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Electronic Structure and Reactivity of Metal Carbenes

Thomas Strassner (✉)

Institut für Physikalische Organische Chemie, Technische Universität Dresden,
Mommsenstr. 13, 01062 Dresden, Germany
thomas.strassner@chemie.tu-dresden.de

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Abstract Metal carbenes have for a long time been classified as Fischer or Schrock carbenes depending on the oxidation state of the metal. Since the introduction of *N*-heterocyclic carbene complexes this classification needs to be extended because of the very different electronic character of these ligands. The electronic structure of these different kinds of carbene complexes is analysed and compared to analogous silylenes and germylenes. The relationship between the electronic structure and the reactivity towards different substrates is discussed.

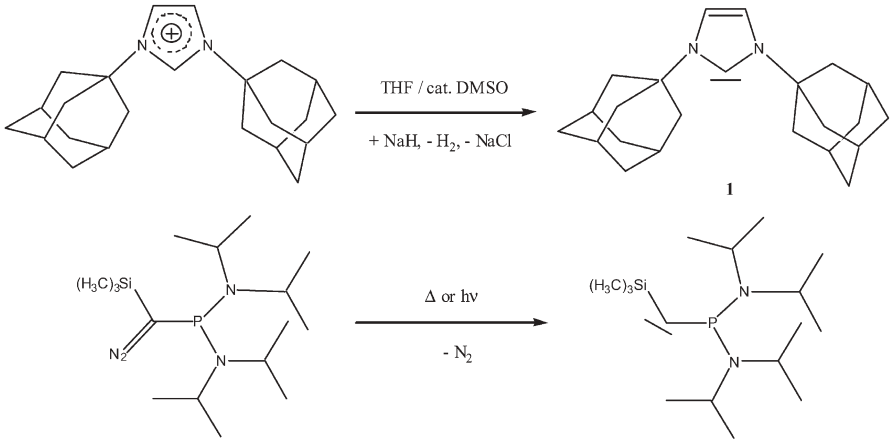
Keywords Reactivity · Theory · Density functional theory (DFT) calculations · Carbenes

Abbreviations

BDE	Bond dissociation energy
CDA	Charge decomposition analysis
Cp	Cyclopentadienyl
Cy	Cyclohexyl
DFT	Density functional theory
EDA	Energy decomposition analysis
Hal	Halogen
HF	Hartree–Fock
Me	Methyl
Ph	Phenyl
PPh_3	Triphenylphosphine
post-HF	post-Hartree–Fock
TM	Transition metal

1 Introduction

Carbenes – molecules with a neutral dicoordinate carbon atom – play an important role in all fields of chemistry today. They were introduced to organic chemists by Doering and Hoffmann in the 1950s [1] and to organometallic chemists by Fischer and Maasböl about 10 years later [2, 3]. But it took another 25 years until the first carbenes could be isolated [4–8]; examples are given in Scheme 1.

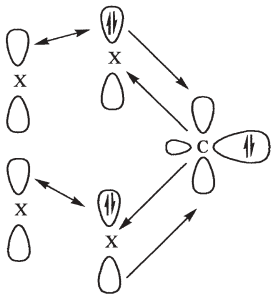


Scheme 1 Examples of isolated carbenes

The surprising stability of *N*-heterocyclic carbenes was of interest to organometallic chemists who started to explore the metal complexes of these new ligands. The first examples of this class had been synthesized as early as 1968 by Wanzlick [9] and Öfele [10], only 4 years after the first Fischer-type carbene complex was synthesized [2, 3] and 6 years before the first report of a Schrock-type carbene complex [11]. Once the *N*-heterocyclic ligands are attached to a metal they show a completely different reaction pattern compared to the electrophilic Fischer- and nucleophilic Schrock-type carbene complexes.

Wanzlick showed that the stability of carbenes is increased by a special substitution pattern of the disubstituted carbon atom [12–16]. Substituents in the vicinal position, which provide π-donor/σ-acceptor character (Scheme 2, X), stabilize the lone pair by filling the p-orbital of the carbene carbon. The negative inductive effect reduces the electrophilicity and therefore also the reactivity of the singlet carbene.

