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Ni(II) complexes with ligands derived from phenylpyridine, active for selective dimerization and trimerization of ethylene

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ABSTRACT

An electrophilic substitution–carbonylation reaction on phenylpyridine based on the concept of 'umpolung' was used to prepare a series of pyridine based carbonyl compounds and bispyridine derivatives. The key intermediate which enhances this reaction is a base aggregate formed by the association of BuLi with lithium 2-dimethylaminoethanolate (LiDMAE) which is stabilized in nonpolar solvents. The presence of polar chelating amides that are used as acyl donors was found to collapse the superbase aggregates liberating nucleophilic 'free' BuLi. These nucleophiles lead a classical nucleophilic reaction to introduce butyl tails on the pre-ligand molecules. Pyridine carbonyl compounds produced by these electrophilic substitution–carbonylation reactions, on treatment with 2,6-diisopropylaniline and (DME) $NiBr_2$ in glacial acetic acid at reflux temperature, gave Ni(II) complexes in good yields in a one pot protocol. These complexes are active toward ethylene, producing selective dimerization and trimerization products.

1. Introduction

Nitrogen chelating ligands having [N^N], [N^N^N] and [N^N^N^N] structures are well known for their ability to coordinate with various transition elements giving complexes which are active catalysts in C–C bond forming reactions [1]. [N^N] and [N^N^N] complexes bearing various transition elements such as Ni, Pd, Al, Co, Fe and Cr are widely accepted catalysts in ethylene polymerization/oligomerization reactions [1–4]. Designing the ligands of these complexes in a reasonable way, they were found to produce industrially important oligomers [5]. Complexes used in catalytic purposes are preferred to have completely inert and non-labile ligands for their stability. Realization of these characteristics has been accomplished only for a few non-cyclopentadienyl systems and remains a vibrant area of research. To achieve new ligand structures and to finely tune them for better catalytic activity, a good understanding in the successful design and synthesis of organometallic complexes is required. In this background, we have investigated in the recent years for new types of complexes having [N,N] and [N,O] chelating ligands based on 'ligand oriented catalyst design concept', yielding industrially important ethylene oligomers [6,7].

The famous [N^N] structures, α-diimines, with Ni and Pd complexes have paved dramatic changes in the field of single site non-metallocene catalysts mediated olefin polymerization/oligomerization reactions [3]. After identifying heterocyclic compounds as the efficient candidates providing nitrogen chelating ligands, growing demand for such compounds has made chemists to design efficient and selective methods to introduce functionalities on such heterocyclic compounds [8–16]. In pyridine derivatives, the nitrogen atom polarizes the ring π-system, resulting in a decreased electron density on carbon atoms that make electrophilic substitution difficult on the rings. After Seebach and Corey have developed the concept of 'umpolung' [17,18], a large number of investigations have been conducted on various electrophilic/nucleophilic reactions, enabling this concept potential to employ on pyridine based compounds. Most efficient electrophilic substitution reported on pyridines involves the use of lithiated pyridines as intermediates [19]. Halopyridines are classically used as a potential substrate, because they can be converted to lithiated pyridines [19]; however, the π-deficiency of pyridine ring favors nucleophilic attack rather than lithiation. This leads to investigate on a non-nucleophilic and strongly basic reagents that can act as lithiating agents for pyridines. Fort and coworkers have

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modified strongly nucleophilic n-BuLi by associating with lithium chelating 2-dimethylaminoethanol (DMAE) in order to effectively conduct a regioselective α-lithiation on pyridine rings directly [20]. Association with DMAE considerably increases the basicity/nucleophilicity ratio of BuLi by enhancing basicity through complexation and inhibiting nucleophilicity through the formation of sterically hindered aggregates. The key intermediate which enhances this reaction is a base aggregate formed by the association of BuLi with lithium 2-dimethylaminoethanolate (LiDMAE) which is stabilized in nonpolar solvents. It has been found that the presence of chelating polar solvents influences the stability of this super-base aggregate, resulting in changing the reaction pathways and hence such solvents can be used as trapping solvents to produce new compounds based on pyridine [20]. It is appropriate to explore the potential of such reactions to produce different pyridine based ligands.

In this regard, an attempt to synthesize various pre-ligands based on phenylpyridine using reactions mediated by BuLi-LiDMAE superbase has been made. A new method to preparare pyridine-imine ligands based nickel complexes with [N,N] chelation structure using an electrophilic substitution–carbonylation reaction on phenylpyridine is explained. Certain interesting observations during the ligand synthesis, which are useful for future design and development of organometallic complexes based on ligand-oriented design are also described.

