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{*N*-alkyl-*N*-[pyridin-2-ylmethylene] amine}dichloro palladium(II) complexes: synthesis, crystal structures and evaluation of their catalytic activities for ethylene polymerization

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Abstract

Three pyridinylimine palladium(II) complexes of the type $[(C_5H_4N)HC{=}N{-}(CH_2)n{-}CH_3]\ PdCl_2$ ($n = 4, 7, 11$) were synthesized by reacting $(COD)PdCl_2$ with the appropriate pyridyl-imine ligand. The crystal structure of the complex, where $n = 7$ was determined using single crystal X-ray crystallography and this displays a striking co-planar geometry, with the pyridine ring, the metal coordination sphere N(1)–C(5)–C(6)–N(2)–Pd and the alkyl backbone all being in the same plane. The three complexes prepared were evaluated as catalyst precursors for ethylene polymerization. Activation with methylaluminoxane (MAO) leads to the formation of an active catalyst species, which produces only high-density polyethylene. The effect of the chain length of the alkyl substituent at the imino nitrogen on the catalytic activity was evaluated. It was found that the molecular weight of the polymer increases as the chain length increases, although a higher level of MAO was required to reach optimum activity.

Keywords: Palladium; Pyridylimine; Pyridyl-2-methanimine; Ethylene polymerization; HDPE; Polyethylene

1. Introduction

In recent years, there has been increasing interest in developing late transition metal catalysts for olefin polymerization. Initially, Brookhart discovered that Pd(II) and Ni(II) diimine catalyst systems, of the type $\{[ArN{=}C(R){-}(R)C{=}NAr]M(CH_3)(OEt_2)\}^+BAr'_4{}^-$ ($Ar = 2,6\text{-}(Me)_2C_6H_3$, $2,6\text{-}(i\text{-}Pr)_2C_6H_3$), were capable of polymerizing ethylene and α-olefins to high-molecular weight polymers with controlled level of polymer branching [1]. The key feature of their catalysts is the presence of bulky *ortho* aryl substituents at the imino nitrogen, which serve to block the axial coordination sites thus retarding the rate of chain termination. Subsequently, Gibson [2] and Brookhart [3] both reported that tridentate iron and cobalt-based complexes bearing pyridine bis-imine ligands with bulky aryl groups were also capable of converting ethylene to high-molecular weight polymers (M_w of up to 1.83×10^5 at 1 atm and 6.11×10^5 at 10 atm). Other groups [4] have recently further studied asymmetrical bidentate aryl-substituted pyridylimine-type catalysts and found that only oligomerization of ethylene was possible with Ni(II) catalysts while Pd(II) analogues were found to be inactive. Currently Pd/Ni complexes with hetero-donor chelate ligands, such as P–N, P–P and P–O for ethylene homo/co-polymerization have also received attention [5]. These investigations indicate that both electronic and steric environments of ligands are crucial in stabilizing the metal ions and in controlling the activity of polymerization.

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Recently, we synthesized a novel pyridylimine-type Pd(II) complex with long straight alkyl group attached to imino nitrogen and reported the results of our preliminary evaluation of this as a catalyst precursor for ethylene polymerization [6]. In this paper we now report the results of our investigation into the catalyst activity of other pyridyl-imine compounds, which contain different alkyl substituents at the imino nitrogen.

2. Experimental

2.1. General information

All manipulations involving air- and/or moisture-sensitive compounds were performed in a nitrogen-filled glove box or under an atmosphere of purified dry nitrogen using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer with chloroform-*d* as solvent at room temperature (for ligands **L$_1$**–**L$_3$** and Pd(II) complexes **1**–**3**) or 1,2,4-trichlorobenzene as solvent at 100 °C (polymeric products, benzene-d_6 as chemical shift reference). Elemental analyses were carried out by the microanalytical services of the Chemistry Department at University of the Western Cape. IR spectra in the range 500–4000 cm^{-1} were recorded as liquid films or DRIFTS on a Perkin–Elmer Paragon 1000PC FTIR spectrophotometer. Melting points of polyethylene were determined by differential scanning calorimetry using a Perkin–Elmer DSC-7 calorimeter, operating at the rate of 10 °C min^{-1}. For polymer molecular weights, gel permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene stabilized with 0.0125% BHT at 160 °C using a Polymer Labs, PL-GPC 220 instrument equipped with three columns packed with a polystyrene/divinylbenzene copolymer.

