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Abnormal NHC Palladium Complexes: Synthesis, Structure, and Reactivity

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Abstract: Developments in palladium chemistry have been spurred predominantly by the outstanding application potential of this metal in catalysis. The quest for new ligands in order to modulate the catalytic activity and selectivity of the palladium center has been greatly stimulated by the discovery of N-heterocyclic carbenes as formally neutral, strongly donating, and covalently binding ligands. Abnormal variations of N-heterocyclic carbenes, even though known (yet not recognized) for 30 years, have received very little attention until recently. In parts this may have been due to the fact that the **free abnormal carbene** ligand is much less stable than the normal carbene analogues. In the last decade, significant progress has been made in abnormal carbene palladium chemistry and reliable synthetic routes as well as promising catalytic applications have been developed. As a consequence, these type of complexes have gradually transformed from laboratory curiosities to unique formally neutral ligands with exceptional donor ability. Here, the advances in abnormal carbene palladium chemistry are summarized. In an attempt to stimulate the entry of newcomers in this fascinating field of research, elementary aspects of synthesis are discussed as well as progress in characterization of the complexes. Most recent (catalytic) applications may highlight the potential of this rapidly growing area of palladium chemistry.

Keywords: palladium – N-heterocyclic Carbenes – abnormal bonding mode – selective bond activation – bonding mode analysis – ligand-induced reactivity – catalysis

1. INTRODUCTION AND SCOPE OF THIS REVIEW

Palladianism is a type of architecture that refers to a unique style developed by Andrea Palladio in the 16th century, long before the element palladium was discovered [1]. Even though the element's name is not directly related with Andrea Palladio [2], it is worth noting that Palladian architecture is typically characterized by a balance of esthetic principles, functionality, and the opportunities offered by the specific location and the environment [1]. Much of this—admittedly oversimplified—description also holds for current activity in palladium chemistry and hence, Palladianism may serve also as a term to illustrate a great portion of the aims of contemporary research in using palladium for catalytic transformations. Besides heterogeneous versions of catalytically active palladium, much effort has been devoted to the development of homogeneous catalysts based on molecular and well-defined palladium complexes, which allow activity and selectivity to be tuned [3]. Initially, the area of homogeneous palladium catalysis was dominated by phosphine-containing systems. With the discovery of N-heterocyclic carbenes (NHCs) as powerful ligands in transition metal chemistry, however, a significant drift in activities has occurred during the last two decades [4]. Currently, a major fraction of research activity in palladium-mediated catalysis concentrates on using and optimizing NHCs as spectator ligands. Within these activities, abnormal versions of NHC ligands have been discovered rather serendipitously [5]. These new variations of NHC ligands have developed during only a short period of time from niche compounds to ligands with remarkable synthetic potential for variations, thus entailing new and unprecedented reactivity patterns [6,7]. In this account, we aim at reviewing the progress that has been achieved by using abnormal carbene ligands in palladium chemistry until early 2010. Strong emphasis is directed to specific aspects of abnormal carbene chemistry that are particularly relevant or well-developed in palladium chemistry. The material is divided into sections covering synthetic methods towards abnormal carbene palladium complexes,

structural aspects, specific reactivity patterns, and catalytic applications. The focus on palladium chemistry allows for discussing some hypothesis in more detail and distinguishes this account from previous reviews covering the transition metal chemistry of abnormal carbenes [6–9], and also from a book chapter that highlights the catalytic activity of various abnormal carbene complexes [10]. In being a personal account, it concentrates particularly on achievements from our laboratories, though we have tried to place these results in appropriate perspective.

Historically, the term ‘abnormal carbene’ has been used to describe Arduengo-type imidazolylidene ligands that are bound to the metal center in the wrong way, thus abnormally, via C4 as opposed to C2 [5]. Later, this description has been expanded to a more general concept, encompassing all isomers of heterocyclic carbenes for which a neutral totally covalent Lewis structure cannot be written (Fig. 1) [6,7]. Resonance structures of abnormal NHC complexes that include a M=C double bond, *i.e.* a metal-carbene fragment, thus require the introduction of two opposite charges within the heterocycle, which classifies these species as mesoionic complexes, a subclass of betaines [11]. Due to historical constraints and in an attempt to emphasize the isomeric relationship between normal and abnormal NHC complexes, we will use the term ‘carbene’ throughout this review, even though various arguments will be put forward that a mesoionic description may be at least equally appropriate [12].

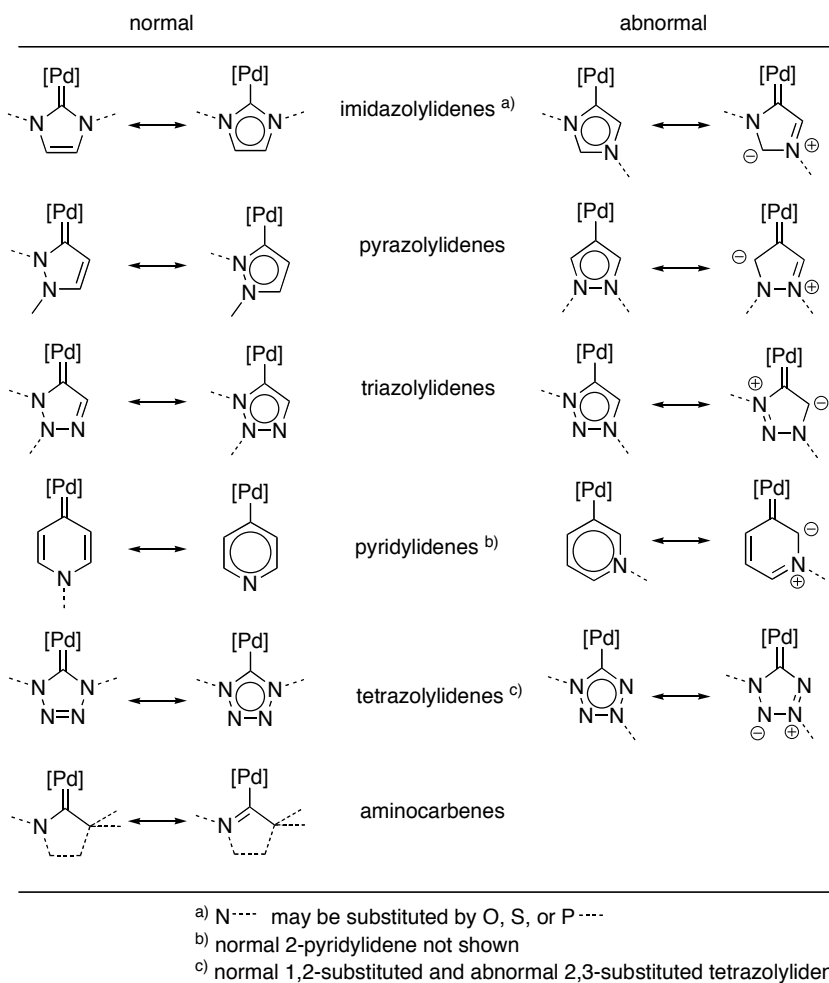


Figure 1. Normal and abnormal NHC palladium complexes shown in their carbene resonance form (featuring a M=C double bond) and in a resonance form comprising a M–C single bond emphasizing delocalized charges. Only one of the numerous charge-localized structures is shown for the abnormal carbene palladium series. All systems apart from the normal triazolylidene complexes are known.

The definition of ‘abnormal carbene’ as defined above excludes complexes comprising cyclic (alkyl)(amino)carbenes, (amino)(ylide)carbenes and related ligands. Even though these systems are closely related to abnormal NHCs in many aspects due to the reduced heteroatom stabilization of the carbene moiety, they are not further covered in this account. These subclasses of N-heterocyclic carbenes have been comprehensively reviewed recently [13].

