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Novel hemi-labile pyridyl-imine palladium complexes: Synthesis, molecular structures and reactions with ethylene

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ABSTRACT

Ligands (2-pyridyl-2-furylmethyl)imine, (**L1**), (2-pyridyl-2-thiophenemethyl)imine (**L2**), and (2-pyridyl-2-thiopheneethyl)imine (**L3**) were synthesized by condensation reactions and obtained in good yields. Reactions of **L1**–**L3** with either [PdClMe(cod)] or [$PdCl_2$(cod)] gave the corresponding monometallic palladium(II) complexes **1–5** in very good yields. Molecular structures of complexes **1**, **4** and **5** indicated that the ligands are bidentate and coordinate to the palladium metal through the imine and pyridine nitrogen atoms. When complexes **3**–**5** were treated with $NaBAr_4$, cationic species, **3a**, **4a**, and **5a** were produced which catalyzed polymerization of ethylene though with very low activities. ^{1}H NMR spectroscopy studies showed that these cationic species were very stable in solution. DFT calculations showed high ethylene coordination barriers to the cationic species **3a, 4a** and **5a**.

1. Introduction

The development of nitrogen-donor late transition metal catalysts as olefin oligomerization and polymerization catalysts has witnessed significant growth since the discovery of Brookhart and co-workers [1] that α-diimine nickel and palladium complexes produce active catalysts for ethylene polymerization reactions. To date several reviews have been written on late transition-metal olefin oligomerization and polymerization catalysis [2]. From these literature reports, it is evident that catalyst performance (activity and selectivity) in these reactions can be regulated through ligand modification as well as changing the identity of the metal centre.

While catalyst selectivity towards the formation of either oligomers or polymers has generally been understood to be controlled by steric factors of the ligand backbone [2a], understanding the balance between catalyst activity and stability still remains a dark horse. Generally, catalysts containing more electrophilic metal centre tend to be more active owing to the ease of olefin coordination to the vacant metal site, a crucial step in olefin oligomerization or polymerization process. However, it has been shown that more electrophilic metal centres give rise to unstable catalysts leading to rapid decomposition of the active species [3,4]. On the other hand, use of electron-rich ligands produce stable catalysts but exhibit very low activities [5,6]. One approach to the design of stable and more active olefin oligomerization and polymerization catalysts has been through the use of "hemi-labile ligands" first introduced by Jeffrey and Rauchfuss in 1979 [7]. The role of the hemi-labile donor group is to stabilize the active cationic species, hence improving stability of the catalysts. The crucial interplay in using hemi-labile ligands is the balance between the donor ability of the hemi-labile group and the incoming monomer. It is essential that the incoming monomer be more strongly coordinating than the hemi-labile group in order to gain access to the metal centre [2b,c].

Several examples of ethylene oligomerization and polymerization catalysts that contain hemi-labile ligands have been reported in literature. For example, palladium complexes of hemi-labile P^N^O ligands [8] have been shown to give active or inactive ethylene oligomerization catalysts depending on the donor strength of the O–R functionality (Eq. (1)). While catalysts bearing methoxy group show low activity (86 mg product after 24 h), no catalytic activity was observed for those containing an O–H group.

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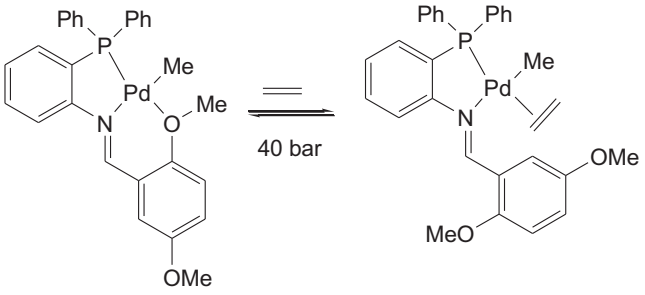


(1)

It is believed that the non-labile phenolate group coordinates to the metal centre without disassociation as required for an active catalyst and hence blocks ethylene coordination. However, these catalysts showed high stability in solution, presumably due to the stabilizing role of the phenolate group. In our current attempt to develop both active and stable ethylene oligomerization and polymerization catalysts, we report the synthesis of new palladium complexes of imino-pyridine ligands containing potential hemi-labile thiophene or furan groups. Molecular structures of these palladium complexes and attempts to use them as ethylene oligomerization or polymerization catalysts are discussed.

2. Experimental

2.1. Materials and methods

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Dichloromethane and hexane were refluxed and distilled from calcium hydride (CaH_2) while diethyl ether was dried over sodium wire and benzophenone. Methanol was dried from magnesium. Starting materials, [PdClMe(cod)] and [$PdCl_2$(cod)] were prepared following literature methods [9]. The following materials, anhydrous magnesium sulfate, 2-pyridinecarboxaldehyde, 2-furylmethylamine, 2-thiopheneethylamine, tetramethyltin, 1,5-cyclooctadiene, palladium(II)chloride and 2-thiophenemethylamine were purchased from Sigma–Aldrich and used without any further purification. The NMR experiments were done on a Varian XR200 MHz spectrometer. Chemical shifts are given in ppm while all coupling constants are reported in Hz. IR spectra in solution were recorded on a Perkin–Elmer Spectrum 100 Series FT-IR instrument using Nujol mulls on NaCl plates. Elemental analyses was performed on Server 1112 Series Elemental Analyzer. Melting points were recorded on open capillaries using SMP10 melting point apparatus.

