ISSN:
Print - 2277 - 0593
Online - 2315 - 7461
© FUNAAB 2012

Journal of Natural Science, Engineering and Technology

AN IMPROVED SYNTHESIS OF ETHYL 6-(BENZIMIDAZOL-2-YL) PYRIDINE-2-CARBOXYLATE AND APPLICATION OF ITS NICKEL COMPLEX TOWARDS ETHYLENE CATALYTIC BEHAVIOR

S. ADEWUYI[a,*], S. A. AMOLEGBE[a], C. A. AKINREMI[a], AND A. SOBOLA[b]

[a] Department of Chemistry, University of Agriculture Abeokuta, P M B 2240, Abeokuta, Ogun State, Nigeria.
[b] Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa.
***Corresponding author:** E-mail: adewuyis@unaab.edu.ng , kafcheff@yahoo.co.uk

ABSTRACT

Ethyl 6-(benzimidazol-2-yl)-pyridine-2-carboxylate (EBIPC) was efficiently synthesized by condensation reaction of β-keto ester pyridine carboxylate and o-phenylenediamine. The compound was characterized by elemental analysis and spectroscopic techniques (IR and NMR) to confirm its molecular structure. This new protocol afforded a product with higher yield (65.1%) and reduced number of reaction steps. Upon activation with trimethylaluminum (Me_3Al) as the co-catalyst, the nickel complexes exhibited high catalytic activities for ethylene oligomerization (up to 1.26×10^6 g $mol^{-1}(Ni)$ h^{-1}). Various polymerization reaction conditions significantly influenced the catalytic properties of the complexes.

Key words: benzimidazolylpyridine, nickel complex, co-catalyst, ethylene oligomerization

INTRODUCTION

The modern chemical industries greatly rely on alkenes (commonly α-olefins) as essential starting material for ethylene oligomerization and polymerization. The development of new catalysts for this purpose is of high interest to academic and industrial considerations. Ni (II) complexes bearing bidentate mono-anionic ligands have been reported to be effective ethylene oligomerization catalysts (Keim *et al.,* 1978 & 1983; Keim, 1990). Establishing further the effect of other ligating organic moieties, nickel complexes bearing different ancillary ligations such as phosphinosulfonamide (Rachita *et al.,* 2000), 2-pyridylbenzamide (Sun *et al.,* 2004), anilinotropone (Jenkins & Brookhart, 2004), oxazoline (Speiser *et al.,* 2004), benzamidinate- acetylacetonate (Nelkenbaum *et al.,* 2005), pyrazolyl (Ajellal *et al.;* Hou *et al.,* 2006), salicylaldiminato (Wehrmann *et al.,* 2006), imino-1,10-phenanthrolines (Sun *et al.,* 2006), quinoxalinyl-6-iminopyridines (Adewuyi *et al.,* 2007), pyridinealdoxime (Mukherjee *et al.,* 2009) and formazanates (Zaidman *et al.,* 2010) have also been described for their various level of catalytic activities. Following this trend, a six-coordinated methyl derivative of benzimidazol-2-ylpyridine-2-carboxylate nickel complex with distorted octahedral geometry (Fig. 1) successfully oligomerized ethylene when activated by diethylaluminumchloride (Et_2AlCl) co-catalyst (Hao *et al.,* 2007). This new catalyst system produced mainly C_4 and C_6 oligomers with increased catalytic activity.