2.2. Materials

Toluene, diethyl ether, and hexane were distilled from sodium under nitrogen. Dichloromethane was distilled from phosphorus pentoxide under nitrogen. Pentylamine (95%), octylamine (98%), dodecylamine (98%), pyridine-2-carboxaldehyde (99%), anhydrous magnesium sulfate and methylaluminoxane (10 wt.% solution in toluene) were obtained from Aldrich Chemicals and used without further purification. (η^4-1,5-cyclooctadiene)PdCl$_2$ was prepared according to a published procedure [7].

2.3. Synthesis of ligands L$_1$, L$_2$ and L$_3$

The ligands were prepared using a similar procedure described by Haddleton et al. [8]. The alkylamine (1.8 mmol) was added dropwise to a stirred solution of pyridine-2-carboxaldehyde (1.8 mmol) in dry diethyl ether (20 ml) cooled in an ice bath. After the addition was complete, the reaction was allowed to warm to room temperature. Anhydrous magnesium sulfate (3 g) was added and the slurry stirred for 24 h at this temperature. The solution was filtered and the ether was removed from the filtrate by evaporation. The crude product was purified by extraction with hexane. The product was obtained as a clear oil after removal of hexane and drying in vacuo.

2.3.1. L$_1$ (Pentyl-pyridin-2-ylmethylene-amine)

Light-yellow oil. Yield: 75%. ^{1}H NMR (CDCl$_3$): δ 8.62(d, 1H, py-6), 8.35(d, 1H, imino-H), 7.94(d, 1H, py-3), 7.72(t, 1H, py-4), 7.30(m, 1H, py-5), 3.64(t, 2H, =N–CH_2), 1.70(t, 2H, =NCH$_2$CH_2), 1.25(brs, 4H, –(CH_2)$_2$–), 0.86(t, 3H, CH_3); ^{13}C NMR (CDCl$_3$): δ 163.06, 154.44, 149.29, 136.28 124.31, 120.99, 61.99, 31.79, 29.13, 22.47, 14.79; *Anal*. Calc. for C$_{11}$H$_{16}$N$_2$: C, 74.96; H, 9.15; N, 15.89%. Found: C, 74.92; H, 9.11; N, 15.95%.

2.3.2. L$_2$ (Octyl-pyridin-2-ylmethylene-amine)

Light-yellow oil. Yield: 73%. ^{1}H NMR (CDCl$_3$): δ 8.62(d, 1H, py-6), 8.36(d, 1H, imino-H), 7.96(d, 1H, py-3), 7.72(t, 1H, py-4), 7.30(m, 1H, py-5), 3.65(t, 2H, =N–CH_2), 1.70(t, 2H, =NCH$_2$CH_2), 1.25(brs, 10H, –(CH_2)$_5$–); 0.86(t, 3H, CH_3). ^{13}C NMR(CDCl$_3$): δ 161.49, 154.62, 149.22, 136.30 124.36, 121.01, 61.41, 31.68, 30.56, 29.22, 29.07, 27.19, 22.49 13.89; *Anal*. Calc. for C$_{14}$H$_{22}$N$_2$: C, 77.01; H, 10.86; N, 12.83%. Found: C, 77.05; H, 10.68; N 12.31%.

2.3.3. L$_3$ (Dodecyl-pyridin-2-ylmethylene-amine)

Light-yellow oil. Yield: 70%. ^{1}H NMR (CDCl$_3$): δ 8.61(d, 1H, py-6), 8.36(d, 1H, imino-H), 7.96(d, 1H, py-3), 7.72(t, 1H, py-4), 7.32(m, 1H, py-5), 3.66(t, 2H, =N–CH_2), 1.70(t, 2H, =NCH$_2$CH_2), 1.24(brs, 18H, –(CH_2)$_9$–), 0.86(t, 3H, CH_3); ^{13}C NMR (CDCl$_3$): δ 161.63, 154.77, 149.38, 136.45, 124.15, 121.14, 61.56, 31.89, 30.71, 29.65, 29.61, 29.59, 29.42, 29.32, 27.33, 22.66, 14.07; *Anal*. Calc. for C$_{18}$H$_{30}$N$_2$: C, 78.77; H, 11.02; N, 10.21%. Found: C, 78.62; H, 11.14; N, 10.28%.

