Nickel N-heterocyclic carbene complexes in homogeneous catalysis

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Chapter 1

Introduction

Abstract. *The chemistry of N-heterocyclic carbenes (NHCs) is reviewed and discussed. First an overview is given of the electronic structure of free carbenes, followed by a discussion on the structure of transition-metal NHC complexes, with an emphasis on nickel complexes. Then synthetic routes leading to such complexes are evaluated. In addition, an overview of reactions catalyzed by transition-metal NHC complexes is presented, followed by a description of the contents of this thesis.*

1.1 Introduction

An old definition of the word 'carbene' is 'a bitumen soluble in carbon disulfide but insoluble in carbon tetrachloride'.[1] Nowadays, the term carbene is used for a divalent carbon compound in which the carbene carbon atom is linked to two adjacent groups by covalent bonds and has two non-bonding electrons (Figure 1.1), which are either in a singlet or in a triplet state.

A special class of carbenes is the group of N-heterocyclic carbenes (NHCs),[2-9] which is the subject of this thesis. Since the first isolation of a free NHC in 1991,[10] the study and application of these compounds is a fast growing field, as can be seen in Figure 1.2. In this figure the number of hits in a literature search using the SciFinder Scholar program for the phrase 'N-heterocyclic carbene', ordered by year of publication, is depicted.[11] It reveals a linear increase in the number of papers published on this subject between 2002 and 2008.

The great interest for NHCs may mostly be attributed to the fact that they are highly versatile ligands for transition-metal complexes, especially of complexes used in homogeneous catalysis. A famous example of the successful use of NHCs in catalysis is the Grubbs catalyst. The first generation Grubbs catalyst, a ruthenium complex with two phosphane ligands was found to be highly active in the metathesis of olefins. The second generation catalyst, in which one of the phosphane ligands

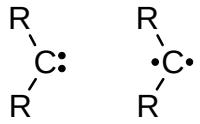


Figure 1.1. Singlet and triplet carbenes.

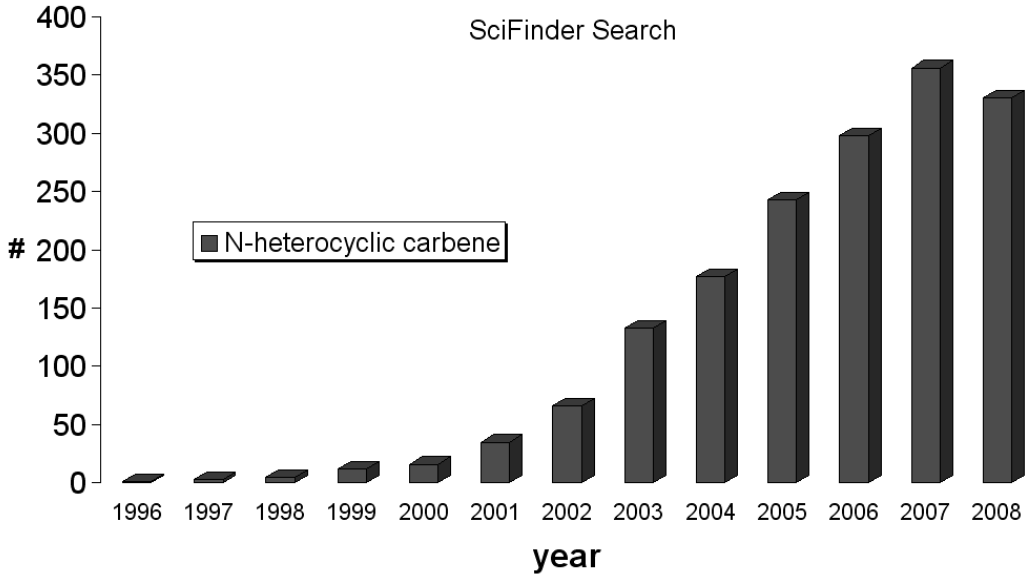


Figure 1.2. Number of papers on the subject of N-heterocyclic carbenes, ordered by publication year, found using the SciFinder Scholar program.

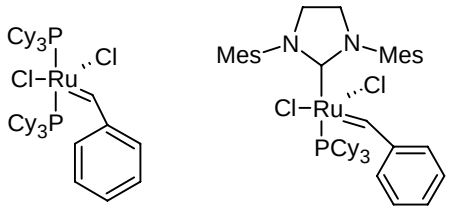


Figure 1.3. First and second generation Grubbs catalysts.

was replaced by a NHC ligand, proved to be even more active and more stable (Figure 1.3).[12] In 2005 Robert Grubbs was awarded the Nobel Prize in chemistry for his work on the metathesis reaction.

In this chapter a short overview is given of the properties of carbenes and of N-heterocyclic carbenes in particular. Then their properties as ligands in transition-metal complexes are discussed, followed by a short overview of catalytic reactions in which NHC complexes have been investigated. The discussion will be focused on the synthesis and use of nickel NHC complexes.

Nomenclature

Some inconsistencies appear to be present in the literature in the nomenclature of imidazole derivatives and carbenes thereof. In this thesis the nomenclature shown in Figure 1.4 will be followed. Furthermore, it should be noted that metal N-heterocyclic carbene complexes derived from imidazole have been depicted differently in literature (Figure 1.4, **A** - **D**). Representation **A** is used throughout this thesis.

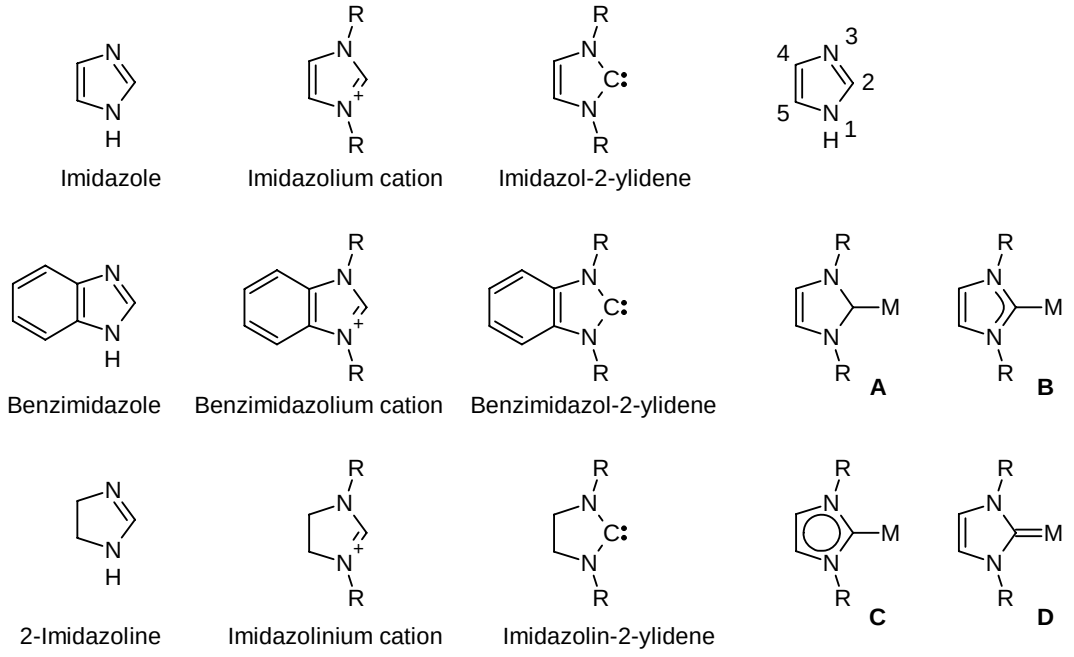


Figure 1.4. Nomenclature of imidazole-derived structures, atom numbering, and a variety of common representations of metal NHC complexes (**A** – **D**).

1.2 Carbenes

Reactants in organic synthesis

Free carbenes are known in organic synthesis as useful reactants. A common reaction involving a carbene is given in Scheme 1.1.[13] In this case, the dichlorocarbene may be generated by reaction of chloroform with a strong base. Subsequent reaction with an olefin leads to the formation of a cyclopropane.

Singlet vs triplet state – theoretical discussion

Having only two substituents, the geometry around the divalent carbene carbon atom can be either bent or linear. The latter geometry is based on an sp-hybridized carbon atom. Most carbenes, however, have an sp^2-hybridized carbon atom and the geometry is not linear. The energy of one p orbital, p_π, does not change by going from the sp to the sp^2-hybridization state. Due to its partial s character the sp^2 orbital, which is described as a σ orbital, is energetically stabilized relative to the original p orbital (Figure 1.5).[7]

The two nonbonding electrons available on the sp^2-hybridized carbene carbon atom can have antiparallel spins, with the two electrons occupying the σ-orbital

Scheme 1.1. Dichlorocarbene in organic synthesis.

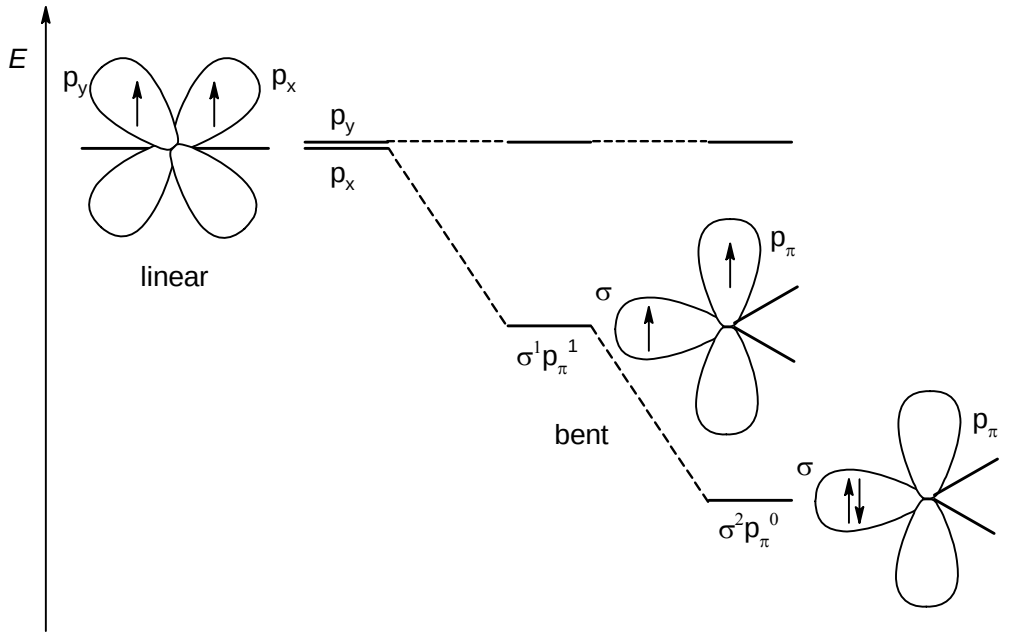
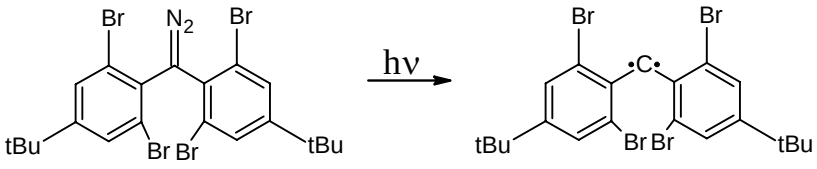


Figure 1.5. Energy diagram with possible electron configurations for the frontier orbitals of carbene carbon atoms.[7]



Scheme 1.2. Generation of a triplet carbene.

