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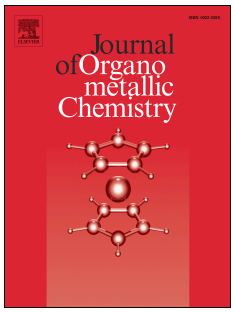


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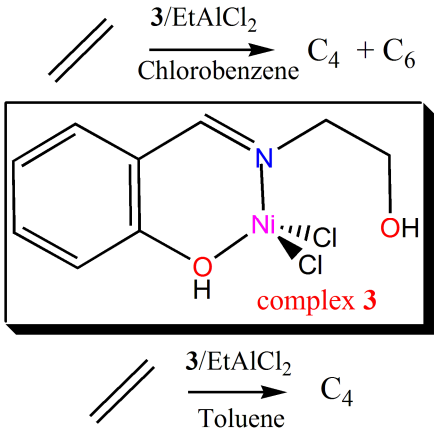

# Structural and ethylene oligomerization studies of chelated N^O (imino/amino)phenol nickel(II) complexes

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**Abstract**

Condensation reactions of 2-aminoethanol with the appropriate aldehyde gave ligands 2-[1-[(2-hydroxyethyl)imino]ethyl]phenol (**L1**) and 2-[(2-hydroxyethyl)imino] methyl]phenol (**L2**) respectively. Subsequent reductions of **L1** and **L2** with $NaBH_4$ afforded the corresponding amine ligands 2-[1-[(2-hydroxyethyl)amino]ethyl]phenol (**L3**) and 2-{[(2-hydroxyethyl)amino]methyl}phenol (**L4**). Reactions of **L1**-**L4** with either $NiCl_2$ or $NiBr_2$(DME) produced the nickel(II) complexes Ni(**L1**)$Br_2$] (**1**), [Ni(**L1**)$Cl_2$] (**2**), [Ni(**L2**)$Cl_2$] (**3**) and [Ni(**L3**)$Br_2$] (**4**) respectively. Structural elucidation of the compounds were performed using NMR, IR, mass spectrometry, elemental analyses and single crystal X-ray crystallography for complex **3**. All the nickel(II) complexes formed active catalysts in ethylene oligomerization reactions upon activation with $EtAlCl_2$ co-catalyst to afford butenes (20% - 100%) and hexenes (31% - 80%) as the major products. Higher catalytic activities of up to 11 830 kg $mol^{-1}$ $h^{-1}$ and formation of exclusively butenes were realized depending on the complex structure and reactions conditions.

**Keywords:** imine ligands; nickel; structures; ethylene; oligomerization

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## Introduction

Catalyst design constitute a great interest in the development of new late transition metal based complexes for ethylene transformation reactions.[1-2] Most research revolve around the variation of the ligand architecture in order to control the electronic and steric properties of the resulting complex.[3-7] Over the past decades, nickel complexes of range of ligands including P^O (the SHOP process),[8] N^N,[9-11] N^P,[12-14] N^N^N[15-17] and O^N[18-20] donor ligands have been applied as catalyst in olefin oligomerization reactions with varied outcomes. To date, numerous reports show nickel(II) complexes as promising olefin oligomerization catalysts due to their high catalytic activity and selectivity especially in the oligomerization of ethylene. For example, Yu *et al*,[21] reported *N*-(-2-substituted-5,6,7-trihydroquinolin-8-ylidene)arylamino nickel complexes as highly active catalysts upon activation with ethylaluminium sesquichloride in ethylene dimerization and trimerization reactions.

However, despite the progress made with nickel complexes, challenges such as balancing the catalytic activity, stability and selectivity still remain unsolved.[22] The use of hybrid ligands (N^P, N^O, N^P or N^O^P) appear to be an attractive avenue to achieve this catalytic balance due to tunable electronic effect of the catalysts in addition to conferring possible hemilibility.[4, 12, 23-24] For instance, Gao *et al*,[6] recently reported salicylaldimito N^O ligated nickel(II) complexes to as highly active ethylene polymerization catalystscatalysts. On the other hand, Zhou and his co-workers reported another series of nickel(II) complexes ligated by N,O donor ligands based on 4,6-didenzihydryl-2-[(arylimino)methyl]phenol derivatives, which exclusively dimerize ethylene to butenes.[7]

We recently reported the use of N^N-donor (imino/amino)pyridine palladium(II) and nickel(II) complexes as ethylene dimerization and oligomerization catalysts.[25-26] In order to

further investigate the role of the ligand architecture and effect of mixed donor ligands on the catalytic behaviour of these complexes, we now report the use of N^O donor nickel(II) complexes based on (imino/amino)phenol ligands as ethylene dimerization and trimerizations catalysts. The structural elucidation of these nickel(II) complexes and their catalytic behaviour towards ethylene oligomerization under various reaction conditions have been investigated and would be discussed.

