

## Review

## Coordination chemistry of ditopic carbanionic N-heterocyclic carbenes



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## ABSTRACT

The chemistry of N-heterocyclic carbenes, particularly imidazol-2-ylidenes, has been exhaustively documented in the literature. Amongst the many bond activation reactions available for such species (C–H, C–C and N–C), it has recently become apparent that deprotonation of the alkenic backbone can give rise to ditopic carbanionic carbenes, *i.e.* anionic species capable of bonding to Lewis acidic centres *via* two different carbon sites (C2 and C4 or C4 and C5). In this article, we aim to provide a comprehensive review of the chemistry of such species, with a particular focus on their isolation as alkali-metal salts and their subsequent reactivity.

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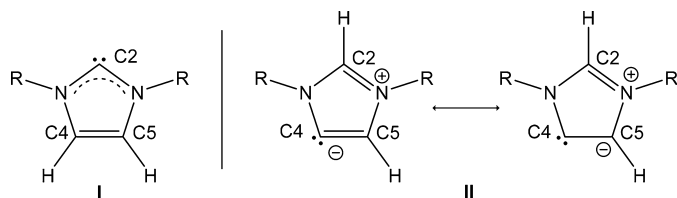
## 1. Introduction

The importance of N-heterocyclic carbenes (NHCs) as supporting ligands in transition-metal chemistry is indisputable and has been extensively documented in the chemical literature [1–12]. This (now mature) area of chemistry was initiated by the

pioneering work of Wanzlick and Öfele [13,14], and accelerated by Arduengo and co-workers following their seminal report describing the isolation of the first structurally authenticated carbene, 1,3-bis(adamantyl)-imidazol-2-ylidene (IAd) [15]. The extraordinary stability of NHCs, compared to that of other acyclic all-carbon analogues, is a result of  $\pi$ -donation by adjacent N-heteroatoms into the empty  $p_{\pi}$  orbital at the carbenic centre. This increased stability has allowed for the synthesis of a wide variety of N-heterocyclic carbenes. The electronic and steric parameters of such species can be specifically tailored by both nitrogen and backbone-carbon

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**Fig. 1.** Bonding modes of imidazol-2-ylidenes: “classical” (I; left), and “abnormal” or mesoionic (II; right). The term mesoionic is employed because such species cannot be represented by a Lewis structure without invoking two opposing charges on the ligand.

functionalization [16]. Accordingly, there are several reviews already published documenting the use of NHCs as ligands for the formation of transition-metal complexes [1–12]. Similarly, the strong  $\sigma$ -donor ability of NHCs has also been employed in main-group chemistry for the isolation of low-coordinate, low-oxidation state diatomic species,  $E_2(\text{NHC})_2$  ( $E = \text{Si}, \text{Ge}, \text{Sn}, \text{P}, \text{As}$ ) [17–21], including, most recently a  $B_2(\text{IPr})_2$  species (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), which features a boron–boron triple bond [22].

## 2. Bonding modes of N-heterocyclic carbenes

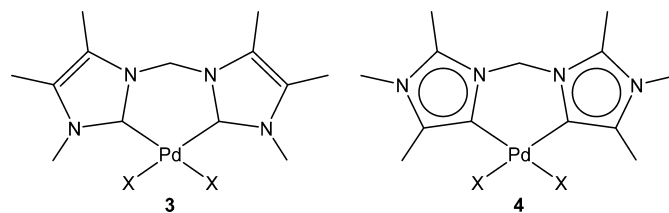
Arguably, the most ubiquitous family of N-heterocyclic carbenes are those consisting of a five-membered ring core with an unsaturated backbone, *i.e.* imidazol-2-ylidenes. The coordination chemistry of these NHCs is dominated by so-called “classical” coordination *via* the C2 position (Fig. 1, I). Numerous examples of metal complexes bearing NHCs bonded in such a manner were documented over the 30-year period before other coordination modes were discovered.

### 3. “Abnormal” or mesoionic N-heterocyclic carbenes (aNHCs)

#### 3.1. Transition-metal aNHC complexes

The first documented example of a so-called “abnormal” (or mesoionic) N-heterocyclic carbene (aNHC; Fig. 1, II), was reported by Crabtree and co-workers and isolated from the reaction of 2-pyridylmethylimidazolium salts with the iridium polyhydride  $\text{IrH}_5(\text{PPh}_3)_2$  (Fig. 2) [23–25]. Direct metallation of imidazolium salts occurs at either the C2 or C4 position, favouring one isomer or another as a result of either steric factors due to the nature of the R group, or electronic factors associated with the counter-anion of the imidazolium salt and/or the nature of the solvent [26].