2. SYNTHETIC ASPECTS

The synthetic procedures for the formation of abnormal carbene palladium complexes include *i*) C_{azolium}-H bond activation (direct metallation), *ii*) oxidative addition to a C_{azolium}-halide bond, *iii*) alkylation or protonation of the corresponding anionic azolyl ligand, *iv*) transmetallation from azolyldene Ag^I intermediates, and *v*) metal coordination to the free carbene. These procedures have been covered by and large in recent reviews [6,7,9]. Here, we only point out some recent developments and highlight particular aspects that are specific for installing palladium as metal at the carbene scaffold.

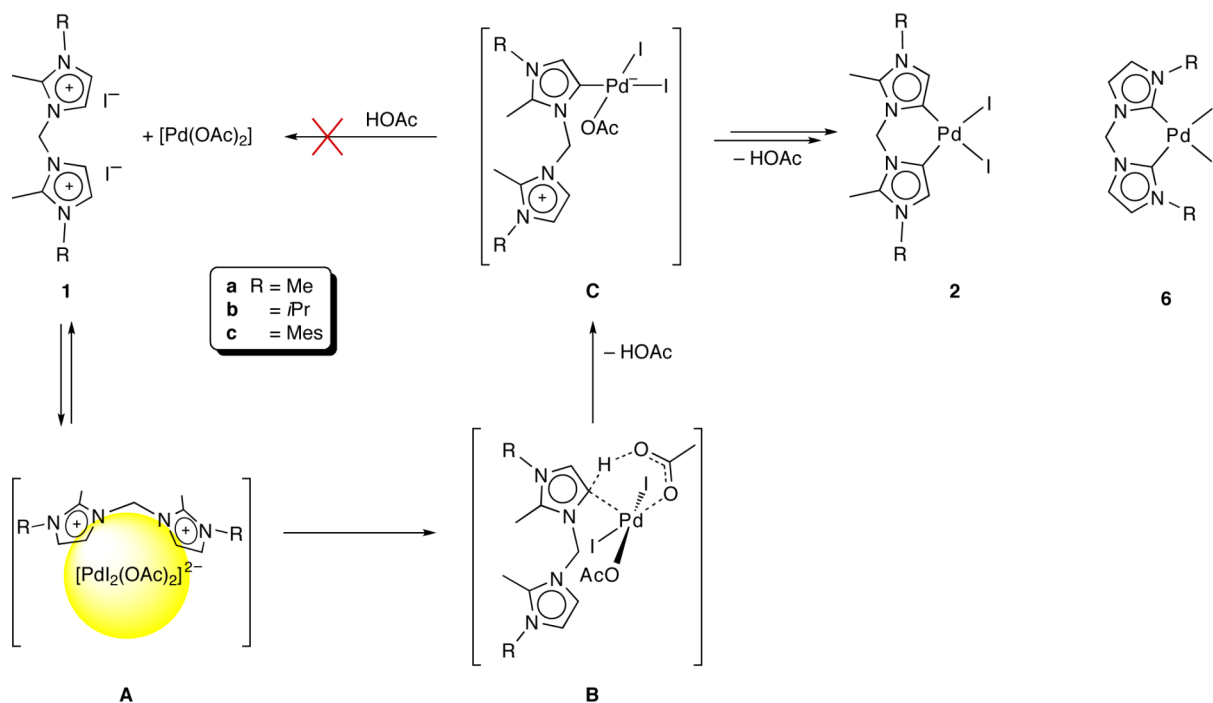
2.1. C-H Bond Activation

Heterocyclic C-H bond activation, arguably one of the most useful procedures to generate abnormal carbene palladium complexes, is often thermally induced and has been demonstrated with Pd(OAc)₂, Pd(acac)₂ (acac = acetylacetonate) [14], and K₂PdX₄ (X=Cl, Br) [15] as metal precursor. The latter two precursors have been used predominantly for C_{pyridinium}-H bond activation, while Pd(OAc)₂ has been more widely applied, including C-H activation of imidazolium, pyridinium, and triazolium salts. The bond activation with Pd(OAc)₂ presumably involves the formation of an azolium palladate precursor (diimidazolium)[PdI₂(OAc)₂] originating from coordination of the halide of the azolium salt to the palladium center [16]. Support for such a palladate formation has been obtained through NMR investigations and from the fact that palladation using azolium salts with non-coordinating PF₆⁻ or BF₄⁻ anions fail to undergo C-H bond activation.

Experiments using the diimidazolium system **1** have indicated that the first Pd-C formation is irreversible (Scheme 1; Mes = mesityl) [16]. Unlike strong acids such as HCl, weaker acidic HOAc—which is the side product from acetate-mediated palladation of azolium salts—cannot cleave the Pd-C bond in intermediate **C**. The irreversibility of the bond forming process

together with the high yield of cyclopalladated dicarbene complex **2** point to an early pre-equilibrium that triggers the regioselectivity of C–H bond activation to the ‘inner’ carbon. Steric factors seem to be less relevant as even *N*-methylated diimidazolium salts (**1a**) yield the desired complex in over 90% yield [17]. Taking these results into account, a model has been proposed for the palladation of these diimidazolium salts, which comprises an ion pair **A** as dynamic intermediate. Such an intermediate arranges the Pd(OAc) fragment in closer proximity **to the inner rather than outer** C–H bond. This interaction is much akin to heteroatom coordination in heteroatom-assisted cyclopalladation [18], and subsequent C–H bond activation may thus ensue along an electrophilic pathway, involving either an intermediate **B** reminiscent to electrophilic aromatic substitution chemistry, or via an agostic intermediate.

Scheme 1

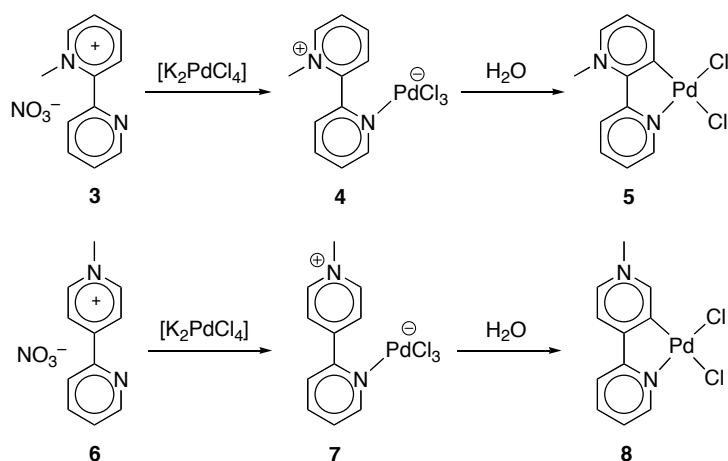


Notably, addition of an alkyl substituent at the ‘outer’ carbon (formally C4 in **1**) increases the barrier for C–H bond activation, and palladation only proceeds with diimidazolium chlorides, but not with iodides [19]. According to the mechanistic model sketched above, such a reactivity difference may be rationalized by considering the electron-donating effect of the methyl group at C4, which reduces the cationic character of the heterocycles. Hence, ion pairing is less tight with $[\text{PdI}_2(\text{OAc})_2]^{2-}$ as compared to $[\text{PdCl}_2(\text{OAc})_2]^{2-}$. Alternatively, steric congestion in the ligand periphery may discriminate the larger $[\text{PdI}_2(\text{OAc})_2]^{2-}$ and may thus prevent access to the C–H bond.