**Experimental section**

*Materials and methods*

All synthetic manipulations were performed using standard Schlenk-line techniques under a nitrogen atmosphere. The solvents were obtained from Merck and dried or distilled using appropriate methods. The chemicals; 2'-hydroxy acetophenone (98%), 2-methoxy amine (99%), ethanolamine (99 %), *N*,*N*-(diethyl)ethylenediamine (99%), sodium borohydride (98%), nickel(II) bromide (98%), nickel(II) bromide-1,2-dimethoxyethane (97%) and nickel(II) chloride (98%) were obtained from Sigma Aldrich and used as received. $^{1}$H NMR and $^{13}$C {$^{1}$H} NMR (100 MHz) spectra were recorded on a 400 MHz Bruker Ultra shield NMR spectrometer in $CDCl_3$ and DMSO-$d_6$ solvents. The infrared spectra were recorded on a Perkin Elmer, Spectrometer 100. LC Premier micro-mass Spectrometer model LCMS-2020, was used for mass spectral analyses. Elemental analyses were performed on a Thermal Scientific Flash 2000. The magnetic moments were determined using Evans balance (Sherwood MK-1). Varian CP-3800 gas chromatograph equipped with a CP-Sil 5 CB (30 m x 0.2 mm x 0.25 µm) capillary column was used for GC analyses while GC-MS analyses were performed on a Shimadzu GCMS-QP2010SE.

**Syntheses of ligands and their respective nickel(II) complexes**

*2-[1-[(2-hydroxyethyl)imino]ethyl]phenol, (**L1**)*

To a solution of 2'-hydroxy acetophenone (1.50 g, 11.00 mmol) in ethanol (30 ml) was added ethanolamine (0.67 g, 11.00 mmol) and a catalytic amount of para tolyl sulfonic acid (5.00 mg) to give a light green solution which was refluxed for 24 h at 60 °C. After the reaction period, the solvent was removed under vacuum to give **L1** as light brown oil. Yield: 2.58 g (80%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta_H$/ppm: 2.37 (s, 3H, C-$CH_3$); 3.75 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz, N-$CH_2$); 3.99 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz, O-$CH_2$); 6.75 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, 6-ph); 6.92 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz 4-ph); 7.28 (dd, 1H, $^{3}J_{HH}$ = 8.0 Hz, 5-ph), 7.48 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, 3-ph). $^{13}$C{$^{1}$H} NMR ($CDCl_3$): δ/ppm: 42.6, 58.3, 63.7, 116.6, 128.3, 130.7, 133.1, 136.5, 162.4, 173.4. FT-IR ($cm^{-1}$): $\nu_{(O-H)}$: 3164; $\nu_{(O-H)}$: 2865; $\nu_{(C=N)}$:1604. TOF MS ESI: *m/z* (%), 180.1028 ($[M + H]^+$, 100%). HRMS calc for $C_{10}H_{13}NO_2$, 180.1025. Found, 180.1028

*2-[[(2-hydroxyethyl)imino]methyl]phenol (**L2**)*

Compound **L2** was synthesized following the same procedure adopted for **L1** using salicyladehyde (1.50 g, 0.01 mol) and ethanolamine (0.73 g, 0.01 mol) to give **L2** as a brown oil. Yield: 1.87 g (84%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta_H$/ppm: 3.79 (t, 2H, $^{3}J_{HH}$ = 4.0 Hz, N-$CH_2$); 3.96 (t, 2H, $^{3}J_{HH}$ = 4.0 Hz, O-$CH_2$); 6.89 (t, 1H, $^{3}J_{HH}$ = 8.0 Hz, 6-ph); 6.98 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, 4-ph); 7.28 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, 5-ph); 7.36 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, 3-ph), 8.42 (s, 1H, N=CH). $^{13}$C {$^{1}$H} NMR ($CDCl_3$): δ/ppm: 61.7, 62.1, 117.1, 118.7, 131.5, 132.5, 161.2, 166.94. FT-IR ($cm^{-1}$): $\nu_{(O-H)}$: 3353; $\nu_{(O-H)}$: 3057; $\nu_{(C=N)}$:1631. TOF MS ESI: m/z (%), 166.09 ($[M + H]^+$, 100%). HRMS for $C_9H_{11}NO_2$, 166.0868. Found, 166.0866

*2-[1-[(2-hydroxyethyl)amino]ethyl]phenol (**L3**)*

To a solution of compound **L1** (0.50 g, 2.79 mmol) in methanol (30 ml) was added $NaBH_4$ (0.54 g, 13.90 mmol) to give a clear solution which was stirred under reflux for 4 h at 50 °C. The solvent was reduced under vacuum and the residue re-dissolved in chloroform (30 ml) and washed with distilled water (3 x 20 ml) to remove excess $NaBH_4$. The organic layer was then separated and dried over $MgSO_4$, filtered and solvent removed under reduced pressure to afford **L3** as a light yellow oil. Yield: 0.16 g (32%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$/ppm: 1.51 (d, 3H, $^3J_{HH}$ = 4.0 Hz, C-$CH_3$); 2.74 (t, 2H, $^3J_{HH}$ = 4.0 Hz, N-$CH_2$); 3.79 (t, 2H, $^3J_{HH}$ = 4.0 Hz, N-$CH_2$); 4.00 (q, 1H, $^3J_{HH}$ = 4.0 Hz, N-CH); 6.80 (d, 1H, $^3J_{HH}$ = 8.0 Hz, 6-ph); 6.98 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, 4-ph), 7.15 (d, 1H, $^3J_{HH}$ = 8.0 Hz, 5-ph); 7.20 (d, 1H, $^3J_{HH}$ = 8.0 Hz, 3-ph). $^{13}$C {$^1$H} NMR ($CDCl_3$): δ/ppm: 22.4, 49.1, 58.91, 61.3, 116.8, 119.2, 126.4, 128.1, 128.4, 157.1. FT-IR ($cm^{-1}$): $\nu_{(N-H)}$: 3309; $\nu_{(O-H):}$ 3047; $\nu_{(O-H)}$: 2963. TOF MS ESI: m/z (%), 180.1023 ($[M - H]^+$, 100%), 181.1078 ($[M]^+$, 14%). HRMS calc. for $C_{10}H_{15}NO_2$, 180.1025. Found, 180.1023.

