

Catalyst precursors for ethylene polymerization based on novel mono- and bi-nuclear pyridylimine-type palladium(II) complexes with long straight chain alkyl substituents at the imino nitrogen

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Abstract

The synthesis and characterization of novel mono- and bi-nuclear pyridylimine-type palladium(II) complexes with long chain alkyl groups attached to the imino nitrogen are described. These complexes were evaluated as catalyst precursors for ethylene polymerization under relatively mild reaction conditions. Unlike *N*-aryl substituted pyridylimine-type analogues, these complexes when activated with methylaluminoxane (MAO) were capable of producing highly linear polyethylene with high molecular weights, the values of which can be tuned from 6×10^5 to 1×10^6 by varying polymerization temperature and the ratio of Al to Pd.

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1. Introduction

Late transition metal-catalyzed olefin polymerization has received greater prominence over the recent years as a result of Brookhart's report on Pd(II) and Ni(II) diimine catalyst systems, which were capable of polymerizing ethylene and other α -olefins to form high molecular weight polymers [1–3]. The key feature of their catalysts is the symmetrical presence of bulky *ortho* aryl substituents at the imino nitrogen atoms, which effectively block the axial coordination sites thus retarding the rate of chain termination. Reduced steric bulk results in a decrease in polymer molecular weight. For this class of catalysts, Pd(II)-based systems produce highly branched polymers from ethylene with up to 125 branches per 1000

carbon atoms. Analogous Ni(II) catalysts are also quite sensitive to polymerization conditions, e.g. ethylene pressure, ligand structure and temperature, and can thus be tuned to produce polyethylene ranging from high to low density.

Subsequent to Brookhart's initial work on Ni and Pd, he as well as Gibson discovered that iron and cobalt-based complexes bearing tridentate pyridine bis-imine ligands with bulky aryl groups were also capable of converting olefins to high molecular weight polymers (M_w of polyethylene up to 1.83×10^5 at 1 atm and 6.11×10^5 at 10 atm) as well as co-polymers [4–8]. In the past year, other groups [9–11] have also reported on studies dealing with asymmetrical bidentate aryl-substituted pyridylimine-type catalysts. In these latter cases, it was found that only oligomerization of ethylene was possible with Ni(II) catalysts while Pd(II) analogues were found to be inactive.

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Evidently, there exists a very complex link between ligand architecture and catalyst activity as well as polymer properties. To understand this better, we have designed a novel bi-nuclear pyridylimine-type Pd(II) complex in which two diimine centers are linked via a C12 hydrocarbon bridge. Each of the termini of the hydrocarbon bridge is bound to the imino nitrogen of the two pyridylimine units. In addition, we have also synthesized a mono-nuclear derivative, in which a single pyridylimine unit interacts with one palladium center. These complexes have been evaluated in ethylene polymerization. Our findings are reported here.

2. Experimental

2.1. General procedures

All manipulations involving air- and/or water-sensitive compounds were performed in a nitrogen-filled glove-box or under an atmosphere of purified dry nitrogen using standard Schlenk techniques. ^1H (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded on a Varian Gemini 2000 spectrometer with CDCl_3 as solvent at room temperature (for ligands and mono-nuclear Pd(II) complex) or 1,2,4-trichlorobenzene as solvent at 100°C (for polymeric products, benzene- d_6 as chemical shift δ reference). Elemental analyses were carried out by the micro-analytical services of the Chemistry Department at University of the Western Cape. IR spectra in the range of $4000\text{--}500\text{ cm}^{-1}$ were recorded as liquid films or DRIFTS on a Perkin-Elmer Paragon 1000 P spectrophotometer. Melting points of polyethylene were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 calorimeter operating at the rate of $10^\circ\text{C}/\text{min}$. For polymer molecular weights, gel permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene at 135°C using a Waters GPC 2000 equipped with Waters HT 3, 4, 5, and 6 columns and the curves were calibrated against polystyrene standards.

