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FULL PAPER

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Synthesis and characterization of (pyrazolylethylphosphinite)nickel(II) complexes and catalytic activity towards ethylene oligomerization

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Compounds (2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L1**), 2-(3,5-di-tert-butyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L2**), and 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L3**) were prepared using the synthetic routes reported in literature. These compounds were reacted with [$NiCl_2(DME)_2$] or [$NiBr_2(DME)_2$] under appropriate reaction conditions to afford six new nickel(II) compounds ([$NiCl_2$(**L1**)] (**1**), [$NiCl_2$(**L2**)] (**2**), [$NiCl_2$(**L3**)] (**3**), [$NiBr_2$(**L1**)] (**4**), [$NiBr_2$(**L2**)] (**5**) and [$NiBr_2$(**L3**)] (**6**)). The new nickel(II) pre-catalysts catalyze the oligomerization of ethylene, in the presence of ethylaluminium dichloride as co-catalyst, to produce butenes, hexenes, octenes and higher carbon chain ethylene oligomers with very little Friedel-Crafts alkylation products when the reactions were run in toluene.

KEYWORDS
ethylene, nickel complexes, oligomerization, pyrazolylphosphinite

1 | INTRODUCTION

Nickel based pre-catalysts have become popular in the development of olefin oligomerization processes following the pioneering work by Keim and co-workers for the SHOP process.[1] The oligomers produced are industrially important and the short-chain alkenes (C_4-C_{10}) can be used as co-monomers and as precursors to plasticizers, detergents and polyalphaolefins.[2] The role of oxidation state of the metal in the catalytic activity in oligomerization is not clearly understood. For example in the ethylene oligomerization catalyzed by nickel containing molecular sieves, it is assumed that nickel(II) ions in high-coordination unsaturated environments are the active sites.[3] In contrast, another school of thought supports the notion that low-valent nickel ions, most likely nickel(I) species, are the active sites for ethylene oligomerization.[4] Despite the numerous arguments about the active species being either nickel(I)[5] or nickel(II),[6,7] there is no conclusive evidence on the role of the oxidation state in the catalytic activity.

In recent times, ligand design has focused on mixed donor concept, where different chemical donor functionalities, such as hard and soft donor atoms or groups are employed. This stems from the discovery that neutral bidentate scaffolds afford active species that efficiently oligomerize ethylene at relatively lower temperatures and pressures.[7] Of particular interest is the combination of neutral chelating P^N ligands with nickel(II). This has been proven to be effective in the catalytic oligomerization of ethylene by tuning the electronic and steric properties of these ligands to influence activity and selectivity.[8] Noteworthy is Brookhart's α-diimine ligand systems which when complexed with palladium or nickel produced either oligomers or polymers depending on the steric bulk of the substituent used.[7a]

There have been reports on P^N nickel catalysts which oligomerize ethylene followed by Friedel-Crafts alkylation of toluene by the ethylene oligomers formed in the oligomerization reaction.[9] Dyer *et al.*[9e] used a P^N donor nickel complex with ethylaluminium dichloride (EADC) as co-catalyst to produce butene and hexene followed by alkylation of toluene, the solvent used for the reaction. Interestingly, the alkyl toluenes were only produced when the complex has phenyl groups attached to the phosphorus atom. When groups such as di-isopropylamino (*i*-Pr_2N), dimesityl (Mes) and diphenylamino (Ph_2N) groups were used, there was no alkylation. Song *et al.*[9f] on the other hand, used MAO as co-catalyst with another (P^N) nickel(II) complex to produce the active catalyst that oligomerized ethylene to butene, hexene and octene followed by alkylation of the solvent (toluene) by the oligomers. Again other studies[9a, 9b, 9c, 9d] reported nitrogen based nickel complexes activated with aluminum co-catalysts resulting in ethylene oligomerization followed by Friedel-Crafts alkylation of the solvent. They further stated that where ethylene oligomerization is followed by Friedel-Crafts alkylation the two reactions occur in tandem and promoted by a tandem catalytic system.

In this work, we report (pyrazolylethylphosphinite) nickel(II) complexes as pre-catalysts for ethylene oligomerization reaction with EADC as co-catalysts in different reaction solvents.

