Nickel(II) Dibromide Complexes Bearing Bis(benzimidazolyl)amine and Bis(benzimidazolyl)pyridine Ligands for Ethylene Oligomerizations

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Abstract A series of bis(benzimidazolyl)amine and bis(benzimidazolyl)pyridine ligands and their respective nickel(II) dibromide complexes were synthesized and fully characterized. After activation of the nickel complexes with ethylaluminum sesquichloride showed productivity in excess of 10^6 (g-oligomer)(mol-Ni)⁻¹h⁻¹bar⁻¹ towards ethylene oligomerization, producing butenes as major products. The bis(benzimidazolyl)pyridine nickel complexes showed higher activity and dimerization selectivity than corresponding bis(benzimidazolyl)amine nickel complexes.

Keywords Catalysis · Ethylene oligomerization · Ligands · Nickel complex · Transition metal catalysts

1 Introduction

The modern chemical industry has much reliance on α -olefins, and development of new catalysts for oligomerization and polymerization of ethylene is of great interest in both academic and industrial pursuits. One of the major industrial processes in ethylene oligomerizations, the Shell higher olefin process (SHOP), employs nickel complexes as catalyst [1, 2]. Over the past decade, research into nickel complexes as catalysts for olefin reactivity has attracted much attention due to the substantial breakthrough by the

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group of Brookhart with the development of highly active catalysts for ethylene polymerization [3–5]. The important progress of ethylene reactivity promoted by nickel complexes is reflected by the recent review articles [6-11]. Both oligomerization and polymerization can be occurred in the same batch with the mechanistic difference of chain termination and propagation. Recent challenges in the application of nickel complexes in ethylene oligomerization are improving their catalytic activity and selectively for the formation of α -olefins and controlling the polymer properties of produced polymers. From an academic view, the fundamental points in designing novel complexes as good homogeneous catalysts are based on designing and synthesizing suitable ligands to provide a conductive environment. Since the initial reports of ethylene polymerization with non-metallocene-based catalysts, there has been a significant focus on developing alternative variants of the bis(imino)pyridine ligand with varying degrees of success [10, 12–15]. One direction of exploration has been the replacement of the central pyridine ring with alternative heterocycles including pyrimidine, pyrazine, triazine, pyrrole, carbazole, furan, or thiophene [16]. Subtle changes to the ligand structure appear to have a dramatic effect upon catalysis, as well as the ability of the ligand to ligate zirconium, chromium, iron or cobalt.

In general, for ligand oriented metal complexes for ethylene oligomerization, ligands with no substantial adjacent substituents, facilitating β -hydrogen transfer, are preferred. In that aspect bis(benzimidazolyl)amine/pyridine (Fig. 1) with a wide open coordination site can be an ideal candidate. The transition metal complex of similar ligand systems Co, Cr and V have been utilized for ethylene and 1,3-butadiene polymerizations [12–16]. In polar organic solvents, tridentate aromatic and aliphatic ligands possessing three heterocyclic nitrogen donor atoms can

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Fig. 1 Bis(benzimidazolyl)pyridyl (a) and bis(benzimidazolyl)amine (b) ligands and their geometry optimized structures [(c) and (d)] with R = Me by density functional theory

displace solvent molecules and/or anions from the first coordination sphere of divalent nickel salts, NiX₂, to give a plethora of [NiLX₂] complexes (L = ligand). Moreover, the bis(benzimidazole)amine/pyridine backbone is easy to derivatize, which allows its facile incorporation into extended segmental ligands for the design of electronically modulated complexes. In order to utilize the potential of Ni as catalyst for ethylene oligomerizations we are reporting synthesis and characterization of a series of new nickel(II) complexes bearing the tridentate bis(benzimidazolyl)amine/pyridine ligands. Ethylene oligomerizations were performed at different reaction parameters for process optimization.

2 Experimental

2.1 Material

All manipulations involving air or moisture sensitive compounds were carried out under a purified nitrogen atmosphere. Toluene was distilled over Na/benzophenone and stored over molecular sieves (4 Å). Tetrahydrofuran used for the precatalyst synthesis was dried over calcium hydride and stored over molecular sieves (4 Å). Polymerization grade of ethylene was purified by passing it through columns of Fisher RIDOXTM catalyst and molecular sieve 5 Å/13X. Ethylaluminum sesquichloride (EASC) in toluene solution was obtained from Aldrich and used without further purification. All other chemicals (Sigma Aldrich Co.) used without further purifications unless otherwise mentioned.

