarbene complexes reported by Field and co-workers were successfully tested in the intramolecular hydroamination of aminoalkynes (Scheme 42) [48]. At a catalyst loading of 1.5 mol%, complex **50** catalyzes the cyclization of 4-pentyn-l-amine to 2-methyl-l-pyrrolidine with conversions of up to 80% after 16 h at 60 °C.

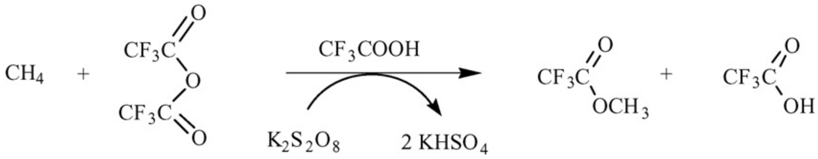
Rh and Ir trinuclear compounds with TIMEN^{Me} ligand (Scheme 21) also displayed good activities in this catalytic test, the Rh complex being among the most active in this type of reaction [66].

Palladium(II)-based biscarbene complexes have also been considered for other catalytic applications. Dicationic complexes such as **51** (Scheme 43) catalyze the copolymerization of C_2H_4 and CO to give high molecular weight, strictly alternating poly(C_2H_4-alt-CO) under mild conditions (50 °C) and low pressure [44].



Scheme 43.

The activity of complexes **52a** and **52b** in the catalytic conversion of methane into methanol was reported by Herrmann and co-workers [87]. These compounds proved to be highly resistant under the acidic conditions required for C–H activation and their high thermal and chemical stability allowed the reactions to be carried out at high temperatures and in the presence of a strong oxidant. A suspension of potassium peroxodisulfate in a mixture of trifluoroacetic acid and its anhydride at a methane pressure of 20–30 bar and 80–90 °C in the presence of a catalytic amount of the palladium complex, afforded the formation of trifluoroacetic acid methyl ester (Eq. (1)).



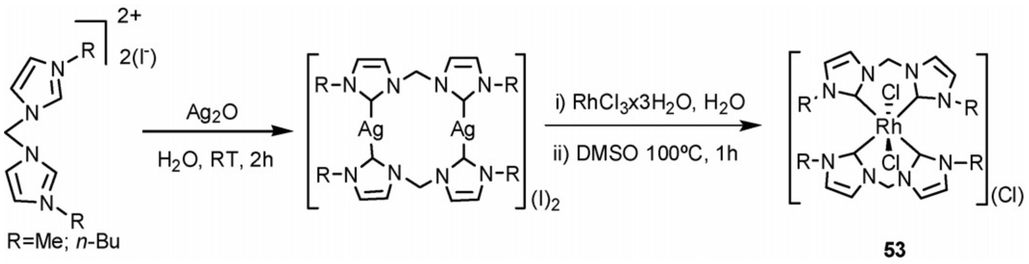
$$CH_4 + (CF_3CO)_2O \xrightarrow[K_2S_2O_8 \;\to\; 2\,KHSO_4]{CF_3COOH} CF_3C(O)OCH_3 + CF_3C(O)OH \quad (1)$$

$$\begin{aligned} CH_4 &\longrightarrow CH_3^{+} + H^{+} + 2e^{-} \\ O_2^{2-} + 2e^{-} &\longrightarrow 2O^{2-} \end{aligned} \quad (2)$$

Potassium peroxodisulfate provides the redox equivalents to balance the conversion of methane (Eq. (2)). In these conditions complexes **52a** and **52b** gave TONs of 500 and 980, respectively, whereas, the catalytic systems of Periana (Pt) and Sheldon (Pd), successfully used for C–H activation of alkanes and arenes, did not show any methane activation. Since the analogues of such complexes with iodide ligands did not show any activity in the activation of methane, the same research group investigated the possibility of an influence of the coligands in the reaction, but this seemed not to have any influence in the reaction output [88].

