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#### Earth abundant metal complexes of donor functionalised N-heterocyclic carbene ligands: synthesis, characterisation and application as amination catalysts

Halliru Ibrahim, Muhammad Dabai Bala\*

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa

#### Abstract

Six new imidazolium salts of the form 3-R-1-picolylimidazolium bromide (1a: R = 4nitrophenyl, **1b**: R = 4-acetylphenyl, **1c**: R = 4-cyanophenyl, **1d**: R =allyl, **1e**: R =butenyl, **1f**: R = pentenyl) were synthesised and isolated in high yields. Corresponding Ag-NHC intermediate complexes 2a, 2d, and 2e were transmetalated to yield  $[M(NHC)_2Cl_2 M = Co, Ni]$ complexes in good to excellent yields. The Co-NHC (3a, 3d, 3e) and Ni-NHC (3a', 3d', 3e') complexes were relatively stable in air, insoluble in chlorinated solvents but very soluble in methanol and DMSO. Poorly resolved NMR spectra and magnetic susceptibility values of 2.53 and 2.73  $\mu_B$  for 3d and 3e respectively suggest both to be paramagnetic cobalt complexes. All the imidazolium salts, isolated Ag-NHC complexes and the corresponding Co and Ni-NHC complexes were characterised by spectroscopic and analytical techniques. Low catalyst loading (1 mol%) of the complexes were active for the C-N coupling of aniline with phenyl bromide under mild reaction conditions. In addition, the *in situ* generated catalyst obtained from a mixture of NiCl<sub>2</sub>/1a (1:2 mole ratio) initiated the C-N coupling of several aryl amines with substituted aryl bromides bearing a wide variety of functional groups. Good to excellent yields of the desired diaryl amine products were obtained. The yields are comparable to data obtained with palladium catalysts or harsher temperature conditions of Cu mediated Ullman reactions.

#### Keywords

NHC, Pyridyl, Imidazolium salts, In situ catalysis, C-N coupling, Co, Ni, Monoarylation

#### 1. Introduction

Since the pioneering works of Öfele, Wanzlick and Arduengo [1], *N*-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands in organic & inorganic synthetic transformations and organometallic homogeneous catalysis [2]. Their ability to tolerate many functional groups, work at ambient temperatures and strongly coordinate to metal centres in catalytic systems without ligand dissociation due to excellent sigma donating ability meant NHCs are now the preferred options in organometallics, coordination chemistry and homogeneous catalysis over other two-electron donor ligands like ethers, amines, and even the

<sup>\*</sup> Correspondence to: e-mail- bala@ukzn.ac.za; fax-+27 31 260 3091

ubiquitous phosphines [3]. In spite of all these, it is interesting to note that metal-NHC<sup>Ricle Online</sup> complexation especially when applied to homogeneous catalysis, is still dominated by the platinum group metals (PGM) mainly rhodium, iridium, ruthenium & palladium. While to date comparatively much fewer complexes are known of earth abundant, non-PGM; first row transition metals like nickel or cobalt [1a, 3-5].

Although bidentate hemilabile ligands containing a mixture of strong and weak donor groups have found widespread applications in homogeneous catalysis [6], their complexes with nickel and especially cobalt are scarce [7]. Hence, except for a few examples that are stabilised by classical donor ligands like cyclopentadiene, phosphines, heterocyclic systems and CO [8], few examples of multidentate functionalised Ni- or Co-NHC complexes are available [9]. The study of multidentate carbene complexes has been an interesting field of study [10a-b], because during catalysis, the ligand exhibits coordinative and electronic unsaturation due to variability in binding strengths of the donor atoms to the metal centre. The presence of weak donors help provide the hemilabile character of such ligands, which accounts for possible reversible dissociation from the metal centre to generate empty site(s) for the coordination of substrate(s) without catalyst decomposition [10].

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Due to their cost effectiveness and distinct catalytic abilities, interest in the development of catalyst systems based on earth abundant, non-PGM; first row transition metals is gaining ground amongst chemists worldwide and several systems based on NHC and Co(II) [11], Ni(0) [2j,12] and Ni(II) [13] are gradually complementing PGM-based catalysts. Such complexes have proven to be active in C-S coupling [14], cyclo addition [15], addition polymerization of norbornane [16], aryl amination [2j, 11b, 13, 17], styrene polymerization [18], Suzuki and Kumada coupling reactions [19]. More specifically, C-N coupling is very important in organic synthesis as a route to important groups of chemicals for synthetic, pharmaceutical and fine chemical industrial applications. Although, most aryl C-N coupling reactions are catalysed by Pd(0) or copper mediated Ullman reactions; the use of the former is neither economically nor ecologically advantageous [20] while the latter proceeded via harsh conditions, high temperatures or requires stoichiometric amounts of a copper catalyst [21,22]. Except for the use of Ni(0)/bis-arylimidazolium salts by Kuhl *et al.* [2] and more recent work by Matsubara and co-workers where they used a nickel(II) halide complex bearing a mixed PPh<sub>3</sub>/NHC ligand as a catalyst precursor [13], efficient catalyst systems containing nickel as the central metal for arylation of aromatic amines are still rare. To the best of our knowledge the use of functionalised, bidentate and sterically demanding metal-NHC complexes

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incorporating cobalt or nickel as catalysts for the arylation of amines is still novel Dependence on the synthesis of new functionalised imidazolium salts and their Ag, Co and Ni complexes. Findings on the application of the Co and Ni complexes as catalysts for the coupling of aryl amines with aryl halides to selectively yield diaryl amines products are also reported.

#### 2. Experimental

#### 2.1. General procedures

All experiments except when otherwise mentioned were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were analytical grade and dried using standard techniques: THF and hexane in benzophenone were distilled over sodium wire; methanol in iodine was distilled twice over magnesium ribbon; 1,2-dichloroethane was distilled over CaCl<sub>2</sub> and stored with molecular sieve and dichloromethane was distilled over calcium hydride or P<sub>2</sub>O<sub>5</sub>. Methanol washed 4Å molecular sieves were activated by drying in an oven at 150 °C for 24 h followed by heating in a furnace at 500 °C for 2 d and cooled in a desiccator. Deuterated solvents were obtained from Merck and are used without further purification. Both CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> were prepared using a standard procedure [23]. N-substituted imidazoles were prepared by the modification of established procedures [24], while the corresponding salts were purified and isolated using a recently reported technique [25]. The aryl amines used were analytically pure; obtained from Sigma-Aldrich and distilled prior to use then stored with molecular sieves. Potassium tertiary butoxide, 2bromomethyl pyridine hydrobromide, allyl bromide, butenyl bromide, pentenyl bromide and all aryl halide substrates used were analytically pure; obtained from Sigma-Aldrich and used without further purification. NMR spectra were recorded on a Bruker AVANCE<sup>TM</sup> 400 Ultrashield spectrometer operating at room temperature and samples were dissolved in CDCl<sub>3</sub>, CD<sub>3</sub>OD or DMSO-d<sub>6</sub>. The spectra were internally referenced relative to solvent peak(s) and chemical shift values recorded ( $\delta$  ppm) with respect to  $\delta = 0$  ppm for tetramethylsilane in both <sup>1</sup>H and <sup>13</sup>C NMR spectra [26]. Hysteresis loop measurement for determination of saturated magnetization was conducted on vibrating sample magnetometer (VSM) Lakeshore 735. Infrared spectra were recorded on a PerkinElmer universal ATR Spectrum 100 FT-IR spectrometer. Mass spectrometry and elemental analysis (where applicable) were recorded on Waters Micromass LCT Premier TOF MS-ES+ and ThermoScientific Flash2000 elemental analyser respectively.