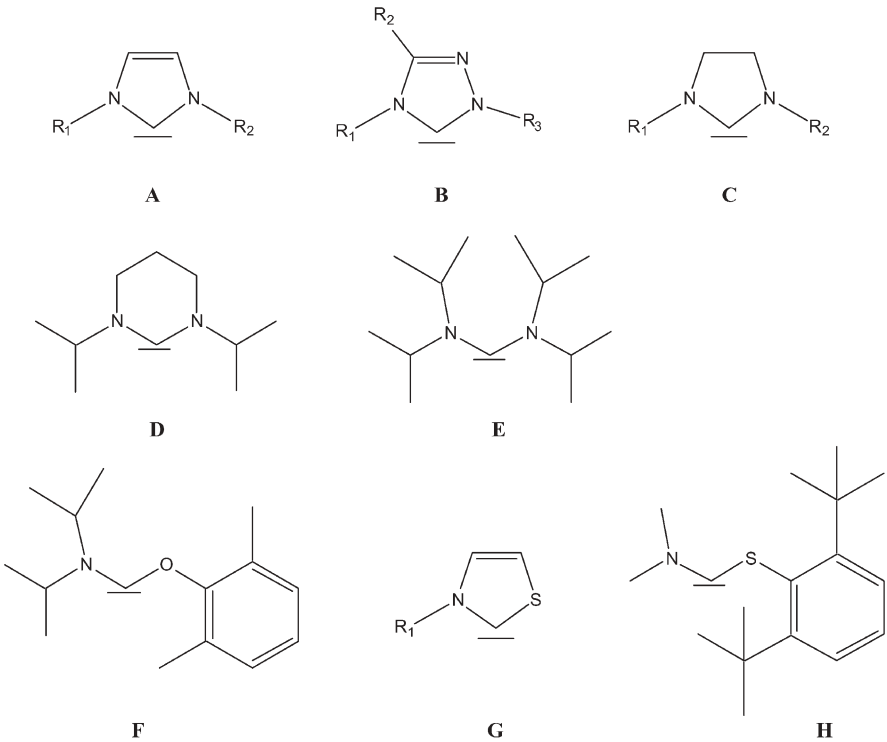
Based on these assumptions many different heteroatom-substituted carbenes have been synthesized. They are not limited to unsaturated cyclic diaminocarbenes (imidazolin-2-ylidenes; Scheme 3, A) [17–22] with steric bulk to avoid dimerization like **1**; 1,2,4-triazolin-5-ylidenes (Scheme 3, B), saturated



Scheme 2 Stabilization by vicinal substituents with π-donor/σ-acceptor character

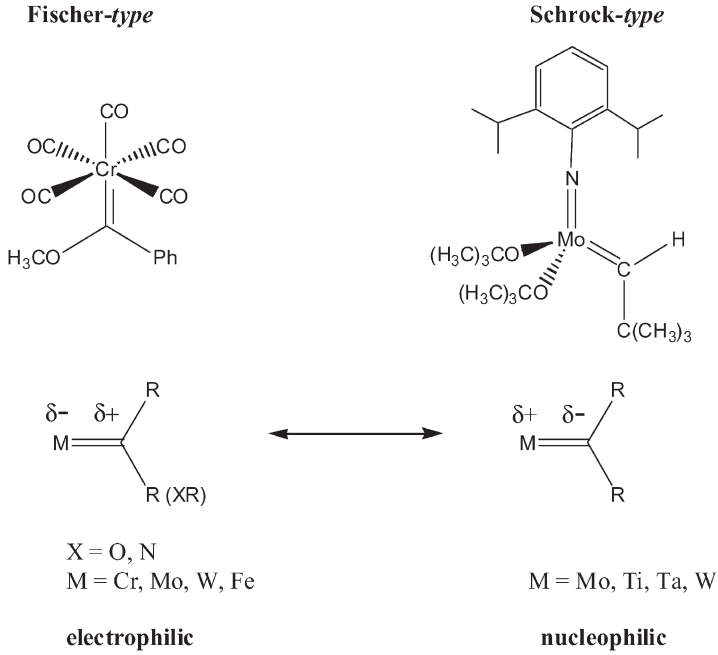
imidazolidin-2-ylidenes [6, 7, 23] (Scheme 3, C), tetrahydropyrimid-2-ylidenes [24, 25] (Scheme 3, D), acyclic structures [26, 27] (Scheme 3, E), or systems where one nitrogen was replaced by an oxygen (Scheme 3, F) or sulphur atom (Scheme 3, G and H) have also been synthesized [28]. Several synthetic routes from different precursors can be found in the literature [29–31].

During the last decade *N*-heterocyclic carbene complexes of transition metals have been developed for catalytic applications for many different or-



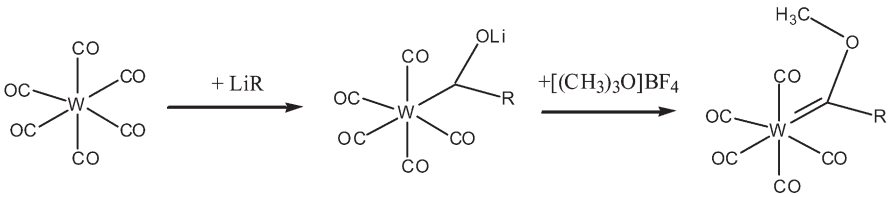
Scheme 3 Different classes of synthesized (*N*-heterocyclic) carbenes

ganic transformations. The most prominent examples are probably the olefin metathesis reaction by the Herrmann/Grubbs catalyst or the methane functionalization, which are described later in more detail.



Scheme 4 Schrock-type and Fischer-type carbene complexes

Fischer-type carbene complexes (Scheme 4) are electrophilic heteroatom-stabilized carbenes coordinated to metals in low oxidation states. They can be prepared from $M(CO)_6$ (M=Cr, Mo, W) by reaction of an organolithium compound with one of the carbonyl ligands to form an anionic lithium acyl "ate" complex. This is possible because of the anion-stabilizing and delocalizing effect of the remaining five π-accepting electron-withdrawing CO ligands. The first synthesis of a Fischer-type carbene complex is shown in Scheme 5.