Generally, the C2-position of imidazolium salts needs to be protected by an alkyl or aryl group in order to direct palladation to the abnormal position. Indirect protection can be achieved when using bulky *tert*-butyl substituents at nitrogen, which shield the C2–H bond and promote C4/5–H bond activation [20,21]. Metallation of the C2 position constitutes another, rather special method for protecting the normal position. In an unusual reaction, bimetallic imidazole-based palladium systems have been isolated from intramolecular C4/5–H bond activation [22]. The formed product features a C2–Pd and a C4/5–Pd bond and may thus be formulated either as a normal or as an abnormal carbene palladium complex.

A different bond activation mechanism may operate in the cyclopalladation of the pyridine-pyridinium salt **3** with K_2PdX_4 ($\text{X}=\text{Cl}, \text{Br}$; Scheme 2) [15]. Initial formation of the zwitterionic coordination compound **4** has been evidenced by solution and solid state analyses. Cyclometallation requires prolonged heating in aqueous media and produces the abnormal pyridylidene complex **5** [23]. Similar cyclopalladation has been observed when starting from the isomeric pyridine-pyridinium salt **6**. Again, water is essential for the C–H bond activation process in intermediate **7** [24], and formation of complex **8** proceeds easier when chloropalladate is used rather than the bromo analogue [25].

Scheme 2



2.2. Oxidative Addition

Oxidative addition reactions to palladium(0) precursors require the prefunctionalization of the azolium salt. In highly electron-poor heterocycles such as tetrazolium salts, oxidative C–Cl addition occurs smoothly [26], though typically, iodide functionalization is safer. Specific routes for the iodination of most abnormal carbene precursors have been developed and may thus provide a general access to abnormal carbene palladium complexes [27]. Oxidative addition has been successfully demonstrated with the most abundant palladium(0) sources such as $Pd_2(dba)_3$, $Pd(dba)_2$, and $Pd(PPh_3)_4$. Interestingly, oxidative addition may not require the protection of more acidic positions of the heterocycle, such as the C(2) position in imidazolium salts. A comparative study using oxidative addition to 2-, 3-, and 4-chlorinated pyridinium salts to give the palladium complexes **9–11** (Fig. 2) reveals marked reactivity differences, since formation of the abnormal pyridylidene complex **10** requires significantly longer reaction times (3d vs. 17 h for **9** or **11**) [28].

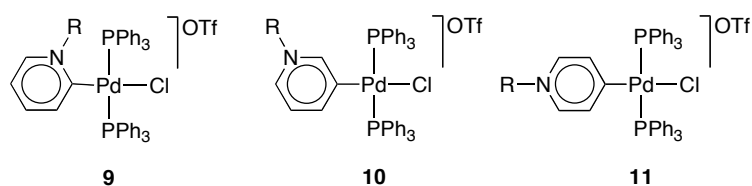


Figure 2. Isomeric pyridylidene palladium complexes featuring normal (**9**, **11**) and abnormal (**10**) pyridylidene bonding.

2.3. Transmetallation Reactions

Transmetallation via silver carbene complexes is not particularly versatile with abnormal carbenes, mostly because the corresponding silver carbene intermediates are unstable and decompose too rapidly. Useful transmetallation protocols have only been established for the synthesis of palladium triazolylidene complexes, involving carbene transfer to $\text{PdCl}_2(\text{NCR})_2$ [29,30]. The stability of the silver carbene intermediate is strongly dependent on the substitution pattern at the triazolylidene ligand. Incorporation of appropriate groups has thus allowed the intermediate to be stabilized sufficiently for performing crystallographic analyses [30].

2.4. Coordination to Free Carbenes

While the formation of free abnormal carbenes has been shown to be feasible [31], this route has not yet been applied for palladium complexation to abnormal carbenes. Coordination of related less heteroatom stabilized, yet normal, cyclic (alkyl)(amino) carbenes to $[\text{PdCl}(\text{allyl})]_2$ has been demonstrated [32]. Presumably, this procedure may also be extrapolated to free abnormal carbene complexation.

The free carbene route is generally more difficult because the reduced number of heteroatoms in close proximity to the carbene carbon destabilizes the free carbene [33]. For example, the stability of the parent 4-imidazolylidene has been computed to be about 80 kJ mol^{-1} lower than that of the corresponding 2-imidazolylidene [33b]. In addition, non-aryl substituents at the heterocycle tend to react with bases to form ylid-type compounds due to exocyclic deprotonation rather than the desired abnormal carbene. Recent calculations have suggest that

the introduction of electron-donating and strongly shielding substituents may render pyridylidenes stable [34].

3. STRUCTURAL FEATURES

While abnormal carbene palladium(0) and palladium(IV) complexes have been suggested to be formed, all crystallographically analyzed abnormal carbene complexes comprise a +2 oxidation state of the palladium center and hence a distorted square-planar metal coordination geometry. Structural characterization has focused predominantly on bond length analyses, especially on the Pd–C_{carbene} bond length, on the distance between the palladium center and the ligand *trans* to the abnormal carbene, and on perturbations within the heterocycle upon abnormal carbene complex formation.

3.1. Pd–C_{carbene} Bond Length Analysis

Abnormal carbene NHC ligands are considered better σ -donors than their normal analogs, and support for this notion has initially been sought from investigation of palladium–carbon bond length variations. Analysis of the Pd–C_{carbene} bond lengths in all crystallographically characterized abnormal NHC complexes reveals an average bond length of 1.99(3) Å (Fig. 3). This distance does not differ from typical Pd–C bond lengths in normal carbene palladium complexes, and it is slightly shorter than the average palladium–carbon distance in cyclic (alkyl)(amino)carbenes or (amino)(ylide)carbenes (average 2.03(1) Å) [32,35].

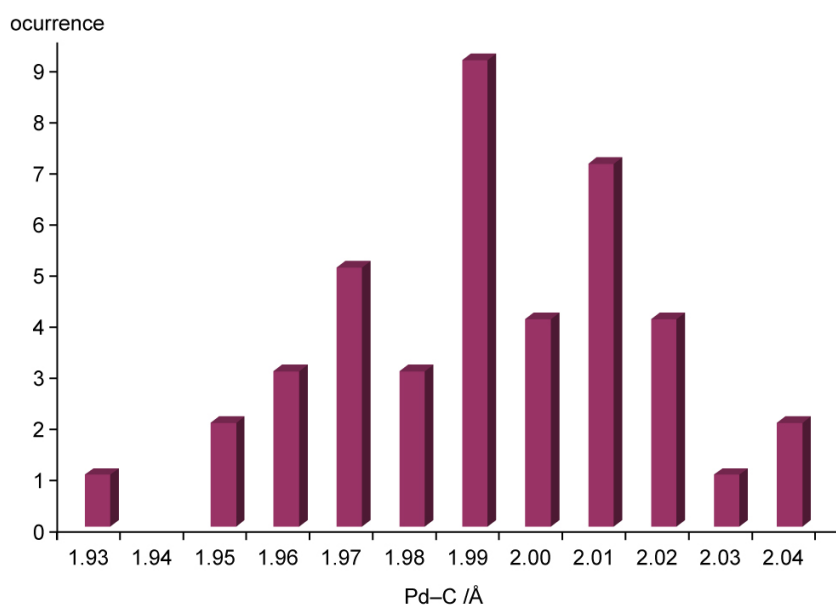


Figure 3. Histogram illustrating the occurrence of Pd–C bonds in abnormal carbene palladium complexes within a ± 0.005 Å range.