#### 2.2. General synthetic procedure for the ligand precursors la-f

The imidazolium salts which are NHC ligand precursors were synthesised by the modification of literature procedures [25, 27]. Spectroscopic and analytical data obtained are presented. A typical and generic procedure for the synthesis of the imidazolium salts 3-R-1-(2-pyridylmethyl)imidazolium bromide (**1a-f**) is described:

A saturated solution of Na<sub>2</sub>CO<sub>3</sub> was first used to neutralize 2-(bromomethyl)pyridine hydrobromide at 0 °C. The neutral pink solution obtained was then extracted with diethyl ether (3 x 10 ml) at 0 °C and the clear solution of liberated 2-(bromomethyl)pyridine dried over anhydrous MgSO<sub>4</sub> and filtered. The colourless filtrate was then reduced to 1/3 of the initial volume under reduced pressure and added to a solution of *N*-substituted imidazole (1 mole equivalent) in dry acetonitrile (40 ml) at 0 °C. The remaining ether was removed at reduced pressure and the contents of the flask subjected to gentle reflux for 18 h. Progress of the reaction was monitored by TLC. The solvent was then removed under reduced pressure and the TLC of the crude obtained in methanol: ethyl acetate (1: 4) solvent system. This showed unreacted starting materials with Rf values 0.7-1.0 while the salt remained unmoved at the spot. Purification was thus obtained with column chromatography. The starting materials were eluted out with ethyl acetate and the salt obtained as methanol eluent. All volatiles were then removed at reduced pressure to give the salts in excellent yields.

#### 2.2.1. 3-(4-nitrophenyl)-1-(2-pyridylmethyl)imidazolium bromide (1a)

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Prepared from 2-(bromomethyl)pyridine (1.6 mmol) and equimolar *para*-nitrophenyl imidazole in acetonitrile. Product obtained as reddish-orange solid, yield (0.52 g, 90%; mp 220-222 °C). IR (ATR cm<sup>-1</sup>):  $v_{\text{moisture}}$  3404,  $v_{\text{C-H}}$  aromatic 3017,  $v_{\text{C=C}}$  1625,  $v_{\text{NO}}$  1538 ,  $v_{\text{C=N}}$  1349,  $v_{\text{Ar}}$  744;  $\delta_{\text{H}}$  (400 MHz, DMSO-d<sub>6</sub>): 10.3 (1H, s, NCHN), 8.58-8.50 (4x1H, dd, phenyl), 8.15-8.13 (3x1H, m, pyridyl), 9.91-7.92 (1H, m, pyridyl), 7.60 (1H, d, *J* 6.9 Hz, CH=CH imidazoyl), 7.43 (1H, d, *J* 6.9 Hz, CH=CH imidazoyl) and 5.70 ppm (2H, s, NCH<sub>2</sub>).  $\delta_{\text{C}}$  (400 MHz, DMSO-d<sub>6</sub>): 152.9 (NCHN), 149.6 (C pyridyl), 147.6 (CH pyridyl), 139.2 (C ph), 137.5 (C ph), 136.9 (CH pyridyl), 125.5 (CH pyridyl), 124.4 (CH ph), 123.8 (CH imidazoyl), 122.9 (CH ph), 122.7 (CH pyridyl), 121.2 (CH imidazoyl) and 53.6 ppm (NCH<sub>2</sub>). HRMS (m/z) for C<sub>15</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub>: calcd 281.1039 [M - Br]<sup>+</sup>, found 281.1030 [M - Br]<sup>+</sup>.

#### 2.2.2. 3-(4-acetylphenyl)-1-(2-pyridylmethyl)imidazolium bromide (1b)

Prepared from 2-(bromomethyl)pyridine (0.31 g, 1.21 mmol) and 1-(4-(1H-imidazol-1-yl)phenyl)ethanone (0.23 g, 1.21 mmol) in acetonitrile. Product obtained as air sensitive

shiny orange-brown microcrystal, yield (0.39 g, 91%; mp 199-202 °C). IR (ATR cm<sup>-1</sup>):  $v_{\text{MMPRURIOIII3G}}$  3381,  $v_{\text{C-H}}$  3061, 2955,  $v_{\text{C=O}}$  1675,  $v_{\text{C-N}}$  1237,  $v_{\text{Ar}}$  836;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>): 11.1 (1H, s, NCHN), 8.51 (1H, d, *J* 4.4 Hz, CH=CH imidazoyl), 8.19 (1H, d, *J* 4.4 Hz, CH=CH imidazoyl), 8.07 (2x2H, dd, *J* 16.5 Hz, phenyl), 7.97 (1H, s, pyridyl), 7.83 (1H, d, *J* 7.7 Hz, pyridyl), 7.74-7.71 (1H, m, pyridyl), 7.35-7.26 (1H, m, pryridyl), 5.96 (2H, s, NCH<sub>2</sub> pyridine) and 2.60 ppm (3H, s, CH<sub>3 acetyl</sub>).  $\delta_{\text{C}}$  (400 MHz, CDCl<sub>3</sub>): 196.4 (C=O), 152.1 (NCHN), 149.8 (C pyrdyl), 137.8 (CH pyridyl), 137.7 (C Ph), 137.5 (C Ph), 136.0 (CH pyridyl), 130.5 (CH Ph), 124.2 (CH pyridyl), 124.1 (CH imidazoyl), 124.0 (CH Ph), 121.8 (CH pyridyl), 120.6 (CH imidazoyl), 54.2 (NCH<sub>2</sub>) and 26.8 ppm (CH<sub>3</sub>). HRMS (m/z) for C<sub>17</sub>H<sub>16</sub>N<sub>3</sub>O: calcd 278.1289 [M - Br]<sup>+</sup>, found 278.1293 [M - Br]<sup>+</sup>.

#### 2.2.3. 3-(4-cyanophenyl)-1-(2-pyridylmethyl)imidazolium bromide (1c)

Dry acetonitrile solution of liberated 2-(bromomethyl)pyridine (0.30 g, 1.18 mmol) was refluxed with acetonitrile solution of 4-imidazoylbenzonitrile (0.20 g, 1.18 mmol). Crude product was obtained as distinct off-white precipitate within reddish-pink solution. Precipitate of the salt was filtered out of the mixture under atmosphere of nitrogen using vacuum filtration, rinsed with dried acetonitrile and dried in a desiccator. Yield (0.37 g, 93%; mp 265-267 °C). IR (ATR cm<sup>-1</sup>):  $\nu_{\text{moisture}}$  3345,  $\nu_{\text{CH}}$  3050,  $\nu_{\text{CN(nitrile)}}$  1597,  $\nu_{\text{Ar}}$  748;  $\delta_{\text{H}}$  (400 MHz, DMSO-d<sub>6</sub>): 10.2 (1H, s, NCHN), 8.57 (1H, d, *J* 4.4 Hz, pyridyl), 8.49 (1H, d, *J* 1.4 Hz, pyridyl), 8.23 (2x1H, dd, CH=CH imidazoyl), 8.12—7.61 (4H, dd, phenyl), 7.59 (1H, d, *J* 7.8 Hz, pyridyl), 7.42 (1H, d, *J* 5.1 Hz, pyridyl) and 5.69 ppm (2H, s, NCH<sub>2</sub>).  $\delta_{\text{C}}$  (400 MHz, DMSO-d<sub>6</sub>): 153.0 (NCHN), 149.5 (C pyridyl), 137.9 (CH pyridyl), 137.5 (C Ph), 136.8 (CH pyridyl), 134.4 (CH Ph), 124.4 (CH pyridyl), 123.8 (CH Ph), 122.7 (CH imidazoyl), 122.6 (CH pyridyl), 121.0 (CH imidazoyl), 117.8 (CN), 112.3 (C Ph) and 53.6 ppm (NCH<sub>2</sub>). HRMS (m/z) for C<sub>16</sub>H<sub>13</sub>N<sub>4</sub>: calcd 261.1140 [M - Br]<sup>+</sup>, found 261.1131 [M - Br]<sup>+</sup>.