2 | EXPERIMENTAL SECTION

2.1 | Materials and instrumentation

All ligands and complexes were synthesized under dry Nitrogen/Argon using standard Schlenk techniques. All solvents were of analytical grade and were dried using MBRAUN SPS-800 solvent drying system and or distilled before used. 2,4-pentanedione, triethylamine, 2-hydroxyethylhydrazine, chlorodiphenylphosphine, 2,2,6,6-tetramethyl-3,5-heptanedione, 1,3-diphenyl-1,3-propanedione (all of reagent grade) were used as received from Sigma Aldrich. The triethylamine was dried over potassium hydroxide prior to use. Compounds (3,5-dimethylpyrazol-1*H*-yl)ethanol, (3,5-di-*tert*-butylpyrazol-1*H*-yl)ethanol and (3,5-diphenylpyrazol-1*H*-yl)ethanol, were synthesized following the solvent-free methods reported by Darkwa and co-workers.[10] **(**2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L1**), 2-(3,5-di-*tert*-butyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L2**), and 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)ethyldiphenylphosphinite (**L3**) were prepared using the synthetic routes reported in literature.[11]

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were analyzed on a Bruker Ultrashield 400 (^1H NMR 400.17 MHz, $^{13}C\{^1H\}$ NMR 100.62 MHz and $^{31}P\{^1H\}$ NMR 161.99 MHz) in $CDCl_3$ at room temperature. The coupling constants were calculated in Hertz (Hz) and ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts referenced to residual proton or carbon signals of the $CDCl_3$ which are quoted in δ (ppm) ($CDCl_3$: 7.24 and 77.00 respectively. GC analyses were performed using a Varian 3900 with 15 m x 0.25 mm dimethylpolysiloxane column set to an initial temperature of 40 °C and then increased to 300 °C at 5 °C/min. GC–MS data was recorded using a Shimadzu GC–MS-QP2010 fitted with a single quadrupole mass detector. Atmospheric Pressure Chemical Ionization (APCI) was performed on Bruker micrOTOF-QII 10390 at a dry gas flow of 8.0 L/min and heater at 200 °C. Crystal data analyses were performed on a Bruker APEX-II CCD diffractometer at the University of Johannesburg. Elemental analyses were performed on a Thermo Scientific FLASH 2000 CHNS-O Analyzer at the University of Johannesburg. ESI-MS were recorded on a Waters Synapt G2 spectrometer at the University of Stellenbosch, South Africa. The magnetic susceptibility measurements were performed on a Magway MSB Mk1 balance at room temperature and the effective magnetic moment (μ_{eff}) calculated as described in literature.[12]

2.2 | Syntheses of nickel(II) complexes

2.2.1 | Synthesis of [$NiCl_2$(L1)] (1)

A dry dichloromethane solution (10 ml) of compound **L1** (0.05 g, 0.15 mmol) was added to a stirring dichloromethane solution of [$NiCl_2$(DME)] (0.03 g, 0.14 mmol). The reaction mixture turned orange immediately and was left for 24 h under N_2 atmosphere at room temperature. The solvent was then reduced to about 5 ml and dry hexane added to precipitate the product. The product was filtered, washed with hexane and dried in *vacuo* to afford brown solid. Yield = 0.05 g (79%). ESI-MS: *m/z* (calc) $[M]^+ = 456.02$; Found $[M]^+ = 456.15$ (25%). Anal. Calc.: $C_{19}H_{21}Cl_2N_2NiOP$: C, 50.27%; H, 4.66%; N, 6.17%. Found: C, 50.16%; H, 4.27%; N, 6.20%. $\mu_{eff} = 3.55$ BM.

Similar procedure used to prepare compound **1** was used for compounds **2–6** using the appropriate reagents.

2.2.2 | Synthesis of [$NiCl_2$(L2)] (2)

Compound **L2** (0.14 g, 0.35 mmol) was added to [$NiCl_2$(DME)] (0.05 g, 0.25 mmol) to afford an orange solid. Yield = 0.05 g (79%). HR-ESI-MS: *m/z* (calc) $[M + H + Na]^+ = 563.12$; Found $[M + H + Na]^+ = 563.05$ (100%). Anal. Calc.: $C_{25}H_{33}Cl_2N_2NiOP$: C, 55.8%; H, 6.18%; N, 5.21%. Found: C, 50.16%; H, 4.27%; N, 6.20%. $\mu_{eff} = 3.43$ BM.

