On the Electronic Impact of Abnormal C4-Bonding in N-Heterocyclic Carbene Complexes


Abstract: Sterically similar palladium dicarbene complexes have been synthesized that comprise permethylated dicarbene ligands which bind the metal center either in a normal coordination mode via C2 or abnormally via C4. Due to the strong structural analogy of the complexes, differences in reactivity patterns may be attributed to the distinct electronic impact of normal versus abnormal carbene bonding, while stereoelectronic effects are negligible. Unique reactivity patterns have been identified for the abnormal carbene complexes, specifically upon reaction with Lewis acids and in oxidative addition-reductive elimination sequences. These reactivities as well as analytical investigations using X-ray diffraction and X-ray photoelectron spectroscopy indicate that the C4 bonding mode increases the electron density at the metal center substantially, classifying such C4-bound carbene ligands amongst the most basic neutral donors known thus far. A direct application of this enhanced electron density at the metal center is demonstrated by the catalytic H2 activation with abnormal carbene complexes under mild conditions, leading to a catalytic process for the hydrogenation of olefins.

Keywords: coordination modes · electronic tuning · metal nucleophilicity · N-heterocyclic carbene ligands · palladium

Introduction

In the last few years, N-heterocyclic carbenes (NHCs) have emerged as versatile ligands in organometallic chemistry and homogeneous catalysis.[1] Their successful application has been attributed generally to the covalent M–C bond character and to the stronger donor properties as compared to other neutral donor ligands such as phosphines. Recently, abnormal C4-bonding of NHCs, discovered few years ago,[2] has been suggested to further increase the donor properties of this class of ligands substantially.[3] As a consequence, enhanced reactivity of C4-bound carbene metal complexes has been observed for stoichiometric and catalytic bond activation processes.[3b,4] Stronger ligand donation may be rationalized by the presence of only one heteroatom adjacent to the carbene carbon.[5] While the absence of a second heteroatom reduces the stability of the free carbene,[6] the σ-donor ability is increased due to the lower inductive influence of the nitrogen atoms. Furthermore, in abnormal carbenes, that is, in carbenes that do not possess a neutral M=C carbene resonance structure,[7] the charges in the zwitterionic resonance forms are typically better separated than in normal NHCs, where the positive and negative charge are both localized within the amidinium NCN fragment.[8] Better charge separation is thought to reinforce the anionic character of the metal-bound carbon and hence to enhance its donor ability. An increased relevance of the zwitterionic resonance form as ground state has been postulated also for related pyrazolylidene complexes.[9,10]

Owing to the higher acidity of the proton bound to C2 as compared to C4,[11] abnormal NHC bonding is most often[12] promoted by protection of the C2 position and subsequent metallation at C4 (or C5) via direct C–H bond activa-
In part as a consequence of this approach, the C5 carbon in the ortho position of C4-metallated imidazolylidenes generally features a proton substituent only.\textsuperscript{[14]} In contrast, normal NHCs possess alkyl or aryl substituents on both ortho-positions, that is, on the heteroatoms.\textsuperscript{[15]} When comparing the two carbene bonding modes, hence, stereo-electronic effects often interfere with electronic alterations due to different substitution of the ortho positions.

To unambiguously evaluate the electronic impact of normal and abnormal NHCs we have devised the sterically strongly related dicarbene ligands shown in Figure 1, comprising a completely methylated periphery of the heterocycles. Considering that the N–CH\textsubscript{3} and the C–CH\textsubscript{3} bond lengths are equal within standard deviations (1.485(9) Å and 1.503(11) Å, respectively),\textsuperscript{[16]} the two dicarbene ligands in complexes A and B impose an identical steric environment around the metal center, yet they feature normal C2- and abnormal C4-bonding,\textsuperscript{[17]} respectively. The cis-chelating binding mode of these dicarbene ligands restricts the number of available coordination sites at the metal center, in particular when bound to square-planar d\textsuperscript{8} platinum group metals. In addition, such chelation prevents any isomerization of the carbene ligands into a mutual trans orientation, which would abrogate most of the expected electronic effects such as the trans influence and, catalytically presumably more relevant, the trans effect. Here we report on the synthesis, the reactivity differences, and the remarkably changed catalytic activity of palladium(II) complexes comprising such sterically strongly related dicarbene ligands and provide unambiguous evidence for the unique electronic impact of C4-bound imidazolylidenes.

### Results and Discussion

#### Synthesis of complexes:

The potentially C2-binding permethylated dicarbene ligand precursor was prepared starting from the known\textsuperscript{[18]} 4,5-dimethylimidazole 1 (Scheme 1). N-alkylation with MeI gave the 1,4,5-trimethylimidazole 2, which was subsequently treated with CH\textsubscript{3}I or CH\textsubscript{2}Cl\textsubscript{2} to yield the diimidazolium salts 3a and 3b, respectively. Both products can be converted into the corresponding BF\textsubscript{4}– salt 3c by halide abstraction with two molar equivalents of AgBF\textsubscript{4}. Metallation of 3a with Pd(OAc)\textsubscript{2} in DMSO at elevated temperature according to established procedures\textsuperscript{[19]} afforded the expected cyclopalladated dicarbene complex 4a in high yields. Likewise, complex 4b was obtained from the diimidazolium diiodide 3b and Pd(OAc)\textsubscript{2} by thermally induced cyclometallation. The chloride complex 4a was also available from the imidazolium salt 3e with Pd(OAc)\textsubscript{2} in the presence of excess KCl. The \textsuperscript{1}H NMR spectra of complexes 4a and 4b are similar and reveal significant changes when compared with those of the imidazolium ligand precursors. In particular, the resonance due to the bridging methylene group is shifted upfield by nearly 1 ppm and appears as an AB doublet centered at 6.04 and 5.88 ppm in 4a and at 6.02 and 5.87 ppm in 4b. The inequivalence of these CH\textsubscript{2} protons indicates a rigid boat-type configuration and a restricted flexibility about the Pd–C bond. Such steric constraints may arise due to the repulsive interactions of methyl groups in the C4/C5 position and the CH\textsubscript{2} protons, which disfavor an inversion of the metallaecly. In complexes having protonated C4 and C5 nuclei, metallaecly inversion

