



## Synthesis and characterization of a dinuclear Ni complex containing a bridging CNC pincer ligand

Agnes Mrutu<sup>a</sup>, Karen I. Goldberg<sup>b</sup>, Richard A. Kemp<sup>a,c,\*</sup>

<sup>a</sup> Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131, USA

<sup>b</sup> Department of Chemistry, University of Washington, Box 351700, Seattle, WA 98195, USA

<sup>c</sup> Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87106, USA

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Dedicated to our friend Arnold L. Rheingold

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### ABSTRACT

The reaction of the bis(carbene) pincer ligand <sup>Me</sup>CNC with nickel acetate and Bu<sub>4</sub>NBr produced [(<sup>Me</sup>CNC)<sub>3</sub>Ni<sub>2</sub>]<sup>4+</sup>[Br]<sub>4</sub> (**2**), a complex that contains the <sup>Me</sup>CNC ligand in both traditional tridentate chelating modes as well as in a unique, bridging mode between two Ni<sup>2+</sup> ions. While **2** could not be crystallized or isolated in a pure form, the anion exchange of bromide with triflate yielded [(<sup>Me</sup>CNC)<sub>3</sub>Ni<sub>2</sub>]<sup>4+</sup>[OTf]<sub>4</sub> (**4**), which could be recrystallized from methanol and isolated pure. Single-crystal X-ray analysis of **4** confirmed the unusual dual-coordination modes of the <sup>Me</sup>CNC ligand towards Ni<sup>2+</sup> in these species, and represents the initial example of a Group 10 complex of a bridging CNC ligand.

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### 1. Introduction

Since the initial discovery and report by Arduengo of stable N-heterocyclic carbenes (NHC) [1,2], NHCs have been widely used and studied as donor ligands in metal complexes. An attractive feature common to NHC ligands is their chemical versatility and they serve as a valuable alternative to the traditional phosphines found in many inorganic compounds and organometallic catalytic processes. In an electronic sense, NHC ligands are believed to be better σ-donors than alkylphosphines and can produce complexes that are more air and moisture tolerant than their phosphine-based counterparts [3]. Like phosphines, NHC ligands can be easily modified to vary both steric and electronic effects on structure and reactivity.

The past several years has also seen the significant development and utilization of multidentate pincer-type ligands that can impart valuable properties to their transition metal complexes. In many cases, these pincer ligands exhibit similar advantages of increased thermal stability and decreased reactivities with air and water that are seen by NHC ligands [4–7]. This stability is largely believed to be due to the rigid nature of the pincer ligand and its strong coordination complexation with the metal. Advances in the develop-

ment of pincer ligands have been covered in a recent monograph [5].

We are interested in a unique class of compounds that combines these two structural moieties into one family – pincer ligands that contain NHC binding sites. Herein we report our investigations of two interesting new Ni complexes of the bis(imidazolynylidene)-2,6-pyridine (<sup>R</sup>CNC) ligand (Fig. 1 (right)) [8]. Regarding nomenclature, pincer ligands are commonly named by listing the three atoms that serve as points of attachment to the metal, with the alkyl group on the ring nitrogen atom shown as the R group.

Most transition metal complexes of pincer ligands, regardless of the precise donor atoms used, are monometallic and take advantage of the significant stabilization afforded by the so-called chelate effect. More recently however, pincer ligands in general, and this bis(carbene) CNC ligand specifically, have been shown to yield novel bi-metallic complexes in which the pincer ligand bridges two metals rather than acting as a chelating ligand to a single metal. Only a very limited number of these examples have been prepared. Depending on the overall metal/ligand ratio (M:L; L = <sup>R</sup>CNC) one can obtain solid-state structures in which the <sup>R</sup>CNC ligand simply bridges two separate metal complexes (M:L = 2:1) (found in Group 9) [9,10], or a helical-type structure in which two <sup>R</sup>CNC ligands bridge two metals to form a ring (M:L = 1:1) (found in Groups 11 and 12) [11–16] (discussed below). These types of coordination are shown in a general format in Fig. 2. We now report the synthesis and characterization of the initial examples of <sup>R</sup>CNC-bridging Group 10 complexes containing two Ni centers. Additionally, we also describe the solid-state structure

\* Corresponding author at: Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131, USA. Tel.: +1 505 272 7609; fax: +1 505 272 7336.

E-mail address: [rakemp@unm.edu](mailto:rakemp@unm.edu) (R.A. Kemp).

