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## **Abnormal N-heterocyclic carbenes: more than just exceptionally strong donor ligands**

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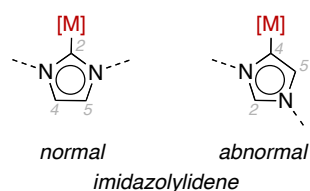
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### **Abstract**

Complexes comprising a so-called abnormal carbene ligand, which displays pronounced mesoionic character, have recently been shown to be competent catalyst precursors for bond activation processes and oxidative transformations, including base-free alcohol oxidation and water oxidation. In this highlight we propose that these abnormal carbene ligands are not just useful spectator ligands but also actively participate in the bond activation step. This mode of action is partially based on the exceptionally strong donor properties of the ligand and, specifically, on the mesoionic character of these abnormal carbenes. The mesoionic properties provide a reservoir for charges and holes and thus induce efficient ligand-metal cooperativity, which is beneficial in particular for oxidation catalysis that involves concerted proton and electron transfer processes.

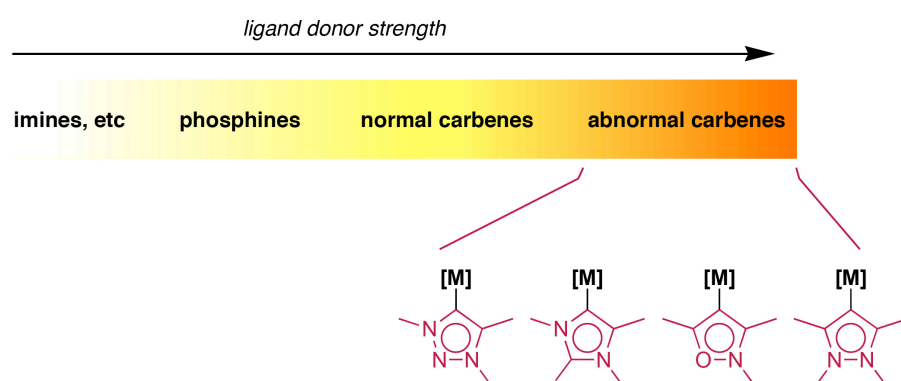
Once discovered to be stable and crystalline,<sup>[1]</sup> N-heterocyclic carbenes (NHCs) were soon recognized as excellent spectator ligands for catalytically active metal centers.<sup>[2]</sup> The great success of NHCs, which are typically derived from imidazolium or 1,2,4-triazolium salts, has often been attributed to their strong donor ability and to the covalent M–L bond. The latter property has significant synthetic and catalytic implications. In contrast to classic donor ligands that coordinate to the metal center by a dative bond, the covalent character of the M–C<sub>NHC</sub> bond decreases the relevance of thermodynamic factors in complex formation processes, since reversible ligand dissociation is generally suppressed.<sup>[3]</sup> For example, a bridging coordination mode of dicarbenes and formation of dinuclear complexes is not rare, while diphosphine or diimine systems generally form chelates that afford mononuclear species.<sup>[4]</sup> As a consequence, NHCs are typically considered as kinetically robust spectator ligands that do not — in contrast to *e.g.* phosphines — provide transient coordination sites for substrate coordination and do not re-coordinate to stabilize catalyst resting states.



**Figure 1.** General representation and numbering scheme of C2-bound, normal imidazolylidene metal complexes and C4-bound, abnormal analogues.

The second key feature of NHCs, *viz.* their strong donor ability, is partially compromised by the two heteroatoms adjacent to the carbene. Their inductive electron-withdrawing effect has been alleviated to some degree by positioning one or both heteroatoms to more remote sites (Fig. 1).<sup>[5]</sup> Remotely stabilized carbenes have been referred to as abnormal carbenes, when no neutral resonance structure is available.<sup>[6]</sup> A direct consequence of the remote heteroatom position is the weaker stabilization of the free carbene through  $\pi$ -push/ $\sigma$ -pull effects, thus