![Figure 1. Metal complexes comprising sterically identical cis-chelating di-carbene ligands for investigating the electronic impact of C2-binding (A) as opposed to C4-binding of the metal center (B).](image-url)

Scheme 1. a) Reagents and conditions: a) MeI, DMSO 65°C, 18 h; b) CH\textsubscript{3}I, 150°C, 14 h; c) Pd(OAc)\textsubscript{2}, (for 3c: Pd(OAc)\textsubscript{2}, KCl), DMSO 120°C, 3 h; d) Ac\textsubscript{2}O, benzene 80°C, 2 h, then MeI, 140°C, 16 h; e) CH\textsubscript{2}Cl\textsubscript{2}, 150°C, 0.5 h, or CH\textsubscript{3}I, toluene 110°C, 14 h; f) Pd(OC\textsubscript{2})\textsubscript{2}, Pd(OAc)\textsubscript{2}, KCl, DMSO 120°C, 3 h; g) for 7e Pd(OAc)\textsubscript{2}, KCl, DMSO 120°C, 3 h; h) AgBF\textsubscript{4}, MeCN, 18 h, then Bu\textsubscript{4}NI, MeCN 1 h.

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is fast at room temperature. In the $^{13}$C NMR spectrum the signal for the metal-bound carbon appears at $\delta = 155.8$ and 161.1 ppm for 4a and 4b, respectively, a frequency that is typical for related C2-bound dicarbene palladium complexes. The chemical shift difference between 4a and 4b may be, in part, due to weaker bonding of iodide in 4b, perhaps as a consequence of steric congestion (cf. X-ray results below).

The permethylated diimidazolium salt precursor for the analogous C4-bound dicarbene complexes was synthesized from commercially available 2,4-dimethylimidazole (5) by regioselective alkylation (Scheme 1). For this purpose, the sterically less shielded nitrogen nucleus was protected in situ with acetic anhydride prior to N-alkylation using MeI. Subsequent cleavage of the acyl group under basic conditions afforded the 1,2,5-trimethylimidazole 6 in moderate yield. NOESY experiments confirmed the formation of the desired isomer. For example saturation of the signal at $\delta = 3.66$ ppm, attributed to the N-bound CH$_3$ group, induced a positive Overhauser effect for both methyl signals at $\delta = 2.76$ (C2-CH$_3$) and $\delta = 2.26$ ppm (C5-CH$_3$), but did not affect the C4-bound proton. Conversely, the signal at $\delta = 2.26$ ppm revealed a correlation to the C4-bound proton and to the N-bound proton. Conversely, the signal at $\delta = 2.26$ ppm revealed a correlation to the C4-bound proton and to the N-bound proton. 

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Subsequent quaternization of 1,2,5-trimethylimidazole (6) with CH$_3$Cl$_2$ or CH$_3$I$_2$ yielded the diimidazolium salts 7a and 7b, respectively, and after anion exchange using AgBF$_4$ the halide-free analogue 7c. Metallation of 7a with Pd(OAc)$_2$ in DMSO, under conditions identical to those used for the preparation of the C2-bound dicarbene complexes yielded the abnormal dicarbene complex 8a (Scheme 1). Successful palladation was indicated by $^1$H NMR spectroscopy due to the disappearance of the C4-bound proton and a splitting of the CH$_3$ group into an AB doublet located at $\delta_H = 6.33$ and $5.93$ ppm ($J_{HH} = 12.9$ Hz). The analogous iodide complex 8b was obtained by successive addition of first AgBF$_4$ and then Bu$_3$NI to 8a in MeCN solution. In solution, complexes 8a and 8b feature diastereotopic methyl groups at the C5 and the C5’ carbon, as revealed by two distinct singlets in the $^1$H and $^{13}$C spectra, respectively. Such diastereotopicity may arise from solvolysis of one Pd–X bond.

Remarkably, direct palladation of the iodide 7b failed under similar reaction conditions. Higher temperatures, longer reaction times, or addition of an external base such as NaOAc or Et$_3$N did not afford the expected palladium complex, and instead only the starting ligand was recovered. Possibly, the palladate [Pd(OAc)$_2$I]$_2$ [19], which is expected to be generated from 7b and Pd(OAc)$_2$, [19] is not nucleophilic enough to activate the diimidazolium C4–H bond of 7. In contrast, activation of this bond is obviously successful with the more electron-rich precursor [Pd(OAc)$_2$Cl$_2$]$_2$, formed from 7a and Pd(OAc)$_2$. Palladation of the imidazolium salt 7c comprising BF$_4^-$ anions in the presence of KCl afforded, unlike its potentially C2-bonding analogue 3c, the dimeric palladium complex 9 in good yields. The $^1$H NMR spectrum of monomeric 8a and dimetallc 9 are highly similar, and unambiguous confirmation of the dimeric nature of 9 required single crystal structure determinations and elemental analyses. Notably, depending on the solvent used for the crystallization pseudo-polymorphs are formed. From DMSO, the compound crystallized as colorless blocks in the centrosymmetric triclinic space group P$ar{1}$ with three molecules of DMSO. Crystals obtained from MeCN/Et$_2$O mixtures were yellow needles and monoclinic (P$2_1$/$n$), and they contained half a molecule of H$_2$O per asymmetric unit. In both pseudo-polymorphs, the palladium complexes are virtually identical and bond lengths and angles do not differ significantly.[21] The molecular structure of one of the polymorphous complexes of 9 is shown in Figure 2 and reveals a di-
**Structural impact of the carbene bonding mode:** To identify the structural consequences of C2 versus C4 bonding of the dicarbene ligand, the molecular structures of 4a, 4b, 8a, and 8b were determined by single-crystal X-ray diffraction (Figure 3). Selected bond lengths and angles are listed in Table 1. In all complexes the palladium center resides in a distorted square-planar configuration. The Pd–C bond length is slightly shorter in the chloride complexes 4a and 8a than in the iodide analogues 4b and 8b, perhaps due to the higher trans influence of iodide versus chloride. In contrast the carbene bonding mode seems to have no influence on the Pd–C bond length, all Pd–C distances are around the expected value of 1.98(2) Å.[19,20,22] Notably, the Pd–Cl bonds are significantly longer in the abnormal complex 8a than in 4a, suggesting a higher trans influence of C4-bound carbenes. No such trend is observed for the palladium–iodide bonds in 4b and 8b, probably due to steric repulsion between the large iodide nucleus and the CH3 group in ortho position (attached to N3 and C5 respectively). The heterocyclic C–C bond tends to be slightly longer in abnormally bound carbenes (av 1.365(17) Å) than in normal C2-bound carbene complexes (av 1.352(8) Å), though the effect is much less pronounced than in the C3-protonated analogues.[22] The torsion between the palladium square plane and the heterocycles as defined by the N-C-Pd-C dihedral angles varies in the 38–48° range and is essentially independent of the carbene bonding mode.

