

# Complexes with Poly(N-heterocyclic carbene) Ligands: Structural Features and Catalytic Applications

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## 1. Introduction

The continuous growth of N-heterocyclic carbene (NHC) chemistry is a fact that is pointed out in all the introductions of the publications regarding NHCs that have appeared in the past decade. Two main scientific achievements may have constituted the initial spur to this growth: (i) the first use by Herrmann and co-workers of NHC complexes in catalysis<sup>1</sup> and (ii) the preparation of the Grubbs' second generation catalyst and related catalysts,<sup>2</sup> which undoubtedly had its contribution in the award of the Nobel Prize for Chemistry 2005.

Without disregarding Lappert's<sup>3</sup> and Wanzlick's<sup>4</sup> pioneering works on the preparation of NHC–metal complexes, we may consider that the isolation of thermally stable carbenes by Arduengo in 1991<sup>5</sup> and the statement made by Herrmann that the use of N-heterocyclic carbenes constitutes “a new structural principle for catalysts design in homogeneous catalysis” in 1995,<sup>1</sup> established a new renaissance of these ligands that may now be considered in its early adolescence. With a full set of great scientific achievements on their back, NHCs are still far from being fully explored, and great potential can be envisaged not only in the homogeneous metal-catalysis field but also in organocatalysis,<sup>6</sup> design of metal-based drugs,<sup>7</sup> and other potential applications that can lead NHCs to their maturity.

Chemical stability and coordination versatility are two of the many properties of NHCs that may have helped their great development. The easy preparation of NHC-precursors has allowed an almost infinite access to new organometallic topologies, in which the only limitation seems to be the imagination of the researchers. Apart from the most widely used NHCs, imidazolylidenes (let us call them *normal*-NHCs), a wide set of other N-heterocyclic frameworks has allowed the preparation of carbenes in which the electronic and steric parameters can be modified compared with the normal ones. This may include not only the variety of five-membered ring carbenes (*abnormal*-NHCs, pyrazolylidenes, triazolylidenes, tetrazolylidenes, benzoimidazolylidenes, etc.) but also six-<sup>8</sup> and even four-<sup>9</sup> and seven-membered rings.<sup>10</sup> Scheme 1 depicts some of the known NHC frameworks.

NHCs have been widely studied from any possible point of view, including their preparation,<sup>11,12</sup> stability,<sup>13</sup> stereo-electronic properties,<sup>14,15</sup> coordination strategies,<sup>12,16,17</sup> and use in homogeneous<sup>18</sup> and asymmetric catalysis,<sup>19</sup> and some

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Macarena Poyatos graduated in Chemistry in 2001 at Jaume I University (Castellón, Spain). She received her Ph.D. Degree with honors (2005) at Jaume I University, under the supervision of Prof. Eduardo Peris. She then moved to Strasbourg as a postdoctoral fellow and worked in the synthesis and coordination of chiral oxazoline-based ligands and asymmetric catalysis, under the supervision of Prof. Lutz H. Gade and Dr. Stéphane Bellemin-Laponnaz. In 2006, she joined Prof. Robert H. Crabtree's group at Yale University, where she stayed for two years, working on the use of organic liquids for hydrogen storage and design of new NHC ligands. In 2008, she returned to Jaume I University with the "Juan de la Cierva" program (2008–2010). Her research interest focuses on the development of new and improved homogeneous catalysts for C–H activation processes, and the study of the potential biomedical applications of NHC-based complexes.



Jose A. Mata was born in Vila-real, Castellón, in 1974. He received a B.S. in chemistry from University of Valencia (1997) and completed his Ph.D. with honors at University Jaume I under the supervision of Prof. Eduardo Peris in 2002 where he worked on functionalized ferrocenes with nonlinear optical properties (NLO). He was a postdoctoral fellow at Yale University with Prof. Robert Crabtree (2002–2003) working on rhodium complexes with N-heterocyclic carbene ligands. In 2004, he moved to Toulouse as a postdoctoral fellow at the Laboratoire de Chimie de Coordination (CNRS) with Prof. Rinaldo Poli and worked on atom transfer radical polymerization (ATRP). He returned to University Jaume I with the "Ramón y Cajal" program (2005–2008) and became Assistant Professor of chemistry in 2008. His research interests are focused on the development of new catalytic processes based on metal complexes with N-heterocyclic carbene ligands.

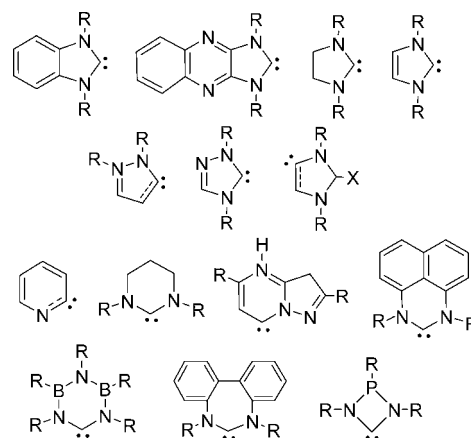
books<sup>20</sup> and journal volumes<sup>21</sup> have been entirely devoted to the chemistry of this type of ligand.

Among NHCs, poly(N-heterocyclic carbene)s have attracted great attention because they allow the preparation of organometallic compounds with a variety of geometries. We now have a wide set of complexes with bis-, tris-, and tetra-NHCs, that can act as bischelating, pincer, tripodal, or bridging ligands, in which the combination with chiral motifs may allow the preparation of asymmetric catalysts. In the search of a rationalized description of the specific coordination modes of



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#### Scheme 1. Some of the NHC Frameworks

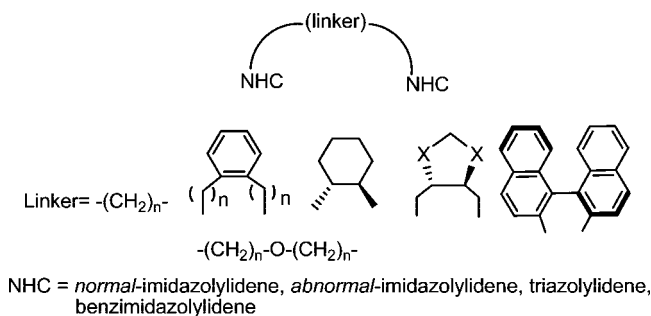


poly-NHCs and their applications in catalysis, some review articles have appeared regarding the properties of bis- and tris-chelating<sup>22</sup> and pincer NHCs,<sup>23,24</sup> thus covering the chemistry of most poly-NHCs that have been described until recently. Still, the development of NHC chemistry is so fast that new achievements are made every year.

This review will concentrate on the properties and catalysis of complexes with poly-NHCs (ligands containing more than one NHC branch) in the period from 2002, but we will focus our attention on the most recent articles (last three years) since some recent reviews have already covered the period until 2006. Some overlap with the already existing related reviews is inevitable, but we will try to cover aspects not reported in previous published articles. For example, all the articles regarding poly-NHCs that have been reported so far deal with either chelating<sup>22</sup> or pincer NHCs,<sup>24,25</sup> while the chemistry of bridging and NHC-based diylidenes has not been considered. These will be covered in this review.

With all this in mind, the present review will focus on the description of the chemistry of poly-NHCs and those structural and electronic aspects that can be related to the

Scheme 2



search of an enhancement of their catalytic properties. The review is subdivided into the following categories: (a) types of poly-NHC ligands, (b) structural properties of coordinated bis-NHC ligands, (c) groups 3–7 metal complexes, (d) group 8 metal complexes, (e) group 9 metal complexes, (f) group 10 metal complexes, (g) group 11 metal complexes, and (h) f-block metal complexes. Each of these categories will focus its attention on the catalytic properties of the complexes comprised therein.

## 2. Types of Poly-NHC Ligands

Attending to their composition (considerations about their coordination capabilities will be discussed later), poly-NHC ligands may be classified as bis-NHCs, tris-NHCs, and tetra-NHCs. Since NHCs can admit other donor-functional groups, the coordination capabilities of these poly-NHCs may not be restricted to the coordination by the carbene fragments only (this means that, for example, we can find many compounds in which biscarbenes are tricoordinated, because the ligand also contains a pyridine, amino, phosphino, alkoxy, aryl, or any other coordinating group).<sup>26</sup>

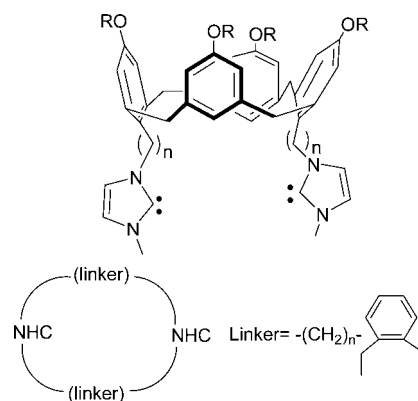
Among those cited above, bis-NHCs are by far the most abundant ones. The first ones to be prepared were those in which the two NHC fragments are bound with an aliphatic linker (Scheme 2).<sup>1,27–36</sup> The easy preparation of this type of ligand has allowed a controlled study of their coordination to metals by modifying the length of the aliphatic linker, and some important implications on the structural properties and reactivity of the resulting products have been extensively researched.<sup>37–41</sup> Other linkers include ethers,<sup>42</sup> amines,<sup>43</sup> or aromatic rings<sup>35,44–47</sup> that provide some rigidity to the bridge and can even introduce  $C_2$ -chirality.<sup>48,49</sup> The properties of these bis-NHCs can also be modified by changing the nature of the NHC, and hence some bistriazolidenes,<sup>50–52</sup> bisimidazolidenes, abnormal-bis-NHCs<sup>53–55</sup> and even mixed normal/abnormal-bis-NHCs<sup>55</sup> have been prepared. Typical frameworks are shown in Scheme 2.

Annularly linked bis-NHCs, including cyclophane<sup>44</sup> and calix[4]arene-based<sup>56</sup> NHCs have also been described, providing interesting coordination modes that result in an increase of the stability to air and heat due to the rigidity imposed by the cyclic structure (Scheme 3).

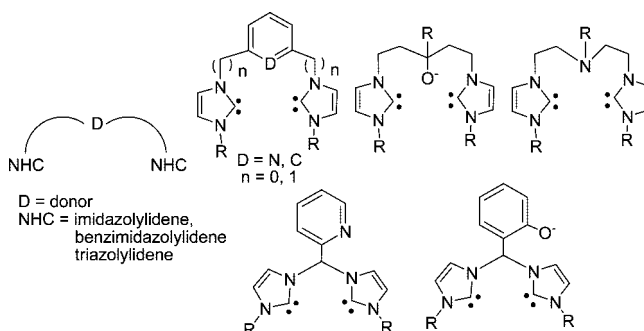
An important class of bis-NHCs is that introducing a donor-functional group between the two carbene edges. P, O, S, N, and C atoms are among the potential donors, and the tris-chelating coordination of these ligands has provided pincer<sup>23</sup> and tripodal<sup>57,58</sup> bis-NHC complexes that have attracted great attention (Scheme 4).

Most of the bis-NHCs described above are often designed to preferentially bind to one metal in a chelating fashion. However, the design of non-chelating bis-NHCs is also of

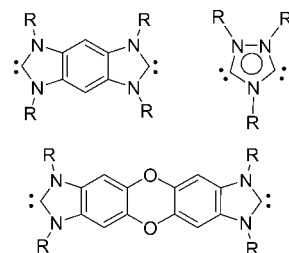
Scheme 3



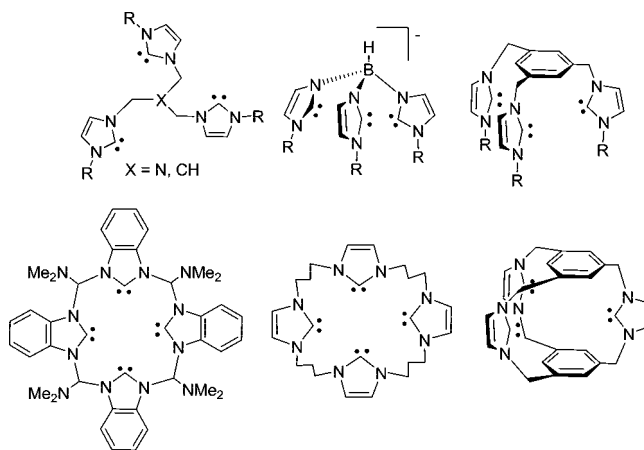
Scheme 4



Scheme 5

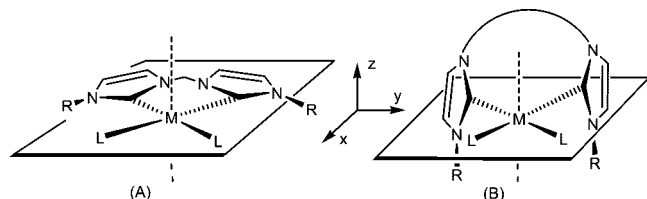


Scheme 6



great interest since this type of ligand can provide bimetallic structures that may lead to new advances in the development of electronic materials.<sup>59</sup> A series of ditopic NHCs have been reported in which the coordination to the same metal is avoided by the linearly opposed disposition of the two carbenes. In this regard, triazolidenes<sup>60,61</sup> and benzobis(imidazolidene)s<sup>62–65</sup> have appeared as interesting scaffolds that





**Figure 1.** Linker length determines the orientation of the azole ring: (A) short linkers (in-plane conformation); (B) long linkers (perpendicular orientation).

can bridge transition metals and provide enhanced electronic and catalytic properties (Scheme 5).

Tris- and tetra-NHCs are less abundant than bis-NHCs. One of the reasons for this may be the complicated multistep synthesis for this type of polycarbene and that the resulting tris- and tetracationic imidazolium salts are often difficult to purify due to their low solubility in most organic solvents. Some of the tris-NHC ligands that have been reported show a  $C_3$ -symmetry through the linkage of the three NHCs to a central  $C(sp^3)$ , amine, or arene (Scheme 6).<sup>66</sup> Just two examples of tetra-NHCs have been reported to date,<sup>67,68</sup> both introducing the NHCs into a macrocyclic structure, as shown in Scheme 6.

### 3. Structural Properties of Coordinated Bis-NHC Ligands

The general principles governing the steric properties of NHCs arise from their fan-shaped profile. When free rotation about the  $M-C$  bond is possible (mostly in mono-NHC ligands), the azole ring is expected to orientate its slim axis to the bulky plane of the complex, minimizing the steric repulsions. When a bis-NHC ligand is used, the ligand can coordinate either to one metal (chelating) or to two metals (bridging), and for each of these two coordination modes, several parameters can affect the orientation of the azole rings.

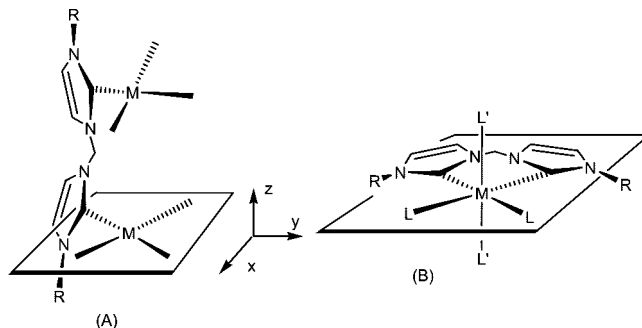
In the chelating coordination form, several structural parameters have to be taken into account, such as the coordination bite angle, the angle between the azole ring and the coordination plane of the complex, and the “in-plane” distortion of the NHC. All these parameters are discussed in this section.

#### 3.1. Chelating versus Bridging Coordination of Bis-NHC Ligands

With the aim to rationalize the preferential chelating or bridging coordination of bis-NHC ligands, several studies have been recently published.<sup>38,41,69,70</sup> When sterically small N-substituents are used (Me, *n*Bu), it seems clear that the main factor that determines the type of coordination of the bis-NHC ligand is the length of the linker between the two azole rings.<sup>38</sup>

For chelate bis-NHC compounds, the rotation about the  $M-NHC$  bond is restricted, so the bulky ligand axis may 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 depends on the linker length, as illustrated by Figure 1. Short linkers (diagram A) force the NHC rings to lie in the  $xy$  plane, while long linkers (diagram B) allow the azole rings to align close to the  $z$ -axis.

In principle, this anisotropic behavior of the bis-NHC ligands determines the reactivity of the metal fragments to



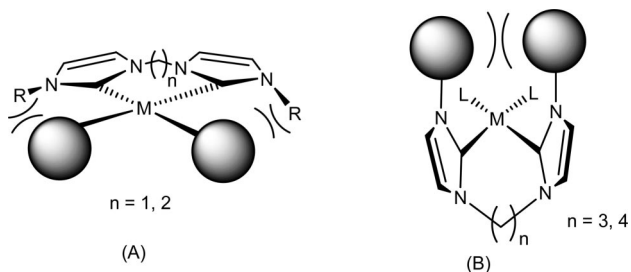
**Figure 2.** (A) Bridging 2:1 (M/L) coordination in square-planar complexes and (B) chelating coordination in an octahedral complex

which they are bound. This effect has been studied in detail for Rh,<sup>38,41</sup> Ir,<sup>40</sup> and Pd<sup>34</sup> complexes. In the case of bis-NHCs with long linkers, if we have a pseudo-square-planar complex with bulky coligands (typically cod or nbd), the bis-chelating coordination of the ligand affords a sterically relieved structure in which the bulky angle of the ligand is oriented toward the unoccupied  $z$ -axis. This means that the coordination of axial ligands to this metal fragment is going to be restricted by the bulkiness of the N-groups of the azole rings. This also prevents the metal from achieving a pseudo-octahedral structure by means, for example, of an oxidative addition, and this has to be taken into account if we plan to use a catalyst in a process that requires an oxidative addition in any of the steps of the catalytic cycle.

On the other hand, bis-NHCs with short linkers force the two azole rings to lie on the sterically crowded plane of the molecule. In the cases that the metal prefers the pseudo-square-planar geometry, the coordination of the bis-NHC can release steric strain by bridging two metal fragments, so that each individual azole ring can now align close to the  $z$ -axis (Figure 2A).

The chelating coordination of bis-NHCs can be achieved if the metal has small coligands (typically CO, halides, CN,  $CH_3CN$ ,  $\eta^2-AcO$ , etc.) that produce a low steric hindrance in the  $xy$  plane. This chelating coordination can be seen in pseudo-square-planar and also in pseudo-octahedral complexes. In the cases where group 9 metals are used, most of the synthetic routes to chelating bis-NHCs start from  $[MCl(cod)]_2$  ( $M = Rh, Ir$ ), so the use of bis-NHCs with short linkers often provides the 2:1 (metal/ligand) species in which the ligand is bridging (Figure 2A). However, for these metals, the oxidation to the +3 oxidation state affords pseudo-octahedral complexes in which the sterically crowded cod ligand is easily substituted by other less sterically demanding ligands (MeCN, AcO, halides, etc) and hence the bis-chelating coordination of the short-linked bis-NHC is allowed (Figure 2, B).

In principle, all the above-mentioned considerations were accepted as valid, until Crabtree and co-workers carried out a more detailed study covering other aspects such as the steric size of the N-substituents (R) and the nature of the counterion.<sup>41</sup> If small R substituents are used, the longer linkers favor chelation due to their ability to avoid the steric clash between R and the other ligands (L). However, when bulkier R groups are used (that is, *t*Bu), longer linkers are expected to bring the two bulky substituents too close to each other. This new steric clash explains why chelation is avoided when long linkers and bulky steric R groups are used, while short linkers and bulky R groups can then form chelates. In



**Figure 3.** (A) Wingtip—ligand ( $R\cdots L$ ) and (B) wingtip—wingtip ( $R\cdots R$ ) steric interactions.

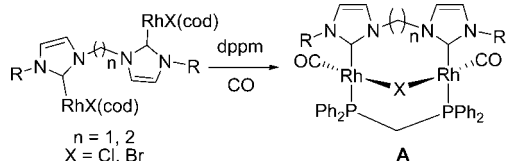
summary, two steric considerations must be taken into account in order to predict the chelation ability of a bis-NHC ligand: (a) the length of the linker between the azole rings and (b) the steric size of the N-substituents ( $R$ ). The steric considerations determine that chelation is possible when both the steric clash between the  $R$  groups and the  $L$  ligand ( $R\cdots L$ ), and that between the two  $R$  groups ( $R\cdots R$ ) are avoided (Figure 3). This dependence of the coordination form of the bis-NHC ligand with the steric bulkiness of the  $R$  groups was earlier proposed by Slaughter and co-workers.<sup>69</sup>

The nature of the anion also affects the formation of either the chelated or the bridged species. This was suggested by Crabtree and co-workers<sup>41</sup> and helped to justify the formation of the chelated bis-NHC compounds with short linkers previously obtained by Slaughter<sup>69</sup> and Field,<sup>70</sup> that otherwise would not fit into the previously discussed reactivity pattern. It has been proposed<sup>41</sup> that the absence of halides in the reaction medium (either by abstraction of the halides in the metal precursors or by directly using a metal precursor without halide ligands) favors the formation of cationic chelate complexes instead of the 2:1 metal/ligand ones. Typical examples to produce the chelate species are the coordination of the bis-NHC ligand by transmetalating the ligand with a  $Ag-NHC$  reagent that does not contain halides and then retains the ability to abstract the halide from the metal precursor<sup>41,69</sup> or use of metal precursors such as  $[M(OR)(cod)]_2$  ( $M = Rh, Ir$ ), which directly provides the non-halide chelate cationic compounds.<sup>70</sup> An additional effect of using halide-free coordination conditions is the avoidance of the oxidative decomposition that tends to occur in the presence of halides. This oxidative decomposition of the four-coordinate  $M(I)$  species often provides six-coordinate  $M(III)$  species. Figure 4 summarizes the different reactivity patterns for the coordination of the bis-NHC ligands under the conditions described in the present section.

