Beyond Conventional *N*-Heterocyclic Carbenes: Abnormal, Remote, and Other Classes of NHC Ligands with Reduced Heteroatom Stabilization

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1. Introduction

The organometallic chemistry of *N*-heterocyclic carbenes (NHCs) has experienced explosive development during the last few years, and the topic remains the main focus of many outstanding research programs.[1] The ongoing popularity of this research area is certainly due to the development of extremely active catalyst systems comprising such carbene ligands. This is perhaps most clearly illustrated by the second-generation olefin metathesis catalysts developed by Grubbs and Nolan,[2] or by the cross-coupling catalysts introduced by Organ and currently commercialized by Aldrich.[3]

The potential of NHCs as ligands for transition metals has been pioneered, in particular, by the independent work of Öfele and Wanzlick, and, later, also by Lappert and Stone in the 1960s and early 1970s.[4] Despite the considerable progress achieved by these groups, the topic did not attract widespread attention until Arduengo reported on the isolation and stability of free *N*-heterocyclic carbenes.[5] This discovery marked a watershed in carbene complex chemistry, and these ligands became available from convenient and inexpensive precursors such as imidazolium salts. A key factor in the remarkable stability of Arduengo-type free carbenes lies in the almost-excessive heteroatom stabilization, because of the presence of two heteroatoms, at least one of which is typically a nitrogen in a position α to the carbene carbon (**A** in Figure 1).[5] The chemistry—and, specifically, the coordination behavior—of these "classical" heterocyclic carbenes has been reviewed extensively: monographs as well as special issues have dwelled on this topic.[1]

Rather dormant in the beginning of the new millennium, the concept of heterocyclic carbene ligands that are not stabilized by two adjacent heteroatoms, as in Arduengo-type carbenes, and also not necessarily with heteroatoms placed in a position α to the carbene carbon was revived by a serendipitous discovery of C4 bonding in imidazolylidenes.[6] The large class of heterocyclic carbenes that can be grouped together under the title of this review include, in particular, imidazolium-derived ligands that bind the metal via the C4 or C5 carbon (**B** and **C** in Figure 1) as well as the pyridylidene family with only one heteroatom present in the heterocyclic skeleton (**D**−**F** in Figure 1). Variations on this

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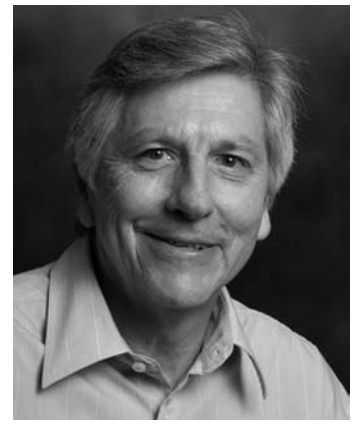
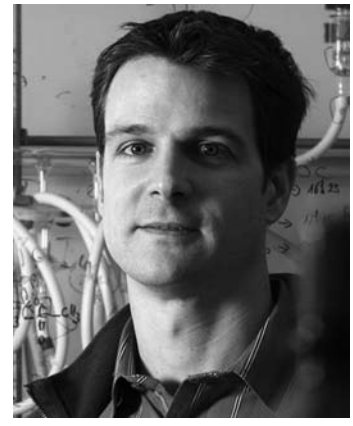
Oliver Schuster studied chemistry at the Technical University of Munich (Germany) and obtained his Ph.D. there in 2005, under the supervision of Prof. Hubert Schmidbaur. For postdoctoral studies, he moved as a Feodor Lynen Fellow (Alexander von Humboldt Foundation) to Prof. Helgard Raubenheimer's group (University of Stellenbosch) in South Africa, where he investigated the concept of remote *N*-heterocyclic carbenes. Oliver is currently a Leopoldina Postdoctoral Fellow (German Academy of Sciences) in the laboratory of Prof. Martin Albrecht at the University of Fribourg in Switzerland. His current efforts are dedicated toward the establishment of new routes to 4-pyridylidene metal complexes to overcome limitations in their synthesis.



Helgard G. Raubenheimer was born in South Africa. He studied at the University of Stellenbosch near Cape Town, and, after 28 years as senior lecturer, professor, and HOD at the University of Johannesburg (then RAU), he returned in 1998 to Stellenbosch as Head of Department (Chemistry and Polymer Science) and Professor in Inorganic Chemistry. His main research interests are the chemistry of gold and reactivity of complexes with carbene ligands. A long time ago, he worked for two years with E.O. Fischer in Munich and with Dieter Seebach in Zurich. Recent collaborators include Hubert Schmidbaur, Wolfgang Herrmann, and Gernot Frenking.

Liangru Yang is a native of People's Republic of China. She obtained her B.Sc. in Chemistry in 1998 and Ph.D. in 2003 at Zhengzhou University, working with Academician Yangjie Wu on ferrocene chemistry. After postdoctoral research at Innsbruck University with Prof. M. R. Buchmeiser, at University of Fribourg with Prof. A. von Zelewsky and Prof. M. Albrecht, and EPFL with Dr. O. Mamula, she joined He'nan University of Technology in 2007. Her current research interests focus on the development of transition-metal-catalyzed reactions and their application in organic synthesis.



Martin Albrecht studied chemistry at the University of Bern (Switzerland) and received his Ph.D. under the supervison of Prof. Gerard van Koten from Utrecht University (The Netherlands) in 2000. After postdoctoral studies with Robert H. Crabtree (Yale) and with Ciba SC (Basel, Switzerland), he joined the University of Fribourg as an Alfred Werner Assistant Professor. His research program currently revolves around (bio)organometallic themes, with a special emphasis on developing new carbene ligands for catalytic and electronic applications. He has recently been awarded a prestigious ERC Starting Grant from the European Research Council.

theme are found via the replacement or displacement of one N atom, thus providing carbenes derived from pyrazolium, isothiazolium, and even quinolinium salts that contain a stabilizing heteroatom in a remote position (**G**−**J** in Figure 1). Recently, carbenes such as **K**, which are comprised of only one heteroatom and lack delocalization through the heterocycle, have been discovered as versatile ligands, thus constituting another important class of carbenes with low heteroatom stabilization. Both the synthesis of the organometallic complexes of these ligands as well as the (catalytic) properties of the coordinated metal centers generally show distinct differences, compared to the more classical NHC complexes, such as C2-metallated imidazolylidenes. This review intends to describe such differences and highlights the chemical peculiarities of these types of *N*-heterocyclic carbene complexes. It introduces, in a qualitative manner, the synthetic routes that have been established for the preparation of such complexes, covering the literature from the very beginning of activities in this area up to 2008. While specialized reviews on some aspects of the present topic have recently appeared,[7] a comprehensive overview of the subject has not been available thus far. Rather than just being descriptive, the present account is mainly directed toward the impact of these still unusual metal-carbene bonding modes on the electronic properties and on the new catalytic applications that have been realized by employing such new carbene complexes. As a consequence of our focus on complexes with less-stabilized *heterocyclic* ligands, systems comprising *acyclic* carbenes have not been included, and the interested reader is, instead, referred to the pioneering and

Table 1. Available Methods for NHC Metallation

metallation method	ligand system
via free carbene	• 2-imidazolylidenes and related ligands[a] • 4-imidazolylidenes (via 2-imidazolylidene rearrangement) • cyclic (amino)(alkyl)carbenes (CAACs) and (amino)(ylide)carbenes (AYCs)
C−H bond activation	• 2-imidazolylidenes and related ligands[a] • 4-imidazolylidenes • 4-triazolylidenes • 3-pyrazolylidenes • 2-, 3-, 4-pyridylidenes • CAACs and AYCs
C−E bond activation	• 2-imidazolylidenes ($E = CH_3$: activation with Ag^I; $E = CO_2^-$: activation with d^8 metals; C=C activation of enetetramines) • 2-pyridylidenes ($E = PR_2$: activation with Pd^{II})
C−X oxidative addition	• 2-imidazolylidenes and related ligands[a] • 4-imidazolylidenes • 3- and 4-pyrazolylidenes • 2-, 3-, 4-pyridylidenes • CAACs
transmetallation	• 2-imidazolylidenes (predominantly from Ag complexes) • 3-pyrazolylidenes (from Ag, Cr) • 4-imidazolylidenes • 4-triazolylidenes • 2-pyridylidenes (from Cr)
heteroatom alkylation	• 3-pyrazolylidenes • 2-, 3-, 4-pyridylidenes
cycloaddition to Fischer carbenes	• 2-imidazolylidenes and related ligands[a] • 3-pyrazolylidene • 2- and 4-pyridylidene • expanded ring NHCs

[a] Includes NHCs with two different stabilizing heteroatoms in a position α to the carbene.

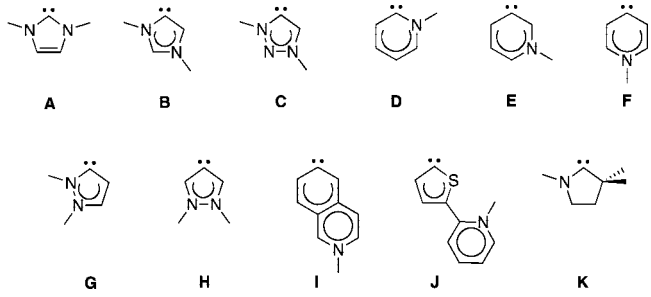
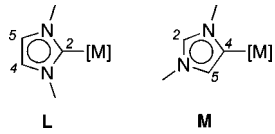


Figure 1. *N*-heterocyclic carbenes, including the "classical" NHC representative (**A**) and representatives of subclasses comprising reduced heteroatom stabilization (**B**−**K**); all are shown in their carbene form.

ongoing work of Bertrand and co-workers.[8,9] Similarly, heteroatom-free cyclic carbenes are not further detailed here.[10]

In the literature, different terms have been coined to describe the bonding of such less-stabilized carbenes to metal fragments. For example, terms such as "wrong way", "abnormal", "unusual", or "nonclassical" have been used to describe C4/C5-bound imidazolylidenes (**B**). Throughout this review, we refer to "abnormal" carbenes as those NHC ligands for which a canonical valence bond representation requires the introduction of additional formal charges on some nuclei (e.g., **B**, **C**, **E**, or **I** in Figure 1). The term "remote" carbene indicates that no heteroatom is located in a position α to the carbene carbon (e.g., **E**, **F**, **H**, **I** in Figure 1); it may be possible to write uncharged contributing resonance structures for the free ligand.[11]

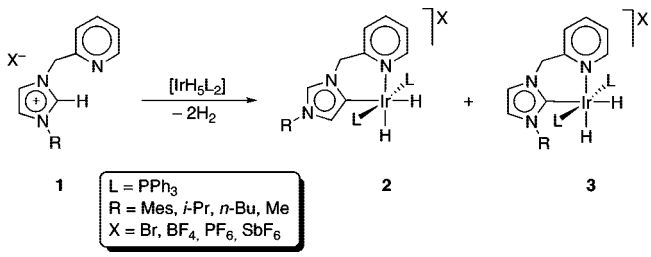
A final preliminary remark concerns the controversial classification of all these ligands as "carbenes". While this classification implies that the ligand is a neutral donor, in all instances, a zwitterionic canonical representation consisting of a carbanionic and a cationic iminium center may be similarly appropriate and even necessary. When bonded, this negative charge is obviously transferred to the metal in one canonical form. Clearly, the borderline between the two limiting representations is continuous, and the issue of whether a ligand is, in reality, a carbene or not may become semantic. In the case of the C2-bound imidazolylidenes, experimental and theoretical studies are in agreement with a relatively small π-contribution to the M−C bond only (M = electron-rich metal center),[12−14] and, hence, the M−C interaction is typically represented by a single bond. However, detailed studies involving less-stabilized *N*-heterocyclic carbenes are still rare. Often, crystallographic and NMR spectroscopic arguments have been put forward to support one resonance form or the other. Despite the fact that the metal−carbon bonds in Fischer carbenes and in *N*-heterocyclic carbenes are very much related, different means of representation have evolved in the literature. In this review, single bonds are used to represent $M-C_{carbene}$ interactions, which is consistent with the accepted representations of conventional NHC−metal bonds and even other metal−ligand bonds that are known to comprise significant π-character (e.g., the M−CO bond in carbonyl complexes). Classical Fischer-type carbene complexes are written with an M=C double bond, in agreement with a different convention developed in the 1960s. A more complete discussion of these



L M

Figure 2. Metal complexes comprising normal (**L**) and abnormal (**M**) imidazolylidene ligands bound at the C2 and the C4 position, respectively.

Scheme 1



1 2 3

considerations is provided in Section 3, after synthetic strategies have been introduced. The review concludes with applications of such carbene complexes in catalysis.

2. Methods of Ligand Complexation

A variety of different methods have been established for the complexation of less-heteroatom-stabilized NHC ligands. Some of these methods are very similar to those yielding normal C2-bound imidazolylidene complexes, while others are unique to a particular subclass of NHC ligands. The different methods of NHC ligand complexation are compiled in Table 1. Further details are provided in this section, which has been organized according to the different ligand systems involved, rather than according to the methods used.

2.1. Complexes with C4-Bound Imidazolylidenes

2.1.1. C−H Bond Activation of Unsubstituted 2H−Imidazolium Salts

Crabtree and co-workers[15] were the first to observe abnormal C4 metallation of imidazolium salts a few years ago (Figure 2). The reaction of pyridine-functionalized imidazolium salt **1** with the iridium polyhydride $IrH_5(PPh_3)_2$ also afforded the iridium (III) complex **2**, which is comprised of a carbene that is abnormally bound through C4 rather than C2 (see Scheme 1). The coordination mode was deduced from NMR spectroscopy and was unambiguously confirmed by X-ray crystallographic analysis. No interconversion to the presumably more-stable normal carbene complex **3** was detected. Hence, product formation seems to be kinetically controlled. These results indicated, for the first time, that it may not always be safe to assume C2 bonding when preparing NHC complexes *in situ* from imidazolium salts and a metal precursor.

The activation of the C4−H bond in imidazolium salts such as **1** is remarkable when considering the acidity difference between the two types of heterocyclic protons. The acidity of the proton attached to C2 has been determined experimentally and by calculation ($pK_a = 24 \pm 1$).[16] This value is 9 pK_a units lower than that calculated for the C4-bound proton ($pK_a = 33$).[17] The difference suggests that aspects other than the acidity of the protons control the regioselectivity of metallation.

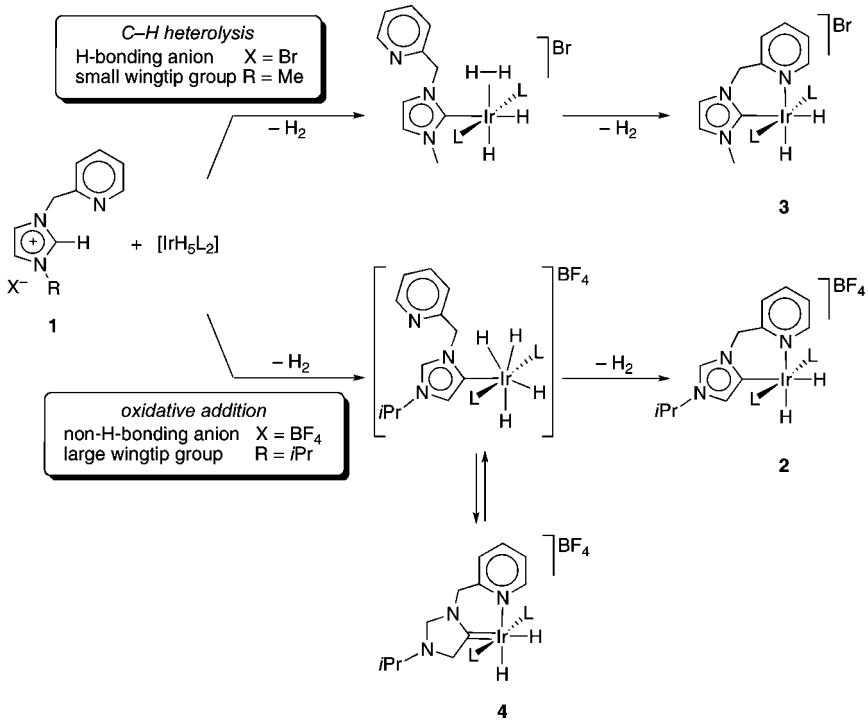
The selective formation of C4- or C2-bound carbene complexes with iridium hydrides seems to be dependent on multiple factors.[18] Calculations suggest that C2 bonding and C4 bonding proceed via distinctly different reaction pathways involving either C2−H heterolytic bond cleavage or C4−H oxidative addition, implicating an iridium(V) species (see Scheme 2).[19] Such mechanistic proposals were further supported by experimental data, which demonstrate that product distribution—and, thus, the site of metallation—is strongly anion-dependent. Large anions such as BF_4^- typically are only weak partners for hydrogen bonding and effect small changes in charge distribution. Consequently, such anions favor an oxidative addition pathway, leading to carbene C4 bonding. In contrast, smaller counterions such as Br^- accelerate heterolytic C−H bond cleavage through hydrogen bonding, thus supporting a proton migration from the imidazolium moiety to the metal-bound hydride. Accordingly, such anions preferentially yield C2-bound carbenes. Time-dependent NMR analysis of the formation of **2** has revealed the intermediate formation of a hydrogenated imidazolinylidene species **4**.[15] This result is consistent with an oxidative addition pathway that is comprised of an $[IrH_4]^+$ species, which may reversibly transfer H_2 from the metal center to the imidazolylidene heterocycle. Notably, chelation of the pyridine moiety is not essential and similar selectivities in C−H bond activation have been observed with simple imidazolium salts upon reaction with $[IrH_5(PPh_3)_2]$ in the presence of pyridine.[20]

Recent studies by Esteruelas et al. on the metallation of imidazolium salts such as **1** with the osmium hydride precursor $[OsH_6(PiPr_3)_2]$ have confirmed the relevance of the counteranion for the regioselectivity of metallation.[21] Metallation at the C4 position is again favored with large and unpolarized $[BPh_4]^-$ anions, whereas imidazolium bromides afford, almost exclusively, the C2-metallated carbene. Time-dependent analysis of carbene formation indicated that kinetic factors are more relevant for C4 coordination than for C2 coordination. In addition, isomerization of the C4-bound carbene to its thermodynamically favored C2-bound isomer has been accomplished under strongly acidic conditions in the presence of HBF_4.

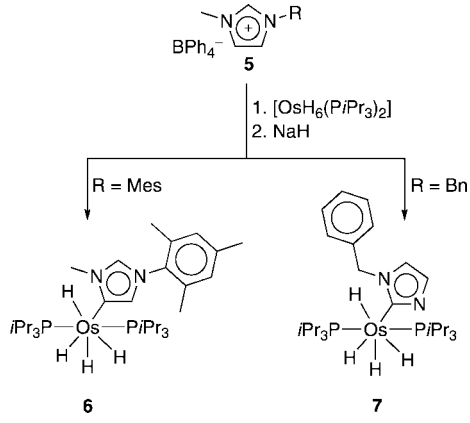
The regioselectivity of metallation is further influenced by the wingtip substituents on the imidazolium salt.[22] A mesityl substituent promotes C4 bonding to the Os center **6**, while the corresponding benzyl-substituted imidazole gives the C2-bound carbene complex **7** in high yields (see Scheme 3). The outcome of this reaction can be explained by invoking steric hindrance between the isopropyl groups of the phosphines and the imidazolium wingtip groups, which is more pronounced for mesityl than for the comparatively flexible benzyl substituent.

A driving force different from counterion effects and steric discrimination is required to rationalize the selective C4 metallation of the imidazolium salt **8**, which is comprised of a chelating phosphine wingtip group to give complex **10** (see Scheme 4).[23] With $[Ir(cod)Cl]_2$ (where cod = 1,5-cyclooctadiene), initial phosphine coordination and formation of **9** has been observed. Subsequent C−H bond activation occurs exclusively at the C4-position and is reversible with ethylene-linked bidentate ligands, yet slow and irreversible with the analogous methylene-bridged derivative **9a**. Base-mediated reductive elimination affords the corresponding iridium(I) complexes **11**. Furthermore, neither a small wingtip group nor a hard chloride counterion (not shown) succeeds in promoting C2−H bond activation. Perhaps the affinity of iridium(I) for olefinic C=C bonds

Scheme 2



Scheme 3



might also play a role in the regioselectivity of iridation. In addition, the constrained bulk of the coordinated phosphine ligand could increase the steric sensitivity of the Ir center.

