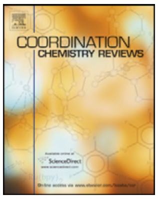
Coordination Chemistry Reviews 253 (2009) 862–892

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Carbenes: Synthesis, properties, and organometallic chemistry

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doi:10.1016/j.ccr.2008.05.018

ARTICLE INFO

Article history:
Received 29 February 2008
Accepted 24 May 2008
Available online 4 June 2008

Keywords:
Fischer carbene
N-Heterocyclic carbene
Schrock carbene
Stereoelectronic
Stabilization

ABSTRACT

Carbenes, thought of only as transient species for a long time, have become ubiquitous in organometallic chemistry. Their interaction with a metal center, which allows for their classification as a function of the nature of the carbene–metal bond, has inspired the investigations of many research groups in every area of chemistry, from physical chemistry to organic synthesis. In this *Review*, we intend to give a general overview of carbenes in a broad sense, discussing singlet and triplet carbenes with all variations within these families. More precisely, we describe here, for Fischer- and Schrock-type carbenes, N-heterocyclic carbenes and non-stabilized ones, the different synthetic routes to both the immediate precursors of carbenes and their metal complexes. Additionally, their steric and electronic properties are discussed in the light of both experimental and theoretical studies.

1. Introduction

Carbenes – compounds possessing a neutral divalent carbon atom with six electrons on its valence shell (Fig. 1) – have enjoyed a long and fruitful history in the field of chemical sciences that started almost a 150 years ago [1].

They remained simple proposals for a long time and generated numerous theoretical and experimental interrogations. Among the most noticeable questions, their electronic configuration – singlet or triplet – along with the geometry around the carbenic carbon took a prominent place. Continuous research efforts, spanning from physical chemistry to organic chemistry, have shed light on the nature of carbenes and have permitted their use in a more systematic manner. These intriguing species, primarily postulated and studied as intermediates in the context of organic transformations, later became a central topic in coordination chemistry [2]. Following the interrogations about their chemical nature, the way they interact with a metal center has grown to be a topic of intense investigation. Indeed, besides an unequivocal and formal definition, there is more than *one unique carbene* to be considered in the field of organometallic chemistry. Hence, as a function both of the metal and the carbene substituents, the bond order witnesses great variation. More fascinating, the carbenic carbon can be nucleophilic or electrophilic, encompassing every nuance in between these two opposite states. Taking advantage of these properties, the applications of metal–carbene species have truly impacted synthetic chemistry. Lately, the irresistible rise of N-heterocyclic carbenes (NHCs) has revealed another facet of the ability of carbenic species to act as supporting ligands in catalysis.

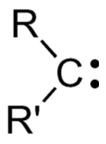


Fig. 1. Schematic representation of a carbene.

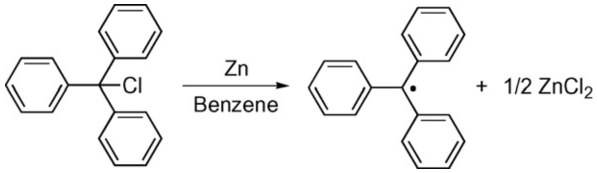
In this review, we will focus on the different aspects of the metal–carbene interaction, including steric and electronic properties considering theoretical and experimental data. The different types of carbenes, along with their synthesis and properties, will be discussed in close relation to the metal complexes they form. After a concise historical background, the different types of metal–carbene species will be described with a strong highlight on NHC-containing complexes.

2. The history of carbenes

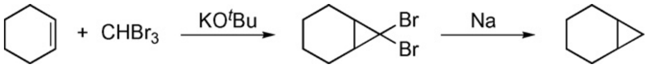
2.1. Early works, radical chemistry

The first assumption of a carbene species was made in 1855 by Geuther and Hermann [1]. They suggested that the alkaline hydrolysis of chloroform proceeds though the formation of a reaction intermediate with a divalent carbon called dichlorocarbene. In 1897, Nef proposed the same reaction intermediate for the Reimer–Tiemann reaction and the transformation of pyrrol to α-chloropyridine in chloroform [3]. They both showed a lot of intuition and courage for their postulations considering that most chemists did not even believe in the existence of free radicals at that time. Indeed, it was only 3 years later that Gomberg characterized the first example of a free radical, triphenylchloromethylene (Scheme 1), through elemental analysis and chemical reactivity [4]. Its discovery was freshly welcomed by the scientific community [5].

Prior to the Great War, Staudinger and Kupfer contributed to the recognition of carbenic reaction intermediates by studying the formation of methylene derivatives [6] and diazomethane [7].



Scheme 1. Generation of the first stable radical.



Scheme 3. Alkene cyclopropanation via a methylene intermediate.

Throughout the 1920s and 1930s, the existence of free radicals was finally well recognized, and their use in organic chemistry as reaction intermediates was growing extremely rapidly [5]. In this context, carbene moieties were regarded as diradicals [8]. The methylene carbene was seen as a linear species, with two degenerate p-orbitals inevitably leading to a triplet state [9]. At the beginning of the 1950s, there was a resurgence of interest in the organic chemical reactions of carbenes [10]. In 1953, Doering and Knox disclosed an elegant synthesis of tropolones via an addition of methylene to substituted benzene (Scheme 2) [11].

The most important contribution of Doering and his collaborators came a year later when they proved the existence of a dibromomethylene intermediate, in the first cyclopropanation operating via the addition of bromoform to an alkene (Scheme 3) [12].

Then more organic synthesis involving the use of methylene were reported [13], prompting chemists and physicists to have a closer look at this carbenic intermediate.

2.2. Electronic configuration and geometry

In 1951, Lennard-Jones and Pople used quantum mechanics to determine the geometric structures and properties of small molecules [14]. They assumed the existence of two different ground states for the methylene carbene (still seen as a diradical) but could not determine which one was of lowest energy. One of the ground states they proposed was a singlet state with triangular geometry possessing three orbitals filled with two paired electrons and an empty orbital. The other proposed ground state was a triplet state with a linear geometry possessing two orbitals filled with paired electrons and two orbitals filled with unpaired electrons [14,15]. Two years later, Duschenne and Burnelle proved that :CF$_2$ had a singlet ground state with a sp^2 hybridization and the orbital bearing the nonbonding pair of electrons s in character [16]. In 1964, Zimmerman et al. assumed that steric protection would enhance the stability of carbenes. They successfully synthesized dimesitylmethylene but could not isolate it [17]. Analysis of the rearrangement products suggested that the carbene had a triplet ground state with an unexpected nonlinear geometry (Scheme 4).

In 1968, Hoffmann et al. accurately determined the minimum splitting energy required between both ground states to have a methylene with a singlet state [18]. They also suggested that the singlet state could be favored by π-overlap between the p-orbitals of the carbene and the α-substituents (Fig. 2).

During the 1970s and 1980s, numerous theoretical works using *ab initio* quantum calculations were published to rationalize the electronic structures and the geometries of methylene moieties such as :CH$_2$, :CHF, :CHBr, :CF$_2$, and :CCl$_2$ [19]. It became more and more obvious that inductive and mesomeric effects act synergistically to determine the energy gap between both ground states [20]. In 1992, Goddard et al. were able to predict accurately the ground state configuration of a series of carbenes :CXY (X, Y = H, F, Cl, Br, I, SiH$_3$), with a method using only low accuracy level calculations and which is applicable to other arbitrary carbenes [21]. It should be noted that it is important to predict the ground states of carbenes as it will directly affect their stability and reactivity [22].

2.3. Stabilization and reactivity of carbenes

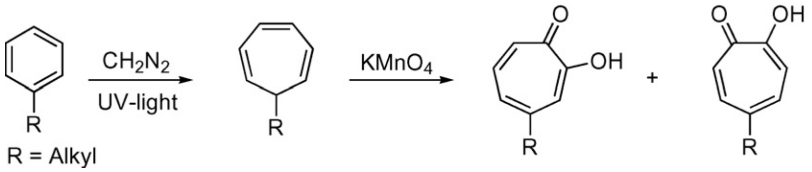
2.3.1. Triplet carbenes

Diazo compounds, most of which are very fragile and prone to degradation, are used to generate triplet carbenes by photolysis (UV-light or XeCl excimer laser). They usually bear two α-phenyl groups, as most α-dialkylmethylenes appear to be singlet carbenes [23]. Their diradical behavior makes them very reactive and difficult to isolate [24]. Triplet carbenes can be trapped by oxygen and form ketones via a ketone oxide intermediate [25]. They also rearrange/decompose by alkene dimerization [17,26], C–H insertion [26a,27], cyclopropanation of alkenes ([2 + 1] cycloaddition) [28], H-abstraction from an alkene [29] or a C–H bond leading to a simple radical [30]. They are generated at low temperature (77 K) and can be characterized by ESR. More than 30 years after the unique (and unsuccessful) attempt by Zimmerman to isolate a triplet carbene [17], Tomioka et al. overcame this challenge [31], and synthesized a triplet carbene stable up to 1 week in solution at room temperature (Scheme 5) [32].

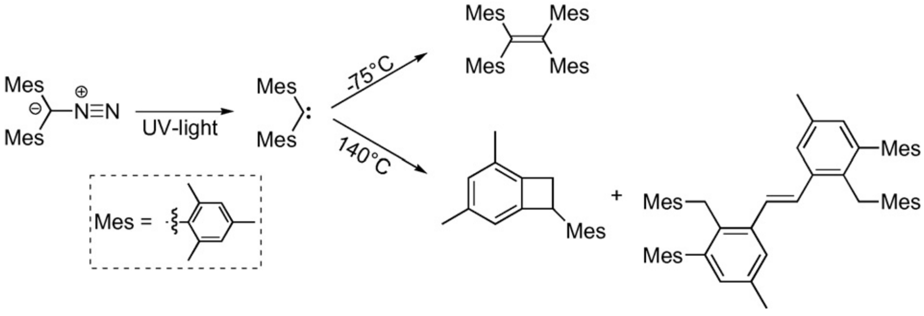
Contrary to their singlet cousins, the triplet carbenes do not react with carbon–halogen bonds [33] and they can be stabilized by steric protection with bromo and trifluoromethyl groups placed in their vicinity [29c,34]. Hydrogen-containing alkyl groups are prohibited because any close C–H bond would be activated [30]. Triplet carbenes can also be stabilized by delocalization of the unpaired electrons in an aromatic network such as an anthryl group [32]. It is worthy to note that these stable carbenes can be linked together to form polycarbenes with interesting ferromagnetic properties [35].

2.3.2. Singlet carbenes

Carbene multiplicity is greatly determined by the electronegativity of both α-substituents. σ-electron-withdrawing groups (negative inductive effect: −I) favor the singlet state by stabilizing the filled non-bonding orbital, increasing its s character [20,21]. On the other hand, electronic delocalizations (mesomeric effects: ±M) between the methylene and its α-substituents determine the carbene geometry (linear or bent) and play an active role in its thermodynamic stabilization [18b]. Depending upon the mesomeric effects and the stabilization brought by each α-group, singlet carbenes fall into five categories: +M/+M [36], −M/−M [36], −M/+M [36], +M/− [37], and the recently isolated aromatic cyclopropyli-



Scheme 2. Synthesis of tropolone-derivatives via the insertion of a methylene intermediate.



Scheme 4. Generation of a triplet carbene and rearrangement products.

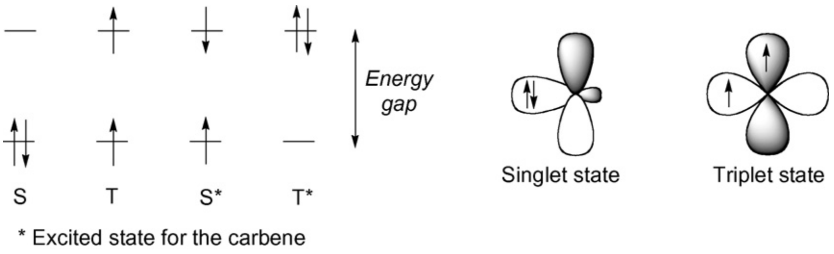


Fig. 2. Electronic states of a carbene.

denes [38]. They are amphiphilic and can react as nucleophilic or electrophilic species [39]. Unstable singlet carbenes usually decompose/rearrange by alkene dimerization [40], 1,2-shifts [41], C–H insertion, fragmentation [42] or [2 + 1] cycloaddition to alkenes [43].

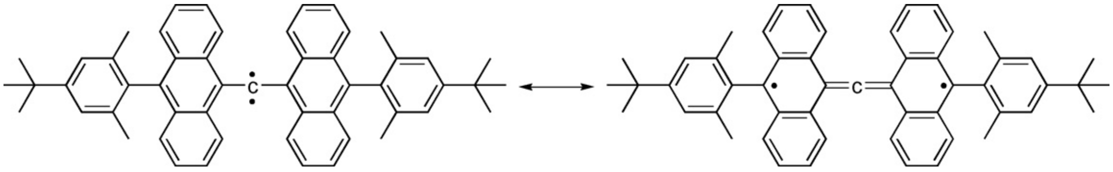
2.3.2.1. +M/+M α-groups. +M/+M singlet carbenes bear two electron-donating α-groups such as F, Cl, Br, I, OR, SR, SR_3, NR_2, PR_2 [36]. They are predicted to have a bent geometry [20,21] Their stabilization occurs by donation from the p orbital of the substituents to the methylene empty p-orbital. Dihalocarbenes [44], dioxacarbenes [45], and oxahalocarbenes [46] are transient species; they spontaneously dimerize. Their reactivity can be monitored in terms of their ability to promote the cyclopropanation of alkenes ([2 + 1] cycloaddition) [45,46]. They are cleanly generated by thermolysis or photolysis from the corresponding diazirines (Scheme 6); or by oxygen atom transfer reaction from urea and carbonate compounds to non-heteroatom stabilized fluorenylidene and methylene carbenes (Scheme 7) [47].

In contrast aminoxycarbenes [48], aminothiocarbenes [48], diphosphinocarbenes [49] and especially diaminocarbenes [36] (including NHCs) are kinetically stable in solution or in the solid state at ambient temperature (Scheme 8). While their dimerization is thermodynamically favored, it occurs only in presence of a Brønsted acid (Scheme 9) [50]. They are conveniently prepared by deprotonation of the corresponding salt [36,51].

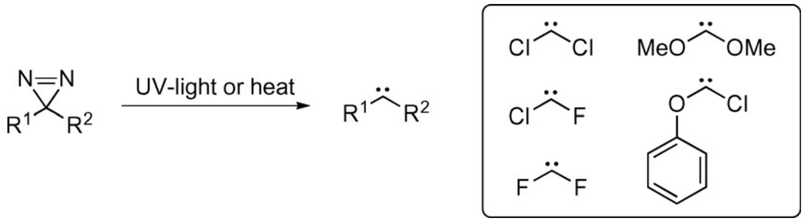
2.3.2.2. −M/−M α-groups. −M/−M singlet carbenes bear two electron-withdrawing α-groups such as COR, CN, CF_3, BR_2, and SiR_3 [36]. They are predicted to have a linear geometry [20,21]. Stabilization occurs by donation from the methylene filled p-orbital to the substituents empty p-orbital. They have never been isolated. However, some masked analogues, such as the borinanylideneboranes [52], have been synthesized and react like electrophilic carbenes toward trapping reactions with germylenes and stannylenes (Scheme 10) [53].

2.3.2.3. +M/−M (or −I) α-groups. +M/−M singlet carbenes bear two α-groups with opposite electronic effects. Their geometry is predicted to be quasi linear [20,21]. They are stabilized simultaneously by a strong donation from the p-orbital substituents to the methylene empty p-orbital and by a weaker donation from the methylene filled p-orbital to the substituents empty p-orbital (push–pull effect). At low temperatures alkoxycyanocarbenes [54] and alkoxytrifluoromethylcarbenes [55] are transient, while phosphinosylilcarbenes [56] and phosphinophosphoniocarbenes [57] are stable at ambient temperature. They are cleanly generated by photolysis or thermolysis of the corresponding diazarine or diazo compound. The phosphinocarbenes, stabilized by extensive delocalizations, can also react like phosphavinylylides or phosphacumulenes (Scheme 11) [36,58].

