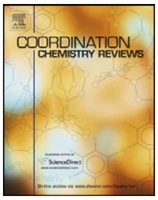
Coordination Chemistry Reviews 253 (2009) 2481–2492

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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



Review

Sterically induced differences in N-heterocyclic carbene transition metal complexes

Olaf Kühl

Institut für Biochemie, Bioinorganic Research Group, EMA Universität Greifswald, Felix-Hausdorff-Str. 4, D-17489 Greifswald, Germany

Contents

1. Introduction 2481
2. *Trans*–*bis*-carbene complexes 2483
3. Abnormal NHC complexes 2484
4. Trigonal bipyramidal and octahedral complexes of formula $MX_n(NHC)_m$ 2485
5. Complexes with bent NHC 2486
6. Square pyramidal complexes 2487
7. Unsymmetrically coordinated NHC ligands 2488
8. Donation into the "empty" p-orbital of NHC ligands? 2489
9. Summary and outlook 2490
Acknowledgements 2490
References 2491

ARTICLE INFO

Article history:
Received 1 April 2009
Accepted 27 July 2009
Available online 3 August 2009

Keywords:
Carbenes
Structure
Ligands
Transition-met. (early) compl.
Organometallic compd

ABSTRACT

The steric implications of the wingtip groups and tether length in bidentate N-heterocyclic carbene ligands on the structural features of NHC complexes are still not fully understood. Steric crowding causes pitch and yaw angles of unsymmetrically coordinated NHC ligands, equatorial or axial coordination of the carbene in trigonal bipyramidal complexes and the close approach of halogen atoms to the C2 atom in some complexes, although electronic factors have been implicated in all instances.

1. Introduction

N-heterocyclic carbenes, NHC, popular ligands ever since their first isolation some twenty years ago, sparked not only a renaissance [1–3] of their transition metal chemistry, but prompted the development of a host of related stable carbenes of unprecedented and rich diversity [4]. As these carbenes "traditionally" replace the ubiquitous phosphane ligands in transition metal complexes [5], questions relating to their stereoelectronic properties are increasingly important for the rational design of NHC ligands [6], especially for applications in catalysis. The modification of wingtip[1] substituents and alterations of the imidazole ring have notable influences on their electronic properties due to annelation [7,8] and their steric properties due to folding [9]. The early perception that NHC act solely as innocent spectator ligands had to be revised in view of the observed reductive elimination of imidazolium salts from transition metal alkyl complexes with *cis*-NHC ligands, a main catalyst degradation pathway [10,11] (see Fig. 1).

The main contribution to the stability of NHC or Wanzlick–Arduengo carbenes comes from a combination of the large electron withdrawing effect of the electronegative nitrogen atom on the σ-electrons of the C–N single bond paired with a $\pi_N \rightarrow \pi_C$ back-donation via the p-orbitals [12–14]. The presence of a C═C double bond in the backbone provides additional thermodynamic stabilisation of at least 20 kcal/mol [15]. To destabilise the $N_{p\pi} \rightarrow C_{p\pi}$ interaction and make the "empty" p-orbital on carbon available for a donor interaction, π-electron density has to be withdrawn from the nitrogen p-orbital, either by annelation [7,8,16] or by introducing

---

E-mail address: dockuhl@gmail.com.

[1] Wingtip or wingtip group is an established term and denotes the N-substituents on the NHC. The term arises from the likening of the Wanzlick–Arduengo carbene's structure to a bird in flight with the N-substituents as the wings.

0010-8545/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2009.07.019

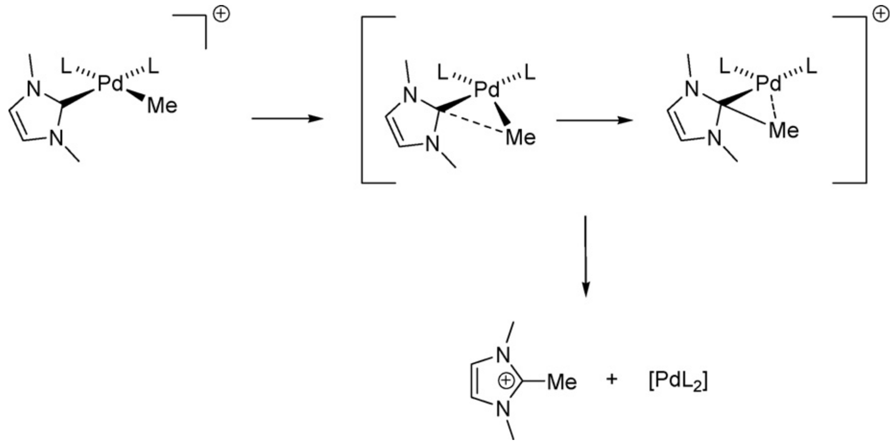


Fig. 1. Reductive elimination of 2-alkylimidazolium salts from transition metal NHC complexes.

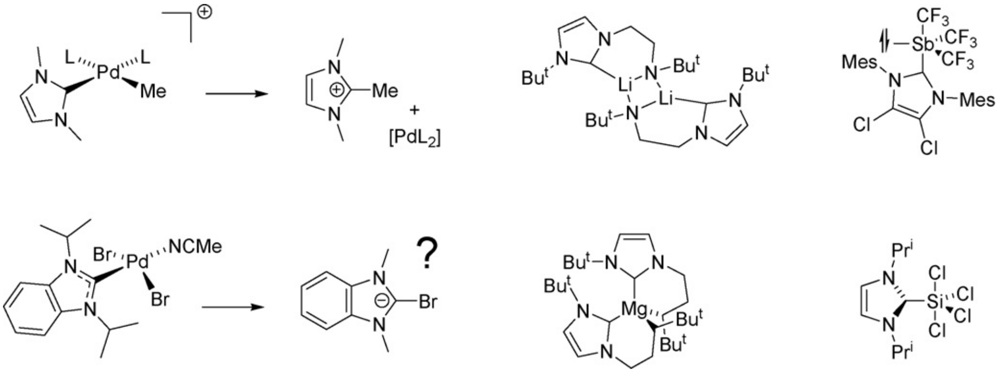


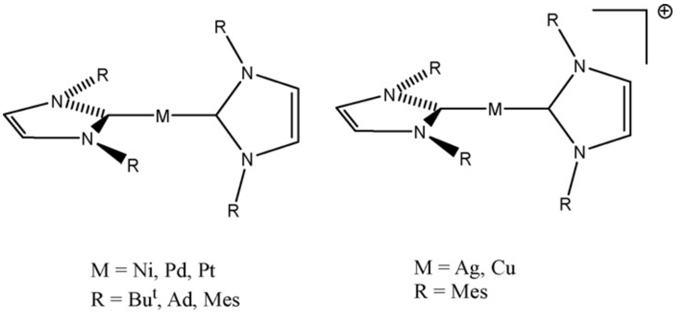
Fig. 2. Three pairs of structurally different NHC complexes.

suitable electron withdrawing substituents on the imidazole backbone (C4/C5) [8]. There is strong experimental evidence against the possibility of a Wanzlick–Arduengo carbene to act as a Lewis acid or electrophile towards a σ-donor ligand [17]. There is only limited π-backbonding observed in transition metal NHC complexes precisely because the receiving p-orbital on carbon is already sufficiently filled with π-electron density from the nitrogen lone pairs. The π-acceptor strength of NHC is believed to be rather low [18], although it is no longer thought to be negligible [19]. It is well known that despite the excellent σ-donicity of NHC, excess of free NHC added to transition metal NHC complexes does not result in a bonding interaction between the lone pair of the singlet carbene and the p-orbital of the coordinated NHC. No such interactions have been observed in crystal structures of free NHC, although electronically destabilised NHC are known to coexist with their dimers [20–22].

Against this background, could crystal structures that feature nucleophilic coligands in close proximity to the C2 p-orbital [23–25] be explained by steric considerations rather than by weak donor interactions into an already occupied orbital that is fully embedded into a delocalised 6 π-electron system? Could the unsymmetrical coordination of a tethered and chelating NHC ligand [26] not be explained by an insufficient tether length rather than undirected “ionic” bonding [27,28] and could the equatorial coordination of NHC ligands in a trigonal bipyramidal coordination geometry [24,29–31] not be caused by the steric demand of the wingtip groups rather than any irregularities of the NHC's electronic structure (see Fig. 2)? In its accustomed axial position [32,33], the wingtip groups of the NHC cannot avoid all three ligands in the equatorial plane simultaneously making steric clashes between the wingtip groups and third row elements in the equatorial plane inevitable.

The steric demand of an NHC ligand is largely governed by the planar imidazole ring creating a wedge like ligand whose steric properties can be described in terms of two angles – a small one describing the height of the wedge and a large one for its width – very similar to the phosphinidine ligands [34]. Alternatively, one can describe the steric demand of an NHC ligand in terms of the area it shades in the metal's coordination sphere, a parameter known as V_{burr} [6]. In either model, the wingtip substituents on the nitrogen atoms are easily identified as the determining factors for the steric demand of these carbene ligands.

The steric influence of the wingtip substituents on the structure of a transition metal carbene complex is most readily seen in the non-parallel coordination of the carbene ligands in the homoleptic $[M(NHC)_2]$ complexes (M = Ni, Pd, Pt) [35–43] (see Fig. 3). The same structural features are observed in the cationic homoleptic group 11 complexes $[M(NHC)_2]X$ (X = anion) [44–47]. It is perhaps inter-



M = Ni, Pd, Pt
R = Bu^t, Ad, Mes

M = Ag, Cu
R = Mes

Fig. 3. Homoleptic and cationic *trans*-$[M(NHC)_2]$ complexes.