2.4. General procedure for the preparation of complexes 1, 2 and 3

A solution of ligand **L$_1$**, **L$_2$** or **L$_3$** (0.35 mmol) in 2 ml CH$_2$Cl$_2$ was added dropwise to a stirred solution of (COD)PdCl$_2$ (0.35 mmol) in 20 ml CH$_2$Cl$_2$ at room temperature. The reaction mixture was stirred for 72 h during which time a precipitate was observed. The micro-crystalline solid was recovered by filtration and washed with dry CH$_2$Cl$_2$. Reduction of the volume of the filtrate by evaporation allows for the isolation of additional product. Recrystallization from CH_2Cl_2 yielded a yellow crystalline solid.

2.4.1. Complex *1*

Yield: 66%. m.p. 264–266 °C. ^1H NMR ($CDCl_3$): δ 9.28(d, 1H, py-6), 8.13(overlapping, d, 2H, py-4 and imino-H), 7.79(d, 1H, py-3), 7.66(t, 1H, py-5), 3.91(t, 2H, $=N-CH_2$), 1.90(t, 2H, $=NCH_2CH_2$), 1.35(brs, 4H, $-(CH_2)_2-$), 0.91(t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 168.51, 155.43, 151.35, 140.08 127.82, 126.09, 61.64, 31.86, 29.02, 22.04, 13.95; *Anal*. Calc. for $C_{11}H_{16}N_2Cl_2Pd$: C, 37.37; H, 4.56; N, 7.92%. Found: C, 37.21; H, 4.08; N, 7.42%.

2.4.2. Complex *2*

Yield: 72.%. m.p. 139–140 °C. ^1H NMR ($CDCl_3$): δ 9.27(d, 1H, py-6), 8.13(overlapping, d, 2H, py-4 and imino-H), 7.81(d, 1H, py-3), 7.66(t, 1H, py-5), 3.90(t, 2H, $=N-CH_2$), 1.90(t, 2H, $=NCH_2CH_2$), 1.31(brs, 10H, $-(CH_2)_5-$), 0.87(t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 166.97, 155.61, 151.37, 140.17, 127.84, 126.83, 61.06, 31.75, 30.71, 29.12, 26.63, 22.59, 14.05; *Anal*. Calc. for $C_{14}H_{22}N_2Cl_2Pd$: C, 42.5; H, 5.60; N, 7.08%. Found: C, 41.95; H, 5.37; N, 6.57%.

2.4.3. Complex *3*

Yield: 42%. ^1H NMR ($CDCl_3$): δ 9.28(d, 1H, py-6), 8.13(overlapping, d, 2H, py-4 and imino-H), 7.80(d, 1H, py-3), 7.64(t, 1H, py-5), 3.90(t, 2H, $=N-CH_2$), 1.90(t, 2H, $=NCH_2CH_2$), 1.31(brs, 18H, $-(CH_2)_9-$), 0.88(t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 167.29, 155.17, 151.75, 140.36, 128.47, 126.98, 61.25, 31.11, 30.03, 29.97, 29.91, 29.71, 29.60, 28.98, 27.00, 23.08, 14.25; *Anal*. Calc. for $C_{18}H_{30}N_2Cl_2Pd$: C, 47.85; H, 6.69; N, 6.20%. Found: C, 47.43; H, 6.56; N, 6.01%.

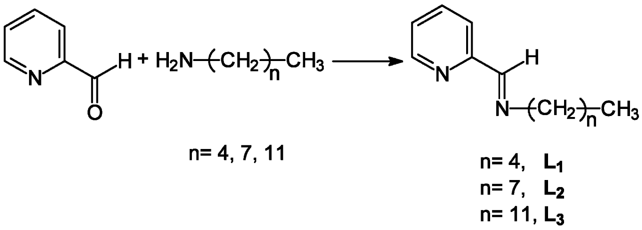
2.5. General procedure for ethylene polymerization

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 into the reactor; the pressure was maintained at 5 atm, throughout the polymerization process, after which the autoclave was vented. The reaction was quenched by adding ethanol. The polymer was collected, treated with 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

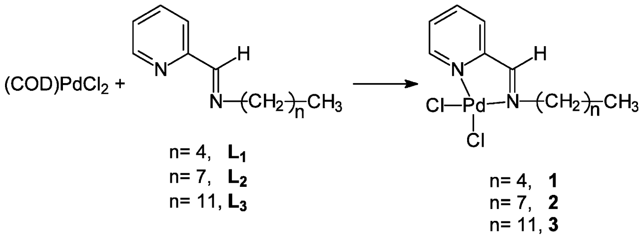
3.1. Synthesis of ligands and palladium complexes

