# Synthesis, Characterization and Ethylene Oligomerization Studies of Nickel Complexes Bearing Novel Bis-α-diimine Ligands

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Abstract Sterically modulated, diazine bridged bis- $\alpha$ diimine Ni(II) complexes have been synthesized to provide a versatile set of catalytic systems for ethylene oligomerization in combination with methyl aluminoxane (MAO) as cocatalyst. All the dinickel catalysts efficiently oligomerize ethylene to produce C<sub>4</sub>–C<sub>20</sub> fractions at activities of up to 1,123 kg-oligomer mol-Ni<sup>-1</sup> bar<sup>-1</sup> h<sup>-1</sup> at 30 °C with Al(MAO)/Ni ratio at 300. The change in potential of metal center induced by substituents, as evidenced by cyclic voltammetric measurements, influences the oligomerization activity. Complexes C1 and C3 produces traces of polyethylene at 30 °C, while at higher temperature all the complexes yielded oligomers only.

**Keywords** Binucleating ligands · Ethylene oligomerization · Methylaluminoxane · Square planar Ni(II) complex · Crystal structures

Dedicated to our teacher, Professor S.T. Nandibewoor on the occasion of his 60th birthday.

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#### 1 Introduction

The oligomerization of ethylene is the major industrial process for the production of linear  $\alpha$ -olefins, which are important reactants used in the preparation of detergents, lubricants, plasticizers, oil field chemicals, and monomers for copolymerization. Current industrial processes employ catalysts including either alkylaluminum compounds or a combination of alkylaluminum compounds and early transition metal compounds, specially, nickel(II) complexes together with bidentate monoanionic [P, O] ligands which have evidentially been proved as ideal catalysts for ethylene oligomerization (the SHOP process). But since the pioneering work by Brookhart's group on  $\alpha$ -diimino nickel complexes for high molecular weight polyethylene, interest in these  $\alpha$ -diimine systems based complexes and various derivatives thereof have arose extensively in both academic and industrial research [1-8]. These  $\alpha$ -diimine ligands form cationic complexes with late transition metal halides, which are the active catalysts in the poly/oligomerization of ethylene and other  $\alpha$ -olefins to form high molecular weight polymers. Further, their higher tolerance of polar functional groups in the monomer has been recognized as a key advantage over early transition metal catalyst systems [9-17]. The key feature of these catalytic systems is the symmetrical presence of bulky ortho-aryl substituents at the imine-nitrogen atoms, which effectively block the axial coordination sites and prevents β-hydrogen elimination, and thus retarding the rate of chain termination [4-7, 17-20]. The geometry and 3-dimensional orientation of  $\alpha$ -diimine ligand systems is also of fundamental importance as it defines the environment around the metal centers. Therefore, both electronic and steric environments of ligands are crucial in stabilizing the late transition metal ions and controlling their activity in olefin poly/oligomerizations.

In more recent years much effort has been devoted towards designing new ligand frameworks for improved catalyst performance leading to intense research focusing on discovering unique as well as more efficient catalytic systems and processes benefiting from cooperative effects between adjacent active metal centers in multinuclear complexes [21-35]. In the perspective, multinuclear group-X metal complexes serve as efficient catalysts in olefin poly/oligomerizations due to the electronic interactions found in the form of cooperative effects between metal centers. The same electronic effects cannot be expected in their mononuclear counterparts [36-39]. Steric modulations in the ligands of multinuclear group-X metal complexes affect ethylene polymerization behavior not only from the viewpoint of yield but also product distribution. Subsequently, there are few works on modified  $\alpha$ -diimine ligand systems, however, only few reports showed the use of bis- $\alpha$ -diimine ligands in the formation of active group-X metal complexes for ethylene poly/oligomerizations [40-43]. Bridged and non bridged binuclear Ni(II) complexes and bimetallic palladium(II) complexes have been studied for ethylene poly/oligomerization and have been found to oligomerize ethylene to higher olefins with remarkably high activity and selectivity [37-39, 44, 45]. Focused in developing alternative nickel complexes as unique and efficient catalytic systems for ethylene activation, benefiting from cooperative effects between adjacent active metal centers, in this work, we report the synthesis, characterization and oligomerization behaviour of three new bis-adiimine Ni(II) complexes of the type [Ni<sub>2</sub>(bis-α-diimine)Cl<sub>4</sub>], which are sterically modulated by varying the substitutions at the 2,6-aryl position. These bis- $\alpha$ -diimine ligands are derived from simple azine scaffold-based ketimines, in order to study the influence of different steric



Scheme 1 Catalyst precursor under investigation for ethylene oligomerization. The part enclosed under *rectangle* represents Brookhart's type core

effects and electron densities at the metal centers (Scheme 1) and their behaviour towards oligomerization of ethylene with methyl aluminoxane (MAO) as co-catalyst.

