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Cobalt and Nickel Complexes Bearing Pyrazolyliminophosphorane Ligands: Synthesis, Characterisation and Catalytic Ethylene Oligomerisation Behaviour

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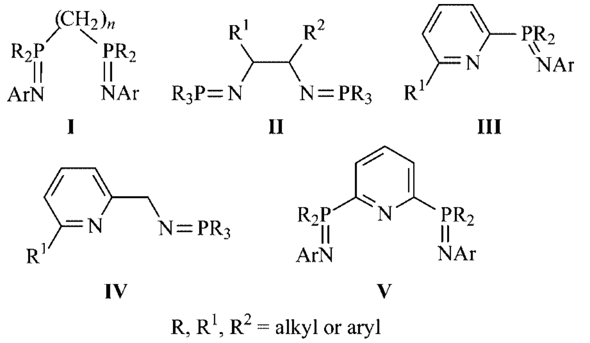
Treatment of 1-(2′-azidophenyl)-3,5-dimethylpyrazole (**1**) with Ph_2PR (R = Ph, Me) and $(Ph_2P)_2CH_2$, respectively, affords the pyrazolyliminophosphoranes **2**, **3** and **4**. Reaction of **2** or **3** with $[NiCl_2(dme)]$ or $NiBr_2$ yields the N,N-chelate nickel complexes **5**–**8**, and with $CoCl_2$ complexes **9** and **10**. Reaction of **4** with $[NiCl_2(dme)]$, $NiBr_2$ and $CoCl_2$, respectively, affords the N,N,P-chelate complexes **11**–**13**. Compounds **2**–**4** were characterised by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy and elemental analysis, while complexes **5**–**13** were characterised by IR spectroscopy and elemental analysis. The structures of complexes **5**, **9** and **12** were further characterised by single-crystal X-ray diffraction techniques. Complexes **5**–**13** are active catalysts for ethylene oligomerisation upon activation with alkylaluminium derivatives (Et_2AlCl, MAO or MMAO). These complexes exhibit good to high catalytic activities (up to $3.54\times10^{6}\,\mathrm{g\,mol^{-1}\,h\,atm}$ for the nickel complexes and $5.48\times10^{5}\,\mathrm{g\,mol^{-1}\,h\,atm}$ for the cobalt complexes). The effects of varying ethylene pressure, temperature and aluminium co-catalyst/Ni or Co ratios with complexes **5**, **9**, **11** and **12** are reported.

Introduction

Ethylene oligomerisation to form linear α-olefins has become a topic of considerable interest in both academia and industry as these oligomers are used as co-monomers with ethylene and for the preparation of a variety of important compounds such as detergents, synthetic lubricants, additives for high-density polyethylene production and surfactants.[1] Late transition metal complexes have demonstrated potential as catalysts for ethylene oligomerisation. A representative example is the nickel catalysts in the Shell higher olefin process (SHOP).[2] Other late transition metal complexes have also proved to be active. These complexes are supported by extensive didentate and tridentate ligands, including N,N,[3] N,P,[1,4] N,O,[5] P,O,[6] P,P,[7] N,N,P,[8] N,N,N,[1b,3b,9] N,P,N[10] and P,N,P[11] ligands. Recently, chelating nitrogen ligands featuring iminophosphorane moieties have attracted considerable attention. Examples include **I**–**V** (Scheme 1).[3a–3d,12] Some of the late transition metal complexes with these ligands exhibit ethylene polymerisation or oligomerisation activities in the presence of appropriate co-catalysts. Pyrazole-based ligands have also received extensive attention in recent years for the preparation of olefin polymerisation catalysts, including poly(pyrazolyl)borates, didentate bis-pyrazolyl ligands and mixed donor ligands.[1b,4f,9b,13] Our aim was to examine a set of new ligands that combine pyrazolyl and iminophosphorane units for late transition metals relevant for catalysis of ethylene polymerisation or oligomerisation. Herein we report the synthesis, characterisation and catalytic performance for ethylene oligomerisation of cobalt and nickel complexes bearing pyrazolyliminophosphorane ligands.



Scheme 1.

Results and Discussion

Synthesis and Characterisation of Compounds 2–13

Compound **1** was prepared according to a literature method.[4f,14] Syntheses of ligands **2**–**4** and cobalt and nickel complexes **5**–**13** are summarised in Scheme 2. Treatment of **1** with one equivalent of phosphane Ph_2PR (R = Ph or Me) or $Ph_2PCH_2PPh_2$ yielded iminophosphoranes **2**–**4** in high yields. Reaction of **2** or **3** with MX_2 (M = Ni, X

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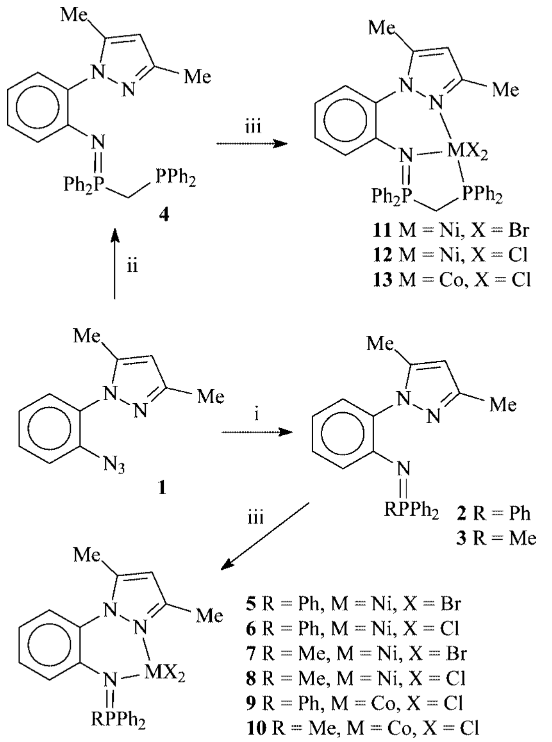
= Br; M = Co, X = Cl) or [$NiCl_2$(dme)] afforded complexes **5**–**10** in good to excellent yields. A similar reaction between **4** and the metal halides gave complexes **11**–**13**. Compounds **2**–**4** are yellow (**2** and **4**) or orange (**3**) solids and were fully characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy and elemental analyses. Complexes **5**–**13** are blue (**5**–**10** and **13**), purple (**11**) or yellow (**12**) crystals or powder. Complexes **5** and **7**–**13** are air stable and complex **6** forms an H_2O adduct after being exposed to air for a long period. These complexes are paramagnetic and were characterised by IR spectroscopy and elemental analyses, as well as by single-crystal X-ray diffraction techniques (for **5**, **9** and **12**).