($\sigma^2p_\pi^0$, singlet state) or parallel spins, with the electrons divided over the two orbitals ($\sigma^1p_\pi^1$, triplet state). A less-stable singlet state with both electrons in the p_π-orbital and an excited singlet state with antiparallel occupation of the two orbitals are theoretically feasible, but are not considered to be of importance.[7]

Whether a carbene is in the singlet or the triplet ground state is determined by the relative energies of the σ and the p_π orbitals. If the gap between the two states is greater than about 40 kcal/mol, a singlet ground state is favored.[14] The relative energies of the two orbitals are determined by the substituents. For instance, large, electron-withdrawing groups give rise to singlet carbenes, while electron-donating groups favor the more reactive triplet state.[3] Three types of substituents may be distinguished: (1) substituents that are part of a conjugated system, (2) substituents that withdraw π electrons from the carbene center and (3) substituents that donate π electrons. To the first type belong triplet carbenes in which the carbene carbon atom has two alkene, alkyne or aryl groups. An example of such a reactive triplet carbene is shown in Scheme 1.2. Even with the steric bulk provided by the substituents, this species has a half-life of 16 seconds in a benzene solution.[15]

Examples of the second type of substituent are π-accepting substituents such as Li, BH_2 or BeH. Often these carbenes have a linear or nearly linear geometry.

Substituents belonging to the third type enhance the nucleophilicity of the carbon atom and the thermodynamic stability. To this type belong N, O, S and P substituents, as well as halides. The interaction of the π electrons of the substituents with the p_π orbital of the carbene center leads to a four-electron-three-center π system, with multiple bond character for the carbene-substituent bond (Figure 1.6).

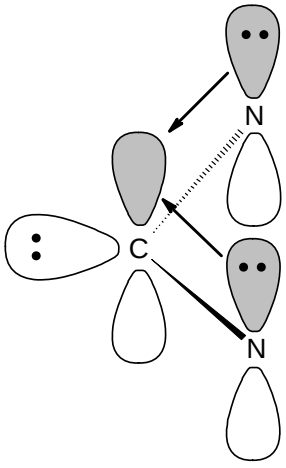


Figure 1.6. Stabilization of NHCs by π interaction.

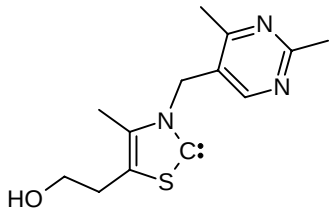


Figure 1.7. N,S-heterocyclic carbene involved in enzymatic benzoin condensation.

Several combinations of heteroatoms (N, O, S, P) are conceivable, and a number of different carbenes with these substituents has been isolated in the solid state.[3] An N,S-substituted heterocyclic carbene was proposed, and later found, to be involved in the enzymatic benzoin condensation in 1958 (Figure 1.7).[16] N-heterocyclic carbenes, in which two N-substituents are incorporated into a 5-membered ring, are the major topic of this work.

Fischer and Schrock carbene complexes

Although many early attempts to prepare or isolate free carbenes failed, complexes of carbenes have been known for decades. The first example of a carbene in coordination chemistry was given by Fischer in 1964 with the synthesis of $W(CO)_5(C(CH_3)OCH_3)$ (Figure 1.8, **A**).[17] The metal-carbon bond of this type of carbene complex is a donor-acceptor bond with σ-donation from the carbene to the metal and π-back donation from the metal to the carbene.[3] Fischer carbenes are generally found with low oxidation state metals with π-accepting ligands and π-donor substituents on the carbene carbon. The Fischer carbene is in a singlet spin state. In contrast, Schrock carbenes are found with high oxidation state metals with non-π-accepting ligands and without π-donor substituents on the carbene carbon. Schrock carbenes are in the triplet spin state. The first example was reported by Schrock in 1974 (Figure 1.8, **B**).[18] Both the Fischer and the Schrock carbenes are commonly depicted with a metal-carbon double bond.

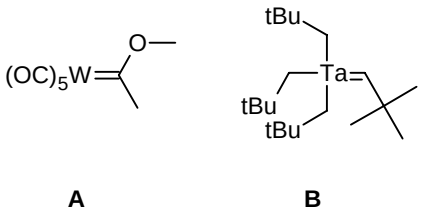


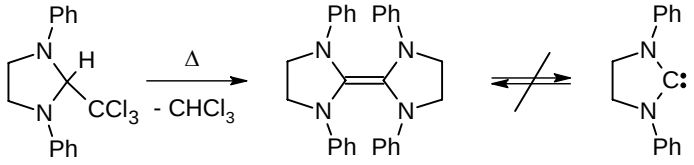
Figure 1.8. Examples of a Fischer (**A**) and a Schrock (**B**) carbene.

1.3 N-Heterocyclic carbenes (free)

Imidazole derivatives

The type of carbene that has received the most attention is the N-heterocyclic carbene (NHC), in which the carbene carbon atom has two nitrogen substituents and is part of a 5-membered ring. In the 1960's attempts to obtain this type of carbenes starting from N,N′-disubstituted imidazolines were made by Wanzlick *et al*.[19] Thermal α-elimination of chloroform from the corresponding imidazole adduct, however, gave the dimerized electron-rich olefin, which was shown not to be in equilibrium with the monomer (Scheme 1.3). In addition, attempts to isolate the free carbene derived from unsaturated N,N′-disubstituted imidazoles were unsuccessful, although the existence of the NHC was proven by trapping the free species as a transition-metal complex.[20]

The first stable carbene was reported by Arduengo *et al*. in 1991 (Figure 1.9).[10] This first example of a stable N-heterocyclic carbene was obtained by deprotonation of the corresponding imidazolium chloride with sodium hydride in the presence of a catalytic amount of DMSO. Some characteristics of the imidazolium salt and the carbene are collected in Table 1.1. The colorless crystals of **B** are thermally stable and



Scheme 1.3. Dimerization of imidazoline-based carbenes.

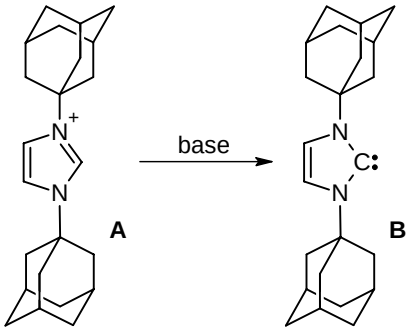


Figure 1.9. 1,3-Diadamanylimidazolium cation **A** and the first isolated N-heterocyclic carbene **B**.

Table 1.1. Some characteristic bond distances (Å), angles (°) and ^{13}C NMR shift (ppm) of structures **A** and **B** (Figure 1.9).

	A BPh_4^-	**B**
C-2 - N-1	1.326	1.367
C-2 - N-3	1.332	1.373
C-4 - C-5	1.334	1.338
N-C-N	109.7	102.2
δ(C) C-2	136	211

melt at 240 °C without decomposition.

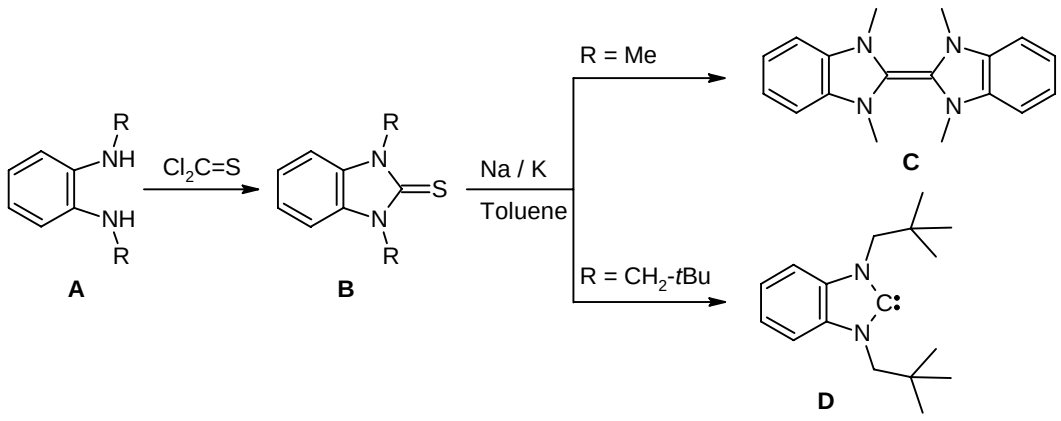
The basicity of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene in DMSO was reported as pK_a = 24, which makes it more basic than strong nitrogen bases such as 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).[21] Other experimental and theoretical investigations revealed similar values for related compounds.[22, 23]

Electronic structure/Stability of imidazol(in)-2-ylidenes

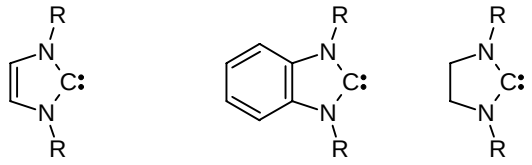
Initially it was thought that the stability of the first isolated free carbene could be explained by the steric properties of the adamantyl groups, however, in 1992 Arduengo showed that 1,3,4,5,-tetramethylimidazol-2-ylidene is a stable solid as well.[24, 25] It has been calculated that the gap between the triplet and the singlet ground state in N-heterocyclic carbenes is about 65-85 kcal/mol, which clearly indicates that the singlet ground state is preferred.[26] The stability of the singlet state is explained by the inductive effect of the σ-electron withdrawing substituents, which stabilizes the σ orbital on the carbene carbon atom, by increasing the singlet-triplet gap. In addition, the singlet state is stabilized by p_π donation from the nitrogen atoms into the empty p_π orbital of the carbene C atom.[27] It was calculated that the highest occupied molecular orbital corresponds to the σ lone pair of the carbene carbon atom.[28]