2. Experimental

2.1. General procedures

All reactions and operations were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX™ catalyst and molecular sieve 5 Å/13X. All solvents used for synthesis and oligomerization experiment were purified according to the standard procedure and stored over molecular sieves (4 Å) under nitrogen condition. Methylalumoxane (MAO) (8.4 wt.% total Al solution in toluene) was donated by LG Chemicals, Korea and was used without purification. All other reagents were purchased from Aldrich Chemical Co. and were used without further purification.

2.2. Characterizations

UV–vis spectra were recorded on a Shimadzu UV-1650 PC spectrometer in toluene at room temperature under nitrogen atmosphere. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer by making CsI pellets of the samples. Fast atom bombardment mass spectroscopy (FAB-MS) was determined using a JMS-700 (JEOL Instrument). Electron impact mass spectroscopy (EI-MS) was determined using a JMS-600 (JEOL Instrument). Elemental analyses were carried out using a Vario EL analyzer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Gemini 2000 spectrometer and the chemical shifts were reported in parts per million relative to internal $(CH_3)_4Si$ (^{1}H, ^{13}C) standard. FAB-MS spectra of the complexes were recorded on a JMS-AX505WA/HP5890 Series II GC–mass spectrometer. Oligomerization products were analyzed by a 7890A GC System (Agilent Technologies) with a J&W Scientific 30 m column with 0.250 mm inner diameter.

2.3. Crystallographic studies

The crystal was picked up with Paraton N oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source and a nitrogen cold stream (−100 °C). The data were corrected for Lorentz and polarization effects (SAINT), and semi-empirical absorption corrections based on equivalent reflections were applied (SADABS). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL). All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

2.4. Oligomerization procedure

Ethylene oligomerizations were performed in a 250 mL glass reactor equipped with septum adapter and a magnetic stir bar. The required amount of catalyst was added to the reactor and kept under vacuum for 30 min and then purged with N_2. The reactor was then charged with toluene (80 mL) under N_2 and then pressurized with ethylene (1.3 bar) at the desired temperature with stirring. The oligomerization was started by the addition of cocatalyst. The ethylene flow to the reactor was monitored by a mass flow meter from the rate of consumption, measured by a hotwire flow meter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. After the given reaction time the reactor was cooled to 0 °C and samples for oligomer analysis were collected from the reactor by passing a 10 mL of this cold mixture through a silica column to remove Al species. Oligomers were analyzed by gas chromatography.

2.5. Synthesis of pre-ligands

To a cold (0 °C) solution of dimethylaminoethanol (1 mL, 10 mmol) in *n*-hexane (25 mL) a solution 8 mL (20 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise over a period of 10 min. After stirring for 30 min, 2-phenylpyridine (0.6 mL, 4 mmol) in *n*-hexane was added at 0 °C and was stirred for another 30 min. After the temperature was brought down to −78 °C. an acylating agent [4 mmol of *N,N*-dimethylformamide (DMF; 0.3 mL), *N,N*-dimethylacetamide (DMAc; 0.4 mL) or *N,N*-dimethylbenzamide (DMB; 0.6 g)] was added slowly. After keeping the solution at −78 °C for 1 h, it was warmed to room temperature overnight. The reaction mixture was again cooled to -5-0 °C and carefully hydrolyzed with chilled water. The aqueous layer was extracted with diethyl ether, dried over $MgSO_4$ and then removed solvents under vacuum to get the crude product. The reactions using DMF, DMAc and DMB as the acyl donor gave products **1**, **4** and **7**, product **2**, **5** and **7**, and product **3**, **6** and **7**, respectively, in high purity, after purifying using column chromatography (*n*-hexane/ethyl acetate).

2.5.1. (2-Phenylpyridine-6-yl)-methanone (**1**)

Yield = 0.07 g (12.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.01 (s, 1H, CHO), 8.16–7.11 (m, 8H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2, 158.6, 153.5, 141.7, 134.2, 128.4, 127.5, 123.3, 118.4. MS (EI+): 182.

2.5.2. Methyl(2-phenylpyridine-6-yl)-methanone (**2**)

Yield = 0.01 g (13.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10–7.31 (m, 8H, Ar), 2.45 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.1, 169.4, 154.4, 139.9, 136.0, 129.9, 127.6, 124.1, 122.2, 24.4. MS (EI+): 197.

2.5.3. Phenyl(2-phenylpyridine-6-yl)-methanone (**3**)

Yield = 0.16 g (15.6%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74–7.18 (m, 13H, Ar), ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 156.0, 153.9, 138.8, 137.7, 136.9, 136.7, 133.0, 132.9, 129.4, 127.8, 122.9. MS (EI+): 259.