*2-{[(2-hydroxyethyl) amino]methyl}phenol (**L4**)*

Compound **L4** was prepared according to the procedure described for **L3** using **L2** (0.54 g, 3.25 mmol) and $NaBH_4$ (0.62 g, 16.25 mmol). Yield: 0.058 g (11%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$/ppm: 2.89 (t, 2H, $^3J_{HH}$ = 4.0 Hz, N-$CH_2$); 3.83 (t, 2H, $^3J_{HH}$ = 4.0 Hz, O-$CH_2$); 4.06 (s, 2H, N-$CH_2$); 6.85 (p, 2H, $^3J_{HH}$ = 8.0 Hz, 3,5-ph); 7.02 (d, 1H, $^3J_{HH}$ = 8.0 Hz, 6-ph); 7.21 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, 4-ph). $^{13}$C {$^1$H} NMR ($CDCl_3$): δ/ppm: 50.45, 52.3, 61.2, 116.4, 119.1, 12.4, 128.43, 128.8, 158.1. FT-IR ($cm^{-1}$): $\nu_{(N-H)}$: 3263; $\nu_{(O-H)}$: 3228; $\nu_{(O-H)}$: 2837. TOF MS ESI: m/z (%), 166.09 ($[M - H]^+$, 100%). HRMS calc. for $C_{11}H_{17}NO_2$, 166.0868. Found, 166.0864.

*[Ni(**L1**)$Br_2$] (**1**)*

Complex **1** was synthesized by adding a solution of [$NiBr_2$ (DME)] (0.10 g, 0.33 mmol) in dichloromethane (5 ml) to a solution of **L1** (0.12 g, 0.66 mmol) in dichloromethane (5 ml). Then the solution was allowed to stir for 24 h at room temperature to give a yellow precipitate which was filtered and washed with dichloromethane (10 ml). Yield: 0.04 g (28%). TOF MS ESI: m/z (%), 397.1000 ([M-$CH_3$], 18%). FT-IR ($cm^{-1}$): $\nu_{(O-H)}$: 3292; $\nu_{(O-H)}$: 2858; $\nu_{(C=N)}$: 1626. $\mu_{obs}$ = 3.10 BM. Anal. Calcd for $C_{11}H_{17}NO_2NiBr_2{\cdot}3H_2O$: C, 26.59, H, 4.24, N, 3.10. Found (%): C 26.58, H 4.37, N 3.26.

Complexes **2 - 5** were synthesized following procedure described for complex **1** using appropriate ligand and nickel(II) salts.

*[Ni(**L1**)$Cl_2$] (**2**)*

$NiCl_2$ (0.10 g, 0.80 mmol) and **L1** (0.15 g, 0.80 mmol). Green solid. Yield: 0.07 g (30 %). TOF MS ESI: m/z (%), 236.02 ([M - 2Cl]$^+$, 100%). FT-IR ($cm^{-1}$): $\nu_{(O-H)}$: 3307; $\nu_{(O-H)}$: 3009; $\nu_{(C=N)}$: 1630. $\mu_{obs}$ = 3.14 BM. Anal. Calcd. for $C_{10}H_{13}NO_2NiCl_2{\cdot}CH_2Cl_2$: C, 33.55; H, 3.84; N, 3.56. Found (%): C 33.23, H 3.93, N 3.81.

*[Ni(**L2**)$Cl_2$] (**3**)*

**L2** (0.22 g, 1.32 mmol) and $NiCl_2$ (0.17 g, 1.32 mmol). Recrystallization from methanol/diethyl-ether solution mixture afforded blue crystals suitable for single-crystal X-ray analysis.. Yield: 0.22g (59 %). TOF MS-ESI: m/z (%), 222.00 ([M - 2Cl]$^+$, 100%). FT-IR ($cm^{-1}$): $\nu_{(O-H)}$: 3426; $\nu_{(O-H)}$: 2922; $\nu_{(C=N)}$: 1644. $\mu_{obs}$ = 3.55 BM. Anal. Calcd. for $C_9H_{11}NO_2NiCl_2{\cdot}H_2O$: C 34.56, H 4.19, N 4.48. Found (%): C 34.92, H 4.39, N 4.02.

*[Ni(**L3**)$Br_2$] (**4**)*

Ligand **L3** (0.10 g, 0.56 mmol and [$NiBr_2$ (DME)] (0.15 g, 0.55 mmol). Blue solid. Yield: 0.20 g (90%). TOF MS ESI: m/z (%), 237.99 ([M-2Br]$^+$, 50%). FT-IR (cm$^{-1}$): $\nu_{(N-H)}$: 3237; $\nu_{(O-H)}$: 3058; $\nu_{(O-H)}$: 2837. $\mu_{obs}$ = 3.75 BM. Anal. Calcd. for $C_{10}H_{15}NO_2NiBr_2$: C, 30.05; H, 3.78; N, 3.50. Found (%): C, 30.24; H, 3.95; N, 3.28.