2.2 Characterization

Elemental analysis of metal complexes was carried out using Various EL analyzer. Fast atom bombardment mass spectroscopy (FAB-MS) was recorded by using JMS-700, JEOL instrument. ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) spectra were recorded at 25 °C on a Varian Gemini 2000 spectrometer in CDCl₃ containing tetramethyl silane as standard. Fast atom bombardment mass spectra (FAB-MS) were obtained from the Korea Basic Science Institute on a JEOL JMS AX 505 spectrometer, operated at 3 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 10 mA emission current, producing a beam of 6 keV xenon. Nitrobenzyl alcohol was used as matrix. Data acquisition and processing were accomplished using JEOL Complement software. The oligomers were analyzed by gas chromatography (GC) (HP6890), performed using a J&W Scientific DB608 column (30 m \times 0.53 mm) with a flame ionization detector (FID). The injector and detector temperatures were kept constant at 250 °C. The program set the initial temperature to 30 °C (held for 2 min) and finishing temperature to 250 °C (held for 10 min), with a heating rate of 10 °C/min.

2.3 Synthesis of Ligands 1a-1c and 2a-2c

Synthetic procedures of ligands and Ni(II) complexes are illustrated in Scheme 1. The preparation and characterization of Cr [12, 13], Mn and Fe [17], and Cu [18] complexes bearing *bis*(benzimidazol)amine/pyridine ligands are well studied for ethylene oligo-/polymerizations [12, 13] and DNA binding [19]. Previously reported literature procedures were employed to synthesize compounds **1a** and **2a** [12], **1b** [17], **2b** [13] and **2c** [18].

For the preparation of *N*-methyl-*N*,*N*-*bis*[(1-benzyl-1*H*-benzimidazol-2-yl)methyl]amine (1c), to 1a (0.50 g, 1.72 mmol) in 15 mL of THF at 0 °C, sodium hydride (85%) (0.20 g, 6.87 mmol) was added. After 1 h, benzyl bromide (1.63 mL, 13.73 mmol) was added to the reaction mixture. The temperature was slowly raised to 50 °C and

Scheme 1 Synthesis of complexes: *i* methyliminodiacetic acid *ii* pyridine-2,6 dicarboxylic acid *iii* NaH/R-X (Me-I, Bn-Br) *iv* (DME) NiBr₂



R=H; 4a, R=Me; 4b, R=Bn; 4c

stirred the reaction mixture over night. The mixtures were then added to the water, the off-white precipitate formed was filtered, washed extensively with water and one time with cold methanol. The compound was dried at 50 °C under vacuum to get a yield of 75.4% (0.61 g). Mp: 180–181 °C. ¹H NMR (300 MHz, CDCl₃, δ , ppm): 2.43 (s, 3H), 3.84 (s, 4H), 5.06 (s, 4H), 6.74 (m, 4H), 7.19 (br m, 12H) 7.77 (m, 2H). ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 151.13, 142.30, 135.96, 135.58, 128.80, 127.65, 125.89, 123.03, 122.22, 119.90, 109.84, 54.15, 46.53, 43.63. Anal. Calcd. For C₃₁H₂₉N₅: C, 78.95; H, 6.20; N, 14.1185. Found: C, 79. 08; H, 6.14; N, 14.78.

2.4 Synthesis of Nickel Complexes 3a-3c and 4a-4c

All complexes were synthesized using the same procedure. An equimolar mixture of ligand (2.0 mmol) and (DME)-NiBr₂ (2.0 mmol) was stirred in 10 mL of THF for 12 h at room temperature. The precipitated complex was washed once with THF (20 mL) and three times with diethyl ether (20 mL), and then dried under vacuum.