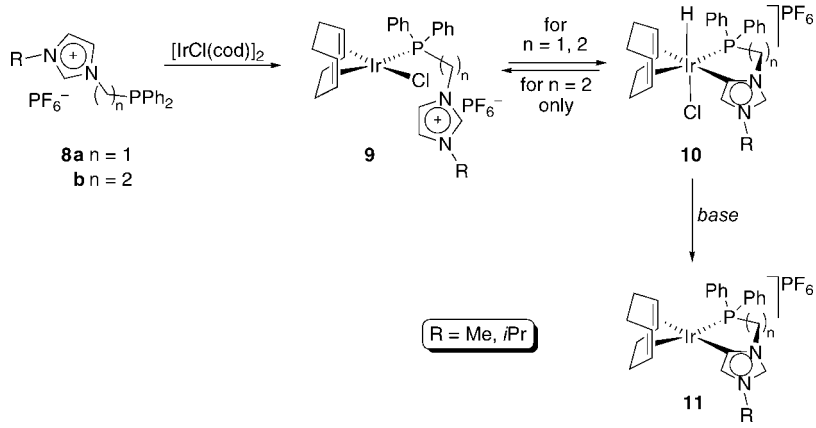
Additives also have a distinct influence on the regioselectivity of imidazolium palladation. Metallation of the hydrochloride adduct of *N*,*N*′-dimesitylimidazol-2-ylidene (IMes·HCl) with $Pd(OAc)_2$, in the presence of Cs_2CO_3 as a base, occurs selectively at the C2-position, thus affording the normal bis(carbene) complex **12** (see Scheme 5).[24] In the absence of Cs_2CO_3, however, the heteroleptic complex **13** is formed. It is comprised of one C2-bound NHC ligand and one carbene that is bound abnormally at C4 to the palladium center (see Scheme 5). Interestingly, an X-ray structure analysis shows that the two different Pd−C bond lengths are identical within experimental error (Pd−C = 2.019(13) and 2.021(11) Å for the normal and abnormal carbene, respectively). According to the mechanistic model used for iridium metallation (*vide supra*), the CO_3^{2-} anion may promote heterolysis of the most acidic C−H bond, thus favoring formation of C2-bound complexes. In the absence of a base, the C4−H bond is activated, probably by oxidative addition, to give **13**. The *trans* orientation of the two carbene ligands seems to play a decisive role for C4 bonding. In rigidly *cis* coordinating, chelating bis(carbene) complexes, exclusive C2 bonding is observed under identical base-free metallation conditions.[25,26]

2.1.2. C−H Bond Activation of C2-Substituted Imidazolium Salts

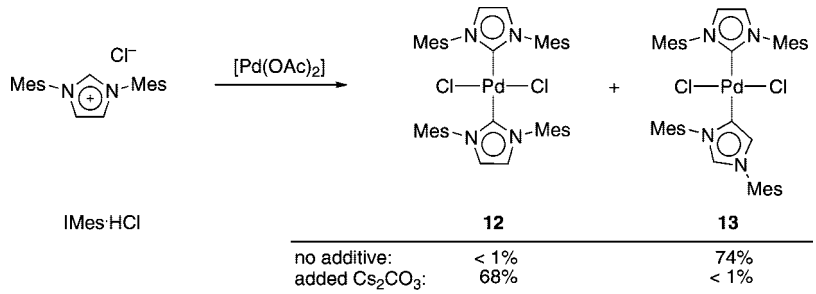
Although the previous section illustrates the feasibility of C4 bonding with 2*H*-imidazolium salts, which may be particularly relevant for *in situ* complex formation, unprotected imidazolium salts are primarily metallated at the C2-position. A rational route toward C4-bound carbenes therefore includes the selective protection of the most acidic C2-position, e.g., by incorporating alkyl or aryl substitutents. Thus, oxidative addition of the C4−H bond of the tetraalkylated C2-blocked imidazolium salt **14** to zerovalent Pt(norbornene)$_3$, in the presence of equimolar amounts of the free carbene IMes, yields the platinum hydride complex **15** with the mixed C2- and C5-bound carbenes both attached to platinum (see Scheme 6).[27] The formation of this complex has been proposed to occur stepwise. Initial coordination of the basic IMes provides the necessary electron density at the central metal to allow for subsequent oxidative addition of the imidazolium C4−H bond. A similar reaction sequence may apply to the formation of the abnormal/normal $[Pd(IMes)_2Cl_2]$ complex **13** (*vide supra*). When using the asymmetrically 1,2,3-trialkylated imidazolium precursor **16**, a mixture of C4- and C5-bound isomers **17a** and **17b** is formed in a 3:1 ratio. This product distribution might reflect a moderate steric preference in the transition state of the oxidative addition.

Complexes **17** are unstable in the presence of certain alkenes, such as styrene, and undergo reductive elimination. The C4-bound carbene is significantly more prone to reductive elimination than the C2-bound IMes ligand, leading to the exclusive formation of the imidazolium salt **16** and

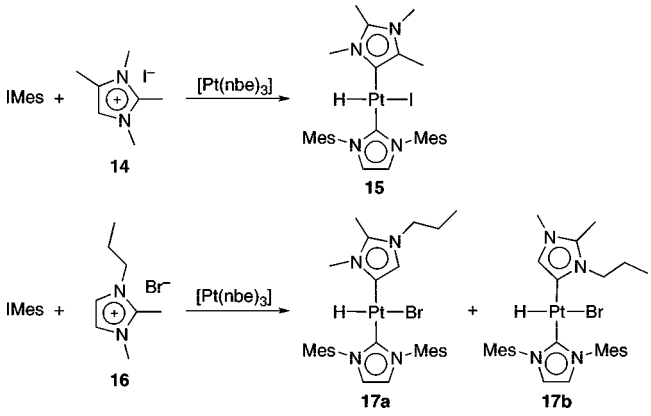
Scheme 4



Scheme 5



Scheme 6



the Pt^0 complex, Pt(IMes)(diolefin). No products resulting from reductive elimination of the normal C2-bound carbene nor from alkene insertion into the Pt−H bond are observed. Both, electronic and steric reasons may account for the observed reaction outcome, and further investigations are clearly desirable.

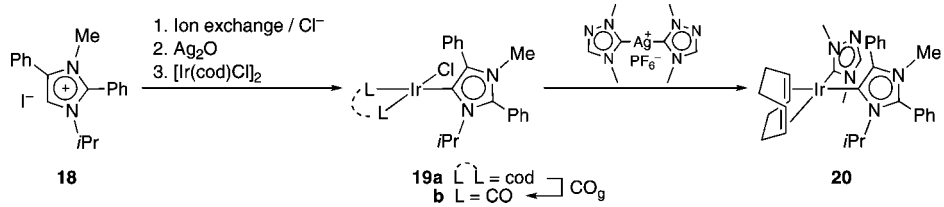
C4-bound carbene metal complexes can also be made by transmetallation from the corresponding silver complexes. Precursor Ag−NHC complexes are typically generated from silver oxide (Ag_2O) and imidazolium salts.[28] To achieve selective metallation, it is necessary to protect both the C2- and C5-positions. For example, the disubstituted imidazolium salt **18** undergoes clean deprotonation in the presence of Ag_2O.[20] Subsequent transmetallation of the presumably formed silver complex with $[Ir(cod)Cl]_2$ yields the Ir^+ complex **19a**, and after the exchange of spectator ligands (cod for CO) complex **19b** (see Scheme 7). IR spectroscopy of this dicarbonyl complex allows for an estimation of the electron-donating ability of such C4-bound carbenes. From the observed stretching frequencies ($\nu_{CO} = 2045, 1961\ cm^{-1}$), a Tolman electronic parameter (TEP)[29] of $\nu = 2039\ cm^{-1}$ has been estimated. This value is considerably lower than for analogous C2-bound carbenes ($\nu \approx 2050\ cm^{-1}$) or basic phosphines (cf. PCy_3, $\nu = 2056\ cm^{-1}$). Hence, such C4-bound carbenes are among the best neutral donors known.

Complex **19a** has been demonstrated to be a useful metal precursor for transmetallation. In the presence of a Ag-triazolylidene, swift formation of the normal/abnormal bis-(carbene) complex **20** is observed.[30] Complexes such as **20** generally exist as multiple diastereoisomers, since rotation about the Ir−$C_{carbene}$ bonds is hampered by the two *cis*-coordinated carbene ligands. Initial attempts to separate the diastereoisomers of **20** by recrystallization have been unsuccessful; yet, this may become an attractive methodology for application in asymmetric catalysis.

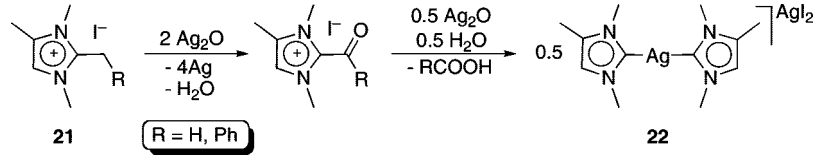
Notably, the formation of stable abnormal silver carbene complexes for transmetallation is often limited to imidazolium salts with aryl substituents at the C2-position, because primary or secondary alkyl groups have been found to be unreliable protecting groups.[31] Reaction of Ag_2O with 2-methylated or 2-benzylated imidazolium salts **21** initiates an unexpected C−C bond activation process, thus yielding the normal Ag-carbene complex **22** (see Scheme 8). A detailed analysis of the course of reaction reveals that Ag_2O is gradually oxidizing the carbon that is attached to C2 to yield acyl imidazolium salts and metallic silver. In the presence of water that is formed during this redox reaction, acyl functionalities seem to be good leaving groups and, hence, promote metallation at the C2 carbon. Consistent with this mechanistic scheme, the highest yields are obtained when a large excess of silver salt is used. A similar oxidation is effectively suppressed when a quaternary carbon (e.g. a phenyl group) is attached to C2.

A transmetallation protocol has been applied for the synthesis of a series of complexes **24** that are comprised of abnormally bound imidazolylidene-derived ligands (see

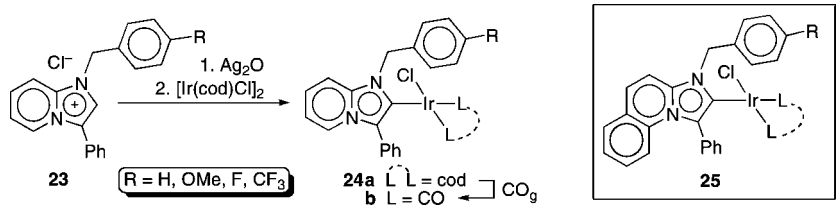
Scheme 7



Scheme 8



Scheme 9



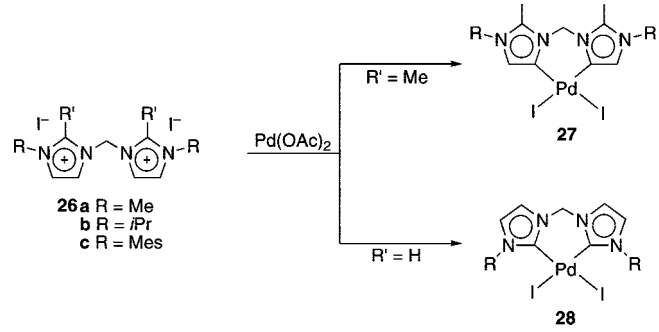
Scheme 9).[32] Remarkably, the donor properties of these ligands, according to ν_{CO} IR analyses, seem to be tunable by remote ligand modification, such as the incorporation of functional groups R in the benzyl wingtip group or by annealing another benzene unit to the carbene ligand **25**. The carbene ligand in complex **25** becomes a stronger σ donor and a better π acceptor, because of the presence of the annelated aromatic ring. However, remote ligand functionalization may also affect the CO ligand by stereoelectronic effects, which do not directly reflect the ligand donor properties (cf. Section 4).

Despite the notorious instability of C4-bound carbene silver complexes, successful transmetallations have recently been reported from silver carbenes derived from 1,2,3-trimethylimidazolium salts, which are comprised of a hydrogen at the C5-position.[33,34] While yields are generally low, product formation at room temperature indicates that the stability of the Ag complex may be sufficiently high to provide access to the desired product.

In contrast to the silver complexation with Ag_2O, palladation of C2-alkylated imidazolium salts does not affect the C−C bond. For example, metallation of the potentially bidentate carbene precursor **26** with $Pd(OAc)_2$ affords the dicarbene complex **27** without any detectable amounts of C2-bound products (see Scheme 10).[35] This procedure is virtually identical to the C2 metallation of 2*H*-imidazolium salts and avoids the presence of any free base (cf. **28**). Mechanistically, the metallation probably proceeds via an ion-pair association, which is initiated by iodide coordination to the palladium precursor to form the nucleophilic palladate $[PdI_2(OAc)_2]^{2-}$.

Because of the availability of the corresponding normal (**28**) and abnormal (**27**) palladium dicarbene complexes,[26] it has been possible to compare the respective bonding effects imposed by C2 and C4 on the metal. X-ray photoelectron spectroscopy (XPS) indicates a 0.6 eV higher bonding energy for the palladium core electrons when coordinated to the normal carbenes. This difference in electron attraction again suggests that abnormally bound carbenes are considerably

Scheme 10



stronger donors than normal carbenes. Such a conclusion is corroborated by a shift toward lower frequency in the infrared stretching vibrations of related dicarbonyl Ir^+ complexes, as previously mentioned. Moreover, the abnormal dicarbene complexes **27** are very sensitive to acids and, in the presence of H_2SO_4, demetallation occurs within a few minutes. In contrast, the normal analogues **28** are stable under identical conditions, even at elevated temperatures.[36] The former reactivity has been suggested to reflect an increased nucleophilicity of the palladium(II) center in **27**, because of the stronger donor ability of the C4-bound carbene, compared to the 2-imidazolylidenes. Theoretical studies by Frenking and co-workers support this conclusion.[37] The difference in donor ability has been rationalized predominantly by the higher energy of the σ lone-pair that belongs to the carbon in C4-bound carbenes. Interestingly, these calculations further suggest a virtually equal relative π contribution to the overall $M-C_{carbene}$ bond from C2- and C4-bound carbenes.

Unequivocal evidence for a strong electronic impact of the imidazolylidene bonding mode has been provided by studies on the sterically comparable dicarbene complexes **29** and **30** with C2- and C4-bound dicarbene ligands, respectively (see Figure 3).[38] Structural disparity between the two complexes arises predominantly because of the different Pd−Cl bond lengths, as a consequence of the stronger *trans* influence of the C4-bound carbene ligand. However, the

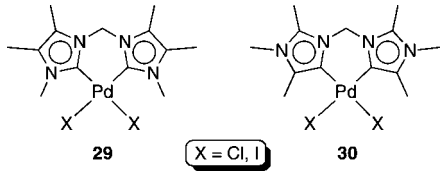
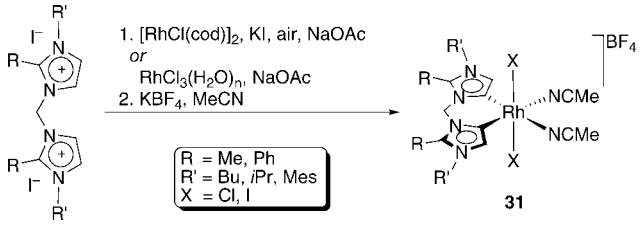


Figure 3. Sterically identical palladium(II) complexes that are comprised of differently bound dicarbene ligands.

Scheme 11



reactivity of the complexes varies considerably. Coordination to Ag^+, acid lability, and easier reductive carbene elimination occur in the C4-bound carbene complexes, while the C2-bound complexes **29** are inert under identical conditions. These results indicate that the carbene ligand binding modes in the two complexes differ to such an extent that the complex reactivity, which is typically determined by the molecular orbitals located on the metal, is substantially influenced.

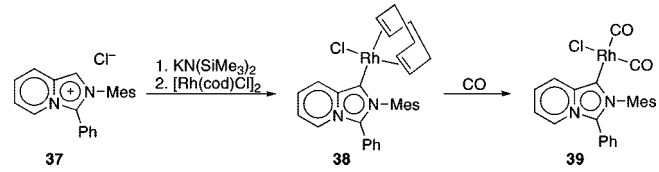
Using a similar C−H bond activation protocol, related rhodium(III) dicarbene complexes **31** were also prepared (see Scheme 11).[39] The metallation, using $[Rh(cod)Cl]_2$, proceeded considerably better when the reaction was performed in the presence of air and potassium iodide (KI) as well as acetate. Detailed investigations revealed that the acetate acts as a proton scavanger rather than as a deprotonating agent. In addition, a sequential oxidation of iodide (by aerobic O_2) and, subsequently, rhodium(I) (via the *in situ* formed I_2) was proposed prior to Rh−C bond formation. The mechanism was further supported by the fact that, when starting directly from rhodium(III) precursors, diimidazolium metallation occurred in higher yields and with the formation of less side products.

With iridium(III) precursors, however, C−H bond activation at the *C*-bound CH_3 group of the diimidazolium salt **26a** was observed, thus yielding complex **33** (see Scheme 12).[33] This $C(sp^3)$−H activation pathway is similar to that observed with Ag_2O (*vide supra*). It was partially suppressed by extending the linker between the two imidazolium moieties from a methylene unit to an ethylene unit. This modification provided the abnormal dicarbene complex **34b** as the major product. These studies indicated that the direct metallation must be used with caution, because selectivity is not always guaranteed.

A related metallation procedure was applied for the successful iridation of a mixed abnormal/normal dicarbene

Scheme 13

Scheme 14

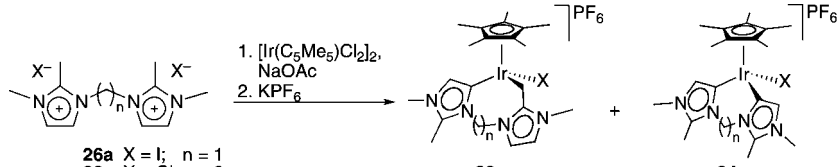


ligand precursor **35**.[33] In the presence of NaOAc, smooth formation of the chelate **36** was observed (see Scheme 13). No activation of the exocyclic C−H bond was evidenced, suggesting that the formation of complexes such as **33** might be a consequence of the initial carbene bonding to the iridium center in the abnormal bonding mode.

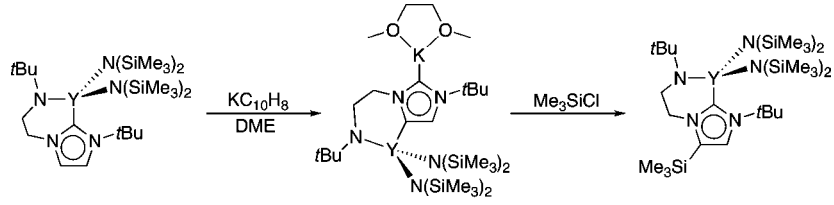
Lassaletta and co-workers synthesized NHC rhodium(I) complexes, which were comprised of a C4-bound carbene ligand (see Scheme 14).[40] The base-containing metal precursor was prepared *in situ* by reacting $[Rh(cod)Cl]_2$ with $K[N(SiMe_3)_2]$.[41] Subsequent metallation of the pyridine-anellated imidazolium salt **37**, featuring a phenyl-protected C2-position, thus yielded the C4-bound carbene rhodium(I) complex **38**. IR spectroscopic data of the corresponding dicarbonyl complex **39** were very similar to those of related iridium complexes with abnormal carbene ligands (e.g., **19b**; recall Scheme 7), in agreement with a strong electron donation by the C4-bound carbene in **39**.[9,42] The iridium(I) complex analogous to **38** was prepared by transmetallation from the corresponding Ag complex, a method which failed for rhodium.[40]

A particular type of C4 metallation is shown in Scheme 15. Upon exposure of the C2-metallated yttrium(III) carbene complex **40** to potassium naphthalenide, a rearrangement occurs that furnishes a C4-bound yttrium(III) complex **41** with a K^+ ion now attached to C2.[43] Formally, this process may be regarded as a carbene transfer from the yttrium center to potassium—a transmetallation process that is usually observed in the reverse direction. Complex **41** exists as a dimer and represents a rare example of a stable potassium carbene complex that does not undergo demetallation via a 1,2-alkyl shift. Notably, a second transmetallation with Me_3SiCl ensues, again effecting a rearrangement of the yttrium fragment to the C2-position, and concomitant formation of a new C4−Si bond in the product (complex **42**). Clearly, such a two-step metallation has great potential, in particular when different (e.g., catalytically or redox active) metal centers would be involved.

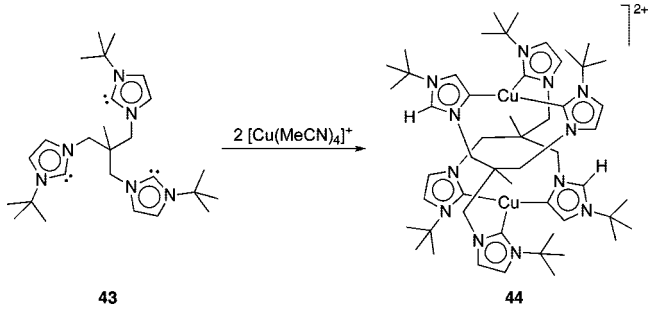
Scheme 12



Scheme 15



Scheme 16



2.1.3. Coordination to Free Carbenes

Normal C2-bound imidazolylidene metal complexes are often synthesized by a stepwise procedure that first includes the generation of a free carbene from the azolium salt with a strong base and subsequent metal coordination. Despite the attractiveness of such a method, only a few reports have appeared that describe abnormal NHC complex formation that is preceded by free carbene formation. In most instances, C4 metallation has been an unexpected result and rational protocols are not available. Copper complexes that contain nonclassical C4-bound carbene ligands have been isolated from the reaction of copper(I) salts with the tripodal carbene ligand **43** (see Scheme 16).[44] The resulting bimetallic complex **44** has each copper center bound to two C2-bound carbene units and one C4-bound carbene unit. This reaction presumably involves tautomerization of the carbene site by proton migration from C4 to C2. The NMR spectroscopic data reflect the different bonding modes ($\delta_C = 189$ for a C2 carbene, $\delta_C = 169$ for a C4 carbene). In the solid state, however, the Cu−C bonds are all identical within the 3σ range (1.983 Å ≤ Cu−C ≤ 1.988 Å).

A similar rearrangement has been observed during the reaction of the *C,N,C* pincer dicarbene ligand **45** with an Fe(II) complex (see Scheme 17).[45] X-ray analysis of the isolated complex **46b** unambiguously revealed a heteroleptic complex in which one pincer ligand displays a mixed C2/C4 bonding mode, while the other one binds via two C2 carbene carbons. Again, the similar Fe−C bond distances are independent of the bonding mode, and all fall within the 1.933−1.938 Å range.

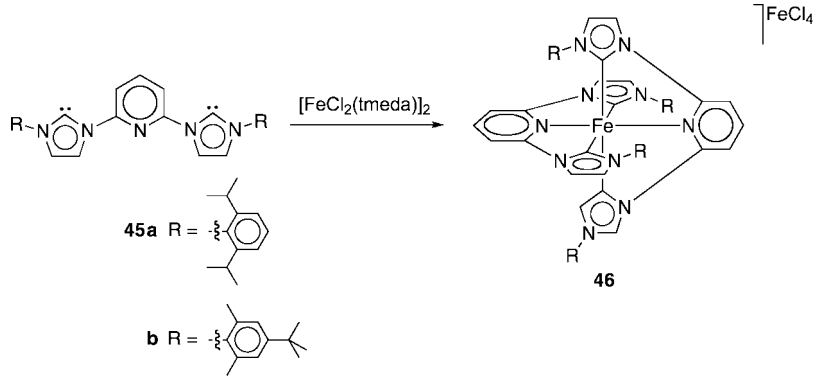
Probably a related carbene rearrangement occurs after deprotonation of the phosphine-functionalized imidazolium precursor (**47**). Reaction of the presumed carbene *in situ* with $[Ir(cod)(\mu\text{-}H)(\mu\text{-}Cl)_2]_2$ gave complex **48**, which is comprised of a C4-bound carbene (see Scheme 18).[46] A similar complex has been obtained from direct metallation of the imidazolium salt via C−H bond activation (cf. **10**; recall Scheme 4).