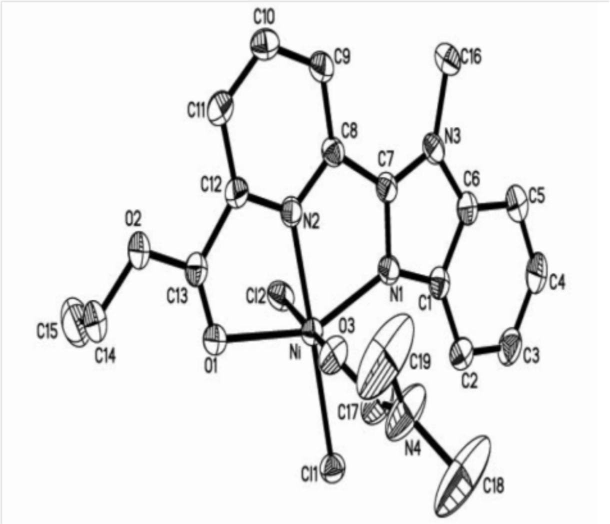
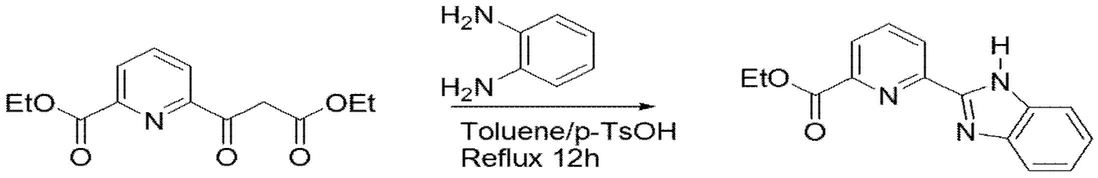


Figure 1: Molecular Structure of benzimidazol-2-ylpyridine-2-carboxylateNiCl_2 complex (Hao *et al.,* 2007)

Remarkably, the synthetic literature methods for the preparation of the ligand group in the complex are condensation reaction of o-phenylenediamine and pyridine-2-carboxylic acid in the presence of phosphoric acid (PPA) or o-phenylenediamine and 2,6-lutidine through oxidation reaction by sulfur. However, this procedure will yield an intermediate, 2-(2-benzoimidazole)-6-methylpyridine. Oxidation of the methyl end is necessary to obtain 6-(benzimidazol-2-yl)-pyridine-2-carboxylic acid and subsequent esterification with ethanol to form Ethyl 6-(benzimidazol-2-yl)-pyridine-2-carboxylate (Barni & Savarino, *1977;* Sun *et al.,* 2007).

These methods do not only involve too many steps, the several work up processes indeed affect the yield of the final product. In order to resolve this problem, direct condensation reaction between o-phenylenediamine and β-ester carboxylate, an isolated by-product in the transformation of dicarbethoxy pyridine into acetylpyridine (Asma *et al.,* 2008) was proposed. Expectedly, the reaction furnished the desired product in good yield (Scheme 1). Herein, we report the new synthesis route for the preparation of ethyl 6-(benzimidazol-2-yl)-pyridine-2-carboxylate (EBIPC) as well as the catalytic activity of its Ni (II) complex activated by trimethylaluminum (Me_3Al) for ethylene conversion.



Scheme 1: Synthesis protocol of EBIPC

MATERIALS AND METHODS

All manipulations of air and/or moisture sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by literature methods (Furniss *et al.,* 1989). All reagents were purchased from Aldrich and were directly used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. Elemental analysis was performed on a Flash EA 1112 microanalyser. GC analysis were performed with a Carlo Erba strumentazione gas chromatograph equipped with a flame ionization detector and a 30m (0.2 mm i.d., 0.25 µm film thickness) DM-1 silica capillary column. The yield of oligomers was calculated by referencing with the mass of the solvent based on the prerequisite that the mass of each fraction is approximately proportional to its integrated areas in the GC trace.

Synthesis of EBIPC:

O-phenylenediamine (3.78 g, 0.035 mol), β-ester carboxylate (6.89 g, 0.027 mol) and p-TsOH (0.04 g) were dissolved in 50 ml toluene. The mixture was refluxed for 12 h, after which the resultant solution was cooled to room temperature to allow precipitation of the crude product (Scheme 1). The precipitate was filtered, washed with diethylether and dried under vacuum. After column separation (Silca-gel, Pet-ether: EtOAc, 1:4), the pure product was obtained as a light yellow powder.

Ethylene oligomerization at ambient and elevated temperatures:

Ethylene oligomerization at 1 atm of ethylene was carried out as follows: The precatalysts (5 µmol) were added to a Schlenk flask under nitrogen. The flask was backfilled three times with N_2 and twice with ethylene and thereafter charged with toluene and co-catalyst solutions in turn under ethylene atmosphere. The reaction solution was vigorously stirred under 1 atm of ethylene at the set temperature. At the end of the desired period of time, the reaction was quenched by 5% aqueous hydrogen chloride and the products were analyzed by GC.

