

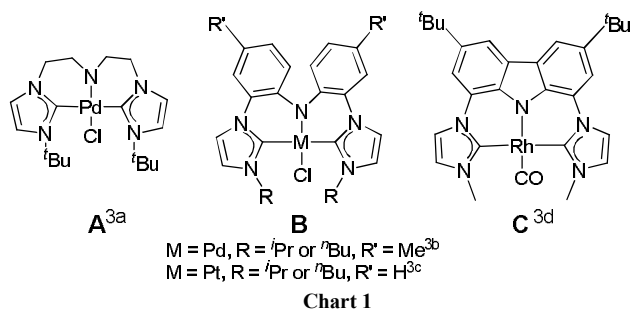
# Isolation of a potassium bis(1,2,3-triazol-5-ylidene)carbazolide: A stabilizing pincer ligand for reactive late transition metal complexes

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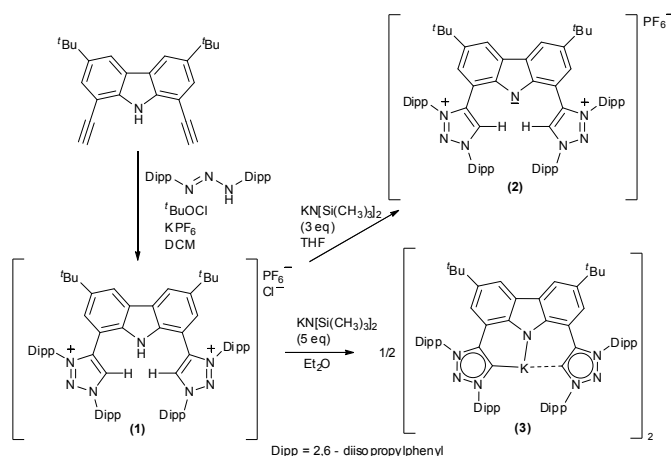
The synthesis and X-ray crystal structure of a potassium adduct of a monoanionic CNC-pincer ligand featuring two mesoionic carbenes is reported. Owing to the peculiar electronic and steric properties of this ligand, the first neutral stable Ni(II)-hydride, and an unusual Cu(II) complex displaying a seesaw 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.<sup>1</sup> 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.<sup>2</sup> 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).<sup>3</sup> Moreover, pincer ligands based on the novel generation of carbenes, namely mesoionic carbenes (MICs),<sup>4</sup> 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,<sup>4,5</sup> whereas with 1,2,3-triazol-5-ylidenes,<sup>6</sup> binuclear bridged complexes<sup>7</sup> or mononuclear complexes with bidentate ligands where the central C-atom does not ligate,<sup>8</sup> 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.<sup>9</sup> 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.

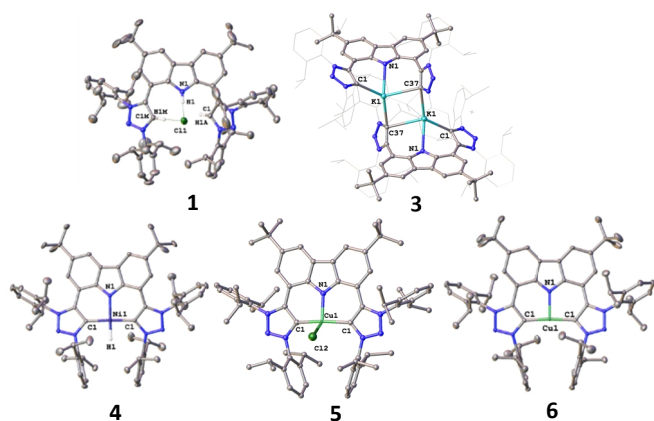
The planar carbazole backbone with its rigid geometry seemed an attractive choice for the design of a bis(mesoionic carbene)amido pincer-type ligand. The synthesis of the dicationic salt precursor, namely the bis(1,2,3-triazolium)carbazole **1**, was achieved in 43%



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).<sup>6a</sup> Addition of 3 equivalents of potassium hexamethyldisilazide (KHMDs) to a THF solution of **1** at -78°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 <sup>1</sup>H NMR spectrum, and by the presence of a triazolium C-H signal (2 H) at 10.03 ppm (see SI). 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°C, the potassium salt **3** could be isolated in good yield (72%) after extraction with hexanes. In the <sup>1</sup>H 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 <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, a singlet at 195 ppm, characteristic of a K-C<sub>carbene</sub> adduct, was observed.<sup>10</sup> Interestingly, the bis(carbene)amido potassium adduct is indefinitely stable in solution and in the solid state, in the absence of oxygen and water.



