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#### Research paper

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#### Transfer hydrogenation of ketones catalyzed by a trinuclear Ni(II) complex of a Schiff

#### base functionalized N-heterocyclic carbene ligand

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#### Abstract

A new Schiff base-functionalized N-heterocyclic carbene ligand precursor 3-benzyl-1-[2-((2hydroxy-benzylidene)-amino]-ethyl-3H-imidazol-1-ium bromide (3), and its trinuclear Ni(II) complex [LNiL-Ni-LNiL].2Br (4) where L = 2-[2-(3-benzylimidazol-1-yl) ethyliminomethyl]phenol, were synthesized via the solventless and free carbene routes respectively. Both compounds were characterized by spectroscopic and X-ray diffraction techniques. Single crystal XRD analysis of 4 showed that it is composed of a central square planar Ni(II) ion symmetrically linked to two distorted square planar Ni(II) ions via two bridging ligands. The central Ni(II) ion is only bound to the Schiff base moieties of the bridging ligands via the phenolate oxygen donor (O1) and imine nitrogen donor (N1) atoms in a trans [N^O^(Ni<sup>2+</sup>)^N^O] mode, whilst the carbene moieties of each bridging ligand and a tridentate L are coordinated in a distorted square planar C<sub>NHC</sub>-(Ni<sup>2+</sup>)^N^O^C<sub>NHC</sub> mode to stabilise each of the terminal Ni(II) ions. Complex 4 showed significant activity as a catalyst in the transfer hydrogenation of a range of aliphatic and aromatic ketones, at a catalyst concentration of 0.1 mol%. An excellent conversion up to 100% was achieved for aromatic ketones after 4 h.

Keywords: Trinuclear Ni(II); Solventless synthesis; *N*-heterocyclic carbene; Schiff base; Bifunctional ligand; Transfer hydrogenation.

#### 1. Introduction

The successful isolation and full characterization of stable *N*-heterocyclic carbenes (NHCs) has revolutionized the field of organometallic chemistry and homogeneous catalysis.<sup>1</sup> This is because NHCs have proven to be good stabilizing ligands to a wide range of metal ions and have over the last few decades been accepted as credible alternatives to traditional ligands like the amines and phosphines.<sup>2</sup> Added to this is the ease of preparation and relatively long shelf lives of their precursor salts. Monodentate NHCs have been widely studied and complexed to a range of transition metals, usually applied as catalysts in a variety of small molecule activation studies that include reduction of ketones, C-N and C-C coupling reactions.<sup>3</sup> However, there is a limitation to the range and scope of reactivity and structural variations obtainable from monodentate carbene ligands, hence one of the current challenges in this field is the development of new multi-functional or polydentate NHC ligands by the

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functionalization of the imidazolyl wingtip positions with other donor groups. This is driven by the need to expand the rich chemistry of NHC based compounds aimed at the development of even more active and stable catalysts and materials. Hence, it is not surprising that the number of publications on this topic is on the rise.<sup>4</sup>

In addition, since their first isolation over a century ago, Schiff bases have become well established as exceptional ligands capable of stabilizing most metal centers,<sup>5</sup> and have yielded very efficient homogeneous catalysts. <sup>6</sup> The idea of incorporating them as wing-tip *N*-substituents to an imidazolium core thereby yielding polydentate NHC ligands is a very interesting prospect<sup>7</sup>, and Li *et al.* were amongst the first to report a Schiff base functionalized NHC (SB/NHC) nickel complex.<sup>8</sup> Peters and coworkers have synthesized the first bimetallic complexes of Pd, Ni, Ag and Au incorporating NHC and Salen in the ligand architecture.<sup>9</sup> As catalysts, such complex systems have shown effective selectivity for stereoselective bond formation in asymmetric catalysis.<sup>10</sup>