#### 2.2.4. 3-allyl-1-(2-pyridylmethyl)imidazolium bromide (1d)

Acetonitrile solution of 2-(bromomethyl)pyridine (1.34 g, 5.3 mmol) was added drop wise to allyl imidazole (0.57 g, 5.3 mmol) in acetonitrile at 0 °C and the mixture subjected to reflux for 24 h. The salt was obtained as methanol eluent from column chromatography of the crude. All volatiles were then removed under reduced pressure to yield the pure salt as a brownish-grey waxy solid. Yield (1.29 g, 87.0%). IR (ATR cm<sup>-1</sup>):  $v_{\text{moisture}}$  3401,  $v_{\text{C-H}}$  3050,  $v_{\text{C=C}}$  1551,  $v_{\text{C=N}}$  1497,  $v_{\text{Ar}}$  759;  $\delta_{\text{H}}$  (400 MHz, DMSO-d<sub>6</sub>): 9.78 (1H, s, NCHN), 8.51 (1H, m, pyridyl), 8.23 (1H, m, pyridyl), 7.98 (2H, dd, CH=CH imidazoyl), 7.36 (1H, m, pyridyl), 7.22 (1H, d, *J* 12.9 Hz, pyridyl), 6.51 (1H, m, CH=CH<sub>2</sub> allyl), 5.69 (2H, s, NCH<sub>2</sub>), 3.44 (2H, s, CH<sub>2</sub>=CH

allyl) and 1.78 ppm (2H, s, CH<sub>2</sub>-N <sub>allyl</sub>).  $\delta_{C}$  (400 MHz, DMSO-d<sub>6</sub>): 153.2 (NCHN) 149 Key (micle Online pyridyl), 137.5 (CH <sub>pyridyl</sub>), 135.3 (CH <sub>pyridyl</sub>), 123.7 (CH <sub>allyl</sub>), 123.6 (CH <sub>pyridyl</sub>), 122.9 (CH <sub>imidazoyl</sub>), 122.6 (CH <sub>imidazoyl</sub>), 121.7 (CH <sub>pyridyl</sub>), 119.5 (CH<sub>2</sub> <sub>allyl</sub>), 53.0 (NCH<sub>2</sub>) and 14.4 ppm (CH<sub>2</sub>-N <sub>allyl</sub>). HRMS (m/s) for C<sub>12</sub>H<sub>14</sub>N<sub>3</sub>: calcd 200.1188 [M - Br] <sup>+</sup>, found 200.1183 [M - Br] <sup>+</sup>.

#### 2.2.5. 3-butenyl-1-(2-pyridylmethyl)imidazolium bromide (1e)

Liberated 2-(bromomethyl)pyridine (1.34 g, 5.3 mmol,) in acetonitrile was added at 0 °C to acetonitrile solution of butenyl imidazole (0.65 g, 5.3 mmol) and refluxed. Isolated yield from column (1.23 g, 79%) brown waxy solid. IR (ATR cm-1):  $v_{\text{moisture}}$  3358,  $v_{\text{C-H}}$  3050, 2973,  $v_{\text{C=C}}$  1628,  $v_{\text{C=N}}$  1450,  $v_{\text{Ar}}$  785;  $\delta_{\text{H}}$  (400 MHz, CD<sub>3</sub>OD): 9.20 (1H, s, NCHN), 8.57 (1H, d, *J* 4.6 Hz, pyridyl), 7.90 (1H, m, pyridyl), 7.69 (2x1H, d, *J* 2.0 Hz, CH=CH imidazoyl), 7.55 (1H, m, pyridyl), 7.43-7.41 (1H, m, pyridyl), 5.84-5.79 (1H, m, CH=CH<sub>2</sub> alkenyl), 5.58 (2H, s, NCH<sub>2</sub>), 5.10-5.06 (2H, m, CH<sub>2</sub>=CH alkenyl), 4.37-4.33 (2H, m, CH<sub>2</sub> alkenyl) and 2.68-2.66 ppm (2H, m, CH<sub>2</sub> alkenyl).  $\delta_{\text{C}}$  (400 MHz, CD<sub>3</sub>OD): 154.4 (NCHN), 151.0 (C pyridyl), 139.2 (CH pyridyl), 134.2 (CH pyridyl), 125.3 (CH alkenyl), 124.2 (CH pyridyl), 123.6 (CH imidazoyl), 122.9 (CH imidazoyl), 119.6 (CH pyridyl), 54.8 (NCH<sub>2</sub>), 50.2 (CH<sub>2</sub> alkenyl), 47.1 (CH<sub>2</sub>-N alkenyl) and 35.3 ppm (CH<sub>2</sub> alkenyl). HRMS (m/s) for C<sub>13</sub>H<sub>16</sub>N<sub>3</sub>: calcd 214.1344 [M - Br]<sup>+</sup>, found 214.1337 [M - Br]<sup>+</sup>.

#### 2.2.6. 3-pentenyl-1-(2-pyridylmethyl)imidazolium bromide (1f)

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Liberated 2-(bromomethyl)pyridine (1.34 g, 5.3 mmol) in acetonitrile was added to acetonitrile solution of pentenyl imidazole (0.72 g, 5.3 mmol) and refluxed. Isolated yield from column (1.31 g, 81%) brown waxy solid. IR (ATR cm<sup>-1</sup>):  $v_{(moisture)}$  3402,  $v_{C-H}$  3072,  $v_{C=N}$  1437, 1158, and  $v_{Ar}$  756  $\delta_H$  (400 MHz, DMSO-d<sub>6</sub>): 9.42 (1H, s, NCHN), 8.54 (1H, d, *J* 4.8 Hz, CH=CH imidazoyl), 7.90-7.87 (2x1H, m, pyridyl), 7.84 (1H, d, *J* 4.8 Hz, CH=CH imidazoyl), 7.52 (1H, m, pyridyl), 7.40-7.38 (1H, m, pyridyl), 5.85-5.81 (1H, m, CH=CH<sub>2</sub> alkenyl), 5.60 (2H, s, NCH<sub>2</sub>), 5.05-4.95 (2H, m, CH<sub>2</sub>-N alkenyl), 4.29 (2H, t, *J* 7.1 Hz, CH<sub>2</sub>=CH alkenyl), 2.03-1.99 (2H, m, CH<sub>2</sub> alkenyl) and 1.94-1.89 ppm (2H, m, CH<sub>2</sub> alkenyl).  $\delta_C$  (400 MHz, DMSO-d<sub>6</sub>): 153.5 (NCHN), 149.5 (C pyridyl), 137.5 (CH pyridyl), 136.9 (CH pyridyl), 123.6 (CH alkenyl), 123.3 (CH pyridyl), 122.6(CH imidazoyl), 122.4 (CH imidazoyl), 115.7 (CH pyridyl), 52.9 (NCH<sub>2</sub>), 48.4 (CH<sub>2</sub> alkenyl), 29.6 (CH<sub>2</sub>-N alkenyl), 28.3 (CH<sub>2</sub> alkenyl) and 12.4 ppm (CH<sub>2</sub> alkenyl). HRMS (m/s) for C<sub>1</sub>4H<sub>18</sub>N<sub>3</sub>: calcd 228.1501 [M - Br]<sup>+</sup>, found 228.1495 [M - Br]<sup>+</sup>.

#### 2.3. Generic synthesis of Ag complexes 2a, 2d, and 2e

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Equimolar quantities of the required imidazolium salt (**1a**, **1d**, or **1e**) and Ag<sub>2</sub>O were loaded into oven dried Schlenk tube containing 4 Å molecular sieves initially cooled under nitrogen. To this was then added 1,2-dichloroethane (30 ml) and the mixture subjected to vigorous stirring and refluxed in the absence of light for 3 d. By then, the dark colour of the silver(I) oxide had faded. The solvent was then removed under reduced pressure and the resulting residue extracted with DCM and filtered through a bed of celite. We wanted to confirm that the Ag-NHC complex was indeed formed; hence, complex **2a** was isolated from the DCM soluble filtrate. The filtrate was first concentrated and the resulting residue was stirred with hexane or toluene. Removal of solvents to dryness afforded 88% of pure **2a**. Compounds **2d** and **2e** were not as stable as **2a**, hence, once generated (confirmed by the absence of imidazolium C2-H at  $\delta > 9$  in the <sup>1</sup>H NMR spectrum of the crude) they were utilised *in situ* and immediately transmetalated to the desired Co or Ni. However characterisation data for the stable **2a** are presented and fully discussed as a representative of the Ag-NHC family of compounds.

