Symmetrically and Unsymmetrically Substituted Bis(pyrazole)-palladium(II) and Nickel(II) Halides as Pre-catalysts for Ethylene dimerization and Friedel-Crafts Alkylation of Toluene and Benzene

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ABSTRACT

Bis(pyrazole)-palladium(II) and nickel(II) halide complexes, [(pz)₂PdCl₂] (1), [(3,5-Me₂pz)₂PdCl₂] (2), [(3,5-ⁱBu₂pz)₂PdCl₂] (3), [(3,5-Ph₂pz)₂PdCl₂] (4), [(3-CF₃,5-Phpz)₂PdCl₂] (5), [(pz)₄NiBr₂] (6), [(3,5-Me₂pz)₂NiBr₂] (7), [(3,5-ⁱBu₂pz)₂NiBr₂] (8), [(3,5-Ph₂pz)₂NiBr₂] (9) and [(3-CF₃,5-Phpz)₂NiBr₂] (10), were investigated as catalysts for ethylene oligomerization using four alkylaluminium compounds as co-catalysts in toluene, benzene and chlorobenzene. The palladium complexes with ethylaluminium dichloride (EtAlCl₂) in toluene selectively produced ethyl- and butyl- toluenes *via* a Friedel-Crafts alkylation of toluene from the ethylene and butenes formed from the dimerization of ethylene. On the other hand, the nickel complexes produced a mixture of butenes and their Friedel-Crafts toluene alkylation products, but very little ethyltoluene. Changing the solvent to benzene produced similar alkyl-aromatics but in chlorobenzene the reaction produced butenes and a yellow oil, with a molecular weight between 501 to 509 g mol⁻¹; representing C₁₈-C₂₀ carbon-containing compounds. Similarly changing the co-catalyst to methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminium chloride (Et₂AlCl) and ethylaluminiumsesquichloride (Et₃Al₂Cl₃) also selectively produced butenes and little or no alkylaromatics.

KEYWORDS

Substituted pyrazoles, palladium(II) and nickel(II) halides, ethylene dimerization, Friedel-Crafts alkylation.

1. Introduction

The last two decades have witnessed increased activity in developing single-site homogeneous ethylene oligomerization and polymerization catalysts in attempts to address some of the problem associated with heterogeneous catalysts for the polymerization of ethylene and other linear α -olefins.¹ These unique compounds have the potential to control product distribution and microstructure while displaying high catalytic activity through the modification of both the steric and electronic properties in a manner that is impossible with heterogeneous catalysts.² Interest in late transition metals olefin oligomerization and polymerization catalysts has particularly grown recently, especially nickel and palladium catalysts that have nitrogen-donor ligands. These are of particular interest due to their ease of synthesis and stability to air and moisture.^{3–5} The remarkable ability of these nitrogen-donor ligands nickel and palladium catalysts to produce olefin oligomers has resulted in the development of pyrazolyl palladium and nickel complexes as the new nitrogen-donor late transition metals ethylene transformation catalysts.^{6,7} In 2002 Li *et al.*⁶ synthesized the first examples *bis*-pyrazole palladium complexes as ethylene polymerization catalysts. Nelana *et al.*⁷ later reported nickel analogues of the palladium compounds as highly active ethylene polymerization catalysts that produced linear high-density polyethylene (LHDPE) when the co-catalyst is methylaluminoxane (MAO).

Several groups have since developed other nitrogen-donor nickel ethylene oligomerization and polymerization catalysts.⁸ Much of the catalyst development has been on P[^]N and N[^]N