The conformational similarity of the two dicarbenes ligands in complexes 4a and 8a is further illustrated by the superimposition of the two molecular structures (Figure 4). Using the C(1)-Pd(1)-C(7) bonding as anchoring point, only slight deviations in the ligand periphery are detectable, arising predominantly from the relative orientation of the heterocycles with respect to the metal coordination plane. Minor differences are also noted in the N–CH3 versus C–CH3 bond lengths. For example the N(1)–CH3 distance in 4a is 1.403(6) Å, whereas the C(2)–CH3 bond length is 1.481(14) Å in 8a. Since these structural differences are very small only, it is probably safe to ignore any stereoelectronic contributions and to attribute the diverting reactivity and stability patterns of the complexes to the electronic impact of the carbene bonding mode.

**X-ray photoelectron spectroscopy:** The variation of electron density at the palladium center as a consequence of the different carbene bonding in complexes 4a and 8a was probed by X-ray photoelectron spectroscopy (XPS). Quantitative analyses of the measurements were complicated by the fact that both complexes were charged under XPS conditions, which required appropriate referencing. When taking the average kinetic energy of the 1s electrons of C, N, and O as a reference, the binding energy of the palladium 3d electrons in 8a is 0.5 eV lower than that of palladium in a C2-bound dicarbene environment as in 4a (Figure 5). This implies a higher electron density at the palladium when bound to abnormal C4-bound carbenes and corroborates previous analysis using structurally less similar C2- and C4-bound di-

![Figure 3. Molecular structure of complexes 4a (a), 4b (b), 8a (c), and 8b (d) (ORTEP representation, 50% probability level, hydrogen atoms and co-crystallized solvent molecules omitted for clarity).](image)

![Figure 4. Superimposition of the molecular structures of 4a (dashed) and 8a (solid) using the C(1)-Pd(1)-C(7) plane as a reference.](image)

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**Table 1.** Selected bond lengths [Å] and angles [°] in complexes 4a, 8a, 4b, and 8b.

<table>
<thead>
<tr>
<th></th>
<th>4a</th>
<th>8a</th>
<th>4b</th>
<th>8b</th>
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<tr>
<td>X-CI</td>
<td>1.979(4)</td>
<td>1.976(9)</td>
<td>2.007(4)</td>
<td>2.007(7)</td>
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<tr>
<td>Pd(1)–C(1)</td>
<td>1.976(5)</td>
<td>1.981(9)</td>
<td>1.981(4)</td>
<td>1.993(8)</td>
</tr>
<tr>
<td>Pd(1)–C(7)</td>
<td>2.3587(12)</td>
<td>2.400(2)</td>
<td>2.6648(5)</td>
<td>2.6734(9)</td>
</tr>
<tr>
<td>Pd(1)–X(1)</td>
<td>2.3556(13)</td>
<td>2.407(2)</td>
<td>2.6717(4)</td>
<td>2.6646(8)</td>
</tr>
<tr>
<td>C(1)–Pd(1)–C(7)</td>
<td>1.342(7)</td>
<td>1.353(13)</td>
<td>1.361(6)</td>
<td>1.363(12)</td>
</tr>
<tr>
<td>C(1)–Pd(1)–X(1)</td>
<td>1.349(6)</td>
<td>1.355(13)</td>
<td>1.355(6)</td>
<td>1.390(11)</td>
</tr>
<tr>
<td>C(1)–Pd(1)–X(2)</td>
<td>0.92(12)</td>
<td>0.86(14)</td>
<td>0.82(16)</td>
<td>0.84(6)</td>
</tr>
<tr>
<td>N(1)–C(1)–Pd(1)–C(7)</td>
<td>42.7(4)</td>
<td>–43.5(7)</td>
<td>47.6(3)</td>
<td>–40.7(6)</td>
</tr>
<tr>
<td>C(1)–Pd(1)–C(7)–N(3)</td>
<td>–44.8(4)</td>
<td>38.9(7)</td>
<td>–48.3(7)</td>
<td>45.0(6)</td>
</tr>
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</table>

[a] C(1)–C(2)–C(3) for 4a and (C1)–(C2) for 8a. [b] C(5)–C(6) for 4b and (C6)–(C7) for 8b.

