Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 241 (2005) 93–100
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Pyridine linker pyrazolyl palladium complexes: Synthesis, characterization and ethylene polymerization activity

M. Sarah Mohlala [a], Ilia A. Guzei [b], James Darkwa [a,*], Selwyn F. Mapolie [a]

[a] *Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa*
[b] *Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, USA*

Received 13 December 2004; received in revised form 11 May 2005; accepted 23 June 2005
Available online 15 August 2005

Abstract

A series of pyrazolyl compounds with 2,6-pyridinedicarbonyl linker, $\{RR'pz(CO)\}_2py$, R = R′ = ^{t}Bu (**L1**); R = R′ = Me (**L2**); R = R′ = H (**L3**), R = H, R′ = Me (**L4**) has been prepared from the reaction of 2,6-pyridinedicarbonyl chloride with the appropriate pyrazole and a mild base. Ligands **L1**–**L3** reacted with $Pd(NCMe)_2Cl_2$ to form mononuclear complexes while the reaction with **L4** produced an intractable product. Complexes **1** and **2** were tested for their catalytic activities for the polymerization of ethylene after activation with methylaluminoxane (MAO). Active polymerization catalysts were formed in situ with MAO and that catalyzed the polymerization of ethylene to high-density linear polyethylene. The effects of co-catalyst concentration and temperature are reported. The optimum co-catalyst to catalyst ratio is 3000:1 and catalyst activity decreases above 40 °C due to catalyst deactivation.

Keywords: Pyridine pyrazolyl ligand; Palladium complexes; X-ray structures; Ethylene polymerization catalysis

1. Introduction

The last decade has seen a tremendous surge in the development of late transition metal catalyzed olefin polymerization chemistry. Two recent reviews on this subject demonstrate the extent of research activities in this area [1,2]. Much of the focus has been on nitrogen donor complexes that incorporate α-diimine [3] or bipyridine [4] ligands precisely because their cationic metal complexes, which are the active catalysts in the polymerization reaction, are highly electrophilic. These nitrogen donor catalysts exhibit high catalytic activities due to their electrophilic nature. A key discovery for the α-diimine ligand catalysts is the recognition that bulky substituents on the ligand blocks apical coordination sites and prevents β-hydrogen elimination that normally leads to the formation of oligomers [5]. Thus, a combination of electronic and steric factors defines the polymerization reaction.

Whereas electronic factors affect the rate of propagation (k_p), steric factors affect the rate of chain transfer (k_{ct}). The balance between these two competing factors therefore determine the microstructure and molecular weight of polymers produced with these nitrogen ligand catalysts. Catalysts with sterically encumbering substituents produce high molecular weight polymers, implying that k_p is greater than k_{ct} [6]. For catalysts containing α-diimine ligands this observation is generally true. However, we have recently discovered that pyrazole nickel and palladium complexes and pyrazolyl palladium complexes, without bulky axial ligands, produce high molecular weight polyethylene [7]. The high molecular weight polyethylene produced with pyrazole based catalysts therefore suggest k_p is much greater than k_{ct} in the pyrazole based ethylene polymerization reactions, because the cationic nickel and palladium species that catalyze the reactions are more electrophilic than catalysts containing α-diimine ligands. This is especially true for catalysts with pyrazolyl ligands.

Our approach to producing catalysts with enhanced electrophilic metal centres is based on using linkers for pyrazolyl

* Corresponding author. Tel.: +27 219593053; fax: +27 219593055.
E-mail address: jdarkwa@uwc.ac.za (J. Darkwa).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.06.040

units that have electron-withdrawing functional groups. This approach first used benzenedicarbonyl linkers [7b] and produced nitrogen donor ligands that had the right donor properties to form bimetallic pyrazolyl complexes. The formation of bimetallic complexes is a sign that the donor behaviour of these ligands is only strong enough to stabilize the metal centres, with the support of bridging chlorides. There are a number of questions that arise from these findings. One of them is the effect a heterocyclic linker that has a potential donor atom would have on the structures and the chemistry of pyrazolyl complexes with such linkers. This report answers this question.