The tendency of saturated NHCs to dimerize is correlated to their smaller singlet-triplet gap of about 70 kcal/mol, compared to the gap of about 80 kcal/mol for unsaturated NHCs.[26] To obtain the free saturated carbene species, bulky substituents such as 2,4,6-trimethylphenyl are needed.[29, 30]

While unsaturated NHCs do not show a tendency to dimerize and unsaturated NHCs dimerize readily, in the case of benzimidazol-2-ylidenes the equilibrium depends highly on steric parameters.[31] The first free benzimidazol-2-ylidenes were reported by Hahn *et al*.[32] As shown in Scheme 1.4, *o*-phenylenediamines **A** were reacted with thiophosgene to yield the corresponding benzimidazol-2-thiones (**B**), which were treated with potassium to generate either the free carbene (**C**), or the



Scheme 1.4. Synthesis of benzimidazol-2-thione **B**, dibenzotetraazafulvalene **C** and benzimidazol-2-ylidene **D**.



d(C_2) [ppm]	211.4-220.8	231.5 (THF-d_8)	238.2-244.5
N-C-N [°]	101.2(2)-102.2(2)	103.5(1), 104.3(1)	104.7(3)-106.4(1)

Figure 1.10. Comparison of ^{13}C NMR spectroscopic and structural parameters for imidazol-, benzimidazol- and imidazolin-2-ylidene.

dibenzotetraazafulvalene (**D**). The solid-state structures of free benzimidazol-2-ylidenes suggest that, compared to the unsaturated imidazol-2-ylidenes the benzimidazole based carbenes have less aromatic character at the carbene carbon.[33] Furthermore, not only the tendency to dimerize, but also structural and ^{13}C NMR spectroscopic parameters are intermediate between the saturated and unsaturated imidazole-based carbenes (Figure 1.10).

Other N-heterocycles and topologies

An overview of other N-heterocyclic carbene topologies is shown in Figure 1.11. Some have been characterized in the free state, while others have been under investigation as a ligand. The use of these alternative topologies allows for the fine-tuning of the electronic properties of the ligand and the corresponding complex. For instance, the six- and seven-membered ring NHCs (**A**, **B**) have been shown to be more basic than their five-membered analogues and due to the larger NCN angle, the substituents of the larger rings are closer to the metal center.[34] Structure **C** was obtained by reaction of bipyridine with a suitable CH_2-precursor ($[Ph_3AsCH_2OTf]^+$), followed by deprotonation, and may formally be described as a bipyridine complex of singlet carbon.[35] Carbene **D** is another example of a way to bring steric bulk in the vicinity of the metal center. With this oxazoline topology, several chiral ligands have

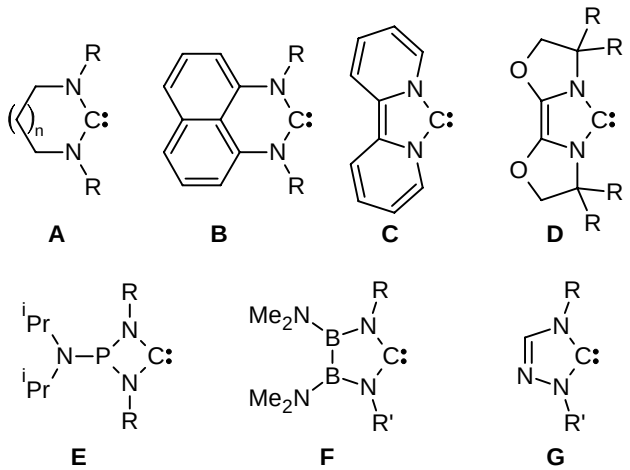


Figure 1.11. Alternative common N-heterocyclic carbene topologies.

been prepared as well.[36]

The backbone of the N-heterocycle is not limited to carbon atoms. Some variations, including phosphorus (**E**)[37] and boron (**F**)[38] containing NHCs have been synthesized as well. The phenyl substituted triazole-based NHC (**G**) was the first commercially available free carbene.[39]

1.4 N-Heterocyclic carbene complexes

1.4.1 General

Even though several N-heterocyclic carbene complexes had been isolated and characterized from the 1960s onward,[20, 40, 41] study of these compounds became widespread only after the isolation of the first free NHC in 1991. Early attempts to trap the free NHC by Öfele and Wanzlick resulted in metal-NHC complexes shown in Figure 1.12, **A** and **B**.[20, 40] Lappert *et al.* used the NHC dimers earlier described by Wanzlick to obtain several transition-metal complexes (**C**).[41]

In NHC complexes the π-back-bonding is less pronounced, in contrast to the Fischer-type carbenes. For this reason, in literature the M-C bond in this type of complex is often depicted as a single bond. A more detailed discussion of the bonding of N-heterocyclic carbenes to transition metals is given in the next section.

1.4.2 Electronic and sterics properties of NHCs

Comparison with phosphanes

NHCs have often been compared to phosphanes, PR_3, the first major class of spectator ligands in homogeneous catalysis. Because of the availability of the Tolman's parameters (electronic parameter Δν, steric parameter Θ) they have predictable and tunable steric and electronic effects.[42] Based on spectroscopic measurements it was concluded early on that NHCs have comparable electronic structures (good σ-donors, poor π-acceptors). Later, it was shown that NHCs are stronger donors than the most basic phosphanes,[43] and that NHCs may also act as a π-acceptor in a number of complexes.[44, 45]

When compared to other σ-donating ligands, NHCs show relatively high

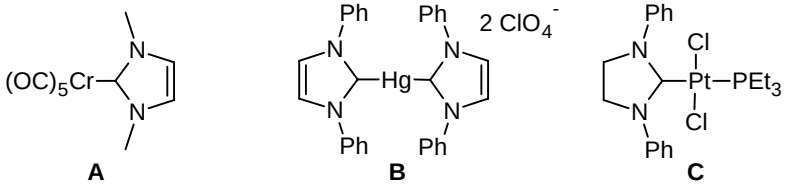


Figure 1.12. Early examples of NHC complexes.

dissociation energies. For example, calculations showed that the loss of PMe_3 from *trans*-[$PdCl_2(PMe_3)$(NHC)] requires 38.4 kcal/mol, while the loss of the NHC (unsubstituted imidazol-2-ylidene) requires 54.4 kcal/mol.[46]

Another important difference between phosphanes and NHCs is the orientation of the steric bulk. In phosphane ligands the three substituents point away from the metal center, while in NHCs the two substituents may flank the metal center. Furthermore, in contrast to phosphanes, the substituents of the NHC are not directly linked to the coordinating atom. This allows, in principle, for the electronic and steric factors to be tuned independently.

Steric parameter

Defining steric parameters for NHCs is subject of ongoing research; however, this is hampered by the fan shape of the NHC ligands compared to the cone shape of the phosphane ligands.[47-50] The cone angle, the parameter used by Tolman to quantify the steric properties of tertiary phosphane ligands, is not a suitable measure of bulk in NHCs. In general, the steric congestion around the metal center is due to the bulkiness of the N-substituents and the metal-carbon distance. Therefore, instead of only one cone angle, two angles may be defined; one angle describing the occupancy of the ligand in the plane of the imidazolium ring, and one angle perpendicular to the plane.[47] Alternatively, the percentage of the volume occupied by ligand atoms in a 3 Å sphere around the metal center may be calculated (Figure 1.13).[51, 52] A plot of the (calculated) bond dissociation energy against the (calculated) volume percentage showed a linear correlation between the two parameters, thereby showing the usefulness of these models.[52]

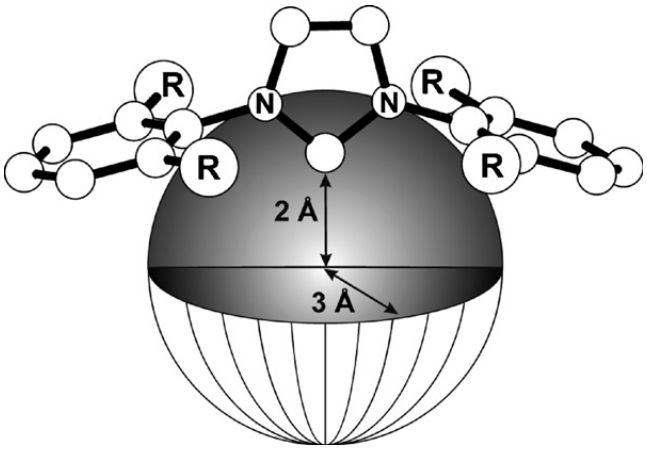


Figure 1.13. Representation of the sphere dimensions for steric parameter determination of NHC ligands (Figure was reproduced from ref. 51).

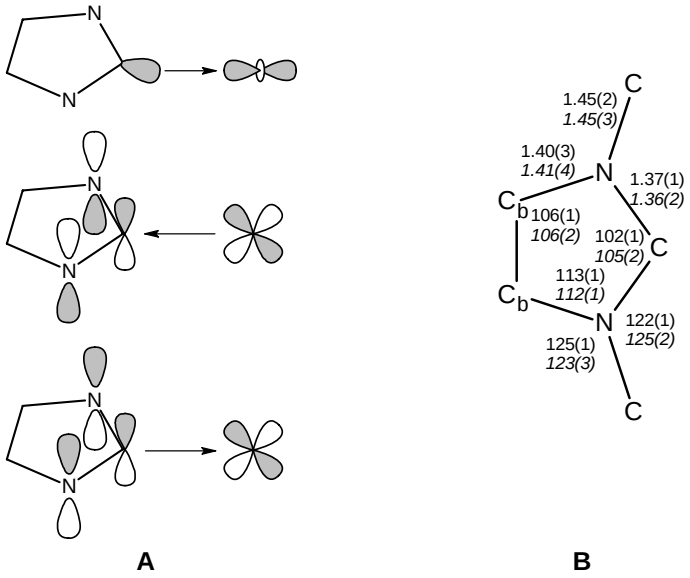


Figure 1.14. The three bonding contributions to the NHCs to metal centers (**A**), and comparison of average bond distances (Å) and angles (°) of 13 examples of free NHCs and 156 NHC complexes (in italics) (**B**).

