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(Ferrocenylpyrazolyl)nickel(II) catalysed ethylene oligomerisation

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Abstract

Compounds **L1**-**L6** (3-ferrocenylpyrazole (**L1**), 3-ferrocenyl-5-methylpyrazole (**L2**), 3-ferrocenylpyrazolyl-methylenepyridine (**L3**), 3-ferrocenyl-5-pyrazolyl-methylenepyridine (**L4**), 3-ferrocenylpyrazolyl-ethylamine (**L5**) 3-ferrocenyl-5-pyrazolyl-ethylamine (**L6**)) reacted with [$NiBr_2$(DME)] or [$NiCl_2.6H_2O$] to give the mononuclear nickel complexes [$NiBr_2$(κ^1-**L1**)$_2$] (**1**), [$NiBr_2$(κ^1-**L2**)$_2$] (**2**), [$NiBr_2$(κ^2-**L3**)] (**3**), [$NiBr_2$(κ^2-**L4**)] (**4**), [$NiBr_2$(κ^2-**L5**)] (**5**), [$NiBr_2$(κ^2-**L6**)] (**6**), [$NiCl_2$(κ^2-**L3**)] (**7**) and [$NiCl_2$(κ^2-**L4**)] (**8**). Because these nickel complexes are paramagnetic they were characterised by a combination of IR spectroscopy, mass spectrometry, elemental analysis and in selected cases by single crystal X-ray crystallography. Activation of complexes **1-8** with $EtAlCl_2$ in chlorobenzene produced active species that catalysed ethylene oligomerization to butenes and C_{16}-C_{64} olefins; showing a non-Schulz-Flory distribution of products. Complexes **2** and **3** were the most active (1 989 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} and 1 776 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} respectively) and in toluene produced isomers of butene and small amounts of butyltoluenes *via* Friedel-Crafts alkylation of toluene by the butenes.

Introduction

Nickel complexes bearing bidentate ligands are known to exhibit higher catalytic activities for ethylene oligomerisation and polymerisation reactions than those containing tridentate ligands.[1] As a result progress in using bidentate nickel complexes to catalyse ethylene reactions has been rapid in recent years. Majority of bidentate ligands for single-site nickel complexes are made from homo- or hetero- donor ligands such as P^P, P^N, P^O, N^O and N^N and these complexes tend to catalyse the production of branched polymers.[2] The branching in the polymers are mainly the result of β-hydride elimination reactions during the polymerisation process leading to methyl branches and "chain walking" that form longer branches such as propyl and amyl.[3] This has led to increased interest in both academia and industry to further study new nickel(II) catalysts, especially modifications of bidentate N^N ligands. As a result of these modifications, various nitrogen donor ligands such as α-diimine derivatives,[4] 1,10-phenanthroline derivatives[5] and quinolone derivatives,[6] and recently pyrazoles[7] have been studied as ligands in nickel catalysed ethylene oligomerisation and polymerisation reactions. The extent of progress with these N^N ligands is seen in the several review articles on this subject.[8] However, the utilisation of these newly developed nickel(II) catalysts in industrial applications is yet to be realised due to a number of critical issues concerning both the nature of the catalytic systems and the usefulness of the resulting products that still remain. To overcome these shortcomings, nickel catalysts bearing ligands with bulky substituents such as benzhydryl-groups have been explored to produce thermally stable catalysts that have high catalytic activities and also to understand the effect of such bulky substituents.[9]

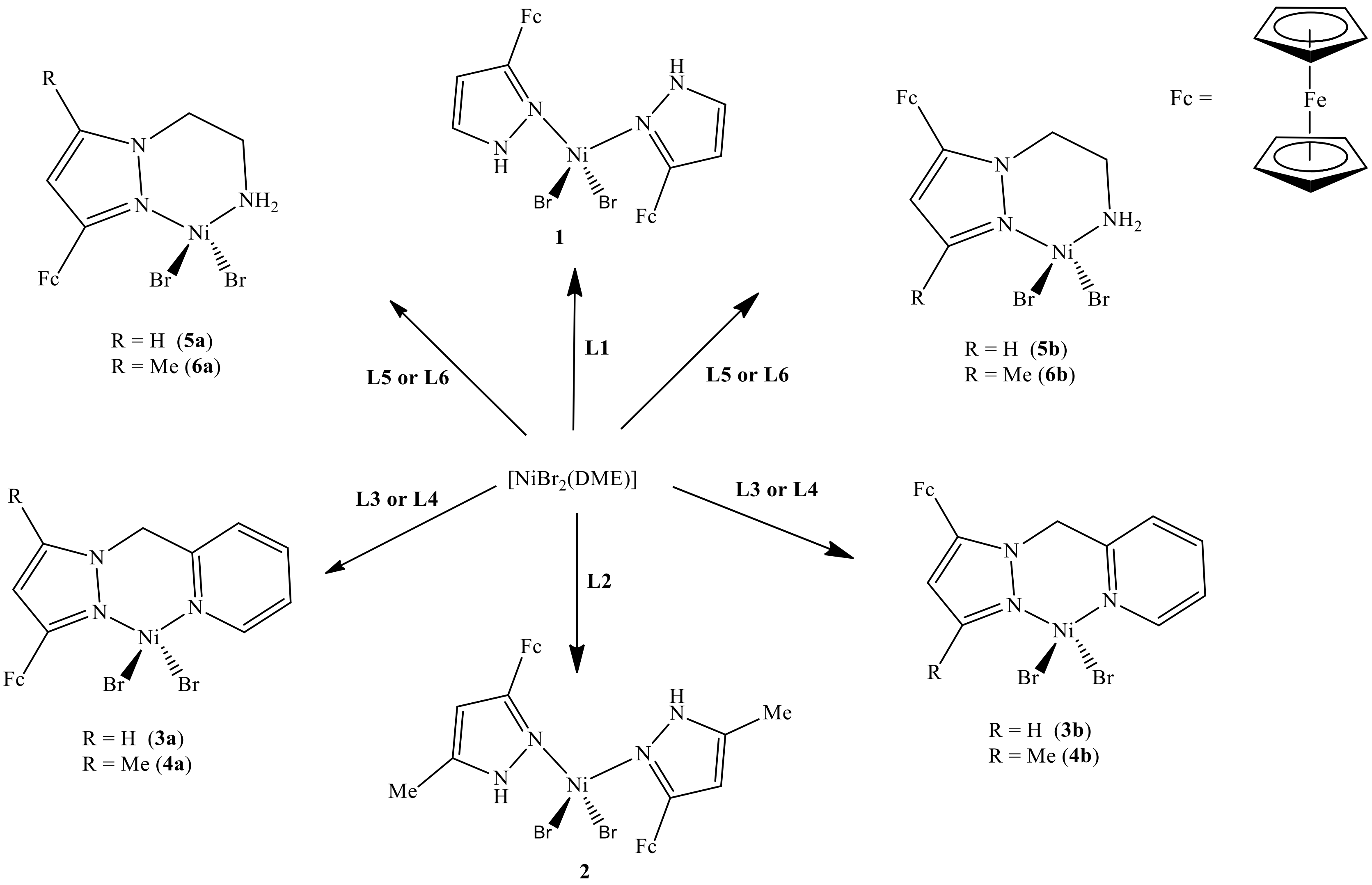
Our contribution to enhancing catalyst stability and high activity include using bulky ferrocenyl group(s) to make pyrazolyl ligands to prepare nickel precatalysts. Herein we report novel nickel catalysts that oligomerises ethylene to butenes but skip the usually observed Schultz-Flory product distribution to form C_{16}+ olefins.