donor nickel ethylene oligomerization reactions which produce mainly dimerization and trimerization products. But in these dimerization and trimerization reactions, the role of alkylaluminium co-catalysts has only recently been brought into focus following reports by Dyer *et al.*,⁹ Gao *et al.*,¹⁰ Ojwach *et al.*¹¹ and Budhai *et al.*¹² These reports on ethylene oligomerization and post-oligomerization Friedel-Crafts alkylation of toluene show the importance of EtAlCl₂ as a co-catalyst and the solvent in which the ethylene oligomerization reactions are run. Dyer *et al.*,⁹ Gao *et al.*,¹⁰ Ojwach *et al.*¹¹ and others¹² have all reported the formation of alkyltoluenes as secondary products. However, only selected nickel catalysts from the Dyer⁹ and Gao¹⁰ systems gave Friedel-Crafts alkylation secondary products. But what is unique about the nickel catalysts reported by Ojwach *et al.*¹¹ and Budhai^{12b} is that they all catalyze ethylene oligomerization followed by the formation of large amounts of alkyltoluenes *via* the Friedel-Crafts alkylation of toluene with the ethylene oligomers formed in the reaction. This points to the possible role the pyrazolyl ligands in the nickel catalysts play in promoting the alkylation reactions; although the exact nature of how this promotes the Friedel-Crafts alkylation remains a subject of much speculation. Nonetheless, a catalyst system that can simultaneously produce ethylene oligomers and alkyltoluenes is highly desirable as alkyltoluenes can be starting materials for detergents and surfactants.

In this project we sought to investigate the effect of varying alkylaluminium co-catalysts on ethylene reactions when bis(pyrazole)palladium and nickel complexes were used as pre-catalysts.

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2. Results and Discussions

2.1. Synthesis of Bis(pyrazole) Palladium and Nickel Complexes

Bis(substituted-pyrazole)palladium(II) and nickel(II) halides were prepared according to literature procedures from $[\text{PdCl}_2(\text{NCMe})_2]$ ⁶ and $[\text{NiBr}_2(\text{DME})]$;⁷ except for compounds **5** and **10**, which are new and were prepared from (3-trifluoromethyl-5-phenylpyrazole) (**L5**) and $[\text{PdCl}_2(\text{NCMe})_2]$ and $[\text{NiBr}_2(\text{DME})]$, respectively (Scheme 1).

Comparison of the ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectral data of compounds **1–4** and **6–9** are similar to those reported in the literature.^{1,7} Compounds **L5**, **5** and **10** were characterized by a combination of ^1H , $^{19}\text{F}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopy, by elemental analysis and HR-MS as shown in the supplementary materials (Figs. S1–S4). $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **L5** and **5** showed singlets at -62.22 ppm and -60.41 ppm, respectively, representing the three fluorine atoms in the trifluoromethyl substituents on the pyrazole ring in **L5** and **5** (Fig. S3). No coupling of carbon to fluorine in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectra was observed; this is due to the low natural abundance of ^{13}C . However, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **L5** and **5** showed coupling of the three fluorine atoms to the carbon atoms with the trifluoro-

methyl substituents on the pyrazole resulting in quartets (Fig. S2). The peak for the carbon in position 4 of the pyrazole ring showed a slight downfield shift from 100.9 ppm in **L5** to 101.5 ppm in **5**, while the quaternary carbons were very low intensity upfield peaks at 142.5 ppm and 144.6 ppm in the ligand and the palladium complex, respectively.

2.2. Oligomerization of Ethylene and Subsequent *in situ* Friedel-Crafts Alkylation Reactions

2.2.1. Screening of Complexes **1–10** and Determination of Optimum Co-catalyst Concentrations

Preliminary investigation of the suitability of these pyrazole palladium and nickel complexes as catalysts for ethylene oligomerization was conducted with EtAlCl_2 as a co-catalyst. All the palladium and nickel complexes were found to be active for the dimerization of ethylene and the subsequent Friedel-Crafts alkylation of toluene by ethylene and butenes, but the palladium complexes formed less butenes and more ethyltoluenes (Table 1). Complexes **5** and **10** had the highest catalytic activities among the complexes tested which can be attributed to the CF_3 group on the pyrazole. In fact, the CF_3 functional group has been reported to increase catalytic activity of some metal complexes.¹³

Scheme 1

General reaction scheme for the preparation of palladium(II) and nickel(II) halide pre-catalysts.

Table 1 Screening of pre-catalysts 1–10 for ethylene oligomerization reactions using ethylaluminium dichloride as co-catalyst.