2.2. Materials

Toluene, diethyl ether, and hexane were distilled from sodium/benzophenone under nitrogen. Dichloromethane was distilled from diphosphorus pentoxide

under nitrogen. Dodecyl amine, 1,12-dodecanyl diamine, pyridine-2-carboxaldehyde, anhydrous magnesium sulfate and methylaluminoxane (MAO, 10% solution in toluene) were purchased from Aldrich and were used as received. $(\text{COD})\text{PdCl}_2$ was prepared according to a published procedure [12].

2.3. Synthesis of *N*-(dodecyl)pyridyl-2-methanimine (**1a**)

This compound was prepared using a procedure described by Haddleton and co-workers [13]. Dodecylamine (1.8 mmol) was added dropwise to a stirred solution of pyridine-2-carboxaldehyde (1.8 mmol) in diethyl ether (20 ml) cooled in an ice bath. The reaction was allowed to proceed at room temperature. Anhydrous magnesium sulfate (3 g) was added and the slurry stirred for 24 h. The solution was filtered, the ether removed from the filtrate, and the crude residue extracted with hexane. The compound was obtained as a yellow oil after removal of hexane and drying in vacuum. Yield: 70%. Analytically calculated for $\text{C}_{18}\text{H}_{30}\text{N}_2$: C 78.77%, H 11.02%, N 10.21%. Found: C 78.62%, H 11.14%, N 10.28%. ^1H NMR (CDCl_3): δ 8.61 (1H, d, py-6); 8.36 (1H, d, imino-H); 7.98 (1H, d, py-3); 7.70 (1H, t, py-4); 7.32 (1H, m, py-5), 3.66 (t, 2H, =N-CH₂); 1.70 (t, 2H, =NCH₂CH₂); 1.24 (brs, 18H, -(CH₂)₉-); 0.86 (t, 3H, CH₃). ^{13}C NMR (CDCl_3): δ 161.63, 154.77, 149.38, 136.45, 124.52, 124.15, 121.14, 61.56, 31.89, 30.71, 29.65, 29.61, 29.57, 29.42, 29.32, 27.33, 22.66, 14.07.

2.4. Synthesis of *N,N'*-(1,12-dodecanediyl)-bis(pyridyl-2-methanimine) (**2a**)

This was prepared using a similar procedure as for **1a** with the exception that absolute ethanol replaced ether as solvent. The compound is a pale yellow solid. Yield: 56%. Analytically calculated for $\text{C}_{24}\text{H}_{34}\text{N}_4$: C 76.15%, H 9.05%, N 14.80%. Found: C 76.28%, H 9.28%, N 14.65%; m.p. $64\text{--}66^\circ\text{C}$. ^1H NMR (CDCl_3): δ 8.63 (2H, d, py-6); 8.37 (2H, d, imino-H); 8.00 (2H, d, py-3); 7.74 (2H, t, py-4); 7.31 (2H, m, py-5), 3.66 (t, 4H, =N-CH₂); 1.83–1.68 (br m, 4H, =NCH₂CH₂); 1.26 (brs, 16H, -(CH₂)₈-). ^{13}C NMR (CDCl_3): δ 161.57, 154.58, 149.33, 136.45, 124.52, 121.10, 61.56, 30.61, 29.51, 29.36, 27.26.

2.5. Synthesis of (*N*-dodecyl-pyridyl-2-methanimine) palladium(II) dichloride (**1b**)

A solution of **1a** (0.35 mmol) in CH₂Cl₂ (2 ml) was added dropwise to a stirred solution of (COD)PdCl₂ (0.35 mmol) dissolved in CH₂Cl₂ (20 ml) at room temperature. The reaction mixture was stirred for 72 h during which time a precipitate was observed. The pale yellow powder was isolated by filtration and washed with fresh CH₂Cl₂. Additional product can be obtained by reducing the volume of the filtrate. The pale yellow product can be re-crystallized from CH₂Cl₂ at -20 °C giving microcrystals. Yield: 42%. Analytically Calculated for C₁₈H₃₀N₂Cl₂Pd: C 47.85%, H 6.69%, N 6.20%. Found: C 47.43%, H 6.56%, N 6.01%; m.p. 144–145 °C. ¹H NMR (CD₂Cl₂): δ 9.26 (1H, d, py-6); 8.13 (2H, overlapping d, pyr-4 + imino-H); 7.80 (1H, d, py-3); 7.64 (1H, t, py-5); 3.90 (t, 2H, =N-CH₂); 1.90 (t, 2H, =NCH₂CH₂); 1.29 (brs, 18H, -(CH₂)₉-); 0.88 (br t, 3H, CH₃). ¹³C NMR (CD₂Cl₂): 167.29, 151.75, 140.68, 128.47, 126.98, 61.25, 32.32, 31.11, 30.03, 29.97, 29.91, 29.60, 27.00, 23.08, 14.25.