Results and discussion

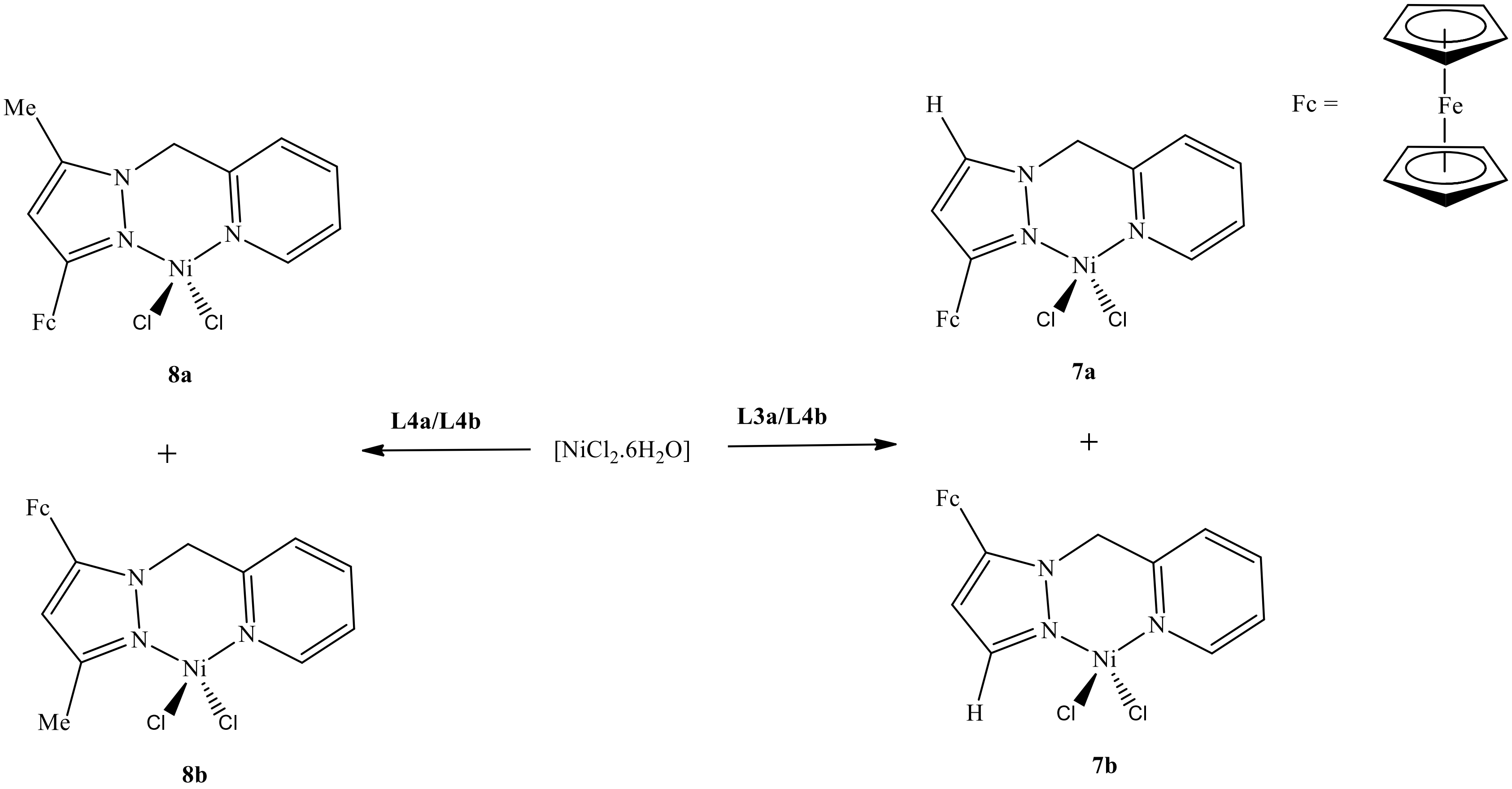
Synthesis and characterisation of nickel complexes

Compounds **L1-L6** were prepared as reported in literature[10] and reacted with the nickel precursors [$NiBr_2$(DME)] and [$NiCl_2.6H_2O$] to produce eight new (ferrocenylpyrazolyl)nickel complexes (Schemes 1 and 2). Complexes **1** and **2** were prepared by reacting **L1** or **L2** and [$NiBr_2$(DME)] in a 2:1 ratio while the reaction of [$NiBr_2$(DME)] or [$NiCl_2.H_2O$] in a 1:1 ratio with ligands **L3-L6** gave complexes **3-8**. Complexes **1** and **2** are light orange solids, while **3-8** are light brown solids. Complexes **1-4**, **7** and **8** are air and moisture stable and were stored without special precautions, but **5** and **6** are extremely moisture sensitive and had to be stored in a glovebox. All these nickel complexes are soluble in most organic solvents but insoluble in diethyl ether and hexane.

Because complexes **1-8** are paramagnetic they were characterised by IR spectroscopy, mass spectrometry, magnetic moment, micro analysis and for **3a** and **4a** by single crystal X-ray crystallography.



Scheme 1: Synthesis of (ferrocenylpyrazolyl)nickel(II) bromide complexes



Scheme 2: Synthesis of (ferrocenylpyrazolyl)nickel(II) chloride complexes

IR spectroscopic data for complexes **1-8** showed the presence of N-containing functional groups. Complexes **1** and **2** contain a secondary amine where the N-H stretching vibrations showed a shift to higher frequencies from 3078 cm^{-1} (**LI**) and 3118 cm^{-1} (**L2**) for the respective ligands to between 3244 cm^{-1} (**1**) and 3257 cm^{-1} (**2**) for the respective complexes. Complexes **5** and **6** that have primary amine functional groups showed N-H stretching vibration shifting to lower frequencies of 3111 cm^{-1} (**5**) and 3193 cm^{-1} (**6**) in the complexes from 3313 cm^{-1} (**L5**) and 3324 cm^{-1} (**L6**). Their bending vibration also shifted from 1555 cm^{-1} (**L5**) and 1585 cm^{-1} (**L6**) to 1616 cm^{-1} (**5**) and 1626 cm^{-1} (**6**). Complexes **3**, **4**, **7** and **8** showed υ(C=N) bands for the corresponding ligands between 1620 cm^{-1} and 1628 cm^{-1}. These suggest that in all complexes the nickel atom is coordinated to the respective ligands.[11] Mass spectrometry of the complexes showed various fragments of their proposed structures (Schemes 1 and 2). For instance, the mass spectrum of complex **7** (Figure S1) showed a molecular ion at *m/z* = 493.9389 corresponding to $[M+Na]^+$ and other fragments with *m/z* values of 437.9782, 402.0028 and 366.0674 which represents $[M\text{-}Cl]^+$, $[M\text{-}2Cl]^+$ and $[M\text{-}NiCl_2+Na]^+$ respectively, supporting the proposed molecular structures in Schemes 1 and 2. Magnetic susceptibility measurement at room temperature on complexes **1-8** gave μ_{eff} in the range 3.34 to 3.94 BM, typical of tetrahedral nickel complexes that have two unpaired electrons.[12-15]