Scheme 2. Synthesis of compounds **2**–**13**. Reagents and conditions: i) Ph_2PR (R = Ph, Me), CH_2Cl_2, room temperature, 12 h; ii) $Ph_2PCH_2PPh_2$, CH_2Cl_2, room temperature, 12 h; iii) MX_2 (M = Ni, X = Br; M = Co, X = Cl) or [$NiCl_2$(dme)], thf, room temperature, 15 h.

The structure of **5** is presented in Figure 1. Crystalline **5** is monomeric. Its Ni atom is four coordinate and has a distorted tetrahedral geometry. The N1–C19–C24–N2 atoms lie in the same plane. The N1–Ni1–N3–N2 atoms are also approximately co-planar, with a torsion angle of 4°. The six-membered metallacycle shows a boat conformation. The Ni1–N1 distance of 2.002(6) Å is longer than those found in [{2-[Ph_2P=N($C_6H_3Me_2$-2′,6′)]-6-($SiMe_3$)-C_5H_3N}$NiBr_2$] [1.996(8) Å] and [{2-(Ph_3P=NCH_2)-6-MeC_5H_3N}$NiBr_2$] [1.983(3) Å].[3c] The Ni1–N3 distance of 2.007(6) Å is close to that in [{1-(2′-$Ph_2PC_6H_4$)-3,5-$Me_2C_3HN_2$}$NiCl_2$] [2.003(4) Å],[4f] but slightly shorter than those found in [{NH(1-CH_2CH_2-3,5-Me_2-C_3HN_2)$_2$}$NiCl_2$] [2.069(2) and 2.0334(19) Å, respectively].[1b] The two Ni–Br bond lengths are very similar and are typical for this class of compounds.[3c,15] The P–N distance of 1.624(6) Å is normal for metal-coordinated iminophosphoranes.[3b,16]

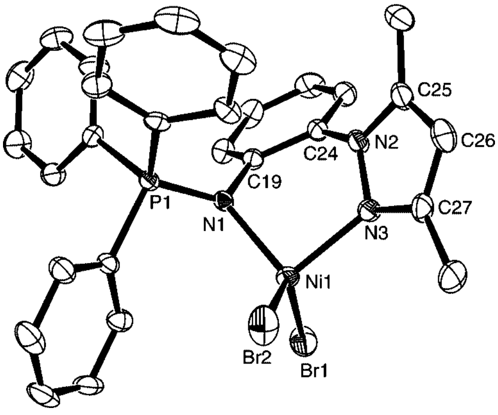


Figure 1. ORTEP drawing of complex **5** (thermal ellipsoids at 30% probability). Selected bond lengths [Å] and angles [°]: Ni(1)–N(1) 2.002(6), Ni(1)–N(3) 2.007(6), Ni(1)–Br(1) 2.3614(13), Ni(1)–Br(2) 2.3743(13), P(1)–N(1) 1.624(6), N(1)–C(19) 1.421(9), N(2)–N(3) 1.388(8), N(2)–C(24) 1.434(9), C(19)–C(24) 1.412(10); N(1)–Ni(1)–N(3) 92.2(2), N(1)–Ni(1)–Br(1) 104.75(17), N(3)–Ni(1)–Br(1) 108.5(2), N(1)–Ni(1)–Br(2) 113.81(16), N(3)–Ni(1)–Br(2) 106.71(18), Br(1)–Ni(1)–Br(2) 125.71(6), C(19)–N(1)–Ni(1) 113.3(4), P(1)–N(1)–Ni(1) 124.4(3), C(27)–N(3)–Ni(1) 127.4(5), N(2)–N(3)–Ni(1) 118.3(4), C(19)–N(1)–P(1) 121.5(5), N(3)–N(2)–C(24) 119.1(6).

The structure of **9** is shown in Figure 2. Crystalline **9** is monomeric and the Co centre is in a distorted tetrahedral environment. Like complex **5**, the six-membered metallacycle also exists in a boat conformation in the solid state. The Co–N distance (av. 2.045 Å) is close to that in [{CH_2(Ph_2P=NPh)$_2$}$CoCl_2$] (av. 2.032 Å).[3b] The Co–Cl

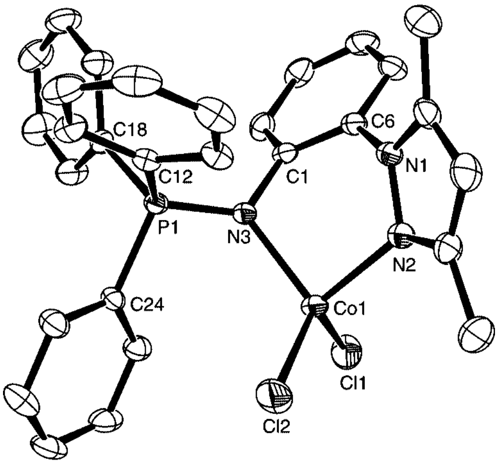


Figure 2. ORTEP drawing of complex **9** (thermal ellipsoids at 30% probability). Selected bond lengths [Å] and angles [°]: Co(1)–N(2) 2.052(2), Co(1)–N(3) 2.038(2), Co(1)–Cl(1) 2.2376(10), Co(1)–Cl(2) 2.2476(10), P(1)–N(3) 1.610(2), N(1)–N(2) 1.385(3), N(1)–C(6) 1.435(4), C(1)–C(6) 1.401(4), N(3)–C(1) 1.427(3); N(3)–Co(1)–N(2) 91.54(9), N(3)–Co(1)–Cl(1) 108.60(7), N(2)–Co(1)–Cl(1) 113.27(8), N(3)–Co(1)–Cl(2) 115.95(7), N(2)–Co(1)–Cl(2) 107.75(8), Cl(1)–Co(1)–Cl(2) 117.01(4), N(1)–N(2)–Co(1) 117.84(18), C(1)–N(3)–Co(1) 111.62(17), N(2)–N(1)–C(6) 119.4(2), C(1)–N(3)–P(1) 122.10(18), C(1)–N(3)–Co(1) 111.62(17), P(1)–N(3)–Co(1) 125.55(13).

