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Journal Name

COMMUNICATION

Transmetalation from CCC-NHC Pincer Zr Complexes in the Synthesis of Air-Stable CCC-NHC Pincer Co (III) Complexes and Initial Hydroboration Trials

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Development of CCC-NHC pincer Co pincer complexes via transmetalation from Zr is reported. Formation of these air-stable Co(III) complexes was achieved through use of a CoCl_2 or $\text{Co}(\text{acac})_3$ in situ or with a discrete CCC-NHC pincer Zr transmetalating agent. Preliminary activity in the hydroboration of styrene is reported. This facile methodology will further the development of CCC-NHC pincer first-row transition metal complexes.

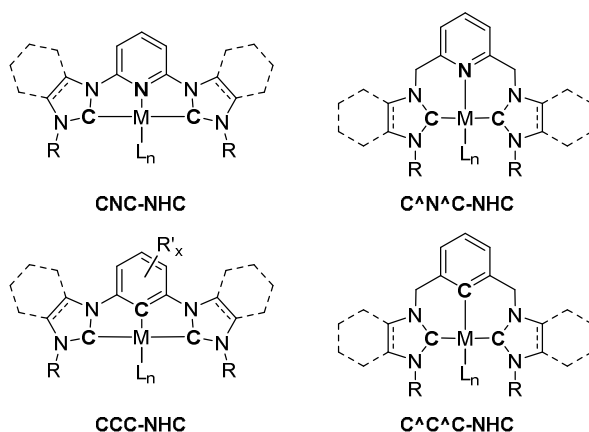
The pincer ligand architecture continues to play a significant role in the development of homogeneous catalysis despite being introduced in the 1970's almost 40 years ago.¹ The tridentate meridional architecture of pincer ligands has been demonstrated to be a durable framework for many transition metals catalyses and reactions, most notably N_2 fixation,² C–C bond formation,³ C–H bond activation,^{3a-c, 4} and small molecule activation^{4b, 5} including NH_3 ,⁵⁻⁶ CO_2 ,^{3b, 3c, 7} and H_2O .^{3a, 8} N-heterocyclic carbenes (NHCs) increase the durability of these ligand systems due to their strong σ -electron-donating properties, resulting in pincer scaffolds with profound metal–NHC bond strengths.^{1d, 9} As a result, these NHC's have become an attractive ligand to incorporate into catalysts systems with base-metal centers such as Fe, Ni, and Co.¹⁰

Numerous NHC base-metal pincer complexes have been reported with a CNC-NHC framework (Chart 1).¹¹ Danopoulos reported some of the first examples of CNC-NHC pincer complexes with low valent Fe and Co centers.^{11a, 11b} Chirik and co-workers have illustrated several examples of catalytically active CNC-NHC Fe and Co complexes in hydrogenation¹² and hydroboration.¹³ More specifically, Co pincer complexes have been shown to be effective catalysts in alkene¹⁴ and nitrile¹⁵ hydrogenation, alcohol dehydrogenation,¹⁶ CO_2 activation,^{7c, 17} alkene hydroboration¹⁸ and silylation¹⁹, and C–H borylation.^{4f}

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Electronic Supplementary Information (ESI) available: Experimental details, catalytic procedure, CIF files, figures, and tables giving full crystallographic data of **2** (CCCD # 1440681) and **4** (CCDC # 1440682), and exact mass data for complexes **3** and **4** and NMR spectra for **3**, **4** and **B** are reported. See DOI: 10.1039/x0xx00000x

Chart 1. Select CNC- and CCC-NHC Pincer Variants with Phenyl or Pyridyl Linkers



Despite increasing reports of base-metal pincer complexes, the CCC-NHC variants are exceedingly rare. In fact, the only reported CCC-NHC late transition base-metal complexes to date are the Ni complexes recently reported by the Hollis²⁰ and Fout groups.²¹ The only other late transition metal monoanionic tridentate carbene pincer complexes were the bis(arylimidazol-2-ylidene) tetrahydro-piperidine ($i^{\text{Pr}}\text{CNC}$)Co complexes formed due to the redox active ligand published by Chirik and co-workers in 2013.^{12a} To promote metalation of the (CCC-NHC) H_3 imidazolium salt pre-cursor (or proligand), activation of the aryl C–H bond and both NHC protons of the CCC-NHC proligand are required. The need for an electrophile to activate the aryl C–H bond, compounded with the inherently weak nature of M–C bonds of first row metals, has hindered the advance in CCC-NHC base-metal complexes. However, use of early transition-metal amido starting materials have been effective in activating proligands providing access to multidentate complexes.²² The electrophilic nature of the d^0 metal center and the basicity of the amido ligands serve the two fold purpose needed to synthesize CCC-NHC pincer complexes. This method also provides a synthetic route to late transition metal CCC-NHC pincer complexes through transmetalation. In 2005 and 2008,

