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(Pyrazol-1-yl)carbonyl palladium complexes as catalysts for ethylene polymerization reaction

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ABSTRACT

Reactions of two equivalents of {3,5-(dimethylpyrazol-1-yl)-4-methoxy-1-carbonyl}benzene (L1), {3,5-(dimethylpyrazol-1-yl)-4-ethoxy-1-carbonyl}benzene (L2), {3,5-(dimethylpyrazol-1-yl)-4-hexyloxy-1-carbonyl}benzene (L3), and {3,5-(dimethylpyrazol-1-yl)-4-dodecycloxy-1-carbonyl}benzene (L4) with one equivalent of [Pd(NCMe)₂Cl₂] produced the corresponding monometallic complexes, [Pd(L1)₂Cl₂) (1), [Pd(L2)₂Cl₂) (2), [Pd(L3)₂Cl₂) (3) and [Pd(L4)₂Cl₂) (4) in good yields. Solid state structures of 2 and 4 confirmed the monodentate character of L1–L4 and *trans* configuration of the palladium complexes. Activation of 1–4, and the furanyl and thiophenyl carbonyl pyrazolyl palladium complexes: [Pd(Mepz-COfn)₂Cl₂] (5), [Pd(MepzCOth)₂Cl₂] (6), [Pd(t_{Bu}pzCOfn)₂Cl₂] (7) and [Pd(t_{Bu}pzCOfn)₂Cl₂] (8) (fn = furan, th = thiophene) with MAO produced catalysts for the polymerization of ethylene with moderate activities; forming linear high density polyethylene. The structure of the complexes had a significant effect on both the activity of the catalysts and nature of the polymers obtained.

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1. Introduction

Transition metal-catalyzed alkene polymerization has evolved as one of the most important reactions both in academic and industrial arenas [1]. Since the discovery by Brookhart and co-workers in 1996 that α -diimine nickel and palladium complexes give active olefin polymerization catalysts, significant amount of research has been directed towards the design of other late transition metal nitrogen-donor catalysts [2]. The success of these nitrogen-based late transition metal catalysts has largely been attributed to the ability to control both the steric and electronic properties of the catalysts. This has led to the development of a plethora of catalysts containing ligands with different steric and electronic properties [3].

Over the past decades, pyrazolyl nickel(II) and palladium(II) complexes have emerged as potential catalysts in olefin oligomerization and polymerization reactions [4]. The ease with which their electronic and steric properties can be regulated has made it possible to investigate the structure–activity relationship of a series of pyrazolyl metal complexes [5]. In one such design, the use of benzene-carbonyl linker pyrazolyl palladium catalysts led to higher catalytic activities but reduced stability compared to simple pyrazole palladium catalysts in ethylene polymerization reactions [4b]. The observed higher activity is believed to emanate from an increase in the electrophilicity of the palladium center and hence facilitate coordination of the ethylene monomer. In a related work, a change of benzene linker to pyridine carbonyl linker resulted in a potential tridentate ligand system which showed good stability but reduced catalytic activity [6]. This is presumably due to the tridentate coordination of the ligand; thus blocking ethylene access to the palladium center. This hypothesis was in deed confirmed in attempts to use 2,6-bis(pyrazol-1-ylmethyl)pyridine palladium complexes as catalysts in ethylene polymerization reactions where chloride abstraction resulted in the formation of stable tridentate cationic species which were inactive towards ethylene oligomerization or polymerization reactions [7].

In this current work, we report the use of pyrazol-1-yl palladium complexes containing alkoxybenzene-carbonyl and heterocylic carbonyl units, in the polymerization of ethylene (Chart 1). The furanyl and thiophenyl carbonyl units are expected to display hemilability and hence produce more stable catalysts to compensate for the weaker donor ability of the pyrazol-1-yl unit in the ligand motif. The structures of these compounds and the catalytic results obtained are discussed.

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Chart 1. Palladium complexes used in polymerization of ethylene.

2. Results and discussion

2.1. Synthesis of (pyrazolyl)alkoylbenzene ligands and their palladium(II) complexes

Reactions of an appropriate 4-alkoxybenzoyl chloride with 3,5dimethylpyrazole in a 1:1 mol ratio gave the corresponding compounds **L1–L4** in moderate to good yields (Scheme 1). While compounds **L2** and **L4** did not require any purification, **L1** and **L3** were purified by column chromatography on silica gel using a 4:1 mixture of dichloromethane:hexane as eluent. Subsequent reactions of **L1–L4** with [Pd(NCMe)₂Cl₂] in a 2:1 mol ratio afforded the corresponding palladium complexes [Pd(**L1**)₂Cl₂] (**1**), [Pd(**L2**)₂Cl₂] (**2**), [Pd(**L3**)₂Cl₂] (**3**) and [Pd(**L4**)₂Cl₂] (**4**) in moderate to high yields (Scheme 2). All the complexes were isolated as air stable yellow solids.