These principles can be applied to selectively obtain chelating or bridging coordination forms of complexes containing bis-NHC ligands. For example, with the aim to obtain dirhodium architectures in which the dicarbene and a bisphosphine ligand bridged the two metals forming “A-frame” frameworks, Cowie and co-workers recently used a series of methylene- and ethylene-bridged dicarbenes to prepare complexes **A**, as shown in Scheme 7.<sup>71</sup>

Although the vast majority of examples of chelating bis-NHC ligands refer to their coordination in the *cis* form, there

**Scheme 7**



are several examples describing *trans*-bis-NHC complexes. This type of coordination has been observed mainly for  $Ni^{48}$  and  $Pd^{43,47,48,72}$  complexes, although some  $Ag^{72,73}$  and  $Ru^{74}$  complexes have also been described. Scheme 8 shows some of these compounds. Apart from the examples describing the coordination of tridentate-pincer bis-NHC ligands, in which the two carbenes are forced to adopt a *trans* configuration,<sup>23</sup> the coordination of bidentate bis-NHCs in the *trans* form is achieved only if the rigidity of the bridging tether avoids the coordination in the *cis* form. This rigidity can be introduced by using long chains containing cycles that often provide an additional interest to the resulting complexes by bringing chirality (complexes **B–D** in Scheme 8). An interesting example in which the *trans* coordination of the dicarbene is observed, is the use of bis(imidazolydene)calix[4]arene frameworks (compound **E** in Scheme 8).<sup>75</sup>

## 3.2. Structural Consequences of Chelating Bis-NHCs

The fan-shaped arrangement of the azole rings in bis-NHCs gives rise to a number of structural parameters that are described in detail below.

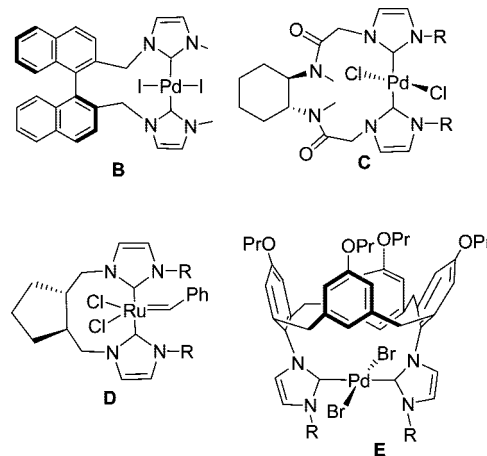
### 3.2.1. Bite Angle

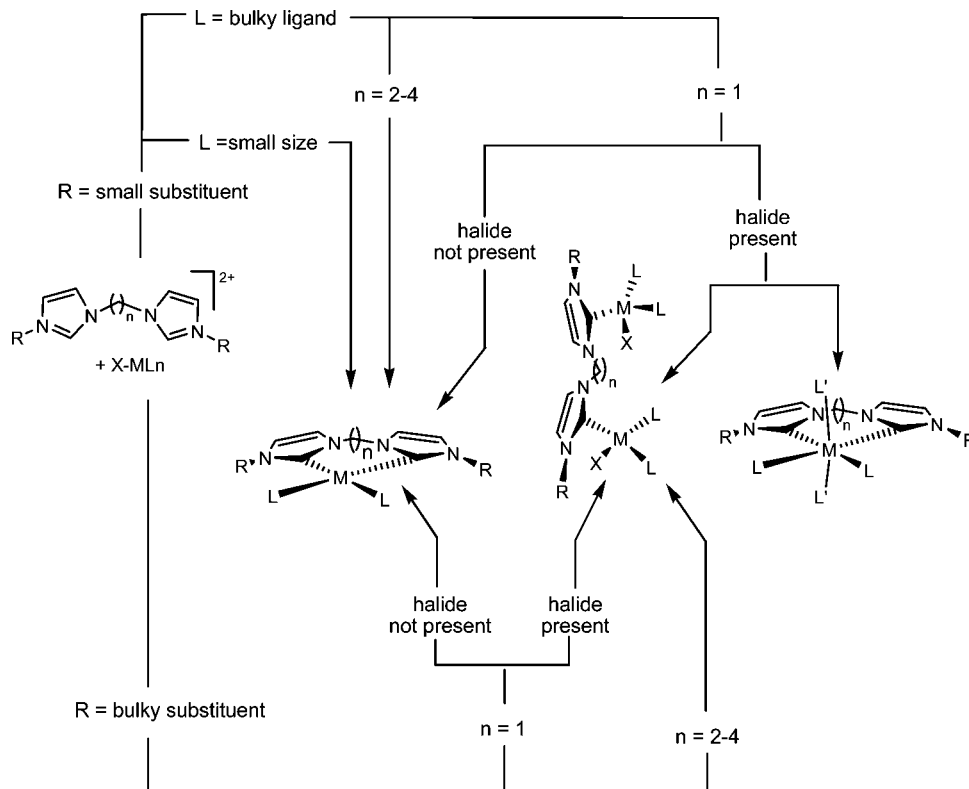
One of the first structural parameters that has to be considered is the coordination bite angle. In the case of chelating bis-NHCs, a systematic study of the variation of the bite angle upon varying the number of methylene groups in the  $-(CH_2)_n-$  bridging chain between the azole rings can be made by taking a close look at the data reported in the literature, which has been recently reviewed.<sup>38,41</sup> With values ranging from  $79.5^\circ$  to  $94^\circ$ , assigned to  $W(0)^{16}$  and  $Ir(I)^{40}$  complexes, respectively, the bite angles strongly depend on the linker length but are also affected by the nature of the coligands, the metal, and its oxidation state (Table 1). Remarkably, the recently described bitriazolyldiene ligand (bitz) with a direct N–N bond linking the azole rings<sup>52</sup> displays the smallest bite angle for a chelating bis-NHC with a value of  $79.1^\circ$  in a  $Pd(II)$  complex.<sup>51</sup>

### 3.2.2. $\alpha$ Angle

The  $\alpha$  angle is defined as the average of the two imidazole ring planes and the  $xy$  plane of the coordination compounds. As observed from the representative data shown in Table 1, this angle strongly depends on the linker length, although

**Scheme 8**





**Figure 4.** Reactivity patterns expected for bis-NHC ligands.

the size of the R wingtips and the geometry of the complexes have an important influence. For the square-planar species with ligands with short linkers (typically  $n = 1$ ),  $\alpha$  is rather large, because of the absence of apical ligands (angles typically ranging from  $40^\circ$  to  $57^\circ$ , entries 3–15). Among these complexes, those with the bulkier wingtips (R) are the ones to show larger  $\alpha$  values, because this affords a situation in which the steric repulsion between the bulky R groups and the other ligands of the complex is minimized. This is exemplified by the data shown in Table 1, where it can be seen that all the complexes with *t*Bu wingtips show  $\alpha$  values above  $55^\circ$  (entries 3, 7, 9, 13, and 14), while other wingtips present values below  $50^\circ$ . Hexacoordinated complexes show lower  $\alpha$  values due to the presence of ligands in the  $\pm z$  direction, with a minimum value of  $11.9^\circ$  for a Rh(III) complex (entry 19). For longer linkers ( $n = 2-4$ ), square-planar complexes are typically formed, and  $\alpha$  ranges from  $63^\circ$  to  $90^\circ$ .

### 3.2.3. $\theta$ (Yaw) Angle

The in-plane distortion of the NHC that Crabtree and co-workers defined as “yaw” distortion<sup>41</sup> (Figure 5) is mainly due to the steric constrain imposed by the formation of the metallacycle. The bis-chelating NHC complexes with shorter linkers show the highest yaw distortions, as can be seen in Table 1. For the directly N–N linked ( $n = 0$ ) biscarbenes (entries 1 and 2),  $\theta$  is  $13^\circ$ . For the complexes with short linkers ( $n = 1$ ), the angle typically ranges from  $4^\circ$  to  $14^\circ$  for square planar complexes, although one exception is found with negligible distortion (entry 11). For these complexes, a clear dependence of  $\theta$  on the size of the R group is found, with higher  $\theta$  values shown for those complexes with *t*Bu wingtips, due to the stronger steric clash of this bulky group with the coligands (Figure 5).

### 3.2.4. M–C Bond Distances

As described above, the plane of the azole ring is inevitably at an angle ( $\alpha$ ) to the coordination plane of the complex. Table 1 shows that this angle varies with the many conditions that have already been described, and it ranges from  $0^\circ$  to  $90^\circ$  without showing any specific preferences at any fixed angle values. It has been long discussed whether the  $\pi$ -interaction between the metal and the NHC would have any participation in the M–NHC bond.<sup>15</sup> If this interaction was important, it would be expected that certain  $\alpha$  values provided a preferential orientation of the  $p_z$  orbital of the carbene carbon to favor the overlapping with the corresponding  $d_{\pi}$  orbital of the metal. This, in turn, implies that at “effective” angles the double bond character of the M–NHC should increase, and hence the M–C bond should be shorter.

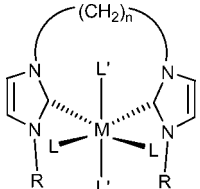
A close analysis of the M–C distances shown in Table 1 shows that it seems that there are not any “preferential”  $\alpha$  values providing any shorter M–C distances. In fact, M–C distances do not seem to vary with any of the structural parameters discussed above. This observation supports the idea of the negligible  $\pi$ -interaction, but it should not be taken as a definitive proof because both the  $\sigma$ - and the  $\pi$ -interactions influence the M–NHC distances. For a more definitive conclusion, a complete deconvulsion of these two factors ( $\sigma$ - and  $\pi$ -contributions) should be clearly established.

## 4. Poly-NHC Ligands in Complexes of Groups 3–7

### 4.1. Preparation and Properties

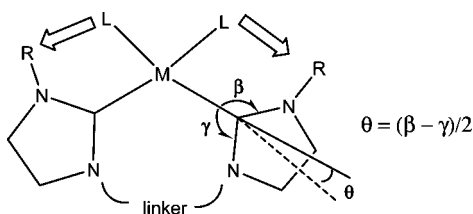
Whereas NHC ligands have been widely used to support late transition metal complexes, early transition metals have been somewhat neglected, and their chemistry is fairly underdeveloped. However, there is an increasing interest in

Table 1. Representative Literature Structural Data on Chelating Biscarbenes



entry	M	linker (n)	R	L	L'	bite angle C-M-C (deg)	$\alpha^a$ (deg)	$\theta^b$ (deg)	M-C (Å)	ref
1	Rh(III)	0	CH <sub>3</sub>	I, CH <sub>3</sub> CN	2 I	79.4	2.3	13	1.977	52
2	Pd(II)	0	CH <sub>3</sub>	CH <sub>3</sub> CN		79.14	1.5	13	1.979	52
3	Ni(II)	1	<i>t</i> Bu	bis-NHC		83.6	55.1	13	1.932	76
4	Ni(II)	1	CH <sub>3</sub>	bis-NHC		86.6	42.5	7	1.909	27
5	Pd(II)	1	CH <sub>3</sub>	2 I		83.2	47.3	8	1.989	77
6	Pd(II)	1	EtOH	2 I		83.6	45.5	6	1.991	78
7	Ni(II)	1	<i>t</i> Bu	Cl, PMe <sub>3</sub>		84.9	57.5	10	1.941	76
8	Pd(II)	1	CH <sub>3</sub>	2 CH <sub>3</sub> CN		84.1	40.2	4	1.966	29
9	Pd(II)	1	<i>t</i> Bu	2 I		83.4	56.4	14	2.004	32
10	Pd(II)	1	CH <sub>3</sub>	bis-NHC		81.8	41.5	0	2.137	79
11	W(0)	1	CH <sub>3</sub>	CO, PPh <sub>3</sub>	2 CO	79.5	30.9	1	2.229	16
12	Rh(I)	1	CH <sub>3</sub>	cod		83.2	45.7	8	2.025	70
13	Rh(I)	1	<i>t</i> Bu	cod		81.5	56.9	14	2.064	41
14	Rh(I)	1	<i>t</i> Bu	2 CO		81.5	53.6	13	2.078	41
15	Rh(I)	1	CH <sub>3</sub>	2 CO		83.5	45.0	7	2.062	70
16	Rh(III)	1	<i>n</i> Bu	CH <sub>3</sub> COO	I, I	87.3	19.7	1	1.976	80
17	Rh(III)	1	CH <sub>3</sub>	2 CH <sub>3</sub> CN	I, I	87.8	26.3	4	2.026	80
18	Ir(III)	1	<i>neo</i> -pentyl	CH <sub>3</sub> COO	I, I	87.2	21.6	1	1.984	81
19	Rh(III)	1	<i>n</i> Bu	CH <sub>3</sub> COO	I, ntc <sup>c</sup>	86.2	11.9	0	1.956	50
20	Pd(II)	2	<i>t</i> Bu	2 CH <sub>3</sub>		88.1	65.2	11	2.079	46
21	Ni(II)	2	<i>t</i> Bu	Cl, PPMe <sub>3</sub>		88.4	70.3	5	1.915	76
22	Pd(II)	1	CH <sub>3</sub>	2 Cl		83.78	49.47	6	1.966	34
23	Pd(II)	2	CH <sub>3</sub>	2 Cl		87.84	57.9	6	1.979	34
24	Pd(II)	3	CH <sub>3</sub>	2 Cl		87.63	74.1	1	1.969	34
25	Pd(II)	4	CH <sub>3</sub>	2 Cl		91.15	70.32	3	1.976	34
26	Rh(III)	<i>o</i> -phenyl	<i>n</i> Bu	CH <sub>3</sub> COO	2 I	92.2	33.4	2	2.000	82
27	Rh(I)	2	<i>n</i> Bu	cod		84.0	63.0	6	2.041	38
28	Rh(I)	3	<i>n</i> Bu	cod		87.6	78.0	3	2.034	38
29	Rh(I)	4	<i>n</i> Bu	2 CO		91.0	84.3	1	2.082	38
30	Rh(I)	<i>o</i> -xylyl	CH <sub>3</sub>	cod		90.6	86.6	3	2.050	37
31	Ir(III)	1	CH <sub>3</sub>	cod	H, Cl	84.6	40.2	7	2.056	40
32	Ir(I)	3	<i>n</i> Bu	cod		84.6	90.5	0	2.039	40
33	Ir(I)	4	CH <sub>3</sub>	cod		94	90.0	1	2.032	40

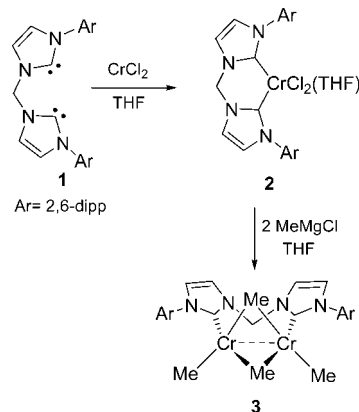
<sup>a</sup> Average of the dihedral angles evaluated using N'-C<sub>carbene</sub>-M-C<sub>carbene</sub>. <sup>b</sup> As defined in Figure 5. <sup>c</sup> ntc = nortricyclyl.

Figure 5. The in-plane (yaw,  $\theta$ ) distortion in coordinated NHCs.

this area, and several homogeneous catalyst systems that combine a Lewis acidic metal cation and an NHC have been recently described.

The first studies on early transition metal complexes bearing NHC ligands were reported by Öfele in 1993.<sup>83</sup> Group 6 biscarbene complexes of the type *cis*-M(CO)<sub>4</sub>(NHC)<sub>2</sub> were synthesized by reaction of the alkoxide precursor K<sub>4</sub>[M<sub>4</sub>(μ<sub>3</sub>-OCH<sub>3</sub>)<sub>4</sub>(CO)<sub>12</sub>] (M = Cr, Mo, W) and the corresponding bisimidazolium salt.<sup>16,83</sup> A few years later, Hahn reported the preparation of a biscarbene tetracarbonyl molybdenum complex that was characterized by X-ray diffraction.<sup>84</sup> In this particular example, the high donor ability of the carbene ligands is clearly illustrated by the different Mo-CO bond lengths of the carbonyls that are *cis* and *trans* to the NHC ligands, although the valuable IR  $\nu$ (CO) stretching frequencies were not reported.

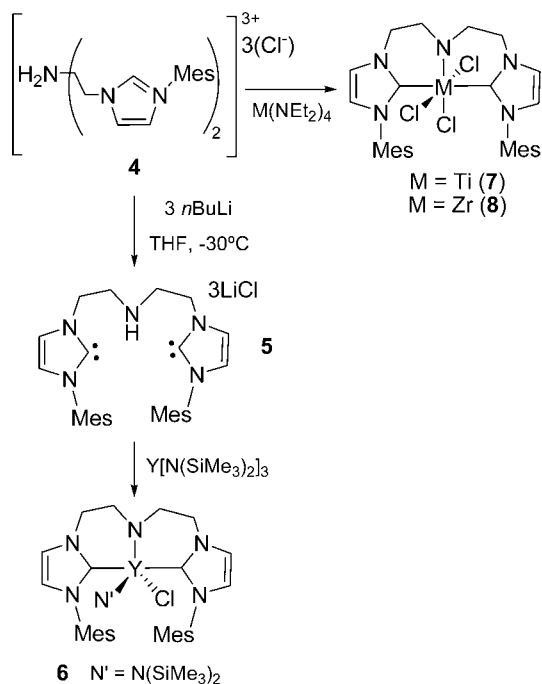
Scheme 9



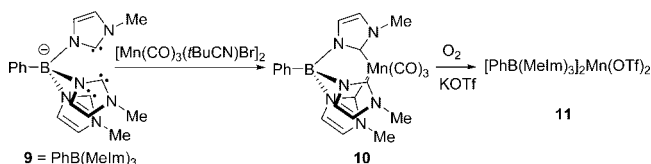
More extensive studies on the preparation of chromium NHC-based complexes were performed by Theopold and co-workers.<sup>85,86</sup> Several Cr(III) and Cr(II) complexes with the bis-NHC ligand 1,1'-methylene-3,3'-di-2,6-diisopropylphenylimidazole-2,2'-diylidene (**1**, Scheme 9) were prepared and fully characterized. Noteworthy, the same group recently described a bimetallic Cr(II)-NHC complex **3** (Scheme 9) that exhibits an unusually short Cr-Cr bond length.<sup>86</sup> The reaction of the free bis-NHC **1** with CrCl<sub>2</sub>



Scheme 10



Scheme 11

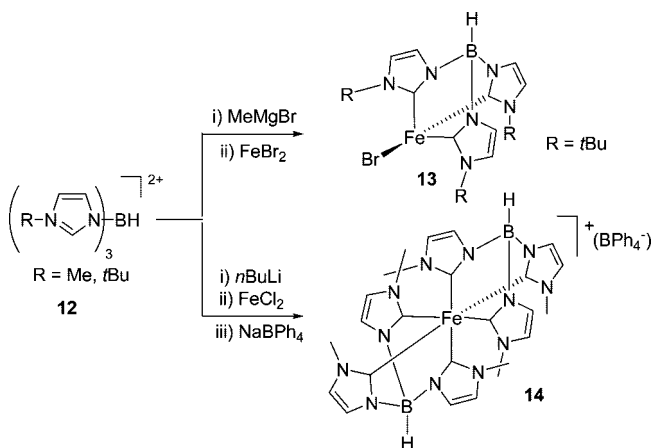


afforded the isolation of the Cr(II) compound **2** (Scheme 9). In an attempt to isolate the corresponding alkyl complex by abstraction of the chloride ligands, compound **2** was further reacted with  $\text{MeMgCl}$ , yielding the bimetallic compound **3** in which the biscarbene ligand is bridging two Cr(II) atoms, also bridged by two methyl ligands.

