



## 2,6-Lutidine-linked bis-saturated NHC pincer ligands, silver complexes and transmetallation

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### ABSTRACT

Pincer ligands have proven to be valuable tools in the formation of robust transition metal complexes. To date, pincer ligands have featured an extremely diverse array of structural motifs, backbones and donor units. Carbene ligands have been easily integrated into a variety of pincer ligand structures and yet there are very few examples in which saturated NHC donor moieties are featured. Saturated NHCs are known to have unique donor and acceptor properties compared to their unsaturated analogs and therefore their implementation into pincer structures should lead to new electronic properties of the coordinated metal. To expand the use of saturated NHCs in pincer ligand chemistry, a bis-NHC pincer ligand, featuring a 2,6-lutidine linker, has been synthesized. The proligand can be directly metalated using silver oxide and the silver salt has been used in transmetallation chemistry to generate Ni(II) pincer complexes. This ligand is an excellent addition to known pincer ligands and will have applications in catalysis and other areas.

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### 1. Introduction

Tridentate ligands that coordinate meridionally – pincer ligands – are a valuable class of chelating ligands that generate robust metal complexes and have broad applications in catalysis. Perhaps the best known and largest category of pincer ligands are those that feature an aromatic (phenyl or pyridine) group with *meta*-substituents that have ligating moieties. Phosphine-based systems such as the PCP [1], POCOP [2], and PNP [3] ligands are perhaps the most widely used and best known because they are relatively easy to synthesize and can be readily modified sterically and electronically. Additionally, transition metal complexes featuring pincer ligands have proven to be excellent catalysts for a broad range of catalytic transformations [4].

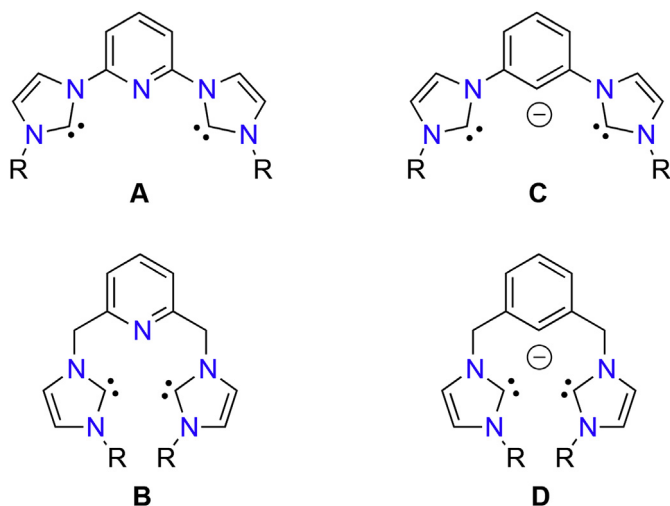
In the last 25 years carbenes have become ubiquitous ligands in transition metal and main group chemistry [5]. They are renowned for their strong  $\sigma$ -donor and weak  $\pi$ -acceptor properties, which create unreactive ligand-metal bonds and electron rich transition metal complexes. These unique properties have made carbenes an

important complement to phosphine-based ligands. Unsurprisingly, carbenes have been integrated into multidentate ligand systems, including pincers [5c,6]. The first systems featured two unsaturated N-heterocyclic carbene (uNHC) moieties connected by a pyridine linker, either directly **A** [7] or by a methylene group **B** [8], were reported in the early 2000's (Fig. 1). The anionic systems **C** [9] and **D** [8a] have also been reported. Complexes featuring ligands **A–D** with a wide variety of transition metals have been reported, many of which have been used as catalysts.

Interestingly, nearly all of the early pincer systems featured uNHC moieties, despite the fact that saturated NHCs (sNHCs) have been known since 1995 [10]. In fact, to date only systems of type **E** [11] and **F** [12] have been reported (Fig. 2), the former only very recently. The effects of saturation on the ligand properties of NHCs is a complex issue but has been investigated thoroughly via a variety of experimental and computational means [13]. The general consensus of these studies is that despite having nearly identical Tolman Electronic Parameters (TEPs) [14] the  $\sigma$ -donor and  $\pi$ -acceptor properties are, in fact, quite unique and therefore lead to sometimes starkly different reactivities of the corresponding transition metal complexes. This is particularly evident in the case of Ru-based metathesis catalysts for monodentate sNHCs [15] and selective tritiation catalysis of iron complexes of **E** [11]. However, to

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**Fig. 1.** Neutral pyridine-linked uNHC pincer ligands **A** and **B** and the anionic aryl-linked uNHC pincer ligands **C** and **D**.

date, no pincer ligands featuring two sNHCs and a 2,6-lutidine linker **G** have been reported (Fig. 2).

One disadvantage of NHC based pincer systems is that the ligation process is complicated by generation of the carbene. One easy method with broad application is the use of silver carbene complexes, which, while somewhat light sensitive, are much more stable and easier to handle than free carbene ligands [16]. These silver complexes have proven to be excellent transmetallation reagents and can be used to generate a variety of complexes that can then be used as catalysts. Additionally, there has been significant investigation into the behavior of NHC silver complexes in medicinal chemistry as anti-tumor and anti-bacterial agents [17].

In order to broaden the scope of carbene based pincer ligands, we have synthesized the first 2,6-lutidine-linked bis-sNHC proligands. These ligands easily undergo metalation to form silver complexes, which in turn can be used for transmetallation chemistry. To demonstrate the viability of the transmetallation reactivity, Ni(II) complexes have been synthesized. All of these species have been isolated and fully characterized. These ligands will allow for further tuning of the electronics of transition metal pincer complexes.

