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Ferrocenylpyrazolyl palladium complexes as catalysts for the polymerisation of 1-heptene and 1-octene to highly branched polyolefins

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Reactions of $[PdCl_2(NCMe)_2]$ with the ferrocenylpyrazolyl compounds: 3-ferrocenyl-1*H*-pyrazole-5-carboxylate (**L1**), ethyl-1-(2-bromoethyl)-3-ferrocenyl-1*H*-pyrazole-5-carboxyalte (**L2a**), ethyl-1-(2-bromoethyl)-5-ferrocenyl-1*H*-pyrazole-3-carboxylate (**L2b**), 3-ferrocenylpyrazolyl-methylenepyridine (**L3**) and 3-ferrocenyl-5-methylpyrazolyl-methylenepyridine (**L4**) at room temperature afforded $[PdCl_2$(**L1**)] (**1**), $[PdCl_2$(**L2a**)] (**2a**), $[PdCl_2$(**L2b**)] (**2b**), $[PdCl_2$(**L3**)] (**3**) and $[PdCl_2$(**L4**)] (**4**) respectively. Compounds **L1**-**L4** and their palladium complexes were obtained in moderate to high (50-90%) yield and characterized by NMR spectroscopy, elemental analysis, and in selected cases by single crystal X-ray crystallography. Complexes **1**-**4** were used as pre-catalysts for the reactions of 1-heptene and 1-octene with $EtAlCl_2$ as a co-catalyst. The activities of **1**, **2a** and **3b** were relatively low (10 083-18 250 g/molPd.h) with 1-heptene being a better monomer for these complexes. However, pre-catalysts **3** and **4** showed moderate activities (123 000-448 000 g/molPd.h) 1-octene being the better monomer. The polyolefins obtained were characterized by both ^1H and $^{13}C\{^1H\}$ NMR to be highly branched polyolefins with degree of branching up to 270 branches per 1 000 carbon atoms. However, low molecular weights between 888 and 1 198 were recorded with narrow PDI between 1.02 and 1.44.

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Introduction

For many years the key building blocks in the petrochemical industry have been ethylene, propylene, and butene. This is due to their availability, low cost and reactivity; thus allowing for their conversions to a wide array of commercially useful products.[1] Although these petrochemical building blocks are still useful today, the improved availability of linear α-olefins *via* oligomerisation of ethylene, generally in the range between C_6 and C_{20}, provide access to alternate building blocks to ethylene, propylene and butene in the petrochemical industry.[2] Products made from linear α-olefins have unique and valuable characteristics for commercial proposes. For instance, copolymerisation of monomers such as 1-octene with ethylene gives stronger and tougher linear low density polyethylene, which has superior properties as packaging materials.[3] Furthermore other higher α-olefins like 1-heptene and 1-dodecene are used in making various biodegradable surfactants for household and industrial applications.[1a]

The polymerisation of these linear α-olefins is pre-dominantly performed with Ziegler-Natta type catalysts. However, in recent times Ziegler-Natta catalysts are used less since the discovery of late transition metal catalysts that have high activity toward ethylene polymerisation.[4] The two most studied late transition metals for these reactions are nickel and palladium[5] with the best known nickel catalyzed reaction being the Shell Higher Olefin Process (SHOP);[6] the success of which is driven by the chain termination properties it offers. Palladium on the other hand was considered incapable of oligomerising or polymerising olefins until the seminal work by Brookhart.[4] Since then several groups have used palladium complexes as catalysts in olefin oligomerisation and polymerisation reactions as demonstrated by several review articles on this subject.[7] Although there are several catalysts that have been used for olefin transformation reactions, their success appears to be dependent on the ligand

system. Nearly all late transition metal catalysts for olefin oligomerisation and polymerisation reactions have nitrogen donor atoms. Examples can be found in ligand systems such as α-diimine,[8] pyrazole,[9] mixed pyrazolyl-pyridine[10] and phenanthroline.[11]

Pyrazole and pyrazolyl metal complexes have attracted attention in coordination chemistry[9,10] and in catalysis,[11,12] as well as their potential applications in medicine.[13] For catalysis, pyrazole and pyrazolyl containing metal complexes are interesting because they have weaker σ-donor ability that makes their metal containing complexes more electrophilic than other nitrogen-donor ligands like imines and pyridines.[7a,14] Thus, in order to have the best electrophilicity for pyrazole and pyrazolyl metal complexes for catalytic applications, the substituents on the pyrazolyl unit are crucial. Much of the tuning for steric and electronic properties on pyrazoles have been alkyl and aryl substituents in the 3,5-positions,[12,15] but a recent report on the synthesis of ferrocenylpyrazoles opens avenues to use ferrocenyl groups as alternatives to alkyl and aryl groups.[16] A few reports on ferrocenyl supported palladium catalysts for ethylene oligomerisation or polymerisation have appeared in the literature,[17] but these are not extensive.

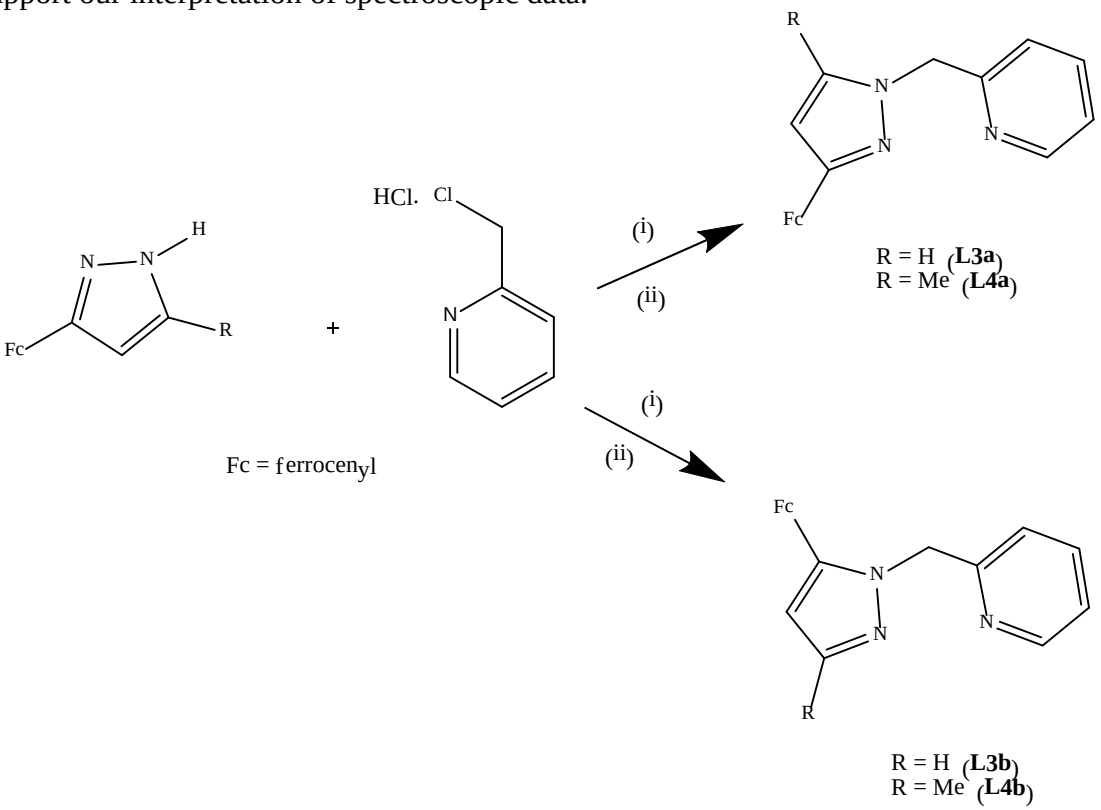
We have started a systematic search for ferrocenylpyrazolyl-supported late transition metal catalysts for α-olefin oligomerisation and polymerisation reactions. Herein we report our initial results for a series of palladium complexes that serve as efficient catalysts for higher α-olefins resulting in highly branched polyolefins.

Results and discussions

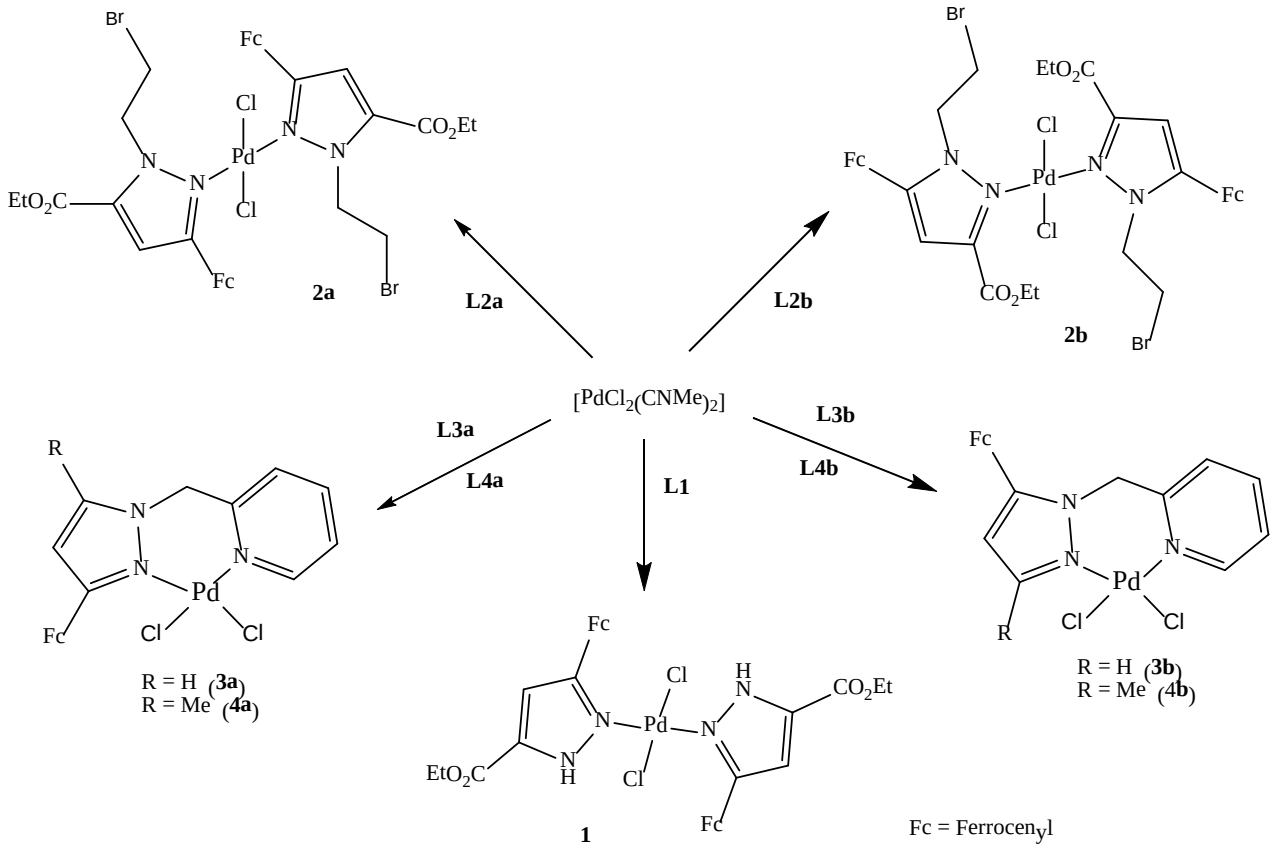
Synthesis of ligands and their palladium complexes