Entry	Pre-catalyst	Al:M	Activity ^a	α -C ₄	%Product distribution					
					A	B	C	D	E	F
1	1	400	43.0	–	65.1	34.9	–	–	–	–
2	2	400	54.0	–	64.2	35.8	–	–	–	–
3	3	400	93.0	–	63.3	36.7	–	–	–	–
4	4	400	100.0	–	62.0	38.0	–	–	–	–
5	5	400	112.0	–	62.2	37.8	–	–	–	–
6	6	350	190.0	43.3	1.8	25.5	4.5	13.0	1.5	10.3
7	7	350	150.0	44.2	1.7	24.6	4.5	13.9	0.6	10.4
8	8	350	173.0	43.2	1.8	24.9	4.6	13.0	2.1	10.4
9	9	350	180.0	44.2	1.7	26.29	2.3	13.6	1.3	10.6
10	10	350	216.0	44.3	1.2	25.87	2.5	14.6	0.6	10.5

Conditions: amount of pre-catalyst Pd or Ni = 10 μ mol, 10 mL toluene, 10 bar, 1 h, 30 °C.^aActivity in kg product mol^{−1} metal h^{−1}.

Experiments were run in triplicate.

Characterization of products by GC (Fig. 1) and GC-MS confirmed that the palladium catalysts gave only two products, mono-ethyltoluenes (**A**) and mono-butyltoluenes (**B**) (Scheme 2). So the palladium catalysts are selective in oligomerizing ethylene to butenes but with the low amount of butenes present in the reaction, the large amount of ethylene present appears to promote alkylation of toluene by to ethyltoluenes *via* a Friedel-Crafts alkylation process. However, with the nickel catalysts, the products were butenes and six alkyltoluenes, namely mono-butyltoluenes (**B**), di-butyltoluenes (**D**) and tri-butyltoluenes (**F**) as major products; and mono-ethyltoluenes (**A**), ethyl-butyltoluene (**C**) and ethyldi-butyltoluenes (**E**) as minor

products (Scheme 2). For the palladium catalysts selectivity towards **A** ranged from 62 to 65 %, but the nickel catalysts are selective towards butene oligomers as primary product and butyltoluenes (**B**, **D** and **F**) as secondary products (Table 1). The alkyltoluenes have regioisomers; formed as a result of toluene being activated at the *ortho* and *para* positions. For example compound **B** has three regioisomers; two can be attributed to butyl groups in *ortho* and *para* positions of the toluene and the third as branched, possibly from 2-butene from the isomerization of 1-butene before alkylation. The other alkylation products would have similar regioisomers if one considers alkylation in *ortho* and *para* positions and possible butene isomers.

Scheme 2

Ethylene oligomerization and Friedel-Crafts reactions, showing typical alkyltoluene products.

Figure 1 GC illustrating the alkylated toluene products and their respective regioisomers. Experiments were run in triplicate.

Having established that complexes **5** and **10** were the most active catalysts amongst the palladium and nickel compounds, respectively, we investigated effect of the concentration of EtAlCl_2 on the ethylene reactions with **5** and **10**. Table 2 is a summary of the data from this variation, indicating that for **5** and **10** the optimum co-catalyst:catalyst ratio was 370:1 and 550:1, respectively. These ratios were used in the subsequent variations of other parameters in the ethylene reactions with these two metal complexes.

2.2.2. Effects of Temperature, Time and Pressure Variation on Catalysis

A steady increase in catalyst activity was observed when temperature of the ethylene reactions was increased from 30 °C to 50 °C while time and pressure remained constant, but catalyst activity decreased above 50 °C (entries 1–4, Table 3). For complex **5** at 30 °C and 40 °C only two products, **A** and **B**, were observed. As the temperature increased to 50 °C and above, we observed the formation of **C**, **D**, **E** and **F** as additional products and a drastic reduction in the amount of **A** formed. When pressure and time were varied for this catalyst only changes in the proportions of products **A**–**F** were observed (entries 6–10, Table 3). Complex **10** produced mainly butenes, the alkyltoluene products **B**, **D** and **F**, and very small amounts of products that contain ethyl groups. For this catalyst optimum activity was $563.8 \text{ kg mol}^{-1} \text{ Ni h}^{-1}$ at 50 °C compared to activity of $216.2 \text{ kg mol}^{-1} \text{ Pd h}^{-1}$ for **5** at the same conditions. Increase in ethylene pressure increased activity for both **5** ($372.8 \text{ kg mol}^{-1} \text{ Pd h}^{-1}$) and **10** ($606.9 \text{ kg mol}^{-1} \text{ Ni h}^{-1}$) (Table 3), with optimum activities at 20 bar. This is typical as increase in pressure of ethylene in the reactor would make more substrate available for the reaction.¹⁴ What is, however, unique is that for the palladium catalyst as temperature increased to 50 °C and above and also as time and pressure increased above 1 h and pressure above 10 bar, amounts of alkylation products also increased. This signifies that when the amount of butenes in the reactor is low, ethyltoluenes is the major product; but as the amount of butenes increased the main alkylation products are alkyltoluenes. Nickel catalysts are generally known for dimerizing ethylene, and since low amounts of butenes in these reactions resulted in more ethyltoluenes, it is