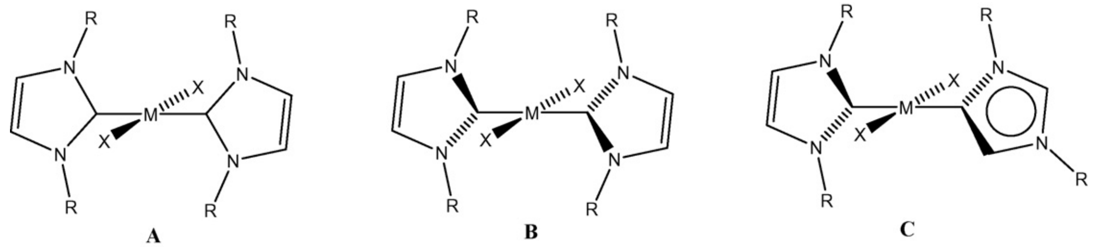


Fig. 4. Structural differences in *trans*-[$M(NHC)_2X_2$] complexes.

esting to note that the corresponding phosphane complexes feature three or four ligands compared to the two ligands in the case of the carbene complexes [48] highlighting the different steric shielding properties of the two ligand families.

2. *Trans–bis*-carbene complexes

The known, structurally characterised compounds *trans*-[$M(NHC)_2X_2$] (M = Ni, Pd, Pt; X = Cl, Br, I) [49–62] (see Fig. 4) show a remarkable likeness to the homoleptic complexes [$M(NHC)_2$] (M = Ni, Pd, Pt) [35–43]. Contrary to those, they realise two different structural types **A** and **B**. Type **B** is realised by both series of complexes and shows the two linearly arranged NHC ligands tilted against each other whereas in **A** the two carbene ligands are coplanar. The axis of the NHC ligands is perpendicular to the axis of the halogens in both structure types.

There are roughly an equal number of examples for structure types **A** (see Fig. 5) [49–54] and **B** (see Fig. 6) [55–62]. Examples for *cis*-[$M(carbene)_2X_2$] (M = Ni, Pd, Pt; X = Cl, Br, I) often, but not always, feature *bis*-carbene chelate ligands [63–65].

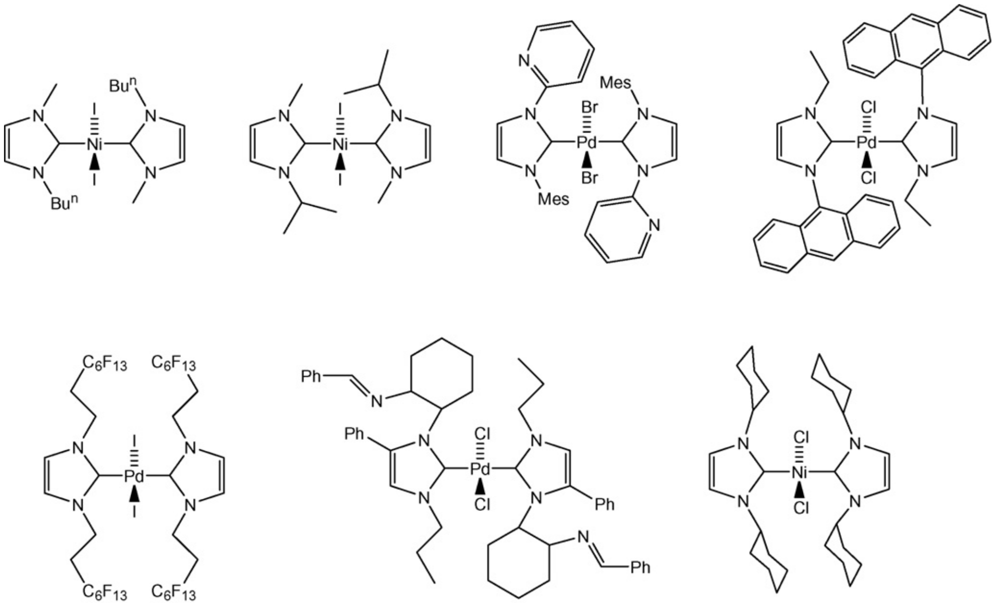


Fig. 5. *trans*-[$M(NHC)_2X_2$] complexes of structure type **A**.

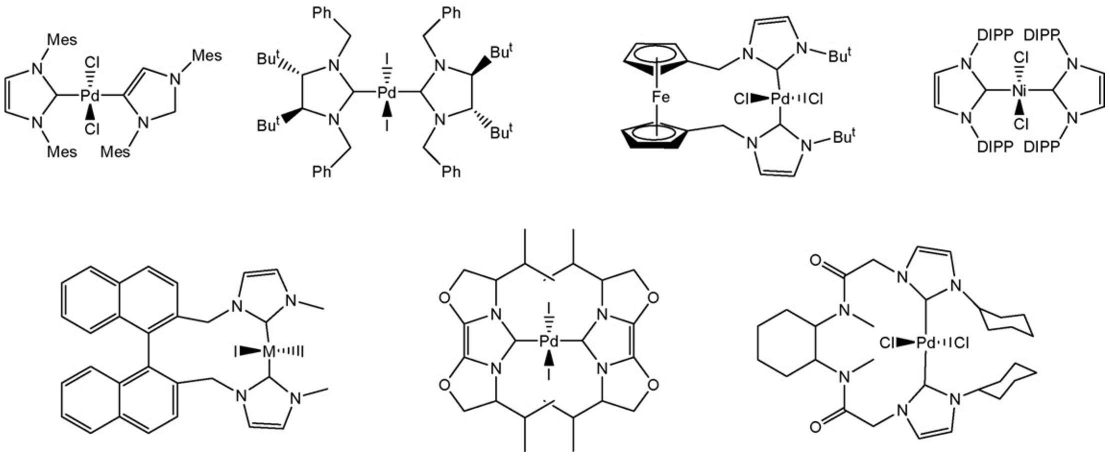


Fig. 6. *trans*-[$M(NHC)_2X_2$] complexes of structure type **B**.

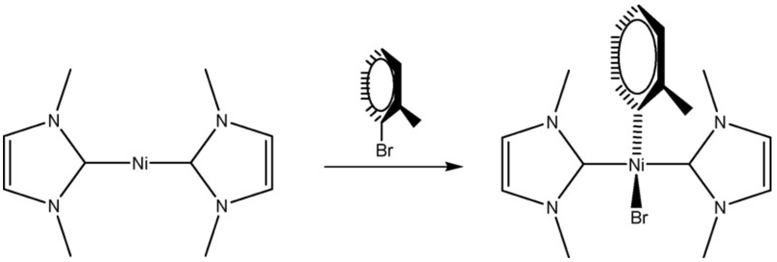


Fig. 7. The reaction between [Ni(IMe)$_2$] **1** and *o*-bromotoluene to form the square planar complex *trans*-[Ni(IMe)$_2$Br(*o*-tolyl)] **2**.

The question presents itself, what is the driving force for the realisation of structure type **A** or **B**. In the structurally determined homoleptic *bis*-carbene complexes of the zero valent metals nickel, palladium and platinum, only structure type **B** is found [35–43]. The carbene ligands in these complexes have sterically demanding substituents at the nitrogen atom (mesityl, *tert*-butyl, adamantyl) [38–43], which raises the suspicion that the tilting of the carbene ligands may have steric reasons. The only described homoleptic complex with methyl substituted carbene ligand [Ni(IMe)$_2$] **1**[2] was not structurally determined. However, it readily adds *o*-bromotoluene to form the square planar complex *trans*-[Ni(IMe)$_2$Br(*o*-tolyl)] **2** with almost coplanar carbene ligands (4.16°) [35] (see Fig. 7).

The complexes of structure type **A** (see Fig. 5) are distinguished by substituents at the carbene nitrogen atom that are sterically indifferent or are unsymmetrically substituted in such a way that the sterically demanding substituents avoid each other in the complex [49–54]. The complexes with unsymmetrical carbene ligands are centrosymmetric with the metal atom located on the centre of inversion. The coplanar arrangement of the carbene ligands is evidently independent of the halogen atom on the metal. There are examples for iodine, chlorine and bromine. It is interesting to note that examples for the sterically demanding substituents mesityl and anthracenyl are only described for palladium which is larger than nickel. This could be connected with the greater steric tolerance of a 12 pm longer M–C bond [66] in the palladium complexes.

In contrast, structure type **B** is reserved for structurally more demanding and/or chelating carbene ligands. In the latter, *trans*-coordination is enabled via alkyl bridges between the imidazole rings and the ligand backbone; a coplanar arrangement is prevented by geometrical constraints. The sterically demanding carbene ligands carry mesityl, DIPP (2,6-diisopropylphenyl) or benzyl groups [54–62]. Interestingly, the steric hindrance in the benzyl substituted carbene is generated by *tert*-butyl groups in 4,5 position that prevent a backfolding of the phenyl groups and thus cause tilting of the carbenes. The chelate carbenes possess a binaphthyl, ferrocenyl or cyclohexyl scaffold.

The closely related homoleptic complexes [M(NHC)$_2$] (M = Ni, Pd, Pt) and [M(NHC)$_2$]$^+$ (M = Cu, Ag, Au) [44–47] crystallise in structure type **B**, except for some gold(I) complexes that realise type **A** structures. In the silver(I) *bis*-carbene complex [Ag(MesI)$_2$]CF$_3$SO$_3$ **3** [45], the carbene ligands are tilted by 39.7° and thus it is the first representative of structure type **B**. At the time, the authors pointed to the sterically demanding mesityl substituents as the likely cause for the observed tilting. This assumption proves correct. The neutral representatives [M(NHC)$_2$] (M = Ni, Pd, Pt) (see Fig. 3) [36–43] without exception realise structure type **B** as far as they are structurally characterised. This is obviously due to the sterically demanding substituents.