2.6. Synthesis of *N,N'*-(μ-1,12-dodecanediyl)bis-(pyridyl-2-methanimine)palladium(II) dichloride (**2b**)

The **1b** (0.175 mmol) dissolved in CH₂Cl₂ (2 ml) was added dropwise into a stirred solution of (COD)PdCl₂ (0.35 mmol) in CH₂Cl₂ (20 ml) at room temperature. A precipitate formed immediately and the reaction mixture was stirred overnight. A pale yellow powder was isolated by filtration, washed with fresh CH₂Cl₂, and dried under vacuum. Yield: 91%. Analytically Calculated for C₂₄H₃₄N₄Pd₂Cl₄: C 39.31%, H 4.67%, N 7.64%. Found: C 39.36%, H 4.44%, N 7.42%; m.p. 268–273 °C (dec.).

2.7. General procedure for ethylene polymerization

A mechanically stirred stainless steel 300 ml Parr autoclave was heated under vacuum for at least 1 h at 70 °C and cooled to room temperature prior to being charged with 150 ml toluene, MAO, and catalyst precursor in a nitrogen-purged glove-box. After sealing the autoclave, it was removed from the glove-box and flushed with ethylene. The reaction mixture was

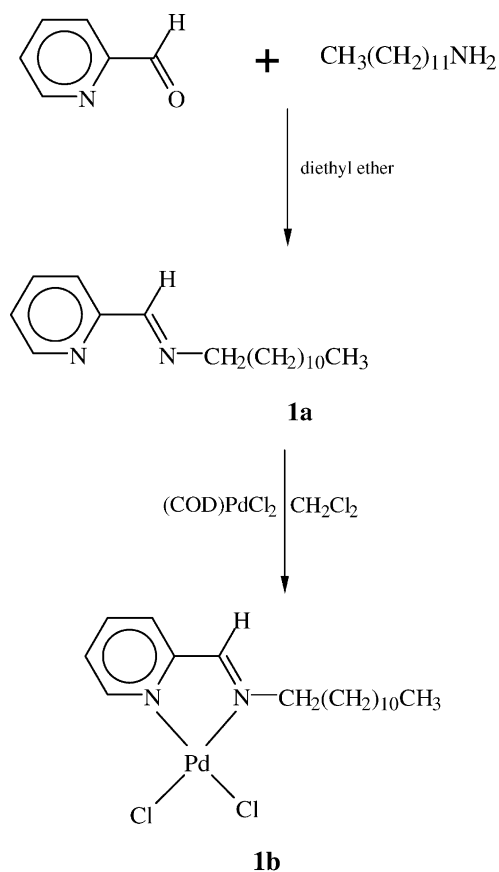
heated to the desired reaction temperature; ethylene was introduced to a pressure of 5 atm. The reactor pressure was maintained at 5 atm throughout the polymerization. At the end of the polymerization, the unreacted ethylene was vented and the reaction quenched with ethanol. The polymer was collected, treated with a 1 M solution of HCl for 48 h to remove any palladium residues. After filtration, the polymer was washed with water followed by fresh ethanol, and then dried at 80 °C under vacuum to constant weight.