2.2. Synthesis of ligands and palladium complexes

2.2.1. (2-Pyridyl-2-furylmethyl)imine (*L1*)

To a solution of 2-pyridinecarboxaldehyde (0.20 g, 1.89 mmol) and anhydrous magnesium sulfate (1.00 g) in methanol (15 mL) at 0 °C was added dropwise a solution of 2-furylmethylamine (0.18 g, 1.89 mmol) in methanol (15 mL). The reaction was allowed to proceed at room temperature for 12 h. After the reaction period, the light orange mixture was filtered and solvent removed under vacuum to obtain the crude product. The crude product was washed with water (10 mL) and the organic material extracted with dichloromethane (2 × 10 mL) and dried over anhydrous magnesium sulfate. The solvent was then removed to afford compound **L1** as a light brown oil. Yield = 0.33 g (93%). IR (Nujol cm^{-1}); ν(C=N) 1649, ν(C–O–C) 1325, ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.60 (t, 1H, J = 7.6, furan); 6.22 (d, 1H, J = 7.2, furan); 6.16 (d, 1H, J = 3.0, furan); 4.71 (s, 2H, –CH_2); 8.30 (s, 1H, –CH=N); 8.51 (d, 1H, J = 4.6, py); 7.19 (dd, 1H, J = 6.2, py); 7.88 (d, 1H, J = 7.8, py); 7.92 (d, 1H, J = 8.0, py); ^{13}C NMR (200 MHz, $CDCl_3$) δ 142.29, 110.33, 107.79, 151.74; 163.67; 56.67; 154.36, 149.36, 124.83, 136.45, 121.35; *Anal.* Calc. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.58, H, 5.24, N, 14.88%.

2.2.2. (2-Pyridyl-2-thiophenemethyl)imine (*L2*)

Compound **L2** was synthesized following the procedure described for **L1** using (2-pyridinecarboxaldehyde (0.51 g, 4.76 mmol) and 2-thiophenemethylamine (0.54 g, 4.76 mmol). Light yellow oil was obtained. Yield = 0.89 g (92%). IR (Nujol cm^{-1}); ν(C=N) 1648, ν(C–S–C) 1314, ^{1}H NMR (200 Hz, $CDCl_3$) δ 7.78 (t, 1H, J = 5.0, thiophen); 7.27 (t, 1H, J = 6.0, thiophen); 7.02 (d, 1H, J = 7.2, thiophen); 5.07 (s, 2H, –CH_2); 8.48 (s, H-8, –CH=N); 8.67 (d, 1H, J = 3.8, py); 7.37 (t, 1H, J = 6.6, py); 8.07 (d, 1H, J = 8.0, py); 8.11 (d, 1H, J = 7.6, py). ^{13}C NMR (200 MHz, $CDCl_3$) δ 58.89, 121.39, 124.91, 125.37, 126.30, 126.89, 136.53, 141.17; 149.38, 154.36, 163.05. *Anal.* Calc. for $C_{11}H_{10}N_2S$: C, 65.32; H, 4.98; N, 13.85. Found: C, 65.12; H, 5.06; N, 14.09%.

2.2.3. (2-Pyridyl-2-thiopheneethyl)imine (*L3*)

This compound was also prepared according to the procedure used for **L1** using 2-pyridinecarboxaldehyde (0.38 g, 3.56 mmol) and 2-thiopheneethylamine (0.45 g, 3.56 mmol). Light yellow oil was obtained. Yield = 0.74 g (92%). IR (Nujol cm^{-1}); ν(C=N) 1650, ν(C–S–C) 1336, ^{1}H NMR (200 Hz, $CDCl_3$) δ 7.32 (dd, 1H, J = 5.8, thiophen); 6.95 (t, 1H, J = 7.0, thiophen); 7.50 (t, 1H, J = 5.4, thiophen); 3.21 (t, 2H, J = 6.4 = N–CH_2); 3.91 (t, 2H, J = 6.8, –CH_2); 8.31 (s, 1H, –CH=N); 8.65 (d, 1H, J = 4.2, py); 7.46 (t, H, J = 7.2, py); 7.92 (d, 1H, J = 7.6, py); 7.98 (t, 1H, J = 7.4, py); ^{13}C NMR (200 MHz, $CDCl_3$) δ 30.60, 61.40, 120.53, 124.10, 125.21, 125.36, 126.83, 136.98, 141.97; 149.37, 153.98, 162.56. *Anal.* Calc. for $C_{12}H_{12}N_2S$: C, 66.63; H, 5.59; N, 12.95. Found: C, 66.77; H, 5.76; N, 12.57%.

2.2.4. Dichloro-[(2-pyridyl-2-furylmethyl)imine]palladium (II) (*1*)

To a solution of [$PdCl_2$(cod)] (0.10 g, 0.35 mmol) in CH_2Cl_2 (20 mL) was added a solution of **L1** (0.07 g, 0.35 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 6 h to give a light yellow precipitate. The precipitate was filtered to obtain a light yellow solid. Recrystallization from a mixture of CH_2CN: hexane solution afforded single crystals suitable for X-ray analysis. Yield = 0.11 g (88%), mp: 173 °C. IR (Nujol cm^{-1}); ν(C=N) 1597, ν(C–O–C) 1301, ^{1}H NMR (200 MHz, DMSO) δ 6.84 (t, 1H, J = 4.0, furan); 5.56 (d, 1H, J = 3.2, furan); 5.48 (t, 1H, J = 2.4, furan); 4.01 (s, 2H, –CH_2); 7.56 (s, 1H, –CH=N); 7.91 (d, 1H, J = 5.2, py); 6.67 (t, 1H, J = 2.4, py); 7.15 (d, 1H, J = 5.4, py); 7.29 (t, 1H, J = 6.0, py); ^{13}C NMR (200 MHz, DMSO) δ 53.47, 111.10, 111.52, 128.95, 141.39, 143.89, 147.77, 150.24; 155.62, 172.31. *Anal.* Calc. for $C_{11}H_{10}Cl_2N_2PdO$: C, 36.34; H, 2.77; N, 7.71. Found: C, 36.78; H, 2.70; N, 7.50%.