3a: light green crystals in 84.0% yield. Anal. Calcd. For $C_{31}H_{29}N_5NiBr_2$: C, 40.05; H, 3.36; N, 13.74 Found: C, 40.53; H, 3.59; N, 13.58. FAB-MS (*m/z*): 430 [M-Br]⁺. **3b**: light green crystals in 86.0% yield. Anal. Calcd. For $C_{31}H_{29}N_5NiBr_2$: C, 42.42; H, 3.94; N, 13.02. Found: C, 42.86; H, 4.08; N, 12.86. FAB-MS (*m/z*): 458 [M-Br]⁺. **3c**: light green crystals in 87.0% yield. Anal. Calcd. For $C_{31}H_{29}N_5NiBr_2$: C, 53.95; H, 4.24; N, 10.15. Found: C, 53.58; H, 4.86; N, 10.57. FAB-MS (*m/z*): 610 [M-Br]⁺.

4a: greenish yellow crystals in 90.0% yield. Anal. Calcd. For $C_{31}H_{29}N_5NiBr_2$: C, 43.07; H, 2.47; N, 13.22. Found: C, 43.26; H, 3.01; N, 13.76. FAB-MS (*m/z*): 450 [M-Br]⁺.

4b: greenish yellow crystals in 88.0% yield. Anal. Calcd. For $C_{31}H_{29}N_5NiBr_2$: C, 45.21; H, 3.07; N, 12.55. Found: C, 45.32; H, 3.21; N, 12.12. FAB-MS (*m/z*): 568 [M-Br]⁺.

4c: greenish yellow crystals in 89.0% yield. Anal. Calcd. For C₃₁H₂₉N₅NiBr₂: C, 55.82; H, 3.55; N, 9.86. Found: C, 56.17; H, 3.70; N, 9.55. FAB-MS (*m/z*): 620 [M-Br]⁺.

2.5 Ethylene Oligomerizations

Ethylene oligomerizations were performed at 1.3 bar in a 250-mL round-bottomed flask kept at constant temperature by a thermostat and equipped with a magnetic stirrer and a thermometer, and the oligomer products were analyzed by GC according to the literature procedures [19].

2.6 Computational Details

The quantum chemical calculations were carried out by density functional theory (DFT) since it usually gives realistic geometries, relative energies and vibrational frequencies for transition metal compounds. All calculations were performed with the DMol³ DFT code [20] as implemented in Accelrys Materials Studio[®] 4.3 (http://www. accelrys.com/) on a personal computer (Pentium[®] dualcore CPU at 2.50 GHz, 4.00 gigabytes ram) operated with Microsoft Windows XP. The non-local generalized gradient approximation (GGA) functional by Perdew-Burke-Ernzerhof (PBE) [21] was used for all geometry optimizations. The convergence criteria for these optimizations consisted of threshold values of 2×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å for energy, gradient and displacement convergence, respectively, while a self-consistent field density convergence threshold value of 1×10^{-5} Ha was specified. DMol³ utilizes a basis set of numeric atomic functions, which are exact solutions to the Kohn-Sham equations for the atom [22]. A polarized split valence basis set, termed double numeric polarized (DNP) basis set was used. All geometry optimizations employed highly efficient delocalized internal coordinates [23]. The use of delocalized coordinates significantly reduces the number of geometry optimization iterations needed to optimize larger molecules compared with the use of traditional Cartesian coordinates. Some of the geometries optimized were also subjected to full frequency analyses at the same GGA/PBE/ DNP level of theory to verify the nature of the stationary points.

3 Results and Discussion

3.1 Synthesis and Characterization of Complexes

Ligand **1a** was prepared by condensation reaction of 1,2phenylenediamine and methyl iminodiacetic acid in ethylene glycol at 190 °C [12]. Ligand **2a** was also synthesized in the same way using pyridine-2,6-dicarboxylic acid. The ligands **1b**, **1c**, **2b**, and **2c** were obtained in high yields by the simple *N*-alkylation using corresponding alkyl halides via Na salts of **1a** and **2a** in THF [13].