2.2.3 | Synthesis of [$NiCl_2$(L3)] (3)

Compound **L3** (0.20 g, 0.45 mmol) was added to [$NiCl_2$(DME)] (0.07 g, 0.30 mmol) to give a. yellow solid. Yield = 0.15 g (88%). HR-ESI-MS: *m/z* (calc) $[M\text{-}Ph + Na]^+ = 521.99$; Found $[M\text{-}Ph + Na]^+ = 522.45$(97.4%); *m/z* (calc) $[M\text{-}4Ph + Na]^+ = 294.87$; Found $[M\text{-}4Ph + Na]^+ = 294.68$ (39%). Anal. Calc.: $C_{29}H_{25}Cl_2N_2NiOP$: C, 60.25%; H, 4.36%; N, 4.85%. Found: C, 59.93%; H, 4.58%; N, 4.33%. $\mu_{eff} = 3.49$ BM.

2.2.4 | Synthesis of [NiBr$_2$(L1)] (4)

Compound **L1** (0.24 g, 0.75 mmol) and [NiBr$_2$(DME)] (0.15 g, 0.50 mmol) were reacted together to give a green solid. Yield = 0.23 g (85%). ESI-MS: *m/z* (calc) $[M\text{-}Br]^+ = 462.95$; Found $[M\text{-}Br]^+ = 463.05$ (100%). Anal. Calc.: $C_{19}H_{21}Br_2N_2NiOP$: C, 42.04%; H, 3.90%; N, 5.16%. Found: C, 42.08%; H, 3.78%; N, 5.33%. $\mu_{eff} = 3.68$ BM.

2.2.5 | Synthesis of [NiBr$_2$(L2)] (5)

Compound **L2** (0.26 g, 0.65 mmol) and [NiBr$_2$(DME)] (0.15 g, 0.50 mmol) were reacted to afford a pale green solid. Yield = 0.25 g (81%) HR-ESI-MS: *m/z* (calc) $[M]^+ = 628.00$; Found $[M]^+ = 629.44$(75%); (calc) $[M + Na]^+ = 646.99$; Found $[M + Na]^+ = 647.45$ (43%). Anal. Calc.: $C_{25}H_{33}Br_2N_2NiOP$: C, 55.80%; H, 6.18%; N, 5.21%. Found: C, 54.97%; H, 6.20%; N, 5.33%. $\mu_{eff} = 3.83$ BM.

2.2.6 | Synthesis [NiBr$_2$(L3)] (6)

Compound **L3** (0.15 g, 0.33 mmol) and [NiBr$_2$(DME)] (0.07 g, 0.23 mmol) were reacted to afford a yellow solid. Yield = 0.11 g (73%). HR-ESI-MS: *m/z* (calc) $[M]^+ = 663.94$; Found $[M]^+ = 662.86$ (50%). Anal. Calc.: $C_{29}H_{25}Br_2N_2NiOP$: C, 52.22%; H, 3.78%; N, 4.20%. Found: C, 51.68%; H, 4.10%; N, 4.18%. $\mu_{eff} = 3.52$ BM.

2.3 | Catalysis

2.3.1 | Procedure for ethylene oligomerization reactions

Ethylene oligomerization was performed in a 50 ml stainless steel autoclave which was dried at 100 °C and cooled under nitrogen prior to usage. In a nitrogen-purged glove box, the autoclave was loaded with the respective catalyst and the required amount of co-catalyst. The general procedure involved charging of the autoclave with the complex and co-catalyst in 5 ml dry toluene. The Ni:Al ratio used was between 1:00–1:600. The autoclave was sealed, removed from the glove box and loaded into the reactor chamber which was heated to the required temperature. The autoclave was then flushed three times with ethylene and the desired ethylene pressure set to a constant flow and maintained throughout the reaction time. At the end of the reaction, the ethylene supply was closed, put under liquid nitrogen trap and the autoclave vented. The reaction was quenched by addition of 2 M HCl and an aliquot of the product mixture was taken for GC analysis. The solvent in the remaining products in the reactor was removed in *vacuo* and the mass of the total non-volatiles products determined. Analysis of the oligomers was performed by GC–MS and the molecular weight determined by APCI.