not surprising the nickel catalyst produced mainly butyltoluenes. But compared to other pyrazolyl nickel catalysts reported in the literature^{11,12} that convert all ethylene oligomers from ethylene to alkyltoluenes, the current nickel catalysts are not able to convert all the butenes produced to butyltoluenes in spite of the large amount of EtAlCl_2 used in these reactions. This suggests that the Friedel-Crafts alkylation is not catalyzed by the excess EtAlCl_2 alone, otherwise all the ethylene reactions with the nickel complexes **6**–**10** would have produced exclusively butyltoluenes from butenes present in the product mix.

2.2.3. Effect of Solvent on Ethylene Oligomerization and Friedel-Crafts Alkylation Reactions

Since the observed Friedel-Crafts alkylation of toluene occurred because toluene is an activated aromatic compound for Friedel-Crafts reactions, we investigated the ethylene reactions with complex **10** in less activated aromatic solvents like benzene and chlorobenzene and in a non-aromatic solvent hexane. Of the two aromatic solvents, the more activated benzene produced butylbenzenes; but the less activated chlorobenzene produced butenes and high molecular weight ethylene oligomers (Table 4). The high molecular weight ethylene oligomers were isolated as viscous oily yellow liquids after evaporating the chlorobenzene. After initial attempt to characterize the oil by GC-MS failed, we run mass spectra of the oils using atmospheric pressure chemical ionization (APCI). The oils showed molecular weight in the region $501\text{--}580 \text{ g mol}^{-1}$ representing a mixture of C_{18} to C_{20} olefins. In hexane, only ethylene oligomers (C_{12} to C_{16} olefins) with molecular weight between $344\text{--}484 \text{ g mol}^{-1}$ were identified by APCI. It is worth noting that in chlorobenzene and in hexane ethylene oligomers of similar high molecular weight were produced. Formation of these high molecular weight ethylene oligomers are unusual and could be due to further oligomerization of initially form $\text{C}_4\text{--C}_8$ that nickel and palladium catalysts are known to form when they oligomerize ethylene. It is also interesting to note reports on other nickel complexes and EtAlCl_2 systems for ethylene reactions in toluene that do not yield any Friedel-Crafts alkyltoluenes products,^{9,10} which therefore confirms the role a ligand plays in this catalysis. Our

Table 2 Determination of optimum co-catalyst and pre-catalyst ratios for complex **5** and **10**.

Entry	Pre-catalyst	Al:M	T/°C	Time/h	Pressure/bar	Activity ^a	α -C ₄	%Product distribution					
								A	B	C	D	E	F
1	5	200	30	1	10	25.0	–	62.1	37.9	–	–	–	–
2	5	300	30	1	10	53.0	–	62.0	38.0	–	–	–	–
3	5	350	30	1	10	100.0	–	62.3	37.7	–	–	–	–
4	5	370	30	1	10	140.0	–	62.9	37.1	–	–	–	–
5	5	400	30	1	10	112.0	–	62.2	37.8	–	–	–	–
6	5	500	30	1	10	110.0	–	60.1	39.9	–	–	–	–
7	10	300	30	1	10	200.0	43.2	1.8	24.8	4.7	14.0	10.4	2.1
8	10	400	30	1	10	305.0	44.3	1.7	23.9	2.3	16.6	10.6	1.3
9	10	500	30	1	10	350.0	44.4	1.7	26.0	2.5	15.7	10.5	0.6
10	10	550	30	1	10	433.0	44.3	1.7	26.3	2.5	13.6	10.5	1.1
11	10	600	30	1	10	420.0	44.5	1.8	26.1	2.7	13.9	10.5	0.7
12	10	700	30	1	10	340.0	44.6	1.7	26.2	2.6	13.8	10.3	0.8

Conditions: amount of pre-catalyst Pd or Ni = 10 μ mol, 10 mL toluene, 10 bar, 1 h, 30 °C. ^a Activity in kg product mol⁻¹ metal h⁻¹. Experiments were run in triplicate.