Electronic structure

Initially, NHC ligands were considered to be almost pure σ-donors, through donation of the σ electrons of the carbene carbon atom into an empty d orbital of the metal. More recently it has been suggested that NHCs are electronically more flexible, since filled and empty π and π* orbitals on the NHC ring may contribute to the NHC-metal bond (Figure 1.14, **A**).[53] Electron rich metals may be stabilized through additional back donation of d electrons of the metal to a π* orbital of the NHC, while electron-deficient metals can be stabilized through donation of π electrons of the NHC into an empty d orbital of the metal.[52] The structure of the five-membered ring changes only slightly on going from the free carbene species to the metal complex, as can be seen from a comparison of the solid state structures of free NHCs and metal NHC compounds. Selected bond distances and angles averaged over a number of NHCs and complexes are given in Figure 1.14, **B**.[54]

Several studies have been performed in order to determine the bond dissociation energy of metal-NHC bonds and to quantify the contribution of π electrons to the metal-NHC bond in various systems. For example, in several studies the carbonyl stretching frequencies of metal (Ni, Ir) NHC carbonyl complexes have been determined experimentally[50] and by quantum chemical calculation[55]. Comparison of different NHCs and phosphanes showed that the difference between various NHCs is not very large and that NHCs are better σ-donors than phosphanes. In addition, attempts were undertaken to measure calorimetrically the bond dissociation energy (BDE) of a number of $NiL(CO)_n$ complexes.[56] Depending on the complex and the bulk of the ligand the BDE of the Ni-NHC bond was measured to be about 30-40 kcal/mol.

Density functional calculations on d^{10} metal NHC complexes such as $Ni(NHC)(CO)_2$ revealed as much as 25% π contribution to the total bonding interaction in the case of nickel(0), most of which is due to back donation.[45] Other studies revealed that the π contribution decreases in the order Ni > Pd > Pt.[57]

The investigations regarding the nature of various metal-NHC bonds were reviewed in 2008.[27]

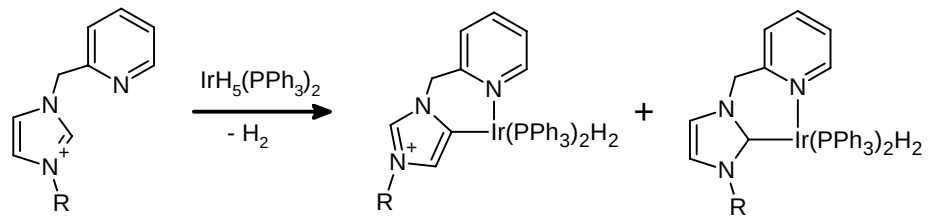
1.4.3 Other topologies

Abnormal binding

The C-4 and C-5 CH groups of imidazolium salts are quite acidic. This is clear for example, from the fact that the backbone of IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) is readily chlorinated by CCl_4.[58] In 2002 Gründemann *et al*. reported a pyridine functionalized imidazolium ligand that, on reacting with $IrH_5(PPh_3)_2$, gave a mixture of two carbene complexes: one with regular binding at C-2 and one with binding at C-4, as shown in Scheme 1.5.[59, 60] This binding motive was coined abnormal binding.

Once the normal or abnormal compounds have formed they do not easily interconvert, even not after prolonged heating in DMSO. IR-spectroscopy data suggest that abnormal C-4 bound NHCs would be substantially stronger electron donors than normal C-2 bound carbenes,[61] which may be beneficial for some catalytic applications. For instance, it was shown that palladium complexes bearing two NHCs (IMes), one in the normal, one in the abnormal binding mode, could be used as active catalysts in C-C coupling reactions.[62] When the two ligands are both in the normal binding mode the catalyst is inactive. Whether the normal or the abnormal complex is obtained depends on the reaction conditions: when cesium carbonate is used as a base, abnormal binding occurs more frequently.

More recently, abnormal NHCs have been observed with other metals, such as rhodium,[63] osmium,[64] and platinum.[65] The abnormal binding of NHC ligands was reviewed in 2007.[66]



Scheme 1.5. Abnormal binding mode in NHC coordination. BF_4 anions are not shown.

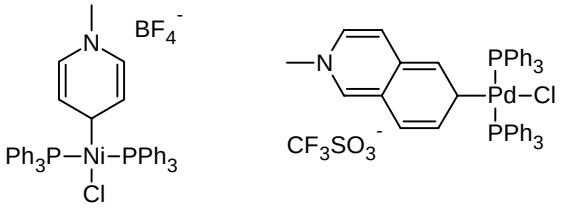


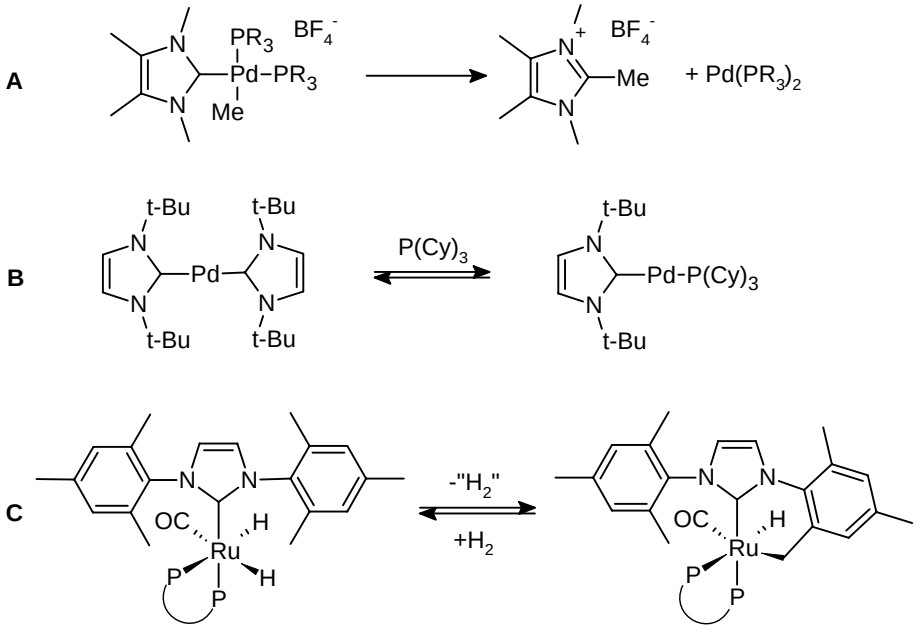
Figure 1.15. Examples of transition metal rNHC complexes.

Remote N-heterocyclic carbenes

A new class of metal NHC complexes was discovered recently, in which the heteroatom is not directly bound to the carbene carbon atom. Even though to date free remote N-heterocyclic carbenes (rNHCs) have not been isolated, a number of rNHC metal complexes have been prepared via oxidative addition of d^{10} metal centers into a suitable carbon-halide bond.[67, 68] Two examples of rNHC metal complexes are depicted in Figure 1.15. A number of rNHC metal complexes have been used in catalytic reactions.[68]

1.4.4 Decomposition pathways

Although NHCs are usually considered to be spectator ligands and some NHC complexes are stable in boiling solvents in air, they are not always inert. Potential decomposition or deactivation pathways are depicted in Scheme 1.6 and include reductive elimination of the carbene with a *cis*-coordinated ligand (**A**),[69] decomplexation or displacement by a competing ligand (**B**),[70] C-H or C-C activation of a substituent (**C**).[71] Another pathway leads to abnormal binding of the carbene ligand (see for example section 1.4.3). The rate of reductive elimination is considered



Scheme 1.6. Examples of possible decomposition pathways of NHC complexes.

to be lowered by the use of bidentate ligands, because of restriction of the bite angle.[72]

The imidazol-2-ylidene C=C (back-bone) double bond is relatively inert, possibly because of the aromatic character of the ring. For example, IMes is unchanged when $RhCl(H)_2(IMes)_2$ is used as a catalyst in a hydrogenation reaction. Because catalysts are rarely recovered, it is difficult to say whether imidazol-2-ylidenes remain unsaturated in all cases.

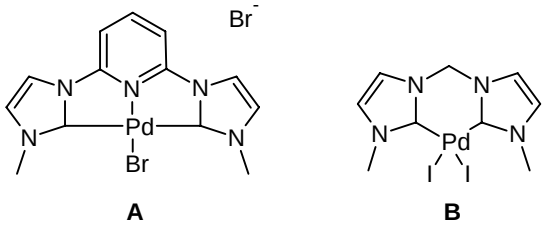
The reactivity of stable NHCs towards O_2, CO, NO and water was reported in 2001.[73] It was shown that 1,3-di-*tert*-butylimidazol-2-ylidene and its saturated analogue were stable towards O_2 and CO. Reactions with NO yielded the C-2 ketone and reactions with water gave the hydrolysis products (*e.g.* R-N=CHCH$_2$-N(CHO)-R). The air sensitivity is therefore due to the attack of water, which in the case of the imidazolin-2-ylidene is very fast. The hydrolysis of the imidazol-2-ylidene requires months to complete. Furthermore, it was reported that in the presence of platinum the imidazol-2-ylidene could be hydrogenated to the corresponding imidazolidine.

The stability and reactivity of NHC complexes was reviewed in 2004.[74]

1.4.5 Chelating N-heterocyclic carbene ligands

Given the successful use of chelating phosphane ligands in transition-metal catalyzed homogeneous catalysis, several studies into the properties of chelating N-heterocyclic carbenes have been undertaken. A 2004 review on chelating NHCs concludes: "In view of the increasing success of monodentate NHCs in catalysis, we can expect a rise in the use of chelating NHCs".[43] Indeed, since then many complexes bearing chelating NHCs have been reported as homogeneous catalysts.[72, 75]

A first advantage of chelating NHCs is the entropically enhanced stability. For example, pincer-type complex **A** (Figure 1.16) can be refluxed for 24 hours in dimethylacetamide (bp 165 °C) in air without decomposition, while bisNHC complex **B** deposits Pd black after 8 hours of reflux in the same solvent.[76] Furthermore, the bridging moiety provides another means of fine-tuning the properties of the complex, by modulation of the bite angle and a more rigid conformation, as shown in Figure 1.17.[75]



A **B**

Figure 1.16. Palladium complexes of chelating NHC ligands.