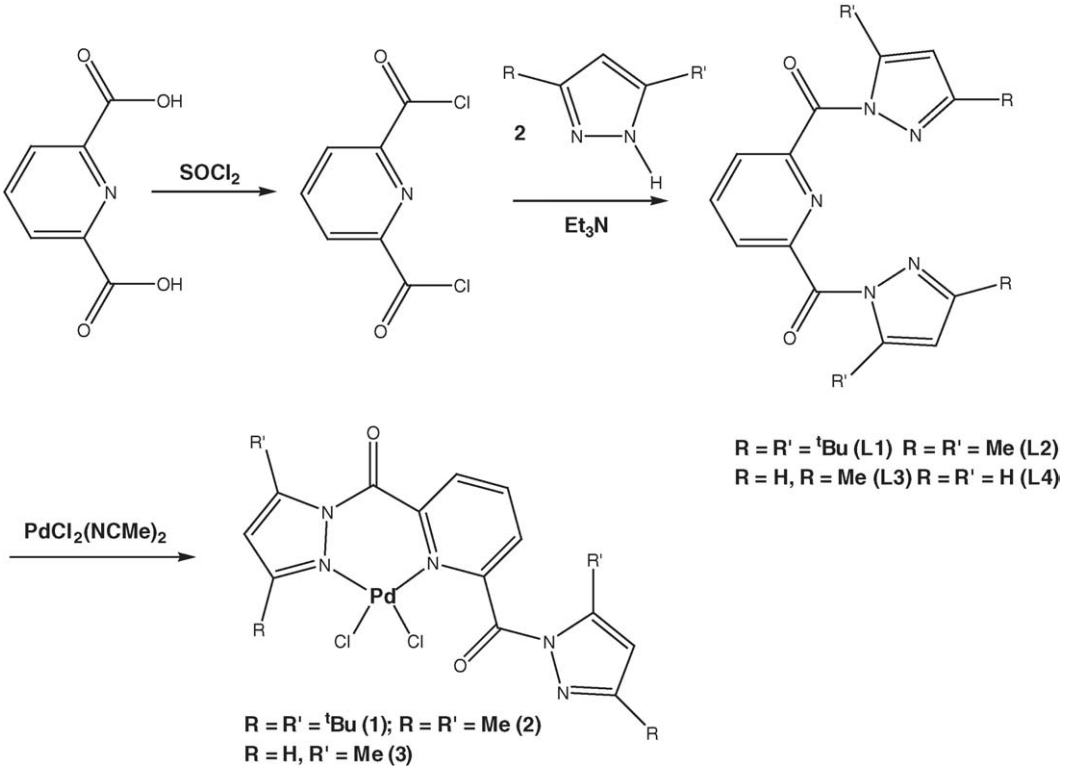
2. Results and discussion

2.1. Synthesis of ligands and complexes

Compounds **L1**–**L4** were synthesized from the reaction of 2,6-pyridinedicarbonyl dichloride with 3,5-ditertiarybutylpyrazole, 3,5-dimethylpyrazole, 3-methylpyrazole and pyrazole respectively; using the procedure recently reported by us [7b] (Scheme 1). Analytically pure compounds were obtained after purification by chromatography on silica gel in 40–70% yield.

Compounds **L1**–**L4** are very stable in air and can be stored at room temperature for a long period of time. These compounds (**L1**–**L4**) were characterized by mutlinuclear NMR and IR spectroscopy, as well as by microanalysis and X-ray crystallography for **L3**. ^{1}H NMR spectra of **L1** and **L2** show two singlets associated with the tertiarybutyl or methyl protons in positions 3 and 5 of the pyrazolyl ring, a singlet for the proton in position 4 of the pyrazolyl ring (**L1** and **L2**), a singlet for the methyl group at position 3 and two doublets at positions 4 and 5 of the pyrazolyl ring for **L3** and two doublets and a triplet for the pyrazolyl protons in **L4**. In addition, all the ligands (**L1**–**L4**) show multiplets (7.69–7.84 ppm) for pyridinyl protons (**L1**–**L4**). Infrared spectra of **L1**–**L4** have the characteristic carbonyl stretching frequencies in the 1680–1716 cm^{-1} range.

Complexes **1**–**3** were prepared by the reaction of ligands **L1**–**L3** with $PdCl_2(NCMe)_2$ in moderate yields of 58–63% (Scheme 1). However, no reaction was observed between **L1** and PdClMe(COD) during attempts to synthesize PdClMe(**L1**) (**1**). This is consistent with our earlier findings that bis(pyrazolylcarbonyl)benzene ligands do not react with PdClMe(COD) [7b]. The reaction of **L4** with $PdCl_2(NCMe)_2$ gave an intractable product and was not pursued further. With the exception of **1**, which is a crystalline orange solid, all the other complexes were isolated as pinkish-orange powders; insoluble in common organic solvents. Complex **2** is, however, soluble in dimethylsulfoxide (DMSO) but complex **3** is insoluble in DMSO. Because of the insoluble nature of complexes **2** and **3** in common organic solvents, the proposed structures of these compounds are mainly deduced from the elemental analysis, which suggests that it has one palladium and one **L4** ligand, indicating complex **3** has a structure similar to complex **1**.



Scheme 1.

The ^{1}H NMR spectrum for complex **1** is characteristic of the bonding mode of the bis(pyrazolylcarbonyl)pyridinyl ligands. Instead of one singlet associated with pyrazolyl backbone proton, there are two singlets (6.21 and 6.38 ppm) for the pyrazolyl backbone protons with equal intensity. In addition, there are four different peaks for the tertiarybutyl protons at positions 3 and 5 of the pyrazole ring. The infrared spectrum of **1** shows two carbonyl groups at 1727 and 1712 cm^{-1}. This spectroscopic data suggests that the palladium metal is coordinated to only one of the two pyrazolyl units in **L1**, leaving the other pyrazolyl unit uncoordinated. Single crystal X-ray crystallography later confirmed this. The ^{1}H NMR spectrum for complex **2** in DMSO has a similar pattern as that of **1**; hence **2** should have the same structure as **1**.