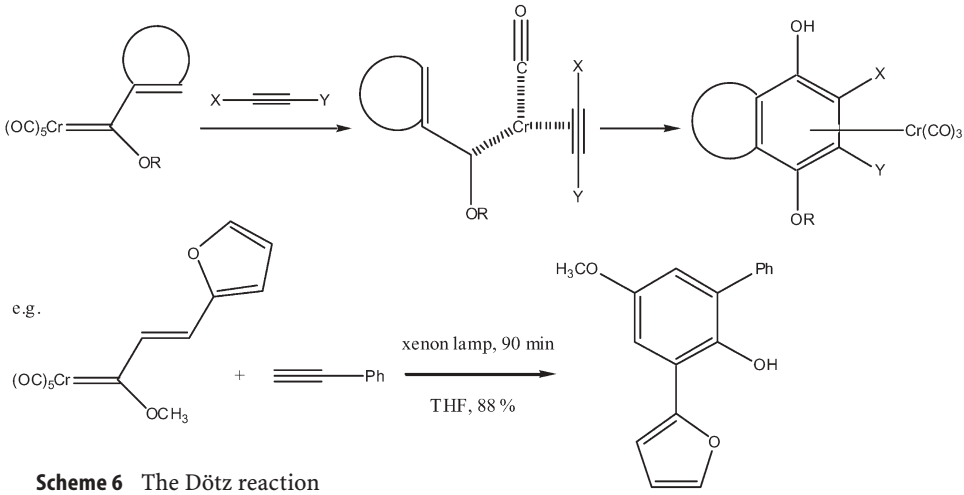


Scheme 5 Synthesis of the first Fischer-type carbene complex

The reactivity of these carbene complexes can be understood as an electron-deficient carbene carbon atom due to the electron-attracting CO groups, while

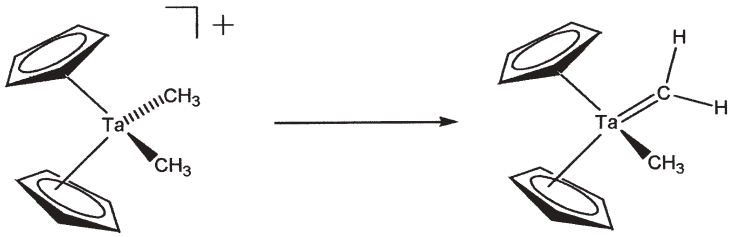
the alkoxy group stabilizes the carbene. They are therefore strongly electrophilic and can easily be attacked by nucleophiles. Derivatives can be synthesized by replacing the alkoxy group by amines via an addition-elimination mechanism [32–34]. Additionally, the hydrogens at the α-carbon are acidic and can be deprotonated with a base. Electrophiles therefore would attack at the α-carbon.

Because of the strongly electron-withdrawing character of the $Cr(CO)_5$ unit, the reaction with alkynes to hydroquinone and phenol derivatives [35–37] (Dötz reaction) is possible according to Scheme 6 (see also Chap. 4 "Chromium-templated Benzannulation Reactions").

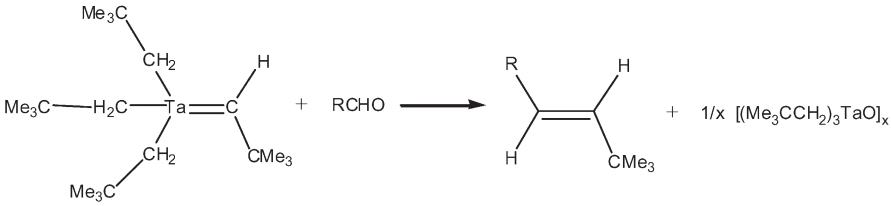


Scheme 6 The Dötz reaction

Schrock-type carbenes are nucleophilic alkylidene complexes formed by coordination of strong donor ligands such as alkyl or cyclopentadienyl with no π-acceptor ligand to metals in high oxidation states. The nucleophilic carbene complexes show Wittig's ylide-type reactivity and it has been discussed whether the structures may be considered as ylides. A tantalum Schrock-type carbene complex was synthesized by deprotonation of a metal alkyl group [38] (Scheme 7).



Scheme 7 Synthesis of the first Schrock-type carbene complex



Scheme 8 Typical reaction of alkylidene complexes

These alkylidene complexes are reactive and add electrophiles to the alkylidene carbon atom according to Scheme 8. Wittig-type alkenation of the carbonyl group is possible with Ti carbene compounds, easily prepared in situ by the reaction of CH_2Br_2 with a low-valent titanium species generated by treatment of $TiCl_4$ with Zn, where the presence of a small amount of Pb in Zn was found to be crucial [39, 40]. It is synthetically equivalent to $Cl_2Ti{=}CH_2$. Replacement of the chlorine by cyclopentadienyl ligands leads to the so-called Tebbe reagent [41–44]. It is formed by the reaction of Cp_2TiCl_2 with $AlMe_3$. Due to the high oxophilicity it reacts smoothly with ketones, esters and lactones to form oxometallacycles.