Recent studies by Arnold and co-workers showed that the incorporation of an anionic functional group (alkoxide, amido, or amino) in an NHC unit allows the preparation of tridentate ligands capable of coordinating to  $d^0$  early transition metals such as yttrium, titanium, and zirconium.<sup>87</sup> The lithium aminodicarbene chloride complex **5** reacts with  $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$  affording the yttrium(III) complex **6** (Scheme 10). Hexacoordinated titanium (**7**) and zirconium (**8**) complexes were synthesized by reaction of **4** with  $M(\text{NEt}_2)_4$  ( $M = \text{Ti}$ ,  $\text{Zr}$ ) (Scheme 10). Complexes **7** and **8** constituted the first examples of group 3 and 4 metal complexes with monoanionic biscarbene ligands.

Another interesting example of early transition metal NHC-based complexes was described by Smith and co-workers.<sup>88</sup> By the reaction shown in Scheme 11, the tris(NHC)borate **9**<sup>89,90</sup> afforded a tricarbonyl complex of Mn(I) with a tripodal tris-NHC ligand, **10**. The analysis of the  $\nu(\text{CO})$  bands on the IR spectrum of this complex showed that **9** is the most electron-donating tripodal ligand compared with all others that have been bound to the same Mn-tricarbonyl fragment. Compound **10** is air-sensitive and is easily oxidized to a homoleptic Mn(IV) complex (**11**, Scheme 11), which is the first example of a Mn(IV)–NHC complex reported to-date.

Scheme 12



## 4.2. Catalytic Applications

Although many catalytic applications of late transition metal complexes bearing poly-NHC ligands have been described, those of early transition metals are restricted to a few examples. In 2003, Gibson and co-workers reported Cr(III)-based ethylene oligomerization precatalysts that incorporate a CNC-pincer carbene ligand.<sup>91,92</sup> More recently, McGuinness shed some light on the mechanism of the reaction with the mentioned pincer complexes in combination with MAO.<sup>93</sup> The Cr(II) and Cr(III) complexes described by Theopold were tested for polymerization of ethylene with a MAO cocatalyst, showing low activities and a broad weight distribution of the polymers.<sup>85</sup> In particular, Cr(II) compounds such as **2** (Scheme 9) were unreactive to ethylene when exposed to MAO, showing that the more Lewis acidic Cr(III) performs better in this reaction. The authors pointed out the ease with which the Cr(III) complexes are reduced to Cr(II), arguing that very strong  $\sigma$ -donating but soft NHC ligands may have a stronger affinity for the softer Cr(II) rather than the harder Cr(III). Thus, they concluded that this ligand system may be better suited for lower oxidation state chromium chemistry and that, due to the inactivity of the Cr(II) compounds tested, it would not lead to successful results in ethylene polymerization.

## 5. Poly-NHC Ligands in Complexes of Group 8 Metals

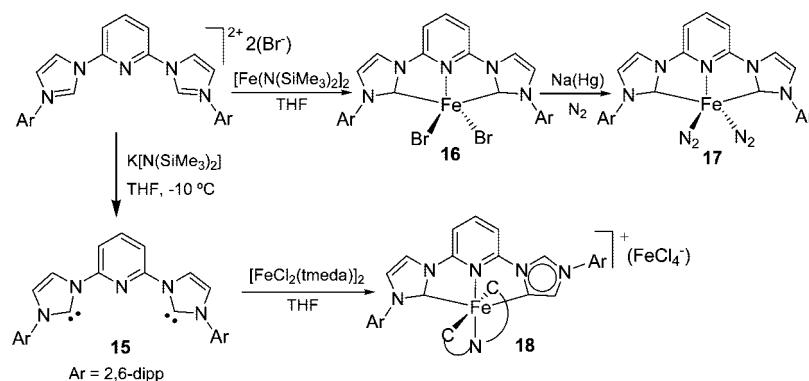
### 5.1. Iron

Poly(N-heterocyclic carbene)–iron complexes with a topology analogous to tris(pyrazolyl)borate (Tp) have been known since 1996.<sup>94</sup> Smith and co-workers described the coordination of a tris(NHC)borate ligand to Fe(II) using a magnesium complex as an effective ligand transfer agent.<sup>90</sup> The reaction of the tris(imidazolyl)borate salt with  $\text{MgMeBr}$  yielded the magnesium complex, which was subsequently reacted with  $\text{FeBr}_2$ , affording complex **13** (Scheme 12), in which the tris-NHC ligand is in a tripodal coordination form. The use of  $n\text{BuLi}$  for the deprotonation of **12** led to the homoleptic hexacarbene iron(III) complex **14** (Scheme 12).<sup>94</sup>

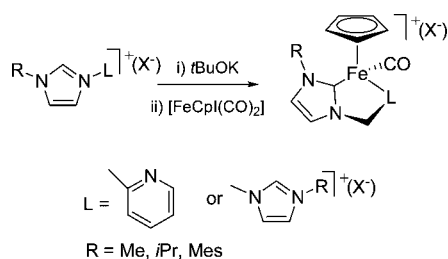
In the course of poly-NHC iron chemistry, the development of thermally stable CNC-pincer 2,6-pyridyl-bis-NHC ligands (such as **15**, Scheme 13) had an important implication. Depending on the reaction conditions and the iron(II) precursor employed, different pincer poly-NHCs were achieved (**16** and **18**, Scheme 13).<sup>95</sup> The catalytic properties of the



Scheme 13



Scheme 14



iron pincer bis-NHC complexes were tested for ethylene oligomerization and polymerization in combination with several cocatalysts. Unfortunately, these catalysts were inactive, most probably due to decomposition via reductive elimination of an alkylimidazolium cation. Conversely, the same pincer ligand provides highly active catalysts for ethylene oligomerization when coordinated to earlier transition metals such as Ti, V, and Cr,<sup>91</sup> as previously mentioned (section 4). The reduction of the Fe(II) complex **16** using Na(Hg) under N<sub>2</sub>, afforded the first dinitrogen complex stabilized by a NHC ligand (**17**, Scheme 13).<sup>96</sup>

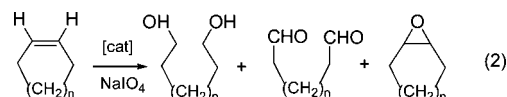
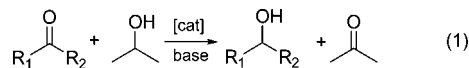
A series of piano stool Fe(II)–NHC complexes of general formula [FeCpCO(NHC–L)]X (L = Py, NHC) were prepared by deprotonation of the corresponding imidazolium salt with a strong base followed by the addition of [FeCpI(CO)<sub>2</sub>] (Scheme 14).<sup>97</sup> The basicity of the ligands was evaluated based on Lever's<sup>98</sup> and Tolman's<sup>99</sup> electrochemical parameters and computational studies. The authors concluded that in these examples NHCs do not behave as pure  $\sigma$ -donor ligands but also a small  $\pi$ -backbonding contribution should be considered.

## 5.2. Ruthenium

Several ruthenium complexes with poly-NHC ligands were obtained starting from 2,6-pyridyl-bisimidazolium salts. A variety of Ru–CNC complexes were subsequently developed by changing the ruthenium precursor (complexes **19**–**24**, Scheme 15). The synthetic methodologies normally implied deprotonation with an external weak base with further addition of the ruthenium precursor. The isolation of the 2,6-pyridyl-bis-NHC ligand was also possible and was the coordination strategy for complexes **20** and **22**.

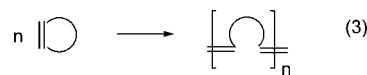
All the complexes shown in Scheme 15 showed interesting properties from the catalytic point of view. Complexes **19**<sup>100</sup> and **22**<sup>101</sup> catalyzed the hydrogenation of carbonyl groups from ketones via hydrogen transfer from *i*PrOH in the presence of strong bases such as KOH, *t*BuOK, or *i*PrOK (eq 1). Aryl and alkyl ketones were converted to the

corresponding alcohols in quantitative yields with TONs up to 125 000.<sup>100</sup> The high stability of the complexes **19** and **22** allowed the catalytic reactions to be carried out under air and without pretreatment of commercially available solvents.

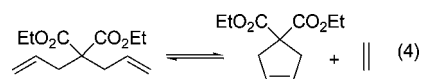


Compound **19** was also a good catalyst for the oxidation of cyclic olefins to aldehydes in the presence of NaIO<sub>4</sub> (eq 2).<sup>100</sup> Remarkably, the process is selective toward the dialdehyde, and no side-products derived from overoxidation were observed. The [Ru(CNC)<sub>2</sub>]<sup>2+</sup> complex **21** turned out to be completely inactive in the two above-mentioned catalytic processes, most probably due to the difficulty of generating a vacant site.

The benzylidene complex **20** was tested for the ring-opening metathesis polymerization (ROMP, eq 3) of cyclic alkenes and ring-closing metathesis of diethyl 2,2-diallylmalonate (RCM, eq 4).<sup>102</sup> The activities observed were low compared with Grubbs' first and second generation catalysts. However, full conversions were achieved at 45 °C using a 10% catalyst loading. Most probably, the low activity observed arose from the blocking of three coordination sites and the low lability of the metal–NHC bond.



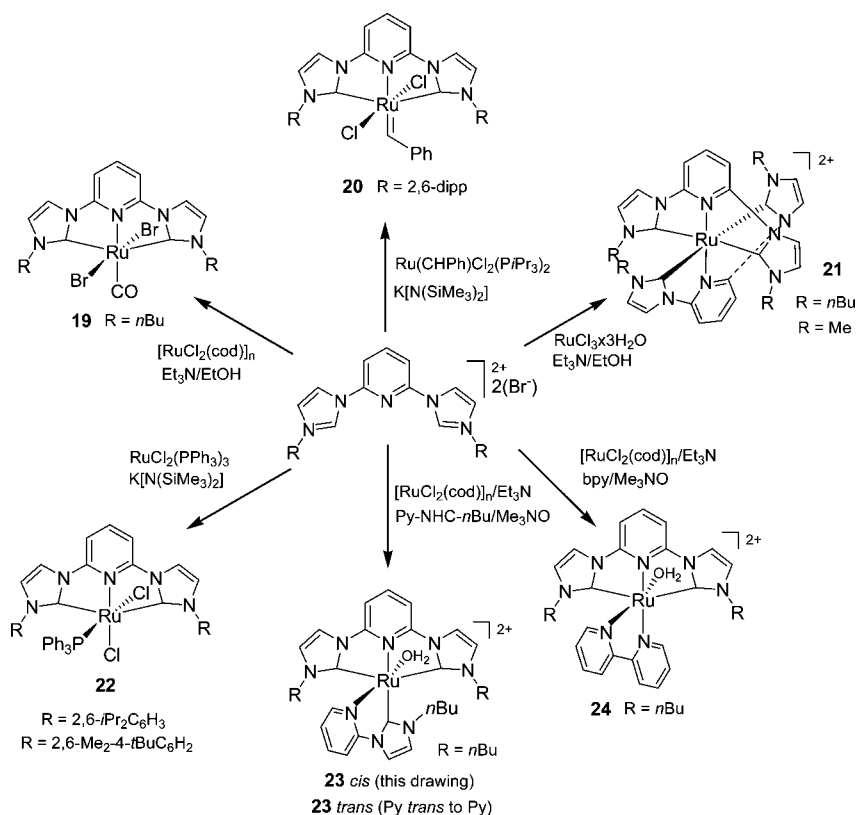
cyclic alkene = cod, coe, nbd, nbe



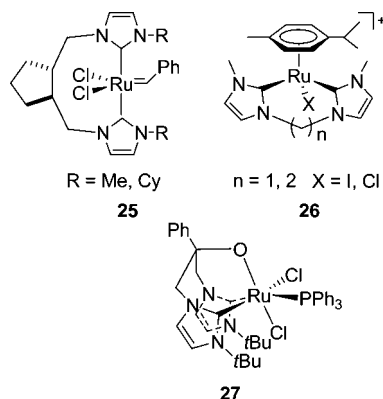
The photoluminescence properties of complex **21** (R = Me) were evaluated and compared with those of [Ru(terpy)<sub>2</sub>]<sup>2+</sup> and [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. According to the spectroscopic properties and emission kinetic curves in acetonitrile and water, the luminescence lifetime of complex **21** is the longest among those reported for similar bis- and tris-pyridyl ruthenium derivatives.<sup>103</sup>

The synthetic methodology for ruthenium–NHC–aqua complexes **23** and **24** involved the coordination of the biscarbene using a weak base and subsequent halide and

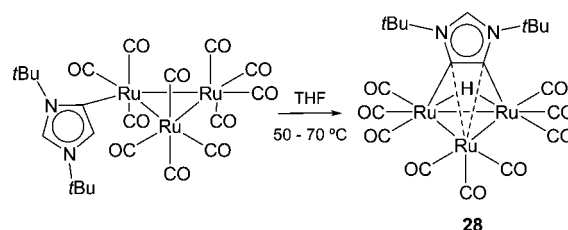
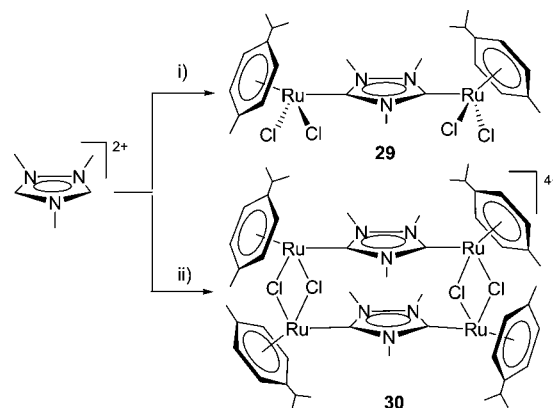
Scheme 15



Scheme 16



Scheme 17

Scheme 18<sup>a</sup>

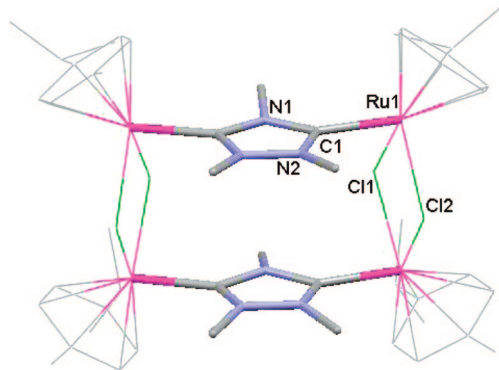
<sup>a</sup> (i)  $K[N(SiMe_3)_2]$ ,  $[RuCl_2(p\text{-cymene})]_2$ ; (ii)  $AgOAc$ ,  $[RuCl_2(p\text{-cymene})]_2$ .

carbonyl group substitution. The Ru–aqua complexes containing polypyridyl ligands are known to lose protons and electrons to reach higher oxidation states.<sup>104</sup> The  $Ru^{IV}=O$  complexes showed excellent oxidative properties toward a wide variety of substrates.<sup>105</sup> Complexes **23** and **24** were tested in the epoxidation catalytic reaction of *cis*- $\beta$ -methylstyrene. The results showed that complexes **23** (*cis*/*trans*) are highly stereoselective toward the *cis*-epoxide.

Other chelating ruthenium complexes with *trans*, *cis*, and tripodal coordination were described in the last years (Scheme 16). The coordination of the ligands was carried out by generating the free carbene (complex **25**),<sup>74</sup> by using a weak base for deprotonation of the imidazolium salt (complex **26**),<sup>39</sup> and by transmetalation from silver (complex **27**).<sup>58</sup> Unfortunately, the catalytic activity of these complexes was very low. For example, complex **26** was tested in the hydrosilylation of terminal alkynes and intramolecular hydroamination, although it proved to be inactive. The inactivity of complex **26** is most probably due to the stability of the

M–NHC bond, which prevents the complex from opening a coordination vacant site.<sup>39</sup>

Interestingly, recent examples of monoazole dicarbene have been reported (Schemes 17 and 18). Whittlesey and co-workers described the unprecedented formation of a bis-abnormal-di-NHC, in which the azole ring is bridging two Ru atoms of a trinuclear Ru cluster (**28**, Scheme 17).<sup>106</sup>



**Figure 6.** Molecular structure of tetranuclear complex **30** (counterions and hydrogen atoms have been omitted for clarity).

The coordination of a triazole-di-ylidene ligand (ditz) to  $[\text{RuCl}_2(p\text{-cymene})]_2$  yielded two different products depending on the methodology used. The external base procedure led to the dimetallic complex **29** in contrast to the transmetalation from silver that led to the tetranuclear complex **30** (Scheme 18).

Both complexes proved to be highly active in the  $\beta$ -alkylation of secondary alcohols with primary alcohols (eq 5) and, in fact, lie among the most active catalysts for this reaction. For most of the substrates, the process was found to be selective in the production of the alkylated alcohols, although in some cases small amounts of the alkylated ketones were observed.<sup>107</sup>

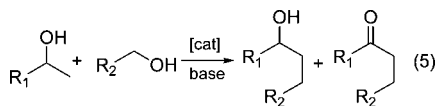
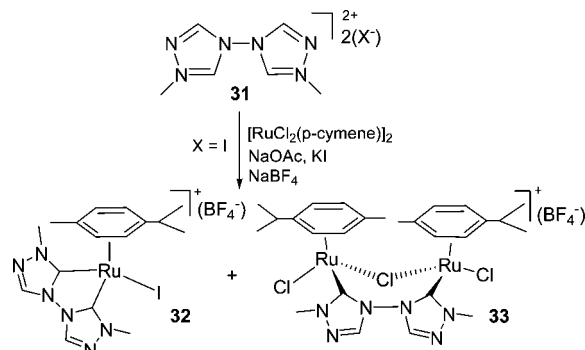


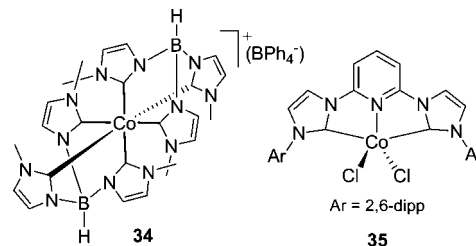
Figure 6 shows the molecular diagram of the cation of the tetranuclear complex **30**. As can be seen in the figure, the compound is the sum of two dinuclear structures with one ditz bridging ligand, bridged by four chlorine ligands. The use of the ditz ligand has afforded many other homo- and even heterodimetallic complexes in which the two metals are disposed in a linearly opposed disposition, thus confirming ditz as an effective new type of a Janus-head-type ligand. Other examples of Rh and Ir complexes with ditz will be discussed later.

Noteworthy, all the reports on chelating poly-NHC complexes involve ligands in which the carbene units are joined by a linker, with the only exception of an example described recently by Peris and Crabtree.<sup>52</sup> In order to avoid possible side-reactions on the linker groups when strong bases are employed, a bitriazolyliidene ligand (bitz), in which the two carbene units are directly linked, was obtained as the simplest possible chelating bis-NHC ligand. The bitz ligand, which might be considered the NHC analogue of the ubiquitous N-donor ligand 2,2'-dipyridyl, reliably chelates on metalation to Ru, Rh, and Pd.<sup>51,52</sup> For instance, the reaction of bitz ligand iodide precursor **31** with  $[\text{RuCl}_2(p\text{-cymene})]_2$  in the presence of NaOAc afforded a mixture of the chelate complex **32** and the dinuclear species **33** (Scheme 19).