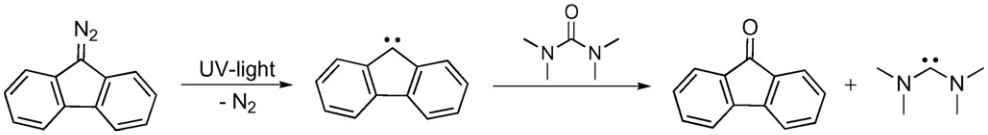
2.3.2.4. +M/− α-groups. While alkylhalogenocarbenes are transient [59], Bertrand et al. synthesized a series of stable arylphosphinocarbenes [60], alkylaminocarbenes [61] and silylaminocarbenes (Fig. 3) [62]. They are stabilized by only one amino- or phosphino-group. The second α-group acts as a spectator and provides a marginal electronic effect toward the carbene center. They are nucleophiles and can be generated by depronation of the corresponding salt. Additionally, a transient pyrazolylidene stabi-



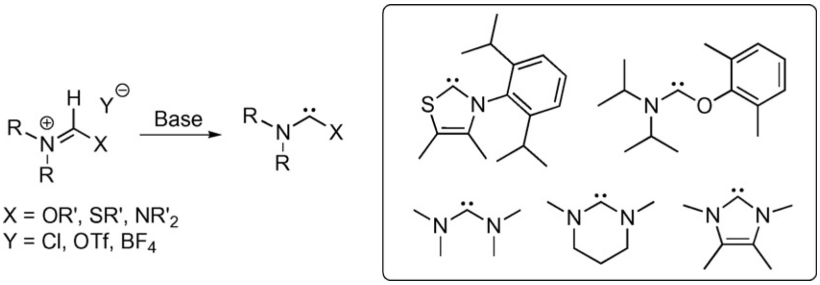
Scheme 5. Stable triplet carbene.



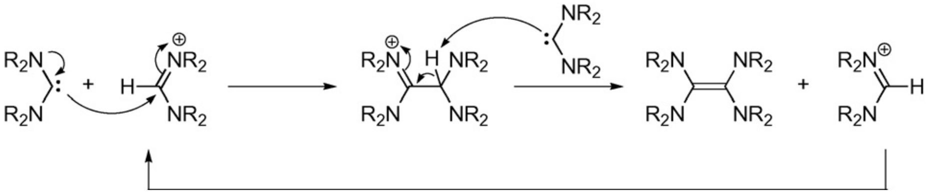
Scheme 6. Generation of carbenes from diazarine precursors.



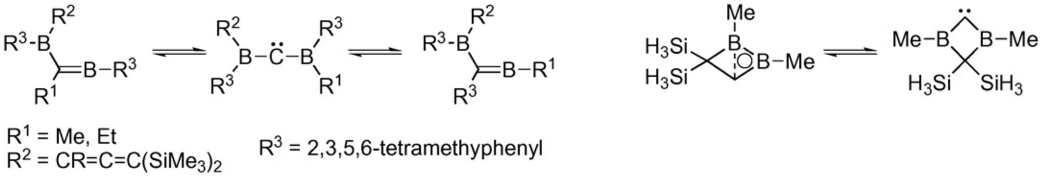
Scheme 7. Generation of carbenes by oxygen atom transfer.



Scheme 8. Generation of carbenes by deprotonation.



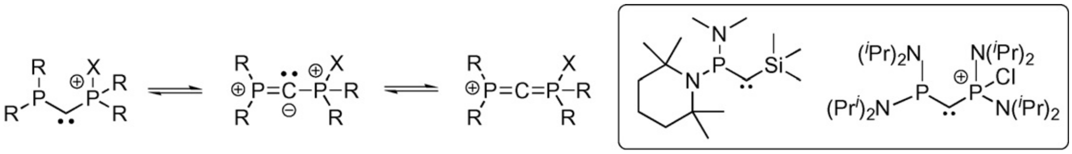
Scheme 9. Carbene dimerization assisted by a Brønsted acid.



Scheme 10. Masked analogues of −M/−M carbenes.

lized by one amino-group has been synthesized by decarboxylation of a betaine pyrazolium-3-carboxylate precursor [37].

2.3.2.5. Cyclopropenylidenes. Cyclopropylidenes largely present in combustion flames and interstellar space [63] were considered as transient carbenes in regular laboratories conditions until the recent isolation of bis(diisopropylamino)cyclopropenylidene by Bertrand et al. in low yield [38]. This aromatic carbocyclic carbene, bearing no stabilizing α-groups, is synthesized by deprotonation of the corresponding cyclopropenium tetrafluoroborate



Scheme 11. Phosphinocarbenes and mesomeric forms.

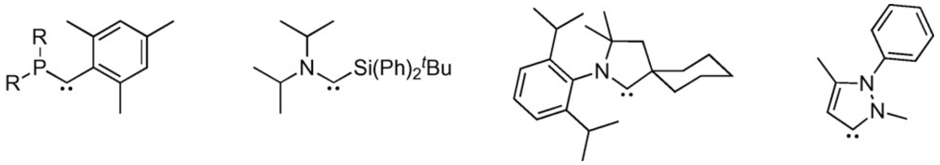
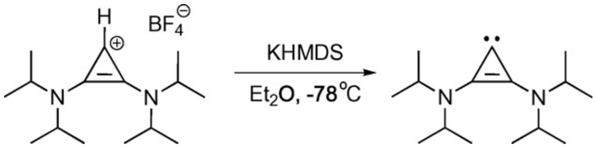
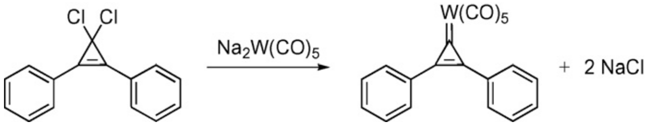


Fig. 3. Carbenes stabilized by only one α-group.



Scheme 12. Bis(diisopropylamino)cyclopropenylidene synthesis.



Scheme 16. Synthesis of the first non-stabilized carbene–metal complex.

salt: a very classical method to generate Fischer-type carbene (Scheme 12).

3. Carbenes and organometallic chemistry

3.1. Early works and first complexes

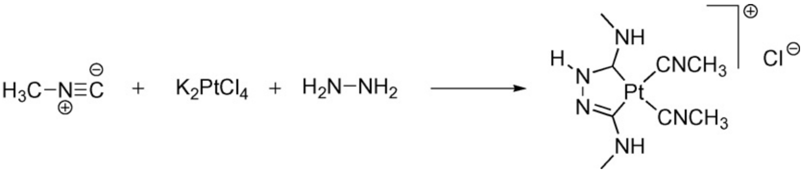
In 1915, Chugaev et al. reported that hydrazine reacts with isocyanide complexes of platinum(II) to yield new hydrazine-bridged platinum complexes [64]. Unfortunately they did not have the required spectroscopic techniques to reveal, in fact, the first synthesis of a metal–carbene complex (Scheme 13). A carbene-containing structure was first proposed in 1970 [65], based on previous related observations [66], and triggered further studies on the generation of carbene–metal complexes from isocyanide and hydrazine [67]. The definitive structure was later resolved in 1973 by NMR and X-ray single crystal diffraction [68].

During the 1960s, Fischer and Öfele were working on alkene–metal–carbonyl (Mn, Re) complexes [69]. In 1964, while carbenes were in vogue in organic chemistry, Fischer reported and characterized unambiguously the first metal–carbene complex [70]: methoxyphenylmethylene tungsten(0) pentacarbonyl (Scheme 14). The authors extended the synthesis to chromium(0), iron(0) and manganese(0) complexes with different alkoxy- and alkyl-groups [71].

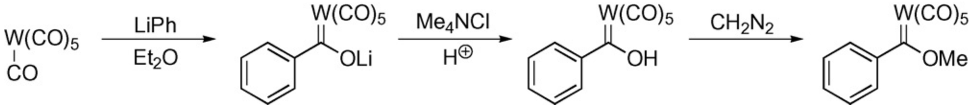
During the same period, Wanzlick was interested in isolating carbenes and believed that diaminocarbenes would be stable. He proposed the synthesis of the 1,3-diphenyl-2-imidazolidinylidene via 1,3-diphenyl-2-trichloromethylimidazolidine [72]. The carbene was not isolated and only the corresponding enetetramine was recovered. He also reported different carbene adducts by using thiophosgene, thionylchloride, cyclopentanone or benzaldehyde [73]. In 1968, Wanzlick and Öfele separately reported two different NHC–metal complexes [74] (Scheme 15) more than 20 years before the first isolation of a NHC.

The same year, Öfele also reported the first complex bearing a non-stabilized carbene without any α-heteroatoms (Scheme 16) [75].

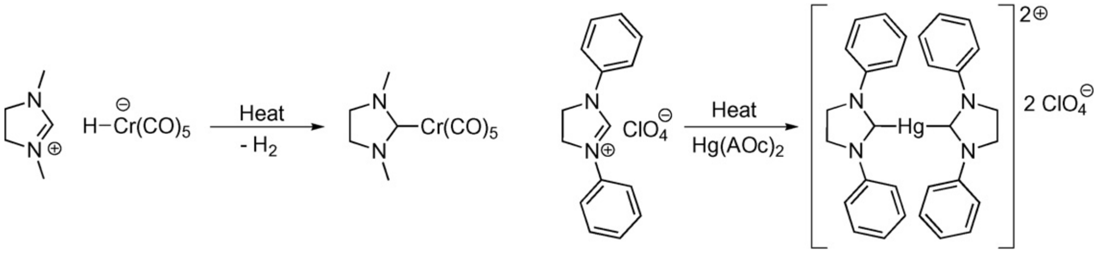
In 1974, Schrock reported the first synthesis of a high oxidation state (d^0) metal–alkylidene complex [76] by an α-hydrogen



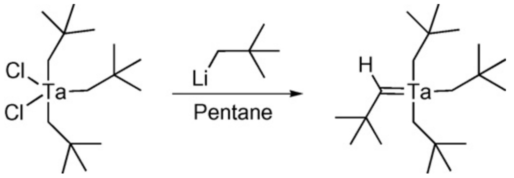
Scheme 13. Synthesis of the Chugaev's salt.



Scheme 14. Synthesis of the first recognized metal–carbene complex.



Scheme 15. Synthesis of the first NHC–metal complexes.



Scheme 17. Synthesis of the first alkylidene–metal (d^0) complex.

abstraction on the tris(2,2-dimethylpropyl)methyl tantalum(V) dichloride precursor (Scheme 17).

3.2. Carbene–metal bond formation

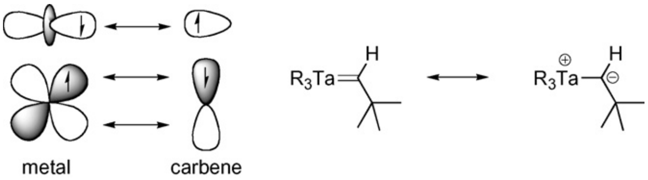
3.2.1. Geometric considerations

The formation of the C–M bond of a carbene–metal complex by orbitals overlapping requires a narrowing of the valence angle (XCY) at the carbene center [77]. Carbenes stabilized by donation from both α-groups (+M/+M), such as diaminocarbenes or dialkoxycarbenes, adopt a bent geometry with a small valence angle at the central carbon [20,21]. They have the required geometry to strongly and easily bind a metal fragment. In contrast push–pull carbenes, alkylidenes, and triplet carbenes adopt a widened valence angle and tend to be linear [20,21]. They do not have the adequate geometry to bind the metal fragment and any changes of conformation to narrow their valence angle are energetically unfavorable [77]. Consequently, they are very reluctant to form a metal complex and give a weaker metal–carbon bond.

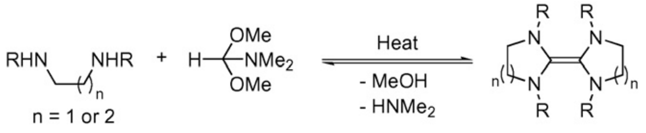
3.2.2. Electronic considerations

3.2.2.1. Fischer carbene complexes. Well-stabilized heteroatom-containing singlet carbenes, such aminocarbenes and alkoxycarbenes have a significant gap between their singlet and triplet ground states [36]. They form a metal–carbon bond constituted by mutual donor–acceptor interaction of two closed-shell (singlet) fragments. The dominant bonding arises from carbene–metal σ-donation and simultaneously from metal–carbene π-back donation (Scheme 18) [78]. The π-electrons are usually polarized toward the metal and the carbon–metal bond has a partial double bond character, which diminishes with the stabilization of the carbene by its α-groups [71,78]. For instance, in diaminocarbenes, including NHCs, the metal–carbon bond is seen as a simple bond; the π-back donation is usually weak because the carbenic carbon is already well stabilized by π-donation from its amino-groups [79,80]. Fischer carbene complexes are electrophilic at the carbon–metal bond and are prone to nucleophilic attack at the carbene center (OMe/NMe_2 exchange for instance) [77–79]. They are associated with low oxidation state metals [78–80].

3.2.2.2. Schrock carbene complexes. Poorly stabilized carbenes such as dialkylcarbenes or alkylidenes have a small gap between their singlet and triplet ground state. They form a covalent metal–carbon bond in nature created by the coupling of two triplet fragments (Scheme 19) [77b,81]. The π-electrons are nearly equally distributed between the carbon and the metal, and the metal–carbon bond is seen as a true double bond [78,81]. Schrock carbene complexes are nucleophilic at the carbon–metal bond and are susceptible to react at the carbene center with electrophiles as in a Wittig reaction involving an ylide instead of a carbene [79]. They are found exclusively among early transition metals with the highest oxidation state (d^0) [78].



Scheme 19. Metal–carbon bonding in Schrock carbene complexes.



Scheme 20. Synthesis of enetetramines.

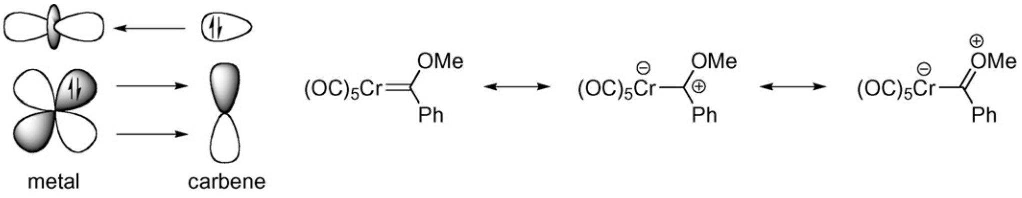
3.2.2.3. Other type of metal–carbene complexes. Non-heteroatom stabilized carbenes can be bound to late-transition metals and low oxidation state early transition metals. The complexes formed are usually electrophilic at the metal–carbon bond in contrast with the Schrock carbene complexes. They represent the borderline between traditional Fischer- and Schrock-type complexes, and they fit partially the definition of both categories. Schrock mentioned that in such complexes the carbene moieties should be called phenylcarbenes and alkylcarbenes because benzylidenes and alkylidenes stand for Schrock carbene complexes [82]. Nevertheless, it is acceptable to call non-heteroatom stabilized carbenes alkylidenes and benzylidenes in complexes, regardless of the metal involved or its oxidation state.

3.3. Synthesis of Fischer carbene complexes

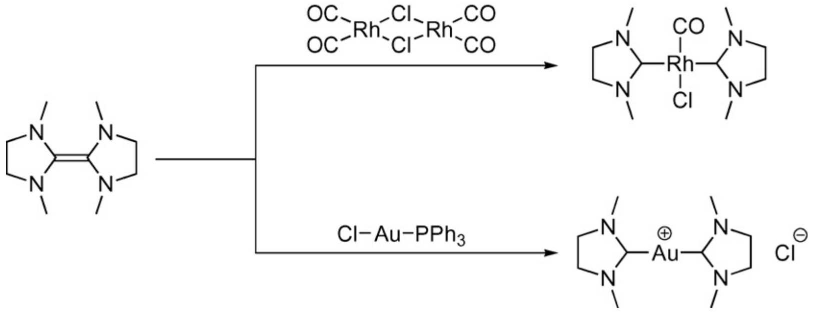
3.3.1. Enetetramines

Enetetramines are electron-rich alkenes bearing four amino groups [83]. They are synthesized from diamines and *N,N*-dimethylformamide. The reaction is a succession of equilibria, which are driven toward the alkene by removal (distillation) of methanol and dimethylamine (Scheme 20) [84]. The synthesis is restricted to primary alkyl- and unhindered aryldiamines [79,85].

They are generally oxygen- and moisture-sensitive, being chemiluminescent in air due to the formation and decay of dioxetane [86]. Their weak C=C bond reacts with electrophiles or protic reagents to yield the corresponding aminals [86]. They are also strong reducing agents and form in presence of alkyl-, organosilyl-, organogermanyl-, and organotin halides the corresponding radicals by halide abstraction [79]. They generate imidazolidinylidene



Scheme 18. Metal–carbon bonding in Fischer carbene complexes.



Scheme 21. Carbene–metal complex derived from enetetramines.

(NHC) or tetrahydropyridinylidene transition metal complexes by di-μ-halogenodimetal bridge splitting or by the displacement of a neutral or anionic ligand depending upon the metal source chosen (Scheme 21).