Catalytic transfer hydrogenation (CTH) is a simple but chemically important transformation that yields value added products that include alcohols, amines and thiols which serve as building blocks to fine chemicals and pharmaceuticals.<sup>11</sup> Since the extensive works of Noyori and co-workers utilising transition metal complexes as catalysts with 2-propanol (or formates) as source of hydrogen, CTH has gained recognition as an attractive alternative to the use of molecular hydrogen for the reduction of unsaturated molecules.<sup>12</sup> Until quite recently, when first row transition metals, especially Fe, Co and Ni have begun to be recognized as credible catalytic centres, most reported CTH processes are based on heavy transition metals such as Ru, Rh and Ir.<sup>13</sup> The obvious advantages to the use of earth abundant metal based complexes as catalysts has been widely recognized to include their moderate cost, relative non-toxicity and the fact that they are readily available and may provide alternative reaction pathways that are more efficient and selective than current systems.<sup>14</sup> Hence, excellent catalytic results have been reported with Fe<sup>15</sup> and guite recently with Ni based catalysts. <sup>16</sup> On this basis, we herein report the first trinuclear nickel complex of a bifunctional SB/NHC ligand framework and its application as an effective catalyst for the transfer hydrogenation of aliphatic and aromatic ketones.

#### 2. Results and discussion

#### 2.1. Synthesis and characterization

2-bromoethyliminomethylphenol 1 and 1-benzylimidazole 2 were prepared according to published procedures.<sup>17</sup> The SB/NHC ligand precursor was prepared using adapted solventless methods in which equimolar quantities of 1 and 2 were heated neat for 30 min to

yield 98% of pure  $3^{.18}$  <sup>1</sup>H-NMR spectrum of 3 in CDCl<sub>3</sub> showed all the expected signals typical of an imidazolium salt. The characteristic C2-H imidazolium proton resonance signal was observed downfield at 9.4 ppm.<sup>19</sup> The aromatic C4,5-H protons of 3 were observed as a multiplet at 6.90 ppm due to the deshielding effects of the positively charged imidazolium ring system.<sup>20</sup> As expected, a singlet that is typical of phenolic OH groups was observed downfield at 12.64 ppm, while all other signals corresponding to the imine and aromatic protons of 3 were observed and well resolved. In addition, the <sup>13</sup>C NMR spectrum shows the characteristic imidazolium C2 signal at 137 ppm, this signal is usually observed downfields for all related compounds.<sup>21</sup> Other spectroscopic techniques including IR confirmed the isolation of 3, with distinct signals corresponding to the O–H (3400 cm<sup>-1</sup>) and C=N (1631 cm<sup>-1</sup>) functionalities distinctly observed. Positive mode ESI MS analysis gave the molecular ion of the salt with the loss of the Br<sup>-</sup> counter ion at m/z value of 306.<sup>22</sup>

The free carbene route is the easiest and most direct method of generating NHC from an imidazolium salt such as **3** and coordinating it to a metal of choice. Most other popular methods require extra steps for the formation and isolation of metal-NHC complexes. The first step in the free carbene route requires deprotonation of **3** via the addition of excess of base (KO*t*Bu) to extract the acidic C2-H thereby generating the free carbene which was then coupled to nickel by the slow addition of an equimolar amount of the metal precursor (NiCl<sub>2</sub> diglyme). Change of colour from the reddish brown suspension of the carbene mixture to a greenish solution that was allowed to stir overnight was an initial indication of metalation. Filtration of the supernatant and removal of all volatiles in vacuo yielded air stable yellow microcrystals of the trinuclear nickel complex **4**. The complex is insoluble in chlorinated solvents and acetone, but soluble in methanol.



Scheme 1: Synthetic route to the trinuclear Ni(II) complex **4**. (i) Solvent free, 60 °C; (ii) MeOH, KOtBu, NiDME.