### 2 Experimental

#### 2.1 General Considerations

All manipulations involving air-sensitive materials were performed under a purified nitrogen atmosphere using Schlenk techniques. Dichloromethane was distilled from calcium hydride; toluene and hexane were distilled from sodium. All reagents used in this study were purchased from Sigma-Aldrich and used without further purification. MAO solution (10 %) in toluene was purchased from Sigma-Aldrich to be used directly without any treatment.

Metal and chloride contents were estimated according to standard methods [46]. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 500 MHz and 100 MHz spectrometer respectively, in DMSO- $d_6$  or CDCl<sub>3</sub> at room temperature using TMS as internal reference. IR spectra were recorded in a KBr disc matrix using an Impact-410 Nicolet (USA) FTIR spectrometer over the range of 4,000–400 cm<sup>-1</sup>. The electronic spectra were measured on a Hitachi 150-20 spectrophotometer over the range of 1,000–200 nm. TG and DTA measurements were recorded in nitrogen atmosphere on a Universal V2.4F TA instrument using a final temperature of 1,000 °C and heating rate of 20 °C/min. All of the olefin estimations were monitored by gas chromatography equipped with FID detector using an HP-5 column.

#### 2.2 Synthesis of Ligands (L1-L3)

A 50 ml round bottom flask was charged with (2.73 g, 22.7 mmol) 2,6-dimethylaniline, (1.96 g, 22.7 mmol)/ (3.4 g, 22.7 mmol) 2,6-diethylaniline/(4.03 g, 22.7 mmol) 2,6-diisopropyllaniline, 2,3-butanedione, ethanol (20 mL) and glacial acetic acid (0.4 mL). The pale yellow solution was stirred for 36 h at room temperature without isolation of the product. The completeness of the reaction was monitored by TLC by the consumption of reactants. Then, hydrazine hydrate (0.55 mL, 11 mmol) in 10 mL ethanol was added drop wise with stirring. After few hours yellow solid began to separate. The mixture was further stirred overnight. The yellow precipitate was isolated by filtration, washed with  $2 \times 10$  mL ethanol, and dried in vacuum. Slow evaporation of ethanolic solution yielded yellow colored crystals of L1 and L3 suitable for X-ray diffraction analysis. Schematic representation for the synthesis of ligands and numbering pattern for NMR assignment is given in Scheme 2.

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### 2.2.1 2,6-Dimethyl-phenyl-{1-methyl-2-[(1-methyl-2methylimino-propylidene)-hydrazono]-propylidene}amine (L1)

Yield: 70% Anal. Calc. for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub> (%): C, 76.97; H, 8.07; N, 14.96. Found (%): C, 76.95; H, 8.06; N, 14.99. IR cm<sup>-1</sup>: 1628, (C=N), 2963, (CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 2.008 (s, 12H, Benz–CH<sub>3</sub>), 1.992 (s, 6H, methyl, C10H<sub>3</sub> and C11H<sub>3</sub>), 2.204 (s, 6H, methyl, C7H<sub>3</sub> and C14H<sub>3</sub>), 7.06 (d, 4H, *J*=7.5 Hz, C3H, C5H, C17H and C19H), 6.93 (t, 2H, *J*=7.5 Hz, C4H and C18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 166.04 (–*C*8N1 and –*C*13N4), 156.19 (–*C*9N2 and –*C*12N3), 123.10 (*C*4H and *C*18H), 124.83(*C*5H, *C*3H, *C*17H and *C*19H), 127.89 (*C*2H, *C*6H, *C*16H and *C*20H), 148.33(*C*1H and *C*15H), 17.87 (Benz–CH<sub>3</sub>), 15.65 (–*C*7H<sub>3</sub> and –*C*14H<sub>3</sub>), 12.85 (*C*10H<sub>3</sub> and *C*11H<sub>3</sub>).  $\lambda_{max}$  (nm): 255, 370. *m/z*: 374.

## 2.2.2 2,6-Diethyl-phenyl-{1-methyl-2-[(1-methyl-2methylimino-propylidene)-hydrazono]-propylidene}amine (L2)

Yield, 60 %. Anal. Calc. for  $C_{28}H_{38}N_4$  (%): C, 78.10; H, 8.89; N, 13.01. Found (%): C, 78.13; H, 8.87; N, 13.0. IR cm<sup>-1</sup>: 1630, (C=N), 2963, (CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.170 (t, 12H, *J*=7.5 Hz, CH<sub>2</sub>–CH<sub>3</sub>), 2.035 (s, 6H, methyl, C10H<sub>3</sub> and C11H<sub>3</sub>), 2.239 (s, 6H, methyl, C7H<sub>3</sub> and C14H<sub>3</sub>), 2.367 (q, 8H, *J*=7.5 Hz, CH<sub>2</sub>–CH<sub>3</sub>), 7.127 (d, 4H, *J*=7.5 Hz, C3H, C5H, C17H and C19H), 7.050 (t, 2H, *J*=7.5 Hz, C4H and C18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 165.82 (–C8N1 and –C13N4), 156.43 (–C9N2 and –C12N3), 123.48 (C5H, C3H, C17H and C19H), 125.98 (C4H and C18H), 130.63 (C2H, C6H, C16H and C20H), 147.39 (C1H and C15H), 24.62 (CH<sub>2</sub>–CH<sub>3</sub>), 16.02 (–C7H<sub>3</sub> and –C14H<sub>3</sub>), 13.67 (CH<sub>2</sub>–CH<sub>3</sub>), 12.80 (C10H<sub>3</sub> and C11H<sub>3</sub>).  $\lambda_{max}$  (nm): 256, 376. *m/z*: 430.