All compounds were characterized by a combination of ¹H, ¹³C NMR, IR, mass spectrometry, microanalyses and for L2, complexes 2 and 4 by single X-ray crystallography. IR spectra of L1–L4 showed characteristic carbonyl peaks between 1689 cm⁻¹ and 1702 cm⁻¹. This feature was useful in determining coordination of L1–L4 to palladium to form the corresponding palladium complexes 1-4. Generally, shifts towards higher frequencies were observed upon coordination of the ligands. For example, the $v_{(C=0)}$ cm⁻¹ were found at 1689 cm^{-1} and 1708 cm^{-1} for **L4** and its corresponding palladium complex, 4, respectively. This is consistent with electron flow from the ligand to the palladium atom [8]. ¹H NMR spectra of all the compounds (L1–L4) and palladium complexes (1–4) showed two characteristic upfield singlets in the range 2.18-2.61 ppm for the two methyl groups on the pyrazolyl unit and triplets between 3.86 and 4.16 ppm corresponding to O-CH₂ in the alkoxy chain. The CH2-protons for the longer alkoxy chains appeared as multiplets between 1.27 ppm and 1.85 ppm. Microanalyses data of complexes **1**-**4** were consistent with the structures shown in Scheme 2.

2.2. Molecular structures of compounds L2, 2, and 4

Single crystals suitable for X-ray analyses for compounds **L2** were grown by slow evaporation of a CH₂Cl₂ solution at RT whereas those of complexes **2** and **4** were grown by slow diffusion of hexane into dichloromethane solution at RT for about 3–4 days. Table 1 shows the crystallographic data whereas Table 2 contains selected bond lengths and bond angles for **L2**, **2**, and **4**. The molecular structures of **L2**, **2** and **4** are depicted in Figs. 1–3, respectively.

The bond distances and bond angles in compound **L2** are typical. The conjugated π -system deviates from planarity due to the steric conflict between the H atom on atom C12 and the lone pair of electrons on atom N1. Consequently the dihedral angles between the pz plane and the plane defined by atoms O1, N2, C6, C7 is 33.62(1)°, and the dihedral angle between the latter plane and the benzene ring is 16.68(9)°.

The Pd atom in both **2** and **4** adopts a slightly distorted square planar geometry, with the pyrazolyl ligands *trans* to each other. In both structures, the Pd atom resides on a crystallographic inversion center, thus only one half of each complex is symmetryindependent. The N–Pd–N and Cl–Pd–Cl angles are linear due to the symmetry, whereas the other angles about the palladium centers range between 88.34 (4)° and 91.66(4)°. The Pd–Npz bond lengths of 2.0301(14) Å and 2.025(2) and Pd–Cl bond distances of 2.3076 (4) Å and 2.3036 (6) Å in compounds **2** and **4** respectively are similar and fall within the normal ranges for these types of bonds [9]. The average Pd–Npz bond length of 2.027(2) Å correlates well





Scheme 2.

with those in the benzenedicarbonyl and benzenetricarbonyl palladium complexes [2.0332(5) Å [5,6]]. This indicates minimal electronic influence from the alkoxy chains in the ligand structure.

The non-planarity of the conjugated π -system in the ligands in **2** and **4** resembles the conformational behaviour of **L2** in the solid state. Namely, the dihedral angles between the pz plane and the plane defined by atoms N2, O1, C6, C7 in **2** is 44.96(8)°, whereas the

Table 1

Crystal data and structure refinement for compounds L2, 2 and 4.