We attempted to acquire the <sup>1</sup>H-NMR data for complex **4** using a 400 MHz NMR spectrometer; but only obtained a signal for CDCl<sub>3</sub> at around 7.27 ppm which is surprising given our assumption that the complex contains square-planar Ni(II) centres. However, literature reports on magnetic susceptibility studies of some square planar trinuclear nickel compounds revealed that all the complexes possessed weak antiferromagnetic interactions and no NMR data were reported for their characterisation.<sup>23</sup> Hence, we also conducted magnetic susceptibility measurements on compound 4 which also indicated weak paramagnetism (0.72 µB) at room temperature. Similarly, analysis of compound 4 by X-ray diffraction (vide infra) shows distortions from normal square-planar geometry around two of the three metal coordination sites that may account for the ferromagnetic interactions in solutions of 4 prepared for NMR analysis. However, significant changes were observed in the IR spectrum of the complex in comparison to that of the ligand 3, further affirming coordination of **3** to nickel. In addition to the disappearance of the strong O–H absorption band (3400 cm<sup>-1</sup> in 3), there is also a general shift towards lower wavenumbers for the absorption bands of other functional groups, indicating Ni-L interactions. For instance, the distinct, imine N=C absorption band ( $1631cm^{-1}$  in 3) was observed at  $1609 cm^{-1}$  in 4. Likewise, the aromatic C=C band was observed around 1540  $\text{cm}^{-1}$  in **4** as compared to its positon of 1559 cm<sup>-1</sup> in **3**. Also, the phenolic C–O stretching vibration observed at 1148 cm<sup>-1</sup> in 3 shifted to 1337 cm<sup>-1</sup> in 4 due to higher Ph-O bond order as a result of the loss of hydrogen from the Ph-OH donor arm. This is in line with similar observations reported in the literature for related compounds.<sup>24</sup> Furthermore, due to the high symmetry of **4** (*vide infra*), its ESI MS spectrum supports the formation of a trinuclear complex. The isotopic pattern of 4 has the signal of highest abundance at m/z = 667 which matches the dicationic [(M–Ni) - $2BF_4$ <sup>2+</sup> fragment.<sup>25</sup>

Ultraviolet-visible spectra of the ligand precursor **3** and corresponding complex **4** were measured in methanol between the range 800 to 200 nm (Fig. S8). The spectrum of **3** shows two strong absorption bands at 255 nm and 319 nm, which we assigned to the  $\pi$ - $\pi$ \* transitions of the aromatic rings and n- $\pi$ \* transitions of the imine (C=N) groups respectively.<sup>26</sup> Whilst that of the complex **4** is characterised by high energy absorption bands at 244 (sh) and 383 nm which are attributed to the O-Ni, and N-Ni ligand to metal charge transfer transitions respectively.<sup>26-27</sup> However, the expected d-d transitions, characteristic of

diamagnetic square planar complexes normally observed as weak bands at 400-600 nm for  $Ni^{2+} d^8$  ions were not observed in **4**.<sup>28</sup>

#### 2.2. Single crystal X-ray diffraction analysis of compounds 3 and 4

Colorless block crystals of **3** suitable for structural analysis by XRD were grown from acetonitrile by slow cooling of a hot solution. The SB/NHC ligand precursor crystallized in the P-1 space group of the triclinic system. The Schiff base moiety of the molecule is almost coplanar (Fig. 2) with the oxygen (O1) and nitrogen (N1) donor arms lying on the same plane, which led to intramolecular O–H---N hydrogen bonding.<sup>4a</sup>



**Fig. 2:** Thermal ellipsoid plot of the asymmetric unit of **3** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): C(2)-O(1) 1.356(2);C(7)-N(1) 1.275(3); C(8)-N(1) 1.462(3); C(8)-C(9) 1.517(3); C(9)-N(2) 1.468(3); C(12)-N(2) 1.329(3); C(12)-N(3) 1.335(3); C(13)-N(3) 1.447(3); N(2)-C(12)-N(3) 108.39(17); C(8)-N(1)-C(7) 116.96(17); O(1)-C(2)-C(1) 121.01(18); O(1)-C(2)-C(3) 119.13(17).