## 2.2.3 2,6-Diisopropyl-phenyl-{1-methyl-2-[(1-methyl-2methylimino-propylidene)-hydrazono]-propylidene}amine (L3)

Yield, 75 %. Anal. Calc. for  $C_{32}H_{46}N_4$  (%): C, 78.96; H, 9.53; N, 11.51. Found (%): C, 78.91; H, 9.57; N, 11.52.

IR cm<sup>-1</sup>: 1632, (C=N), 2963, (CH<sub>3</sub>), <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.186 (dd, 24H, J=4.5, 7 Hz, CH( $CH_3$ )<sub>2</sub>), 2.052 (s, methyl, 6H, C10 $H_3$  and C11 $H_3$ ), 2.259 (s, 6H, methyl, C7 $H_3$  and C14 $H_3$ ), 2.691 (sep, 4H, J=7 Hz, CH(CH<sub>3</sub>)), 7.186 (d, 4H, J=7.5 Hz, C3H, C5H, C17H and C19H), 7.116 (t, 2H, J=7.5 Hz, C4H and C18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 165.91(-C8N1 and -C13N4), 156.74 (-C9N2 and -C12N3), 122.96 (C5H, C3H, C17H and C19H), 123.73 (C4H and C18H), 135.20 (C2H, C6H, C16H and C20H), 146.08 (C1H and C15H), 28.31 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.11 (CH(CH<sub>3</sub>)<sub>2</sub>), 16.33 (-C7H<sub>3</sub> and -C14H<sub>3</sub>), 12.88 (C10H<sub>3</sub> and C11H<sub>3</sub>).  $\lambda_{max}$  (nm): 256, 370. m/z: 486.

### 2.3 Preparation of Complexes

A 50 mL round bottom flask was charged with 0.55 g (2.5 mmol) NiCl<sub>2</sub>(DME), to which a solution of 0.44 g (1.18 mmol) of **L1**/0. 508 g (1.18 mmol) of **L2**/0.58 g, (1.18 mmol) of **L3**, in 30 ml dichloromethane was added under an inert nitrogen atmosphere. The resulting red/ brown mixture was stirred at room temperature over night. Then the mixture was filtered to remove the unreacted NiCl<sub>2</sub>(DME) to give a clear red/brown solution which yielded a red/brown solid by removing the dichloromethane under reduced pressure. The solid product was washed with  $3 \times 10$  mL hexane, and then dried in vacuum. Schematic representation for the synthesis of complexes and numbering pattern for NMR assignment is given in Scheme 3.

# 2.3.1 2,6-Dimethyl-phenyl-{1-methyl-2-[(1-methyl-2methylimino-propylidene)-hydrazono]-propylidene}amine dinickel(II) chloride (C1)

Yield: 64 %. Anal. Calc. for  $C_{24}H_{30}Cl_4N_4Ni_2$  (%): C, 45.49; H, 4.77; N, 8.84; Ni, 18.52; Cl, 22.38. Found (%): C, 45.51; H, 4.75; N, 8.84; Ni, 18.56; Cl, 22.34. FTIR cm<sup>-1</sup>: 1611, (C=N), 2963, (CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.988 (s, 12H, Benz–CH<sub>3</sub>), 2.263 (s, 6H, methyl, C10H<sub>3</sub> and C11H<sub>3</sub>), 2.361 (s, 6H, methyl, C7H<sub>3</sub> and C14H<sub>3</sub>), 7.095, (d, *J*=7.5 Hz, 4H, C3H, C5H, C17H and C19H), 6.992, (t, *J*=7.5 Hz, 2H, C4H and C18H).  $\lambda_{max}$  (nm): 255, 370, 427. ESI mass, *m/z*: 632.2 [M], 596.3 [M–Cl]

Scheme 3 Synthetic routes for the preparation of sterically tuned dinickel(II) complexes derived from bis-α-diimine ligands



## 2.3.2 2,6-Diethyl-phenyl-{1-methyl-2-[(1-methyl-2methylimino-propylidene)-hydrazono]-propylidene}amine dinickel(II) chloride (C2)

Yield: 70%, Anal. Calc. for  $C_{28}H_{38}Cl_4N_4Ni_2$  (%): C, 48.75; H, 5.55; N, 8.12; Ni, 17.02; Cl, 20.56. Found (%): C, 48.73; H, 5.54; N, 8.14; Ni, 17.04; Cl, 20.56. FTIR cm<sup>-1</sup>: 1619, (C=N), 2963, (CH<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.16 (t, *J*=7.5 Hz, 12H, CH<sub>2</sub>-CH<sub>3</sub>), 2.129 (s, 6H, methyl, C10H<sub>3</sub> and C11H<sub>3</sub>), 2.291 (s, methyl, 6H, C7H<sub>3</sub> and C14H<sub>3</sub>): 2.342, (m, 8H, CH<sub>2</sub>-CH<sub>3</sub>), 7.129, (d, *J*=7.5 Hz, 4H, C3H, C5H, C17H and C19H), 7.092, (t, *J*=7.5 Hz, 2H, C4H and C18H).  $\lambda_{max}$  (nm): 255, 370, 417. ESI mass *m/z*: 689.9 [M], 654.4 [M–CI].