2.2. *Molecular structures of **L3** and **1***

Single crystals of **L3** were obtained from a solution of **L3** in a 1:2 mixture of CH_2Cl_2 and hexane at −15 °C, and crystals of **1** were obtained by a slow evaporation of CH_2Cl_2 solution of **1** at room temperature. The crystal data, together with the data collection and structure refinement parameters are presented in Table 1 and selected bond lengths and bond angles are presented in Table 2. Molecular structures of **L3** and **1** are shown in Figs. 1 and 2 respectively. The structure of **L3** has a two-fold symmetry (C_2). Even though **L3** was prepared from 3-MepzH its structure has the methyl substituents in position 5 of the pyrazolyl units. Dynamic equilibrium between 3- and 5-MepzH is well established [7b,c] and these tautomers allows **L3** to adopt the least sterically hindered isomeric form during its synthesis which results in the structure of **L3** being identical to that of 1,3-bis(3-methylpyrazolyl-1-carbonyl)benzene [7b]. In spite of the different linker in **L3**, its bond parameters are quite similar and comparable to pyrazolyl ligands with benzene linkers. For example the N–N distances in 1,3-bis(3,5-ditert-butylpyrazolylcarbonyl)benzene (1.387(3) and 1.385(3) Å) are similar to N–N distances in **L3** (1.3812(14) Å). Therefore, the different linkers in the two types of pyrazolyl ligands do not have any significant effect on their bond parameters.

Table 1
Crystal data and structure refinement for **L3** and **1**

	L3	**1**
Empirical formula	$C_{15}H_{13}N_5O_2$	$C_{29}H_{41}Cl_2N_5O_2Pd$
Formula weight	295.30	668.97
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$
a (Å)	14.864(3)	9.2796(9)
b (Å)	14.399(2)	14.9316(12)
c (Å)	6.8726(12)	22.369(2)
α (°)	90.00	90.00
β (°)	103.613(3)	90.574(3)
γ (°)	90.00	90.00
V (Å^3)	1429.5(4)	3099.2(5)
Z	4	4
D_c (Mg m^{-3})	1.372	1.434
μ(Mo Kα) (mm^{-1})	0.096	0.805
Crystal size (mm)	0.53 × 0.42 × 0.36	0.40 × 0.30 × 0.20
Absorption correction	Multiscan	Empirical
T_{max}/T_{min}	0.9662/0.9508	1.00/0.54
$R(F)$ (%) [$I > 2\sigma(I)$]	3.76	4.79

Table 2
Bond lengths (Å) and angles (°) for **L3** and **1**

L3			
Bond lengths			
O(1)–C(5)	1.2140(15)	N(1)–C(2)	1.3226(16)
N(1)–N(2)	1.3812(14)	N(2)–C(4)	1.3781(16)
N(2)–C(5)	1.3922(17)	N(3)–C(6)	1.3392(14)
C(1)–C(2)	1.4945(18)	C(5)–C(6)	1.5067(16)
Bond angles			
C(4)–N(2)–C(5)	125.50(10)	N(1)–N(2)–C(5)	121.88(10)
N(1)–C(2)–C(1)	120.42(11)	C(3)–C(2)–C(1)	127.94(12)
O(1)–C(5)–N(2)	120.49(11)	O(1)–C(5)–C(6)	121.70(11)
N(2)–C(5)–C(6)	117.81(10)	N(3)–C(6)–C(7)	124.16(11)
N(3)–C(6)–C(5)	113.38(11)	C(7)–C(6)–C(5)	122.20(11)
1			
Bond lengths			
Pd–N(1)	2.062(4)	N(3)–C(17)	1.350(6)
Pd–N(3)	2.032(4)	N(3)–C(13)	1.358(6)
Pd–Cl(1)	2.2861(13)	N(4)–N(5)	1.388(5)
Pd–Cl(2)	2.2581(12)	N(4)–C(18)	1.397(6)
N(1)–N(2)	1.396(5)	C(12)–C(13)	1.509(6)
N(1)–C(12)	1.412(6)	C(17)–C(18)	1.527(6)
Bond angles			
N(3)–Pd–N(1)	83.87(15)	C(5)–N(1)–Pd	135.6(3)
N(3)–Pd–Cl(2)	92.20(10)	N(2)–N(1)–Pd	112.2(3)
N(1)–Pd–Cl(1)	175.76(11)	C(17)–N(3)–Pd	126.1(3)
N(3)–Pd–Cl(1)	173.11(10)	C(13)–N(3)–Pd	115.0(3)
N(1)–Pd–Cl(1)	93.05(11)	N(1)–N(2)–C(12)	118.7(4)
Cl(2)–Pd–Cl(1)	90.69(5)	N(3)–C(13)–C(12)	121.7(4)

In contrast to the bimetallic structures of bis(pyrazolyl-1-carbonyl)benzene palladium chloride complexes [7b], **1** has a mononuclear structure, with two terminal chloride ligands (Cl(l) and Cl(2)) and two nitrogen atoms (N(3) and N(1)) of the pyridine ring and pyrazolyl unit bonded to the palladium in a distorted square planar geometry. The Pd–Cl distances in **1** (2.286(13) Å) and (2.258(12) Å) fall within the usual ranges of terminal Pd–Cl bonds. For example, in dichloro[(4*S*,7*R*)-7,8,8-trimethyl-2-(pyridin-2-ylmethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole)]palladium(II), the two terminal Pd–Cl bond distances measured 2.289(2) and 2.284(2) Å [8]. The two Pd–N(pz) (2.062(4) Å) and Pd–N(py) (2.032(4) Å) in **1** are also similar to the distances found in dichloro[(4*S*,7*R*)-7,8,8-trimethyl-2-(pyridin-2-ylmethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole)]palladium(II) (Pd–N(pz) (2.035(5) Å) and Pd–N(py) (2.023(5) Å) [8]; but slightly shorter than the average Pd–N(pz) distance of 2.11 Å calculated for 59 Pd–N(pz) distances reported to the Cambridge Structural Database (CSD) [9], though the difference is not statistically significant. Bond angles about the Pd centre in **1** differ by at least 1.2° from those of dichloro[(4*S*,7*R*)-7,8,8-trimethyl-2-(pyridin-2-ylmethyl-