Nickel complexes 3a-3c and 4a-4c were prepared in good yields by the matallation with one equivalents of (DME)NiBr₂ in THF at room temperature (see Scheme 1). The complexes 3a-3c could be envisaged as to originate bis(benzimdazolyl)s from a methyl amine core and 4ac that from a pyridinyl core. All the complexes were consistent with their elemental analyses and FAB-MS. The 2,6-bis(2-benzimidazolyl)pyridine ligand derivatives have been reported to be coordinated to transition metals such as zirconium, chromium, iron and cobalt to form various metal complexes [13, 16, 24–33]. In the case of benzimidazole-substituted pyridines, ligands of the type bis(benzimidazole)pyridine have been applied only to chromium, where in combination with MAO or diethylaluminum chloride (DEAC) they acted as highly effective initiators for ethylene oligomerization [13]. When methylaluminoxane (MAO) was employed as the cocatalyst, the chromium complexes showed high activity for ethylene oligomerization and polymerization. Oligomers were produced with high selectivity towards α -olefins, and polyethylenes were produced with extremely broad polydispersity. Variants of the bis(imino)pyridine ligand where only one imino arm has been replaced with benzimidazole have been reported bound to iron, cobalt, and nickel, all of which successfully initiated ethylene oligomerization [34-36]. The Gibson group reported a mechanism study of ethylene oligomerization by chromium complex bearing 2,6-bis(1Hbenzo[d]imidazol-2-yl)pyridine [37]. More recently the Sun group synthesized a series of [2,6-bis(2-benzimidazolyl)pyridyl]chromium chlorides and tested for ethylene oligo-/polymerizations [13]. When MAO was employed as the cocatalyst, the chromium complexes showed high activity for ethylene oligomerization and polymerization. Oligomers were produced with high selectivity towards α olefins, and polyethylenes were produced with extremely broad polydispersity.

A theoretical calculation was performed to find out the minimum energy structure (Fig. 2) of all nickel complexes (3a-3c, 4a-4c) bearing *bis*(benzimidazolyl)pyridine/amine ligands. The final structure was obtained using a GGA/ PBE/DNP level of theory with the DMol³ DFT code. The complexes were fully optimized and a few selected geometric parameters, i.e. bond length and bond angles are given in Table 1. From the optimized structures of the complexes, it was observed that the Ni centers in 3a-3c lie in a distorted tetragonal-pyramidal environment and those in 4a-4c lie in a distorted trigonal-bipyramidal environment. The N^1 -Ni-Br¹ bond angle is 169.338, 168.043 and 177.964 for the complexes 3a, 3b and 3c, respectively, 124.842, 127.298 and 117.838 for the complexes 4a, 4b and 4c, respectively. According to the bond lengths of Ni- N^1 , Ni– N^2 and Ni– N^3 of the complexes **3a**, **3b** and **3c**, Ni– N^3 has much longer length (3.087–4.454 Å) than the other two ones. Possibly the bis(benzimidazolyl)amine ligands might be coordinated to nickel in a bidentate way, which is quite different from bis(benzimidazolyl)pyridine nickel complexes, 4a, 4b and 4c. The observed differences in the bond angle and bond length between 3a-3c and 4a-4c come from a basic discrepancy of the structure induced by the different ligand backbone structures. In addition there exist differences in the bond angle and bond length in a same series of complexes, attributable to the difference in the steric hindrance due to the presence of the different of alkyl groups on the benzimidazolyl rings.

The Fukui function (FF) [38, 39] was also calculated to determine the local reactivity in the complexes by using a GGA/PBE/DNP level of theory with the DMol³ DFT code (Table 2). Comparing the ratio of FF values for nucleophilic attack to electrophilic attack (f^+/f^{2-}) , *bis*(benzimidazol-yl)amine Ni complexes display higher value than *bis*(benz-imidazolyl)-pyridine Ni complexes. Therefore, for electrophilic attack, the Ni center of the complex **3a–3c** is

Fig. 2 Density functional theory based geometry optimized structure of the complexes



Table 1 Some important bond lengths and bond angles estimated for the complexes 3a-3c and 4a-4c by geometry optimization