### 2.3.3 2,6-Diisopropyll-phenyl-{1-methyl-2-[(1-methyl-2methylimino-propylidene)-hydrazono]-propylidene}amine dinickel(II) chloride (C3)

Yield: 70% Anal. Calc. for  $C_{32}H_{46}Cl_4N_4Ni_2$  (%): C, 51.55; H, 6.22; Cl, 19.01; N, 7.51; Ni, 15.74. Found (%): C, 51.53; H, 6.20; Cl, 19.03; N, 7.54; Ni, 15.73. IR cm<sup>-1</sup>: 1620, (C=N), 2963, (CH<sub>3</sub>), <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.15 (d, *J*=7 Hz, CH(*CH*<sub>3</sub>)<sub>2</sub>), 2.022 (s, 6H, methyl, C10*H*<sub>3</sub> and C11*H*<sub>3</sub>), 2.229 (s, 6H, methyl, C7*H*<sub>3</sub> and C14*H*<sub>3</sub>):, 2.660, (m, 4H, C*H*(CH<sub>3</sub>)), 7.105, (d, *J*=7.5 Hz, 4H, C3*H*, C5*H*, C17*H* and C19*H*), 7.162, (t, *J*=7.5 Hz, 2H, C4*H* and C18*H*).  $\lambda_{max}$  (nm): 255, 370, 426. *m/z*: 745.9 [M], 710.4 [M–Cl].

### 2.4 Olefin Oligomerization Activity

Ethylene oligomerization experiments were performed in a 250 mL round bottom flask equipped with a magnetic stirrer and a thermometer [47–49]. After addition of the nickel complex (C1–C3), the reactor was charged with toluene (60 mL) via syringe and immersed in a thermostat to acquire constant temperature previously set to a temperature of 30 °C. When the reactor was equilibrated to the thermostat temperature, ethylene gas was pressurized into the reactor (1.3 bar) after removing the prefilled nitrogen gas under reduced pressure. When no more absorption of ethylene into toluene was observed, a prescribed amount of

MAO was injected into the reactor and oligomerization commenced. The oligomerization rate was determined every 0.01 s from the rate of ethylene consumption, measured by a hotwire flow meter connected to a computer through an A/D converter. Oligomerization was quenched by the addition of methanol containing hydrochloric acid (5 v/v %), the resulting mixture was passed through an alumina column to remove cocatalyst species and the obtained oligomers were analyzed by GC. The rate of ethylene consumption was directly obtained from the computerized experimental set up and is expressed as in terms of gram-product mol-Ni<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup> [48, 49].

### **3** Results and Discussion

## 3.1 General Characterization and Electrochemistry of the Bis-α-diimine Ligands and Their Ni(II) Complexes

The elemental analyses of all the complexes C1–C3 are consistent with the proposed structures with 2:1 metal– ligand stoichiometry. Comparing the FTIR spectra of bis- $\alpha$ -diimine ligands and their respective Ni(II) complexes gives an idea about the coordination mode of the ligands to the Ni(II) metal ion. The FTIR spectra of all three ligands, L1–L3 exhibit characteristic intense broad band at around 1,630 cm<sup>-1</sup>, which can be assigned to azomethine functionality. Upon metallation, this band is shifted to lower frequency by 10–20 cm<sup>-1</sup> in the spectras of corresponding Ni(II) complexes C1–C3, indicating the involvement of azomethine nitrogen atoms in the coordination. The methyl and aromatic C–H stretching frequencies are observed at around 2,960 and 3,000 cm<sup>-1</sup> in all the compounds.

The acquisition of <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ligands supports their respective structures. The <sup>1</sup>H NMR spectra of bis- $\alpha$ -diimine ligands **L1–L3** consisted of a series of well resolved peaks. The numbering scheme for the assignment of carbons and corresponding protons is given in Scheme 2, detailed chemical shift values for all the carbon and protons are given in experimental section. The protons of the two methyl groups attached to the azine fragment in the ligands **L1–L3** resonated as singlets in the

range 1.992–2.052 and 2.204–2.259 ppm respectively. The methyl/ethyl/isopropyl signals of all the ligands are found in expected ranges in their <sup>1</sup>H NMR spectra and are detailed in experimental section. The aromatic signals in all the ligands were observed in the expected region, ranging 7.06–7.186 and 6.93–7.116 respectively.