Parameters	L2	2	4
Empirical	$C_{14}H_{16}N_2O_2$	$C_{28}H_{32}Cl_2N_4O_4Pd$	C ₄₈ H ₇₂ Cl ₂ N ₄ O ₄ Pd
Formula weight	244.29	665.88	946.40
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	Pna2 ₁	$P2_1/c$	Р
a/Å	14.8463(13)	10.1753(7)	8.6703(9)
b/Å	7.7038(7)	7.6073(5)	8.8030(9)
c/Å	11.5017(10)	17.9819(12)	16.5208(17)
α	90°	90°	$\alpha = 75.443^{\circ}$
β	90°	90.97°	$eta=76.773^\circ$
γ	90°	90°	$\gamma=78.202^{\circ}$
Volume	1315.5(2) Å ³	1391.72(16) Å ³	1173.5(2) Å ³
Ζ	4	2	1
Density (calculated)	1.233 Mg/m ³	1.589 Mg/m ³	1.339 Mg/m ³
Absorption	0.084 mm^{-1}	0.901 mm ⁻¹	0.556 mm^{-1}
coefficient			
F(000)	520	680	500
Theta range for data collection	2.74–26.37°	2.00-26.38°.	2.42–26.45°.
Reflections collected	5492	18,286	9836
Independent	2551	2853	4769
reflections	[R(int) = 0.0190]	[R(int) = 0.0268]	[R(int) = 0.0839]
Completeness to theta	(26.37°) 98.9%	(26.38°) 99.9%	(26.45°) 98.7%
Absorption	Multi-scan	Multi-scan	Multi-scan
correction	with SADABS	with SADABS	with SADABS
Data/restraints/ parameters	2551/1/166	2853/0/181	4769/0/271
Goodness-of-fit	1.031	1.047	0.901
Final R indices	R1 - 0.0331	R1 - 0.0210	R1 - 0.0361
[I > 2 sigma(I)]	wR2 = 0.0907	wR2 = 0.0506	wR2 = 0.0856
R indices	R1 = 0.0397.	R1 = 0.0256.	R1 = 0.0471.
(all data)	wR2 = 0.0969	wR2 = 0.0534	wR2 = 0.0912
Largest diff.	0.133 and	0.474 and	0.891 and
peak	-0.175 e.Å ⁻³	-0.259 e.Å ⁻³	-0.918 e.Å ⁻³
and hole			

corresponding angle in **4** is $41.70(11)^\circ$. The dihedral angle between the N2, O1, C6, C7 plane and the benzene ring in **2** is $12.18(7)^\circ$, whereas the corresponding angle in **4** spans $23.52(10)^\circ$. In all the three reported structures, the dihedral angles involving the pz group are larger than the angles formed to the benzene ring, which indicates that the conjugated system is easier to disturb around the N–C bond rather than between the carbonyl and benzene ring.

2.3. Evaluation of the palladium complexes as catalysts for the polymerization of ethylene

All the palladium complexes shown in Chart 1 were investigated as potential catalysts for the polymerization of ethylene using MAO as the co-catalyst. This was done to probe the effect of pendant group with stabilizing atom on the catalytic activities of the palladium complexes; by comparing the activities of palladium complexes with no donor atoms (**1–4**) and those with donor atoms (**5–8**) (Table 3). First, we screened all the complexes to establish the structure–activity relationship in the polymerization of ethylene (Table 3). Table 3 reveals that complexes **1** and **2**, **5–8** were active in the polymerization of ethylene, with activities between 130 and 471 kg mol⁻¹ h⁻¹. Complexes **3** and **4** bearing longer alkoxy chains were inactive under similar conditions. ¹³C{¹H} NMR spectra of all the polymers obtained exhibited one signal around 30 ppm, indicating the formation of high density linear polyethylene.

Table 2							
Selected bond lengths	[Å] a:	nd angles	[°	for com	pound I	2 , 2 and	14.

Bond lengths [A]		Angles [°]	
L2			
O(1) - C(6)	1.203(2)	C(2) - N(1) - N(2)	105.15(17)
N(1)-C(2)	1.318(2)	N(1)-N(2)-C(4)	112.02(18)
N(1)-C(4)	1.375(2)	N(1)-N(2)-C(6)	121.53(13)
N(1) - N(2)	2.373(2)	C(4) - N(2) - C(6)	126.42(18)
2			
Pd(1)-N(1)	2.0301(14)	N(1)#-Pd(1)-N(1)	180.00(8)
Pd(1)-Cl(1)	2.3076(4)	N(1) - Pd(1) - Cl(1)	88.34(4)
O(1) - C(6)	1.207(2)	N(1)#-Pd(1)-Cl(1)	91.66(4)
N(2)-C(4)	1.370(2)	N(1)-Pd(1)-Cl(1)#	91.66(4)
N(1) - N(2)	1.379(2)	N(1) - Pd(1) - Cl(1)	88.34(4)
4			
Pd-N(1)	2.025(2)	N(1)-Pd-N(1)#1	179.999(1)
Pd-Cl(1)	2.3036(6)	N(1)-Pd-Cl(1)	88.83(6)
O(1) - C(6)	1.205(3)	N(1)#1-Pd-Cl(1)	91.17(6)
N(1)-C(2)	1.342(3)	N(1)-Pd-Cl(1)#1	91.17(6)
N(1)-N(2)	1.387(2)	Cl(1)-Pd-Cl(1)#1	180.00(3)



Fig. 1. Molecular structure of complex L2 drawn with 50% probability.