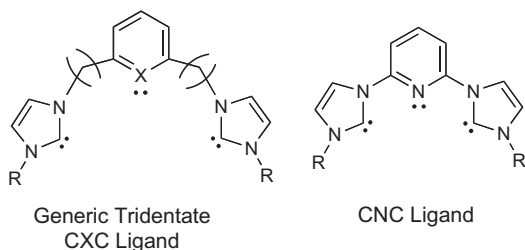


Fig. 1. Structures of CXC ligands.

of one of these complexes with a M:L ratio of 2:3, a novel species in which the CNC ligand is attached to the Ni<sup>2+</sup> ions in both a chelating, tridentate mode as well as the bridging, non-chelating mode.

## 2. Experimental section

All manipulations were carried out in an Ar-filled glovebox or by using standard Schlenk techniques. Anhydrous solvents (dimethylsulfoxide (DMSO), CHCl<sub>3</sub>, CH<sub>3</sub>CN, and CH<sub>3</sub>OH) were purchased from Aldrich and either used immediately upon opening or stored in the glovebox over 4 Å molecular sieves until use. Nickel acetate Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O was obtained from Aldrich and dried by heating at 100 °C for 12 h under dynamic vacuum into a separate P<sub>2</sub>O<sub>5</sub> collector. Tetrabutylammonium bromide [(Bu)<sub>4</sub>NBr] and silver triflate [AgOTf] were purchased from Aldrich and used without further purification. The imidazolium salt precursor **1** for the MeCNC ligand was prepared according to the literature method [11,17]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AMX 250 spectrometer using DMSO-*d*<sub>6</sub> as solvent. Elemental analyses for carbon, hydrogen and nitrogen content were obtained commercially at Columbia Analytical Services, Tucson, AZ.

### 2.1. Syntheses

#### 2.1.1. Preparation of [(<sup>Me</sup>CNC)<sub>3</sub>Ni<sub>2</sub>]<sup>4+</sup>[Br]<sub>4</sub> (**2**)

Ligand precursor **1** (1.60 g, 4.0 mmol) was dissolved in DMSO (20 mL) and then treated with Ni(OAc)<sub>2</sub> (0.47 g, 2.66 mmol) and Bu<sub>4</sub>NBr (1.3 g, 4.0 mmol). The mixture was stirred at room temperature for 12 h and then heated to 130 °C for 1 h. The precipitate was collected by filtration. The solid was washed with CHCl<sub>3</sub> (10 mL × 3) and CH<sub>3</sub>CN (10 mL × 3). The solid was then dried *in vacuo*, yielding **2** as a yellow solid (1.00 g, 32% based on the limiting reagent Ni(OAc)<sub>2</sub>). Mp. >260 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 2.81 (s, 12H, NCH<sub>3</sub>), 4.21 (s, 6H, NCH<sub>3</sub>), 7.64 (d, <sup>3</sup>J<sub>H-H</sub> = 1.98 Hz, 4H, imidazole), 7.83 (d, <sup>3</sup>J<sub>H-H</sub> = 1.95 Hz, 2H, imidazole), 8.05 (d, <sup>3</sup>J<sub>H-H</sub> = 8.14 Hz, 4H, pyridine), 8.17 (d, <sup>3</sup>J<sub>H-H</sub> = 1.95 Hz, 2H, imidazole), 8.29 (t, <sup>3</sup>J<sub>H-H</sub> = 8.14 Hz, 1H, pyridine), 8.49 (d, <sup>3</sup>J<sub>H-H</sub> = 1.98 Hz, 4H, imidazole), 8.62 (t, <sup>3</sup>J<sub>H-H</sub> = 8.14 Hz, 2H, pyridine) 8.84 (d, <sup>3</sup>J<sub>H-H</sub> = 8.14 Hz, 2H,

pyridine). Anal. Calc. for C<sub>39</sub>H<sub>39</sub>Br<sub>4</sub>N<sub>15</sub>Ni<sub>2</sub>: C, 40.56; H, 3.40; N, 18.19. Found: C, 38.23; H, 3.71; N, 16.69%. Despite numerous attempts, we were unable to prepare analytically pure samples of **2**. Notably, exchange of bromide for triflate leads to complex **4** that was isolated in analytically-pure form (see below).