Parameters	3a	3b	3c	4 a	4b	4 c	
		R N ⁴ c ¹ C ² N ¹ C ³ N ² Br ¹ Br ²		$ \begin{array}{c} $			
Bond length (Å)							
Ni–N ¹	2.707	2.081	2.088	1.894	1.892	1.896	
Ni–N ²	1.937	1.934	1.967	1.909	1.912	1.891	
Ni–N ³	4.454	3.919	3.087	1.909	1.892	1.914	
Ni–Br ¹	2.327	2.326	2.331	2.443	2.441	2.455	
Ni–Br ²	2.357	2.343	2.353	2.433	2.444	2.428	
C^1-C^2	1.481	1.482	1.480	1.439	1.445	1.445	
Bond angle (degr	ee)						
N ¹ -Ni-N ²	82.757	82.320	82.660	81.229	81.443	81.462	
N ¹ -Ni-N ³	46.899	51.836	63.311	81.234	81.336	81.402	
N ¹ –Ni–Br ¹	169.338	168.043	177.964	124.842	127.298	117.838	
N ¹ -Ni-Br ²	93.255	93.323	91.560	129.241	126.895	134.143	
N ² -Ni-Br ¹	95.218	95.264	90.084	94.763	94.897	93.384	
N ³ –Ni–Br ²	91.195	93.323	93.775	95.754	95.611	96.294	
Br ¹ -Ni-Br ²	90.685	91.888	90.025	105.919	105.805	108.014	
C ¹ -N ² -Ni	107.263	114.725	113.400	114.358	115.164	115.177	
C ⁴ -N ³ -Ni	33.477	51.836	90.495	114.354	114.432	114.212	

more active than **4a**–**4c**. For both series of complexes, the f^+/f^{2-} value decreases as the alkyl group in benzimidazolyl rings become bulky from hydride to benzyl. These electronic parameters together with the structure of the complexes and steric bulk will play important roles in deciding

oligomerization reactivity (vide infra). Modeling all the NiBr₂ complexes by ab initio calculations showed considerable difference in the electro-static potential fitting (ESP) charge distributions within these molecules. In general the nickel atoms in the complexes bearing *N*-benzyl substituted

Table 2 Some important parameters of the complexes 3a-3c and 4a-4c

Parameters	3a	3b	3c	4a	4b	4c
Optimized E ^a	-7586.96	-7665.45	-8126.67	-7660.74	-7739.26	-8200.90
Binding E ^a	-7.7193	-8.6225	-12.4343	-7.9086	-8.8488	-12.9789
Fukui function ^b : f^+	0.107	0.106	0.027	-0.003	-0.003	-0.001
Fukui function ^c : f^+	0.145	0.143	0.127	0.012	0.011	0.034
Fukui function ^b : f^{2-}	0.224	0.219	0.153	-0.009	-0.011	-0.006
Fukui function ^c : f^{2-}	0.237	0.231	0.249	0.034	0.033	0.139
f^+/f^{2-} (Mullikan)	0.478	0.484	0.177	0.333	0.273	0.167
f^+/f^{2-} (Hirshfeld)	0.612	0.619	0.510	0.353	0.333	0.245
HOMO E ^a	-0.09570	-0.17340	-0.15220	-0.16819	-0.16573	-0.16201
Electro-static potential	fitting (ESP) charge	s ^d				
Metal	0.436	0.321	0.447	0.217	0.268	0.406
Br^1	-0.376	-0.342	-0.400	-0.395	-0.394	-0.401
Br ²	-0.406	-0.396	-0.466	-0.391	-0.394	-0.415
N^1	0.139	0.192	-0.302	-0.043	-0.007	-0.094
N^2	-0.594	-0.423	-0.239	-0.278	-0.322	-0.409
N ³	-0.575	-0.537	-0.399	-0.278	-0.340	-0.411

^a In Hartre

^b Fukui function for nucleophilic (f^+) and electrophilic (f^{-2-}) attacks in Mullikan charge

^c Fukui function in Hirshfeld charge

^d Notation of the type of atom is in Table 1

ligands in each system are more electropositive than other complexes bearing *N*-methyl or non-substituted ligands, as a result the electropositivity of nickel atom decreases in the order of 3c > 3a > 4c > 3b > 4b > 4a. However, on the basis of these calculations the electronic differences among the complexes appear to be less than are suggested by the differences in reactivity towards ethylene.