Single crystal X-ray structures of **3a** and **4a** confirmed the tetrahedral nature of these nickel complexes. In addition to the above techniques used to characterised **1-8**, elemental analyses were consistent with the proposed molecular structures in Schemes 1 and 2 and also confirmed the analytical purity of these complexes. Crystallographic and structural refinement data can be found in Table S1; while molecular structures are in Figures 1 and 2, each of which has selected bond lengths and angles in the figure caption. Bond angles for **3a** and **4a** are in the range 93.72(14)° to 111.35(3)°. The Ni-N bonds in both complexes are in the range 2.000-2.015(18) Å for Ni-N(py) and 1.999-2.004(18) Å for Ni-N(pz) and similar to Ni-N bond lengths of 2.005-2.121(2) Å reported in the literature.[16] The cyclopentadienyl rings in **3a** and **4a** are eclipsed and have dihedral angles of 3.080(1)° and 1.907(4)° respectively.

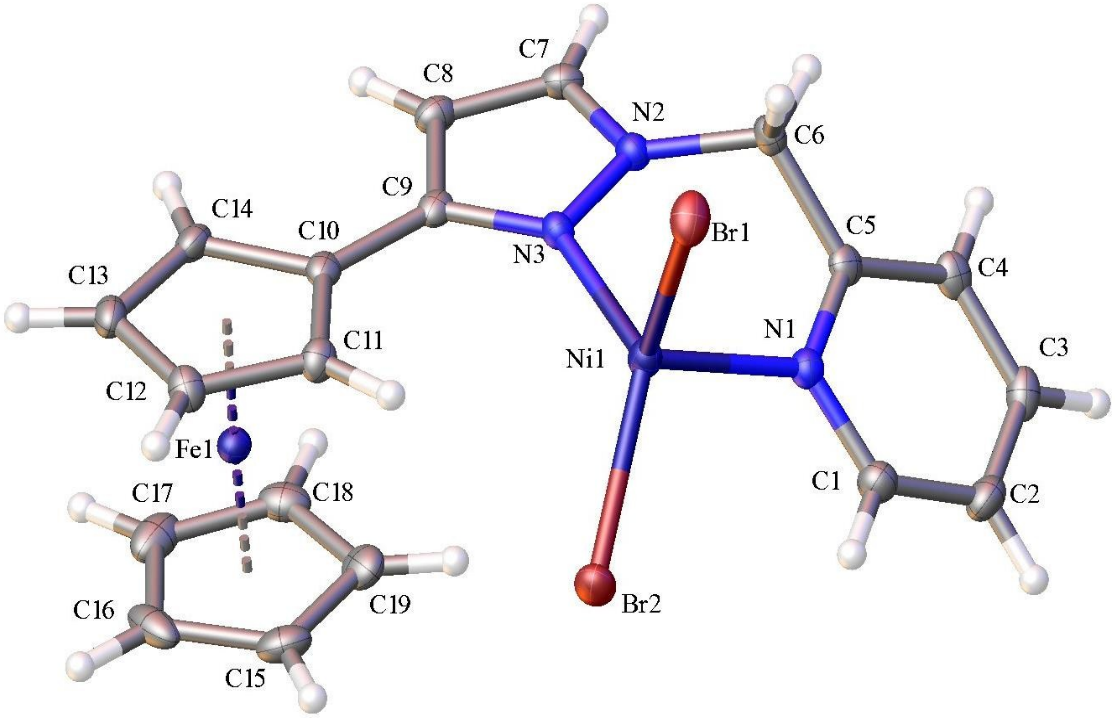


Figure 1: Molecular structure of **3a**, drawn with 50% probability ellipsoids. Selected bond lengths [Å] and bond angles [°]: Br1-Ni1, 2.3715(4); Br2-Ni1, 2.3614(4); Ni1-N1, 2.000(18); Ni1-N3, 2.004(18); N1-C5, 1.352(3); N2-N3, 1.362(3); N2-C6, 1.458(3); N1-Ni1-N3, 94.20(7); N1-Ni1-Br2, 104.24(5); N3-Ni1-Br2, 129.17(5); N1-Ni1-Br1, 106.88(5); N3-Ni1-Br1, 102.68(5); Br2-Ni1-Br1, 115.837(17); N2-C6-C5, 113.59(18).

