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Neutral palladium(II) complexes with *P,N* Schiff-base ligands: Synthesis, characterization and catalytic oligomerisation of ethylene

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ABSTRACT

New *N*-functionalised 2-phosphinobenzaldimino (P^N) ligands bearing 3-picolyl, furfuryl, thiophene-2-methyl, thiophene-2-ethyl, and benzyl groups have been prepared in good yield. The 2-phosphinobenzaldimino ligands were reacted with $PdCl_2$(COD) to give the corresponding metal complexes of the type Pd(L)Cl_2 (L = 2-phosphinobenzaldimino (P^N) ligand). All compounds were fully characterized using spectroscopic and analytical techniques, including ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies, mass spectrometry and elemental analysis. Selected neutral palladium complexes were evaluated as catalyst precursors in ethylene oligomerisation reactions, after activation with a co-catalyst (MMAO, $EtAlCl_2$, or Et_2AlCl).

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1. Introduction

The interest in olefin oligomerisation/polymerisation dates back to 1952 when Gellert and Ziegler reported the reaction of ethylene with lithium aluminium hydride ($LiAlH_4$) in ether at 180–200 °C and observed a rapid drop in the ethylene pressure [1]. Ever since, the selective ethylene dimerisation, trimerisation and tetramerisation have attracted considerable attention and also chemical companies have made efforts to narrow the broad distribution of olefins to high value co-monomers (1-hexene and 1-octene). These attempts have involved increased capital expenditure and operational complexities. Selective ethylene trimerisation has received the most attention (compared to ethylene dimerisation and the recently discovered ethylene tetramerisation) [2,3]. In 1977, Manyik et al. of Union Carbide reported the first selective ethylene trimerisation to 1-hexene [4]. In addition, 1-hexene was found to be an oligomeric by-product in the ethylene polymerisation catalysed by a homogeneous chromium-based system [chromium(III)*tris*(2-ethylhexanoate)/hydrolyzed triisobutylaluminium]. Later, Briggs and others developed a catalyst system involving a donor ligand system (selected from dimethoxybenzene, monoglyme, diglyme, triglyme and *o*-dimethoxybenzene) to give a different kind of catalyst system: [chromium(III)*tris*(2-ethylhexanoate)/donor ligand/hydrolyzed triisobutylaluminium] which produced 1-hexene as a major product with selectivities of up to 74% as well as a small amount of polyethylene [5]. These results prompted companies including Phillips Petroleum Corporation, Mitsubishi Chemical Corporation and Sumitomo Chemical Company to investigate this system further, using pyrrole or 2,5-dipyrrole donor ligands. In particular, the four-component catalyst incorporating halide promoters were investigated, e.g. [chromium(III)*tris*(2-ethylhexanoate)/2,5-dimethylpyrrole/$AlEt_3$/CCl_4]. Chromium(III) complexes containing tridentate ligands have also recently been shown to be highly active and selective catalysts for ethylene trimerisation to 1-hexene when activated with MAO [6–9].

In the 1990s, interest in late transition-metal complexes as catalysts for ethylene reactivity was renewed by the discovery of highly active α-diimine-based complexes by Brookhart [10] and Gibson [11]. An important observation made by Brookhart and co-workers was the marked effect that ligand manipulation has on the product formed. It was observed that by eliminating the steric bulk of the *ortho*-substituent on the aryl-substituted α-(diimine) Pd and Ni complexes, only ethylene oligomers were formed as opposed to the high molecular weight polyethylene produced when bulky *ortho*-substituents were present [10,12,13]. These discoveries

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resulted in many research groups making efforts to design new ligand systems containing N- and also P-donor ligands, in an effort to find highly active and selective catalyst systems, particularly those containing late transition metals (Ni and Pd complexes) [14–17].

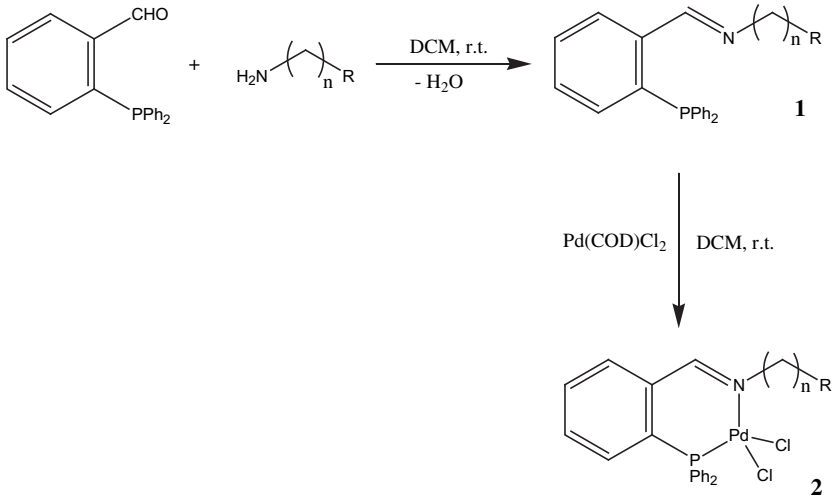
To date, there are a relatively small number of reports in the literature describing ethylene oligomerisation catalysed by palladium catalyst precursors. The main reason is presumably the very low activity (or inactivity) observed with these catalyst systems. The interest in the chemistry of ligands containing both 'hard' nitrogen and 'soft' phosphorus donor atoms [18–20] allows for a variety of coordination possibilities beyond traditional P–P or N–N ligands [21]. The P,N ligands show a particular behaviour in binding to soft metal centres such as palladium(II) and platinum(II) that make their complexes good precursors in catalytic processes [22–25]. The choice of the P^N coordinating ligand system relates to their ability to improve thermal stability [26–28] of the corresponding catalysts, presumably due to the presence of the strong phosphorus-metal bond [29], thereby curbing rapid catalyst deactivation/decomposition at high temperature. The stability of the catalysts at high temperatures is particularly important since ethylene oligomerisation reactions can be highly exothermic [26]. In addition P^N ligands offer unique trans-effects due to the different electron donor and acceptor capabilities of phosphorus and nitrogen that may improve the catalyst's performance [26–28]. In polymerisation reactions, the active catalysts are commonly stabilized by the metal–hydrogen agostic interactions. For the compounds reported herein, third donors on the imine nitrogen were also introduced to study their effect on the stability of the *in situ* generated catalysts. The rationale for this is linked to the position of the lone pairs on oxygen and sulphur of the furyl and thiophenyl groups respectively, which are nearly perpendicular to the ring, and are more aromatic and thus not readily available for coordination. The proposed metal–oxygen or metal–sulphur interaction should thus be strong enough to stabilize the catalyst's vacant site but weak enough to be displaced by the incoming ethylene. Herein, we report the synthesis of a series of neutral, P,N-chelating, palladium phosphinobenzaldimino complexes and investigate their activity as ethylene oligomerisation catalyst precursors.