The <sup>13</sup>C NMR spectral analyses agreed with the <sup>1</sup>H NMR spectral data in demonstrating the architecture of the azine-scaffold-based binucleating ligands **L1–L3**. In the <sup>13</sup>C NMR spectra of ligands **L1–L3**, the signal observed around ~166 ppm is due to azomethine carbon (linkage between aniline and the one side of 2,3-butanedione), at the lowest downfield position of the carbon atoms. Another signal around ~156 ppm in the spectra of ligands was assigned to the azomethine carbon (linkage between two 2,3-butanedione molecules). The appearance of these two signals additionally confirms the successful formation of the bis- $\alpha$ -diimine ligands.

The <sup>1</sup>H NMR of the complexes, **C1–C3** showed downfield shifts of signals compared to respective free ligands **L1–L3**. The two methyl groups attached to the azine fragment in the complex **C1–C3** resonated as singlets in the range 2.022–2.263 and 2.229–2.361 ppm respectively, showing shifts to downfield region and suggesting the coordination through azomethine nitrogen. The methyl/ ethyl/isopropyl signals of all the complexes have again been shifted to downfield region as expected and are detailed in experimental section. The aromatic signals in all the complexes were observed in the region 6.992–7.102 ppm.

Electronic spectra of all the compounds L1-L3 and C1-C3 were recorded in their dichloromethane solution over the scan range 200-800 nm. Electronic spectral data of bis- $\alpha$ -diimine ligands L1–L3 are very similar to each other due to their structural similarity. The electronic absorption spectra of all ligands exhibit a strong band at around 250 nm assignable to  $\pi \rightarrow \pi^*$  and weak band around 380 nm corresponds to  $n \rightarrow \pi^*$  transitions associated with azomethine linkage [50, 51]. The electronic absorption spectral data of the dinickel(II) square planar complexes C1–C3 are also similar since they differ only in substituents on phenyl ring at ortho-aryl position and these do not alter the coordination mode of the ligands. The spectral profiles below 380 nm are similar and are ligand centered transitions (intraligand  $\pi - \pi^*$  and  $n - \pi^*$ ) of benzene and non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base complexes. Since these complexes are diamagnetic, the bands at around 390–445 nm could be assigned to  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  transition consistent with square-planar nickel(II) complexes [50, 51]. UV–Vis spectra are shown in Fig. 1.

The mass spectra of bis- $\alpha$ -diimine ligands, L1–L3 show molecular ion peaks at 374, 430 and 486 respectively, corresponding to their molecular weights. The ESI mass

spectra of complexes, C1–C3 show molecular ion peak with m/z values at 632.2, 689.9 and 745.9 respectively. These values are in good agreement with the proposed composition for the complexes. Further, the complexes C1–C3 also show the fragmentation peak corresponding to [M–C1] at 596.3, 654.4 and 710.4 respectively.

Thermal studies of dinickel(II) complexes were undertaken in order to study their thermal stability and as supportive data for the proposed molecular formulae. The dinickel(II) complexes C1-C3 are hygroscopic and on exposure to atmosphere absorb moisture which is observed in the thermogram of these complexes as weight loss corresponding to water molecules at 65-75 °C. This is further confirmed by the appearance of endothermic signal at the same temperature range for complexes C1-C3. The weight loss of around 55-60 % for complexes C1-C3, in the region of 150-450 °C corresponds to simultaneous decomposition of ligands and elimination of four coordinated chlorine atoms as HCl. The elimination of chlorine atoms is an exothermic process and as expected, is observed as exothermic DTA signal in the range 250-270 °C. The plateau obtained after heating complexes above 500 °C accounts for the formation of stable metal oxides.

The cyclic voltammetric experiments of the free ligands and their Ni(II) complexes were performed at room temperature in DMSO under  $O_2$  free conditions in the potential range -1.0 to +1.0 V, using a glassy carbon working electrode (0.082 cm<sup>2</sup>), a platinum counter electrode and an Ag/Ag<sup>+</sup> reference electrode. The electrochemical studies of the free ligands showed no electrochemical response within the similar working potential range. Therefore, the observed electrochemical responses in the cyclic voltammograms (CVs) of the complexes **C1–C3** are purely due to the presence of metal centers. CVs of the complexes are shown in Fig. 2.

A one-electron quasi-reversible redox behavior for each Ni(II) ion is observed in the CVs of the complexes C1-C3. The oxidation potentials for all the Ni(II) catalysts are in the range -0.15 to 0.05 and 0.35 to 0.5 V at a scan rate of  $0.1 \text{ V s}^{-1}$  differing only slightly from each other, and shift to higher potentials with an increase in scan rate. Correspondingly, in the reverse scan, two reduction waves appear which can be attributed to the reduction of one Ni(III) per wave. The reduction potentials are in the region 0.025 to 0.25 and -0.05 to -0.25 mV, and with increasing scan rate shifts towards more negative potentials. For the complex C3, the separation between the anodic and cathodic peak potentials,  $\Delta Ep = Epa - Epc$  was found to be 200 and 350 mV. For C2,  $\Delta$ Ep was 80 and 300 mV and for C1,  $\Delta$ Ep was found to be 75 and 275 mV. Overall, the difference between the anodic and cathodic peak potentials  $(\Delta Ep)$  is more than 58 mV. This suggests one electron