2.2.5. Dichloro-[(2-pyridyl-2-thiophenemethyl)imine]palladium (II) (*2*)

Complex **2** was prepared in a similar manner to complex **1**. [$PdCl_2$(cod)] (0.10 g, 0.35 mmol) and **L2** (0.07 g, 0.35 mmol). Yellow solid. Yield = 0. 11 g (85%), mp: 171 °C. IR (Nujol cm^{-1}); ν(C=N) 1598, ν(C–S–C) 1306, ^{1}H NMR (200 Hz, DMSO) δ 6.94 (t, 1H, J = 7.0, thiophen); 6.66 (d, 1H, J = 5.2, thiophen); 6.16 (d, 1H, J = 4.8, thiophen); 4.28 (s, 2H, –CH_2); 7.79 (s, 1H, –CH=N); 8.01 (d, 1H, J = 5.2, py); 6.37 (d, 1H, J = 6.8, py); 7.23 (d, 1H, J = 7.6, py); 7.40 (t, 1H, J = 7.4, py); ^{13}C NMR (200 MHz, DMSO) δ 54.74; 127.07, 127.40; 128.76, 128.80, 136.93, 141.20, 150.03, 155.60, 172.21. *Anal.* Calc. for $C_{11}H_{10}Cl_2N_2PdS$: C, 34.80; H, 2.66; N, 7.38. Found: C, 35.98; H, 2.70; N, 7.60%.

*2.2.6. Chloromethyl-[(2-pyridyl-2-furylmethyl)imine]palladium (II) (**3**)*

To a solution of [PdClMe(cod)] (0.04 g, 0.16 mmol) in 1:2 mixture of CH_2Cl_2/Et_2O (15 mL) was added a solution of **L1** (0.03 g, 0.16 mmol) CH_2Cl_2 (2 mL). The yellow solution was stirred for 5 h at room temperature to produce a light yellow precipitate. Recrystallization from CH_2Cl_2:hexane gave **3** as an analytically pure yellow solid. Yield = 0.06 g (98%), mp: 132 °C. IR (Nujol cm^{-1}); ν(C=N) 1590, ν(C–O–C) 1291, ^{1}H NMR (200 Hz, $CDCl_3$) δ 4.97 (s, 2H, CH_2); 8.16 (s, 1H, –CH=N); 1.11 (s, 3H, Pd–Me); 9.07 (d, 1H, J = 5.2, py); 7.94 (t, 1H, J = 7.6, py); 7.45 (t, 1H, J = 6.8, furan); 7.62 (t, 1H, J = 5.4, py); 6.47 (t, 1H, J = 4.6, furan); 7.23 (t, 1H, J = 5.0, furan), 6.53 (d, 1H, J = 4.4, py). ^{13}C NMR (200 MHz, $CDCl_3$) δ: 29.70; 54.67; 111.07, 111.78, 125.85; 128.20, 138.48, 141.20, 143.86, 149.62, 166.61. *Anal.* Calc. for $C_{12}H_{13}ClN_2PdO$: C, 42.01; H, 3.82; N, 8.16. Found: C, 42.21; H, 3.50; N, 8.25%.

*2.2.7. Chloromethyl-[(2-pyridyl-2-thiophenemethyl)imine]palladium (II) (**4**)*

The complex was prepared following the method described for **3** using [PdClMe(cod)] (0.05 g, 0.20 mmol) and **L2** (0.04 g, 0.20 mmol). Recrystallization from CH_2Cl_2:hexane solution afforded yellow single crystals suitable for X-ray analysis. Yield = 0.07 g, 0.19 g (95%). mp: 129 °C. IR (Nujol cm^{-1}); ν(C=N) 1591, ν(C–S–C) 1309, ^{1}H NMR (200 Hz, $CDCl_3$) δ 5.16 (s, 2H, CH_2); 8.16 (s, 1H, –CH=N); 1.12 (s, 3H, Pd–Me); 9.06 (d, 1H, J = 5.4, py); 8.56 (d, 1H, J = 3.8, py); 7.07 (dd, 1H, J = 4.6, thiophen); 7.23 (t, 1H, J = 4.2, py); 7.35 (dd, 1H, J = 7.0, thiophen); 7.59 (t, 1H, J = 7.2, thiophen); 7.94 (d, 1H, J = 7.2, py). ^{13}C NMR (200 MHz, $CDCl_3$) δ: 29.70, 56.37, 125.90, 127.10, 127.46, 128.18, 129.13, 1135.66, 38.49, 148.84, 149.62, 160.74, 166.28. *Anal.* Calc. for $C_{12}H_{13}ClN_2PdS$: C, 40.13; H, 3.65; N, 7.80. Found: C, 39.99; H, 3.23; N, 7.43%.

*2.2.8. Chloromethyl-[(2-pyridyl-2-thiopheneethyl)imine]palladium (II) (**5**)*

Complex **5** was prepared in a similar manner to **3** using [PdClMe(cod)] (0.05 g, 0.19 mmol) and **L3** (0.04 g, 0.19 mmol). The light yellow solid was recrystallized from CH_2Cl_2:hexane solution to give single crystals suitable for X-ray analysis. Yield = 0.06 g (90%). mp: 126 °C. IR (Nujol cm^{-1}); ν(C=N) 1590, ν(C–S–C) 1296, mp: °C, ^{1}H NMR (200 Hz, $CDCl_3$) δ 3.37 (s, 2H, =N–CH_2); 3.99 (s, 2H, –CH_2); 7.79 (s, 1H, –CH=N); 1.08 (s, 3H, Pd–Me); 9.09 (d, 1H, J = 5.8, py); 7.91 (d, 1H, J = 4.2, py); 7.62 (t, 1H, J = 4.2, thiophen); 7.49 (t, 1H, J = 4.8, py); 7.15 (d, 1H, J = 5.2, thiophen); 6.85 (t, 1H, J = 5.6, thiophen). ^{13}C NMR (200 MHz, $CDCl_3$) δ: 29.73; 61.56, 30.58; 124.77, 125.31, 126.54, 128.07, 127.24, 127.77; 138.53; 141.42, 149.64, 166.44. *Anal.* Calc. for $C_{13}H_{15}ClN_2PdS$: C, 41.84; H, 4.05; N, 7.51. Found: C, 41.65; H, 4.25; N, 7.23%.