one of us utilized this methodology to access the CCC-NHC pincer Rh²³ and Ir²⁴ complexes, respectively. Herein, we extend this methodology to Co, improve it using an isolated CCC-NHC pincer complex and demonstrate an application of the CCC-NHC pincer Co pincer complex in hydroboration.

Preliminary studies involved the screening of Co(acac)₃ for transmetalation. Investigations began with the addition of 2.5 equiv of Zr(NMe₂)₄ to the (1,3-bis(3'-butylimidazolium)benzene diiodide **1** proligand to generate Zr diamido complex **A** in-situ (Figure 1), followed by addition of Co(acac)₃ (Scheme 1).

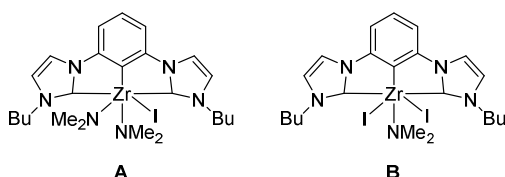
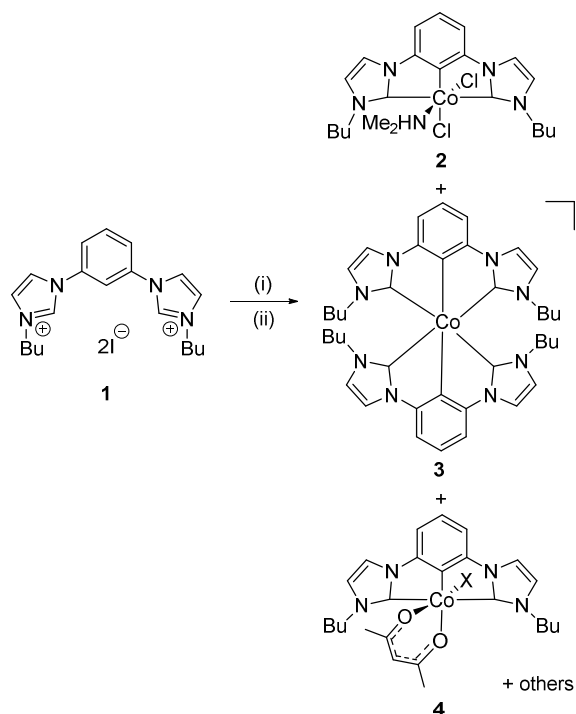


Figure 1. CCC-NHC pincer Zr complexes utilized as transmetallating reagents.

The ¹H NMR spectrum obtained from this reaction mixture indicated a shift in signals from Zr complex **A** after addition of the Co source that was indicative of transmetalation. However, a complex mixture of species was formed (Figure S1). The ¹H NMR spectrum included signals assignable to complexes **3** and **4** (vide infra) and more (Scheme 1, see Figure S1). A single red crystal was retrieved from the reaction mixture and identified as **2** from X-ray analysis (see Figure 2). Currently, the additional species are anticipated to include, minimally, halide variants of **2** and **4**.

Scheme 1. Attempted in situ metallation/transmetalation (Zr → Co) producing a



mixture of **2**, **3**, **4** and others.^a

^aConditions: (i) 2.5 equiv Zr(NMe₂)₄, CH₂Cl₂, rt, 1h; (ii) 1.1 equiv Co(acac)₃, 12 h