The preparation of the *N*-alkyl substituted pyridylimine ligands **L$_1$**–**L$_3$** was carried out by condensation of pyridine-2-carboxaldehyde with the corresponding alkylamines with removal of water using anhydrous magnesium sulfate (Eq. (1)). After isolation by filtration and reduction of the solvent by evaporation, the pyridylimine compounds were easily purified by extraction with hexane. ^1H NMR spectra of ligands **L$_1$**–**L$_3$** show the signal for $=N-CH_2$ appearing around 3.65 ppm; while the imino proton appears at 8.36 ppm. The latter appears upfield compared to the signal of the aldehydic proton of the starting material. Infrared investigation of the three ligands shows three strong bands are apparent at approximately 1650, 1588 and 1568 cm^{-1}, ascribed to C=N vibration and pyridine-ring vibrations, respectively.



(1)

Subsequent reactions of equimolar amounts of ligands (**L$_1$**–**L$_3$**) with (COD)PdCl$_2$ resulted in the formation of {*N*-alkyl-*N*-[pyridin-2-ylmethylene] amine}dichloro palladium complexes **1**–**3** (Eq. (2)). IR spectra for the palladium complexes, in comparison with those of their corresponding ligands, show only a single absorption band in the region around 1600 cm^{-1}, which is assigned to the pyridine-ring vibration. Disappearance of the imino C=N absorptions in their IR spectra might be ascribed to an infrared inactive C=N vibration [9] in the Pd(II) complexes as result of coordination of the diimine ligand to the palladium metal as well as a reduction in electron density in the C=N bond arising from electron density flowing from the ligand to the metal center. ^1H NMR data for the these Pd(II) complexes **1**–**3** show, large downfield shifts of the protons of the pyridylimine group, py-*H*(1), py-*H*(4) and the imino group *H*–C=N, and $=N-CH_2$. This reveals the existence of strong coordination of the pyridine nitrogen and the imine nitrogen to the palladium center. Corresponding downfield shifts in the ^{13}C NMR spectra of these complexes are also observed. Thus the signals for py-*C*(1), py-*C*(4), py-*C*(5), imino H–*C*=N, and $=N-CH_2$ are deshielded by coordination to the palladium.



(2)

These pyridinylimine Pd complexes can be recrystallized from CH_2Cl_2 at −20 °C. The X-ray structure of complex **2** is shown in Fig. 1. The crystal data and selected bond lengths and bond angles are presented in Tables 1 and 2. Complex **2** has a very similar crystal structure to that of compound **3**, which was recently reported by us [6]. Interestingly, unlike other reported diimine complexes possessing aryl groups at the imino nitrogen, whose planes are either bent or entirely perpendicular to the plane of the complex, our complexes display a striking co-planar geometry, i.e. the pyridine ring, the metal coordination sphere N(1)–C(5)–C(6)–N(2)–Pd and the alkyl backbone are in the same plane.

3.2. Ethylene polymerization

Table 1
Crystal data and structure refinement for complex **2**

Formula	$C_{14}H_{22}Cl_2N_2Pd$
CCDC no.	CCDC 208097
Color/shape	yellow
Formula weight	395.64
Temperature (K)	173(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimension	
a (Å)	8.7561(2)
b (Å)	9.4916(3)
c (Å)	10.3464(3)
α (°)	80.177(2)
β (°)	67.738(2)
γ (°)	87.9700(10)
V (Å^3)	783.72(4)
Z	2
D_{calc} (Mg m^{-3})	1.677
Absorption coefficient (mm^{-1})	1.513
F(0 0 0)	400
Crystal size (mm^3)	0.17 × 0.15 × 0.10
θ Range for data collection	2.16–28.29
Index ranges	$-11 \le h \le 6$, $-12 \le k \le 11$, $-13 \le l \le 12$
Reflections collected	8870
Independent reflections	3848 ($R_{int} = 0.025$)
Completeness to $\theta = 28.29°$	98.8%
Max. and min. transmission	0.8634 and 0.7830
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3847/22/174
Extinction coefficient	0.0009(6)
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0260$, $wR_2 = 0.0476$
R indices (all data)	$R_1 = 0.0359$, $wR_2 = 0.0501$
Largest difference peak and hole (e Å^{-3})	0.490 and −0.498

The palladium complexes were activated in toluene by the addition of a toluene solution of MAO (10% w/w) at room temperature. Ethylene polymerization experiments were carried out at 5 atm of ethylene pressure in an autoclave. The results are shown in Table 3. All the polymeric products are white granular solids. Complexes **1** and **2** exhibited their highest productivities of polyethylene at Al/Pd ratio of 1030 and 2030, respectively, while Complex **3** bearing the longest alkyl group of the three didn't show significant yield in this range or