2.5.4. 4-Butyl-6-phenyl-pyridine-2-carbaldehyde (**4**)

Yield = 0.76 g (78.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 1H, CHO), 7.79–7.10 (m, 7H, Ar), 2.78 (t, 2H, CH_2), 1.50 (qn, 2H, CH_2), 1.02 (sx, 2H, CH_2), 0.91 (t, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$):

δ 196.7, 158.1, 155.8, 145.8, 145.3, 131.4, 129.1, 126.7, 116.3, 37.0, 33.5, 22.6, 13.9. MS (EI+): 238.

*2.5.5. 1-(4-Butyl-6-phenyl-pyridin-2-yl)-ethanone (**5**)*

Yield = 0.79 g (77.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16–6.98 (m, 7H, Ar), 2.71 (t, 2H, CH_2), 2.40 (S, 3H, CH_3), 1.52 (qn, 2H, CH_2), 1.01 (sx, 2H, CH_2), 0.92 (t, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.7, 163.7, 162.4, 156.8, 139.2, 130.5, 129.2, 128.1, 127.9, 36.8, 33.9, 25.2, 22.4, 13.9. MS (EI+): 253.

*2.5.6. (4-Butyl-6-phenyl-pyridin-2-yl)-phenyl-methanone (**6**)*

Yield = 0.95 g (75.1%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06–7.08 (m, 12H, Ar), 3.0 (t, 2H, CH_2), 1.52 (qn, 2H, CH_2), 0.99 (sx, 2H, CH_2), 0.91 (t, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 155.1, 153.8, 139.3, 138.6, 137.8, 134.8, 133.4, 130.9, 129.0, 128.3, 125.7. 121.6, 36.5, 33.8, 22.2, 13.9. MS (EI+): 315.

*2.5.7. 6,6′-diphenyl-[2,2′]bipyridinyl (**7**)*

Yield (*N*,*N*-dimethylformamide reaction) = 0.02 g (3.4%), Yield (DMAc reaction) = 0.02 g (3.0%), and Yield (*N*,*N*-dimethylbenzamide reaction) = 0.02 g (2.8%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62–7.08 (m, 16H, Ar), ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.7, 155.1, 138.1, 135.8, 129.5, 129.0, 126.3, 124.0, 119.0. MS (EI+): 308.

2.6. Synthesis of complexes

Complexes **8**–**13** were synthesized in a similar manner using nickel(II) bromide ethylene glycol dimethyl ether complex [(DME)$NiBr_2$]. A suspension of (DME)$NiBr_2$ (1 mmol), 2-phenyl pyridine-6-aldehydes or ketones **1**–**6** (1 mmol) and 2,6-diisopropyl aniline (1 mmol) in glacial acetic acid (10 mL) was refluxed for 4 h. The precipitate was filtered and washed with diethyl ether (5 mL × 3). The residue collected were redissolved in dichloromethane and concentrated to saturated solution, and then reprecipitated using diethyl ether, filtered and washed with diethyl ether (5 mL × 3). The solid residue was dried under vacuum overnight at 40 °C.

Complex **14** was synthesized by refluxing compounds **7** (1 mmol) with (DME)$NiBr_2$ (1 mmol) in glacial acetic acid (10 mL) for 4 h. The precipitate was filtered and washed with diethyl ether (5 mL × 3). The residue collected were redissolved in dichloromethane and concentrated to saturated solution and then reprecipitated using diethyl ether, filtered and washed with diethyl ether (5 mL × 3). The solid residue was dried under vacuum overnight at 40 °C.

*2.6.1. N-((2-phenylpyridine-6-yl)methylene)-2,6-diisopropylanilineNiBr$_2$ (**8**)*

The complex was obtained as brown crystals in 56.0% yield. Anal. Calcd for $C_{24}H_{26}Br_2N_2Ni$: C, 51.38; H, 4.67; N, 4.99. Found: C, 49.99; H, 4.56; N, 5.01. IR (CsI, cm^{-1}) 3398, 3066, 1620, 1566, 1543, 11,497, 1458, 1419, 1303, 1126, 1038, 1010, 810, 764, 443, 328, 278. MS (FAB+): 480 [M − Br].

*2.6.2. N-((2-phenylpyridine-6-yl)methylmethylene)-2,6-diisopropylanilineNiBr$_2$ (**9**)*

The complex was obtained as a brown crystals in 56.3% yield. Anal. Calcd for $C_{25}H_{28}Br_2N_2Ni$: C, 52.22; H, 4.91; N, 4.87. Found: C, 51.39; H, 5.08; N, 4.65. IR (CsI, cm^{-1}) 3420, 2959, 1636, 1558, 1521, 1506, 1458, 1409, 1382, 1340, 1319, 1192, 1126, 1039, 1012, 813, 765, 444, 327, 280. MS (FAB+): 495 [M − Br].