The mechanism of the metal–carbene formation is unlikely to proceed via generation and trapping of a free carbene [79]. Lappert et al. have synthesized enetetramine-derived complexes, having between one and four carbene ligands, of $Cr^{0/I}$, $Mo^{0/II}$, $W^{0/II}$, Mn^{I}, $Fe^{-II/0/I/II}$, $Ru^{-II/0/II}$, Os^{II}, $Co^{-I/II/III}$, $Rh^{I/III}$, $Ir^{I/III}$, $Ni^{0/I/II}$, Pd^{II}, Pt^{II}, Au^{I} and Hg^{II} [79,87]. Nevertheless, in some rare exceptions the C=C bond is not cleaved, and there is chelation with both amino-groups [79]. Of note, in the presence of metal-hydrides the imidazolidinium salt can be formed instead of the metal–carbene complex.

3.3.2. *Isocyanide–metal complexes (carbenoid precursor)*

The first isocyanide was prepared by Lieke in 1859 by reaction of allyl iodide and silver cyanide [88]. They are usually synthesized by dehydration of formamides (Ugi reaction) [89], by reaction of primary amines with dichlorocarbene [90] or by metalation/ring-opening of oxazoles (Scheme 22) [91].

They are strong bases and either polymerize or are hydrolyzed under acidic conditions [92]. They can be stabilized via metal coordination and functionalized [93]. Isocyanides are notorious for their bad smell, which might have seriously hindered their use by chemists [89]. They are sufficiently obnoxious to have been included in non-lethal weapons [94]! In terms of bonding, they are isoelectronic with CO and react with metal salts or carbonyl to access the corresponding isocyanide–metal complexes (Scheme 23) [93,95].

Isocyanide–metal complexes, when the metal center is sufficiently acidic, react promptly by nucleophilic attack at the coordinated carbon to form aminocarbene–metal complexes [96]. They react with protic nucleophiles such as primary and secondary amines or alcohols to yield acyclic diamino- and aminoalkoxycarbenes complexes (Scheme 24) [97].

They also yield oxazolidinylidene, thiazolinylidene, tetrazolylidene, triazolylidene, imidazolylidene, and imidazolidinylidene (NHCs) complexes by spontaneous cyclization, base-promoted cyclization, reaction with 1,3-dipolarophiles, and reaction with 1,3-dipoles (Scheme 25) [98].

In the case of benzannulated carbenes, such as benzoxazolylidenes and benzimidazolinylidenes, the precursors 2-hydroxyaryl isocyanide and 2-aminoaryl isocyanide which undergo spontaneous cyclization, need to be protected before their metalation (Scheme 26) [95].

Isocyanide–metal complexes are valuable species because they give access to numerous carbene complexes derived from non-isolable carbenes, including acyclic aminoalkoxycarbenes, oxazolidinylidenes, 1,3-H,H-NHCs and 1,3-H,alkyl-NHCs. Moreover, NH,NH-carbenes can be alkylated stepwise leading to unsymetrically *N*,*N*′-substituted ligands [95]. They also lead to high oxidation state metal complexes with an unusual large number of coordinated carbenes, such as tetra- or hexacarbene complexes [99].

3.3.3. *Carbonyl–metal complexes*

Complexes of acidic metals bearing an electron-deficient carbonyl ligand react with aliphatic amines to give carbamoyl complexes [100]. Under basic conditions, they also react with amines and alcohols bearing a good leaving group in α-position, leading to oxazolidinylidene and dioxolanylidene complexes (Scheme 27) [101].

The reaction proceeds also with carbonyl ligands under neutral conditions by using oxirane, aziridine and azetidine, and leads to the corresponding dioxolanylidene, oxazolidinylidene and oxazinanylidene complexes [102]. It is worthy to note that thiocarbonyl ligands can undergo the same type of reaction. In the presence of aziridine or thiirane, they lead to thiazolinylidene and dithiolanylidene complexes, while oxathiolanylidenes complexes are not formed (Scheme 28).

3.3.4. *Diazirines*

In 1965, Graham discovered a remarkable one-pot hypohalite oxidation of imidamides, leading to alkyl-, phenyl-, alkoxy-, or vinylhalodiaziridines [103]. They can undergo further exchange reactions and be functionalized by nucleophilic attack at the halide position (Scheme 29) [104].

Carbenes are cleanly produced by thermal decomposition of diazirines (Scheme 6). Nevertheless, attempts to generate metal complexes directly from diazirines have been quite unsuccessful, leading to very low yields (at the most 16%) [105]. The reaction does not proceed via coupling between a metallic fragment and the free carbene but via an insertion route leading to a metal–diazo-intermediate (Scheme 30) [105b].

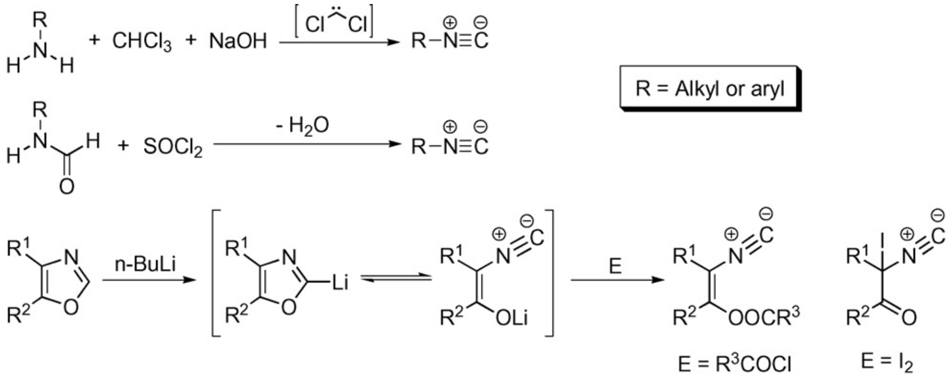
3.3.5. *Vilsmeier salts*

The first chloroiminium salt was prepared by Vilsmeier in 1927, by the reaction of phosphoryl trichloride and *N*,*N*′-dimethylformamide [106]. The synthesis has been extended to *N*,*N*′-dialkylcarbamic chloride and *N*,*N*,*N*′,*N*′-tetraalkylurea (Scheme 31) [87c,107].

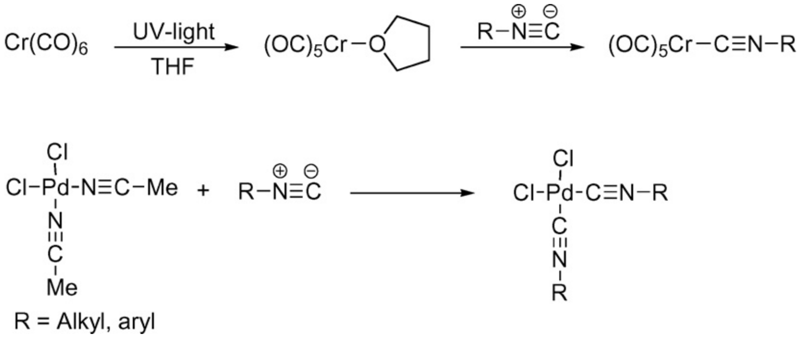
In the presence of a tertiary amine, usually the Hünig's base [108], iminium salts are deprotonated. The resulting unstable aminocarbenes can mediate the synthesis of isatins and quinolines [109]. When reacted with an electron-rich metal center, Vilsmeier salts lead to stable aminocarbenes complexes by oxidative addition of the C–Cl bond (Scheme 32) [110].

3.3.6. *Transmetalation from Group 6 metal–carbene complexes*

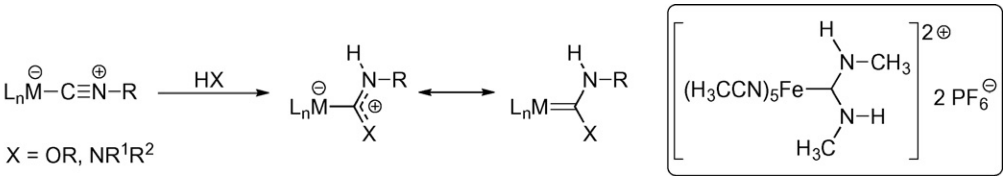
The first example of stoichiometric carbene ligand transfer between metal ions was reported by Fischer and Beck in 1970 [111]. The reaction of a molybdenum carbene complex with photochem-



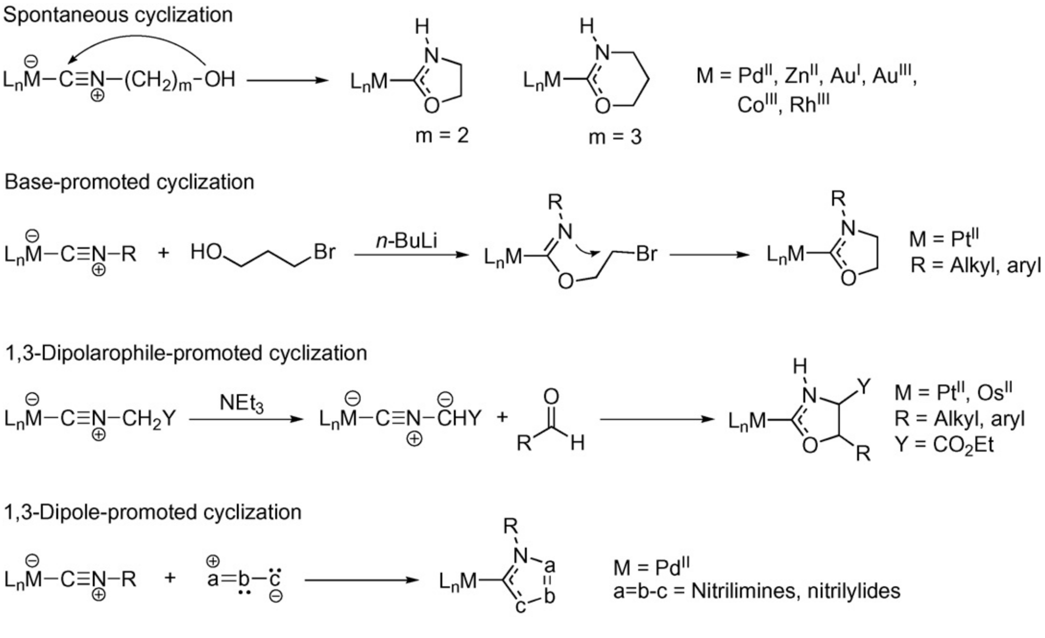
Scheme 22. Synthesis of isocyanides.



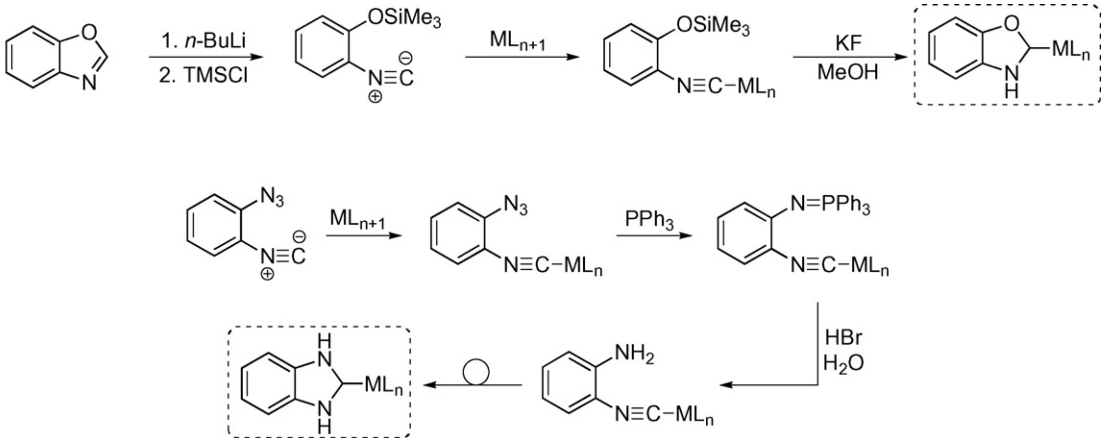
Scheme 23. Synthesis of isocyanide–metal complexes.



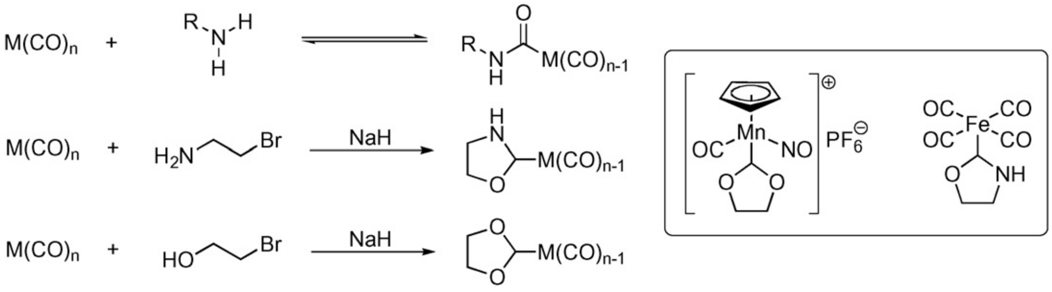
Scheme 24. Synthesis of aminocarbene complexes via isocyanide metal complexes.



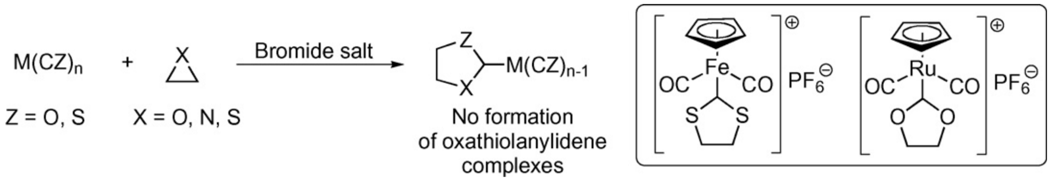
Scheme 25. Mechanisms for the cyclization of isocyanide complexes.



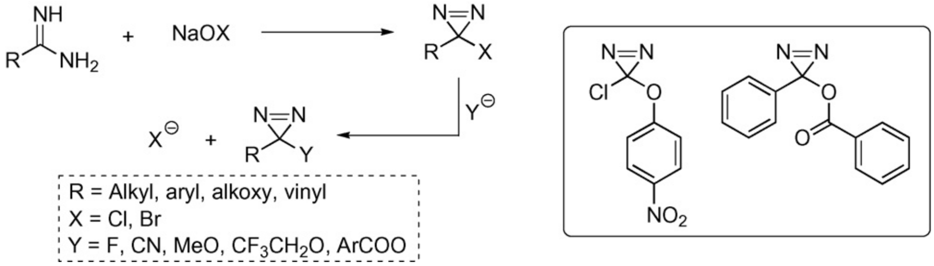
Scheme 26. Formation of benzannulated carbene complexes.



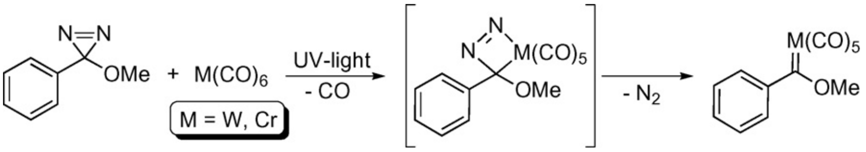
Scheme 27. Synthesis of alkoxycarbene complexes via carbonyl–metal complexes.



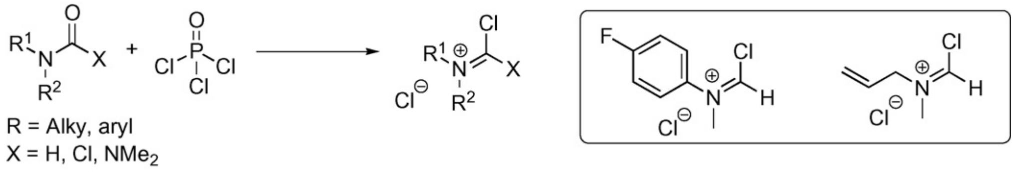
Scheme 28. Synthesis of carbene complexes via heterocycles.



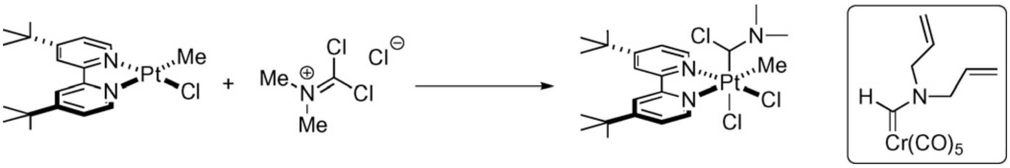
Scheme 29. Synthesis of diazirines.



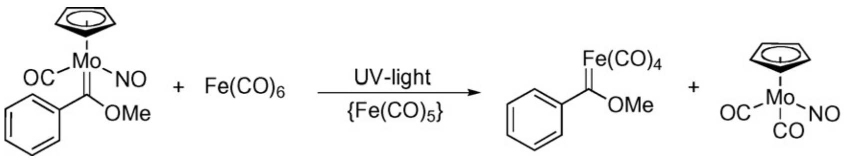
Scheme 30. Synthesis of carbene complexes via diazirines.