The activities found for the active compounds were generally moderate according to the Gibson scale $(10-100 \text{ kg PE mol Pd h}^{-1} \text{ bar}^{-1})$ [10], but lower compared to the benzene-carbonyl [5] and pyridine carbonyl [6] linker pyrazolyl palladium catalysts. This is rather interesting as complexes **1–8** are expected to be sufficiently electrophilic to allow ethylene coordination. In ethylene polymerization mechanism, it has been shown both experimentally and theoretically that the turnover limiting step is the migratory insertion of coordinated ethylene monomer into the Pd–Me bond [2,11–13]. For this insertion to occur, the coordinated ethylene must be in a cis position relative to the coordinated alkyl group. Considering the steric demands of the pyrazolyl ligands in **1–8**. a *cis* conformation *via* a *trans–cis* labilization would be energetically unfavourable. Thus the lower activities of 1-8 could be attributed to the higher migratory insertion barriers of the coordinated ethylene. Using this hypothesis, the trends in activities of 1-8 as depicted in Table 3 would be largely due to steric factors. Catalysts 5–6, containing the smaller furanyl and thiophenyl carbonyl groups showed higher catalytic activities than catalysts 1-4, containing the more sterically demanding alkoxy benzene groups. In deed complexes 3 and 4, containing bulkier hexyl and dodecyl groups were inactive. Similarly, complexes 7 and 8, bearing *tert*-butyl groups on the pyrazolyl unit showed lower catalytic activities of 176 kg mol^{-1} h^{-1} and $125 \text{ kg mol}^{-1} \text{ h}^{-1}$ compared to the methyl analogues **5** and **6** which gave activities of 301 kg mol⁻¹ h⁻¹ and 426 kg mol⁻¹ h⁻¹ respectively.

The nature of the catalyst also affected the molecular weight of the polymers obtained. No determination of the polymer molecular weight was performed on the polymers obtained from catalysts 1-4 due to higher amounts of palladium black deposits. From Table 3, entries 5–8, it is evident that the molecular weight of the polymers decreased with increase in steric bulk in the ligand



Fig. 2. Molecular structure of complex 2 drawn with 50% probability.

backbone. For instance, replacing methyl groups in **4** with *tert*-butyl groups in **7** resulted in a reduction of polymer Mw from 8.41×10^5 g/mol to 5.74×10^5 g/mol. This is in sharp in contrast to the expected trends; where an increase in steric bulk is expected to hinder β -hydride elimination and produce higher molecular weight polymers [2,10,11]. Similar observations have been made by Brookhart et al. using phosphine—imine palladium complexes [14].

Having established the best catalyst system, the effect of Al:Pd ratio on the ethylene polymerization was studied using complex **2** (Table 4). This was done by varying the Al:Pd ratio from 500:1 to 6000:1. The optimum Al:Pd ratio was found to be 4000:1 (Table 4, entry 5). This ratio is quite high compared to those reported for related nitrogen-donor palladium catalysts [15]. The higher amount of MAO required to activate complexes **1–8**, could result from coordination of oxygen and sulfur atoms (furanyl, alkoxy and thiophenyl groups) to the Al centers in the co-catalyst. This assumption is further reinforced by higher activity reported for catalyst **6**, since sulfur (a soft base) does not form stable complexes with Al metal (a hard acid) compared to catalyst **5**, containing a harder oxygen donor.

The Lewis acidity of boron compounds has been utilized to improve the catalytic activities of palladium and nickel catalysts in olefin polymerization reactions [16–19]. To probe if the addition of a boron compound, $B(C_6F_5)_3$, would enhance the activities of our complexes; two equivalents of $B(C_6F_5)_3$ was added to complex **6** and MAO (Table 4, entries 8–9). We observed a significant increase in activity from 62 kg mol⁻¹ h⁻¹ to 462 kg mol⁻¹ h⁻¹ at Al:Pd ratio of 500:1 and 1000:1 respectively (Table 4, entries 2 and 9). This is consistent with increase in electrophilicity of the palladium metal center thus facilitating ethylene coordination [2,10] and hence increase in catalytic activity.

The molecular weights of the polyethylene obtained were also affected by the amount of co-catalyst used. Inspection of Table 4 reveals that an increase in the Al:Pd ratio from 500:1 to 4000:1 resulted in a concomitant increase in Mw from 3.30×10^5 g/mol to 8.01×10^5 g/mol. Beyond this ratio, polymer molecular weight decreases with further increase in the amount of MAO.