Five compounds, three known:(3-ferrocenyl-1*H*-pyrazole-5-carboxylate (**L1**), **(**ethyl-1-(2-bromoethyl)-3-ferrocenyl-1*H*-pyrazole-5-carboxyalte) (**L2a**) and (ethyl-1-(2-bromoethyl)-5-ferrocenyl-1*H*-pyrazole-3-carboxylate) (**L2b**),[18] and two new ones: (3-ferrocenylpyrazolyl-methylenepyridine) (**L3**) and (3-ferrocenyl-5-methylpyrazolyl-methylenepyridine) (**L4**) were used to prepare five palladium complexes **1**-**4** respectively (Schemes 1 and 2). Compounds **L3** and **L4** were prepared by refluxing a chlorobenzene solution of the appropriate ferrocenylpyrazolyl compound with 2-chlormethyl-pyridine hydrochloride in a 1:1 ratio, excess KOH after adding and TBAB (10 drops) (Scheme 1). When the synthesis of **L3** and **L4** were performed in either toluene or THF, the yields were very low but in chlorobenzene the yields were excellent (~90%). In both reactions two structural isomers of **L3** and **L4** are formed, arising from the tautomerisation of the hydrogen atom in the ferrocenylpyrazoles used as starting materials. The presence of the two isomers is clear from ^{1}H NMR spectra. Attempts to separate the two isomers of **L3** and **L4** by column chromatography were unsuccessful. In the ^{1}H NMR spectrum (Figure S1) two singlets for the methyl protons for **L4** were found at 2.19 ppm (**L4a**) and 2.30 ppm (**L4b**) in a 4:1 intensity ratio, signifying that **L4a** is the major product based on steric factors that are expected to control the reaction of the ferrocenylpyrazoles. High resolution mass spectrometry gave molecular ions for both compounds, **L3** (m/z = 344.0844 (100%) and **L4** (m/z = 358.1000 (100%), and elemental analysis was used to confirm their purity. A similar tautomerisation occurs in the formation of **L2**, but could be separated using preparative TLC to **L2a** and **L2b**. The compounds were subsequently used to prepare their respective palladium complexes **2a** and **2b**; and their solid state structures (vide infra) attest to the structural isomers of the compounds.

Reactions of **L1-L4** with $[PdCl_2(NCMe)_2]$ in a 1:1 ratio produced the palladium complexes **1-4** (Scheme 2) in moderate to high yields (51-86%). All the palladium complexes were partially soluble in THF and toluene but quite soluble in dichloromethane. Complexes **1**, **2a** and **2b** are orange whereas **3** and **4** are light brown in colour. The ^{1}H NMR spectra of **1**, **2a** and **2b** show no special features, however they revealed downfield chemical shifts for all protons compared to the free ligands. The ^{1}H NMR spectra of complexes **3** and **4** showed peaks of the two isomers similar to the free ligands. For example, complex **4** has a ^{1}H NMR spectrum (Figure S2) with peaks at 2.44 ppm (**4a)** and 2.66 ppm (**4b**) in a 3:1 ratio instead of the 4:1 ratio found for the free ligands (**L4a** and **L4b**). Also in this case, steric factors would support **4a** being the major product, and the chemical shift of the methyl group lends further credence to **4a** as the major products since its methyl group is expected to be the most downfield chemical shift in a ^{1}H NMR spectrum. We have used the solid state structures of most of these compounds to support our interpretation of spectroscopic data.



Scheme 1: Synthesis of ferrocenylpyrazolylmethylenepyrindine compounds: (i) KOH/TBAB; (ii) chlorobenzene reflux



Scheme 2: Synthesis of ferrocenylpyrazolyl palladium(II) complexes **1-4**

Molecular structures of L2, L3a, L4a, 2a, 2b.C_7H_8 and 3a.CH_2Cl_2

Single crystals suitable for X-ray analysis of **L2**, **L3a**, **L4a**, **2a**, **2b.C_7H_8** and **3a.CH_2Cl_2** were obtained by slow evaporation of their toluene or CH_2Cl_2/hexanes solutions at 25 ^oC. Crystallographic data are tabulated in Table 1, whereas the molecular geometries and selected bond lengths and angles are presented in Figure 1-6.

Compound **L2** crystalizes as two independent molecules (conformational isomers) in the asymmetric unit, **L2a** (Figure 1) and **L2b** (Figure S3). In **L2a** the atoms O1, C10 and C11 are disordered over two positions with a major contribution of 68.2(5)%; whereas in **L2b** the

unsubstituted cyclopentadienyl ring is disordered over two positions with a major component contribution of 63.7(12)%. There were no conformational isomers observed in the crystal structures of **L3** and **L4** but in both cases the isomer in the solid state was the one with the ferrocenyl unit in position 3 of the pyrazolyl ring (i.e **L3a** and **L4a**). In crystal structures of **L2**, **L3a** and **L4a** the pyrazolyl unit is coplanar with one cyclopentadienyl ring of the ferrocene moiety. The cyclopentadienyl rings in **L1**, **L3a** and **L4a** are nearly parallel in an eclipsed conformation with dihedral angles of 1.80(3)^{o}, 0.76(6)^{o} and 4.99(7)^{o} respectively. The N–N bond lengths of the pyrazolyl units in **L2a** (1.333(5) Å and **L2b** are similar at 1.338(5) Å, although the N–N bonds in **L3a** (1.3559(15) Å) and **L4a** (1.363(19) Å) are slightly longer but the difference is not statistically significant.

The crystal structures of **2a**, **2b.C$_7$H$_8$** and **3a.CH$_2$Cl$_2$** all show slightly distorted square planar geometries about the Pd centre with bond angles between 87.42(15)-91.90(11)^{o}. In **2a** and **2b.C$_7$H$_8$** the smallest N-Pd-Cl angles are 88.88(12)^{o} and 89.90(8)^{o}, whereas the largest N-Pd-Cl angles are 91.12(12)^{o} and 90.10(8)^{o}. In **3a.CH$_2$Cl$_2$** the N-Pd-Cl angle range is 87.42(8)^{o} - 91.90(11)^{o}. The two cyclopentadienyl rings in **2a**, **2b.C$_7$H$_8$** and **3a.CH$_2$Cl$_2$** are nearly parallel, with dihedral angles of 3.60(3)^{o}, 4.71(16)^{o} and 2.59(19)^{o}, respectively. The cyclopentadienyl rings of ferrocenyl moiety for all palladium complexes also show staggered conformation as found in most compounds with ferrocenyl groups. The Pd-N bond lengths for **2a** (2.013(4) Å), **2b.C$_7$H$_8$** (2.011(3) Å) and **3a.CH$_2$Cl$_2$** (2.017(4) Å) are somewhat shorter than the Pd-N bond lengths found in pyrazolyl palladium complexes that have Pd-N($_{pz}$) bonds where they range from 2.034(3) to 2.060(3) Å;[19] and the Pd-Cl bond lengths for **2a** (2.304(13) Å), **2b.C$_7$H$_8$** (2.298(8) Å) and **3a.CH$_2$Cl$_2$** (2.2816(11) Å) are in the normal range (2.242-2.516 Å) as 1776 palladium complexes to which two nitrogen atoms and two chloride ions are ligated to the palladium that are reported in the Cambridge Structural Database (CSD).[20]

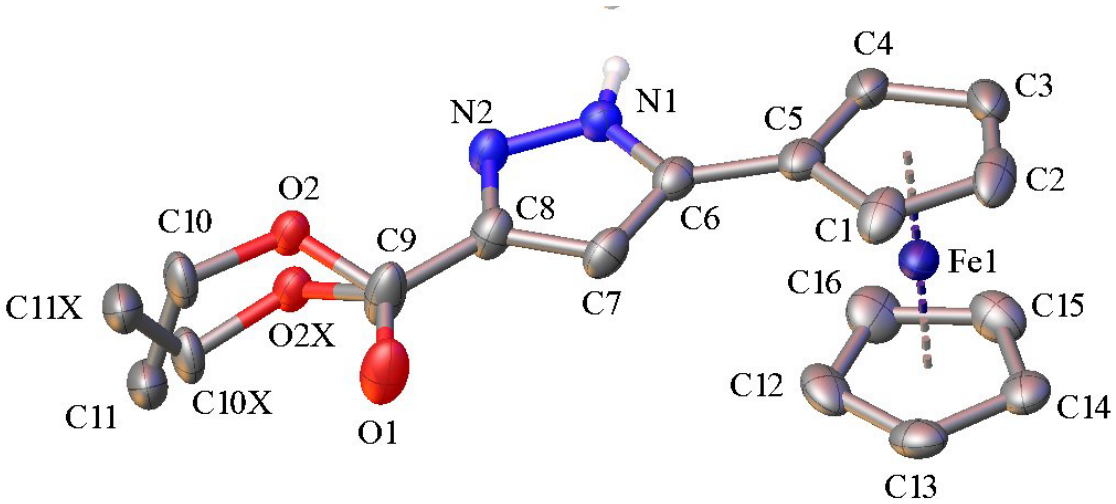


Figure 1: A molecular drawing of **L2a** with 50% probability ellipsoids. Both disordered components of OEt group are shown. Hydrogen atoms were removed for clarity. Selected bond lenght [Å] and angles [^{o}]: N1-N2, 1.333(5); Fe1-C1, 2.041(5); Fe1-C5, 2.041(5); C5-C6, 1.471; C6-N1, 1.345(6); C3-Fe1-C12, 163.10(2); C2-Fe1-C5, 68.90(2); C5-C6-N1, 123.00(4); N2-N1-C6, 113.60(4).