These carbene (or alkylidene) complexes are used for various transformations. Known reactions of these complexes are (a) alkene metathesis, (b) alkene cyclopropanation, (c) carbonyl alkenation, (d) insertion into C–H, N–H and O–H bonds, (e) ylide formation and (f) dimerization. The reactivity of these complexes can be tuned by varying the metal, oxidation state or ligands. Nowadays carbene complexes with cumulated double bonds have also been synthesized and investigated [45–49] as well as carbene cluster compounds, which will not be discussed here [50].

2 Fischer-Type Complexes

Fischer-type carbene complexes, generally characterized by the formula $(CO)_5M{=}C(X)R$ (M=Cr, Mo, W; X=π-donor substitutent, R=alkyl, aryl or unsaturated alkenyl and alkynyl), have been known now for about 40 years. They have been widely used in synthetic reactions [37, 51–58] and show a very good reactivity especially in cycloaddition reactions [59–64]. As described above, Fischer-type carbene complexes are characterized by a formal metal-carbon double bond to a low-valent transition metal which is usually stabilized by π-acceptor substituents such as CO, PPh_3 or Cp. The electronic structure of the metal–carbene bond is of great interest because it determines the reactivity of the complex [65–68]. Several theoretical studies have addressed this problem by means of semiempirical [69–73], Hartree–Fock (HF) [74–79] and post-HF [80–83] calculations and lately also by density functional theory (DFT) calculations [67, 84–94]. Often these studies also compared Fischer-type and

Schrock-type carbenes [67, 74, 75, 93] and the general agreement is that Schrock-type carbenes can be characterized by the interaction of a triplet carbene ligand with a transition metal fragment in the triplet state (Fig. 1B). This leads to a balanced electronic interaction and nearly covalent σ and π bonds. On the other hand, Fischer-type carbene complexes are formed by coordination of a singlet carbene ligand to a transition metal fragment in the singlet state, with significant carbene to metal σ donation and metal to carbene π back-donation (Fig. 1A). Both interactions have been found to be important for the correct description of the bond and the electrophilic character at the carbene carbon atom [86, 88, 93, 94].

The kinetic and thermodynamic properties of Fischer-type carbene complexes have also been addressed by Bernasconi, who relates the strength of the π-donor substituent to the thermodynamic acidity [95–101] and the kinetics and mechanism of hydrolysis and reversible cyclization to differences in the ligand X [96, 102].

A recent study by Frenking [84] investigated in great detail the influence of the carbene substitutents X and R at a pentacarbonyl-chromium Fischer-type complex. The electronic characteristics of these substituents control the reac-

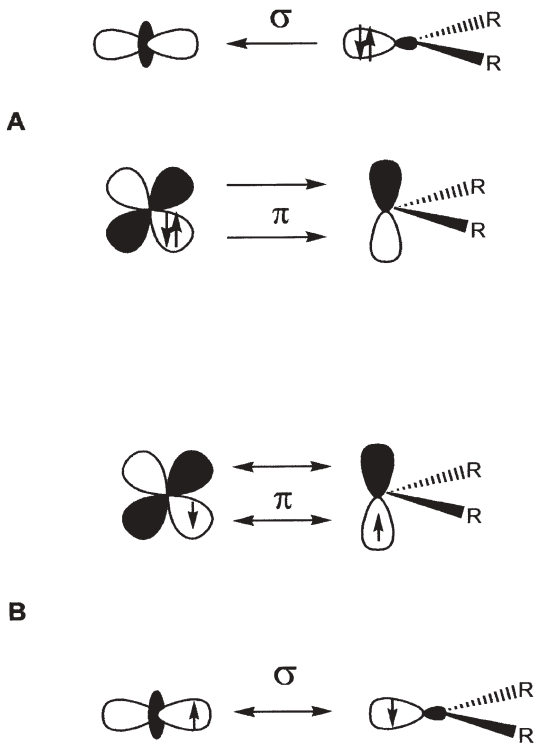


Fig. 1A,B Dominant orbital interactions in Fischer-type carbene complexes (**A**) and Schrock-type carbene complexes (**B**)

tivity of these complexes, which have been shown to be useful in many synthetic applications, most prominently the Dötz benzannulation reaction [36]. As described above (Scheme 6) this reaction, starting from aryl- or alkenyl-substituted alkoxycarbene complexes of chromium affords alkoxyphenol derivatives by insertion of the alkyne and one CO ligand in an α,β-unsaturated carbene and subsequent ring closure. In general, phenols are the main reaction product, which was investigated by a theoretical study and found to be the thermodynamically preferred product [103].

The study by Frenking investigated 25 different chromium carbene complexes, varying the σ- and π-donor strength by systematically combining different ligands X (X=H, OH, OCH_3, NH_2, $NHCH_3$) and R (R=H, CH_3, $CH{=}CH_2$, Ph, C≡CH). To analyse the nature of the metal–carbon bond they conducted an energy [104–108] and charge [109, 110] decomposition analysis.