The ethylene oligomerization at elevated-pressure was performed in a stainless autoclave (500 ml) through a solenoid clave for continuous feeding of ethylene at desired pressures. The complexes (5 µmol) were dissolved in 100 ml of freshly distilled toluene under nitrogen atmosphere, and the solution was subsequently transferred to the fully dry reactor via a syringe. The required amount of co catalyst was then injected into the reactor using a syringe, and the reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene. The reaction was terminated and analyzed by using the same method as described above for the reaction with 1 atm.

Ethylene oligomerization at ambient and elevated temperatures:

Ethylene oligomerization at 1 atm of ethylene was carried out as follows: The precatalysts (5 µmol) were added to a Schlenk flask under nitrogen. The flask was backfilled three times with N_2 and twice with ethylene and thereafter charged with toluene and co-catalyst solutions in turn under ethylene atmosphere. The reaction solution was vigorously stirred under 1 atm of ethylene at the set temperature. At the end of the desired period of time, the reaction was

quenched by 5% aqueous hydrogen chloride and the products were analyzed by GC.

The ethylene oligomerization at elevated-pressure was performed in a stainless autoclave (500 ml) through a solenoid clave for continuous feeding of ethylene at desired pressures. The complexes (5 µmol) were dissolved in 100 ml of freshly distilled toluene under nitrogen atmosphere, and the solution was subsequently transferred to the fully dry reactor via a syringe. The required amount of co catalyst was then injected into the reactor using a syringe, and the reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene. The reaction was terminated and analyzed by using the same method as described above for the reaction with 1 atm.

RESULTS AND DISCUSSION

Synthesis and characterization of EBIPC:

The pure product was obtained as a light yellow powder in 65.1% yield. The IR, ^{1}H- and ^{13}C NMR data are assigned as: IR (KBr; cm^{-1}): 3364; 3068; 2978; 1719 ($\nu_{C=O}$); 1593; 1459; 1406; 1386; 1301; 1251; 1176; 742.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 11.59 (s, 1H, O-H), 8.62(d,1H, Py-Hm), 8.14 (d, 1H, Py-Hm), 8.0 (t, 1H, Py-Hp), 7.85 (td, 1H, Bz), 7.53 (td,1H, Bz), 7.33 (dd, 2H, Bz),4.54 (q, 2H,O–CH_2),2.50 (s, 2H, N=C(CH_2), 1.49 (t,3H,CH_2(CH_3).

^{13}C NMR (75.45 MHz, $CDCl_3$, δ): 164.66, 149.73, 148.72, 147.17, 144.00, 137.94, 133.90, 125.

The assigned peaks agree with the previous old methods (Sun *et al.,* 2007). The compound was further confirmed by elemental analysis as: Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.32; H, 4.86; N, 15.69.

Investigation of the effect of various parameters on ethylene oligomerization:

The influence of Al/Ni molar ratio and reaction temperature on ethylene reactivity was studied with Ni/Me_3Al system (Table 1). Increasing the Al/Ni molar ratio from 50 to 500, its productivity of ethylene oligomerization was greatly enhanced (6.3-7.32 x 10^5 g mol^{-1}(Ni) h^{-1}). However, further increasing of the Al/Ni molar ratio to 1000 resulted in lower activities of oligomerization of ethylene (2.23 x 10^5 g mol^{-1}(Ni) h^{-1}). This result is comparable with the various organoaluminum co-catalyst systems (Hao *et al.,* 2007) as well as Ni-phenoxy imine/MAO catalyst (Dolinsky *et al.,* 2006). In view of these observations, further experiments were performed at molar ratio of Al/Ni at 500.

Table 1: Ethylene oligomerization with EBIPC-$NiCl_2$ System at different Al/Ni molar ratio[a]

Al/Ni	Activity[b]	Oligomers distribution (%)[c]	
		C4	C6
50	6.30	95.5	4.3
100	7.21	85.5	14.5
200	7.03	81.1	18.9
500	7.32	94.5	5.5
1000	2.23	93.8	6.2

[a] Conditions: 5 µmol of complexes, 100 mL of toluene, 0.5 h. 20 atm. 20 °C.
[b] 10^5 g mol^{-1}(Ni) h^{-1} [c] Weight percent determined by GC analysis.