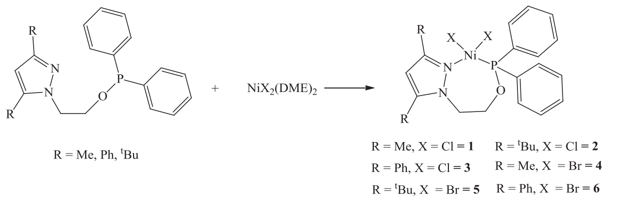
2.3.2 | General characterization of catalytic products

The characterization of the oligomers produced was performed using GC and 2D–GC. The instrument was first calibrated using authentic standard samples of various oligomers of C_6-C_{20} range in order to accurately determine the retention times of the products. Thus the oligomer components in the reaction product mixture were identified by comparison of their reaction times with the standard samples. Additionally, the alkyltoluenes were identified using GC–MS. The molecular weights of the higher carbon content oligomers were determined using APCI.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of nickel complexes

The nickel dichloride complexes (**1–3**) were prepared by reacting the various ligands with the [NiCl$_2$(DME)] precursor whereas the dibromide analogues (**4–6**) used the [NiBr$_2$(DME)] precursor as shown in Scheme 1. This was achieved by reacting equimolar amount of the ligand of interest with the corresponding precursor under inert atmosphere in dichloromethane at room temperature for 24 h. The complexes were obtained in high yields and characterized by mass spectroscopy, magnetic moment and elemental analysis. Due to their paramagnetic nature, satisfactory NMR analysis could not be performed on these complexes. The results of the micro-analysis are consistent with the empirical formulae for the proposed structures of the complexes. These nickel complexes are



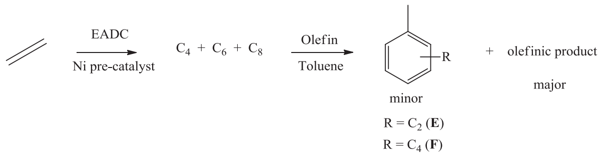
SCHEME 1 Synthesis of pyrazolylphosphinite nickel(II) complexes **1–6**

air and moisture sensitive so they were handled accordingly and stored in a glove box.

The mass spectrometry data for these complexes showed the molecular ion peaks and fragments of the proposed structures as shown in Figure S1. The magnetic susceptibility measurements were performed on the Magway MSB Mk1 balance and the effective magnetic moment (μ_{eff}) calculated from the results obtained. Nickel(II) ($3d^8$) complexes generally assume tetrahedral, square planar or octahedral geometries. Magnetic moment values have successfully been used to predict the geometries of most complexes.

The effective magnetic moment as show in literature of tetrahedral nickel(II) complexes lie between 3.20 BM and 4.10 BM whereas that of the octahedral complexes are between 2.90 BM and 3.30 BM.[13]

The various effective magnetic moment (μ_{eff}) values of complexes **1–6** are 3.55, 3.68, 3.43, 3.83, 3.49 and 3.52 BM respectively. These confirmed the paramagnetic nature of the complexes with crystal field splitting of (eg^4)(t_2g^6) and also suggest that the geometry could be tetrahedral for these complexes.



SCHEME 2 Ethylene oligomerization reaction catalyzed by nickel(II) pre-catalysts. R = C_2H_5; C_4H_9

3.2 | Evaluation of complexes 1–6 as ethylene oligomerization catalysts

Pre-catalyst **1–6** were screened in order to determine their catalytic activity towards ethylene oligomerization. The preliminary reactions were performed in toluene and ethylaluminium dichloride (EADC) used as co-catalyst. Scheme 2 gives the general reaction scheme for the ethylene reactions. All the complexes were found to be active towards ethylene oligomerization producing butenes, hexenes, octenes, trace amounts of Friedel-Crafts alkyltoluenes and other olefinic products which are oily in nature after the volatiles were evaporated.

Pre-catalyst **5** recorded the highest catalytic activity and was therefore used to determine the optimum reaction conditions of temperature, time, ethylene pressure (Table 1) and Ni:Al ratio. The product distribution observed is similar to what was reported in earlier studies.[14] After analyzing the catalytic products with GC (Figure S2–S4), all the volatiles were pumped off, leaving an oily product which was characterized by ^{1}H–NMR, Atmospheric Pressure Chemical Ionization (APCI) technique and 2D–GC as shown in Figure S5–S7.