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carbene palladium (II) complexes. Independent DFT calculation of the binding energy of the palladium 3d electrons revealed a 0.8 eV lower energy in abnormally bound dicarbene complexes than in the normal analogue (336.1 eV vs. 336.9 eV). The slight shift in absolute energies may be attributed to the charging of the complexes under experimental conditions. These XPS measurements are in line with earlier IR analyses of νCO stretching frequencies in abnormal carbene iridium dicarbonyl complexes, and they demonstrate unequivocally that C4-bound carbenes are exceptionally strong donors and considerably stronger than their C2-bound analogues.

Impact of carbene C4-bonding on reactivity: The steric similarity of complexes 4 and 8 also allowed the investigation of the relevance of electronic effects on the reactivity of the coordinated metal centers. Upon reaction of complex 8 with AgBF₄, the silver adduct 11 was isolated, whereas the normally bound dicarbene complex 4 only underwent halide abstraction and gave the bissolvento complex 10 (Scheme 2; Figure 6a). Formation of such a bimetallic complex 11 suggests that Pd···Ag bond formation is a general process in C4-bound carbene palladium complexes. This behavior may become attractive for exploiting new types of direct metal–metal interactions.

A crystal structure analysis of the bimetallic complex 11 revealed that, most notably, the Pd···Ag bond length is significantly longer (3.1120(10) Å; Figure 6b) than in a related complex comprising a proton at the C5 position (Pd···Ag 2.8701(6) Å). Presumably, this is a consequence of the different steric repulsion between the C5-bound substituent (crystallographically labeled C(2) and C(6) in Figure 6b) and the acetonitrile ligands around the silver nucleus. The silver ion is significantly shifted towards the carbene ligands, which is reflected by the acute Ag-Pd-C angles (Ag(1)-Pd(1)-C(1) 64.6(2)° and Ag(1)-Pd(1)-C(7) 64.7(2)°). This bonding situation compares well with that in the previously reported Ag-Pd(dicarbene) complex with a proton at the C5-position, which shows Ag-Pd-C angles of 65.8(2)° and 68.3(1)°.

The observed geometry indicates that silver bonding occurs not only via the dₓ orbital of the palladium center, expected to be the HOMO within the Pd(dicarbene) fragment, since such a donor interaction should position the silver nucleus in an apical position. Significant donor contributions may also originate from the palladium–carbene bond, either by an agostic bonding (i.e., electron density from the Pd···Ag bond) or by interaction with the Pd···Ag bond. Theoretical analyses using BP86/TZ2P suggested that the two metal fragments of complex 11 dissociate spontaneously in the gas phase. No minimum could be located on the potential energy surface that would be close to the crystallographically characterized structure. Optimization of the structure with constrained Ag/C0-Pd and Ag···C distances based on the crystallographically determined values allowed, however, the identification of the relevant bonding interactions. Accordingly, substantial stabilization of the silver cation arises from orbital interactions between the filled dₓ orbital of palladium and the LUMO of Ag⁺ (predominantly s character, ΔE = −12 kcal mol⁻¹). A weaker interaction of −4.4 kcal mol⁻¹ involves electron donation from a silver 4d orbital to the Pd···Ag π* orbital (Figure 7). While this contribution is relatively small, it may rationalize the observed shift of the silver ion from the palladium z axis towards the dicarbene ligand. Furthermore, these calculations reveal 1 eV higher energy levels for the carbene orbitals in the C4 coordination mode as compared to that in 2-imidazolylidenes. This energy difference indicates a substantially larger charge transfer from the carbene lone pair to the coordinated metal center when bound via C4 and may hence provide...
a rational explanation for the enhanced nucleophilicity of the palladium center in complexes 8.

Similarly to the reaction with Lewis acidic Ag⁺, complexes 8 comprising C4-bound dicarbene also react with strong Brønsted acids. Both Pd–C bonds in 8 are acid sensitive and are cleaved within minutes. For example, exposure of complex 8a to HCl (0.4 M in MeCN) led to the rapid acidolysis and formation of the imidazolium salt 7a. A similar reaction outcome was observed when using H₂SO₄, while complexes 4a and 4b are stable for weeks under such acidic conditions, even upon heating to 80 °C. Clearly, steric protection of the palladium center and of the Pd–C bonds can be excluded as an argument for rationalizing this distinctly different reactivity of C2- and C4-bound dicarbene complexes. Possibly, oxidative addition of HX and subsequent reductive elimination of an imidazolium cation from a putative PdIV(dicarbene)(hydride) intermediate may occur. Reductive carbene elimination is known to be promoted by C4-bound carbene ligands.[26] Alternatively, a Lewis acid/base adduct similar to the silver complex 11 may form, in which the proton is located at a similar position as Ag⁺ in 11 and hence in close proximity to both Pd–C bonds. Subsequent rearrangement of such an intermediate into a Pd–H–C three-center, two-electron transition state followed by thermodynamically driven metal–carbon bond breaking is then conceivable. Irrespective of the exact mechanism, the acid lability and the nucleophilic character of the palladium center in 8 appeared to be a direct consequence of the ligand-induced difference of electron density, both at the metal center and at the metal-bound carbon.