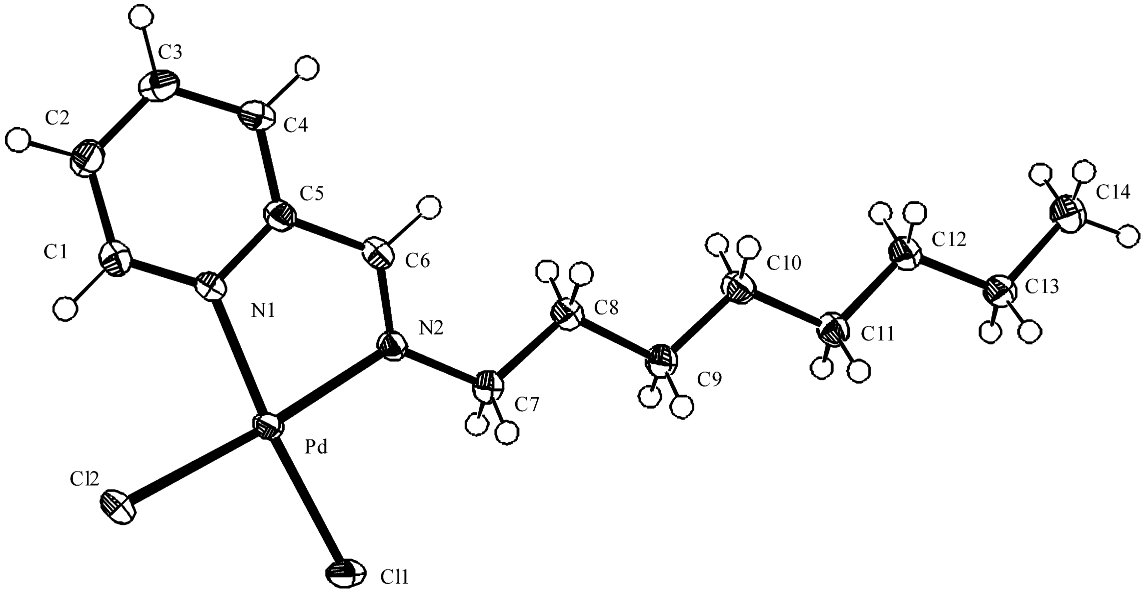


Fig. 1. X-ray structure of complex **2**.

Table 2
Selected bond distances (Å) and angles (°) for complex **2**

Bond lengths	
Pd–N(1)	2.037(2)
Pd–N(2)	2.029(2)
Pd–Cl(1)	2.2764(7)
Pd–Cl(2)	2.2956(7)
N(1)–C(1)	1.332(3)
N(1)–C(5)	1.358(3)
N(2)–C(6)	1.278(3)
C(5)–C(6)	1.447(4)
N(2)–C(7)	1.476(3)
Bond angles	
Cl(1)–Pd–Cl(2)	90.75(3)
Cl(1)–Pd–N(2)	93.80(6)
N(2)–Pd–Cl(2)	175.44(6)
N(2)–Pd–N(1)	80.94(8)
N(1)–Pd–Cl(2)	94.51(6)
N(1)–Pd–Cl(1)	174.71(6)

even when the Al/Pd ratio reached 2839. It seems that the Pd(II) complex with a longest alkyl group might need significantly higher ratios of Al/Pd or a higher concentration of MAO to activate it and to reach its optimum productivity. It appears that the steric bulk of ligands affects activation of the Pd complexes.

Based on the evidence of a number of previous studies [10] that cationic alkyl complexes are the active species in ethylene polymerization, a probable activation process for the Pd complexes is shown in Scheme 1. Species of the type (N–N)$Pd^+(CH_3)$ is considered increasingly difficult to form as the steric bulk of the long chain alkyl substituents increases. Siedle's study on the activation process of dialkylzirconocenes with MAO showed that increased steric hindrance at zirconium increases the free energy of activation [11]. Thus it is proposed that the complex **3** shows a lower catalytic activity for ethylene polymerization in this study as a result of the bulky steric effect on its activation with MAO.

