The effect of bulky substituents on the olefin polymerisation behaviour of nickel catalysts bearing [P,O] chelate ligands

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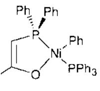
Incorporation of bulky substituents adjacent to the oxygen donor site of [P,O]Ni catalysts affords dramatic increases in olefin polymerisation activities

Nickel catalysts have provided some of the most significant advances in late transition metal olefin polymerisation catalysis and have given some of the most promising results with regard to polar monomer incorporation into polyolefinic materials.[1–4] One of the earliest systems to be investigated was the nickel-ylide oligomerisation system (**1**) introduced by Keim *et al.*[5] and subsequently developed by the groups of Starzewski[6] and Klabunde[7] for olefin polymerisation and copolymerisation. However the intrinsic activities of these catalysts are not high.

Bulky substituents have been shown to have a strong influence on the activities and selectivities of α-diimine[8] and salicylaldimine[9] nickel catalysts, yet the influence of sterically demanding groups has not been fully explored in the [P,O]Ni system. Several sites around the ligand are amenable to modification (see **2** below†): (i) the tertiary phosphine substituents (R^1), (ii) the backbone carbon substituent (R^2) adjacent to the phosphine donor, and (iii) the backbone carbon substituent (R^3) adjacent to the enolate oxygen. It was also recognised that an alternative approach to changing the steric influence at the enolate oxygen site is to exchange the oxo group for the isoelectronic [NR] unit. Here, we describe a series of new nickel catalysts containing [P,O] chelate ligands which reveal a dramatic enhancement in ethylene polymerisation activities, in some cases in excess of two orders of magnitude, on introduction of bulky substituents, especially at the site adjacent to the oxygen donor group.

The phosphorus ylide ligand precursors **3**–**5** (Scheme 1) were synthesised *via* modified literature procedures.[10,11] The ligand precursors **6**–**8** were prepared *via* Diels–Alder addition of crotonic acid or fumaric acid to anthracene, followed by conversion to the acyl chloride and subsequent treatment with benzylidenetriphenylphosphorane. For **8**, the bis(acyl chloride) is used to introduce the pendant phosphonium group. The catalysts **3a**–**8a** were then generated *in situ* by treatment of $Ni(cod)_2$ with the phosphorus ylide ligand precursor. *In situ* $^{31}P\{^1H\}$ NMR studies show that oxidative addition of **3**–**8** to the Ni(0) species occurs very rapidly in the presence of an olefin to form [P,O]Ni chelates.



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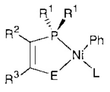
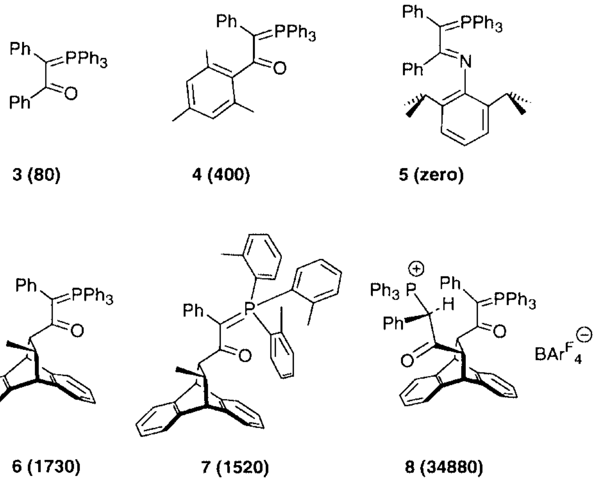


2

R^1 = Ph, o-tol
R^2 = H, Ph
R^3 = Ph,
2,4,6-$Me_3C_6H_2$
9,10-DH-9,10-EA †
E = O, N(2,6-$Pr^i_2C_6H_2$)
L = PPh_3, Py, $PPhMe_2$

Complexes containing these chelate ligands were also synthesised and isolated‡ from the corresponding ligand precursors and $Ni(cod)_2$ in the presence of an auxiliary ligand, typically triphenyl- or dimethylphenyl-phosphine, or pyridine. A crystal structure of the complex **6b**§ containing the ligand from catalyst system **6a** and the stabilising triphenylphosphine ligand is shown in Fig. 1. Complex **6b** crystallises with two independent molecules **A** and **B** in the asymmetric unit both of which have very similar conformations, the differences being in the relative orientations of the phenyl substituents. The geometry at nickel is only very slightly distorted square planar, the nickel and the four coordinated atoms being coplanar to within *ca.* 0.028 Å in both molecules. The plane of the C(43) phenyl ring is, in both molecules, oriented almost orthogonally



Scheme 1 Ligand precursors (LP) used in the corresponding *in situ* catalyst systems LP/$Ni(cod)_2$/olefin, **3a**–**8a** (olefin = ethylene, propylene or hex-1-ene) and their catalytic activities (g $mmol^{-1}$ h^{-1}) for ethylene polymerisation; BAr^F_4 = [3,5-$(CF_3)_2C_6H_3$]B.