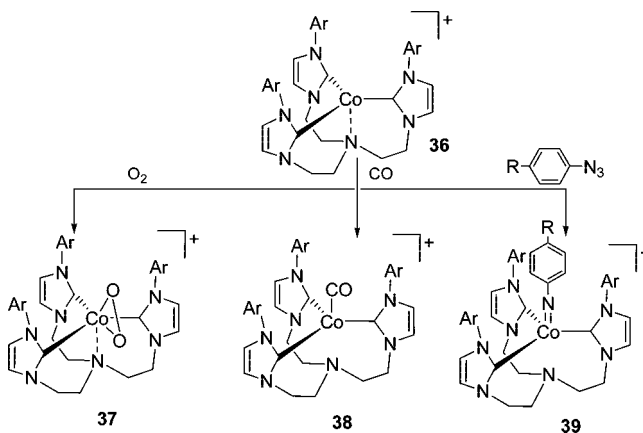
**Scheme 19**



**Scheme 20**



**Scheme 21**



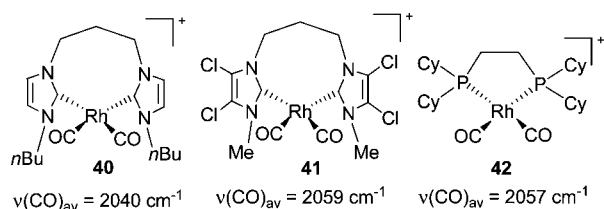
## 6. Poly-NHC Ligands in Complexes of Group 9 Metals

### 6.1. Cobalt

Cobalt–NHC complexes are not common, and just a few examples of Co compounds with poly-NHC ligands have been described. The bis[hydrotris(3-*R*-imidazolin-2-ylidene)borate] cobalt(III) complex **34** (Scheme 20) was the first polycarbene–cobalt compound described.<sup>108</sup> The Co(III) complex is isostructural to the previously mentioned Fe(III) compound **14** (Scheme 12).<sup>109</sup> The pincer CNC-coordination is also known in cobalt, as in complex **35** (Scheme 20).<sup>91</sup>

The tetradentate tris-NHC ligand tris[2-(3-arylmethylimidazole-2-ylidene)ethyl]amine (TIMEN<sup>Ar</sup>) developed by Meyer and co-workers was coordinated to cobalt, affording cobalt(I)/(II) complexes with high-spin electronic configurations (Scheme 21).<sup>110</sup> The cobalt(I) complexes proved to be active in the activation of small molecules.<sup>66</sup> For example, the reaction of complex **36** with dioxygen formed cobalt(III) peroxo complex **37**, which is capable of transferring an oxygen atom to organic electrophiles. The same complex also reacted with carbon monoxide and with aryl azides to form cobalt(I) carbonyl (**38**) and cobalt(III) imido complexes.

Scheme 22



The imido complexes show intramolecular imido insertion to form cobalt(II) imine species **39** (Scheme 21).

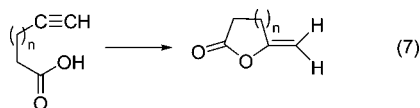
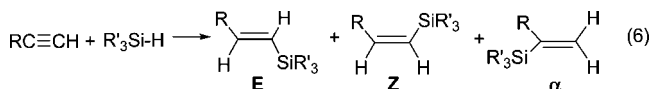
## 6.2. Rhodium

Together with palladium, rhodium is the metal that has given more examples of complexes with poly-NHC ligands. Two very recent reviews covered the chemistry of all these complexes until late 2006,<sup>22,23</sup> so we will focus our attention on the more recent examples.

The introduction of chloro substituents at the C4 and C5 positions of the imidazole ring provided new chelating NHC complexes of rhodium (**41**, Scheme 22) and iridium.<sup>111</sup> The electronic properties were evaluated on the basis of the  $\nu(\text{CO})$  of the carbonyl derivatives, showing that the chloroimidazolylidene ligand is significantly less  $\sigma$ -donating than the nonchlorinated analogue, and its electron-donating power can be compared with that shown by basic diphosphines.

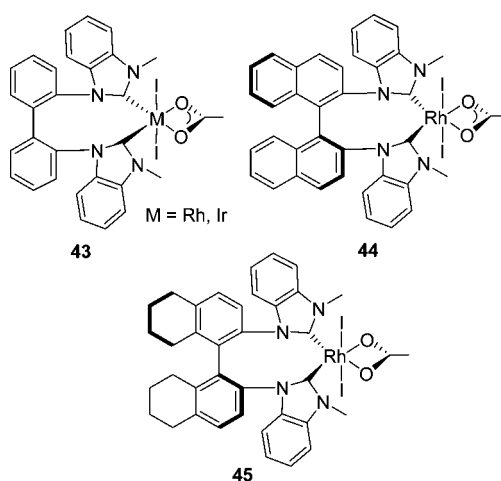
The electronic properties of chelating NHCs and phosphines were evaluated for rhodium carbonyl complexes and compared with other related nonchlorinated bisimidazolylidene (**40**) and bisphosphine ligands (**42**) (Scheme 22).<sup>112</sup> The introduction of the chloro substituents in the azole rings shifts carbonyl frequencies higher when compared with the nonchlorinated rhodium complex, indicating a reduction of the electron-donating character. In fact, complex **41** has a  $\sigma$ -donating character similar to that of complex **42**, in which bis(dicyclohexylphosphino)ethane is coordinated to Rh(I).

The tuning of the electronic properties of the ligand has important implications for the catalytic properties of the compounds obtained. An enhanced activity of the chlorinated NHC catalyst was observed in the hydrosilylation of terminal acetylenes (eq 6) and cyclization of alkynoic acids (eq 7).

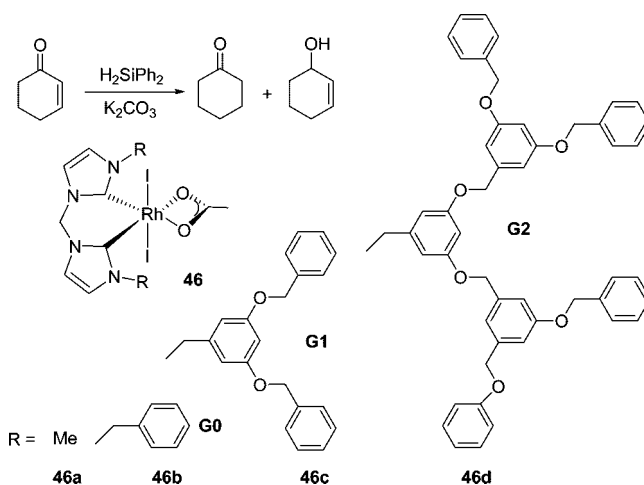


Shi et al. reported a new family of chelating bis-NHC ligands where the linker between the two imidazole rings is derived from a diamine source (Scheme 23). The achiral complexes **43** were active in the hydrosilylation of ketones using diphenylsilane at room temperature.<sup>113</sup> Complex **45** was found to be active in the enantioselective hydrosilylation of methyl ketones under the same conditions. For a range of substrates, good to excellent enantioselectivities and yields were obtained.<sup>114</sup> The chiral BINAM derivatives, complexes **44** and **45**, were highly active in the enantioselective hydrosilylation of 3-oxo-3-arylpropionic methyl or ethyl esters.<sup>115</sup>

Scheme 23



Scheme 24



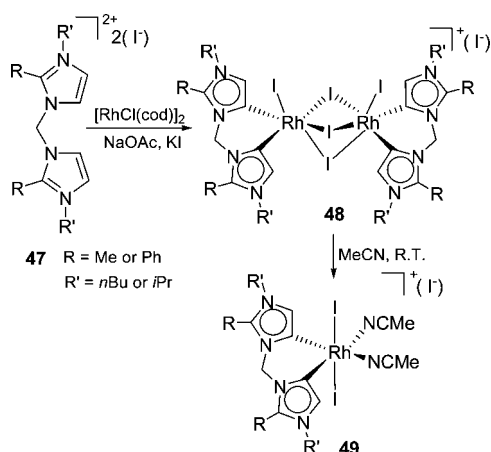
A series of bis-NHC chelating carbenes bearing the Fréchet-type dendritic frameworks were synthesized and tested in ketone hydrosilylation (Scheme 24).<sup>116</sup> The introduction of polybenzylether moieties in the wingtip groups (complexes **46b–d**) enhanced the catalytic activity and selectivity in the hydrosilylation of 2-cyclohexen-1-one compared with that shown by methyl complex **46a**. Unfortunately, no dendrimer generation effect was observed in the hydrosilylation as happened in monodentate NHC carbene complexes.<sup>117</sup>

Rhodium(III) complexes containing bis-*a*NHC carbenes were described by Albrecht et al. (Scheme 25).<sup>54</sup> Coordination of the C2-protected bisimidazolium salts **47** to  $[\text{RhCl}(\text{cod})]_2$  using an external base afforded the dimetallic species **48** bridged by three  $\mu^2$ -I ligands.<sup>37,38,82</sup> In the presence of a weak coordinating solvent, **48** afforded the monometallic species **49**. The two complexes were active in catalytic transfer hydrogenation of ketones with *i*PrOH in the presence of a strong base.<sup>82</sup>

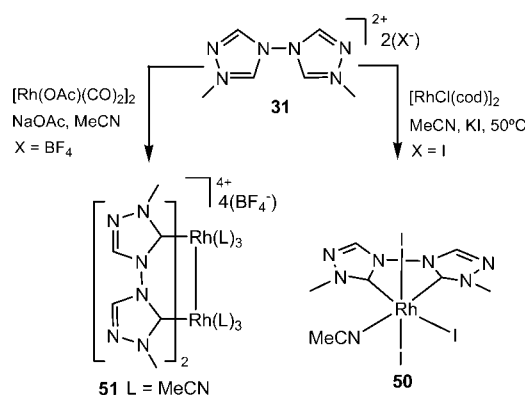
The coordination of the bitz ligand to rhodium gave different complexes depending on the reaction conditions employed.<sup>51,52</sup> The reaction of the bitz precursor **31** with  $[\text{RhCl}(\text{cod})]_2$  in the absence of any external base, afforded chelating Rh(III) mono-bitz complex **50** (Scheme 26). The coordination of bitz to Rh(III) therefore occurred under milder conditions than usually found for other NHC precursor salts, which normally require prior activation. When the reaction was carried out in the presence of NaOAc, a



Scheme 25

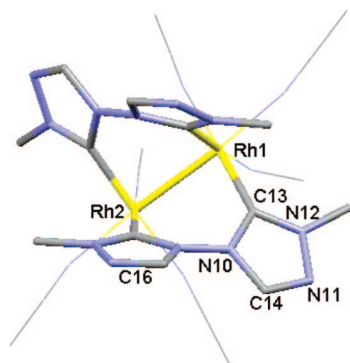


Scheme 26



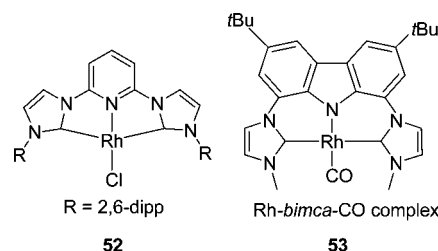
chelating Rh(III)–bis-bitz complex was isolated even when a precise 1:1 ratio of Rh/bitz was employed. Interestingly, the reaction of the tetrafluoroborate salt of **31** with  $[\text{Rh}(\text{OAc})(\text{CO})_2]_2$  afforded an unexpected metal–metal-bonded dirhodium(II) complex (**51**, Scheme 26), which constituted the first example of a dirhodium(II) complex bearing an NHC ligand. The molecular structure of the cation of complex **51**, illustrated in Figure 7, shows the two rhodium atoms in an octahedral environment with two bridging bitz ligands forming two six-membered metallacycle rings.

Pincer-NHC complexes of rhodium have been extensively studied<sup>23</sup> and continue to give interesting new complexes. 2,6-Pyridyl-bis-NHC ligands, coordinate to  $[\text{RhCl}(\text{CH}_2=\text{CH}_2)_2]_2$  to afford the pincer chloro-Rh(I) complex **52** (Scheme 27). The Rh(I)-carbonyl and Rh(III)-trihalide analogue complexes had already been described.<sup>37,118</sup> An

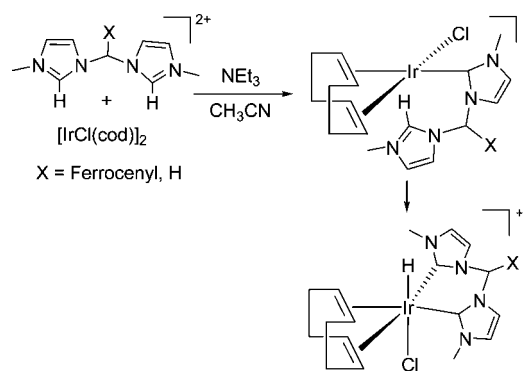


**Figure 7.** Molecular structure of the dirhodium(II) complex **51** (counterions and hydrogen atoms have been omitted for clarity).

Scheme 27



Scheme 28



interesting variation of the CNC-pincer framework was proposed and successfully coordinated to rhodium. The 3,6-di-*tert*-butyl-1,8-bis(3-methylimidazolin-2-yliden-1-yl)carbazole (bimca) is a monoanionic, meridionally coordinating tridentate ligand. The coordination of bimca ligand to Rh(I) was carried out using a strong base (LDA) and  $[\text{RhCl}(\text{CO})_4]_2$  and yielded complex **53**.<sup>119</sup>

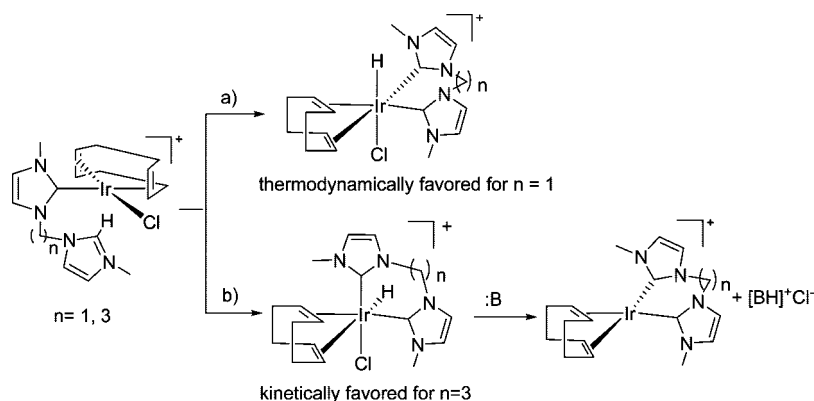
### 6.3. Iridium

Most of the studies and complexes based on poly-NHC iridium complexes that have been reported are in close relation to their rhodium analogues.<sup>22</sup> The fine-tuning of the linker in chelating bis-NHC ligands has provided important information about the metalation process. In the case of bis-NHC Ir(I) complexes, the C–H oxidative addition of the imidazolium salt plays a decisive role. The reaction of a ferrocenyl-bisimidazolium salt with  $[\text{IrCl}(\text{cod})]_2$  provided the first evidence of the intermediacy of a stable NHC–Ir<sup>III</sup>–H complex by direct oxidative addition of the imidazolium salt (Scheme 28).<sup>120</sup>

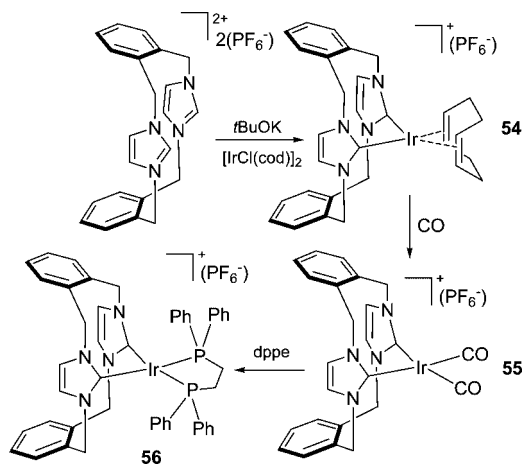
A combined experimental and computational approach provided a mechanism for the metalation of a series of bisimidazolium salts with different linkers between the azole rings. It was concluded that the metalation of the second imidazolium ring proceeds by C2–H oxidative addition.<sup>40</sup> The final formation of the bis-NHC–Ir<sup>III</sup>–H (short linker) or bis-NHC–Ir<sup>I</sup> (long linker) depends on whether the oxidative addition product yields the *trans* (short linker, *n* = 1, mechanism a) or *cis* (long linker, *n* = 3, mechanism b) products as shown in Scheme 29. The *trans* products are the thermodynamically favored complexes, but in the case of the ligands with long linkers, the *cis* complexes are kinetically favored, thus providing the bis-NHC–Ir<sup>I</sup> reductive elimination products.<sup>40</sup>

A large number of chelating bis-NHC–iridium complexes have been described.<sup>81,111,113,121</sup> As an example of the general reactivity of the chelating Ir(I) complexes, a cyclophane–bis-NHC has been chosen (Scheme 30).<sup>122</sup> The reaction of a imidazolium-linked *ortho*-cyclophane salt with  $[\text{IrCl}(\text{cod})]_2$

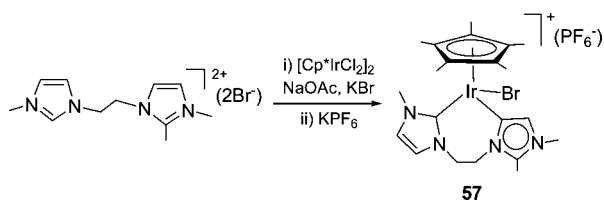
Scheme 29



Scheme 30



Scheme 31

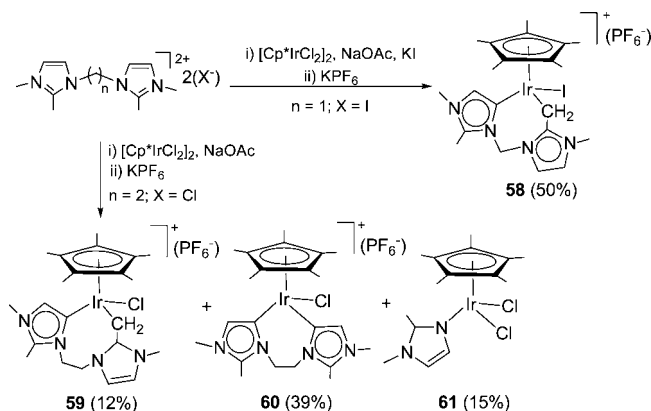


in the presence of a strong base yielded the cationic Ir(I) complex **54**. The 1,5-cyclooctadiene can be displaced by bubbling CO to give the dicarbonyl complex **55**. The carbonyl groups can also be displaced by dppe to yield complex **56**.