An ORTEP plot of CCC-NHC pincer Co chloride complex **2** is presented in Figure 2, and selected metric data are presented in Table 1. The X-ray data unambiguously allowed the identification of the chlorides. Due to the meridional coordination and rigidity of the tridentate CCC-NHC ligand, Co complex **2** contained a distorted-octahedral center resulting in a (C_{NHC})–Co–(C_{NHC}) bond angle of 145.6° (Table 1). The Co–(C_{NHC}) bonds length is 2.174 Å, which is 0.214 Å longer than the Co–(C_{NHC}) bonds length of the (CNC-NHC)CoBr₃ pincer reported by Danopoulos in 2004.^{11a} This trend of longer bond lengths for the CCC-NHC versus the CNC-NHC ligand was also observed when compared to the Co(I) complex Co–(C_{NHC}) bond length of 1.9015 Å (0.273 Å shorter in the CNC-NHC complex) for Chirik's (4-CPh₂CH₃-^{iPr}CNC)-CoN₂ pincer complex.^{12a} Although the imidazolium proligand **1** contained iodide halogens, complex **2** contained two chloride ligands from exchange with dichloromethane.

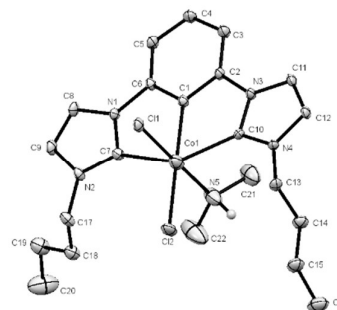


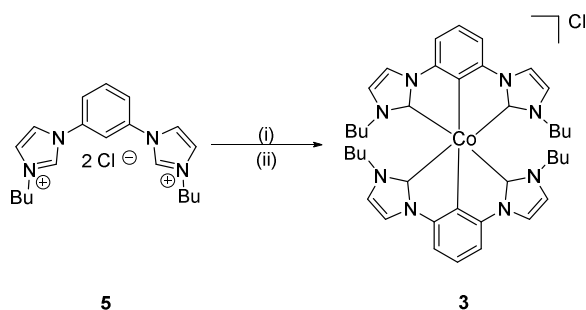
Figure 2. Molecular structure of 2-(1,3-bis(N-butylimidazol-2-ylidene)phenylene)(dimethylamido)bis(chloro)cobalt(III) (**2**). The hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (°)

	length (Å)	angle (°)	
Co(1)–Cl(1)	2.411(1)	C(1)–Co(1)–C(7)	72.7(2)
Co(1)–Cl(2)	2.360(1)	C(1)–Co(1)–C(10)	73.0(2)
Co(1)–N(5)	2.135(5)	C(7)–Co(1)–C(10)	145.6(2)
Co(1)–C(1)	2.107(4)	Cl(2)–Co(1)–Cl(1)	90.06(4)
Co(1)–C(7)	2.203(4)	N(5)–Co(1)–Cl(2)	87.63(13)
Co(1)–C(10)	2.174(4)	C(10)–Co(1)–Cl(2)	106.04(10)

With many recent Co pincer reports exhibiting a chloride coordinated to the Co center,^{15b, 18a, 25} it was hypothesized that the chloride imidazolium proligand would be a more appropriate pre-cursor to synthesize the desired Co complex **2** in high yield. In addition, CoCl₂ was examined as a Co source in hopes of further favoring the formation of **2**. However, when chloride salt **5** was metallated with 2.5 equiv of Zr(NMe₂)₄ in situ followed by addition of CoCl₂ as outlined in Scheme 2, the formation of a single product, **3**, with coordination of two CCC-NHC ligands to the Co center. Presumably, air oxidation occurred. Accurate mass measurements of **3** contained the

correct isotopic distribution pattern at $m/z = 701.3453$ as compared to a calculated $m/z = 701.3490$ for $[M-Cl]^+$ for the formulation of $M = C_{40}H_{50}CoN_8Cl$ (see ESI, Figure S6). Further evidence of the structure of **3** was obtained in the 1H NMR spectrum with a single methylene peak shifted upfield at δ 2.80 (see ESI, Figure S4), compared to the diastereotopic methylene peak shift of around δ 4.0-5.5 commonly observed for other mono-ligated CCC-NHC pincer complexes.²⁶ In addition, the butyl chain peaks of **3** overlapped and were also shifted upfield at δ 0.66-0.73. Nonetheless, the Co-C_{NHC} and the Co-C_{aryl} peaks were observed at δ 183.9 and δ 176.0, respectively, in the ^{13}C NMR spectrum (see Figure S5), consistent with metalation of the Co. It should also be noted this hexa-coordination has been reported with several CNC and scorpionato NHC Fe complexes as well.^{10a} While further studies continue on air-stable **3**, investigation was continued into developing a facile methodology that would allow access