3. Results and discussion

3.1. Synthesis of ligands and complexes

The *N*-alkyl substituted mono- and bi-functional pyridylimines **1a** and **2a** were prepared by the condensation of pyridine-2-carboxaldehyde with the appropriate amine or diamine with removal of water using anhydrous magnesium sulfate (Schemes 1 and 2). Since, 1,12-diaminododecane is sparingly soluble in diethyl ether, absolute ethanol was used as solvent to maintain a homogeneous medium. Subsequent to the preparation of the ligands the Pd(II) dichloride complexes **1b** and **2b** were obtained from the reaction of the pyridylimine ligands with (1,5-cyclooctadiene)palladium(II) dichloride in dichloromethane at room temperature (also illustrated in Schemes 1 and 2). Some of the bi-nuclear Pd(II) complex **2b** precipitated from solution during the initial 10 min, although an extended reaction time was needed to optimize the yield. Complete characterization of **2b** was not possible due to its lack of solubility in common organic solvents. Elemental analysis however showed the result for **2b** to be in agreement with the calculated values based on our expected chemical formulation.

IR spectra for the palladium complexes are as shown in Fig. 1 together with those of the corresponding ligands. In both the ligands **1a** and **2a**, three strong bands are apparent at ca. 1650, 1588, and 1568 cm⁻¹, assigned to C=N vibration and pyridine-ring vibrations, respectively. While for both the Pd(II) complexes **1b** and **2b**, only a single absorption occurs at ca. 1600 cm⁻¹. Disappearance of C=N absorptions in the IR spectra of complexes were reported by Lavery and Nelson [14], who ascribed this to be an infrared inactive C=N vibration in the Pd(II) complexes. On



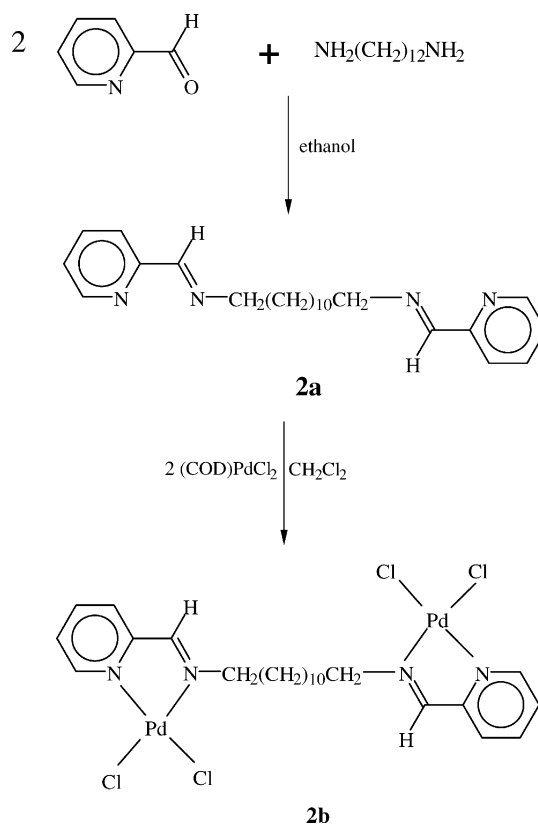
Scheme 1. Synthesis of pyridylimine-type ligand **1a** and its corresponding palladium(II) dichloride complex **1b**.

the other hand, another plausible explanation could be a reduction in electron density in C=N bond as a result of bonding of the diimine ligand to the metal center. This would lead to a lower ν (C=N) value.

¹H and ¹³C NMR data for the ligands and the mono-nuclear Pd(II) complex **1b** are listed in Tables 1 and 2. Comparison of ligand **1a** with the correspond-

Table 1
¹H NMR spectral data for the ligands and complexes in CDCl₃

Compound	δ (ppm)						
	H2	H3	H4	H5	H6	H7	
1a	7.96	7.72	7.28	8.63	8.36	3.65	
2a	7.96	7.74	7.31	8.62	8.37	3.66	
1b	7.80	8.13	7.64	9.28	8.13	3.90	
2b	–	–	–	–	–	–	



Scheme 2. Synthesis of pyridylimine-type ligand **2a** and its corresponding palladium(II) dichloride complex **2b**.

ing complex **1b** shows large downfield shifts of the protons attached to the carbons of the pyridylimine group (C3, C4 and C5, as shown in Fig. 2). The protons of the CH₂ group attached to the imino functionality (C7) show a similar downfield shift.