*2.3. Molecular structures of **1**, **4** and **5***

Single-crystal X-ray diffraction data for compounds **1**, **4** and **5** were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo Kα radiation (χ = 0.71073 Å). The crystal structure was solved by direct methods using SHELXS-97 [10] and refined by full-matrix least-squares methods based on F [10] using SHELXL-97 [10] and using the graphics interface program X-SEED [11,12]. The programs X-SEED and POV-RAY [12] were both used to prepare molecular graphic images.

*2.4. Preparation of compound **5a** its ^{1}H NMR spectroscopy study*

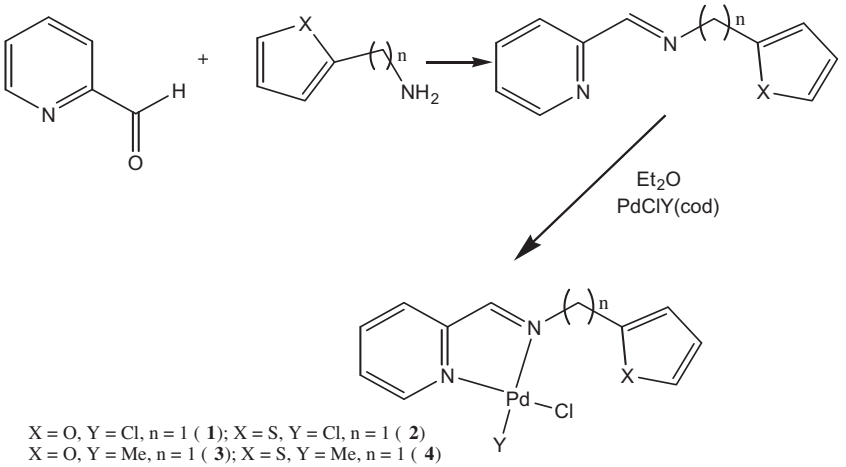
To a mixture of **5** (0.10 g, 0.24 mmol) and $NaBAr_4$ in an NMR tube was added $CDCl_3$ (1.00 ml) to give **5a**. The solution was shaken and ^{1}H NMR spectrum of the solution acquired at various intervals for 7 days. ^{1}H NMR of **5a** after 15 min (200 Hz, $CDCl_3$) d: 1.11 (s, 3H, Pd–CH_3); 3.20 (t, 2H, J = 5.6, CH_2); 3.92 (t, 2H, J = 4.4, CH_2); 7.07–8.47 (m, 7H, thiophene and py); 7.50 (s, 4H, BAr_4), 7.71 (s, 8H, BAr_4); 8.01 (s, 1H, H-imine).

3. Results and discussion

3.1. Synthesis of the ligands and metal complexes

Compounds **L1**–**L3** were prepared by condensation reactions of 2-pyridinecarboxaldehyde with the appropriate (furylalkyl)amine or (thiophenylalkyl)amine (Scheme 1). The compounds were isolated as light brown oils in quantitative yields. Reactions of **L1**–**L3** with either [$PdCl_2$(cod)] or [PdMeCl(cod)] afforded the corresponding complexes, **1**–**5**, in moderate yields (Scheme 1).

IR spectra of the ligands generally exhibited strong absorption bands at around 1650 cm^{-1}, typical of an imine functionality [13–16]. Coordination of **L1**–**L3** to the palladium atom could be deduced from the IR spectra of complexes **1**–**5**, which showed typical lower absorption bands between 1590 and 1598 cm^{-1} [17] compared to the respective ligands. ^{1}H NMR spectra of the compounds also provided a useful tool for their elucidation. For instance, singlet peaks between 8.36 and 8.76 ppm in **L1**–**L3** were indicative



Scheme 1.

of the presence of the imine protons [18]. In addition, singlet at 4.83 and 5.00 ppm were assigned to the CH_2 linker protons in **L1** and **L2**, respectively [19]. ^{1}H NMR spectra of complexes **1**–**5** showed upfield shifts of the imine protons in the region of 7.5–8.16 ppm. In the ^{13}C NMR spectra, the imine carbons in **1**–**5** appeared downfield between 166.00 and 173.00 ppm compared to 162.00 ppm in the free imine ligands. Zhang et al. reported a similar trend in related imino-pyridyl palladium complexes where they observed a downfield shift from 167.00 to 165.4 ppm in the free imine compounds [13].

3.2. Molecular structures of complexes *1*, *4* and *5*

Single crystals of complexes **1**, **4** and **5** suitable for X-ray analyses were grown by slow diffusion of hexane into a dichloromethane solution at room temperature. Crystallographic data and structural refinement parameters are given in Table 1 while selected bond lengths and angles are contained in Table 2. Molecular structures of complexes **1**, **4** and **5** are shown in Figs. 1–3. The geometry around the palladium atom in the three complexes (**1**, **4** and **5**) could be described as distorted square planar. For instance, the bond angles around the Pd metal atoms of N(1)–Pd(1)–N(2) (79.10(6)°) in **1** and N(8)–Pd(1)–N(1) (80.5(2)°) in **4** show significant deviations from planarity. The reported bond angle for N(1)–Pd(1)–Cl(2) of (90.59(5)°) in **1** is slightly higher than the angle N(1)–Pd(1)–Cl(1) of (88.81(6)°) observed in **4**. The bond angles for N(1)–Pd(1)–N(2) of 80.5(2)° in **1**, 79.10(6)° in **4** and 79.33(6)° in **5** are all statistically similar and compare well with bond angles in related 2-methoxycarbonyl-6-iminopyridine palladium compounds which averaged 79.4(2)° [13]. The average Pd–N(2) bonds lengths of 2.044(4) Å in **1**, **4** and **5** compare well with bond lengths of 2.045(2) Å reported for the unconjugated diimine palladium complexes [20]. The differences between Pd(1)–Cl(1) and Pd(1)–Cl(2) bond lengths in **1** reflects the stronger *trans* influence of the pyridyl group compared to the imine group. This is consistent with the observations of Doherty et al. [21]. In general, the Pd–Cl distances in the three complexes are normal, averaging 2.290(13) Å. This value is in good agreement with the Pd–Cl bond distance of 2.298(15) Å averaged for 491 Pd complexes as reported in the Cambridge Structural Database (CSD) [22]. The Pd(1)–N(1) bond length of 2.1322(16) Å in **4** is significantly longer than the Pd(1)–N(2) bond length of 2.0509 (16) Å; this difference reflects the greater *trans* influence of the methyl group compared to the chloride ligand [23]. Similar trend is also observed in complex **5**. The Pd–CH_3 bond length in **4** was reported as 2.0366(18) Å, and compares well with the bond lengths of 2.005(12) Å observed in other related palladium complexes [22].