Based on the exceptionally high donor ability of C4-bound carbene ligands, the palladium centers in 8 are expected to promote redox reactions considerably better than in 4, comprising normally bound carbene ligands. We have probed such reactivity patterns by exposing different palladium complexes to a Cl₂ atmosphere. Under these conditions, the C2-bound dicarbene systems 4b and 13b underwent halide metathesis and afforded complexes 4a and 13a, respectively, containing metal-bound chlorides (Scheme 3). Substitution of the metal-bound halides was confirmed by a diagnostic shift of the metal-bound carbon in the ¹³C NMR spectrum, for example, in complex 13 from δ_C= 162.5 to 156.5 ppm. Similarly the isopropyl protons are displaced in the ¹H NMR spectrum from δ_H= 5.37 to 5.53 ppm, probably due to intramolecular hydrogen bonding of the isopropyl protons to the metal-bound halides.[19b] The structure of 13a was further confirmed by crystallographic analysis.[23]

FIGURE 6. Reaction products from the reaction of C2- and C4-bound dicarbene palladium complexes with AgBF₄ in MeCN. Molecular structure of the cationic portions of complexes 10 (a) and 11 (b; ORTEP representation, 50% probability, hydrogen atoms, non-coordinating BF₄⁻ anions and cocrystallized solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: for 10: Pd1–C1 1.955(4), Pd1–N3 2.071(4); C1-Pd1-C1a 83.2(2), C1-Pd1-N3 173.40(15), C1-Pd1-N3a 4.70(15), N3-Pd1-N3a 86.72(19). For 11: Pd1–Ag1 3.1120(10), Pd1–C1 1.970(7), Pd1–C7 1.966(7), Pd1–N3 2.075(6), Pd1–N6 2.082(7), C1–C2 1.367(9), C6–C7 1.373(10); C1-Pd1-C7 85.8(3), Ag1-Pd1-C1 64.6(2), Ag1-Pd1-C7 64.68(18).

FIGURE 7. Calculated interactions that are relevant for stabilizing the silver cation in the bimetallic complex 11 (color code: Pd purple, Ag light blue, N blue, C gray).


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anistically, formation of the chloride complex may be rationalized by an oxidative addition of Cl₂ to the palladium center followed by reductive I₂ or ICl elimination. In the presence of excess Cl₂, the postulated palladium(IV) oxidative addition product [PdCl₄(dicarbene)] is apparently unstable and reverts back to complex 13a.

In contrast, the C₄-bound carbene complex 8b afforded the dichloro dimidazolium salt 14 upon exposure to Cl₂ (Scheme 4). While the removal of I₂ may proceed according to a process similar to that suggested for 4b, apparently reductive elimination of C₅H₄C=Cl is relatively facile in C₄-bound carbene palladium(IV) complexes. In solution, probably [PdCl₄]²⁻ is formed initially as anion of the dichloro dimidazolium salt and perturbation of the original 2:1 imidazolium/palladium stoichiometry occurred only upon recrystallization from DMSO solution. Both elemental analyses and a crystal structure determination (Figure 8a) of recrystallized samples indicated a 4:3 imidazolium/palladium ratio due to the presence of one [PdCl₄]²⁻ and two [PdCl₃(DMSO)]⁻ ions, and two dimidazolium dications. Reductive elimination of the carbene ligand was also observed from the C₅-protonated dicarbene palladium complex 15 in the presence of excess Cl₂ (Scheme 4). Demetallation occurred, however, not via C₅H₄C=Cl bond formation but via C₅H₄C=C₅H₄ bond making, thus affording the tricyclic dimidazolium salt 16 (Figure 8b). The molecular structure of this dimidazolium salt revealed a strained arrangement of the heterocycles as reflected by the C(3)-C(4)-C(5) bond angle of 147.3(9)°, which is unusually large for a formally sp²-hybridized carbon center. The ¹³C NMR resonance of the bridging C₄ nucleus was observed in the usual region (δC = 123.5 ppm), while the remarkable high-field shift of the resonance due to the proton-bound C₅ carbon (δC = 111.9 ppm) may reflect the strained geometry. In the ¹H NMR spectrum of 16, the signal attributed to the aromatic proton is displaced to lower field (δH = 7.16 ppm in 15 versus δH = 8.34 ppm in 16). The presence of only little steric bulk at C₅ in complex 15 as compared to the permethylated ligand in complex 8 may play a key role for distinguishing the outcome of the reductive elimination processes. The methyl groups at C5 in complex 8a and in the putative Pd⁴⁺ intermediate may be sterically too demanding to allow an arrangement of the two carbene ligands that would induce C=C reductive elimination as observed from complex 15.

Reductive carbene elimination and formation of 14 and 16 is in agreement with previous findings, which indicated that C₄-bound carbene ligands are more prone to reductive elimination from MII centers than the C₂-bound analogues (M = Ni, Pd, Pt). Based on our observations, reductive elimination from Pd⁴⁺ decreases in the sequence I—I > C₄sub-C₄sub > C₄sub-C₅ > C₅sub-C₅ > C₅sub-C₅sub-C₅sub. Clearly, further mechanistic and theoretical investigations are warranted to substantiate this trend.

Catalysis: The electronic implications due to the different carbene bonding have also significant consequences on the catalytic activity of the coordinated metal center. This impact has been observed with sterically similar dicarbene complexes. Here, it is illustrated by the distinctly different performance of complexes 10 and 12 as catalyst precursors for alkene hydrogenation (Scheme 5).

Hydrogenation of cyclooctene (coe) to cyclooctane (coa) was used as a model reaction. Catalytic runs were performed at room temperature and under atmospheric pres-
sure of H₂. Under these conditions, the C4-bound carbene complex 12 showed appreciable catalytic activity, conversions reached 57% after 1 h and were essentially complete after 8 h. In contrast, the C2-bound analogue 10 is inactive and even after 20 h, no coa was formed. These results are in line with our preliminary studies on the hydrogenation of CO₂,[30] which suggested that the C4-carbene bonding mode is pivotal for imposing high catalytic activity. Steric modifications appear to play only a minor role yet they may become relevant for catalyst optimization. Assuming that catalytic hydrogenation involves oxidative addition of H₂ to the metal center,[27] the high catalytic activity of 12 may be rationalized by the substantial electron density at the palladium center as a consequence of the exceptionally strong donor ability of the two C4-bound carbene ligand residues. Furthermore, reductive elimination of either the product or the heterocycle may occur,[30] in analogy to the specific reactivity patterns established for the reaction of C4-bound carbene complexes with Cl₂ (see above). The latter reaction trajectory may generate a palladium polyhydride species as the catalytically active species. Mechanistic studies directed towards a better understanding of this palladium-catalyzed hydrogenation are currently ongoing in our laboratories.