3.2 Ethylene Oligomerizations

The oligomerization rate of ethylene under constant pressure using *bis*(benzimidazolyl)amine Ni (**3a–3c**) and *bis*(benzimidazolyl)pyridine Ni (**4a–4c**) complexes combined with EASC changes markedly with time, as shown in Fig. 3. These kinetic curves can be divided into two parts: i.e. induction period where the rate increases rapidly to a maximum followed by a decay period during which the rate decreases monotonously, even though the induction and decay periods are somewhat changed depending on the type of catalyst. Note that the preliminary screening tests for the type of cocatalyst such as AlR₃ (R = Me, Et, ⁱBu), AlEt₂Cl and MAO show that EASC is the best cocatalyst for Ni catalysts of this study. In fact all alkyl aluminum cocatalysts, except EASC, gave only negligible activities.

The oligomerization results are summarized in Table 3. All the ethylene oligomerization reactions were performed employing EASC as the cocatalyst and toluene as a solvent under a semi-batch condition. The complexes derived from



Fig. 3 Ethylene oligomerization rate profiles obtained by different Ni(II) complexes combined with ethylaluminum sesquichloride (EASC): **a 3a, b 3b, c 3c, d 4a, e 4b,** and **f 4c**. Oligomerization conditions: catalyst = 5 μ mol, [EASC]/[Ni] = 200, ethylene pressure = 1.3 bar, toluene = 80 mL, T = 30 °C and time = 30 min

pyridine with their activity ranging from $1.662 \text{ to } 2.803 \times 10^6 \text{ (g-oligomer)(mol-Ni)}^{-1}\text{h}^{-1}\text{bar}^{-1}$ were more active than those derived from methylamine $[1.086-1.622 \times 10^6 \text{ (g-oligomer)(mol-Ni)}^{-1}\text{h}^{-1}\text{bar}^{-1}]$. As a result the activity (as the

Entry	Catalyst	[Al]/[Ni]	T (°C)	Yield (g)	$R_{p,avg}^{a}$	Oligomer distribution (%) ^b		
						C_4	α-C ₄	C ₆
1	3 a	200	30	3.53	1086	84.1	15.9	15.9
2	3b	200	30	5.40	1622	83.8	12.3	16.2
3	3c	200	30	3.81	1172	84.3	13.7	15.7
4	4a	200	30	5.56	1711	86.3	36.1	13.7
5	4 b	200	30	5.27	1662	87.2	35.7	12.8
6	4 c	200	30	9.11	2803	84.4	30.8	15.6
7	3a	50	30	3.91	1203	77.2	12.7	22.8
8	3a	100	30	6.32	1945	81.9	14.2	18.1
9	3a	200	30	3.53	1086	84.1	15.9	15.9
10	3a	800	30	2.47	760	90.4	15.1	9.6
11	3a	100	10	0.62	191	86.4	10.4	13.6
12	3a	100	50	1.56	480	87.0	28.7	13.0
13	3a	100	70	0.51	157	92.5	26.3	7.5

Table 3 Ethylene oligomerization results obtained by bis(benzimidazolyl)amine Ni (3a-3c) and bis(benzimidazolyl)pyridine Ni (4a-4c) complexes combined with ethylaluminium sesquichloride (EASC)

Oligomerization condition: catalyst = 5 μ mol, P_{C2H4} = 1.3 bar, toluene = 80 mL, and time = 30 min

^a Average rate of polymerization over a polymerization period in kg (mol-Ni)⁻¹h⁻¹bar⁻¹

^b Determined by GC

average rate of oligomerization over a period of oligomerization) decreases in the order of 4c > 4a > 4b > 3b >3c > 3a. The activity changes might be arising from the variation of electronic nature due to structural differences of these two classes of complexes. The pyridyl rings in complexes 4a-4c with their resonance effect possibly draw the lone pair of electrons from N atom into the ring, thereby reducing the availability of these lone pair of electrons to Ni metal center in comparison with N-methyl groups in 3a-3c, in which the positive inductive of methyl group makes the lone pair electron more easily available for central metal. Note that the f^+ and f^{2-} values and their ratio f^+/f^{2-} (Table 2) of **3a–3c** complexes are larger than 4a-4c complexes and the higher values of these parameters are not favorable to achieve high activity. In addition to these electronic factors, the intrinsic planar nature of the bis(benzimidazolyl)pyridine complexes may facilitate the accessibility of the incoming monomers.