*2.6.3. N-((2-phenylpyridine-6-yl)phenylmethylene)-2,6-diisopropylanilineNiBr$_2$ (**10**)*

The complex was obtained as a brown crystals in 58.6% yield. Anal. Calcd for $C_{30}H_{30}Br_2N_2Ni$: C, 56.56; H, 4.75; N, 4.40. Found: C, 56.06; H, 4.88; N, 4.45. IR (CsI, cm^{-1}) 3421, 3182, 1616, 1585, 1550, 1500, 1462, 1388, 1292, 1253, 1188, 1118, 1060, 1033, 960, 802, 736, 354, 282. MS (FAB+): 476 [M-(2Br + H)].

*2.6.4. [(4-butyl-6-phenyl-pyridin-2-ylmethylene)-(2,6-diisopropyl-phenyl)-amine]NiBr$_2$ (**11**)*

The complex was obtained as pink crystals in 57.6% yield. Anal. Calcd for $C_{28}H_{34}Br_2N_2Ni$: C, 54.50; H, 5.55; N, 4.54. Found: C, 54.96; H, 5.08; N, 4.85. IR (CsI, cm^{-1}) 3422, 3180, 1618, 1581, 1551, 1500, 1462, 1388, 1292, 1253, 1188, 1118, 1060, 1033, 960, 802, 736, 354, 282. MS (FAB+): 457 [M − 2Br].

*2.6.5. [1-(4-butyl-6-phenyl-pyridin-2-yl)-ethylidene]-(2,6-diisopropyl-phenyl)-amine]NiBr$_2$ (**12**)*

The complex was obtained as pink crystals in 58.9% yield. Anal. Calcd for $C_{29}H_{36}Br_2N_2Ni$: C, 55.19; H, 5.75; N, 4.44. Found: C, 55.06; H, 5.28; N, 4.65. IR (CsI, cm^{-1}) 3421, 3182, 1616, 1585, 1550, 1500, 1462, 1388, 1292, 1253, 1188, 1118, 1060, 1033, 960, 802, 736, 354, 282. MS (FAB+): 551 [M − Br].

*2.6.6. [[(4-butyl-6-phenyl-pyridin-2-yl)-phenyl-methylene]-(2,6-diisopropyl-phenyl)-amine]NiBr$_2$ (**13**)*

The complex was obtained as pink crystals in 59.0% yield. Anal. Calcd for $C_{34}H_{38}Br_2N_2Ni$: C, 58.91; H, 5.53; N, 4.04. Found: C, 58.29; H, 5.36; N, 4.81. IR (CsI, cm^{-1}) 3424, 3179, 1619, 1580, 1549, 1498, 1461, 1388, 1291, 1254, 1187, 1118, 1061, 1036, 959, 801, 735, 354, 286. MS (FAB+): 613 [M − Br], 532 [M-(2Br + H)].

*2.6.7. [6,6′-diphenyl-[2,2′]bipyridinyl]NiBr$_2$ (**14**)*

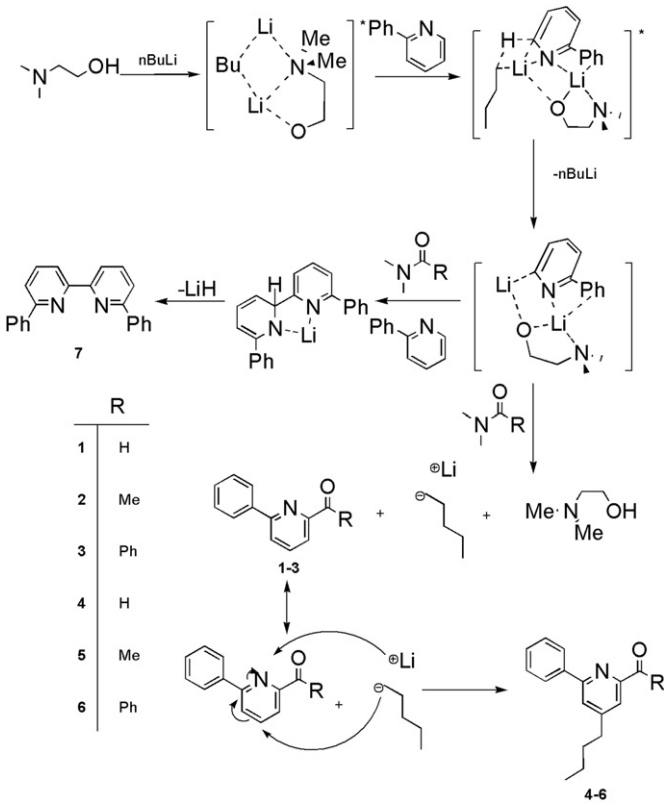
The complex was obtained as a reddish yellow crystals in 58.6% yield. Anal. Calcd for $C_{22}H_{16}Br_2N_2Ni$: C, 50.15; H, 3.06; N, 5.32. Found: C, 49.86; H, 3.21; N, 4.66. IR (CsI, cm^{-1}) 3423, 3179, 1614, 1585, 1550, 1503, 1459, 1389, 1291, 1253, 1188, 1120, 1062, 1033, 961, 802, 735, 355, 281. MS (FAB+): 366 [M − 2Br].