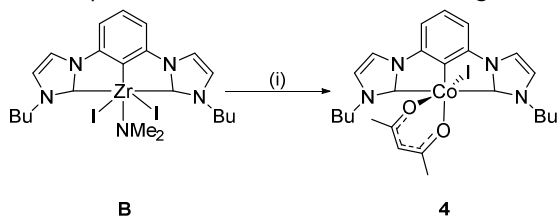


to a single, mono-coordinated CCC-NHC pincer Co complex.

Scheme 2. Synthesis of CCC-NHC Co Complex **3**^a

^aConditions: (i) 2.5 equiv Zr(NMe₂)₄, CH₂Cl₂, rt, 1h; (ii) 1.1 equiv CoCl₂, 12 h

Despite numerous experimental designs to directly access a single mono-coordinated CCC-NHC pincer Co complex, incomplete metalation or mixtures resulted. It was surmised that the *in-situ* formed Zr diamido species **A** with excess Zr amido could be correlated to these experimental shortcomings. Isolated Zr diido complex **B** was then considered as a transmetallating reagent. Ultimately, Zr diido complex **B** was found to be a competent transmetallating reagent resulting in the formation of a single CCC-NHC Co(acac) pincer complex (Scheme 3, **4**). Due to the lower solubility of complex **B**, compared to that of **A**, increased reaction temperatures were required to carry out the reaction efficiently. Typical spectroscopic data were obtained for **4** including clean NMR



and exact mass data (See ESI).

Scheme 3. Synthesis of CCC-NHC Co Complex **4**^a

^aConditions: (i) 1.1 equiv Co(acac)₃, toluene, 90 °C, 12h

X-ray quality crystals were grown by recrystallization using a chloroform/hexane solvent system. The chelation of the acac ligand was further confirmed through X-ray analysis along with an iodide coordinated to the Co center. An ORTEP plot of Co acac complex **4** is presented in Figure 3 along with selected metric data in Table 2. Compared to **2**, Co complex **4** adopts a less distorted octahedral geometry due to the chelation of the bidentate acac ligand. The Co-C_{aryl} bond length in **4** was measured at 1.874 Å (Table 2), noticeably shorter than the analogous bond distance in **2** (2.107 Å). Furthermore, the trans coordinated NHC ligands had an (C_{NHC})-Co-(C_{NHC}) angle of 159.9°, which is greater than any of the previously published CCC-NHC pincer complexes of Zr, Hf, Ti, Ta, Rh, or Ir.^{23-24, 26a, 26b, 27}

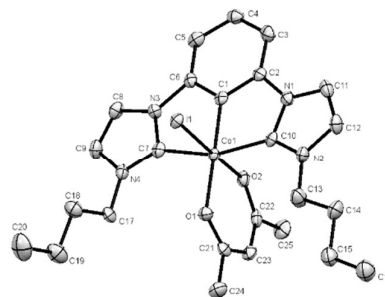


Figure 3. Molecular structure of 2-(1,3-bis(N-butylimidazol-2-ylidene)phenylene)(2,4-pentanedionato)(iodo)cobalt(III) **4**. The hydrogens and a chloroform molecule found in the lattice were omitted for clarity. ORTEP thermal ellipsoids are shown at 50% probability.

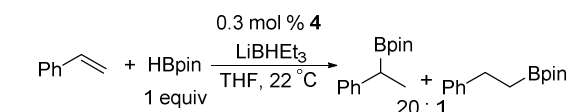
Table 2. Selected Bond Lengths (Å) and Angles (°)

length (Å)		angle (°)	
Co(1)-C(1)	1.874(5)	C(1)-Co(1)-C(10)	80.09(19)
Co(1)-O(2)	1.941(3)	C(1)-Co(1)-C(7)	79.84(19)
Co(1)-C(10)	1.965(4)	C(10)-Co(1)-C(7)	159.9(2)
Co(1)-C(7)	1.971(4)	O(2)-Co(1)-O(1)	92.81(13)
Co(1)-O(1)	2.002(3)	C(1)-Co(1)-O(2)	89.48(16)
Co(1)-I(1)	2.5685(6)	C(1)-Co(1)-I(1)	89.73(12)