Given the quantity of structures available up to now, consideration of subclasses of abnormal carbene palladium complexes is only meaningful for imidazolylidene and triazolylidene palladium complexes at this point (>15 entries each). Average Pd–C_{carbene} bond distances in these complexes are identical within standard deviations, 1.983(25) Å for abnormal imidazolylidene palladium complexes [16,17,19,20,22,36] and 1.995(26) Å for the triazolylidene analogues [30,37]. In pyrazolylidene palladium complexes, the bond distances are slightly longer and average to 2.012(13) Å (seven structures) [38], yet statistically still identical within the 3σ range. Only two structures have been reported for abnormal pyridylidene palladium complexes [28,39] and a single complex comprising an isoxazolylidene ligand [40]. Bond lengths analysis of these latter ligand classes is thus hampered by the small number of data available and may be biased by special situations. For example, the *ortho*-substituted phenyl groups in complex **12** may induce substantial repulsion from the palladium center due to the presence of two bulky PPh₃ ligands (Figure 4) [38c]. The

relatively long Pd–C bond, 2.038(4) Å) may thus reflect this repulsion rather than a weak palladium–isoxazolylidene bond.

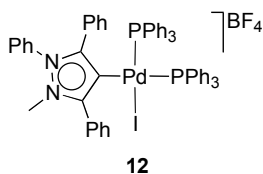


Figure 4. Palladium complex comprising an abnormally bound isoxazolylidene ligand.

An interesting comparison is offered by a series of *N*-methyl-pyridinium-derived palladium salts comprising the metal bound to C2, to C3, or to C4 (*cf.* Fig. 2) [28]. The more remote the stabilizing nitrogen is located from the carbene, the shorter the Pd–C bond length is, decreasing from 2.002(3) in **9** to 1.996(7) in **10** to 1.979(7) in **11** [41]. This trend lends further support to the notion that Pd–C bond length analyses do not reflect any difference between the normal and abnormal carbene bonding mode, but may be dictated by steric, conformational and other constraints.

3.2. Carbene *trans* Influence

A more useful probe for the impact of abnormal carbene bonding may be provided by monitoring the *trans* influence of different carbenes. While different stereoelectronic effects often preclude the comparison of various types of ligands, trends may emerge from structurally related systems. For example, picoline-substituted imidazolylidene complexes feature a significantly longer Pd–Br bond *trans* to abnormal carbenes as opposed to normal carbenes (2.514(1) Å vs. 2.481(1) Å) [36a]. Furthermore, *ortho*-dimethylated isoxazolylidene seems to exert a lower *trans* influence than the *ortho*-dimethylated pyrazolylidene analogue based on the shorter *trans* Pd–I bond in the former palladium complex (2.647(2) vs. 2.670(3), respectively) [38b,40]. We have recently investigated sterically identical pairs of complexes **13** and **14**, which comprise a fully methylated periphery (Fig. 5) [19]. The only difference

between the two complexes is the carbene bonding mode. While most bond lengths and angles are very similar in both complexes, the Pd–Cl bonds differ considerably (2.35 Å in **13a** vs. 2.40 Å in **14a**). The longer Pd–Cl bond lengths in **14** reflect a higher *trans* influence of abnormal imidazolylidenes as compared to the normal C2-bound analogues. Remarkably, this trend is absent when comparing the corresponding iodide complexes **13b** and **14b** (Pd–I 2.68 Å and 2.67 Å). Probably steric repulsion between the large iodide nucleus and the CH₃ group in **the** *ortho* position (attached to N3 and C5, respectively) are dominating in these complexes, thus overwriting the generic *trans* influence of the carbene ligand. This example may illustrate the relevance of stereoelectronic effects, which need to be cautiously considered when comparing even closely related ligand systems.

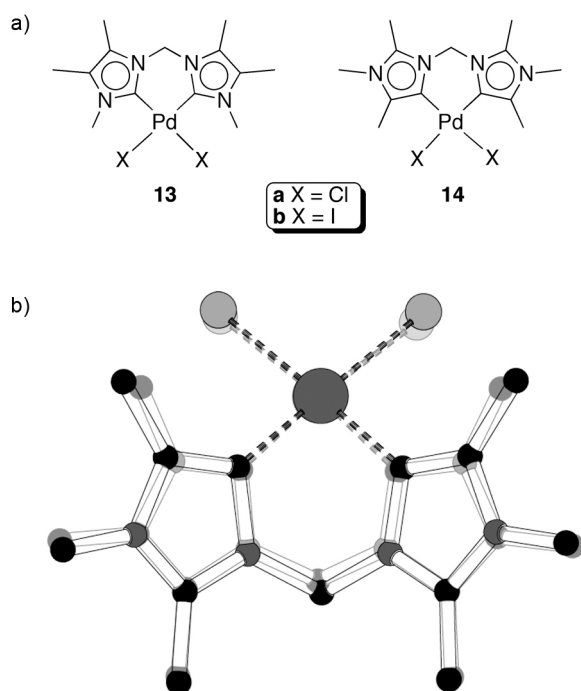


Figure 5. a) Isostructural palladium complexes featuring normal (**13**) and abnormal (**14**) bonding modes of N-heterocyclic carbene ligands; b) superimposition of the crystal structures of **13b** (faint) and **14b** (full), illustrating the longer Pd–Cl bond distances.

3.3. Perturbation Within the Heterocycle

Bond length differences within the heterocyclic ligand may, sometimes, provide an indirect probe for the nature of the M–C bond and may thus give information on the transfer of

electron density along the metal-ligand vector. For example, in abnormal imidazolylidene palladium complexes, the heterocyclic C4–C5 bond is typically around 1.39 Å [16,17,19,36], indicating a fully π -conjugated system. In contrast, normal C2-bound imidazolylidene palladium analogues feature substantially shorter C–C bonds (generally around 1.33 Å), reminiscent to a localized olefinic C=C bond. The NCN fragment is not modified significantly upon changing the carbene bonding mode. These findings suggest different charge stabilization in normal and abnormal imidazolylidene complexes. In the normal version, both the positive and the negative charge may thus be located within the NCN amidinylidene fragment, thus invoking a dissection of the NCN and the CC π electron densities in the heterocycle (Fig. 6a) [42]. In abnormal carbene complexes, similar considerations lead to a better charge separation and entail a cationic amidinium fragment and a vinyl (or perhaps vinylidene-like) portion (Fig. 6b). Such a limiting structure insinuates a higher anionic character of the abnormal imidazolylidene ligand and suggests stronger electron donation to palladium as compared to the normal imidazolylidene.

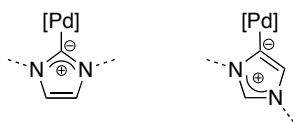


Figure 6. Perturbation of the bonding situation in heterocycles upon carbene complex formation as a consequence of minimal overlap between the NCN fragment and the CC unit in imidazolylidenes: a) limiting structure in normal imidazolylidene palladium complexes featuring a mesoionic NCN π system and a neutral olefinic C=C unit, and b) limiting structure in abnormal imidazolylidene palladium complexes comprising a positively charged NCN amidinium fragment and an anionic vinyl-type unit.

While in triazolylidene palladium complexes, similar comparison of abnormal and normal carbene bonding modes is hampered by the lack of complexes comprising normally bound carbenes, palladium pyridylidene complexes have been investigated in more detail [28]. In contrast to the normal C2- and C4-pyridylidene isomers, the abnormal C3-pyridylidene

palladium complex **10** lacks any characteristic bond length modifications in the heterocycle. In the normal isomers, the bond lengths are highly reminiscent **to** related pyridones and implicate a considerable degree of C=E double bond (E = O or Pd), whereas bond lengths in the abnormal carbene complex resemble those of pyridyl-derived ligands. Hence, significant π backbonding from the palladium center to the carbene is only postulated for normal pyridylidene ligands while the abnormal pyridylidene ligand is essentially a σ bound ligand. It should thus be a stronger donor than the normal isomers. This conclusion is corroborated by an earlier study on pyridylidene palladium complexes analogous to **9–11**, but comprising an acidic hydrogen rather than a methyl group at the heterocyclic nitrogen [5b]. The acidity of this hydrogen decreases in the series 3-pyridylidene > 4-pyridylidene > 2-pyridylidene. Notably, a theoretical study suggests that the π orbital term of the Pd–C bond is not affected by changes in the bonding mode of the pyridylidene ligand, but the bond strength is altered [43].