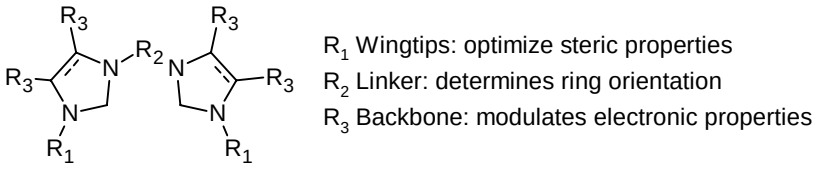


Figure 1.17. Influence of various substituents of chelating N-heterocyclic carbenes on the properties of the corresponding complex. Reproduced from ref. 75.

It has been noted that the effect of the linker on the bite angle of bisNHCs is small, in comparison with bisphosphanes. This is due to rotation of the imidazole rings out of the preferred orientation perpendicular to the coordination plane.

A disadvantage of chelating NHCs may be the irreversible coordination of the NHC to transition metals. Therefore, in some cases care must be taken because of the possibility that a chelating ligand binds monodentately,[77] or that it will bind two metal centers.[78, 79]

The properties of functionalized NHCs were reviewed in 2007,[80] and 2008.[72]

1.4.6 Nickel complexes

Monodentate nickel NHC complexes

The main focus of the research described in this thesis lies on the synthesis and use of nickel complexes of N-heterocyclic carbenes. In this section an overview is given of the most common nickel NHC complexes reported to date.

The first isolated Ni NHC complex was serendipitously synthesized by reaction between DMF and a Ni(SNNS) complex to yield a dinuclear nickel(II) complex bearing two (SCS) pincer-type ligands of a saturated NHC with thiophenolate substituents (Figure 1.18).[81] This complex is highly stable and does not decompose in concentrated H_2SO_4, although strong nucleophiles (Nu), such as PMe_3 are able to react to give mononuclear Ni(SCS)Nu complexes. Two years later the first isolated nickel(0) NHC complex was reported by Arduengo *et al*.[25] Coordination of the free carbene IMes to $Ni(COD)_2$ gave a $Ni(NHC)_2$ species, which was shown to exhibit a nearly linear geometry. The nickel complexes of monodentate NHC ligands isolated since, may be divided into five categories, depicted in Figure 1.19.

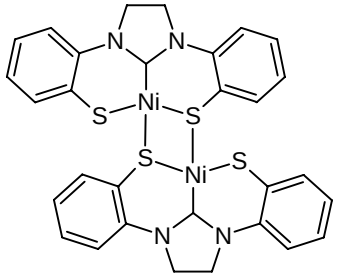


Figure 1.18. The first isolated nickel NHC complex reported in literature.

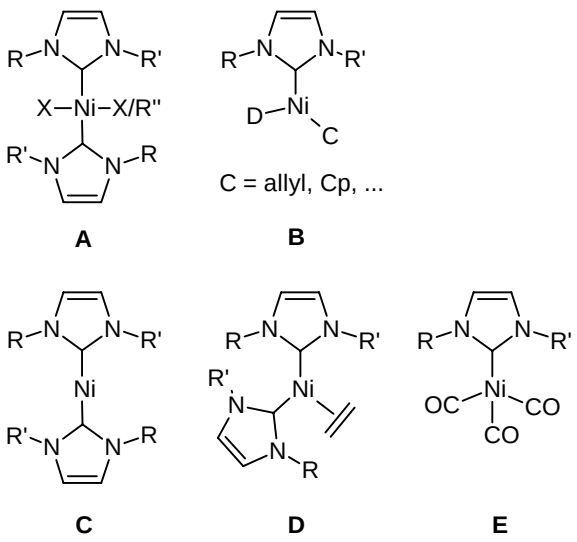


Figure 1.19. Overview of types of nickel complexes with monodentate NHC ligands isolated to date. For clarity, only unsaturated NHCs are shown.

The largest category (**A**) is that of nickel(II) complexes with two monodentate NHCs and two additional anionic groups. In most cases two halides are present, [82-84] but two pseudohalides, such as cyanide, have been used as well.[85] In addition, structures with one halide and one alkyl or aryl substituent on the nickel ion have been isolated.[86] These complexes are the result of oxidative addition of alkyl or aryl halides to the corresponding Ni(0) species. A second type of nickel NHC complex has one monodentate NHC, one anionic carbon-donor moiety, such as cyclopentadienyl,[87] or allyl,[88] and one additional anionic ligand, such as a halide,[87]or a thiophenolate (**B**).[89] The other types comprise Ni(0) NHC species (**C**), the first of which includes Arduengo's $Ni(IMes)_2$ and a $Ni(NHC)_3$ species.[90] Furthermore, some $Ni(0)(NHC)_2$ complexes bearing an additional olefin or alkyne coordinated to the nickel center have been characterized (**D**).[90] The last category of common Ni(0) NHC complexes consists of complexes with the general formula $Ni(NHC)_n(CO)_m$ (**E**). Several combinations of *n* and *m* have been found, depending mainly on the size of the NHC. These complexes were prepared mainly to study the electronic properties of N-heterocyclic carbenes.[50]

Chelating NHC ligands

Nickel complexes bearing polydentate ligands may be divided into two groups: (1) those where all the donor groups are NHCs and (2) those where, next to one NHC other donor groups (P, N, O, S, olefin) are present. Only a few members of the first group were successfully prepared, and are shown in Figure 1.21. Examples are a nickel dihalide complex bearing a cyclophane-based bisNHC,[91] and a nickel dihalide complex of a *trans* chelating bisNHC ligand with a BINOL-derived bridge have been obtained to date.[92] Other nickel complexes bearing one bisNHC include a dimethyl complex Ni(C^C)Me_2,[78] and a cationic complex bearing one bisNHC, one phosphane

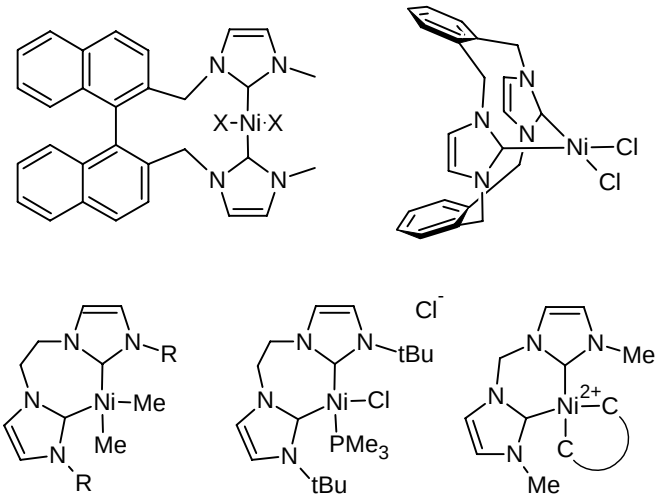


Figure 1.21. Known nickel complexes with chelating bisNHC ligands (C = NHC).

ligand and one halide.[93] Attempts to prepare complexes of the type $Ni(C\hat{}C)_2X_2$, where C^C is a chelating bisNHC in which the two NHCs are linked with one alkyl chain bridge and X is a halide, lead to homoleptic $Ni(C\hat{}C)_2$ complexes,[77, 93, 94] or intractable mixtures.[78] In comparison, palladium dihalide complexes bearing chelating bisNHC ligands are ubiquitous.[95, 96]

The group of nickel complexes with donor-functionalized polydentate ligands mainly consists of compounds with bidentate ligands. Three examples are shown in Figure 1.20. The most common neutral donor moieties are phosphanes,[97] and pyridines,[98, 99] while anionic donor moieties include amido,[100] and phenolato groups.[101-103] Most complexes are obtained as the homoleptic complex with two ligands (**A** or **C**) or the dihalide complex with one chelating ligand (**B**). Recently, some penta- and hexacoordinated nickel complexes with various N-donor functionalized NHC ligands have been reported, as well.[104]

Tridentate NHC ligands are mainly of the pincer type. In addition to the (SCS) pincer-type complexes mentioned before, several others have been reported, for example with a (CNC) donor configuration.[105] Few other tridentate ligands have been investigated, such as a (CNO^-) ligand.[106] As nickel prefers a square planar geometry, an additional donor ligand is required for this type of ligands. To fill all four

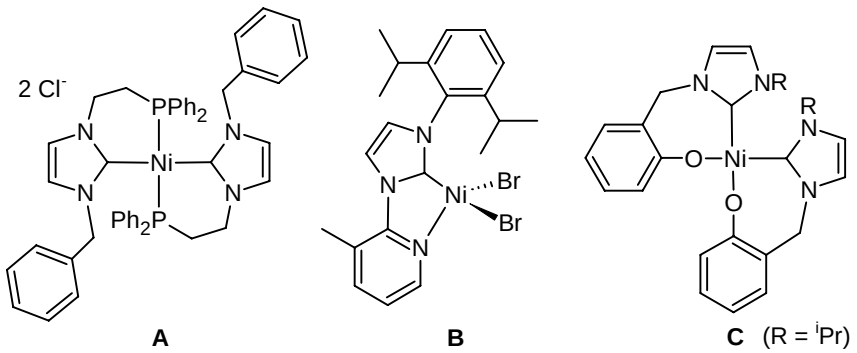


Figure 1.20. Nickel(II) NHC complexes with coordinating pendant arms.

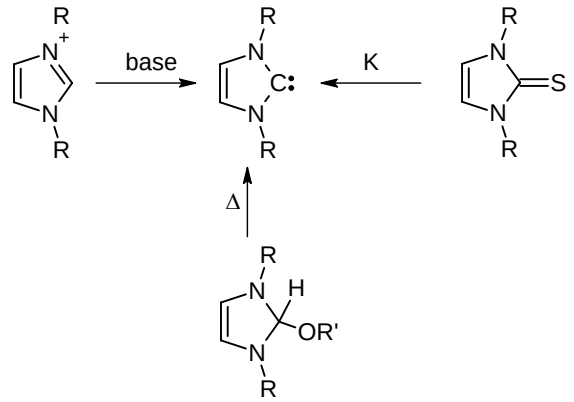
coordination sites a number of tetradentate NHC ligands have been prepared, including a macrocyclic ligand of two NHCs and two pyridines,[107] and ligands consisting of two coupled pyridine functionalized NHCs.[108]

1.5 Synthetic methods

1.5.1 Free carbene

In order to obtain a transition-metal complex of an N-heterocyclic carbene, it is often required to synthesize the NHC in the free state. Three common routes to generate the free carbene are depicted in Scheme 1.7. In this scheme, only unsaturated imidazole rings are shown, although in principle these methods may be used to generate saturated and benzimidazole-based NHCs. Generally, carbenes derived from imidazoles are obtained by deprotonation of the 1,3-disubstituted imidazolium salts. A number of different bases and solvents have been reported in the literature for this reaction. An early example is the use of NaH in THF, sometimes in combination with a catalytic amount of KO^{t}Bu. If the imidazole has base-sensitive substituents more selective bases may be used, such as *sec*-BuLi or KN(SiMe$_3$)$_2$.[2, 93] Alternatively, the carbene may be generated by addition of a base (NaH or KNH$_2$) to a suspension of the imidazolium salt in liquid ammonia. This technique, introduced by Herrmann *et al*.[109] yields the carbene within minutes and was shown to be especially useful for deprotonation of diimidazolium salts. Other methods leading to the free NHC include the desulfurization of imidazol-2-thiones with potassium,[30, 32] and the thermolysis of 2-alkoxy substituted NHC-precursors (Scheme 1.7).[12]

In the case of imidazolin-2-ylidenes and benzimidazol-2-ylidenes, the free NHC may be in equilibrium with its dimeric species, as discussed in section 1.3. Still, the free species may be present long enough to be able to coordinate to a metal center.