## 2. Experimental

### 2.1. General considerations

All manipulations of air and moisture-sensitive materials were carried out using standard vacuum line, Schlenk, and cannula techniques. Solvents were dried according to standard methods: acetonitrile and dichloromethane were lyophilized and distilled from

calcium hydride, tetrahydrofuran and toluene were lyophilized over a potassium mirror and distilled. All reagents were purchased from Sigma-Aldrich, Chemical Co. and used as received. The 1-mesityl-4,5-dihydro-1H-imidazole and 1-(2,6-diisopropylphenyl)-4,5-dihydro-1H-imidazole were prepared following a slight modification of the reported methods [18]. NMR data were recorded on JEOL GX300 (300 MHz), Bruker Fourier (300 MHz) and Bruker AVANCE III HD (500 MHz) NMR machines. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are expressed in ppm and Hz, respectively. The spectra were referenced internally using the signal from the residual protio-solvent ( $^1\text{H}$ ) or the signals of the solvent ( $^{13}\text{C}$ ). The NMR spectra of all compounds can be seen in the supplementary information document associated with this article. Elemental analysis of the compounds was performed with a Vario-Micro V2.0.11 elemental (CHNS) analyzer. The melting points of the compounds were obtained using a MEL-TEMP melting point apparatus with a Fluke 51 II electronic thermometer and are reported uncorrected. Mass spectra were obtained using a JEOL The MStation JMS-700 instrument (FAB+), a JOEL The AccuTOF:JMS-T100LC (DART+) or an Agilent Technologies 6210 G1969A LCTOF multimode ESI/APCI with direct injection.

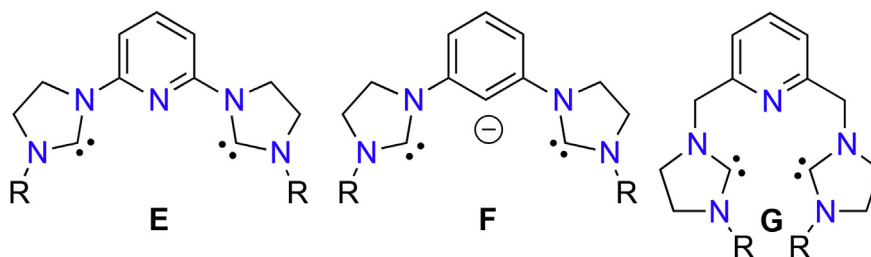
### 2.2. Proligand synthesis

#### 2.2.1. 2,6-bis((1-mesityl-dihydroimidazolium)methyl)pyridine dibromide **1a**

A mixture of 1-(2,4,6-trimethylphenyl)-4,5-dihydro-1H-imidazole (2.4 g, 12.9 mmol) and 2,6-bis(bromomethyl)pyridine (1.6 g, 6 mmol) in DMF (4 mL) was heated to 80 °C for 18 h. After cooling to room temperature, diethyl ether (100 mL) was added to the reaction mixture. The pale yellow solid was filtered and washed with diethyl ether (3  $\times$  50 mL) to yield 4.0 g, (99%) of an off white solid. m.p. = 240.0–241.1 °C. X-ray quality crystals were grown by adding warm water to an oily mixture of **1a**, dichloromethane and chloroform.  $^1\text{H}$  NMR (300 MHz, Acetonitrile- $d_3$ , 25 °C):  $\delta$  2.22 (s, 6H,  $\text{CH}_3$  *p*-mesityl), 2.32 (s, 12H,  $\text{CH}_3$  *o*-mesityl), 4.16–4.20 (m, 8H,  $\text{CH}_2$  imidazolium), 5.08 (s, 4H,  $\text{CH}_2$  linker), 7.05 (s, 4H,  $\text{CH}$  *m*-mesityl), 7.59 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 2H,  $\text{CH}$  3,5-pyridine), 7.96 (t,  $^3J_{\text{HH}} = 7.7$  Hz, 1H  $\text{CH}$  4-pyridine), 9.22 (s, 2H, 2-imidazolium)  $^{13}\text{C}$  { $^1\text{H}$ } NMR (75 MHz, Acetonitrile- $d_3$ , 25 °C):  $\delta$  17.68 ( $\text{CH}_3$  *o*-mesityl), 20.62 ( $\text{CH}_3$  *p*-mesityl), 49.77 ( $\text{CH}_2$  imidazolium), 51.54 ( $\text{CH}_2$  imidazolium), 52.87 ( $\text{CH}_2$  linker), 123.45 ( $\text{CH}$  3,5-pyridine), 130.16 ( $\text{CH}$  *m*-mesityl), 131.53 ( $\text{C}$  *p*-mesityl), 136.30 ( $\text{C}$  *o*-mesityl), 139.34 ( $\text{CH}$  4-pyridine), 140.81 ( $\text{C}$  *ipso*-mesityl), 154.12 ( $\text{C}$  2,6-pyridine), 160.22 ( $\text{CH}$  2-imidazolium). FAB $^+$  (Acetonitrile)  $m/z$ :  $[\text{M}-\text{Br}]^+ = 560.2394$  (calc'd = 560.2389).

#### 2.2.2. 2,6-bis((1-(2,6-diisopropylphenyl)-dihydroimidazolium)methyl)pyridine dibromide **1b**

Compound **1b** was prepared in a procedure analogous to **1a** from 2,6-bis(bromomethyl)pyridine (1.02 g, 3.85 mmol) and 1-(2,6-diisopropylphenyl)-4,5-dihydro-1H-imidazole (1.8 g, 7.81 mmol) in DMF (3 mL). Yield: 4.1 g, (69%). m.p. = 248.3–250.2 °C.  $^1\text{H}$  NMR



**Fig. 2.** Reported sNHC pincer ligands **E** and **F** and the new sNHC pincer **G**.

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