4. SPECIFIC REACTIVITY PATTERNS

4.1. Impact of the Ligand

Two factors are most **critical in governing** the metal-centered reactivity of palladium carbene complexes: electron density at palladium, and steric shielding of the metal center and of the *cis* positions in the palladium coordination sphere. While much effort has been devoted recently to evaluate the electronic effect of a variety of (ab)normal carbenes, true appreciation of steric effects has been more recent [44]. While being one of the predominant factors for high activity of normal carbene palladium catalysts, *e.g.* in PEPPSI-type cross-coupling reactions (PEPPSI = pyridine-enhanced precatalyst preparation, stabilization and induction)

[45,46], steric engineering of palladium complexes in abnormal carbene chemistry has only been little explored.

The impact of abnormal carbene bonding on the electronic properties of the palladium center are largely associated with the donor ability of the abnormal carbene ligand. Often, the ligand donor strength is quantified by IR spectroscopy using the **stretching frequencies** of coordinated CO spectator ligand(s) (Tolman electronic parameters, TEPs) [47,48], or by electrochemical analysis (Lever electronic parameters, LEPs) [49]. Both these measurements are not practical for palladium chemistry, and in particular not for palladium(II) complexes because the corresponding palladium(II) carbonyl complexes are extremely rare, and because the redox potentials of palladium(II) complexes are typically beyond the electrochemical window of classical solvents [50]. Extrapolation of data from other metal complexes may sometimes give a useful approximation of the ligand donor ability. However, since the donor ability is not an intrinsic property of the ligand but a result of ligand-metal interactions, such extrapolation may be misleading. A variety of alternative probes for measuring the electron density at palladium and for comparing the donor properties of the spectator carbene ligands have thus been developed. The most frequently used techniques are critically summarized below.

X-ray photoelectron spectroscopy has been used to determine the bonding energies of the palladium 3d electrons as a function of the carbene bonding mode in palladium diimidazolylidene palladium complexes such as **13** and **14** (*cf.* Fig. 5a) [17,19]. Electron dissociation from the palladium center in abnormal complex occurs consistently at lower energy costs by 0.6 eV than from the normally bound analogues. Such less tight electron binding implies a substantially higher electron density at the palladium center when bound to abnormal carbenes and supports the notion that abnormally bound imidazolylidenes are considerably stronger electron donors to the palladium(II) center than the C2-bound

analogues. While XPS perhaps provides the most direct technique to observe the (ligand-induced) electron density at the palladium center, analyses are far from being routine and require sophisticated instrumentation. In addition, the relatively low resolution of the measurements may preclude subtle ligand effects **from being** detected.

NMR spectroscopy has been used to estimate the electron density at various nuclei. For example, the deshielding of the carbon nucleus upon formal pyridylidene complex formation is significantly smaller for abnormal 3-pyridylidene ($\Delta\delta$ 30 ppm) than for normal 2- or 4-pyridylidene ($\Delta\delta$ 50 ppm) systems [28]. Notably, the absolute chemical shift of the carbene carbon provides a tempting though often also a misleading probe, because the chemical shift is strongly influenced by a number of parameters other than the carbene donor power, including inductive effects of neighboring (and more remote) nuclei, paramagnetic shift components, hybridization changes, bond angles, and related steric constraints [7,51]. Hence, the chemical shift of the carbene carbon is usually unsuitable for donor power measurements. Recently, Huynh and coworkers have developed a method that uses the NMR frequency of a spectator ligand nucleus as a more reliable indicator. In their system, the metal-bound carbon of a benzimidazolylidene (bim) ligand serves as reporter for the donor properties of a *trans*-positioned ligand L (Fig. 7) [52]. Variation of the ligand L in complexes [(L)PdBr₂(bim)] to an abnormal imidazolylidene ligand (*cf.* complex **15**, Fig. 7) induces a considerable deshielding of the diagnostic benzimidazolylidene carbon resonance ($\Delta\delta_C$ ca. 3 ppm with respect to the normal carbene analog). This shift is in good agreement with the stronger *trans* influence deduced from structural analyses (see above). Practical disadvantages of this method such as the required synthetic efforts may be counterbalanced by its broad scope, if the ¹³C NMR scale correlates well with other techniques. Moreover, it may be necessary to correct the obtained values for eventual stereoelectronic effects.

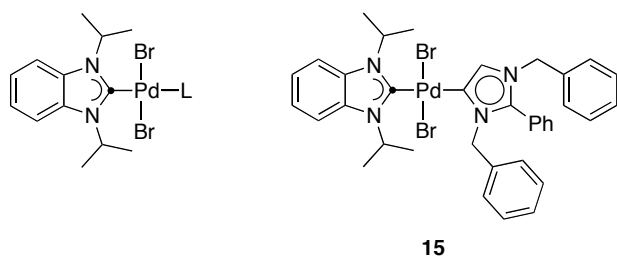


Figure 7. Generic complex used for probing the donor ability of a ligand L to palladium(II) by ^{13}C NMR spectroscopy (the diagnostic carbon nucleus is highlighted), and the specific abnormal imidazolylidene palladium(II) complex **15** that has been analyzed by this method.

In an attempt to minimize geometrical effects due to different ligand substitution patterns, we have recently prepared a series of abnormal carbene palladium complexes **16–20** which feature a five-membered N-heterocyclic skeleton and methyl groups in both *ortho* positions (Fig. 8) [40]. Coordination of these abnormal carbene ligands to a $\text{Pd}(\text{PPh}_3)_2\text{I}$ fragment then allows for evaluating the modulated electron density at the palladium center by ^{31}P NMR spectroscopy. The paramagnetic contribution to the shielding constant is dependent on the HOMO-LUMO gap, which in turn is a direct response of the donor ability [53]. Hence, the more a ligand is donating, the smaller the HOMO-LUMO gap becomes, and hence the less shielded are the ^{31}P nuclei. Indeed a good correlation has been found between the measured ^{31}P NMR chemical shifts and the calculated TEPs [54] for the series of isosteric complexes **16–20** [40]. Accordingly, the donor ability of abnormal carbenes decreases in the series pyrazolylidene > isoxazolylidene > imidazolylidene, and all abnormal carbenes are stronger donors than the normal 2-imidazolylidene. The practicality of this method may be underlined by the ease of ^{31}P NMR measurements on modern spectrometers. In addition, synthetic routes for installing an iodide substituent on various different heterocycles are available as are well-established procedures to perform oxidative addition of C–I bonds to $\text{Pd}(\text{PPh}_3)_4$. Obviously steric alterations in the abnormal carbene skeleton remain a major issue. In parts this has been

resolved by using isosteric ligands, though comparison of 5- and 6-membered heterocyclic carbene complexes is still ambiguous.