#### 2.3.1. [1-(4-nitrophenyl)-3-(2-pyridyl)imidazol-2-ylidene]silver(I)chloride (2a)

Both 1-(4-nitrophenyl)-3-(pyridine-2-ylmethyl)-1H-imidazol-3-ium bromide **1a**, (0.50 g; 1.38 mmol) and silver(I)oxide (0.32 g; 1.38 mmol) were added into a Schlenk tube and refluxed in 1,2-dichloroethane (30 ml) in the dark for 3 d. Yield: brown microcrystalline powder, stable in air and unstable in chloroform but soluble in DCM and DMSO (0.510 g, 88%; mp. 173-176 °C). IR (ATR cm<sup>-1</sup>):  $v_{C-H}$  3084, 2946  $v_{C-N}$  1515,  $v_{N-O}$  1336,  $v_{Ar}$  844, 750;  $\delta_{H}$  (400 MHz, DMSO-d<sub>6</sub>): 8.50 (1H, d, *J* 4.4 Hz, pyridyl), 8.29 (2x1H, d, *J* 9.0 Hz, phenyl), 8.04-8.02 (1H, m, pyridyl), 8.02 (2x1H, d, *J* 1.9 Hz, phenyl), 7.85 (1H, d, *J* 4.9 Hz, CH=CH imidazoyl), 7.81-7.80 (1H, m, pyridyl), 7.39 (1H, d, *J* 4.9 Hz, CH=CH imidazoyl), 7.34 (1H, t, *J* 2.2 Hz, pyridyl) and 5.58 ppm (2H, s, NCH<sub>2</sub>).  $\delta_{C}$  (400 MHz, DMSO-d<sub>6</sub>): 180.4 (NCN; C-Ag), 155.3 (C pyridyl), 149.5 (CH pyridyl), 146.8 (C Ph), 144.4 (C Ph), 137.4 (CH pyridyl), 125.7 (CH pyridyl), 124.9 (CH Ph), 124.4 (CH imidazoyl), 123.3 (CH Ph), 122.4 (CH pyridyl), 120.4 (CH imidazoyl) and 56.4 ppm (NCH<sub>2</sub>). MS-ES<sup>+</sup>: m/z(%) 667(10) [Ag(ligand)<sub>2</sub>]<sup>+</sup>, 281(100) [(ligand + H)]<sup>+</sup>.

DOI: 10.1039/C6NJ01118G

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2.4. Synthesis of Co and Ni complexes 3a and 3a'
2.4.1. Co[3-(4-nitrophenyl)-1-picolyimidazolin-2-ylidene]<sub>2</sub>Cl<sub>2</sub> (3a)

To a solution of CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.15 g; 0.24 mmol) in DCM (20 ml) was added dropwise a DCM (20 ml) solution of silver-NHC complex 2a (0.10 g, 0.24 mmol). The green precipitate that formed was continuously stirred at room temperature in the dark for 2 d. At the expiration of the reaction time, the supernatant liquid was filtered via cannula and the solid green residue washed with more DCM till the washings became clear. Dry methanol (40 ml) was then used to extract the solid and the orange-brown extract filtered through a bed of celite. The clear orange-brown filtrate was then concentrated under reduced pressure to afford green, air stable microcrystals of the cobalt-NHC complex: 3a. Yield (0.114 g, 69%; mp 275-278 °C). IR (ATR cm<sup>-1</sup>): *v*<sub>moisture</sub> 3364, *v*<sub>C-H</sub> 3092, *v*<sub>NO</sub> 1522, *v*<sub>CN</sub> 1300, *v*<sub>Ar</sub> 852, 748; δ<sub>H</sub> (400 MHz, CD<sub>3</sub>OD): 8.42 (2x1H, s, pyridyl), 8.25 (2x(1H, 1H), m, pyridyl), 8.02 (2x1H, m, pyridyl), 7.80-7.70 (2x4H, dd, phenyl), 7.42 (2x1H, s, J 4.6 Hz, CH=CH imidazovi), 7.20 (2x1H, s, CH=CH imidazovl) and 5.46 ppm (2x2H, s, NCH<sub>2</sub>). δ<sub>C</sub> (400 MHz, CD<sub>3</sub>OD): 153.7 (C <sub>pyridyl</sub>), 150.8 (CH pyridyl), 149.6 (C Ph), 140.5 (C Ph), 139.1(CH pyridyl), 137.7 (CH pyridyl), 126.6 (CH Ph), 125.5(CH imidazovl), 124.6 (CH Ph), 124.4(CH pyridyl), 122.9 (CH imidazovl) and 55.5 (NCH<sub>2</sub>). MS-ES<sup>+</sup>: m/z(%) 690(5)  $[(M + H)]^+$ , 619(10)  $[(M - 2Cl)]^{2+}$ , 562(10)  $[(M - CoCl_2 + 2H)]^{2+}$ , 282(18)  $[(\text{ligand} + 2\text{H})]^{2+}$ , 281(100)  $[(\text{ligand} + \text{H})]^+$ .

#### 2.4.2. Ni[3-(4-nitrophenyl)-1-picolyimidazolin-2-ylidene]<sub>2</sub>Cl<sub>2</sub> (3a')

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To a dark blue solution of NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.15 g; 0.23 mmol) in DCM (20 ml) was added an equimolar DCM solution (20 ml) of **2a**. This prompted a yellow precipitate to be formed and the mixture stirred in the absence of light at room temperature for 2 d. The DCM soluble extract was filtered via cannula and the residue washed with more DCM (2 x 20 ml). The resulting yellow residue was then extracted with dry methanol (40 ml) and filtered through celite. Removal of all volatiles under reduced pressure yielded **3a'** as orange-yellow microcrystals that became moist when exposed for a while in air. Yield (0.153 g, 96%; mp 283—285 °C). IR (ATR cm<sup>-1</sup>):  $v_{broad moisture}$  3289,  $v_{C=C}$  1523,  $v_{C-N}$  1340,  $v_{Ar}$  680;  $\delta_{H}$  (400 MHz, CD<sub>3</sub>OD): 8.84 (2x1H, bs, pyridyl), 8.42 (2x2H, d, *J* 8.8 Hz, phenyl), 8.14 (2x1H, s, CH=CH imidazoyl), 7.95 (2x1H, s, CH=CH imidazoyl), 7.89-7.73 (2x(1H, 1H), m, pyridyl), 7.54 (2x1H, d, *J* 7.9 Hz, pyridyl), 7.34 (2x2H, d, *J* 6.2 Hz, phenyl), 5.59 (2x2H, s, NCH<sub>2</sub>). No <sup>13</sup>C NMR spectrum was available due to possible decomposition during the accumulation of FID. HRMS (m/s) for C<sub>30</sub>H<sub>24</sub>N<sub>8</sub>O<sub>4</sub>ClNi: calcd 653.0963 (M<sup>+</sup> - Cl<sup>-</sup>), found 653.0983 (M<sup>+</sup> - Cl<sup>-</sup>).

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2.5. Generic procedure for synthesis of Co and Ni complexes 3d, 3d', 3e and 3e' View Article Online Online

Equimolar amounts of the imidazolium salt and Ag<sub>2</sub>O were mixed together in a Schlenk tube containing molecular sieves and refluxed in 1,2-dichloroethane (30 ml) in the dark for 3 d. All volatiles were removed and the dark grey solid extracted with DCM (40 ml) and filtered through a bed of celite. The dark brown filtrate was then reduced to about 1/3 of the initial volume and added drop wise to a Schlenk tube containing a DCM solution of 1 mole equivalent of the metal precursor [MCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>; M= Co, Ni]. The resulting suspension was then stirred in the dark at room temperature for 2 d. The coloured suspension was filtered via cannula and the precipitate washed with more DCM and filtered till the washings became colourless, and then extracted with dry methanol (40 ml). Filtration through a bed of celite and subsequent removal of all volatiles afforded the desired complex in high yield.

#### 2.5.1. Co(3-allyl-1-picolyimidazolin-2-ylidene)<sub>2</sub>Cl<sub>2</sub> (3d)

Imidazolium salt **1d** (0.67 g, 2.39 mmol), Ag<sub>2</sub>O (0.55 g, 2.40 mmol) and CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.57 g, 2.40 mmol) were reacted accordingly. Yield: dark green powder that decompose on long exposure to air (1.20 g, 93%; mp 185-188 °C). IR (ATR cm<sup>-1</sup>):  $v_{(broad moisture)}$  3378,  $v_{C-H}$  3105,  $v_{C=C}$  1596,  $v_{C=N}$  1438, and  $v_{Ar}$  718;  $\delta_{H}$  NMR (400 MHz, CD<sub>3</sub>OD): 8.32 (2x1H, bs, pyridyl), 7.59 (2x1H, bm, pyridyl), 7.51 (2x1H, d, *J* 7.9 Hz, CH=CH imidazoyl), 7.47-7.40 (2x1H, bm, pyridyl), 7.29 (2x1H, d, *J* 7.9 Hz, CH=CH imidazoyl), 7.13 (2x1H, d, *J* 5.2 Hz, pyridyl), 6.59-6.57 (2x1H, bm, CH=CH<sub>2</sub>), 5.82 (2H, d, *J* 7.6 Hz, NCH<sub>2</sub>), 5.31 (2H, s, NCH<sub>2</sub>), 5.26 (2x2H, s, CH<sub>2</sub>=CH) and 1.56 ppm (2H, d, *J* 6.9 Hz, CH<sub>2</sub>-N allyl).  $\mu_{eff} = 2.53 \,\mu_{B}$ . MS-ES<sup>+</sup>: m/z(%) 492(60) [(M - Cl)]<sup>+</sup>, 457(20) [(M - 2Cl)]<sup>2+</sup>, 200(100) [(ligand + H)]<sup>+</sup>.