Table 3 Variation of temperature, time and pressure using complexes **5** and **10** and ethylaluminium co-catalyst.

Entry	Pre-catalyst	Al:M	T/°C	Time/h	Pressure/bar	Activity ^a	α -C ₄	%Product distribution					
								A	B	C	D	E	F
1	5	370	30	1	10	140.0	–	64.9	35.1	–	–	–	–
2	5	370	40	1	10	153.1	–	54.6	45.4	–	–	–	–
3	5	370	50	1	10	416.2	–	5.5	58.8	4.6	23.5	2.8	7.3
4	5	370	60	1	10	69.4	–	2.5	60.3	4.6	23.5	2.8	7.3
5	5	370	30	4	10	93.5	–	8.33	63.1	3.5	19.0	2.5	3.45
6	5	370	30	8	10	56.2	–	11.2	65.5	2.3	15.3	1.4	4.32
7	5	370	30	16	10	27.1	–	11.5	77.9	–	10.6	–	5.23
8	5	370	30	1	20	372.8	–	35.3	32.6	15.4	10.9	9.9	4.07
9	5	370	30	1	30	69.4	–	32.4	30.4	14.3	11.3	10.1	1.5
10	5	370	50	1	20	433.4	–	36.4	33.4	10.7	4.7	12.9	2.0
11	10	550	30	1	10	433.0	44.3	2.9	26.3	1.4	13.6	2.8	10.1
12	10	550	40	1	10	462.8	45.0	2.8	26.4	1.5	13.3	2.7	9.2
13	10	550	50	1	10	563.6	57.0	8.1	25.7	–	8.8	–	3.5
14	10	550	60	1	10	416.8	78.0	0.6	16.3	–	6.5	–	–
15	10	550	30	4	10	186.1	56.0	–	25.0	–	19.0	–	–
16	10	550	30	8	10	156.0	62.1	–	20.8	–	17.1	–	–
17	10	550	30	16	10	83.6	73.2	–	13.9	–	6.9	–	–
18	10	550	30	1	20	606.9	69.1	1.6	11.8	<1	18.5	<1	7.6
19	10	550	30	1	30	316.7	56.7	1.4	16.9	1.2	12.1	1.4	10.4
20	10	550	50	1	20	780.3	70.1	<1	13.9	<1	14.2	–	<1

Conditions: amount of pre-catalyst Pd or Ni = 10 μ mol, 10 mL toluene, 10 bar, 1 h, 30 °C. ^a Activity in kg product mol⁻¹ metal h⁻¹. Experiments were run in triplicate.

Table 4 Products formed upon solvent variation using ethylaluminium dichloride as co-catalyst and pre-catalyst **10**.

Solvent	Al:Ni	Activity	% α -C ₄	% Alkyl toluenes	% Alkyl benzenes	Molar mass/g mol ⁻¹
Toluene	550	563	44.3	55.7	–	–
Chlorobenzene	550	1272	68.0	–	–	508.98
Benzene	550	1044	–	–	100	–

Conditions: amount of Ni pre-catalyst = 10 μ mol, Al:Ni = 550:1, ethylene pressure = 10 bar, 10 mL toluene, 50 °C. Experiments were run in triplicate.

catalysts therefore favour the formation of alkylaromatics.

We also investigated the effect of co-catalysts on the ethylene reactions using complex **10** (Table 5). With ethylaluminium-sesquichloride, Et₃Al₂Cl₃, (EASC) there was considerable amount of butenes formed, up to twice as much as when the co-catalyst was EtAlCl₂. EASC also produced very small amounts of alkyltoluenes. The best EASC co-catalyst to nickel ratio was 600:1 and this was ratio used for further variations (Table 6). At low temperatures (e.g. at 20 °C) and low co-catalyst concentrations butene formation was 100 %, but at 50 °C, only 4 % of the product mix are alkyltoluenes. Activity with EASC was as high as 3130 kg mol⁻¹ Ni h⁻¹, compared to EtAlCl₂ (780 kg mol Ni h⁻¹). The high activity from the EASC reactions indicate the effectiveness of this ethylaluminium compound as a co-catalyst.¹⁶ Shorter reaction times also resulted in better selectivity towards the formation of butenes, while increased reaction times allowed for Friedel-Crafts alkylated products (entries 8–10). This proves that oligomerization initially occurs followed by alkylation of toluene with the oligomers formed or the monomer itself. Methylaluminoxane (MAO) and modified methylaluminoxane