Fig. 1 UV-Vis spectra of ligands L1-L3 and complexes C1-C3



Fig. 2 Cyclic voltammograms of complexes C1–C3, at scan rate  $0.1 \ \mathrm{Vs}^{-1}$ 

transfer quasi-reversible redox process assignable to the Ni(II)/Ni(III) couple, for each Ni(II) ion. The oxidation and corresponding reduction reactions obey the diagnostic criteria, i.e., Ipc/Ipa is almost constant but not unity for a quasi-reversible electron transfer [52–54]. The stepwise nickel-based redox processes of the catalysts can be assigned as shown in Eqs. 1 and 2.

Oxidation: Ni(II), Ni(II) - 
$$e^- \rightarrow Ni(III)$$
, Ni(II)  
-  $e^- \rightarrow Ni(III)$ , Ni(III) (1)

Reduction: Ni(III), Ni(III) + 
$$e^- \rightarrow Ni(II)$$
, Ni(III)  
+  $e^- \rightarrow Ni(II)$ , Ni(II) (2)

Although the two Ni(II) ions in complexes, C1–C3 are in the same chemical environments, the overall twoelectron transfer process appear as separate one-electron processes, indicating that oxidation/reduction at one site is influenced by the steric and electronic factors on the other site, and hence induces a positive/negative shift in the oxidation/reduction potential of the metal ion. The shift in CVs of complexes C1–C3 is due to the perturbation on the nickel center caused by substituents at 2,6-positions. These result strongly supports the influence of these substituents on nickel center and hence the oligomerization activity. This redox mechanism can be explained in terms of the flexibility and size of the coordination cavity in these catalysts, in addition to the geometric requirements and the size of the nickel ions in different oxidation states.

#### 3.2 Crystallographic Studies of L1 and L3

The X-ray diffraction data were collected using a Bruker SMART APEX2 CCD area-detector diffractometer. The structures were solved by direct methods, and refined by full-matrix least-square on  $F^2$ . Each hydrogen atom was placed in a calculated position, and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed using SHELXL-97 package [55].

The single crystal X-ray structure of bis-α-diimine ligand L1  $[C_{36}H_{45}N_6]$  was unambiguously determined at 296 K and was shown to be monoclinic space group P 1 21/n 1, with a = 18.4500(6) Å, b = 6.1307(2) Å, c = 30.3580(10) Å,  $\beta = 94.183(2)^{\circ}$ , volume = 3424.69(19) Å<sup>3</sup>. Details of the data collection and refinements are given in Table 1. Selected bond lengths, torsion angles and bond angles are given in Tables 3, 4 and 5 respectively (in Supplementary data). A perspective view of the ligand is shown in Fig. 3 showing 50 % probability ellipsoids. The asymmetric unit of the compound crystal shows two independent ligand molecules A and B. The C–C bond distances (1.38 Å) and C–C–C bond angles (120°) of pendent phenyl rings are comparable with similar reported structures [37-39]. [N2A=C11A, N3A=C14A and C15A=N4A [1.275(4), 1.274(4) and 1.270(4) Å respectively] bond distances in molecule A are comparable with reported structures [37-39] and show slight deviation with respect to molecule B where N=C [N2B=C11B, N1B=C10A and C6B=N1B [1.275(4), 1.271(4) and 1.419(4) Å respectively] agrees well with the values for double bond character, confirming the formation of bis-imine bonds [37-39]. Bond angles C6A-N1A- $C10A = 121.0(3)^{\circ}, C11A-N2A-N3A = 117.7(3)^{\circ} C15A-$ N4A-C23A 121.0(3)° and C24A-C23A-N4A =  $119.6(4)^{\circ}$ 

Table 1 Crystal data and structure refinement details for bis- $\alpha$ -diimine ligands L1 and L3

Crystal Data	L1	L3 C <sub>32</sub> H <sub>46</sub> N <sub>4</sub>			
Empirical formula	C <sub>36</sub> H <sub>45</sub> N <sub>6</sub>				
Formula mass	561.78	490.76			
Crystal size (mm)	$0.45 \times 0.32 \times 0.21$	$0.40 \times 0.35 \times 0.35$			
Crystal system	Monoclinic	Triclinic			
Space group	$P_{2_1}/n$	P-1			
a(Å)	18.4500(6)	10.0113(4)			
$b(\text{\AA})$	6.1307(2)	12.5354(5)			
$c(\text{\AA})$	30.3580(10)	13.4582(5)			
$\alpha(^{\circ})$	90	66.076(2)			
β(°)	94.183(2)	84.287(3)			
γ(°)	90	82.065(3)			
Volume [pm3 $\times$ 106]	3424.69 (19)	1527.29 (10)			
Z	4	2			
$D_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.090	1.067			
$\mu$ (cm <sup>-1</sup> ) (Mo $K_{\alpha}$ )	0.71073	0.063			
Temperature (K)	296 (2)	296 (2)			
Index range					
h	$-16 \rightarrow 16$	$-11 \rightarrow 12$			
k	$-5 \rightarrow 5$	$-15 \rightarrow 15$			
l	$-27 \rightarrow 27$	$16 \rightarrow 16$			
Reflections collected	22771	22161			
Unique reflections $(R_{int})$	2263 (0.0308)	5497 (0.0582)			
Reflections with $F_{\rm o} > 4\sigma(F_{\rm o})$	2776	2713			
Number of parameters	380	337			
$R_1$	0.0537	0.0734			
$wR^2$ (all data)	0.1687	0.2467			
Max. and min. residual density ((e $pm^{-3}) \times 10^{-6}$ )	0.216, -0.180	0.389, -0.236			