Scheme 31. Vilsmeier salts synthesis.



Scheme 32. Synthesis of aminocarbene complexes via Vilsmeier salts.



Scheme 33. Transmetalation and carbene transfer.

ically generated pentacarbonyl iron(0), produced a new iron(0) complex by transmetalation (Scheme 33).

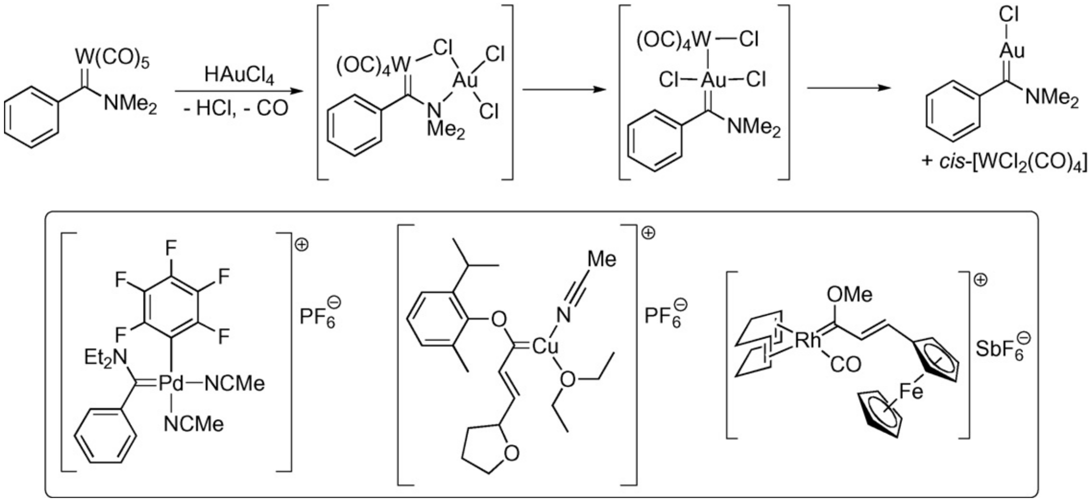
Mechanistic studies have ruled out the involvement of free carbenes and the transmetalation process occurs via a carbene transfer between two metal centers [112]. Hence, alkene formation (decomposition products) does not occur via carbene dimerization, but via elimination of a bis-carbene complex formed during a second transmetalation reaction [113]. Late-transition metal complexes, including Rh^{I}, Rh^{III}, Ir^{I}, Pd^{0}, Pd^{II}, Pt^{II}, Cu^{I}, Ag^{I}, Au^{I}, Au^{III} have been synthesized from Group 6 metal (Cr, Mo, W) complex precursors (Scheme 34) [113,114].

This method applies for all Fischer-type carbenes and is extremely efficient with diaminocarbene complexes, including NHCs (Section 4.9.5). In a few cases, carbene-bridged complexes are formed by transmetalation. They can be di- or even tri-nuclear, with a cluster core (Scheme 35) [113,115].

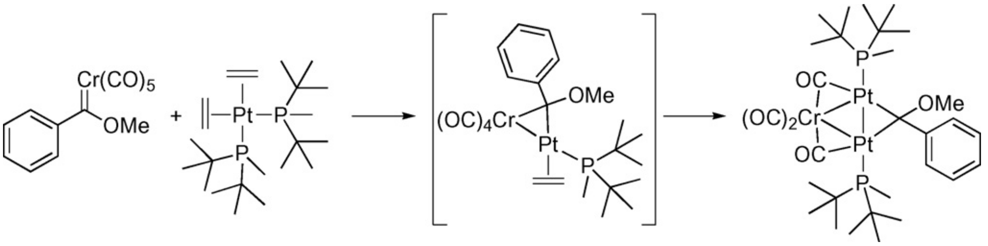
Interestingly, until 2000 the chemistry of the Group 6 metal Fischer carbene complexes was quite forsaken. Now the trend is reversed and a number of efficient catalysts for organic transformations such as carbene self-dimerizations, C–H insertions, cyclizations, cyclopropanations are generated by transmetalation [116]. It should also be noted that chromium- and tungsten-containing Fischer carbenes are now widely used as stoichiometric reagents for late-transition metal-catalyzed reactions [117].

3.3.7. *Modification of Fischer carbene complexes by nucleophilic attack*

Most transition metal–carbene complexes of the Fischer-type are electrophilic at the carbenic carbon (Scheme 18) [77–79,118]. They can be easily modified by nucleophilic substitution when they bear some alkoxy-, alkylthio-, or silyloxygroups [71,119]. For aminocarbenes the substitution is more difficult as amines are not good leaving groups, and it does not occur with NHC-complexes



Scheme 34. Synthesis of carbene complexes via transmetalation.



Scheme 35. Synthesis of polynuclear carbene complex via transmetalation.

[120]. Nucleophiles range from neutral to anionic, including ammonia [71,118] amines [71,118,119], hydrazines [118,121], oximes [118,122], alkoxides [118,123], thiolates [118,124], carbanions (usually aryl- or alkyllithium) [125], malonitrile anion [119], imidazolide [126] and benzimidazolide anions [126]. The first nucleophilic substitution was reported by Fischer et al. in 1967 [127]. The mechanism is similar to the reaction of nucleophilic addition to carboxylic esters, involving a tetrahedral intermediate before extrusion of the leaving group [128]. For neutral nucleophiles a proton transfer is included as additional and mandatory step for the elimination. If there is no acidic proton available, the reaction stops at the zwitterion adduct stage (Scheme 36) [128].

In the presence of metal–carbonyl anions, methoxycarbene complexes display an unusual reactivity. The nucleophilic attack occurs at the methyl group and leads to acylmetalate complexes by demethylation (Scheme 37) [129]. Similar reactivity is encountered with silyloxycarbene complexes, which undergo desilylation in the presence of amines or sodium methoxide [130].

3.3.8. Tautomerization of pyridines to pyridinylidene complexes

The possible isomerization of pyridinium salts to pyridin-2-ylidenes was first proposed in 1937 [131] whereas a carbene tautomer was finally characterized 60 years later, in the gas phase [132]. Pyridin-2-ylidenes are 40 kcal mol^{-1} less stable than pyridines but strongly stabilized by coordination to a transition metal fragment [132]. Quinolines, bipyridines, and other 2-substituted pyridines react with ruthenium(IV) [133], osmium(IV) [133], rhodium(I) [134], and iridium(III) [135] complexes to form *N*-metal adducts which tautomerize further to pyridin-2-ylidene complexes by 1,2-H shift from carbon to nitrogen (Scheme 38) [136].

3.4. Synthesis of Schrock carbene complexes

3.4.1. Metal alkyl complexes

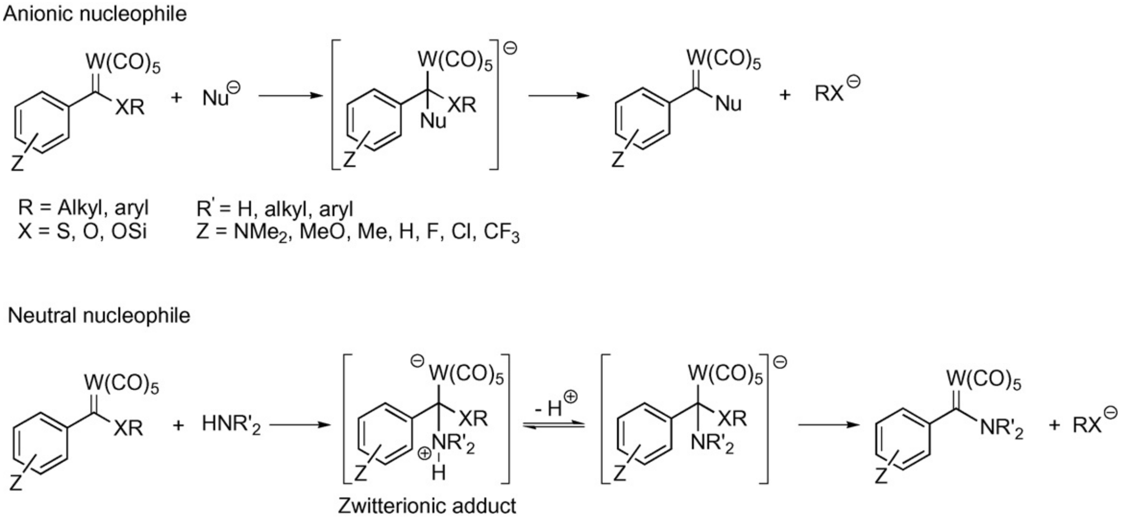
Alkyl metal complexes are easily prepared by reaction of metal halides with alkyl lithium or Grignard reagents [137]. Di- or polyalkyl complexes of coordinatively saturated early transition metals with high oxidation state (d^0) lead to alkylidene complexes by α-deprotonation [138]. The reaction requires the generation of a thermodynamically and kinetically favored leaving group, usually an alkane or a weak conjugated acid (Scheme 39). Complexes lacking β-hydrogens and bearing some methyl, neopentyl, or *tert*-butyl groups are preferred to avoid any competition between α- and β-deprotonation [138]. The reaction can be promoted thermally, photochemically, sterically, or with a base. It is a general method to prepare alkylidene complexes of Ti^{IV}, Zr^{IV}, Hf^{IV}, V^{V}, Nb^{V}, Ta^{V}, Cr^{VI}, Mo^{VI}, W^{VI} and Re^{VII} [82,138].

Di- and polyalkyl complexes of early transition metals which are not at their highest oxidation state, typically d^1 metals such as Ti^{III}, Zr^{III} or V^{IV}, Nb^{IV}, can be oxidized to alkylidene complexes by Ag^{I} salts or iodine (Scheme 40) [138e].

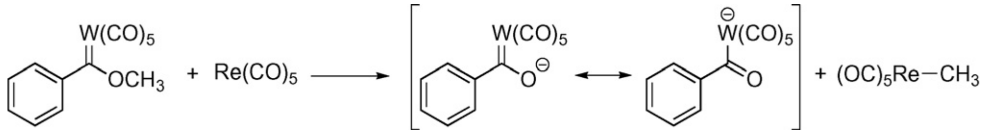
3.4.2. Cyclopropenes

Cyclopropenes are conveniently prepared by dehalogenation of mono- or dihalocyclopropane precursors under strongly basic conditions, involving alkoxides, amides, or alkyllithium reagents [139]. Cyclopropenone ketals are prepared by induced amide ring closure of 1-bromo-3-chloro-2,2-dialkoxypropane (Scheme 41) [140].

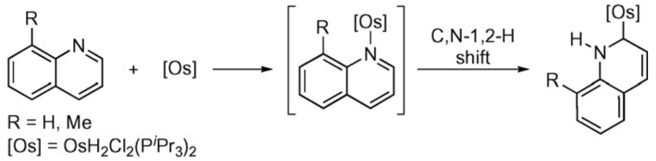
Investigations on the 1,3-dipolar cycloaddition of cyclopropenone ketals have shown that they are best characterized as a



Scheme 36. Mechanism of nucleophilic substitution on Fischer carbene complexes.



Scheme 37. Formation of acylmetalate by demethylation.



Scheme 38. Formation of pyridinylidene complex by tautomerization.

nucleophilic and π-delocalized singlet vinylcarbene. Both species are in thermal equilibrium (Scheme 42) [140].

Following this reactivity, transition metal vinylalkylidene complexes of Ti^{IV}, Zr^{IV}, W^{VI} and Re^{VII} have been synthesized by rearrangement of 3,3-diphenylcyclopropene, 3-methyl-3-phenylcyclopropene and 4,8-dioxaspiro[2,5]oct-1-ene [141]. The reaction can be induced thermally, photochemically or by using Hg^{II} salts (Scheme 43) [141].

3.4.3. Phosphiranes

Phosphines react with organic halides, forming phosphonium salts in high yield [142]. Further deprotonation by NaH yields phosphiranes (Scheme 44). They can be described as phosphorus ylides bearing a nucleophilic carbon and are commonly used for the Wittig reaction [143].

Phosphiranes react with phosphine reduced-metal complexes of Ti^{II}, Zr^{II}, V^{III} and W^{IV} to yield alkylidene complexes via a transfer reaction [138b,144]. The reaction proceeds through the loss of a phosphine from the metal center, followed by nucleophilic attack by the ylide carbon onto the metal [144c]. The zwitterionic adduct formed rearranges to alkylidene complex, relieving the steric crowding brought by the phosphirane group (Scheme 45).

Transfers from partially resonance-stabilized phosphorus ylides are greatly favored because the formed alkylidenes (such as benzylidenes, and vinylidenes) have their nucleophilic carbon stabilized by delocalization [144c].

3.4.4. Transmetalation from Group 5 metal alkylidenes

In 1982, Schrock et al. readily obtained a series of tungsten(VI) oxoneopentylidene complexes by alkylidene transfer from tantalum(V) alkylidene precursors [145]. The reaction proceeds via a bridged tungsten–tantalum alkylidene intermediate (Scheme 46). Since then no other examples of transmetalation between alkylidene complexes have been reported.

3.5. Synthesis of alkyl- and phenylcarbene complexes

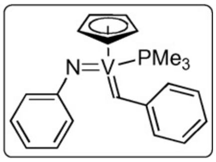
3.5.1. Diazo compounds

In 1906, bronze copper and copper(II) salts were found to catalytically promote the decomposition of diazoalkanes [146]. Nevertheless, the development of efficient catalysts for diazo decomposition reactions only began in earnest in the 1960s with the introduction of well-defined phosphite or acetylacetonate copper complexes [147]. The reaction proceeds via the formation of a diazo–metal adduct [148]. Depending upon the metal complexes used, this adduct can be stable or rearrange to a carbene complex by

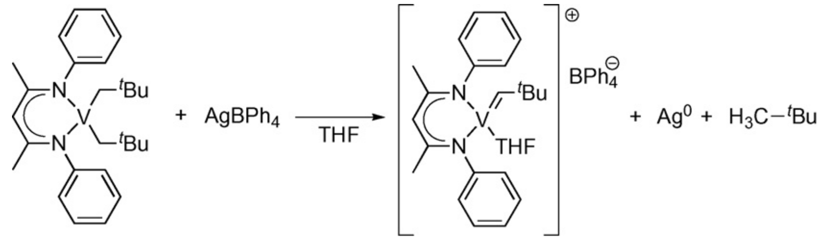
$$L_mM^n(CH_2R)_2 \xrightarrow[\text{Heat}]{\text{UV - light}} L_mM^n{=}CHR + CH_3R$$

$$L_mM^n(CH_2R)_2 + x\,PR_3 \longrightarrow L_mM^n{=}CHR(PR_3)_x + CH_3R$$

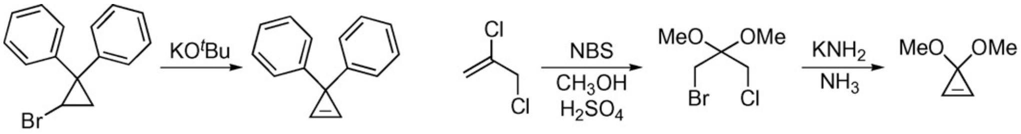
$$L_mM^n(CH_2R)X + B^{\ominus} \longrightarrow L_mM^n{=}CHR + BH + X^{\ominus}$$



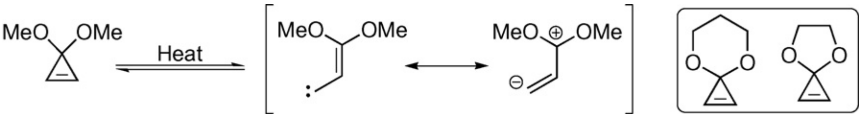
Scheme 39. Formation of alkylidene complexes via α-hydrogen elimination.



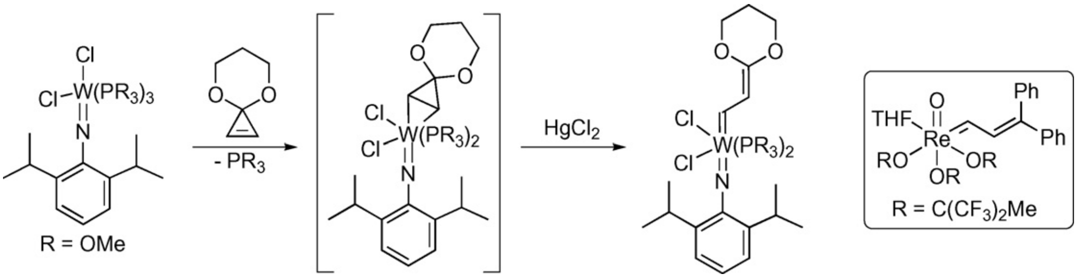
Scheme 40. Generation of alkylidene complexes via oxidation.