The BP86 calculations together with a basis set of triple-ζ quality reproduce the geometries of experimentally known structures of that series very well, underestimating the Cr–$C_{carbene}$ bond length by only 0.048 Å with the differences for the Cr–CO and C–O bond lengths even smaller. According to Ziegler and co-workers the BP86 functional is especially well suited for $Cr(CO)_6$ and its accuracy is comparable to that of CCSD(T) calculations [111]. The shortest Cr–$C_{carbene}$ bond lengths for any given substituent R always correspond to the complex where X=H, the weakest π-electron donor. Increasing the π donation, e.g. by changing R=OH to R=NH_2, leads to a significant shortening of the Cr–$C_{carbene}$ bond length by about 0.05 Å.

This can be interpreted in terms of the Dewar–Chatt–Duncanson (DCD) model [112, 113] as a regular behaviour where larger Cr–$C_{carbene}$ bond lengths are supposed to go along with shorter Cr–CO_{trans} and C–O_{trans} bond distances. In line with that expectation the Fischer-type complexes with NH_2 or $NHCH_3$ show the shortest Cr–CO_{trans} bond lengths (1.886–1.897 Å), those with OH or OCH_3 substituents distances of 1.899–1.915 Å and for R=H bond lengths of 1.916–1.937 Å. The calculated bond dissociation energies range from 64.5 to 97.9 kcal/mol and a direct relationship between them and the Cr–$C_{carbene}$ bond lengths is not observed, although in general a larger Cr–$C_{carbene}$ bond length relates to a smaller BDE. The π-electron-donating character does play a major role; for any substituent X the complex with R=H always shows the largest BDE and the larger π donation of the amino group reduces the back-donation to the carbene.

The CDA analysis provides the amount of electronic charge transfer in the carbene→metal donation and metal→carbene back-donation. For most investigated systems of the study [84] the carbene→metal donation is more than two times larger than the metal→carbene back-donation. Correlation of bond lengths with charge donation values is poor, while the back-donation values give a reasonable agreement. The authors explained the greater influence of the back-donation on the structural parameters of the complexes by the fact that the donation values are almost uniform for all complexes analysed, while the charge back-donation differs quite a bit over all complexes. This compares well with a previous CDA study of $M(CO)_5L$ complexes (M=Cr, Mo, W; L=CO, SiO,

CS, N_2, NO^+, CN^-, NC^-, HCCH, CCH_2, CH_2, CF_2, H_2), which showed that the metal→ligand back-donation correlates well with the change of the M–CO_{trans} bond length, while the ligand→metal donation does not [88].

The energy decomposition analysis of the chromium–carbene bond dissociation energy into a deformation (ΔE_{def}) and an interaction (ΔE_{int}) energy term proved that the interaction term is responsible for the differences between the Fischer-type carbene complexes. Pauli repulsion and electrostatic terms basically cancel out and the orbital interaction term exhibits a good correlation with the Cr–$C_{carbene}$ bond lengths. The results from the EDA are in good agreement with the conclusions from the CDA. The electrophilicity results from the difference between donation and back-donation, leading to a charge separation with a partially positive charge on the carbene carbon atom, which was quantified by the electrophilicity index ω [114]. The calculated values show a clear dependence of the electrophilicity from the π-donor substituents. Strong donors reduce the electrophilicity because the acceptor orbital of the carbene becomes occupied by π donation. For a given substituent R, back-donation increases in the order H>OH>OCH_3>NH_2>$NHCH_3$, and it becomes larger with decreasing π-donor character of the group X.

3
Schrock-Type Complexes

A decade after Fischer's synthesis of [$(CO)_5W{=}C(CH_3)(OCH_3)$] the first example of another class of transition metal carbene complexes was introduced by Schrock, which subsequently have been named after him. His synthesis of [$((CH_3)_3CCH_2)_3Ta{=}CHC(CH_3)_3$] [11] was described above and unlike the Fischer-type carbenes it did not have a stabilizing substituent at the carbene ligand, which leads to a completely different behaviour of these complexes compared to the Fischer-type complexes. While the reactions of Fischer-type carbenes can be described as electrophilic, Schrock-type carbene complexes (or transition metal alkylidenes) show nucleophilicity. Also the oxidation state of the metal is generally different, as Schrock-type carbene complexes usually consist of a transition metal in a high oxidation state.

The different chemical behaviour was explained by a different bonding situation in Schrock-type complexes, where more covalent double bond character from the combination of a triplet carbene with a transition metal fragment in a triplet state was attributed. The nature of this bond was the subject of several theoretical studies [77–81, 85, 87, 115–119] using different levels of theory. In a pioneering study, Hall suggested that the difference in the chemical behaviour results from changes in the electronic configuration of the transition metal [80]. In a recent paper [93], Frenking reported accurate ab initio calculations on several low-valent carbene complexes of the type [$(CO)_5WCX_2$] and high-valent alkylidenes of the type [$(Hal)_4WCX_2$], the bonding situation being examined by Bader [120–122], NBO [123] and CDA [109, 110] analyses. They