Increased catalytic activity was observed at reaction temperature of 20 °C which produced largely C_4 oligomers (7.32 x 10^5 g mol^{-1}(Ni) h^{-1}, Table 2). However, as the reaction temperature increases, the catalytic activity decreases with marginal increase in C_6 proportion. This can be ascribed to the decomposition of some active species and lower ethylene solubility at higher temperature (Dolinsky *et al.,* 2006).

Table 2: Ethylene oligomerization with EBIPC-NiCl$_2$ System at different temperatures [a]

Temp (oC)	Activity[b]	Oligomers distribution (%)[c]	
		C4	C6
20	7.32	94.5	5.5
40	1.72	85.8	14.2
50	1.51	88.6	11.4
60	1.28	84.6	15.4
80	0.91	81.5	18.5

[a] Conditions: 5 µmol of complexes, 100 mL of toluene, 0.5 h. Al/Ni 500, 20 atm.
[b] 10^5 g mol^{-1}(Ni) h^{-1} [c] Weight percent determined by GC analysis.

Table 3: Ethylene oligomerization with EBIPC-NiCl$_2$ System at different pressure [a]

Pressure (atm)	Activity [b]	Oligomers distribution (%)[c]	
		C4	C6
1	0.50	96.8	3.6
10	1.85	89.8	10.2
20	7.32	94.5	5.5
30	12.6	93.1	6.9
40	12.5	92.7	7.3

[a] Conditions: 5 µmol of complexes, 100 mL of toluene, 0.5 h. Al/Ni 500, 20°C.
[b] 10^5 g mol^{-1}(Ni) h^{-1} [c] Weight percent determined by GC analysis

Conspicuously, the ethylene concentration significantly affects the catalytic behavior of the complex. The catalytic system was investigated under different ethylene pressure. The activities of the complex rose sharply with increasing ethylene pressure and at 30 atmospheres, value of 1.26 x 10^6 g mol^{-1}(Ni) h^{-1} was obtained (Table 3).

CONCLUSION

Ethyl 6-(benzimidazol-2-yl)-pyridine-2-carboxylate was prepared by direct condensation reaction between o-henylenediamine and β-ester carboxylate. This method is preferred over the literature method as it reduces the number of steps and afforded an improved product yield. Upon activation with trimethylaluminum (Me_3Al), the nickel complex afforded good activity for ethylene oligomerization at low temperature and high pressure.

REFERENCES

Adewuyi, S., Li, G., Wang, W., Hao, P., Sun, W. –H., Tang, N., Yi, J. 2007. Nickel (II) complexes chelated by 2-quinoxalinyl -6-iminopyridines: Synthesis, crystal structures and ethylene oligomerization. *J. Organomet. Chem.,* 692: 3532–3541.

Ajellal, N., Kuhn, M.C.A., Boff, A.D.G., Horner, M., Thomas, C.M., Carpentier, J. –F., Casagrande, O. L. Jr., 2006. Nickel complexes based on tridentate pyrazolyl ligands for highly efficient dimerization of ethylene to 1-butene. *Organometallics,* 25: 1213–1216.

Asma, M., Adewuyi, S., Kuang, X., Amin, B., Sun, W.–H. 2008. An improved synthetic protocol and plausible mechanism in forming acetylpyridines from 2,6-dicarbethoxypyridine. *Letters in Organic Chemistry,* 5**:** 296–299.

Barni, E., Savarino, P.J. 1977. 2-(Methylpyridyl or quinolyl)benz-X-azoles. *Heterocyclic Chem.,* 14: 937–940.

Furniss, B.S. Hannaford, A.J., Smith, P.W.G., Tatchell, A.R. 1989. Vogel's Textbook of Practical Organic Chemistry. England: ELBS/Longman, pp. 786–790.

Dolinsky, M.C.B., Lin, W.O., Dias, M.L. 2006. Ethylene polymerization with nickel complexes containing aminophosphine ligands. *Journal of Molecular Catalysis A: Chemical,* 258: 267–274.

Hao, P., Zhang, S., Sun, W.–H., Shi, Q., Adewuyi, S., Lu, X. & Li, P. 2007. Synthesis, characterization and ethylene oligomerization studies of nickel complexes bearing 2-benzimidazolylpyridine derivatives. *Organometallics*, 26: 2439–2446.