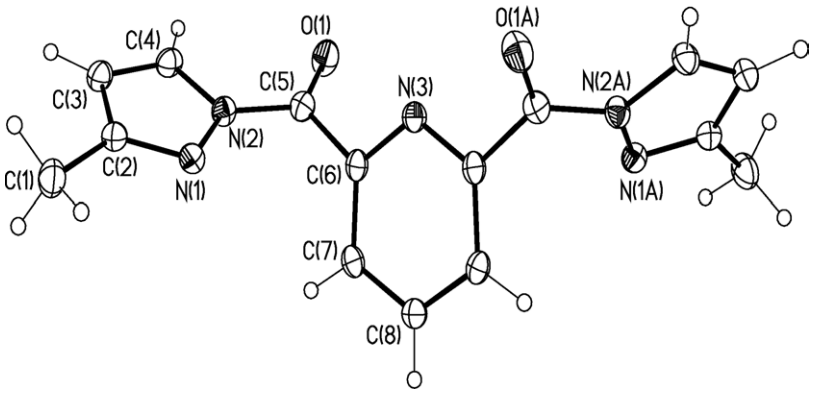


Fig. 1. Molecular structure of 2,6-bis(3-methylpyrazolylcarbonyl)pyridine (**L3**).

4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole)]palladium(II) due to the steric effect of the uncoordinated pyrazolyl unit in **1**. Overall there is not much difference in bond parameters caused by the presence of the carbonyl groups in **1** versus the methylene group in dichloro[(4*S*,7*R*)-7,8,8-trimethyl-2-(pyridin-2-ylmethyl-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole)]palladium(II).

2.3. Ethylene polymerization

Ethylene polymerization reactions were performed using complexes **1** and **2**, with methylaluminoxane (MAO) as a co-catalyst. Because of the poor solubility complex **3** was not used in the polymerization experiments. The polymerization data are in Table 3. Complex **1** formed the most active catalyst. High temperature ^{1}H and ^{13}C NMR spectra of the polyethylene isolated from these reactions have chemical shifts of 1.28 and 30.00 ppm, respectively, and melting points determined by DSC were in the range 134–138 °C. These data identified the polymers isolated as linear, with no branching. Typically ethylene polymerization late transition metal catalysts with nitrogen donors form branched polymers [4a,6,10], with the exception of pyrazole and pyrazolyl ligand nickel and palladium catalysts [7b,c]. A critical feature in the formation of linear polymers is that the rate of chain transfer (k_{ct}) is much slower than the rate of chain propagation (k_p).

The polymers isolated have molecular weights ranging from 4×10^5 (Table 3, entry 10) to 2×10^6 (Table 3, entry 1). These results are comparable to high molecular weights of polyethylene produced by α-diimine Ni(II) (3×10^5), Pd(II) (1×10^5) [3a], pyridylimine Pd(II) (1×10^6) [11] and tris(pyrazolylcarbonyl)Pd(II) (1×10^6) [7b] catalyst systems. Unimodal polymer molecular weight distribution from gel permeation chromatography (GPC) indicates there is only one kind of active catalyst species in the polymerization reactions. Details of how changes in polymerization

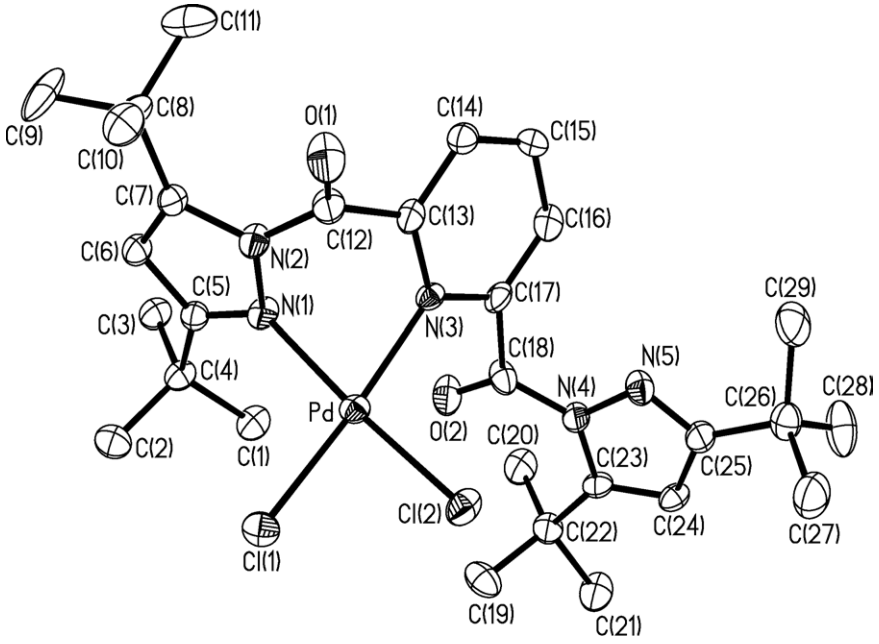


Fig. 2. Molecular structure of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridine palladium dichloride (**1**).