Similarly, yellow block crystals of **4** were obtained by slow evaporation of a methanol solution of the complex. The complex crystalized in the monoclinic P 21/n space group, with a centre of symmetry passing through the central Ni(1) in a linear arrangement of three Ni<sup>2+</sup> ions (Fig. 3).<sup>29</sup> This is in contrast to an analogous trinuclear Cu-NHC complex, in which Cu<sup>2+</sup> ions occupied the three corners of an equilateral triangle.<sup>30</sup> The trinuclear complex (**4**) consists of four tridentate SB/NHC ligands (**3**) coordinated to three square planar Ni(II) centres. There are two distinct coordination modes for the three nickel ions in **4** with the

central ion Ni(1) bound to two bridging SB moieties of **3** via their phenolate oxygen donors (O1) and imine nitrogen donors (N1) in a *trans* (ONON) coordination mode designated  $[N^O^{(Ni^{2+})}N^O]$ .<sup>31</sup>



**Fig. 3:** Thermal ellipsoid plot of the asymmetric unit of **4** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): N(1)-Ni(1), 1.916(2); Ni(1)-O(1), 1.8303(19); C(10)-Ni(2) 1.876(3); C(29)-Ni(2) 1.896(3); N(1)-Ni(1)-N(1)\*, O(1)-Ni(1)-O(1)\*180.0; O(1)-Ni(1)-N(1), O(1)\*-Ni(1)-N(1)\* 86.50(9); O(1)-Ni(1)-N(1)\*, O(1)\*-Ni(1)-N(1) 93.50(9).

Although **3** is a mixed SB/NHC ligand, all the bond lengths are within the typical values observed for salicyldo Ni(II) Schiff base complexes.<sup>31-32</sup> The bond angles involving the five central entities O(1)–Ni(1)–O(1) and N(1)–Ni(1)–N(1) are 180°, typical of perfectly square planar molecules.<sup>33</sup> On the other hand, the terminal nickel centres Ni(2) are each bound to a tridentate **3** in a C^N^O fashion and the NHC moiety (C<sub>NHC</sub>-) of respective bridging **3** to complete a four coordinate distorted square planar CNOC arrangement of donor atoms designated  $C_{NHC}$ -(Ni<sup>2+</sup>)^N^O^C<sub>NHC</sub>. The net effect of this distorted square planar arrangement is responsible for the induced paramagnetic character observed in the NMR data of **4**.<sup>34</sup> Furthermore, the observed bond lengths: 1.876 (3) for [C(10)-Ni(2)], 1.918(2) for [N(6)-Ni(2)] and 1.855(2) for [Ni(2)-O(2)] are all within values reported for similar distorted square planar compounds with paramagnetic disposition.<sup>35</sup>

#### 2.3. Catalytic transfer hydrogenation of ketones based on complex 4

The reduction of covalent bonds by CTH which utilizes protic solvents such as 2-propanol as the solvent and hydrogen donor is a very simple and convenient, yet powerful synthetic

technique. This is partly because, from a safety viewpoint, CTH is a safer alternative to the use and handle of potentially explosive hydrogen gas. These and associated environmental concerns have sustained the ever increasing worldwide interest in CTH.<sup>15c, 36</sup> In this study, complex **4** was utilized as the catalyst for initiating the transfer hydrogenation of a wide range of ketones (Table 1), beginning with the optimization of reaction conditions presented in Figs. 4 and 5.



**Fig. 4.** Influence of catalyst concentration on the conversion of acetophenone using **4**. Conditions: acetophenone (2.1 mmol); **4** (0.05-0.3 mol%); (KOH, 30 mole%, 0.112 g, 2 mmol in 10 ml isopropanol and then 3ml was used from the stock); 2-propanol (solvent, 3 mL); 4 h. Conversion determined by GC based on duplicate runs that agree within ±5%.

