

Isolation of a potassium bis(1,2,3-triazol-5-ylidene)carbazolide: a stabilizing pincer ligand for reactive late transition metal complexes†

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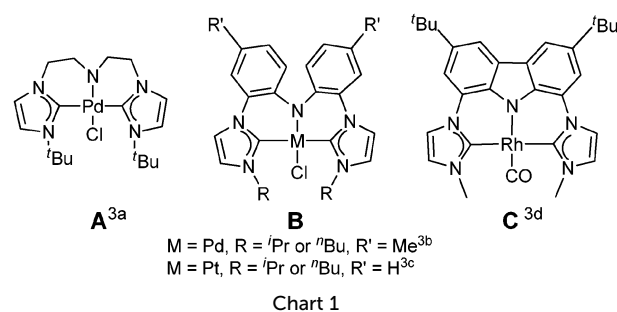
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The synthesis and X-ray crystal structure of a potassium adduct of a monoanionic CNC-pincer ligand featuring two mesoionic carbenes is reported. Owing to the peculiar electronic and steric properties of this ligand, the first neutral stable Ni(II)-hydride, and an unusual Cu(II) complex displaying a seesaw geometry, have been isolated.

It is well known that tridentate pincer ligands not only give rise to robust catalysts, but also allow for isolating extremely reactive metal centers.¹ A large number of both neutral and monoanionic pincer ligands featuring N-heterocyclic carbenes (NHCs) have been prepared, and the corresponding complexes used as catalysts for various chemical transformations.² However, only four complexes, featuring a strongly donating amido-moiety as the central coordinating atom, flanked by two NHC wing-tip groups in a CNC-fashion, have been reported (A–C) (Chart 1).³ Moreover, pincer ligands based on the novel generation of carbenes, namely mesoionic carbenes (MICs),⁴ which are even stronger donors than NHCs, have been even less explored. For the CCC-tridentate binding mode, a handful of examples are known with imidazol-4-ylidenes,^{4,5} whereas with 1,2,3-triazol-5-ylidenes,⁶ binuclear bridged complexes⁷ or mononuclear complexes with bidentate ligands where the central C-atom does not ligate,⁸ are exclusively found. A neutral CNC-analogue of tridentate terpyridine, [2,6-bis(1,2,3-triazol-5-ylidene)-pyridine], is the only example of a bisMIC pincer acting as a tridentate ligand.⁹ Here we report the synthesis of the first stable *anionic* CNC-tridentate ligand featuring terminal 1,2,3-triazol-5-ylidenes and a central



amido functionality, its mononuclear tridentate Ni(II)-hydride and Cu(II) complexes.

The planar carbazole backbone with its rigid geometry seemed an attractive choice for the design of a bis(mesoionic carbene)amido pincer-type ligand. The synthesis of the dicationic salt precursor, namely the bis(1,2,3-triazolium)carbazole **1**, was achieved in 43% yield by an adapted version of the formal 1,3-dipolar cycloaddition between a 1,3-diaza-2-azoniaallene salt and a 1,8-diethynylcarbazole (Scheme 1).^{6a} Addition of 3 equivalents of potassium hexamethyldisilazide (KHMDS) to a THF solution of **1** at $-78\text{ }^{\circ}\text{C}$ resulted only in the deprotonation of the carbazole, keeping unchanged the two pendant 1,2,3-triazolium moieties. The cationic salt **2** was isolated in 93% yield as an air- and moisture-stable red solid. The monodeprotonation of **1** is indicated by the absence of the N–H resonance in the ¹H NMR spectrum, and by the presence of a triazolium C–H signal (2H) at 10.03 ppm (see ESI†). The structure of **1** was confirmed by an X-ray diffraction study (Fig. 1). When a large excess of KHMDS (5 equivalents) was added to a diethylether suspension of **1** at $-78\text{ }^{\circ}\text{C}$, the potassium salt **3** could be isolated in good yield (72%) after extraction with hexanes. In the ¹H NMR spectrum, the disappearance of the acidic N–H and triazolium C–H signals confirmed the formation of the triply deprotonated compound **3**. In the ¹³C{¹H} NMR spectrum, a singlet at 195 ppm, characteristic of a K–C_{carbene} adduct, was observed.¹⁰ Interestingly, the bis(carbene)amido potassium adduct is indefinitely stable in solution and in the solid state, in the absence of oxygen and water.