Table 3
Ethylene polymerization data with **1** and **2** as catalysts[a]

Catalyst	Entry	Al:Pd ratio	Temperature (°C)	TON (kg PE/mol Pd h)	T_m[b] (°C)	M_n[c] (10^5)	M_w/M_n
1	1	1000:1	25	228.9	137.20	5.21	3.89
1	2	2000:1	25	691.1	137.25	4.84	3.50
1	3	3000:1	25	844.8	137.65	4.67	3.50
1	4	4000:1	25	803.3	137.52	4.74	3.90
1	5	3000:1	30	135.7	137.58	3.72	3.47
1	6	3000:1	40	714.3	136.80	2.97	3.51
1	7	3000:1	45	662.0	137.41	3.02	3.13
1	8	3000:1	50	507.1	136.45	2.60	3.57
1	9	3000:1	60	529.1	136.13	2.30	3.23
1	10	3000:1	70	484.4	134.04	1.38	3.03
2	11	3000:1	25	24.5	138.58	3.75	3.89

[a] Polymerization conditions: [Pd] = 4.48×10^{-6} M (**1**), 5.99×10^{-6} mmol (**2**); MAO as co-catalyst; 150 mL toluene; 5 atm ethylene pressure; 3 h.
[b] Determined by differential scanning calorimetry (DSC).
[c] Molecular weight data was determined by GPC vs. polystyrene standards at 145 °C.

conditions affect the polymerization reaction are discussed below.

2.3.1. Effect of catalysts on polymerization

Our catalysis studies with ethylene were mainly focused on **1**. The results in Table 3 show that **1** is by far a better catalyst than **2**. Complex **1** has a moderate catalytic activity (TON = 844 kg PE/mol Pd h) and gave a high molecular weight polymer (1.6×10^6). Complex **2** (Table 3) shows a much lower catalytic activity compared to **1**. The presence of carbonyl groups in the ligands was expected to affect the electrophilicity of the complex to give faster monomer insertion, which in turn should lead to high catalytic activities. The results obtained with catalysts **1** and **2** show lower activity than the pyrazolyl catalysts, $[Pd_2(3,5\text{-}^tBupzCO)_3(\mu\text{-}Cl)_2Cl_2]$ (TON = 1099 kg PE/mol Pd h) [7b] and $[Pd(3,5\text{-}^tBu_2pz)_2Cl_2]$ (TON = 1006 kg PE/mol Pd h) [7a], reported by Darkwa and co-workers. The lower catalytic activities of catalysts **1** and **2** compared to the two catalysts, $[Pd_2(3,5\text{-}^tBupzCO)_3(\mu\text{-}Cl)_2Cl_2]$ and $[Pd(3,5\text{-}^tBupz)_2Cl_2]$ [7a,b], could be due to a lower electrophilicity displayed by catalysts **1** and **2**.

2.3.2. Effect of co-catalyst to catalyst molar ratio (Al:Pd) on polymerization

To examine of co-catalyst to catalyst ratio in the polymerization, several experiments in which the co-catalyst to catalyst (Al:Pd) molar ratio was varied from 1000:1 to 4000:1 were carried out (Table 3, entries 1–4) using **1** as the catalyst. Catalytic activity increased with increase in the Al:Pd ratio, with the highest activity obtained at 3000:1 molar ratio of Al:Pd (entry 3) (844 kg PE/mol Pd h) and thereafter decreased with increasing Al:Pd ratio. We observed a similar trend for ethylene polymerization catalyzed by $[Pd_2(3,5\text{-}^tBupzCO)_3(\mu\text{-}Cl)_2Cl_2]$ [7b]. Even though co-catalyst/catalyst ratio in MAO activated catalyst system is usually high, the ratio used here is higher than usual. It is possible that the larger concentration of MAO needed to effectively activate **1** is due to MAO reacting with both the uncoordinated pyrazolyl unit in **1** and the palladium centre. As such optimum activation of the catalyst is not reached until the Al:Pd ratio becomes 3000:1. The formation of Al–pyrazolyl adducts when MAO is used to activate **1** is not unexpected as formation of Al–nitrogen adducts with nitrogen containing ligands is well documented [12]. Examples of pyrazolyl–Al compounds have also been reported in the literature $[Al(1,3,5\text{-}Me_3pz)]$ [13] and $[Tp^*_2Al][AlCl_4]$ (Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate) [14]. Therefore, the possibility of MAO's catalytic activity reduction due to its binding to uncoordinated pyrazolyl moieties cannot be ruled out.

2.3.3. Effect of temperature on polymerization

The effect of temperature on ethylene polymerization was investigated using catalyst **1** (Table 3, entries 5–10). An initial increase in catalyst activity was observed in increasing temperature from 30 to 40 °C (135 kg PE/mol Pd h (30 °C) to 714 kg PE/mol Pd h (40 °C)), but the catalytic activity decreased as temperature increased with activity of 484 kg PE/mol Pd h at 70 °C. Such decrease in activity as temperature rises is associated with decomposition of the catalyst. Similar temperature effects on catalytic activity have been reported when the binuclear pyridylimine palladium(II) [1], diimine nickel(II) [10a] and Cp_2ZrCl_2 [15] were used to catalyze the polymerization of ethylene with MAO as a co-catalyst. The molecular weights of polyethylene produced by **1** are strongly dependent on temperature (Table 3); the higher the temperature the lower the molecular weight of polyethylene produced. Increasing reaction temperature enhances chain transfer, leading to shorter polymer chains and hence lower molecular masses. The polymer polydispersity indices were found to be in the range 3.03 and 3.90, indicating no significant influence of temperature on polymer molecular weight distribution as temperature was varied. Although the polymer polydispersity indices found are high compared to polymers obtained from other single-site late transition metal catalysts, there is no evidence to suggest that our catalysts are multi-site. GPC traces show only one peak, typical of a unimodal distribution characteristic of single-site

catalysts and therefore our catalysts can only be considered to be single-site in spite of the slightly higher than usual polydispersity indices.