From Fig. 4 it is clear that the TH of acetophenone requires a combination of the catalyst **4** and the base KOH for attainment of reasonable conversion (93%) to the alcohol. A low conversion (22%) was observed with only the base KOH, an earlier study reported 66% in 18 h based on 20 mole% of KOH.<sup>37</sup> Variations in catalyst concentration established 0.1 mol% as the optimum. Detrimental effects to substrate conversion and significant decreased in conversion was observed with catalyst concentrations lower or higher than the optimum (Fig. 4).

The influence of stoichiometric quantities of various bases (KOH, NaOH, KO*t*Bu and Et<sub>3</sub>N) on the catalytic activities of **4** was also explored and the results are presented in Fig. 5.



**Fig. 5:** Base dependence of the transfer hydrogenation of acetophenone with 0.1 mol% of **4** as catalyst.

The more effective auxiliary co-catalysts are NaOH and KOH at 89 and 90% conversions respectively, while the least activity was observed with the organic bases KO*t*BU (42% conversion) and triethylamine (no conversion was recorded). This trend is consistent with the order of stability and strengths of the bases and agrees with reports indicating that strong bases are required for supporting the active species in CTH.<sup>38</sup>

We further investigated the scope and limitations of the CTH based on complex **4** and KOH by utilizing a variety of aromatic and aliphatic ketones and the results are presented in Table 1. All the aromatic ketones gave quantitative conversions to the alcohol (**5a** - **5e**) which is similar to values obtained using a more expensive Ru complex at a catalyst concentration of 0.25 mol% and 10 mol% KOH in 5h.<sup>39</sup>

**Table 1.** Scope of products in the transfer hydrogenation of ketones with complex 4 as catalyst.





<sup>a</sup> General conditions: same as Fig. 4. Catalyst **4** (0.1 mol%); <sup>b</sup> Turnover number = mole product / mole catalyst; <sup>c</sup> Turnover frequency ( $h^{-1}$ ) = mole product / (mole catalyst x time) @ 4 h; <sup>d</sup> TOF @ 0.5 h; <sup>e</sup> TOF @ 3 h.

With the substrate 1-phenyl-2-butanone (**5e**) and complex **4** as catalyst a reactivity/ time study was conducted and the profile (Fig. 6) of the results indicates that progress of the catalytic reaction is time dependent. In general, all the substrates yielded quantitative conversions to the alcohol within 4h reaction time and product **5c** provided the highest turnover frequency of  $2000 \text{ h}^{-1}$ .



Fig. 6. Time profile of product 5e. General conditions: same as in Fig. 4.

Furthermore, with the cyclic aliphatic ketones, **4** yielded 65% of 2-methyl-cyclohexanol (**5f**), 82% 4-methylcyclohexanol (**5g**) and 95% of cyclohexanol (**5h**). This order of reactivity is clearly due to steric hindrance (**5f**) and electronic deactivation by the methyl substituent to the reactive C=O bond (**5g**) as compared to **5h**. In addition, **4** effectively achieved 70 and 78% reduction of 3-methyl-2-butanone and 3-hexanone to 3-methyl-2-butanol (**5i**) and 3-hexanol (**5j**) respectively. Finally, the selective reduction of 5-hexene-2-one to 5-hexene-2-ol (**5k**) was recorded, with a conversion of 78%. Generally, these results are significant improvements for Ni in CTH when compared to a series of Ni-diamine.<sup>40</sup> In fact, it is still better than systems based on Rh(I) and Ir(I) NHC complexes under similar conditions but with 10 times the catalyst concentration (1 mol%) at extended reaction times.<sup>41</sup>

#### 3. Conclusion

In summary, we synthesized a new Schiff base functionalized NHC ligand precursor **3**, using environmentally benign (solvent free) methods. Similarly, **3** was used to synthesize the first trinuclear Ni-NHC complex **4**, using a straight forward one-pot free carbene route. Complex **4** exhibited paramagnetic character, due to distorted ligand coordination around Ni(II) centres. The molecular compositions of compounds **3** and **4** were unambiguously determined by a variety of techniques. The trinuclear complex **4** exhibited high catalytic activity in the transfer hydrogenation of both aliphatic and aromatic ketone substrates, at a low catalyst

concentration of 0.1 mol%. Significantly, a TOF of 2000 h<sup>-1</sup> was recorded for the production of 1-phenyl-2-propanol from phenyl acetone.