(MMAO) as co-catalysts also produced butenes and but no alkyl toluenes, although catalysts activities were generally low (**10** gave activities of 280 kg mol⁻¹ Ni h⁻¹ and 250 kg mol⁻¹ Ni h⁻¹ MAO and MMAO, respectively). The production of alkyltoluenes appear to be driven by the acidity of the co-catalysts, so the least acid co-catalysts MAO and MMAO produced no alkyltoluenes at all whereas the most acidic co-catalyst EtAlCl₂ produced the most alkyltoluenes.

3. Conclusions

Like other reported pyrazolyl nickel and palladium dihalides in the literature, bis(pyrazole)- and (bis-substitutedpyrazoles)-palladium and nickel can be activated with EtAlCl₂ to produce catalysts for the dimerization of ethylene in toluene, benzene and chlorobenzene; but in toluene and benzene Friedel-Crafts alkylation of the solvents by ethylene and butenes occur and with selectivity towards mono-butyl and dibutyl-toluenes. Interestingly, the less active palladium catalysts resulted in significant amounts of mono-butyltoluenes compared to the nickel catalysts making the palladium complexes more selective

Table 5 The use of co-catalysts other than ethylaluminium dichloride and pre-catalyst **10**.

Entry	Co-catalyst	Al/Ni	T/°C	Time/min	Activity ^a	% Product distribution	
						α -C ₄	Butyltoluene
1	MAO	1500	30	30	280	100	–
2	MMAO	1500	30	30	250	100	–
3	Et ₂ AlCl	500	30	30	820	100	–
4	Et ₃ Al ₂ Cl ₃	500	30	30	2290	99	1

Conditions: amount of Ni pre-catalyst = 4 μ mol, toluene: 100 mL.

^a Activity as: kg mol⁻¹ Ni h⁻¹, pressure: 10 bar.

Experiments were run in triplicate.

Table 6 Variation of reaction parameters using EASC as co-catalyst for pre-catalyst **10**.

Entry	Al:Ni	T/°C	Time/min	Activity ^a	Pressure/bar	% Product distribution	
						α C ₄	F-C
1	400	30	30	1760	10	>99	<1
2	500	30	30	2290	10	99	1
3	600	30	30	2580	10	97	3
4	700	30	30	2390	10	92	8
5	600	20	30	900	10	100	–
6	600	40	30	1990	10	98	2
7	600	50	30	1790	10	96	4
8	600	30	15	3130	10	100	–
9	600	30	45	2430	10	96	4
10	600	30	60	1280	10	90	10
11	600	30	30	420	5	80	20
12	600	30	30	48	1	>99	<1
13 *	600	30	30	490	10	>99	<1

Conditions: amount of Ni pre-catalyst = 4 μ mol, toluene: 100 mL.

^a Activity as: kg mol⁻¹ Ni h⁻¹.

* Pd pre-catalyst = 4 μ mol.

Experiments were run in triplicate.

towards this product. Changing solvents also has a significant effect on the ethylene reaction, with chlorobenzene and hexane producing viscous oils that is made up of C₁₂ to C₁₈ olefins. It is also clear that only EtAlCl₂ as a co-catalyst produces catalysts that act in tandem to produce butenes and ethyl- and butyl-toluenes; as such the combination of these bis(pyrazoles)-palladium and nickel dihalides and EtAlCl₂ can be seen in tandem for the production of these alkylaromatics.