3. Conclusions

In spite of the potential of the pyridine linker pyrazolyl ligands to be tridentate, they form monometallic complexes with one uncoordinated pyrazolyl unit. The two complexes investigated (**1** and **2**) can be activated with MAO to form active catalysts for the polymerization of ethylene to form high-density linear polyethylene, however their catalytic activities are lower than the benzene linker analogues. The best catalyst was found to be **1**, the most soluble catalyst in the polymerization solvent; as such the solubility of the catalysts could be a factor in the activity trend observed for these catalysts. Catalytic activities were also found to be sensitive to the co-catalyst to catalyst ratio as well as temperature. The best co-catalyst to catalyst ration is 3000:1 and above 40 °C catalyst decomposition lowers activity. Polymerization temperature strongly affects polymer molecular weight, with lower molecular weight polymers produced as temperature increased from 25 to 70 °C; this trend is normal.

4. Experimental

4.1. Materials and instrumentation

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Dichloromethane (CH_2Cl_2) was dried by distilling over diphosphorous pentoxide (P_2O_5) and stored over molecular sieves. Toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried by distilling over sodium/benzophenone and stored over dry molecular sieves, while thionyl chloride was obtained from Merck and distilled before use. 3,5-Ditertbutylpyrazole was prepared by a literature procedure [16], while 2,6-pyridinedicarboxylic acid, pyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole were obtained from Aldrich and used as received. The NMR spectra were recorded on a Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50.3 MHz). The chemical shifts are reported in δ (ppm) and referenced to residual protons and ^{13}C NMR signals of deuterated chloroform as internal standard. Elemental analysis was performed in-house on a Carlo Erba NA analyzer in the department of chemistry, University of the Western Cape.

4.2. Synthesis of ligands and complexes

4.2.1. Synthesis of 2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine (*L1*)

To a solution of 2,6-pyridinedicarbonyl dichloride (0.57 g, 2.83 mmol), obtained from the reaction of 2,6-pyridinedicarboxylic acid and thionyl chloride, in toluene (60 mL) was added 3,5-ditert-butylpyrazole (1.00 g, 5.67 mmol), followed by Et_3N (3 mL). The reaction mixture was refluxed for 24 h. The salt, $Et_3N{\cdot}HCl$, gradually formed and was removed by filtration and the filtrate evaporated to give a white solid. A pure product was obtained after chromatography using silica gel and CH_2Cl_2:ether (8:1) as eluent. Yield = 1.01 g, 73%. $C_{29}H_{41}N_5O_2$ (491.67): calcd. C 70.84, H 8.41, N 14.24; found C 69.95, H 8.91, N 13.67. ^{1}H NMR ($CDCl_3$): δ 7.68–7.82 (m, 3H, py); 6.18 (s, 2H, 4-pz); 1.49 (s, 18H, 5-^{t}Bu); 1.17 (s, 18H, 3-^{t}Bu). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 166.2, 163.6, 158.0, 153.4, 134.6, 125.7, 106.5, 33.2, 32.3, 29.6, 29.5. IR (nujol mull): ν(C=O) = 1716 cm^{-1}, ν(C=N) = 1564 cm^{-1}.

Compounds **L2**, **L3** and **L4** were synthesised using the same procedure as described for **L1**.

4.2.2. Synthesis of 2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine(*L2*)

Compound **L2** was prepared from the reaction of 3,5-dimethylpyrazole (1.00 g, 10.40 mmol) and 2,6-pyridinedicarbonyl dichloride (1.06 g, 5.20 mmol). Yield = 0.99 g, 59%. $C_{17}H_{41}N_5O_2$ (323.35): calcd. C 63.15, H 5.30, N 21.66; found C 62.51, H 5.06, N 21.20. ^{1}H NMR ($CDCl_3$): δ 7.88–7.98 (m, 3H, py); 6.05 (s, 2H, 4-pz); 2.65 (s, 6H, 5-Me); 2.20 (s, 6H, 3-Me). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 165.9, 153.2,151.9, 145.2, 136.2, 126.5, 111.7, 97.4, 14.2, 13.7, 11.8. IR (nujol mull): ν(C=O) = 1709 cm^{-1}, ν(C=N) = 1583 cm^{-1}.