Over the past few years, Co²⁸ and Fe^{13, 29} catalyzed alkene hydroboration has been an attractive area of research due to the lower cost of first-row metals³⁰ compared to precious metals. A recent report by Huang and co-workers demonstrated excellent turnover numbers with (ⁱPrPNN)CoCl₂ complex, (ⁱPrPNN=(diisopropylphosphino)methyl-2,2'-bipyridine), in alkene hydroboration.^{18a} Therefore, complex **4** was screened for catalytic activity in the hydroboration of styrene at room temperature, and the first results employing literature conditions are presented in Table 3.

Initially, no activity was observed when employing **4** without a hydride source (see Table 3, entry 1). However, upon combination of superhydride and **4**, quantitative conversion of styrene was obtained in one hour (entry 2) yielding as the

major product the Markovnikov hydroboration product by 20:1, similar to what has been observed for a few Co complexes recently.^{28a, 28b} An additional 1.1 mmol of styrene and pinacolborane were added to the reaction mixture yielding 95% conversion after another hour (entry 3). Control experiments conducted in the absence of **4** and/or superhydride (entries 4 and 5) verified their necessity to obtain conversion. While **4** was highly selective for the formation of the Markovnikov product, the catalytic activity was also comparable to other recently reported catalysts. For example the (^tBuPNN)CoCl₂ complex^{18a} at 1 mol % produced the anti-Markovnikov hydroboration styrene product in 93% yield in 1 hour under similar conditions. Other reducing agents, in addition to scope and optimization, are currently being investigated to better understand the regioselectivity, scope



entry	precat.	LiBHET ₃ (mol %)	t (min)	conv. ^b
1	4	--	60	0
2	4	1.0	60	>99 ^c
3 ^d	4	1.0	60	95 (92) ^e
4	--	--	60	0
5	--	1.0	60	0

and limitations of **4** in alkene hydroboration.

Table 3. Alkene Hydroboration of Styrene^{a, 5}

^aStyrene (1.1 mmol), HBpin (1.1 mmol), **4** (3.3 μmol), LiBHET₃ (3.3 μmol) and solvent (1.0 mL) were added to a 1 dram vial with a magnetic stir bar, and stirred for 1 h at 22 °C. ^bConversion of styrene was determined by GC-MS analysis. ^cTrace ethylbenzene (< 2%) observed. ^dAdditional 1.1 mmol of styrene and pinacolborane were added to the reaction mixture of entry 3. ^eIsolated yield.

In conclusion, air stable CCC-NHC pincer Co complexes have been synthesized efficiently via transmetalation from an isolated CCC-NHC pincer Zr complex allowing access to more economic catalyst design. Three new complexes, **2**, **3**, and **4**, were isolated and characterized, which are the first mono-anionic CCC-NHC Co pincer complexes reported to date. Complex **4** was found to rapidly hydroborate styrene strongly favouring the rare Markovnikov regiochemistry instead of the usual anti-Markovnikov products. Studies are on-going to examine the scope and limitations of this reactivity. Due to previous reports of Co(III) complexes being active catalysts in C–H activation,³¹ studies are currently underway to expand the activity of these CCC-NHC Co complexes, expand the synthetic methodology, and to access various oxidation states of the Co metal center.

Acknowledgements

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Notes and References

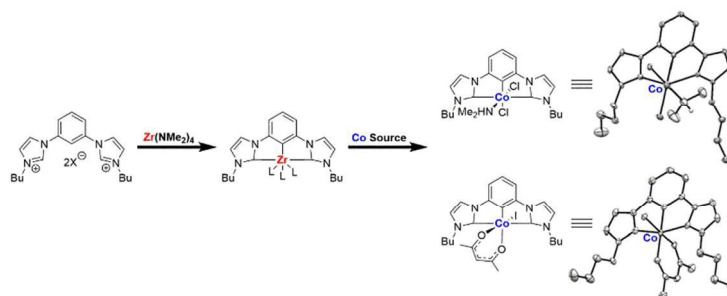
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Transmetalation from an isolated CCC-NHC Zr complex efficiently produces the Co complex, which catalyzes hydroboration.