Conversely, coordination of a related free carbene ligand to $[Rh(coe)_2(acac)]$ has exclusively yielded the C2-bound phosphino-carbene complex.[46] Metal−hydride formation could perhaps play an important role in the unexpected carbene rearrangement when using iridium precursors. However, further studies are required to evaluate other potential reaction pathways, such as proton migration from C4 to C2 during metallation. If the latter process indeed occurs, rearrangements may become more feasible than expected.

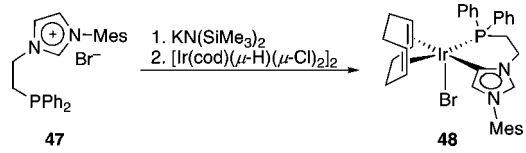
Notably, chelating groups are not required for such a carbene rearrangement. A recent study on the reactivity of the cluster compound $Ru_3(CO)_{12}$ toward free carbenes containing bulky wingtip groups has revealed the selective formation of the abnormal carbene complexes **50** (see Scheme 19).[47] The steric bulk imposed by the nitrogen substituents has been identified as a major driving force for this carbene rearrangement. When using imidazolylidenes that contain smaller methyl wingtip groups, the major product of the reaction is the trinuclear C2-bound imidazolylidene cluster **49**. Upon warming of the C4-bound carbene complex **50**, a second irreversible C−H bond activation occurs, to afford the trimetallic complex **51** in which the heterocyclic ring adopts a κ^2-bridging mode.

A related, thermally induced carbene rearrangement was observed in the Os cluster **52**, which consisted of a normally bound IMes ligand (see Scheme 20).[48] Upon thermolysis of **52** at 200 °C, the abnormal carbene complex **53** was

Scheme 17

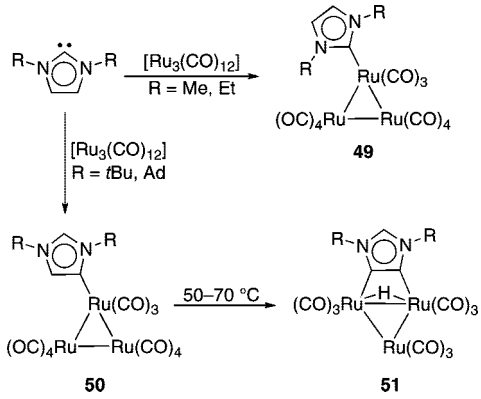


Scheme 18



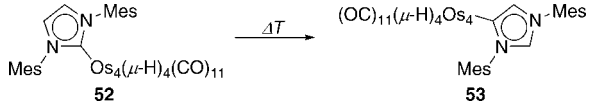
47 48

Scheme 19



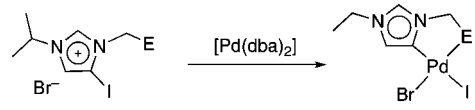
49 50 51

Scheme 20



52 53

Scheme 21



54a E = 2-pyridyl
b E = CH_2SCH_3 55

obtained, along with various other products. Because of the unusual reaction conditions, insufficient data are available to make a sensible mechanistic proposal. Undoubtedly, exciting further developments may be expected from the interaction of NHC ligands with transition-metal clusters.[49]

2.1.4. Oxidative Addition

As early as 1973, Stone and co-workers introduced the oxidative addition of thiazolium salts to low-valence metal fragments as a route to carbene complexes.[50] This protocol is particularly attractive because metallation is entirely independent of ligand CH acidity. Accordingly, the oxidative addition of 4-haloimidazolium salts also represents a rational access to C4-metallated carbenes. The potentially chelating ligand precursors **54** were prepared by sequential regioselective *H*-substitution and *N*-alkylation of iodoimidazole. Oxidative addition to zerovalent $Pd(dba)_2$ then afforded the corresponding complexes **55** that carry abnormal carbenes (see Scheme 21).[51]

2.2. Triazolylidene Complexes

The formation of carbene ligands with reduced neighboring heteroatom stabilization has recently been demonstrated when 1,2,3-triazolium salts were used as ligand precursors.[52] The neutral triazol heterocycles are available by [3 + 2] cycloaddition reactions ("click chemistry"), which is a procedure that is highly flexible and allows a variety of functionalities to be introduced in the ligand backbone. Nitrogen alkylation of the 1,4-disubstituted triazols **56** at the N3-position gives compounds **57** as precursors for abnormal carbene bonding (while N2-alkylation would provide normal carbene precursors; see Scheme 22). Metallation of triazolium salts (**57**) via C−H bond activation using $Pd(OAc)_2$ or Ag_2O, and subsequent transmetallation of the silver carbene complex with ruthenium(II), iridium(I), and rhodium(I) has been demonstrated. A preliminary assessment of the donor strength of these 1,2,3-triazolylidene ligands has been accomplished, based on the ν_{CO} stretching frequences of the iridium dicarbonyl complex **59a**. The resulting Tolman electronic parameter[29,53] compares well with those of the most basic normal carbenes (cf. also **19b**; recall Scheme 7). Adjustment of the electronic effects of the heterocycle substituents has been proposed as a method for fine-tuning the donor strength of these ligands.

2.3. Pyrazolylidene and Isothiazolylidene Complexes

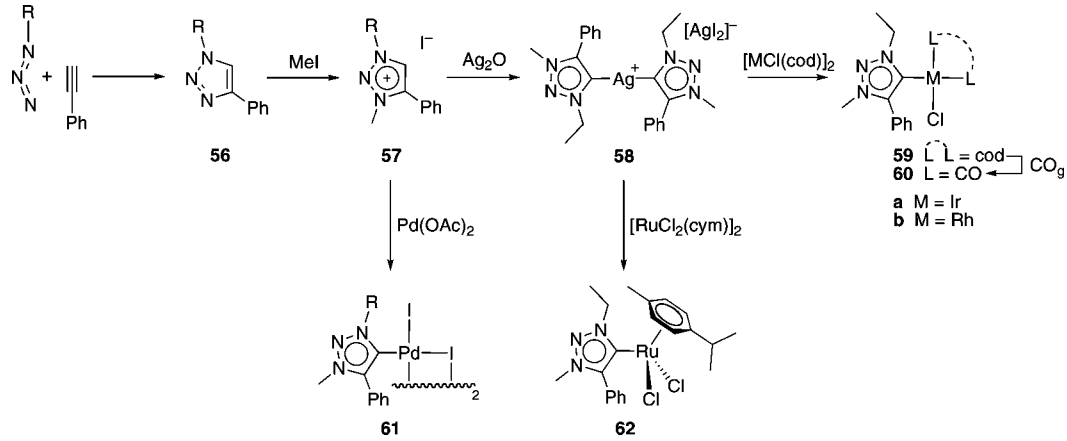
Similar to imidazolium-derived carbenes, pyrazolium metallation may give either normal or abnormal carbene ligands. However, the heteroatom stabilization in pyrazolylidenes is reduced, compared to that in imidazolylidenes. In normal C3-bound carbenes, a single N atom is located adjacent to the carbene carbon, which may increase the donor properties of these ligands, compared to normal C2-imidazolylidenes. In abnormal C4-bound carbenes, only remotely located heteroatoms are available for carbene stabilization (see Figure 4). Although the chemistry of abnormal pyrazolylidenes is somewhat underdeveloped, different routes to normal C3-bound pyrazolyidenes have been disclosed. The properties of the corresponding complexes reveal that this type of ligand indeed is complementary in many respects to its imidazolylidene counterpart.

2.3.1. C−H Bond Activation

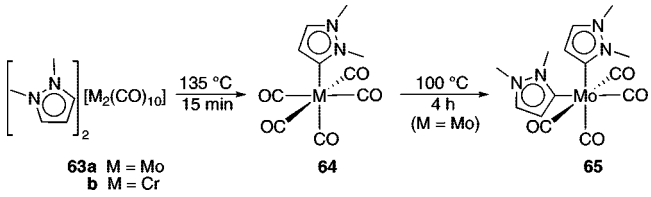
The pyrazolylidene complexes **64** were made via thermolysis of the pyrazolium salt of the decacarbonyl dimetallates **63** (see Scheme 23).[54] Extended heating of the molybdenum carbene **64a** induced a ligand redistribution and yielded the *cis*-bis(carbene) complexes **65** and $Mo(CO)_6$. Although the corresponding 2-imidazolylidene complex that contains a *N*,*N*-dimethylimidazol-2-ylidene (IMe) ligand, *cis*-$(IMe)_2Mo(CO)_4$, readily undergoes photochemical *trans* isomerization, complex **65** is inert toward such a rearrangement. This may be a consequence of the larger *trans* effect exhibited by the carbene ligand in **65**. Based on carbonyl stretching frequencies in $Mo(CO)_5$ (carbene) complexes, Öfele and co-workers have attributed stronger donor properties to the pyrazolylidene in **64** than to 2-imidazoylidenes such as IMe or benzimidazolylidenes. However, the *trans* influence is similar, i.e., the crystallographically determined metal−carbonyl bonds in the Cr complex **64b** and (IMe)$Cr(CO)_5$ are of equal length ($Cr-CO_{trans}$ = 1.86 and 1.87 Å, respectively).[55]

Quantum mechanical investigations suggest that the nitrogen lone pairs of these heterocyclic carbenes are largely localized, thus allowing (some) mesomeric interaction solely via the carbon framework.[55] This result is in marked contrast to the general assumption that the stability of imidazol-2-ylidene systems can be predominantly attributed to π-donation by the N atoms.[1]

Scheme 22



Scheme 23



Scheme 24

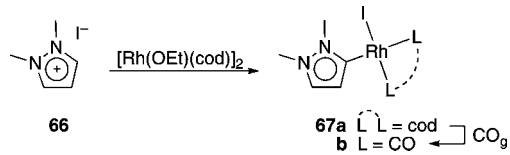


Table 2. Spectroscopic Data for Rhodium Complexes Comprising Pyrazolylidene and 2-Imidazolylidene Ligands

compound	ν_{CO} (cm^{-1})	$\delta_{C(carbene)}$	$^1J_{RhC}$ (Hz)
67b	2066, 1993	169.2	25.8
cis-(IMe)Rh(CO)$_2$I	2073, 2000	168.9	40.8
cis-(SIMe)Rh(CO)$_2$I	2072, 1999	195.2	n/a

In an attempt to compare the relative donor strengths of different carbenes, Herrmann et al. have synthesized a range of NHC complexes of the type *cis*-RhI(NHC)(CO)$_2$.[56] The complexes are prepared via *in situ* deprotonation of the corresponding azolium salts by a metal complex that contains a basic ligand and the subsequent introduction of carbon monoxide, as illustrated in the synthesis of complex **67b** (see Scheme 24).[41,57] The rhodium alkoxide precursor is effective for the rhodation of various azolium salts; however, attempts to use analogous alkoxide precursors of other metals have been unsuccessful.

The reported carbonyl IR stretching frequencies support the notion that the pyrazolylidene ligand exerts a higher σ-donor/π-acceptor ratio than the unsaturated normal imidazolylidene IMe or its saturated analog (*N*,*N*-dimethylimidazolin-2-ylidene, SIMe; see Table 2). Neither $^1J_{RhC}$ coupling constants nor the ^{13}C NMR resonances of the metal-bound carbon correlate with the IR data, illustrating how uncertain it could be to use such spectroscopic data to explain or deduce the bonding features of complexes.

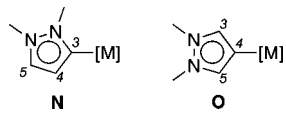
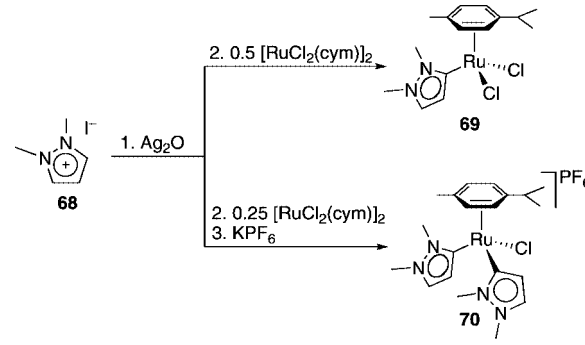
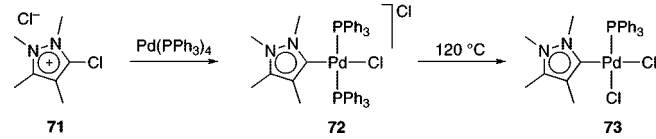


Figure 4. Normal pyrazolylidene (**N**) bound via C3, and abnormal (and remote) pyrazolylidene (**O**), coordinating to the metal center at C4.

Scheme 25



Scheme 26



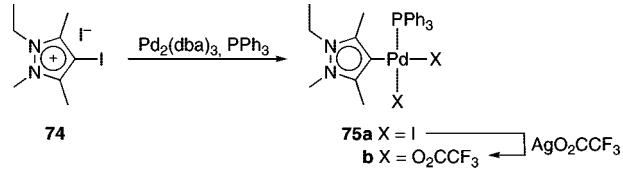
2.3.2. Transmetallation

Transmetallation methods are rather unexplored in pyrazolylidene chemistry. Without isolation of the presumed silver carbene complex, successful ruthenation afforded the complexes **69** and **70** (see Scheme 25).[34] The stoichiometry of the reactants could be utilized to access either the monocarbene **69** (0.5 mol equiv ruthenium dimer, with respect to pyrazolium salt) or the bis(carbene) complex **70** (0.25 mol equiv).

2.3.3. Oxidative Addition

The low CH acidity of pyrazolium salts has restricted their metallation by C−H bond activation to only few metal precursors thus far. Oxidative addition provides an alternative approach (e.g., for the preparation of palladium complexes **72** from the 3-chloropyrazolium salt **71**; see Scheme 26).[57] At elevated temperatures, displacement of a phosphine ligand by the nucleophilic Cl$^-$ anion is observed, yielding the neutral *cis* isomer **73**. The metal-bound carbon appears at 162.7 ppm in the ^{13}C NMR spectrum, which is only 1.6 ppm downfield from **72**.

Scheme 27



Oxidative addition was also successfully used for the synthesis of the first abnormally C4-bound pyrazolylidene complex **75a** (see Scheme 27).[58] To increase the solubility for ^{13}C NMR analysis, iodide was substituted for trifluoroacetate to yield **75b**. The carbene in the trifluoroacetate complex **75b** appeared at unusually high field ($\delta_C = 113.8$), thus representing one of the most shielded carbene-type resonances known. This result could be a consequence of the combination of both abnormal and remote features in this strongly electron-donating carbene. Further support for strong ligand donation is provided by the low average ν_{CO} values (2018 cm^{-1}) of analogous [$Rh(CO)_2Cl$ (carbene)] complexes, which are comprised of related C4-bound pyrazolylidene ligands.[58c]

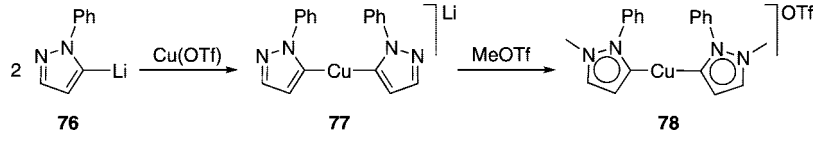
2.3.4. Nitrogen Functionalization of Metallated Pyrazolyl Ligands

Another approach to preparing less-stabilized NHC complexes involves first installing the metal on the heterocycle (**R**), followed by protonation or alkylation of the heteroatom to induce carbene-type bonding (**S**) (see Scheme 28).

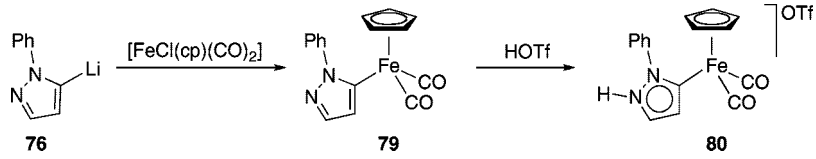
This approach has been successfully applied to the preparation of a variety of carbene complexes with different metals.[59] Typically, metallation has been performed via lithiation of the azole-ligand precursor, followed by transmetallation and protonation or alkylation. For example, transmetallation of the pyrazolyl lithium complex **76** with Cu(OTf) afforded the cuprate **77** and, after *N*-methylation, the bis(carbene) complex **78** (see Scheme 29).[60]

Scheme 28

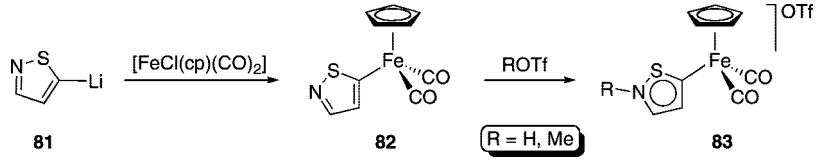
Scheme 29



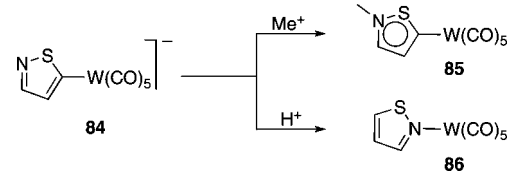
Scheme 30



Scheme 31



Scheme 32

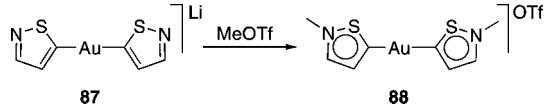


Similar results were obtained using a cationic iron fragment (see Scheme 30).[61] Carbene formation was assumed, based on a 19-ppm downfield shift of the metal-bound carbon resonance upon remote protonation of the neutral precursor **79**. This assumption was further supported by a concomitant bathochromic shift of the carbonyl absorption bands from $\nu_{CO} = 2031$ and 1979 cm^{-1} in **79** to $\nu_{CO} = 2048$ and 1989 cm^{-1} in **80**. However, neutral ligand formation alone could contribute to a decrease in metal-to-carbonyl back-donation. Single-crystal structure determinations revealed no significant change in the Fe−C bond lengths upon carbene formation.

A similar procedure involving first transmetallation and subsequent *N*-alkylation has also been used to prepare the isothiazolylidene complex **83** (see Scheme 31).[62] A significant downfield shift of the metal-bound carbon resonance ($\Delta\delta = 25$) occurs upon quaternization, and the carbonyl stretching frequencies again shifted to higher energies, presumably reflecting the formation of a metal−carbene bond. Such a bonding mode is further supported by a relatively short C−S distance in the molecular structure of **83**.

Related carbene formation has been also noted upon alkylation of the anionic tungsten complex **84** to form **85** (see Scheme 32).[63] Remarkably, protonation instead of alkylation does not yield the expected product. Instead, attack at the metal-bound carbon provided, after a rearrangement, the *N*-coordinated isomer **86**. Analysis of the $^{183}W-^{13}C$ coupling constant of the isothiazolylidene complex **85** ($\delta_C = 197.8$; $^1J_{WC} = 75.0$ Hz) indicates that the s character of

Scheme 33



the overlapping orbitals at the carbene carbon is substantially smaller in **85** than in the analogous C2-bound thiazolylidene complex (δ_C = 208.3; $^1J_{WC}$ = 98.1 Hz). This fact might explain the protonation at carbon to form the coordination complex **86**.

In contrast, alkylation of the imine N atoms in the bis(isothiazolyl) aurate **87** have imparted only a small downfield shift of the metal-bound carbon resonance ($\Delta\delta$ = 2.3).[64] This concurs with little metal-to-ligand π-interaction in complex **88** (see Scheme 33). Hence, an iminium rather than a neutral carbene-type ligand resonance structure has been postulated to make the more important contribution.

2.3.5. Cycloaddition to Fischer Carbene Complexes

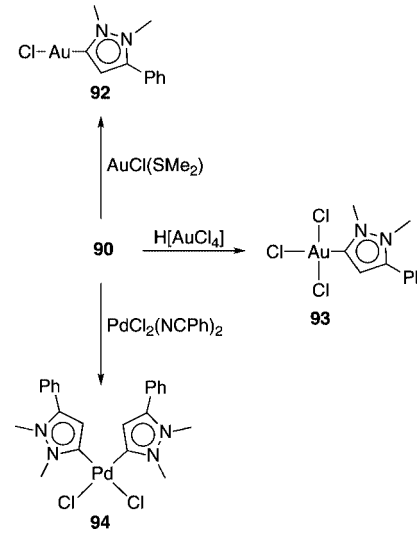
Cycloaddition of dinucleophiles to unsaturated Fischer-type carbenes represents an alternative route to *N*-heterocyclic carbenes.[65] For example, the pyrazolylidene complex **90** has been obtained upon addition of dimethylhydrazine to the alkynyl carbene **89** or to the allenylidene **91** (see Scheme 34).