2. Results and discussion

2.1. Synthesis and characterization of the iminophosphine ligands (*1a–1f*)

The iminophosphine ligands were isolated as off-white powders via a Schiff-base condensation reaction of 2-(diphenylphosphino) benzaldehyde with the appropriate amine (Scheme 1), following modified literature methodologies [30–34]. The iminophosphine ligand (**1e**), is a known compound and was prepared using the reported method [35].

The ^{31}P NMR spectra of the iminophosphine ligands show only one singlet between −13.2 and −13.9 ppm and attest to the formation of only one product. This signal was shifted slightly upfield compared to the starting 2-diphenylphosphinobenzaldehyde signal, which appears at −11.7 ppm. The disappearance of the aldehyde proton signal at 10.5 ppm and appearance of a doublet (J_{HP} = 4.9–5.8 Hz) for the imine fragment (**HC**=N) at 8.39–9.02 ppm confirmed condensation of the aldehydes and the respective amines [33,34]. The coupling of phosphorus with the imine proton is presumed to be due to a through-space coupling, arising from the ligand's conformation in which the imine proton points towards the phosphorus lone pair. This observation is consistent with that reported by Rauchfuss and others for related ligands [32,36–38]. IR



Compound	n	R
1a	1	3-pyridyl
1b	1	2-furyl
1c	1	2-thiopheneyl
1d	2	2-thiopheneyl
1e	1	Ph
1f	1	4-tolyl

Complex	n	R
2a	1	3-pyridyl
2b	1	2-furyl
2c	1	2-thiopheneyl
2d	2	2-thiopheneyl
2e	1	Ph
2f	1	4-tolyl

Scheme 1.

spectroscopy was used to confirm the successful formation of the imine functionality. Strong absorption bands in the region 1625–1636 cm^{-1} are observed in the IR spectra for all the iminophosphine ligands **1a**–**1f**, in agreement with literature values for related compounds [32,37,38]. Elemental analysis and mass spectroscopic data support and are in agreement with the proposed structures.

2.2. Synthesis and characterization of the palladium complexes (*2a*–*2f*)

The reaction of the ligands **1a**–**1f** with $Pd(COD)Cl_2$ in DCM at room temperature resulted in the precipitation of the corresponding palladium dichloride complexes **2a**–**2f** (Scheme 1), which were isolated by filtration as yellow powders in 64–83% yield. Spectroscopic and analytical data for these complexes are in agreement with the proposed structures.

The ^1H NMR spectra of complexes **2a**–**2f** show imine protons in the region between 8.34 and 8.72 ppm that are shifted upfield by 0.27–0.7 ppm with respect to the free ligands, which could be due to the change in the conformation of the ligand to enable κ^2–P^N coordination to the metal centre [39]. In addition, all the imine protons appeared as singlets as opposed to the doublets observed for the free ligands. A more significant downfield shift to 31.7–37.3 ppm of the single ^{31}P resonances of complexes **2a**–**2f**, compared to −13.2 to −13.9 ppm for the free ligands, was observed due to coordination of the phosphine moiety to the palladium centre. The IR spectroscopic data of complexes **2a**–**2f** revealed a bathochromic (red) shift of about 8–20 cm^{-1} with respect to the free ligands, with $\nu_{C=N}$ stretching vibration bands appearing in the region 1626–1630 cm^{-1}, which confirmed the coordination of the imine nitrogen to the palladium metal centre. The mass spectral data for these complexes show $[M-Cl]^+$ as the highest molecular weight fragment. This is a common phenomenon in the mass spectra of analogous palladium complexes.

2.3. Oligomerisation of ethylene

Selected neutral iminophosphine palladium complexes (**2a**–**2e**) were investigated as ethylene oligomerisation catalyst precursors under various reaction conditions. The principle steps (reaction mechanism) in ethylene oligomerisation entail (i) activation of a neutral catalyst precursor using a co-catalyst to generate the cationic active catalyst, (ii) chain propagation through insertion of ethylene into the metal–alkyl bond (Cossee mechanism), and β-hydride elimination to restore the very active metal hydride species which catalyses subsequent ethylene reactions. Parameters such as co-catalyst concentration (Al/Pd molar ratio), reaction time, reaction temperature, and ethylene pressure, have a significant effect on the type of olefin product distribution and these parameters were varied in this study to determine the optimal reaction conditions.

2.3.1. The selection of a co-catalyst

To establish the most efficient co-catalyst, various co-catalysts (MMAO, Et_2AlCl and $EtAlCl_2$) were used to activate a representative palladium catalyst precursor (**2b**) in the oligomerisation of ethylene. The co-catalyst molar ratios (Al/Pd) were also varied for each co-catalyst to determine optimum molar ratios (i.e. Al/Pd = 100 and 1000 for MMAO, Al/Pd = 100, 300, 500 for Et_2AlCl, Al/Pd = 4, 10, 50, 100 for $EtAlCl_2$). The palladium catalyst generally displayed only low catalytic activities, which were also observed by Guan, Rieger and co-workers in their ethylene polymerisation studies [40,41]. In fact, no catalytic activity was observed when MMAO was used to activate the catalyst precursor **2b**. This could be due to the lower Lewis acidity of MMAO or deactivation of the active catalyst by the $^tBu_3Al$ impurities in MMAO [42–44]. Low catalytic activities of up to 1.9×10^2 g mol^{-1} Pd h^{-1} (Table 1, entry 4) were observed when Et_2AlCl was employed as a co-catalyst. Increasing the Al/Pd ratio from 100 to 300 led to an improvement in the catalytic activity. Further increasing the Al/Pd ratio to 500 resulted in a decrease in the catalytic activity. This trend was observed for all catalysts investigated and could be ascribed to the increased amount of trialkylaluminium impurities present in the solutions of MMAO and Et_2AlCl [42,43]. In addition, increasing the co-catalyst molar ratio could facilitate dialkylation of the Pd centre, consequently deactivating the catalyst by rapid reductive elimination to give inactive Pd(0) species [45]. The same behaviour was observed when $EtAlCl_2$ was used as a co-catalyst, with catalytic activities increasing appreciably when the Al/Pd molar ratio was increased from 10 to 50. No catalytic activity was observed at low co-catalyst molar ratio (Al/Pd = 4), presumably due to insufficient activation of the catalyst precursors. When larger molar ratios (Al/Pd = 10 and 50) were employed, only low catalytic activities were observed (e.g. 6.8 and 7.5×10^2 g mol^{-1} Pd h^{-1} respectively with **2b**/$EtAlCl_2$, Table 1, entries 7 and 8), while further increasing the Al/Pd ratio to 100 led to a decline in the catalytic activity (7.4×10^2 g mol^{-1} Pd h^{-1}, Table 1, entry 9). Of the three co-catalysts investigated, $EtAlCl_2$ gave the best catalytic activities which could be attributed to its stronger Lewis acidity compared to MMAO and Et_2AlCl, and was therefore used in subsequent investigations.