The homoleptic compounds are coordinatively and electronically unsaturated, which explains their reactivity regarding oxidative addition [35–37], coordination of donor molecules [35] and their activity in various catalytic reactions [39]. The compounds are stabilised by sterically demanding substituents and therefore crystallise in structure type **B**. Sterically less demanding carbenes should be able to form homoleptic complexes of stoichiometry [M(NHC)$_n$] (n = 3,4). In contrast, some homoleptic gold(I) complexes realise structure type **A**, since the greater stability of gold(I) NHC adducts [67–73] enables less bulky NHC ligands to form stable complexes.

Within the crystal structure, the transition metal NHC complexes adopt a minimum energy conformation that is not identical with the structure in solution. In solution, the NHC ligands can usually rotate fairly freely around the metal carbene bond, since it is essentially a single bond. So, what is the practical significance of this minimum energy conformation when it is not preserved in solution. In many catalytic applications, the catalytic cycle is thought to go via a [M(NHC)$_2$] intermediate that coordinates and subsequently couples the substrates. The substrates are obviously larger than the halide atoms they replace in the coordination sphere of the metal and thus require more space. This forces the NHC ligands to adopt a conformation that minimises steric interaction between the wingtip groups. The solid state structures of the *trans*-[M(NHC)$_2$X$_2$] serve as a good model for this situation and assist us in designing sterically optimised transition metal NHC complexes.

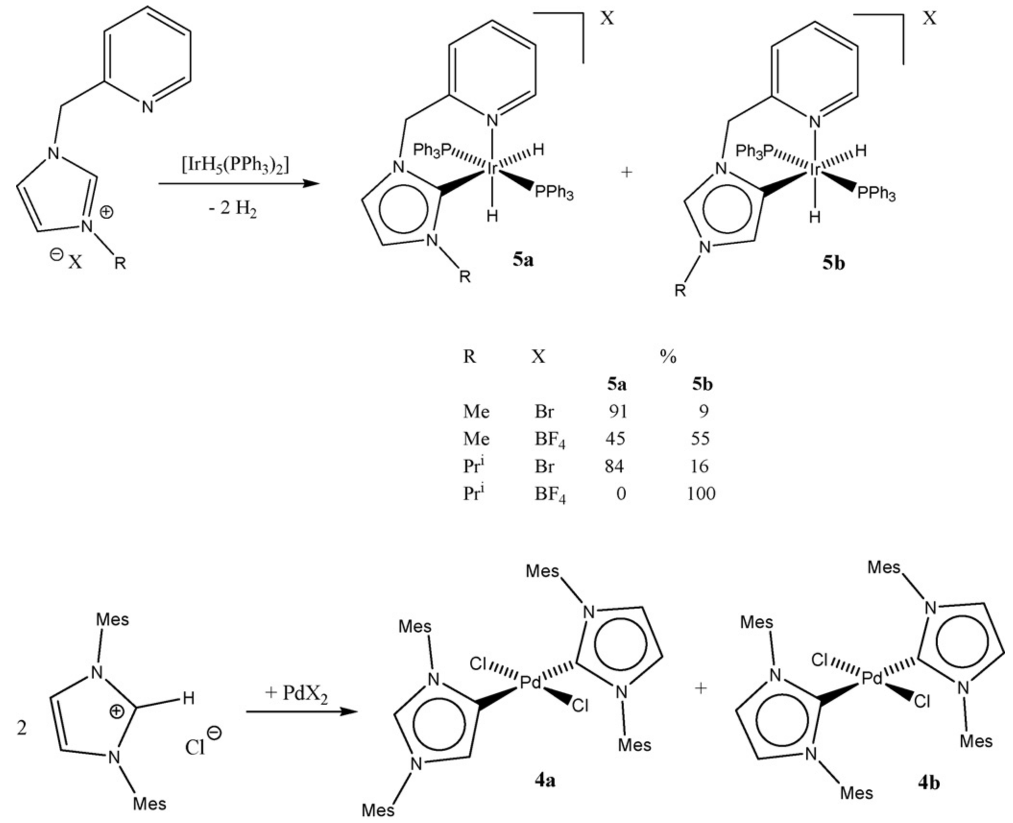
3. Abnormal NHC complexes

In abnormal NHC complexes, an NHC is coordinated by the C4 or C5 carbon atom to the metal rather than by the customary C2 atom. Excellent reviews on this topic have recently appeared from Arnold and Pearson [74] and Albrecht [75]. Here, it suffices to say that the factors governing the occurrence of abnormal coordination are not entirely clear, but steric congestion seems to play a major role. This steric congestion can be caused by the steric bulk of the wingtip groups, the tether length (and thus the bite angle) and indeed the nature of the anion of the imidazolium salt or the ligand on the metal. Some typical examples are given in Fig. 8.

The complex [Pd(IMes)$_2$Cl$_2$] **4** is formed with two normal coordinated IMes ligands and structure type **B** **4b** or alternatively with one abnormal coordinated IMes ligand and structure type **C** **4a** depending on the steric bulk of the ligand on the starting material PdX$_2$ (X = Cl, OAc). The sterically more demanding acetate yields the abnormal complex with structure **C** [59]. In the methylpyrido functionalised NHC iridium complexes the formation of the abnormal complex **5b** depends on both the steric bulk of the wingtip group of the carbene and the size of the anion of the imidazolium salt [76]. The former is rather unsurprising, but the latter needs an explanation. Crabtree et al. showed that the anion assists in the abstraction of a proton from the imidazolium salt and in doing so becomes sterically relevant within the coordination sphere of the iridium atom. The larger tetrafluoro borate anion thus causes abnormal coordi-

---

[2] IMe: I = imidazole stands for the NHC scaffold; Me = methyl stands for the N-substituents on the NHC.



R	X	%	
		5a	**5b**
Me	Br	91	9
Me	BF_4	45	55
Pr^i	Br	84	16
Pr^i	BF_4	0	100

X	%	
Cl	<1	68
OAc	74	<1

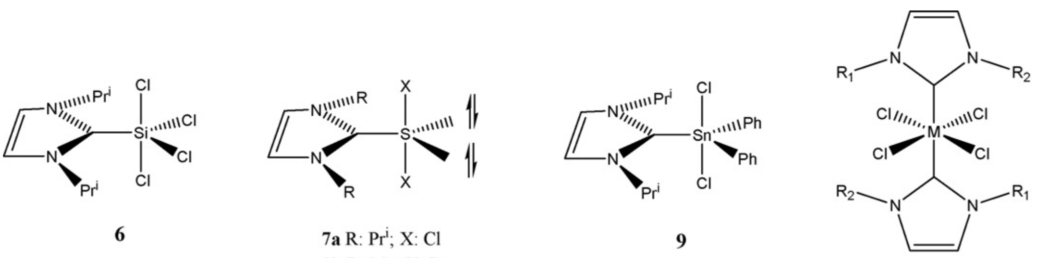
Fig. 8. Normal and abnormal coordination in transition metal NHC complexes.

nation of the carbene to a much greater extent than the sterically less cumbersome bromide anion. Shortening the tether between the imidazole ring and the pyridine substituent decreases the bite angle of the ligand and increases the steric impact of the wingtip group. Abnormal coordination relieves the steric strain [51].

4. Trigonal bipyramidal and octahedral complexes of formula $MX_n(NHC)_m$

In the structures of some NHC adducts of main group and transition metal halides of the general formula $MX_n(NHC)_m$ (M = S, Si, Sn, Ti, Zr, Hf; n = 2–4; m = 1,2) (see Fig. 9), the N-heterocyclic carbene is either seen in the equatorial position of a trigonal bipyramidal tbp coordinated central atom or the conformation within the octahedral complex is not the one that is electronically favoured.

An example of the former is the complex [Si(IPr^i)Cl$_4$] **6** [31], where the carbene occupies an equatorial position in the Ψ-trigonal bipyramidal arrangement around silicon. Due to the electron withdrawing nitrogen atoms and the formal positive charge on the carbene carbon atom, the effective electronegativity of this carbon atom should be greater than those of the chlorine atoms [30] and thus the carbene should be in the axial position (see Fig. 10). The situation in the related compound [S(IPr^i)Cl$_2$] **7a** [30] is very similar, except that the two electron lone pairs on sulphur take the equatorial positions of two chlorine atoms in [Si(IPr^i)Cl$_4$]. In both compounds, the Cl–M–Cl bond angles of the axial substituents



6

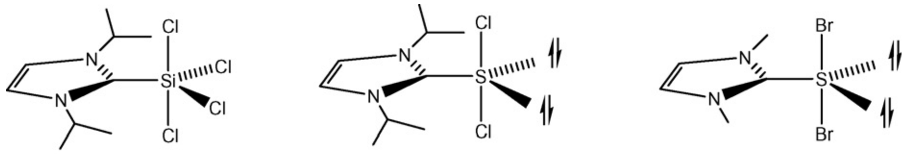
7a R: Pr^i; X: Cl
8b R: Me; X: Br

9

10

R_1	Pr^i	Bu^s	Me
R_2	Pr^i	Pr^i	CH_2Mes
M	Zr, Hf	Zr	Zr

Fig. 9. Size matters—“axial” as opposed to “equatorial” coordination.