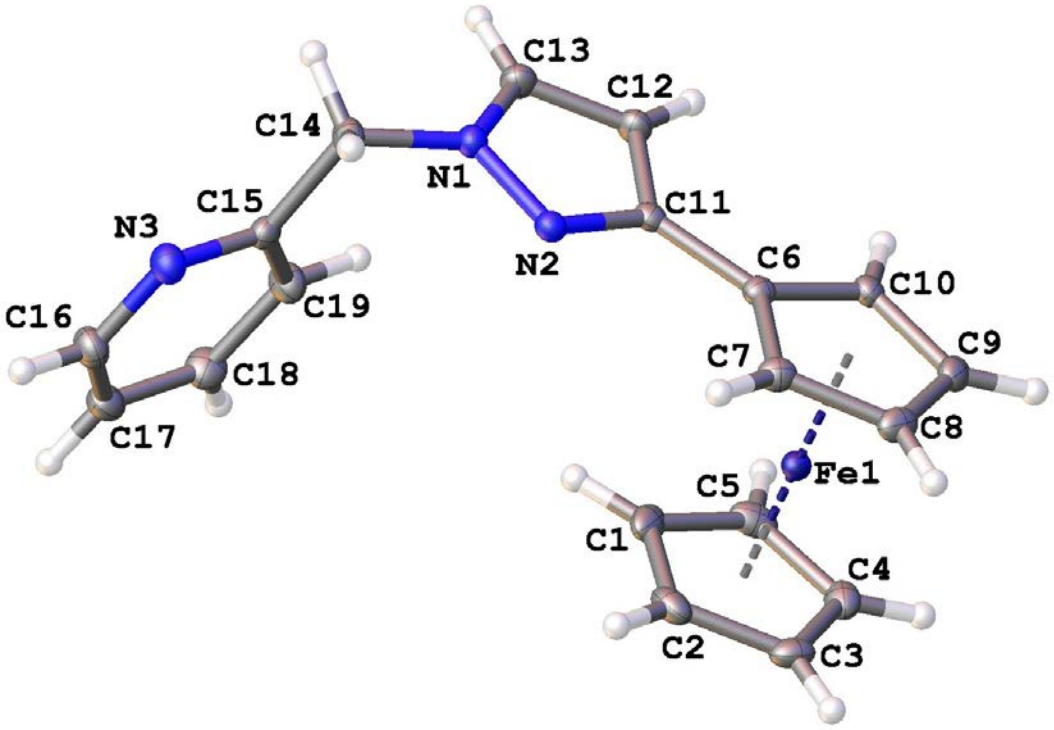


Figure 2: Molecular structure of **L3a**, drawn with 50% probability ellipsoids. Selected bond lengths [Å] and bond angles [^{o}]: N1-N2, 1.355(15); N1-C13, 1.353(18); N1-C14, 1.447(17); C14-C15, 1.515(18); N3-C15, 1.336(18); N2-C11, 1.340(17); C13-N1-N2, 112.18(11); N2-N1-C14, 119.07(11); N2-N1-C13, 112.18(11); C8-Fe-C3, 107.11(5); C1-Fe-C6, 107.54(5).

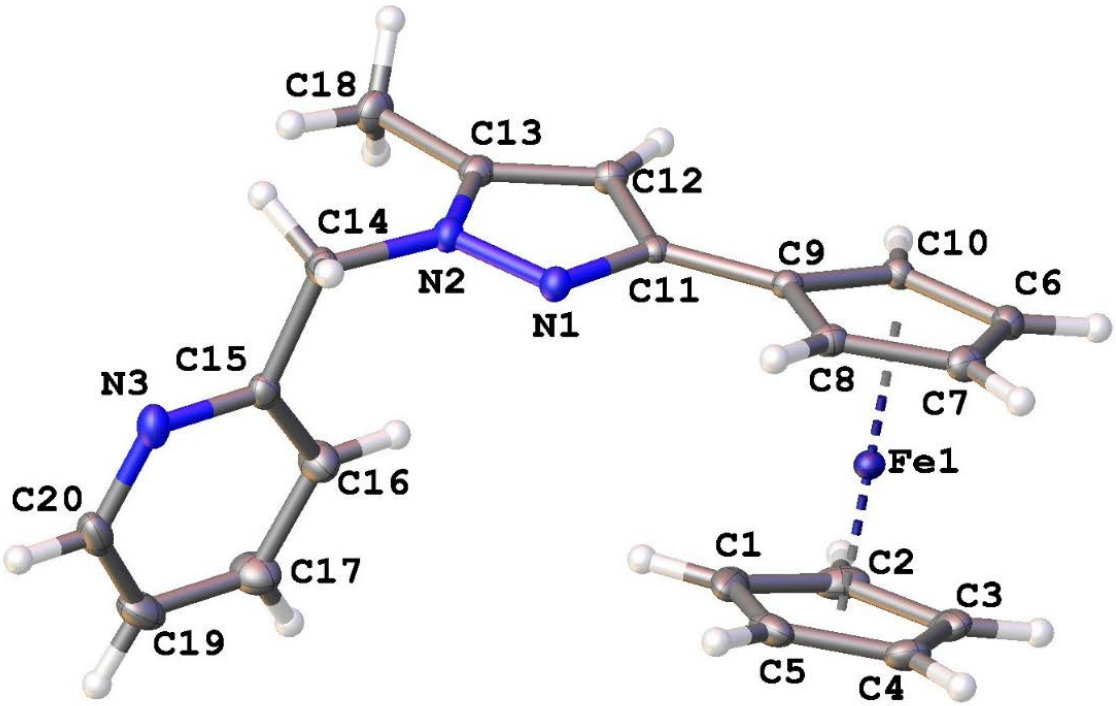


Figure 3: Molecular structure of **L4a**, drawn with 50% probability ellipsoids. Selected bond lengths [Å] and bond angles [^{o}]: N1-N2, 1.363(19); C20-N3, 1.339(2); C15-N3, 1.346(2); C14-N2, 1.449(2); C13-N2, 1.360(2); C11-N1, 1.339(2); C7-Fe1, 2.034(17); C1-Fe1, 2.043(17); C11-N1-N2, 104.48(13); C13-N2-C14, 128.55(14); C7-Fe1-C10, 68.61(6); C1-Fe1-C2, 40.56(8); C20-N3-C15, 116.95(16).

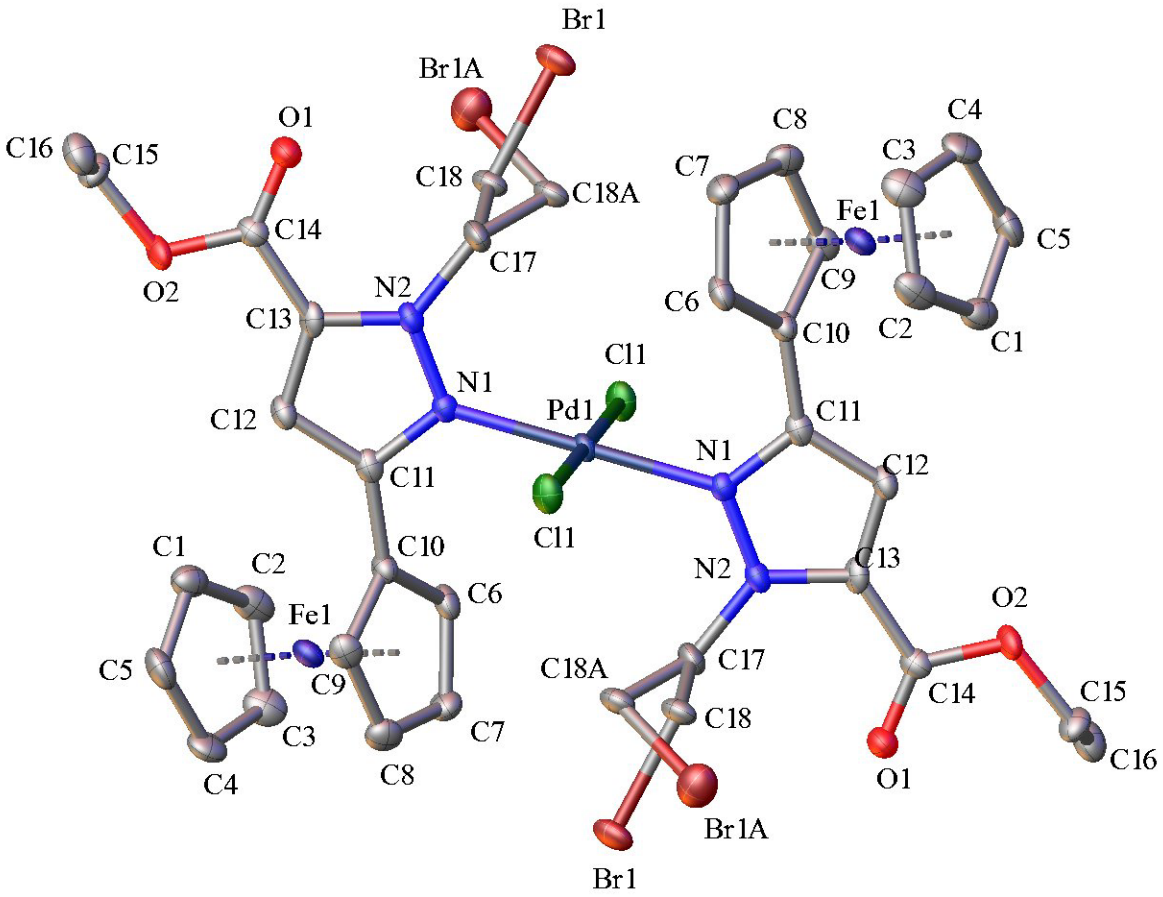


Figure 4: Molecular structure of **2a** drawn with 50% probability ellipsoids. Selected bond lenghts [Å] and bond angles [^{o}]: Pd1-N1, 2.013(4) Å; Pd1-Cl1, 2.304(13) Å; N1-N2, 1.356(6) Å; Fe1-centroid C1-C5, 1.653(3) Å; Fe1-centroid C6-C10, 1.645(2) Å. N1-Pd-N1A, 180.0^{o}; Cl1-Pd-Cl1A, 180.0^{o}; N1-Pd-Cl1, 88.88(12)^{o}; N1A-Pd-Cl1, 91.12(12)^{o}.