All catalysts predominantly produced ethylene dimers and small quantities of ethylene trimers (<1%; see Table 1). In all cases, the oligomerisation product distribution (C_4 and C_6) was not affected by the Al/Pd molar ratios at lower concentrations (i.e Al/Pd = 100–300 for Et_2AlCl and Al/Pd = 10–50 for $EtAlCl_2$). For example, only a slight increase in the C_4 fraction (99.1 and 99.8% at Al/Pd = 100 and 300) was observed with catalyst **2b**/Et_2AlCl (Table 1, entries 3 and 4). At higher co-catalyst concentrations (Al/Pd = 500) the selectivity for C_4 decreased slightly to 98.1% (Table 1, entry 5) with the same catalyst.

Upon activation with Et_2AlCl and $EtAlCl_2$, the palladium catalysts yielded besides 1-butene (1-C_4) also 2-butene (2-C_4). This suggests that the palladium catalysts have a dual role, namely the oligomerisation of ethylene to 1-C_4 as well as the isomerization of the formed product (1-C_4) to the corresponding 2-C_4 isomers (*cis* and *trans*). The selectivity for 2-C_4 increased with increasing co-catalyst concentration (Table 1, entries 3–5 and 7–9), where in the case of $EtAlCl_2$, 2-C_4 is the major component of the C-4 fraction. The minor C_6 components comprised of a mixture of 3-methyl-1-pentene, *trans*-3-methyl-2-pentene, *cis*-3-methyl-2-pentene, and

Table 1
Influence of the co-catalyst and the co-catalyst/catalyst precursor ratio on catalytic activity and product distribution with complex **2b**.[a]

Entry	Co-catalyst	Al/Pd	Activity[b]	Oligomers		
				C_4	C_6	1-C_4
1	MMAO	100	–	–	–	–
2	MMAO	1000	–	–	–	–
3	Et_2AlCl	100	1.3	99.1	0.9	84
4	Et_2AlCl	300	1.9	99.8	0.2	81
5	Et_2AlCl	500	1.8	98.1	1.9	67
6	$EtAlCl_2$	4	–	–	–	–
7	$EtAlCl_2$	10	6.8	99.0	1.0	32
8	$EtAlCl_2$	50	7.5	99.5	0.5	21
9	$EtAlCl_2$	100	7.4	96.1	2.9	12

[a] General conditions: 10 μmol of catalyst precursor; 50 ml toluene; 15 min, 10 bar, error estimate = ±0.1, 1-C_4 component is the proportion within the C_4 fraction.
[b] Activity = $\times 10^2$ g(product) mol^{-1} Pd h^{-1}.

2-ethylbutene, as well as 1-hexene, *trans*-2-hexene, and *cis*-2-hexene, which presumably are secondary products formed by the co-dimerisation of butene with ethylene [46–51].

2.3.2. The influence of temperature

The effect of temperature on ethylene oligomerisation was explored using catalysts **2a**–**2e** and $EtAlCl_2$ as the co-catalyst (Al/Pd = 50, at 30 bar ethylene for 15 min). The details of this study are given in Table 2. Three reaction temperatures (10, 50, 80 °C) were investigated.

Increasing the reaction temperature proved to have an effect on the catalytic activity, but very little influence on the product distribution (i.e. relative amounts of C_4 and C_6). In all cases, increasing the reaction temperature from 10 to 50 °C resulted in a significant improvement in the catalytic activity (e.g. 2.2 to 5.2×10^2 g mol^{-1} Pd h^{-1} for **2e**/$EtAlCl_2$, Table 2, entries 13 and 14). Further increasing the reaction temperature from 50 to 80 °C led to a decrease in the catalytic activity (e.g. 3.9×10^2 g mol^{-1} Pd h^{-1} for **2e**/$EtAlCl_2$, Table 2, entry 15). It is most likely that catalyst deactivation occurs at the elevated temperatures. This behaviour is consistent with that of Brookhart's Pd(II)-α-diimine catalysts [52]. A reason for the drop in the catalytic activity could also be ascribed to the lower ethylene solubility in toluene at 80 °C (i.e. 0.12 mol kg^{-1} bar^{-1} at 50 °C and 0.080 mol kg^{-1} bar^{-1} at 80 °C) [46–48,53,54].

All of the catalysts investigated showed mainly ethylene dimerisation (up to 100% C_4 with **2e**/$EtAlCl_2$, Table 2, entry 13) and to a minor extent trimerisation to C_6. In all cases, high temperatures favoured 1-C_4 double bond isomerization since the selectivity for 1-C_4 gradually decreased with increasing temperature. For instance, at 10, 50, and 80 °C, the selectivities for 1-C_4 were 39, 19, and 11% respectively, for the iminophosphine catalyst **2b**/$EtAlCl_2$ (Table 2, entries 4, 5, and 6).

2.3.3. The influence of reaction time

Subsequently, the effect of the reaction time on the catalytic activity and the product distribution was studied. The start of the reaction was taken when the autoclave was filled with the appropriate pressure of ethylene (working pressure). At the end of a catalytic run (after 1, 5, 15, and 30 min), the ethylene pressure was discontinued and the autoclave was rapidly cooled to −25 to −35 °C before the residual ethylene was vented. Catalysts **2a**–**2e**/$EtAlCl_2$ displayed selectivities for C_4 up to 99%, but proved to have rather short lifetimes as in all cases the best catalytic activities were observed when the catalytic reactions were carried out for 1 min (see Table 3). Reactions carried out beyond 1 min showed a gradual decrease in the catalytic activities. For example, catalyst system **2b**/$EtAlCl_2$ afforded 7.6, 7.1, 6.2 and 4.2×10^2 g mol^{-1} Pd h^{-1} after 1, 5, 15, and 30 min (Table 3, entries 5, 6, 7, 8) respectively. In addition, increasing the reaction time from 1 to 30 min led to a slight reduction in the amount of C_4 (e.g. 99.5 and 98.5% at 1 and 30 min respectively for catalyst **2b**/$EtAlCl_2$), together with an increase in the 2-C_4 fraction from 64 to 85% (Table 3, entries 5–8). The mode of catalyst deactivation is not clear at this stage, but the role of palladium black can be ruled out as this was not observed in any of the cases investigated.