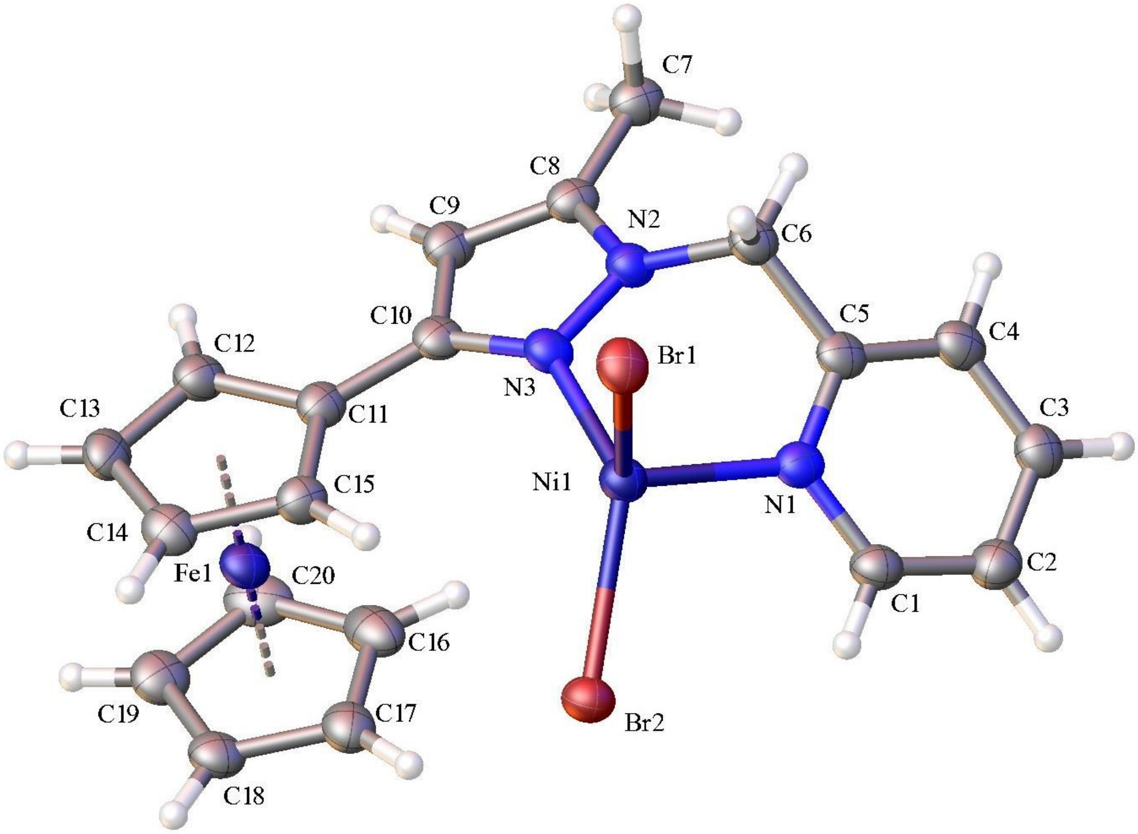


Figure 2: Molecular structure of **4a**, drawn with 50% probability ellipsoids. Selected bond lengths [Å] and bond angles [°]: Br1-Ni1, 2.3728(8); Br2-Ni1, 2.3637(7); Ni1-N1, 2.015(4); Ni1-N3, 1.999(3); N1-C5, 1.347(5); N2-N3, 1.372(5); N2-C6, 1.452(5); N1-Ni1-N3, 93.72(14); N1-Ni1-Br2, 106.09(10); N3-Ni1-Br2, 133.62(10); N1-Ni1-Br1, 107.67(10); N3-Ni1-Br1, 101.29(10); Br2-Ni1-Br1, 111.35(3); N2-C6-C5, 112.4(3).

Ethylene oligomerisation reactions using precatalysts 1-8

Precatalysts **1**-**8** were activated with $EtAlCl_2$ as co-catalyst and investigated for their activities towards oligomerisation or polymerisation of ethylene in chlorobenzene. Optimum Al:Ni ratio and catalyst loading were established with precatalyst **2**. On adding the co-catalyst the temperatures of the reactions increased rapidly from 25 °C to between 50 °C and 60 °C for about 20 min before dropping to the set temperature, usually within 10 min. A similar temperature increase has been reported by Darkwa and co-workers with other (pyrazolylmethylenepyridine)nickel(II) and (pyrazolylmethylenebenzene)nickel(II) catalysed ethylene reactions where temperature increase were even higher, rising to between 80 °C and 110 °C.[15a,17] Catalytic activity increased steadily from a Al:Ni ratio of 100:1 (348 kg.molNi^{-1}.h^{-1}) to a ratio of 400:1 (1 989 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1}) before decreasing to 1 356 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} at Al:Ni ratio of 500:1 (Table 1). Amount of precatalyst used in a catalytic reaction has influence on the activity of the active species and the products obtained, so the influence of catalysts loading on the activity of the ethylene oligomerisation was studied using precatalyst **2**. We observed an increase in catalyst activity from a catalyst loading of 6 µmol to 10 µmol but activity decreased at 11 µmol (Table 1: entries 4, 6-8).

Table 1: Determination of optimum Al:Ni ratio and precatalyst loading

Entry	Al:Ni	Precatalyst loading (µmol)	[a]Yield (g)	Activity (kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1})	[b]Oligomer molecular weight (Da)
1	100:1	10	3.5	348	378.0
2	200:1	10	7.9	786	481.0
3	300:1	10	15.1	1 506	567.0
4	400:1	10	19.9	1 989	611.0
5	500:1	10	13.6	1 356	521.0
6	400:1	6	6.9	1 151	456.0
7	400:1	8	10.5	1 315	561.0
8	400:1	11	19.7	1 788	610.0

Conditions: 6 mL of chlorobenzene; co-catalyst = $EtAlCl_2$; ethylene = 10 bar; precatalyst = **2**; temperature 25 °C; time 1 h; [a]determined by mass difference of 6.0 mL chlorobenzene (6.66 g) and mass of final solution; [b]determined by APCI.

The rest of the nickel complexes were tested as catalyst for the ethylene reaction described earlier using Al:Ni ratio 400:1 and 10 μmol catalyst loading. Precatalyst **2** produced the most active catalyst (Table 2). In all these reactions (Tables 1 and 2) GC analyses of the products showed four product peaks in the chromatogram (Figure 3). These product peaks were identified as 1-butene, *cis*-2-butene, *trans*-2-butene and 2-methylpropene (Figure 3); indicating that the ethylene dimerised to 1-butene, which further transformed into the remaining C_4 products. The formation of the *cis*- and *trans*- 2-butenes suggest that there is "chain-walking" of the 1-butene to form the internal butenes in a similar manner reported by Brookhart and co-workers.[19] Furthermore, the formation of 2-methyl-propene suggests that there is cleavage of the C-C bond of a coordinated internal butene to the nickel centre, which then undergoes rapid recombination as proposed by Jacobson *et. al*.[20] The selectivity of these catalysts towards 2-methylpropene is unique and seems to be at the expense of 1-butene (Table 2); hence the small amount of 1-butene in the product mix. A similar observation has been made by Braunstein and co-workers when they used (pyridyl-triazole)nickel(II) and $EtAlCl_2$ co-catalyst to catalyse ethylene dimerization to butenes. The selectivity of these (pyridyl-triazole)nickel(II) catalysts to 1-butene was only 10%,[21] contrary to typical 1-butene selectivity of > 80% for most catalysts.[22] There was no evidence of the formation of hexenes and octenes with precatalysts **1-8** unlike (pyrazolylethylpyridylamine)nickel(II) and (pyrazolylethylpyrroleamine)nickel(II) complexes that produced 1-butene and 1-hexene when the solvent is chlorobenzene and $EtAlCl_2$ co-catalyst.[17b] There was also no evidence from the GC analysis (Figure S2) of olefins between C_{10} and C_{14} and Friedel-Crafts alkylation of chlorobenzene by the butene oligomers from any of the catalytic reactions with ethylene and precatalysts **1-8**.

Table 2: Ethylene oligomerisation data using precatalysts **1-8**, $EtAlCl_2$ as co-catalyst

Entry	Precatalyst	Pressure (bar)	[a]Yield (g)	Activity (kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1})	Temperature (^{o}C)	Time (min)	[b]Selectivity for 1-butene (%)	[c]Oligomer molecular weight (Da)
1	**1**	10	12.2	1 221	25	60	8	551.0
2	**2**	10	19.9	1 989	25	60	10	611.0
3	**3**	10	17.8	1 776	25	60	9	581.0
4	**4**	10	10.2	1 023	25	60	7	546.0
5	**5**	10	6.7	671	25	60	6	486.0
6	**6**	10	5.8	578	25	60	5	477.0
7	**7**	10	8.2	823	25	60	6	492.0
8	**8**	10	7.1	710	25	60	6	461.0
9	**2**	5	12.2	1 221	25	60	8	399.0
10	**2**	20	22.2	2 220	25	60	10	887.0
11	**2**	10	10.2	1 023	40	60	9	481.0
12	**2**	10	6.3	634	50	60	8	310.0
13	**2**	10	4.1	412	60	60	8	210.0
14	**2**	10	21.3	1 066	25	120	9	679.0
15	**2**	10	24.1	803	25	180	10	788.0

Conditions: 6.0 mL of solvent; Chlorobenzene, catalyst loadings = 10 µmol, Al:Ni = 400:1; [a]determined by mass difference of 6.0 mL chlorobenzene (6.66 g) and mass of final solution; [b]determined by GC; [c]determined by APCI.