*[Ni(**L4**)$Cl_2$] (**5**)*

$NiCl_2{\cdot}6H_2O$ (0.12 g, 0.48 mmol) and **L4** (0.08 g, 0.48 mmol). Green solid. Yield: 0.03 g (21 %). TOF MS-ESI: m/z (%), 224.01 ([M - 2Cl]$^+$, 100%), 225.02 ([M - 2Cl]$^+$, 40 %). FT-IR (cm$^{-1}$): $\nu_{(N-H)}$: 3250; $\nu_{(O-H)}$: 3179; $\nu_{(O-H)}$: 2932. $\mu_{obs}$ = 3.58 BM. Anal. Calc. for $C_9H_{13}NO_2NiCl_2$ (%): C 36.42, H 4.41, N 4.72. Found (%): C 36.39, H 4.38, N 4.65.

*X-ray crystallography data collection*

X-ray crystallographic data collection for compound **3a** was recorded on a Bruker Apex Duo diffractometer equipped with an Oxford Instrument Cryojet operating at 100(2) K and an Incoatec microsource operating at 30 W power. Crystallographic and structure refinements data of **3a** is provided in Table 1. The data was collected with Mo Kα (λ = 0.71073 Å) radiation at a crystal-to-detector distance of 50 mm. The data collections were performed using omega and phi scans with exposures taken at 30 W X-ray power and 0.50˚ frame width using APEX2.[27] The data was reduced with the program SAINT[27] using outlier rejection, scan speed scaling, as well as standard Lorentz and polarisation correction factors. A SADABS semi-empirical multi-scan absorption correction was also applied to the data.

Direct methods, SHELXS-2014[28] and WinGX[29] were used to solve the structure. All non-hydrogen were located in the difference map and refined anisotropically with SHELXZ-2014.[28] All the hydrogen atoms were included as idealized contributors in the least squares process. Their positions were calculated using a standard riding model with C-$H_{aromatic}$ distances of 0.93 Å and $U_{iso}$ = 1.2 $U_{eq}$ and C-$H_{methylene}$ distances of 0.99 Å and $U_{iso}$ = 1.2 $U_{eq}$ and C-$H_{methyl}$ distances of 0.98 Å and $U_{iso}$ = 1.5 $U_{eq}$. The amine N-H and hydroxyl O-H hydrogen atoms were located in the difference density map and refined isotropically.

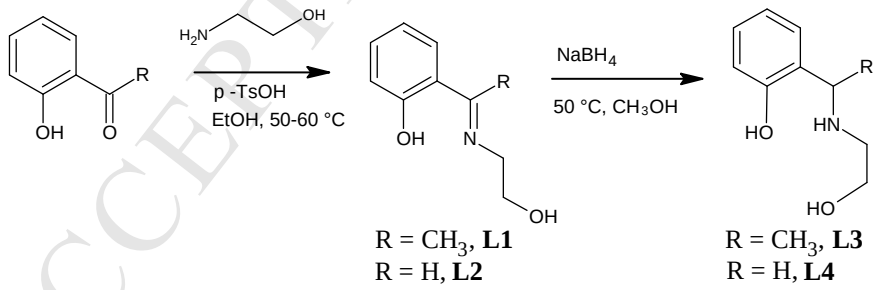
*General procedure for ethylene oligomerization reactions*

Ethylene oligomerization reactions were performed in a 400 ml stainless steel Parr reactor equipped with a mechanical stirrer, temperature controller and an internal cooling system. The reactor was pre-heated to 100 °C in *vacuo* and then cooled to room temperature. The appropriate amount of the synthesized catalyst precursor (10.0 µmol) was weighed out and transferred into a dry Schlenk tube under nitrogen and toluene (20 ml) was added utilizing a syringe. The required amount of a co-catalyst was then injected into the Schlenk tube containing the pre-catalyst. The mixture was then transferred *via* a cannula into the reactor followed by addition of 60 ml of toluene *via* a cannula to the reactor to give a total of 80 ml. The reactor was then flashed three times with ethylene and the appropriate temperature and pressure was set and the reaction started by switching the stirrer. After the reaction period, the reactor was cooled to approximately -10 °C using ice and liquid nitrogen and the excess ethylene vented off. The reaction was then quenched by the addition of 10 % hydrochloric acid (5 ml) and a portion of the reaction mixture was sampled in a GC-vial for GC and GC-MS analyses to determine the product distribution. The mass of the product formed was determined from the calibration curve of the R-factors for the standards *vs* the number of carbons[30] and using n-heptane as an internal standard.