7. Other applications

Another interesting application of chelating biscarbene complexes was reported by Youngs and co-workers. The biscarbene



Scheme 44.

rhodium(III) complexes **53** were obtained by transmetallation from a silver(I) carbene to $RhCl_3 \cdot 3H_2O$ (Scheme 44) [89]. These complexes may have applications in radiation therapy. ^{105}Rh is an excellent choice for tumor therapy since it has a $t_{1/2}$ of 36.4 h, which is sufficient time to kill tumor cells but short enough to avoid the accumulation of radioactive material in the body. Since ^{105}Rh is only available from $RhCl_3 \cdot 3H_2O$, the easy access to highly stable complexes such as **53** directly from $RhCl_3 \cdot 3H_2O$ (Scheme 44), may make such biscarbene–^{105}Rh complexes appropriate for radiation therapy.

Acknowledgements

We gratefully acknowledge financial support from the MEC of Spain (project CTQ2005-05187), Bancaixa (P1.1B2004-07 and P1.1A2005-04) and Generalitat Valenciana (GV05/107). J. A. M. thanks the Spanish Ramón y Cajal program for a fellowship. M.P. thanks the MEC of Spain for a postdoctoral fellowship.

References

[1] K. Ofele, J. Organomet. Chem. 12 (1968) 42.
[2] H.W. Wanzlick, H.J. Schonher, Angew. Chem. Int. Ed. 7 (1968) 141.
[3] A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.
[4] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1291.
[5] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, G.R.J. Artus, Angew. Chem. Int. Ed. Engl. 34 (1995) 2371.
[6] E. Peris, R.H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239.
[7] E. Peris, R.H. Crabtree, C.R. Chimie 6 (2003) 33.
[8] M. Albrecht, R.H. Crabtree, J. Mata, E. Peris, Chem. Commun. (2002) 32.
[9] M. Albrecht, J.R. Miecznikowski, A. Samuel, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 3596.
[10] C. Kocher, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 261.
[11] D.S. Clyne, J. Jin, E. Genest, J.C. Gallucci, T.V. RajanBabu, Org. Lett. 2 (2000) 1125.
[12] L.G. Bonnet, R.E. Douthwaite, R. Hodgson, Organometallics 22 (2003) 4384.
[13] A.R. Chianese, R.H. Crabtree, Organometallics 24 (2005) 4432.
[14] M.C. Perry, X.H. Cui, M.T. Powell, D.R. Hou, J.H. Reibenspies, K. Burgess, J. Am. Chem. Soc. 125 (2003) 113;
A.A. Gridnev, I.M. Mihaltseva, Synth. Commun. 24 (1994) 1547.
[15] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[16] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 2485.
[17] J.A. Mata, A.R. Chianese, J.R. Miecznikowski, M. Poyatos, E. Peris, J.W. Faller, R.H. Crabtree, Organometallics 23 (2004) 1253.
[18] A.M. Magill, K.J. Cavell, B.F. Yates, J. Am. Chem. Soc. 126 (2004) 8717.
[19] T. Weskamp, V.P.W. Bohm, W.A. Herrmann, J. Organomet. Chem. 600 (2000) 12.
[20] D. Enders, H. Gielen, J. Organomet. Chem. 617 (2001) 70.
[21] D.J. Cardin, B. Cetinkaya, M.F. Lappert, Chem. Rev. 72 (1972) 545.
[22] W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, G.R.J. Artus, Chem. -Eur. J. 2 (1996) 772.
[23] R.E. Douthwaite, D. Haussinger, M.L.H. Green, P.J. Silcock, P.T. Gomes, A.M. Martins, A.A. Danopoulos, Organometallics 18 (1999) 4584.
[24] G.T.S. Andavan, E.B. Bauer, C.S. Letko, T.K. Hollis, F.S. Tham, J. Organomet. Chem. 690 (2005) 5938.
[25] R.E. Douthwaite, M.L.H. Green, P.J. Silcock, P.T. Gomes, J. Chem. Soc. -Dalton Trans. (2002) 1386.
[26] P.B. Hitchcock, M.F. Lappert, P. Terreros, K.P. Wainwright, J. Chem. Soc. -Chem. Commun. (1980) 1180.
[27] M.F. Lappert, J. Organomet. Chem. 358 (1988) 185.