4. Experimental

4.1 Materials and Manipulations

All syntheses of palladium and nickel complexes were carried in an inert atmosphere. Toluene was dried over sodium and benzophenone, distilled and stored under a nitrogen atmosphere. Chlorobenzene was dried over 3 Å molecular sieves. Hexane was dried over sodium lumps, distilled and stored under 3 Å molecular sieves. Ethylene (99.9 %) was purchased from AFROX (South Africa) and used as received. The co-catalyst, ethylaluminium dichloride (EtAlCl₂), 25 wt.% (1.0 M) solution in hexanes was purchased from Sigma-Aldrich and used as received. The palladium starting material, [PdCl₂(NCMe)₂], was synthesized according to literature procedure.¹⁷ Compounds [(pz)₂PdCl₂] (1), [(3,5-Me₂pz)₂PdCl₂] (2), [(3,5-^tBu₂pz)₂PdCl₂] (3),⁶ and [(pz)₄NiBr₂] (6), [(3,5-Me₂pz)₂NiBr₂] (7),⁷ were synthesized according to the literature procedures. Infrared (IR) spectra were recorded on a Bruker Tensor 27 equipped with a diamond ATR, elemental analyses were performed in house at the University of Johannesburg on a Flash 200 organic CHNS analyzer and at Rhodes University with a Varioelementar III microcube CHNS analyzer. The mass spectrometry unit at the University of Stellenbosch performed the HR-ESI-MS spectra on a Waters API Quattro micro spectrophotometer. NMR spectra were recorded on a Bruker 400 MHz instrument (¹H at 400 MHz and ¹³C{¹H} at 100 MHz). The chemical shifts are reported in δ (ppm) and referenced to the residual proton and carbon signals 7.24 ppm and 77.0 ppm for CDCl₃ and 2.49 and 39.5 ppm for DMSO-*d*₆ for each respective NMR solvent. ¹⁹F{¹H} NMR spectra were also run with no internal standard in DMSO-*d*₆ or CDCl₃ depending on solubility of the compound analyzed. GC and GC-MS were used to identify the products from the oligomerization and Friedel-Crafts reactions. GC-MS were recorded in-house at the University of Johannesburg on a Shimadzu GC-MS-QP2010 fitted with a quadrupole mass detector.

Synthesis of (3,5-Ph₂pz)₂PdCl₂ (4)

3,5-Diphenyl-1H-pyrazole (0.170 g, 0.772 mmol) was added to a suspension of [PdCl₂(NCMe)₂] (0.10 g, 0.39 mmol) in toluene (20 mL). Yield: 0.20 g (85 %). δ_H (400 MHz, DMSO-*d*₆): 6.81 (1H, s, 4-H pz), 7.39 (3H, t, J 7.6 Hz, 3'-H, 4'-H and 5'-H), 7.39 (3H, t, J 7.6 Hz 3''-H, 4''-H and 5''-H), 7.91 (2H, d, J 7.2 Hz, 2'-H, 6'-H), 8.11 (2H, d, J 7.6 Hz, 2''-H, 6''-H) and 13.75 ppm (1H, s, N-H); δ_C (100 MHz, DMSO-*d*₆): 103.0 (C-4-pz), 125.9 (C-3', C-5'), 128.3 (C-3'', C-5''), 129.4 (C-4', C-4''), 128.2 (C-2', C-6'), 129.5 (C-2'', C-6''), 130.2 (C-1'), 133.3 (C-1''), 156.7 (C-3-pz) and 164.9 ppm (C-5-pz); HR-MS (ESI): *m/z* (%) = 616.9883 (70) [M+H]⁺. Found: C, 57.93; H, 4.03; N, 8.73 %. Calc. for C₃₀H₂₄Cl₂N₄Pd: C, 58.32; H, 3.92; N, 9.07 %.

Synthesis of (3-CF₃,5-Phpz)₂PdCl₂ (5)

A suspension of [PdCl₂(NCMe)₂] (0.453 g, 1.175 mmol) in toluene (20 mL) was mixed with 5-phenyl-3-(trifluoromethyl)-1H-pyrazole (0.50 g, 2.35 mmol). Yield: 0.83 g (79 %). δ_H (400 MHz, DMSO-*d*₆): 6.34 (1H, s, 4-H pz), 7.44 (3H, t, J 7.6 Hz, 3'-H, 4'-H and 5'-H), 7.91 (2H, d, J 7.6 Hz, 2'-H, 6'-H), 13.75 (1H, s, N-H