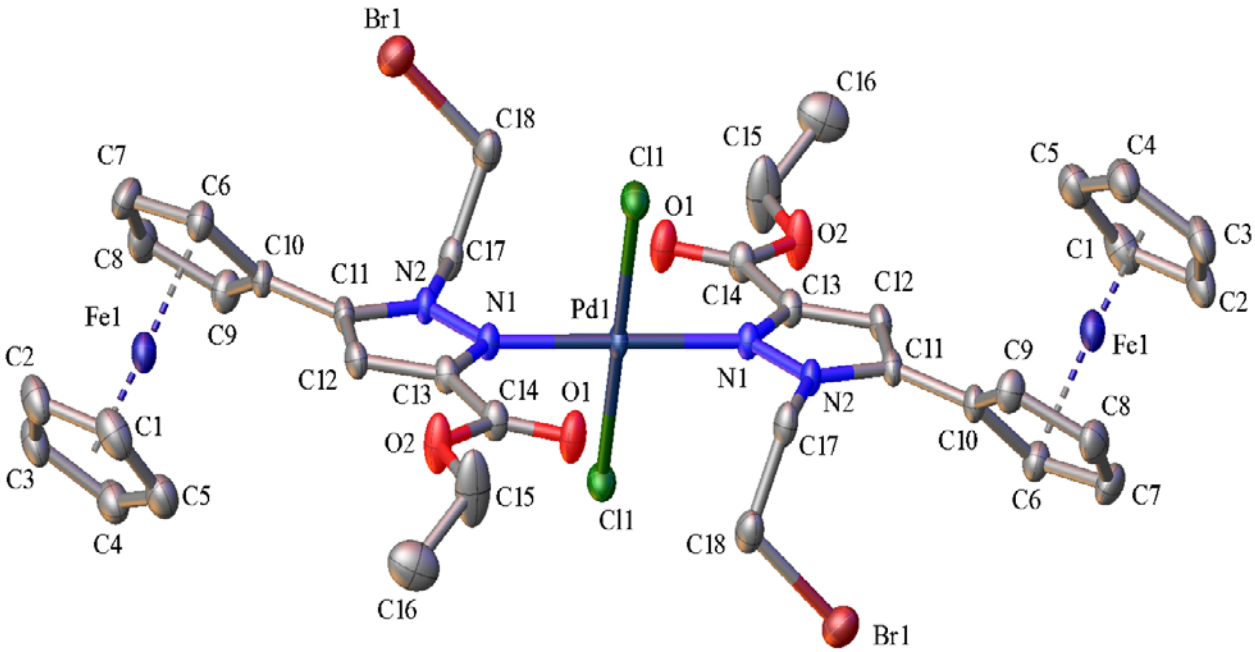


Figure 5: Molecular structure of **2b** drawn with 50% probability ellipsoids. Hydrogen atoms and toluene were removed for clarity. Selected bond lengths [Å] and bond angles [°]: Pd1-N1, 2.011(3); Pd1-Cl1, 2.298(8); N1-N2, 1.349(4); Fe1-centroid C1-C5, 1.653(2); Fe1-centroid C6-C10, 1.641(2). N1-Pd-N1A, 180.0(2); Cl1-Pd-Cl1A, 180.0; N1-Pd-Cl1, 90.10(8); N1A-Pd-Cl1, 89.90(8).

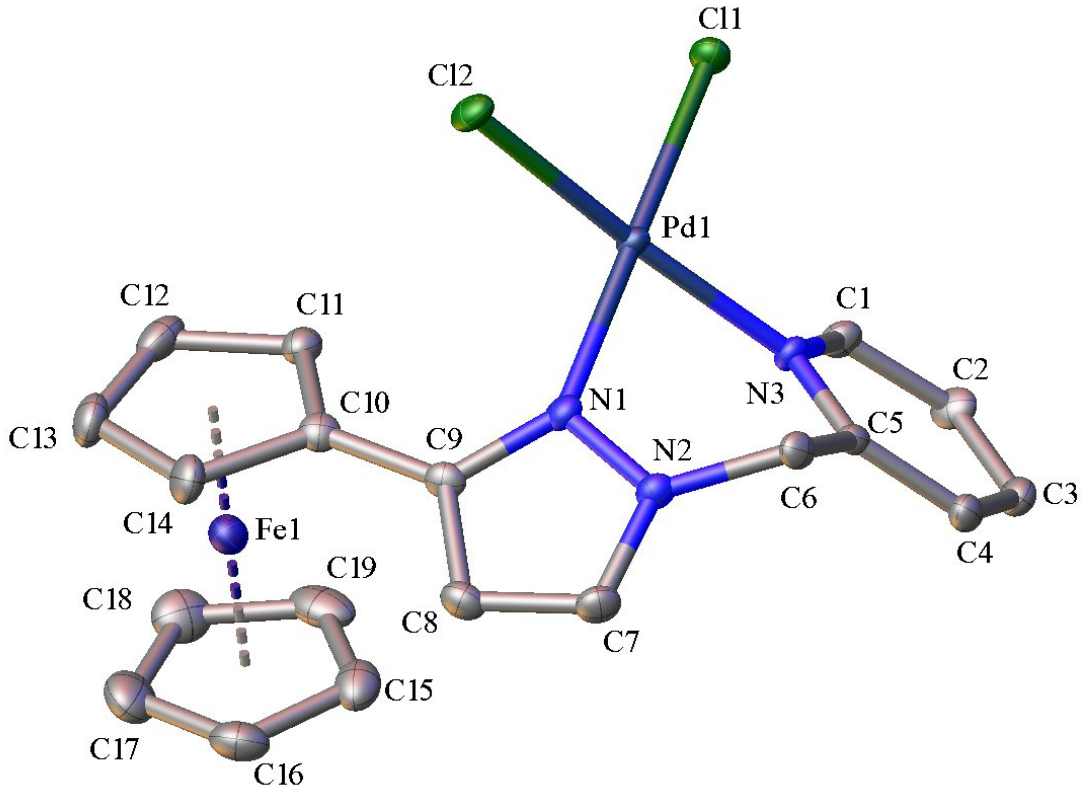


Figure 6: Molecular structure of complex **3a**, drawn with 50% probability ellipsoids. Hydrogen atoms and dichloromethane were removed for clarity. Selected bond lengths [Å] and bond angles [^{o}]: Pd1-Cl1, 2.282(11); Pd1-Cl2, 2.295(12); N1-N2, 1.363(5); Pd1-N1, 2.017(4); Pd1-N3, 2.03594(4); N2-C6, 1.463(5); N3-C1, 1.362(6); Cl2-Pd1-Cl1, 90.33(4); N1-Pd1-Cl1, 176.04(11); N1-Pd1-Cl2, 91.90(11); N3-Pd1-Cl1, 90.82(11); N3-Pd1-Cl2, 171.92(10);N3-Pd1-N1,87.42(15);C5-C6-N2,110.8(3).

Table 1: Crystal data and structure refinement for compounds **L2**, **L3a, L4a**, **2a**, **2b.C_7H_8** and **3a.CH_2Cl_2**

	L2	**L3a**	**L4a**	**2a**	**2b.C_7H_8**	**3a.CH_2Cl_2**
Empirical formula	$C_{16}H_{16}FeN_2O_2$	$C_{19}H_{17}FeN_3$	$C_{20}H_{19}FeN_3$	$C_{36}H_{38}Br_2Cl_2Fe_2N_4O_4Pd$	$C_{36}H_{38}Br_2Cl_2Fe_2N_4O_4Pd.C_7H_8$	$C_{20}H_{21}N_3Cl_2FePd.CH_2Cl_2$
Formula weight	324.16	343.24	359.25	1039.52	1131.66	605.46
Temperature/ K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength/Å	1.54178	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	C2/c	P21 /c	P21 /c	$P\bar{1}$	$P\bar{1}$	C2/c
a/ Å	29.416(8)	14.563(12)	10.412(8)	8.987(3)	10.379(10)	36.226(5)
b/ Å	11.924(3)	9.913(8)	14.067(10)	9.377(3)	10.641(10)	8.037(9)
c/ Å	21.477(5)	10.7526(8)	10.833(8)	11.493(4)	11.720(11)	15.450(19)
α/ (^{o})	90	90	90	82.844(5)	73.826(10)	90
β/ (^{o})	129.709(13)	103.195(2)	91.106(2)	86.976(5)	65.091(10)	103.443(3)
γ/ (^{o})	90	90	90	78.416(5)	68.185(10)	90
Volume (Å^3)	5795.2(3)	1511.4(2)	1586.4(2)	941.0(5)	1078.52(18)	4375.2(10)
Z	16	4	4	1	1	8
Density (Mg/m^3)	1.486	1.517	1.504	1.834	1.742	1.8382
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1632	R1 = 0.0244, wR2 = 0.0612	R1 = 0.0308, wR2 = 0.0837	R1 = 0.0472, wR2 = 0.1077	R1 = 0.0443, wR2 = 0.1187	R1 = 0.0501, wR2 = 0.1283

Olefin polymerisation catalysis

The ability of **1**-**4** to oligomerize or polymerize 1-heptene and 1-octene (Table 2) was investigated. A typical reaction was run with 5 μmol of palladium pre-catalyst, 200 equivalents of $EtAlCl_2$ as co-catalyst, and 4 mL of the olefin monomer in hexane. After sampling for GC analysis it was established that no heptene or octene oligomers were formed (Figure S4) but upon work-up of the reaction viscous oily products were isolated. NMR spectra of these oils indicated they were highly branched polyolefins. A typical ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are shown in Figures S5 and 7 of these branched polymers.

For pre-catalysts **1**, **2a** and **2b** conversion of 1-heptene and 1-octene to the respective polyolefins were in the first 3 h. It took 24 h to obtain the conversion reported in table 2 (Entries 1-6). However, pre-catalysts **3** and **4** showed good conversions even within 1 h (Table 2, entries 7-18), with almost complete conversion of 1-octene in 7 h by pre-catalyst **3** (Table 2, entry 18). It appears the nature of the ligands in the pre-catalyst play a significant role in the catalyst activity, with **1**, **2a** and **2b** that have only pyrazolyl donor group being less active compared to **3** and **4** that have pyrazolyl and pyridyl donor groups. For instance, the best activity of the pre-catalyst containing only pyrazolyl was 18 250 g/molPd.h for complex **1** whereas the best activity for the pre-catalyst with pyrazolyl-pyridine donor was 448 000 g/molPd.h for complex **3**.