The ^{1}H–NMR signals between 0.80 and 2.00 ppm indicated different CH_3 and CH_2 protons from the oligomeric mixture. The ^{1}H–NMR chemical shift around 5.10 ppm is a vinylene olefinic end group which is suggestive of termination by β-hydride elimination[15] as shown in Figure S8. For the reactions performed in toluene, the aromatic protons also confirmed the production of alkyltoluenes in the process (Figure S9).

TABLE 1 Summary of the optimization of reaction parameters

Entry	Temp (°C)	Time (h)	Pressure (bar)	Activity (g.molNi^{-1}.h^{-1})	Product(%)				
					C_4	C_6	C_8	E	F
1	25	1	10	191 000	61.0	37.7	0.8	0.3	0.2
2	30	1	10	253 000	76.1	22.2	0.9	0.5	0.3
3	40	1	10	210 000	71.3	26.3	0.6.	1.3	0.5
4	50	1	10	173 000	55.0	41.0	0.3	2.5	1.2
5	30	0.5	10	187 000	57.1	40.2	0.5	1.2	1.0
6	30	2	10	229 000	72.4	26.0	0.6	0.6	0.4
7	30	3	10	204 000	56.1	40.0	1.8	1.3	0.8
8	30	4	10	199 000	65.0	33.2	1.0	0.5	0.3
9	30	1	5	122 000	61.6	37.1	0.8	0.3	0.2
10	30	1	15	279 000	69.3	29.5	0.6	0.4	0.2
11	30	1	20	279 000	58.0	40.5	0.5	0.6	0.4
12	30	1	25	277 000	53.0	45.3	0.7	0.7	0.3
13[d]	30	1	10	306 000	38.3	35.0	26.7	-	-
14[e]	30	1	10	197 000	41.6	29.9	28.5	-	-

Conditions: 5 ml toluene; catalyst = **5**; catalyst loading = 10 μmol; co-catalyst = EADC; Ni:Al = 1:400; [d]5 ml chlorobenzene; [e]5 ml hexane.

APCI technique was used to determine the molecular weight of the higher carbon content products. APCI, as the name suggests, is a soft ionization technique and has the advantage of producing fewer fragments. The envelop shape of the spectrum as shown Figure S5 indicates that single catalytically active species were produced after activation with the co-catalyst.[16] The molecular weights range from 325.0 Da and 548.0 Da which also suggest that the oily products are oligomers. Additionally, the observed molecular weight difference between two adjacent peaks is around 28 units which correspond to ethylene fragment. The distribution of product as observed in the APCI spectrum shows a range from C_8 to C_{26} and this falls within the lubricant range. The oily products were further characterized using 2D–GC separation technique. The blobs in the 2D show that the components were separated and they can be identified as shown by 2D and 3D chromatograms respectively. Combining the other characterization techniques with the 2D–GC, the chromatograms were identified as butyltoluene, hexyltoluene and higher molecular weight oligomers.

One way by which the catalytic oligomerization reaction was optimized was to vary the pre-catalyst:co-catalyst ratio. Using complex **5**, it was seen from the results that Ni:Al ratio of 1:400 is the optimum pre-catalyst to co-catalyst loading. Again it was observed that the both the activity and molecular weight of the oligomers produced increased as the ratio was increased from 1:100 to 1:400. Thus activity increased from 107 000 to 191 000 $\text{g.molNi}^{-1}\cdot\text{h}^{-1}$ while molecular weight increased from 344.3 Da to 372.4 Da. When the pre-catalyst to co-catalyst ratio was further increased to 1:500, both activity and molecular weight decreased marginally. Huang *et al.*[17] attributed the reduction of the molecular weight with increasing Ni:Al ratio to chain-transfer to excess co-catalyst.

From the results, we observed an increase in activity from 161 000 to 255 000 $\text{g.molNi}^{-1}\cdot\text{h}^{-1}$ when temperature was increased from 25 °C to 30 °C. However, increasing the temperature further from 30 °C to 50 °C resulted in a decrease in activity to 173 000 $\text{g.molNi}^{-1}\cdot\text{h}^{-1}$ as well as decrease in molecular weight. Britovsek *et al.*[18] attributed this observation to deactivation or decomposition of the active species as well as low solubility of ethylene at elevated temperatures. Also, increasing the temperature favors the formation of more alkylated toluenes whereas the amount of butenes produced decreased drastically. This means that at elevated temperatures, the butenes produced rapidly alkylate the solvent. Song *et al.*[9f] also observed an increased formation of alkyl toluenes when the temperature was increased from 20 °C to 60 °C. They then concluded that Friedel-Crafts alkylation is favored at high temperatures.