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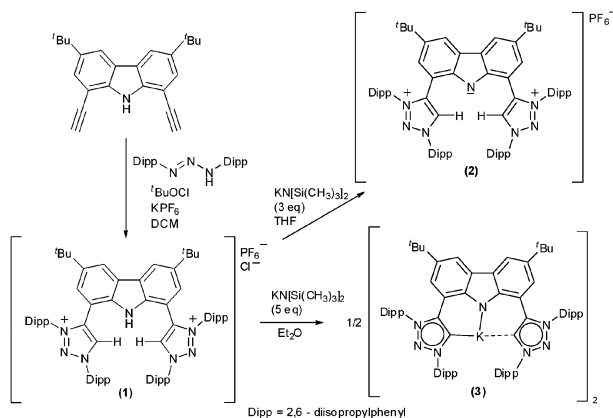
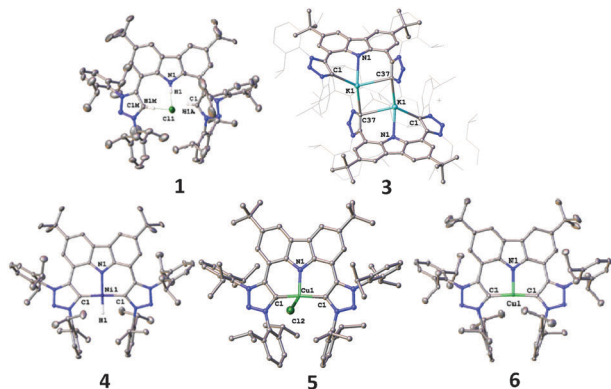
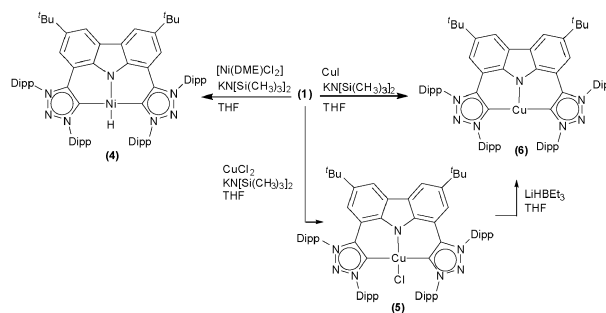
Scheme 1 Synthesis of ligand precursors **1** and **2**, and ligand **3**.

Fig. 1 Molecular structures of **1**, **3**–**6** (thermal ellipsoids at 50% probability level). Hydrogen atoms (except triazolium C–H's, N–H and Ni–H), solvent molecules and counteranions (PF_6^-) were omitted for clarity except in the case of **1**. The diisopropylphenyl-groups of **3** were drawn as wireframe structures for the sake of clarity.

Crystals of **3**, suitable for an X-ray diffraction study, were obtained from a mixture of deuterated benzene and toluene. The structure of **3** (Fig. 1) features a $[(\text{CNC})\text{-K-K}(\text{CNC})]$ dimer centered on a distorted rhombic K_2C_2 core, with the two three-coordinated potassium atoms acting as a bridge between two CNC ligands. The two 1,2,3-triazol-5-ylidene rings are planar with bond distances between that found for single and double bonds, and are not coplanar with the carbazolidone backbone. The bond angles $[\text{N}2\text{-C}1\text{-C}2 = 100.49(14)^\circ]$ and $[\text{N}5\text{-C}37\text{-C}38 = 100.66(15)^\circ]$ in **3** are more acute than the corresponding angle $[\text{N}2\text{-C}1\text{-C}2 = 104.06(19)^\circ]$ in **1** as always observed when comparing a carbene and its precursor.⁴ Each potassium binds to one N atom and one carbene carbon from a CNC unit plus one carbene carbon from the adjacent (CNC) ligand. The bond distances ($\text{K}1\text{-N}1 = 2.624(15)$; $\text{K}1\text{-C}1 = 2.869(17)$; $\text{K}1\text{-C}37' = 2.9684(19)$ Å) are well in accordance with other potassium-carbene bond lengths of 3.000(13)–3.048 Å;¹⁰ additionally, long carbon–K distances are observed ($\text{K}1\text{-C}37 = 3.158(17)$ Å).^{10b}

When the cationic pincer derivative **1** was reacted with excess base and 1.1 equivalent of nickel(II) dichlorodimethoxyethane adduct ($[\text{Ni}(\text{DME})\text{Cl}_2]$) in THF at -78 °C, the unexpected nickel-hydride complex $[(\text{CNC})\text{NiH}]$ **4** was obtained in 39% yield (Scheme 2).