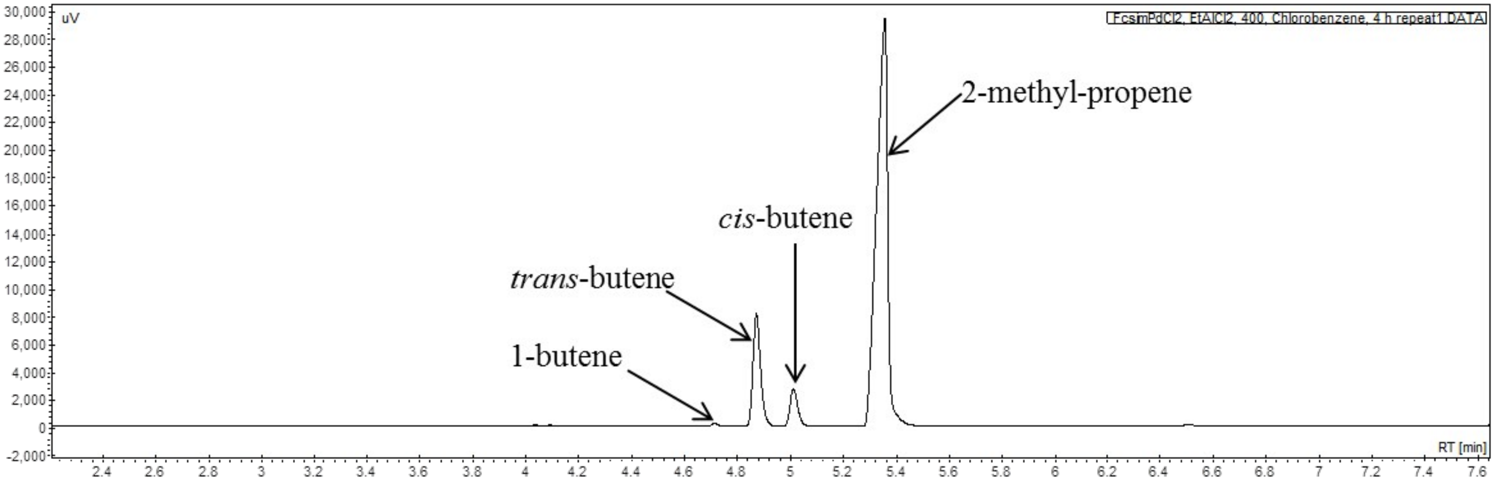


Figure 3: Expanded GC showing the four isomers of butene formed in the ethylene oligomerisation reaction

When the chlorobenzene was evaporated from the product mix, oily liquids were obtained. Attempts to determine the molecular weights of these oils by GPC were unsuccessful as their molecular weights were lower than 1 000 Da. Atmospheric pressure chemical ionization (APCI) was therefore used to determine the molecular weight of these oils. A typical APCI mass spectrum is Figure 4, and with this technique molecular weights of the oily products were found to be between 210.0 and 887.0 Da, which shows that these were compounds that have C_{16}-C_{64} carbon atoms. An expanded form of the spectrum showed isotopic distributions (Figure 4 insert) and differences between two sets of isotopic of 14.0 units that corresponds to a methylene group fragmentation. Further analysis of the oils by ^{1}H NMR spectroscopy showed olefinic end groups signals between 4.75 ppm and 5.48 ppm (Figure S3). These are vinylene ($-CH_2CH=CH_2$) and vinylidene ($-CHC(R)=CH_2$) end groups that results when β-hydride elimination is the dominant chain-transfer pathway[23] and that chain transfer to alkyl-Al is negligible.[24]

We have also used the nomenclature by Usami[25] and Mclain.[26] to assigning the peaks in the $^{13}C\{^1H\}$ NMR spectra of the oils (Figure S4). From the $^{13}C\{^1H\}$ NMR spectrum (Figure S4) the major peaks are butyl branching (at 14.20 ppm, 22.90 ppm and 27.40 ppm), and some amount of longer chain branching that has a signal at 29.50 ppm. The presence of the later chain could explain why the oils are very fluid. Combining the mass spectral data and the ^{1}H NMR spectral end group analyses allowed us to conclude that the oily products are indeed a mixture of oligomers that have C_{16} to C_{64} carbon atoms. It is interesting to note that ethylene oligomerisation products have no C_6 to C_{14} components; however it is not clear why there are no C_6 to C_{14} olefins in the product mix; although it is possible that formation of C_{16} to C_{64} olefins could be from further reactions of butenes and other lower carbon content olefins in the oligomerisation reaction to the oily olefins. Examples of oily products from ethylene oligomerisation catalysed by N,N-iminopyridine nickel(II) complexes supported on dendritic framework have been reported by Flores[27a] and Mapolie[27b]. Both reactions produce olefins with up to C_{34} atoms; and while olefinic products from the Flores catalysts follow Schulz-Flory distribution, the Mapolie catalysts give a mixture of alkyltoluenes and C_{22}+ olefins. As such it is difficult to firmly establish that the Mapolie catalysts oligomerise ethylene in a Schulz-Flory manner, but the MALDI-TOF of their oily product show olefin carbon content above C_{60}. Nevertheless, the both Flores and Mapolie catalysts produce high carbon content olefinic oils similar to our catalysts.

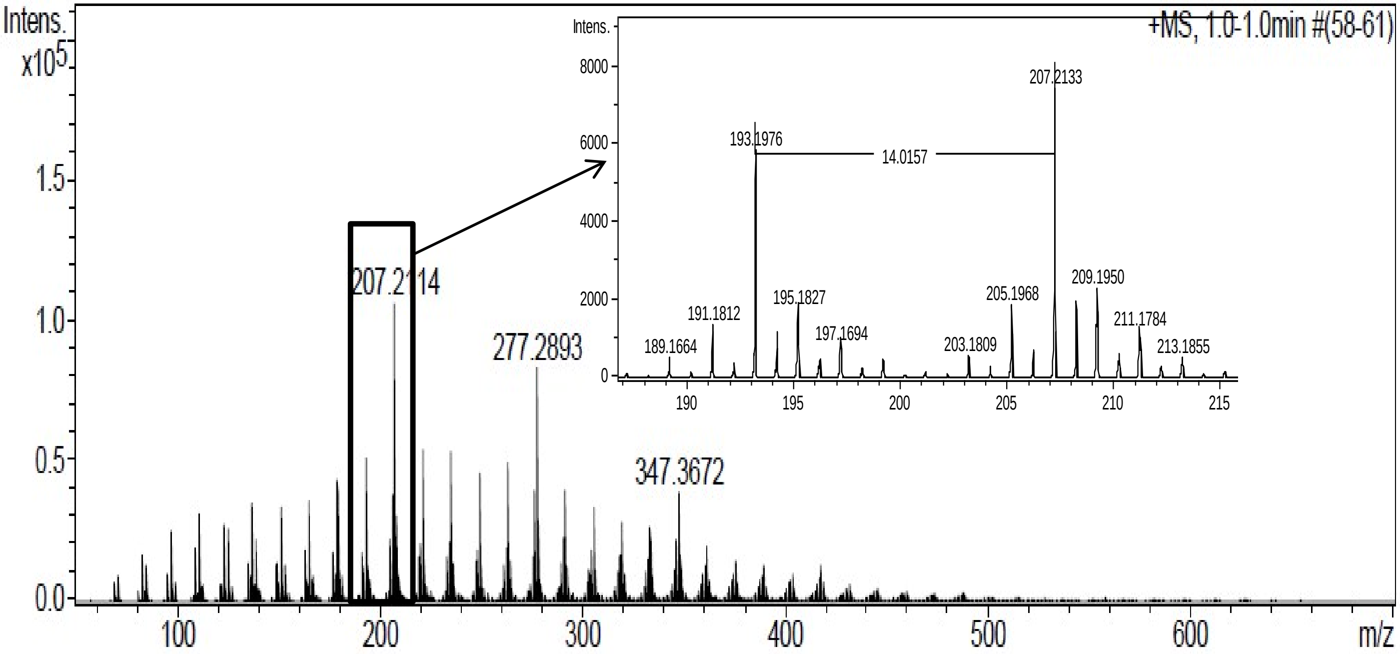


Figure 4: A typical APCI spectrum of the oligomer synthesised using precatalyst **2.** Insert is an expansion of the a portion of the spectrum showing fragmentation pattern and isotopic distribution