3. Conclusions

Several palladium(II) complexes containing (pyrazol-1-yl)-4alkoxy-1-benzene ligands have been successfully prepared and characterized. The ligands are monodentate, forming monometallic complexes in which the ligands are *trans* to each other in the solid state. Activation of these complexes and the furanyl and thiophenyl carbonyl palladium(II) complexes with MAO produced catalysts for the polymerization of ethylene with moderate activities. Generally, the heterocylic carbonyl palladium complexes showed better catalytic activities than the alkoxy carbonyl benzene palladium catalysts. The steric bulk imposed by the heterocylic and alkoxy benzene-carbonyl linkers is largely responsible for the reduced activities of the resultant catalysts. This has the overall effect of hindering the formation of the *cis*-isomers required for the migratory insertion of ethylene to form polyethylene.

4. Experimental

4.1. Materials and instrumentation

All manipulations were performed under a dry, deoxygenated nitrogen atmosphere using standard Schlenk tube techniques. All solvents were analytical grade and were dried and distilled prior to use. Toluene and dichloromethane were dried over sodium-benzophenone and P_2O_5 respectively. The compounds, 4-alkoxybenzoyl chloride (alkoxy = methoxy, ethoxy and hexyloxy), 4-dodecycloxybenzoicacid and



Fig. 3. Molecular structure of complex 4. Selected atoms are labeled while the H atoms are omitted.

3,5-dimethylpyrazole were purchased from Sigma–Aldrich and used as received. The starting materials $[PdCl_2(NCMe)_2]$ and 4-dodecycloxybenzylchloride were prepared following literature procedures [20,21]. The pyrazolyl furoyl and thiophene carbonyl palladium complexes **5**–**8** were prepared according to our published methods [22]. IR spectra were recorded as nujol mulls on a Perkin–Elmer, Paragon 1000 PC FTIR spectrometer. NMR spectra were recorded on a Gemini 2000 instrument (¹H at 200 MHz, ¹³C at 50 MHz). Microanalyses were performed on a Carlo Erba NA analyzer.

4.2. Synthesis of (pyrazolyl)alkoxycarbonyl benzene ligands and their palladium complexes

4.2.1. {3,5-(dimethylpyrazol-1-yl)-4-methoxy-1-carbonyl}benzene (L1)

To a solution of 3,5-dimethylpyrazole (1.41 g, 14.70 mmol) in toluene (50 mL), 4-methoxybenzoyl chloride (2.50 g, 14.70 mmol) and Et₃N (1.00 g, 14.70 mmol) was added. The mixture was refluxed for 24 h and solvent evaporated in *vacuo* to give a white residue. Purification of the crude product using column chromatograph on silica gel with CH₂Cl₂:hexane (4:1) as an eluent afforded an oily product which solidified within 24 h to a white solid. Yield = 2.65 g (78%). ¹H NMR (200 MHz, CDCl₃) δ 2.25 (s, 3H, pz-CH₃); 2.60 (s, 3H, pz-CH₃); 3.86 (s, 3H, O-CH₃(alkoxy)); 6.03 (s, 1H, pz-H); 6.96 (d, 2H, ³J_{HH} = 8.8 Hz, ph); 8.05 (d, 2H, ³J_{HH} = 8.8 Hz, ph). ¹³C NMR (50 MHz, CDCl₃) δ 13.8; 14.2; 55.4; 110.7; 163.2; 167.5. IR (nujol cm⁻¹); v(C= 0) 1702.05. Anal. calcd for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.12; N, 12.17. Found: C, 67.57; H, 6.21; N, 12.18.

4.2.2. {3,5-(dimethylpyrazol-1-yl)-4-ethoxy-1-carbonyl}benzene (**L2**)

Compound **L2** was prepared in a similar manner to **L1** using 4-ethoxybenzoylchloride (1.06 g, 6.29 mmol) and 3,5-dimethylpyrazole (0.60 g, 6.29 mmol). Evaporation of the solvent in *vacuo* gave an oily product which solidified after 24 h to white single crystals suitable for

Table 3					
Ethylene	polymerization	data	for	complexes	1-8 ^a .