2.3.4. The influence of ethylene pressure

As the final parameter, the effect of the ethylene pressure on catalytic activity and product distribution was studied. It was observed that increasing the ethylene pressure resulted in the improvement of both the catalytic activity and the selectivity (for C_4) for all the catalysts investigated (see Table 4). For example, catalyst **2b**/$EtAlCl_2$ provided activities of 2.5, 6.8 and 7.1×10^2 g mol^{-1} Pd h^{-1} (Table 4, entries 4, 5, 6) when the reactions were carried out at 10, 30, and 50 bar respectively. The selectivity for the C_4 fraction improved as well with increasing ethylene pressure (e.g. for **2b**/$EtAlCl_2$: 98.6, 99.1, and 99.7% at 10, 30, and 50 bar respectively, Table 4, entries 4, 5, 6). Due to the higher ethylene concentrations in solution (and thus more availability) ethylene will out-compete butene and therefore less co-dimerisation (to make C_6) will be observed.

The 1-C_4 component within the C_4 fraction was observed to increase gradually as the ethylene pressure was increased from 10 to 50 bar (e.g. from 28 to 37% for the **2b**/$EtAlCl_2$ catalyst system; Table 4, entries 4 and 6), which is believed to be due to the

Table 2
Influence of temperature on ethylene oligomerisation with complexes **2a**–**2e**.[a]

Entry	Complex	Temp. (°C)	Activity[b]	Oligomerisation (wt %)		
				C_4	C_6	1-C_4
1	**2a**	10	5.5	99.3	0.7	48
2		50	6.9	99.5	0.5	25
3		80	4.3	98.6	1.4	12
4	**2b**	10	6.7	99.7	0.3	39
5		50	7.4	99.0	1.0	19
6		80	5.1	99.6	0.4	11
7	**2c**	10	5.4	99.4	0.6	41
8		50	6.3	99.2	0.8	33
9		80	5.5	98.9	1.1	13
10	**2d**	10	4.5	99.4	0.6	46
11		50	4.8	99.8	0.2	29
12		80	4.5	99.1	0.9	16
13	**2e**	10	2.2	100	–	50
14		50	5.2	99.3	0.7	23
15		80	3.9	99.8	0.2	17

[a] General conditions: Time = 15 min; 10 μmol of catalyst precursor; 50 ml toluene; co-catalyst: $EtAlCl_2$; Al/Pd = 50; pressure = 30 bar, temperature = 25 °C, error estimate = ±0.1, 1-C_4 component is the proportion within the C_4 fraction.
[b] Activity = $\times 10^2$ g(product) mol^{-1} Pd h^{-1}.

Table 3
Influence of reaction time on the catalytic activity with **2a**–**2e**/$EtAlCl_2$.[a]

Entry	Complex	Time (min)	Activity[b]	Oligomerisation (wt %)		
				C_4	C_6	1-C_4
1	**2a**	1	6.9	99.3	0.7	45
2		5	6.4	99.3	0.7	33
3		15	6.0	99.1	1.9	20
4		30	4.9	98.0	1.8	19
5	**2b**	1	7.6	99.5	0.5	36
6		5	7.1	99.3	0.7	29
7		15	6.2	98.7	1.3	22
8		30	4.2	98.5	1.5	15
9	**2c**	1	6.9	99.3	0.7	43
10		5	6.6	98.9	1.1	38
11		15	5.9	98.7	1.3	29
12		30	4.0	98.1	1.9	21
13	**2d**	1	5.6	99.0	1.0	33
14		5	5.3	99.2	0.8	27
15		15	4.3	98.6	1.4	23
16		30	3.4	98.4	1.6	20
17	**2e**	1	6.0	99.2	0.8	37
18		5	5.4	99.1	0.9	32
19		15	4.1	99.2	0.8	25
20		30	3.6	98.8	1.2	16

[a] General conditions: Temp = 50 °C; 10 μmol catalyst precursor; 50 ml toluene; 30 bar, error estimate = ±0.1, 1-C_4 component is the proportion within the C_4 fraction; Al/Pd = 50.
[b] Activity = $\times 10^2$ g(product) mol^{-1} Pd h^{-1}.

Table 4
Influence of ethylene pressure and catalyst concentration on ethylene oligomerisation with complexes **2a**–**2e**.[a]

Entry	Complex	Pressure	Activity[b]	Oligomerisation (wt %)		
				C_4	C_6	1-C_4
1	**2a**	10	3.1	98.1	1.9	33
2		30	7.3	98.9	1.1	39
3		50	7.7	99.6	2.3	44
4	**2b**	10	2.5	98.6	1.4	28
5		30	6.8	99.1	0.9	33
6		50	7.1	99.7	0.3	37
7	**2c**	10	5.9	98.9	1.1	36
8		30	6.2	99.4	0.6	42
9		50	6.4	99.3	0.5	43
10	**2d**	10	2.6	98.3	1.7	26
11		30	6.5	98.8	1.2	36
12		50	6.8	99.6	0.4	42
13	**2e**	10	3.6	99.0	1.0	31
14		30	5.1	99.3	0.7	39
15		50	6.5	100	–	45

[a] General conditions: Temp = 50 °C, time = 5 min, 5 μmol of catalyst precursor, 50 ml toluene, error estimate = ±0.1, 1-C_4 component is the proportion within the C_4 fraction; Al/Pd = 50.
[b] Activity = $\times 10^2$ g(product) mol^{-1} Pd h^{-1}.

competition between chain transfer and chain isomerization [55]. Thus, at high ethylene concentrations formation of 1-C_4 is favoured due to rapid chain transfer versus chain isomerization.