The effect of the ligand systems on the catalyst activity

There are three ligand types, namely mono-dentate ferrocenylpyrazolyl (**L1** and **L2**), bidentate ferrocenylpyrazolyl-pyridine (**L3** and **L4**) and bidentate ferrocenylpyrazolyl-amine (**L5** and **L6**) that were used to prepare the nickel precatalysts. Of the nickel complexes that have mono- dentate ligands, precatalyst **2** was the most active whilst the nickel complexes that have bi-dentate ligands precatalysts with pyridine groups (**3** and **4**) were more active than precatalysts with amine group (**5** and **6**). Overall the most active was precatalyst **2**. The observed differences in catalytic activity could come from the electrophilicity differences at the nickel centre the ligands have on the catalysts. This is supported by the σ-donor abilities of the nitrogen donor atoms in the ligands which increases in the order pyrazolyl < amine < pyridyl. This explains the higher catalytic activity of precatalyst **2**.

It appears that the type of halide has effect on catalyst activity. Comparing the activities of precatalysts **3**, **4**, **7** and **8** (Table 2: entries 3, 4, 6 and 7), the dibromide precatalysts are more active compared to the dichloride precatalysts. This could be due to the higher solubility of the dibromide complexes compared to the dichloride analogues. Similar observations have been made for (pyrazolyliminophosphorane)-nickel(II) precatalysts[28] and 2-quinoxalinyl-6-iminopyridine nickel(II) precatalysts[29] where bromide complexes were more active than the chloride analogues in the oligomerisation of ethylene. Generally, these complexes upon activation catalysed ethylene to butenes and higher ethylene oligomers between C_{16} and C_{64}. We attribute the selectivity of these complexes to the presence of the ferrocenyl unit in the ligands due to the fact a similar ligand system without ferrocenyl substituents reported by us[15a] produce oligomers in the C_4-C_8 range;

although the actual role of the ferrocenyl unit in the current ethylene catalytic reaction is not clear to us.

Effect of pressure, time, temperature on the product obtained with 2

Pressure

Kinetic experiments reported in literature show that increasing ethylene pressure results in increased activity and molecular weight of oligomers produced.[30] Therefore, it was not surprising that increasing the pressure of ethylene from 5 bar to 10 bar resulted in increase in both activity and molecular weights of the ethylene oligomers (Table 2: entries 2 and 9). The activity and molecular weight at 10 bar showed nearly a twofold increase compared to 5 bar. However, a further increase of pressure to 20 bar gave activity of 2 220 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1}, which is a smaller increase than when pressure was increased by 5 bar (Table 2: entries 2 and 10). This could be due to saturation of the reaction mixture by ethylene.[31] Also, pressure increase from 5 bar to 20 bar had very small influence on the selectivity of 1-butene which marginally increased from 8% to 10%. Because of the smaller increase of activity at 20 bar, time and temperature variations were performed at 10 bar.

Time

When the ethylene reactions were run with precatalysts **2** at different times namely 60 min, 120 min and 180 min (Table 2: entries 2, 14 and 15), there was increase in the amounts of ethylene oligomers formed and the molecular weight of the oligomers. However, the catalyst activity gradually decreased from 1 989 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} at 60 min to 803 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} at 180 min. This could be due to catalyst deactivation or mass transfer limitation of the ethylene to the catalyst. Selectivity toward the formation of 1-butene was also not influenced by increase in time.

Temperature

The effect of temperature on the ethylene reactions was investigated by varying temperature from 25 ^oC to 60 ^oC with **2** (Table 2: entries 2 and 4-6). Activity and molecular weight decreased significantly from 1 989 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} and 611.0 at 25 ^oC to 412 kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1} and 210.0 at 60 ^oC respectively (Table 2: entries 2, 11-13). This observation is similar to α-diimine nickel[32] or 2-iminopyridine nickel[33] catalysts reported in literature; and the decrease could be due to decomposition or deactivation of the active species and fast termination of the growing chain at high temperature. We were also able to establish through the temperature variation experiments that 25 ^oC is the optimum temperature for this precatalyst and that increase in temperature beyond 25 ^oC did not influence the activity and selectivity towards 1-butene by much.

Effect of solvent on products using precatalysts 2 and 3

When reaction with precatalysts **2** and **3** were performed in toluene at optimum conditions of Al:Ni = 400, 1 h, precatalyst loading of 10 μmol and 25 ^oC temperature, the products obtained from these reactions were butenes and butyltoluenes (the butyltoluenes is as a result of Friedel-Crafts alkylation of toluene). Typical GC and GC-MS for the reaction in toluene are shown in Figures S5-S7. Here too GC also shows four signals for butene, which was also observed when chlorobenzene was used as reaction solvent. However, a larger amount of 1-butene was obtained in toluene than in chlorobenzene (Table 3). Furthermore, the major butene product in the toluene reaction is *trans*-2-butene (Figure S6). The selectivity towards 1-butene improved significantly in toluene compared to the reaction in chlorobenzene. The selectivity for 1-butene was as high as 25% (Table 3). These results suggest that the type of solvent plays a role in the isomerisation process, and is in agreement with results recently reported by Nyamato *et al*.[34] that used (chloromethylpyrazolylmethylpyridine)nickel(II) precatalysts to produce 1-butene is solvent dependent.

In the work up of products from the reactions performed in toluene, the solvent was pumped off to afford oily products which were identified by ^{1}H NMR spectroscopy and GC-MS as Friedel-Crafts butyltoluenes. Table 3 shows the product distribution at different reaction conditions. Interestingly very low levels (20%) of Friedel-Crafts alkylation were recorded compared to previous reports where alkylation levels were as high as 80%.[15a,17] Changes in reaction conditions resulted in changes in product distribution. For example increasing ethylene pressure from 5 bar to 20 bar for precatalysts **2** and **3** saw high levels of butenes been produced compared to butyltoluenes (Table 3: entries 1-3 and 7-9). Under the same conditions, precatalyst **2** produced more butenes and less butyltoluenes than for precatalyst **3**. This could be attributed to the type of active species formed during the activation of the precatalyst upon abstraction of the halides. Gao and co-workers have shown the influence of temperature on the Friedel-Crafts alkylation process with nickel precatalysts.[35] They reported that Friedel-Crafts alkylation occurs at high temperature. So observing higher alkylation products as high as 30% at 60 °C when we increased temperature from 25 °C to 60 °C compared to 20% at 25 °C for precatalyst **2** was no surprise (Table 3: entries 2, 4-6). For precatalyst **3** alkylation products was about 60% at 60 °C from 40% at 25 °C (Table 3: entries 8, 10-12). Also alkylation can be dependent on the type of precatalyst used; an observation made by Dyer and co-workers,[36] where out of the four nickel precatalysts investigated only one of them resulted in Friedel-Crafts alkylation products. It is therefore worth noting of all the pyrazolyl nickel precatalysts investigated by us[15a,17] the (ferrocenylpyrazolyl)nickel complexes in this report produced the least alkyltoluene products and could be the reason why higher carbon content olefins were produced from further incorporation of lower carbon content olefins in the oligomerisation reactions.