distances [2.2376(10) and 2.2476(10) Å, respectively] are within the normal range for four-coordinate Co complexes.[3b,3c,17]

Single crystals of complex **12** suitable for X-ray crystallography were grown from toluene. The molecular structure of complex **12** is presented in Figure 3. Complex **12** is monomeric and co-crystallises with one toluene molecule. The coordination geometry around the nickel atom is distorted trigonal bipyramidal in which the P1–Ni1–N3 angle is 167.57(9)° as a result of the strain imposed by the five- and six-membered chelate rings. The N1–Ni1–Cl1–Cl2 atoms are nearly co-planar. The N1–C26–P2–Ni1 atoms are also approximately in the same plane, the sum of the angles around N1 being 359.92°. The Ni–N distance (av. 2.063 Å) is slightly longer than that in complex **5** and comparable to those in [{NH(1-CH_2CH_2-3,5-$Me_2C_3HN_2$)$_2$}$NiCl_2$] [2.069(2) and 2.0334(19) Å, respectively].[1b] Both P1 and P2 exhibit distorted tetrahedral geometries. The Ni1–P1 distance of 2.4001(11) Å is longer than that in [{1-(2′-$Ph_2PC_6H_4$)-3,5-$Me_2C_3HN_2$}$NiCl_2$] [2.281(2) Å],[4f] but still within the normal range.[8]

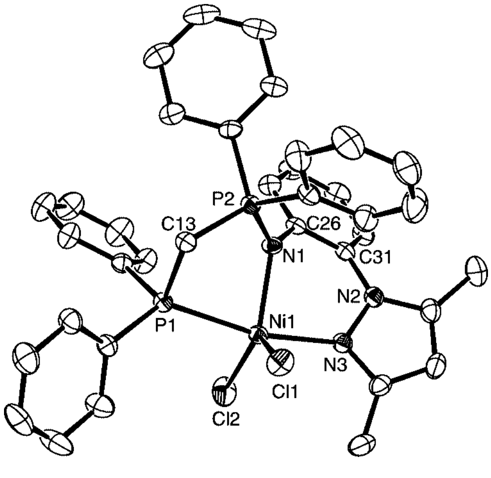


Figure 3. ORTEP drawing of complex **12** (thermal ellipsoids at 30% probability). Selected bond lengths [Å] and angles [°]: Ni(1)–N(1) 2.066(3), Ni(1)–N(3) 2.060(3), Ni(1)–Cl(2) 2.3012(11), Ni(1)–Cl(1) 2.3187(11), Ni(1)–P(1) 2.4001(11), P(2)–N(1) 1.603(3), P(1)–C(13) 1.842(3), P(2)–C(13) 1.806(3), N(2)–N(3) 1.377(4), N(2)–C(31) 1.424(5), N(1)–C(26) 1.405(4), C(26)–C(31) 1.412(5); N(1)–Ni(1)–N(3) 87.00(11), N(1)–Ni(1)–Cl(2) 129.22(9), N(3)–Ni(1)–Cl(2) 92.76(9), N(1)–Ni(1)–Cl(1) 102.94(9), N(3)–Ni(1)–Cl(1) 94.35(9), Cl(2)–Ni(1)–Cl(1) 127.65(5), N(1)–Ni(1)–P(1) 80.64(8), N(3)–Ni(1)–P(1) 167.57(9), Cl(2)–Ni(1)–P(1) 96,05(4), Cl(1)–Ni(1)–P(1) 87.20(4), P(2)–N(1)–Ni(1) 118.82(15), C(26)–N(1)–Ni(1) 114.9(2), C(26)–N(1)–P(2) 126.2(2), N(2)–N(3)–Ni(1) 122.8(2), C(13)–P(1)–Ni(1) 99.02(12), N(1)–P(2)–C(13) 106.93(15).

Catalytic Properties of Complexes 5–13 for Ethylene Oligomerisation

We initially examined the catalytic activities of complexes **5**–**10** using Et_2AlCl as activator; the results are displayed in Table 1. At an Al/metal molar ratio of 300 and 20 °C under 1 atm of ethylene the cobalt complexes **9** and **10** are inactive, whereas complexes **5**–**8** catalyse the dimerisation and trimerisation of ethylene with high activity (2.09×10^5 to 1.86×10^6 $g\,mol^{-1}\,h$; entries 3 and 11–13 in Table 1). The influence of the Al/Ni ratio, the reaction temperature and ethylene pressure was investigated for complex **5**. At 20 °C under 1 atm of ethylene, when the ratio of Al to Ni was 300 complex **5** showed the highest catalytic activity (1.34×10^6 $g\,mol^{-1}\,h\,atm$). Variation of the reaction temperature also influences the catalytic activity and product distribution. Thus, with a rise of the temperature from 20 °C to 40 °C and finally to 55 °C the catalytic activity of **5** gradually decreased and the proportion of C_6 component increased (entries 3, 7 and 8 in Table 1). At 0 °C the catalytic activity of **5** was close to that at 40 °C. However, the proportion of C_6 component at 0 °C was far lower than that at 40 °C (entry 3 in Table 1). This decrease of catalytic activity with a rise of temperature may be attributable to the lower solubility of ethylene and the decomposition of the active sites at higher temperature. The catalytic activities of complexes **6** and **7** at 20 °C under 1 atm of ethylene and with a 300:1 Al/Ni molar ratio (7.67×10^5 and 2.09×10^5 $g\,mol^{-1}\,h\,atm$, respectively) are lower than that of complex **5**. Complex **8** exhibits the highest catalytic activity (1.86×10^6 $g\,mol^{-1}\,h\,atm$). Enhancement of the ethylene pressure does not increase the catalytic activity of **5** in unit pressure (entry 10 in Table 1). Comparison of the catalytic

Table 1. Ethylene oligomerisation with **5**–**8**.[a]