often requiring the metal carbene complexes to be generated by an organometallic approach rather than by coordination chemistry via a free base.<sup>[6b,7]</sup> Support for a considerably stronger donor ability of 4(5)-imidazolyliidenes compared to their normal analogues has been obtained from computational work including  $pK_a$  calculations<sup>[8]</sup> and energy decomposition analyses.<sup>[9]</sup> Experimentally, these bonding principles have been confirmed by the markedly lowered CO stretch vibrations in (NHC)Ir(CO)<sub>2</sub>Cl complexes,<sup>[10]</sup> the higher kinetic energy of d-electrons in abnormal dicarbene palladium complexes,<sup>[11]</sup> and by the larger *trans* influence of isostructural dicarbene palladium complexes in comparative studies.<sup>[12]</sup> These data suggest that the gap in donor properties between abnormal and normal carbenes is similar or even larger than the gap between normal imidazolyliidenes and (alkyl) phosphines. An array of different abnormal carbene scaffolds has been developed in the last few years,<sup>[13]</sup> indicating that the donor properties can be significantly influenced by the number and position of heteroatoms within the heterocycle, thus providing a wide diversity of ligand systems with strong to exceptional donor characteristics (Fig. 2).



**Figure 2.** Schematic and simplified donor ability scale illustrating the donor ability of different abnormal NHC ligands.

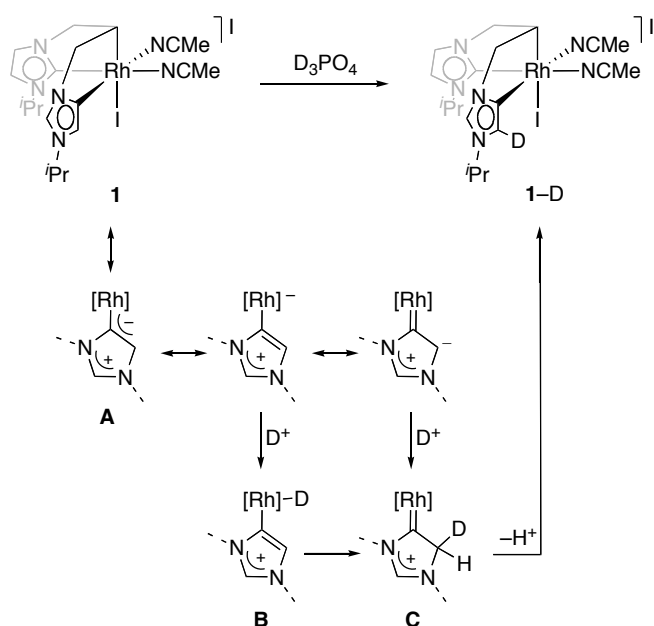
The strong ligand donor properties directly affect the catalytic activity of the metal center, and a variety of transformations have been accomplished with abnormally bound carbene metal complexes.<sup>[14]</sup> In a number of bond activation processes, the catalytic performance is

significantly higher than in normal carbenes.<sup>[11,15]</sup> In parts, these results have been attributed to the higher propensity of the metal center to undergo oxidative addition because of the distinct donor properties of the abnormal carbene ligand. Recent work suggests, however, that the increased mesoionic character<sup>[6c]</sup> of these abnormal carbenes may also be of high relevance in rationalizing the observed reactivity patterns.

A first indication for unusual reaction trajectories has stemmed from attempts to cleave the Rh–C<sub>alkyl</sub> bond in complex **1** comprising an abnormally and a normally bound NHC in one single molecule (Scheme 1). While H<sub>3</sub>PO<sub>4</sub> does not seem to affect the complex, the deuterated analog D<sub>3</sub>PO<sub>4</sub> cleanly affords the monodeuterated complex **1-D** in which the C5-carbon of the abnormally bound heterocycle is deuterated exclusively.<sup>[16]</sup> The most acidic proton in this molecule, *i.e.* the C2-bound proton of the abnormal carbene, is inert and no isotope incorporation has been detected at this site. When an analogue of **1** featuring both carbenes in the abnormal bonding mode is exposed to D<sub>3</sub>PO<sub>4</sub>, the corresponding doubly deuterated product is isolated comprising a deuterium bound to each heterocyclic carbon adjacent to the rhodium-bound nucleus.<sup>[17]</sup> The combination of these results does not support a simple electrophilic aromatic substitution mechanism, as may be surmised for the deuteration of metal-free 2-imidazolylidene.<sup>[18]</sup> A more probable mechanism may be based on the separation of the  $\pi$ -electron system in imidazolylidenes into an olefinic C=C fragment and a cationic amidinium unit NCN<sup>+</sup>.<sup>[19]</sup> Metalation at the C2 position hence leads to effective charge compensation due to the introduction of a formal negative charge (carbanion formation) within the NCN<sup>+</sup> unit. In contrast, metalation of C4 or C5 affords a metala-allyl unit comprising a formally anionic vinyl site bound to the metal center and the amidinium unit as an intramolecular remote cation (resonance structure **A**, Scheme 1).<sup>[20]</sup> This model may help rationalize the stronger donor properties of the abnormal carbene. In addition, allyl-type reactivity of the M–C=C unit is commensurate with the observed deuteration at the