Conclusions

Novel mono-dentate ferrocenylpyrazolyl, bi-dentate ferrocenylpyrazolylmethylpyridine and ferrocenylpyrazolylethylyamine nickel(II) complexes can be activated with $EtAlCl_2$ to catalyse ethylene oligomerisation to butene isomers and C_{16}-C_{64} ethylene oligomers. It is interesting to note that products formed in these ethylene oligomerisation reactions do not follow a Schulz-Flory distribution. It begins with the formation of butenes and then skip C_6-C_{14} products but then gets to C_{16}-C_{64} olefins. This is unique and represents a rare example where products from nickel catalysed ethylene oligomerisation reaction do not have C_6-C_{14} but has C_{16+}. The products from the reactions were greatly influenced by the solvent used. In chlorobenzene the butene isomer 2-methylpropene was the major product, whilst in toluene the *trans*-2-butene isomer was the major product but also only small amounts of butyl-toluenes were formed.

Table 3: Ethylene oligomerisation and Friedel-Crafts alkylation reactions data, using precatalysts **2** and **3**, with $EtAlCl_2$ as co-catalyst

Entry	Catalyst	Pressure (bar)	[a]Yield (g)	Activity (kg of ethylene oligomer.mol.$^{-1}$(Ni).h^{-1})	Temperature (^{o}C)	[b]Oligomer and FC distributions (%)				[b]Selectivity (%)
						C_4	**A**	**B**	**C**	**1-C_4**
1	**2**	5	8.23	823	25	57.50	21.52	11.36	9.62	10
2	**2**	10	17.73	1 773	25	80.10	11.22	5.01	3.67	15
3	**2**	20	21.56	2 156	25	93.03	4.43	1.20	1.25	20
4	**2**	10	8.70	870	40	79.23	13.09	4.56	3.12	20
5	**2**	10	7.09	609	50	78.23	13.52	6.12	2.13	19
6	**2**	10	5.14	514	60	72.19	15.13	7.23	5.45	18
7	**3**	5	4.56	456	25	54.10	39.90	6.00	-	13
8	**3**	10	12.45	1 245	25	61.66	24.53	8.42	3.12	18
9	**3**	20	19.24	1 924	25	71.23	13.45	9.93	5.39	25
10	**3**	10	10.56	1 056	40	52.45	27.12	10.45	9.98	20
11	**3**	10	8.12	812	50	48.12	31.24	12.12	8.52	17
12	**3**	10	5.67	567	60	40.34	35.78	13.10	10.78	15

Conditions: 6 mL of toluene; catalyst loading = 10 μmol of precatalyst; monomer = ethylene; co-catalyst = $EtAlCl_2$; Al:Ni = 400:1; time 1 h. [a]Determined by mass difference of 6.0 mL toluene (5.22 g) and final mass of solution. FC = Friedel-Crafts alkylated product. [b]Determined by GC; **A** = mono-butyltoluene; **B** = di-butyltoluene; **C** = tri-butyltoluene.

Experimental

Materials and general instrumentations

Complexes were synthesised using standard Schlenk techniques under N_2. Organic solvents such as methanol were dried over CaH_2, chlorobenzene over $CaCl_2$, Hexane over Na lamps while tetrahydrofuran (THF) was dried over Na with benzophenone as indicator. [$NiBr_2$(DME)] and [$NiCl_2.6H_2O$] were purchased from Sigma Aldrich and used as received. Compounds **L1**-**L6** were synthesised following procedures described in literature,[10] were used to prepare the nickel(II) complexes **1**-**8**. Magnetic moments of the nickel complexes were measured using a Magway MSB MK1 magnetic susceptibility balance. Effective magnetic moments, μ_{eff} were calculated as described in literature.[37] GC analyses were performed on a Varian 3900 with 50 m x 0.21 mm with a CP coated silica pona column. The GC experiments were run at initial temperature of 40 ^oC and then ramped to 250 ^oC at 5 ^oC/min. GC-MS analyses were performed on a Shimadzu GC-MS-QP2010 fitted with a quadrupole mass detector. Elemental analyses were performed on a Vario elementar III microcube CHNS analyser at Rhodes University. The mass spectrometry unit at the University of Stellenbosch performed the ESI-MS spectra on a Waters API Qualtro micro spectrophotometer. Atmospheric pressure chemical ionization (APCI) was run on Burker micrOTOF-Q II 10390 at a dry gas flow of 8.0 L/min and dry heater at 200 ^oC.

Syntheses of nickel complexes

Synthesis of [{bis(3-ferrocenyl-1H-methylpyrazolyl}nickel(II) bromide] (1)

A THF solution (20 mL) of compound **L1** (0.09 g, 0.35 mmol) was added to a stirring THF solution (30 mL) of [$NiBr_2$DME] (0.05 g, 0.17 mmol). The reaction mixture turned dark orange and was allowed to stir for 12 h under N_2 at room temperature. The solution was then reduced to 10 mL and hexane was added to precipitate the product as an orange solid. The product was filtered, washed three times with hexane and dried in *vacuo*. Yield = 89% (0.11 g). IR (Diamond ATR, cm^{-1}): 3244 υ(N-H) amine. High resolution ESI-MS *m/z* (%) = 652.8664 (70%) $[M-Br]^+$. Anal. Calcd. for $C_{26}H_{34}Br_2Fe_2N_4Ni$: C, 43.21; H, 3.35; N, 7.75%. Found: C, 42.84; H, 3.75; N, 7.32%. μ_{eff} = 3.60 BM.

Complexes **2-6** were prepared using the procedure described for **1**.

Synthesis of [{bis(3-ferrocenyl-5-methylpyrazolyl}nickel(II) bromide] (2)

Compound **L2** (0.13 g, 0.50 mmol) was reacted with $[NiBr_2(DME)]$ (0.08 g, 0.25 mmol) to give an orange solid. Yield = 92% (0.17 g). IR (Diamond ATR, cm^{-1}): 3257 υ(N-H) amine. High resolution ESI-MS *m/z* (%) = 761.1672 (70%) $[M+1]^+$. Anal. Calcd. for $C_{28}H_{38}Br_2Fe_2N_4Ni$: C, 44.80; H, 3.76; N, 7.46%. Found: C, 44.89; H, 3.93; N, 7.42%. μ_{eff} = 3.57 BM.