pz); δ_C (100 MHz, DMSO-*d*₆): 101.5 (C-4 pz), 123.5 (q, ¹J_{F,C} = 38.2 Hz, C-F₃), 125.9 (C-3', C-5'), 129.4 (C-4'), 129.6 (C-2', C-6'); 128.5 (C-1'), 144.6 (C-3 pz), 150.1 (C-5 pz). δ_F (DMSO-*d*₆): -60.41 (CF₃). IR (Diamond ATR, cm⁻¹): ν(N-H) = 3226 cm⁻¹; ν(C=N) = 1611 cm⁻¹. HR-MS (ESI): *m/z* (%) = 600.9453 (100) [M+H]⁺. Found: C, 39.90; H, 2.35; N, 9.31 %. Calc. for C₂₀H₁₄Cl₂F₆N₄Pd: C, 39.92; H, 2.35; N, 9.31 %.

Synthesis of (3,5-^tBu₂pz)₂NiBr₂ (8)

3,5-Di-*tert*-butyl-1H-pyrazole (0.50 g, 2.35 mmol) and [NiBr₂(DME)] (0.54 g, 1.175 mmol) were dissolved in CH₂Cl₂ (20 mL) and gave a clear green solution. The mixture was allowed to react for 10 min. After evaporation and purification a dark blue powder was obtained. Yield: 0.19 g (88 %). HR-MS (ESI): *m/z* (%) = 578.0965 (56) [M+H]⁺. Found: C, 45.65; H, 6.88; N, 9.56 %. Calc. for C₂₂H₄₀Br₂N₄Ni: C, 45.63; H, 6.96; N, 9.68 %.

Synthesis of (3,5-Ph₂pz)₂NiBr₂ (9)

The preparation of 9 followed the same procedure as for 6 starting with 3,5-di-phenyl-1H-pyrazole (2.5 g, 11.44 mmol) and [NiBr₂(DME)] (1.25 g, 5.72 mmol) over a 24 h period yielding a green solid. Yield: 3.01 g (80 %). HR-MS (ESI): *m/z* (%) = 658.0546 (40) [M+H]⁺. Found: C, 55.09; H, 3.51; N, 8.33 %. Calc. for C₃₀H₂₄Br₂N₄Ni: C, 54.67; H, 3.67; N, 8.50 %.

Synthesis of (3-CF₃,5-Phpz)₂NiBr₂ (10)

5-Phenyl-3-(trifluoromethyl)-1H-pyrazole (0.50 g, 2.35 mmol) and [NiBr₂(DME)] (0.54 g, 1.175 mmol) were dissolved in CH₂Cl₂ (20 mL). Yield: 0.65 g (86 %). IR (Diamond ATR, cm⁻¹): ν(NH) = 3228, ν(C=N) = 1612. HR-MS (ESI): *m/z* (%) = 641.8819 (100) [M]⁺. Found C, 37.36; H, 2.20; N, 8.72 %. Calc. for C₂₀H₁₄Br₂F₆N₄Ni: C, 37.37; H, 2.20; N, 8.72 %.

4.2. General Procedure for Ethylene Oligomerization and Friedel-Crafts Alkylation Reactions

Oligomerization and Friedel-Crafts alkylation reactions were carried out in a 40 mL high-pressure reactor, which was dried at 100 °C and cooled under nitrogen to the desired temperature before use. An appropriate amount of pre-catalyst was added to the reactor under nitrogen together in degassed toluene (10 mL) and an appropriate amount of ethyl aluminium dichloride added with a syringe. Immediately after the addition of the EtAlCl₂, the reactor was charged with ethylene and the reactor temperature was maintained at the desired temperature. Ethylene pressure was set at the desired pressure maintained at this pressure during the reaction. After the set reaction time, excess ethylene was vented and the reaction quenched by adding 2 M HCl in methanol. The oily yellow product formed was filtered to remove any solid matter, washed with 2 M HCl in methanol and volatiles removed in *vacuo*. All experiments were run in triplicate.

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Figure S1: ¹H NMR spectrum for complex 5.

FigureS2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 5.

Figure S3: $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **L5** at -62.22 ppm with that of complex **5** at -60.44 ppm.

LM C25
JD_UJ_130920_9 (0.039) Is (0.50,1.00) C₂₀H₁₄N₄F₆NiBr₂

FigureS4: High resolution Mass Spectrum of complex **10**.