Entry	Complex	Al/Ni	*P* [atm]	Time [h]	*T* [°C]	Activity[b]	C_4 [%][c]	C_6 [%][c]
1	**5**	50	1	0.5	20	2.24	67.3	32.7
2	**5**	200	1	0.5	20	7.99	82.1	17.9
3	**5**	300	1	0.5	20	13.4	78.8	21.2
4	**5**	400	1	0.5	20	7.30	73.4	26.6
5	**5**	600	1	0.5	20	7.09	54.1	45.9
6	**5**	300	1	0.5	0	5.50	74.0	26.0
7	**5**	300	1	0.5	40	5.64	13.3	86.7
8	**5**	300	1	0.5	55	2.86	5.4	94.6
9	**5**	300	1	1	20	14.3	76.9	23.1
10	**5**	300	10	0.5	20	71.3	79.2	20.8
11	**6**	300	1	0.5	20	7.67	64.7	35.3
12	**7**	300	1	0.5	20	2.09	77.8	22.2
13	**8**	300	1	0.5	20	18.6	72.1	27.9

[a] Conditions: 5 µmol of pre-catalyst, Et_2AlCl as co-catalyst, 30 mL of toluene (120 mL of toluene with 10 atm of ethylene). [b] 10^5 $g\,mol^{-1}\,h$. [c] Weight percent determined by GC analysis.

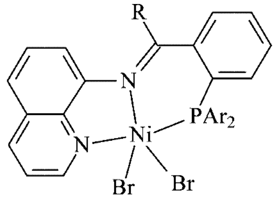
Table 2. Ethylene oligomerisation with complexes **11** and **12**.[a]

Entry	Complex	Al/Ni	P [atm]	Time [h]	t [°C]	Activity[b]	C_4 [%][c]	C_6 [%][c]
1	**11**	50	1	0.5	20	1.80	76.6	23.4
2	**11**	200	1	0.5	20	2.12	78.8	21.2
3	**11**	300	1	0.5	20	2.97	61.0	39.0
4	**11**	500	1	0.5	20	2.63	57.4	42.6
5	**11**	700	1	0.5	20	2.23	61.8	38.2
6	**11**	300	1	0.5	0	2.38	80.5	19.5
7	**11**	300	1	0.5	40	3.54	72.2	27.8
8	**11**	300	1	0.5	60	1.07	68.0	32.0
9	**11**	300	1	1	20	1.41	50.4	49.6
10	**11**	300	10	0.5	40	8.52	76.2	23.8
11	**12**	300	1	0.5	20	2.85	70.5	29.5
12	**12**	300	1	0.5	40	2.53	62.0	38.0
13	**12**	300	1	0.5	0	2.42	68.9	31.1
14	**12**	300	1	0.5	60	1.88	66.0	34.0

[a] Conditions: 5 µmol of pre-catalyst, Et_2AlCl as co-catalyst, 30 mL of toluene (120 mL of toluene when determined at 10 atm). [b] 10^6 g mol^{-1} h. [c] Weight percent determined by GC analysis.

activities of complexes **5**–**8** showed that under the same conditions the activity order is **8** > **5** > **6** > **7**. Unfortunately, it is difficult to establish a relationship between the catalytic activities and the electronic and steric effects of the groups attached to the phosphorus and nickel atoms from these results.

It has been reported that the nickel complexes of N,N,P-tridentate ligands **VI** show high catalytic activity for ethylene oligomerisation in the presence of $EtAlCl_2$.[8] We therefore added a Ph_2P group to the *P*-methyl of ligand **3** to construct the new N,N,P tridentate ligand **4**. The nickel complexes of the ligand (**11** and **12**) show high catalytic activity for ethylene oligomerisation in the presence of Et_2AlCl (Table 2). In each case the reaction produced a mixture of C_4 and C_6 species. The quantity of aluminium co-catalyst affected the outcome of the reaction. For complex **11**, enhancement of the Al/Ni molar ratio from 50:1 to 300:1 gave an increase in catalytic activity. With further augmentation of the Al/Ni ratio the catalytic activity gradually decreased (entries 1–5 in Table 2). The effect of reaction temperature was also studied. The reaction was carried out at 0, 20, 40 and 60 °C, and the results showed that the highest catalytic activity was achieved at 40 °C. It seems that in this example the lowering of ethylene solubility at higher temperature is not the main factor affecting the catalytic activity of **11**. It was also noted that prolonging the reaction time led to a decrease of catalytic activity and an increase of the C_6 fraction in the products. This increase of the proportion of C_6 component may be due to co-oligomerisation of C_4 accumulated in the reaction vessel. The influence of pressure was similar to that with complex **5**. Thus, an increase of ethylene pressure did not obviously



VI

Table 3. Ethylene oligomerisation with complexes **9**, **10** and **13**.[a]

Entry	Complex	Co-catalyst	Al/Co	Activity[b]	C_4 [%][c]	C_6 [%][c]
1	**9**	MAO	300	very low		
2	**9**	MAO	500	2.56	82.7	17.3
3	**9**	MAO	800	3.18	20.7	79.3
4	**9**	MAO	1000	3.85	27.9	72.1
5	**9**	MAO	1500	4.51	16.9	83.1
6	**9**	MAO	1800	5.62	19.1	80.9
7	**9**	MAO	2400	8.60	21.0	79.0
8	**10**	MAO	2400	7.01	16.9	83.1
9	**13**	MAO	2400	7.12	22.6	77.4
10	**9**	MMAO	300	15.5	97.6	2.4
11	**9**	MMAO	500	24.2	>99	
12	**9**	MMAO	800	26.0	>99	
13	**9**	MMAO	1000	27.3	>99	
14	**9**	MMAO	1500	52.3	>99	
15	**9**	MMAO	2000	53.3	>99	
16	**10**	MMAO	2000	54.8	>99	
17	**13**	MMAO	2000	33.6	>99	

[a] Conditions: 5 µmol of pre-catalyst, 20 °C, 30 mL of toluene, 1 atm of ethylene, 0.5 h. [b] 10^4 g mol^{-1} h. [c] Weight percent determined by GC analysis.

enhance the catalytic activity of **11** in unit pressure (entry 10 in Table 2). For complex **12**, the highest activity was observed at 20 °C and 1 atm of ethylene in the presence of 300 equiv. of Et_2AlCl.