heterocyclic C5 position exclusively, either through metal hydride formation and a subsequent 1,3-allylic shift of a metal-bound deuterium cation via intermediate **B**, or due to  $D^+$ -bonding by the partially negative carbon directly to form intermediate **C**. Intermediate **C** comprises a formal metal-carbene  $M=C$  bond and induces, upon reversible  $C-H/D$  bond making and breaking, the observed isotope exchange yielding **1-D**.

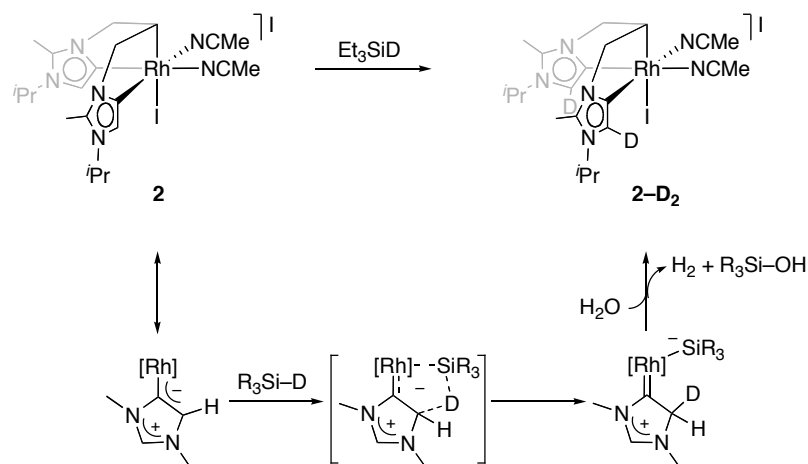
**Scheme 1**



A similar reactivity pattern has been uncovered when investigating the mechanism of catalytic Si-H bond activation with complex **2** (Scheme 2).<sup>[21]</sup> When employing the monodeuterated silane  $Et_3SiD$  as substrate, selective deuteration of the C5 position and formation of **2-D<sub>2</sub>** occurs, corroborating ligand participation in the bond activation step. Accordingly, Si-H bond cleavage may proceed either through oxidative addition and a subsequent 1,3-shift of the metal-bound deuteride (*cf* conversion of **B** to **C** in Scheme 1), or through a 5-membered transition state involving C5 and the rhodium center (Scheme 2), similar to a complex-assisted metathesis process.<sup>[22]</sup> Such cooperativity between the metal center and the ligand has been noted in different contexts and may be a key factor for various metal-catalyzed bond activation processes.<sup>[23]</sup> Accordingly, previously reported catalytic reactions involving

abnormal carbene ligands may require a mechanistic reconsideration. For example, the higher performance induced by abnormal carbene ligands in the palladium-catalyzed H<sub>2</sub> activation may include ligand participation.<sup>[24]</sup> Similarly, the Rh-catalyzed transfer hydrogenation may be more efficient with abnormal carbene ligands<sup>[15a]</sup> because the abnormal carbene may assist the C<sub>isopropoxide</sub>-H bond activation step. Obviously, the type of cooperativity highlighted here is not restricted to abnormal carbenes only and may also be relevant for normal carbenes that contain an unsaturated carbon adjacent to the metal-bound nucleus, *e.g.* in 3-pyrazolylienes,<sup>[25]</sup> and it may also be effective, though presumably less pronounced, in normal 2-imidazolylienes.<sup>[26]</sup>