This synthetic route is particularly useful for the introduction of specific substitution variations into heterocyclic carbenes; yet, the yields for the cyclization step are typically low. Recently, it has been shown that the pyrazolylidene in complex **90** is readily transferred to late transition metals. This has been demonstrated by the synthesis of Au^+, Au^{3+}, and Pd^{2+} complexes (see Scheme 35), thus disclosing an interesting cycloaddition−transmetallation sequence for preparing different pyrazolylidene metal complexes.[66]

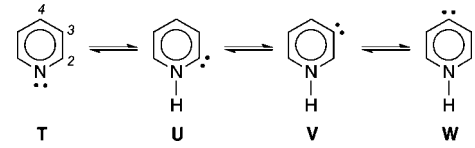
2.4. Pyridylidene Complexes

Pyridinium salts represent a subclass of carbene precursors that are remarkable in their own right. First, deprotonation of a ring carbon formally produces six-membered *N*-heterocyclic carbenes that are stabilized by one heteroatom, viz, the pyridylidene isomers **U**, **V**, and **W** (see Scheme 36). The reactivity of such a putative carbene is high, and complex formation according to a free carbene route is difficult. To date, free pyridylidenes, which were proposed by Hammick 70 years ago,[67] have been characterized only in the gas phase by mass spectrometry.[68,69] A recent computational study suggests that free 2-pyridylidenes may be stable if the heterocycle is extensively substituted by electron-donating amino groups.[70] Second, metal coordination at the *ortho*, *meta*, and *para* positions may provide normal, abnormal, and remote carbene complexes. According to the definition of the terms "abnormal" and "remote" (cf. Section 1), the abnormal 3-pyridylidene **V** belongs also to the class of remote pyridylidenes. Similarly, the remote pyridylidene **W** is simultaneously a normal NHC. Regioselectivity is obviously relevant, and electronic as well as steric influences

Scheme 35



Scheme 36



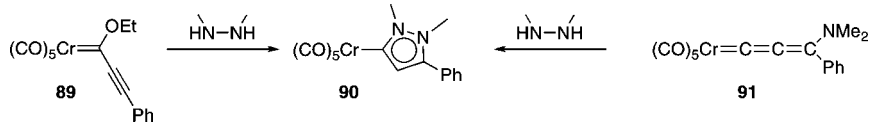
might be involved. Calculations have indicated that, in the absence of steric constraints, the *ortho*-pyridylidene (**U**) is more stable than the corresponding *meta*-pyridylidene (**V**) and *para*-pyridylidene (**W**) by 10−15 kcal/mol.[69] Third, chemical functionalization of pyridine is well-established, which allows the carbene to be connected to a variety of functionalities and be embedded in a variety of chelating environments. It is indeed surprising that the organometallic chemistry of pyridinium-derived carbenes is still much less explored than the related imidazolylidene chemistry. This may be the result of an intuitively wrong appraisal of the strength of such metal−carbene bonds.

2.4.1. Oxidative Addition

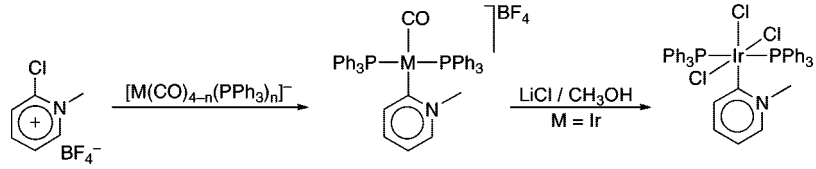
The first pyridylidene-type transition-metal complexes were prepared in 1974, via the oxidative addition of pyridinium salts to low-valent metal centers. Reaction of the chloropyridinium salt **95** with iridium(−I) and rhodium(−I) precursors gave the complexes **96a** and **96b** (see Scheme 37), respectively.[71] Based on the pertinent CO stretching frequencies, the electron-donor capability of the *N*-methylpyridylidene ligand was determined to be similar to that of other neutral ligands, such as PPh_3 or DMSO. Upon reaction with methanolic LiCl, however, remarkably facile metal oxidation to the neutral Ir^{3+} complex **97** indicated an appreciable electron density at the metal center in **96a**.

A similar reaction was observed with the manganate $Na[Mn(CO)_5]$ as metal precursor.[71] This method is also applicable to 4-chloropyridinium salts such as **99**, thus affording the remote NHC complex **100** (see Scheme 38).[72]

Scheme 34

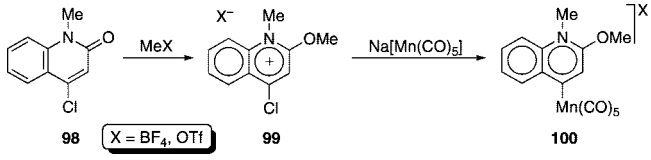


Scheme 37



95 **96a** M = Ir; n=1 **b** M = Rh; n=2 **97**

Scheme 38



98 X = BF_4, OTf **99** **100**

Upon metallation of **99**, the ^{13}C NMR resonance of C4 experiences a significant downfield shift ($\delta_C = 156$ in **99** vs 226 in **100**). This result, together with the increased ν_{CO}, has been the basis for proposing carbene complex formation.

Reaction of the chloropyridinium salt **95** with dianionic metalate complexes $[M(CO)_n]^{2-}$ (M = Cr, $n = 5$; M = Fe, Ru, $n = 4$) yielded neutral complexes of the type [M(pyridylidene)$(CO)_n$], which is analogous to **100**.[71,73] Because of the limited availability of dianionic precursors $[ML_n]^{2-}$, Schubert et al. explored the potential of monoanionic metal silyl and metal stannyl complexes $[M(ER_3)L_n]^-$ (ER_3 = $SiMe_3$, $SnMe_3$) as synthons for $[ML_n]^{2-}$, because the ER_3 ligand is readily removed in the form of R_3ECl.[74,75] The feasibility of this approach was demonstrated by synthesizing the pyridylidene complex **102** from the chloropyridinium salt **95** and the silyl-protected manganate precursor **101** (see Scheme 39). Spectroscopic properties of the pyridylidene complex **102** are very similar to those of related Fischer carbene complexes (e.g., **103**), which suggests a related influence of the heteroatom on both metal−carbene bonds. A similar approach was used for the preparation of a rhodium bis(pyridylidene) complex, which seems to be highly unstable.[76]

The oxidative addition of halopyridinium salts to several zerovalent precursors of Ni, Pd, and Pt allowed for systematic study of the consequences of metallation at various positions on the pyridinium ring.[72,77−81] The metallation procedure has a broad scope and was extended also to the metallation of polyaromatic systems such as quinolinium and acridinium salts, thus providing access to abnormal and remote NHC complexes (see Figure 5).[11]

The carbene carbons of the nickel and palladium complexes **104**−**111** resonate at 200 ± 10 ppm and are significantly deshielded ($\Delta\delta_C = 40-50$), compared to the corresponding precursor pyridinium salts. The nickel-bound pyridylidene carbons are located at lower field strength than their palladium analogues, which is opposite to the trend observed for the related 2-imidazolylidene complexes.[77,78] Crystallographic analysis of complexes **104**−**111** reveals metal−carbon bond lengths that are in a range typically observed for M−C_{aryl} single bonds. These distances are also in good agreement with those of related nickel(II) and palladium(II) imidazolylidene complexes. Based on bond length analyses, the *trans* influence of pyridylidenes increases with the distance between the heteroatom and the carbene. This points to stronger donor properties of the remote pyridylidenes.

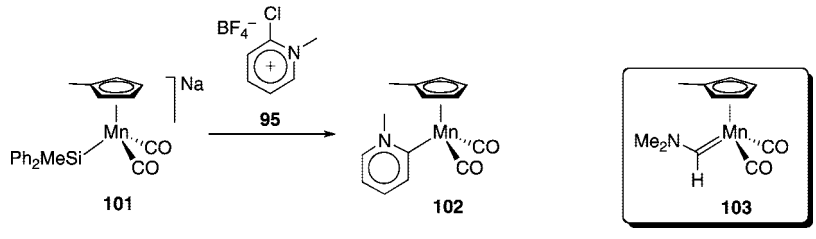
The electron redistribution within the *N*-heterocycle upon formation of the complexes **104**, **108**, and **112** by successive methylation and metallation of 2-, 3-, and 4-chloropyridine, respectively, has been evaluated by means of ^{13}C NMR spectroscopy.[81] An additive contribution of the two independent steps can be deduced, which suggests that carbene formation is an incremental process. The degree of synergy between both contributions is also reflected by the carbene carbon NMR shift, which decreases in the corresponding palladium complexes in the order

remote ($\delta_C = 197.7$) > normal ($\delta_C = 189.3$) > abnormal ($\delta_C = 165.0$)

Notably, the metal fragments exert a push/pull effect, which is consistent with a carbene-type donor/acceptor bond. When compared to related chemical shifts in free pyridine, metal complexation in the normal analogue **104** seems to affect only the immediate site of metallation, while a notable charge redistribution within the heterocycle is induced in the remote congener **108**. A diene character of the normal and remote pyridylidene ligands is further supported by the bond alternation observed in the X-ray crystal structures of **104** and **108**. The data for the corresponding abnormal pyridylidene complexes **112** are more complex and cannot be rationalized in terms of valence bond theory only.

Calculations using free reaction energies predict that oxidative addition occurs more readily for 2-pyridylidenes than for 4-pyridylidenes, but, interestingly, the metal−carbon bond strength shows an opposite trend.[78] Adjacent π-donor atoms may stabilize a free carbene toward nucleophilic attack but simultaneously weaken the M−C bond. Similar results have been obtained for Fischer-type carbene complexes.[82] Metallation of the dichlorinated pyridinium salts **113** either with Ni^0 or with Pd^0 exclusively provided the remote pyridylidene product **114** (see Scheme 40).[81] Taking into

Scheme 39



101 **102** **103**

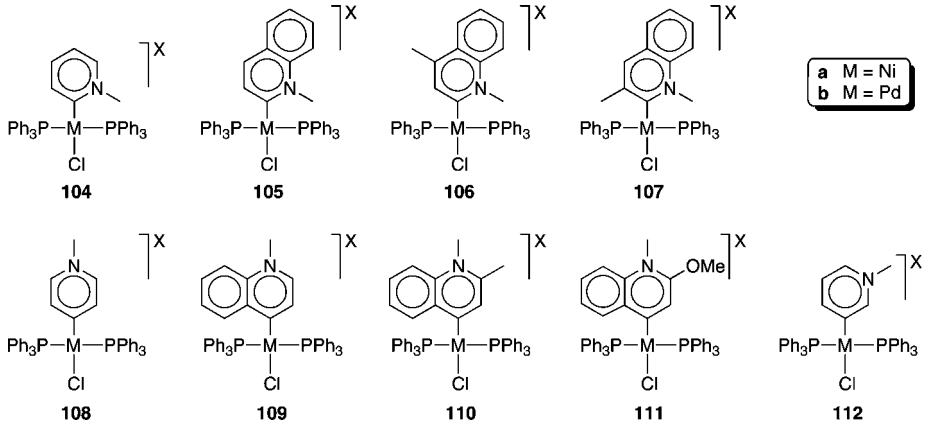
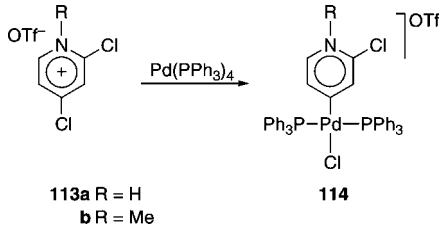
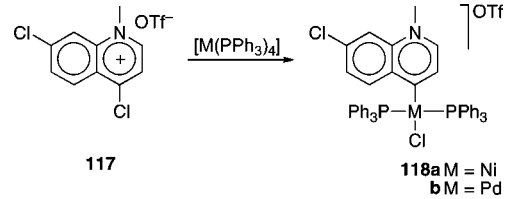


Figure 5. Pyridylidene nickel(II) and palladium(II) complexes, featuring different types of carbene bonding.

Scheme 40



Scheme 41



account the absence of steric differentiation between the 2-position and the 4-position in the protonated pyridinium salt **113a**, these results indicate that electronic considerations predominantly determine the regioselectivity of metallation. Thus, F-strain,[83] which is induced by the substituents at nitrogen, may have a less-important role in directing the metallation to the 4-position than expected.

Recently, the remote NHC concept has been extended to ligands in which the heteroatom and the carbene are located in different aromatic rings.[84] The Pd^{2+}-bound carbon atoms of **115** and **116** resonate at relatively high field ($\delta_C = 180.7$ and 187.0, respectively; see Figure 6). Carbene bonding has been proposed based on the significant downfield shift of these signals, with respect to the corresponding ligand precursor salts.

However, results of intramolecular competition experiments using the dichloride **117** have shown that oxidative addition occurs exclusively at the heterocycle, yielding the remote pyridylidene-type complex **118**. The C−Cl bond on the annelated ring is not affected at all, even in the presence of an excess of $M(PPh_3)_4$ (see Scheme 41).[81]

Energy decomposition analysis of the M−C bond in various pyridylidene quinolylidene and isoquinolylidene complexes have indicated that the attractive metal−ligand interactions are predominantly electrostatic, with only about one-third due to orbital contributions.[77,78,85] The covalent portion consists of some 20% π-bonding, which compares well with the π-character calculated for Fischer-type amino carbene complexes.[86] Both the σ- and π-contributions to the M−C bond have been calculated to be larger in pyridinium-derived NHC complexes than in the corresponding 2-imidazolylidene systems.[77] Although the relative composition of the M−C bond seems to be remarkably insensitive to the position of the heteroatom, the calculated bond strengths vary considerably.[85] The total metal−ligand interaction energies correlate well with the energy level of the HOMO in the free carbene ligand. Therefore, according to these computational results, a less-stable free carbene yields a stronger metal−carbon bond.

Cyclometallation of pyridinium derivatives via C−H bond oxidative addition has been successfully utilized for the synthesis of normal and remote pyridylidene iridium(III) complexes. To increase the regioselectivity for C2 metallation, Li and co-workers have protected the potentially remote carbenoidal position by alkylation. Oxidative C−H bond addition to $[Ir(cod)_2]PF_6$ gives the iridium(III) pyridine−pyridylidene chelates (**119** and **120**) (see Figure 7).[87] The remote pyridylidene analog of **120** (viz., **121**) undergoes *cis*−*trans* isomerization. The **121**-*cis* complex has been crystallographically characterized and is also the major species in solution. Such a regioselective C−H bond oxidative addition protocol provides an attractive methodology for pyridylidene complex synthesis, because ligand prefunctionalization becomes redundant.

2.4.2. Nitrogen Functionalization of Metallated Pyridyl Ligands

In the early 1980s, the groups of Isobe[88,89] and Crociani[90−95] successfully prepared nickel, palladium, and platinum py-

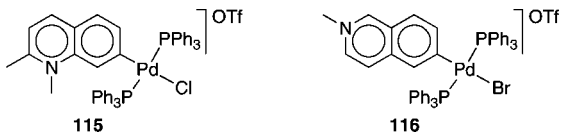


Figure 6. Extension of the remote carbene theme: isoquinolylidene complexes, which are comprised of the heterocycle and the metal-bound carbene carbon associated with different rings.

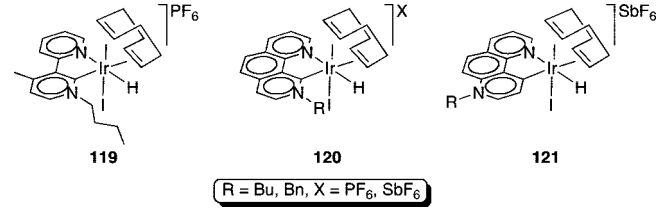
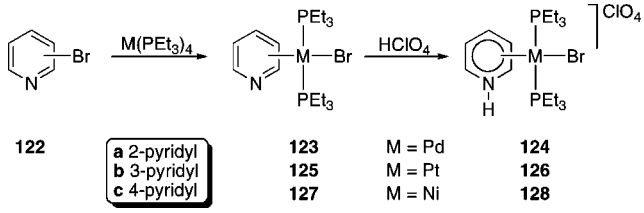
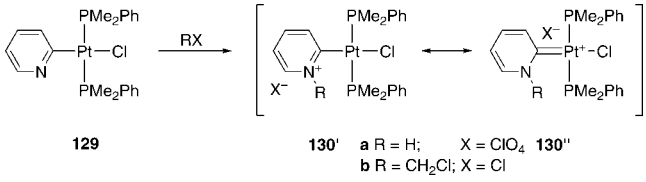


Figure 7. Normal pyridylidene Ir^{3+} complexes (**119** and **120**) and remote pyridylidene Ir^{3+} complexes (**121**), accessible by oxidative C−H bond addition.

Scheme 42



Scheme 43



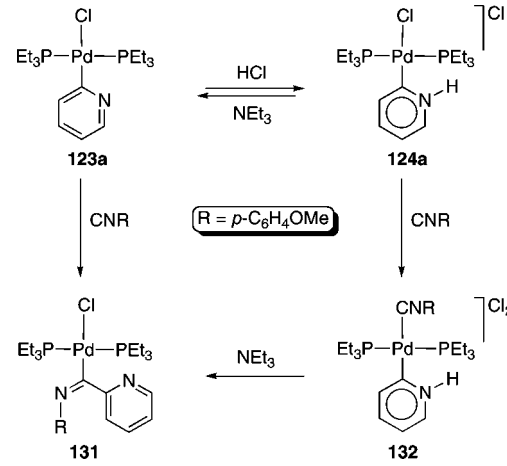
ridylidene complexes via the protonation or alkylation of pyridyl complexes (see Scheme 42).

These early studies focused on the effect of the metal fragment on the reactivity of the pyridine, rather than on the carbene-type bonding of the ligand. Titration experiments showed that the Brønsted basicity of pyridine in the palladium complex **123a** is ~4 orders of magnitude higher than that of unsubstituted pyridine.[89] Systematic studies revealed a strong dependence of the basicity on the pyridyl substitution pattern. The basicity decreases in the order of metal substitution as C2 ≫ C4 > C3, and it is larger for the platinum complexes **125** than for the corresponding palladium complexes **123**.[89,95]

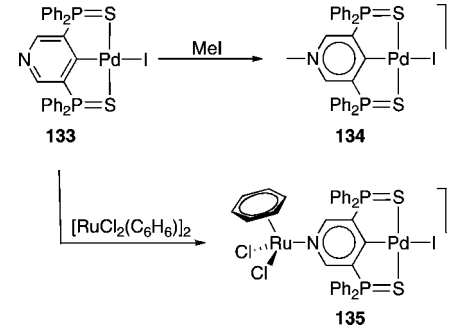
Contribution of a carbene resonance structure in the protonated species **124a** was inferred from ^{13}C NMR spectroscopy. The resonance frequency of the metal-bound carbene ($\delta_C = 184.9$) indicated a downfield shift, compared to the precursor pyridyl system **123a** ($\Delta\delta \approx 5$). Moreover, the Pt−C and Pt−P coupling constants decreased upon protonation. These changes were rationalized by invoking an enhanced M−C bond order. This conclusion was corroborated by results of ^1H NMR studies, which revealed a hindered rotation about the M−C bond in 2-pyridylidene complexes prepared by protonation, such as **124a**.[90,92] Steric effects might have only a minor role in explaining this increased rigidity, because, in the precursor complexes **123a** that contain an anionic pyridyl ligand, this rotation is fast on the NMR scale. Finally, the observed high-frequency shift of the M−Br stretching vibration upon protonation was attributed to a decreased *trans* influence of the carbene, compared to the anionic pyridyl ligand.[90]

The high basicity of 2-metallated pyridines has been further illustrated by the successful activation of CH_2Cl_2 by complex **129** to form the *N*-alkylated chloride salt **130b** (see Scheme 43).[94] Replacing the *trans*-coordinated phosphine spectator ligands by bidentate *cis*-chelating ligands such as1,2-bis(diphenylphosphino)ethane (dppe) or dimethyldithiocarbamate (dmtc) does not influence this reactivity pattern.[93,95−97] Because the 2- and 4-metallated congeners differ considerably in their reactivity, the contribution of a zwitterionic pyridinylium-type resonance structure (**130′**; see Scheme 43) has been suggested to be more relevant than the neutral pyridylidene structure **130″**.[95,96] Comparison of the Pt−C bond distances in **100**, its protonated form **130a**, and **130b** is not conclusive for establishing metal−carbon π-interactions (see Table 3).[94] Interestingly, the heterocycles in the carbenoid complexes **130** are oriented almost perpendicular

Scheme 44



Scheme 45



to the metal coordination plane, while in the pyridyl complex **129**, the ligand is tilted only by ~10°.

The metal−carbon bond in 2-pyridylidene complexes such as **124a** displays a pronounced inertness. For example, migratory insertion of isocyanide into the Pd−C bond is unsuccessful in the pyridylidene **124a**, while it occurs readily in the pyridyl complex **123a** to give **131** (see Scheme 44). Instead, the pyridylidene complex undergoes a ligand exchange, affording the dicationic complex **132**.[98] Isocyanide insertion can be initiated subsequently by the addition of a base. A similar reactivity pattern has been observed for the analogous nickel complexes.[92]

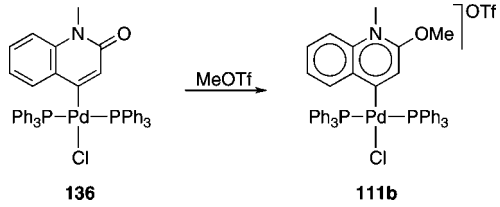
The palladium pyridyl complex **133** that features an *S*,*C*,*S*-tridentate coordinating pincer ligand has been alkylated to yield the corresponding carbene complex **134** (see Scheme 45).[99] UV−vis measurements reveal a bathochromic shift of the metal-to-ligand charge transfer (MLCT) band upon alkylation, which has been attributed to a lowering of the π^*-level. Interestingly, coordination of **133** as a metalloligand to a $RuCl_2(\eta^6\text{-}C_6H_6)$ fragment (complex **135**) induces a similar MLCT band shift as methylation.