To test the stability of these catalysts a second aliquot of the monomer was added to these reactions, using **1** or **3**. In the case of **1**, 1-heptene (4 mL) was added while for **4**, 1-octene (4 mL) was added. However, neither of these catalysts was able to completely convert the second aliquot of 4 mL of the monomer, no matter how long these reactions were run. It is possible that the incomplete conversion of the second aliquot of monomer could be due to mass transport problems as the reaction mixture became very viscous with the second batch of

monomers. Nevertheless, it is also possible that in both cases there was some degree of catalyst deactivation.

We investigated the effect of temperature of the activity of these pre-catalyst using complex **3** and 1-octene table 2 (Entries 8-10), confirmed that increase in temperature drastically reduced activity from 160 000 g/molPd.h at 25 ^{o}C to 82 000 g/molPd.h at 60 ^{o}C. Here, it is clear that higher temperature caused the catalyst to deactivate, hence the lower activity. Increase in reaction time resulted in increase in polymer molecular weight while increase in reaction temperature resulted in lower polymer molecular weight (Table 2). Both of these trends are expected, but what is significant is that PDI of the polymers remained narrow (1.02-1.44) (Table 2) strongly suggesting that these catalysts are single-site catalysts. This would also suggest that most of the catalytically active species remain active with time. A typical GPC trace (Figure S6) show monomodal molecular distribution; consistent with single-site catalysts system formed upon activation of pre-catalysts **1**-**4** with $EtAlCl_2$. Generally, catalyst activity increases with increasing polymerisation temperature but causes chain transfer[21] or faster chain termination,[7a] which may result in high branching or broad PDI. Similar observation has also been reported by Marques *et al*.[22] where narrow polydispersity indexes (1.12-1.21) have been achieved at temperatures between -11 to 25 ^{o}C.

NMR spectroscopy was used to characterize the polymers produced. ^{1}H NMR spectra for the various polymers obtained were similar. A typical ^{1}H NMR spectrum (Figure S5) showed two peaks at 0.87 ppm, which was assigned to CH_3, and at 1.26 ppm assigned to CH_2 and CH groups in the polymers. Integration of these two peaks suggests that the polyolefins synthesized are highly branched with degree of branching per 1000 carbon atoms between 198 and 270 (Table 2). Similar highly branched polyolefins have been reported by Brookhart and

co-worker.[21] Their degree of branching was as high as 297 per 1000 carbons when they polymerize propylene, 1-hexene and 1-octadecene with α-dimminenickel(II) chloride pre-catalyst using MAO as co-catalyst. Normally highly branched polyolefins are associated with nickel catalysts[23] which have high incidence of β-hydride migration. Our palladium catalysts appear to have similar levels of β-hydride migration, which would explain why they produce such highly branched polymers.

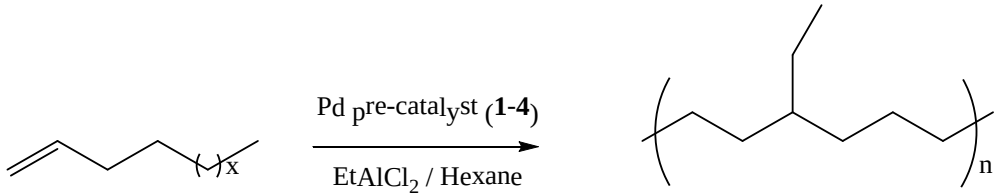
The $^{13}C\{^{1}H\}$ NMR spectra provided additional evidence of branching in the polyolefins produced. A typical $^{13}C\{^{1}H\}$ NMR spectrum is shown in Figure 7. We have used the $^{13}C\{^{1}H\}$ NMR spectra to propose a structure for the branched polyolefin produced (Figure 8); adopting the nomenclature used by Usami[24] and Mclain[25] for such branched polymers. From the $^{13}C\{^{1}H\}$ NMR data there are three main branches in our polymers, namely ethyl, propyl and butyl.

The ethyl and propyl branches in the polymers are low. A $^{1}B_2$ peak associated with ethyl branches, usually found around 11 ppm is not found in our spectra. However, low intensity $^{2}B_2$ peaks around 26.6 ppm and brB_2 at 39.5 ppm in our spectra suggest the presence of, but not extensive, ethyl branches. Similarly less extensive propyl branches in the polymers are depicted by the peaks at 14.6 ppm ($^{1}B_3$) and 36.6 ppm ($^{3}B_3$). The formation of ethyl and propyl branches in the polymer is the result of 2,1-insertion of monomers into the Pd-C bond of the catalyst, followed by successive elimination and reinsertion steps.

The characteristic peaks for butyl branches are: (i) the terminal methyl peak at 14.16 ppm (ω-1), and (ii) methylene peaks in the range 23.01–23.77 ppm and 29.5 ppm represented as $^{3}B_4$. Generally butyl branch arises from sequential 1,2-insertions of monomer into Pd-C bond.

Longer butyl branches were also observed in the polymer as high intensity peaks at 22.86 ppm ($^2B_5$) and 32.04 ppm (1,4-α'B_n) (Figure 7). These longer chain branches arise from 2,1-insertion of monomers, but are also promoted by metal migration to the primary carbon of the polymer and subsequent enchainment. There are also methyl branches in our polymers. These are the peaks at 27.95 ppm (1,6-βB_1) and 28.22 ppm (1,6-β'B_1) in Figure 7. The proposed mechanism for the formation of these branches is as reported in literature.[26]

Table 2: Olefin polymerisation data using pre-catalysts **1-4**[a] and $EtAlCl_2$ in hexane



x = 2, 3 Branched polyolefin

Entry	Catalyst	Olefin	Time (min)	Temp (^oC)	% Conversion	Yield (g)	*Activity (g/molPd.h)*	Branching[b]	M_n[c] (Da)	PDI
1	**1**	1-heptene	1440	25	79	2.19	18 250	260	825	1.22
2	**1**	1-octene	1440	25	63	1.79	14 917	265	910	1.07
3	**2a**	1-heptene	1440	25	78	2.18	18 167	256	849	1.29
4	**2a**	1-octene	1440	25	47	1.33	11 083	250	864	1.02
5	**2b**	1-heptene	1440	25	51	1.43	11917	256	836	1.44
6	**2b**	1-octene	1440	25	42	1.21	10 083	255	889	1.04
7	**3**	1-heptene	120	25	52	1.44	144 000	226	1 023	1.24
8	**3**	1-octene	120	25	56	1.60	160 000	233	1 135	1.20
9	**3**	1-octene	120	40	40	1.15	115 000	220	981	1.18
10	**3**	1-octene	120	60	29	0.82	82 000	198	888	1.16
11	**4**	1-heptene	120	25	44	1.23	123 000	206	1 059	1.19
12	**4**	1-octene	120	25	58	1.65	165 000	241	1 075	1.19
13	**3**	1-octene	15	25	18	0.52	416 000	227	1 070	1.16
14	**3**	1-octene	30	25	39	1.12	448 000	234	1 094	1.21
15	**3**	1-octene	45	25	45	1.30	346 667	245	1 105	1.20
16	**3**	1-octene	60	25	50	1.42	284 000	250	1 124	1.20
17	**3**	1-octene	180	25	65	1.86	124 000	262	1 167	1.20
18	**3**	1-octene	420	25	98	2.80	80 000	270	1 198	1.17

[a]Conditions: 6 mL of hexane; catalyst loading = 5 µmol of pre-catalyst; 4 mL of monomer; Al:Pd = 200:1; [b]branching per 1000 carbon atoms determined by ^1H NMR; [c]Determined by GPC.

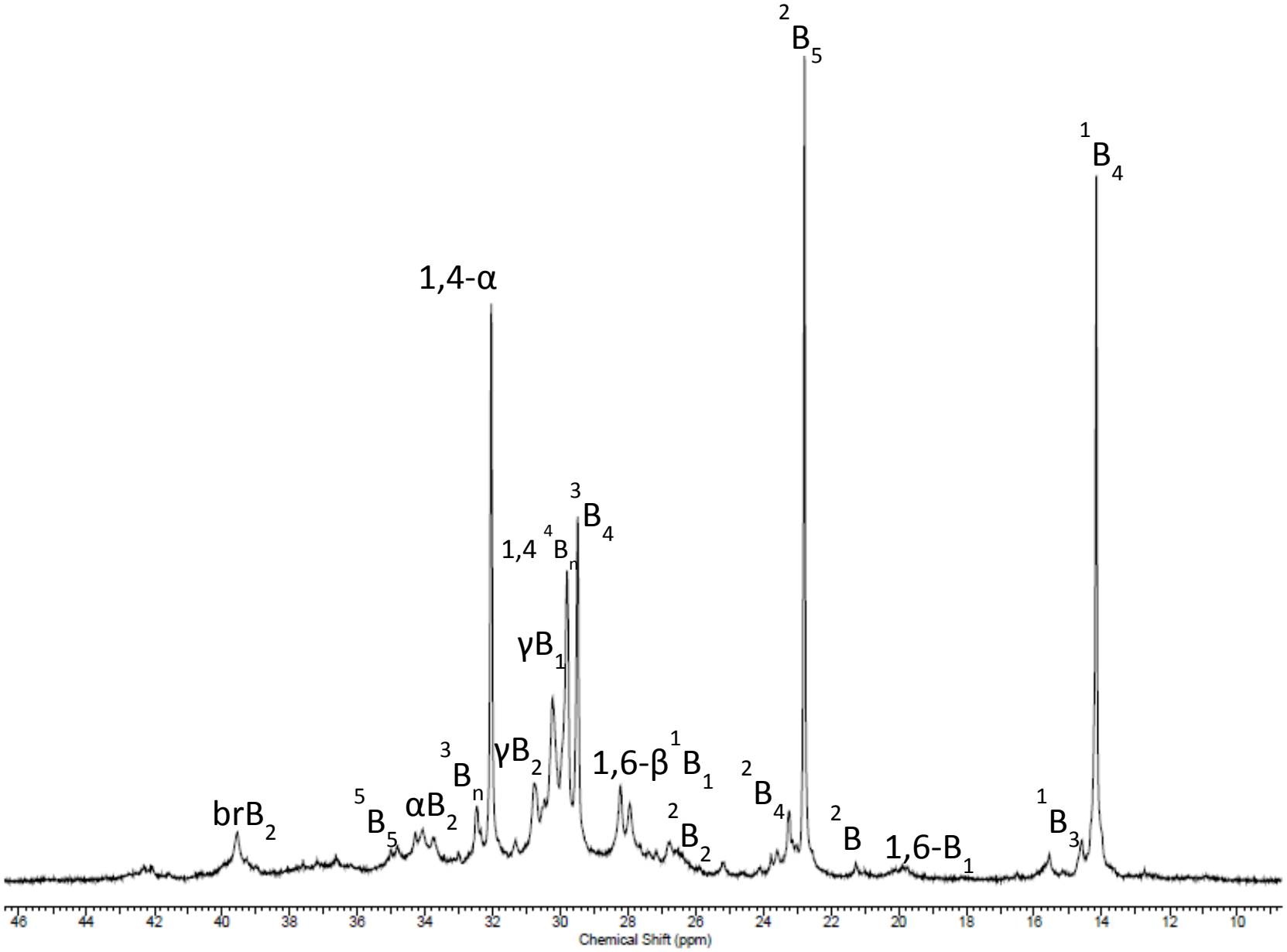


Figure 7: $^{13}C\{^{1}H\}$ NMR spectrum of a branched poly-olefin using pre-catalyst **3** with 1-octene