3. Results and discussion

An attempt to synthesize various pre-ligands based on phenylpyridine, using reactions mediated by BuLi-LiDMAE superbase has been made. This superbase can easily α-lithiate phenylpyridine. The treatment of the lithiated product with an N,N-dialkyl substituted amides of suitable monocarboxylic acids, which can act as an acyl donor, results in α-acylation of phenylpyridine. DMF, DMAc and DMB are employed as the acylating reagents. Finally phenylpyridine based acyl products were obtained by hydrolysis of macrocomplexes with water.

As these acylating agents can act as chelating agents as well, they are able to deviate the reaction mechanism to produce unexpected products based on phenylpyridine. Various products obtained from one reaction could be purified using column chromatographic method. A lengthy silica flash column was employed for the separation, with n-hexane/ethyl acetate as eluent. Three classes of compounds were separated as indicated in Scheme 1. The compounds **1**–**3** were obtained in 12.2–15.6% yield and compounds **4**–**6** in 75.4–78.2% yield. The compounds **4**–**6** show aliphatic signals assignable to a butyl tail in the molecule. A third product, compound **7** was obtained in all the three reactions with varying yield (2.8–3.4%).

Compounds **1**–**3** are formed according to an expected mechanism: i.e. a reaction mediated by highly basic BuLi-LiDMAE aggregate. However, the chelating amides that are used as acyl donors can also act as trapping agents. Due to their polar presence, the superbase aggregate can collapse to liberate nucleophilic, free BuLi. At this condition there is a high probability for compounds **1**–**3** to undergo the classical nucleophilic reaction. Such a reaction



Scheme 1. Synthesis of ligands **1**–**7**.

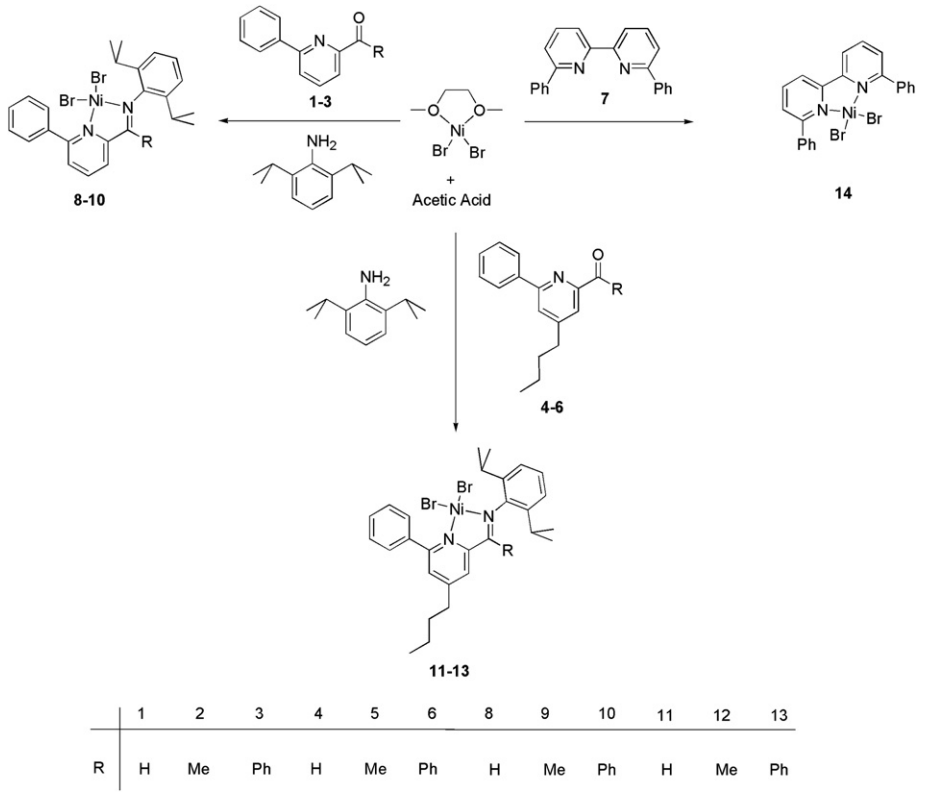
introduces a butyl tail at the para position of compounds **1**–**3** producing compounds **4**–**6**. It has also been reported that, when polar trapping agents such as THF is used in these reactions; there is a chance for dimerization of pyridine derivatives to yield bipyridine derivatives [20]. The structure of all these compounds was intensively analyzed using different NMR spectroscopy, elemental analysis and EI-Mass spectra.