Hou, J., Sun, W.-H., Zhang, S., Ma, H., Deng, Y. & Lu, X. 2006. Synthesis and characterization of tridentate nickel complexes bearing P^N^N and P^N^P ligands and their catalytic property in ethylene oligomerization.. *Organometallics,* 25: 236–244.

Jenkins, J.C., Brookhart, M. 2004. A mechanistic investigation of the polymerization of ethylene catalyzed by neutral Ni (II) complexes derived from bulky anilinotropone ligands. *J. Am. Chem. Soc.,* 126: 5827–5842.

Keim, W. 1990. Nickel: An element with wide application in industrial homogenous catalysis. *Angew. Chem. Int. Ed. Engl.*, 29: 235–244.

Keim, W., Behr, A. , Limbacker, B., Kruger, C. 1983. Novel nickel-oligomerization catalysts with arsenic-oxygen chelate ligands. *Angew. Chem. Int. Ed. Engl.*, 22: 503–504.

Keim, W., Kowaldt, F.H., Goddard, R., Kriige, C. 1978. Novel coordination of (Benzoy1methylene)triphenylphosphorane in a nickel oligomerization catalyst. *Angew. Chem. Int. Ed. Engl.,* 17(6): 466–467.

Mukherjee, S., Patel, B. A., Bhaduri, S. (2009). Selective ethylene oligomerization with nickel oxime complexes. *Organometallics,* 28(10): 3074–3078.

Nelkenbaum, E., Kapon, M., Eisen, M. S. 2005. Synthesis and molecular structures of neutral nickel complexes: Catalytic activity of (benzamidinato)(acetylacetonato)nickel for the addition polymerization of norbornene, the oligomerization of ethylene, and the dimerization of propylene. *Organometallics,* 24: 2645–2659.

Rachita, M. J., Huff, R. L., Bennett, J. L., Brookhart, M. 2000. Oligomerization of ethylene to branched alkenes using neutral phosphinosulfonamide nickel (II) complexes. *J. Polym. Sci. Part A: Polym. Chem.*, 38: 4627–4640.

Speiser, F., Braunstein, P. & Saussine, L. 2004. Nickel and iron complexes with oxazoline- or pyridine-phosphonite ligands: synthesis, structure and application for the catalytic oligomerization of ethylene. *J. Chem. Soc., Dalton Trans*, 1539–1545.

Sun, W.–H., Hao, P., Zhang, S., Shi, Q., Zuo, W. & Tang, X. 2007. 2-(Benzoimidazole)-6-(1-aryliminoethyl)pyridyl complexes of iron (II) and cobalt (II) as highly active catalysts for ethylene oligomerization and polymerization: Synthesis, characterization and their catalytic behaviors. *Organometallics,* 25: 666–708.

Sun, W.–H., Zhang, S., Jie, S., Zhang, W., Li, Y., Ma, H., Chen, J., Wedeking, K., Fröhlich, R. J. 2006. Synthesis, characterization and ethylene oligomerization studies of nickel complexes bearing 2-imino-1, 10-phenanthrolines. *J. Organomet. Chem.,* 691: 4196–4203.

Sun, W.–H., Zang,W., Gao, T., Tang, X., Chen, L., Li, Y., Jin, X. 2004. Synthesis and characterization of N-(2-pyridyl) benzamide-based nickel complexes and their activity for ethylene oligomerization. *J. Organomet. Chem.,* 689: 917–929.

Wehrmann, P., Zuideveld, M., Thomann, R., Mecking, S. 2006. Copolymerization of ethylene with 1-butene and norbornene to higher molecular weight copolymers in aqueous emulsion. *Macromolecules,* 35: 5995–6002.

Zaidman, A.V., Kayumoy, R.R., Beloy, G.P., Pervova, I.G., Lipunov, I.N., Kharlampidi, Kh. E. 2010. Ethylene oligomerization in the presence of catalytic systems based on nickel (II) formazanates. *Petroleum Chemistry*, 50(6): 450–454.

(Manuscript received: 20th June, 2012; accepted: 25th January, 2013).