#### 2.5.2. Ni(3-allyl-1-picolyimidazolin-2-ylidene)<sub>2</sub>Cl<sub>2</sub> (3d')

Imidazolium salt **1d** (0.67 g, 2.39 mmol), Ag<sub>2</sub>O (0.55 g, 2.40 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.57 g, 2.40 mmol) were reacted accordingly. Yield: lemon-green microcrystals relatively stable in air (1.19 g, 93%; mp 243-245 °C). IR (ATR cm<sup>-1</sup>):  $v_{(broad moisture)}$  3323,  $v_{C=C}$  1610,  $v_{C-N}$  1437,  $v_{Ar}$  743;  $\delta_{H}$  (400 MHz, DMSO-d<sub>6</sub>): 8.16 (2x1H, s, pyridyl), 8.05 (2x1H, m, pyridyl), 7.83 (2x1H, s, CH=CH imidazoyl), 7.69 (2x1H, s, pyridyl), 7.37 (2x1H, s, CH=CH imidazoyl), 7.16 (2x1H, m, pyridyl), 6.57 (2x1H, d, *J* 13.5 Hz, CH=CH<sub>2</sub> allyl), 5.97 (2H, s, NCH<sub>2</sub>), 5.81 (2H, d, *J* 13.6 Hz, NCH<sub>2</sub>), 4.09 (2x2H, s, CH<sub>2</sub>=CH allyl) and 1.48 ppm (2x2H, s, CH<sub>2</sub>-N allyl). MS-ES<sup>+</sup>: m/z (%) 491(100) [(M – Cl)]<sup>+</sup>, 455(10) [(M – 2Cl)]<sup>2+</sup>.

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2.5.3. Co(3-butenyl-1-picolyimidazolin-2-ylidene)<sub>2</sub>Cl<sub>2</sub> (3e)

Imidazolium salt **1e** (0.56 g, 2.0 mmol), Ag<sub>2</sub>O (0.44 g, 2.0 mmol) and CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.25 g, 2.0 mmol) were reacted accordingly. Yield: dark green air sensitive powder (0.79 g, 71%; mp 120-123 °C). IR (ATR cm<sup>-1</sup>):  $v_{(broad moisture)}$  3365,  $v_{C=C}$  1596,  $v_{C-N}$  1437,  $v_{Ar}$  762;  $\delta_{H}$  (400 MHz, DMSO-d<sub>6</sub>): 8.81-7.80 (2x6H, bm: 4H, pyridyl; 2H, CH=CH imidazoyl), 7.57-7.49 (2x1H, bm, CH=CH<sub>2</sub>), 5.93 (2H, d, *J* 5.8 Hz, NCH<sub>2</sub>), 5.75 (2H, s, NCH<sub>2</sub>), 5.05 (2x2H, t, *J* 12.2 Hz, CH<sub>2</sub>=CH), 4.11-4.01 (2x2H, m, CH<sub>2</sub>-N <sub>alkenyl</sub>) and 2.23 ppm (2x2H, s, CH<sub>2</sub>).  $\mu_{eff}$  = 2.73  $\mu_{B}$ . MS-ES<sup>+</sup>: m/z (%) 557(7) [(M + 2H)]<sup>2+</sup>, 520(22) [(M - Cl)]<sup>+</sup>, 485(20) [(M - 2Cl)]<sup>2+</sup>, 214(100) [(ligand + H)]<sup>+</sup>.

#### 2.5.4. Ni(3-butenyl-1-picolyimidazolin-2-ylidene)<sub>2</sub>Cl<sub>2</sub> (3e')

Imidazolium salt **1e** (0.56 g, 2.0 mmol), Ag<sub>2</sub>O (0.44 g, 2.0 mmol) and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.25 g, 2.0 mmol) were reacted accordingly. Yield: yellowish green air sensitive powder (0.92 g, 83%; mp 108-110 °C). IR (ATR cm<sup>-1</sup>):  $v_{(broad moisture)}$  3329,  $v_{C=C}$  1610,  $v_{C-N}$  1438,  $v_{Ar}$  769;  $\delta_{H}$  (400 MHz, DMSO-d<sub>6</sub>): 8.25 (2x1H, s, pyridyl), 8.06 (2x1H, m, pyridyl), 7.84 (2x1H, s, CH=CH <sub>imidazoyl</sub>), 7.71 (2x1H, s, CH=CH <sub>imidazoyl</sub>), 7.44 (2x2H, m, pyridyl), 6.93 (2x1H, m, CH=CH<sub>2</sub>), 5.90 (2H, d, *J* 14.9 Hz, NCH<sub>2</sub>), 5.65 (2H, s, NCH<sub>2</sub>), 4.81-4.77 (2x2H, m, CH<sub>2</sub>=CH), 4.11-3.70 (2x2H, m, CH<sub>2</sub>-N <sub>alkenyl</sub>) and 2.32 ppm (2x2H, s, CH<sub>2</sub> <sub>alkenyl</sub>). MS-ES<sup>+</sup>: m/z (%) 519(50) [(M – Cl)]<sup>+</sup>, 484(10) [(M – 2Cl<sup>-</sup>)]<sup>2+</sup>, 214(100) [(ligand + H)]<sup>+</sup>.

#### 2.6. Analysis of magnetic susceptibility measurement data

The numeric data obtained from the hysteresis loop measurement using the VSM when analysed as a plot of magnetic moment/mass (emu/g) against field (Oes) gave an initial magnetization curve which qualitatively confirmed the paramagnetic nature of the complexes. The experimentally determined value of saturated magnetization Ms is a function of the number of moles 'n' used per atom (0.025-0.031g). This was used to determine the magnetic susceptibility (µeff) of each paramagnetic complex in µB which was compared with the calculated magnetic moments consistent with the number of un-paired electrons. The quotient Ms/n divided by a constant 5584.9 (derived from the equation: mu\_B\*N\_A = 5584.9 emu/mole; where N\_A is Avogadro's number) gave the magnetic susceptibility of the complexes [28].

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#### 2.7. Typical procedure for the 3a' activated arylation of aniline with phenyl bromide

To an oven dried Schlenk tube initially cooled under nitrogen was added aniline (1.0 g, 1 ml, 0.010 mol), phenyl bromide (2.0 g, 1.4 ml, 0.013 mol), KO'Bu (1.46 g, 0.013 mol) and **3a'** (0.069 g, 0.0001 mol). The mixture was vigorously stirred in refluxing THF (20 ml) under an atmosphere of nitrogen for 12 h with reaction progress monitored by TLC. The contents of the Schlenk tube were then allowed to cool to room temperature after which DCM (30 ml) was added into the flask, stirred for an hour and filtered through a bed of celite. All volatiles in the filtrate were removed under reduced pressure and the crude residue obtained was mixed with silica and loaded onto a column. The desired product (diphenyl amine) was obtained as an eluent of hexane: DCM (4:1). Removal of all volatiles gave isolated yield of a low melting yellowish-brown solid (1.13 g, 67%). IR (ATR cm<sup>-1</sup>): v<sub>N-H</sub> 3380 (bs, 2° amine), v<sub>C-H</sub> 3041, v<sub>C-N</sub> 1307, v<sub>Ar</sub> 741;  $\delta_{\rm H}$  (400 MHz, DMSO-d<sub>6</sub>): 8.12 (1H, bs, N-H), 7.21 (2x2H, d, *J* 7.4 Hz), 7.06 (2x2H d, *J* 7.6 Hz), 6.81 (2x1H t, *J* 7.3 Hz,).  $\delta_{\rm C}$  (400 MHz, DMSO-d<sub>6</sub>): 143.4 (C <sub>Ph</sub>), 129.1 (CH <sub>Ph</sub>), 119.6 (CH <sub>Ph</sub>), 116.7 (CH <sub>Ph</sub>).