For the phenylpyridine carbonyl compounds **1**–**6**, the synthesis of imino-pyridyl ligands was attempted through classical imine reaction. However, this protocol was not effective since a major portion of the product was decomposed during the separation steps by column chromatography. Thus, a one-pot synthesis is advantageous to synthesize metal complexes in high yield [15,21]. A one-pot synthetic technique has been adopted to prepare the desired Ni complexes **8**–**13** from compounds **1**–**6** (Scheme 2). The phenylpyridine carbonyl compounds **1**–**6** on treatment with 2,6-diisopropylaniline and (DME)$NiBr_2$ in glacial acetic acid gave Ni complexes **8**–**13** in good yields. Complex **14** was prepared from **7** by refluxing with (DME)$NiBr_2$ in glacial acetic acid. All complexes were characterized by FAB-MS, elemental analysis and IR spectroscopy. Among the complexes **8**–**13**, those complexes with methylinic phenyl groups easily yielded crystals from their dichloromethane solution on vapor deposition of n-pentane. More idea about their structure was obtained from the crystallographic information of their solid state structure.

Deep orange-brown crystals of imino-pyridyl Ni complex **13** suitable for solid state structure measurements were obtained by vapor deposition of n-pentane to a CH_2Cl_2 solution of the complex. The solid state structure was obtained by single crystal XRD measurements. Selected bond angles and bond lengths are displayed in Table 1 and ORTEP diagram is depicted in Fig. 1. The complex crystallized as monomeric unit with a tetrahedral Ni metal center coordinates to the neutral ligand through two sp^2 hybridized nitrogen atoms. The remaining two coordinations are fulfilled by bonding with two bromide ions. Previous report showed that the Ni complexes of this general type are dimeric when steric interactions permit the monomeric halves $LNiX_2$ (where L is ligand molecule) to come sufficiently close [22]. It may be the steric properties of the ligand molecule that prevents the close approach of monomeric halves. The angles, the four coordinations in the tetrahedron making with one another, range from 80.9(7) to 131.8(5)°, deviating largely from the standard tetrahedral angle 109.5° indicating a severe distortion. The bond length between central Ni atom and the nitrogen from pyridine ring and that between Ni atom and imine nitrogen are non-identical. That between Ni and pyridyl nitrogen is found slightly shorter than the other (see Fig. 1 and Table 1). From the plane passing through the atoms N2, C16 and C11, the other nitrogen atom N1 deviates by a distance 0.203 Å. These deviations from standard tetrahedral angle and the non-planar arrangement of the ligands with metal center can be resulted from the steric demands within the ligand molecule to orient toward most stable conformations. The torsional angle between the planes that is formed between N1-C11 and N2-C16 is −16.1°. Accordingly the N2 deviates 0.194 Å from the plane where the pyridine ring (mean: N1, C7, C8, C9, C10, C11) lies. The plane of phenyl ring (C23, C24, C25, C26, C27, C28) that is attached to the imine nitrogen N2 is located nearly vertical to the plane of pyridine ring (N1, C7, C8, C9, C10, C11). The methylinic phenyl ring (C17, C18, C19, C20, C21, C22) makes 53.04° through one direction with the plane of pyridine ring. The plane that runs through the third phenyl ring (C1, C2, C3, C4, C5, C6) in the molecule that is directly attached to the pyridine ring makes an angle of 42.22° with the plane that passes through all atoms in pyridine ring. It indicates that all the conformation possibilities have been utilized to orient different groups in three dimensional planes to get a structure with minimum strain.

Pink colored crystals of complex **14** were obtained at conditions that are similar for complex **13**. Selected bond angles and bond lengths of this molecule from its crystallographic measurements are displayed in Table 1 and ORTEP diagram is depicted in Fig. 2. The metal complex exists as monomeric unit with a metal to ligand ratio of 1:1. The coordination geometry of the complex **14** is similar to that of previously reported symmetrical phenanthroline or bipyridine Ni complexes [22]. The Ni center is in tetrahedral geometry being four coordinated by the two nitrogen donors of the bidentate ligand and two bromide ions. The distortions from the standard tetrahedral structure are very clearly observed from the bond angles that Ni makes with its four coordination sites. The bond angle values 83.19(19), 118.69(11), 100.64(11), 98.18(11), 116.49(10) and 130.45(4)° indicates the deviation from the standard tetrahedral angle value of 109.5°. The dihedral angle of the N–Ni–N and Br–Ni–Br planes is 75.6° indicating slightly flattened tetrahedral. The two Ni–N bond distances are 2.00(4) and 2.02(4) Å which are very close to a typical value of 2 Å. The Ni–Br bond lengths 2.36(11) and 2.37(10) Å in the molecule are also around the standard value of 2.3 Å. The two pyridyl rings constituting the bipyridyl ligand backbone are not located in a single plane. The two planes in which each of this pyridyl units are located are separated from each other by an angle of 21.76°. The plane passing through one pyridyl ring (mean: C1, C2, C3, C4, C5, N1) makes an angle of 45.71° with the plane passing through the phenyl ring (mean: C6, C7, C8, C9, C10, C11) attached to it. The angle between plane passing through the other pyridyl ring (mean: C12, C13, C14, C15, C16, N2) and that passing through the phenyl ring attached to it (mean: C17, C18, C19, C20, C21, C22) is 36.55°.