This reveals the existence of strong coordination of the pyridine nitrogen and the imine nitrogen to the palladium center. The slight shifts observed for

Table 2
¹³C NMR spectral data for the ligands and complexes in CDCl₃

Compound	δ (ppm)						
	C1	C2	C3	C4	C5	C6	C7
1a	154.8	121.1	136.4	124.5	149.4	161.6	61.6
2a	154.6	121.1	136.5	124.5	149.3	161.7	61.5
1b	155.1	126.2	139.9	127.7	151.0	166.6	60.5
2b	–	–	–	–	–	–	–

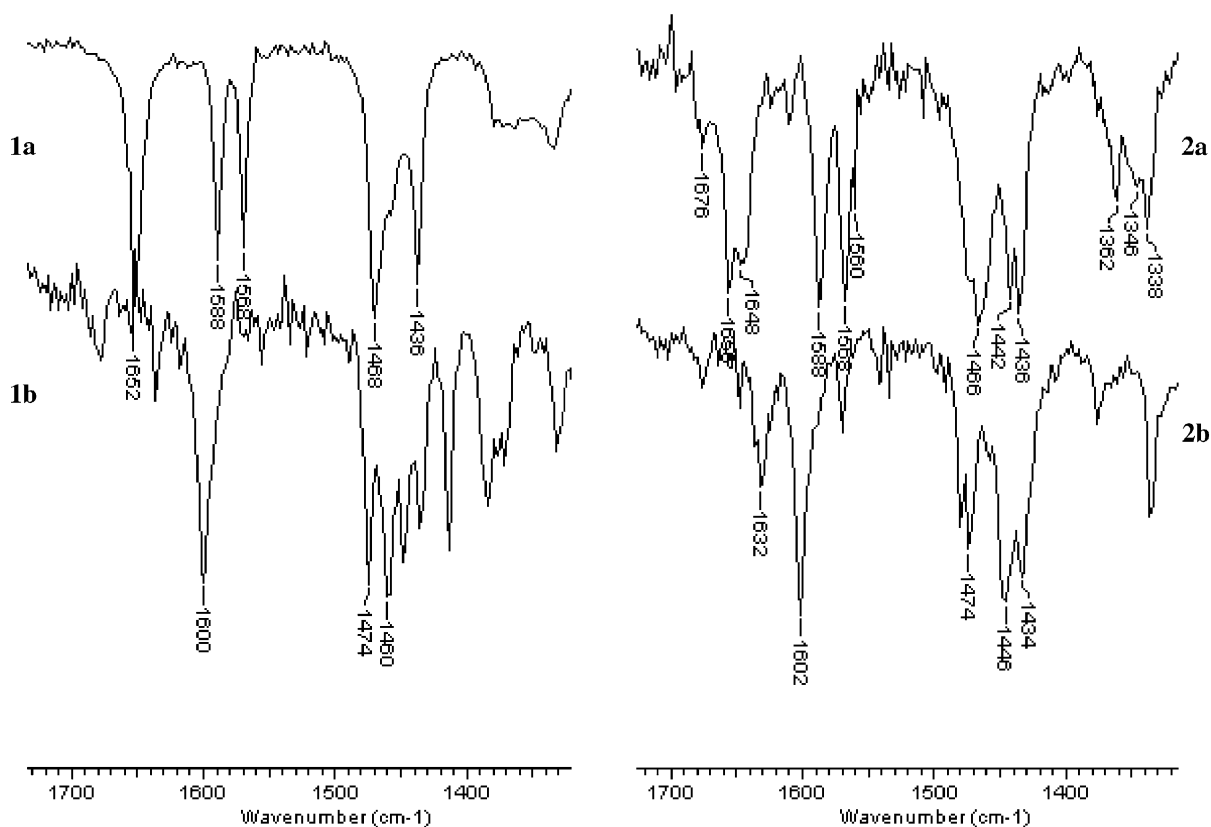


Fig. 1. IR spectra of ligands and the corresponding palladium complexes.