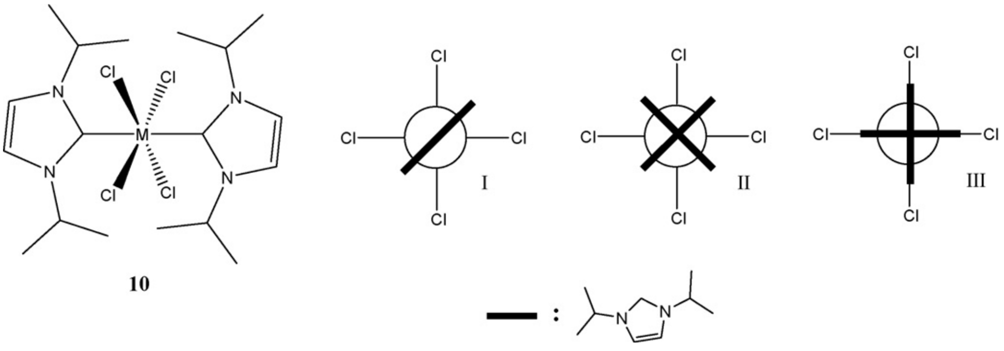


6
$Si(IPr^i)Cl_4$

7a
$S(IPr^i)Cl_2$

8b
$S(IMe)Br_2$

Fig. 10. Trigonal bipyramidal main group element NHC complexes with the carbene in equatorial position.



10

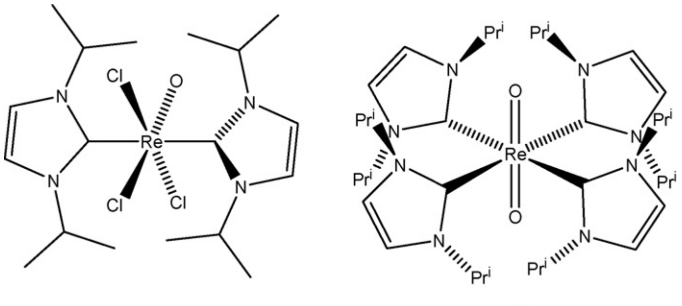
Fig. 11. The different relative positions of NHC ligands in *trans*-$[M(NHC)_2X_4]$ complexes.

deviate from linearity, 175.2(1)° for $[Si(IPr^i)Cl_4]$ and 175.9(1)°for $[S(IPr^i)Cl_2]$ and the chlorine atoms bend towards the carbene as predicted by the VSEPR-concept [32,33]. It appears that the comparatively large Cl and Br atoms force the carbene into the equatorial position, where the NHC wingtip groups have more space and thus steric strain is released.

Arduengo and Burgess published a related series of $[S(IMe)X_2]$ (X = Cl, Br, I) complexes [29] of which the bromide compound **8b** was structurally characterised featuring the carbene ligand in equatorial position (S–C 173(2) pm) and the bromine atoms axially with exact linear orientation.

Let us first examine an example where the structural deviations from the electronically preferred conformation are comparatively small. Erker et al. have synthesised a series of *trans*-$[M(NHC)_2Cl_4]$ complexes **10** (M = Zr, Hf; NHC = IPr^i, Bu^sIPr^i, $MeICH_2Mes$) [77] and calculated their preferred conformations using DFT methods. In the electronically preferred conformation of the calculated molecule *trans*-$[Zr(IH)_2Cl_4]$ the two carbene ligands are perpendicular to each other and each carbene is coplanar with a $ZrCl_2$ unit (see Fig. 11). In the structurally determined complex *trans*-$[Zr(IPr^i)_2Cl_4]$ **10a**, the actual conformation changes to an arrangement where the carbene ligands are coplanar, but bisect the Cl–Zr–Cl angle of the central $ZrCl_4$ plane. The difference in the two possible conformations is low and was calculated as 0.1 kcal/mol between the two conformations with the carbenes coplanar or perpendicular to each other. It appears that the two carbenes do not interact sterically when the $M–C_{carbene}$ bond length is 243.2(3) pm as in *trans*-$[Zr(IPr^i)_2Cl_4]$. The same holds true for *trans*-$[Hf(IPr^i)_2Cl_4]$ **10b**, where the $M–C_{carbene}$ bond length is shorter at 240.1(2) pm and the energy difference somewhat larger at 0.3 kcal/mol. Interestingly, the transition state, where the isopropyl groups of the carbenes interact with the chlorine atoms of the $ZrCl_2$ plane, is very low at 2.7 and 2.8 kcal/mol and indicative of a weak steric interaction at such a long $M–C_{carbene}$ bond length.

In contrast, the $M–C_{carbene}$ bond lengths in $[Si(IPr^i)Cl_4]$ **6** [31], $[Sn(IPr^i)Ph_2Cl_2]$ **9** [31] and $[S(IPr^i)Cl_2]$ **7a** [30] are much smaller at 191.1(7), 217.9(3) and 173.2(3) pm, respectively. They are some 52, 25 and 70 pm shorter than in *trans*-$[Zr(IPr^i)_2Cl_4]$ **10a**.



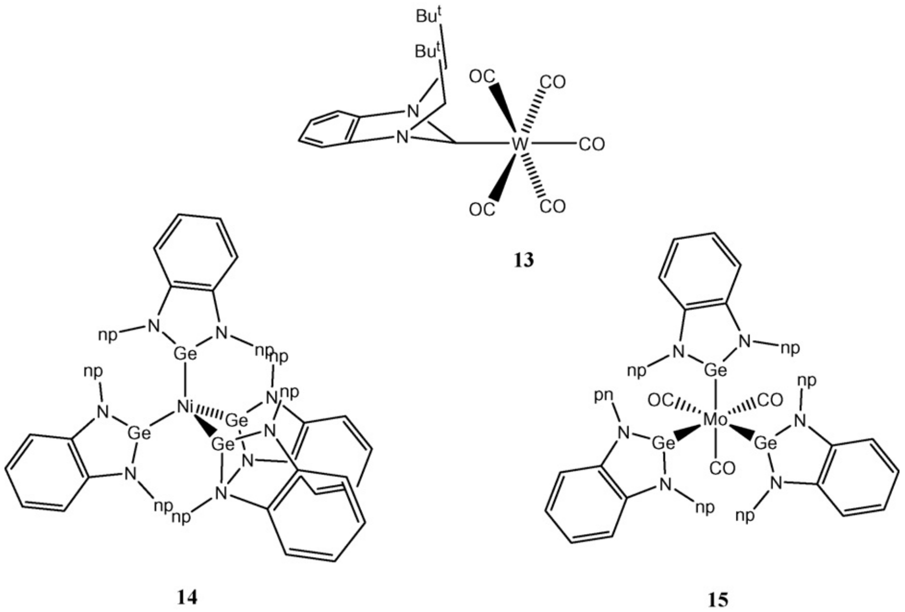
11 **12**

Fig. 12. Size matters—a minimum of distortion in rhenium NHC complexes.

An octahedral complex featuring a short $M–C_{carbene}$ bond length of 218.1(4) pm, similar to that of the tin(IV) compound, and coplanar IPr^i ligands was published by Royo et al. [78] (see Fig. 12). The two carbene ligands in *trans*-$[Re(IPr^i)_2OCl_3]$ **11** are coplanar whereas the four carbene ligands in the closely related complex *trans*-$[Re(IPr^i)_4O_2]$ **12** are arranged in a propeller mode around the linear O═Re═O unit. Although the $M–C_{carbene}$ bond length at 218.4(3)–220.8(5) (av. 219.6) pm is almost identical to that in *trans*-$[Re(IPr^i)_2OCl_3]$, the carbene ligands are no longer coplanar. It is interesting to note that one of the carbene ligands in *trans*-$[Re(IPr^i)_2OCl_3]$ is coplanar with the O═Re═Cl unit meaning that there is no steric repulsion to this second row element at a $M–C_{carbene}$ bond length of 218.5(5) pm.

5. Complexes with bent NHC

An interesting structure of an annelated carbene ligand coordinated to a $W(CO)_5$ moiety **13** was published by Hahn et al. [9] (see Fig. 13). It constitutes the first example of a bent NHC ligand. The ligand, *N,N′-bis*-neopentylbenzimidazolin-2-ylidene, is reported to have its carbene carbon atom dislodged from the plane of the imidazole ring by 20.7(11) and 19.0(11) pm (two crystallographically different molecules in the asymmetric unit),



13

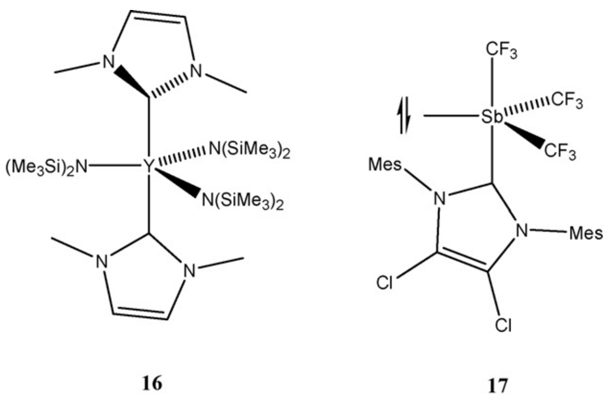
14

15

Fig. 13. Transition metal complexes with folded NHE (E = C, Ge) ligands.

respectively. A recent search of the CCSD reveals that such a dislocation is very rare for coordinated carbene ligands and if it occurs is limited to a few pm [9,79–83]. However, for the higher homologues, N-heterocyclic silylenes NHSi [84–89] and germylenes NHGe [26,90,91] the occurrence is far more frequent and appears to be the rule for annelated NHSi and NHGe. In a recent publication, Ullah et al. described the extent and causes for the bending of *N,N′-bis*-neopentylbenzimidazolin-2-ylidene in the nickel complex [Ni(NHGe)$_4$] **14** and the molybdenum complex *fac*-[Mo(NHGe)$_3$(CO)$_3$] **15** [92]. The authors concluded that the delocalised π-electron system in the five-membered ring features a reduced heteroaromatic stabilisation that enables bending, but that actual bending is triggered by steric factors, i.e. increased bulk and non-symmetry in the *N*,*N′*-substituents. Although heteroaromatic stabilisation is significantly greater in NHC than in the homologous NHGe [14,15,93], annelation destabilises the heteroaromatic five membered ring [8,9,17,94] and may make the separation into two delocalised π-electron systems possible: the annelated phenyl ring and a N–Ge–N entity with 4 π-electrons. Bending is then observed on the two “hinges” the $C_N–C_N$ and the N–N vectors.