3. Conclusions

A series of new bidentate iminophosphine ligands have been synthesized in good yield and characterized by spectroscopic and analytical methods. Palladium dichloride complexes were isolated in high yields by the reaction of the ligands with Pd(COD)Cl_2. These complexes were used as catalyst precursors for ethylene oligomerisation and were activated with a variety of co-catalysts (MMAO, $EtAlCl_2$, and Et_2AlCl) in an effort to determine an efficient co-catalyst for each catalyst system. $EtAlCl_2$ was found to be an efficient co-catalyst for the neutral palladium catalyst precursors. For each catalyst system, reaction conditions such as temperature, reaction time, and ethylene pressure were investigated in an effort to establish optimum catalytic reaction conditions. The neutral palladium/$EtAlCl_2$ catalyst system performed best at a temperature of 50 °C with an ethylene pressure of 50 bar. The palladium catalysts generally gave low catalytic activities (up to 7.7×10^2 g mol^{-1} Pd h^{-1}). These catalysts also gave ethylene dimerisation (up to 100%) and trimerisation (up to 2.3%) products, and within the C4 fraction, selectivities for 1-C_4 of up to 50% were obtained. The catalyst systems bearing P^N ligands employed in this project proved to be highly stable as no formation of palladium black was observed implying that the ligand remained bound to the palladium metal centre throughout the catalytic cycle.

4. Experimental

4.1. General remarks

All reactions were carried out under a nitrogen or argon atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques unless stated otherwise. Solvents were dried and purified by heating at reflux under argon in the presence of a suitable drying agent. All reagents were purchased from Aldrich and used without further purification. 2-Diphenylphosphinobenzaldehyde [56], Pd(COD)Cl_2 [57], and ligand **1e** [58] were prepared by published procedures. Melting points were recorded on a Kofler hotstage microscope (Reichert Thermovar). Elemental analyses were carried out on a Fisons EA 1108 CHNS Elemental Analyzer in the microanalytical laboratory at the University of Cape Town. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Varian Mercury-300 MHz (^{1}H: 300 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121 MHz) or Varian Unity-400 MHz (^{1}H: 400 MHz; ^{13}C: 100.6 MHz) spectrometer. ^{1}H NMR spectra were referenced internally using the residual protons in the deuterated solvents ($CDCl_3$: δ 7.27; DMSO: δ 2.50 ppm) and values reported relative to the internal standard tetramethylsilane (δ 0.00). ^{13}C NMR spectra were referenced internally to the resonance ($CDCl_3$: δ 77.0; DMSO: δ 39.4) and the values reported relative to tetramethylsilane (δ 0.0). IR absorptions were measured on a Perkin Elmer Spectrum one FT-IR spectrophotometer. GC analyses were performed using a Varian 3900 gas chromatograph equipped with an FID and a 50 m × 0.20 mm HP-PONA column (0.50 μm film thickness). The carrier gas was helium at 40 psi. The oven was programmed to hold the temperature at 32 °C for 4 min and then to ramp the temperature to 200 °C at 10 °C/min and then to hold it at 200 °C hold for 5 min. The sample in a screw-cap vial was cooled in liquid nitrogen before being injected into the GC, in an attempt to minimize the loss of the volatile product.

4.2. General procedure for preparation of ligands (*1a*–*f*)

To a dichloromethane solution (15 mL) of 2-diphenylphosphinobenzaldehyde (*ca.* 3 mmol) was added an equimolar amount of the appropriate substituted amine. An excess of magnesium sulphate was also added to the reaction mixture to remove the water by-product. The reaction was left to stir at room temperature for 16 h, after which time the magnesium sulphate was filtered off and the solvent removed from the filtrate *in vacuo* to give a yellow–orange oil. The oily crude products of ligands **1a**–**1f** were solidified by dissolving the oil in hot hexane, followed by quick hot filtration of the liquid product. The resultant solution was then cooled at −16 °C overnight to give an off-white powder, which was filtered and dried *in vacuo*.

4.2.1. Preparation of (2-diphenylphosphino-benzylidene)-pyridin-3-ylmethyl-amine ($C_{25}H_{21}N_2P$) (*1a*)

This compound was prepared from the reaction of 2-diphenylphosphinobenzaldehyde (1.00 g, 3.50 mmol) and 3-aminomethylpyridine (0.38 g, 3.5 mmol) using the general procedure. The pure product was obtained as an off-white powder (1.13 g, 86%). M.p. 79–81 °C. IR (KBr): 1635 cm^{-1} ($\nu_{C=N}$, imine). ^{1}H NMR ($CDCl_3$): δ 9.02 (d, 1H, J_{HP} = 4.9 Hz, H-imine), 8.45 (dd, 1H, J_{HH} = 1.7, 4.8 Hz, H-pyridyl), 8.42 (d, 1H, J_{HH} = 1.7 Hz, H-pyridyl), 8.01 (ddd, 1H, J_{HH} = 1.4, 3.9, 7.6 Hz, Ar–H), 7.24–7.43 (m, 13H, Ar–H), 7.12 (ddd, 1H, J_{HH} = 0.8, 4.8, 7.8 Hz, Ar–H), 6.90 (ddd, 1H, J_{HH} = 7.7, 4.7, 1.1 Hz, Ar–H), 4.67 (s, 2H, N–CH_2). ^{13}C NMR ($CDCl_3$) δ: 161.4 (d, J_{CP} = 21.0 Hz, C-imine), 149.4 (C-pyridyl), 148.3 (C-pyridyl), 137.8 (d, J_{CP} = 19.6 Hz, Ar–C), 137.1 (d, J_{CP} = 17.0 Hz, Ar–C), 136.4 (d, J_{CP} = 9.4 Hz, Ar–C), 135.5 (C-pyridyl), 134.6 (C-pyridyl), 134.1 (d, J_{CP} = 20.0 Hz, Ar–C), 133.4 (Ar–C), 130.6 (Ar–C), 129.0 (Ar–C), 128.7 (d, J_{CP} = 7.2 Hz, Ar–C), 127.9 (d, J_{CP} = 4.1 Hz, Ar–C), 123.4 (Ar–C), 122.6 (C-pyridyl), 62.34 (N–CH_2). ^{31}P NMR ($CDCl_3$): δ −13.2 (s). EI–MS: *m*/*z* 379.92 $[M]^+$. Anal. Calc. for $C_{25}H_{21}N_2P$ (380.42): C, 78.93; H, 5.56; N, 7.36. Found: C, 78.91; H, 5.49; N, 7.22.