In some instances, alkylation of an exocyclic oxygen rather than the internal heteroatom may provide a method for the formation of pyridylidene complexes.[91] For example, alkylation of **136** occurs at an oxygen as the most nucleophilic

Table 3. Structural Parameters of Platinum Pyridyl and Pyridylidene Complexes

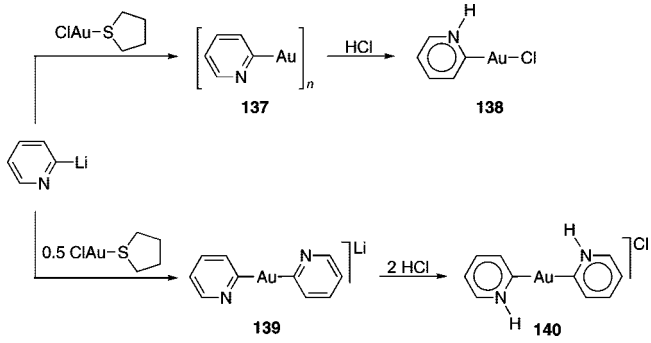
	Bond Length (Å)		
complex	*d*(Pt−C)	*d*(Pt−Cl)	dihedral angle, ∠(N−C−Pt−P) (deg)
129	1.996(8)	2.408(3)	102.47, 83.20
130a	1.986(9)	2.372(3)	92.86, 92.66
130b	1.956(6)	2.378(2)	90.41, 91.32

Scheme 46



136 111b

Scheme 47

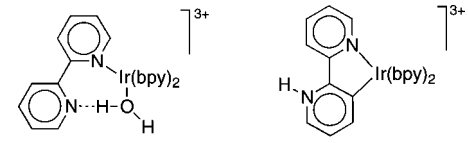


137 138 139 140

site, providing an alternative approach toward the formation of **111b** (see Scheme 46).[72] Examination of the molecular structure of this pyridylidene-type complex shows significant alteration of the bond length within the heterocycle, indicating castabilization of the carbene center by the nitrogen and the exocyclic heteroatom. Similarly, the complexes **100**[72] and **116**[86] have been synthesized by this route, i.e., by alkylation *after* heterocycle metallation. In all examples, the metal-bound carbon resonance shifts significantly downfield upon methylation. This effect has been explained in terms of an increased M−C bond order.

Pyridyl complex protonation has also been used to prepare carbene complexes of gold. Depending on the metal/ligand stoichiometry used in the preceding transmetallation, the 2-pyridyl gold precursor is either oligomeric **137** (1 mol equiv gold) or occurs as the bis(pyridyl) aurate **139** (0.5 mol equiv gold). Both species can be protonated to produce the monometallic monopyridylidene and dipyridylidene complexes **138** and **140**, respectively (see Scheme 47).[100]

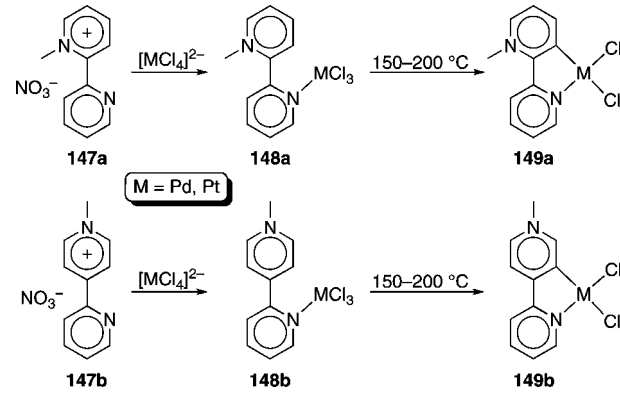
While transmetallation from lithiated reagents has been used in the preparation of 2-pyridyl precursor complexes only, Maitlis and co-workers showed that all three pyridyl isomers—and, hence, also all three pyridylidene complexes—are accessible upon decarbonylative activation of pyridine aldehydes **141** in the presence of the Rh^{3+} complex **142** (see Scheme 48). Subsequent alkylation of the pyridyl nitrogen in **143** yields the corresponding carbene complexes **144**.[101] Comparision of the spectroscopic data of the 2-, 3-, and 4-substituted pyridylidene isomers **144** with their related precursors **143** indicates significantly higher CO stretching frequencies for the 2- and 4-pyridylidenes only. This is in



145 146

Figure 8. Proposed iridium structure **145**, and the crystallographically determined complex **146**, obtained from reacting $IrCl_3$ and bpy in the presence of NaOMe (bpy = 2,2′-bipyridine).

Scheme 49



147a 148a 149a 147b 148b 149b

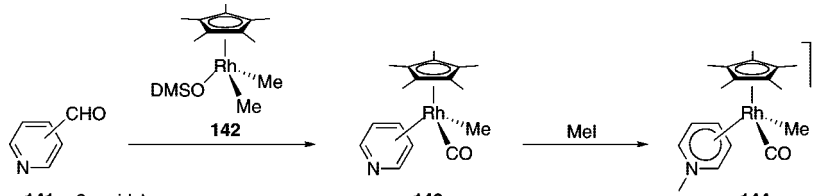
agreement with a smaller σ-donor/π-acceptor ratio for the 2- and 4-pyridylidene complexes as compared to the abnormal 3-pyridylidene analogues. A similar synthetic protocol has also been successfully used to prepare an analogous 4-pyridylidene Ir^{3+} complex, which is much more stable to reductive elimination than the corresponding rhodium complex (**144c**).

2.4.3. C−H Bond Activation

Watts et al., in 1977, reported on the synthesis of a cationic iridium(III) complex that contained three 2,2′-bipyridine (bpy) ligands, one of which was claimed to bind in a monodentate mode (**145**; see Figure 8).[102] The exact binding mode of that ligand raised a controversy,[103] which was finally clarified by a single crystal structure determination (**146**; see Figure 8).[104] The structure demonstrated that this complex contains the first, initially unrecognized, abnormal pyridylidene ligand.

In a more rational approach, Wimmer and co-workers demonstrated the successful cyclometallation of monoalkylated 2-pyridyl and 4-pyridyl pyridinium salts **147**, using tetrachloropalladate and tetrachloroplatinate precursors.[105] The initially formed coordination complexes **148** were isolated and converted to the corresponding metallacycles upon heating in aqueous solutions or in the solid state (see Scheme 49). Analysis of the resulting abnormal 3-pyridylidene complexes **149** was hampered by their poor solubility in common solvents, and, perhaps as a consequence

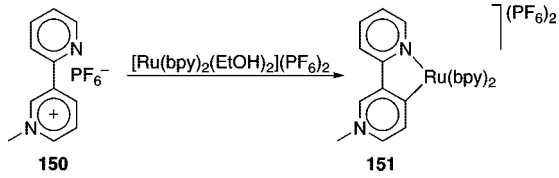
Scheme 48



141a 2-pyridyl
b 3-pyridyl
c 4-pyridyl

143 144

Scheme 50



of the lack of conclusive data, the carbenoid character of the metal−carbon bond in these complexes has not been discussed.

Obviously, cyclometallation of the pyridinium salts **147** will direct the metal center to the pyridinium *meta* position to yield abnormal carbenes. In contrast, cyclometallation of 3-pyridyl pyridinium salts such as **150** may afford normal or remote pyridylidene complexes. Reaction of **150** with the *in situ* formed metal precursor $[Ru(bpy)_2(EtOH)_2](PF_6)_2$ has led to the remote isomer **151** exclusively (see Scheme 50).[106] Based on the discussion in the previous section, this reaction outcome may be understood by considering a synergistic interplay between the electronic preference for pyridinium C4 metallation and the steric protection of the pyridinium *ortho* positions by the methyl group (F-strain[83]).

The pyridine-assisted cyclometallation protocol has been further extended to prepare Ru complexes that contain terpyridinium-derived *N,C,N*- and *N,N,C*-chelating pyridylidenes.[107−109] Particularly interesting for comparative purposes are complexes **152** and **153**, which feature remote and abnormal pyridylidenes, respectively (see Figure 9).[109] A distinctly different bonding situation is indicated by the NMR chemical shift of the metal-bound carbon ($\delta_C = 183.7$ in **152**, 225.6 in **153**), which could indicate a higher carbene character in the complex **153**. This result is further supported by a 50-mV anodic shift of the ruthenium(II)/ruthenium(III) oxidation potential in **153**, compared to **152**. This shift has been rationalized in terms of a rise of the ligand π^*-level, which is due to better π-back-donation from the metal and reflects a reduced electron transfer from the ligand to the metal in **153**. This model is consistent with a change from (zwitter)ionic pyridyl-type coordination in **152** toward neutral carbene-like pyridylidene donation of the ligand in **153**. Similar effects have been observed in the electronic spectra of related Ru(N^C)$(bipy)_2$ complexes, where N^C is an *N,C*-bidentate coordinating pyridine-pyridylidene ligand.[108] Displacement of the alkylated nitrogen from the *meta* position (abnormal carbene) to the *para* position (remote carbene) induces a 38-nm hypsochromic shift of the MLCT band.[106] Note that the crystallographically determined Ru−C bond distance is only slightly shorter in **153** (2.014(5) Å) than in **152** (2.033(5) Å).

Cyclometallation of pyridinium derivatives has been successfully utilized also for the preparation of normal 2-pyridylidene complexes. To increase the regioselectivity for C2-metallation, it seems advantageous to install the chelating donor site on the functional group that is used for pyridine *N*-quaternization. Using this methodology, Bercaw and co-workers have accomplished the synthesis of *N*-heterocyclic carbene Pt^{2+} complexes **154** when starting from monocationic *N*-(2-pyridyl)-pyridinium salts **155** (see Scheme 51).[110]

Structural data from X-ray analysis of various carbene complexes **154** indicate substantial bond length alteration in the heterocycles and point to partially localized double bonds in certain instances. In particular, such bond length alteration seems to be dependent on the substitution pattern of the pyridinium ring. A pyridylidene-type structure featuring a relatively short Pt−C bond distance of 1.959(3) Å has been proposed for unsubstituted carbenes such as **154a**. While the ^{13}C NMR resonance of the metal-bound carbon is located at a relatively low chemical shift ($\delta_C < 180$), the $^1J_{PtC}$ coupling constants are exceptionally large (1200−1330 Hz) and could serve as a probe for the Pt−C bond order. In the *para*-amino-functionalized complex **154b**, stabilization of the iminium form occurs predominantly from the NMe_2 donor substituent, rather than from the metal. Accordingly, the Pt−C bond is significantly longer than that in **154a** (2.011(2) Å), and the aromatic C−C bonds of the NMe_2 substituted ring alternate in length. In the isomeric **154c** complex, having an NMe_2 substituent in the *meta* position, a similar π-involvement of the two N atoms is not possible and no bond alteration occurs. The Pt−C bond length (2.004(6) Å) is similar to that in **154b**, indicating that charge compensation in this system still occurs predominantly via the NMe_2 substituent rather than through π-backbonding from platinum. Remarkably, however, the activation energy for rotation about the C−NMe_2 bond is considerably higher in **154c** than in the resonance-stabilized system **154b**.

Investigation of ligand substitution reactions in the 2-pyridylidene complexes **154** has indicated an associative DMSO exchange mechanism. The exchange rate for the carbene complex **154a** is ~3 orders of magnitude higher than for its neutral 2-phenyl pyridine analogue. Orbital considerations of the assumed trigonal bipyramidal transition state suggest that the exchange rate is enhanced by the presence of π-acidic ligands. According to this model, the higher rate for **154a** implies M−C backbonding in the transition state and a pronounced *trans* effect by the carbene ligand. In the ground state, the Pt−S bond distances are statistically identical for the two complexes under discussion, thus revealing no difference in *trans* influence.

Chelated 2-pyridylidene complexes **156** of different Group 10 metals have been prepared using $[M(acac)_2]$ (M = Ni, Pd, Pt; see Scheme 51) as metal precursors.[111] X-ray crystal structures reveal a higher *trans* influence of the carbene donor, relative to the pyridine-type donor. The UV−vis absorption spectra of these complexes show a metal-dependent MLCT absorption maximum and, hence, are indicative of metal−ligand backbonding.

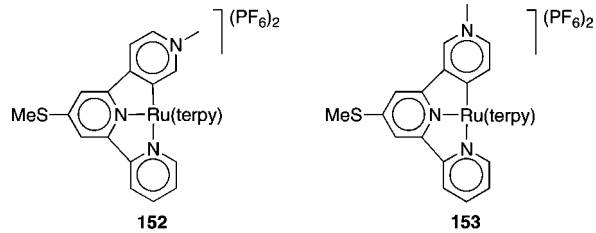
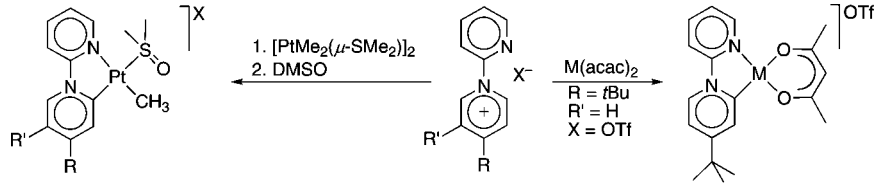
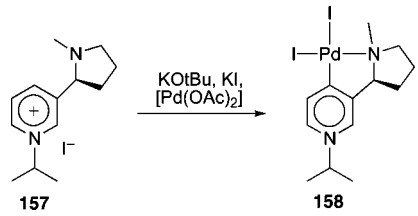


Figure 9. Redox-active terpyridine Ru^{2+} complexes featuring abnormal (**152**) and remote (**153**) pyridylidene bonding.

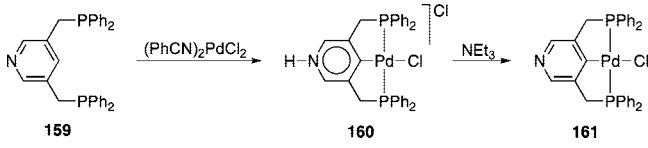
Scheme 51



Scheme 52



Scheme 53



The asymmetric palladium complex **158** has been prepared from the nicotinium-derived chiral ligand precursor **157** under very mild conditions (see Scheme 52).[112] C−H bond activation occurs selectively at the less-acidic C4 position, most likely because of effective shielding of the *ortho* positions by the isopropyl group. Palladation has been postulated to occur by initial formation of a palladate species and subsequent ion pairing with the cationic heterocycle prior to Pd−C bond formation.[25,26] The metal-bound carbon in **158** resonates at higher field strength (δ_C = 176.2) than the cationic complex **108b** (δ_C = 197.7). This NMR shift difference emphasizes again the strong dependence of the carbene carbon resonance on the ligand environment of the metal.

Cycloaddition of the 3,5-diphosphino-pyridine pincer ligand **159** to $PdCl_2(PhCN)_2$ proceeds smoothly in the absence of a base to generate the remote pyridylidene complex (**160**) (see Scheme 53).[113] Formally, this reaction corresponds to a pyridine tautomerization involving a 1,4-migration of the proton. UV−vis spectrosopic comparison of the pyridylidene complex **160** and the deprotonated pyridyl complex **161** indicates that protonation induces a 16-nm hypsochromic shift of the relevant absorption band in the visible region. This shift has been rationalized by a reduction of the HOMO energy and thus an increase of the highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) gap upon protonation, because of reduced electron density at the metal center. Coordination of the pyridine nitrogen to BEt_3 or to a $PdCl_2$ fragment results in a much smaller shift of the absorption band ($\Delta\lambda$ = 2 nm), thus suggesting a related but less-pronounced effect.

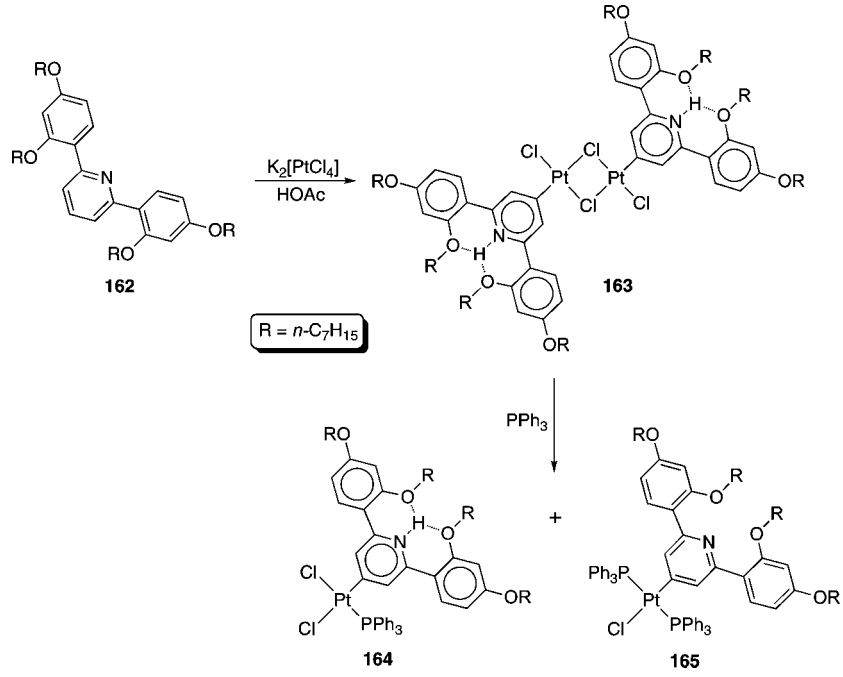
A similar proton migration has been observed during the metallation of ligand **162**. Although this ligand seems to be well-suited for *C*,*N*,*C*-terdentate pincer-type metal coordination,[45b,c] exclusive activation of the pyridyl C4-position is observed. This created the dimeric complex **163**, featuring two remote NHC ligands (see Scheme 54).[114] Crystallographic analysis shows a Pt−C bond distance of 1.951(9) Å, which is short for a nonchelating ligand. The dihedral angle between the ligand heterocycle and the metal square plane in **163** deviates remarkably (~39°) from the in-plane or perpendicular orientation that would be expected for effective d−π back-donation. In solution, however, carbene-type bonding seems to be supported by an extraordinarily deshielded resonance for the metal-bound carbon (δ_C = 324.3). The addition of PPh_3 cleaves the dimeric structure and gives a mixture of complexes **164** and **165**.[115] Complex **164** has been assigned a zwitterionic structure as the predominant resonance form, based on the virtually identical ^{13}C NMR shifts of the metal-bound carbons in **164** and in the pyridyl complex **165** (δ_C = 177.0 and 176.1, respectively).

The η^2-complex **166**, obtained from $[Os(NH_3)_5]^{3+}$ and a methylpyridinium salt, is metastable and undergoes a slow C−H bond activation to afford the C4-bound NHC complex **167** (see Scheme 55).[116] Such a transformation seems to be unique for pyridine-derived heterocycles, because related complexes with η^2-arene or η^2-imidazolium ligands do not show similar reactivities. Interestingly, the more-acidic C2-position is not activated, even if C4 is protected by a methyl group. This might be attributed to the steric demand of the *N*-methyl group.

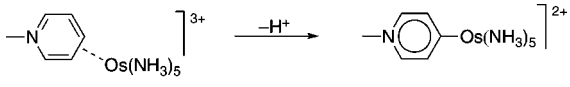
Carmona and Poveda have exploited a similar F-strain[83] to access pyridylidene complexes. The iridium trispyrazolborate complex, $IrTp(Ph)_2(N_2)$, which contains a labile N_2 ligand activates the C6−H bond of picoline **168a** at elevated temperatures and yields the carbene complex **169a**, thus inducing a formal proton shift from C6 to nitrogen to afford the tautomeric carbene ligand (see Scheme 56).[117] The course of the reaction is sensitive to the applied reaction conditions, the substituents on the pyridine ring, and modifications to the iridium complex. For example, at 60 °C **168a** was shown to coordinate with the N atom to the metal precursor to form isomer **170a**, which rearranged to **169a** at 90 °C. In contrast, unsubstituted pyridine does not undergo a proton shift with the same precursor $IrTp(Ph)_2(N_2)$, even at 150 °C, and afforded **170d** exclusively.

Nitrogen coordination has been partly suppressed by incorporating mesityl substituents in the Tp ligand of the iridium precursor. Thus, the reaction of $IrTp'(N_2)$ with pyridine results in the formation of a 1:1 mixture of the *C*- and *N*-bound isomers (**171** and **172**) (see Scheme 57).[118] In this situation, thermal interconversion of the two isomers has not been achieved, indicating that the *N*-bound complex is probably not an intermediate during carbene formation but rather a side product that is formed under kinetic control. Crystal structure determination of different complexes **169** shows significant bond alterations within the 2-pyridylidene ligand, thus supporting a carbene-type Pd−C bond and a heterocycle featuring substantial diene character.[117−119]

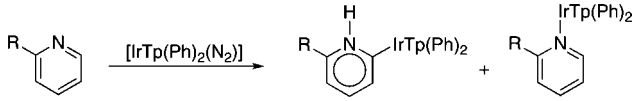
Scheme 54



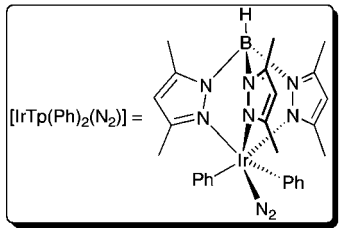
Scheme 55



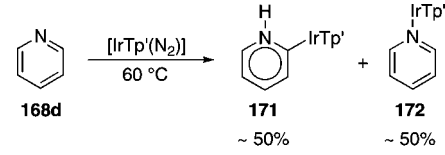
Scheme 56

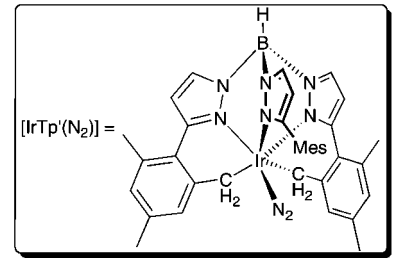


168	R	T/ °C	169	170
a	Me	60	---	> 50%
		90	> 80%	---
b	Ph	90	> 80%	---
c	2-pyridyl	90	> 90%	---
d	H	150	---	> 80%

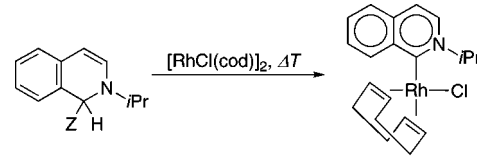


Scheme 57





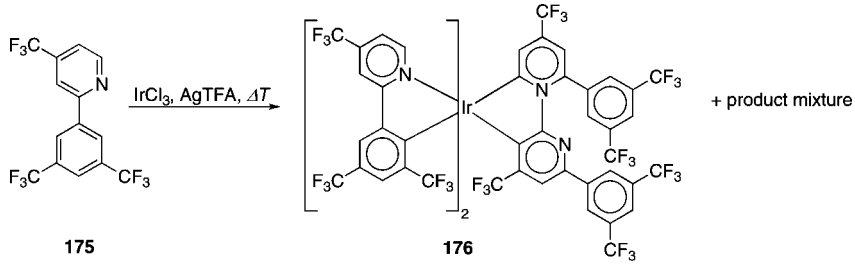
Scheme 58



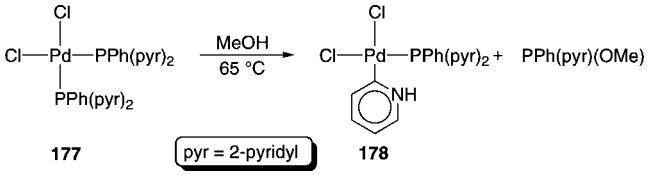
Deuterium labeling experiments provide evidence that the iridium-bound mesityl substituents of the IrTp′ fragment are involved in the proton shift process, possibly acting as hydrogen reservoirs. Moreover, the observed depletion of the deuterium content at the pyridine C3- and C4-positions suggests that carbene formation at these C atoms is also occurring. Yet, these remote products are unstable and rearrange to the thermodynamically more-stable C2-bound product, which is consistent with theoretical considerations.[69] Hence, in *N*-alkylated pyridylidenes, F-strain[83] may well be a relevant driving force for remote NHC formation (i.e., for the high regioselectivity to metallate the C4-position). A similar tautomerization with metal involvement has been observed recently upon reaction of quinolines with ruthenium(IV) and osmium(IV) hydrides ($MH_2Cl_2(PiPr_3)_2$),[120] and also upon treatment of 2,3′-bipyridines with $[Ir(cod)_2]BF_4$.[121] In the latter case, an amide functionality as a hydrogen-bond acceptor group was determined to be essential for stabilizing the pyridylidene tautomer, as opposed to a metal−hydride species. These recent results indicate that such tautomerization reactions may have a more general scope than initially believed.