### 2.8. Typical procedure for NiCl<sub>2</sub>/**1a** in situ activated arylation of aniline with phenyl bromide

Anhydrous NiCl<sub>2</sub> (0.013 g, 0.0001 mol), imidazolium salt **1a** (0.072 g, 0.0002 mol) and 4Å molecular sieves were loaded into a Schlenk tube under an atmosphere of nitrogen and stirred together in THF for 1 h at room temperature. To the resulting suspension was then added KO'Bu (1.46 g, 0.013 mol), aniline (1.0 g, 0.010 mol) and phenyl bromide (2.0 g, 0.013 mol). The Schlenk tube was then equipped with a condenser and subjected to reflux for 12 h. After cooling to room temperature, DCM (30 ml) was added and the contents filtered through a bed of celite. The resulting filtrate was then concentrated and the crude obtained was mixed with silica and loaded onto a column. The diarylamine product was isolated as an eluent of hexane: DCM (4:1) after removal of all volatiles.

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#### 3. Results and discussion

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#### 3.1. Synthesis: - picolyl functionalised salts

In the synthesis of the *N*-substituted imidazoles; conventional synthetic strategy applicable to the type of *N*-substituent were applied [24]. The picolyl functionalised ligand precursors (**1a-f**) were synthesised using modification of established procedures [Scheme 1 (a)] [27].



**Scheme 1.** Synthesis of (a) functionalised imidazolium salts with picolyl moiety and (b) picolyl functionalised imidazol-2-ylidene(NHC)-Ni(II) and Co(II) complexes.

All the imidazolium salts were obtained in excellent yields via a purification technique we described for similar salts [25]. In the synthesis of the imidazolium salts, it seems the type of solvent used has an effect on the reaction rate and we observed that under similar conditions, when compared to DCM, methanol or toluene as the reaction medium acetonitrile tends to give higher yields with great ease of purification [27, 29]. Both 3-(4-nitrophenyl)-1-picolylimidazolium bromide **1a**, and 3-(4-cyanophenyl)-1-picolylimidazolium bromide **1c**, precipitated out from the reaction solution after about 12 h of reaction; and were eventually

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obtained by a simple filtration of the salts under an atmosphere of nitrogen which were purified online by simple washing with dry acetonitrile. Alternatively, the crude product may be concentrated and the salt isolated as methanol eluent via column chromatography [25]. Both **1b** and the alkenyl picolyl imidazolium salts **1d-f**, were purified in a similar fashion as methanol eluents which were then isolated as either grey-brown highly hygroscopic solid (**1b**), brown waxy substance (**1d**) or light brown oils (**1e & f**).

#### 3.2. Characterisation of salts

The <sup>1</sup>H NMR spectrum of each of the salts (**1a-f**) showed the distinct C-2 proton singlet peaks at 9-11 ppm, a clear indication of imidazolium salt formation [6a, 30]. Coupling of the imidazole with the picolyl moiety in all the salts **1a-f** was confirmed by the appearance of a distinct singlet characteristic of the methylene (NCH<sub>2</sub>) protons observed at 5.5-5.7 ppm [7a, 27]; integrating for 2H. The alkenyl C2 protons (CH<sub>2</sub>=CH) appeared as a multiplet in 1d-f, while the distinct singlet at 2.60 ppm corresponded to the methyl group on the acetyl functional group in 1b (analyses spectra available as supporting information). The rest of the protons in the <sup>1</sup>H NMR spectra of all the salts were within the aromatic region and were consistent with expected integration and coupling multiplicities for such compounds. The corresponding <sup>13</sup>C NMR spectra of the salts showed the methylene carbon peak (NCH<sub>2</sub>) at the range 53.5-54.9 ppm with the characteristic down field peak of the imidazolium carbons at 152-154 ppm [27, 30a]. All the salts (1a-f) are extremely hygroscopic and quickly imbibed varying quantities of moisture (FTIR broad peaks at 3349-3355 cm<sup>-1</sup>), a common reported problem for related salts [25]. However, the clean NMR data and exact HRMS results established their purity (see supporting information). The HRMS (TOF-MS ES+) of all the salts exhibited peaks due to the molecular ion with the loss of one bromide counter ion. The found values are all within the acceptable limits of the calculated values of the parent-derived ion peak. The three solid microcrystalline salts had narrow melting point ranges within expected limits of their molecular compositions of 220-222, 199-202 and 265-267 °C respectively for **1a-c.** These are indicative of pure solids and comparable to related published data.

#### 3.3.Synthesis and characterisation of metal-NHC complexes

All the nickel and cobalt complexes reported herein were synthesised via transmetalation from corresponding Ag-NHC complexes (Scheme 1b). It is worthy to note that for this to succeed we chose to use Ag<sub>2</sub>O in refluxing 1,2-dichloroethane as a convenient means to alleviate well documented difficulties [7,10b,27,31] with the formation of Ag-NHC

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compounds of bulky ligand precursors following conventional methods. We also added by Atticle Online molecular sieves to the reaction medium during formation of the Ag-NHC complexes, it served to improve product yield by the elimination of moisture and other impurities. Hence, Ag-NHC complexes of **1a**, **1d** and **1e** were prepared by refluxing the corresponding mixtures of the salts and excess Ag<sub>2</sub>O in 1,2-dichloroethane for 3 d, within which the dark colour of Ag<sub>2</sub>O disappeared. Complete formation of the Ag-NHC complexes was monitored by the disappearance of the C2 imidazolium protons (9-11 ppm) by <sup>1</sup>H NMR of crude products (Fig. 1).



Figure 1: Comparative <sup>1</sup>H NMR spectra of **1a** (top) and **2a** (bottom).

Concentration of the crude and extraction with DCM afforded the Ag-NHC complexes **2a**, **2d** and **2e** [19]. Complex **2a** was stable to air and light, hence it was isolated and fully characterised. The relatively lower melting range of **2a** (173-176 °C) as compared to the imidazolium salt **1a** (220-222 °C) is a clear indicator to the formation of a thermally weak Ag-NHC complex [32]. Compounds **2d** and **2e** derived from **1d** and **1e** were less stable to air; moisture and light, hence were directly transmetalated to Co and Ni. We monitored the disappearance of the downfield C2 imidazolium protons from the ligand precursors as a guide and sign of successful deprotonation by the basic Ag<sub>2</sub>O. Also, further analysis of **2a** confirmed

its successful isolation; <sup>13</sup>C NMR data showed a downfield shift of the C2 carbon from Vigy 57 icle Online ppm in **1a** to 180 ppm in **2a** (Figure 2); typical of a carbene-metal bond [33].



Figure 2: Comparative <sup>13</sup>C NMR spectra of 1a (top) and 2a (bottom).

The methylene protons in the picolyl moiety also shifted up-field (5.70 to 5.58 ppm) in the <sup>1</sup>H NMR data of **2a** with a corresponding downfield shift of the methylene carbon peak (53.5 to 56.4 ppm; Figure 2) as reported for similar Ag-NHC complexes [27]. Elemental analysis (CHN) data obtained for **2a** agree with the formation of Ag(ligand)Cl and the MS-ES<sup>+</sup> results gave the molecular ion as  $[Ag(NHC)_2]^+$  characteristic of Ag-NHC complexes of the form Ag(NHC)X [27].