#### 4. Experimental

#### 4.1. General information

All reactions were performed using standard Schleck techniques under an inert atmosphere. All solvents were dried and purified using standard procedures prior to use. Glassware were dried in an oven at 120 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance-III 400 MHz spectrometer at ambient temperature with tetramethylsilane (TMS at 0.00 ppm) as internal standard. All chemical shifts are quoted in  $\delta$  (ppm) and coupling constants in Hertz (Hz). Abbreviations used for the multiplicity of the NMR signals are: s = singlet, d =doublet, t = triplet, m = multiplet, dd = doublet of doublet. Infrared spectra were recorded on a Perkin Elmer universal ATR Spectrum 100 FT-IR spectrometer. Mass spectrometry and elemental analysis (where applicable) were recorded on Waters Micromass LCT Premier TOF MS-ES<sup>+</sup> and ThermoScientific Flash2000 Elemental Analyser respectively. UV-vis was measured on Shimadzu UV-vis-NIR Spectrophotometer UV-3600. Hysteresis loop measurements for determination of saturation magnetization at room temperature were conducted on a Lakeshore 735 vibrating sample magnetometer. Thin Layer Chromatography (TLC) was carried out on Machery-Nagel polygramSil/G/UV254 pre-coated plates. Melting points analysis were recorded using an Electrothermal 9100 melting point apparatus. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

#### 4.1.1. Synthesis of the NHC/SB ligand precursor (3)

Into a clean Schleck tube charged with a stirrer bar and nitrogen gas was placed an equimolar amounts of both the Schiff base **1** (0.227 g, 1 mmol) and the corresponding substituted imidazole **2** (0.158 g, 1 mmol). The mixture was heated neat at 60 °C for 30 min, with the progress of reaction monitored using TLC. Salt **3** was isolated as a colourless solid, yield 0.378 g, 98%. mp 138–140 °C. <sup>1</sup>H-NMR (400 MHz, DMSO) 4.04 (2H, t, J = 5.5 Hz, CH<sub>2</sub>-N), 4.59 (2H, t, J = 5.5 Hz, N-CH<sub>2</sub>-), 5.42 (2H, s, CH<sub>2</sub>), 6.90 (2H, m, imidazole), 7.33 (8H, m, Ar), 7.82 (1H, d, Ar), 8.49 (1H, s, N=CH-), 9.36 (1H, s, NCHN), 12.64 (1H, s, OH). <sup>13</sup>C{<sup>1</sup>H}-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  50.79 (NC-Ar), 53.69 (NC  $\alpha$  to imine), 58.35 (C  $\beta$  to imine), 116.89, 118.32, 119.19, 121.33, 123.05, 128.88, 129.51, 129.60, 132.22, 132.48, 133.10, 133.7, 137.34 (NCN), 160.64 (OH-C, Ar), 168.97 (C=N). IR (ATR cm<sup>-1</sup>): 3400, (OH), 3095, (CH, sp<sup>2</sup>), 2930, (CH, sp<sup>3</sup>), 1631, (C=N), 1559, (C=C), 1276, (N-C-N), 1148, (C-O). ESI-MS: [M<sup>+</sup>-Br<sup>-</sup>] calculated for C<sub>19</sub>H<sub>20</sub>N<sub>3</sub>O: 306.1601, found 306.1605. CHN Anal.

Calculated for [C<sub>19</sub>H<sub>20</sub>N<sub>3</sub>OBr. 0.5H<sub>2</sub>O] C, 57.73; H, 5.35; N, 10.63 found C, 57.64; H, 5.32; N, 10.67.