## Results and discussion

*Syntheses of N^O ligands and their respective nickel (II) complexes*

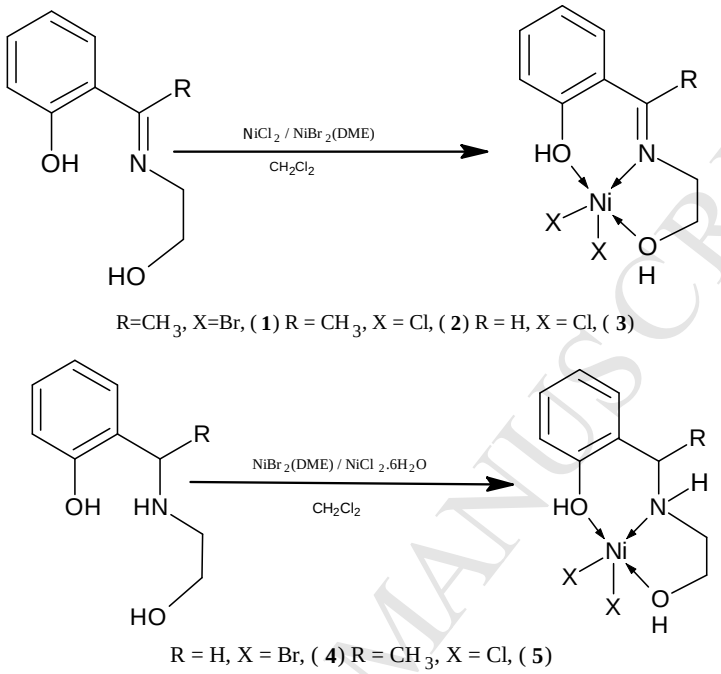
The (imine)phenol ligands **L1** and **L2** were synthesized by reacting equimolar amounts of 2-aminoethanol with 2'-hydroxy acetophenone and salicylaldehyde using para tolyl sulphonic acid as a catalyst (Scheme 1). Reductions of compounds **L1** and **L2** with $NaBH_4$ afforded the corresponding (amine)phenol ligands **L3** and **L4** respectively (Scheme 1). The imine ligands **L1** and **L2** were obtained in high yields (84% and 80%),. On the other hand, the corresponding amine compounds **L3** and **L4** were isolated in very low yields of 32% and 11% respectively, pointing to possible low efficiency of the $NABH_4$ reducing agent used. Reactions of ligands **L1-L4** with appropriate nickel(II) salts gave the corresponding nickel(II) complexes **1-5** (Scheme 2). All the complexes were isolated as hygroscopic solids in low to high yields (21%-90%).




**Scheme 1**: Synthesis of N^O donor ligands and their respective nickel(II) pre-catalysts **1**–**5**.

The compounds were characterized by a combination of $^{1}H$ and $^{13}C$ NMR spectroscopy (**L1**-**L4**), mass spectrometry, IR spectroscopy, micro-analyses and single crystal X-ray crystallography for complex **3**. As an illustration, $^{1}H$ NMR spectrum of **L2** (Fig. S1) showed a singlet peak around 8.42 ppm, which was diagnostic of the imine proton. Reduction

of **L2** to give the amine ligand **L4**, resulted in the appearance of a new signal at 4.06 ppm in the $^{1}$H NMR spectrum, consistent with the presence of an amine proton. The $^{13}$C {$^{1}$H} NMR spectra (Fig. S2) of the ligands were consistent with the $^{1}$H NMR spectral data.




**Scheme 2**: Synthesis of the N^O ligated nickel(II) complexes **1**-**5**

IR spectroscopy was also used in the structural elucidation of ligands **L1**–**L4** and their nickel(II) complexes **1**-**5**. For example, the formation of imine ligands was established from the presence of the $\nu_{(C=N)}$ signal at 1 615cm$^{-1}$ and 1 604 cm$^{-1}$ for **L1** and **L2** respectively (Fig. S3). The absence of these signals in the IR spectra of **L3** and **L4** confirmed the successful reduction of the corresponding ligands **L1** and **L2**. Formation of the nickel(II) complexes **1**-**5** was also deduced by comparing their IR spectra to those of the respective ligands. For instance, a shift of the $\nu_{(C=N)\ signals}$ from 1 615 cm$^{-1}$ in **L1** to 1 630 cm$^{-1}$ in complex **1** was observed. Similarly, the $\nu_{(O-H)}$ signals at around 3 059 cm$^{-1}$ and 3 292 cm$^{-1}$ in **L1** and its corresponding complex **1** respectively established the coordination of the phenolic O atom to nickel(II) atom; and more importantly, absence of deprotonation and coordination of the

ligands in their neutral forms. Fig. S4 shows the IR spectra of ligand **L4** and its corresponding complex **5**.

Mass spectrometry was also used to establish the identity of the ligands their corresponding complexes. For example, the mass spectrum of complex **3** showed an m/z value at 443.0172 amu formed after the loss of the two $Cl^-$ ligands and stabilization of the fragment by another ligand unit. The base peak at 222.0113 amu results from the loss of secondary ligand unit (Fig. S5). The magnetic moments of complexes **1**-**5** were obtained in the range of 3.10 – 3.76 BM. These values were slightly higher than spin only magnetic moments of 2.83 BM[31] but fall within the expected range for high spin nickel(II) complexes of 2.9-4.2 BM.[31] The elemental analyses data of complexes **1**-**5** were found to be consistent with one ligand motif per nickel(II) atom in good agreement with the proposed structures in Scheme 2.