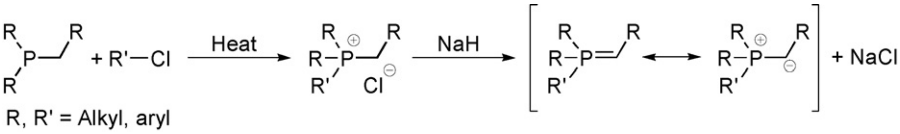
Scheme 41. Cyclopropenes and cyclopropenone ketals synthesis.



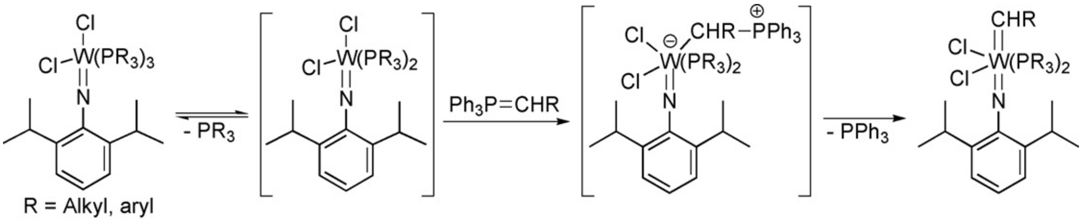
Scheme 42. Equilibrium between cyclopropenone ketals and vinylcarbenes.



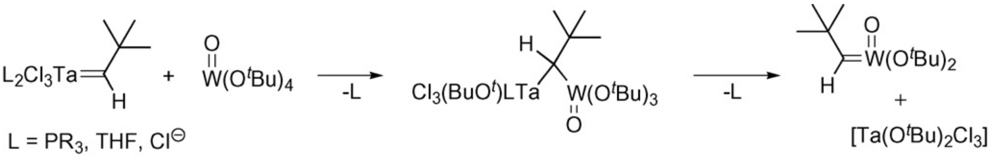
Scheme 43. Vinylalkylidenes formation by cyclopropene rearrangement.



Scheme 44. Synthesis of phophorus ylides.



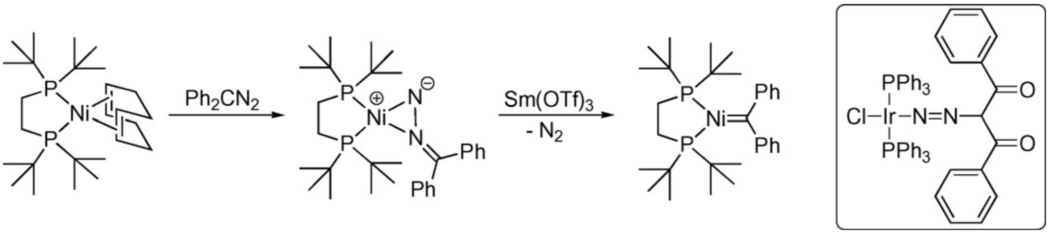
Scheme 45. Transfer of alkylidene from phosphorus ylides.



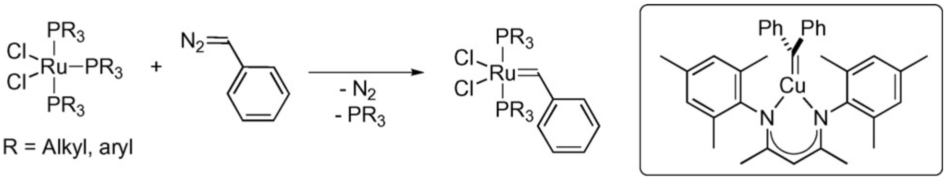
Scheme 46. Transmetalation of alkylidenes complexes.

nitrogen extrusion (Scheme 47) [149]. For instance, Cu^{I} [148,150], Rh^{II} [151], Ru^{II} [151], Ni^{0} [152], Co^{II} [153], Pd^{II} [154], Ag^{I} [155], Au^{I} [156] complexes lead to carbenic species while Ta^{V} [157], Nb^{V} [157], Mo^{IV} [158], Fe^{II} [159], Ir^{I} [160] lead to stable diazo-complexes.

Most of the carbene complexes formed by decomposition are further used to promote organic transformations via carbene transfer reactions such as cyclopropanation of alkenes [161], cyclopropenation of alkynes [161], cycloaddition to aromatic rings [161], ylide formation [161], ketene formation [162] and insertion reactions [161,163]. They are generally very reactive but are sufficiently stabilized by binding with the metal to avoid any competing carbene dimerization [164]. As a matter of fact, some phenylcarbene



Scheme 47. Mechanism of diazo decomposition.



Scheme 48. Synthesis of carbene complexes using diazo compounds.

complexes of Ni^0 [165], Cu^I [166], Ru^{II} (including the Grubbs catalyst) [167], Ru^{IV} [168], Fe^{IV} [169], and Os^{IV} [170] porphyrins were stable enough to be structurally characterized by single crystal X-ray diffraction (Scheme 48).

Diazoalkanes react also with metal–metal double or triple bonds and form metal–diazo adducts, which undergo thermally or photochemically induced loss of nitrogen, to rearrange to bridged metal–carbene complexes [171]. The reaction usually proceeds via a 1,3-dipolar cycloaddition pathway and allows the formation of dimetallacyclopropane and dimetallacyclopropene scaffolds (Scheme 49) [172].

3.5.2. Alkene isomerization

Recently, powerful π-donor ligands, such as the anionic PNP [173] or silox ligands [174], have been used to bind early transition metals and form π-basic metal centers. In presence of alkenes, they lead to alkylcarbenes [175] or alkylidenes [176] via an isomerization reaction. Back-donation from the metal stabilizes the carbene and favors its formation. In that case, the alkene–metal π-complex is not formed (Scheme 50).

3.5.3. α-Ionization

Metal α-ethers and α-thioethers are conveniently synthesized by hydride reduction of the parent Fischer alkoxy- and thiocarbene complexes [177]. They undergo α-ionization in the presence of Lewis or Brønsted acids to form alkyl- and phenylcarbene complexes via the dissociation of alcohols or thiols (Scheme 51) [178]. Complexes of W^0, Fe^{II} and Ni^{II} have been synthesized from metal α-ethers and used for cyclopropanations [178].

3.5.4. Cyclopropenes

Grubbs et al. have reported and patented the synthesis of two vinylcarbene complexes of Ru^{II} and Os^{II} by thermal rearrangement of 3,3-diphenylcyclopropene [179] (see Section 3.4.2 for an insight on the mechanism of formation). Nevertheless, this route has not been applied to synthesize further vinylcarbene complexes since.

3.6. Carbocyclic carbenes

Singlet carbocyclic carbenes, non-stabilized by heteroatoms, are generally transient with the notable exception of the bis(diisopropylamino)cyclopropenylidene recently isolated [38]. In 1968, Öfele reported the stable diphenylcyclopropenylidene chromium(0) pentacarbonyl complex [75]. Since then, a few examples of cyclopropenylidene and heptatrienylidene complexes were synthesized by oxidative addition of 1,1-dichloro-2,3-diarylcyclopropene or 1,1-dibromocycloheptatriene to platinum(0) or palladium(0) phosphine complexes (Scheme 52) [180]. These carbenes are almost exclusively σ-donor with their p-orbitals partially filled and involved in the aromaticity of the carbocyclics. They lead to stable palladium(II) complexes with excellent activity in cross-coupling reactions [181].

4. N-Heterocyclic carbenes

4.1. Definition

NHCs, also called Arduengo carbenes, are diaminocarbenes and form Fischer-type complexes with transition metals. Since the seminal work of Wanzlick [72–74] during the 1960s, numerous NHC–metal complexes have been synthesized following the traditional route to Fischer complexes without the involvement of any free carbene ligand (See Section 3.3). Nevertheless, the real breakthrough came in 1991, when Arduengo et al. synthesized and isolated the first stable NHC, 1,3-bis(adamantyl)imidazol-2-ylidene [182]. Since then, a great variety of NHCs bearing different scaffolds have been synthesized (Scheme 53) and reacted with transition metals leading to well-defined complexes [183]. Today, these carbenes are recognized as an exciting alternative to the limitations of phosphine ligands in the field of organometallic chemistry and its related catalysis [184,185].

Slight changes to the NHC architectures have a dramatic change on the electronic donor properties of the carbene moieties and impose geometric constraints on the *N*-substituents, influencing their steric impact [186]. These *N*-substituents allow for a modulation of the steric pressure on both the carbene and the coordinated metal [187]. Nevertheless, five-membered ring, imidazolylidenes and imidazolidinylidenes are widely used to generate NHC-complexes, while the other frameworks are rarely employed.

4.2. Five-membered ring iminiums and their NHCs

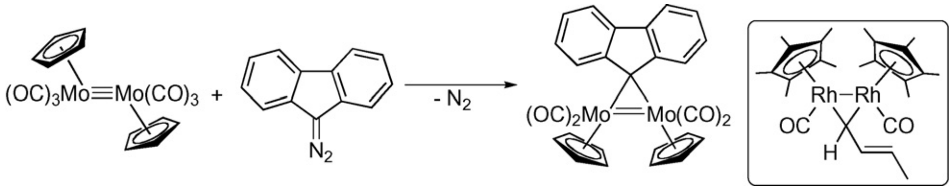
4.2.1. Imidazolium salts and imidazolylidenes

Various reliable routes are available to prepare imidazolium precursors [188]. One of the most straightforward is a one-pot synthesis, using, a primary amine, and formaldehyde [189]. Under acidic conditions the reaction proceeds through a coupling between the amine and the glyoxal, which forms the corresponding Schiff base. Condensation with formaldehyde leads to the imidazolium salt (Scheme 54).

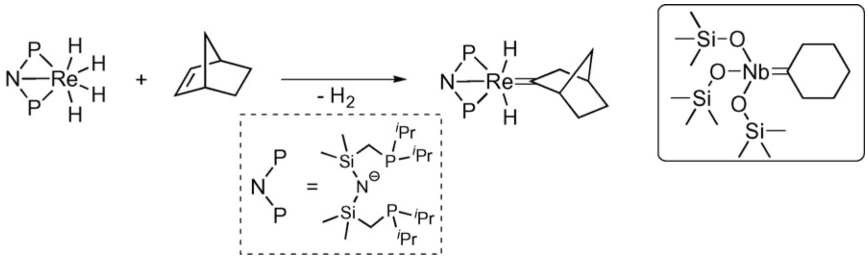
The reaction can be split in two distinct steps, with the isolation of the Schiff base (diimine) [190]. It allows for the synthesis of symmetrically *N*,*N*′-substituted imidazolium salts with various aryl- and alkyl-groups such as the 1,3-bis(2,6-diisopropylphenyl)imidazolium (IPr·HX), 1,3-bis(2,4,6-trimethylphenyl)imidazolium (IMes·HX), 1,3-bis(cyclohexyl)imidazolium (ICy·HX), 1,3-bis(adamantyl)imidazolium (IAd·HX), 1,3-bis(*tert*-butyl)imidazolium (ItBu·HX) and 1,3-bis(dodecyl)imidazolium (IDD·HX) (Scheme 55) [191].

Nevertheless, with sterically demanding salts the cyclization step becomes disfavored and reveals the limitation of this route [192]. Recently, Glorius et al. proposed an alternative approach for the synthesis of sterically hindered imidazolium salts [193]. The reaction of silver triflate with chloromethyl pivalate generates, in situ, an alkylating reagent, which efficiently cyclizes hindered and non-hindered diimines (Scheme 56) [193].

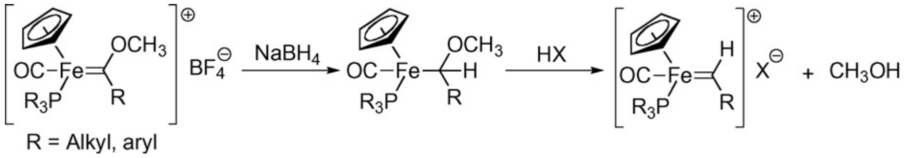
The one-pot reaction between glyoxal, ammonium chloride, paraformaldehyde, and only one equivalent of primary amine leads



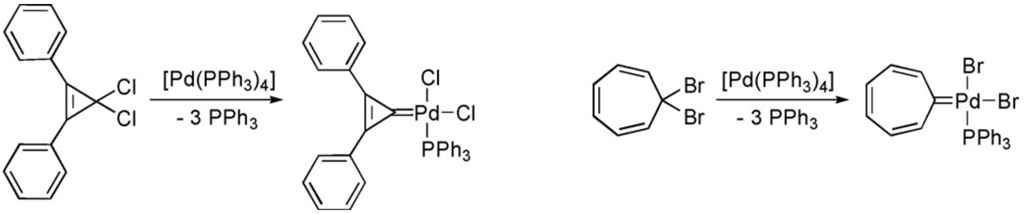
Scheme 49. Reaction of a diazo-group with metal–metal multiple bonds.



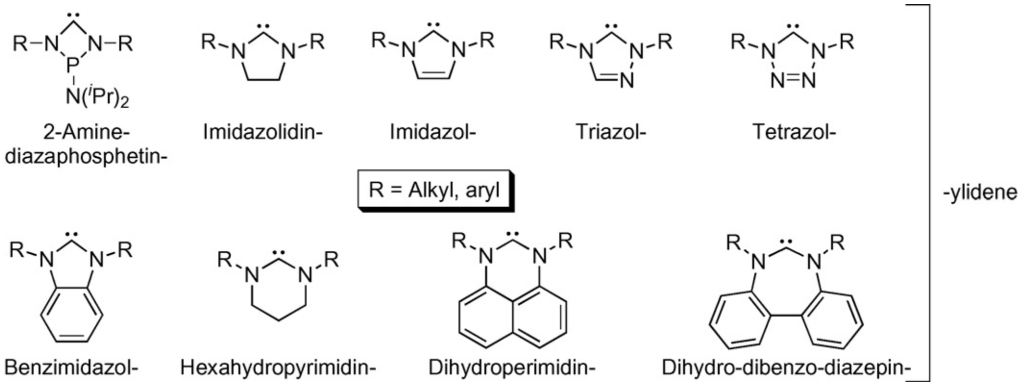
Scheme 50. Isomerization of alkenes to alkylcarbenes.



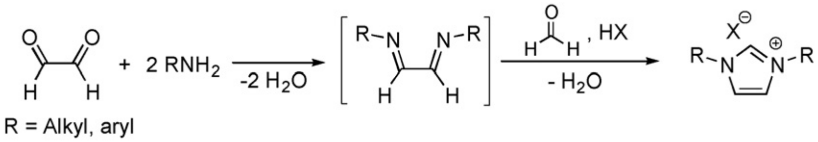
Scheme 51. α-Ionization of metal α-ethers.



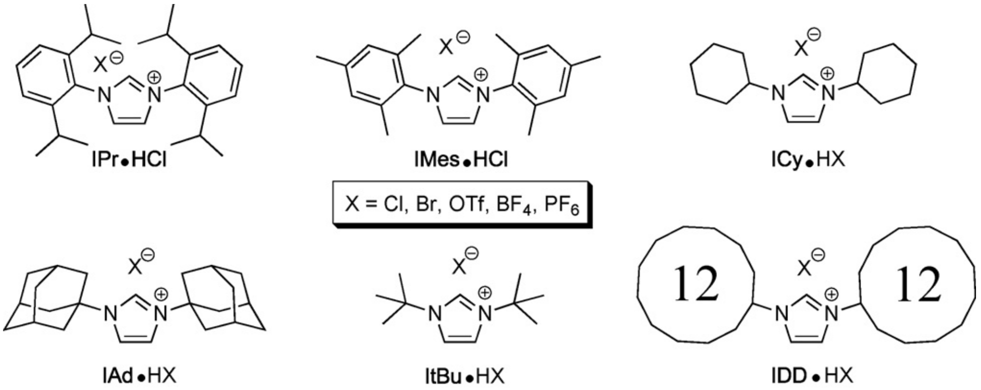
Scheme 52. Synthesis of carbocyclic carbene complexes by oxidative addition.



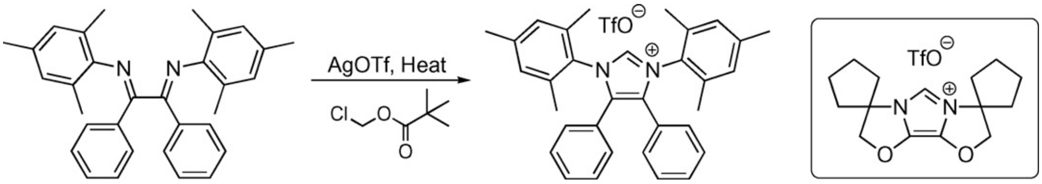
Scheme 53. Scaffolds of NHCs currently found in the literature.



Scheme 54. One-pot synthesis of imidazolium salts.



Scheme 55. Imidazolium salts used as carbene precursors.



Scheme 56. Cyclization of diimines with chloromethyl pivalate.