4.2.2. Preparation of (2-diphenylphosphino-benzylidene)-furan-2-ylmethyl-amine ($C_{24}H_{20}NOP$) (*1b*)

This compound was prepared from the reaction of 2-diphenylphosphinobenzaldehyde (1.00 g, 3.44 mmol) and furfurylamine (0.33 g, 3.44 mmol) using the general procedure. The pure product was obtained as an off-white powder (1.03 g, 81%). M.p. 76–77 °C. IR (KBr): 1634 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 9.01 (d,

J_{HH} = 5.1 Hz, H-imine), 8.07 (ddd, 1H, J_{HH} = 7.7, 4.0, 1.4 Hz, Ar–H), 7.25–7.42 (m, 13H, Ar–H), 6.91 (m, 1H, H-furan), 6.27 (m, 1H, H-furan), 6.05 (dd, 1H, J_{HH} = 3.3, 0.7 Hz, H-furan), 4.65 (s, 2H, N–CH_2). ^{13}C NMR ($CDCl_3$) δ: 161.5 (d, J_{CP} = 23.0 Hz, C-imine), 152.3 (C-furan), 142.0 (C-furan), 139.3 (d, J_{CP} = 17.3 Hz, Ar–C), 137.7 (d, J_{CP} = 19.8 Hz, Ar–C), 136.4 (d, J_{CP} = 9.7 Hz, Ar–C), 134.1 (d, J_{CP} = 19.9 Hz, Ar–C), 133.3 (Ar–C), 130.5 (Ar–C), 129.0 (Ar–C), 128.8 (Ar–C), 128.6 (d, J_{CP} = 7.1 Hz, Ar–C), 127.6 (d, J_{CP} = 4.2 Hz, Ar–C), 110.3 (C-furan), 107.4 (C-furan), 57.0 (N-CH_2). ^{31}P NMR ($CDCl_3$): δ −13.9 (s). EI–MS: *m/z* 369.81 $[M+H]^+$. Anal. Calc. for $C_{24}H_{20}NOP$ (369.40): C, 78.03; H, 5.46; N, 3.79. Found: C, 77.79; H, 5.56; N, 3.60.

4.2.3. Preparation of (2-diphenylphosphino-benzylidene)-thiophen-2-ylmethyl-amine ($C_{24}H_{20}NPS$) (**1c**)

This compound was prepared from the reaction of 2-diphenylphosphinobenzaldehyde (1.00 g, 3.44 mmol) and 2-thiophene-methylamine (0.39 g, 3.44 mmol) using the general procedure. The pure product was obtained as an off-white powder (0.97 g, 73%). M.p. 70–72 °C. IR (KBr): 1625 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 9.02 (br d, 1H, J_{HP} = 4.9 Hz, H-imine), 8.11 (m, 1H, Ar–H), 7.25–7.45 (m, 12H, Ar–H), 7.20 (dd, 1H, J_{HH} = 5.1, 1.1 Hz, H-thiophene), 6.95 (m, 2H, H-thiophene + Ar–H), 6.78 (dd, 1H, J_{HH} = 3.1, 1.0 Hz, H-thiophene), 4.86 (s, 2H, N–CH_2). ^{13}C NMR ($CDCl_3$) δ: 160.8 (d, J_{CP} = 23.2 Hz, C-imine), 141.8 (C-thiophene), 139.3 (d, J_{CP} = 17.2 Hz, Ar–C), 137.7 (d, J_{CP} = 19.3 Hz, Ar–C), 136.3 (d, J_{CP} = 9.7 Hz, Ar–C), 134.1 (d, J_{CP} = 20.8 Hz, Ar–C), 133.3 (Ar–C), 130.6 (Ar–C), 129.1 (Ar–C), 128.9 (Ar–C), 128.7 (d, J_{CP} = 7.1 Hz, Ar–C), 127.8 (d, J_{CP} = 4.2 Hz, Ar–C), 126.8 (C-thiophene), 125.1 (C-thiophene), 124.6 (C-thiophene), 59.9 (N–CH_2). ^{31}P NMR ($CDCl_3$): δ −13.99 (s). EI–MS: *m/z* 385.56 $[M]^+$. Anal. Calc. for $C_{24}H_{20}NPS$ (385.46): C, 74.78; H, 5.23; N, 3.63; S, 8.32. Found: C, 74.29; H, 5.29; N, 3.35; S, 8.26.

4.2.4. Preparation of (2-diphenylphosphino-benzylidene)-thiophen-2-ylethyl-amine ($C_{25}H_{22}NPS$) (**1d**)

This compound was prepared from the reaction of diphenylphosphinobenzaldehyde (2.00 g, 6.89 mmol) and 2-thiopheneethylamine (0.88 g, 6.89 mmol) using the general procedure. The pure product was obtained as an off-white powder (2.54 g, 92%). M.p. 64–65 °C. IR (KBr): 1636 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): δ 8.91 (d, 1H, J_{HP} = 4.9 Hz, H-imine), 8.03 (m, 1H, Ar–H), 7.26–7.45 (m, 12H, Ar–H), 7.08 (dd, 1H, J_{HH} = 5.1, 1.1 Hz, H-thiophene), 6.93 (m, 1H, Ar–H), 6.88 (m, 1H, H-thiophene), 6.77 (dd, 1H, J_{HH} = 3.3, 0.9 Hz, H-thiophene), 3.78 (t, 2H, J_{HH} = 3.2 Hz, N–CH_2–), 3.02 (t, 2H, J_{HH} = 3.2 Hz, N–CH_2–CH_2). ^{13}C NMR ($CDCl_3$): δ 160.6 (d, J_{CP} = 21.3 Hz, C-imine), 142.4 (C-thiophene), 139.6 (d, J_{CP} = 17.3 Hz, Ar–C), 137.6 (d, J_{CP} = 19.5 Hz, Ar–C), 136.7 (d, J_{CP} = 9.6 Hz, Ar–C), 134.1 (Ar–C), 134.0 (J_{CP} = 19.9 Hz, Ar–C), 133.5 (Ar–C), 130.3 (Ar–C), 130.0 (Ar–C), 128.9 (Ar–C), 127.8 (d, J_{CP} = 4.3 Hz, Ar–C), 126.7 (C-thiophene), 125.0 (C-thiophene), 123.5 (C-thiophene), 62.5 (N–CH_2–), 31.4 (N–CH_2–CH_2). ^{31}P NMR ($CDCl_3$): δ −13.55 (s). EI–MS: *m/z* 400.04 $[M]^+$. Anal. Calc. for $C_{25}H_{22}NPS$ (399.49): C, 75.16; H, 5.55; N, 3.51; S, 7.75. Found: C, 75.03; H, 5.64; N, 3.05; S, 8.06.