In addition, compared with the nickel complexes with didentate ligands **5**–**8**, complexes **11** and **12** exhibit higher catalytic activity under similar reaction conditions.

The nature of the aluminium co-catalyst affects the catalytic properties of the pre-catalysts greatly. As we mentioned above, the cobalt complexes are inactive for ethylene oligomerisation with Et_2AlCl as co-catalyst. However, they showed good catalytic activities for ethylene oligomerisation with MAO or MMAO as activator (Table 3). Complexes **9**, **10** and **13** showed similar catalytic activities when MAO was used as co-catalyst (Al/Co = 2400) at 20 °C under 1 atm of ethylene. The catalytic reaction yielded a mixture of C_4 and C_6 species.

When MMAO was used as co-catalyst, **13** revealed lower activity than **9** and **10**. However, each of complexes **9**, **10** and **13** exhibits higher activities than that with MAO as activator under similar reaction conditions. We also tested the effect of the Al/Co ratio for complex **9**. Increase of the MAO/Co or MMAO/Co ratio resulted in an enhancement of catalytic activities (entries 1–7 and 10–15 in Table 3). An important feature of the cobalt complex/MMAO systems was the selectivity: in each case the reaction gave almost single C_4 species.

Conclusions

We have synthesised and characterised a set of novel N,N and N,N,P chelating ligands and their nickel and cobalt complexes. Upon activation with Et_2AlCl, the nickel complexes reveal high catalytic activity for the dimerisation and trimerisation of ethylene under the optimal conditions, whereas the cobalt complexes are inactive. When activated with MAO or MMAO the cobalt complexes exhibit high catalytic activities. It was also observed that the catalytic activity of complex **9** increases with an increase of the Al/Co ratio. When activated with MMAO, the cobalt complexes show high selectivity, forming almost single C_4 species. Investigation of the action of the ligands revealed that the nickel complexes with the tridentate ligand have a higher catalytic activity than those with didentate ligands when activated with Et_2AlCl. However, the cobalt complexes with tridentate ligands exhibit lower activity than those with didentate ligands when activated with MMAO. When MAO was used as activator, the cobalt complexes with either tridentate or didentate ligands show similar catalytic activity.

Experimental Section

General Procedure: All air- or moisture-sensitive manipulations were performed under dry N_2 using standard Schlenk and vacuum-line techniques. Solvents were distilled under N_2 over sodium/benzophenone (toluene, *n*-hexane, thf and Et_2O) or CaH_2 (CH_2Cl_2) and degassed prior to use. NMR spectra were recorded with a Bruker av300 spectrometer at ambient temperature (300 MHz for ^1H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P). The chemical shifts of ^1H and ^{13}C NMR spectra are referenced to internal solvent resonances; the ^{31}P NMR spectra are referenced to external 85% H_3PO_4. IR spectra were recorded with a Bruker VECTOR-22 spectrometer. Elemental analyses were performed by the Analytical Centre of the University of Science and Technology of China. GC analyses were performed with a Carlo Erba Strumentazione gas chromatograph equipped with a flame ionisation detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) DM-1 silica capillary column. High purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. Et_2AlCl was purchased from Fluka as a 1.90 M solution in hexane. 3,5-Dimethyl-1-(2′-azidophenyl)pyrazole and $[NiCl_2(dme)]$ were prepared according to literature methods.[4f,14,18]

Preparations

1-{*o*-$(Ph_3PN)C_6H_4$}-3,5-$Me_2C_3HN_2$ (2): A solution of **1** (2.09 g, 9.8 mmol) in CH_2Cl_2 (20 mL) was added to a stirred solution of PPh_3 (2.57 g, 9.8 mmol) in CH_2Cl_2 (10 mL) at room temperature and the mixture was stirred overnight. Volatiles were removed in vacuo and the residue was dissolved in diethyl ether. Filtration of the solution and concentration of the filtrate afforded **2** as a yellow powder (3.95 g, 90.2%), m.p. 126–127 °C. ^1H NMR ($CDCl_3$): δ = 2.02 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 5.89 (s, 1 H, CH), 6.42 (d, *J* = 7.8 Hz, 1 H, C_6H_4), 6.58 (t, *J* = 7.5 Hz, 1 H, C_6H_4), 6.81 (dt, *J* = 7.5, 8.1 Hz, 1 H, C_6H_4), 7.14–7.20 (m, 1 H, C_6H_4), 7.25–7.31 (m, 6 H, Ph), 7.35–7.39 (m, 3 H, Ph), 7.47–7.54 (m, 6 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.8, 13.9, 104.0, 117.1, 122.1 (d, *J* = 9.4 Hz), 128.5 (d, *J* = 12.1 Hz), 128.7, 130.5, 131.6 (d, *J* = 2.7 Hz), 131.8, 132.6 (d, *J* = 9.8 Hz), 134.5, 134.8, 141.7, 147.5 ppm. ^{31}P NMR ($CDCl_3$): δ = –3.56 ppm. IR: $\tilde{\nu}$ = 3049 cm^{-1} w, 3017 vw, 2960 vw, 2925 w, 1591 m, 1548 m, 1496 vs, 1472 s, 1460 s, 1438 s, 1378 m, 1366 m, 1343 vs, 1314 m, 1288 m, 1164 w, 1137 w, 1109 vs, 1054 m, 1033 m, 1020 m, 997 m, 930 w, 780 m, 768 m, 764 s, 718 vs, 694 s, 657 w, 648 w. $C_{29}H_{26}N_3P$ (447.511): calcd. C 77.83, H 5.85, N 9.39; found C 77.50, H 5.87, N 9.49.