*Solid state structure of nickel(II) complex **3a***

Single crystals suitable for X-ray analysis of complex **3a** (derivative of **3**) were grown by slow diffusion of diethyl ether into methanol solution of complex **3** at room temperature and used for its solid state structure determination. Table 1 gives a summary of the crystallographic data and structure refinement parameters, while Figure 1 represents the molecular structure and selected bond parameters for complex **3a**. The solid state structure of **3a** revealed the formation of a dinuclear species in which the coordination sphere around each nickel(II) atom contains one tridentate bound ligand unit, one terminal chloride ligand and one methanol solvent to give an octahedral arrangement. The phenolate O atom bridges the two nickel atoms, confirming deprotonation of the O-H group during crystallization. The empirical formula of the solid state structure of **3a** thus differs from that of complex **3**, which contains one ligand unit and two chloride ligands per nickel(II) center. Such transformations

have been reported in literature and relate to relative stabilities of the dinuclear and mononuclear species and may also be solvent driven. For example, the structure of **3a** compares favorably to the one reported by Dey *et al.*[32] for bis($\mu_2$-2-((2-Hydroxyethyl)iminomethyl)phenolato-N,O,O,O')-bis(acetate-O)-diaqua-di-nickel(II) complex.

**Table 1**: Crystal data and structure refinement for complex **3a**.

| **Parameter** | **Value** |
|---|---|
| Empirical formula | $C_{20}\ H_{28}\ Cl_2\ N_2\ Ni_2\ O_6$ |
| Formula weight | 580.72 g/mol |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P $2_1$/n |
| a | 8.3440(7) Å |
| b | 8.9628(7) Å |
| c | 16.4951(13) Å |
| α | 90° |
| β | 101.127(2)° |
| γ | 90° |
| Volume | 1210.41(17) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.593 $Mg/m^3$ |
| Absorption coefficient | 1.814 $mm^{-1}$ |
| F(000) | 600 |
| Crystal size | 0.520 x 0.240 x 0.150 $mm^3$ |
| Theta range for data collection | 2.517 to 28.299°. |
| Reflections collected | 10761 |
| Completeness to theta = 25.242° | 100.0 % |
| Max. and min. transmission | 0.789 and 0.446 |

| | |
|---|---|
| Data / restraints / parameters | 2994 / 2 / 154 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final R indices [I>2sigma(I)] | R1 = 0.0197, wR2 = 0.0472 |
| R indices (all data) | R1 = 0.0206, wR2 = 0.0476 |
| Largest diff. peak and hole | 0.450 and -0.281 e.$Å^{-3}$ |

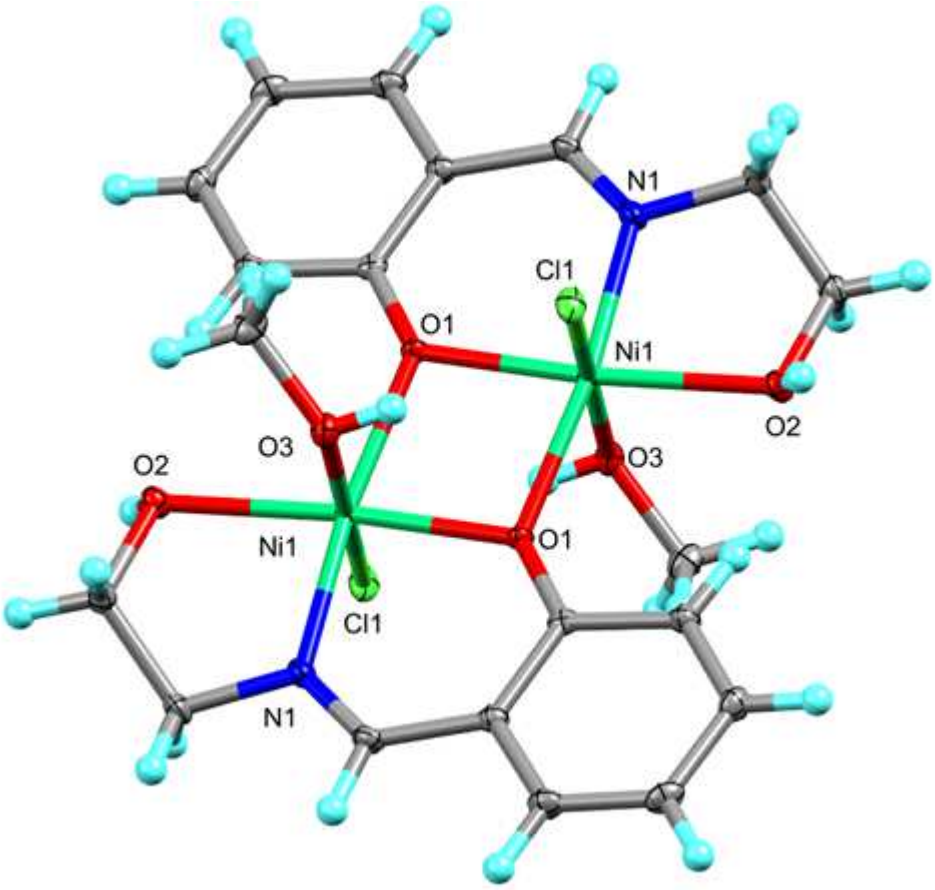



**Figure 1.** Molecular structure diagram of complex **3a** with 50 % probability ellipsoid. Selected bond lengths (Å) and angles (˚): Ni(1)-N(1), 2.0012(10); Ni(1)-O(1), 2.0619(8); Ni(1)-O(2), 2.1400(9); Ni(1)-O(3), 2.1303(9); Ni(1)-Cl(1), 2.4083(4); N(1)-Ni(1)-O(1), 91.45(4); O(1)-Ni(1)-O(1), 80.40(4); N(1)-Ni(1)-O(2), 80.65(4); O(1)-Ni(1)-O(2), 107.15(3); O(3)-Ni(1)-Cl(1), 173.20(3); O(2)-Ni(1)-Cl(1), 90.85(3).