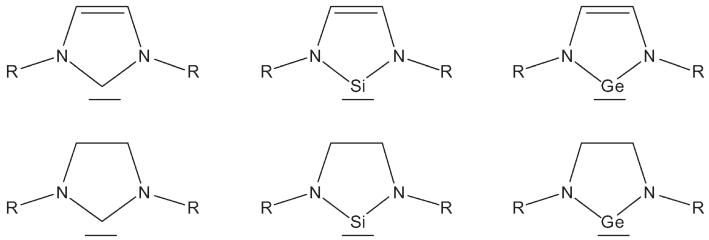
did find that the bonding situation in the neutral low-valent and high-valent complexes is significantly different. The Schrock-type carbene complexes have a much shorter W–$C_{carbene}$ bond than the low-valent complexes, which is in agreement with experimentally known geometries [38]. This can be explained by the smaller radius of the metal atom in a higher oxidation state or a different type of metal–carbene bonding interaction, which was found to be the case in the complexes studied. Topological analysis of the electron density distribution (Bader analysis) clearly shows the differences between Fischer-type and Schrock-type carbene complexes. The Laplacian distributions show that the charge distribution around the carbene carbon atom, i.e. the lone-pair electrons of the carbene, are independent of the metal fragment in both types of complexes, while the Laplacian distribution in the π plane of the carbene ligand shows significant differences. Fischer complexes show an area of charge depletion in the direction of the p(π) orbitals, leading to holes in the electron concentration and therefore possible sites of nucleophilic attack, while the Schrock complexes are shielded by continuous areas of charge concentration. It was found that the Laplacian distribution in Fischer carbenes is similar to the situation in a singlet ($^1A_1$) methylene group, while the Laplacian distribution in Schrock complexes agrees well with a triplet ($^3B_1$) methylene group [93]. Evaluation of the calculated bond critical points of the tungsten–carbene bond shows that in the case of the Schrock complexes, the bond critical point is closer to the charge concentration of the carbene carbon atoms compared to the Fischer-type complexes. The calculated values show that the energy density at the bond critical point of the tungsten–carbene bond has much higher negative values for the Schrock complexes, indicating a larger degree of bond covalency [124]. Another measure of the double bond character is the calculated ellipticities, which demonstrate that the Schrock-type complexes show a much larger double bond character.

This is in agreement with the results of the NBO calculations, where Fischer-type complexes show a tungsten–carbene bond which is polarized towards the metal end, while the Schrock-type complexes show σ and π bonds that are both polarized towards the carbon end. The carbene ligands carry a significant negative partial charge and the population of the p(π) carbene orbital is higher in the Schrock-type complexes. The results of the NBO analysis, which focuses on the orbital structure, are in good agreement with the Bader analysis, which is based on the total electron density. The CDA results clearly show that the Schrock carbene complexes should be interpreted as an interaction between a triplet metal moiety and a ($^3B_1$) triplet carbene.

4
N-Heterocyclic Carbene (NHC) Complexes, Silylenes and Germylenes

The report of the successful isolation of a stable carbene by Arduengo in 1991 [6, 7] (Scheme 1, **1**) and the realization of the extraordinary properties of these

new ligands stimulated the research in this area, and many imidazol-2-ylidenes have been synthesized in the last 10 years [8]. The 1,3-diadamantyl derivative of the imidazol-2-ylidenes is stable at room temperature and the 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene [125] is reported to be even air-stable. A variety of stable carbenes have been synthesized in between (Scheme 3), and it was shown that steric bulk is not a requirement for the stability (the 1,3-dimethylimidazolin-2-ylidene can be distilled without decomposition [126]), although it certainly influences the long-term stability by preventing dimerization. Applying the same principles which made the isolation of these carbenes possible led to the synthesis of the analogous silylenes [127, 128] and germylenes [129] (Scheme 9).



Scheme 9 Saturated and unsaturated carbenes, silylenes and germylenes

Scheme 3 shows clearly that it is absolutely not necessary to have a cyclic delocalization of π electrons in those NHC ligands to be able to isolate stable carbenes, as was believed in the beginning, although this provides additional stability [14, 130, 131]. Generally these ligands are formally neutral, two-electron donors which, contrary to Fischer-type or Schrock-type carbene complexes, are best described as pure σ-donor ligands without significant metal-ligand π back-bonding [132–135]. This might be due to a rather high occupancy of the formally empty p_π orbital of the carbene carbon atom by π delocalization [136].

Early theoretical studies [133, 135, 137–147] investigated the electronic structure of the carbenes, silylenes and germylenes shown in Scheme 9 to elucidate the reasons for the surprising stability, and came to different conclusions concerning the importance of the stabilizing effect of the π delocalization. Early studies predicted that the C–N π interaction does not play a major role [130], while others found that the p_π population at the carbene carbon atom is 30% higher for the unsaturated case, indicating that cyclic delocalization is clearly enhanced in the unsaturated carbene [147] as well as in unsaturated silylenes and germylenes [135, 146]. The electronic structure of silylenes and germylenes is thought to be qualitatively similar to that of carbenes [128, 136]. A photoelectron spectroscopy [148] study on a series of *tert*-butyl-substituted unsaturated compounds, together with an interpretation based on Kohn–Sham orbitals, gave surprising differences concerning the nature of the highest

occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals compared to previous ab initio studies [146, 147]. Analysis of the chemical shielding tensors supported a non-conjugated resonance structure over a π-bonded ylidic resonance structure.