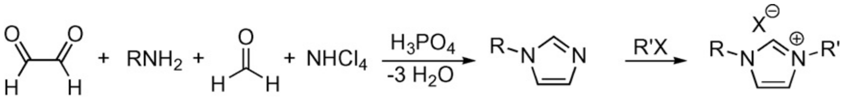
to the mono *N*-substituted imidazole. It can be further *N*-alkylated by reaction with an alkyl halide to form an unsymmetrically *N*,*N*′-substituted imidazolium salt (Scheme 57) [188].

Another route to synthesize unsymmetrical imidazolium salts is the stepwise alkylation of an imidazolide anion generated from the reaction of imidazole with potassium (Scheme 58) [188].

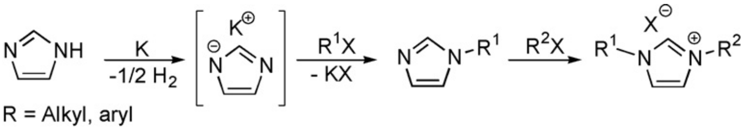
Imidazolium salts lead to imidazolylidenes by deprotonation. The reaction can be carried out in ammonia or in non-protic solvents such as THF or ethers. The deprotonation requires anhydrous conditions and the use of strong bases, with pK_a values above 14. Usually, potassium or sodium hydride with a catalytic amount of *tert*-butoxide is employed, but *tert*-butoxide itself, lithium aluminum hydride, *n*-butyllithium, potassium hexamethyldisilazide (KHMDS) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) are also efficient alternatives (Scheme 59) [188,190,194].

Last year, Astruc et al. proposed a surprising route to deprotonate a series of imidazolium salts. The role of the base was played by a radical anion superoxide formed in situ by reduction of ambient dioxygen with a 19-electron sandwich complex of Fe^I (Scheme 60) [195].

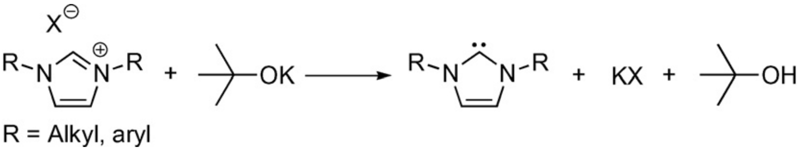
Finally, imidazolylidenes can be synthesized by electrochemical or chemical reduction of imidazolium salts [190a,196]. Cyclic voltammograms indicate a very negative potential at −2.28 V, and an excess of potassium in boiling THF is required to perform the chemical reduction. Coulometric analysis reveals a single electron



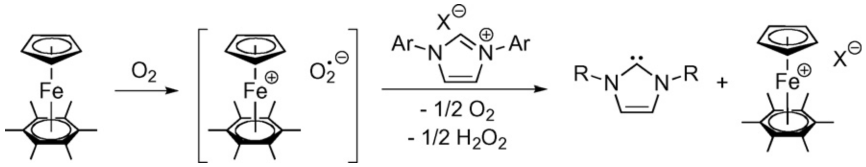
Scheme 57. Synthesis of *N*-alkylimidazoles and further *N*-alkylation.



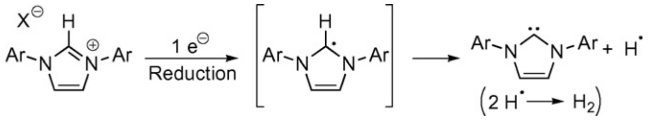
Scheme 58. Stepwise alkylations of imidazoles.



Scheme 59. Imidazolylidene formation via deprotonation.



Scheme 60. Deprotonation of imidazolium salts by the radical anion superoxide.



Scheme 61. Reduction of imidazolium salts.

event and the reduction is likely to proceed via a radical imidazole intermediate, which undergoes a further loss of a hydrogen radical (Scheme 61) [196].

4.2.2. *Imidazole-2-thiones and imidazolylidenes*

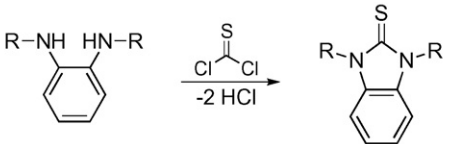
The condensation reaction of thioureas with 3-hydroxy-2-butanone in refluxing hexanol leads to 4,5-dimethyl-1,3-dialkylimidazole-2-thiones [197]. The reaction requires harsh conditions, but it is a general route to produce, in one step, tetraalkylimidazole-2-thiones in good yields. For instance, 1,3,4,5-tetramethylimidazole-2-thione (ITM·S), 1,3-diisopropyl-4,5-dimethylimidazole-2-thione (IPrMe·S) and 1,3-diethyl-4,5-dimethylimidazole-2-thione (IEtMe·S) are conveniently synthesized by this method (Scheme 62) [197].

Under acidic conditions, aryl- or alkyl isothiocyanates react with 2,2-diethoxyethaneamine to form mono *N*-substituted imidazole-2-thiones. These can react further with an alkyl halide to form *N*,*N*′-substituted imidazole-2-thiones (Scheme 63) [198].

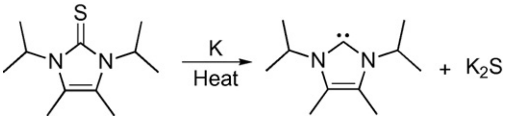
Alternatively, the cyclization reaction of *N*,*N*′-dialkylbenzene-1,2-diamines with thiophosgene leads to benzimidazole-2-thiones in high yield (Scheme 64) [188,199].

Imidazole-2-thiones lead to imidazolylidenes by reduction. The reaction is carried out in boiling THF with an excess of potassium. Despite the drastic conditions required, the yields are generally almost quantitative (Scheme 65) [197,199,200]. However, this route is not appealing as working with potassium metal is cumbersome.

Finally, it is worthy to note that imidazole-2-thiones are easily formed by reaction of imidazolium halides with elemental sulfur under basic conditions [201].



Scheme 64. Synthesis of benzimidazole-2-thiones.



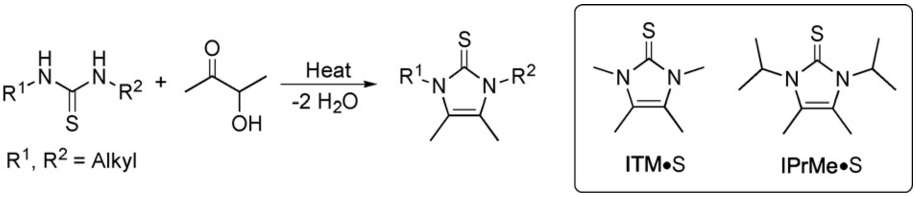
Scheme 65. Imidazolylidene formation by reduction with potassium.

4.2.3. *Imidazolinium salts and imidazolidinylidenes*

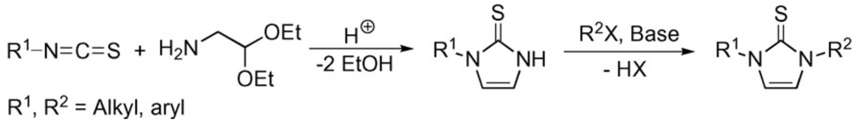
Diazobutadienes (Schiff bases) obtained by condensation of glyoxal with two equivalents of primary amine are reduced to ethane-1,2-diamines by action of sodium borohydride or Red-Al [202]. They react with triethyl orthoformate under acidic conditions to form imidazolinium salts [190]. The cyclization is an equilibrium which is driven by removal (distillation) of ethanol. The reaction time can be reduced from hours to a few minutes using microwave heating [203]. It allows for the synthesis of symmetrically *N*,*N*′-substituted imidazolinium salts with various aryl groups such as the 1,3-bis(2,6-diisopropylphenyl)imidazolinium (SIPr·HX) and 1,3-bis(2,4,6-trimethylphenyl)imidazolinium (SIMes·HX) for instance (Scheme 66) [191].

Ethyl-2-chloro-2-oxoacetate can react with two different amines, stepwise, to form an oxalamide. Its reduction with borane·THF or lithium aluminum hydride yields ethane-1,2-diamines which can be cyclized to form unsymmetrically *N*,*N*′-substituted imidazolinium salts (Scheme 67) [204].

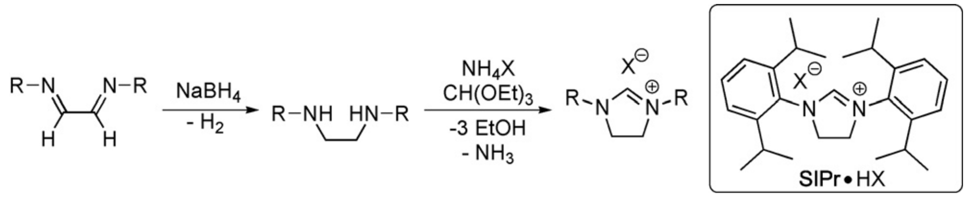
Imidazolinium salts lead to imidazolidinylidenes by deprotonation (Scheme 68). The reaction conditions are similar to that used with imidazolium salts. Nevertheless, ammonia, alkoxides and any other nucleophilic bases have to be avoided because they form adducts with imidazolidinylidenes [205]. Of note, even a rare



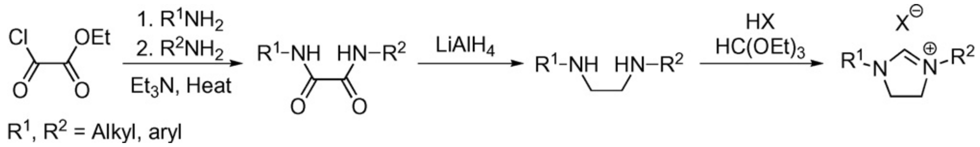
Scheme 62. Synthesis of imidazole-2-thiones by condensation.



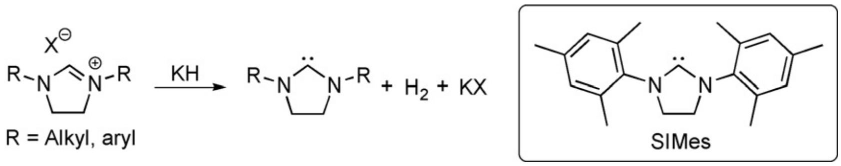
Scheme 63. Synthesis of imidazole-2-thiones in two steps.



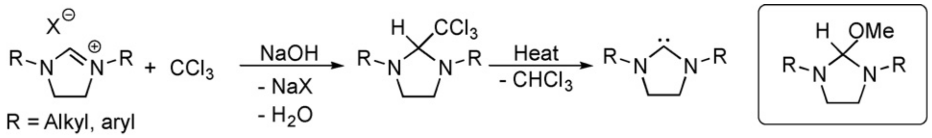
Scheme 66. Synthesis of imidazolinium salts.



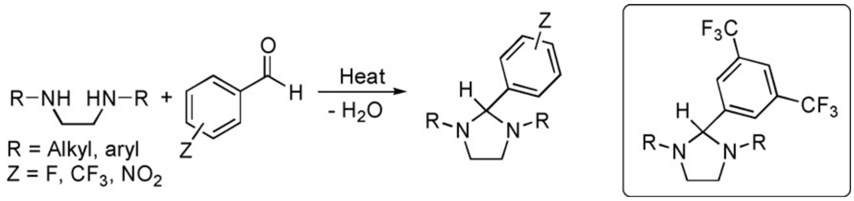
Scheme 67. Synthesis of unsymmetrical imidazolinium salts.



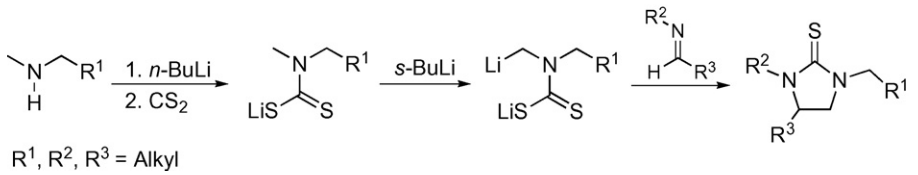
Scheme 68. Imidazolidinylidenes formation via deprotonation.



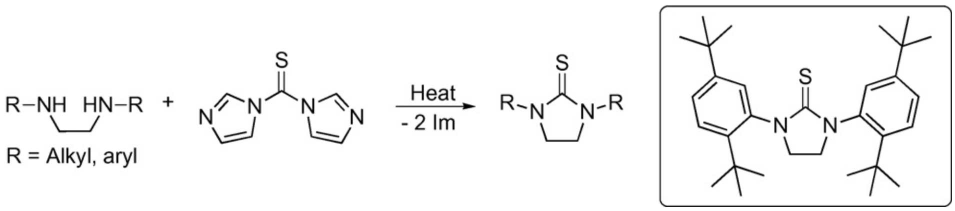
Scheme 69. Synthesis of imidazolidine adducts under basic conditions and their thermolysis to imidazolidinylidenes.



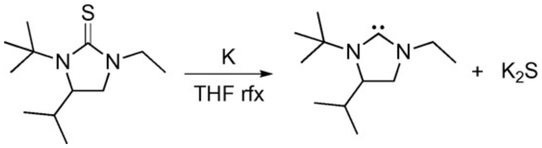
Scheme 70. Synthesis of imidazolidine adducts by condensation of diamine.



Scheme 71. Synthesis of imidazolidine-2-thiones by condensation of aldimines.



Scheme 72. Synthesis of imidazolidine-2-thiones by condensation of diamines.



Scheme 73. Imidazolidinylidenes formation by reduction with potassium.

imidazolinium salt with a diboron backbone could be deprotonated without decomposition, leading to the first stable NHC with a diboron backbone [206].

4.2.4. Imidazolidine-adducts and imidazolidinylidenes

Imidazolinium halides can be converted to 2-methoxyimidazolidine [207], 2-*tert*-butoxyimidazolidine [207,208] and 2-trichloromethylimidazolidine [209] with methanol, *tert*-butanol, and chloroform under basic conditions. These adducts act as masked carbenes and can be chemically manipulated in air. They generate imidazolidinylidenes by thermolysis without the need for a strong base (Scheme 69) [207–209].

Another possible route for the synthesis of masked NHCs is the condensation–cyclization of ethane-1,2-diamines onto benzaldehydes leading to diaminoketals [210]. In the case of benzyl-, pentafluorophenyl-and *p*-nitrophenyl-2-imidazolidine adducts (Scheme 70), they can be used as surrogates for NHC-containing transition metal complexes [211].

4.2.5. Imidazolidine-2-thiones and imidazolidinylidenes

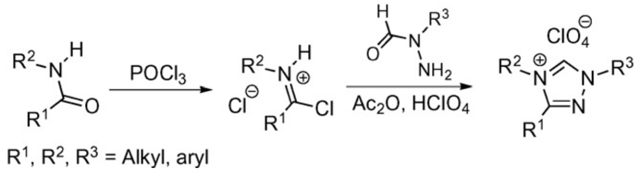
In a one-pot reaction, secondary amines are deprotonated with *n*-butyllithium and treated with carbon disulfide to yield lithium dithiocarbamates. A second lithiation with *sec*-butyllithium yields lithium *N*-lithiomethyldithiocarbamate compounds. Finally, addition of an aldimine yields imidazolidine-2-thiones (Scheme 71) [212]. Even if this route leads to mediocre yields of thiones (around 50%), it remains a rapid synthesis for unsymmetrically *N*,*N*′-substituted imidazolidinylidene precursors.

An alternate route to yield imidazolidine-2-thiones in better yield is the cyclization reaction of ethane-1,2-diamines with thiophosgene or 1,1′-thiocarbonyldiimidazole (Scheme 72) [213].

Imidazolidine-2-thiones are reduced similarly to imidazole-2-thiones with an excess of potassium in boiling THF. The reaction leads to imidazolidinylidenes in high yield (Scheme 73) [197,212].

4.2.6. Triazolium salts and triazolylidenes

1,4-Disubstituted triazolium salts can be synthesized in a three-step procedure described by Boyd [214]. In the presence of formic acid and acetic anhydride, aryl- or alkylhydrazines form bisformylhydrazines. Further condensation with a mixture of acetic anhydride and perchloric acid affords the corresponding oxadiazolium salts. The last step of the synthesis is the ring-opening/ring-closing reaction (RORC-reaction) using a primary amine, in which the oxygen atom is substituted by an amino group (Scheme 74).



Scheme 75. Synthesis of 1,3,4-trisubstituted triazolium salts.

1,3,4-Trisubstituted triazolium salts can be synthesized in a one-pot procedure patented by Teles et al. [215]. *N*-Alkyl-*N*-formylhydrazines, prepared by condensation reaction of alkylhydrazines with methylformate, react with an imidoylchloride, which can be prepared in situ. Then, the cyclization is achieved using acetic anhydride and perchloric acid (Scheme 75).