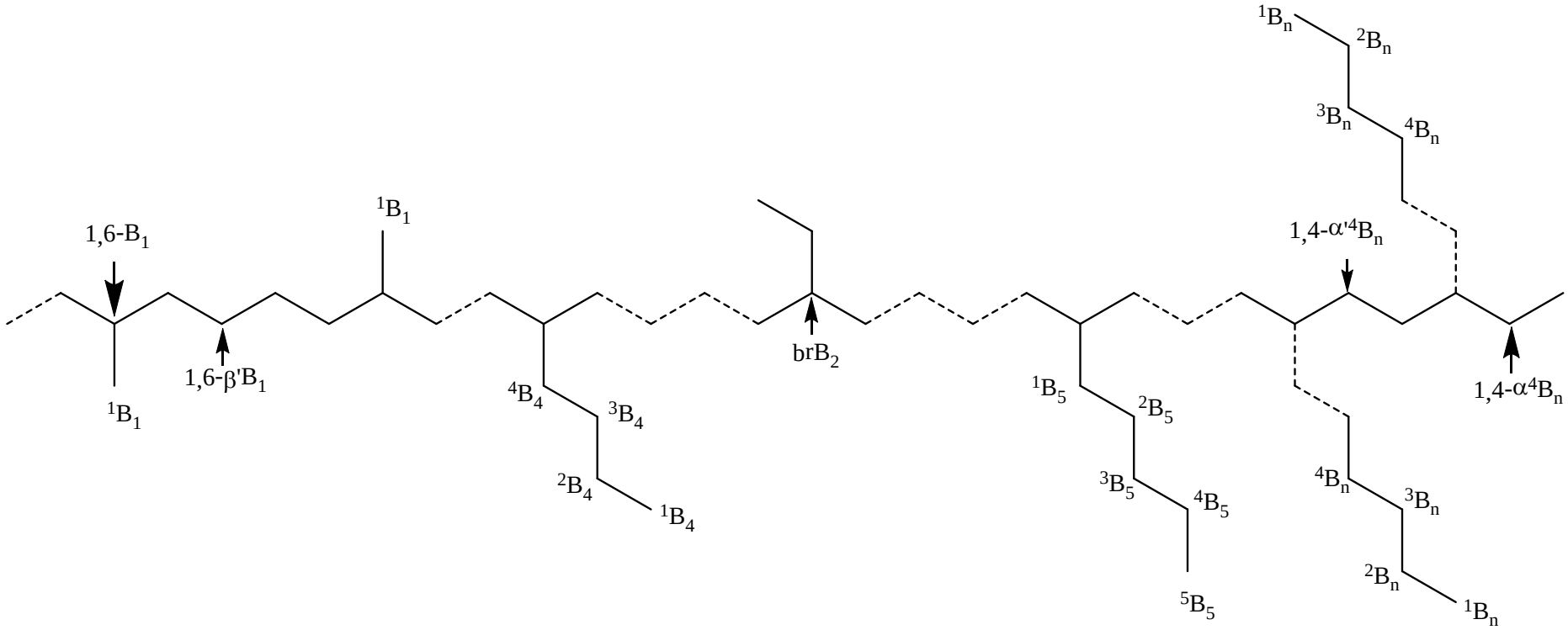


Figure 8: Proposed structure of branched polymers

Conclusion

All five ligands formed monometallic palladium complexes that were used as pre-catalysts for the polymerisation of 1-heptene and 1-octene after activation with $EtAlCl_2$ to highly branched polyolefins. The polyolefins were of low molecular weight with narrow PDI irrespective of the reaction condition and the $^{13}C\{^1H\}$ NMR spectra show that there are three main branches namely ethyl, propyl and butyl branching.

Experimental

General information

Synthesis of air sensitive compounds was carried out under N_2 inert atmosphere. Solvents were dried under nitrogen before use. All organic solvents were dried and purified by distillation over standard reagents under N_2 prior to use. Ferrocene was purchased from Aldrich and used without further purification. Acetylferrocene,[27] 3-ferrocenyl-*1H*-pyraozlyl-5-carboxylate (**L1**),[18] ethyl-1-(2-bromoethyl)-3-ferrocenyl-*1H*-pyrazolyl-5-carboxylate (**L2a**),[18] ethyl-1-(2-bromoethyl)-5-ferrocenyl-*1H*-pyrazole-3-carboxylate (**L2b**)[18] and $[PdCl_2(NCMe)_2]$[28] were synthesized using literature procedures. NMR spectra were recorded on a Bruker 400 MHz instrument (^1H at 400 MHz and $^{13}C\{^1H\}$ at 100 MHz). The chemical shifts are reported in δ (ppm) and referenced to the residual proton and carbon signals at 7.24 ppm and 77.0 ppm respectively of $CDCl_3$ NMR solvent. Elemental analyses were performed on a Vario elementar III microcube CHN analyzer at Rhodes University. The mass spectrometry unit at the University of Stellenbosch performed the ESI-MS spectra on a Waters API Qualtro micro spectrophotometer. The SEC instrument consists of a Waters 1515 isocratic HPLC pump, a Waters 717plus auto-sampler, Waters 600E system controller (run by Breeze Version 3.30 SPA) and a Waters in-line Degasser AF. A Waters 2414 differential refractometer was used at 30°C in series with a Waters 2487 dual wavelength absorbance UV/Vis detector operating at variable wavelengths. Tetrahydrofuran (THF, HPLC grade,

stabilized with 0.125% BHT) was used as eluent at flow rates of 1 mL min^{-1}. The column oven was kept at 30 ^{o}C and the injection volume was 100µL. Two PLgel (Polymer Laboratories) 5µm Mixed-C (300x7.5 mm) columns and a pre-column (PLgel 5 µm Guard, 50x7.5 mm) were used. Calibration was done using narrow polystyrene standards ranging from 580 to $2x10^6$ g mol^{-1}. All molecular weights were reported as polystyrene equivalents. Samples for SEC were dissolved in BHT stabilized THF (2 mg/mL). Sample solutions were filtered via syringe through 0.45 µm syringe filters before subjected to analysis.

Synthesis of ligands

Synthesis of ferrocenylpyrazolyl-methylenepyridine (L3a and L3b)

To a 20 mL chlorobenzene solution of 3-ferrocenylpyrazole (0.40 g, 1.58 mmol) was added 2-chloromethylpyridine hydrochloride (0.26 g, 1.58 mmol), KOH (0.44 g, 7.93 mmol) and 10 drops of TBAB. The mixture was refluxed for 18 h and the resulting mixture filtered and solvent evaporated to obtain a dark orange solid product of yield 87% (0.47 g).^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.03 (s, 5H, η^5-C_5H_4); 4.05 (s, 5H, η^5-$C_5H_4)_{iso}$; 4.23 (s, 2H, η^5-C_5H_4); 4.38 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.67 (s, 2H, η^5-C_5H_4); 5.42 (s, 2H, CH_2); 5.67 (s, 2H, $CH_2)_{iso}$; 6.33 (s, 1H, pz-H); 6.37 (s, 1H, pz-H)$_{iso}$; 6.76 (d, 1H, J_{HH} = 7.6 Hz, py)$_{iso}$; 6.91 (d, 1H, J_{HH} = 7.6 Hz, py); 7.17 (t, 1H, J_{HH} = 5.2 Hz, py); 7.41 (s, 1H, pz); 7.52 (s, 1H, pz)$_{iso}$; 7.60 (t, 1H, J_{HH} = 7.2 Hz, py); 8.54 (d, 1H, J_{HH} = 4.0 Hz, py); 8.60 (d, 1H, J_{HH} = 3.6 Hz, py)$_{iso}$. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 55.2; 57.4; 66.5; 68.1; 68.4; 69.0; 69.4; 69.5; 103.9; 105.8; 120.9; 121.3; 122.3; 122.5; 130.8; 137.0; 139.4; 149.2; 149.3; 151.9; 157.2; 157.9. High resolution ESI MS: calc. $[M+1]^+$: $C_{19}H_{18}N_3Fe$: 344.2000. Found = 344.0844. Anal. Calcd for $C_{19}H_{17}N_3Fe$: C, 66.49; H, 4.99; N, 12.24% Found: C, 66.76; H, 5.23; N, 12.51%

Compound **L4** was prepared in a similar manner as described for **L3**, using the appropriate reagents.

Synthesis of ferrocenylmethylpyrazolyl-methylenepyridine (L4a and L4b)

Compound 3-ferrocenyl-5-methylpyrazole (0.50 g, 1.88 mmol) was added to 2-chloromethylpyridine hydrochloride (0.31 g, 1.88 mmol), KOH (0.53 g, 9.39 mmol) and 10 drops of TBAB to obtain a light orange solid product of yield 90% (0.60 g).^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.19 (s, 3H, CH_3); 2.30 (s, 3H, $CH_3)_{iso}$; 4.05 (s, 5H, η^5-C5H4); 4.23 (s, 2H, η^5-C_5H_4); 4.34 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.65 (s, 2H, η^5-C_5H_4); 4.75 (s, 2H, η^5-$C_5H_4)_{iso}$; 5.39 (s, 2H, CH_2); 5.61 (s, 2H, $CH_2)_{iso}$; 6.13 (s, 1H, pz-H); 6.17 (s, 1H, pz-H)$_{iso}$; 6.74 (d, 1H, J_{HH} = 8.0 Hz, py); 6.78 (d, 1H, J_{HH} = 8.4 Hz, py)$_{iso}$; 7.16 (t, 1H, J_{HH} = 5.2 Hz, py); 7.59 (t, 1H, J_{HH} = 8.0 Hz, py); 8.54 (d, 1H, J_{HH} = 4.8 Hz, py); 8.60 (d, 1H, J_{HH} = 4.0 Hz, py)$_{iso}$. ^{13}C{^{1}H} NMR ($CDCl_3$) δ:11.1; 13.5; 54.6; 55.0; 66.4; 67.9; 68.0; 68.3; 68.9; 69.4; 69.5; 103.8; 105.5; 120.7;120.8;122.2; 122.3; 137.0; 139.7; 142.4; 148.3; 149.1; 149.3; 150.0; 157.5; 158.2. High resolution ESI MS: calc. $[M+1]^+$: $C_{20}H_{20}N_3Fe$: 358.0900. Found = 358.1000. Anal. Calcd for $C_{20}H_{19}N_3Fe$: C, 67.24; H, 5.36; N, 11.76% Found: C, 67.58; H, 5.91; N, 12.01%.