Transmetalation of the Ag-NHC complexes **2a**, **2d**, and **2e** to the desired cobalt or nickel with either  $CoCl_2(PPh_3)_2$  or  $NiCl_2(PPh_3)_2$  as the metal precursors was achieved by a slight modification of an established transmetalation procedure [7a]. A distinct colour change in each of the reactions was an early indicator of successful transmetalation. For example, the blue colour of the DCM solution of  $NiCl_2(PPh_3)_2$  was observed to gradually fade and develop a yellow/orange precipitate of the product  $Ni(NHC)_2Cl_2$ . Unreacted Ag-NHC, the metal precursor and displaced PPh<sub>3</sub> were recovered as DCM soluble components. Extraction of the solvent under reduced pressure afforded the respective fairly air stable orange powders of  $Ni(NHC)_2Cl_2$  (**3a',3d',3e'**) or dark green powders of  $Co(NHC)_2Cl_2$  (**3a, 3d, 3e**) complexes. The cobalt complexes turned into dark orange solutions when dissolved in methanol while the

nickel complexes maintained their colour in methanol solutions. None of the Complexesticle Online showed a peak around 9-11 ppm in their respective <sup>1</sup>H NMR spectra, a confirmation of successful deprotonation of the imidazolium protons and formation of carbene-metal bonds (see accompanying supporting information). Absence of a peak around -6 ppm characteristic of PPh<sub>3</sub> in the <sup>31</sup>P NMR data is indicative of the purity of the complexes to be free of liberated phosphine ligand. All the complexes were further characterised by melting point, IR (ATR), MS-ES<sup>+</sup> and HRMS.

The <sup>1</sup>H NMR data of **3a** accounted for all the expected protons, but interestingly the expected doublet and singlet peaks that usually account for the diastereotropic methylene protons in the ligand moiety of similar complexes [7a, 9a]; was observed as a singlet in **3a**. The appearance of the singlet slightly shifted up-field from 5.58 ppm in **2a** to 5.47 ppm in **3a** was attributed to possible dynamic atropisomerisation in the three aromatic rings that composed the ligand backbone as observed in related metal-NHC complexes bearing pincer CNC architecture [11b, 34]. In such systems, only at a fast rate of inter-conversion would the two methylene (NCH<sub>2</sub>) protons be observed on the same plane to generate a singlet, hence giving an insight into the solution phase geometry of the metal complex.

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The related yellow microcrystalline Ni-NHC complex 3a' gave a <sup>1</sup>H NMR data similar to that obtained for the Co-NHC analogue. Although the peaks were not as sharp, all the protons were accounted for and the expected diastereotropic protons representing NCH<sub>2</sub> methylene protons also appeared as a singlet peak within a similar region to the corresponding Co complex **3a**.

Conversely, both **3d** and **3e** are ferromagnetic/paramagnetic species as observed from the respective magnetic susceptibility (2.53 and 2.73  $\mu_B$ ) measurements [28]. These values are in agreement with data reported for related cobalt complexes which are consistent with one unpaired electron [11]. Hence, only broad <sup>1</sup>H NMR spectra were recorded for these compounds (supporting information). However, fully resolved <sup>1</sup>H NMR spectra were obtained for the corresponding nickel complexes **3d'** and **3e'**, with all the expected proton peaks accounted for. The characteristic doublet and singlet peaks accounting for the diastereotropic protons of each methylene bridge in the ligand moieties appeared in **3d'** at  $\delta$  5.81 and 5.97 ppm and for **3e'** at  $\delta$  5.90 and 5.65 ppm a confirmation of dicarbene complexation to nickel (supporting information).

#### 3.4. Catalytic arylation of aniline

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The pioneering works of Migita and co-workers [35] paved the way to transition metal catalysed arylation of amines with aryl halides, although credit for C-N coupling is attributed to Buchwald and Hartwig after whom the well-known Buchwald–Hartwig amination is named [20a, 36]. Most C-N coupling reactions are base initiated with the base serving to reduce the catalyst precursor to an active state. The organo-alkali metal salts KO'Bu and NaO'Bu are the most effective in a variety of catalytic coupling reactions that include C-C coupling of  $\alpha$ -ketones with aryl halide [13], metal-NHC catalysed arylation of aromatic amines [2j, 11b, 13, 20b], and CuTC catalysed arylation of amines and amides [22d]. The organic nature of these bases and the ease of isolation and removal of their precipitates are some of the advantages that make them prominent in coupling reactions. Although, the use of commoner bases such as KOH and K<sub>3</sub>PO<sub>4</sub> may seem advantageous for C-N coupling reactions, they are unsuitable because KOH for instance is known to react with the substrate yielding mainly phenolic products while the use of K<sub>3</sub>PO<sub>4</sub> usually resulted in poor yields [37]. However, in Cu-catalysed aryl C-N coupling reactions, simple inorganic bases like K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>PO<sub>4</sub> are specifically preferred [37-38].

Results of a preliminary and optimisation study presented in Table 1 investigated the KO<sup>t</sup>Bu promoted C-N coupling reaction of aniline (**4**) and phenyl bromide (**5**) to preferentially yield the desired monoarylated amine (**7**).

#### Table 1

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Optimization of reaction conditions for arylation of aniline (4) with phenyl bromide (5)



Entry	Catalyst	Substrates' mole		Solvent	Yield (%) <sup>a</sup>	
		equivalents				
		4	5	_	6	7
1	None	1.2	1	THF	13	-
2 <sup>b</sup>	None	1.2	1	THF	-	-
3	None	-	1.2	THF	-	-
4 <sup>c</sup>	None	1	1.2	THF	-	-
5	3d	1.2	1	THF	28	32
6	3d	1	1.2	THF	27	40
7	3d'	1	1.2	THF	21	60
8	3d'	1	1.2	Acetonitrile	Trace	Trace
9	3d'	1	1.2	Dioxane	29	41
10	3a'	1	1.2	THF	28	67
11	3a	1	1.2	THF	30	15
12	3e'	1	1.2	THF	21	40
13	3e	1	1.2	THF	13	20
14 <sup>d</sup>	3a'	1	1.2	THF	12	Trace
15 <sup>e</sup>	3a'	1	1.2	THF	18	20
16 <sup>f</sup>	3a'	1	1.2	THF	31	68
17 <sup>g</sup>	3a'	1	1.2	THF	38	28
18 <sup>h</sup>	3a'	1	1.2	THF	23	69
19 <sup>f</sup>	NiCl <sub>2</sub>	1	1.2	THF	Trace	Trace
20 <sup>f</sup>	NiCl <sub>2</sub> /1a (1:1)	1	1.2	THF	25	60
$21^{\mathrm{f}}$	NiCl <sub>2</sub> /1a (1:2)	1	1.2	THF	28	65
22	NiCl <sub>2</sub> /1a (1:2)	1	1.2	THF	24	63

Except otherwise mentioned, all reactions were done with 1 mol% of catalyst, 1.2 mole equivalent KO'Bu, under an atmosphere of nitrogen and refluxing solvent for 12 h. Progress of reaction monitored by TLC. <sup>a</sup> Isolated yield from column chromatography, average of two runs. <sup>b</sup> Reaction done at room temperature. <sup>c</sup> Reaction done in the absence of a base. <sup>d</sup> 1.2 mole equivalent of K<sub>2</sub>CO<sub>3</sub> used as the base. <sup>e</sup> 1.2 mole equivalent of Na<sub>2</sub>PO<sub>4</sub> used as the base. <sup>f</sup> Reaction done for 18 h. <sup>g</sup> 0.5 mol% of catalyst used. <sup>h</sup> 2 mol% of catalyst used.

#### **New Journal of Chemistry**

As the primary control reaction, the two substrates were reacted together in the absence detection of any catalyst (entry 1) and as expected no traces of the desired monoarylated product (diphenyl amine) were observed. However, a 13% yield of biphenyl, **6**, (a yellowish-white solid, confirmed by NMR, IR and mp = 70-72 °C) was isolated as a by-product in what is believed to be a competing C-C coupling reaction, which has been identified by others as a variant of the Hiyama coupling reaction [39]. Further studies were conducted on the blank control reaction by conducting the reaction at room temperature (entry 2), conducting the reaction in the absence of the aryl amine (entry 3) or a base (entry 4). The results indicate an interesting relationship such that heat, base and both substrates are all required for any reaction to take place.

We then introduced 1 mol% of Co(allylNHC)<sub>2</sub>Cl<sub>2</sub>, **3d** as the catalyst with a slight molar excess of the aniline (entry 5). This yielded a modest quantity of the desired product (32%) along with a corresponding increase in the quantity of the biphenyl product. By changing the relative mole ratios of the substrates (entry 6) such that a slight excess of the aryl halide was used with the same catalyst **3d**, an increase in the isolated yield of the product **7** and a slight decrease in that of the side product **6** was observed. This confirms the observation in entry 3 (absence of **4**) that the aniline may be responsible for promoting the unwanted reduction of the aryl halide to biphenyl.