Ethylene oligomerizations have been performed with all the Ni(II) complexes at moderate conditions. Due to the open structure



Scheme 2. Synthesis of complexes **8**–**14**.

of the metal center, which exists as a common feature in all of these complexes, when activated with ethylaluminum sequichloride (EASC), yielded oligomers as summarized in Table 2. All the experiments have been conducted in chlorobenzene at 30 °C and 1.3 bar ethylene pressure for 30 min. It is interesting to note that the complexes give dimerization and trimerization products exclusively regardless of structure. Complexes **8**–**13** can be divided into two categories. Complexes **8**–**10** represent an (imino)pyridine structure with varying methylenic substituents: –H (complex **8**), -Me (complex **9**), and –Ph (complex **10**). Complexes **11**–**13** are characterized by the same structure with an n-butyl substituent at the para-position of the core pyridine ring. The activity of these two sets of complexes toward ethylene is significantly influenced by the methylenic substituents. Complexes **8** and **11** with methylenic hydrogen show low activity: i.e. 16.0 and 16.3 × 10^6 g-oligomer/mol-Ni h bar, respectively. Complexes **10** and **13** with methylenic phenyl substituent exhibit high activity: i.e. 34.9 and 35.7 × 10^6 g-oligomer/mol-Ni h bar, respectively, while complexes **9** and **12** with methylenic methyl substituent display intermediate activity: i.e. 25.2 and 26.5 × 10^6 g-oligomer/mol-Ni h bar, respectively. Comparing the two complexes in different categories, the

Table 1
Selected bond lengths (Å) and bond angles (o) For complexes **13** and **14**.

Bond lengths (Å)	Bond angles (°)
Complex 13	
Ni(1)–N(1) 2.0049(18)	N(1)–Ni(1)–N(2) 80.99(7)
Ni(1)–N(2) 2.0138(16)	N(1)–Ni(1)–Br(2) 131.87(5)
Ni(1)–Br(1) 2.3581(4)	N(2)–Ni(1)–Br(2) 104.33(5)
Ni(1)–Br(2) 2.3536(4)	N(1)–Ni(1)–Br(1) 93.50(4)
N(2)–C(16) 1.287(3)	N(2)–Ni(1)–Br(1) 112.98(4)
N(2)–C(23) 1.448(2)	Br(2)–Ni(1)–Br(1) 125.161(17)
C(11)–C(16) 1.490(3)	N(1)–C(11)–C(16) 114.32(18)
	N(2)–C(16)–C(11) 115.36(18)
Complex 14	
Ni(1)–N(1) 2.009(4)	N(1)–Ni(1)–N(2) 83.19(7)
Ni(1)–N(2) 2.021(4)	N(1)–Ni(1)–Br(2) 118.69(11)
Ni(1)–Br(1) 2.3719(10)	N(2)–Ni(1)–Br(2) 100.64(11)
Ni(1)–Br(2) 2.3597(11)	N(1)–Ni(1)–Br(1) 98.18(11)
N(1)–C(1) 1.350(6)	N(2)–Ni(1)–Br(1) 116.49(10)
N(2)–C(12) 1.361(6)	Br(2)–Ni(1)–Br(1) 130.45(4)
	N(1)–C(1)–C(12) 115.2(4)
	N(2)–C(12)–C(1) 115.2(4)

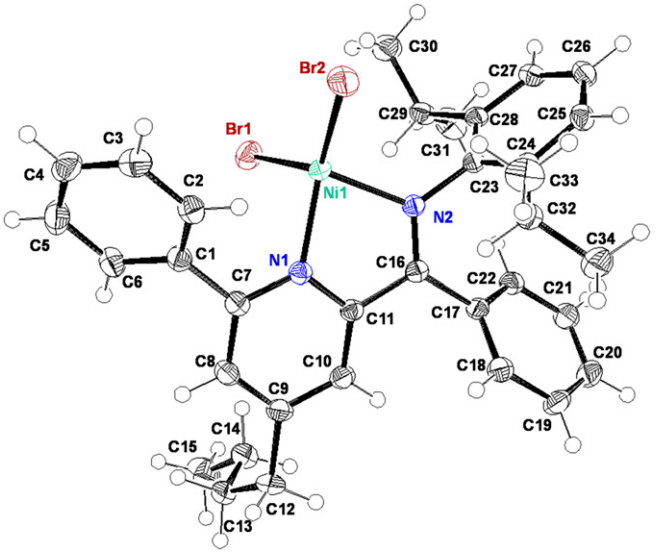


Fig. 1. ORTEP diagram of the solid-state molecular structure of complex **13**. Thermal ellipsoids are drawn at the 50% probability level.