Synthesis of palladium complexes

Synthesis of [{bis(3-ferrocenyl-1H-pyrazole-5-carboxylate}palladium(II) chloride] (1)

To a mixture of the **L1** (0.113 g, 0.349 mmol) and $[PdCl_2(NCMe)_2]$ (0.045 g, 0.174 mmol) was added 20 mL of CH_2Cl_2 and stirred at room temperature for 18 h. After evaporating the solvent, the crude product obtained was recrystallized by slow evaporation of a solution of the product in a 2:1 mixture of dichloromethane-toluene to afford **1** as an orange solid. Yield = 87% (0.125 g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.59 (t, 3H, $OCH_2\mathit{CH_3}$), 4.03 (s, 5H, η^5-C_5H_4), 4.25 (q, 2H, OCH_2CH_3), 4.56 (s, 2H, η^5-C_5H_4), 4.65 (s, 2H, η^5-C_5H_4), 6.43 (s, 1H, pz). Anal. Calcd for $C_{32}H_{31}Cl_2Fe_2N_4O_4Pd$: C, 46.66; H, 3.67; N, 6.80. Found: C, 46.68; H, 4.06; N, 6.88%.

Complexes **2-4** were prepared in a similar manner as described for **1**, using the appropriate reagents and ratios.

Synthesis of [{bis(ethyl-1-(2-bromoethyl)-3-ferrocenyl-1H-pyrazolyl-5-carboxylate}-palladium(II) chloride] (2a)

Compound **L2a** (0.122 g, 0.349 mmol) was reacted with $[PdCl_2(NCMe)_2]$ (0.045 g, 0.174 mmol) to give an orange solid. Yield = 58% (0.105 g). ^{1}H NMR ($CDCl_3$, 400 MHz,): δ 1.42 (t, 3H, $OCH_2\underline{CH_3}$), 3.94 (t, 2H, $CH_2\underline{CH_2}Br$), 4.21 (s, 5H, η^5-C_5H_4), 4.43 (q, 2H, $O\underline{CH_2}CH_3$), 4.58 (s, 2H, η^5-C_5H_4), 5.31 (s, 2H, η^5-C_5H_4), 5.73 (t, 2H, $\underline{CH_2}CH_2Br$), 6.94 (s, 1H, pz). Anal. Calcd for $C_{36}H_{38}Br_2Cl_2Fe_2N_4O_4Pd$: C, 41.59; H, 3.68; N, 5.39. Found: C, 41.70; H, 3.83; N, 5.32%.

Synthesis of [{bis(ethyl-1-(2-bromoethyl)-5-ferrocenyl-1H-pyrazolyl-3-carboxylate)}-palladium(II) chloride] (2b)

Compound **L2b** (0.122 g, 0.349 mmol) was reacted with $[PdCl_2(NCMe)_2]$ (0.045 g, 0.174 mmol) to give an orange solid. Yield: 51% (0.100 g).^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.47 (t, 3H, $OCH_2\underline{CH_3}$), 4.21 (s, 5H, η^5-C_5H_4), 4.46 (m, 2H, $CH_2\underline{CH_2}Br$, 2H, η^5-C_5H_4), 4.58 (m, 2H, $O\underline{CH_2}CH_3$, 2H, η^5-C_5H_4), 5.89 (t, 2H, $\underline{CH_2}CH_2Br$), 6.83 (s, 1H, pz). Anal. Calcd for $C_{36}H_{38}Br_2Cl_2Fe_2N_4O_4Pd.C_7H_8$: C, 44.14; H, 3.82; N, 5.23. Found: C, 44.54; H, 3.91; N, 4.97%.

Synthesis of [{ferrocenylpyrazolyl-methylenepyridine} palladium(II) chloride] (3a and 3b)

A mixture of **L3a** and **L3b** (0.0995 g, 0.290 mmol) was added to $[PdCl_2(NCMe)_2]$ (0.0751 g, 0.290 mmol) to afford a light brown mixture of **3a** and **3b**. Yield = 80% (0.12 g). ^{1}H NMR, ($CDCl_3$, 400 MHz): 3.97 (s, 5H, η^5-C_5H_4); 4.04 (s, 5H, η^5-$C_5H_4)_{iso}$; 4.36 (s, 2H, η^5-C_5H_4); 4.41 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.45 (s, 2H, η^5-C_5H_4); 4.80 (s, 2H, η^5-$C_5H_4)_{iso}$; 5.68 (s, 2H, CH_2); 5.85 (s,

2H, $CH_2)_{iso}$; 6.37 (s, 1H, pz)$_{iso}$; 6.42 (s, 1H, pz); 7.41 (d, 1H, J_{HH} = 6.8 Hz, py); 7.47 (d, 1H, J_{HH} = 6.8 Hz, py)$_{iso}$; 7.61(d, 1H, J_{HH} = 6.8 Hz, py); 7.71 (s, 1H, pz); 7.92 (m, 1H, py); 9.08 (d, 1H, J_{HH} = 4.0 Hz, py); 9.30 (d, 1H, J_{HH} = 3.6 Hz, py)$_{iso}$. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 56.3; 58.0; 67.6; 68.8; 69.2; 69.9; 70.4; 70.7; 105.7; 106.4; 121.9; 122.8; 123.8; 124.5; 131.6; 137.7; 140.1; 150.5; 150.7; 153.2; 158.3; 159.0. Anal. Calcd. for $C_{19}H_{17}Cl_2FeN_3Pd$: C, 43.84; H, 3.29; N, 8.07%. Found: C, 43.86, H, 3.61; N, 7.80%.

Synthesis of [{3-ferrocenyl-5-methylpyrazolyl-methylenepyridine}palladium(II) chloride] (4a and 4b)

A mixture of **L4a** and **L4b** (0.0997 g, 0.280 mmol) was added to a $[PdCl_2(NCMe)_2]$ (0.0725 g, 0.280 mmol) to give a light brown solid of **4a** and **4b**. Yield = 82% (0.12 g). ^1H NMR, ($CDCl_3$, 400 MHz): δ 2.44 (s, 3H, $CH_3)_{iso}$; 2.64 (s, 3H, CH_3); 4.00 (s, 5H, η^5-C_5H_4); 4.20 (s, 5H, η^5-$C_5H_4)_{iso}$; 4.30 (s, 2H, η^5-C_5H_4); 4.43 (s, 2H, η^5-C_5H_4); 4.81 (s, 5H, η^5-$C_5H_4)_{iso}$; 5.54 (s, 2H, CH_2); 5.82 (s, 2H, $CH_2)_{iso}$; 6.17 (s, 1H, pz); 6.20 (s, 1H, pz)$_{iso}$; 7.28 (d, 1H, J_{HH} = 7.6 Hz, py); 7.43 (d, 1H, J_{HH} = 8.0 Hz, py); 7.49 (t, 1H, J_{HH} = 6.0 Hz, py); 7.85 (t, 1H, J_{HH} = 7.6 Hz, py)$_{iso}$; 7.92 (d, 1H, J_{HH} = 7.6 Hz, py); 9.08 (d, 1H, J_{HH} = 4.0 Hz, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ:12.1; 13.9; 55.7; 56.1; 69.6; 69.9; 71.2; 72.0; 74.9; 75.2; 76.1; 105.9; 106.6; 122.6; 123.3; 123.9; 124.3; 137.2; 140.0; 142.5; 149.3; 115.0.; 150.1; 152.4; 158.6; 159.7. Anal. Calcd for $C_{20}H_{19}Cl_2FeN_3Pd$: C, 44.94; H, 3.58; N, 7.86%. Found: C, 44.54, H, 3.78; N, 7.56%.

Molecular structure determination by single crystal X-ray analysis

Single-crystal X-ray diffraction data for **L2**, **L3a**, **L4a**, **2a**, **2b.C_7H_8** and **3a.CH_2Cl_2** were collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and diffractometer to crystal distance of 5.00 cm. The following is a typical experiment conducted in the case of structure **L2**.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.[29] A successful solution by the direct methods of SHELXS97 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.[30]

Catalysis procedure

In a typical reaction a parallel reactor tube was charged with 5 µmol of a catalyst precursor and 30 mL of dry hexane. The tube was mounted on the reactor, filled with nitrogen and evacuated three times before finally filling it with nitrogen followed by addition of 4 mL of monomer. A 10 mL solution $EtAlCl_2$ (200 equivalents) in hexane was then added to the reaction vessel. The reaction mixture was stirred for the appropriate time, after which the reaction was quenched with about 5 mL of 10% HCl in methanol and water. The organic phase was then separated from the aqueous phase and washed three times with water. The organic phase was dried over anhydrous $MgSO_4$, some sampled for GC analysis and solvent evaporated to obtain the oily product.

General characterization of branched polyolefin

Branched polymers were characterized using GPC, ^{1}H (Figure S4) and $^{13}C\{^{1}H\}$ NMR (Figure 7) spectroscopy.