H2 could be explained in terms of two opposite effects, viz. a low-field shift caused by the inductive effect and a high-field shift caused by the disappearance of the paramagnetic effect of the imine nitrogen atom upon coordination. This was previously found for pyridylimine complexes of tin [15]. Similar observed downfield shifts in the ^{13}C NMR spectrum of the complex **1b** indicate that the imino-group carbon

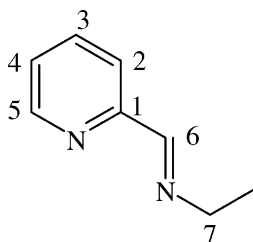


Fig. 2. Numbering scheme for pyridylimine group.

and the pyridine carbons are deshielded by coordination to palladium.

3.2. Polymerization of ethylene

The precursors **1b** and **2b** were activated in situ in toluene by the addition of MAO and the polymerizations were performed at 5 atm of ethylene pressure, affording solid polyethylene. Data for the ethylene polymerization are summarized in Table 3. The polymers, obtained using these pyridylimine Pd(II) complexes with aliphatic chains attached to the imino nitrogen are highly linear polyethylene as determined by DSC ($T_m = 135\text{--}137^\circ\text{C}$). This is in contrast to the branched ethylene oligomers produced in aryl-substituted pyridylimine nickel and palladium catalyst systems. The appearance of only one signal in the high temperature ^1H and ^{13}C NMR spectra of the polymerization products reinforced their

Table 3

Mono- and bi-nuclear palladium(II) complexes **1b** and **2b** as catalyst precursors for ethylene polymerization^a

Entry no.	Precursor	[MAO]/[Pd]	Temperature (°C)	Yield (g)	Productivity (g PE mol ⁻¹ Pd atm ⁻¹ h ⁻¹)	T _m (°C) ^b	M _n × 10 ^{-5c}	M _w × 10 ^{-5c}	M _w /M _n
1	1b	60	25	0.0639	270	135.88	3.35	7.09	2.12
2	1b	100	25	0.1817	760	138.02	3.84	8.08	2.11
3	1b	260	25	0.7314	3060	137.80	4.07	8.53	2.10
4	1b	1040	25	1.1236	4070	137.75	4.52	9.19	2.03
5	2b	50	25	0	0	–	–	–	–
6	2b	100	25	0.714	3010	135.50	2.94	6.43	2.19
7	2b	260	25	0.137	580	137.83	4.58	11.2	2.45
8	2b	1050	25	0.148	620	138.52	5.12	11.7	2.28
9	2b	100	15	0.914	3850	137.25	5.31	10.3	1.93
10	2b	100	5	0.0045	20	137.76	–	–	–
11	2b	100	35	0.174	730	137.64	3.63	7.56	2.08

^a Polymerizations conditions: [Pd] = 0.016 mmol, MAO as co-catalyst, 150 ml toluene, and 5 atm of ethylene, 3 h.^b Determined by differential scanning calorimetry (DSC).^c Molecular weight data was determined by GPC vs. polystyrene standards.