Triazolium halides or perchlorate salts are converted to 5-methoxytriazolines in methanol under basic conditions. Whereas the deprotonation of triazolium salts result in carbene decomposition, these adducts yield quantitatively triazolylidenes by thermolysis (Scheme 76) [36,188,216].

4.3. Six and seven-membered ring iminium salts and NHCs

Only a few examples of six- and seven-membered ring NHCs have been reported [217,218]. The synthesis of the precursor salts follows the one proposed for imidazolinium salts: propane-1,3-diamines or butane-1,4-diamines are condensed with triethyl orthoformate under acidic conditions. The carbenes are generated by deprotonation with KHMDS or bis(trimethylsilyl)mercury(II) while *tert*-butoxide forms adducts [219].

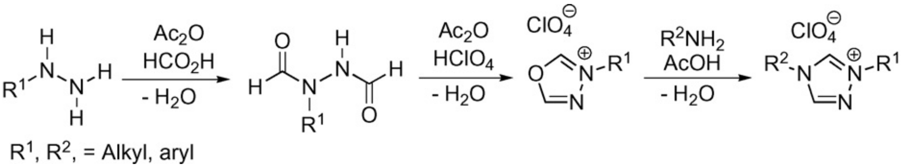
4.4. Four-membered ring iminium salts and NHCs

The only examples of four-membered ring NHCs were reported by Grubbs et al. in 2004 [186]. Two equivalents of primary amine react with triethyl orthoformate under acidic conditions to form *N*,*N*-disubstituted formamidines [220]. They are converted to silylamidines by addition of *n*-butyllithium and trimethylsilyl chloride. They finally form the four-membered ring iminium salts by cyclization in the presence of dialkylaminodichlorophosphine and trimethylsilyl-trifluoromethanesulfonate (TMSOTf) at room temperature (Scheme 77).

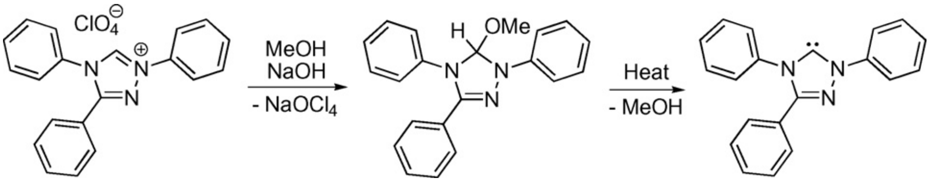
Iminium salts are depronated with mesityllithium or KHMDS to generate the four-membered ring NHCs. When a less hindered or more nucleophilic base is employed, the ring opens by P–N bond cleavage and forms an *N*-phosphino-*N*,*N*′-disubstituted formimidamide rather than a NHC (Scheme 78) [186].

4.5. Stability of NHCs toward dimerization

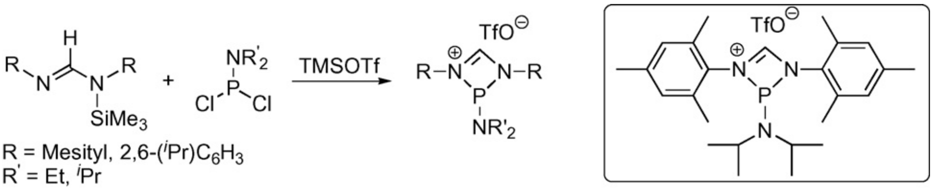
The major limitation to the design of stable diaminocarbenes is their dimerization into enetetramines [201c,221]. This reaction has likely prevented the isolation of the 1,3-diphenylimidazolinylidene by the Wanzlick group more than 40 years ago [72]. The dimerization follows a nonleast motion pathway that involves the attack of the occupied σ lone pair of one carbene center on the vacant p_π



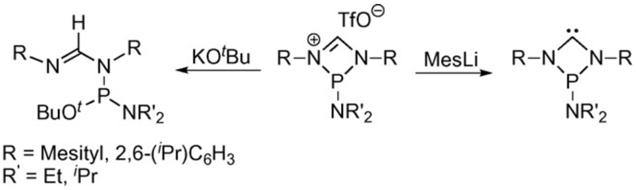
Scheme 74. Synthesis of 1,4-disubstituted triazolium salts.



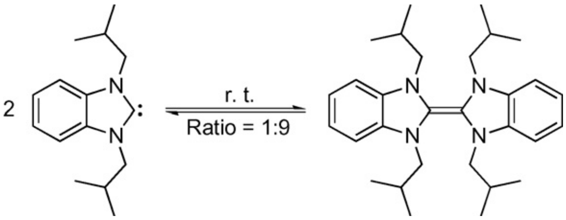
Scheme 76. Triazolylidenes formation by thermolysis.



Scheme 77. Synthesis of four-membered ring iminium salts.



Scheme 78. Synthesis of four-membered ring NHCs.



Scheme 80. Equilibrium between a NHC and its dimer.

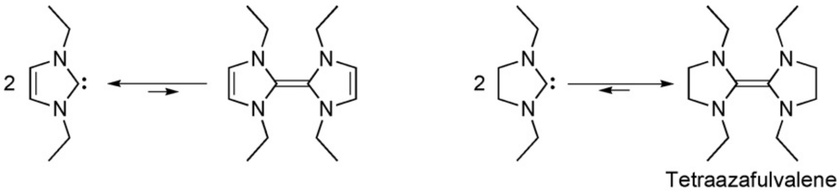
orbital of a second carbene [222]. Whereas imidazolidinylidenes require sterically demanding ligands to prevent their dimerization to tetraazafulvalenes [223], imidazolylidenes exhibit a thermodynamically unfavorable dimerization even for small ligands such as methyl groups (Scheme 79) [223,224].

The strength of the C=C bond in enetetramines can be approximated by the strength of the (sp^2–sp^2)σ and the (p–p)π bonds in ethylene (172 kcal mol^{-1}) [225], minus the sum of the singlet–triplet energy gap for both dissociated carbenes [226]. The energy gap between singlet and triplet state is higher for imidazolidinylidenes (85 kcal mol^{-1}) than for imidazolinylidenes (70 kcal mol^{-1}) due to an extra-stabilization provided by the partial aromatic character of the imidazole ring [221,227]. Consequently imidazolylidenes do not form enetetramines easily as the C=C bond would be very weak or even energetically disfavored. In contrast, imidazolidinylidenes readily form enetetramines, which are difficult to dissociate. The dimerization reaction has to be kinetically hampered by steric protection. For symmetrically *N*,*N′*-substituted imidazolinylidenes, the demarcation line separating stable from unstable carbenes is established as ^{t}Bu vs. ^{i}Pr for alkyl and Mes vs. Ph for aryl [223].

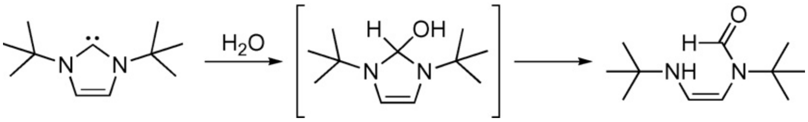
4.6. Wanzlick equilibrium

Wanzlick believed that imidazolidinylidenes could be generated from tetraazafulvalenes. He assumed that both species were present together through an equilibrium reaction. Nevertheless, Winberg et al. showed that metathesis reaction between acyclic and cyclic enetetramines did not lead to cross-metathesis products [84], while Lemal et al. showed that cross-metathesis could only proceed in presence of electrophiles [40a]. Finally, Wanzlick's postulate was rejected in the mid-1960s. In 1999, Denk et al. reinvestigated the cross-metathesis reaction between two enetetramines and uncovered some cross-metathesis products formed at high temperature (150 °C) without the presence of any electrophiles [228]. They supported a Wanzlick equilibrium, but could not prove it, as the cross-metathesis products could have been formed by a [2 + 2] cycloaddition/[2 + 2] cycloreversion of the enetetramines, favored at high temperatures. One year later, Hahn et al. demonstrated the existence of the Wanzlick equilibrium by evidencing the formation of some benzimidazolylidene by partial dissociation of the corresponding dimer dibenzotetraazafulvalene, at room temperature without the use of any electrophile (Scheme 80) [229]. It is important to note that if benzannulated NHCs possess the topology of imidazolylidenes, they are prompt to dimerize and exhibit mainly the reactivity of imidazolidinylidenes [212,230].

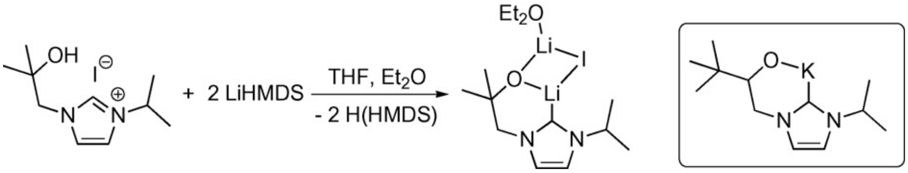
Finally, the rate of dimerization for some unsymmetrically substituted imidazolidinylidenes has been reduced, making possible the observation of the carbene and its dimers over weeks by adjusting the steric constraint of *N*-alkyl groups [212].



Scheme 79. Dimerization of NHCs.



Scheme 81. Hydrolysis of NHCs.



Scheme 82. NHC alkali metals complexes.

4.7. *General reactivity of NHCs*

Imidazolylidenes and sterically stabilized imidazolidinylidenes are thermodynamically stable. They do not react with triplet dioxygen for kinetic reasons, even if the formation of ketones appears to be very exothermic [231,232]. They are inert toward carbon monoxide (no formation of ketenes) and oxidating agents such as CuO and HgO. They react slowly with dihydrogen to form aminals by 1,1-addition in the presence of a catalytic amount of palladium or platinum [232]. On the other hand, they are extremely sensitive to moisture and have to be handled under dry atmosphere [233]. They hydrolyze through the insertion of the carbene into H_2O, or by nucleophilic attack of OH^-. Both pathways lead to a formamide by ring opening of a cyclic α-diaminomethanol intermediate (Scheme 81) [232].

NHCs react with acids and form iminium salts quantitatively due to their high pK_a values, ranging from 20 to 30 (in water) [234]. They are among the most powerful neutral organic bases and their strength is comparable to DBU and pentacyclic vinamidines [235].

4.8. *Organometallic chemistry of NHCs*

4.8.1. *Bonding to metal and π-back donation*

The distance between the carbenic carbon and the metal in organometallic complexes gives an insight on the ability of the carbene to accept any transfer of electron density from the metal (π-back donation) [71]. A short distance accounts for a partially metal–carbon double bond due to a π-back donation. Studies of different types of carbenes show that the π-accepting ability decreases from Schrock- to Fischer-type (non-diaminocarbenes) to NHCs [236]. It is well accepted that NHCs bind strongly to metals by σ-bonding while the π-back bonding can be considered negligible [237]. Nevertheless, the bonding between a metal center and a NHC always presents a π-back bonding component which, while marginal in most cases, becomes significant for Group 11 metals, copper, silver and gold [238]. Furthermore, it has been shown that π-back donation is favored in saturated imidazolidinylidenes when compared to unsaturated imidazolylidenes [239]. It is important to add that the 6π-delocalization in NHCs, such as imidazolylidenes, only provides a marginal effect in the bonding nature of NHCs [236].

4.8.2. *Bonding properties, comparison with phosphines*

In metal complexes, NHCs share with phosphines the characteristics of being monodendate two-electron donor ligands [240]. Carbonyl–metal complexes bearing a CO group placed in *trans* position to an NHC or a phosphine ligand are of special interest in infrared spectroscopy. The vibrational frequency of C–O stretching is known to be proportional to the π-back donating ability of the NHC or phosphine ligand. In a totally symmetric vibrational mode, more basic ligands (σ-donors) induce lower vibrational frequencies. Studies of different complexes of nickel(0) have shown that NHCs appear to be more electron-donating than most basic phosphines [241]. They bind more firmly the metal center than phosphines ligands. Finally, contrary to the phosphines, NHCs bind with alkaline, lanthanides and high oxidation state metals in which π-back donation is not possible [242].

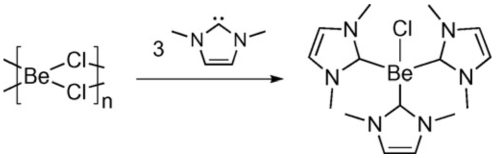
4.8.3. *Reaction between metals and isolated NHCs*

4.8.3.1. Alkali metals (Group 1). In THF, the 4,5-dimethyl-1,3-diisopropylimidazolium salt is deprotonated with lithium, sodium, or potassium hexamethyldisilazide to form the corresponding carbene alkali metal adducts [217a]. The bonding with the metal induces a slight shift upfield for the ^{13}C NMR signals of the carbenic carbon and can be suppressed by trapping the alkali metals with crown ethers. Interactions between the metals and imidazolylidenes appear to be purely electrostatic, but are sufficient to enhance the stability of the carbene in air [217a]. Recently, the synthesis of a bidentate alkoxy-*N*-imidazolylidene has allowed for the isolation of lithium and potassium NHC adducts with good thermal stability (Scheme 82) [243].

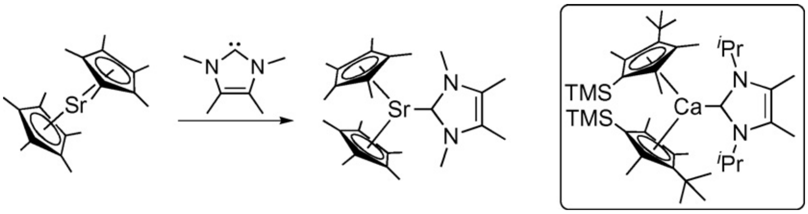
4.8.3.2. Alkaline earth metals (Group 2). Beryllium(II) chloride, one of the strongest Lewis acids known, reacts with three equivalents of a sterically unencumbered NHC to form the corresponding adduct (Scheme 83) [244].

Metallocenes of magnesium, calcium, strontium, and barium react with one equivalent of NHC to form the corresponding adducts [245]. The metal–carbon bond has a pronounced covalent character for magnesium, and becomes more ionic for the heavier alkaline earth metals. Using an excess of carbene with calcium, strontium, and barium leads to the bis-NHC adduct in which the second NHC is weakly bound to the metal (Scheme 84) [237a,245].

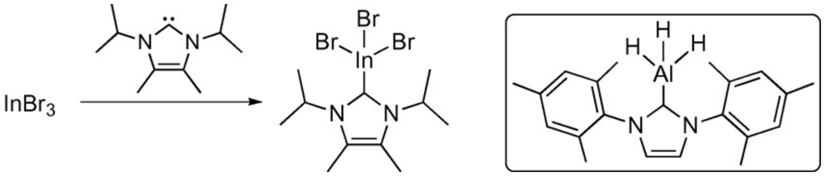
4.8.3.3. Group 13 complexes. Aluminum(III) and gallium(III) trihalides react with one equivalent of NHC to form a four-coordinate adduct [246]. Indium(III) and thallium(III) trihalides react with



Scheme 83. NHC–beryllium complex.



Scheme 84. NHC alkaline earth metal complexes.



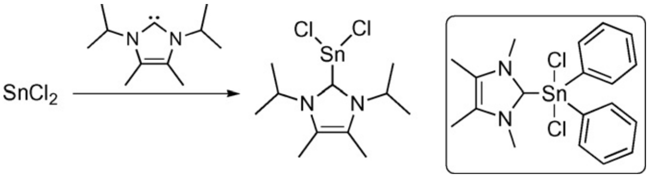
Scheme 85. NHC–Group 13 metal complexes.

one or two equivalents of NHC to form respectively a four-coordinate adduct or a five-coordinate (hyper valent) bis-NHC adduct (Scheme 85) [247]. The electronic structure of the imidazole fragment is an intermediate between those of the free carbene and imidazolium ion [36,248].

Alanes, galanes, and indanes are well stabilized by bulky NHCs. The formed adducts are thermally stable in contrast with the phosphine-containing ones [249]. The only known complex of thallium(I) exhibits a metal center coordinated with three NHCs from the same pincer ligand [250].

4.8.3.4. Groups 14, 15, and 16 complexes. The carbene chemistry of these metals appears to be extremely underdeveloped. Complexes of tin and tellurium [251] have been described only in few reports while there is no reference available for lead and bismuth. Tin(II) dichloride leads to a tetravalent bis-NHC adduct with sterically unencumbered carbenes and to a trivalent mono-NHC adduct with bulkier carbenes (Scheme 86) [237a,252]. The C–Sn bond is strongly polarized and fragile. Although the complexes are stable in the solid state, they decompose slowly in solution and rapidly in gas phase. They do not belong to the stannene family because there is no π-back-donation from tin to the carbene [253]. A mono-NHC adduct of pentavalent tin(IV) has been synthesized by reaction of diphenyltin(IV) dichloride and tetramethylimidazolylidene (Scheme 86) [237a].