are comparable with the reported values for analogous compound [37–39] and corresponding angles in the molecule B are also in agreement with the literature values. The torsion angles [72.17°] between the two planes [C10A–C11– N2–H9A2] and [C1A–C2A–C3A–C4A–C5A–C6A], suggests that the phenyl rings of the molecule are almost perpendicular to the azine fragment, due to which the ligand is non-planar in nature. The torsion angle 172.3(3) exhibited by N1A–C10A–C11A–N2A and -8.0(5) by C9A–C10A– C11A–N2A indicates that N1A and N2A atom are *trans*, and N2A and C9A are *cis* to each other., 166.9(3)° by N3A– C14A–C15A–N4A and -13.8(5) N3A–C14A–C15A–C16 A indicates that N3A and N4A atom are *trans* to each other and N3A and C16A are *cis* to each other.

The single crystal X-ray structure of bis-α-diimine ligand L3 was unambiguously determined at 296 K and was shown to be triclinic space group P-1, with a = 10.0113(4) Å, b = 12.5354(5) Å, c = 13.4582(5) Å,  $\beta = 84.287(3)^{\circ}$ , volume = 1527.29(10) Å<sup>3</sup>. Details of the data collection and refinements are given in Table 1. Selected bond lengths, torsion angles and bond angles are given in Tables 3, 4 and 5 respectively. A perspective view of the ligand is shown in Fig. 4 showing 50 % probability ellipsoids. In the compound crystal, the C-C bond distances (1.38 Å) and C-C-C bond angles (120°) of pendent phenyl rings are in accordance with the values reported in literature [37-39]. The bond distances of N4-C8, N3-C7, N2-C6 and N1-C5 [1.271(3), 1.279(3), 1.274(3), and 1.274(3) Å respectively] agrees well with the values for double bond character, confirming the formation of bis-imine bonds [37-39]. The torsion angle  $167.41(13)^{\circ}$ exhibited by N1-C5-C6-N2 and -12.33(13)°by N1-C5-C6-C17 indicates that N1 and N2 atom are trans, and N1 and C17 are *cis* to each other. Similarly, the torsion angle for N4–  $C7-C8-N3 = 173.15(2)^{\circ}$  clearly shows that N4 and N3 are trans to each other. A close look at the torsion angles [69.78°]



Fig. 3 ORTEP projection of bis-α-diimine ligand L1 showing 50 % probability ellipsoids

Fig. 4 ORTEP projection of bis- $\alpha$ -diimine ligand L3 showing 50 % probability ellipsoids



Table 2 Results of ethylene oligomerization with dinickel(II) complexes C1-C3 combined with MAO at 30 and 50 °C

Entry	Catalyst	Temperature (°C)	Activity $R_p^a$	Distribution of olefins (%) <sup>b</sup>						
				$C_4$	$\alpha$ -C <sub>4</sub>	C <sub>6</sub>	C <sub>8</sub>	C <sub>10</sub>	C <sub>12-20</sub>	Polymer
1	C1	30	662.2	76.3	87.0	12.2	6.3	2.1	3.1	_
2	C2	30	889.6	70.3	28.4	15.6	8.9	3.2	Wax	Trace
3	C3	30	1,123.4	85.1	60.4	4.7	4.1	3.1	3.0	Trace
4	C1	50	371.7	77.2	45.5	13.5	4.8	3.1	Wax	-
5	C2	50	439.7	67.8	13.7	20.2	5.8	4.0	2.2	-
6	C3	50	530.0	78.4	24.7	12.2	6.1	2.4	Wax	-

Conditions: catalyst = 5  $\mu$ mol; [MAO]/[Ni] = 300; toluene solvent = 60 mL; PC<sub>2</sub>H<sub>4</sub> = 1:3 bar; reaction time = 30 min

<sup>a</sup> Rate of oligomerization in kg-oligomer mol-Ni<sup>-1</sup> bar<sup>-1</sup> h<sup>-1</sup>

<sup>b</sup> Determined by GC using calibration curves with standard solutions

between the two planes [C9, C10, C13, C14, C15, C29] and [C8, C7, N3, N2 C6, C5, N1], suggests that the phenyl rings of the molecule are perpendicular to the azine fragment, due to which the ligand is non-planar in nature.