The monomer pressure was varied while keeping the reaction time at 1 h and the temperature at 30 °C (Table 1; entries 9–12). As expected, increase in ethylene pressure led to higher catalytic activities. For instance, the activity increased from 122 000 $\text{g.molNi}^{-1}.\text{h}^{-1}$ at 5 bar to 279 000 $\text{g.molNi}^{-1}.\text{h}^{-1}$ at 15 bar. This trend has been attributed to the increase in ethylene concentration in solution which makes more monomer available for coordination on to the active site.[19] However, further increase in the ethylene pressure resulted in no significant change in activity. Even though kinetically the rate of oligomerization or polymerization increases with increase in ethylene pressure[20] the observed decrease in activity could be due to saturation and diffusion limitations.[21]

The reaction time was also varied in order to determine the stability of the active species over time. Table 1 (entries 2 and 5–8) shows the results obtained. For example when the reaction time was increased from 0.5 h to 1 h, there was a considerable increase in activity while further increase from 1 h to 2 h resulted in a decrease in activity. This clearly shows that the active species deactivates with time.

In order to effectively evaluate the effect of solvent on catalytic activity and product distribution, three different solvents were used; toluene, chlorobenzene and hexane. Table 1 (entries 2 and 13–14) shows the activities and product distributions when the reactions were performed in toluene, chlorobenzene and hexane respectively under similar conditions. In toluene, 77% of the products formed are butenes, 22% hexenes and 1% alkyl toluenes. No significant amounts of octenes were evident. However, in chlorobenzene and hexane there was significant amount of octenes produced but no Friedel-Crafts product was formed. The absence of alkylated toluenes is further confirmed by ^{1}H–NMR data.

It is evident from the above results that the nature of solvent used has an effect on the catalytic products. Thus when activated aromatic solvent such as toluene is used under favorable reaction conditions, there is subsequent alkylation of the solvent to produce Friedel-Crafts alkylated products. In terms of activity, chlorobenzene recorded the highest catalytic activity, followed by toluene and hexane. This trend can be attributed to the relative solubility of the catalyst in the various solvents used.

It is also evident from the initial screening of the pre-catalysts that the environment around the nickel(II) metal centre as well as the substituent on the pyrazole has a considerable effect on the catalytic behaviour of the catalysts. We have observed that the nickel dibromide precursors are in all case more active than their dichloride counterparts as shown in Table 1. This observation agrees with earlier studies and is attributed to the higher solubility of the dibromides in toluene than the dichlorides.[22] Furthermore, when the complexes with bulky (tertiary butyl) groups on the pyrazole are used, there is increased activity. The activity follows the order ^{t}Bu > Ph > Me. This indicates that the steric bulk of the pyrazolyl substituent plays an important role in the catalytic activity of the complex.

4 | CONCLUSION

Six new pyrazolylphosphinite nickel(II) complexes were synthesized and were all active ethylene oligomerization catalysts. Reactions of ethylene with the nickel(II) pre-catalysts and EADC in toluene uniquely produced a mixture of ethylene oligomer ranging from C_4 to C_{26} and minor amounts of butyl and hexyltoluenes which are favored at elevated temperatures. When chlorobenzene is used as solvent, regioisomers of C_4, C_6 and C_8 as well as higher carbon content oligomer were formed. The environment of the nickel and the substituent on the pyrazolyl ligands has considerable effect on the catalytic activity of the complexes. The best performing pre-catalyst **5**, which has bulky tertiary butyl groups on the pyrazole and dibromide nickel centre. Due to higher solubility of the nickel bromide precursors in toluene medium, their catalytic performances for ethylene oligomerization are slightly higher than nickel chloride analogue. Additionally, the variation of the ethylene pressure, Ni:Al ratio, solvent system, reaction time and nature of complex have significant effects on the activity and products formed. It is therefore evident that when the various reaction parameters are varied, the process can be fine-tuned towards desired products.

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