Frenking [133] showed that the higher stability of the imidazolin-2-ylidenes is caused by enhanced p_π–p_π delocalization leading to a significant electronic charge in the formally "empty" p_π orbital of the carbene carbon atom. The unsaturated imidazolin-2-ylidenes as well as the saturated imidazolidin-2-ylidenes are strongly stabilized by electron donation from the nitrogen lone pairs into the formally "empty" p_π orbital. The cyclic 6π-electron delocalization shows some aromatic character according to energetic and magnetic analysis. Silylenes and germylenes are also stabilized by p_π–p_π delocalization. The electronically less stable saturated imidazolidin-2-ylidenes need additional steric protection of the carbene carbon atom to become isolable.

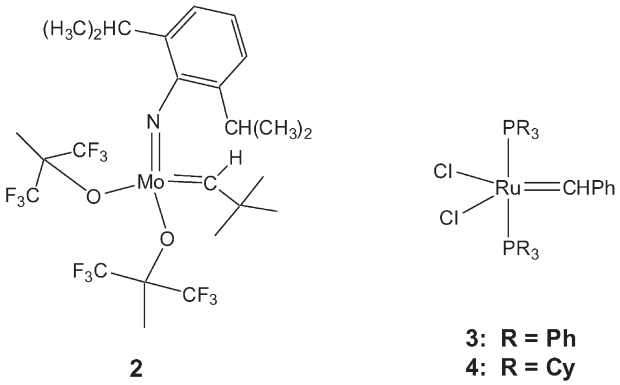
N-heterocyclic carbenes show a pure donor nature. Comparing them to other monodentate ligands such as phosphines and amines on several metal-carbonyl complexes showed the significantly increased donor capacity relative to phosphines, even to trialkylphosphines, while the π-acceptor capability of the NHCs is in the order of those of nitriles and pyridine [29]. This was used to synthesize the metathesis catalysts discussed in the next section. Experimental evidence comes from the fact that it has been shown for several metals that an exchange of phosphines versus NHCs proceeds rapidly and without the need of an excess quantity of the NHC. X-ray structures of the NHC complexes show exceptionally long metal–carbon bonds indicating a different type of bond compared to the Schrock-type carbene double bond. As a result, the reactivity of these NHC complexes is also unique. They are relatively resistant towards an attack by nucleophiles and electrophiles at the divalent carbon atom.

A study [134] of the complexation of MCl (M=Cu, Ag, Au) to carbenes, silylenes and germylenes showed that metal→ligand bond dissociation energies follow the order C>Si>Ge. The strongest bond is predicted for the carbene-AuCl complex, which has a higher BDE than the classical Fischer-type complex $(CO)_5W$–CH(OH). The most important change of the ligand geometries is the shortening of the N–X (X=C, Si, Ge) bond, indicating a stronger π donation. While σ donation is still the dominant term, metal→ligand π back-donation becomes somewhat stronger for silylenes and germylenes, while it is negligible for the carbenes. The weak aromaticity of the *N*-heterocyclic ligands increases only slightly when they become bonded to the different metal chlorides.

A theoretical study of methyl-Pd heterocyclic carbene, silylene and germylene complexes revealed a very low activation barrier for the methyl migration in the silylene and germylene ligands [136]. Unlike the reaction of the carbene ligand, which experimentally occurs via concerted reductive elimination, the reaction in the silylene and germylene case is better described as an alkyl migration to the neutral ligand.

5
Grubbs/Herrmann Metathesis Catalysts

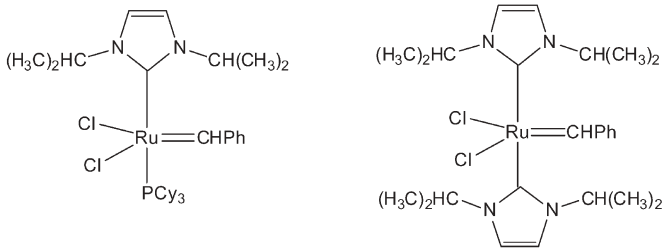
Metal-carbene complexes of the Fischer and Schrock types have been very useful for the transfer of CR_2 moieties (R=H, alkyl, aryl, alkoxy, amino) in cyclopropanation reactions and olefin metathesis. Ring-opening polymerization (ROMP), acyclic diene metathesis (ADMET) and ring-closing metathesis (RCM) are the best-known examples. Together with Schrock's molybdenum-imido complex **2**, the ruthenium-phosphine complexes **3** and **4** (Scheme 10) have been very successful olefin metathesis complexes. Excellent reviews [149] on these topics have been written and one of the chapters of this book, written by B. Schmidt, is devoted to the principles and applications of this reaction towards organic synthesis. Therefore I will only focus on the development of what are nowadays known as the Grubb's catalysts. Ruthenium became the most promising metal mostly because of its tolerance of various functional groups and mild reaction conditions.