1-{*o*-$(Ph_2MePN)C_6H_4$}-3,5-$Me_2C_3HN_2$ (3): This compound was prepared using a similar method to that for **2**. Reaction of Ph_2PMe (1.67 g, 8.4 mmol) with **1** (1.78 g, 8.4 mmol) in CH_2Cl_2 (30 mL) gave orange crystals of **3** (2.74 g, 84.5%), m.p. 86–87 °C. ^1H NMR ($CDCl_3$): δ = 1.96 (d, *J* = 12.6 Hz, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 5.93 (s, 1 H, CH), 6.54 (d, *J* = 8.1 Hz, 1 H, C_6H_4), 6.71 (t, *J* = 7.2 Hz, 1 H, C_6H_4), 6.95–7.01 (m, 1 H, C_6H_4), 7.24–7.27 (m, 1 H, C_6H_4), 7.32–7.49 (m, 6 H, Ph), 7.57–7.63 (m, 4 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.9, 13.8, 14.0 (d, *J* = 62.4 Hz), 104.2, 117.4, 123.0 (d, *J* = 10.9 Hz), 128.6 (d, *J* = 12 Hz), 128.8 (d, *J* = 3.8 Hz), 131.2 (d, *J* = 9.8 Hz), 131.5 (d, *J* = 2.9 Hz), 134.7, 135.0, 141.7, 147.6, 147.9 ppm. ^{31}P NMR ($CDCl_3$): δ = –2.14 ppm. IR: $\tilde{\nu}$ = 3051 cm^{-1} m, 3039 m, 2951 w, 2915 m, 1591 s, 1549 m, 1499 vs, 1427 s, 1436 s, 1417 m, 1358 vs, 1316 m, 1289 m, 1276 m, 1160 w, 1116 s, 1055 m, 1033 m, 1022 m, 998 w, 927 vw, 879 m, 869 m, 768 m, 753 s, 741 s, 732 s, 711 m, 692 s, 648 m. $C_{24}H_{24}N_3P$ (385.441): calcd. C 74.79, H 6.27, N 10.90; found C 74.69, H 6.29, N 11.16.

1-[*o*-$\{Ph_2PCH_2P(Ph)_2N\}C_6H_4$]-3,5-$Me_2C_3HN_2$ (4): A solution of **1** (3.33 g, 15.6 mmol) in CH_2Cl_2 (20 mL) was added to a stirred solution of $Ph_2PCH_2PPh_2$ (6.01 g, 15.6 mmol) in CH_2Cl_2 (10 mL) at 0 °C and the mixture was stirred overnight at room temperature. Volatiles were removed in vacuo and the residue was dissolved in diethyl ether (20 mL). Filtration of the solution and concentration of the filtrate produced **4** as a yellow powder (7.36 g, 82.7%), m.p. 130–131 °C. ^{1}H NMR ($CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 3.07 (d, J = 12.5 Hz, 2 H, CH_2), 5.81 (s, 1 H, CH), 6.38 (d, J = 8.0 Hz, 1 H, C_6H_4), 6.64 (t, J = 7.6 Hz, 1 H, C_6H_4), 6.80–6.85 (m, 1 H, C_6H_4), 7.11–7.24 (m, 15 H, Ph, C_6H_4), 7.32 (d, J = 7.1 Hz, 2 H, Ph), 7.47–7.53 (m, 4 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.0, 13.9, 29.6 (dd, J = 61.8, 70.8 Hz), 104.2, 117.4, 123.3 (d, J = 10.3 Hz), 128.4, 128.49, 128.54, 128.65, 128.75, 131.5, 131. 9 (d, J = 9.1 Hz), 132.7, 133.0, 134.6, 134.9, 142.0, 147.5 ppm. ^{31}P NMR ($CDCl_3$): δ = –1.98 (d, J = 51.9 Hz), –31.42 (d, J = 52.6 Hz) ppm. IR: $\tilde{\nu}$ = 3054 cm^{-1} m, 2923 m, 1595 m, 1547 m, 1498 vs, 1468 s, 1433 s, 1365 vs, 1357, 1309 w, 1289 w, 1182 vw, 1155 vw, 1118 m, 1060 w, 1022 m, 998 w, 930 vw, 798 w, 778 m, 765 w, 735 vs, 694 s, 643 w. $C_{36}H_{33}N_3P_2$ (569.615): calcd. C 75.91, H 5.84, N 7.38; found C 75.79, H 5.91, N 7.68.

[{1-[*o*-(Ph_3PN)C_6H_4]-3,5-$Me_2C_3HN_2$}$NiBr_2$] (5): A solution of **2** (0.552 g, 1.23 mmol) in thf (10 mL) was added to a suspension of $NiBr_2$ (0.270 g, 1.23 mmol) in thf (10 mL) and the mixture was stirred overnight at room temperature. The solvent was then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 3 mL. Toluene was added to the solution to give **5** as a blue powder (0.693 g, 93.6%), m.p. 311–312 °C. IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} w, 3047 w, 2958 vw, 2922 w, 1590 w, 1549 m, 1497 m, 1483 m, 1438 vs, 1366 m, 1279 m, 1263 vs, 1232 m, 1187 w, 1125 m, 1107 vs, 1058 w, 1047 m, 1005 m, 993 s, 811 s, 783 m, 753 s, 741 m, 721 s, 694 s, 667 w, 622 w. $C_{29}H_{26}Br_2N_3NiP$ (666.01): calcd. C 52.29, H 3.93, N 6.31; found C 52.34, H 3.88, N 6.48.

[{1-[*o*-(Ph_3PN)C_6H_4]-3,5-$Me_2C_3HN_2$}$NiCl_2$] (6): A solution of **2** (0.407 g, 0.91 mmol) in thf (10 mL) was added to a stirred suspension of [$NiCl_2$(dme)] (0.200 g, 0.91 mmol) in thf (10 mL) at room temperature and the mixture was stirred overnight at room temperature. The volatiles were removed under vacuum and the residue was dissolved in CH_2Cl_2 (10 mL). The solution was filtered and the filtrate was concentrated to about 2 mL. Hexane was added to the solution to give **6** as a blue powder (0.477 g, 90.8%), m.p. 275–276 °C. IR (KBr): $\tilde{\nu}$ = 3065 cm^{-1} w, 2970 vw, 2926 vw, 1591 m, 1549 m, 1497 s, 1487 s, 1437 vs, 1389 w, 1368 m, 1283 m, 1263 s, 1233 m, 1188 w, 1140 w, 1110 s, 1048 m, 1029 w, 994 m, 812 s, 783 m, 756 s, 744 m, 723 s, 695 s, 678 w, 612 w. $C_{29}H_{26}Cl_2N_3NiP$ (577.11): calcd. C 60.35, H 4.75, N 7.28; found C 60.39, H 4.64, N 7.29.