Entry	Catalyst	TON ^b	$M_{ m w}{}^{ m c} imes 10^5$	$M_{ m n}{}^{ m c} imes 10^5$	$M_{\rm w}/M_{\rm n}^{\rm c}$
1	1	130	n.d.	n.d.	n.d.
2	2	123	n.d.	n.d.	n.d.
3	3	Trace	n.d.	n.d.	n.d.
4	4	Trace	n.d.	n.d.	n.d.
5	5	301	8.41	4.05	2.08
6	6	426	8.01	3.98	2.01
7	7	176	5.74	2.88	1.99
8	8	125	6.17	1.90	1.90

^a Conditions: [Pd] = 9.76×10^{-6} mol Al:Pd, 4000:1; temperature, 50 °C; time, 2 h; solvent, toluene, 100 mL; pressure, 5 bar.

^b TON in kg of polymer per mol. Pd per h (kg mol⁻¹ h⁻¹).

^c Determined by GPC using polystyrene standards. n.d., not determined.

X-ray analyses. Yield = 1.32 g(86%). ¹H NMR (200 MHz, CDCl₃) δ 1.12 (t, 3H, ³*J*_{HH} = 6.6 Hz, CH₃(alkoxy)); 2.26 (s, 3H, pz-CH₃); 2.61 (s, 3H, pz-CH₃); 4.13 (m, 2H, O-CH₂(alkoxy)); 6.04 (s, 1H, pz-H); 6.96 (d, 2H, ³*J*_{HH} = 8.8 Hz, ph); 8.06 (d, 2H, ³*J*_{HH} = 8.8 Hz, ph). ¹³C NMR (50 MHz, CDCl₃) δ 13.3; 13.7; 14.2; 63.2; 110.7; 162.1; 167.0. IR (nujol cm⁻¹); v(C=O) 1691.80. Anal. calcd for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.48; H, 6.68; N, 12.19.

4.2.3. {3,5-(dimethylpyrazol-1-yl)-4-hexyloxy-1-carbonyl}benzene (L3)

Compound **L3** was prepared in a similar manner to **L1** by reacting 4-(hexyloxy)benzoyl chloride (1.00 g, 3.08 mmol) and 3,5dimethylpyrazole (0.30 g, 3.08 mmol). Purification by column chromatograph on silica gel using CH₂Cl₂:hexane (4:1) as an eluent afforded an oily product which solidified to a white solid after 24 h. Yield = 0.74 g (80%). ¹H NMR (200 MHz, CDCl₃) δ 0.94 (t, 3H, ³J_{HH} = 6.6 Hz, CH₃(alkoxy)); 1.47 (m, 6H, CH₂(alkoxy)); 1.84 (m, 2H, CH₂(alkoxy)); 2.26 (s, 3H, pz-CH₃); 2.61 (s, 3H, pz-CH₃); 4.06 (t, 2H, ³J_{HH} = 6.6 Hz, O-CH₂(alkoxy)); 6.04 (s, 1H, pz-H); 6.95 (d, 2H, ³J_{HH} = 8.8 Hz, ph); 8.05 (d, 2H, ³J_{HH} = 8.8 Hz, ph). ¹³C NMR (50 MHz, CDCl₃) δ 14.8; 23.3; 26.3; 29.8; 32.2; 68.9; 111.3; 114.9; 125.7; 132.9; 134.7; 145.7; 152.3; 163.6; 171.0. IR (nujol cm⁻¹); v(C=O) 1689.14. Anal. calcd for C₁₈H₂₄N₂O₂: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.31; H, 8.16; N, 9.04.

4.2.4. 3,5-dimethylpyrazol-1-yl-4-dodecycloxy-1-carbonyl benzene (L4)

Compound **L4** was prepared in a similar manner to **L1** using 4-(dodecycloxy)benzoylchloride (1.00 g, 3.08 mmol) and 3,5dimethylpyrazole (0.30 g, 3.08 mmol). Removal of solvent under vacuum produced **L4** as a white solid. Yield = 0.97 g (82%). ¹H NMR (200 MHz, CDCl₃) δ 0.93 (t, 3H, ³*J*_{HH} = 6.6 Hz, CH_{3(alkoxy)}); 1.23 (m, 18H, CH_{2(alkoxy)}); 1.74 (m, 2H, CH_{2(alkoxy)}); 2.26 (s, 3H, pz-CH₃); 2.61

Table 4	
Effect of Al:Pd ratio on ethylene polymerization activity of complex 2^a .	