4.2.3. Synthesis of 2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine (*L3*)

Compound **L3** was prepared from the reaction of 3-methylpyrazole (0.64 g, 0.63 mL, 7.82 mmol) and 2,6-pyridinedicarbonyl dichloride (0.80 g, 3.92 mmol). Yield = 0.65 g, 56%. $C_{15}H_{13}N_5O_2$ (295.30): calcd. C 61.01, H 4.44, N 23.72; found C 60.31, H 4.24, N 23.44. ^{1}H NMR ($CDCl_3$): δ 8.79 (d, 2H, 5-pz); 8.34 (d, 2H, py); 8.13 (t, 1H, py); 6.35 (d, 2H, 4-pz); 2.39 (s, 6H, 3-Me). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 167.9, 162.3, 155.4, 149.5, 149.1, 143.4, 138.4, 138.2, 138.1, 133.9, 133.6, 132.6, 129.2, 128.7, 127.6, 127.2, 111.3, 110.9, 104.9, 13.9, 11.6. IR (nujol mull): ν(C=O) = 1712 cm^{-1}, ν(C=N) = 1554 cm^{-1}.

4.2.4. Synthesis of 2,6-bis(pyrazolyl-1-carbonyl)pyridine (*L4*)

Compound **L4** was prepared from the reaction of pyrazole (0.53 g, 7.82 mmol) and 2,6-pyridinedicarbonyl dichloride (0.80 g, 3.92 mmol). Yield = 0.41 g, 41%. $C_{29}H_{41}N_5O_2$ (295.55): calcd. C 52.82, H 4.43, N 23.70; found C 52.56, H 4.61, N 18.90. ^{1}H NMR ($CDCl_3$): δ 8.79 (d, 2H, 5-pz); 8.34 (d, 2H, py); 8.17 (t, 1H, py); 7.85 (d, 2H, 3-pz); 6.54 (t, 2H, 4-pz). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 162.7, 149.6, 145.4, 137.9, 132.4, 128.8, 110.1. IR (nujol mull): ν(C=O) = 1710 cm^{-1}, ν(C=N) = 1569 cm^{-1}.

*4.2.5. Synthesis of {2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (**1**)*

To a yellow solution of $PdCl_2(CH_3CN)_2$ (0.25 g, 0.95 mmol) in CH_2Cl_2 (40 mL), was added a solution of 2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine (0.47 g, 0.95 mmol) in CH_2Cl_2 (20 mL). The solution gradually turned orange-red and after stirring for 48 h, the solvent was evaporated to give an orange residue. Recrystallization from CH_2Cl_2 at room temperature or CH_2Cl_2:ether (2:1) at −15 °C gave analytically pure product as orange crystals suitable for X-ray analysis. Yield = 0.30 g, 62%. $C_{29}H_{41}Cl_2N_5O_2Pd{\cdot}(1/4)CH_2Cl_2$ (689.71): calcd. C 50.46, H 5.98, N 10.15; found C 50.97, H 5.81, N 10.07. ^{1}H NMR ($CDCl_3$): δ 8.02–8.18 (m, 3H, py); 6.36 (s, 1H, 4-pz); 6.19 (s, 1H, 4-pz); 1.77 (s, 9H, 5-^{t}Bu); 1.57 (s, 9H, 3-^{t}Bu); 1.47 (s, 9H, 5-^{t}Bu); 1.18 (s, 9H, 3-^{t}Bu). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 175.2, 164.9, 162.8, 162.4, 160.8, 158.5, 156.9, 151.4, 138.5, 131.0, 127.6, 109.9, 107.6, 33.9, 33.3, 32.4, 30.0, 29.5, 29.3, 29.2. IR (nujol mull): ν(C=O) = 1727 and 1712 cm^{-1}, ν(C=N) = 1557 cm^{-1}.

Complexes **2** and **3** were prepared in a similar manner as described for **1**.

*4.2.6. Synthesis of {2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (**2**)*

Complex **2** was prepared from 2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine (**L2**) (0.47 g, 0.95 mmol) and $PdCl_2(CH_3CN)_2$ (0.25 g, 0.95 mmol). Yield = 0.37 g, 51%. $C_{17}H_{17}Cl_2N_5O_2Pd$ (500.66): calcd. C 50.46, H 5.98, N 10.15; found C 50.97, H 5.81, N 10.07. ^{1}H NMR (DMSO): δ 8.19 (m, 3H, py); 5.97 (s, 1H, pz); 5.91 (s, 1H, 4-pz); 2.36 (s, 3H, 5-Me); 2.18 (s, 9H, 3-Me); 2.17 (s, 9H, 5-Me); 2.08 (s, 3H, 3-Me). IR (nujol mull): ν(C=O) = 1719 and 1723 cm^{-1}, ν(C=N) = 1576 cm^{-1}.

*4.2.7. Synthesis of {2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (**3**)*

Complex **3** was prepared from 2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine (**L3**) (0.50 g, 1.69 mmol) and $PdCl_2(CH_3CN)_2$ (0.44 g, 1.69 mmol). Yield = 0.39 g, 49%. $C_{15}H_{13}Cl_2N_5O_2Pd.1/2CH_2Cl_2$ (515.07): calcd. C 33.16, H 2.41, N 12.89; found C 33.61, H 2.12, N 12.34. IR (nujol mull): ν(C=O) = 1723 and 1734 cm^{-1}, ν(C=N) = 1546 cm^{-1}.