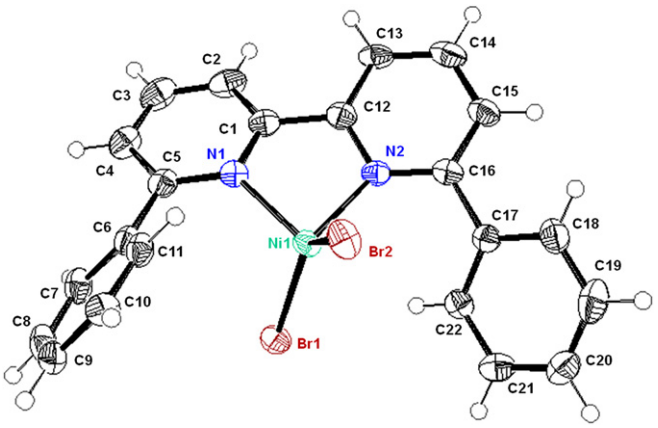


Fig. 2. ORTEP diagram of the solid-state molecular structure of complex **14**. Thermal ellipsoids are drawn at the 50% probability level.

complexes with n-butyl substituents (complexes **11**–**13**) show higher activity than the corresponding complexes with no n-butyl substitution (complexes **8**–**10**).

Complex **14** comes under a different class of ligand having bipyridine architecture when compared with other complexes of (imino)pyridine structure. This again provides an open metal center leading to oligomerization of ethylene when activated with EASC in ethylene atmosphere. This complex shows only a moderate activity of 0.2×10^6 g-oligomer/mol-Ni h bar toward ethylene.

All the complexes produced 1-butene (81–88%) as a major product together with 1-hexene (3–9%) as a minor product, demonstrating they tend to favor chain termination over propagation. It was difficult to find a specific trend according to the structure of the complexes. In general nickel catalysts tend to yield internal olefins in ethylene oligomerization reactions [23,24]; however, the complexes of this study produces only negligible amount of internal olefins. These results demonstrate that (i) reversible β-H elimination after ethylene insertion, followed by reinsertion with the opposite regiochemistry and chain transfer to give 2-butene or (ii) a re-uptake mechanism leading to isomerization of 1-butene is not activated in the present catalyst system.

A detailed investigation on the properties of these complexes in ethylene oligomerization reactions based on ion-pair concept along with a DFT investigation on the background of these results are currently ongoing and will be reported elsewhere in due course.

Table 2
Summary of ethylene oligomerization results over various N(II) complexes **8**–**14** in combination with EASC at standard conditions[a]..

Run no	Complex	Activity[b]	Selectivity[c]			
			$C_4^=$		$C_6^=$	
			α = [d]	ΣC_{4i} = [e]	α = [d]	ΣC_{6i} = [e]
1	**8**	16.0	86	4	6	4
2	**9**	25.2	83	3	8	6
3	**10**	34.9	82	7	7	4
4	**11**	16.3	86	5	5	4
5	**12**	26.5	84	2	9	5
6	**13**	35.7	81	7	8	4
7	**14**	0.2	88	7	3	1

[a] Oligomerization conditions: catalyst = 2.5 μmol, solvent = 80 mL, time = 30 min, and [EASC]/[Ni] = 150.
[b] Average rate of oligomerization in $R_p \times 10^{-6}$ (g-oligomer)(mol-Ni)$^{-1}$h^{-1} bar^{-1}.
[c] Determined by GC.
[d] α-olefin.
[e] Sum of internal olefins other than α-olefin.

4. Conclusions

A series of [N-N] type bidentate Ni(II) complexes based on phenylpyridine have been synthesized using a direct method to activate the α-CH in pyridine. This method has found to be a very efficient to synthesize pyridine related ligands in that various metal complexes with different structures are produced in a single reaction in good yields. Solid state structure obtained from single crystal XRD measurement sheds light on the details of three dimensional arrangements of atoms and groups in the complex molecules. The distortions from the standard tetrahedral structure are very clearly observed from the bond angles that Ni makes with its four coordination sites. All these complexes showed high activity toward ethylene when activated with EASC, yielding exclusively 1-butene (81–88%) and some amounts of 1-hexene (3–9%) together with negligible internal olefins.

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Appendix A. Supplementary material

CCDC 756871 and 758995 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.08.005.

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