The polymers, obtained with these pyridylimine Pd(II) complexes with aliphatic chains attached to the imino nitrogen are high-density linear polyethylene as determined by DSC ($T_m = 135–137$ °C). This is in contrast to the branched ethylene oligomers produced using 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 confirm their linear nature. GPC analysis showed these palladium catalyst precursors produced significantly high-molecular weight polyethylene. The catalyst precursor **3** with the longest chain group of the three, produced higher molecular weight polyethylene ($M_n = 6.3–6.8 \times 10^5$, $M_w = 22 \times 10^5$); than complexes **1** and **2**, ($M_n = 4.5–5.1 \times 10^5$, $M_w = 11–14 \times 10^5$). The molecular weight distribution of polymers obtained from precursor **3** are also a bit wider, having PDI values in the range 3.28–3.58 as compared to 2.56–2.77 for polymers obtained from precursors **1** and **2**. The GPC curves shows that the molecular weight distribution is unimodal, indicating that only one kind of active species is operative in the polymerization reactions.

It should be noted that by changing the substituents on the imino nitrogen from an aryl group to a long chain alkyl group has the effect of greatly increasing the molecular weights and producing linear polyethylene. These results can be explained using conventional mechanistic assumptions, i.e. β-hydride (β-H) isomerization (chain-running) leads to branching while β-H elimination leads to chain transfer. The unique coplanar structure of our precatalysts is likely a decisive factor affecting the polymer properties. The long straight alkyl chain lying in the same plane of the active center would impart higher steric bulk than is formed in the angled aryl group systems. Ziegler et al. using a QM/MM approach calculated that, for the imine-type catalysts with bulky ligands, the relative magnitudes of the free energy barriers are in the following order:

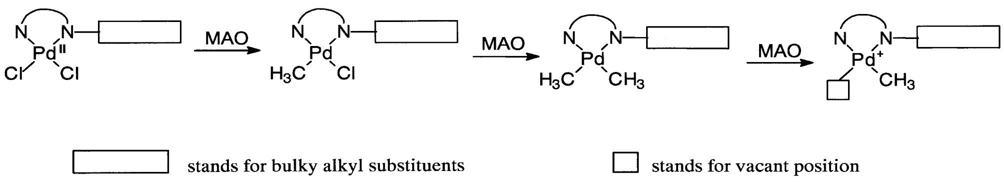
Table 3
Results of ethylene polymerization catalyzed by palladium complexes **1**–**3**

Catalysts	Al/Pd	Activity kg PE (mol Pd atm h)$^{-1}$	M_n [a] $\times 10^{-5}$	M_w [a] $\times 10^{-5}$	PDI [b]
1	815	9.98	4.74	12.9	2.73
1	1037	15.4	4.75	12.4	2.60
1	1260	7.54	5.12	14.2	2.77
2	810	0.45	4.13	10.77	2.61
2	1208	1.39	4.39	11.94	2.72
2	1706	1.78	4.46	12.22	2.74
2	2132	12.7	4.52	11.8	2.63
2	2558	3.94	5.16	13.2	2.56
3	987	0.19	6.12	21.29	3.48
3	2130	1.71	6.32	22.3	3.56
3	2839	2.43	6.85	22.2	3.28

Polymerization conditions: [Pd] = 0.016 mmol, MAP as co-catalyst, 150 ml toluene, 5 atm, 3 h.

[a] Molecular weight data determined by GPC vs. polyethylene standards at 160 °C.

[b] PDI = M_w/M_n.



Scheme 1.

propagation < branching < termination [12]. Clearly, a higher energy is needed for the growing polymer chain to undergo β-H isomerization and β-H elimination. Therefore, chain running and chain transfer processes are retarded, and the rate of chain propagation is far faster than chain running and chain transfer rates. Thus permitting the formation of high-density linear polyethylene with high-molecular weight. Furthermore, the longer alkyl group in complex **3** shows a greater hindrance in polymer chain transfer and elimination than the other two complexes, which might explain why complex **3** leads to the formation of higher molecular weight polyethylene.

4. Conclusion

The {*N*-alkyl-*N*-[pyridin-2-ylmethylene] amine}dichloro palladium(II) complexes bearing long alkyl group at the imino nitrogen were successfully synthesized, characterized and applied as catalyst precursors in ethylene polymerization. This work allowed us to study the effects of alkyl substituents on olefin polymerization. On the one hand, the coplanar features of our complexes are deemed to favour chain propagation and retard chain transfer and chain running rates. Therefore, polymers produced here are highly linear polyethylene with high-molecular weights, different from those prepared with recently reported *N*-aryl pyridylimine-type complexes. On the other hand, the steric feature affects the activation reaction of the palladium complexes with MAO. It is also indicated that ligand environments play a crucial role on catalyst activity and polymer microstructure.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 208097 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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