The average Ni-O bond length of complex **3a** of 2.0619(8) Å was found to be longer than the average Ni-O bond length of 2.039 Å reported in 78 similar structures, a trend that could result due to the bridging O atom.[33] In contrast, the Ni-$N_{imine}$ bond length of 2.0012(10) Å obtained was found to be shorter than the average Ni-$N_{imine}$ bond length of 2.003 Å reported literature for 78 similar structures.[33] The selected bond angles of **3a** for O(1)-Ni(1)-O(1), N(1)-Ni(1)-O(2), O(3)-Ni(1)-Cl(1) of 80.40(4)˚ and 80.65(4)˚ respectively significantly deviate from the expected 90$^{o}$ and thus demonstrate a distorted octahedral geometry.[33]

*Catalytic behavior of nickel(II) complexes **1–5** in ethylene oligomerization reactions*

The catalytic abilities of the nickel(II) complexes **1-5** in ethylene oligomerization reactions were investigated using $EtAlCl_2$ as the activator in chlorobenzene solvent. Table 2 gives a summary of the results obtained for the nickel(II) pre-catalysts **1-5**. The ethylene oligomerization reactions predominantly produced $C_4$ and $C_6$ oligomers as the main products. The oligomeric products were characterized using a combination of GCand GC-MS (Fig. S6).

**Table 2**: Ethylene oligomerization data obtained for nickel(II) complexes **1-5** using $EtAlCl_2$.[a]

| **Entry** | **Catalyst** | **$T_{min}/T_{max}$ (°C)[b]** | **Yield (g)[c]** | **Activity (kg.mol$^{-1}$ .h$^{-1}$)[d]** | **Product distribution (%) [e]** | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | **$C_4$** | **$C_6$** | **α-$C_4$** | **α-$C_6$** |
| 1 | **1** | 25/30 | 25 | 2 500 | 27 | 73 | 85 | 91 |
| 2 | **2** | 25/27 | 26 | 2 600 | 29 | 71 | 99 | 74 |
| 3 | **3** | 25/29 | 19 | 1 900 | 31 | 69 | 87 | 75 |
| 4 | **4** | 25/26 | 20 | 2 000 | 20 | 80 | 98 | 87 |
| 5 | **5** | 25/33 | 15 | 1 500 | 22 | 78 | 93 | 86 |

[a]Reaction conditions: [Ni] =10 µmol; solvent, chlorobenzene, 80 ml (90 g); temperature, 25 °C; time, 1 h; pressure,10 bar; Al/Ni=250.

[b]Initial temperature was 25 °C, $T_{min}$ and $T_{max}$ = lowest and highest temperatures obtained during the reaction period.
[c]Determined using n-heptane as an internal standard.
d Activity, kg oligomer produced per mol catalyst per hour
[e]Determined by GC.

From Table 2, it was evident that the ligand architecture and the identity of the halides influenced the catalytic activities of the nickel(II) complexes. For instance, catalytic activities of 2 600 $kg.mol^{-1}.h^{-1}$ and 1 900 $kg.mol^{-1}.h^{-1}$ were observed for the methyl substituted and unsubstituted complexes **2** and **3** respectively (Table 2, entries 2 and 3). This can be attributed to improved solubility of complex **2** in comparison to the non-substituted complex **3**.[34] Significantly, the imine catalysts were more active compared to their amine analogues. For example, the imine and amine complexes **1** and **4** exhibited catalytic activities of 2 500 $kg.mol^{-1}.h^{-1}$ and 2 000 $kg.mol^{-1}.h^{-1}$ respectively (Table 2, entries 1 *vs* 4). This was expected due to greater electrophilicity of the imine complexes. It was also observed that the chloride complex **2** was more active than its bromide analogue complex **1**, in good agreement with the reports of Zhang *et al.*[35] using 2, 6-pyridicarboxamide nickel(II) complexes. In general, the selectivity towards the formation of $C_4$ (20%-31%) and $C_6$ (69% -80%) oligomers was not significantly affected by the ligand motif. This is reasonable from the comparable steric parameters around the nickel atom in complexes **1**-**5**.

*Investigation of the effect of reaction conditions on the catalytic behavior complex **3***

The effect of varying the reaction parameters was investigated using **3**/$EtAlCl_2$ catalyst system and the results are summarized in Table 3. Both the catalytic activities and the product distribution were significantly affected by the variation of pressure, Al/Ni ratio, time

and solvent medium. The Al/Ni ratio was varied from 150 to 300 (Table 3, entries 1 - 4) to give an optimum catalytic activity of 3 900 $kg.mol^{-1}.h^{-1}$ at Al/Ni ratio of 200. A decrease in the catalytic activity was observed at higher Al/Ni ratios of 250 and 300, which has been attributed to increased alkylaluminium impurities which might result in catalyst deactivation.[35] As the Al/Ni ratio was increased from 150 to 300, the selectivity of $C_4$ oligomer was observed to increase from 32% to 73% due to possible increased chain transfer to the co-catalyst. Another plausible explanation for increased $C_4$ oligomers at higher Al/Ni ratios could be increased chain termination arising from enhanced catalytic activity.[22]