Table 1
Crystal data and structure refinement parameters for complexes **1**, **4** and **5**.

Parameter	**1**	**4**	**5**
Formula	$C_{11}H_{10}Cl_2N_2OPd$	$C_{22}H_{13}ClN_2PdS$	$C_{23}H_{15}ClN_2PdS$
Formula weight	363.51	359.5	373.18
T (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P21/c*	*P21/c*	*P21/c*
a (Å)	7.1568(9)	8.7860(2)	9.7013(13)
b (Å)	21.642(3)	8.8009(2)	17.425(2)
c (Å)	8.2697(10)	9.5884(2)	8.5427(12)
α (°)	90	88.2940(10)	90
β (°)	108.788(5)	63.3111(10)	107.723(4)
γ (°)	90	77.8350(10)(2)	90
Volume (Å^3)	1212.6(3)	645.76(2)	1375.6(3)
Z	4	2	4
D_{Calcd} (mg/m^3)	1.991	1.847	1.802
Absorption coefficient (mm^{-1})	1.95	1.78	1.677
F (0 0 0)	712	356	744
Final R indices (R_1)	0.1316	0.020	0.1404
R indices all data (R_1)	0.0526	0.050	0.1631
Reflections collected	9213	12 231	23 515
Completeness to theta (%)	99.4	99.6	98.8
Goodness of Fit (GOF) on F^2	0.982	1.05	1.106
Largest difference peak and hole (e Å^{-3})	0.411 and −0.261	2.923 and −0.567	2.944 and −1.908

Table 2
Selected bond lengths and angles for complexes 1, **4** and **5**.

	1 X = Cl(1)	**4** X = Cl(1)	**5** X = C(13)
Bond lengths (Å)			
Pd(1)–N(1)	2.033(2)	2.028(5)(5)	2.137(4)
Pd(1)–N(2)	1.983(2)	1.985(5)	2.057(16)
Pd(1)–X	2.3191(7)	2.3121(17)	2.079(5)
Bond angles (°)			
N(1)–Pd(1)–N(2)	80.5(2)	79.10(6)	79.33(16)
N(1)–Pd(1)–X	93.8(1)	96.06(4)	174.15(6)
N(2)–Pd(1)–X	95.1(1)	95.1(1)	95.30(7)

3.3. Reactions of complexes *3*–*5* with ethylene

The chloromethyl palladium complexes (**3**–**5**) were investigated for their ability to oligomerize or polymerize ethylene using $NaBAr_4$ (Ar = 3,5-$(CF_3)C_6H_3$) as the activator. In a typical experiment, approximately 0.05 mmol of the respective complex was reacted with an equivalent amount of $NaBAr_4$ in CH_2Cl_2 (80 mL). Ethylene pressure of 40 bar, time of 2 h and temperature of 30 °C was employed (Scheme 2). After the reaction time, the volatile components were trapped using liquid nitrogen and analyzed for the presence of dimers (butenes). The GC chromatogram did not show the presence of any volatile oligomers. Then, excess ethylene was vented off and the reaction quenched by addition of a small amount of MeOH. The solvent was then removed under reduced pressure to give a white residue (Yield = 0.08 g). ^{1}H NMR spectrum of the product showed signature peaks of low density polyethylene at 0.87 and 1.25 ppm [1]. From the ^{1}H NMR spectrum, the degree of branching in the polymer was calculated to contain 28 carbons atoms/1000 carbon atoms. In addition, the ^{1}H NMR spectrum also showed signals at 7.48 and 7.68 ppm corresponding to the BAr_4 protons. Attempts to optimize the catalytic conditions to improve the product yields were made. For instance, catalyst loading was increased by 10-fold to 0.5 mmol and longer reaction time of 5 h was employed. However, all these variations did not improve the activity of the catalysts and negligible amounts of products were obtained. Interesting though, no palladium black was observed, indicating the absence of catalyst decomposition, thus ruling out the possibility of catalyst instability. Therefore, this poor activity of catalysts derived from complexes **3**–**5** could be due to; one, poor electrophilicity of the Pd metal centre which hinders ethylene coordination, and two, stronger binding affinity of the furan or thiophene groups, which blocks ethylene coordination.