The use of methylene- and ethylene-bridged bisimidazolium salts with one of the azole rings blocked at the C2 position by a methyl group (C2-Me) gave unexpected results. Depending on the length of the linker and on the nature of the bisimidazolium salt used, the corresponding *a*NHC-complexes or the products resulting from the activation of the C–H bond in the C2-Me group were obtained. As depicted in Scheme 31, the reaction of 1,1'-ethylene-2,3,3'-trimethylbis(1*H*-imidazolium) dibromide with  $[\text{Cp}^*\text{IrCl}_2]_2$  in the presence of NaOAc in refluxing acetonitrile allowed the preparation of compound **57**, in which the chelating biscarbene ligand is coordinated by both the abnormal and normal modes (Scheme 31).<sup>55</sup>

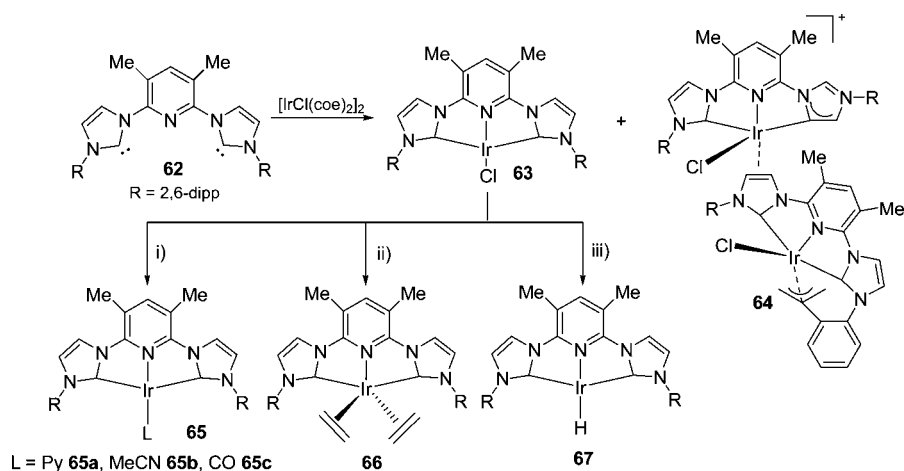
The reaction gave completely different products when doubly C2-Me substituted bisimidazolium salts were used, for which the length of the linker clearly determined the reaction outcome. For the methylene linker ( $n = 1$ ), the only

Scheme 32



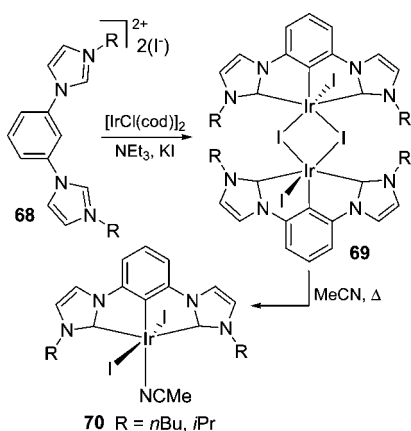
compound obtained showed an unusual type of coordination in which the chelating ligand is coordinated through an *a*NHC and a methylene group resulting from the C–H activation of the C2-Me group (complex **58**, Scheme 32). For the ethylene linker ( $n = 2$ ) a mixture of three different products was obtained, the expected bis-*a*NHC together with the chelating C2-Me activated compound, as well as a neutral species bearing a 1,2-dimethylimidazole ligand (**59**, **60**, and **61**, respectively, in Scheme 32). DFT calculations could not discriminate the nature of the first metalations, but it pointed out a kinetic preference for the second metalation through C–H activation at the C5 position.<sup>55</sup>

Although pincer 2,6-pyridyl-bis-NHC ligands have been coordinated to many transition metals, their coordination to Ir remained elusive until very recently.<sup>123,124</sup> In a remarkable work, Danopoulos and co-workers described the coordination of the 2,6-pyridyl-bis-NHC ligand **62** to an Ir(I) center using  $[\text{IrCl}(\text{coe})_2]_2$  to afford complex **63** (Scheme 33). In the same reaction, a minor amount of the unexpected complex **64** was also obtained. Complex **64** is a double pincer cation containing one Ir(I) and one Ir(III) center. The Ir(I) fragment shows the coordination of the pincer ligand through one normal- and one abnormal-NHC. The coordination sphere about the Ir(I) center is completed by a chloride ligand and the unprecedented  $\eta^2$ -ethylene coordination of one imidazol-2-ylidene from the other pincer fragment. The Ir(III) fragment shows the pincer ligand, one chloride, and one  $\eta^3$ -allyl group originated by C–H activation of one *i*Pr of the NHC substituent. Halide abstraction of **63** afforded the coordination of pyridine, acetonitrile, carbon monoxide, or ethylene, depending on the reaction conditions (complexes **65** and **66**, Scheme 29). Treatment of **63** with *i*PrONa in THF yielded

Scheme 33<sup>a</sup>

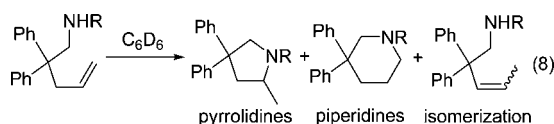
<sup>a</sup> (i) **65a**, Py,  $\text{NaBARF}_4$  [ArF = 3,5-bis(trifluoromethyl)phenyl]; **65b**,  $\text{KPF}_6$ , MeCN; **65c**,  $\text{KPF}_6$ , CO; (ii)  $\text{KPF}_6$ ,  $\text{CH}_2=\text{CH}_2$ , (iii)  $i\text{PrONa}$ , THF.

Scheme 34

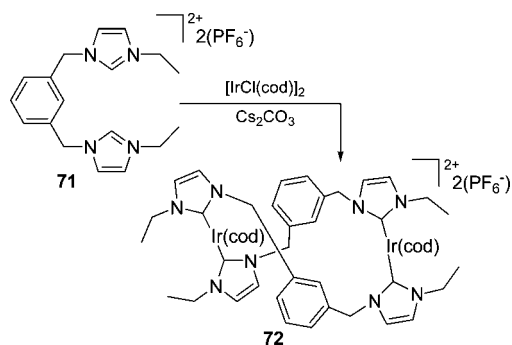


the unusual Ir(I)-hydride **67**, an interesting compound that combines an Ir(I)-hydride and an NHC ligand.

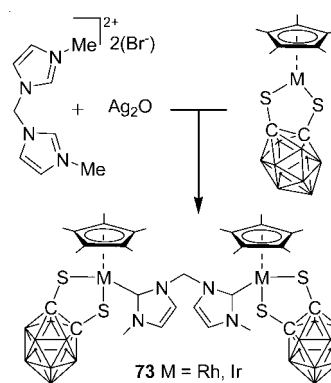
The substitution of the pyridyl ring by a phenyl in the 2,6-pyridyl-bis-NHC ligand led to the CCC pincer bisimidazolium salt **68** (Scheme 34).<sup>123</sup> The coordination of this ligand to  $[\text{IrCl}(\text{cod})]_2$  afforded the Ir(I) pincer dimer complex **69**. The dimeric nature was broken by heating or ultrasonic activation to yield the monomeric species **70**. Complex **69** and its rhodium analogue were also obtained simultaneously using a different synthetic methodology.<sup>125</sup> This new methodology implies deprotonation and C–H phenyl activation using  $\text{Zr}(\text{NMe}_2)_4$  and subsequent transmetalation to  $[\text{MCl}(\text{cod})]_2$  (M = Rh, Ir). Complex **69** and its rhodium analogue were tested in the intramolecular hydroamination/cyclization of secondary amines (eq 8).<sup>125</sup> Both complexes were effective catalysts in this reaction, achieving full conversions after 16 h at 110 °C even in the presence of air and water. In the catalytic experiments, only pyrrolidine derivatives were observed. No piperidines were observed, and just in some cases, traces of isomerization products were observed. The catalytic results using water as solvent showed no appreciable loss of activity.



Scheme 35



Scheme 36



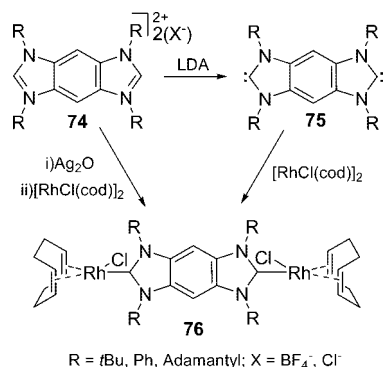
The reaction of the *m*-xylyl-bridged bisimidazolium salt **71** with  $[\text{IrCl}(\text{cod})]_2$  in the presence of  $\text{Cs}_2\text{CO}_3$  afforded the figure-eight 20-membered ring dimetallacycle complex **72** (Scheme 35).<sup>123</sup>

A new type of poly-NHC carbene complexes based on carboranes was described by Jin and co-workers.<sup>126</sup> As shown in Scheme 36, the coordination of the methylene-linked bis-NHC ligand to a  $\text{Cp}^*$ -carborane metal fragment afforded complexes **73**.

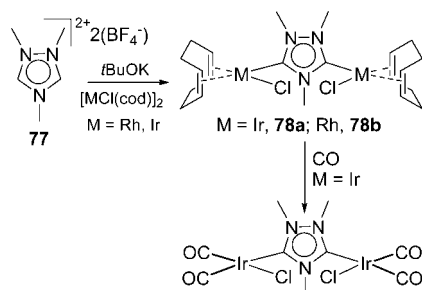
#### 6.4. Dicarbenes for a Linearly Opposed Coordination

The design of poly-NHC ligands with different topologies has increased the architectural diversity and coordination modes in organometallic catalysts. The first examples of

Scheme 37



Scheme 38



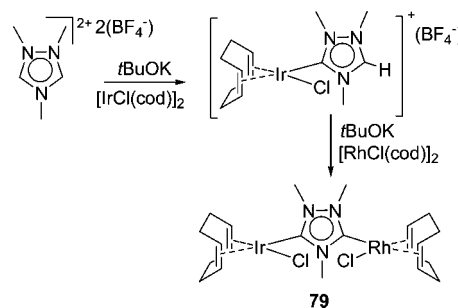
linearly opposed coordination of NHCs were elegantly shown by Bielawski and co-workers.<sup>65</sup> A series of benzobis(imidazolylidene)s were coordinated forming homobinuclear rhodium,<sup>63–65</sup> palladium,<sup>62,63,65</sup> platinum,<sup>62,63,65</sup> nickel,<sup>65</sup> silver,<sup>63–65</sup> and iron<sup>127</sup> complexes. These ligands showed facially opposed coordination abilities (Janus-head-type) between the two metal fragments.<sup>64</sup> Deprotonation of benzobis(imidazolium) salts (**74**) using LDA yielded the free dicarbene ligands (**75**). Subsequent treatment with 1 equiv of [RhCl(cod)]<sub>2</sub> afforded the homobinuclear Janus-head-type rhodium complexes **76** (Scheme 37). The same final products can be obtained through the silver–NHC complexes by the transmetalation procedure. These complexes represent a modular approach to main-chain organometallic polymers.<sup>62,63</sup>

A related situation to that shown in Scheme 37 can be obtained starting from simple triazolylidenes. The possibility of obtaining dicationic triazolium dicarbene precursors (**77**)<sup>128</sup> to potentially bind two metal centers was suggested by Bertrand and co-workers,<sup>129</sup> who described a polymeric silver dicarbene compound.<sup>61</sup> The 1,2,4-trimethyl-triazolium precursor reacted with [MCl(cod)]<sub>2</sub> (M = Rh, Ir) in the presence of *t*BuOK to afford the dinuclear homobimetallic compounds **78** (Scheme 38). Complex **78a** readily reacts with CO to yield the tetracarbonyl complex. The determination of the Tolman electronic parameter (TEP) indicates that the triazol-di-ylidene ligand is electronically similar to phosphines, with lower electron-donating power than other known NHCs. Preliminary results in catalysis showed that complexes **78** are active in transfer hydrogenation and intramolecular cyclization of alkynoic acids, being among the most active catalysts for this latter process.<sup>130</sup>

The sequential deprotonation of the trimethyltriazolium dication was also possible under similar reaction conditions to afford the dinuclear heterobimetallic compound **79** (Scheme 39). The Ir–Rh complex confirmed the ligand's capability to easily coordinate to two different metals.

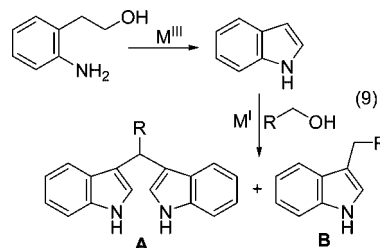
An extension of this work provided a detailed study of the synthetic pathways to obtain heterobimetallic complexes

Scheme 39



(Scheme 40).<sup>131</sup> The reaction of 1,2,4-trimethyltriazolium tetrafluoroborate in methanol with 1 equiv of NaH and 1 equiv of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> or [IrCl(cod)]<sub>2</sub> afforded the cationic compounds **80** and **81**, respectively in which the azole ligand is acting as a monocarbene (Scheme 40). Compounds **80** and **81** were isolated and characterized by means of NMR and mass spectroscopy. Both complexes are valuable synthons for the preparation of heterobimetallic dicarbene species, since a second CH bond at the azole ring can be activated to generate the second carbene. The reaction of **80** with [MCl(cod)]<sub>2</sub> (M = Rh, Ir) afforded the dimetallic species **82** (Ir<sup>III</sup>/Ir<sup>I</sup>) and **83** (Ir<sup>III</sup>/Rh<sup>I</sup>), two special cases of mixed-valence metal complexes (Scheme 40). Figure 8 depicts the molecular structure of heterobimetallic complex **83** and shows the triazolidene ligand connecting the Rh(I) and the Ir(III) centers.

Complexes **82** and **83** were tested in a tandem catalytic reaction implying the consecutive oxidative cyclization of 2-aminophenyl ethyl alcohol and the alkylation of the resulting indole with a series of primary alcohols (eq 9). The cyclization reaction is normally catalyzed by Cp\*Ir(III)<sup>132</sup> complexes and the indole alkylation by Ir,<sup>133</sup> Ru,<sup>134</sup> and In.<sup>135</sup> The new catalysts showed high activity in the overall reaction process and the selectivity in the production of the bisindolylmethane (A) or monoalkylated indole (B) could be tuned by changing the indole/alcohol ratio.<sup>131</sup>

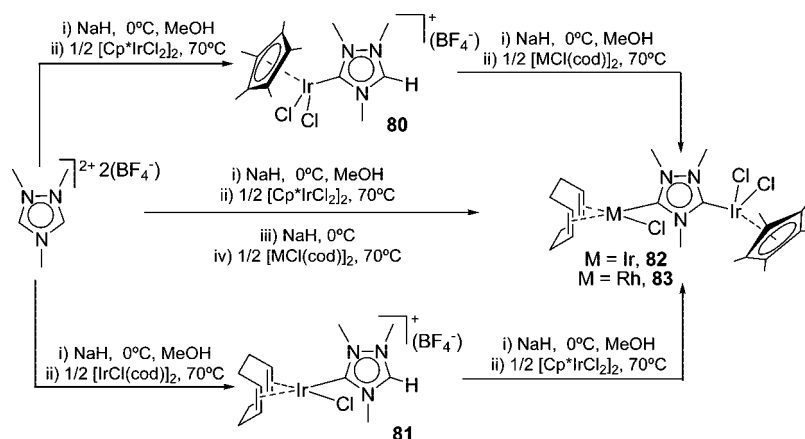


## 7. Poly-NHC Ligands in Complexes of Group 10 Metals

Group 10 metal complexes have been used as a test bed for the coordination of NHC ligands with many different topologies. Most NHC ligands were first coordinated to palladium, and then their coordination was extended to other transition metals. In this section, we decided to classify the complexes with poly-NHC ligands attending first to the ligand topologies and then to the different metals. The vast majority of examples refer to Pd complexes, and all Ni and Pt complexes have followed the trends opened for Pd. We believe that this type of classification may provide a clearer view of the chemistry of this group of metals.



Scheme 40



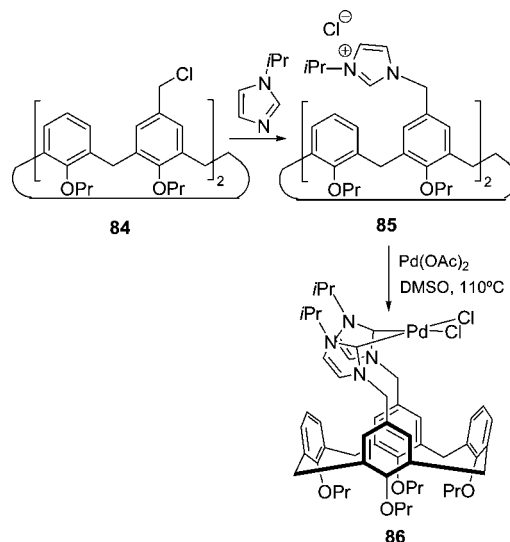
## 7.1. Macrocyclic Chelating NHC Complexes

The combination of NHC and macrocyclic ligands generates an important new class of ligands for supramolecular chemistry and, more interestingly, for catalytic supramolecular chemistry. In this sense, some research groups have focused their interest on the preparation of imidazolium salts based on calix[4]arenes as precursors for a new group of macrocyclic chelating NHC ligands.<sup>56,75,136</sup> Due to the restricted geometry of calix[4]arenes, two different functional sites can be easily identified. The upper rim of the macrocycle may allow the introduction of the ligands at concrete positions. The modification of the upper rim by changing the number of ligands or their geometry is crucial to the design of suitable catalysts for specific reactions. The functionalization of the lower rim fixes the cone conformation and determines the macrocycle solubility.

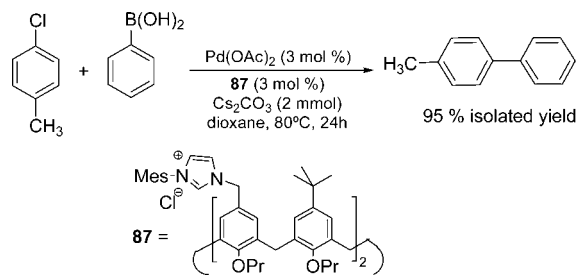
Schatz and co-workers described the first calix[4]arene skeleton, which serves as a platform for attaching NHC ligands.<sup>56</sup> Following a modular synthetic protocol, a series of calixarene-based imidazolium salts were isolated and further reacted with a Pd(II) precursor. For instance, calixarene **84** bearing a chloromethyl group can easily react with isopropyl imidazole to yield the imidazolium salt **85** (Scheme 41). In this particular case, the introduction of the propyl groups at the lower rim enhances the solubility of these complexes in organic solvents. Treatment of the imidazolium salt **85** with Pd(OAc)<sub>2</sub> yielded the *cis*-chelated Pd(II) complex **86**.

The catalytic activity of these palladium complexes was tested in the Suzuki coupling of phenyl boronic acid and 4-aryl halides, using an *in situ* protocol.<sup>56,136</sup> The Pd(OAc)<sub>2</sub>/imidazolium salt systems showed high activity in the coupling of aryl chlorides. Bulky substituents on both the

Scheme 41

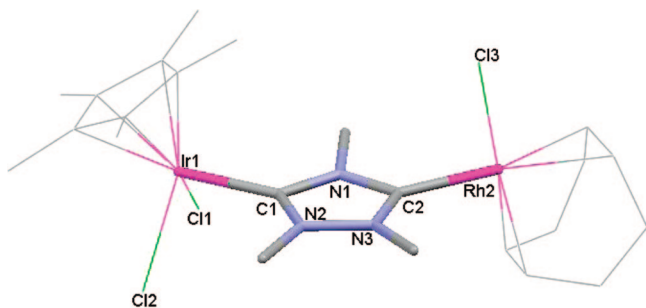


Scheme 42



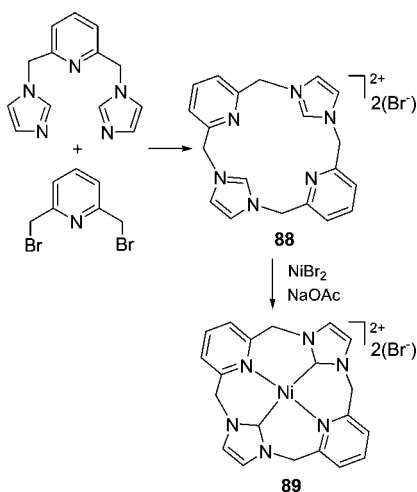
imidazole unit and the macrocyclic skeleton enhanced the catalytic efficiency. The bisimidazolium salt **87** (Scheme 42), with a mesityl N-substituent and a *tert*-butyl group at the upper rim of the calixarene scaffold, provided the best results. Although the catalytic activity was significantly lower, it was possible to form biaryls even in pure water, an environmentally benign reaction media.<sup>136</sup>

A similar calixarene-based ligand has been described and successfully coordinated to Pd(OAc)<sub>2</sub>.<sup>75</sup> In this particular case, the bidentate ligand occupies two *trans* positions of the square plane (**E**, Scheme 8). The isolated Pd(II) complexes displayed different activities than those for the *in situ* generated catalyst in the cross-coupling of phenyl boronic acid and 4-aryl halides, thus indicating that the active species involved must be different.

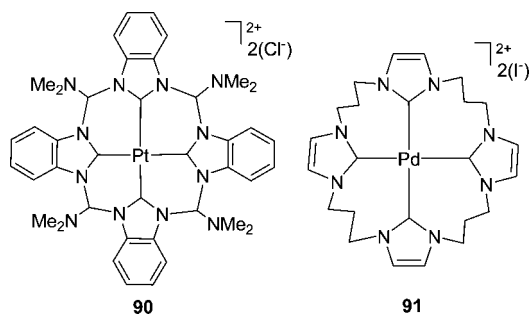


**Figure 8.** Molecular structure of heterobimetallic complex **83** (hydrogen atoms are omitted for clarity).

Scheme 43



Scheme 44



Additionally, some metal complexes with cyclic poly-NHC ligands were described in which rather than acting as a typical bidentate ligand as in the examples above, the ligand encapsulates the metal.<sup>67,137,138</sup> The first example of an NHC-based macrocyclic ligand containing a metal ion within the ligand cavity was reported by Baker and co-workers in 2002.<sup>138</sup> Treatment of cyclophane **88**, prepared by reaction of 2,6-bis(bromomethyl)pyridine with 2,6-bis(imidazol-1-ylmethyl)pyridine,<sup>139</sup> with  $\text{NiBr}_2$  and  $\text{NaOAc}$  afforded the Ni(II) compound **89** (Scheme 43). As depicted in the scheme, the tetradentate ligand is coordinated to the nickel center through two pyridine nitrogens and two carbene units.