[{1-[*o*-(Ph_2MePN)C_6H_4]-3,5-$Me_2C_3HN_2$}$NiBr_2$] (7): A solution of **3** (0.278 g, 0.72 mmol) in thf (10 mL) was added to a stirred suspension of $NiBr_2$ (0.158 g, 0.72 mmol) in thf (10 mL) at room temperature and the mixture was allowed to stir overnight. The solvent was then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 2 mL. Toluene was added to yield blue crystals of **7**·CH_2Cl_2 (0.427 g, 86.1%), m.p. 239–240 °C. IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} w, 2987 w, 2916 w, 1593 m, 1550 m, 1499 s, 1453 m, 1437 s, 1419 m, 1389 w, 1373 w, 1298 m, 1272 s, 1236 m, 1160 w, 1117 vs, 1061 w, 1047 w, 1010 s, 996 s, 894 s, 799 w, 781 m, 743 vs, 716 w, 693 s, 667 s, 615 w. $C_{24}H_{24}Br_2N_3NiP$·CH_2Cl_2 (688.88): calcd. C 43.59, H 3.80, N 6.10; found C 43.72, H 3.82, N 6.17.

[{1-[*o*-(Ph_2MePN)C_6H_4]-3,5-$Me_2C_3HN_2$}$NiCl_2$] (8): A solution of **3** (0.321 g, 0.83 mmol) in thf (10 mL) was added to a stirred suspension of [$NiCl_2$(dme)] (0.183 g, 0.83 mmol) in thf (10 mL) at room temperature and the mixture was allowed to stir overnight. The volatiles were then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 2 mL. Toluene was added to give **8**·CH_2Cl_2·0.3THF as a blue powder (0.414 g, 80.2%), m.p. 117–118 °C. IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} w, 2986 w, 2915 w, 1594 m, 1556 m, 1499 s, 1487 m, 1450 m, 1437 s, 1390 m, 1374 m, 1302 m, 1274 s, 1238 m, 1150 w, 1114 vs, 1067 m, 1010 s, 998 s, 897 s, 866 w, 801 m, 786 m, 780 m, 749 vs, 729 s, 695 s, 668 w, 616 w. $C_{24}H_{24}Cl_2N_3NiP$·CH_2Cl_2·0.3THF (621.60): calcd. C 50.62, H 4.61, N 6.76, found C 50.82, H 4.51, N 7.10.

[{1-[*o*-(Ph_3PN)C_6H_4]-3,5-$Me_2C_3HN_2$}$CoCl_2$] (9): A solution of ligand **2** (0.432 g, 0.96 mmol) in thf (10 mL) was added to a stirred suspension of $CoCl_2$ (0.125 g, 0.96 mmol) in thf (10 mL) at room temperature and the mixture was allowed to stir overnight. The solvent was then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 2 mL. Hexane was added to give **9** as a blue powder (0.535 g, 96.4%), m.p. 268–269 °C. IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} w, 2958 vw, 2922 w, 2853 vw, 1590 m, 1549 m, 1496 s, 1484 s, 1438 vs, 1389 w, 1366 m, 1313 w, 1278 m, 1260 vs, 1232 s, 1188 w, 1158 vw, 1138 w, 1125 s, 1108 vs, 1048 m, 1027 w, 1006 m, 992 s, 807 s, 781 s, 753 s, 742 m, 721 s, 694 s, 666 m, 645 w, 621 m. $C_{29}H_{26}Cl_2CoN_3P$ (577.35): calcd. C 60.33, H 4.54, N 7.28; found C 60.34, H 4.53, N 7.55.

[{1-[*o*-(Ph_2MePN)C_6H_4]-3,5-$Me_2C_3HN_2$}$CoCl_2$] (10): A solution of **3** (0.326 g, 0.85 mmol) in thf (10 mL) was added to a stirred suspension of $CoCl_2$ (0.110 g, 0.85 mmol) in thf (10 mL) at room temperature and the mixture was allowed to stir overnight. The solvent was then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 2 mL. Toluene was added to produce blue crystals of **10**·1.5C_7H_8 (0.404 g, 72.7%), m.p. 125–126 °C. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} w, 2985 w, 2914 w, 1592 m, 1552 m, 1498 s, 1484 m, 1437 s, 1423 m, 1388 w, 1371 m, 1302 m, 1272 s, 1236 m, 1161 w, 1144 w, 1113 s, 1064 m, 998 s, 949 w, 898 s, 798 w, 777 m, 749 s, 728 m, 695 m, 666 w, 614 w. $C_{24}H_{24}Cl_2CoN_3P$·1.5C_7H_8 (653.49): calcd. C 63.41, H 5.55, N 6.43; found C 63.24, H 5.47, N 6.52.

[{1-[*o*-($Ph_2PCH_2PPh_2N$)C_6H_4]-3,5-$Me_2C_3HN_2$}$NiBr_2$] (11): A solution of **4** (0.524 g, 0.92 mmol) in thf (10 mL) was added to a suspension of $NiBr_2$ (0.201 g, 0.92 mmol) in thf (5 mL) at room temperature with stirring and the mixture was allowed to stir for 4 h. The solvent was then removed under vacuum and the residue was dissolved in CH_2Cl_2 (10 mL). The solution was filtered and the filtrate was concentrated to about 4 mL. Hexane (10 mL) was added to produce purple microcrystals of **11** (0.693 g, 95.6%), m.p. 225–226 °C. An analytically pure sample was obtained by recrystallisation from a mixture of dmf and benzene. IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} m, 3016 w, 2987 w, 2960 vw, 2816 w, 1590 m, 1553 m, 1499 vs, 1484 s, 1454 s, 1436 vs, 1389 m, 1366 m, 1298 s, 1241 m, 1190 w, 1160 m, 1114 vs, 1047 m, 997 s, 804 s, 782 vs, 741 vs, 725 s, 691 vs, 642 w, 615 w. $C_{36}H_{33}Br_2N_3NiP_2$·THF·C_6H_6 (938.33): calcd. C 57.54, H 4.93, N 5.96; found C 57.24, H 4.82, N 5.83.