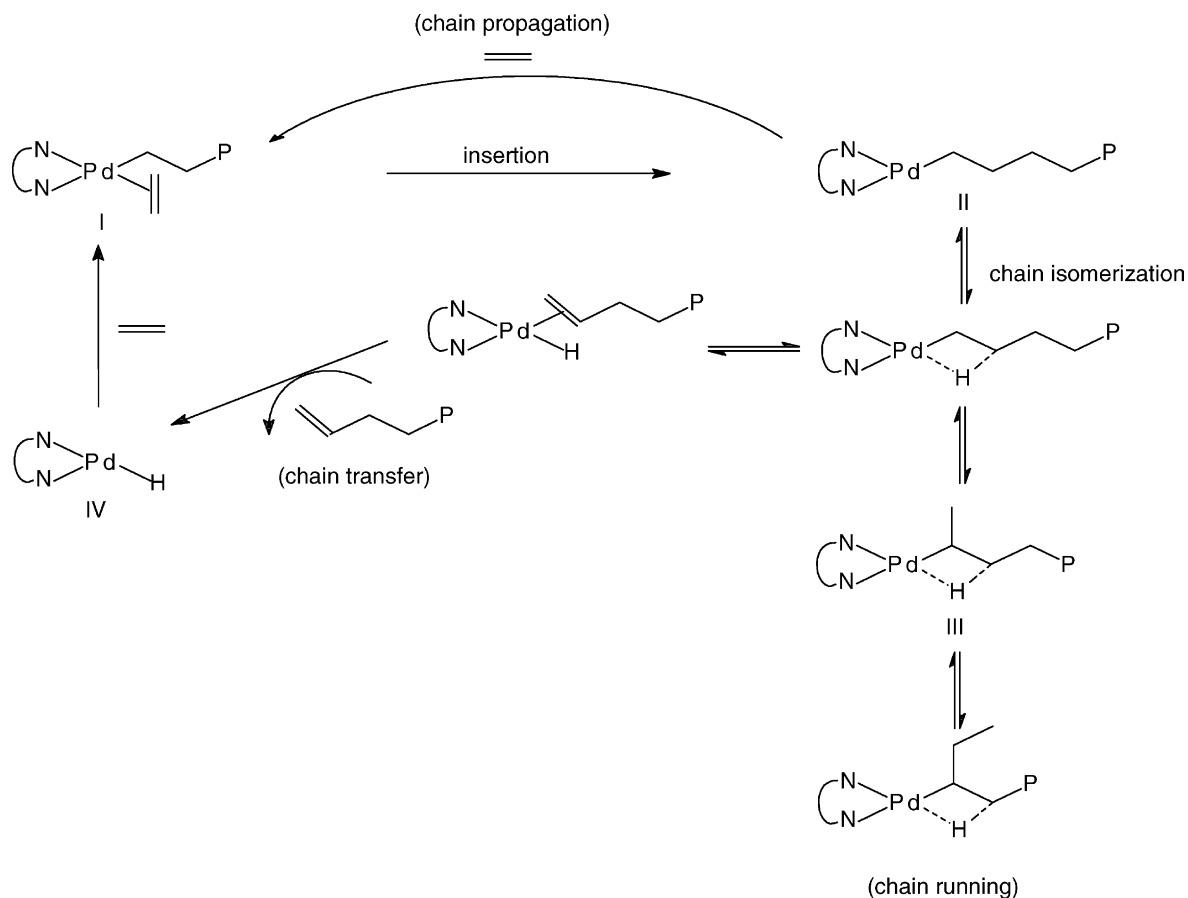
linear nature. Moreover, significantly high molecular weight with M_w values ranging from 6.43×10^5 (entry 6) to 1.17×10^6 (entry 8), were obtained as confirmed via high temperature GPC. This is comparable to polyethylene produced via some Group 4 metallocenes. The unimodal molecular weight distribution curves in the GPC plots indicate only one kind of active species in the polymerization reactions. Polydispersity indices for all these cases are around 2, similar to those reported for other late transition metal catalysts.

It is worth noting that by changing the substituents on the imino nitrogen from aryl groups to long chain alkyl groups leads to a dramatic increase in the molecular weight and yielding only linear polyethylene. These results can be rationalized with the proposed reaction pathway as shown in Scheme 3 together with recent reported assumptions [2,3,16]. The alkyl–ethylene complex **I** is the catalyst resting state; ethylene insertion results in the formation of **II** that can be rapidly trapped by ethylene to reform **I**. Repeating this step leads to chain propagation. **II** can be β -hydride (β -H) isomerized, i.e. undergo reinsertion with opposite regiochemistry to produce a branched alkyl group **III**. Continuous β -H isomerization and reinsertion (chain-running) leads to chain branching. While, β -H elimination releases olefin to yield **IV**, leading to chain transfer.