Conclusion

Palladium complexes comprising sterically strongly related dicarbene ligands that bind the metal center either normally at C2 or abnormally at C4 allowed unambiguous identification of the electronic impact of the abnormal bonding mode of imidazolylidenes. In the solid state, carbene bonding at C2 or abnormally at C4 allowed unambiguous identification is considerably higher. All evidence suggests that C4-bound dicarbene complexes are markedly stronger donors than their C2-bound analogues. Enhanced donation of C4-bound imidazolylidenes may be rationalized, in analogy to C2-bound dicarbene complexes with Cl₂ (see above). The latter reaction trajectory may generate a palladium polyhydride species as the catalytically active species. Mechanistic studies directed towards a better understanding of this palladium-catalyzed hydrogenation are currently ongoing in our laboratories.

Experimental Section

General: The syntheses of the dimethyl imidazole 1[19] and of the palladium complexes 13b[19] and 15[19] were reported previously. All other reagents are commercially available and were used as received. All NMR spectra were recorded on Bruker spectrometers at 25°C unless specified otherwise. The $^1$H and $^{13}$C chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to external SiMe₄. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of Ilse Beetz (Kronach, Germany) or the Microanalytical Laboratory of the ETH (Zürich, Switzerland). Microwave-mediated reactions were carried out on a Biotage Initiator 2.0 instrument. The XPS spectra were measured on a Scienta SES 2002 electron spectrometer with a 5 eV x 10⁻¹⁵ mbar base pressure. The photon source consisted of an X-ray tube emitting Mκα photons at 1253.6 eV.

Synthesis of 2: CH₂ (4.31 g, 30.4 mmol) was added to a solution of 4,5-dimethylimidazole 1 (2.60 g, 27.4 mmol) in DMSO (100 mL). Powdered KOH (3.42 g, 61.0 mmol) was then added in small quantities and the solution was stirred at room temperature for 1 h and at 65°C for 18 h. After the mixture had been cooled to room temperature, KOH (100 mL, 1.09 g, 2.23 mmol) and AgBF₄ (0.87 g, 9.6%), which was recrystallized from MeOH/Et₂O (3/C₁₄)₈ mL) and then dried in vacuo to give 3a as brown solid (1.54 g, 50%). 1H NMR (500 MHz, [D₆]DMSO): δ = 9.53 (s, 2H, Hₐ), 6.75 (s, 2H, NCH₃), 3.78 (s, 6H, NCH₃), 2.31, 2.22 ppm (2×12H, Cₐ−CH₃); 13C{¹H} NMR (125 MHz, [D₆]DMSO): δ = 136.5 (Cₐ−H), 128.3, 126.4 (2×Cₐ−CH₃), 55.3 (CH₂), 34.0 (NCH₃); 11C{¹H} NMR (90 MHz, CDCl₃): δ = 133.5(Cₐ−CH₃), 133.5, 122.5 (2×Cₐ−CH₃), 31.3 (NCH₃), 12.7, 8.1 ppm (2×Cₐ−CH₃).

Synthesis of 3a: A solution of 2 (2.20 g, 20.0 mmol) and CH₂Cl₂ (3 mL) was stirred at 150°C under microwave irradiation for 30 min. A brown oil had formed, which was separated by decantation and washed with toluene (3×20 mL) and EtO (3×20 mL) and then dried in vacuo to give 3a as brown solid (2.39 g, 78%) as a highly viscous oil. All our attempts to crystallize 3a at −30°C under various conditions have failed thus far and elemental analysis was only satisfactory when including solvents. 1H NMR (500 MHz, [D₆]DMSO): δ = 9.53 (s, 2H, Hₐ), 6.75 (s, 2H, NCH₃), 3.78 (s, 6H, NCH₃, 2.30, 2.24 ppm (2×12H, Cₐ−CH₃); 13C{¹H} NMR (125 MHz, [D₆]DMSO): δ = 136.3 (Cₐ−H), 128.3, 126.3 (2×Cₐ−CH₃), 55.1 (CH₃), 33.9 (NCH₃), 8.2, 7.7 ppm (2×Cₐ−CH₃); elemental analysis calcd (%) for C₁₃H₂₂I₂N₄ (488.15): C 31.99, H 5.44, N 13.73; C 31.95, H 5.44, N 13.74.

Synthesis of 3b: A suspension of 1 (1.09 g, 2.23 mmol) and AgBF₄ (0.92 g, 4.73 mmol) in MeCN (20 mL) was stirred at room temperature for 18 h in the absence of light. The suspension was then filtered through Celite and the volatiles were removed in vacuo to give 3b as a red oil (1.54 g, 50%). 1H NMR (500 MHz, [D₆]DMSO): δ = 9.27 (s, 2H, Hₐ), 6.61 (s, 2H, NCH₃), 3.78 (s, 6H, NCH₃), 2.30, 2.24 ppm (2×12H, Cₐ−CH₃); 13C{¹H} NMR (125 MHz, [D₆]DMSO): δ = 136.0 (Cₐ−H), 128.3, 126.3 (2×Cₐ−CH₃), 55.3 (CH₃), 34.0 (NCH₃), 8.3, 7.9 ppm (2×Cₐ−CH₃); elemental analysis calcd (%) for C₁₃H₂₂I₂N₄ (488.15): C 31.99, H 5.44, N 13.74; found: C 31.95, H 5.44, N 13.75.