Entry	Al:Pd	TON ^b	$M_{ m w}{}^{ m c} imes 10^5$	$M_{\rm n}{}^{\rm c} imes 10^5$	$M_{\rm w}/M_{\rm n}^{\rm c}$
1	500:1	24	3.30	1.71	1.93
2	1000:1	62	5.53	2.85	1.94
3	2000:1	104	5.83	2.89	2.01
4	3000:1	126	7.15	3.45	2.07
5	4000:1	426	8.01	3.98	2.01
6	5000:1	471	4.89	2.05	2.38
7	6000:1	141	5.38	1.85	2.90
8 ^d	500:1	48	2.73	1.34	1.94
9 ^d	1000:1	462	4.19	2.06	2.07

^a Conditions: Complex **6**; [Pd] = 9.76×10^{-6} mol; temperature, 50 °C; time, 2 h; solvent, toluene; pressure, 5 bar.

^b TON in kg of polymer per mol. Pd per h (kg mol⁻¹ h⁻¹).

^c Determined by GPC using polystyrene standards.

^d $B(C_6F_5)_3$ used in addition to MAO.

(s, 3H, pz-CH₃); 4.05 (t, 2H, ${}^{3}J_{HH} = 6.6$ Hz, O–CH_{2(alkoxy)}); 6.04 (s, 1H, pz-H); 6.95 (d, 2H, ${}^{3}J_{HH} = 8.8$ Hz, ph); 8.05 (d, 2H, ${}^{3}J_{HH} = 8.8$ Hz, ph). 13 C NMR (50 MHz, CDCl₃) δ 13.31; 22.2; 31.4; 67.7; 110.2; 114.4; 124.9; 137.4; 145.7; 152.3; 162.4; 167.6. IR (nujol cm⁻¹); v(C=O) 1689.14. Anal. calcd for C₂₄H₃₆N₂O₂: C, 76.96; H, 9.66; N, 7.28. Found: C, 75.42; H, 10.42; N, 7.30.

4.2.5. Synthesis of [Pd(L1)₂Cl₂] (**1**)

To a solution of [Pd(NCMe)₂Cl₂] (0.15 g, 0.58 mmol) in dichloromethane (30 mL), 3,5-dimethylpyrazolyl-4-methoxy-1-carbonyl benzene, **L1** (0.27 g, 1.16 mmol) was added. The resultant orangeyellow solution was stirred at room temperature for 24 h. The solution was then concentrated to 15 mL and the product precipitated by addition of hexane to give complex **1** as an analytically pure yellow solid. Yield = 0.20 g (53%).¹H NMR (200 MHz, CDCl₃) δ 2.18 (s, 3H, pz-CH₃); 2.32 (s, 3H, pz-CH₃); 3.91 (s, 3H, O-CH_{3(alkoxy})); 5.95 (s, 1H, pz-H); 7.07 (d, 2H, ³J_{HH} = 8.8 Hz, ph); 7.99 (d, 2H, ³J_{HH} = 8.4 Hz, ph). IR (nujol cm⁻¹); v(C=O) 1698.31. Anal. calcd for C₁₃H₁₄ Cl₂N₂O₂Pd: C, 48.90; H, 4.42; N, 8.78. Found: C, 48.58; H, 3.94; N, 8.37. Complexes **2–4** were prepared following the procedure

described for 1.

4.2.6. Synthesis of $[Pd(L_2)_2Cl_2]$ (2)

Ligand **L2** (0.27 g, 1.09 mmol) and [Pd(NCMe)₂Cl₂] (0.14 g, 0.54 mmol). Slow diffusion of hexane in to a dichloromethane solution of **2** at $-4 \degree$ C produced yellow single crystals suitable X-ray analysis. Yield = 0.23 g (63%). ¹H NMR (200 MHz, CDCl₃) δ 1.12 (t, 3H, ³*J*_{HH} = 6.6 Hz, CH_{3(alkoxy)}); 2.26 (s, 3H, pz-CH₃); 2.61 (s, 3H, pz-CH₃); 4.21 (m, 2H, O-CH_{2(alkoxy)}); 5.96 (s, 1H, pz-H); 7.05 (d, 2H, ³*J*_{HH} = 8.2 Hz, ph); 7.97 (d, 2H, ³*J*_{HH} = 8.8 Hz, ph). IR (nujol cm⁻¹); v(C=O) 1705.89. Anal. calcd for C₁₄H₁₆Cl₂N₂O₂Pd: C, 50.50; H, 4.42; N, 8.41. Found: C, 50.37; H, 4.45; N, 8.09.