[28] Z.Q. Shi, R.P. Thummel, Tetrahedron Lett. 36 (1995) 2741.
[29] H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972.
[30] P.L. Arnold, Heteroat. Chem. 13 (2002) 534;
I.J.B. Lin, C.S. Vasam, Comments Inorg. Chem. 25 (2004) 75.
[31] Y.A. Wanniarachchi, M.A. Khan, L.M. Slaughter, Organometallics 23 (2004) 5881.
[32] D.S. McGuinness, K.J. Cavell, B.F. Yates, Chem. Commun. (2001) 355;
N.D. Clement, K.J. Cavell, C. Jones, C.J. Elsevier, Angew. Chem. Int. Ed. 43 (2004) 1277.
[33] D.S. McGuinness, K.J. Cavell, B.F. Yates, B.W. Skelton, A.H. White, J. Am. Chem. Soc. 123 (2001) 8317.
[34] M. Viciano, E. Mas-Marza, M. Poyatos, M. Sanau, R.H. Crabtree, E. Peris, Angew. Chem. Int. Ed. 44 (2005) 444.
[35] M. Viciano, M. Poyatos, M. Sanau, E. Peris, A. Rossin, G. Ujaque, A. Lledos, Organometallics 25 (2006) 1120.
[36] D.S. McGuinness, W. Mueller, P. Wasserscheid, K.J. Cavell, B.W. Skelton, A.H. White, U. Englert, Organometallics 21 (2002) 175;
W.A. Herrmann, V.P.W. Bohm, C.W.K. Gstottmayr, M. Grosche, C.P. Reisinger, T. Weskamp, J. Organomet. Chem. 617 (2001) 616.
[37] A.R. Chianese, X.W. Li, M.C. Janzen, J.W. Faller, R.H. Crabtree, Organometallics 22 (2003) 1663.
[38] G. Bertrand, E. Diez-Barra, J. Fernandez-Baeza, H. Gornitzka, A. Moreno, A. Otero, R.I. Rodriguez-Curiel, J. Tejeda, Eur. J. Inorg. Chem. (1999) 1965.
[39] E. Diez-Barra, J. Guerra, V. Hornillos, S. Merino, J. Tejeda, J. Organomet. Chem. 690 (2005) 5654.
[40] F.E. Hahn, M. Foth, J. Organomet. Chem. 585 (1999) 241.
[41] W.A. Herrmann, J. Schwarz, M.G. Gardiner, M. Spiegler, J. Organomet. Chem. 575 (1999) 80.
[42] W.A. Herrmann, V.P.W. Bohm, C.P. Reisinger, J. Organomet. Chem. 576 (1999) 23.
[43] J. Schwarz, V.P.W. Bohm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. -Eur. J. 6 (2000) 1773.
[44] M.G. Gardiner, W.A. Herrmann, C.P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239.
[45] W.A. Herrmann, J. Schwarz, M.G. Gardiner, Organometallics 18 (1999) 4082.
[46] W.P. Fehlhammer, T. Bliss, U. Kernbach, I. Brudgam, J. Organomet. Chem. 490 (1995) 149.
[47] K. Ofele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1.
[48] S. Burling, L.D. Field, H.L. Li, B.A. Messerle, P. Turner, Eur. J. Inorg. Chem. (2003) 3179.
[49] M. Poyatos, M. Sanau, E. Peris, Inorg. Chem. 42 (2003) 2572.
[50] J.A. Mata, E. Peris, C. Incarvito, R.H. Crabtree, Chem. Commun. (2003) 184.
[51] M. Poyatos, E. Mas-Marza, J.A. Mata, M. Sanau, E. Peris, Eur. J. Inorg. Chem. (2003) 1215.
[52] M. Poyatos, E. Mas-Marza, M. Sanau, E. Peris, Inorg. Chem. 43 (2004) 1793.
[53] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polyrazolylborate Ligands, Imperial College Press, London, 1999.
[54] R.R. Schrock, Acc. Chem. Res. 30 (1997) 9.
[55] J. Zhou, Y. Tang, Chem. Soc. Rev. 34 (2005) 664.
[56] R. Frankell, C. Birg, U. Kernbach, T. Habereder, H. Noth, W.P. Fehlhammer, Angew. Chem. Int. Ed. 40 (2001) 1907.
[57] R. Frankel, U. Kernbach, M. Bakola-Christianopoulou, U. Plaia, M. Suter, W. Ponikwar, H. Noth, C. Moinet, W.P. Fehlhammer, J. Organomet. Chem. 617 (2001) 530.
[58] H.V.R. Dias, W.C. Jin, Tetrahedron Lett. 35 (1994) 1365.
[59] H. Nakai, Y.J. Tang, P. Gantzel, K. Meyer, Chem. Commun. (2003) 24.
[60] X.L. Hu, I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. 125 (2003) 12237.
[61] X. Hu, I. Castro-Rodriguez, K. Meyer, Organometallics 22 (2003) 3016;
X.L. Hu, Y.J. Tang, P. Gantzel, K. Meyer, Organometallics 22 (2003) 612.
[62] E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, Inorg. Chem. 43 (2004) 2213.