Synthesis of 3c: A suspension of 3b (1.09 g, 2.23 mmol) and AgBF₄ (0.92 g, 4.73 mmol) in MeCN (20 mL) was stirred at room temperature for 18 h in the absence of light. The suspension was then filtered through Celite and the volatiles were removed in vacuo to give 3c as a red oil (1.54 g, 50%). 1H NMR (500 MHz, [D₆]DMSO): δ = 9.27 (s, 2H, Hₐ), 6.61 (s, 2H, NCH₃), 3.78 (s, 6H, NCH₃), 2.30, 2.24 ppm (2×12H, Cₐ−CH₃); 13C{¹H} NMR (125 MHz, [D₆]DMSO): δ = 136.3 (Cₐ−H), 128.4, 126.4 (2×Cₐ−CH₃), 55.1 (CH₃), 33.8 (NCH₃), 8.0, 7.6 ppm (2×Cₐ−CH₃); elemental analysis calcd (%) for C₁₃H₂₂F₂N₄ (407.95): C 38.27, H 5.44, N 13.73; found: C 38.45, H 5.31, N 13.43.
Synthesis of 7b: Neat CH2I2 (1.9 g, 7.2 mmol) was added to 6 (1.40 g, 12.7 mmol) and the mixture was stirred at 140°C for 16 h. The formed brown oil was dissolved in MeOH (20 mL). Upon addition of Et2O (80 mL), crude 7b separated as a reddish oil, which was collected by decantation and dried in vacuo (2.2 g, 63%). Recrystallization from MeOH/Et2O gave 7b as an analytically pure solid. 1H NMR (500 MHz, CD2Cl2): δ = 7.85 (s, 2H, Hn), 6.90 (s, 2H, CH2), 3.66 (s, 6H, NCH3), 2.83, 2.25 ppm (2×, 12H, C148Cimi); 13C{1H} NMR (125 MHz, CD2Cl2): δ = 145.8, 130.7 (2×, C148Cimi) 117.6 (C148Cimi), 56.4 (CH2), 32.2 (NCH3), 10.9, 9.2 ppm (2×, C148Cimi), elemental analysis calcd (%) for C13H22I2N2: C 32.57, H 3.13; found: C 32.00, H 4.60, N 11.48.

Synthesis of 7c: A suspension of 7a (2.21 g, 4.53 mmol) and AgBF4 (1.36 g, 9.55 mmol) in MeCN (20 mL) was stirred at room temperature for 16 h in the absence of light. The suspension was then filtered through Celite and the volatiles were removed in vacuo to give 7c as a red oil (1.57 g, 85%). Microanalytically pure material formed upon crystallization of 7c from MeOH/Et2O. 1H NMR (360 MHz, D2DMSO): δ = 7.52 (2×, 2H, Hn), 6.50 (s, 2H, CH2), 3.59 (s, 6H, NCH3), 2.71 (s, 6H, C148Cimi), 2.24 ppm (2×, 6H, C148Cimi); 13C{1H} NMR (112 MHz, D2DMSO): δ = 145.7, 130.9 (2×, C148Cimi), 117.4 (C148Cimi), 56.2 (CH2), 31.9 (NCH3), 10.2, 8.9 ppm (2×, C148Cimi); elemental analysis calcd (%) for C13H16BF4N4 (497.95) H2O: C 36.66, H 5.8, N 13.15; found: C 36.25, H 5.36, N 12.76.

Synthesis of 8a: Solid Pd(OAc)2 (0.75 g, 3.36 mmol) was added to a solution of 7a (0.56 g, 1.84 mmol) in DMSO (6 mL). The reaction mixture was stirred at 50°C for 2 h and then at 120°C for 3 h. After the mixture had been cooled to room temperature, CH2Cl2 (20 mL) and Et2O (80 mL) were added to give a precipitate which was collected and washed repeatedly by adding CH2Cl2 (20 mL) followed by precipitation with Et2O (80 mL) and dried in vacuo. This afforded 8a as a yellow powder (0.49 g, 65%). An analytically pure sample of 8a was obtained by recrystallization from CH3NO2/Et2O. 1H NMR (500 MHz, D6DMSO): δ = 6.33, 5.93 (2×, 2H, CH2), 3.50 (s, 6H, NCH3), 2.66 (s, 6H, C148Cimi), 2.37, 1.84 ppm (2×, C148Cimi); 13C{1H} NMR (125 MHz, D6DMSO): δ = 145.6, 130.7 (2×, C148Cimi), 117.4 (C148Cimi), 56.3 (CH2), 32.2 (NCH3), 10.8, 9.1 ppm (2×, C148Cimi); elemental analysis calcd (%) for C13H16B2F8N4(OAc)2·0.5H2O: C 43.35, H 5.17, N 13.76; found: C 35.14, H 4.91, N 13.51.

Synthesis of 8b: Excess Nbu4I (0.52 g, 1.41 mmol) was added to a solution of 12 (0.21 g, 0.35 mmol) in MeCN (20 mL) and the mixture was stirred at room temperature for 1 h. Addition of Et2O (80 mL) induced the formation of a red precipitate, which was separated by filtration. 4a (2.21 g, 4.53 mmol) and AgBF4 (0.099 g, 0.51 mmol) in MeCN (20 mL) was stirred for 18 h in the absence of light. The suspension was then filtered through Celite and crude 8b was obtained by recrystallization from CH3NO2/Et2O. 1H NMR (500 MHz, D6DMSO): δ = 6.33, 5.93 (2×, 2H, CH2), 3.50 (s, 6H, NCH3), 2.66 (s, 6H, C148Cimi), 2.37, 1.84 ppm (2×, C148Cimi); 13C{1H} NMR (125 MHz, D6DMSO): δ = 145.6, 130.7 (2×, C148Cimi), 117.4 (C148Cimi), 56.3 (CH2), 32.2 (NCH3), 10.8, 9.1 ppm (2×, C148Cimi); elemental analysis calcd (%) for C13H16B2F8N4(OAc)2·0.5H2O: C 43.35, H 5.17, N 13.76; found: C 35.14, H 4.91, N 13.51.