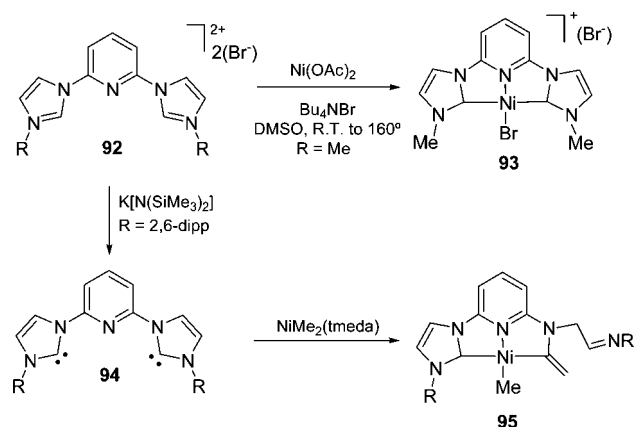
Likewise, the first examples of homoleptic platinum(II)<sup>68</sup> and palladium(II)<sup>67</sup> complexes of tetracarbenes macrocycles were described (**90** and **91**, respectively, in Scheme 44).

## 7.2. Chelating Pincer-NHC Complexes

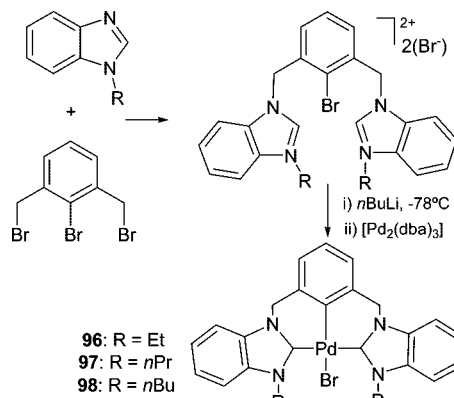
The properties and catalytic applications of metal complexes with NHC-based pincer-type ligands were comprehensively reviewed by Danopoulos and Pugh in 2007.<sup>23</sup> Since then some other interesting examples of group 10 pincer-NHC complexes have been reported, and these will be described herein.

Even though nickel–NHC complexes are commonly used in catalysis, there are just a couple of examples of metal complexes bearing a pincer ligand. The tridentate carbene precursor **92**, isolated by direct reaction of 2,6-dibromopyridine with *N*-methylimidazole, was reacted with  $\text{Ni}(\text{OAc})_2$  in the presence of  $\text{Bu}_4\text{NBr}$  yielding Ni(II) complex **93** (Scheme 45).<sup>140</sup> More recently, a pincer compound was isolated using the free carbene route.<sup>141</sup> In an attempt to prepare the corresponding methyl complex, the reaction of the free carbene **94** with  $\text{NiMe}_2(\text{tmeda})$  was carried out. The

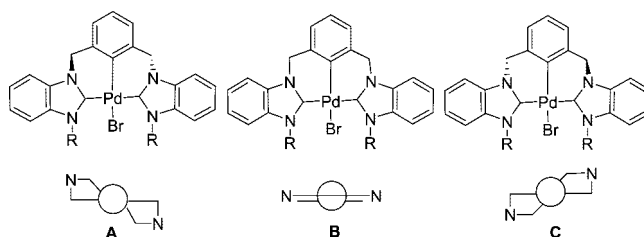
Scheme 45



Scheme 46



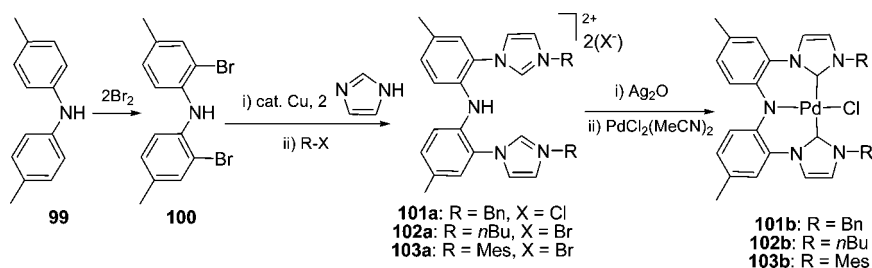
Scheme 47



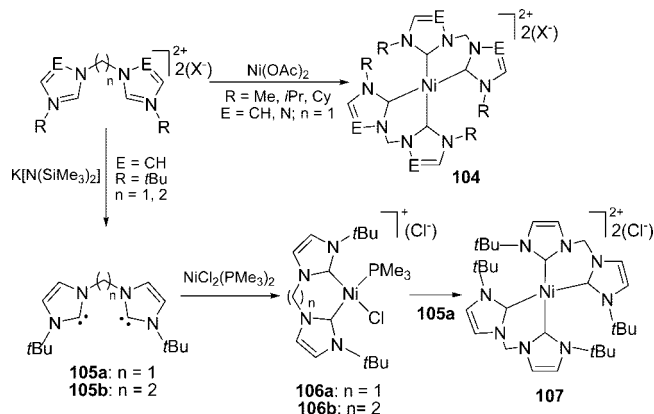
complex thus isolated was unambiguously identified as **95** by means of X-ray diffraction. The formation of **95** (Scheme 45), which is the product of an unusual ring opening of one of the imidazole rings, clearly questions the widely accepted view that NHCs are “innocent” ligands in organometallic chemistry. Although the exact mechanism is still unclear, the authors proposed the following explanation: (1) coordination of **94** to Ni with displacement of *tmeda*; (2) methyl migration from the resultant five-coordinated intermediate to one of the  $\text{C}_{\text{NHC}}$ , followed by catalytic deprotonation of the base (*tmeda*) of the  $\beta$ -hydrogen bearing methyl group; (3) ring-opening of the imidazole in the resulting vinyl group, forming an imine; (4) protonation of the carbanion by *tmeda*- $\text{H}^+$ .

Because of their common application in catalytic C–C coupling reactions, the chemistry of palladium complexes is in continuous development. Some examples of palladium complexes supporting pincer-NHC ligands have been described in the last two years, as well as their catalytic activity. Hahn and co-workers have reported the preparation of xylene-bridged pincer Pd(II) complexes **96**–**98** (Scheme 46), aiming that the unique donor properties of the benzimidazol-

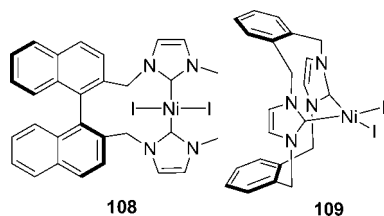
Scheme 48



Scheme 49



Scheme 50



2-ylidene unit would confer on them interesting catalytic properties.<sup>142</sup> The xylene-bridged benzimidazolium salts, prepared by reaction of 1,3-di(bromomethyl)-2-bromophenylene with the corresponding N-alkylated benzimidazole, were deprotonated with *n*-butyl lithium and further reacted with  $[\text{Pd}_2(\text{dba})_3]$ , affording neutral compounds **96**–**98** (Scheme 46).

Interestingly, a direct combination of the puckering of the two six-membered chelate rings and the presence of bulky aromatic substituents on the imidazolylidene rings affords a helical structure with a  $C_2$  proper axis coinciding with the N–Pd–Br vector, providing a complex with axial chirality. Whereas the  $^1\text{H}$  NMR spectra at room temperature of complexes **96**–**98** exhibited two doublets for the resonances of the protons of the bridging methylene group, those of similar lutidine-bridged compounds exhibited broad singlets.<sup>137</sup> As previously reported for other bisimidazolylidene ligands, the authors attributed this behavior to an atropisomerization process hindered by a higher energy barrier for the interconversion between the two possible limiting twisted conformations A and C (Scheme 47). Similar examples of this type of behavior were previously reported for imidazolylidene-based CNC pincer ligands, and Danopoulos and co-workers made a detailed study of the structural features of this type of pincer complex based on X-ray diffraction studies.<sup>137,143–145</sup>

A more recent report concerns the synthesis of a new pincer-type ligand, which combines the electronic properties

inherent to NHC ligands and the presence of a rigid diarylamido backbone.<sup>146</sup> Bis(4-methylphenyl)amine **99** was prepared by a typical Buchwald–Hartwig amination from the corresponding aryl-bromide and aniline.<sup>147</sup> Bromination of **99**, copper-catalyzed coupling to imidazole, and further N-quaternization of the imidazole ring yielded bisimidazolium salts so isolated were coordinated to Pd(II) by transmetalation from a Ag(I)–NHC complex, using  $\text{PdCl}_2(\text{MeCN})_2$  as the palladium source (Scheme 48).

The reaction of **101a**–**103a** with  $\text{PdCl}_2(\text{MeCN})_2$  seems to proceed through elimination of HCl and formation of the corresponding amido compound. In contrast, the tridentate carbene–amine ligands reported by Douthwaite and co-workers in which the two carbene units are bridged by the more flexible diethylamine, behave in a different way.<sup>43,148</sup> In this latter case, a strong base is needed to deprotonate the NH subsequent to Pd(II) coordination, affording the amido-NHC complexes. The authors explained this difference arguing that the more rigid diarylamino ligand points the NH directly to the metal, making it easier to activate.

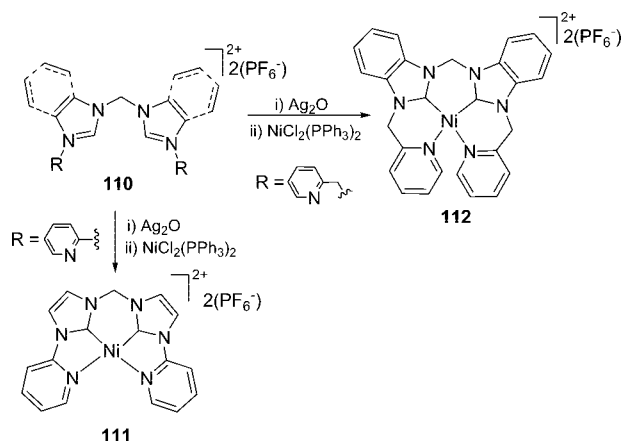
## 7.3. Bidentate Chelating NHC Complexes

### 7.3.1. Nickel Complexes

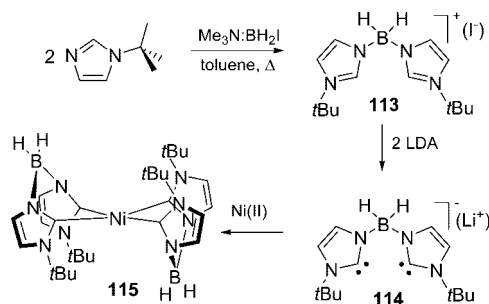
The first reports on the coordination of bidentate chelating NHC ligands to Ni(II) appeared in the literature in 1999.<sup>27,76</sup> The reaction of equimolar amounts of the methylene-bridged bisimidazolium salts with  $\text{Ni}(\text{OAc})_2$  always led to homoleptic Ni(II) carbene complexes with two chelating biscarbene ligands (**104**, Scheme 49).<sup>76</sup> Following this protocol, the formation of the *cis*-dihalide complexes was never observed even when the more sterically demanding N-substituents (*i*Pr and Cy) were present. On the other hand, the deprotonation of methylene- and ethylene-bridged bisimidazolium salts with a strong base, and further reaction with  $\text{NiCl}_2(\text{PMe}_3)_2$  afforded monocationic complexes **106**, in which only one chelating biscarbene ligand was incorporated (Scheme 49).<sup>76</sup> The homoleptic complex **107** was obtained by reacting **106a** with another equivalent of the free carbene **105a**. However, attempts to incorporate a second biscarbene unit to **106b** by reaction with 2 equiv of **105a** yielded complex **107** as well. The formation of **107** clearly indicates that the ethylene-bridged biscarbene ligand is more sterically demanding than its methylene counterpart.

Other examples of the coordination to Ni(II) and Pd(II) to more rigid biscarbene ligands were also reported.<sup>44,48</sup> Nickel(II) complex **108** (Scheme 50) constitutes the only example of a chiral Ni(II) complex bearing a biscarbene ligand.<sup>48</sup> In this particular case, the biscarbene ligand with a 2,2'-binaphthyl backbone occupies the *trans* positions of the square plane, giving the *trans*-dihalo complex, regardless of which metalation strategy is followed. In the same context,

Scheme 51



Scheme 52



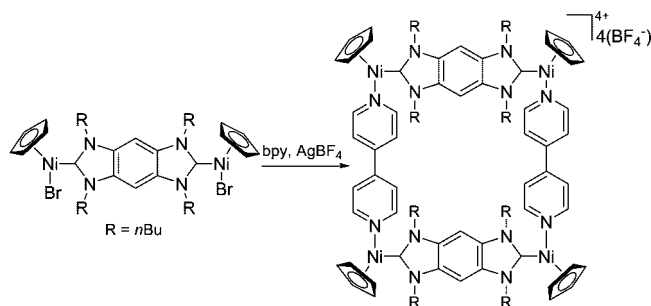
complex **109** (Scheme 50), derived from an imidazolium-linked *ortho*-cyclophane salt, showed extraordinary stability to air and heat as a result of the increased rigidity imposed by the cyclophane skeleton.<sup>44</sup>

During the last years, Lee et al. have been interested in the coordination of tetradentate pyridine-NHC ligands to  $\text{Ni(II)}$  and  $\text{Pd(II)}$  and demonstrated that these ligands provide extra stability to the catalytic species.<sup>149,150</sup> The pseudo-square-planar nickel(II) complexes **111** and **112** were easily prepared by transmetalation from the corresponding  $\text{Ag(I)}$ –NHC complexes to  $\text{NiCl}_2(\text{PPh}_3)_2$  (Scheme 51).

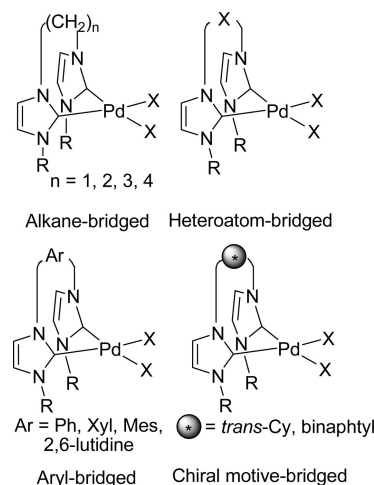
Smith and co-workers described the synthesis and coordination to  $\text{Ni(II)}$  of a bulky biscarbene borate ligand.<sup>151</sup> The ligand precursor salt (**113**, Scheme 52) was prepared as previously described<sup>152</sup> by reaction of 2 equiv of 1-*tert*-butylimidazole with *in situ* prepared  $\text{Me}_3\text{N}:\text{BH}_2\text{I}$ . Deprotonation of the resulting salt **113** with LDA and subsequent reaction with  $\text{NiCl}_2(\text{dme})$ ,  $\text{NiCl}_2(\text{PPh}_3)_2$ , or  $\text{NiCl}_2(\text{PMe}_3)_2$  resulted in the formation of the square-planar, diamagnetic  $\text{Ni(II)}$  complex **115**. In this particular case, the nickel atom is coordinated to two biscarbene borate ligands that are in a *trans* disposition. DFT calculations were performed to explain the structural differences between the isolated complex **115** and the related complex with a bispyrazolyl borate ligand,  $\text{Ni}[\text{H}_2\text{B}(\text{tBupyr})_2]_2$ , which is octahedral and paramagnetic. The authors concluded that the stabilization of the square-planar geometry by the biscarbene borate ligand can be ascribed to its greater donor ability.

Very recently, Hahn et al. described the coordination of a benzobis(imidazolylidene) ligand to  $\text{Ni(II)}$ . The reaction of nickelocene with such a rigid ligand led to a dicarbene-bridged dinuclear  $\text{Ni(II)}$  complex. Subsequent abstraction of the bromo ligands and reaction with bipyridine gave the tetracationic molecular rectangle depicted in Scheme 53.<sup>153</sup>

Scheme 53



Scheme 54



### 7.3.2. Palladium Complexes

Owing to their wide application in C–C coupling reactions, the chemistry of palladium(II)–NHC complexes has become an area of great interest and is therefore under continuous development. Indeed, this type of complex is considered as a new generation of catalysts for such organic transformations, alternatives to the ubiquitous phosphine-based ones. In particular, those bearing biscarbene ligands have received much attention mainly due to their higher stability to heat and air, and their improved catalytic performances.

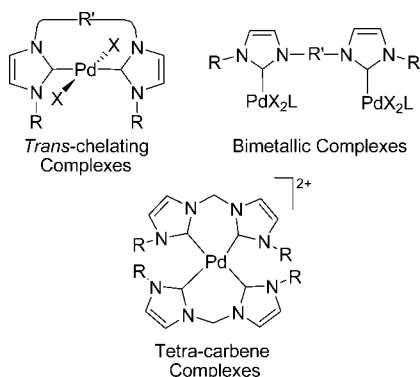
Since the preparation of the first  $\text{Pd(II)}$  complex bearing a chelating biscarbene ligand<sup>1</sup> and its successful application in C–C coupling reactions such as Heck or Suzuki,<sup>28</sup> many other examples have been described and applied to a wide set of organic transformations. In this regard, we have reviewed the structural properties, fluxional behavior, and catalytic applications of late transition metal complexes supporting chelating bis- and tris-NHC ligands, including those that are palladium-based.<sup>22</sup> Likewise, a more recent review by Cavell and Normand focuses on the latest advances in homogeneous catalysis with donor-functionalized (donor = C, N, O, S, or P) NHC complexes of group 9 and 10 metals.<sup>26</sup>

Due to the vast number of reports on palladium(II) bis-NHC chemistry, we present here a compilation of the more relevant examples, as well as a more detailed account of the more recent and interesting ones.

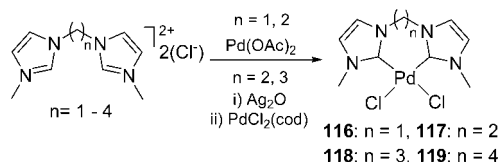
Over the last years, several neutral and cationic *cis*-chelating palladium(II) complexes have been described. They can be classified according to the functional group that bridges the two carbene units (Scheme 54): (i) alkane-bridged,<sup>1,27–36</sup>



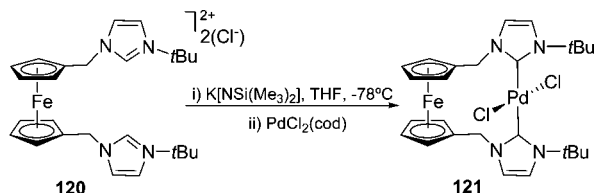
Scheme 55



Scheme 56



Scheme 57



(ii) heteroatom-bridged,<sup>42</sup> (iii) aryl-bridged,<sup>35,44–47</sup> and (iv) chiral motive-bridged.<sup>48,49</sup>

A few examples of bis-chelating tetracarbenes, in which either two identical<sup>79,154</sup> or two different<sup>27</sup> biscarbene ligands are coordinated to the same palladium atom, can also be found in the literature (Scheme 55). In addition, some neutral and cationic palladium(II) complexes in which the bidentate ligand occupies two *trans* positions of the square plane have been described.<sup>43,47,48,72,144</sup> Finally, bimetallic palladium(II) complexes in which the bidentate ligand bridges the two metal centers are scarce.<sup>33,47,144,155,156</sup>

Alkane-bridged bidentate carbenes provide an excellent way to study the effects of the ligand anisotropy on the reactivity of the complexes formed. The study of these effects, earlier performed for Rh<sup>38,41</sup> and Ir,<sup>40</sup> was recently expanded to palladium complexes.<sup>34</sup> Whereas the synthesis of the Pd(II) complexes with short alkyl bridges (**116**, **117**) was possible by reaction of the corresponding bisimidazolium salt with  $\text{Pd}(\text{OAc})_2$ , milder reaction conditions were required to isolate those with longer alkyl bridges (**118**, **119**). The synthesis of the Pd(II) complexes **118** and **119** was carried out by transmetalation of the corresponding Ag(I)–NHC complexes to  $\text{PdCl}_2(\text{cod})$ . As shown in Scheme 56, *cis*-chelating dichloro Pd(II) complexes were isolated in all cases.

There are some reports on palladium(II)–bis-NHC complexes that cannot be included in any of the subgroups proposed above. For instance, the reaction of the ferrocene-bridged bisimidazolium salt **120** with a strong base and subsequent reaction with  $\text{PdCl}_2(\text{cod})$  yielded the *trans*-chelating Pd(II) complex **121** (Scheme 57).<sup>157</sup>

Abnormal coordination was also expanded to *cis*-chelating biscarbene palladium(II) systems. In this regard,

Albrecht and co-workers described the preparation of a series of Pd(II) complexes with a chelating bis- $\alpha$ NHC ligand.<sup>53</sup> The synthetic strategy consisted of the blocking of the C2 position of the azole rings with a methyl group, thus allowing the preparation of bis- $\alpha$ NHC complexes **123–125** (Scheme 58).