[63] X. Hu, K. Meyer, J. Am. Chem. Soc. 126 (2004) 16322;
X.L. Hu, I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. 126 (2004) 13464.

[64] X.L. Hu, I. Castro-Rodriguez, K. Meyer, Chem. Commun. (2004) 2164.

[65] X.L. Hu, K. Meyer, J. Organomet. Chem. 690 (2005) 5474.

[66] E. Mas-Marza, E. Peris, I. Castro-Rodriguez, K. Meyer, Organometallics 24 (2005) 3158.

[67] E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, Organometallics 23 (2004) 323.

[68] E. Mas-Marza, M. Sanau, E. Peris, J. Organomet. Chem. 690 (2005) 5576.

[69] P.L. Arnold, A.C. Scarisbrick, Organometallics 23 (2004) 2519.

[70] W.A. Herrmann, L.J. Goossen, C. Kocher, G.R.J. Artus, Angew. Chem. Int. Ed. Engl. 35 (1996) 2805.

[71] M.T. Powell, D.R. Hou, M.C. Perry, X.H. Cui, K. Burgess, J. Am. Chem. Soc. 123 (2001) 8878.

[72] V. Cesar, S. Bellemin-Laponnaz, L.H. Gade, Chem. Soc. Rev. 33 (2004) 619;
M.C. Perry, K. Burgess, Tetrahedron: Asymmetry 14 (2003) 951.

[73] W.L. Duan, M. Shi, G.B. Rong, Chem. Commun. (2003) 2916.

[74] M.C. Perry, X.H. Cui, K. Burgess, Tetrahedron: Asymmetry 13 (2002) 1969.

[75] C. Marshall, M.F. Ward, W.T.A. Harrison, Tetrahedron Lett. 45 (2004) 5703.

[76] C. Marshall, M.F. Ward, W.T.A. Harrison, J. Organomet. Chem. 690 (2005) 3970.

[77] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C.L. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.

[78] W.A. Herrmann, C.P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.

[79] C.M. Jin, B. Twamley, J.M. Shreeve, Organometallics 24 (2005) 3020.

[80] C.M. Zhang, M.L. Trudell, Tetrahedron Lett. 41 (2000) 595.

[81] M.V. Baker, B.W. Skelton, A.H. White, C.C. Williams, J. Chem. Soc. - Dalton Trans. (2001) 111.

[82] H.M. Lee, C.Y. Lu, C.Y. Chen, W.L. Chen, H.C. Lin, P.L. Chiu, P.Y. Cheng, Tetrahedron 60 (2004) 5807.

[83] G. Zassinovich, G. Mestroni, S. Gladioli, Chem. Rev. 92 (1992) 1051;
P. Dani, T. Karlen, R.A. Gossage, S. Gladiali, C. van Koten, Angew. Chem. Int. Ed. 39 (2000) 743.

[84] J.R. Mecznikowski, R.H. Crabtree, Organometallics 23 (2004) 629.

[85] J.W. Faller, D.G. D'Alliessi, Organometallics 21 (2002) 1743.

[86] S. Lee, J.F. Hartwig, J. Org. Chem. 66 (2001) 3402.

[87] M. Muehlhofer, T. Strassner, W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1745.

[88] T. Strassner, M. Muehlhofer, A. Zeller, E. Herdtweck, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 1418.

[89] C.A. Quezada, J.C. Garrison, M.J. Panzner, C.A. Tessier, W.J. Youngs, Organometallics 23 (2004) 4846.