Scheme 10 Successful catalysts for olefin metathesis

In particular the exchange of the triphenylphosphine ligands by the more electron donating and sterically more demanding tricyclohexylphosphines was accompanied by a significantly higher stability and reactivity [150–152]. Therefore the development of complex **5** (Fig. 2) was the logical extension of that concept, keeping in mind the demonstrated excellence of NHC ligands over standard phosphane ligands.

The synthesis of these complexes can easily be accomplished by substitution of one or both PCy_3 groups of **3** by NHC ligands. The X-ray structure of **6** shows significantly different bond lengths: the "Schrock double bond" to the CHPh group is 1.821(3) Å, while the "NHC bond" to the 1,3-diisopropylimidazolin-2-ylidene is 2.107(3) Å. Complexes with imidazolidin-2-ylidenes were also synthesized and screened in an extensive study by Fürstner [153], who found that the performance of those catalysts depends strongly on the application and that



5 **6**

Fig. 2 Ruthenium-NHC complexes active in catalytic olefin metathesis

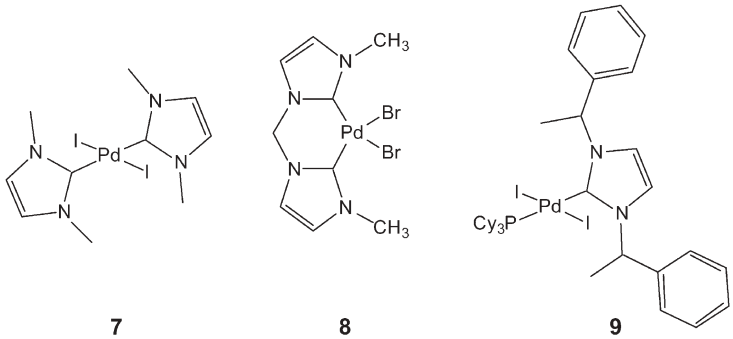
there is not just one single catalyst which outperforms all others. The mixed-ligand olefin metathesis complexes of one phosphane and one NHC ligand were first patented by Herrmann [154] and then communicated at a meeting before appearing in journals in 1999 [155]. Papers on the same topic by Nolan [156] and Grubbs [157] were published later; nevertheless these catalysts are nowadays known as "the Grubbs catalysts".

Mixed phosphane/NHC complexes have been the subject of a DFT study, where theory and experiment agree that the ligand dissociation energy for an NHC ligand is higher than for a phosphane ligand [155]. However, ligand-exchange studies revealed that the π bonding of the olefin might be the decisive factor [158, 159]. But the mechanistic discussion is still going on. Chen et al. conducted electrospray ionization tandem mass spectroscopy investigations [160–163] and concluded that the metallacyclobutane is a transition state rather than an intermediate, while calculations by Bottoni et al. found it to be an intermediate [164]. Additionally several other reaction pathways and intermediates have been proposed [118, 165–170], but there is still the need to collect additional data before a definitive answer on the mechanism of olefin metathesis catalysed by Grubbs/Herrmann catalysts can be given.

6 Platinum and Palladium NHC Complexes

Carbon–carbon bond formation reactions and the CH activation of methane are another example where NHC complexes have been used successfully in catalytic applications. Palladium-catalysed reactions include Heck-type reactions, especially the Mizoroki–Heck reaction itself [171–175], and various cross-coupling reactions [176–182]. They have also been found useful for related reactions like the Sonogashira coupling [183–185] or the Buchwald–Hartwig amination [186–189]. The reactions are similar concerning the first step of the catalytic cycle, the oxidative addition of aryl halides to palladium(0) species. This is facilitated by electron-donating substituents and therefore the development of highly active catalysts has focussed on NHC complexes.

Palladium(II) complexes provide convenient access into this class of catalysts. Some examples of complexes which have been found to be successful catalysts are shown in Scheme 11. They were able to get reasonable turnover numbers in the Heck reaction of aryl bromides and even aryl chlorides [22, 190–195]. Mechanistic studies concentrated on the Heck reaction [195] or separated steps like the oxidative addition and reductive elimination [196–199]. Computational studies by DFT calculations indicated that the mechanism for NHC complexes is most likely the same as that for phosphine ligands [169], but also in this case there is a need for more data before a definitive answer can be given on the mechanism.



Scheme 11 Examples of active palladium-NHC complexes

Bis-chelating NHC complexes like **8** have also been successfully used for the activation and oxidation of methane to methanol in CF_3COOH in the presence of peroxodisulphate [200, 201]. The methanol is deactivated by esterification and therefore protected from further oxidation reactions. The analogous platinum NHC complexes could be synthesized by a new synthetic route and structurally characterized [202]. They have proven to be geometrically very similar to the palladium complexes [203]; the differences in the observed (and calculated) bond lengths and angles are not significant. Unfortunately the bis-chelated platinum NHC complexes are not stable under the reaction conditions used for the palladium complexes and attempts are under way to better stabilize the platinum complexes. Since we first reported the bis-chelated palladium NHC complexes several other reports appeared in the literature [204–207], showing that it is an area of current interest. Several experimental and theoretical projects in our group are currently directed towards the goal of solving the obvious mechanistic questions and we hope to report them soon.

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