4.2.5. Preparation of benzyl-(2-diphenylphosphino-benzylidene)-amine ($C_{27}H_{24}NP$) (**1f**)

This compound was prepared from the reaction of 2-diphenylphosphinobenzaldehyde (1.16 g, 4.0 mmol) and 4-methylbenzylamine (0.49 g, 4.0 mmol) using the general procedure. The pure product was obtained as a yellow–orange oil (1.28 g, 81%). IR (CH_2Cl_2): 1635 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR ($CDCl_3$): 9.00 (1H, d, J_{HH} = 5.1, H-imine), 8.05 (1H, ddd, J_{HH} = 1.5 Hz, 4.0 Hz, 7.7 Hz, Ar–H), 7.68 (1H, ddd, J_{HH} = 0.9 Hz, 3.9 Hz, 7.7 Hz, Ar–H), 6.78–7.32 (15H, m, Ar–H), 6.05 (1H, d, J_{HH} = 5.8 Hz, Ar–H), 4.64 (2H, s, N–CH_2–), 2.34 (3H, s, –CH_3). ^{13}C ($CDCl_3$): 161.3 (d, J_{CP} = 22.9 Hz, C-imine), 143.2 (d, J_{CP} = 18.1 Hz, Ar–C), 137.9 (d, J_{CP} = 19.5 Hz, Ar–C), 137.4 (d, J_{CP} = 21.0 Hz, Ar–C), 134.5 (Ar–C), 133.9 (d, J_{CP} = 11.3 Hz, Ar–C), 133.6 (d, J_{CP} = 19.8 Hz, Ar–C), 130.5 (Ar–C), 129.2 (Ar–C), 128.9 (d, J_{CP} = 8.0 Hz, Ar–C), 128.7 (Ar–C), 128.3 (Ar–C), 127.4 (d, 4.6 Hz, Ar–C), 60.9 (N–CH_2), 21.9 (CH_3). ^{31}P NMR ($CDCl_3$): −13.6. EI–MS: *m/z* 392.79 $[M]^+$. Anal. Calc. for $C_{27}H_{24}NP$ (393.46): C, 82.42; H, 6.15; N, 3.56. Found: C, 81.97; H, 6.61; N, 3.35.

4.3. General procedure for the preparation of palladium complexes (**2a**–**2f**)

To a dichloromethane solution (5 mL) of the appropriate ligand **1a**–**1f** (*ca.*0.2–0.3 mmol) was added a dichloromethane solution (15 mL) of $Pd(COD)Cl_2$. A yellow precipitate formed immediately. The reaction mixture was allowed to stir at room temperature for 6 h and the yellow crude product filtered. The product was then washed three times with 10 mL dichloromethane and dried *in vacuo* to give a yellow powder.

4.3.1. Preparation of [$Pd(C_{25}H_{21}NP)Cl_2$] (**2a**)

This complex was prepared from a reaction of **1a** (0.11 g, 0.29 mmol) and $Pd(COD)Cl_2$ (0.08 g, 0.26 mmol) using the general procedure, to give a pure product as a yellow powder (0.93 g, 64%). M.p. 210–212 °C (decomp.). IR (KBr): 1626 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 8.50 (dd, 1H, J_{HH} = 4.8, 1.8 Hz, H-pyridyl), 8.34 (s, 1H, H-imine), 8.32 (d,1H, J_{HH} = 2.2 Hz, H-pyridyl), 7.96 (dt, 1H, J_{HH} = 1.8, 7.7 Hz, H-pyridyl), 7.78 (m, 2H, Ar–H), 7.56 (m, 4H, Ar–H), 7.39 (m, 4H, Ar–H), 7.16 (m, 4H, Ar–H), 6.99 (m, 1H, Ar–H), 5.48 (s, 2H, N–CH_2–). ^{31}P NMR (DMSO-d_6): δ 37.3 (s). EI–MS: *m/z* 522.11 $[M-Cl]^+$. Anal. Calc. for $C_{25}H_{21}Cl_2NPPd$ (557.75): C, 53.84; H, 3.80; N, 5.02. Found: C, 53.51; H, 3.99; N, 4.86.

4.3.2. Preparation of [$Pd(C_{24}H_{20}NOP)Cl_2$] (**2b**)

This complex was prepared from the reaction of **1b** (0.13 g, 0.35 mmol) and $Pd(COD)Cl_2$ (0.10 g, 0.35 mmol) using the general procedure. The pure product was obtained as a yellow powder (0.15 g, 69%). M.p. 198–199 °C (decomp.). IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 8.72 (s, 1H, H-imine), 8.00 (ddd, 1H, J_{HH} = 1.2, 4.2, 7.6 Hz, Ar–H), 7.89 (dt, 1H, J_{HH} = 1.5, 7.7 Hz, Ar–H), 7.75 (tt, 1H, J_{HH} = 1.4, 7.6 Hz, Ar–H), 7.58 (m, 2H, Ar–H), 7.45 (td, 4H, J_{HH} = 2.9, 4.8 Hz, Ar–H), 7.24 (m, 5H, Ar–H + H-pyridyl), 7.05 (dd, 1H, J_{HH} = 7.8, 10.1 Hz, Ar–H), 6.55 (d, 1H, J_{HH} = 3.2 Hz, H-furan), 6.38 (dd, 1H, J_{HH} = 1.9, 3.2 Hz, H-furan), 5.56 (s, 2H, N–CH_2–). ^{31}P NMR (DMSO-d_6): δ 32.2 (s). EI–MS: *m/z* 511.43 $[M-Cl]^+$. Anal. Calc. for $C_{24}H_{20}Cl_2NOPPd$ (546.72): C, 52.72; H, 3.69; N, 2.56. Found: C, 52.60; H, 3.58; N, 2.35.

4.3.3. Preparation of [$Pd(C_{24}H_{20}NPS)Cl_2$] (**2c**)

This complex was prepared from the reaction of **1c** (0.10 g, 0.26 mmol) and $Pd(COD)Cl_2$ (0.07 g, 0.26 mmol) using the general procedure. The pure product was obtained as a yellow powder (0.97 g, 66%). M.p. 233–234 °C (decomp.). IR (KBr):1629 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (DMSO-d_6): δ 8.81 (s, 1H, H-imine), 7.98 (m, 1H, Ar–H), 7.93 (m, 1H, Ar–H), 7.74 (m, 1H, Ar–H), 7.55 (m, 2H, Ar–H), 7.41 (dt, 5H, J_{HH} = 2.9, 4.9 Hz, Ar–H), 7.91 (dd, 4H, J_{HH} = 7.8, 4.9 Hz, Ar–H), 7.18 (m, 2H, H-thiophene), 6.90 (dd, 1H, J_{HH} = 2.9, 2.0 Hz, H-thiophene), 5.66 (s, 2H, N–CH_2–),. ^{31}P NMR (DMSO-d_6): δ 31.8 (s). EI–MS: *m/z* 526.77 $[M-Cl]^+$. Anal. Calc. For $C_{24}H_{20}Cl_2NPPdS$ (562.79): C, 51.22; H, 3.58; N, 2.49; S, 5.70. Found: C, 51.48; H, 3.44; N, 2.70; S, 5.97.