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 **962789 (2a)**, **962790 (2b)**, **962791 (3a)**, **962792 (L2)**, **962793 (L3a)** and **962794 (L4a)**. 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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References

1. (a) E. F. Lutz; *J. Chem. Edu.* 63, **1986**, 202-203. (b) G. W. Parshall; *Homogeneous Catalysis* Wiley New York, **1980**, 176-177. (c) E. R. Freitas, C. R. Gum, *Chem. Eng. Progress*, **1979**, 73-76.
2. (a) Alpha Olefins (02/03-4), PERP Report, *Nexant Chem Systems*. (b) Plastics Europe Deutschland, WG Statistics and Market Research; cf. *http://www.vke.de/de/infomaterial/download.* (*c*) Y. V. Kissin, In Kirk-Othmer Encyclopedia of Chemical Technology; Wiley & Sons, Inc: **2005**.
3. (a) K. W. Doak, In *Encyclopedia of Polymer Science and Engineering*; H. F. Mark, Ed.; John Wiley & Sons: New York, 1986, **6**, 386. (b) S. J. McLain, K. J. Sweetman, L. K. Johnson, E. F. McCord, *Polym. Mater. Sci. Eng*. 2002, **86**, 320-321; (c) C. S. Propeny, D. H. Camacho, Z. Guan, *J. Am. Chem. Soc.* 2007, **129**, 10062-10063; (d) S. J. Diamanti, P. Ghosh, F. Shimizu, G. C. Bazan, *Macromolecules* 2003, **36**, 9731-9735.
4. L. K. Johnson, C. M. Killian, M. Brookhart; *J. Am. Chem. Soc.* 1995, **117**, 6414-6415.
5. (a) W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger; *Angew. Chem., Int. Ed. Engl.* 1978, **17**, 466-467; (b) W. Keim, A. Behr, B. Limbäcker, C. Krüger; *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 503-504; (c) J. M. Malinoski; M. Brookhart; *Organometallics*, 2003, **22**, 5324-5335; (d) B. L. Small, M. Brookhart, A. M. A. Bennett; *J. Am. Chem. Soc*. 1998,

120, 4049-4050; (e) G. J. P. Britovsek, V.C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams; *Chem. Commun.* 1998, 849-850; (f) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G.A. Solan, S. Stromberg, A. J. P. White, D. J. Williams; *J. Am. Chem. Soc.* 1999, **121**, 8728-8740. (g) S. Wang, W.-H. Sun, C. Redshaw; *J. Organomet. Chem.* 2014, **751**, 717-741.

6. (a) W. Keim, A. Behr, M. Roper; *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, New York, **1982**, vol. 8, ch. 52; (b) W. Keim; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235-244; (c) W. Keim; *J. Mol. Catal.*, 1989, **52**, 19-25; (d) M. Peuckert, W. Keim; *Organometallics*, 1983, **2**, 594-597; (e) A. M. Al-Jarallah, J. A. Anabtawi, M. A. B. Siddiqui, A. M. Aitani; A. W. Al-Sa'doun; *Catal. Today*, 1992, **14**, 1-121; (f) K. Weissermel; H.-J. Arpe, *Industrial Organic Chemistry*, VCH, Weinheim, **1993**.
7. (a) S. D Ittel, L. K. Johnson, M. Brookhart *Chem. Rev.* 2000, **100**, 1169-1203; (b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* 2003, **103**, 283-315; (c) S. Mecking, *Coord. Chem. Rev.* 2000, **203**, 325-351; (d) R. Gao W-H. Sun, C. Redshaw; *Catal. Sci. Technol.* 2013, **3,** 1172-1179.
8. (a) J. D. Azoulay, R. S. Rojas, A. V. Serrano, H. Ohtaki, G. B. G., G. Wu, G. C. Bazan; *Angew. Chem. Int. Ed*. 2009, **48**, 1089-1092. (b) S. Mecking; L. K. Johnson; L. Wang; M. Brookhart; *J. Am. Chem. Soc.* 1998, **120**, 888-899. (c) F. C. Rix, M. Brookhart; *J. Am. Chem. Soc.* 1995, **117**, 1137-1138.
9. (a) R. Mukherjee; *Coord. Chem. Rev.* 2000, **203**, 151-218. (b) M. A. Halcrow; *Coord. Chem. Rev.* 2006, **249**, 2880-2908. (c) M. A. Halcrow; *Coord. Chem. Rev.* 2009, **253**, 2493-2519.
10. (a) S. O. Ojwach, I. A. Guzei, L. L. Benade, S. F. Mapolie, J. Darkwa; *Organometallics* 2009, **28**, 2127-2133. (b) M. S. Mohlala, I. A. Guzei, J. Darkwa, S. F. Mapolie; *J. Mol. Cat. A: Chem.* 2005, **241**, 93-100.
11. (*a*) S. Strömberg, M. Oksman, L. Zhang, K. Zetterberg; *Acta Chem. Scand.* 1995, **49**, 689-695; (*b*) V. De Felice, M. E. Cucciolito, A. De Renzi, F. Ruffo, D. Tesauro; *J. Organomet. Chem.* 1995, **493**, 1-11.
12. (a) S. O. Ojwach, J. Darkwa; *Inorg. Chim. Acta* 2010, **363**, 1947-1964. (b) C. Obuah, B. Omondi, K. Nozaki, J. Darkwa; *J. Mol. Cat. A: Chem*. 2014, **382**, 31-40. (c) C. Obuah, M. K. Ainooson, S. Boltina, I. A. Guzei, K. Nozaki, J. Darkwa; *Organometallics* 2013, **32**, 980-988. (d) M. K. Ainooson, S.O. Ojwach, I.A. Guzei, L.C. Spencer, J. Darkwa; *J.*

Organomet. Chem. 2011, **696**, 1528-1535. (e) K. Li, J. Darkwa, I. A. Guzei, S. F. Mapolie; *J. Organomet. Chem.;* 660, **2002**, 108-115. (f) I. A. Guzei, K. Li, G. Bikzhanova, J. Darkwa, S. F. Mapolie, *Dalton Trans*. 2003, 715-722. (g) A. Budhai, B. Omondi, S. O. Ojwach, C. Obuah, E. Y. Osei-Twum, J. Darkwa; *Catal. Sci. Technol*. 2013, **3**, 3130-3135.

13. (a) F. K. Keter, J. Darkwa; *Biometals* 2012, **25**, 9-21; (b) R. M. Claramunt, L. Bouissane, M. P. Cabildo, M. P. Carnago, J. Elguero, A. Radziwon, C. Medina; *Bioorg. Med. Chem.* 2009, **17**, 1290-1296. (c) P. K. Sharma, N. Chandak, P. Kumar, C. Sharma, K. R. Aneja, *Eur. J. Med. Chem.* 2011, **46**, 1425-1432. (d) S. A. F. Rostom, *Bioorg. Med. Chem.* 2010, **18**, 2767-2776. (e) W. C. M. Duivenvoorden, Y-N. Liu, G. Schatte, H-B. Kraatz, *Inorg. Chim. Acta* 2005, **358**, 3183-3189.
14. C. Bianchini, G. Giambastiani, I. G. Rios, G. Mantovani, A. Meli, A. M. Segarra; *Coord. Chem. Rev.* 2006, **250**, 1391-1418.
15. S. Tsuji, D. C. Swenson, R. F. Jordan; *Organometallics* 1999, **18**, 4758-4764.
16. (a) R. S. Herrick, C. J. Ziegler, M. Precopio, K. Crandall, J. Shaw, R. M. Jarret, *J. Organomet. Chem.* 2008, **693**, 619-624. (b) Y-N. Liu, G. Orlowski, G. Schatte, Y-B. Kraatz ; *Inorg. Chim. Acta* 2005, **358**, 1151-1161. (c) R. S. Herrick, B. R. Franklin, C. J. Ziegler, A. Cetin; *Inorg. Chem. Commun.* 2009, **12**, 1209-1211.
17. (a) Z. Weng, S. Teo, T. S. A. Hor, *Organometallics* 2006, **25**, 4878, (b) Z. Weng, S. Teo, L. L. Koh, T. S. A. Hor; *Chem. Commun.* 2006, 1319–1321 (c) V. C. Gibson, C. K. A. Gregson, C. M. Halliwell, N. J. Long, P. J. Oxford, A. J. P. White, D. J. Williams; *J. Organomet. Chem.* 2005, **690**, 6271-6283.
18. (a) A. Patti, S. Pedotti; *Tetrahedron: Asymmetry* 2006, **17**, 1824-1830. (b) K. Nienzu, J. Serwatowski, S. Trofimenko; *Inorg. Chem.* 1991, **30**, 524-527. (c) Y-S. Xie, X-H. Pan, B-X. Zhao, J-T. Liu, D.S. Shin, J-H. Zhang, L-W. Zheng, J. Zhao, J-Y. Miao; *J. Organomet. Chem.* 2008, **693**, 1367-1374.
19. S. O. Ojwach, I. A. Guzei, J. Darkwa; *J. Organomet. Chem.* 2009, **694**, 1393-1399.
20. F. H. Allen; *Acta Crystallogr*., 2002, **B58**, 380-388.
21. C. M. Killian, D. J. Tempel, L. K. Johnson, M. Brookhart; *J. Am. Chem. Soc.* 1996, **118**, 11664-11665.
22. J-C. Yuan, L. C. Silva, P. T. Gomes, P. Valerga, J. M. Campos, M. R. Ribeiro, J. C.W. Chien, M. M. Marques; *Polymer* 2005, **46**, 2122-2132.
23. (a) M. M. Wegner, A. K Ott, B. Rieger; *Macromolecules* 2010, **43**, 4091-4097. (b) R. Chen, S. F. Mapolie; *J. Mol. Catal. A: Chem.* 2003, **193**, 33-40.
24. T. Usami, S. Takayama, *Macromolecules* 1984, **17**, 1756-1761.

25. S. J. Mclain, E. F. McCord, L. K. Johnson, S. D Ittel, L. J. T. Nelson, S. D. Arthur, M. J. Halfhill, M. F. Teasley, D. J. Tempel, C. Killian, M. Brookhart; *Polym. Prepr*. 1997, **38**, 772.

26. (a) D. H. Camacho, Z. Guan; *Macromolecules* 2005, **38**, 2544-2546; (b) J. M. Rose, A. E. Cherian, J. H. Lee, L. A. Archer, G. W. Coates L. J. Fetters; *Macromolecules* 2007, **40**, 6807-6813. (c) U. Subramanyama, P. R. Rajamohananb, S. Sivaram; *Polymer* 2004, **45**, 4063-4076. (d) F. Peruch, H. Cramail, A. Deffieux; *Macromolecules* 1999, **32**, 7977-7983. (e) J. D. Azoulay, G. C. Bazan, G. B. Galland; *Macromolecules* 2010, **43**, 2794-2800.

27. Z. Szafran, R. M. Pike, M. M. Singh. *Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience*. John Wiley & Sons, Inc.: New York. **1991**, 302

28. G. K. Anderson, M. Lin; *Inorg. Synth.* 1990, **28**, 60.

29. Bruker-AXS. **2009** APEX2, SADABS, and SAINT Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.

30. G. M. Sheldrick; SHELXL. *Acta Cryst.* 2008, **A64**, 112-122.

(Ferrocenylpyrazolyl)palladium complexes that catalyse the polymerization of 1-heptene and 1-octene to highly branched polyolefins are reported.