Since our initial objective in this ligand design was to use the furan or thiophene donor groups as hemi-labile motifs to stabilize the active intermediate species, we further investigated the propensity of these groups to stabilize the active species and their subsequent displacement by an incoming ethylene monomer (Scheme 2). This was done by ^{1}H NMR spectroscopic studies to determine half-lives of the cationic compounds **3a**, **4a** and **5a** (see section 2.4) and Density Functional Theory calculations [24] to evaluate their ethylene coordination barrier. Table 3 gives selected ^{1}H NMR signals, half-lives and thermodynamic data of

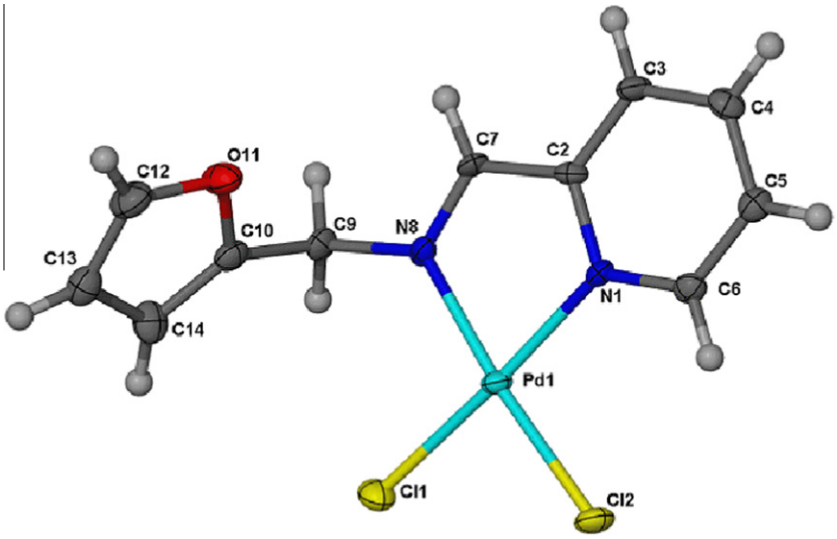


Fig. 1. Molecular structure of **1** shown with 50% probability ellipsoids.

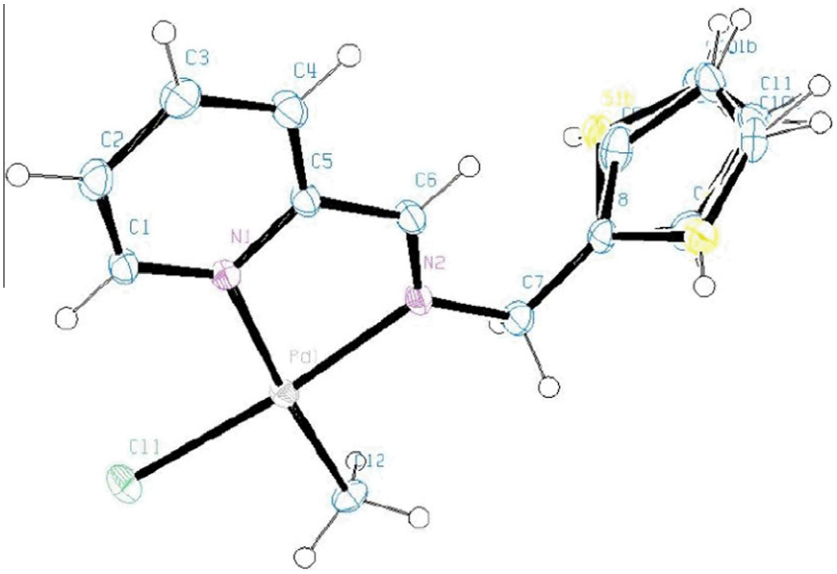


Fig. 2. Molecular structure of **4** shown with 50% probability ellipsoids. The thiophene molecule is severely distorted.

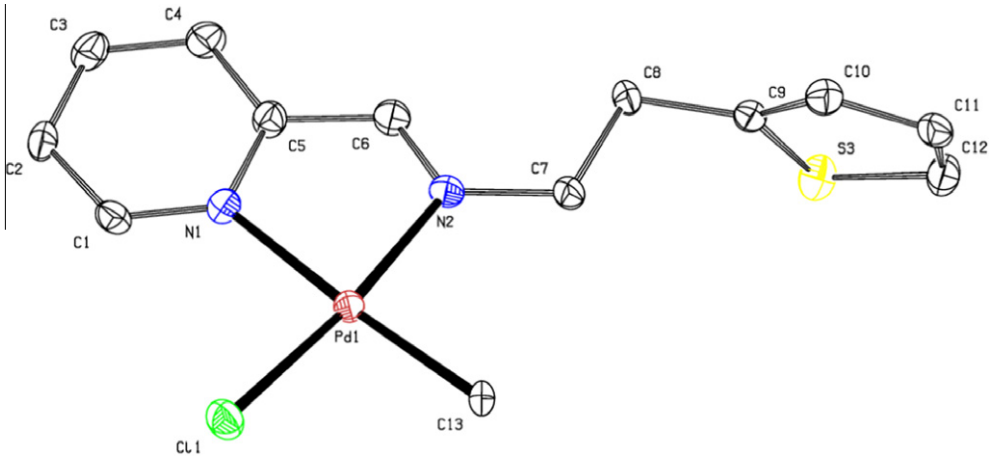
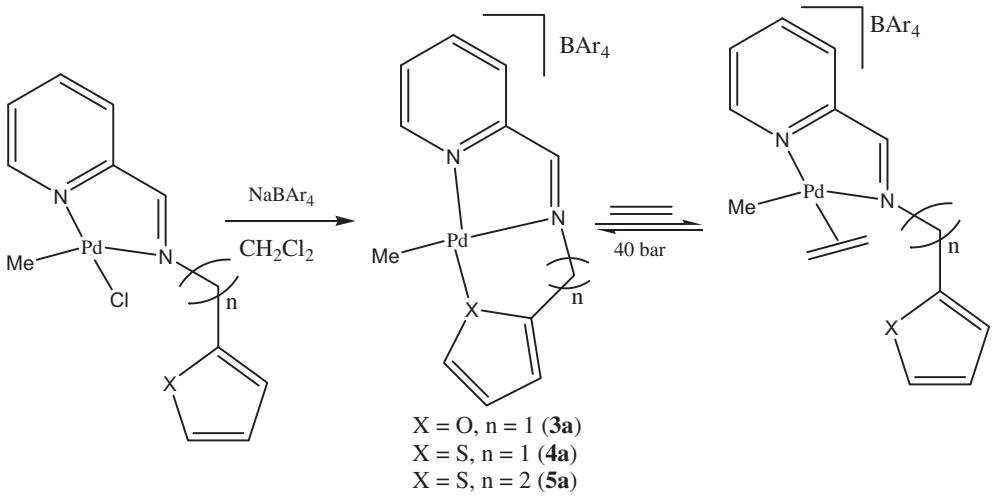


Fig. 3. Molecular structure of **5** shown with 50% probability ellipsoids. Hydrogen atoms are ommitted for clarity.