The bonding mode of **1** was unambiguously confirmed by X-ray crystallography and the presence of a low field resonance in the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  (8.72 ppm) which can be assigned

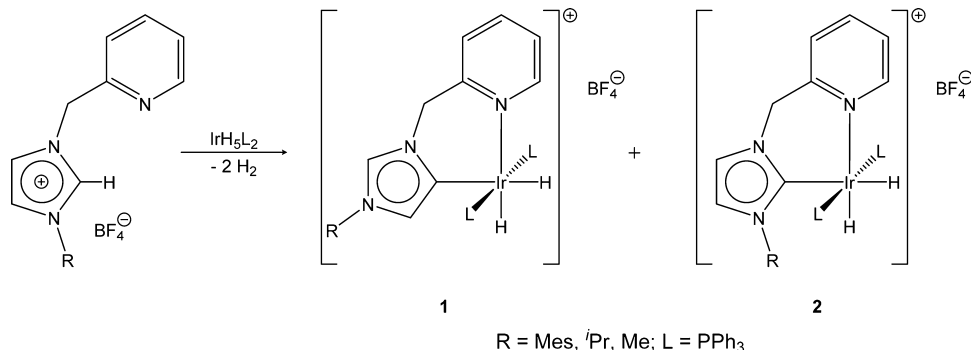


**Fig. 3.** Bis-C2 and bis-C4 chelating NHC ligands [34,36,37].

to the imidazole proton at the C2 position. Bearing in mind that the acidity of the C2 proton has been determined by calculations to be nine  $\text{pK}_a$  units smaller than that of the C4 proton ( $\text{pK}_a = 24$  and 33, respectively) [27,28], it is surprising to find that the *in situ* metallation of the imidazolium salt can occur exclusively at the C4 position. The regioselectivity of metallation can be controlled through the steric bulk of the R group, hence when  $\text{R} = \text{Mes}$  or  $i\text{Pr}$ , the sole product is **1**. When  $\text{R} = \text{Me}$ , a mixture of **1** and **2** is formed. It is important to note that **1** and **2** do not interconvert at room temperature or when heated to  $100^\circ\text{C}$ , which would suggest that **1** is the thermodynamic product of the reaction, despite the greater acidity of the proton at the C2 position.

The discovery of this alternative bonding mode paved the way for an increase in the number of new complexes containing C4-bonded carbenes. This aspect of the coordination chemistry of N-heterocyclic carbenes has been the subject of several review articles in the chemical literature [29–32]. The “abnormal” bonding mode is relevant to further discussions regarding chemical bonding in ditopic carbanionic N-heterocyclic carbenes (*vide infra*) and as such relevant examples are discussed below. For an in-depth review of “abnormal” bonding in N-heterocyclic carbenes, the reader is directed to any of the excellent reviews of the area [29–32]. We will highlight only a handful of representative examples herein.

C4-bonded NHC complexes of palladium are amongst the most numerous “abnormal” complexes in the chemical literature, in all likelihood due to the extensive studies carried out on catalytically active C2-bonded NHC palladium complexes [33–35]. However many other novel complexes containing “abnormally” bonded NHCs with transition metals such as ruthenium, rhodium and iridium are also well documented [29–32]. Rational design of “abnormal” carbene complexes has been demonstrated by Albrecht and co-workers who have developed a range of chelating NHC ligands which give either the bis-C2 or bis-C4-bonded NHC palladium complexes (Fig. 3) by blocking the appropriate position on the imidazole ring with an alkyl or aryl group [34,36,37]. Likewise, “abnormally” bonded platinum(II) complexes of similar chelating NHC ligands can be synthesized by microwave-assisted double C–H bond activation; the corresponding platinum(IV) complexes could be obtained by subsequent reaction with  $\text{PhICl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$  [38].



**Fig. 2.** “Abnormal” (**1**) and “classical” (**2**) isomers of Crabtree’s iridium(III) complex of the 2-pyridylmethylimidazolylidene ligand [23].

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