4.3.4. Preparation of [$Pd(C_{25}H_{22}NPS)Cl_2$] (**2d**)

This complex was prepared from the reaction of **1d** (0.21 g, 0.50 mmol) and $Pd(COD)Cl_2$ (0.14 g, 0.50 mmol) using the general

procedure. The pure product was obtained as a yellow powder (0.23 g, 71%). M.p. 203–205 °C (decomp.). IR (KBr): 1629 cm^{-1} ($\nu_{C=N}$). ^1H NMR (DMSO-d_6): δ 8.52 (s, 1H, H-imine), 7.93 (dd, 1H, J_{HH} = 1.3, 7.6 Hz, Ar–H), 7.87 (m, 1H, Ar–H), 7.73 (tt, 1H, J_{HH} = 1.4, 7.5 Hz, Ar–H), 7.65 (m, 2H, Ar–H), 7.56 (dt, 4H, J_{HH} = 3.0, 7.6 Hz, Ar–H), 7.46 (m, 5H, Ar–H), 7.23 (dd, 1H, J_{HH} = 1.2, 5.1 Hz, H-thiophene), 6.91 (dd. 1H, J_{HH} = 5.6, 7.7 Hz, Ar–H), 6.80 (dd, 1H, J_{HH} = 3.4, 5.1 Hz, H-thiophene), 6.57 (dd, 1H, J_{HH} = 0.7, 3.4 Hz, H-thiophene), 4.55 (t, 2H, J_{HH} = 7.7 Hz, N–CH_2–CH_2–), 3.07 (t, 2H, J_{HH} = 7.7 Hz, N–CH_2–CH_2–). ^{31}P NMR (DMSO-d_6): δ 32.3 (s). EI–MS: m/z 541.33 $[M-Cl]^+$. Anal. Calc. For $C_{25}H_{22}Cl_2NPPdS$ (576.81): C, 52.06; H, 3.84; N, 2.43; S, 5.56. Found: C, 52.22; H, 3.63; N, 2.70; S, 5.49.

4.3.5. Preparation of [Pd($C_{26}H_{22}NP$)Cl_2] (**2e**)

This complex was prepared from the reaction of **1e** (0.21 g, 0.50 mmol) and Pd(COD)Cl_2 (0.14 g, 0.50 mmol) using the general procedure. The pure product was obtained as a yellow powder (0.23 g, 79%). M.p. 199–201 °C (decomp.). IR (KBr): 1627 cm^{-1} ($\nu_{C=N}$). ^1H NMR (DMSO-d_6): δ 8.83 (s, 1H, H-imine), 8.02 (m, 1H, Ar–H), 7.91 (m, 1H, Ar–H), 7.75 (m, 1H, Ar–H), 7.56 (m, 2H, Ar–H), 7.38 (dt, 4H, J_{HH} = 2.7, 7.7 Hz, Ar–H), 7.25 (dd, 4H, J_{HH} = 1.8, 7.9 Hz, Ar–H), 7.13 (m, 5H, Ar–H), 6.98 (m, 1H, Ar–H), 5.50 (s, 2H, N–CH_2–). ^{31}P NMR (DMSO-d_6): δ 34.1 (s). EI–MS: m/z 521.02 $[M-Cl]^+$. Anal. Calc. for $C_{26}H_{22}Cl_2NPPd$ (556.76): C, 56.09; H, 3.98; N, 2.54. Found: C, 55.86; H, 3.76; N, 2.48.

4.3.6. Preparation of [Pd($C_{27}H_{24}NP$)Cl_2] (**2f**)

This complex was prepared from the reaction of **1f** (0.47 g, 1.18 mmol) and Pd(COD)Cl_2 (0.34 g, 1.18 mmol) using the general procedure. The pure product was obtained as a yellow powder (0.34 g, 50%). M.p. 173–175 °C (decomp.). IR (KBr): 1628 cm^{-1} ($\nu_{C=N}$). ^1H NMR (DMSO-d_6): 8.84 (1H, s, H3), 8.17 (1H, m, Ar–H), 7.92 (1H, m, Ar–H), 7.69 (1H, m, Ar–H), 7.60 (2H, m, Ar–H), 7.41 (2H, m, Ar–H), 7.30 (6H, m, Ar–H), 7.19 (4H, m, Ar–H), 7.11 (1H, m, Ar–H), 5.47 (2H, s, H2), 2.26 (3H, s, H1). ^{31}P NMR (DMSO-d_6): 30.7 (s). EI–MS: m/z 535.27 $[M-Cl]^+$. Anal. Calc. for $C_{27}H_{24}Cl_2NPPd$ (570.79): C, 56.81; H, 4.24; N, 2.45. Found: C, 55.90; H, 4.31; N, 2.53.

4.4. Catalytic olefin oligomerisation reactions

A 250 mL stainless-steel Parr-type autoclave equipped with an overhead magnetic stirrer was heated at 100 °C under vacuum for 1 h and then cooled to room temperature. The autoclave was transferred into the glovebox where anhydrous solvent (toluene or cyclohexane (40 mL)), the catalyst precursor complexes ($2-5 \times 10^{-5}$ mol) and a co-catalyst ($EtAlCl_2$, Et_2AlCl, or MMAO), were introduced at room temperature under an inert atmosphere of nitrogen. The autoclave was sealed inside the glovebox before being taken out. The autoclave was then purged three times with ethylene under stirring (300 rpm) before being brought to a working ethylene pressure (10–50 bar). The contents of the autoclave were then stirred for the desired time, while maintaining the ethylene pressure throughout the experiment. At the end of the catalytic run the autoclave was cooled to *ca.* −30 °C in a liquid nitrogen cooled acetone bath, at which temperature the excess ethylene was slowly vented. An internal standard (nonane, *ca.* 1 mL) was then added and a sample of the cooled reaction mixture collected in a cooled screw-cap vial for GC analysis.

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