### 3.3 Ethylene Oligomerizations

Numerous attempts have been made in Schiff-base derived dinickel(II) and their alkyl/aryl-substituted counterparts to obtain exceptionally good activity in olefin oligomerization. This is with the hope that the dinuclear catalysts would be more tolerant to simple monomers as well as functionalized monomers, which is a highly desirable property due to the cooperative effect that exists between the metal centers. Especially, when high molecular weight polymers are targeted, the nature of the cooperative effect between metal centers, steric control, nature of the monomer and cocatalyst become crucial. In this perspective, we have designed a series of sterically tuned dinickel(II) complexes, which mimic the Brookhart catalyst for ethylene oligomerization. For ethylene oligomerization



**Fig. 5** Ethylene consumption rate curves of dinickel(II) complexes C1–C3 at 30 and 50 °C. oligomerization conditions: complex = 5  $\mu$ mol, [MAO]/[Ni] = 300, toluene = 60 mL,  $P_{ethylene} =$  1.3 bar, and reaction time = 30 min

applications, good catalytic performances of dinickel(II) complexes have been recorded as a means of imposing close spatial confinement on multi-nickel centers have also

been suggested. In the case of present dinickel(II) systems C1–C3, maximum steric hindrance offered by the bis- $\alpha$ -diimine ligand systems will not allow the monomer units to enter from axial positions, by which polymer chain termination occurs. The monomer obstruction is offered sufficiently by the steric substituents present on 2,6-positions of bis-anilines, whereas on the other side of the metal center equal monomer obstruction does not occur, which cannot prohibit the axial ethylene insertion that results in the formation of oligomers with only traces of polymer. However, in combination with quantitative amount of MAO, the synthesized dinickel(II) complexes C1–C3,

selectively afforded dimerization to tetramerization of ethylene along with small amounts of higher olefin products and trace amounts of polyethylene. The distribution of oligomers is given in Table 2. All the three dinickel(II) complexes give high 1-butene content as nearly 75 % of the total C4 content formed. Apart from butane contents, in all the cases a considerable amount of higher olefins like C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub> and C<sub>12-20</sub> contents were observed with nearly 12–20, 4–10, 2–4 and 2–3 % compositions, respectively. Among three test samples, dinickel(II) complexes C1 and C3, produce the traces of polyethylene which was hard to characterize using spectral technique. From the ethylene



consumption profile [Fig. 5] it is evident that all the dinickel(II) complexes were highly active in the initial 10–15 min, however, become inactive which is attributed to the deactivation of active sites. The oligomer distribution pattern is consistent with a nickel alkyl species being the active center, where fast elimination of  $\beta$ -hydride limits the formation of higher olefins. Based on this observation, a preliminary mechanism of ethylene oligomerization is suggested in Fig. 6.

At the elevated temperature, the yield of the ethylene oligomers and their distributions are also affected drastically. Interestingly, no polymer was formed at 50 °C, which could be attributed to the increase in the entropy of monomer units. This increase in the temperature produced a sharp 3-5-fold decrease in oligomerization activity as is evident from Table 2. This decrease in activity could be attributed to the formation of *cis*-dinickel(II) complexes at the higher temperature, where on only one side a steric bulk from anilines can guide the monomer insertion, while on other side enough hindrance is not available from a methyl group of butene-backbone. Although it is too premature to conclude anything with the data collected here, all of these results may be originated from the cooperative effects of the dinickel(II) complexes and the steric bulk around them.

### 4 Conclusion

A simple and convenient synthetic approach towards preparation of a series of sterically modulated binickel(II) center catalysts, derived from bulky substituted bis-a-diimine ligands for oligomerization of ethylene is presented. The ligand scaffolds, designed to impose close spatial confinement for the two metal centres, were prepared in two steps by the condensation of 2,3-butanedione with 2,6dialkyl substituted aniline in a 1:1 stoichiometric ratio to give a intermediate, mono-condensed Schiff base product, iminoketone, which upon condensation with half an equivalent of hydrazine hydrate yielded the diazine bridged bis- $\alpha$ -diimine ligands. The corresponding bimetallic Ni(II) catalysts of these ligands showed high activity for ethylene oligomerization combined with MAO as cocatalysts. All the three dinickel(II) complexes showed high selectivity towards 1-butene as nearly 75 % of the total C4 content formed also accompanied by considerable amount of higher olefins like  $C_6$ ,  $C_8$ ,  $C_{10}$  and  $C_{12-20}$  contents which were observed with nearly 12-20, 4-10, 2-4 and 2-3 % compositions, respectively. Among three test samples, dinickel(II) complexes C1 and C3 also yielded the traces of polyethylene, interestingly at only 30 °C but not at slightly higher temperature of 50 °C. Substituents on the aromatic ring reduced the catalytic activity in the order of CH<sub>3</sub>>CH<sub>2</sub>CH<sub>3</sub>>CH(CH<sub>3</sub>)<sub>2</sub>.

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