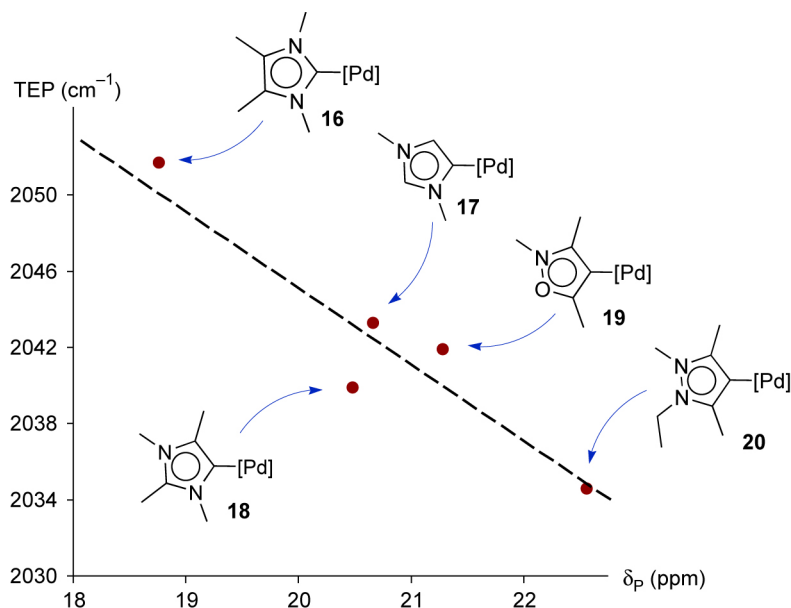


Figure 8. Palladium(II) complexes comprising different types of isosteric abnormal carbene ligands ([Pd] = *trans*-Pd(PPh₃)₂I). The measured ³¹P NMR chemical shifts correlate well with independently calculated Tolman electronic parameters (TEPs).

Despite these current limitations, it is obvious that the expansion of the carbene ligand family to a variety of abnormal systems has significantly expanded the donor capacity range of NHC ligands. Abnormal carbene ligands seem to be tunable over a wider window than normal carbenes. Taking all variations of NHC ligands together, this class of ligand slowly reaches the broadness that made phosphorus-based donor ligands so versatile [47]. Most importantly, variation of the steric impact of abnormal carbene ligands is virtually unlimited due to highly flexible synthetic protocols for fabricating the corresponding heterocyclic precursors. This fact may be underlined, for example by the availability of ‘click’-chemistry for accessing a diversity of triazole-, pyrazole-, and isoxazole-based heterocycles as abnormal carbene precursors. Such synthetic versatility will be particularly attractive for introducing additional functionality that is not palladium-centered, *e.g.*, for immobilization, for the introduction of recognition sites, or for attaching (fluorescent) reporter groups.

4.2. Stoichiometric Reactivity Patterns

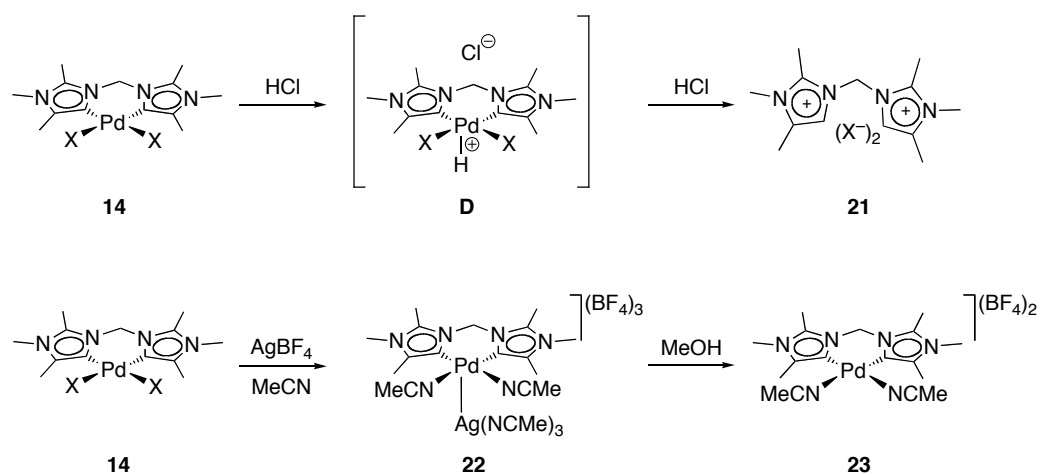
Based on the strong donor properties of the abnormal carbene ligand, two specific reactivity patterns may be particularly stimulated: *i*) reaction with electrophiles and *ii*) oxidative addition reactions. Both types of reaction are expected to be promoted by a metal center that is electron rich and they may have obvious implications also for catalytic reactions. For example, catalytic C–C cross-coupling reactions are generally accepted to be rate-limited by the initial oxidative addition step of the aryl halide to low-valent palladium. The reactivity of abnormal carbene palladium complexes has been studied both towards electrophiles as well as towards oxidizing agents.

4.2.1. Reactivity towards Electrophiles

The permethylated palladium dicarbene complex **14** and related complexes undergo Pd–C_{carbene} bond cleavage when exposed to strong acids [16,19]. While the instability of organometallic compounds towards HCl or H₂SO₄ is not surprising as such, it is worth noting that the Pd–C_{carbene} bonds in the analogous normal dicarbene palladium complex **13** are stable under identical conditions and even survive elevated temperatures (80 °C) for several days. Differences due to unequal steric shielding in the two complexes can be confidently excluded because of the similar structural design of the dicarbene ligands. Electronic activation of the palladium center as a function of the carbene donor properties may constitute a more probable rationale. Thus, increasing ligand donation by the abnormal carbenes in **14** enhances the basicity of the palladium center. In a square-planar geometry, enhanced basicity translates into a higher energy of the d_{z²} orbital. Proton binding to the palladium center via a d_{z²}(Pd)–s(H) orbital interaction may then provide an intermediate Pd···H adduct (**D**, Scheme 3). Subsequent 1,2-migration of the proton from the palladium center to the carbon and

concomitant Pd–C_{carbene} scission may be a possible pathway to explain the observed product formation. According to this model, the substantially lower donor ability of normal carbenes (as in **13**) prevents either the formation of the pentacoordinate adduct or the 1,2-migration of the hydrogen. Based on related reactivity studies using different electrophiles, we tend to favor the former bias, *i.e.* the lack of electron density at the palladium center that stabilizes the normal carbene complexes.

Scheme 3



Substitution of the electrophilic reaction partner of **14** from a proton to a silver cation induces, firstly, abstraction of the palladium-bound halides. In addition, a palladium-silver bond is formed, thus producing the bimetallic adduct **22** [19]. Such an adduct may be regarded as a model intermediate for the intermediate **D** as discussed above for the Pd–C_{carbene} bond acidolysis. No similar product formation has been observed in analogous complexes comprising normal imidazolylidene ligands. Calculations have indicated that the Pd–Ag bond in **22** is in part the result of a stabilizing interaction between an empty 4s orbital at silver and a filled π MO involving the pseudo-vinyl Pd–C=C fragment of the abnormal carbene ligand and the palladium center. These interactions reinforce the bonding scheme within the

heterocycle as depicted above (*cf.* Fig. 6). In addition, they provide strong support for a polarized Ag–Pd bond, with the palladium center as donor and the silver nucleus as acceptor site. This notion implies that the palladium center in complex **22** is formally nucleophilic and that it acts as a ligand. Indeed, in the crystal structure of complex **22**, the silver adopts only a slightly distorted tetrahedral coordination geometry if the palladium center is taken into account as a fourth ligand in addition to the three MeCN molecules.