4.2.8. General procedure for ethylene polymerization

Polymerization was carried out in a 300 mL stainless steel autoclave, which was loaded with the catalyst and co-catalyst, methylaluminoxane (MAO) in a glove box. This was done by charging the autoclave with a palladium complex in dry toluene (150 mL), and the appropriate amount of MAO (10% in toluene) at a co-catalyst to catalyst ratio ranging from 250 to 1000. The reactor was sealed and removed from the glove box and then flushed three times with ethylene after which it was heated to the polymerization temperature. Ethylene was continuously supplied to maintain a constant pressure during the polymerization reaction. After the set reaction time, excess ethylene was vented and the polymerization quenched by adding ethanol. The polymer was filtered, washed with 2 M HCl followed by ethanol and dried in an oven overnight at 50 °C under vacuum.

NMR spectra of polyethylene were recorded in 1,2,4-trichlorobenzene/benzene-d_6 at 115 °C. The number-average (M_n) and weight-average (M_w) molecular weights and polydispersity indices (M_w/M_n) of the polymers were determined by high temperature gel permeation chromatography (GPC) (1,2,4-trichlorobenzene, 145 °C, rate = 1.000 mL/min) at the Group Technologies Research and Development laboratory of SASOL polymers (South Africa) and the Institute of Polymer Science at the University of Stellenbosch (South Africa). Thermal analyses were performed on a Universal V2.3H TA instrument at the University of Botswana and on a Perkin-Elmer PC Series 7 system at the University of Cape Town (South Africa).

4.3. X-ray crystallography

Crystal evaluation and data collection for **L3** and **1** were performed on a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [17]. The structures were solved by direct methods and refined by least-squares techniques using SHELXTL program [18]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients. Additional crystallographic data for the structures are deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-250208 (**L3**) and CCDC-178096 (**1**). The data can be obtained free of charge on application to CCDC, Cambridge, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.as.uk).

Acknowledgement

This work was funded by a grant from the National Research Foundation (South Africa), through its Institutional Research Development Programme.

References

[1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
[2] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.

[3] (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414;
(b) B.L. Small, M. Brookhart, A.M.A. Bennet, J. Am. Chem. Soc. 120 (1998) 4049;
(c) G.P.J. Britovesk, V.C. Gibson, B.S. Kimberly, P.J. Maddox, S.J. McTarvish, G.S. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849;
(d) D.G. Musaev, R.D.J. Froese, K. Morokuma, New J. Chem. 119 (1997) 6177;
(e) C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005;
(f) S.A. Svejda, M. Brookhart, Organometallics 18 (1999) 65.
[4] (a) T.V. Laine, K. Lappalainen, J. Liimatta, E. Aitola, B. Lofgren, M. Leskela, Macromol. Rapid Commun. 20 (1999) 487;
(b) T.V. Laine, M. Klinga, M. Leskela, Eur. J. Inorg. Chem. 959 (1999) 959;
(c) T.V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola, M. Leskela, J. Organomet. Chem. 606 (2000) 112.
[5] S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888.
[6] D.P. Gates, S.A. Svedjda, E. Oňate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, Macromolecules 33 (2000) 2320.
[7] (a) K. Li, I.A. Guzei, J. Darkwa, S.F. Mapolie, J. Organomet. Chem. 660 (2002) 109;
(b) I.A. Guzei, K. Li, G.A. Bikzhanova, J. Darkwa, S.F. Mapolie, Dalton Trans. (2003) 715;
(c) S.M. Nelana, J. Darkwa, I.A. Guzei, S.F. Mapolie, J. Organomet. Chem. 689 (2004) 1835.
[8] D.A. House, P.J. Steel, A.A. Watson, Aust. J. Chem. 39 (1986) 1525.
[9] F.H. Allen, Acta Cryst. B58 (2002) 380.
[10] (a) R.J. Maldanis, J.S. Wood, A. Chandrasekaran, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 645 (2002) 158;
(b) M.A. Zuideveld, P. Wehrmann, C. Rohr, S. Mecking, Angew. Chem. Int. Ed. 43 (2004) 689.
[11] R. Chen, S.F. Mapolie, J. Mol. Catal. A 193 (2003) 33.
[12] (a) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., John Wiley & Sons, New York, 1999;
(b) G.H. Robinson, Coordination Chemistry of Aluminum, VCH, New York, 1993;
(c) M.P. Cole, R.F. Jordan, J. Am. Chem. Soc. 119 (1997) 8125;
(d) E. Ihara, V.G. Young Jr., R.F. Jordan, J. Am. Chem. Soc. 120 (1998) 8277;
(e) J.S. Kim, L.M. Wojcinski, S. Liu, J.C. Sworen, S. Sen, J. Am. Chem. Soc. 122 (2000) 5668;
(f) M. Bruce, V.C. Gibson, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc. Chem. Commun. (1998) 2523.
[13] I.P. Romm, T.A. Zayakina, V.N. Sheinker, E.N. Guryanova, A.D. Garnovskii, O. Osipov, Zh. Obshch. Khim. 46 (1976) 2279.
[14] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[15] P.A. do Couto Jr., M. Nele, F.M.B. Coutinho, Eur. Polym. J. 38 (2002) 1471.
[16] J. Elguero, E.G.R. Jacquier, Bull. Soc. Chim. Fr. 2 (1968) 707.
[17] R.H. Blessing, Acta Crystallgr. Sect. A 51 (1995) 33.
[18] Bruker-AXS, SADABS V.2.05, SAINT V.6.22, SHELXTL V.6.10 & SMART 5.622 Software Reference Manuals, Bruker-AXS, Madison, WI, USA, 2000–2003.