The ligand variation brought about by N-alkylation had a significant effect on oligomerization. For complexes **3a–3c**, the methylated derivative (**3b**) yields the best activity of 1.622×10^{6} (g-oligomer)(mol-Ni)⁻¹h⁻¹bar⁻¹. In the case of complexes **4a–4c**, there is a strong effect on activity by N-alkylation. As a result the complex **4c** bearing benzyl substituent gives very high activity, 2.803×10^{6} (g-oligomer)(mol-Ni)⁻¹h⁻¹bar⁻¹, which is almost 2 times high than that by complex **4a**. There was a drastic decrease in activity due to N-alkylation which is attributed to formation of anion amide group by the deprotonation of the free N–H group by cocatalyst during activation [13].

GC analysis of the products revealed that both the catalytic systems were highly selective towards butenes constituting around 85% of the total product and the remaining fractions were hexenes. Even though selectivity towards C₄ olefins were almost similar level, pyridine derived system showed better selectivity to 1-butene (30.8-36.1%) than methyl amine system (12.3-15.9%). The catalyst activity is comparable to some Ni(II) coordination catalysts with N-donor ligands under similar conditions. Previously, Brookhart reported that catalysts with only one substituent on the *N*-ring for the α -diimine do not yield polymers but instead produce oligomers [40]. The products are mainly butenes and hexenes, with small/moderate amounts of higher oligomers up to C10. The oligomer distribution pattern is consistent with a nickel hydride species being the active center, where fast elimination of β -hydride limits the products to mostly butenes and hexanes; however, in a few cases higher olefins are also observed in trace amounts.

In general the parameters such as cocatalyst concentration and temperature play important roles in determining the reaction profiles and product distribution. The results of ethylene oligomerization gathered at different conditions are summarized in Table 3. In order to investigate the effect of variation of cocatalyst concentration, a series of reactions were performed with increasing [Al]/[Ni] ratios (from 50 to 800) with a **3a**/ EASC system. The activity of the catalyst increases from 1.203×10^6 to 1.945×10^6 (g-oligomer)(mol-Ni)⁻¹h⁻¹bar⁻¹ by increasing [Al]/[Ni] ratio from 50 to 100; however the activity decreases monotonously by further increase of [Al]/ [Ni] ratio. The decrease of activity in the presence of excess amount of cocatalyst is usually observed in transition metal catalyzed olefin oligomerizations. In transition metal catalyzed oligomerization process, the active species are established as cation–anion ion pair, formed through the activation of catalyst precursors by the aluminum cocatalyst and reaction attributes connected with the nature of the ion pairing. At higher concentration of cocatalyst, the ion pair could be stabilized by the excess cocatalyst making monomer insertion difficult and hence a reduced the activity [41]. On increasing the [Al[/[Ni] from 50 to 800 favored formation of C_4 fraction due to extensive chain transfer to Al.

To explore temperature effect oligomerizations were performed at temperatures ranging from 10 to 70 °C using **3a**/EASC system at [Al[/[Ni] = 200 (Table 3). The optimum activity was observed at 30 °C. There is a drastic reduction in activity on increasing temperature from 30 to 70 °C, demonstrating the deactivation of active species is accelerated at elevated temperatures. In addition facilitated chain transfer reactions at high temperatures increase the production of C₄ olefin: 92.5% at 70 °C.

4 Conclusions

Two classes of Ni(II) complex bearing bis(benzimidazolyl)amine and bis(2,6-benzimidazolyl)pyridine ligands with varying N-alkyl substitutents were synthesized and characterized. From the optimized structures of the complexes using a GGA/PBE/DNP level of theory with the DMol³ DFT code, the Ni centers in bis(benzimidazolyl)amine and bis(2,6-benzimidazolyl)pyridine ligands lie in a distorted tetragonal-pyramidal and a distorted trigonal-bipyramidal environment, respectively. All the Ni(II) complexes combined with EASC cocatalyst showed high activity towards ethylene to yield butenes (around 85%) as major product along with hexenes. The Ni(II) complexes bearing planar bis(2,6-benzimidazolyl)pyridine ligands showed higher activity, dimerization and 1-butene selectivity than those bearing bis(benzimidazolyl)amine ligands. The modifications of ligand by N-alkylation had a strong influence on oligomerization profiles. Higher oligomerization temperatures and cocatalyst ratio favored the production C₄ fraction and enhanced selectivity towards 1-butene.

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