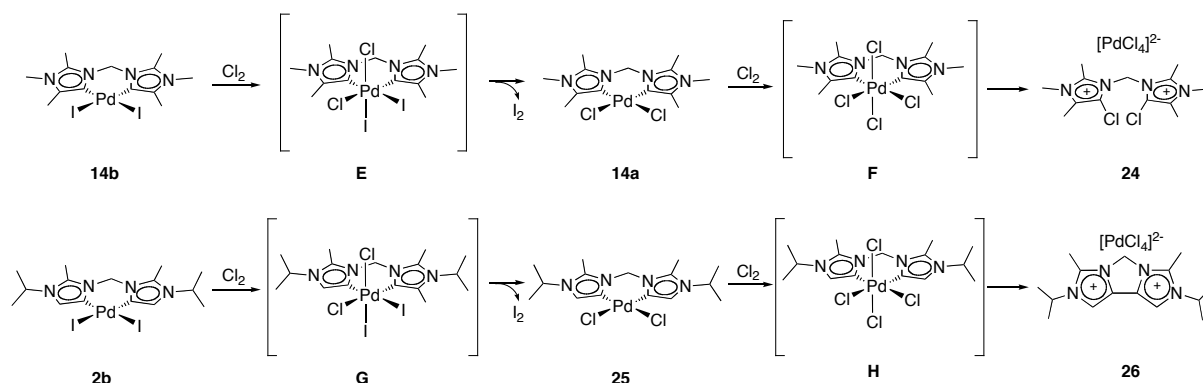
The calculated model for the silver bonding is further supported by the fact that the silver nucleus is not positioned at a fully apical position with respect to the palladium square plane. Perhaps due to the contribution of the π electron density from the C=C bond, the silver is shifted towards the two carbene sites, which is reflected by the strong deviation of the C_{carbene}–Pd–Ag angles from 90° (ideal apical position) to less than 70°. Moreover, addition of a Lewis base that is competitive to the palladium center transfers the silver(I) nucleus from complex **22** to the solvent area. For example, MeOH or DMSO successfully remove the silver ion and afford the bis(solvento) complex **23**, while MeCN is ineffective. Based on these reactivity schemes, the nucleophilicity of the palladium center towards silver(I) can be related to solvent nucleophilicities. The nucleophilicity thus decreases in the order MeOH, DMSO > Pd(abnormal diimidazolylidene) > MeCN > Pd(normal diimidazolylidene).

4.2.2. Oxidative Addition Reactions

The propensity of abnormal carbene palladium complexes for undergoing redox-reactions has been probed specifically with systems comprising abnormal imidazolylidene ligands. Exposure of complex **14b** to strongly oxidizing conditions such as Cl₂ induces a reaction cascade, eventually affording the dichlorinated diimidazolium palladate salt **24** [19]. Such product formation has been proposed to originate from initial oxidative addition of Cl₂ and subsequent reductive C–Cl bond elimination. No trace of iodide incorporation has been

detected. In addition, exposure of the normal dicarbene complex **13b** to identical reaction conditions induces a simple halide exchange and produces the palladium dichloride complex **13a**. These experiments suggest that C–Cl bond formation in **24** is not a result of high chemoselectivity of the elimination process but a consequence of the much faster rate for I₂ and ICl reductive elimination from the putative palladium(IV) intermediate **E**. Hence, a multistep process is likely to take place, involving repetitive switching between palladium(II) and palladium(IV) intermediates (Scheme 4). Apparently, reductive elimination from intermediate **F** is favored with abnormal carbenes, while such a process is prevented with normal dicarbenes. An enhanced propensity of abnormal carbenes to undergo reductive elimination reactions has also been established in related platinum chemistry [55].

Scheme 4



The reaction outcome of the reductive elimination process is strongly influenced by steric parameters. When the abnormal diimidazolylidene palladium complex **1b**, which lacks the *ortho* methyl groups of complex **14**, is subjected to Cl₂, reductive C–C elimination is the preferred pathway. The formed tricyclic salt **26** comprises considerable ring strain in the dicationic portion. Crystallographic analysis reveals C–C–C bond angles of 145.4(9)° and 147.3(9)°, which are unusually wide for sp²-hybridized carbons. Apparently, this strain is compensated by the strength of the newly formed C–C bond from complex **1b**. The

preference of of intermediate **H** to undergo C–C as opposed to C–Cl reductive elimination at palladium may be rationalized by the increased steric flexibility of the palladium(IV) intermediate **H** as compared to **F**, because the *ortho* positions are unsubstituted. Rotation about the carbene–palladium bond in **H** may align the orbitals at the two carbons appropriately and reductive C–C coupling ensues. In the methylated analog **F**, however, twisting of the heterocycles is prevented due to CH₃...Cl interactions, thus making the C–Cl reductive elimination the exclusive pathway. Accordingly, C–C reductive elimination is principally preferred, and C–Cl bond formation only takes place if the former process is blocked.

5. CATALYTIC APPLICATIONS

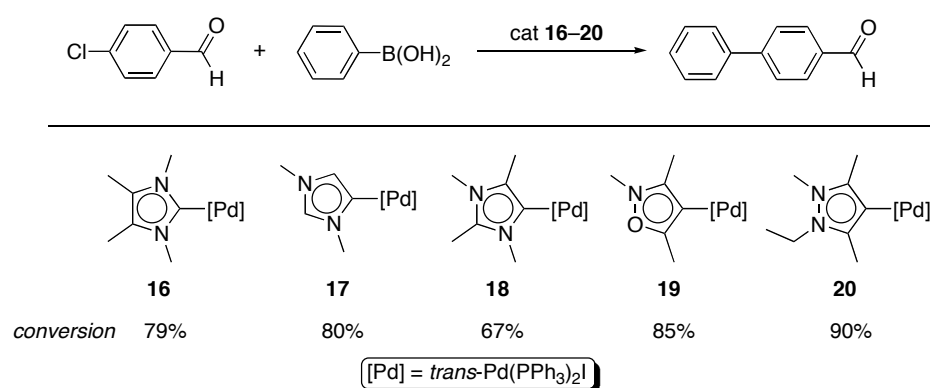
5.1. Cross-Coupling Catalysis

The catalytic activity of abnormal carbene palladium complexes has been summarized recently [7,10]. Following general trends in palladium chemistry, not surprisingly, major efforts have been directed towards cross-coupling catalysis. A theoretical study on a specific bis(carbene) system has predicted little energetic difference for catalysis using normal or abnormal carbene spectator ligands [56]. However, the assumption of two carbene ligands being bound to the palladium center throughout the catalytic cycle may be disputable. Most recent reports have concentrated on using monocarbene palladium complexes which contain (hemi)labile ligands. Such a setting is expected to enhance catalyst activation, *i.e.*, metal reduction to form palladium(0) species. Strong carbene donation to this palladium(0) intermediate should then facilitate the rate-determining step of the catalytic cycle, that is, oxidative C–X bond addition.

Recently, a series of isostructural abnormal carbene complexes **16–20** have been compared in Suzuki-Miyaura cross-coupling (Scheme 5) [40]. Aryl chlorides are fully converted within 3 h

at a 1 mol% catalyst loading, **although** elevated temperatures are required to achieve high conversion (DMF, 140 °C, K₂CO₃). Analysis of the reaction progress reveals a (weak) correlation between donor ability and catalytic activity. **The enhanced catalytic performance may be rationalized by the stronger donor ability abnormal carbene ligands, which destabilize the low-valent palladium(0) intermediate and hence promote oxidative substrate addition, i.e. they accelerate the rate-determining step.** Given the fact that the complexes all comprise small methyl substituents in *ortho* position to the carbene site, steric optimization may result in a further increase of the catalytic activity, especially when considering the relevance of steric bulk for ensuing high catalytic activity [57].