Scheme 2.

Table 3
Selected ^{1}H NMR signals, half-lives ($t_{1/2}$) and energies of ethylene coordination barriers to the cationic complexes **3a**–**5a**.

Compound	^{1}H NMR ($CDCl_3$, ppm)			Energies		
	Pd–Me	–CH_2–	C=N–H	$t_{1/2}$ (h)[a]	ΔH[b]	ΔG[b]
3a	1.07	5.05	8.11	84	−16.53	−5.48
4a	1.12	5.23	7.98	96	−13.18	−2.34
5a	1.11	3.20, 3.92	8.03	72	18.24	−8.26

[a] Determined by ^{1}H NMR spectroscopy using BAr_4 protons as internal standard.
[b] Calculated by Density Functional Theory at the B3LYP/LAN2DZ level of theory. Units, kcal/mol.

compounds **3a**, **4a** and **5a**. Fig. 4 shows the optimized geometries of **4a** and its corresponding ethylene coordinated complex. The identity of the cationic compounds, **3a**, **4a** and **5a** could be easily deduced from their respective ^{1}H NMR spectra obtained after the addition of $NaBAr_4$. For example, in **5a**, the signal corresponding to the Pd-Me protons was observed at 1.11 ppm as compared to 1.05 ppm in **5**. Similarly, upfield shifts were observed for the ethylene linker at 3.20 and 3.92 ppm for **5a** relative to the signals at 3.32 and 4.03 ppm in **5**. More conspicuous change was observed in the signal of the furan proton at 8.47 ppm compared to the downfield signal at 8.62 ppm in complex **5**.

From Table 3, it was evident that these cationic complexes were stable, with half-lives of 84, 96 and 72 h for **3a**, **4a** and **5a**, respectively. This confirms the stabilities of the catalysts obtained from these complexes and the absence of any palladium black formation. Ethylene coordination barriers of $\Delta G = -5.48$ kcal/mo; $\Delta H = -16.53$ kcal/mol (**3a**), $\Delta G = -2.34$ kcal/mol; $\Delta H = -13.18$ kcal/mol (**4a**) and $\Delta G = -8.26$ kcal/mol; $\Delta H = -18.24$ kcal/mol (**5a**) were obtained (Table 3). In an earlier study by Morokuma et al. [25], ethylene coordination barriers for the α-diimine palladium catalysts of $\Delta G = -18.4$ and $\Delta H = -29.4$ kcal/mol were reported. These values are significantly more negative than those obtained for our complexes, **3a**, **4a** and **5a**. It is therefore conceivable that complexes **3**–**5** gave poor activities due to the difficulty of ethylene in displacing the coordinated furan or thiophene groups. Typical ΔG values of ethylene coordination to the vacant metal centres of active ethylene polymerization catalysts are known to be between −30 and −60 kcal/mol [26]. A recent publication by Ojwach et al. [27] on the tridentate bound bis(pyrazolyl)pyridine palladium complexes gave ethylene coordination barriers of $\Delta H = +1.7$ kcal/mol and $\Delta G = +12.6$ kcal/mol. These tridentate bis(pyrazolyl)pyridine palladium complexes are completely inactive towards ethylene oligomerization or polymerization [27]. In another related work, Darkwa and co-workers reported that $[PdCl_2\{(R_2pz\text{-}CO)_2py\}]$ can be activated to afford active catalysts for the polymerization of ethylene [28]. The carbonyl linker group in these complexes makes the Pd–N_{pz} bonds weaker resulting in dissociation of one of the coordinated pyrazolyl units to allow ethylene to coordination to the palladium metal centre and undergo subsequent insertion to form polyethylene. The lack of increased catalytic activity even when complexes **3**–**5** were subjected to high ethylene pressures of 40 atm therefore points to the strength of the Pd–$O_{(furan)}$ or Pd–$S_{(thiophene)}$ bonds in **3a**, **4a** and **5a** relative to the binding affinity of ethylene monomer.

4. Conclusion

The pyridyl-imine compounds containing furan or thiophene hemi-labile groups react with palladium metal precursors to

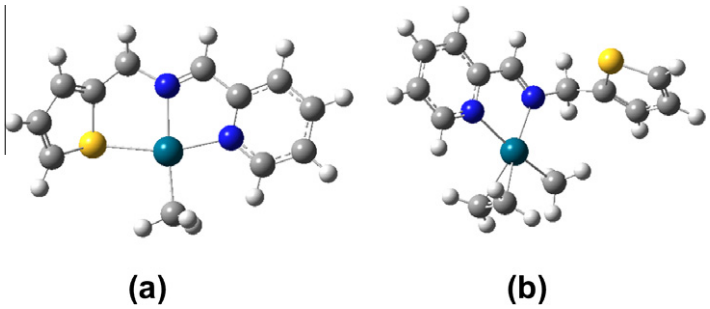


Fig. 4. Optimized geometries of **4a** (a) and its corresponding ethylene complex (b) computed at the B3LYP/LANL2DZ level of theory.

produce monometallic palladium complexes in which the ligands coordinate via the imine and pyridine nitrogen atoms. Reactions of complexes **3**–**5** with $NaBAr_4$ under ethylene atmosphere produced very stable catalysts for the polymerization of ethylene to form low density polyethylene though with very low activities. From Density Functional Theory calculations, competition between the ethylene monomer and the furan or thiophene groups for the vacant metal site upon halide abstraction appears to hinder ethylene coordination to the palladium centre thus limiting the polymerization process.