New examples of *cis*-chelating palladium complexes bearing a bis-NHC ligand with a rigid binaphthyl backbone were described.<sup>158</sup> The reaction of *N*-aryl-substituted benzimidazolium salts **126**<sup>114</sup> with  $\text{Pd}_2(\text{dba})_3$  yielded the corresponding *cis*-chelating Pd(II) complexes **127** with subsequent *ortho*-metalation of the phenyl ring of the wingtip (Scheme 59).

Pyrazole-bridged NHC ligands were also coordinated to Pd(II)<sup>156</sup> and Ni(II).<sup>159</sup> The reaction of salts **128** with  $\text{Ag}_2\text{O}$  and further transmetalation to  $[\text{PdCl}_2(\text{allyl})]_2$  or  $[\text{PdCl}_2(\text{methylallyl})]_2$  yielded the targeted pyrazolate/NHC Pd(II) complexes (**129** and **130**, Scheme 60),<sup>156</sup> in which the ligand behaves both as a CN-bis-chelating ligand and NN-ligand bridging the two Pd fragments. Unfortunately, there are no reports on the catalytic applications of the isolated compounds and thus on whether the proximate palladium centers cooperate during substrate turnover.

While a vast number of symmetrically substituted bis-NHC ligands have been reported, there are only two examples of nonsymmetrically substituted bis-NHC ligands.<sup>55,160</sup> Scheme 61 depicts the synthesis of nonsymmetrically substituted ethylene-bridged bisimidazolium salts **131** and their coordination to Pd(II) via transmetalation, yielding *cis*-chelating complexes **132**.<sup>160</sup>

Yet another example of chiral alkane and aryl-bridged palladium(II) complexes was reported by Herrmann and co-workers.<sup>161</sup> Two new chiral imidazoles were synthesized starting from commercially available chiral amines. The reaction of the isolated chiral imidazoles with the corresponding dibromo compound yielded imidazolium salts **133** (Scheme 62, Table 2), which maintain the (*R*)-configuration of the original amines. As depicted in Scheme 62, the neutral dibromo biscarbene complexes **134** were synthesized by reaction of the chiral imidazolium salts with  $\text{Pd}(\text{OAc})_2$ . Although the authors proposed that the rigidity of the chiral chelating biscarbene ligand can result in higher optical inductions in asymmetric reactions, there are no reports to-date of the catalytic performances of these palladium complexes.

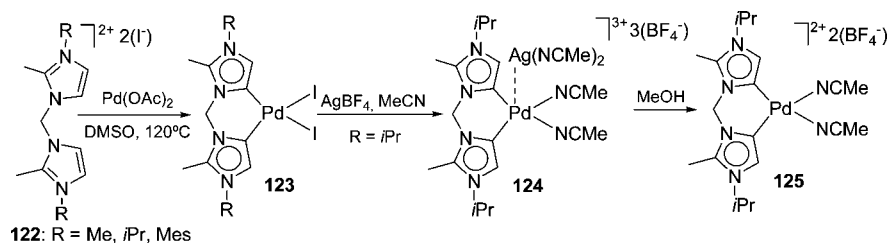
The bitriazolylidene ligand (bitz) was also coordinated to Pd(II).<sup>51</sup> The reaction of the tetrafluoroborate salt of **31** (Scheme 19) with  $\text{Pd}(\text{OAc})_2$  in refluxing MeCN yielded dicationic complex **135** (Scheme 63). As discussed in section 3 of this review, complex **135** displays the smallest bite angle for a chelating bis-NHC, with a value of  $79.1^\circ$ .

### 7.3.3. Platinum Complexes

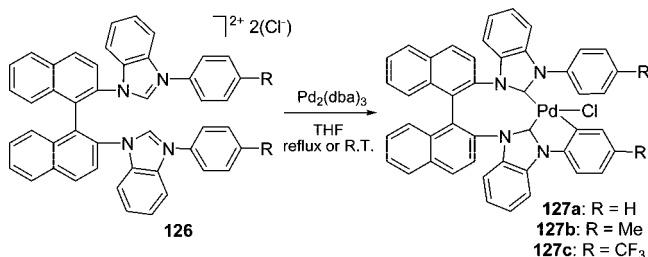
The first examples of chelating biscarbene Pt(II) complexes were described by Fehlhammer and co-workers in 2001.<sup>162</sup> Platinum(II) halide salts, such as  $\text{PtCl}_2$  or  $\text{PtI}_2$  were directly reacted with the bis(imidazolyl)borate biscarbene **136** affording complexes **137**, as shown in Scheme 64. These homoleptic tetracarbene–Pt(II) complexes are neutral, as a consequence of the negative charges of the  $\text{BH}_2^-$  linker of the bisimidazoles.

Replacing  $\text{BH}_2^-$  in **136** by its isoelectronic  $\text{CH}_2$  moiety, Strassner<sup>163</sup> and Youngs<sup>164</sup> reported the first examples of chelating alkane-bridged bis-NHC–Pt(II) complexes. Up to

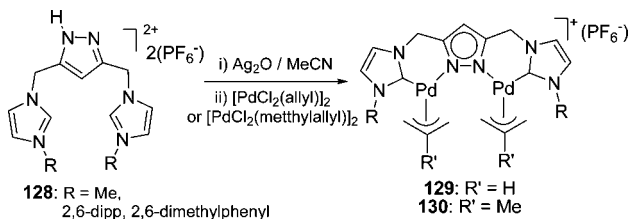
Scheme 58



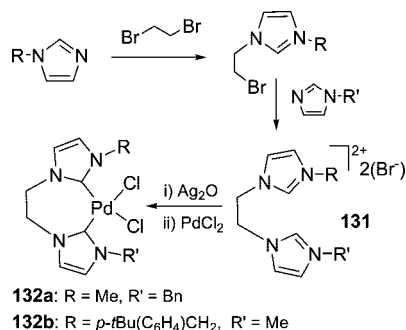
Scheme 59



Scheme 60



Scheme 61



Scheme 62

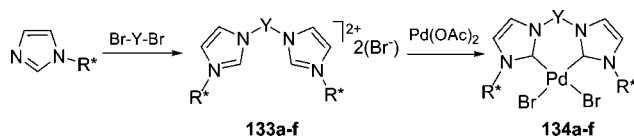
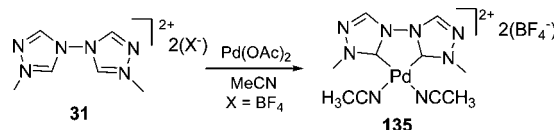


Table 2. Chiral Imidazolium Salts 133a–f

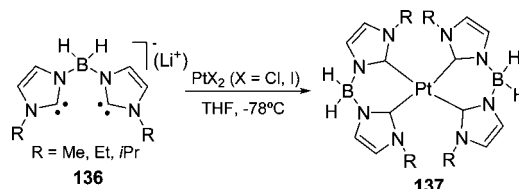
imidazolium salt	R*	Y
133a	( <i>R</i> )-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	CH <sub>2</sub>
133b	( <i>R</i> )-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	<i>o</i> -xyl
133c	( <i>R</i> )-CH(C <sub>10</sub> H <sub>7</sub> )CH <sub>3</sub>	<i>o</i> -xyl
133d	( <i>R</i> )-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	<i>m</i> -xyl
133e	( <i>R</i> )-CH(C <sub>6</sub> H <sub>5</sub> )CH <sub>3</sub>	<i>p</i> -xyl
133f	( <i>R</i> )-CH(C <sub>10</sub> H <sub>7</sub> )CH <sub>3</sub>	2,6-(CH <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>3</sub> N)

that point, only a few examples of Pt(II)–NHC complexes were known, and in most cases, their synthesis involved tedious multistep pathways.<sup>162,165</sup> As illustrated in Scheme 65, the synthesis of the Pt(II) complexes was carried out using the corresponding platinum(II) halides, which are

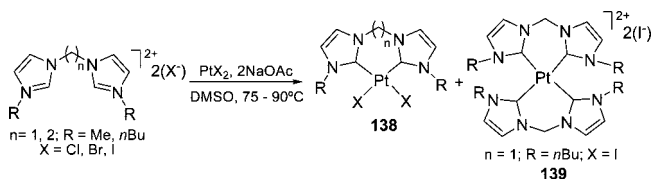
Scheme 63



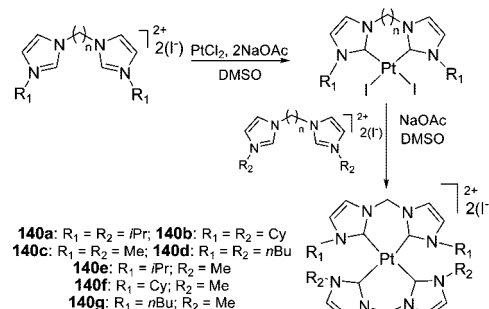
Scheme 64



Scheme 65



Scheme 66

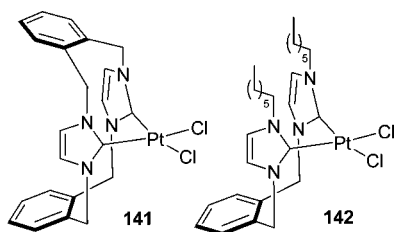


readily available. The deprotonation of a series of bisimidazolium salts with NaOAc in the presence of PtX<sub>2</sub> (X = Cl, Br, I) afforded the chelating biscarbene complexes **138**. Interestingly, the reaction of 1,1'-methylene-bis(*n*-butylimidazolium)diiodide with PtCl<sub>2</sub> under the same reaction conditions also gave the homoleptic chelating tetracarbene **139** (Scheme 65) even when a precise 1:1 ratio of the salt to PtCl<sub>2</sub> was used.<sup>164</sup> Similar complexes can be obtained by direct reaction of platinum(II) acetylacetonate and the corresponding bisimidazolium salt.<sup>166</sup>

Platinum(II) tetracarbene complexes similar to **139**, were also obtained following the sequential procedure depicted in Scheme 66.<sup>167</sup> Using this methodology, homoleptic (**140a–d**) and heteroleptic tetracarbene complexes (**140e–g**) were obtained.

Other examples of highly stable bis-NHC–Pt(II) complexes were reported later. Complexes **141** and **142** (Scheme 67) represent the first examples of platinum(II)–bis-NHC

Scheme 67

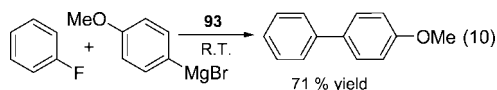


complexes in which the carbene units are linked by a cyclophane motive.

## 7.4. Catalytic Applications

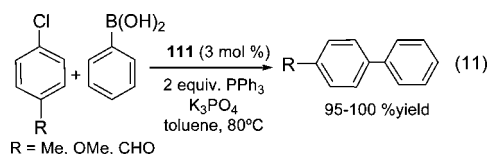
### 7.4.1. Nickel(II) Complexes

The catalytic activity of the pincer nickel(II) complex **93** (Scheme 45) was studied for different C–C coupling reactions, showing good to excellent results.<sup>140,168</sup> High activities were achieved in the Heck coupling of aryl bromides and activated aryl chlorides with butyl acrylate, but the reaction did not work for nonactivated aryl chlorides.<sup>140</sup> It is important to point out that the catalytic activity decreased upon addition of a drop of Hg, thus suggesting that heterogeneous catalytic species could be involved in this transformation. Complex **93** was also tested in Grignard coupling reactions, yielding the desired bisaryl compounds in moderate to good yields when aryl bromides and chlorides were used.<sup>168</sup> More interestingly, several aryl fluorides were successfully coupled to aryl Grignard reagents in the presence



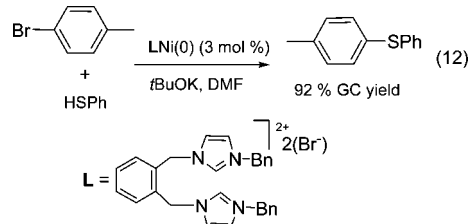
of **93** (eq 10), although longer reaction times were required. Additionally, **93** proved to be active in the Suzuki coupling reaction. The air and moisture stability of the catalyst allowed the reactions to be carried out aerobically and at high temperatures during several hours. These results present chelating Ni(II)–NHC complexes as a much cheaper alternative to Pd(II) in cross-coupling reactions.

The catalytic activity of nickel(II) complexes **111** and **112** (Scheme 51) was tested in the coupling of aryl chlorides with phenylboronic acid, showing moderate activities.<sup>150</sup> However, the activity of complex **111** was dramatically improved by the addition of 1 or 2 equiv of PPh<sub>3</sub>. For instance, 3 mol % of the Ni(II) catalyst **111** together with 2 equiv of PPh<sub>3</sub> achieved nearly full conversion within 10 h even for electron-rich aryl chlorides (eq 11).



More recently, the application of Ni(0) complexes in C–S coupling was studied.<sup>169</sup> The *in situ* generated Ni(0)–NHC species showed good to excellent activities toward various aryl halides in C–S coupling, making them excellent candidates to replace Pd-organophosphanes for this reaction. In particular, aryl-bridged bidentate NHC ligand L provided

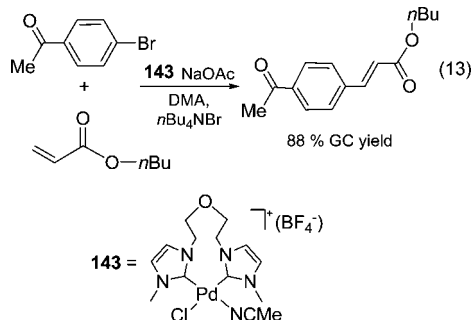
excellent results in the coupling of 4-bromotoluene with thiophenol (eq 12).



### 7.4.2. Palladium(II) Complexes

Complexes **96–98** (Scheme 46) have demonstrated the ability to catalyze Heck and Suzuki coupling reactions with *para*-functionalized aryl bromides.<sup>142</sup> These robust and air- and moisture-stable complexes allowed the reactions to be carried out under aerobic conditions making them suitable for the activation of less reactive aryl halides. Although pincer complexes **101b–103b** (Scheme 48) performed well in the Suzuki coupling of aryl bromides, no activity on the activation of aryl chlorides was reported.<sup>146</sup>

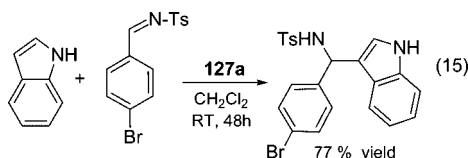
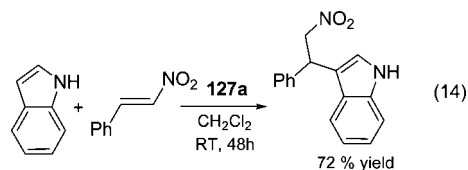
A palladium(II) ether-functionalized bis-NHC complex reported by Cavell and co-workers was tested in the Heck coupling of 4-bromoacetophenone and *n*-butyl acrylate, showing moderate activity (eq 13).<sup>42</sup> Taking into account related examples,<sup>143,170</sup> the authors proposed that the replacement of the *N*-methyl substituents by the bulkier Mes or dipp groups would improve the catalytic activity. However, the solid-state structure of complex **143** revealed that it may not be flexible enough to accept such large *N*-substituents.



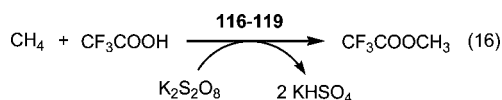
Very recently, Hwang's group examined the catalytic activity of a homoleptic bischelate tetracarbene Pd(II) complex.<sup>154</sup> Contrary to the assumption that the catalytic activity of a biscarbene system might be inhibited by the formation of a bischelate tetracarbene Pd species,<sup>36</sup> they proved that this complex is an excellent precatalyst for the Heck reaction with potential recyclability. For instance, in the coupling of bromo-benzene and styrene, the catalyst was reused six times without detectable loss of activity. The tetracarbene complex displayed good activity in the Heck coupling of a wide variety of aryl bromides and also one activated aryl chloride, 4-chloroacetophenone, while it was barely active with nonactivated aryl chlorides.

Also, some new palladium-based catalysts for the Suzuki–Miyaura cross-coupling reaction were developed. For instance, the activity of the complex **132a** (Scheme 61) was investigated for the coupling of sterically hindered substrates. Although moderate to high yields were obtained when only one of the coupling partners (aryl boronic or aryl halide) was mono- or di-*ortho*-substituted, no coupled products were obtained when both partners were sterically demanding. The

cyclometallated *cis*-chelated complexes **127** (Scheme 59) were successfully applied in the same cross-coupling reactions. The complex **127a** was also applied in the Friedel–Crafts reactions of indole with 2-nitrovinylbenzene and *N*-(4-bromobenzylidene)-4-methylbenzenesulfonamide under mild conditions (eqs 14 and 15, respectively), showing moderate activity.<sup>171</sup>



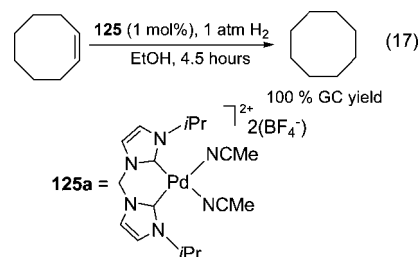
Other catalytic applications for Pd(II) bis-NHC complexes were described besides those implying a C–C bond formation. Alkane-bridged complexes with different alkylidene chain lengths **116–119** (Scheme 56) were tested in the conversion of methane into methanol in the presence of a strong oxidizing agent such as  $K_2S_2O_8$ .<sup>34</sup> One problem in the direct functionalization of methane is that only the first bond, but not the second or more bonds, must be modified. Since the C–H bonds of methanol are less stable than those in methane, a way to avoid further activation of the methanol thus formed is to intercept it in the form of a methyl ester by adding a strong acid in the reaction media. A suspension of  $K_2S_2O_8$  in a mixture of trifluoroacetic acid and its anhydride at a methane pressure of 30 bar and 90 °C in the presence of a catalytic amount of the palladium complex afforded the formation of trifluoroacetic acid methyl ester (eq 16).



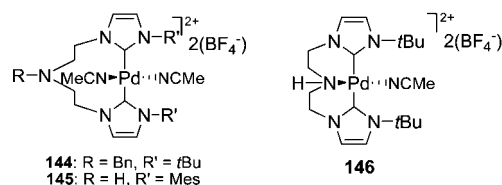
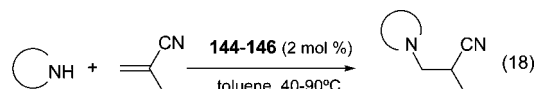
The ethylene-bridged biscarbene complex **117** displayed the best activity for the activation of methane and its oxidation to trifluoroacetic acid methyl ester, being the most active palladium biscarbene complex for this reaction reported to-date.<sup>30</sup> The methylene and butylene-bridged complexes **116** and **119** were also found quite active in the C–H activation of methane, while the reactivity of the propylene-bridged complex **118** was significantly lower.

The effect of electronic properties of the abnormally bound complexes **123–125** (Scheme 58) were studied in catalytic olefin hydrogenation,<sup>53</sup> which involves the activation of  $H_2$  as the key step. The bis(solvent) complex **125** (Scheme 58) performed well as catalyst in the hydrogenation of cyclooctene at room temperature and 1 atm  $H_2$  whereas its C2-bound counterpart **125a**<sup>33</sup> performed poorly (eq 17). The catalytic results suggested that the high electron density imparted by this bonding mode affects the catalytic activity and allows the activation of less reactive bonds such as in  $H_2$ .

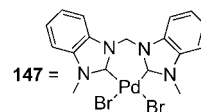
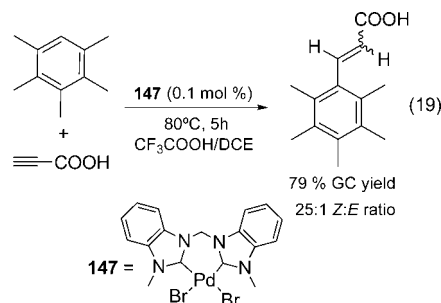
The bis-NHC complexes **144** and **145** and pincer complex **146** were tested in the hydroamination of alkenes (eq 18).<sup>43</sup>



Complexes **144–146** catalyzed the reaction between the activated alkene methacrylonitrile and cyclic secondary alkenes such as piperidine, pyrrolidine, morpholine, and *N*-methyl piperazine. However, much lower activities were achieved when a nonactivated alkene, such as styrene, was employed. In the absence of cocatalyst, complex **145** gave the highest catalytic performances.