**Scheme 2**

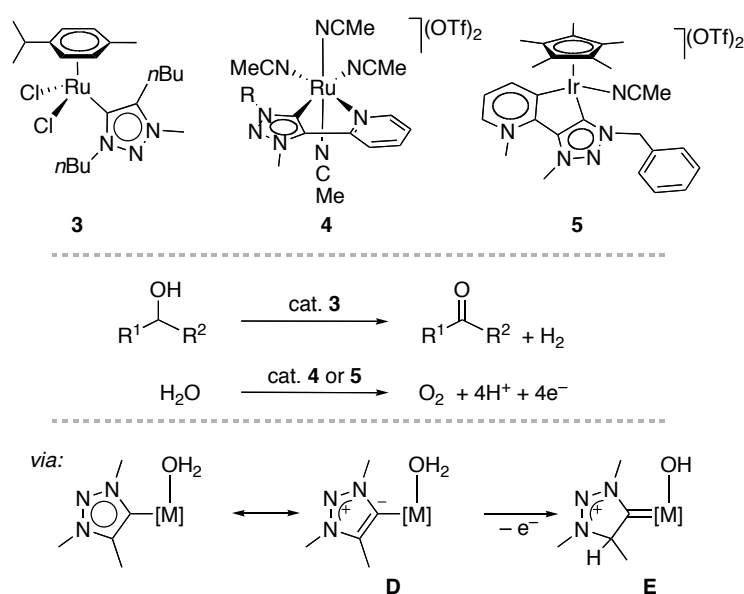


Metal-ligand cooperativity as postulated here for the abnormal carbene metal complexes may be particularly attractive in catalytic oxidation reactions that comprise concomitant proton transfer. For example, the high activity of complex **3** comprising an abnormal 5-triazolyliene in catalyzing the base-free oxidation of alcohols or amines (Scheme 3) may be vindicated by cooperative effects and ensuing coupled transfer of protons and electrons (PCET, proton-coupled electron transfer).<sup>[15b]</sup>

PCET has been recognized as a key component of solar-powered water splitting for energy generation (photosynthesis) and artificial versions have aimed to include such effects in the

water oxidation cycle, *i.e.* the more challenging part of water splitting. In light of the specific properties of abnormal carbene ligands and considering the high catalytic activity of ruthenium and iridium,<sup>[27]</sup> it may not be surprising that complexes **4** and **5** are amongst the most active water oxidation catalysts of their class known to date.<sup>[28]</sup> Specifically, the ruthenium complexes **4** are easily accessible and demonstrate a high tunability of the catalytic activity through appropriate ligand modifications. The active species originating from the iridium complex **5** appears to be catalytically highly robust and turnover numbers are — even under highly dilute conditions — only limited by the availability of the sacrificial oxidant, cerium ammonium nitrate. The remarkable stability of the catalytically competent species may originate from the potential of complex **5** to undergo two sequential proton transfers from the coordinated water molecule in **D** and the hydroxide intermediate **E**, respectively, which are paired with a simultaneous (formal) oxidation of iridium(III) to iridium(V) (Scheme 3).

**Scheme 3**



Cooperative processes in which the ligand is assisting the metal center in bond making and breaking processes may be advantageous yet perhaps not essential for some of the bond



activation processes highlighted above. A plethora of other ligands may display similarly cooperative modes of action, including imines such as (poly-)pyridines. Transient dearomatization, evidenced in some pyridine-based systems<sup>[23b]</sup> and also proposed for the abnormal carbene heterocycles of complexes **1–5** may spring-load the active species for engaging in energy-demanding bond activation processes such as C–H bond activation, or O–H bond activation in metal-bound hydroxides.

The concept of metal-ligand cooperativity may be of general relevance for water splitting and related metal-catalyzed redox processes. While first results point indeed to a non-innocence of the abnormal carbenes and their active participation in bond activations, clearly, the proposal outlined in this highlight is still speculative and further work will be required to support or disprove this hypothesis. For example, cooperative effects based on the enhanced mesoionic character of abnormal carbenes should have implications also on reactions mediated by transition metal centers other than platinum group metals. Current work in our group aims at exploiting these specific properties of abnormal carbenes for the catalytic transformation of other small molecules.

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Abnormal carbene ligands – isomeric to classical N-heterocyclic carbenes but comprising a much more pronounced mesoionic character — are proposed to act cooperatively with the metal center to accomplish demanding bond activation processes.