What are the steric implications in a trigonal bipyramidal geometry around the central metal atom. In an octahedron, the equatorial plane consists of an MX_4 unit with X–M–X bond angles of 90°. The carbene ligand can bisect these and thus avoid interaction with equatorial ligands. In a tbp geometry, the situation is fundamentally different as the X–M–X angle is now 120° and the arrangement of the three equatorial ligands thus that bisecting one angle brings the axial carbene in direct close contact with the third equatorial ligand. We know from *trans*-[Zr(IPr^i)Cl$_4$] that this transition state is only 2.7 kcal/mol higher in energy, but even for tin with a 25 pm shorter $M–C_{carbene}$ bond length, this energy difference is likely to be much higher and prohibitive. Therefore, the equatorial coordination in the trigonal bipyramidal complexes of sulphur(II), silicon(IV) and tin(IV) rather than the axial coordination predicted by the VSEPR-concept [32,33] has purely steric reasons and is not indicative of a reduced electronegativity of the carbene carbon.



16

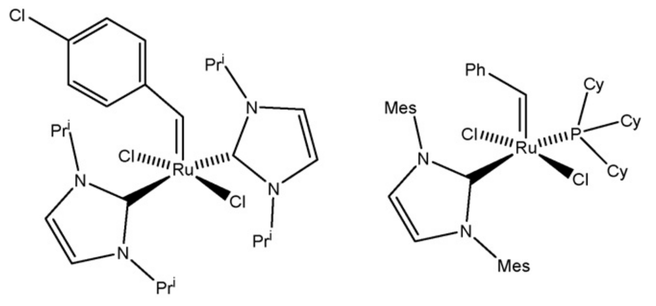
17

Fig. 14. Trigonal bipyramidal NHC complexes with the carbene in axial position.

A good example, where the carbene is located in axial positions of a tbp geometry is given in Fig. 14. In the yttrium complex [Y(IMe)$_2${N(SiMe$_3$)$_2$}$_3$] **16** [95] with $Y–C_{carbene}$ distances of 266 pm (av.), the carbene ligands are tilted by 87.6° against each other and the three equatorial amido ligands feature N–Y–N angles of 132°, 116° and 113°, respectively. In addition, the $C_{carbene}–Y–N_{amido}$ angles reveal the dislocation of one of the amido ligands due to steric interaction with one of the carbene ligands (94° and 84°). In the other example, the carbene ligand in [Sb(IMes)(CF$_3$)$_3$] **17** [26] displays a noticeable pitch angle (see Fig. 16) due to the interaction of the mesityl wingtip substituent with the equatorial CF$_3$ groups. The very long $Sb–C_{carbene}$ bond length of 282.1(5) pm shows the steric crowding in the coordination sphere of the antimony atom and the preference of the carbene for an axial binding site.

6. Square pyramidal complexes

The best known application of NHC in homogenous catalysis is as a ligand in ruthenium catalysed olefin metathesis. The structurally characterised Grubbs catalysts [Ru(NHC)$_2$Cl$_2$(=CR$_2$)] **18** [96] and [Ru(NHC)LCl$_2$(=CR$_2$)] (L = phosphane; usually PCy$_3$) **19** [97–99] feature a square base pyramidal geometry with the Schrock carbene in the apex and the two chlorine atoms trans to each other [98–100] (see Fig. 15). The four ligands in the base move away from the apical carbon atom filling the “void” of the unoccupied position of an imaginary octahedron around the 16 VE ruthenium(II) centre. Again, the deviation from linearity shown by the chlorine atoms can be interpreted as moving towards the p-orbital of the NHC ligands. In the case of [Ru(NHC)$_2$Cl$_2$(=CR$_2$)] the inappropriateness of



18 **19**

Fig. 15. Square pyramidal ruthenium NHC complexes, second generation Grubbs catalysts.

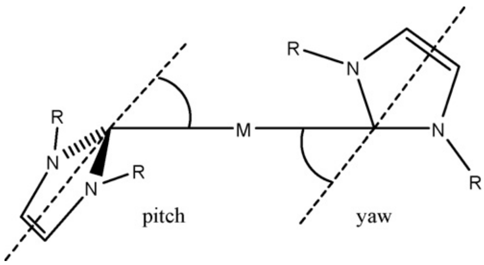


Fig. 18. Graphical definition of the pitch and yaw angles.

such an interpretation is immediately obvious as the pair of chlorine atoms cannot move towards both NHC ligands simultaneously. Rather, the deviation from linearity is the consequence of steric requirements within the square base pyramidal geometry around the ruthenium atom and the absence of a lone pair opposite to the Schrock carbene.

Later, we will see a similar arrangement in related complexes where the interpretation is not so self-evident.

7. Unsymmetrically coordinated NHC ligands

The description of metal complexes with chelating ligands always raises the question whether the ligand or the metal determines the geometric parameters like the bite angle [101,102] or the optimal length of the tether between the two ligating atoms. In this context, it should be noted that N-heterocyclic carbenes are in some respects fundamentally different from other popular ligands like chelating phosphanes [103,104]. In particular, the ligating carbene carbon atom of the NHC is embedded in a rigid heterocyclic framework which places the flexibility of this functional carbene between the extremely flexible $Ph_2P(CH_2)_nPPh_2$ series of chelating diphosphanes [102] and the rigid Xantphos family (see Fig. 16) [105].

It can be expected that this rigidity will have an influence on the optimal tether length between the carbene and a pendant chelating functional group with respect to the size of the metal centre. An excellent example for this was presented by Arnold et al. [27] in a series of amido tethered chelating carbene complexes of lithium, magnesium and uranium with the ligand (see Fig. 17). The ethylene linker between the imidazole ring and amide functional group is ideal to differentiate between central atoms of different size. The second steric factor in the chelate ligand are the wingtip substituents on the amido and the second imidazole nitrogen atoms. In the lithium complex $\{Li[\eta^2\text{-}Bu^tN(CH_2)_2IBu^t]\}_2$ **20**, the carbene unit is unsymmetrically coordinated in two directions to the lithium ion, whereas the corresponding magnesium complex $Mg[\eta^2\text{-}Bu^tN(CH_2)_2IBu^t]_2$ **21** features the unsymmetric coordination of the carbene unit only in one direction. The two directions are described by the pitch (out of plane tilting) and yaw (in plane tilting) angles (see Fig. 18), respectively [106]. Both central ions, lithium and magnesium, prefer tetrahedral coordination [107], but in the present case only the magnesium complex has a four coordinate metal centre whereas the lithium ion is three coordinate (see Fig. 18). As a consequence, the ligand bite angle in the magnesium complex is 94.1° and in the lithium complex 99.7°. Interestingly, using the appropriate trigonometric equation, this translates into a distance between the carbene carbon atom and the amido nitrogen atom of 332 pm for the magnesium and 328 pm for the lithium complex. It seems that for both complexes the ligand is at the end of its tether and thus the occurrence of unsymmetric coordination of the

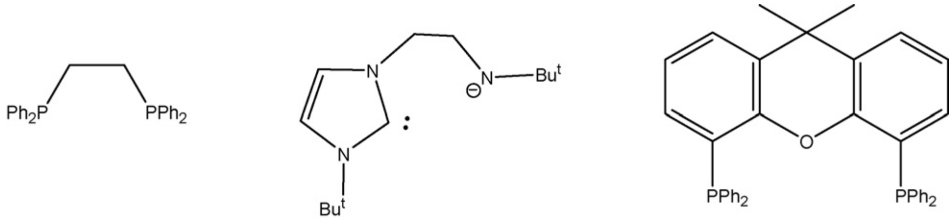
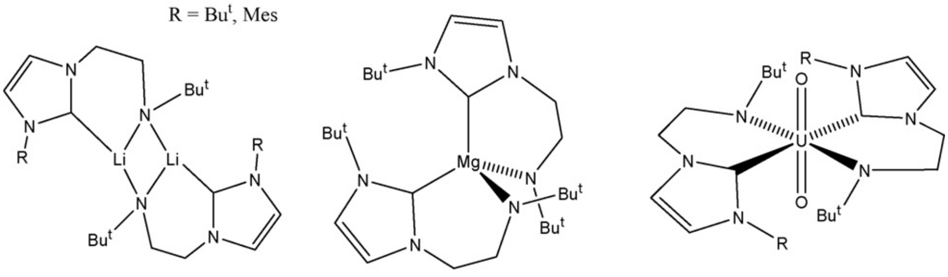


Fig. 16. Bidentate ligands of varying bite angle and rigidity.



20 **21** **22**

Fig. 17. Size matters—pitch and yaw angles as a question of metal and wingtip size.

NHC unit is due to geometrical constraints rather than electronic influences.