A different type of C−H bond activation has been realized recently with the adduct **173**, obtained from the reaction of the corresponding isoquinolinium salt with KO*t*Bu or K[N(SiMe$_3$)$_2$].[122] Reaction with $[Rh(cod)Cl]_2$ (see Scheme 58) readily provides the 2-pyridylidene-type complex **174**. Based

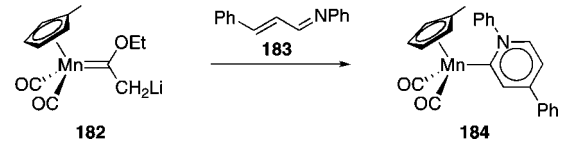
Scheme 59



Scheme 60



Scheme 62



on the reactivity of related adducts of 2-imidazolylidenes,[123] a sequential process has been proposed, first comprising the formation of a still-elusive free pyridylidene via the elimination of HZ, followed by fast metal coordination.

In an attempt to cyclometallate the potentially *C,N*-bidentate chelating ligand precursor **175** with $IrCl_3$, complex **176** has unexpectedly been isolated, along with several other products (see Scheme 59).[124] Note that the pyridylidene-type ligand binds via two carbons (one of which could be considered a normal carbene) to the metal center. While such complexes may be of interest (for example, as novel light-emitting materials), further studies are required to devise a rational synthetic protocol.

2.4.4. P−C Bond Activation

The transfer of an organic substituent from a phosphine ligand onto the central metal in the presence of a nucleophile is a well-known decomposition pathway in homogeneous catalysis.[125] In organometallic synthesis, however, this reactivity has not been much exploited thus far. The neutral 2-pyridylidene complex **178** has been obtained serendipitously when heating the palladium dichloride complex **177**, which is comprised of 2-pyridyl-substituted phosphines in methanol (see Scheme 60).[126] Comparison of the crystallographically determined Pd−Cl bond lengths in **178** indicates that the *trans* influence of the carbene donor is slightly stronger than that of the phosphine.

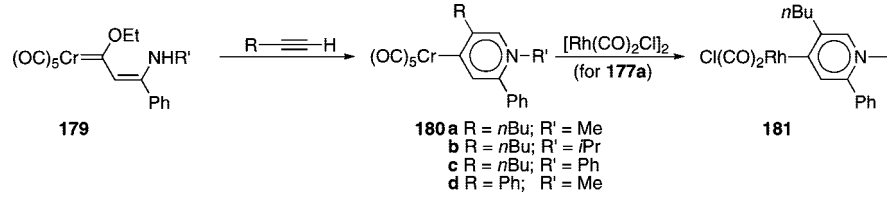
2.4.5. Cycloaddition to Fischer Carbene Complexes

Pyridylidene complexes can be synthesized by modifying existing coordinated carbenes. For example, Aumann and co-workers succeeded in reacting the amino-functionalized Fischer carbene complex **179** with alkynes to yield 4-pyridylidenes such as those in complexes **180** (see Scheme 61).[127] These remote carbene complexes were determined to be remarkably stable, despite the lack of a stabilizing α-heteroatom. The carbene carbon NMR resonance typically shifts ∼50 ppm upfield upon cyclization, because of a significant π-electron contribution from the aromatic pyridylium resonance form. Such a bonding model is supported by the protolysis of the new Cr−C bond by HBF_4. A synthetically very attractive feature of complexes **180** is their propensity to transfer the pyridylidene ligand to late transition metals, as has been illustrated recently with the preparation of the rhodium pyridylidene complex **181** from $[Rh(CO)_2Cl]_2$ and **180a**.[128] Comparison of the low CO stretching frequencies of the *cis* isomer (average $\nu_{CO} = 2014\ cm^{-1}$) with related complexes (*vide supra*) places this 4-pyridylidene system among the strongest carbene-type donor ligands known to date.

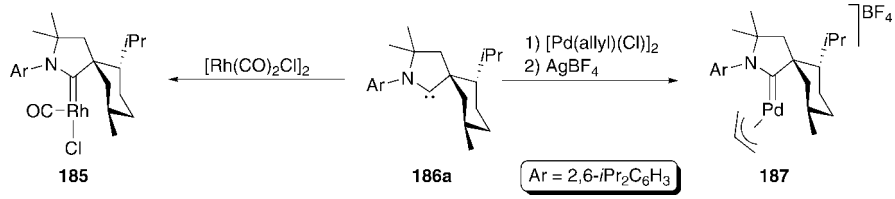
Cycloaddition has also been performed with α,β-unsaturated imines, which does not require the installation of the final heteroatom in the Fischer carbene. For example, the anionic carbene complex **182** reacts with the azabutadiene **183** to afford the 2-pyridylidene manganese(I) complex **184** (see Scheme 62).[129] Analogously, 2-pyridylidene W^0 complexes have been prepared.[130] The molecular structure of complex **184** displays bond lengths that indicate substantial electronic delocalization within the pyridylidene ring. Notably, the carbonyl ^{13}C NMR shift, as well as the IR absorption frequencies, are almost identical to those observed in the analogous 2-thiazolylidene complex.[74] This suggests similar donor properties of these two carbene systems.

The dichotomy in representing Fischer carbene and NHC complexes is perhaps most clearly illustrated in the reaction shown in Scheme 62: while the M−C bond is not altered considerably during the heterocycle formation, the different manners of representation for the complexes **182** and **184** imply a substantial change in the bonding. This dichotomy, grown historically, along with the borderless transition from purely M−C single bonded carbenes to increasing M=C double bond character, both in Fischer carbene and NHC

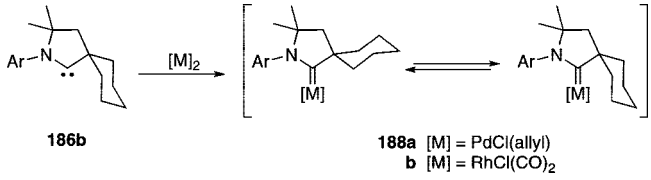
Scheme 61



Scheme 63



Scheme 64



complexes, makes a consistent representation of the formulas in this review impossible. Therefore, we have used the single bond representation for all NHC complexes that have some degree of aromatic character, whereas for Fischer carbene complexes, and also for saturated *N*-heterocyclic carbene complexes, discussed in the subsequent section, a double-bond representation has been adopted. It is our understanding that the different representations heavily overemphasize the effective differences in bonding.

2.5. Complexes Comprising Cyclic (Amino)(Alkyl) or (Amino)(Ylide)Carbenes

2.5.1. Coordination to Free Cyclic (Amino)(Alkyl)Carbenes

Based on the successful preparation of free (amino)(alkyl)-carbenes (AACs),[9] Bertrand and co-workers pursued the synthesis of stable cyclic (amino)(alkyl)carbenes (CAACs) and their transition-metal complexes. Deprotonation of a cyclic aldiminium salt quantitatively afforded the stable carbene **186a**.[131] Subsequent metal coordination gave the complexes **185** and **187** (see Scheme 63).[132] The Rh center spontaneously lost one CO ligand upon carbene bonding to afford **185** complex as a rare 14e species. The 14e palladium carbene complex **187** was accessible by coordination to $[Pd(allyl)Cl]_2$ and subsequent Ag^+-mediated halide abstraction. In contrast to previous attempts to prepare similar 14e complexes with 2-imidazolylidenes,[133] the compounds **185** and **187** were stable and could be crystallized. Structural analysis indicated that at least one of the axial C−H bonds of the menthyl ring was involved in an agostic interaction.

The relevance of agostic interactions in stabilizing these coordinatively unsaturated species has been probed by modifying the substituents in a position α to the carbene carbon. Replacing the menthyl moiety with a sterically more flexible cyclohexyl group **186b**, which can twist away from the metal coordination sphere, results in the exclusive formation of square-planar 16e complexes **188** (see Scheme 64).[131] Attempts to remove one of the ligands induced complex decomposition. Although, apparently, steric bulk and rigidity is essential to stabilize 14e complexes, certain catalytic applications improve when the substituents at this α-position are flexible (cf. section 5). Moreover, the coordinatively saturated rhodium complex **188b** is structurally related to other rhodium carbene complexes and allows comparison of ligand effects. Based on CO stretching frequencies in the corresponding $RhCl(CO)_2$ complexes, these CAACs are stronger donors than classical NHCs, yet weaker than C4-bound abnormal imidazolylidenes. This outcome has been attributed to a combination of relatively strong σ-donor and weak π-acceptor properties of CAACs.

Flexible substituents such as the cyclohexyl group in **186b** provide facile access to bis(carbene) complexes of gold via homoleptic rearrangement from (CAAC)AuCl to $[(CAAC)_2Au]^+$ and $[AuCl_2]^-$.[134] A similar rearrangement can be prevented using bulky ligands such as **186a** or **186c**, which comprise an adamantyl-derived motif to stabilize the gold carbene complex **189**. Remarkably, abstraction of the metal-bound halide in **189** affords **190**, which is a rare example of a stable arene Au^+ π-complex (see Scheme 65).[135]

In an attempt to synthesize Grubbs-type catalysts featuring CAACs, the carbenes **191** were reacted with the Ru precursor complex **192** (see Scheme 66).[136] However, an unexpected air-sensitive product **193** was obtained, in which the phosphine rather than the pyridine was replaced by the carbene ligand. Based on the same principle, the related Grubbs-Hoveyda catalyst **194** was successfully prepared from the corresponding phosphine ruthenium precursor.

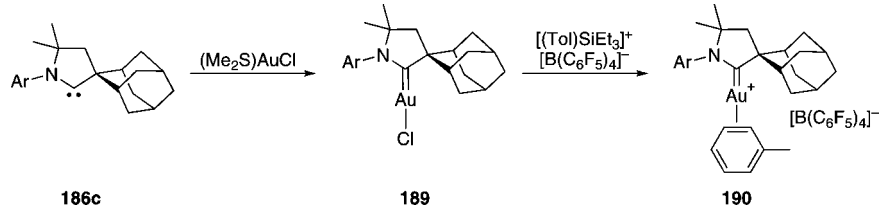
2.5.2. Oxidative Addition

In analogy to other less-stabilized NHC complexation procedures (*vide supra*), oxidative addition was also successfully applied for the preparation of a CAAC complex. Starting from the chloride salt precursor **195**, oxidative addition to Pd^0 occurred smoothly and afforded the neutral complex **196** (see Scheme 67).[137] Both chlorides are coordinated to the Pd center in the product and, in contrast to the pyrazolylidene analogue **73** (cf. Scheme 26), the halides adopt a mutual *trans* disposition.

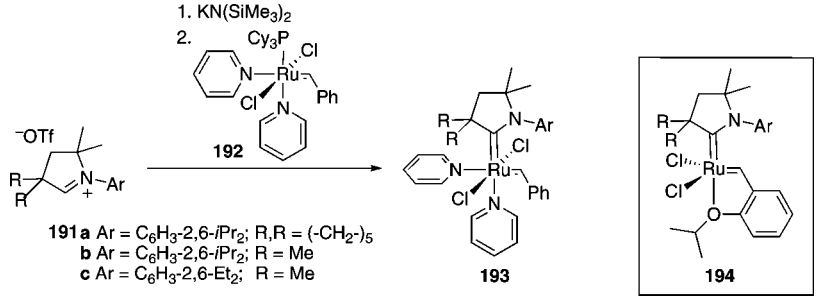
2.5.3. C−H Bond Activation

Direct C−H bond activation has been explored little in the synthesis of carbene complexes that comprise saturated

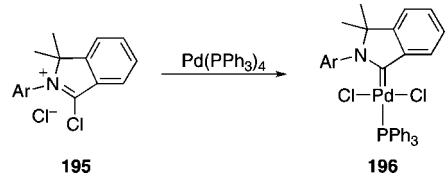
Scheme 65



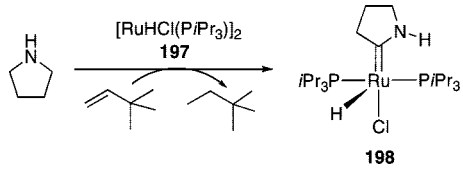
Scheme 66



Scheme 67



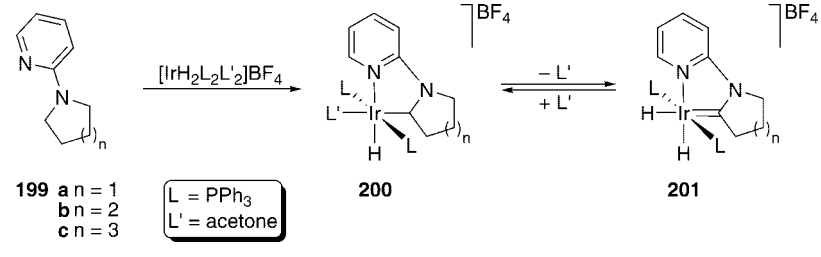
Scheme 68



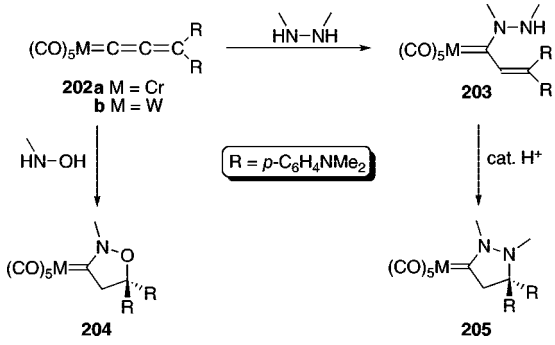
heterocycles. In an unusual approach, the 14-electron species **197** has been used to geminally dehydrogenate pyrrol, thus generating the carbene complex **198** (see Scheme 68).[138] The formation of $RuH(H_2)Cl(PiPr_3)_2$ as a side product is efficiently suppressed in the presence of *t*-butyl ethylene as a H_2 scavenger. Interestingly, piperidine undergoes a similar double dehydrogenation only with the osmium analogue of **197**, $OsHCl(PiPr_3)_2$, but not with the Ru complex itself. Apparently, subtle steric differences in the heterocycle have a pronounced influence on this reaction.

A similar reactivity has also been observed with the iridium complex $[Ir(H)_2(PPh_3)_2(acetone)_2]$. Double sequential α C−H bond activations in **199** produce the carbene complex **201** (see Scheme 69).[139] In a coordinating solvent such as acetone, the second α-elimination is reversed and carbene insertion into the Ir−H bond affords the alkyl iridium complex **200**. Such solvent-induced toggeling between carbene and alkyl bonding modes may provide access to useful (catalytic) applications, perhaps involving hydrogen-transfer reactions. Similarly to ring-expanded classical NHCs (which are comprised of two stabilizing heteroatoms bound to the carbene carbon),[140] an increase of the ring size of the carbene in **201** induces a marked downfield shift of the carbene carbon ^{13}C NMR resonance ($\delta_C = 258.3$ in **201a**, $\delta_C = 262.2$ in **201b**, and $\delta_C = 270.7$ in **201c**), suggesting a higher degree of Fischer carbene character in the ring-expanded systems.

Scheme 69



Scheme 70



2.5.4. Cycloaddition to Fischer Carbene Complexes

Heterocyclic ring formation from Fischer-type allenylidene complexes provides a versatile pathway for the synthesis of nonconjugated heterocyclic carbene complexes. This route is related to the method used in the preparation of pyrazolylidene complexes (cf. Scheme 34). For example, the reaction of the allenylidene complex **202** with hydroxylmethylamine furnishes the unsaturated isoxazolinylidene complex **204** (see Scheme 70).[141] With diamines, complex **203** is obtained and acid catalysis is required to promote cyclization of the carbene ligand.[66,142] The ring closure has only a minor effect on the IR spectroscopic properties of the CO ligands (see Table 4). This result indicates similar donor properties and bonding characteristics for the saturated pyrazolinylidene in **205** and related acyclic Fischer aminocarbene complexes. According to the CO stretching vibrations, pyrazolylidenes are slightly weaker donors than their unsaturated pyrazolylidene analogs (cf. **90** in Scheme 34), yet they are stronger than the corresponding isoxazolinylidene ligand in **204**, although the differences are small. The reactivity differences are more significant: in contrast to the **90** complex, the pyrazolinylidene ligand in complex **205** is inert and not transferable to late transition metals.

Cyclic (amino)(alkyl)carbene complexes related to **204** and **205** have been synthesized via various different methods, including C═O activation in lactames, alkylation of coordinated isocyanides, and heteroatom substitution in oxacycloalkylidene complexes of chromium with an NH unit.

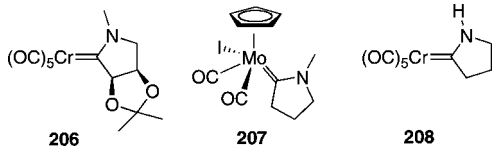
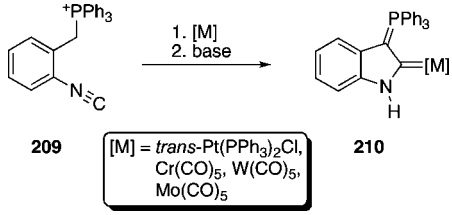


Figure 10. Representative examples of *N*-heterocyclic carbene complexes that may be classified either as cyclic (amino)(alkyl)-carbene or as Fischer carbene complexes, made by lactam C=O activation (**206**), isocyanide alkylation (**207**), and substitution of the heteroatom in cyclopentenylidene complexes (**208**).

Scheme 71



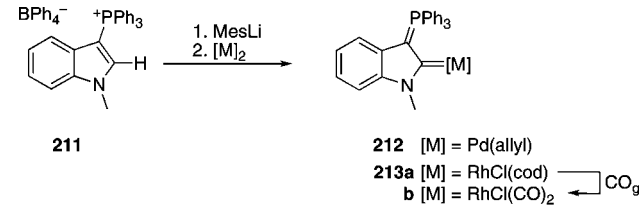
Representative products of these reactions are shown in Figure 10 (**206**−**208**).[143] Because of their chemistry, these complexes are generally called Fischer aminocarbene complexes and, therefore, are not treated any further here; Fischer-type carbene complexes have been reviewed elsewhere.[144]

2.5.5. (Amino)(Ylide)Carbenes

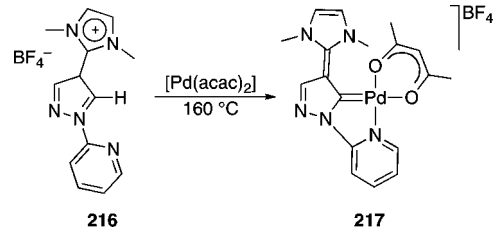
Recently, an important variation within NHC chemistry was revitalized by incorporating heteroatom stabilization by virtue of an exocyclic ylide residue. Ligands such as (amino)(ylide)carbenes (AYCs) had originally been prepared from phosphonium-functionalized isocyanides such as **209** by metal coordination and subsequent base-induced ring closure (see Scheme 71).[145] Electrochemical studies on the formed complexes **210** suggested a weak yet noticeable correlation of the electron density at the metal with the substituents at the phosphorus ylide functionality.

A new synthetic route toward such AYC complexes involves cyclization prior to metal coordination. The phosphonium-substituted indol **211** (Scheme 72) has been deprotonated with a sterically demanding base such as MesLi or K[N(SiMe$_3$)$_2$]. The anticipated free carbene readily coordinates to a suitable Pd^{2+} or Rh^{+} complex to form the complexes **212** and **213**, respectively.[146] Employing such methods, complexes that contain AYCs stabilized by an internal sulfonium-ylide **214** or composed of a pyrazol-derived heterocycle **215** have also been prepared.[147]

Scheme 72



Scheme 73



The observed CO frequencies in the IR spectra of **213b** (average ν_{CO} = 2012 cm^{-1}), **214** (average ν_{CO} = 2014 cm^{-1}), and **215** (average ν_{CO} = 2009 cm^{-1}) indicate a remarkably high electron-donating ability of these carbene ligands (cf. ν_{CO} = 2036 cm^{-1} for the 2-imidazolylidene analogue), as also inferred from the chromium complex **210**. The data further suggest that the donor ability and bonding features of the carbene may be tunable through a judicious choice of the ylide moiety and heterocycle backbone. However, further investigations are warranted to transform these isolated observations into clear and useful trends. Calculations have indicated that the increased electron donor character is predominantly a result of strong σ donation, rather than weak π-acceptor properties.