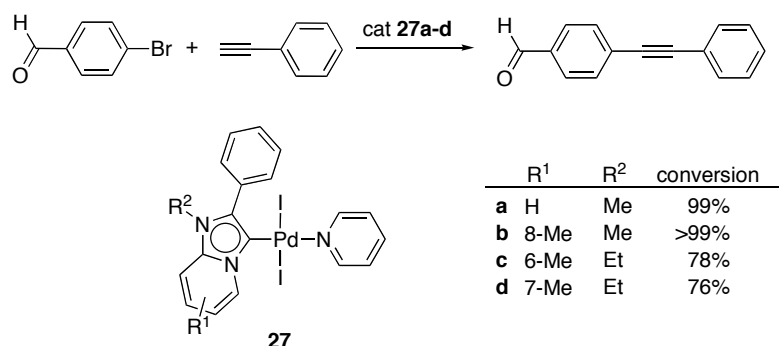
Scheme 5



Attempts to replace the *ortho*-methyl substituents by phenyl groups in the pyrazolylidene palladium complex **12** provides only little improvement in catalytic activity (*cf.* Fig. 4) [38c]. In aqueous media, conversion of activated aryl chlorides is raised from 39% when using precursor **16** to 50% with pre-catalyst **12** (1 mol% cat, H₂O, 80 °C, K₂CO₃, 21 h). A similar increase from 45% to 55% has been noted for Heck-type coupling of 4-chlorobenzaldehyde with *tert*-butyl acrylate (1 mol% cat DMF, 140 °C, NaOAc, 24 h). The vast possibilities for further tuning of the steric impact of the *ortho* substituents and also for modifying the ancillary ligands may illustrate the potential of these systems in cross-coupling catalysis.

The abnormal imidazolylidene palladium complexes **27** have been successfully employed in Sonogashira cross-coupling of aryl halides and terminal alkynes (Scheme 6) [58]. These PEPPSI-themed complexes are active catalysts even under copper- and amine-free conditions, if aryl iodides or activated aryl bromides are used as substrates (4 mol% cat, DMF/H₂O, 90 °C, Cs₂CO₃, 3 h). Activated aryl chlorides have been found to be ineffective, while conversions using normal carbene palladium complexes have been reported to be significantly less efficient. The exact location of the methyl group in the annelated pyridine ring seems to influence the catalytic activity considerably and conversions may vary from 60% to >99%. A suitable rationale for this unusual behavior may, perhaps, provide guidelines for further development of this type of catalyst precursors.

Scheme 6



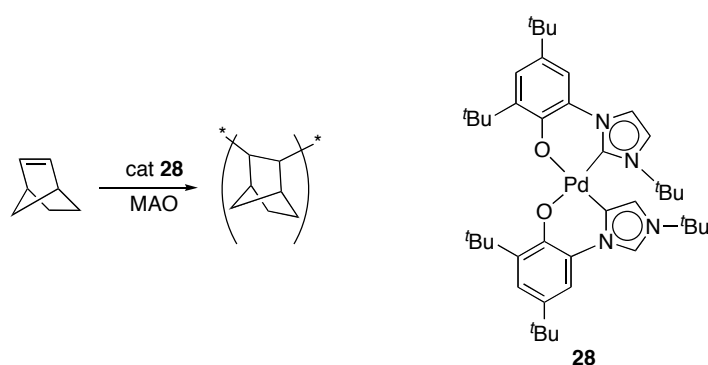
5.2. Other Catalytic Applications

The abnormal imidazolylidene complex **23** has been demonstrated to be a useful catalyst precursor for the hydrogenation of cyclooctene under mild conditions (1 mol%, EtOH, RT, 1 atm H₂) [17]. In contrast, only low conversions have been noted when the palladium is bound to a normal dicarbene ligand. The high catalytic activity of complex **23** may be rationalized by the increased electron density at the palladium center as a consequence of the exceptionally strong donor ability induced by the abnormal carbene bonding mode. In the

presence of H₂, oxidative addition and reductive elimination sequences similar to the reaction patterns developed for **14** with Cl₂ may take place (*cf.* Scheme 4), thus pointing to specific catalyst activation mode that is enabled only with abnormally bound carbene ligands. Such a model also implies that PdH₄²⁻ or, more likely, colloidal material formed from PdH₄²⁻, constitutes the actual catalyst for olefin hydrogenation.

The mixed normal/abnormal biscarbene palladium complex **28** comprising chelating phenoxide groups has been prepared by direct palladation. C–H bond activation is directed to the abnormal rather than the normal position presumably due to the steric congestion imparted by the bulky aryl and *tert*-butyl groups, which effectively shields the imidazolium C2 position and, perhaps more importantly, overcrowds the palladium coordination sphere if both carbenes were normally bound. In the presence of MAO, complex **28** shows excellent catalytic activity in the polymerization of norbornene (2.3×10^7 g polynorbornene per mol Pd and hour with 0.25 μmol catalyst at 40 °C) [20]. The activity is similar to normal analogues that bear less bulky *N*-substituents.

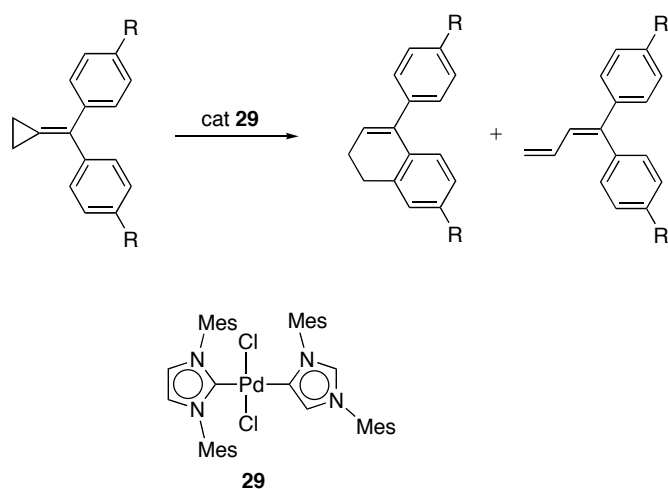
Scheme 7



A peculiar mixture of *N,N'*-dimesitylimidazolium chloride (IMes.HCl) and complex **29**, originally developed by Lebel and coworkers [36b], catalyzes the cycloisomerization of alkylidenecyclopropanes (Scheme 8) [59]. While it has been speculated that the added IMes.HCl may re-activate eventually formed palladium black and thus regenerate complex **29**

(or its normal biscarbene analog), it is worth noting that increasing the ratio of added IMe₃.HCl affects the reaction selectivity and enhances the yield of the 1,1-disubstituted butadiene isomer. A similar selectivity has been observed when the mixed abnormal/normal dicarbene complex **29** at high catalyst loading, while the normal/normal analogue affords almost exclusively the tricyclic product.

Scheme 8



6. CONCLUSIONS

Abnormal N-heterocyclic carbenes, a subclass of mesoionic compounds, have emerged as exceptionally strong donor ligands with appreciable modularity of donor properties. Probably most remarkably in palladium chemistry, coordination of abnormal carbene ligands allows for inverting the typically electrophilic character of the palladium(II) center to become truly nucleophilic, as evidenced for example by the ligating properties of an abnormal dicarbene palladium(II) complex to Lewis acids. This extraordinarily high electron density at the palladium center provides access to new reactivity patterns, which has been exploited in particular in catalysis. Initial studies have underlined the potential of abnormal carbene

palladium complexes in various catalytic reactions. Given the fact that stereoelectronic effects are far from being fully exploited in abnormal carbene chemistry, it is safe to predict substantial further progress in catalyst development. Efforts in these directions will certainly be supported by the recent discovery of free abnormal carbenes that are stable at room temperature.

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