#### 4.1.2. Synthesis of the trinuclear nickel complex (4)

Into a clean Schleck tube containing 0.077 g (0.2 mmol) of **3**, was added methanol (5 mL), followed by 0.09 g (0.8 mmol) of the base KO*t*Bu. The resulting mixture was stirred at room temperature for 1 h. Thereafter, NiCl<sub>2</sub> diglyme (0.04g, 0.2 mmol) was slowly added to the mixture and allowed to stir overnight. The mixture was then filtered over a bed of Celite and all volatiles removed under reduced pressure, affording the complex as yellow microcrystals. Yellow block crystals suitable for XRD were isolated after slow evaporation of a methanol solution of **4** overnight at room temperature. Yield; 0.48 g, 95% (based on **3**). mp 240–242 °C (melt); IR (ATR cm<sup>-1</sup>): 3167, (CH, sp<sup>2</sup>), 2923, (CH, sp<sup>3</sup>), 1609, (C=N), 1540, (C=C), 1338, (C-O). ESI-MS:  $[M - 2Br^- - Ni]^{2+}$  calculated for C<sub>38</sub>H<sub>37</sub>N<sub>6</sub>NiO<sub>2</sub>: 667.2331, found 667.2339.

#### 4.2. Catalytic transfer hydrogenation of ketones

Samples for catalytic study were prepared as follows: The substrate (ketone) was placed into a clean Schleck tube fitted with a reflux condenser and stir bar, followed by the addition of the nickel complex **4**, (0.1 mol %, 3.2 mg, 0.002 mmol); KOH (1 mol equivalent was dissolved in 10 mL of 2-propanol and then 3 mL of the solution was measured and carefully transferred into a Schleck tube using a syringe). The mixture was then refluxed at 82 °C for 4 h. Conversion to product was monitored using GC FID. Each aliquot was taken at a predetermined time and passed through a pad of cotton wool and then injected (0.5  $\mu$ mL) into the GC equipped with a DB1 wax polyethene column. Products were identified by comparison of their retention times with that of standards purchased from Sigma Aldrich. Percentage conversions were calculated from the respective signal peak areas.

#### 4.3. Procedure for structural determination by single crystal X-ray crystal diffraction

Suitable single crystals of **3** or **4** for X-ray analysis were carefully selected, attached onto a Mitagen loop, and centred in the X-ray beam by the aid of a video camera. Intensity data was collected on a Bruker APEXII diffractometer with Mo K $\alpha$  radiation ( $\lambda$ =0.71073Å) equipped with an Oxford Cryostream low-temperature apparatus operating at 100(1) K. The initial cell matrix was determined from three series of scans consisting of twelve frames collected at intervals of 0.5° in a 6° range with the exposure time of ten seconds per frame. Each of the three series of scans was collected at different starting angles and the APEX2 <sup>42</sup> program suite used to index the reflections and refined using SAINT. <sup>43</sup> Data reduction was performed using SAINT software, and the scaling and absorption corrections were applied using

SADABS<sup>44</sup> multiscan technique. The structures were solved by direct methods using SHELXS.<sup>45</sup> Non-hydrogen atoms were first refined isotropically and then by anisotropic refinement with full-matrix least squares based on F<sup>2</sup> using SHELXL.<sup>45</sup> All hydrogen atoms were positioned geometrically, allowed to ride on their parent atoms and refined isotropically.

#### Supplementary data

Crystallographic data of **3** and **4** in .cif format has been deposited with the Cambridge Crystallographic Data Centre, with deposition numbers CCDC 1838594-1838595 respectively. Copy of this information may be obtained free of charge from: The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or http:// www.ccdc.cam.ac.uk.

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# Transfer hydrogenation of ketones catalyzed by a trinuclear Ni(II) complex of a Schiff base functionalized N-heterocyclic carbene ligand

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Highlights:

- 1. New multidentate Schiff base-NHC ligand was synthesised.
- 2. Synthetic route to a new multinuclear Ni complex was developed.
- 3. High activity for catalytic transfer hydrogenation achieved with TOF up to 2000h<sup>-1</sup>.

4. Full characterisation of both ligand and complex achieved.

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