Scheme 2 Synthesis of complexes **4**–**6**.

A characteristic hydride signal appears at -6.30 ppm in the ^1H NMR spectrum, and a single crystal X-ray diffraction study confirmed the structural assignment (Fig. 1). Note that two cationic Ni(carbene)–hydride complexes have been reported to date,¹¹ complex **4** being the first example of an isolated neutral Ni–carbene hydride complex. Formation of the hydride complex is presumed to occur *via* the triazolium C5–H activation, similar to the C2–H activation of the imidazolium ring observed by Cavell *et al.*^{11a} The molecular structure (Fig. 1) shows a distorted square planar geometry around the Ni center, analogous to other nickel hydride complexes featuring pincer ligands with a central amido-ligating atom,¹² and with comparable Ni–N1 and Ni–H1 bond-lengths (see ESI[†]) to these¹² and other Ni–H pincer complexes.¹³ The two 2,6-diisopropylphenyl groups (Dipp) of the mesoionic carbenes shield the hydride. The 1,2,3-triazol-5-ylidenes rings are not coplanar with the carbazolidone backbone: both rings are tilted $[\text{C}4\text{-C}3\text{-C}2\text{-C}1 = -7.7(3)^\circ]$. The two mesoionic carbenes and the metal center ($\text{C}1\text{-N}1\text{-C}1$) form an angle of $177.56(10)^\circ$.

Encouraged by the stability of the Ni–H complex **4**, the synthesis of the first example¹⁴ of a Cu(II)–H complex was attempted. Following a similar procedure as described above, CuCl_2 was employed as starting material (Scheme 2), and the paramagnetic $[(\text{CNC})\text{Cu(II)Cl}]$ complex **5** was obtained in 86% yield.

Although the Cu(II)–carbene fragment is implicated in copper catalysed carbene transfer reactions, it is usually too reactive to be isolated.¹⁵ Again, only two other examples of Cu(II)–carbene complexes are known.¹⁶ No usable NMR data could be obtained due to the paramagnetic nature of the complex, but the single crystal data confirms the structure of this unusual carbene complex. The $\text{C}2\text{-C}1\text{-Cu}1\text{-C}1$ torsion angle of $110.64(5)^\circ$ displays significant deviation from planarity, and the $\text{C}11\text{-Cu}1\text{-N}1$ bond angle of $123.53(6)^\circ$ is indicative more of an unusual seesaw geometry than the expected square planar arrangement around the Cu-atom.^{16,17} Attempts at substituting the chloro ligand with a hydrido employing superhydride (LiHBEt_3) proved unsuccessful; it resulted in the reduction of Cu(II) to Cu(I) and the formation of the brown-colored complex **6** $[(\text{CNC})\text{Cu(I)}]$ (Scheme 2). An independent route, utilizing CuI, KHMDS and **1** as precursor, also led to the isolation of **6**. An X-ray diffraction study (Fig. 1) revealed the rarely found “naked” slightly distorted T-shape geometry of the Cu(I),^{16,18} in which the metal center is coordinated to the central amido and two mesoionic carbenes. The 1,2,3-triazol-5-ylidenes rings are both tilted from the plane of

the carbazolid backbone [C8–C3–C2–C1 = 9.8(3)°], and the N1–Cu bond [2.017(2) Å] is slightly longer than the N1–Cu bond in 5 [1.956(3) Å]. Mono- and dinuclear carbene ligands usually result in the formation of linear copper complexes,¹⁹ while sterically less bulky carbene ligands form Y-shaped complexes.^{17c}

To summarize, the novel anionic CNC-bisMIC ligand with its highly electron-donating backbone allows for the isolation and structural characterization of unusually stable transition metal species that have traditionally been viewed as not isolable under ambient conditions.

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