With the same ligand system, two uranium complexes with a central O═U═O unit were structurally characterised **22 a,b** [27]. Here, the two amido-NHC ligands occupy the equatorial plane of the octahedral complex in a *trans* configuration (see Fig. 17). Whereas in the magnesium complex, the chelate ligands were perpendicular to each other due to the tetrahedral geometry around the metal, in the uranium complexes they are essentially coplanar. This brings the wingtip groups in close proximity to each other. In the case of the *tert*-butyl substituted NHC-ring this leads to steric crowding and large pitch (23°) and yaw (17°) angles, whereas the mesityl wingtip can avoid the *tert*-butyl group on the amido nitrogen atom due to its disc like appearance. The bite angle of the ligand is some 74° and the distance between the carbene carbon and the amido nitrogen atoms 316 pm meaning that the chelate ligand in the uranium complexes is somewhat relaxed.

It should be mentioned that the great majority of structurally determined amino functionalised NHC ligands with two spacer atoms between the imidazole ring and the pendant donor atom is coordinated to metal atoms with square planar or octahedral [108] geometry where the central atom has a preferred bite angle of 90° and thus significantly smaller than the 94.2° or 99.7° observed in the lithium and magnesium complexes (metal preferred bite angle 109.5°), respectively. Unsurprisingly, the corresponding lithium alkoxy-NHC complex $[Li([OCHBu^tCH_2(1\text{-}C\{NCHCHNBu^t\})])\cdot LiI]$ features a similarly large yaw angle of 19° [28].

In Schrock carbenes with the structural element M═C(H)R, a pivoting of the carbene ligand is observed that brings the C–H hydrogen atom in close and bonding proximity of the metal atom [109]. This agostic interaction increases the electron density on the electron deficient metal centre. In contrast, the "pivoting" observed with the Wanzlick/Arduengo carbenes discussed here is clearly different. The most obvious difference is the coordination chemistry: tricoordinate (electronically and coordinatively unsaturated) for lithium in **20** and tetracoordinate (electronically and coordinatively saturated) for magnesium in **21**.

Although an electrostatic bonding situation is described for barium NHC complexes, the corresponding magnesium NHC complexes are described as covalently bonded by the same authors [110] leaving steric reasons as the likely cause for the observed unsymmetrical bonding angles in these tethered chelate complexes.

8. Donation into the "empty" p-orbital of NHC ligands?

Recently, several reports have appeared in the literature concerning the π-donation from *cis*-ligands into the "empty" p-orbitals of NHC ligands coordinated to transition metals. How important or even credible are these claims?

The electronic structure and properties of NHC have been the subject of many experimental and theoretical studies [13–15,93]. It is now universally accepted that these carbenes derive their remarkable stability from the strong N → C carbene π-donation which leads to a largely filled p(π) orbital at the carbene carbon atom [13]. It has long been established that carbenes have a low π-acceptor ability when bonded to transition metals [12,111,112]. Indeed at times, the unsaturated carbenes seem to have a greater net donicity then their saturated analogues [113] suggestive of their ability to act as π-donors [114].

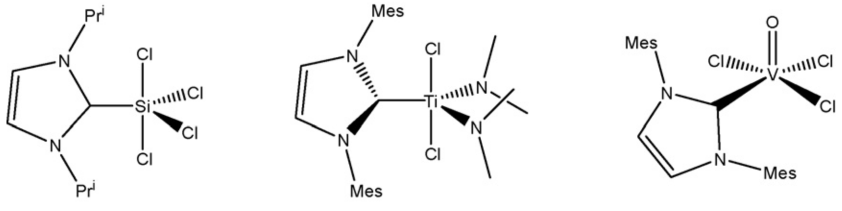
One of the most common degradation pathways involving transition metal carbene complexes in catalysis is reductive elimination forming an imidazolium salt [10,11]. This occurs frequently when an alkyl ligand is positioned *cis* to the NHC ligand on the transition metal. Then the alkyl group attacks the carbene carbon atom electrophilically as a carbocation forming a C2 alkyl substituted imidazolium cation (see Fig. 1).

Against this background, "short intramolecular $Cl\cdots C_{carbene}$ contacts" [23–25] have been reported. These contacts are supposed to be the result of donor interactions involving the halogen lone pairs and the "formally empty" p-orbital of the carbene [23]. But, as described above, the carbon p-orbital is not empty, but filled owing to a strong N → C carbene π-donation. The halogen atom will now attack the carbene carbon atom nucleophilically and thus with opposite polarity to the known reductive elimination pathway above. As evidence, the authors cite crystallographic data and DFT calculations.

Let us consider the compounds $[Si(IPr^i)Cl_4]$ **6** [31], $[Ti(IMes)Cl_2(NMe_2)_2]$ **23** [24] and $[V(IMes)OCl_3]$ **24** [23] (see Fig. 19). Each compound was described in terms of a trigonal bipyramidal geometry around the central metal atom. In each structure, the carbene ligand is reported in equatorial position with the two axial chloride atoms dislocated from linearity and moved towards the equatorial NHC ligand in a way that may suggest $Cl\cdots C_{carbene}$ interactions between the chlorine lone pairs and the formally "empty" p-orbital of the NHC carbon atom.

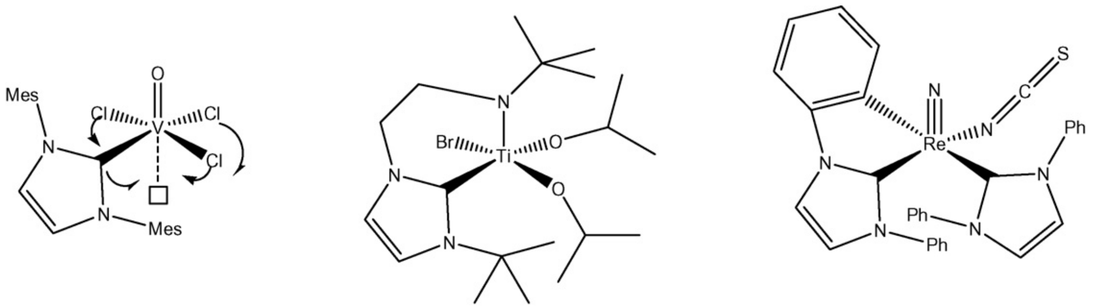
Kuhn et al. correctly remark that the NHC ligand should be found in the axial rather than equatorial position on account of the formally positive charge on the NHC carbon atom upon coordination [31]. They also state that the departure of the axial chlorine atoms from linearity is predicted by VSEPR theory [32,33] and thus a consequence of the coordination geometry and not due to interactions between individual ligands. With other words, there is no need and no evidence for a donor interaction between the chlorine lone pairs and the NHC carbon p-orbital, a fact worth to remember.

In the equally trigonal bipyramidally coordinated compound $[Ti(IMes)(NMe_2)_2Cl_2]$ **23** [27] the NHC is again in the equatorial position. In **23** the Ti–C bond is expectedly much longer (231.3 pm), but some 50 pm shorter than in the antimony complex **17**. As a consequence, the carbene ligand is in the equatorial position in **23**, but axially in **17**. The Ti–N bonds are much shorter (average 187.6 pm). This has steric consequences. Only one of the two NMe_2 groups in **23** can turn its methyl groups into the equatorial plane, the other has to orientate them axially. Because of the short Ti–N bond lengths, the hydrogen atoms of their methyl substituents come in close contact with the axial chlorine atoms (Cl–H 272.7 pm and Cl–H 277.4 pm). These Cl–H distances are in the range of strong Cl–H hydrogen



6 **23** **24**

Fig. 19. "Donation" or just steric crowding?—three NHC complexes with "unusual" structure.



24 25 26

Fig. 20. A selection of square pyramidal transition metal NHC complexes.

bonds [115] and responsible for pushing the chlorine atoms towards the carbene carbon atom.

The high oxidation state of the Ti^{4+} centre is stabilised by strong N–Ti π-donations of the NMe_2 substituents. It should be mentioned that in the synthesis of **23** a second equivalent of carbene IMes is formed that does not bind to the titanium atom. Obviously, the Ti^{4+} centre is sufficiently stabilised by the strong N–Ti interactions to make binding of a second nucleophilic carbene unnecessary. In the absence of NMe_2 substituents MCl_4 (M = Zr, Hf) [70] reacts with two molecules of IPr^i to form $[M(IPr^i)_2Cl_4]$ [77].

A second example for the alleged $Cl\cdots C_{carbene}$ bonding interactions was reported in the compound $[V(MesI)OCl_3]$ **24** [23]. The reported structure was described as a trigonal bipyramidal coordination sphere of the central V^{5+} ion with two chlorine atoms occupying the axial positions. There is no obvious steric reason why the two "axial" chlorines shall form a 158° angle with the vanadium atom at the centre. However, closer inspection of the structure reveals that the E–V–E (E = C, Cl, O) angles formed by the equatorial substituents are 105.83°, 112.09° and 142.08°, respectively. Although the sum is 360°, it is hard to imagine that the carbene should push the "equatorial" chlorine by 22° while drawing the oxygen by 14°. The structural parameters of compound **24** are much better explained by a square base pyramidal arrangement around vanadium in which the unoccupied position *trans* to oxygen is blocked by the mesityl substituent on the carbene. The four substituents (other than the apical oxygen) relax towards the empty position. The carbene carbon atom and the "equatorial" chlorine atom move towards each other as do the "axial" chlorine atoms forming a distorted square base pyramidal geometry. The latter also appear to move towards the carbene carbon atom.