**Table 3**. Ethylene oligomerization reactions of the **3**/$EtAlCl_2$ system[a]

| Entry | Time (h) | Pressure (Bar) | Al/Ni | Yield[b] (g) | Activity ($kg.mol^{-1}.h^{-1}$)[c] | Product Distribution (%)[d] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_4$ | $C_6$ | α-$C_4$ | α-$C_6$ |
| **1** | 1 | 10 | 150 | 29 | 2 900 | 32 | 68 | 73 | 40 |
| **2** | 1 | 10 | 200 | 39 | 3 900 | 45 | 55 | 85 | 57 |
| **3** | 1 | 10 | 250 | 19 | 1 900 | 31 | 69 | 87 | 75 |
| **4** | 1 | 10 | 300 | 17 | 1 700 | 73 | 27 | 97 | 87 |
| **5** | 0.5 | 10 | 200 | 15 | 3 000 | 62 | 38 | 84 | 49 |
| **6** | 2 | 10 | 200 | 57 | 2 800 | 33 | 77 | 91 | 72 |
| **7** | 1 | 20 | 200 | 62 | 6 200 | 66 | 34 | 88 | 69 |
| **8** | 1 | 30 | 200 | 118 | 11 800 | 78 | 22 | 90 | 75 |
| **9**[e] | 1 | 10 | 200 | 21 | 2 100 | 100 | - | >99 | <1 |

[a] Reaction conditions: [**3**]= 10 µmol; solvent, chlorobenzene, 80 ml; Temperature, 25°C.
[b] Determined using n-heptane as an internal standard.
[c] Activity, kg oligomer produced per mol catalyst per hour.
[d] Determined by Gas Chromatography.
[e] In toluene solvent;

To probe the stability of the resultant catalysts, we varied the reaction times from 0.5 h to 2 h using **3**/$EtAlCl_2$ catalyst system (Table 3, entries 2, 5 and 6). Increased catalytic activities from 3 000 kg $mol^{-1}$ $h^{-1}$ to 3 900 kg $mol^{-1}$ $h^{-1}$ with reaction time from 0.5 h to 1 h was

observed, consistent with an induction period within 1 h.[3] However, prolonged reaction times was marked by decreased catalytic activities (2 800 $kg.mol^{-1}.h^{-1}$ within 2 h), indicative of catalyst deactivation.[36] With respect to product distribution, there was a general decrease of $C_4$ oligomer with reaction time followed by a concomitant increase in the $C_6$ fraction. For instance, percentage compositions of $C_4$ of 62%, and 45% were reported at 0.5 h and 1 h respectively. This can be apportioned to chain reinsertion/$C_4$ incorporation with ethylene monomer over prolonged reaction times to give the $C_6$ oligomers.[37] As expected, variation of ethylene pressure from 10 bar to 30 bar resultant in a significant increase in catalytic activity from 3 900 $kg.mol^{-1}.h^{-1}$ to 11 800 $kg.mol^{-1}.h^{-1}$ (Table 3, entries 2 and 8 respectively). The oligomer distribution was also affected by pressure changes as seen from selectivities of $C_4$ oligomer of 33% and 78% at pressures of 10 bar and 30 bar respectively. The observed trends in selectivity of $C_4$ over $C_6$ is consistent with increased catalytic activities which subsequently results in rapid chain termination.[38]

The effect of solvent on ethylene oligomerization reactions was also investigated using **3**/$EtAlCl_2$ system in chlorobenzene and toluene solvents. The solvent used significantly affected both the catalytic activity and selectivity of complex **3**. For example, catalytic activities of 2 100 $kg.mol^{-1}.h^{-1}$ and 3 900 $kg.mol^{-1}.h^{-1}$ were obtained in toluene and chlorobenzene solvents respectively (Table 3, entries 2 *vs* 9). The higher catalytic activities observed in chlorobenzene could be attributed to improved solubility of the complex **3** in chlorobenzene. On the other hand, the use of toluene resulted in higher chemoselectivity for $C_4$ oligomer (100%) compared to compositions of 45% ($C_4$) and 55% ($C_6$) reported in chlorobenzene respectively (Table 3, entries 2 *vs* 9). While the difference in selectivities observed can be attributed to higher catalytic activities in chlorobenzene compared to toluene solvent, the drastic change is rather unusual.

## 4. Conclusion

The N^O donor imine and amine ligands and their respective nickel(II) complexes were successfully synthesized and characterized. The solid state structure of complex **3a** confirmed the formation of a dinuclear species in which the ligand is tridentate and bridges the two metal atoms *via* the phenolate O atom. The nickel(II) complexes formed active catalysts for ethylene oligomerization reactions upon activation with $EtAlCl_2$ co-catalyst to afford mainly butenes and hexenes. The catalytic activities of the nickel(II) complexes were greatly influenced by the structure of the catalyst and the reaction parameters. Higher catalytic activities resulted in lower product selectivity, while lower catalytic activities showed better selectivity of the catalysts.

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**Highlights**

- N^O donor nickel(II) complexes successfully synthesized and characterized
- Tridentate coordination and formation of dinuclear complexes established
- The nickel(II) complexes formed active catalysts for ethylene oligomerization
- The imine complexes more active than amine analogues
- Oligomeric products mains butenes and hexenes depending on reaction conditions