4.2.7. Synthesis of [Pd(L3)₂Cl₂] (3)

Compound **L3** (0.71 g, 2.35 mmol) and Pd(NCMe)₂Cl₂ (0.31 g, 1.18 mmol). A yellow solid product was obtained. Yield = 0.38 g (42%). ¹H NMR (200 MHz, CDCl₃) δ 0.84 (t, 3H, ³*J*_{HH} = 6.6 Hz, CH_{3(alkoxy)}); 1.42 (m, 6H, CH_{2(alkoxy)}); 1.94 (m, 2H, CH_{2(alkoxy)}); 2.17 (s, 3H, pz-CH₃); 2.31 (s, 3H, pz-CH₃); 4.09 (t, 2H, ³*J*_{HH} = 6.6 Hz, O-CH_{2(alkoxy)}); 5.94 (s, 1H, pz-H); 7.05 (d, 2H, ³*J*_{HH} = 8.8 Hz, ph); 7.97 (d, 2H, ³*J*_{HH} = 8.8 Hz, ph). IR (nujol cm⁻¹); v(C=O) 1705.89. Anal. calcd for C₁₈H₂₄Cl₂N₂O₂Pd: C, 55.87; H, 6.22; N, 7.20. Found: C, 56.07; H, 5.91; N, 7.20.

4.2.8. Synthesis [Pd(L4)₂Cl₂] (4)

Compound **I4** (0.56 g, 1.45 mmol) and [Pd(NCMe)₂Cl₂] (0.19 g, 0.73 mmol). A yellow solid product was obtained. Slow diffusion of hexane in to a dichloromethane solution of **4** at -4 °C produced yellow single crystals suitable X-ray analysis. Yield = 0.50 g (73%). ¹H NMR (200 MHz, CDCl₃) δ 0.97 (t, 3H, ³*J*_{*HH*} = 6.6 Hz, CH_{3(alkoxy)}); 1.13 (m, 18H, CH_{2(alkoxy)}); 1.71 (m, 2H, CH_{2(alkoxy)}); 2.19 (s, 3H, pz-CH₃); 2.37 (s, 3H, pz-CH₃); 4.09 (t, 2H, ³*J*_{*HH*} = 6.4 Hz, O-CH_{2(alkoxy)}); 5.95 (s, 1H, pz-H); 7.05 (d, 2H, ³*J*_{*HH*} = 8.6 Hz, ph); 7.97 (d, 2H, ³*J*_{*HH*} = 8.8 Hz, ph). IR (nujol cm⁻¹); v(C=O) 1602.28. Anal. calcd for C₂₄H₃₆Cl₂N₂O₂Pd: C, 60.91; H, 7.78; N, 5.92. Found: C, 60.41; H, 7.78; N, 5.97.

4.3. X-ray crystallography

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_a ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. A typical description is given here for **L2**. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 s per frame. A total of 42 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program [23]. The final cell constants were calculated from a set of 3011 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. A total of 5429 data were harvested by collecting three sets of frames with 0.25° scans in ω with an exposure time 40 s per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. The systematic absences in the diffraction data were consistent for the space groups *Pnma* and *Pna2*₁. The *E*-statistics strongly suggested the non-centrosymmetric space group Pna21 that yielded chemically reasonable and computationally stable results of refinement. A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining nonhydrogen atoms were located in an alternating series of leastsquares cycles and difference Fourier maps. 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 neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 166 parameters against 2551 data resulted in residuals R (based on F^2 for $I > 2\sigma$) and wR (based on F^2 for all data) of 0.0331 and 0.0969, respectively. The final difference Fourier map was featureless.

4.4. General procedure for ethylene polymerization

Ethylene polymerization was performed by loading the required amount of the respective complex and an equivalent amount of methylaluminoxane (MAO) in a 300 mL stainless steel autoclave inside a nitrogen-purged glove box. The autoclave was then sealed, removed from the glove box and mounted on the reactor. The autoclave was flushed three times with ethylene and heated to 50 °C. The desired ethylene pressure was set and a constant flow maintained throughout the reaction time. At the end of the polymerization reaction, the ethylene supply was closed, and excess ethylene vented. The reaction was quenched by addition of ethanol and the polymer was filtered, and 2 M HCl (40 mL) added to remove excess Al or Pd. The pure polymeric material was filtered off and dried in an oven at 60 °C until a constant mass was achieved. The number- and weight-average molecular weights $(M_n \text{ and } M_w)$ and polydispersity (M_w/M_n) of polymers were determined by high temperature gel permeation chromatography (GPC) (1.2.4trichlorobenzene, 160 °C, rate = 1.00 mL/min) on GPC220 instrument using polystyrene standards. High temperature ¹³C NMR spectra in 1,2,3-trichlorobenzene/benzene-d₆ were performed on a Varian 2000 Gemini instrument (50.3 MHz).

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Appendix A. Supplementary material

CCDC numbers; 883906, 883908 and 883907, contains the supplementary crystallographic data for compounds **L2**, **2** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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