Arnold et al. published a compound with very similar geometry to **23** featuring a chelating amido carbene $[Ti(L)Br(O^iPr_2)_2]$ $(L = Bu^tNHCH_2CH_2[C\{Bu^t(CHCH)N\}])$ **25** [116,117] (see Fig. 20). The compound has a square base pyramidal geometry around titanium. The Ti–Br bond length of 267.3 pm is not indicative of a π-donor contribution of the bromine, but the Ti–O bond lengths of 179.1 and 183.5 pm do indicate π-donor contribution from the oxygen atoms with the contribution from the oxygen *trans* to the carbene ligand stronger than from the one *cis* to it. This is reflected in the bond angles where the *trans*-alkoxy ligand features the largest angles moving the bromine and the *cis*-alkoxy ligand closer to the carbene carbon atom. Arnold et al. performed a DFT calculation on compound **6** using the correct geometry and found no evidence for an orbital interaction between either the bromine or oxygen atom and the carbene carbon atom.

A compound with a similar geometry to **24** was published by Braband and Abram [118]. The complex [ReN(SCN)L(L–H)] (L = 1,3,4-triphenyl-1,2,4-triazol-5-ylidene) **26** features an orthometallated phenyl ring on the carbene and the other phenyl ring blocks the coordination site *trans* to the nitrido ligand. In the precursor complex $[ReNCl_2(PMe_2Ph)_2L]$ the Re–P bond *trans* to the carbene is significantly longer than the Re–P bond *cis* to it suggestive of structural evidence for the π-donicity of the carbene. Royo et al. have published a pair of rhenium carbene complexes $[Re(^iPrI)_2OCl_3]$ **11** and $[Re(^iPrI)_4O_2][ReO_4]$ **12** featuring perfect octahedral geometry around rhenium with the carbenes *trans* in **11** and the oxygen atoms *trans* in **12** [70] (see Fig. 11).

It can be said that these close $Cl\cdots C_{carbene}$ distances occur only with sterically crowded metal centres preferably of the 3d or 4p elements such as Ti, V and Sn whereas the 4d and 5d elements Zr, Hf and Re are not affected. These effects are purely steric in nature and are not suggestive of any electronic interaction between the chlorine lone pairs and the 6 π-electron system of the imidazolydine ring. On the contrary, the chlorine lone pairs are usually engaged in π-donor interactions with the central metal to stabilise its high oxidation state.

9. Summary and outlook

It could be shown that in many cases, deviations from the accustomed structures of metal NHC complexes are attributable to steric rather than electronic factors. In *trans–bis*-carbene complexes deviations from the coplanar arrangement of the NHC ligands are due to the steric demands of the wingtip groups. In extreme cases, abnormal coordination of one of the NHC ligands is observed. Although, for electronic reasons, the NHC ligand should be coordinated axially in a metal NHC complex with tbp geometry, for steric reasons it is usually found in equatorial position. The only known exceptions are large central atoms like antimony or small equatorial ligands coordinated through second row elements like nitrogen or carbon.

Even unsymmetric coordination of the carbene ligand and the occurrence of pitch and yaw angles can be attributed to steric factors. Either the avoidance of bulky coligands as in **17** or too short a tether as in certain bidentate functionalised NHC ligands is the reason for these "abnormalities".

Knowledge of these steric factors can be used to optimise ligand design by matching the tether length to the intended metal complex, directing the NHC ligand into the desired position by fine tuning of the wingtip groups, the central metal atom and the size of the coligands. It can also avoid misinterpretation of experimental data by postulating electronic causes that are simply not there.

It is expected that a better knowledge of the steric influence on the structure and reactivity of metal NHC complexes will result in improvements in the design of NHC ligands in practical applications like catalysis and materials science.

Acknowledgements

I thank Prof. A.J. Arduengo III and Prof. J. Heinicke for fruitful discussions.