Synthesis of [{3-ferrocenylpyrazolyl-methylenepyridine}NiBr$_2$] (3)

A mixture of **L3a** and **L3b** (0.10 g, 0.29 mmol) was added to $[NiBr_2DME]$ (0.09 g, 0.29 mmol) to afford a light brown solid. Yield = 0.13 g (82%). IR (Diamond ATR, cm^{-1}): 1626 υ(C=N). High resolution ESI-MS *m/z* (%) = 481.4412 (80%) $[M-Br]^+$. Anal. Calcd. for $C_{19}H_{17}Br_2FeN_3Ni$: C, 40.63; H, 3.05; N, 7.48%. Found: C, 40.58; H, 2.90; N, 7.73%. μ_{eff} = 3.51 BM.

Synthesis of [{3-ferrocenyl-5-methylpyrazolyl-methylenepyridine}NiBr2] (4)

A mixture of **L4a** and **L4b** (0.15 g, 0.42 mmol) was added to [$NiBr_2DME$] (0.13 g, 0.42 mmol) to give light brown solid. Yield = 70% (0.19 g). IR (Diamond ATR, cm^{-1}): 1620 υ(C=N). High resolution ESI-MS *m/z* (%) = 494.6214 (50%) $[M-Br]^+$. Anal. Calcd. for $C_{20}H_{19}Br_2FeN_3Ni$: C, 41.72; H, 3.33; N, 7.30%. Found: C, 41.57; H, 3.36; N, 6.97%. μ_{eff} = 3.94 BM.

Synthesis of [{3-ferrocenylpyrazolyl-ethylamine}NiBr₂] (5)

A mixture of **L5a** and **L5b** (0.15 g, 0.51 mmol) was added to [$NiBr_2DME$] (0.16 g, 0.51 mmol) to afford a light brown solid. Yield = 85% (0.22 g). IR (Diamond ATR, cm^{-1}): 3111 *υ*(N-H) amine stretching vibration, 1626 *υ*(N-H) amine bending vibration. High resolution ESI-MS *m/z* (%) = 536.5312 (50%) $[M+Na]^+$. Anal. Calcd. for $C_{15}H_{17}Br_2FeN_3Ni$: C, 35.07; H, 3.34; N, 8.18%. Found: 35.65; H, 3.71; N, 8.40%. μ_{eff} = 3.41 BM.

Synthesis of [{3-ferrocenyl-5-methylpyrazolyl-ethylamine}NiBr₂] (6)

A mixture of **L6a** and **L6b** (0.11 g, 0.34 mmol) was added to [$NiBr_2DME$] (0.10 g 0.34 mmol) to obtain light brown solid. Yield = 82% (0.15 g). IR (Diamond ATR, cm^{-1}): 3193 *υ*(N-H) amine stretching vibration, 1616 *υ*(N-H) amine bending vibration. High resolution ESI MS *m/z* (%) = 447.6330 (30%) $[M-Br]^+$. Anal. Calcd. for $C_{16}H_{19}Br_2FeN_3Ni$: C, 36.42; H, 3.63; N, 7.96%. Found: C, 36.80; H, 3.71; N, 8.21%. μ_{eff} = 3.36 BM.

Synthesis of [{3-ferrocenylpyrazolyl-methylenepyridine}NiCl$_2$] (7)

A MeOH solution (20 mL) of a mixture of **L3a** and **L3b** (0.12 g, 0.35 mmol) was added to a stirring MeOH solution (30 mL) of $NiCl_2.6H_2O$ (0.08 g, 0.35 mmol). The reaction mixture turned orange and was allowed to stir for 12 h under N_2 at room temperature. The solution was evaporated and the product recrystallized from CH_2Cl_2 and hexane to afford a light brown solid. The product was isolated by filtration, washed three times with hexane and dried in *vacuo*. Yield = 71% (0.12 g). IR (Diamond ATR, cm^{-1}): 1628 υ(C=N). High resolution ESI-MS *m/z* (%) = 493.9389 (10%) $[M+Na]^+$, 437.9782 (70%) $[M-Cl]^+$. Anal. Calcd. for $C_{19}H_{17}Cl_2FeN_3Ni$: C, 48.27; H, 3.62; N, 8.89%. Found: C, 48.48; H, 3.86; N, 8.65%. μ_{eff} = 3.34 BM.

Complex **8** was prepared using the procedure described for **7**.

Synthesis of [{3-ferrocenyl-5-methylpyrazolyl-methylenepyridine}NiCl$_2$](8)

A mixture of **L4a** and **L4b** (0.15 g, 0.42 mmol) in MeOH was added to $NiCl_2.6H_2O$ (0.10 g 0.42 mmol) to give light brown solid. Yield = 73% (0.15 g). IR (Diamond ATR, cm^{-1}): 1621 υ(C=N). High resolution ESI-MS *m/z* (%) = 487.2471 (70%) $[M+1]^+$. Anal Calcd. for $C_{20}H_{19}Cl_2FeN_3Ni.CH_2Cl_2$: C, 44.11; H, 3.70; N, 7.35%. Found: C, 43.99, H, 4.16; N, 7.11%. μ_{eff} = 3.87 BM.

Molecular structure determination by single crystal X-ray analysis

Single-crystal suitable for X-ray diffraction analysis for compounds **3a**, and **4a** were grown and used to determine the molecular structures for the respective compounds. The procedure for compound **3a** is used to describe the general experimental method adopted in X-ray structural determination of all the compounds.

Crystal data was collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about with an exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. Data were harvested by collecting 2982 frames at intervals of 0.5º scans in ω and φ with exposure times of 10 s per frame.[38] A successful solution by the direct methods of SHELXS 2013 provided all non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.[39]

General procedure for ethylene oligomerisation reactions

In a typical reaction, a stainless autoclave (35 mL) containing catalyst a precursor (10 µmol) and stirrer, was transferred the appreciate solvent (6 mL) under nitrogen atmosphere. Ethylaluminum dichloride ($EtAlCl_2$), in hexanes, was added to the reaction mixture. The autoclave was then placed on an Eyela chem-station and pressurised with ethylene to the required pressure and maintained at this pressure throughout the reaction. The reaction was stirred at 1 200 rpm at various temperatures, pressures and time. After the reaction, the excess ethylene was vented off and reaction quenched with 10% HCl in methanol, and the product sampled for GC and GC-MS analyses.

General characterisation of oligomers

Olefin oligomerisation products were characterised using GC. The instruments were calibrated with standard samples, which were used to establish the retention times for various authentic oligomer (C_6-C_{20}) compositions. The oligomer components in the oligomerisation reactions were established by comparing the retention times of products of the oligomerisation runs to that of standard samples. This helped in establishing the identity of the oligomer products. The butyltoluenes were identified by GC-MS. The molecular weight of the high carbon content ethylene oligomers were determined by atmospheric pressure chemical ionization (APCI) technique.

Supporting Information

Electronic Supporting Information (ESI): This material is available free of charge. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre with CCDC 1062600 **(3a)** and 1062601 **(4a)**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336063; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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Ferrocenylpyrazolyl nickel(II) complexes upon activation with $EtAlCl_2$ catalyse ethylene oligomerisation reactions in chlorobenzene to isomers of butenes and C_{16}-C_{64} olefins without Schultz-Flory distribution.