In the context of C–C coupling transformations, Biffis and co-workers proved the high activity of chelating bis-NHC palladium(II) and platinum(II) complexes in the coupling of arenes with alkynes (the Fujiwara reaction).<sup>35</sup> The Fujiwara reaction, in which products of the formal hydroarylation of the triple bond are formed, constitutes an interesting C–C coupling reaction via C–H activation/functionalization, since it involves cheap, commercially available reagents and requires neither directing groups on the arene nor oxidizing agents to regenerate the catalyst.<sup>172,173</sup> In addition, the reaction is highly stereoselective and *cis*-arylalkenes, being the thermodynamically less favored alkenes, are the major products. The employment of the biscarbene–Pd(II) complex **147** allowed performance of the reactions in short times, at higher temperatures, and with only 0.1 mol % of catalyst, notably improving earlier results by Fujiwara. Good to excellent yields and high chemo- and stereoselectivities were achieved with a wide range of alkynes and electron-rich arenes. For instance, the reaction of pentamethylbenzene with propynoic acid gave 79% conversion with 96% selectivity for the *Z*-product (eq 19).

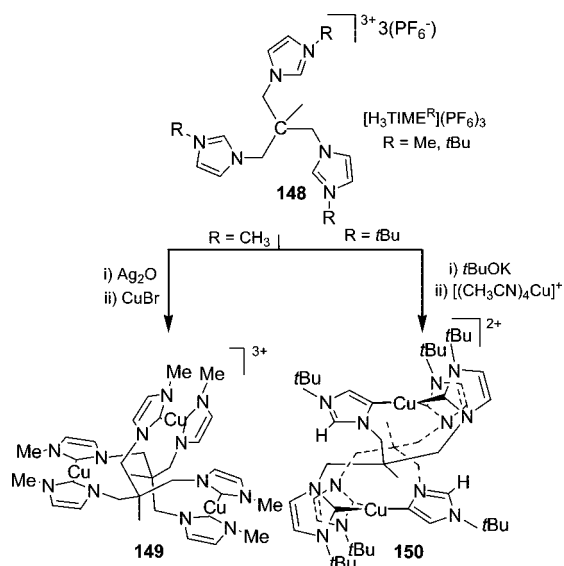


### 7.4.3. Platinum(II) Complexes

Platinum(II) bis-NHC complexes of the type of **138** (Scheme 65), in particular the one bearing methyl *N*-



Scheme 68



substituents and bromide coligands,<sup>163</sup> proved to be efficient in the Fujiwara reaction.<sup>35</sup> This complex displayed slightly lower activity than Fujiwara's systems ( $PtCl_2/2AgOAc$  or  $PtCl_2/2AgOTf$ ) but required lower catalyst loadings and shorter reaction times and did not require the addition of a cocatalyst.<sup>173,174</sup> The Pt(II) complex performed as well as its palladium counterpart in terms of activity and selectivity.

Neutral dichloro bis-NHC Pt(II) complexes were successfully applied in the catalytic C–H activation of methane.<sup>175</sup> The activity of these complexes was studied under the same reaction conditions as those for their Pd(II) analogues,<sup>30,34</sup> in a mixture of trifluoroacetic acid, its anhydride, and  $K_2S_2O_8$  (eq 16). Although both yields and turnover numbers achieved were not very high, the experiments showed that the platinum(II) complexes are stable enough in acidic media and that the reactions work using very low catalyst loadings (0.1 mol %).

## 7.5. Other Applications

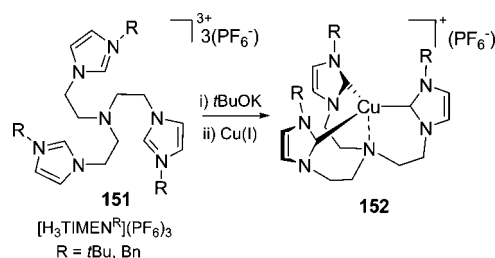
Very recently an interesting application for chelating bis-NHC–Pt(II) complexes was described.<sup>167</sup> The photophysical properties of homoleptic and heteroleptic tetracarbene complexes **140b**, **140d**, and **140f** (Scheme 66), suggested that this class of NHC-based compounds is an interesting structure for blue phosphorescent emitters. Phosphorescent organic light-emitting devices have attracted great attention lately since they would constitute very efficient light sources. However, no emitters for the deep blue are yet available, and many platinum complexes are under study for that purpose.<sup>176</sup> Furthermore, the tetracarbene complexes showed high chemical (decomposition above 340 °C) and photochemical stability.

## 8. Poly-NHC Ligands in Complexes of Group 11 Metals

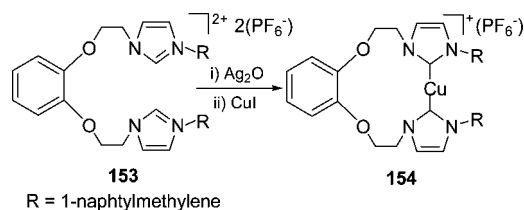
### 8.1. Copper

The first examples of polycarbene–copper complexes were developed by Meyer et al. (Schemes 68 and 69).<sup>177</sup> The coordination of the triscarbene **148** (TIME) to copper led to

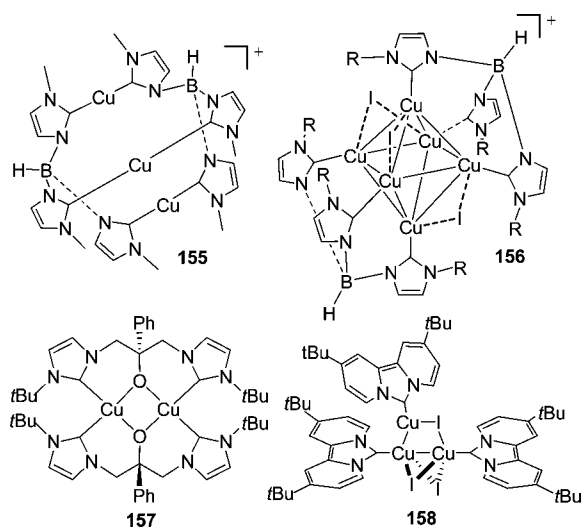
Scheme 69



Scheme 70



Scheme 71



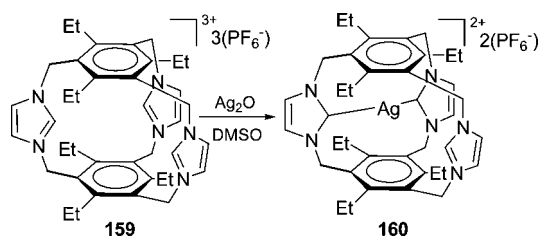
different products (Scheme 68) depending on the reaction conditions and the wingtip groups.<sup>178</sup> When the coordination was carried out by the transmetalation procedure using silver oxide, the trinuclear copper(I) complex **149** was obtained. In contrast, when a strong base was used for deprotonation and  $[(MeCN)_4Cu]^+$  was used as the copper source, a dinuclear complex **150** was observed. This complex shows the coordination of two normal and one abnormal NHC ligands.

When the central carbon in the TIME ligand was changed by nitrogen, the N-centered TIMEN ligand **151** was obtained.<sup>178</sup> Deprotonation using an external base led to the tris-NHC N-anchored tetracoordinated complex **152** (Scheme 69).

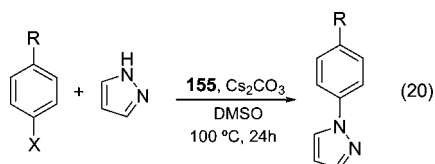
Copper metallacrown ether complexes with NHC ligands were also described. The reaction of the imidazolium 1,2-bis[*N*-(1-naphthyl)methylene]imidazoliummethoxy] benzene hexafluorophosphate (**153**, Scheme 70) with silver oxide in the presence of CuI led to complex **154** (Scheme 70).<sup>179</sup> A 13-membered ring cavity is formed. The complex was structurally and spectroscopically characterized, although no catalytic information was reported.

Deprotonation of a tris(carbene)borate ligand similar to **9** (Scheme 11) using  $nBuLi$  in the presence of  $[CuBr(PPh_3)_3]$  afforded complex **155** (Scheme 71). In this compound, each

Scheme 72



of the two tris-NHC ligands is bridging the three different metal atoms, which display a local linear arrangement.<sup>180</sup> Under the same reaction conditions but with the metal precursor changed to CuCl, the Cu<sub>6</sub>-octahedral complex **156** was obtained.<sup>181</sup> Complex **155** is a good catalyst of Ullmann-type arylation reactions (eq 20). Different kinds of azole rings can be arylated with arylhalides, even using arylchlorides. Other substrates such as aryl alcohols or amides can also be arylated at 100 °C in 24 h.<sup>180</sup> The functionalization of a chelating-NHC ligand with an alkoxide allowed the synthesis of dicopper complex **157**.<sup>182</sup> The most characteristic feature of this compound is that the anionic alkoxide ligand forces the two Cu(I) centers to adopt a nearly square-planar geometry. The coordination of an annulated-NHC ligand to CuI using *t*BuOK led to a Cu(I) trimer with two Cu–Cu bonds and three bridging iodides (complex **158**).<sup>183</sup>



## 8.2. Silver

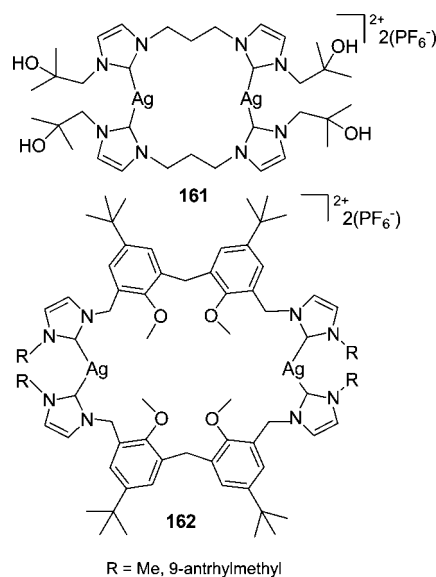
The preparation, properties, and applications of silver–NHC complexes have been extensively reviewed from different points of view,<sup>184,185</sup> and many articles have appeared covering aspects such as structural parameters, transmetalation of NHCs, chelating NHCs,<sup>69,186</sup> silver–silver interactions,<sup>187</sup> and even antimicrobial activity.<sup>188</sup> We will focus on the recent developments in the field of silver–poly-NHC complexes.

The tris(imidazolium) hexasubstituted benzene cage compound **159** was reported in 1995 (Scheme 72).<sup>73</sup> Contrary to other hexasubstituted benzene-type “pinwheel” compounds,<sup>189</sup> **159** is not a good host for anions most probably as a consequence of insufficient free space within the compound. The reaction of compound **159** with silver oxide yielded the silver–NHC complex **160** in which only two of the three imidazolium moieties are activated to form the NHC, while the other remains protonated.

A range of silver dicarbene complexes with an alkyl unit bearing an alcohol were recently described (**161**, Scheme 73).<sup>190</sup> The solid state properties showed that these complexes form channels where the solvent molecules are located.

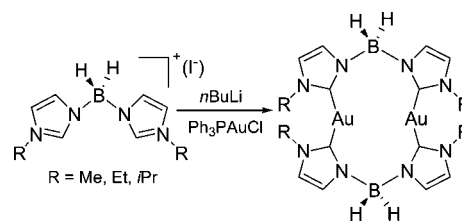
A new family of calixarene analogues based on silver–NHC complexes was described and can be considered as a special class of silver–NHC macrocycles (**162**, Scheme 73). In the solid state, these complexes adopt a twisted 1,2-alternate conformation with the methoxy groups pointing to the void of the cyclic cavity. Complex **162** (R = 9-anthrylmethyl) is an efficient macrocyclic host molecule that complexes [60]fullerene and acts a good fluorescent sensor for [60]fullerene.<sup>191</sup>

Scheme 73



R = Me, 9-anthrylmethyl

Scheme 74



## 8.3. Gold

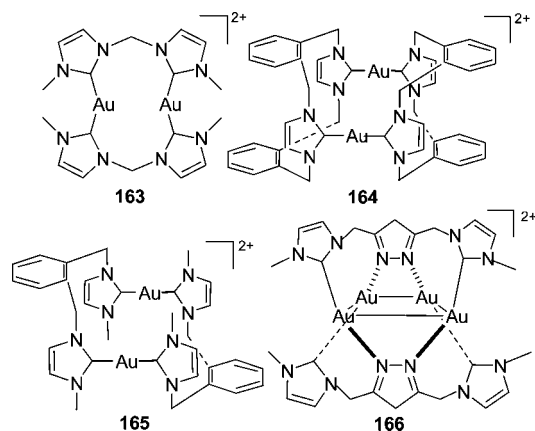
Most of the gold complexes with poly-NHC ligands have been obtained using two different coordination strategies, namely, deprotonation of the imidazolium salt with a strong base and transmetalation from silver–NHC. The most common gold(I) sources are AuCl(PPh<sub>3</sub>) and AuCl(SMe<sub>2</sub>).<sup>192</sup>

One of the first examples of a gold complex with a poly-NHC ligand corresponds to the coordination of bis(imidazol-2-ylidene-1-yl)borate as shown in Scheme 74.<sup>162</sup> Although this ligand forms small chelating rings with palladium and platinum, for gold a bridging coordination is preferred. The crystal structure shows a 12-membered neutral dimetallacycle in a twisted boat-like conformation with a weak Au–Au interaction.<sup>162</sup>

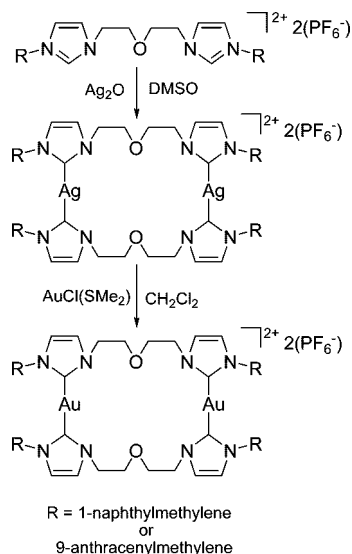
A series of gold complexes with poly-NHC ligands were synthesized from imidazolium-based cyclophanes and related acyclic bis(imidazolium) salts (**163–165**, Scheme 75). The structural diversity of the ligands allowed the synthesis of a series of Au complexes having a range of structural and chemical properties. The non-cyclophane systems are fluxional in solution, while rigid systems are obtained for the cyclophane derivatives (**164**, **165**).<sup>193</sup> These complexes are new potential antitumor agents that selectively target the mitochondria of cancer cells.<sup>194</sup> The reaction of 3,5-bis((*N*-methylimidazolium)methyl)pyrazole bis(hexafluorophosphate) with Ag<sub>2</sub>O and further transmetalation of the Ag(I)–NHC complex to AuCl(SET<sub>2</sub>) yielded a square-planar tetranuclear gold complex (**166**, Scheme 75).

The silver precursor is isostructural and both of them are intensely luminescent in the solid state.<sup>195</sup> Another example of isostructural silver and gold NHC complexes is observed for bis(imidazolium)polyether chain ligands (Scheme 76).

Scheme 75



Scheme 76



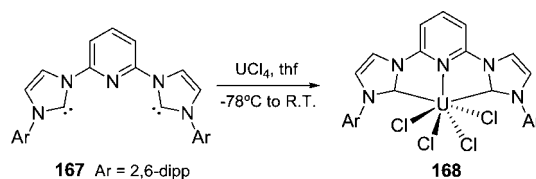
In this case, the Au–Au distance is long enough to prevent metal–metal interaction.<sup>196</sup>

Some other interesting examples of silver(I) and gold(I) complexes have been very recently described.<sup>197–199</sup> Hahn and co-workers reported the preparation of mono- and dinuclear silver(I) complexes starting from a cyclophane-type tetra-imidazolium salt, and their use in transmetalation reactions to yield the corresponding gold(I) complexes. Interestingly, the synthesis of a cyclic hexa-imidazolium salt and the preparation of a hexanuclear silver(I)–NHC derived from this ligand, have been also communicated.<sup>197</sup> Biffis and co-workers reported the preparation of series of silver(I) and gold(I) complexes bearing a tripodal tris(NHC)borate ligand. The silver(I) complexes were tested in the coupling of aryl halides with terminal alkynes (the Sonogashira reaction), showing low activity.<sup>198</sup> New tetracarbene Ag(I) and Au(I) complexes in which two identical bis(triazolylidene)borate ligands are bridging the two metal centers (the triazole version of the complexes depicted in Scheme 74) have been described.<sup>199</sup>

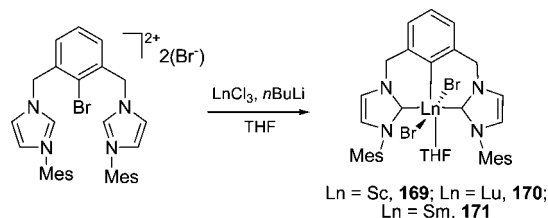
## 9. f-Block Poly-NHC Complexes

There are several reports on f-block-based complexes bearing amido-<sup>200</sup> and phenoxo-tethered,<sup>201</sup> salicylaldiminato-<sup>202</sup> indenyl-<sup>203</sup> and fluorenyl-modified<sup>204</sup> NHC ligands, and these were comprehensively reviewed by Arnold and Lid-

Scheme 77



Scheme 78



dle.<sup>205</sup> However, the examples of poly-NHC ligands in complexes of f-block are restricted to a couple of examples. In 2006, Danopoulos described the first pincer NHC complex of an f-block metal.<sup>206</sup> As depicted in Scheme 77, the reaction of the free carbene **167** and  $\text{UCl}_4$  yielded U(IV) complex **168**, which is the only uranium complex supported by a poly-NHC ligand reported to-date. The molecular structure of complex **168**, determined by X-ray diffraction, showed the metal center in a seven-coordinate geometry best described as a distorted capped trigonal prism.

Another example of a bis-NHC ligand coordinated to various rare-earth metal centers has been recently communicated.<sup>207</sup> The treatment of the xylenyl-bridged CCC pincer bis-NHC ligand precursor and the corresponding lanthanide trichloride ( $\text{LnCl}_3$ ) with  $n\text{BuLi}$  afforded scandium, lutetium, and samarium complexes (**169**, **170**, and **171**, respectively, in Scheme 78). The molecular structures of complexes **169**–**171** were determined by X-ray diffraction as THF-solvated monomeric rare-earth metal dibromides.

## 10. Conclusions

Easy access to NHC precursors has allowed the preparation of a wide set of poly-NHC ligands with an almost unlimited number of architectures. The coordination versatility of this type of ligand has afforded complexes of almost any transition metal in different oxidation states. Parallel to the development of the chemistry of the poly-NHC ligands, new applications are being found, of which catalysis is the one that has had more research devoted. Not only can poly-NHC ligands provide enhanced catalytic properties, but they are also found to afford processes not previously known for complexes with other ligands.

Together with the catalytic applications, these ligands have found their place in the design of complexes with unusual photophysical properties, whose practical applications can be envisaged. Also, the recent examples of the antitumoral and antibacterial properties of some of these species widens their scope of applications where there is every reason to think that they will be equally useful.

## 11. Abbreviations

aNHC	abnormal N-heterocyclic carbene
av	average
<i>t</i> Bu	<i>tert</i> -butyl
bpy	bipyridine
cod	1,5-cyclooctadiene



coe	cyclooctene
Cp	cyclopentadienyl
Cp*	pentamethyl cyclopentadienyl
Cy	cyclohexyl
dba	dibenzylideneacetone
DCE	dichloroethane
DFT	density functional theory
2,6-dipp	2,6-diisopropylphenyl
DMA	dimethylacetamide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
Et	ethyl
iPr	isopropyl
MAO	methylaluminoxane
Me	methyl
MeIm	methyl imidazole
Mes	mesityl; 2,4,6-trimethylbenzyl
MeCN	acetonitrile
nbd	norbornadiene
nbe	norbornene
NHC	N-heterocyclic carbene
ntc	nortricyclyl
Py	pyridine
terpy	terpyridine
THF	tetrahydrofuran
TFA	trifluoroacetic acid
TON	turnover number
Tp	tris(pyrazolyl)borate
tmdea	tetramethylethylenediamine
xyl	xylene

## 12. Acknowledgments

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