#### 2.1.2. Preparation of [(<sup>Me</sup>CNC)<sub>3</sub>Ni<sub>2</sub>]<sup>4+</sup>[OTf]<sub>4</sub> (**4**)

To a suspension of **2** (0.80 g, 0.69 mmol) in 20 mL of methanol held at room temperature was added AgOTf (0.781 g, 2.76 mmol). The mixture was left to stir for 2 h. Silver bromide (AgBr) was removed by filtration through a medium frit. The filtrate was left to crystallize at -32 °C. Analytically-pure, X-ray quality orange crystals of **4** were obtained (0.79 g, 80%). Mp. 199–202 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 2.77 (s, 12H, NCH<sub>3</sub>), 4.22 (s, 6H, NCH<sub>3</sub>), 7.51 (d, <sup>3</sup>J<sub>H-H</sub> = 1.99 Hz, 4H, imidazole), 7.77 (d, <sup>3</sup>J<sub>H-H</sub> = 1.94 Hz, 2H, imidazole), 7.95 (d, <sup>3</sup>J<sub>H-H</sub> = 8.14 Hz, 4H, pyridine), 8.14 (d, <sup>3</sup>J<sub>H-H</sub> = 1.94 Hz, 2H, imidazole), 8.27 (t, <sup>3</sup>J<sub>H-H</sub> = 8.12 Hz, 1H, pyridine), 8.36 (d, <sup>3</sup>J<sub>H-H</sub> = 1.99 Hz, 4H, imidazole), 8.58 (t, <sup>3</sup>J<sub>H-H</sub> = 8.14 Hz, 2H, pyridine), 8.80 (d, <sup>3</sup>J<sub>H-H</sub> = 8.12 Hz, 2H, pyridine). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): 35.9 (N-CH<sub>3</sub>), 108.5 (C<sub>para</sub>), 114.4 (C<sub>imidazole</sub>), 117.9 (imidazole C), 120.8 (q, C-F on triflate, <sup>1</sup>J<sub>C-F</sub> = 321 Hz), 122.1 (C<sub>para</sub>), 126.8 (imidazole C), 127.4 (imidazole C), 144.7 (C<sub>meta</sub>), 148.3 (C<sub>meta</sub>), 148.7 (C<sub>ortho</sub>), 150.3 (C<sub>ortho</sub>), 165.6 (C-Ni, carbene *trans* to N), 166.9 (C-Ni, *trans*-carbenes). Anal. Calc. for C<sub>43</sub>H<sub>39</sub>F<sub>12</sub>N<sub>15</sub>Ni<sub>2</sub>O<sub>12</sub>S<sub>4</sub>: C, 36.08; H, 2.75; N, 14.68. Found: C, 36.20; H, 3.10; N, 14.49%.

### 2.2. X-ray crystallography

Crystallographic data for **4** were collected on a standard Bruker X8 APEX2 CCD-based X-ray diffractometer equipped with an

Table 1  
Crystallographic data and refinement parameters for **4**.

<b>4</b>	
Empirical formula	C <sub>45</sub> H <sub>47</sub> F <sub>12</sub> N <sub>15</sub> Ni <sub>2</sub> O <sub>14</sub> S <sub>4</sub>
Formula weight	1495.64
Crystal size (mm)	0.62 × 0.34 × 0.18
Crystal system	orthorhombic
Space group	<i>Pnma</i>
Temperature (K)	183(2)
<i>a</i> (Å)	13.2812(6)
<i>b</i> (Å)	29.2053(12)
<i>c</i> (Å)	14.9425(7)
α = β = γ (°)	90
Volume (Å <sup>3</sup> )	5795.9(4)
<i>Z</i>	4
Calculated density (g/cm <sup>3</sup> )	1.714
Absorption coefficient μ (mm <sup>-1</sup> )	0.910
Measured reflections	120074
Independent reflections ( <i>R</i> <sub>int</sub> )	9026 [0.0306]
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0737, 0.1734
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0620, 0.1622
Goodness-of-fit GOF on <i>F</i> <sup>2</sup>	1.032

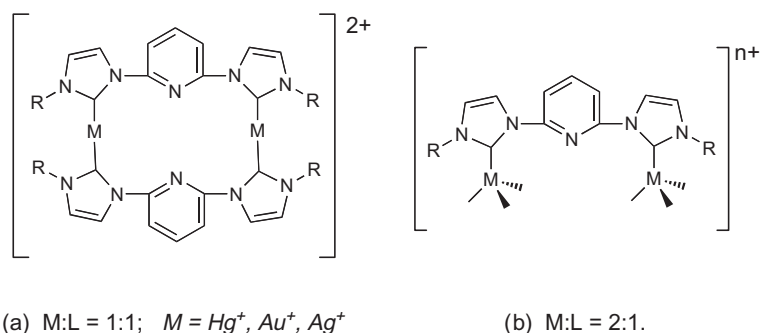


Fig. 2. CNC ligand–metal complexes as a function of metal/ligand ratio.

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