Scheme 1.7. Methods for the generation of a free NHC.

1.5.2 Carbene complexes

Carbene complexes prepared from the free carbene

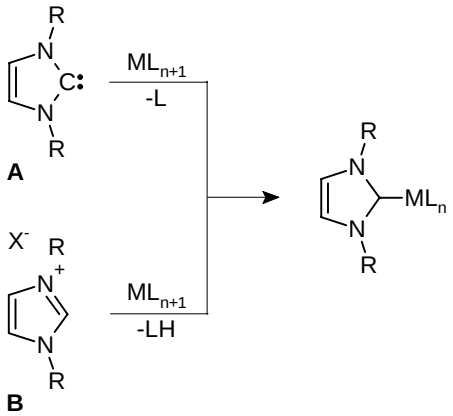
A number of strategies may be distinguished in the synthesis of coordination complexes with carbenes. The majority of NHC complexes have been obtained by substitution of another ligand on the metal center. The first strategy is to mix a suitable metal ion with a free carbene, as shown in Scheme 1.8, **A**. The free carbene may be obtained by methods discussed in the previous section.

For example, treatment of bis(1,5-cyclooctadienyl)nickel(0) with two equivalents of IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) in THF yielding $Ni(IMes)_2$ was reported in 1994.[25] Another example, in which phosphane ligands are replaced by NHCs, has been reported by Herrmann *et al*. in 1997:[110] $NiX_2(PPh_3)_2$ (X = Cl, Br) is reacted with 1,3-dicyclohexylimidazol-2-ylidene (ICy) yielding $NiX_2(ICy)_2$. An example of the synthesis of a coordination complex with a chelating NHC was published by Douthwaite *et al*.:[78] when $Ni(bipy)Me_2$ is reacted with 1,2-ethylene-3,3'-di-*tert*-butyl-diimidazol-2,2'-diylidene at –78 °C the chelating bisNHC ligand replaces the bipy and the complex $[Ni(bisNHC)Me_2]$ is formed.

Alternatively, the carbene may be generated *in situ*, by reaction of the precursor imidazolium salt with an additional external base. For example, a nickel complex with two aryloxo-functionalized NHCs could be prepared by treatment of the ligand precursor salt with $NaN(SiMe_3)_2$ and $Ni(PPh_3)_2Br_2$ in a one-pot procedure.[101]

In the second strategy, an imidazolium salt is deprotonated by reaction with a basic ligand of a suitable metal precursor generating the carbene *in situ* (Scheme 1.8, **B**). An early example of this route is the reaction of $Hg(OAc)_2$ with an imidazolium salt to yield the mercury NHC complex as reported by Wanzlick in 1968.[20]

Nickel NHC complexes may be obtained by reacting $Ni(OAc)_2$ with the imidazolium halide with the loss of acetic acid. This is an example of a reaction in which the carbene is generated *in situ* by a basic metal precursor. In the case that the imidazolium salt has a low melting point, this reaction may even be performed



Scheme 1.8. Reactions leading to transition metal carbene complexes.

without solvent.[82] Alternatively, an additional low-melting, non-reactive salt (ionic liquid) may be added, such as tetrabutylammonium halide, to act as the solvent.[83] When the reaction is finished the salt may be removed by washing with water. Alternatively, $Ni(Cp)_2$ (nickelocene) may be used as a metal precursor with a basic ligand, although in this case only one ligand is replaced.[111]

Nickel(0) complexes may be obtained by reaction of the free carbene with a suitable nickel(0) species, such as $Ni(COD)_2$. Alternatively, the nickel(0) NHC species may be obtained by reductive elimination of ethane from the $Ni(NHC)_2Me_2$ complex.[112]

Alternative, less common strategies leading to NHC complexes are discussed below.

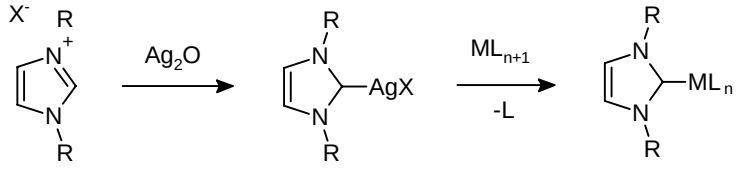
Transmetalation: the Ag_2O route

In recent publications, a number of carbene complexes has been obtained *via* a transmetalation procedure.[98, 113-116] First, the silver complex is obtained by a reaction of an imidazolium salt with Ag_2O. Then, the NHC is transferred from the silver atom to another transition metal, as shown in Scheme 1.9.

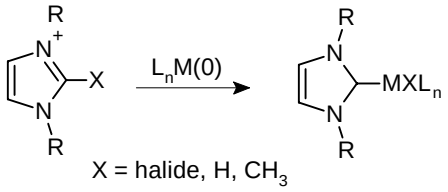
In a typical example 1,3-dialkylimidazolium halide is reacted with Ag_2O in dichloromethane at room temperature yielding the complex [Ag(imidazol-2-ylidene)$_2$][AgX_2]. This complex is subsequently reacted with $[M(COD)Cl_2]$ or $[MCl_2(MeCN)_2]$ to yield the transition-metal complex. This procedure has already been applied with monodentate imidazole carbene ligands, chelating imidazole-based dicarbene ligands and benzimidazole-based carbenes with transmetalation to transition metals, including Pd, Au, Rh, Ir, and Ni. The molecular structures of silver(I) NHC complexes and their use in transmetalation reactions have been reviewed in 2005 and 2007.[53, 117]

In addition to silver NHC complexes, other agents have been developed for transmetalation reactions. For instance, imidazolium salts were reacted with $LiBEt_3H$ to yield the imidazol-2-ylidene-BEt_3 adduct.[118] In subsequent reactions this BEt_3 could be replaced by BH_3, BF_3, and $Mo(CO)_5$. In addition, complexes of the type $[M(NHC)(CO)_5]$ (M = Cr, Mo, W) may be used as NHC-transfer agents.[119]

The generation of silver(I) NHC complexes and the transmetalation reaction of NHCs from silver(I) complexes to other metals will be discussed in more detail in Chapter 2.



Scheme 1.9. The transmetalation route leading to transition metal NHC complexes.



Scheme 1.10. The oxidative insertion of a zerovalent transition-metal complex into a C-X bond.

Oxidative insertion

In the early 1970s the synthesis of several N,S- and N,O-heterocyclic carbene complexes by oxidative addition of a C–Cl bond to suitable Ir, Pd, Pt, and Ni complexes were reported (Scheme 1.10).[120] Later, similar reactions were performed to obtain N-heterocyclic carbene complexes, by oxidative addition of other C–X bonds,[121, 122] In addition, oxidative addition of the C–Cl bond of acyclic carbene precursors to Ni(0) and Pd(0) complexes has been performed.[123]

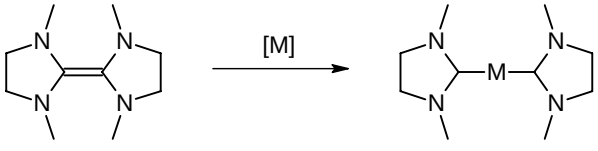
An example of the oxidative addition of a 2-H imidazolium salt was reported by Clement *et al*. in 2004.[124] It involves the addition of 2-H-1,3-dialkylimidazolium salt (with non-coordinating anions) to coordinatively unsaturated $M(NHC)_2$ complexes (M = Ni, Pd) furnishing a stable $[M(NHC)_3H]^+$ complex.

Insertion into electron rich C=C bonds

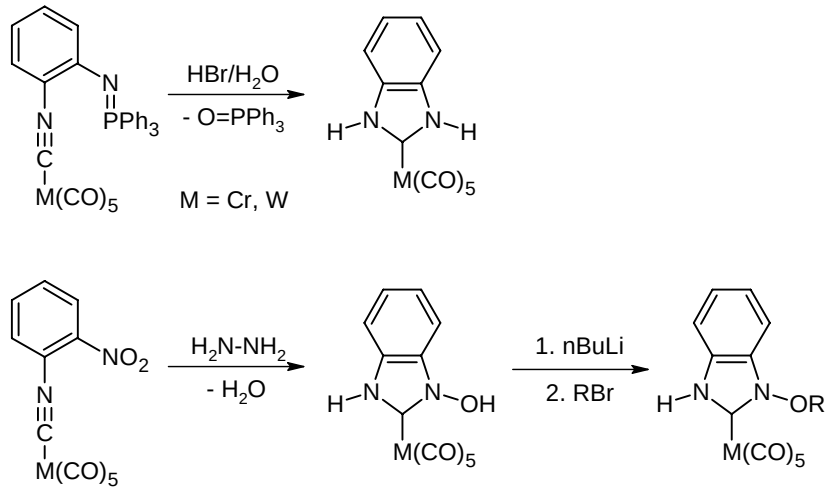
Insertion of a coordinatively unsaturated electrophilic metal complex into the C=C bond of bis(imidazolin-2-ylidene)-based electron-rich olefins is one of the early methods for the synthesis of metal NHC complexes and is known as the Lappert method (Scheme 1.11).[41] This method has been applied mainly for unsaturated NHCs and benzimidazole-based carbenes and for a number of metals, including Pt, Ni, Rh, Pd, W, Cr, Co and Fe.[9] In addition the method may be used to obtain metal complexes of chelating bisNHCs by insertion into N,N′-bridged tetraazafulvalenes.[125]

Synthesis by ring closure on the metal

A conceptually different approach towards benzimidazol-2-ylidene complexes was introduced by Hahn *et al*. in 2003. Instead of using a preformed benzimidazole-scaffold, the imidazole ring was closed while the carbene carbon atom precursor was already attached to the metal by starting from the isocyanide complex (Scheme 1.12).[126] This type of template synthesis yields one of the few examples where the N-substituents are protons, which may subsequently be replaced in a substitution



Scheme 1.11. Insertion of a metal fragment into the C=C bond of a tetraazafulvalene.