[{1-[*o*-($Ph_2PCH_2PPh_2N$)C_6H_4]-3,5-$Me_2C_3HN_2$}$NiCl_2$] (12): A solution of **4** (0.337 g, 0.59 mmol) in thf (10 mL) was added to a stirred suspension of [$NiCl_2$(dme)] (0.130 g, 0.59 mmol) in thf (10 mL) and the mixture was stirred overnight at room temperature. The volatiles were then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 2 mL. Toluene was added to produce yellow crystals of **12**·THF (0.379 g, 83.3%), m.p. 180–181 °C. IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} w, 3028 w, 2963 w, 2904 w, 1590 m, 1556 m, 1496 s, 1486 s, 1447 m, 1435 vs, 1371 m, 1291 s, 1241 m, 1142 m, 1112 s, 1058 m, 1028 w, 996 s, 802 m, 782 s, 770 s, 739 s, 720 s, 693 s, 616 w. $C_{36}H_{33}Cl_2N_3NiP_2$·THF (771.32): calcd. C 62.29, H 5.36, N 5.45;

Table 4. Details of the X-ray structure determinations of complexes **5**, **9** and **12**.

	5	**9**	**12·C_7H_8**
Empirical formula	$C_{29}H_{26}Br_2N_3NiP$	$C_{29}H_{26}Cl_2CoN_3P$	$C_{43}H_{41}Cl_2N_3NiP_2$
Formula mass	666.03	577.33	791.34
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/c$
a [Å]	18.168(4)	16.597(2)	14.793(2)
b [Å]	16.691(4)	18.007(2)	13.929(2)
c [Å]	18.302(4)	18.198(2)	20.250(3)
α [°]	90	90	90
β [°]	90	90	109.793(3)
γ [°]	90	90	90
V [Å^3]	5550(2)	5438.5(12)	3926.2(11)
Z	8	8	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.594	1.410	1.339
$F(000)$	2672	2376	1648
μ [mm^{-1}]	3.660	0.910	0.746
θ range for data collection [°]	2.00 to 26.40	2.01 to 27.19	1.46 to 25.95
No. of reflns. collected	29235	29912	20646
No. of independent reflns. (R_{int})	5662 (R_{int} = 0.0652)	5876 (R_{int} = 0.0681)	7598 (R_{int} = 0.0569)
No. of data / restraints / parameters	5662 / 0 / 327	5876 / 0 / 327	7598 / 0 / 463
Goodness of fit on F^2	1.125	1.050	1.013
Final R indices[a] [$I > 2\sigma(I)$]	R_1 = 0.0615 wR_2 = 0.1973	R_1 = 0.0415 wR_2 = 0.0806	R_1 = 0.0484, wR_2 = 0.1092
R indices (all data)	R_1 = 0.0964 wR_2 = 0.2185	R_1 = 0.0899 wR_2 = 0.0997	R_1 = 0.0960, wR_2 = 0.1353
Largest diff. peak and hole [e Å^{-3}]	1.082 and –0.803	0.364 and –0.384	0.778 and –0.431

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

found C 62.60, H 5.16, N 5.35. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallisation of **12** from toluene (thf was removed from **12**·THF under vacuum prior to recrystallisation).

[{1-[*o*-($Ph_2PCH_2PPh_2N$)C_6H_4]-3,5-$Me_2C_3HN_2$}$CoCl_2$] (13): A solution of **4** (0.482 g, 0.85 mmol) in thf (10 mL) was added to a suspension of $CoCl_2$ (0.110 g, 0.85 mmol) in thf (10 mL) at room temperature with stirring. The volatiles were then removed under vacuum and the residue was dissolved in CH_2Cl_2. The solution was filtered and the filtrate was concentrated to about 2 mL. Toluene was added to produce blue crystals of **13**·0.75C_7H_8 (0.567 g, 86.8%), m.p. 129–130 °C. IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} m, 3021 m, 2950 m, 2924 m, 2902 m, 1590 s, 1572 w, 1556 s, 1495 s, 1481 s, 1467 s, 1435 vs, 1372 s, 1361 s, 1301 s, 1267 vs, 1239 s, 1189 w, 1158 w, 1139 s, 1111 vs, 1057 s, 1044 s, 1028 m, 991 vs, 938 w, 922 w, 825 w, 800 s, 782 vs, 769 vs, 739 vs, 717 vs, 694 vs, 662 s, 638 m, 616 m. $C_{36}H_{33}Cl_2CoN_3P_2$·0.75C_7H_8 (768.56): calcd. C 64.46, H 5.11, N 5.46; found C 64.24, H 5.16, N 5.41.

X-ray Crystallography: Crystals were mounted in Lindemann capillaries under N_2. Diffraction data were collected on a Siemens CCD area detector at 294(2) K with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A semi-empirical absorption correction was applied to the data. The structures were solved by direct methods using SHELXS-97[19] and refined against F^2 by full-matrix least-squares using SHELXL-97.[20] Crystal data and experimental details of the structure determinations are listed in Table 4.

CCDC-606680 (for **5**), -606681 (for **9**) and -617850 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Ethylene Oligomerisation: The oligomerisation with 1 atm of ethylene was carried out in a Schlenk tube. Thus, the pre-catalyst (5 µmol) was added to a dried Schlenk tube and then the tube was back-filled three times with N_2 and twice with ethylene. Toluene (30 mL) was added to the tube and then the appropriate co-catalyst solution was added with a syringe. The reaction mixture was vigorously stirred at the given temperature under 1 atm of ethylene. After the desired period of time (30 or 60 min), the reaction was terminated by adding 10% HCl solution (30 mL). About 1 mL of the organic layer was dried with anhydrous Na_2SO_4 for GC analysis. Ethanol (100 mL) was added to the remaining solution; no polymer was observed.

The oligomerisation with 10 atm of ethylene was carried out in a stainless-steel autoclave (250 mL capacity) equipped with a gas ballast through a solenoid valve for continuous feeding of ethylene at constant pressure. Toluene (120 mL) containing the pre-catalyst was transferred into the fully dried reactor under N_2 atmosphere. The required amount of co-catalyst was injected into the reactor with a syringe. Once the desired temperature had been reached the reactor was pressurised to 10 atm. After stirring for 30 min, the reaction was quenched and worked-up using the same procedure as described above for the reaction at 1 atm.

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