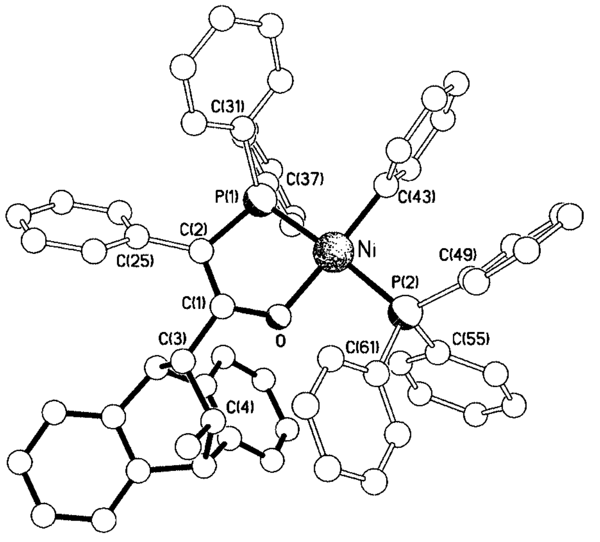


Fig. 1 One of the pair of crystallographically independent molecules present in the structure of **6b**. Selected bond lengths (Å) (data for molecule **B** are given in square brackets); Ni–O 1.901(2) [1.906(2)], Ni–P(1) 2.165(1) [2.174(1)], Ni–P(2) 2.212(1) [2.223(1)], Ni–C(43) 1.921(1) [1.928(1)], P(1)–C(2) 1.784(3) [1.775(3)], O–C(1) 1.309(4) [1.308(4)], C(1)–C(2) 1.374(4) [1.368(4)].

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to this plane. The *cis* angles at nickel are in the ranges 85.74(6)–93.03(7) and 85.43(6)–93.27(6)° in **A** and **B**, respectively, within each case the most acute angle being associated with the bite of the chelating ligand. The Ni–P(1) distance is, in both molecules, 0.05 Å shorter than that to P(2), indicating possibly an extension of the clear pattern of bond delocalisation, that extends from O through to P(1) *via* C(1) and C(2), to include the metal centre. The chelate ring has a slightly folded envelope conformation with the phosphorus atom lying 0.28 Å (molecule **A**) and 0.13 Å (molecule **B**) out of the plane of the remaining four atoms which are coplanar to within 0.007 Å (molecule **A**) and 0.009 Å (molecule **B**). The C(25) phenyl substituent is rotated by *ca.* 55° (**A**) and 68° (**B**) out of the plane of the chelate ring. The O–C(1)–C(3)–C(4) torsion angle is, in both molecules, small (*ca.* 6 and 15° in **A** and **B**, respectively), possibly as a consequence of a C(4)–H···O intramolecular hydrogen bond (the H···O distances are 2.24 and 2.26 Å in **A** and **B**, respectively).

The activities of these neutral catalysts for ethylene polymerisation and the results of product analyses are collected in Table 1. The ligand precursor **3**, and its triphenylphosphine stabilised nickel complex have been described earlier as precursors to ethylene polymerisation catalysts.[3,12] The catalytic performance of **3**/Ni(cod)$_2$ (**3a**) was used as a benchmark for the present study. Polymerisations were carried out both on *in situ* generated catalysts, which do not require the presence of a phosphine scavenger, and on the tertiary-phosphine stabilised pre-catalysts in the presence of Ni(cod)$_2$. Approximately the same activities are found in both cases and the resultant polymers also possess similar properties. In all cases, the polyethylene is essentially linear with number average molecular weights in the range 3000–10 000 and with molecular weight distributions in the range 2.0–3.7. It can be seen that there is an increase in activity upon introduction of a mesityl unit on the carbon adjacent to the enolate oxygen (**4a** *cf.* **3a**). Surprisingly, the activity falls to zero when the oxo group is exchanged for a N(diisopropylphenyl) unit (**5a**). A dramatic increase in activity is found upon introduction of the bulky anthracenyl-derived substituent (**6a**–**8a**), particularly for the phosphonium-containing catalyst **8a** which achieves an activity of almost 35 000 g mmol^{-1} h^{-1}. Comparison of **6a** with **7a** indicates that there is no beneficial effect on activity of increasing the size of the phosphorus substituents.

Another interesting feature of the neutral nickel complexes bearing bulky [P,O] ligands is their ability to oligomerise propylene and hex-1-ene. While co-polymerisations of ethylene with higher α-olefins by nickel phosphinoenolate complexes have been reported,[7] there have been no reports of propylene or hex-1-ene oligomerisations using these or related catalysts. Our attempts to oligomerise propylene with **3a** resulted in formation of only traces of propylene dimers. However **6a**, dissolved in toluene, oligomerised propylene at 4 bar and 70 °C with an activity of 1350 g mmol^{-1} h^{-1} to give a Schultz–Flory distribution (K = 0.64) of C_6–C_{48} olefins. Catalyst **8a** oligomerises propylene with a similar activity to give oligomers with a similar product distribution. Both catalysts homo-oligomerise hex-1-ene to C_{12}–C_{36} oligomers with relatively low activities. Thus, for example, catalyst **6a** shows an activity of 15 g mmol^{-1} h^{-1} for hex-1-ene oligomerisation.