References

[1] K. Öfele, J. Organomet. Chem. 12 (1968) P42.
[2] H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 80 (1968) 154.
[3] M.F. Lappert, J. Organomet. Chem. 358 (1988) 185.
[4] F.E. Hahn, M.C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122.
[5] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290.
[6] S. Diéz-Gonzáles, S.P. Nolan, Coord. Chem. Rev. 251 (2007) 874.
[7] O. Kühl, S. Saravanakumar, F. Ullah, M.K. Kindermann, P.G. Jones, M. Köckerling, J. Heinicke, Polyhedron 27 (2008) 2825.
[8] O. Kühl, K. Lifson, W. Langel, Eur. J. Org. Chem. (2006) 2336.
[9] F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931.
[10] D.S. McGuinness, N. Saendig, B.F. Yates, K.J. Cavell, J. Am. Chem. Soc. 123 (2001) 4029.
[11] C.M. Crudden, D.P. Allen, Coord. Chem. Rev. 248 (2004) 2247.
[12] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39.
[13] D. Nemcsok, K. Wihmann, G. Frenking, Organometallics 23 (2004) 3640.
[14] C. Boehme, G. Frenking, J. Am. Chem. Soc. 118 (1996) 2039.
[15] C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, J. Am. Chem. Soc. 118 (1996) 2023.
[16] O. Kühl, P. Lönnecke, J. Heinicke, New J. Chem. 26 (2002) 1304.
[17] O. Kühl, Cent. Eur. J. Chem. 6 (2008) 365.
[18] W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256.
[19] A.T. Termaten, M. Schakel, A.W. Ehlers, M. Lutz, A.L. Spek, K. Lammertsma, Chem. Eur. J. 9 (2003) 3577.
[20] F.E. Hahn, L. Wittenbecher, D.L. Van, R. Fröhlich, Angew. Chem. Int. Ed. 39 (2000) 541.
[21] A.J. Arduengo III, J.R. Goerlich, W.J. Marshall, Liebigs Ann. (1997) 365.
[22] J. Wolf, W. Böhlmann, M. Findeisen, T. Gelbrich, H.-J. Hofmann, B. Schulze, Angew. Chem. 119 (2007) 3179.
[23] C.D. Abernethy, G.M. Codd, M.D. Spicer, M.K. Taylor, J. Am. Chem. Soc. 125 (2003) 1128.
[24] P. Shukla, J.A. Johnson, D. Vidovic, A.H. Cowley, C.D. Abernethy, Chem. Commun. (2004) 360.
[25] H.V. Huynh, Y. Han, J.H.H. Ho, G.K. Tan, Organometallics 25 (2006) 3267.
[26] A.J. Arduengo III, R. Krafczyk, W. Mahler, W.J. Marshal, R. Schmutzler, Z. Anorg. Allg. Chem. 625 (1999) 1813.
[27] S.A. Mungur, S.T. Liddle, C. Wilson, M.J. Sarsfield, P.L. Arnold, Chem. Commun. (2004) 2738.
[28] P.L. Arnold, M. Rodden, K.M. Davis, A.C. Scarisbrick, A.J. Blake, C. Wilson, Chem. Commun. (2004) 1612.
[29] A.J. Arduengo III, E.M. Burgess, J. Am. Chem. Soc. 99 (1977) 2376.
[30] N. Kuhn, H. Bohnen, J. Fahl, D. Bläser, R. Boese, Chem. Ber. 129 (1996) 1579.
[31] N. Kuhn, T. Kratz, D. Bläser, R. Boese, Chem. Ber. 128 (1995) 245.
[32] R.J. Gillespie, I. Hargittai, The VESPR Model of Molecular Geometry, Allyn and Bacon, Boston, 1991.
[33] R.J. Gillespie, Chem. Soc. Rev. 21 (1992) 59.
[34] C. Müller, D. Vogt, Dalton Trans. (2007) 5505.
[35] D.S. McGuinness, K.J. Cavell, B.W. Skelton, A.H. White, Organometallics 18 (1999) 1596.
[36] N.D. Clement, K.J. Cavell, C. Jones, C.J. Elsevier, Angew. Chem. Int. Ed. 43 (2004) 1277.
[37] M.M. Konnick, I.A. Guzei, S.S. Stahl, J. Am. Chem. Soc. 126 (2004) 10212.
[38] A.J. Arduengo III, S.F. Gamper, J.C. Calabrese, F. Davidson, J. Am. Chem. Soc. 116 (1994) 4391.
[39] C.W.K. Gstöttmayr, V.P.W. Böhm, E. Herdtweck, M. Grosche, W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1363.
[40] G. Altenhoff, R. Goddard, C.W. Lehmann, F. Glorius, Angew. Chem. Int. Ed. 42 (2003) 3690.
[41] S. Caddick, F.G.N. Cloke, P.B. Hitchcock, A.K. de K. Lewis, Angew. Chem. Int. Ed. 43 (2004) 5824.
[42] P.L. Arnold, F.G.N. Cloke, T. Geldbach, P.B. Hitchcock, Organometallics 18 (1999) 3228.
[43] S. Caddick, F.G.N. Cloke, G.K.B. Clentsmith, P.B. Hitchcock, D. McKerrecher, L.R. Titcomb, M.R.V. Williams, J. Organomet. Chem. 617–8 (2001) 635.
[44] X. Hu, I. Castro-Rodriguez, K. Meyer, Chem. Commun. (2004) 2164.
[45] A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, Organometallics 12 (1993) 3405.
[46] X. Hu, I. Castro-Rodriguez, K. Meyer, Organometallics 22 (2003) 3016.
[47] X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, Organometallics 23 (2004) 755.
[48] V.P.W. Böhm, C.W.K. Gstöttmayr, T. Weskamp, W.A. Herrmann, J. Organomet. Chem. 595 (2000) 186.
[49] W.A. Herrmann, G. Gerstberger, M. Spiegler, Organometallics 16 (1997) 2209.
[50] L.G. Bonnett, R.E. Douthwaite, R. Hodgson, J. Houghton, B.M. Kamski, S. Simonovi, Dalton Trans. (2004) 3528.
[51] S. Gründemann, M. Albrecht, A. Kovacewic, J.W. Faller, R.H. Crabtree, J. Chem. Soc., Dalton Trans. (2002) 2163.
[52] L.J. Xu, W.P. Chen, J.F. Bickley, A. Steiner, J.L. Xiao, J. Organomet. Chem. 598 (2000) 409.
[53] G.-X. Liu, H.-B. Song, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Z.-Z. Zhang, Polyhedron 22 (2003) 1515.
[54] D.S. McGuinness, W. Müller, P. Wasserscheid, K.J. Cavell, B.W. Skelton, A.H. White, U. Englert, Organometallics 21 (2002) 175.
[55] K.S. Coleman, S. Turberville, S.I. Pascu, M.L.H. Green, J. Organomet. Chem. 690 (2005) 653.
[56] F. Glorius, G. Altenhoff, R. Goddard, C. Lehmann, Chem. Commun. (2002) 2704.
[57] M.C. Perry, X. Cui, K. Burgess, Tetrahedron: Asymmetry 13 (2002) 1969.
[58] H. Lebel, M.d.R. Sanchez Salvatori, F. Belanger-Gariepy, Acta Cryst. 60E (2004) m755.
[59] H. Lebel, M.K. James, A.B. Charette, S.P. Nolan, J. Am. Chem. Soc. 126 (2004) 5046.
[60] A.C. McKinnon, M.C. Baird, J. Organomet. Chem. 683 (2003) 114.
[61] D.S. Clyne, J. Jin, E. Genest, J.C. Gallucci, T.V. Rajan Babu, Org. Lett. 2 (2000) 1125.
[62] J. Pytkowicz, S. Roland, P. Mangeney, G. Meyer, A. Jutland, J. Organomet. Chem. 678 (2003) 166.
[63] R. Fränkel, J. Kniczek, W. Ponikwar, H. Nöth, K. Polborn, W.P. Fehlhammer, Inorg. Chim. Acta 312 (2001) 23.
[64] R.E. Douthwaite, M.L.H. Green, P.J. Silcock, P.T. Gomes, Organometallics 20 (2001) 2611.
[65] R.E. Douthwaite, D. Häussinger, M.L.H. Green, P.J. Silcock, P.T. Gomes, A.M. Martins, A.A. Danopoulos, Organometallics 19 (1999) 4584.
[66] A. Hollemann, N. Wiberg, Lehrbuch der Anorganischen Chemie, 91st–100th edition, Walter de Gruyter, New York, Berlin, 1985.
[67] J.F. Britten, C.J.L. Lock, Z. Wang, Acta Cryst. 48C (1992) 1600.
[68] H.M.J. Wang, C.S. Vasam, T.Y.R. Tsai, S.-H. Chen, A.H.H. Chang, I.J.B. Lin, Organometallics 24 (2005) 486.
[69] P.J. Barnard, M.V. Baker, S.J. Berners-Price, B.W. Skelton, A.H. White, Dalton Trans. (2004) 1038.
[70] M.V. Baker, P.J. Barnard, S.J. Berners-Price, S.K. Brayshaw, J.L. Hickey, B.W. Skelton, A.H. White, Dalton Trans. (2006) 3708.
[71] H.G. Raubenheimer, P.J. Olivier, L. Linderque, M. Desmet, J. Hrusak, G.J. Kruger, J. Organomet. Chem. 544 (1997) 91.
[72] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 408 (1991) 271.
[73] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 375 (1989) 147.
[74] P.L. Arnold, S. Pearson, Coord. Chem. Rev. 251 (2007) 596.
[75] M. Albrecht, Chem. Commun. (2008) 3601.
[76] L.N. Appelhans, D. Zuccaccia, A. Kovacevic, A.R. Chianese, J.R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R.H. Crabtree, J. Am. Chem. Soc. 127 (2005) 16299.
[77] M. Niehues, G. Kehr, G. Erker, B. Wibbeling, R. Fröhlich, O. Blacque, H. Berke, J. Organomet. Chem. 663 (2002) 192.
[78] B. Royo, E. Herdtweck, C.C. Romão, Eur. J. Inorg. Chem. (2004) 3305.
[79] Search performed by P.G. Jones for the manuscript of Ref. [75].
[80] F.E. Hahn, T. von Fehren, R. Fröhlich, Z. Naturforsch. 59b (2004) 348.
[81] O. Buisine, G. Berthon-Gelloz, J.-F. Briere, S. Sterin, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, I.E. Marko, Chem. Commun. (2005) 3856.
[82] S. Saravanakumar, A.I. Oprea, M.K. Kindermann, P.G. Jones, J. Heinicke, Chem. Eur. J. 12 (2006) 3143.
[83] I.S. Edworthy, M. Rodden, S.A. Mungur, K.M. Davis, A.J. Blake, C. Wilson, M. Schroder, P.L. Arnold, J. Organomet. Chem. 690 (2005) 5710.
[84] T.A. Schmedake, M. Haaf, B.J. Paradise, A.J. Millevolte, D.R. Powell, R. West, J. Organomet. Chem. 636 (2001) 17.
[85] S.B. Clendenning, B. Gehrhus, P.B. Hitchcock, D.F. Moser, J.F. Nixon, R. West, Dalton Trans. (2002) 484.
[86] B. Gehrhus, P.B. Hitchcock, M.F. Lappert, H. Maciejewski, Organometallics 17 (1998) 5599.
[87] A.G. Avent, B. Gehrhus, P.B. Hitchcock, M.F. Lappert, H. Maciejewski, J. Organomet. Chem. 686 (2003) 321.
[88] X. Cai, B. Gehrhus, P.B. Hitchcock, M.F. Lappert, Can. J. Chem. 78 (2000) 1484.
[89] H. Yoo, P.J. Carroll, D.H. Berry, J. Am. Chem. Soc. 128 (2006) 6038.
[90] W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, B. Solouki, M. Wagner, Angew. Chem. Int. Ed. 31 (1992) 1485.
[91] O. Kühl, P. Lönnecke, J. Heinicke, Inorg. Chem. 42 (2003) 2836.
[92] F. Ullah, O. Kühl, G. Bajor, T. Veszprémi, P.G. Jones, J. Heinicke, Eur. J. Inorg. Chem. (2009) 221.
[93] M. Tafipolski, W. Scherer, K. Öfele, G. Artus, B. Pedersen, W.A. Herrmann, G.S. McGrady, J. Am. Chem. Soc. 124 (2002) 5865.
[94] J. Heinicke, A. Oprea, M.K. Kindermann, T. Karpati, L. Nyulaszi, T. Veszpremi, Chem. Eur. J. 4 (1998) 541.
[95] W.A. Herrmann, F.C. Munck, G.R.J. Artus, O. Runte, R. Anwander, Organometallics 16 (1997) 682.
[96] A.H. Hoveyda, A.R. Zhugralin, Nature 450 (2007) 243.
[97] L. Jafarpour, S.P. Nolan, J. Organomet. Chem. 617–8 (2001) 17.
[98] S.T. Nguyen, T.M. Trnka, in: R.H. Grubbs (Ed.), Handbook of Metathesis, Wiley, Weinheim, 2003, p. 61.
[99] A. Fürstner, H. Krause, L. Ackermann, C.W. Lehmann, Chem. Commun. (2001) 2240.
[100] S. Prühs, C.W. Kehmann, A. Fürstner, Organometallics 23 (2004) 280.
[101] O. Kühl, Can. J. Chem. 85 (2007) 230.
[102] P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek, P. Dierkes, Chem. Rev. 100 (2000) 2741.
[103] O. Kühl, Chem. Soc. Rev. 36 (2007) 592.
[104] O. Kühl, Functionalised N-Heterocyclic Carbene Complexes, Wiley & Sons, Chichester, 2009.
[105] L.A. Van der Veen, P.H. Keeven, G.C. Shoemaker, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. Van Leeuwen, M. Lutz, A.L. Spek, Organometallics 19 (2000) 872.
[106] P.L. Arnold, S.T. Liddle, Chem. Commun. (2006) 3959.
[107] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.
[108] S.T. Liddle, I.S. Edworthy, P.L. Arnold, Chem. Soc. Rev. 36 (2007) 1732.
[109] R.J. Goddard, R. Hoffmann, E.D. Jemmins, J. Am. Chem. Soc. 102 (1980) 7667.

[110] A.J. Arduengo III, F. Davidson, R. Krafczyk, W.J. Marshall, M. Tamm, Organometallics 17 (1998) 3375.
[111] N. Fröhlich, U. Pidun, M. Stahl, G. Frenking, Organometallics 16 (1997) 442.
[112] J.C. Green, B.J. Herbert, Dalton Trans. (2005) 1214.
[113] K. Denk, P. Sirsch, W.A. Herrmann, J. Organomet. Chem. 649 (2002) 219.
[114] L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, J. Organomet. Chem. 690 (2005) 5407.
[115] O. Kühl, S. Goutal, Cryst. Growth Des. 5 (2005) 1875.
[116] S.A. Mungur, A.J. Blake, C. Wilson, J. McMaster, P.L. Arnold, Organometallics 25 (2006) 1861.
[117] D. Patel, S.T. Liddle, S.A. Mungur, M. Rodden, A.J. Blake, P.L. Arnold, Chem. Commun. (2006) 1124.
[118] H. Braband, U. Abram, Chem. Commun. (2003) 2436.