Most of the non-precious metal catalyst systems reported to be active in C-N coupling reactions are based on nickel metal and its complexes [2j, 2m, 13], hence when the Ni analogue **3d'** was tested under the same conditions as entry 6, 60% of the desired **7** was isolated (entry 7). What is obvious at this stage is that the catalyst selectively promotes the C-N coupling of the two substrates in competition with the reduction of **5** and its C-C coupling leading to the formation of the biphenyl **6**.

The role of the solvent is important in aryl coupling reactions (entries 7-9). It is clear that THF is the better of the three solvents tested for the current catalyst systems, as both acetonitrile (entry 8) and dioxane (entry 9) negatively affected catalyst productivity. This observation implies that despite the fact that both THF and dioxane are ethereal solvents, mono N-arylation of aromatic amines is more facile in THF which is consistent with observations in a related work by Kuhl *et al.* for the selective mono N-arylation of aromatic diamines in THF, while in refluxing dioxane they reported N,N'-diarylation of the aromatic diamines [2j]. On this basis, we adopted THF as the reaction solvent to study the influence of other reaction

parameters such as the steric and electronic nature of the NHC ligand and influence of variation of the NHC ligand and influence of the NHC ligand and influence of variation of the NHC ligand and influence of variation of the NHC ligand and influence of variation of the NHC ligand and influence of the NHC ligand and the NHC ligand and influence of the NHC ligand and bases.

Entry 13 illustrates the influence of ligand sterics on the catalysis with the bulkier butenyl functionalised catalysts **3e** yielding lower conversions of the desired product as compared to the allyl variants (entry 6). Further studies were conducted with 3a' and in situ generated catalyst systems obtained from the mixture of imidazolium salt **1a** and anhydrous NiCl<sub>2</sub> (entries 15-22). Only traces or low yield (20%) of 7 were obtained with the use of  $K_2CO_3$ and Na<sub>2</sub>PO<sub>4</sub> as bases (entries 14 and 15 respectively). Increasing the reaction time to 18 h (entry 16), did not bring any change in yield of 7 (68%) as compared to the standard 12 h (entry 10, 67%). Entries 17 and 18 indicate that the optimum catalyst concentration for the current system is 1 mol% as the productivity significantly diminished at 0.5 mol% and showed negligible increase when doubled to 2 mol%.

Finally, the study was extended to investigate *in situ* generated catalyst systems. The work of Kuhl et al. [2j], has shown that when combined with appropriate metal sources, bulky imidazolium salts could generate in situ catalysts. We have recently shown that in situ generated Fe-NHC complexes are efficient systems for the transfer hydrogenation of ketones [40]. Therefore, entries 20-22 report on the efficiency of an *in situ* generated Ni-NHC catalysts whereby a mixture of NiCl<sub>2</sub>/1a yielded 63% of the desired product after 12 h which is comparable to the most active catalyst (3a') tested thus far. This is a very important finding given the difficulty and laborious synthetic strategies required for the preparation and isolation of the metal complexes. To illustrate the scope and limitations of the *in situ* generated Ni system, a series of substrates bearing a variety of functional groups were studied. For the purpose of comparison, the most active isolated complex 3a' was run alongside the in situ system under the same reaction conditions, the results are presented in Table 2.

#### Table 2

Metal-NHC complexes catalysed N-mono arylation of aryl amines with aryl bromides



22



All reactions were conducted with either 3a' (1.0 mol%) or a mixture of NiCl<sub>2</sub>/1a (1:2 molar ratio), KO'Bu (1.2 mole equivalent), aryl amine (1.0 mole equivalent), aryl bromide (1.2 mole equivalent), under an atmosphere of nitrogen and refluxing THF (20 ml) for 12 h. Progress of the reaction was monitored by TLC. <sup>†</sup>Isolated yield from column chromatography on average of two runs.

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A recent microwave assisted Pd-NHC catalysed C-N coupling reaction [20b] was reported to display good catalytic activities in Buchwald-Hartwig amination of aryl chlorides. The data presented by Wang and co-workers is comparatively higher than our values, however, what this study has demonstrated is that appreciably good yields of monoarylated products are obtainable under milder conditions based on an earth abundant, non-PGM; nickel catalyst. The results are also comparable to those reported for monodentate [16], bidentate [2m] NHC-metal catalyst systems involving cobalt or nickel centre and even the tridentate NHC-metal complexes of the platinum group of metals [34b]. Hence, an examination of the variety of substrates reveals that the steric position or electronic nature of the substituent on the aryl halide had very little overall influence on the coupling reaction as most of the substrates yielded comparable isolated quantities (circa 70%) of the desired product. A noticeable improvement was observed with aryl bromide bearing the electron withdrawing CN group as a *para*substituent (entry 4-4a, circa 80% yield) which has been established to render the aryl halide more reactive and easily susceptible to oxidative attack by the nickel centre [38].

Under the present reaction conditions with either catalyst system, no products were isolated in the attempted arylation of 2-nitro aniline (entry 9-9a), which is similar to reports on a CuI catalysed reaction for related substrates under harsher conditions [41]. Both catalysts (**3a'** and NiCl<sub>2</sub>/**1a**) also failed to activate formation of the desired diarylamine on a mixture of

#### New Journal of Chemistry

aniline and *p*-chloro- or iodo-acetophenone. In both cases, an aldol product (from the Verticie Online condensation of acetophenone) was isolated in excellent yields which has also been reported by Matsubara *et al.* [13] and recently by us [11b] to be more facile in such base promoted competitive reactions. Finally, it is interesting to note that in all the combinations studied, comparable catalytic efficiencies were recorded for the isolated metal complex **3a'** and the *in situ* generated NiCl<sub>2</sub>/**1a** catalyst, hence opening up a simple, robust and functional group tolerant system for C-N coupling reactions.

As no experimental evidence is available on the mechanism for the catalysed reactions, we have mentioned earlier that recent and past studies on Ni and Pd-NHC complex catalysed aryl C-N coupling reactions have been achieved with the metal in the zero (0) oxidation state. In such studies, the choice of the base was mostly associated with the ease to which it was able to initiate reduction of the metal centre and thereby create the active specie with an oxidation state capable of activating the coupling reagents. On this basis a mechanistic pathway followed by this catalytic reaction could be similar to what we recently reported with similar Co-NHC complexes bearing pincer ligand architecture [11b].

#### 4. Conclusion

Herein we have reported the successful synthesis in excellent yields of six new imidazolium salts bearing a picolyl moiety which were conveniently characterised and some of which were used as precursors of NHC ligands that afforded Ag-NHC complexes in good yields. Transmetalation of both the isolated and *in situ* utilised Ag-NHC complexes afforded the desired Co and Ni complexes in good to excellent yields based on CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> or NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as metal precursors respectively.

All the complexes were active in catalysing *N*-mono arylation of aniline with phenyl bromide, with the highest yield obtained with the Ni based complex **3a'**. The catalyst systems showed excellent selectivity to *N*-mono arylation as no traces of *N*,*N*-diarylated products were observed. The good yields of the products, mild reaction conditions and the use of green, earth abundant, non-PGM; first row transition metals made the current catalyst systems competitive in comparison to classical Cu mediated or CuI catalysed Ullman coupling and Pd catalysed systems for aryl C-N coupling reactions.

New Journal of Chemistry Accepted Manuscript

#### Acknowledgements

We thank the University KwaZulu-Natal and the NRF for financial support. Dr T. Moyo is acknowledged for the use of VSM lakeshore 735. HI thanks FCE (T) Gusau and TET Fund for a study fellowship.

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## Earth abundant metal complexes of donor functionalised N-heterocyclic carbene ligands: synthesis, characterisation and application as amination catalysts

Halliru Ibrahim, Muhammad Dabai Bala\*

School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X54001, Durban 4000, South Africa



Detailed study on Co and Ni complexes of *N*-functionalized chelating NHC ligands applied for the mono-arylation of aniline and substituted aryl amines is presented.

<sup>\*</sup> Correspondence to: e-mail- <u>bala@ukzn.ac.za;</u> fax- +27 31 260 3091