Synthesis of 9: Pd(OAc)2 (0.50 g, 2.23 mmol) was added to a solution of 7e (0.91 g, 2.23 mmol) and KCl (0.83 g, 11.1 mmol) in DMSO (6 mL), and the reaction mixture was stirred at 50°C for 3 h. After the mixture had been cooled to room temperature, CH2Cl2 (20 mL) and Et2O (80 mL) were added and the formed precipitate was collected. Repeated precipitation from CH2Cl2 (20 mL) and Et2O (80 mL) and subsequent drying yielded 9 as an off-white powder (0.73 g, 89%). Analytically pure material was obtained by recrystallization from CH3NO2/Et2O. 1H NMR (500 MHz, D6DMSO): δ = 6.33, 5.94 (2×, 2H, CH2), 3.60 (s, 6H, NCH3), 2.66 (s, 6H, C148Cimi), 2.37, 1.84 ppm (2×, C148Cimi); 13C{1H} NMR (125 MHz, D6DMSO): δ = 145.6, 131.6 (2×, C148Cimi), 117.4 (C148Cimi), 56.3 (CH2), 32.2 (NCH3), 10.8, 9.1 ppm (2×, C148Cimi); elemental analysis calcd (%) for C13H16B2F8N4(OAc)2·0.5H2O: C 43.35, H 5.17, N 13.76; found: C 35.14, H 4.91, N 13.51.

Synthesis of 10: A suspension of 4b (0.10 g, 0.17 mmol) and AgBF4 (0.099 g, 0.51 mmol) in MeCN (20 mL) was stirred for 18 h in the absence of light. The suspension was filtered through Celite and the volatiles were evaporated, yielding 10 as an orange solid (0.10 g, 99%). Recrystallization of 10 from MeCN/Et2O gave an analytically pure sample. 1H NMR (500 MHz, D6DMSO): δ = 6.24, 5.92 (2×, 2H, JHH = 14.0 Hz, 2H, CH2), 3.70 (s, 6H, NCH3), 2.67, 2.24 ppm (2×, 6H, C148Cimi); 13C{1H} NMR (100 MHz, D6DMSO): δ = 140.1, 141.7, 131.2, 130.5, 129.5 (5×, C148Cimi), 126.8 (br, C148Cimi), 59.6 (CH3), 31.5 (NCH3), 11.2, 10.0 ppm (2×, C148Cimi); elemental analysis calcd (%) for C13H16B2F8N4(OAc)2·0.5H2O·0.25Et2O: C 34.48, H 4.55, N 11.91; found: C 34.30, H 4.91, N 11.72.

Synthesis of 11: A suspension of 8a (0.15 g, 0.36 mmol) and AgBF4 (0.24 g, 1.10 mmol) in MeCN (20 mL) was stirred for 18 h at room temperature in the dark. The suspension was filtered through Celite and the volatiles were removed to leave 11 as an orange oil (0.31 g, 94%), which...
was recrystallized from MeCN/Et2O. 1H NMR (400 MHz, CD3CN): δ = 6.76 (bs, 2H, CH2), 3.45 (s, 6H, NCH3), 2.50, 2.21 ppm (2 x 3H, CH3-CH2); 13C{1H} NMR (100 MHz, [D6]DMSO): δ = 143.5 (C mim), 138.3 (C-Pd), 122.6 (C mim), 40.6 (CH3), 32.0 (NCH3), 10.7, 10.3 (2 x CH3-CH2).

Synthesis of 12: Compound 11 (0.31 g, 0.36 mmol) was stirred in MeOH (20 mL) for 5 min at room temperature. The resulting suspension was filtered through Celite. Upon addition of Et2O (80 mL) complex 12 separated as a red oil that was collected, dried (0.13 g, 62%). 1H NMR (500 MHz, [D6]DMSO): δ = 6.2 (bs, 2H, CH2), 3.51 (s, 6H, NCH3), 2.63, 2.21 ppm (2 x 3H, CH3-CH2); 13C{1H} NMR (100 MHz, [D6]DMSO): δ = 142.6 (C mim), 130.5 (C-Pd), 118.2 (C mim), 59.4 (CH3), 31.6 (NCH3), 10.5, 10.2 ppm (2 x CH3-CH2).

Synthesis of 13a: Gaseous Cl2 was passed through a solution of complex 13b (0.14 g, 0.24 mmol) in MeCN (20 mL) for 5 min. After addition of

Table 2. Crystallographic data for the reported complexes.

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[a] R1 = Σ ||Fo|| - |Fc||/|Σ|Fo|| for all I > 2σ(I). [b] wR2 = Σ[w(Fo2 - Fc2)]2/Σ[w(Fo2)]2.
Abnormal C4-Bonding in N-Heterocyclic Carbene Complexes

FULL PAPER

Acknowledgement

We thank F. Fehr and F. Nydegger for technical assistance. This work has been supported by the Swiss National Science Foundation. M.A. gratefully acknowledges an Assistant Professorship from the Alfred Werner Foundation.


[15] Only few examples of 2-imidazolylidene complexes with protonated features C5-bound imidazolylidene ligands. In analogy to previous reports on this type of imida- zolylidene bonding, we refer to this bonding mode as C4 bonding throughout this manuscript. See also refs [6d,7,10].
A world of a difference: While the two diimidazolylidene complexes (see picture) are structurally identical, they feature either abnormal C4-bound (top) or normal C2-bound heterocyclic carbene ligands. This different carbene bonding mode has a marked influence on the stability, reactivity, and catalytic activity of the coordinated metal. The approach presented here allows for an unambiguously differentiation of the electronic impact of abnormal versus normal carbene bonding.