4.8.3.5. Rare earths: lanthanides and Group 3 transition metals. Metallocenes or tris(silylamido) complexes of yttrium, scandium, lanthanum, and of the lanthanides series bearing at least one tetrahydrofuran ligand form NHC-adducts by substitution of the tetrahydrofuran [36,254]. Following this method, complexes bearing one, two, or three carbene ligands have been characterized. The metal–carbene bond is primarily electrostatic and longer than in σ-bonded alkyl lanthanide complexes [255]. The ^{13}C NMR spectra of yttrium(III)–NHCs display a characteristic resonance for the carbene around 195 ppm [237a,256], with a well defined coupling constant $\{^1J(^{13}C\text{-}^{89}Y)\}$ suggesting that the NHC does not dissociate from the rare earth metals, on the NMR time scale (Scheme 87).



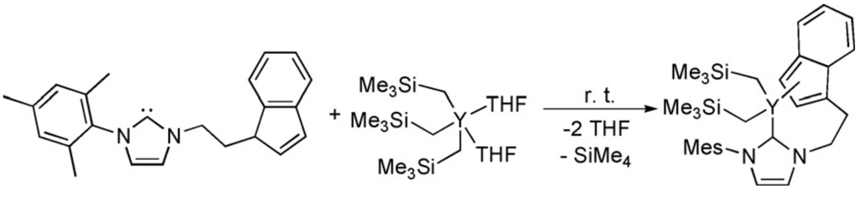
Scheme 86. NHC–tin complexes.

4.8.3.6. Actinides. In 2001, Costa et al. synthesized the first actinide NHC complexes by reacting two equivalents of 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene (IMes) with uranyldichloride [257]. Although a thorium(IV) methylidene complex has been recently synthesized [258], there is no example of NHC–thorium complex. Overall, examples of actinide complexes remain extremely scarce and are restrained to uranium(III) and (VI) [254]. The bonding between the carbene and uranium exhibits some highly unusual properties. The NHC ligands are among the weakest σ-donor for uranyl complexes in contrast to their strong donor character in transition metal complexes [258]. In the meantime, actinyl ions (MO_2^{2+}, M = U, Np, Pu) are hard Lewis acids and the coordination of the uranyl ion with a soft σ-donor NHC is unprecedented [258]. With electron-rich uranium(III), π-back bonding occurs and accounts for the stabilization of the complexes in contrast with transition metals. There is a transfer of electronic density from the uranium f-orbitals to the empty p-orbital of the carbene (Scheme 88) [259].

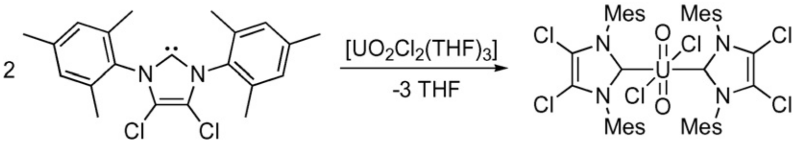
Spent nuclear fuel contains some lanthanides formed from the nuclear fission of actinides [260]. Recent work has shown the stronger affinity of NHCs for 5f ions than for 4f ions [261], which makes them good candidates for potential applications regarding the partitioning/recycling of nuclear waste.

4.8.3.7. Transition metals: Groups 4–12.

4.8.3.7.1. Overview. There is an amazing diversity of transition metal–NHC complexes with a great variety of ligands and oxidation states. All metals from Groups 4 through 12 have been covered, including the radioactive technetium [262]. The motivation for such a large volume of work is the stability/availability of the NHC ligands and the outstanding performances of their metal complexes in catalysis. This paragraph is intended to provide only an overview on the synthesis of metal-transition NHC complexes whereas two detailed reviews on the topic have been written by Herrmann and Bertrand [36,237a,263]. NHCs react with a broad range of organometallic precursors by direct addition or by replacement of two-electron donor ligands. Nitriles, phosphines, tetrahydrofuran, carbonyl (CO), tetrahydrothiophene (THT), pyridines, and dimethylsulfide (DMS) are among the most common ligands displaced by NHCs. Dinuclear precursors featuring halo or aceto bridges are also



Scheme 87. NHC–lanthanide complexes.



Scheme 88. NHC–actinide complexes.

split by the NHCs to form the corresponding monomeric complexes. Depending upon the metal and the stoichiometry of reagent employed, complexes bearing up to three carbene ligands are commonly synthesized (Scheme 89) [264].

4.8.3.7.2. High oxidation state early transition metals. In 2002, Abernethy et al. have reported the synthesis of stable tetrachloro titanium(IV) and trichloro-oxo-vanadium(V) NHC complexes [265]. These complexes demonstrate that both alkylidenes (Schrock-type carbene) and NHCs (Fischer-type carbene) can stabilize transition metals at their highest oxidation state. These complexes exhibit an unsual back bonding from the lone electron pairs of the *cis*-chloride ligand to the empty p-orbital of the carbene. Indeed, the metal centers are strong Lewis acids and the σ-bond between the carbene and the metal is more polarized. This results in a partial positive charge on the carbene carbon, which is stabilized by bonding interactions with the chloride lone pairs (Scheme 90) [265].

4.9. Reaction of masked carbenes

4.9.1. Trialkylborane-2-imidazole

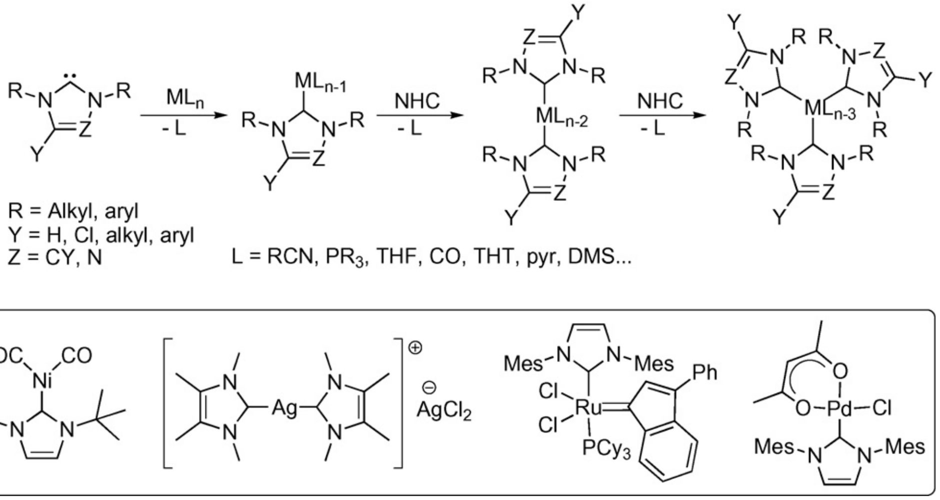
Imidazolium salts are deprotonated by lithium trialkylborohydride and form trialkylborane-2-imidazoles in good yield [266]. These NHC–boron complexes are thermally and air stable as expected for an NHC-Group 13 Lewis acid–base adducts [249,267]. In boiling toluene, they react with hexacarbonylmolybdenum(0) and form the corresponding NHC–molybdenum(0) complex without the need for any base [267]. It is not clear yet if the reaction proceeds by the generation of a free NHC from the boron adduct or if a concerted mechanism should be considered (Scheme 91).

4.9.2. Carboxylate-2-imidazole

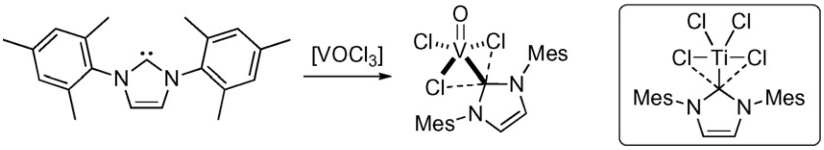
Imidazolium salts react with carbon dioxide or alkyl chloroformates under basic conditions to yield 2-carboxylate or 2-esterimidazoles [268]. They are air stable and can transfer NHCs to a variety of metal salts without the need for any base. At 80 °C, they lead to rhodium, iridium, and palladium complexes in high yield in less than 1 h. The mechanism likely proceeds through metal coordination of the carboxylate via oxygen, followed by β-elimination (Scheme 92) [268b].

4.9.3. Oxidative addition of imidazolium and 2-haloimidazolium salts

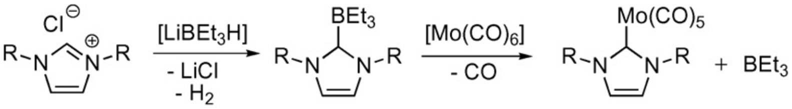
Zerovalent Group 10 metals, especially platinum and nickel complexes, are prompt to react with imidazolium and 2-haloimidazolium salts to form NHC-complexes by oxidative addition [269]. The activation energy barrier of the reaction is very low for bromo- and iodoimidazolium salts. The reaction is also favored with metal(0) complexes bearing bis-chelating ligands



Scheme 89. NHC transition metal complexes.

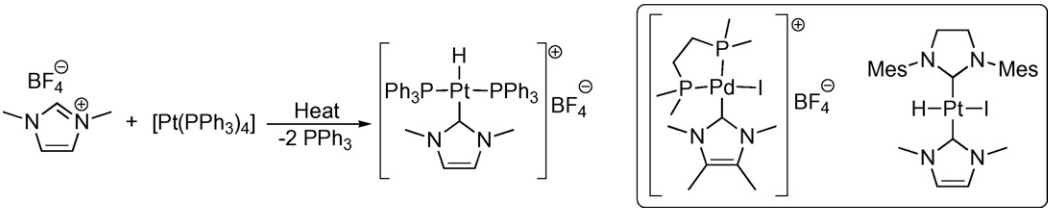


Scheme 90. Synthesis of a NHC–vanadium(V) complex.

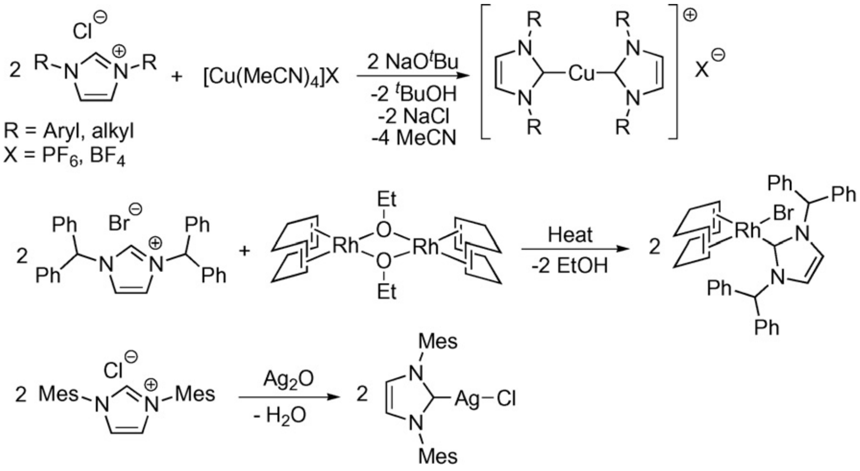


Scheme 91. Formation of NHC-complex via trialkylborane-2-imidazole precursors.

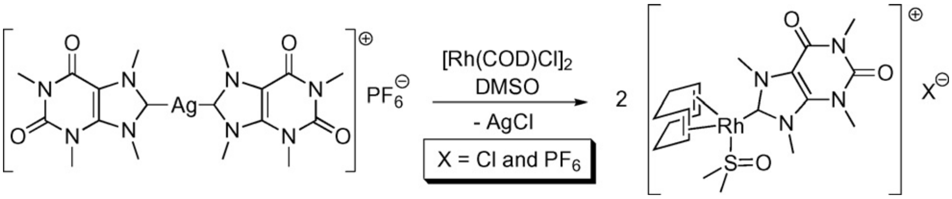
Scheme 92. Formation of NHC-complex via carboxylate-2-imidazole precursors.



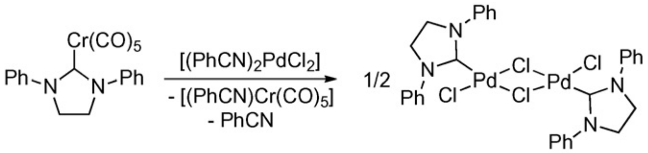
Scheme 93. Formation of NHC-complex via oxidative addition.



Scheme 94. In situ deprotonation of imidazolium salts and formation of NHC–metal complexes.



Scheme 95. Synthesis of a caffeine rhodium(I) complex by transmetalation.



Scheme 96. Synthesis of a palladium(II) complex by transmetalation.

and/or basic ligands, such as phosphines [269a]. The oxidative addition of imidazolium salts is an interesting approach to generate metal hydride NHC complexes (Scheme 93) [270]. Recently, Peris et al. have extended the reaction to the Group 9 metals with the synthesis of an iridium(III) hydride complex by oxidative addition of an imidazolium salt to the chloro(1,5-cyclooctadiene)iridium(I) dimer [271].

Finally, it is important to note that metal-mediated catalysis in ionic liquids is very likely to proceed via the formation of metal–NHC complexes by oxidative addition [269].

4.9.4. *In situ deprotonation of imidazolium salts*

NHC complexes can be obtained by in situ deprotonation of the corresponding imidazolium salts in the presence of metal precursors under basic conditions. A base, such as triethylamine, *tert*-butoxide or a carbonate can be added directly to the reaction media [36,272] or the depronation can arise from an organometallic fragment bearing basic ligands, such as alkoxides, hydride, or acetate [273]. Simple metal oxides, such as silver(I) oxide, can also act as the base and the metal source (Scheme 94) [191,274].

4.9.5. *Transfer of NHC by transmetalation*

4.9.5.1. NHC–silver(I) halide complexes. The air stability and the straightforward synthesis of NHC–silver(I) halide complexes render them attractive for transmetalation reactions [274,275]. In the presence of an organometallic fragment bearing a metal more electronegative than silver, the carbon–silver bond is broken and the carbene transferred while the reaction is thermodynamically favored by the precipitation of solid silver(I) halide. Complexes of ruthenium(IV), rhodium(I), iridium(I), palladium(II), platinum(II) and gold(I) have been synthesized in excellent yields following this procedure (Scheme 95) [274,275]. Recently Abernathy et al. have attempted to transfer some NHCs from silver(I) complexes to titanium(IV) and zirconium(IV) salts. The reaction failed and led to the formation of a bis-NHC–silver(I) complex by abstraction of a chloride ion from the silver by the early transition metal center [276].

4.9.5.2. Group 6 metal(0) complexes. Group 6 metal Fischer-type carbene complexes, including NHCs, are efficient transmetalating agents (Scheme 33) [277]. Rhodium(I), palladium(II), copper(I), silver(I) and gold(I) NHC complexes have been synthesized in good yield from the corresponding pentacarbonyl chromium(0), molybdenum(0) and tungsten(0) NHC precursors [277a]. Nevertheless, these complexes are air sensitive and consequently less employed than silver(I) complexes (Scheme 96).

4.9.5.3. Unusual transmetalating agents. Finally, it should be noticed that three separate recent works describe the synthesis of cerium(III), rhodium(III) and gold(I) complexes from respectively a NHC–lithium(I) adduct, a pincer NHC–zirconium(IV), and a NHC–manganese(0) complex [255,278].

5. Conclusion

This review gathers and recapitulates the synthesis and the properties of carbenes and is dedicated to all the chemists who have contributed to the development of carbene chemistry. These highly active species have slowly emerged from laboratory curiosities to powerful tools in organic, organometallic and material chemistry. They can be reagents, reaction intermediates, or ligands for metal complexes. As the chemistry of carbenes is becoming more explored and understood, it is worth to mention the latest striking advances in carbene chemistry such as the isolation of triplet carbenes stable in solution at room temperature [32]; the detection of a transient singlet palladadiphosphanylcarbene palladium complex with an inverse electronic configuration compared to Fischer-type carbene complexes [279]; or even the synthesis of singlet and triplet transient dicarbomethoxycarbenes from the same precursor, a S,C-sulfonium ylide [280].

NHCs have a very special place in the carbene family thanks to their stability and their straightforward synthesis. They bind metals with various oxidation states, including those normally reserved for alkylidene complexes. They generate organometallic complexes that often show enhanced stability and unique properties in the field of catalysis. In this regard, NHC complexes are outstanding catalysts for a broad array of organic transformations including cross-coupling reactions, metathesis, hydrogenations, polymerizations, hydrosilylations, etc. to cite only a few. Recently, the similarity in term of available orbitals between transition metals fragments and aminocarbenes, including NHCs, has been emphasized and small molecules such as dihydrogen, ammonia and elemental phosphorus have been activated by aminocarbenes [281].

Finally, the interest given to carbenes has been beneficial for other divalent carbon species such as carbodiphosphoranes [282]. These ligands exhibit a carbon(0) center with two lone pairs of electrons non-engaged chemically and even form unsual compounds such as carbon suboxide (C_3O_2) or the dication $[(Ph_3P)_2CH_2]^{2+}$ [283].

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