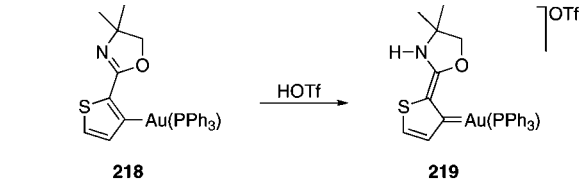
A special type of ylide-stabilized carbene ligand consists of *C*-ylides comprising a carbene as substituent. While metallation of the iminium salt **216** via intermediate formation of a free carbene has failed thus far, cyclometallation using Pd(acac)$_2$ at elevated temperatures produces complex **217** (see Scheme 73).[147]

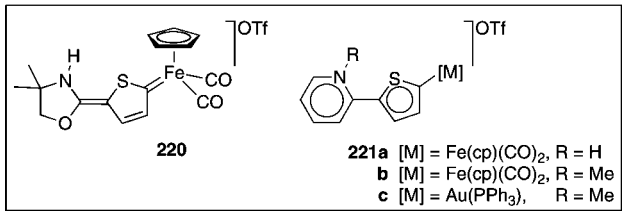
An interesting variation within the theme of exocyclic carbene stabilization has been exploited by inserting a thiene

Table 4. Spectroscopic Data for Chromium Pentacarbonyl Complexes Containing Carbene Ligands

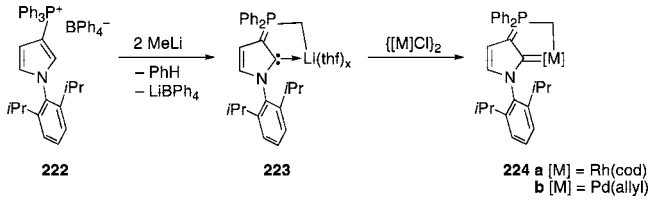
type of carbene	complex	δ_C (carbene)	ν_{CO} (cm^{-1})	reference
3-pyrazolylidene	**90**	190.8	2049, 1938, 1926	65a
3-pyrazolinylidene	**205a**	241.6	2052, 1966, 1926	66
3-oxazolinylidene	**204a**	222.2	2058, 1973, 1932	141
4-pyridylidene	**180a**	236.2	2043, 1919	127a
4-pyridylidene	**180b**	235.0	2043, 1919	127a
4-pyridylidene	**180c**	243.2	2043, 1919	127a
4-pyridylidene	**180d**	225.6	2043, 1923	127a
acyclic (amino)(alkyl)carbene	**206**	265.1	2058, 1978, 1940, 1939	143a
cyclic (amino)(alkyl)carbene	**208**	271.2	2054, 1965, 1927	143c
cyclic (amino)(vinyl)carbene	**225**	249.2	2044, 1956, 1918	65b
cyclic (amino)(vinyl)carbene	**227a**	231.4	2047, 1919, 1902	150
cyclic (amino)(vinyl)carbene	**227b**	229.9	2048, 1920, 1903	150
cyclic (mercapto)(vinyl)carbene	**226**	270.9	2044, 1962, 1924	65b
acyclic (amino)(vinyl)carbene	**203a**	250.1	2052, 1970, 1928	142
acyclic (alkoxy)(vinyl)carbene	**179a**	290.7	2050, 1936, 1930	127b

Scheme 74





Scheme 75



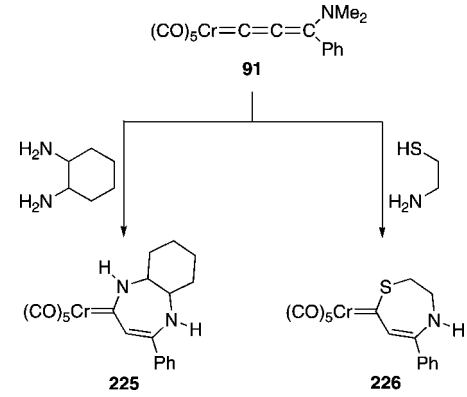
moiety between the metal center and the heterocycle (see Scheme 74).[61,148] Based on IR and NMR data of the complexes **220** and **221**, the metal−carbon bonds in the former compound lay claim to a significant π-contribution from the metal, whereas in complex **221**, the cationic charge is much more localized on the nitrogen-containing heterocycle than toward the metal, suggesting a preponderance of a zwitterionic structure.

The concept of AYCs has recently been expanded to include chelating ligands by resorting to the base sensitivity of the ylide moiety in the free carbenes.[146] When using MeLi (2 mol equiv) as a base for deprotonation of the pyrrol phosphonium ylide **222**, Bertrand and co-workers have observed the substitution of a phenyl residue by a CH_2Li unit, thus yielding the lithium carbene species **223** (see Scheme 75).[149] Mechanistic investigations suggest a stepwise process with, first, the addition of CH_3^- anion to the phosphonium unit and the subsequent base-mediated elimination of Ph−H to form **223**. Transmetallation with Rh^+ and Pd^{2+} precursors provided the new complexes **224**, both comprising a monoanionic *C*,*C*-bidentate coordinating AYC ligand.

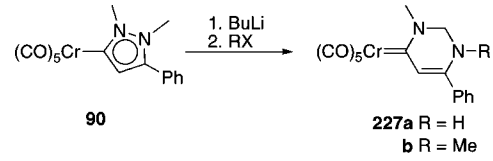
2.6. Miscellaneous *N*-Heterocyclic Carbenes with Low Heteroatom Stabilization

Seven-membered heterocyclic carbenes with only one stabilizing heteroatom adjacent to the carbene carbon have been prepared by cycloaddition of a diamine or an aminothiol to the allenylidene **91**, thus affording complexes **225** and **226**, respectively (Scheme 76).[65b] IR spectroscopic analysis (Table 4) revealed that the seven-membered carbenes transfer slightly less electron density onto the metal than a normal pyrazolylidene ligand (such as **90**, cf. Scheme 34). This trend is not reflected in the corresponding ^{13}C NMR data. Furthermore, related absorption data for complexes **225** and **226** suggest that the type of heteroatom has only a minor influence on the donor properties of these ligands.

Scheme 76



Scheme 77



The six-membered analog of the heterocyclic carbene in **225** has been prepared via an unusual rearrangement in the pyrazolylidene complex **90** (see Scheme 77).[150] Deprotonation with BuLi occurrs selectively at the *N*-methyl group that is situated remote from the carbene C atom and induces a rearrangement to the six-membered ligand. Subsequent protonation or alkylation yielded complex **227**. According to IR spectroscopic measurements (Table 4), the six-membered carbene seems to be a stronger donor than its seven-membered congeners.

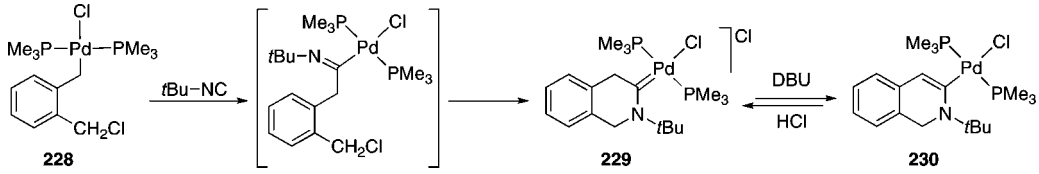
A different synthetic approach involving cyclization at the metal has been utilized for synthesizing the palladium carbene complex **229** (see Scheme 78). The addition of *t*-butyl isocyanide to the *ortho*-xylyl complex **228** results in the formation of a heterocycle and affords the cationic carbene complex **229**.[151] Cyclization is probably initiated by isocyanide insertion into the Pd−C bond of **228**, followed by nucleophilic substitution of the benzylic chloride to form the ring. The acidic proton in a position α to the carbene carbon in **229** can be abstracted in a reversible reaction by relatively mild bases, such as 1,8-diazabicyclo[5.4.0]undecene (DBU), to afford the neutral vinyl complex **230**. Remarkably, the NMR shift of the metal-bound carbon barely changes upon deprotonation ($\Delta\delta_C \approx 6$), despite the significant rehybridization and conformational changes that are associated with this reaction. In the **229** complex, the heterocycle is forced into a boat conformation, whereas, in **230**, it is essentially planar.

3. Carbenes or Zwitterionic Ligands?

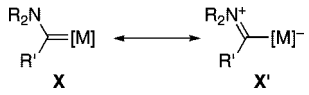
The question of carbene (or carbenoid) character in so-called metal carbene complexes and, more particularly, the importance of $M-C_{carbene}$ π-interaction has been addressed—albeit not always satisfactorily—since the characterization of the first Fischer-type carbene complexes.[152] Aminocarbene complexes of Group 6 metals have become prime examples to illustrate the bonding behavior of such complexes, using two extreme canonical representations (see Scheme 79).

The relevance of the zwitterionic form **X′** is readily appreciated by the chemical nonequivalence of the two *N*-bound R groups in the ^1H and ^{13}C NMR spectra.

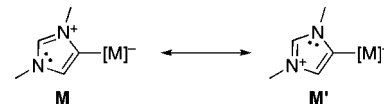
Scheme 78



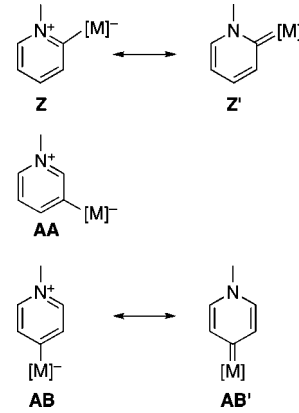
Scheme 79



Scheme 80



Scheme 81



In NHC complex chemistry, the prevalence of metal−ligand π-interaction has become a controversial and still unsettled issue,[153] and with the current boom of homogeneous gold catalysis in organic synthesis, the importance of π-interactions is again being discussed.[154] With the growing relevance of abnormal and remote NHC complexes, the nature of the synergistic metal−carbene bonding is addressed continuously. The biggest impediment to clearing up this problem is probably the general insensitivity of the metal−carbene bond length to small changes in bond order. However, Bercaw and co-workers indicated that such changes can be evoked by providing competing possibilities for diminishing the positive charge on the carbene C atom.[110] Thus, variations in the contributions of limiting structures can be measured.

Various other physical methods have been utilized to study the attachment of nonclassical NHCs to metal fragments. While IR spectroscopic measurements provide a satisfactory method for quantifying the donor power of ligands *trans* to CO (Tolman parametrization), such analyses do not clearly allow for dividing bonds into σ- and π-contributions. Often, the chemical shift of the carbene C nucleus in ^{13}C NMR spectroscopy has been correlated with the carbene character. Such data must be considered with utmost care, because the NMR resonance is affected by multiple components. Factors such as the position of the heteroatom(s), the substitution pattern, contribution from aromaticity, steric constraints, or the nature of *cis*-positioned ligands affect the chemical shift substantially and limit the use of NMR data for bonding-mode analysis. Often, correlation of the ^{13}C NMR data with other analytical techniques is relatively poor (cf. Tables 2 and 4), thus indicating that such data must be critically evaluated. Ideally, comparisons should concentrate on homologous series of compounds or related structural isomers. This is also the situation for metal−carbon coupling constants $^1J_{MC}$. Often they do not follow a consistent trend[56] and their discussion has been contradictory.[93,110]

Inherent in the association of a larger ^{13}C chemical shift with more "carbene character" is the assumption that metal-to-carbene π-back-donation does not effect the same amount of carbon shielding to the donor C atom as participation in π-bond formation within the heterocyclic ring. In the outstanding work of Tanaka and co-workers,[106,108,109] such conclusions are corroborated by significant shifts of the metal oxidation potentials, as a consequence of the expected difference in charge transfer. The sensitivity of the chemical shift of the C donor atom toward the effect exercised by ancillary ligands is probably most dramatically illustrated by the work of Rourke's group. Modification of the ligands in the complexes **163**−**165**, accompanied by changes in structure and by steric effects, induces a shift of >100 ppm (cf. Section 2.4.3).[115]

The two largest groups of compounds treated in this review are the abnormal 4-imidazolylidenes and the pyridinium-derived carbene complexes. For the former group, it is not possible to write formally neutral valence-bond contributing structures wherein the metal participates in π-bonding with the carbene ligand. The formal positive charge is shared between the two nitrogens, whereas the negative charge is directed toward the metal center and the metal-bound carbon (see Scheme 80). Analogous considerations hold for complexes that contain 4-pyrazolylidene ligands (cf. **O** in Figure 4). Nevertheless, with six π-type electrons available, potential M−C π-interactions involving a π^* molecular orbital (MO) of the heterocyclic ring may, of course, not be excluded.[37] All studies consistently indicate that the ligands belonging to these classes are pre-eminently very strong σ-donors and weaker π-acceptors than their normal isomers, and these complexes also exhibit significantly lower ^{13}C chemical shifts than the 2-imidazolylidenes.

Pyridinium-derived carbenes can be of the normal non-remote **Z**, abnormal remote **AA**, and normal remote **AB** type (cf. Scheme 36). The most important contributing neutral resonance structures are illustrated in Scheme 81.

Theoretical studies on the metal−carbon bond by energy decomposition analysis revealed that, in all investigated NHC complexes, this bond is predominantly electrostatic.[14,37,77,78,84] Only about one-third of the bonding energy has been attributed to covalent interactions. This portion can be further separated into ~20 ± 5% π-bonding and 80 ± 5% σ-interactions. Such a bonding situation is highly reminiscient of that in amino carbene complexes of the Fischer type.[85] The exact σ/π bond contribution depends on the type of carbene and also on the electronic configuration at the metal center. In contrast to the composition of the M−C bond, the bond strength is highly sensitive to the number of stabilizing heteroatoms and their position relative to the carbenoid

Table 5. Catalytic Activity of Complexes with Less-stabilized Carbene Ligands

type of carbene ligand	catalyst precursor	catalyzed reaction	reference(s)
C4-bound imidazolylidene	**13**, **55a**	Mizoroki−Heck	24, 51
C4-bound imidazolylidene	**13**, **235**, **236**	Suzuki−Miyaura	24, 164
C4-bound imidazolylidene	**231**	biaryl coupling	162
C4-bound imidazolylidene	**236**	direct hydrogenation	35
C4-bound imidazolylidene	**31**, **238**, **240**	transfer hydrogenation	34, 39
C4-bound imidazolylidene	**245**	hydrosilylation	170
C3-bound pyrazolylidene	**73**	Mizoroki−Heck	57
C3-bound pyrazolylidene	**69**, **70**	transfer hydrogenation	34
C4-bound pyrazolylidene	**233**	Suzuki−Miyaura	58
C2-bound pyridylidene	**156b, 232**	Mizoroki−Heck	111
C2-bound pyridylidene	**104b**	Suzuki−Miyaura	77
C2-bound pyridylidene	**106a**	Kumada−Corriu	80
C2-bound pyridylidene	**174**	hydrosilylation	122
C3-bound pyridylidene	**112b**	Suzuki−Miyaura	77
C4-bound pyridylidene	**111b**	Mizoroki−Heck	77
C4-bound pyridylidene	**108b**, **158**	Suzuki−Miyaura	77, 112
C4-bound pyridylidene	**110a**	Kumada−Corriu	80
cyclic (amino)(alkyl)carbene	**188a**	α-keto arylation	131
cyclic (amino)(alkyl)carbene	**194**	olefin metathesis	136, 171

carbon. Calculations have predicted that adjacent N atoms reduce the energy level of the σ lone pair orbital of the ligand and thus the bonding energy.[82,84] Hence, the higher the stability of the free carbene, the weaker the metal−carbon bond in the complex. The reactivity patterns illustrated in the previous sections indicate, however, that this generalization needs considerable caution. For example, reductive eliminations appear to be much easier in C4-bound imidazolylidenes than in their C2-bound congeners.[7] Similarly, the Ag−C bond in C4-bound imidazolylidene and triazolylidene complexes seems considerably less stable than the analogous bond in Ag complexes of 2-imidazolylidenes.[20,28]

4. Donor Properties of the Ligands

The overall donor ability of ligands has generally been characterized according to two complementary scales: Tolman's electronic parameters (TEPs)[29] and Lever's electronic parameters (LEPs).[155] A recent study successfully illustrated that the two parametrization systems are consistent and can mutually be translated.[156] The TEP of a given ligand is determined by IR spectroscopy, using the pertinent CO stretching vibrations. This method was developed originally for nickel complexes, $Ni(CO)_3(L)$, although it has recently been adapted to other metals as well. Specifically, it has been shown that the associated TEP of ligands L in complexes of general formula $IrCl(CO)_2(L)$ can be determined by using linear regression methods.[53] Hence, the CO stretching frequency, taken as an average of the asymmetric and the symmetric vibration, offers a direct probe for the donor ability of the corresponding ligand. This method has been extensively used in NHC chemistry, and pertinent data are available also for many abnormal carbene ligands.

A similar correlation has been derived for the TEP and the average of the CO stretching vibrations in the complexes $Cr(CO)_5(L)$, which is particularly useful for NHC subclasses prepared from Fischer carbene complexes.[157] In contrast, donor quantification based on $RhCl(CO)_2(L)$ complexes have long been on weak grounds, despite the fact that many studies use this $RhCl(CO)_2$ synthon for the assessment of donor ability.[41,56,131,132,158,159] To the best of our knowledge, the correlation between the TEP (or LEP) and the CO vibrations in these Rh complexes has not yet been established. In a recent study, Wolf and Plenio succeeded, for the first time, in demonstrating a linear relationship of the ν_{CO} frequencies between complexes of the type $IrCl(CO)_2(L)$ and $RhCl(CO)_2(L)$.[160] Several new rhodium (I) and iridium (I) complexes will be required to demonstrate the validity and the sensitivity of the established correlation of the two scales and to identify potential limitations. It is conceivable that stereoelectronic effects influence the *cis*-located CO ligand to such an extent that the IR frequencies may reflect steric effects of the ligand and not only electronic parameters. Therefore, caution is required in using CO stretching frequencies as a unifying concept for probing the ligand donor properties, in particular when comparing sterically very different carbene systems. For example, the size of the heterocyclic carbene (5-membered vs 6-membered) and the presence and nature of substituents (e.g., protons *ortho* to the metallated carbon in many 4-pyridylidene ligands vs alkyl or aryl substituents in 2-imidazolylidenes) may induce a shift of the CO stretching frequencies that cannot be attributed exclusively to electronic effects.

Notably, the second parametrization of ligands by electrochemical methods and leading to LEPs has only rarely been used in carbene chemistry.[13,161] While electrochemical methods require more sophisticated set-ups and are more laborious, they may become relevant with ligand systems where IR absorption spectroscopy is not suitable.[41,132,158]

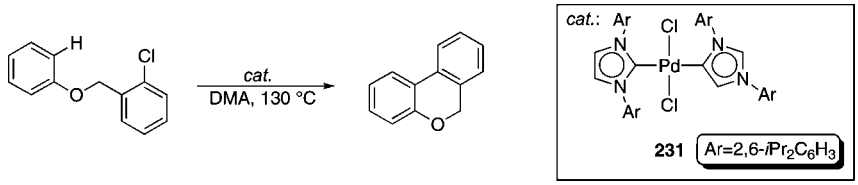
5. Catalytic Applications

The activity of transition-metal complexes in homogeneous catalysis is, by and large, a function of the ligands that are attached to the metal center. The influence and electronic impact of nonclassical carbene ligands on metal centers has been investigated in many situations, which are summarized in Table 5. Not unexpectedly, Pd complexes have received the most attention, although, lately, also catalytic applications of Ni, Rh, and Ru complexes have been reported.

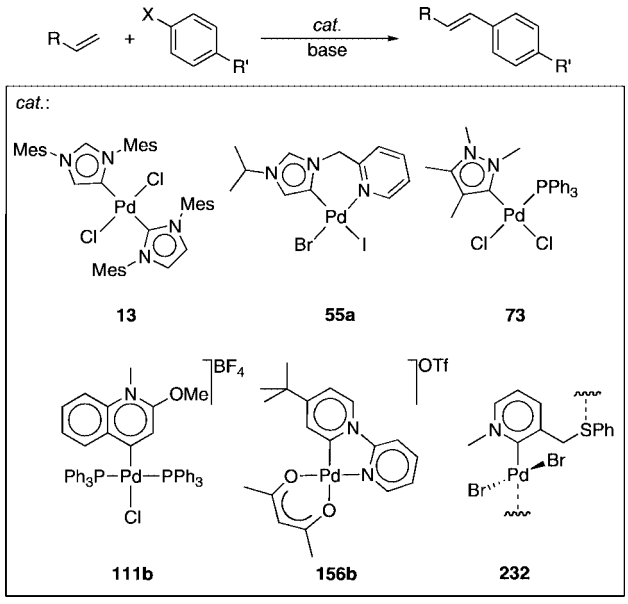
5.1. Carbon−Carbon Cross-Coupling Reactions

Palladium carbene complexes have been used in a variety of C−C bond-forming reactions. For example, the C4-bound carbene complex **13** is an efficient catalyst in the Heck

Scheme 82



Scheme 83



olefination of aryl bromides.[24] In contrast, the corresponding normal analogue **12** is virtually inactive under identical conditions. Remarkably, when preparing the catalyst *in situ* with a mixture of precursor imidazolium salt and $[Pd(OAc)_2]$ in the presence of Cs_2CO_3, i.e., conditions that are used to synthesize normal **12**, the catalytic activity is almost identical to that of **13**. Similar results were obtained for the Suzuki−Miyaura cross-coupling of aryl chlorides with arylboronic acids.

A close analogue of **13**, which comprises diisopropylaryl rather than mesityl wingtip groups **231**, has been used in the intramolecular arylation of aryl chlorides (see Scheme 82).

In these reactions, however, the abnormal complex is significantly less efficient than classical NHC-palladium catalysts or mixtures of $[Pd(OAc)_2]$ and imidazolium salts.[162] Mechanistic investigations suggest that the catalytically active species may also be formed from palladium black and imidazolium salts. These observations could point to a heterogeneous mode of action.