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



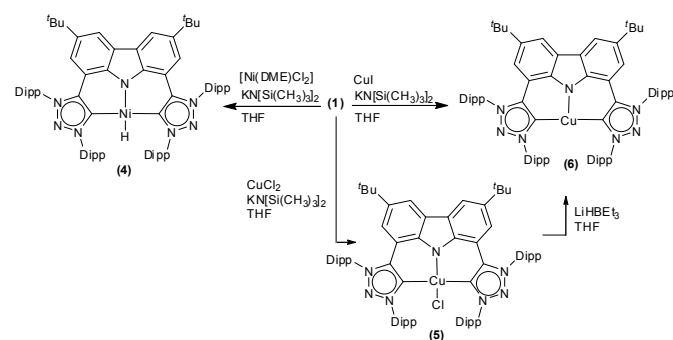
**Fig. 1** Molecular structures of **1**, **3** - **6** (thermal ellipsoids at 50% probability level). Hydrogen atoms (except triazolium C-H's, N-H and Ni-H), solvent molecules and counteranions ( $\text{PF}_6^-$ ) were omitted for clarity except in the case of **1**. The diisopropylphenyl-groups of **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 [(CNC)-K-K-(CNC)] dimer centered on a distorted rhombic  $\text{K}_2\text{C}_2$  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.<sup>4</sup> 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,<sup>10</sup> additionally, long carbon-K distances are observed ( $\text{K}1-\text{C}37=3.158(17)$ Å).<sup>10b</sup>

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  $-78^\circ\text{C}$ , the unexpected nickel-hydride complex [(CNC)NiH] **4** was obtained in 39% yield (Scheme 2). A characteristic hydride signal appears at  $-6.30$  ppm in the  $^1\text{H}$  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,<sup>11</sup> 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.*<sup>11a</sup> 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,<sup>12</sup> and with comparable Ni-N1 and Ni-H1 bond lengths (see SI) to these<sup>12</sup> and other Ni-H pincer complexes.<sup>13</sup> 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 (C1-N1-C1) form an angle of  $177.56(10)^\circ$ .

Encouraged by the stability of the Ni-H complex **4**, the synthesis of the first example<sup>14</sup> of a Cu(II)-H complex was attempted. Following a similar procedure as described above,  $\text{CuCl}_2$  was employed as starting material (Scheme 2), and the paramagnetic [(CNC)Cu(II)Cl] complex **5** was obtained in 86% yield.



**Scheme 2** Synthesis of complexes **4** - **6**

Although the Cu(II)-carbene fragment is implicated in copper catalysed carbene transfer reactions, it is usually too reactive to be isolated.<sup>15</sup> Again, only two other examples of Cu(II)-carbene complexes are known.<sup>16</sup> 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 C2-C1-Cu1-C1 torsion angle of  $110.64(5)^\circ$  displays significant deviation from planarity, and the C11-Cu1-N1 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.<sup>16,17</sup> Attempts at substituting the chloro ligand with a hydrido employing superhydride ( $\text{LiHBEt}_3$ ) proved unsuccessful; it resulted in the reduction of Cu(II) to Cu(I) and the formation of the brown-colored complex **6** [(CNC)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),<sup>16,18</sup> 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 carbazolidone backbone  $[\text{C}8-\text{C}3-\text{C}2-\text{C}1=9.8(3)^\circ]$ , 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,<sup>19</sup> while sterically less bulky carbene ligands form Y-shaped complexes.<sup>16c</sup> 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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## Notes and references

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