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Appendix A. Supplementary data

CCDC 828159, 828093 and 828094 contain the supplementary crystallographic data for compounds **1**, **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[2] (a) S. Ittel, M. Brookhart, L.K. Johnson, Chem. Rev. 100 (2000) 1169;
(b) S. Mecking, Coord. Chem. Rev. 203 (2000) 325;
(c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(d) C. Bianchini, G. Giambastiani, I.G. Rios, G. Mantovani, A. Meli, A.M. Segarra, Coord. Chem. Rev. 250 (2006) 1391;
(e) C. Bianchini, G. Giambastiani, P. Luconi, A. Meli, Coord. Chem. Rev. 254 (2010) 431;
(f) S. Jadwiga, Chem. Rev. 91 (1991) 613;
(g) D.S. McGuinness, Chem. Rev. 111 (2011) 2321;
(h) F. Speise, P. Braunstein, L. Saussine, Acc. Chem. Res. 38 (2005) 784;
(i) W. Kaminsky, A. Ahlers, N. Moeller-Lindenhof, Angew. Chem. 101 (1989) 1304;
(j) S. Mecking, Angew. Chem. Int. 40 (2001) 534;
(k) B. Rieger, L.S. Baugh, S. Kacker, S. Striegler (Eds.), Late Transition Metal Polymerisation Catalysis, Wiley, New Yolk, 2006.
[3] I.A. Guzei, K. Li, G.A. Bikzhanova, J. Darkwa, S.F. Mapolie, Dalton Trans. (2003) 715.
[4] S.O. Ojwach, M.G. Tshivhase, I.A. Guzei, J. Darkwa, S.F. Mapolie, Can. J. Chem. 83 (2005) 843.
[5] S.P. Meneghetti, P.J. Lutz, J. Kress, Organometallics 18 (1999) 2734.
[6] (a) T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskela, J. Organomet. Chem. 606 (2000) 112;
(b) T.V. Laine, J. Liimatta, K. Lappalainen, E. Aitola, B. Lofgren, M. Leskela, Macromol. Rapid Commun. 20 (1999) 487.
[7] (a) J.C. Jeffrey, T.B. Rauchfuss, Inorg. Chem. 18 (1979) 2658;
(b) L. Canovese, F. Visentin, Inorg. Chim. Acta 363 (2010) 2375;
(c) T.B. Rauchfuss, F.T. Patino, D.M. Roundhill, Inorg. Chem. 4 (1974) 652;
(d) R. Lindner, B. van den Bosch, M. Lutz, J.N.H. Reek, J. van der Vlugt, Organometallics 30 (2011) 499.
[8] P.-Y. Shi, Y-H. Liu, S-M. Peng, S-T. Liu, Organometallics 21 (2002) 3204.
[9] (a) E.V. Salo, Z. Guan, Organometallics 22 (2003) 5033;
(b) J. Wiedermann, K. Mereiter, K. Kirchner, J. Mol. Catal. A: Chem. 257 (2006) 67.
[10] G.M. Sheldrick, SHELXS-97, SHELXL-97 and SADABS Version 2.05, University of Göttingen, Germany, 1997.
[11] L.J. Barbour, J. Supramol. Chem. 1 (2001) 189.
[12] J.L. Atwood, L.J. Barbour, Cryst. Growth Des. 3 (2003) 3.
[13] W. Zhang, W.-H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Cheng, P. Hao, J. Organomet. Chem. 691 (2006) 4759.
[14] G. Smith, R. Chen, S. Mapolie, J. Organomet. Chem. 673 (2003) 111.
[15] P. Singh, S. Das, R. Dhakarey, J. Chem. 6 (2009) 99.
[16] Z. Zhang, S. Chen, X. Zhang, H. Li, Y. Ke, Y. Lu, Y. Hu, J. Mol. Catal. A: Chem. 230 (2005) 1.
[17] G.S. Smith, S.F. Mapolie, J. Mol. Catal. A: Chem. 213 (2004) 187.
[18] Y. Song, Z. Xu, Q. Sun, B. Su, Q. Gao, H. Liu, J. Zhao, J. Coord. Chem. (2007) 2351.
[19] D. Pou, A.E. Platero-Prats, S. Perez, C. Lopez, X. Solans, M. Font-Badia, P.W.N.M. van Leeuwen, G.P.F. van Strijdonck, Z. Freixa, J. Organomet. Chem. 692 (2007) 5017.
[20] S.M. Nelana, J. Cloete, G.C. Lisensky, E. Nordlander, I.A. Guzei, S.F. Mapolie, J. Darkwa, J. Mol. Catal. A: Chem. 285 (2008) 72.
[21] S. Doherty, J.G. Knight, T.H. Scanlam, M.R.J. Elsegood, W. Clegg, J. Organomet. Chem. 650 (2002) 231.
[22] F.H. Allen, Acta Crystallogr. B58 (2002) 380.
[23] (a) S.O. Ojwach, I.A. Guzei, J. Darkwa, J. Organomet. Chem. 694 (2009) 1393;
(b) K. Li, I.A. Guzei, J. Darkwa, S.F. Mapolie, J. Organomet. Chem. 660 (2002) 108.
[24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 03, Revision A9, Gaussian Inc., Pittsburgh, Pennsylvania, USA, 1998.
[25] D.G. Musaev, M. Svensson, K. Morokuma, Organometallics 16 (1997) 1933.
[26] L. Deng, P.T. Margl, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 1094.
[27] S.O. Ojwach, I.A. Guzei, J. Darkwa, S.F. Mapolie, Polyhedron 26 (2007) 851.
[28] M.S. Mohlala, I.A. Guzei, J. Darkwa, S.F. Mapolie, J. Mol. Catal. A: Chem. 241 (2005) 93.