Various pyridinium-derived Pd complexes have been used in Mizoroki−Heck olefin arylation (see Scheme 83). Common to all catalysts is their relatively low reactivity toward aryl chlorides and the fact that high reaction temperatures are usually required for appreciable conversions. For example, the cationic pyridylidene complex **111b** couples activated and deactivated aryl bromides with butylacrylate at 145 °C.[77,78] The catalyst is considerably more active than the analogous normally C2-bound imidazolylidene complex. In contrast, the palladium 2-pyridylidene catalyst **156b** is not significantly faster in catalyzing Heck-type olefin arylation than $Pd_2(dba)_3$.[111] Similarly, the pyrazolylidene complex **73** has shown relatively low catalytic performance.[57] However, it is a considerably more-active complex than related Pd complexes that contain 2-imidazolylidene ligands with similar steric bulk.

Along these lines, Heck arylation of olefins with the abnormal imidazolylidene carbene complex **55a** as a catalyst has been tested in the presence of excess Hg^0.[49] A marked decrease in catalyst activity was noted, which indicates a mechanism that involves, at least in part, heterogeneous palladium. In this case, the main function of the carbene ligand seems to be the controlled release of palladium from the complex. Ideally, the rate of palladium dissociation is fast enough to achieve high turnover frequencies (TOFs), yet slow enough to prevent metal aggregation and the formation of palladium black. Similar conclusions have been drawn from mechanistic investigations using the pyridylidene complex **232** in Heck-type coupling reactions.[99b]

Suzuki-type aryl cross-coupling reactions have been tested with a variety of catalysts (see Scheme 84). Given the fact that very low catalyst loadings are usually sufficient to catalyze this reaction,[163] good catalytic activities are not very surprising. Notably, the kinetic reaction profile of some catalytic runs (e.g., **111b**, cf. Scheme 83) indicates remarkably high initial TOFs, followed by a sharp reduction of the conversion rates.[77,78] These features, combined with the high reaction temperatures, may point to ligand dissociation and formation of (colloidal) Pd^0, although palladium black has not been observed at the end of the reaction.

The cationic abnormal carbene complex **233**, derived from the neutral complex **75a** (cf. Scheme 27), catalyzes biaryl cross-coupling reactions at room temperature and in aqueous media.[58] Good yields were obtained for activated aryl bromides, and at 80 °C also for deactivated aryl bromides. An appreciable 37% conversion of aryl chlorides was recorded, which may be further improved by suitable ligand tuning and catalyst optimization.

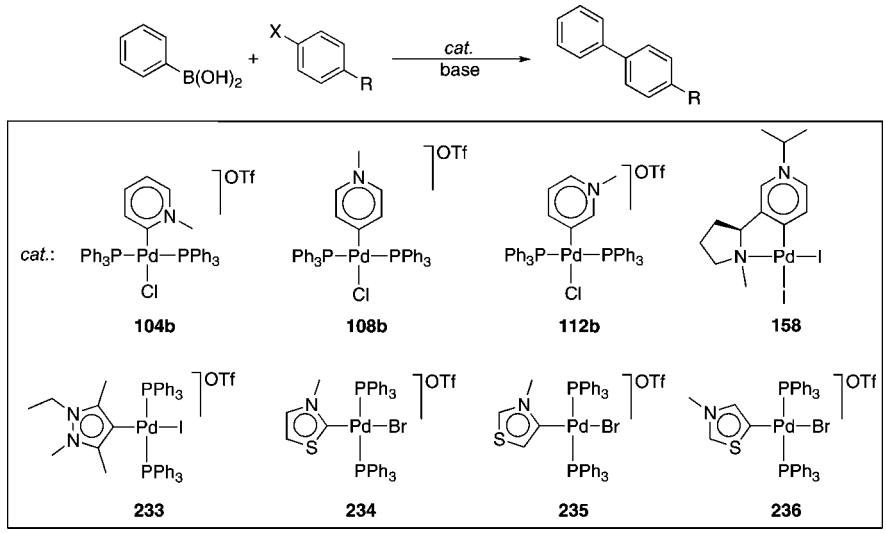
A series of related complexes **234**−**236** (see Scheme 84) that contain a thiazolylidene ligand, featuring either normal or abnormal carbene bonding, has been tested in Suzuki cross-coupling, using phenylboronic acid and bromoacetophenone as an activated substrate (cf. Scheme 84, X = Br, R = $COCH_3$).[164] Reactions performed at 70 °C provide a trend in activity that decreases slightly in the following order:

C2-bound complexes **234** >
C4-bound complexes **235** > C5-bound complexes **236**

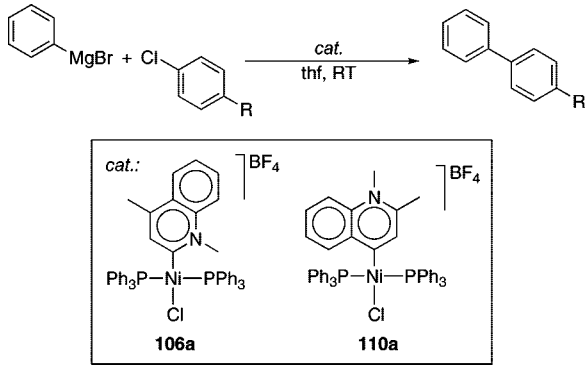
This sequence suggests that abnormal bonding, such as that in **235** and **236**, is disadvantageous, whereas steric bulk in at least one *ortho* position is beneficial. Notably, time-dependent monitoring of the catalytic reaction does not indicate a significant decrease of activity in any of the three systems.

A similar comparison of the influence of different carbene bonding modes has been performed with pyridylidene Pd complexes **104b**, **108b**, and **112b** (cf. Figure 5), which is comprised of a normal C2-bound carbene, a remote (and

Scheme 84



Scheme 85



normal) C4-bound carbene, and an abnormal (and remote) C3-bound carbene, respectively. Initial activity of the normal pyridylidene complexes **104b** and **180b** in the Suzuki cross-coupling are identical, whereas the abnormal pyridylidene complex is slightly less active. In terms of stability, the catalysts generated from remote pyridylidene complexes **108b** or **112b** are superior to the *ortho*-substituted pyridylidene system derived from **104b**, which seems to deactivate after a few hours.

High temperatures are required for Suzuki cross-coupling reactions catalyzed by complex **158**, which is comprised of a chelating remote pyridylidene-type ligand.[112] Interestingly, the activity of this complex is comparable to *in situ*-generated catalysts from $Pd(OAc)_2$ in pyridinium-based ionic liquids.[165] These results could suggest that the active species in both processes is similar.

The cationic pyridylidene nickel(II) complexes **104a**−**111a** have been investigated in the Kumada−Corriu cross-coupling of Grignard compounds with aryl halides (see Scheme 85).[80] The catalytic activity shows a considerable dependence on the substitution of the heterocycle, which, therefore, offers efficient tuning possibilities. With the 2-pyridylidene complex **106a** and the remote carbene complex **110a**, a catalytic performance has been achieved that compares well with the most active system known to date, viz, a mixture of IMes·HBF_4 and $[Ni(acac)_2]$.[166] These pyridylidene Ni systems also allow for the transformation of deactivated aryl chlorides, with good conversions. A color change was observed at the onset of the reaction, which may point to a reduction of the catalyst precursor into a more active nickel(0) form. A related C2-bound bis(2-imidazolylidene) nickel complex appeared to be virtually inactive in this cross-coupling reaction.

Saturated cyclic (alkyl)(amino)carbenes have been successfully used as catalysts for the α-arylation of propiophenones (see Scheme 86).[131] The catalytic performance of the Pd center is strongly dependent on the substitution pattern at the α-carbon of the catalyst. Flexible yet sterically demanding substituents, such as the cyclohexyl group in **188a**, seem to be particularly beneficial, because this group can easily switch between different conformations.

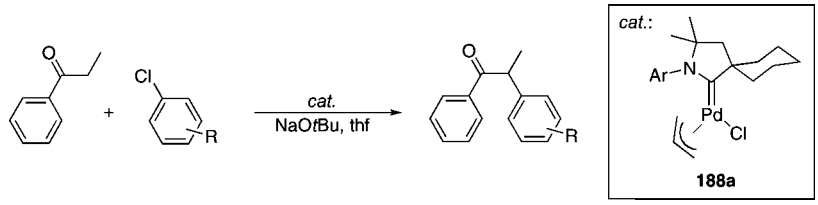
5.2. Hydrogenation and Hydrosilylation Reactions

Apart from C−C bond-forming reactions, certain NHC-metal complexes are also useful catalysts for hydrogenation reactions. Direct hydrogenation under mild conditions has been catalyzed by the cationic Pd(dicarbene) complex **237** (see Scheme 87).[35] The activity of this complex is significantly higher than that of its C2-bound analogue, possibly because of the higher electron density at the metal center, which may facilitate the oxidative addition of H_2 during the catalytic process. Mechanistic studies have also indicated a heterogeneous mode of action of the catalyst due to the formation of nanoparticles.[167] Particle formation may be stimulated under the mildly reducing conditions during hydrogenation.[168] However, these findings do not rule out several modes of actions that operate in parallel, and, at present, it is difficult to draw a definite conclusion.

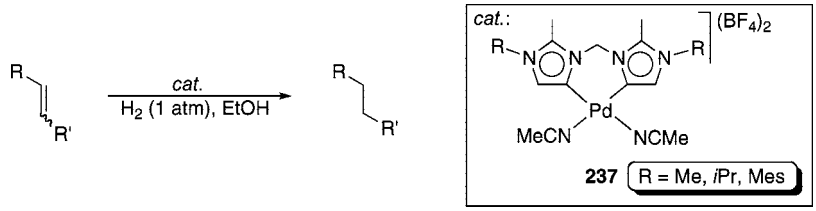
Recently, related Rh complexes such as **238** have been used as catalysts for the transfer hydrogenation of ketones, using *i*-PrOH as a hydrogen source (see Scheme 88).[39] While activities are acceptable (TOF values at 50% conversion are >200 h^{-1}), it is noteworthy that the corresponding C2-bound Rh complexes are virtually inactive in catalyzing such hydrogen-transfer reactions. This behavior may again be a direct consequence of the electronic differences imposed by the C4-bound imidazolylidene ligands, which provide higher electron density at the metal center. Stronger donation is supposed to weaken the rhodium−alkoxide bond, thus facilitating β-hydrogen elimination and product release.

In a recent study, Peris and co-workers have compared different normal and abnormal carbenes in the β-alkylation of secondary alcohols (see Scheme 89).[34] This reaction is

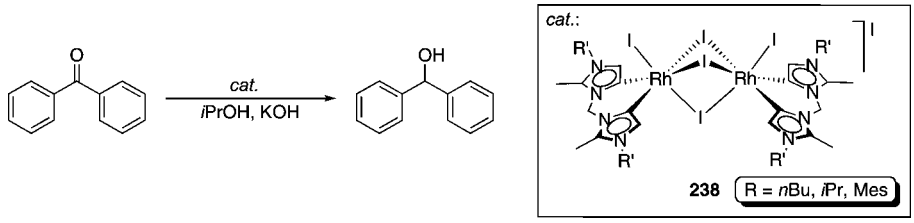
Scheme 86



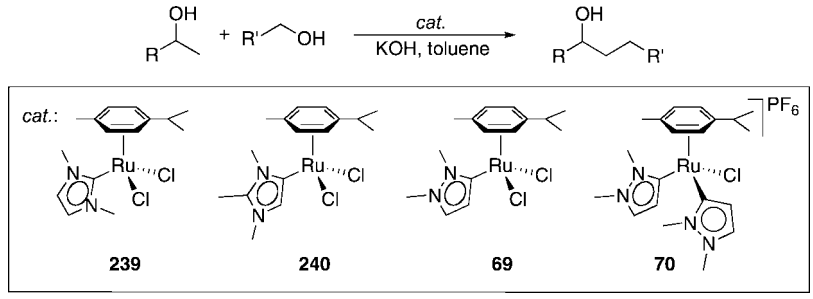
Scheme 87



Scheme 88



Scheme 89



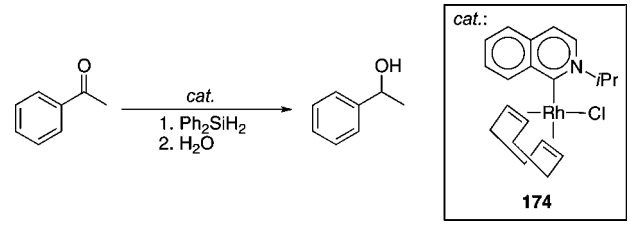
believed to involve a cascade process that is comprised of alcohol dehydrogenation, subsequent aldol condensation, and, finally, hydrogenation of the α,β-unsaturated ketone.[169] The cationic bis(pyrazolylidene) complex **70** seems to be most efficient and converted different secondary methyl alcohols to their higher homologues within 10 h or less. When using complexes with only one carbene ligand, reaction times generally increase in the sequence

pyrazolylidene **69** < abnormal carbene **239** < normal carbene **240**

The observed conversions suggest that strong σ-donation, which is inherent to abnormal carbenes and also to pyrazolylidenes, enhances the catalytic activity of the system.

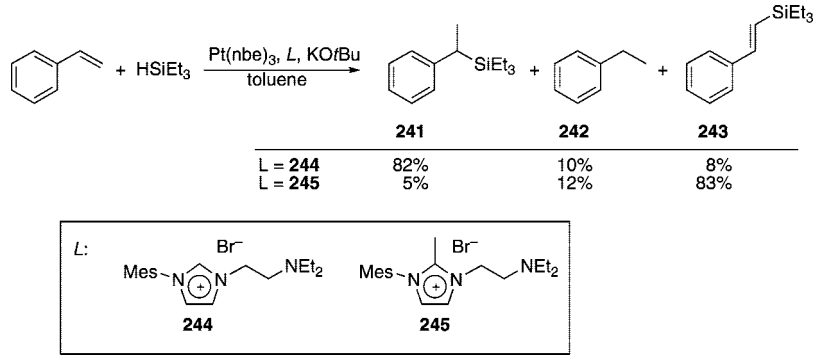
Related to the aforementioned hydrogenation reactions, the pyridylidene Rh complex **174** has been reported to be an active catalyst for the hydrosilylation of ketones (see Scheme 90).[122] After hydrolysis of the silyl ether, the corresponding alcohols are obtained with conversions of up to 50%. This reaction sequence provides an indirect and selective route for carbene metal-mediated hydrogenation of ketones. The catalytic activity of complex **174** appears to be very sensitive to the substitution pattern on the benzene fragment of the isoquinolylidene ligand. Further catalyst optimization is required to make this process competitive and synthetically useful.

Scheme 90

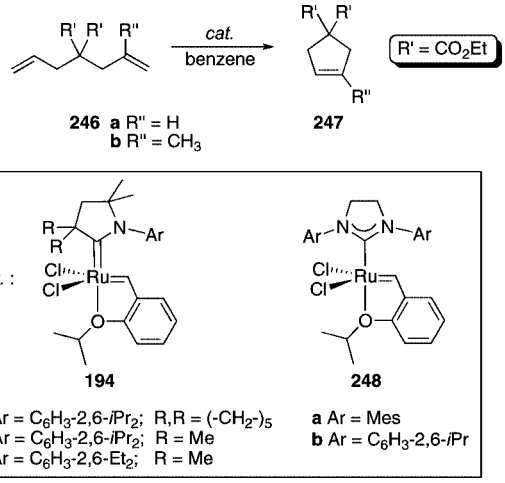


Studies of catalytic hydrosilylation were also undertaken by Cavell and co-workers using a catalyst generated *in situ* from Pt(nbe)$_3$, KO*t*Bu, and different imidazolium salts.[7c,170] The catalyst system based on the 2*H*-imidazolium salt **244** is the most active one and gives predominantly the hydrosilylated product **241** from the reaction of styrene with $HSiEt_3$ (see Scheme 91). Remarkably, with the 2-methylated imidazolium salt **245**, the activity is comparable, yet dehydrogenative silylation is the major pathway and affords predominantly **243** as product. This product is thought to be generated by a β-hydrogen elimination step, following the insertion of styrene into a Pt−Si bond. Apparently, abnormal

Scheme 91



Scheme 92



imidazolylidene coordination has a distinct influence on such a reaction pathway.

5.3. Olefin Metathesis

Cyclic (amino)(alkyl)carbene ruthenium complexes have been exploited as olefin metathesis catalysts.[136,171] The complexes **194**, which feature different bulk at the carbene ligand, can be used for ring-closing metathesis reactions and are compared to the benchmark systems **248** (see Scheme 92 and Table 6). The catalytic activity at the Ru center is strongly dependent on the steric bulk imposed by the ligand. Complex **194a** that contains a large cyclohexyl group adjacent to the carbene moiety is the slowest catalyst and requires heating to 60 °C. The activity of the dimethyl-substituted carbene complex **194b** is considerably higher and has been further improved by reducing the bulk at the aryl nitrogen substituent from diisopropylaryl to diethylaryl groups. Complex **194c** displays ring-closing metathesis activity that is comparable to the most active precursor complexes featuring classical carbene ligands known (e.g., **248b**). The corresponding methyl-substituted analogue, which is supposed to be even more active, could not be prepared thus far. The relevance of steric effects is further emphasized by increasing the bulk on the substrate **246**. For example, the formation of the trisubstituted cyclopentene product **247b** has been slightly slower with the CAAC-ruthenium complex (**194c**) than with the benchmark **248b**; yet, these first results clearly emphasize the potential of less-stabilized carbene ligands in metathesis reactions.

Table 6. Comparison of Catalytic Activities of Ru-Carbene Complexes in Ring Closing Olefin Metathesis

catalyst	R = H			R = CH_3		
	conversion	time	temp	conversion	time	temp
194a	97%	3.3 h	60 °C	95%	20 h	60 °C
194b	95%	10 h	60 °C	96%	48 h	60 °C
194c	95%	15 min	30 °C	95%	60 min	30 °C
248a	95%	20 min	30 °C	95%	45 min	30 °C
248b	97%	13 min	30 °C			

The observed differences in catalytic activity have been attributed to the high sensitivity of the initiation step toward steric modifications. Specifically, rotation about the $Ru{=}C_{benzylidene}$ bond upon Ru−O bond dissociation is critically dependent upon the available space in close proximity to the aryl substituent at nitrogen. The opposite trends in catalyst activity for 2-imidazolylidenes and cyclic (amino)(alkyl) carbenes with bulkier substituents, viz., enhanced activity of **248** vs reduced performance of **194**, is explainable, in part, by the shorter $Ru{-}C_{carbene}$ bond in the CAAC complexes. As a consequence, rotation about the $N{-}C_{aryl}$ bond and about the $C_{aryl}{-}C_{alkyl}$ bonds within the nitrogen substituent is also inhibited.

6. Conclusions

For a long time, the transition-metal chemistry of less-stabilized *N*-heterocyclic carbenes (NHCs) has been a rather neglected area of study. Within the past few years, and certainly stimulated by many serendipitous discoveries as well as rational complex synthesis, the relevance of this type

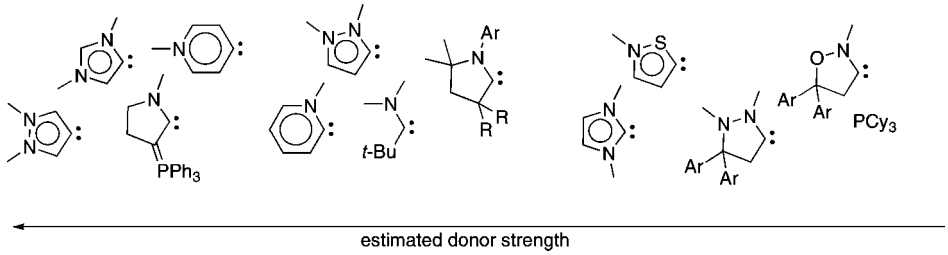


Figure 11. Qualitative estimation of the donor strength of carbenes with reduced heteroatom stabilization, as compared to normal 2-imidazolylidenes and other carbene ligands (based on spectroscopy, reactivity, and calculations).

of carbene ligands has been emphasized. Various preparative routes are now available to make such compounds (cf. Table 1). Although some of these methods are probably rather limited to certain complexes and thus difficult to extrapolate (for example, to include chelate formation or to install a variety of different metal centers), others are more widely applicable and provide coherent approaches toward the synthesis of a broad range of complexes. In such instances, systematic solid-state structural as well as theoretical studies have been undertaken. Based on, among others, NMR, IR, and other spectroscopic studies—culminating in certain instances in Tolman's parametrization concept—it is now evident that the donor strength of these new NHCs varies over a wide range and that the metal center can be tailored for a chosen application (Figure 11). In particular, pyrazolylidenes and C4-bound imidazolylidenes seem to be extraordinary strong donors. Because a consistent methodology for measuring the ligand donor properties is still lacking, comparison is thus far possible only on a punctual level.

Initial catalytic screenings of complexes that contain abnormal, remote, and other classes of NHC ligands with reduced heteroatom stabilization have been performed, and they reveal, indeed, in certain instances, a catalytic scope beyond that which has been observed for phosphine or even classical NHC complexes. Already at this early stage of precatalyst testing and without attempting to significantly involve steric influences, it is safe to predict that highly active systems will become accessible with these exciting new and versatile ligand classes.

7. Acknowledgments

We are most indebted to our many co-workers for their enthusiasm and their dedicated work. Our own work in this research area has been financially supported by the Swiss National Science Foundation, the European Research Council, ERA-net chemistry, BASF, the Alexander von Humboldt Foundation, the Oppenheimer Memorial Trust, and the South African National Research Foundation (Pretoria). Awards of a Feodor Lynen Fellowship by the Alexander von Humboldt Foundation, and a "Leopoldina-Postdoc-Stipendium" by the German Academy of Sciences (BMBF LPD 9901/8-179) to O.S. are gratefully acknowledged. M.A. particularly thanks the Alfred Werner Foundation for an Assistant Professorship.

8. Note Added after ASAP Publication

In the second paragraph of the Introduction, reference 5 was properly cited for the second sentence rather than the first. Additionally, reference 4 was expanded to include seminal work by the early pioneers of the field. The paper originally posted to the Web on March 30, and was reposted on July 22, 2009.

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