Table 1 Results of ethylene polymerisation using catalytic systems **3a**–**8a** in toluene at 70 °C[a]

Cat. system	Ligand amount/ µmol	Mole ratio Ni/L	Ethylene pressure/ bar	PE yield/g	Activity[b]/ g mmol^{-1} h^{-1}	M_n	M_w/M_n
3a	20.0	5	1	0.4	80	6000	2.3
4a	5.0	5	1	0.5	400	4200	2.4
6a	4.4	5	1	1.9	1730	5200	3.6
6b	10.0[c,d]		1	3.2	1280[e]	5100	3.7
7a	10.0	5	1	3.8	1520	3500	2.0
8a	2.5	12	4	21.8	34880	5000	3.6
8a	2.4	12	2	18.3	30500	5200	3.5
8a[f]	2.7	12	4	10.0	14800	9900	5.4[g]

[a] Polymersations carried out in Schlenk tubes or Fisher–Porter bottles, over 15 min. [b] Based on concentration of ligand precursor. [c] 5 equivalents Ni(cod)$_2$ used as phosphine scavenger. [d] Conc. of Ni complex **6b**. [e] g mmol[Ni]$^{-1}$ h^{-1}. [f] Polymerisation carried out at 50 °C. [g] Bimodal molecular weight distribution.

The increase in activity is clearly linked to the introduction of the bulky anthracenyl-derived substituent next to the oxygen donor site. Possible effects of this are to protect the electrophilic nickel centre from binding potentially poisoning donor groups and/or to disfavour the coordination of Lewis acids at the oxygen site, especially another nickel centre which can result in ligand migration and formation of a catalytically inactive bis(chelate) species. Co-polymerisations of ethylene with hydrocarbon and polar co-monomers are presently under investigation.

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Notes and references

† 9,10-Dihydro-9,10-ethanoanthracene.

‡ For example, synthesis of **6b**: a solution of 0.50 g (1.82 mmol) bis(*cis, cis*-cycloocta-1,5-diene)nickel(0), 1.09 g (1.82 mmol) *rac*-*trans*-11-(1-phenyl-1-triphenylphosphoranylideneacetyl)-12-methyl-9,10-dihydro-9,10-ethanoanthracene and 0.48 g (1.82 mmol) triphenylphosphine in toluene (50 ml) was stirred at room temperature for 24 h and at 50 °C for 1 h. The solvent was removed *in vacuo* and the residue was dissolved in toluene (7–8 ml). Addition of *n*-heptane (15–20 ml) gave a yellow precipitate which was filtered, washed with *n*-heptane and dried *in vacuo*. Yield, 1.10 g (66%), Anal. Found: C, 79.56; H, 5.64. $C_{61}H_{50}NiOP_2$ requires C, 79.66; H, 5.64%. ^{1}H NMR (250 MHz, C_6D_6): δ 0.72 (3H, d, J 6.72 Hz, CH_3), 2.17 (1H, m, CH), 2.79 (1H, m, CH), 3.53 (1H, d, J 1.70 Hz, CH), 4.24 (1H, d, J 1.70 Hz, CH), 6.40 (2H, t, Ar), 6.52 (1H, t, Ar), 6.72 (3H, m, Ar), 6.82–6.92 (8H, m, Ar), 6.92–7.09 (14H, m, Ar), 7.11–7.21 (10H, m, Ar), 7.30–7.34 (3H, m, Ar), 7.88–7.95 (2H, m, Ar). ^{31}P{^{1}H} NMR (101 MHz, C_6D_6): δ 22.01 (d, J 281.5 Hz, PPh_3), 33.58 (d, J 281.5 Hz, PPh_2). (+) FAB MS: m/z 918 (M^+), 841 ($M - Ph^+$), 656 ($M - PPh_3^+$).

§ *Crystal data* for **6b**·$0.5C_7H_{16}$: $C_{61}H_{50}OP_2Ni\cdot 0.5C_7H_{16}$, M = 969.8, monoclinic, $P2_1/n$ (no. 14), a = 22.153(2), b = 10.861(1), c = 42.785(4) Å, β = 90.68(1)°, V = 10293(2) Å^3, Z = 8 (2 independent molecules), D_c = 1.252 g cm^{-3}, μ(Cu-Kα) = 14.5 cm^{-1}, T = 203 K, orange–yellow prismatic needles; 15157 independent measured reflections, F^2 refinement, R_1 = 0.050, wR_2 = 0.122, 11797 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°$], 1067 parameters. CCDC 158572. See http://www.rsc.org/suppdata/cc/b1/b101582f/ for crystallographic data in .cif or other electronic format.

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