Scheme 1.12. Ring-closing routes towards benzimidazole-based carbene complexes.

reaction. Following a similar scheme, starting from the *o*-NO_2 phenyl isocyanide, an O-R substituted benzimidazol-2-ylidene could be obtained.[127]

1.6 Catalysis

1.6.1 General

In the past few years N-heterocyclic carbenes have been applied in a large variety of research areas. Apart from an interest from a fundamental point of view, NHC complexes have for example been studied as antibiotics (with silver),[128] anticancer drugs (with gold and palladium),[129, 130] and examples of NHCs in building blocks for supramolecular chemistry,[131] and NHC complex polymers are starting to attract attention.[103, 132] It has been shown that a number of reactions may be catalyzed by free NHCs.[133] For example, 1,3-diadamantylimidazol-2-ylidene (IAd) has been shown to catalyze the transesterification of methyl acetate with benzyl alcohol at room temperature,[134] while several other NHCs have been used as ring-opening polymerization catalysts.[135]

The most studied application of NHCs, however, is as a spectator ligand in homogeneous transition-metal catalyzed reactions. Soon after the first isolation of a free NHC, Herrmann *et al*.[136] recognized the potential of this class of compounds, and with the similarity of the electronic properties of phosphane ligands in mind, attempts were made to modify known transition metal catalysts with NHCs. Early successful examples include $Pd(NHC)_2X_2$ complexes in the Heck reaction,[136] Rh(NHC)(COD)Cl complexes in the hydrosilylation of alkenes,[137] $[Pd(C\hat{}C)(MeCN)_2]^{2+}$ complexes in CO/ethylene copolymerization,[138] and $Ru(NHC)_2Cl_2(=CHPh)$ in olefin metathesis.[139] Inspired by these early successes the field of NHC transition-metal catalysis developed rapidly and was already reviewed in 2002.[140]

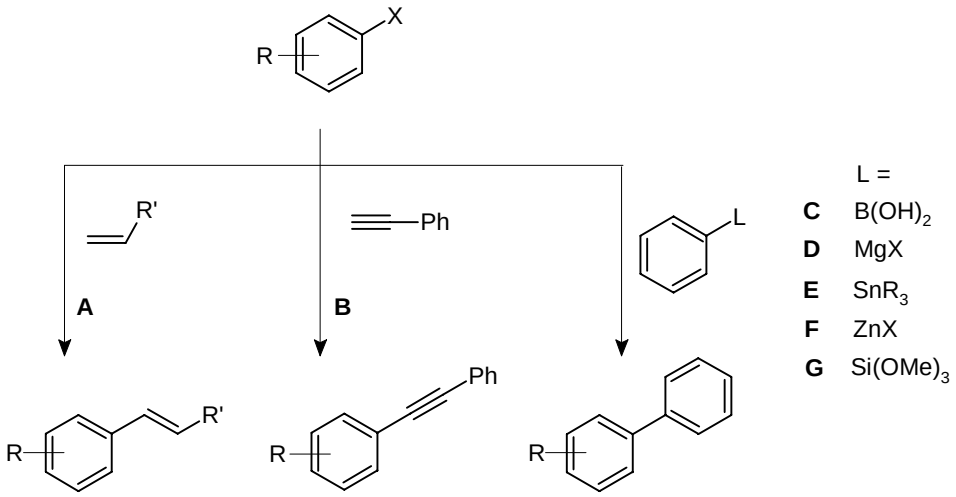
A number of examples in which a known phosphane-based catalyst is modified by replacing one or more of the phosphane ligands with NHCs have been reported. For example, modifications of Crabtree's catalyst $[Ir(cod)(py)(PCy_3)]PF_6$,[141] Wilkinson's catalyst $[RhCl(PPh_3)_3]$,[142] and Grubbs catalyst $[RuCl_2(PPh_3)_2(=CHPh)]$[139] have been reported. More recently, catalytic reactions which are catalyzed uniquely by transition metal NHC complexes are being disclosed. For instance, the use of nickel NHC complexes for catalytic dehydrogenation of ammonia-borane (H_3N-BH_3) for chemical hydrogen storage was recently published.[143]

Due to the stability of the metal-carbene bond, it is assumed that during the catalytic cycle the carbene ligand remains coordinated to the metal. Therefore, in contrast to metal phosphane catalysts, no excess ligand is needed to bring the catalytic reaction to completion. Often the metal NHC catalyst is introduced into the reaction mixture as a preformed complex, although the use of an *in situ* mixture of free carbene or carbene precursor and a suitable metal complex has been reported, as well. The use of preformed NHC complexes avoids handling of free carbenes, while an *in situ* mixture allows for the ligand to metal ratio to be optimized more easily.

In the following sections the most common NHC-complex catalyzed reactions will be discussed, with an emphasis on nickel and other group 10 transition metals. Two types of reactions that are encountered frequently in literature will be reviewed separately, followed by an overview of less common reactions. The reactions that are regularly reported are C-C coupling reactions with aryl halides and olefin metathesis.

Cross-coupling reactions with aryl halides

The vast majority of studies on NHC transition-metal catalyzed reactions has focused on C-C coupling reactions, with an emphasis on coupling reactions with aryl halides. In most cases palladium is the preferred metal, although in some cases also nickel is used. The most common C-C coupling reactions are shown in Scheme 1.13.[144-146] The successful use of NHCs is mostly due to the thermal stability of the metal-NHC bond, as these coupling reactions often require elevated temperatures and previously studied phosphane complexes suffered from degradation. The use of palladium NHC complexes as catalysts in cross coupling reactions was reviewed in 2008.[4]



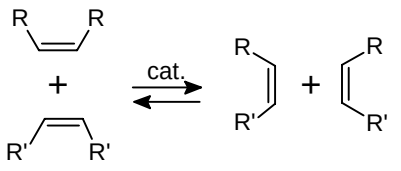
Scheme 1.13. C-C couplings reactions with aryl halides (X = I, Br, Cl): A = Heck reaction, B = Alkyne coupling, C = Suzuki reaction, D = Kumada cross-coupling, E = Stille reaction, F = Negishi coupling, G = siloxane cross-coupling.

Olefin metathesis

A general reaction scheme of olefin metathesis is shown in Scheme 1.14.[147] Homogeneous catalysts for this reaction were devised by Grubbs ($RuCl_2(PCy_3)_2(=CHPh)$)[148] and Schrock ($Mo(OR)_2(=N\text{-}Ar)(=C\text{-}Ar)$).[149] In general, in order to catalyze olefin metathesis a catalyst is needed that has an alkylidene ligand ($=CR_2$) in its active species. A number of metals (Mo, W, Ru, Ta) is known to be able to coordinate alkylidene ligands and to perform these reactions.[147] So far, from these transition metals ruthenium is the only one used in combination with NHC ligands.

Based on the Grubbs-type metathesis catalysts, a number of ruthenium NHC alkylidene complexes were used to perform ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) reactions.[139] The activity of the known catalyst $RuCl_2(PCy_3)_2(=CHPh)$ was comparable to the activity of the complexes with two IPr ligands instead of phosphanes, leading to high yields in both reactions, although the new complex was found to be more stable. It was reported that a similar complex (second generation Grubbs catalyst) bearing one phosphane ligand (PCy_3) and one SIMes (1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) is even more active as metathesis catalyst.[12, 150, 151]

More recently, the O-donor functionalized NHCs were investigated in the ruthenium-catalyzed asymmetric olefin metathesis reactions.[152]



Scheme 1.14. General olefin metathesis reaction.

Other catalytic reactions

Apart from the reactions mentioned in the previous sections, in the literature a large number of reactions has been reported to be catalyzed by transition-metal NHC complexes. As these reactions have not had received a lot of attention, they are not discussed here in detail. Some examples are given in Table 1.2.

Table 1.2. Miscellaneous reactions involving NHC complexes as catalysts.

Reaction	metal center	ref.
Hydrosilylation of alkynes	Rh, Pt	79, 153
Hydrosilylation of ketones	Rh	154
Hydrogenation	Ru, Ir, Pd	155, 141, 156
Furan synthesis	Ru	157
Aryl halide amination	Pd	158
Ethene polymerization	Ti, V, Cr	159, 160
Ethene/CO copolymerization	Pd	138
Hydroformylation	Co, Rh	161, 162
Alkyne coupling	Ru	163
Allylic acetate rearrangement	Au	164
Atom-transfer radical polymerization	Fe	165
Pauson-Khand reaction	Co	166
Hydroamination of olefins	Cu	167

In general, it may be concluded that N-heterocyclic carbenes are versatile ligands capable of stabilizing a variety of metal centers. If an NHC is used as a ligand instead of a phosphane-based ligand a more stable, and often more active catalyst is obtained in a large number of cases.[2]

1.6.2 Nickel NHC complexes in catalysis

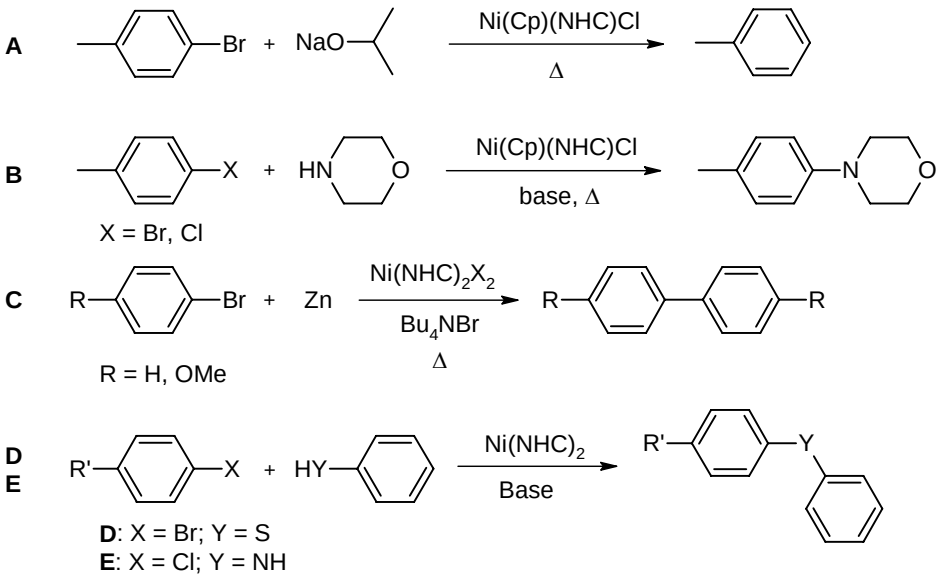
Even though palladium is often the transition metal of choice for catalytic applications in C–C cross coupling reactions, the use of nickel-based catalysts still has a number of advantages: nickel often has a higher reactivity towards aryl chlorides, is cheaper than palladium, and is often easier to remove from the final products.[168] Nickel NHC complexes have been used in a variety of catalytic organic transformations. A short overview of common reaction types is given in this section.