Based on this reaction pathway, the unique coplanar structure of the catalysts precursors **1b** and

2b is likely to be a decisive factor affecting polymer molecular weight and microstructure. The long straight alkyl chain remaining in the same plane as the active center increases steric hindrance as compared to an angled aryl group. This causes an increase in the energy, which is needed to rotate the growing polymer chain about the C_α – C_β bond. The transfer of the β -H to the vacant site on the metal would thus be hindered leading to retardation of chain running and chain transfer processes. Therefore, the rate of chain propagation is far faster than chain running and chain transfer rates, permitting the formation of highly linear polyethylene with high molecular weight. Thus, in these olefin polymerization reactions, not only the nature of the metal center but also the ligand environments have a large influence on catalyst activity as well as polymer microstructure. In general **2b** was found to produce higher molecular weight polyethylene compared to **1b**. This is probably due to the fact that in **2b** the alkyl chain linking the two diimine functionalities is less flexible than the alkyl chain of **1b**. This as alluded to earlier would hinder chain transfer process.

The dependence of catalyst productivity on the ratio of Al: Pd was found to be different for the pre-catalysts **1b** and **2b**. For example, polymerization productivity of **1b** increased with an increase of the ratio Al: Pd ranging from 50 to 1100 (entries 1–4). While for **2b**, the productivity initially showed a rapid increase to reach a maximum at an Al: Pd ratio of 100:1 (entry



Scheme 3. Proposed mechanism of ethylene polymerization.

6). Thereafter, the decrease in productivity with increasing Al:Pd ratio was more pronounced than was the case for **1b**. The bi-nuclear complex was found to have lower polymerization productivity than the mono-nuclear complex at high Al:Pd ratios. The reason is not entirely clear although it would appear to be a result of the lower solubility of the bi-nuclear catalyst precursor species in toluene.

The effect of the Al:Pd ratio on the molecular weight of polyethylene produced appears to be similar for both the mono-nuclear precursor **1b** as well as the di-nuclear analogue **2b**. The molecular weights of the polymers increased with an increase of Al:Pd ratio. This indicates that under our reaction conditions, MAO did not play a significant role in chain transfer of the growing polyethylene. In comparison

with the mono-nuclear palladium catalyst system, the di-nuclear system seems to convert ethylene to higher molecular weight polymers at the same level of Al:Pd ratio, (Al/Pd \geq 260). This is probably due to greater resistance of the di-nuclear catalyst to β -H chain transfer as a result of steric factors. This is less important in the case of the mono-nuclear species with a slightly more flexible alkyl chain.

No significant variation of the molecular weight distribution of the polymers was observed with increasing the ratio of Al:Pd. In almost all the cases, PDI values around 2 were obtained.

We also investigated the effect of reaction temperature on the ethylene polymerization using the bi-nuclear catalyst precursor **2b**, entry 6 and entries 9–11. Good productivities were achieved within the

temperature range of 15–25 °C. A rapid drop of catalytic activity at slightly higher temperatures (>35 °C) was observed. This could be due to the decomposition of the temperature-sensitive active species as well as due to a decrease in ethylene concentration in toluene at high temperature.

4. Conclusions

We have synthesized novel mono- and bi-nuclear pyridylimine palladium(II) complexes with long alkyl groups at the imino nitrogen and applied these as catalyst precursors in ethylene polymerization. The polymers produced here are highly linear polyethylene with high molecular weights, different from those prepared with recently reported *N*-aryl pyridylimine-type complexes. This has demonstrated that selection of suitable ligand structure allows us to tune polymer properties. The co-planar features of our complexes are deemed to favor chain propagation and retard chain transfer and chain running reactions.

Polymerization productivities were found to be sensitive to temperature as well as the amount of the co-catalyst. Different trends are observed for mono- and bi-nuclear pre-catalysts, especially with regards to variation in the ratio of Al: Pd. The bi-nuclear Pd(II) complex display lower catalyst activity than the mono-nuclear analogue. A plausible suggestion is that this is a result of the difference in solubility of these catalyst species in toluene. This is the subject of an ongoing study. In addition, we are also studying the effect of spacer length in the di-nuclear system on catalyst activity.

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