Reactions with aryl halides

In section 1.6.1, a number of C–C cross–coupling reactions starting from aryl halides was listed. In addition to the numerous examples of these reactions catalyzed by palladium compounds, several nickel NHC catalysts have been studied, for instance in the Heck,[105] and Negishi[169] cross-couplings. Several efforts were made to catalyze the Suzuki coupling of aryl halides with aryl boronic acids with nickel NHC

complexes. In some cases the addition of phosphanes to the reaction mixture was necessary to reach full conversion,[100, 170] although a recent example avoids this addition by using phosphane-functionalized NHCs.[97] The Kumada cross-coupling has been studied a number of times and will be discussed in Chapter 4-6. In addition to the cross-coupling reactions mentioned before, the cross-coupling of aryltitanium alkoxides (Ar-Ti(OEt)$_3$) with aryl halides, catalyzed by an *in situ* mixture of Ni(acac)$_2$ and IPr·HCl was investigated.[171] It was found that this reaction runs under mild conditions, leading to a broad scope with high functional-group tolerance.

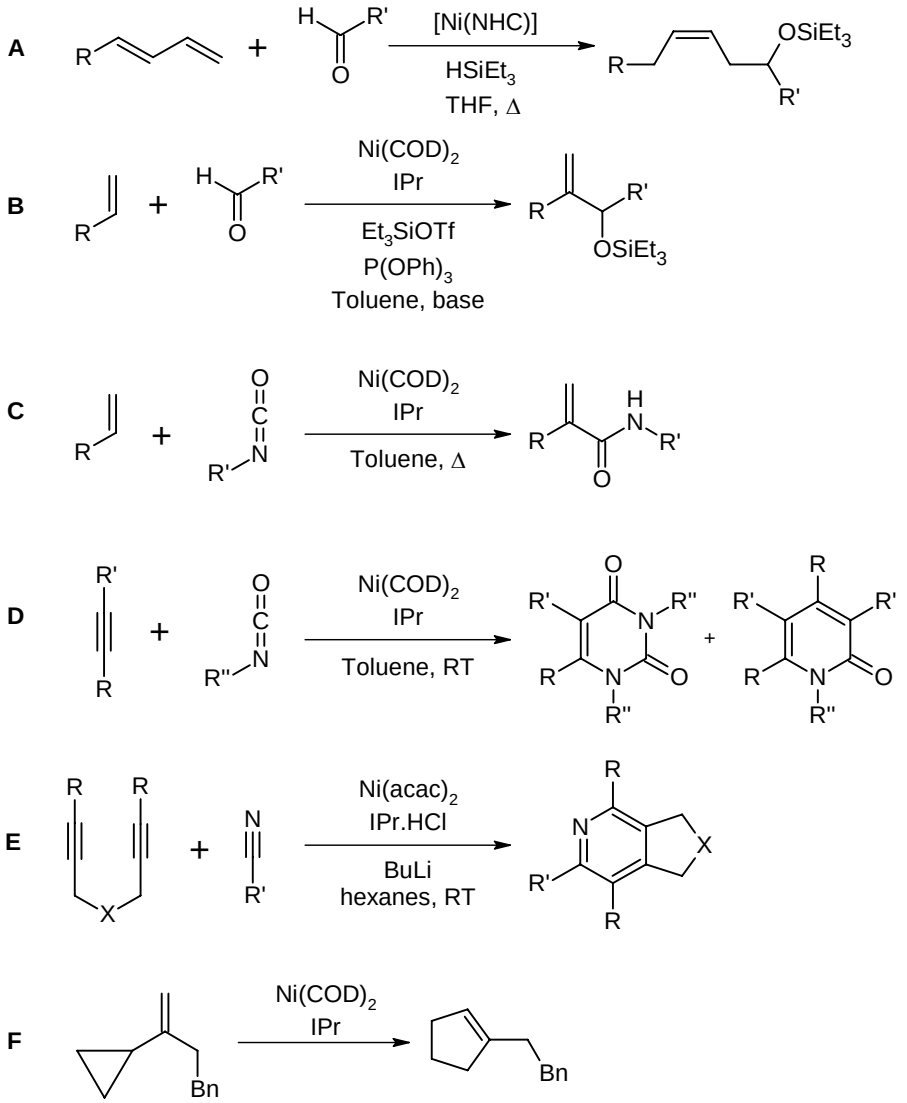
Other reactions starting with aryl halides include the following. Complexes of the type Ni(Cp)(NHC)Cl, which were obtained by reaction of nickelocene (Ni(Cp)$_2$) and bulky imidazol(in)ium halides, were successfully used for the dehalogenation of 4-bromotoluene in the presence of NaO^{i}Pr as a base (Scheme 1.15, **A**).[172] In addition, it was shown that the same complexes could be used for the catalytic aryl amination of aryl halides with morpholine in good yields with KO^{t}Bu as a base and at elevated temperatures (**B**). Benzimidazole-based carbene ligands were used in the nickel catalyzed Ullmann reaction with bromobenzene and 4-bromoanisole in molten tetrabutylammonium bromide to yield symmetric biaryls (**C**).[173] The coupling of aryl chlorides was unsuccessful in this reaction. Nickel(0) complexes bearing two monodentate NHCs could be used for the catalytic aromatic C-S coupling of aryl bromides with thiophenols (**D**),[174] and catalytic C-N coupling of aryl chlorides and with anilines and aryl diamines (**E**).[175]



Scheme 1.15. Aryl halide dehalogenation, amination, homocoupling, aryl amination and aryl thioether formation.

Reactions involving double bonds

A number of variations on catalytic reactions involving C–C double and triple bonds have been disclosed. For instance, the nickel-catalyzed coupling of 1,3-dienes and aldehydes with $HSiEt_3$ is shown in Scheme 1.16, **A**.[176] The nickel NHC complex is generated *in situ* by addition of BuLi to a mixture of $NiCl_2$ and imidazolium salt. The (*Z*)-alkene is obtained in moderate to high yield. Interestingly, when a phosphane ligand is used instead of the NHC, the reaction yields the (*E*)-alkene. Jamison *et al.* used an *in situ* mixture of $Ni(COD)_2$ and IPr (1,3-(2,6-diisopropylphenyl)imidazol-2-ylidene) to catalyze the coupling of olefins with aldehydes (**B**)[177] and terminal olefins with isocyanates to yield acrylamides (**C**).[178] Similar conditions were used to couple two isocyanates with alkynes to give pyrimidine diones (**D**).[179] A reaction of diynes with nitriles catalyzed by an *in situ* prepared nickel NHC complex under basic conditions was reported to give a variety of substituted pyridines (**E**, X = $C(CO_2Me)_2$, H_2CCH_2, O, NTs).[180] Vinyl cyclopropanes could successfully be isomerized to the corresponding cyclopentenes by addition of a mixture of a Ni(0) precursor and a



Scheme 1.16. Organic transformations of C-C multiple bonds catalyzed by nickel NHC complexes.

bulky NHC (**F**).[181]

Other reactions with C–C double bonds in which nickel NHC complexes have been studied are for example the polymerization of styrene,[106, 182] and dimerization of ethene.[183, 184] Often in these reaction the Ni(II) is activated by methylaluminoxane ((-O-Al(Me)$_2$-)$_n$).

Two other nickel NHC complex catalyzed reactions involve hydrogen transfer. It was shown that treatment of various imines with NaO^{i}Pr in the presence of catalytic amounts of Ni(0) and IMes yielded the corresponding amines by transfer hydrogenation.[185] A reaction of catalytic amounts of Ni(0) and a triazol-5-ylidene with H_3NBH_3 leads to the rapid production of dihydrogen gas by dehydrogenation,[143] which, interestingly, was shown to proceed through hydrogen transfer of ammonia-borane to the carbene carbon, followed by C-H activation by the nickel species.[186]

The types of homogeneous catalysis under investigation in this thesis will be presented and discussed in the respective chapters.

1.7 Aim and outline of this thesis

The aim of the research described in this thesis has been to synthesize new nickel complexes with chelating N-heterocyclic carbene based ligands and to use these complexes in homogeneous catalysis.

In the current chapter an overview has been given of the chemistry of N-heterocyclic carbenes and their properties, complexes, and applications in homogeneous catalysis. In Chapter 2 the synthesis and solid-state structure of a monodentate NHC silver(I) complex is described and compared to literature. In addition, the silver complex is used to obtain the corresponding nickel NHC complex. The use of nickel(II) complexes of monodentate NHC ligands in the catalytic hydrosilylation of alkynes is discussed in Chapter 3. In the next three chapters investigations into the Kumada cross-coupling of aryl halides and aryl Grignard reagents are presented. The synthesis of nickel complexes bearing chelating benzimidazole-based bisNHC ligands is described in Chapter 4, together with the use of these novel complexes in this catalytic reaction. Nickel complexes bearing chelating NHC ligands with pendant anionic moieties were synthesized and used in the same catalytic reaction, which is described in Chapter 5. An attempt to rationalize the results described in Chapter 4 by using density functional theoretical calculations is discussed in Chapter 6 and includes the calculation of the full catalytic cycle and a possible route leading to the experimentally observed sideproducts. A number of the complexes were also used in the catalytic vinyl polymerization of norbornene, of which the results are presented in Chapter 7. Chapter 8 contains an evaluation and concluding remarks, as well as future prospects. In addition, the microwave-assisted synthesis of diimidazolium salts, which are potential precursors for chelating

biscarbene complexes, and a comparison to conventional syntheses, are briefly discussed in Appendix A.

Parts of this thesis have been published.[187-189]

1.8 References

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