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Nickel Ethylene Polymerization Catalysts Based on Phosphorus Ligands

Neil A. Cooley, Simon M. Green, and Duncan F. Wass*

BP, Chemicals Stream, Chertsey Road, Sunbury-on-Thames,
Middlesex, TW16 7LL, United Kingdom

Katie Heslop, A. Guy Orpen, and Paul G. Pringle

School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

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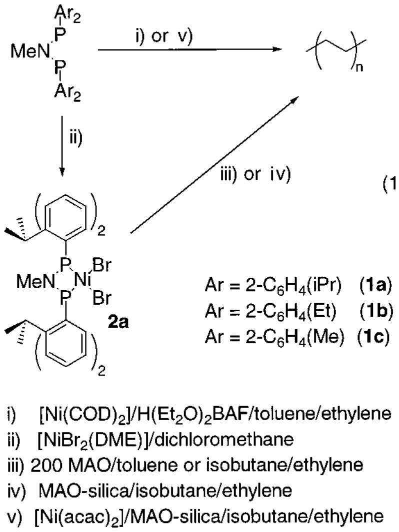
Summary: Nickel(II) complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = ortho-substituted phenyl group) are highly active and poison-tolerant catalysts for the polymerization of ethylene.

The discovery of high-activity nickel and palladium olefin polymerization catalysts by Brookhart and coworkers in 1995 has led to an upsurge of interest in the use of late transition metal polymerization technologies.[1] We report here our discovery of a new class of ethylene polymerization catalyst based on nickel(II) complexes of bulky bis(diarylphosphino)methylamines.[2,3] The growing family of active nickel catalysts is almost exclusively based on hard nitrogen or oxygen donors,[4,5] and despite the central role of diphosphine ligands in many other types of homogeneous catalysis involving late transition metals,[6,7] softer phosphorus donors have been largely unsuccessful in this application.[8]

Several activation methods have been employed (eq 1). Initial polymerization experiments utilized a method developed for the rapid screening of potential nickel catalysts.[4b,9] Treatment of $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene) with the ligand and $H(Et_2O)_2BAF$ (BAF = $B[3,5-(CF_3)_2C_6H_3]_4$) in toluene and exposure of these solutions to ethylene gave polyethylene with moderate activity (Table 1).



(1)

Compound **1a**, bearing isopropyl substituents, produces high molecular weight material with low levels of branching consistent with "chain walking" mechanisms.[4b] Ligands **1b** and **1c**, with less sterically encumbered substitution patterns, yield lower molecular weight material. The tolerance of the systems to traditional poisons for olefin polymerization catalysts matches the most robust existing nickel systems;[10] with water levels as high as 10% by volume, polymerization is still observed, albeit at a tenth the activity.

To investigate a range of other activation methods, a dibromonickel(II) procatalyst complex **2a** was formed by treatment of $[NiBr_2(dme)]$ (dme = 1,2-dimethoxyethane) with ligand **1a** in dichloromethane according to eq 1. A single-crystal X-ray structure of complex **2a** was obtained (Figure 1).[11] The complex is C_2 symmetric with square planar coordination at nickel and a near planar

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[1] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320. (c) Johnson, J. K.; Killian, C. M.; Arthur, S. D.; Feldman, J.; McCord, E. F.; McLain, S. J.; Kreutzer, K. A.; Bennett, A. M. A.; Coughlin, E. B.; Ittel, S. D.; Parthasarathy, A.; Tempel, D. J.; Brookhart, M. WO 96/23010 (to DuPont) **1996** [*Chem. Abstr.* **1996**, *125*, 222773t].

[2] Wass, D. F. WO 01/10876 (to BP Chemicals).

[3] We have recently reported the activity of these ligands in palladium-catalyzed ethylene/CO copolymerization: (a) Dossett, S. J. WO 97/37765 (to BP Chemicals). (b) Dossett, S. J. WO 00/06299 (to BP Chemicals). (c) Dossett, S. J.; Gillon, A.; Orpen, A. G.; Fleming, J. S.; Pringle, P. G.; Wass, D. F.; Jones, M. D. *Chem. Commun.* **2001**, 699.

[4] (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

[5] Mixed hard/soft ligands produce polyethylene under certain conditions: (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (b) Keim, W.; Appel, R.; Gruppe, S.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1012. (c) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123. (d) Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1989.

[6] Notably, palladium phosphine catalysts are well established for the copolymerisation of olefins and carbon monoxide. See: Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

[7] For a recent general overview of the use of phosphine ligands in catalysis, see: van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Diekes, P. *Chem. Rev.* **2000**, *100*, 2741.

[8] Chelating diphosphine ligands demonstrate extremely low activity and give low molecular weight products: (a) Mui, H. D.; Riehl, M. E.; Wilson, S. R.; Girolami, G. S. *ACS Abstracts* **1994**, Vol. 208 (part 1), pp 530-INOR. (c) Hoehn, A.; Lippert, F.; Schauss, E. (BASF) WO 96/37522. (e) Brookhart, M. S.; Feldman, J.; Hauptman, E.; McCord, E. F. (DuPont) WO 98/47934.

[9] Johnson, L. K.; Feldman, J.; Kreutzer, K. A. (DuPont) WO 9702298.

[10] (a) Held, A.; Bauers, F. M.; Mecking, S. *Chem. Commun.* **2000**, 301. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

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Table 1. Ethylene Polymerization Results

entry	catalyst	method[a]	T (°C)	p (bar)	yield (g)	activity[b]	M_w	M_n	PDI	branches[c]/ 1000 C
1	**1a**	i	25	1	1.0	100	120 000	32 000	3.7	2.7
2	**1b**	i	25	1	0.8	80	23 000	9000	2.5	11
3	**1c**	i	25	1	0.6	60	9000	4000	2.2	8.0
4[d]	**1a**	i	25	1	0.1	10	85 000	34 000	2.5	2.5
5	**2a**	iii[e]	25	1	4.1	820	98 000	40 000	2.4	3.1
6	**2a**	iii	25	8	15	1500	148 000	40 000	3.7	1.6
7	**2a**	iii	50	8	22	2200	65 000	17 000	3.8	2.3
8	**2a**	iii	50	20	15	1500	78 000	13 000	5.9	3.1
9	**2a**	iv[f]	50	8	4.2	210	62 000	22 000	2.8	6.2
10	**1a**	v[g]	50	8	11	225	73 000	24 000	3.0	2.5
12	**1b**	v[g]	50	8	1.5	24		42 000[h]		22
13	**1c**	v[g]	50	8	0.4	7		11 000[h]		36
14[i]	**2a**	iv[g]	50	8	1.0	17	63 000	21 000	3.0	11[j]

[a] All runs using 0.01 mmol catalyst and 1 h run time unless otherwise stated. [b] Average activity in g/mmol·h over run time; some catalyst deactivation is observed over this time (see kinetic profile included in Supporting Information) and initial activities are higher. [c] Methyl branches predominate, although smaller amounts of ethyl and longer branches are observed. Typical data included in Supporting Information. [d] Toluene solvent contains 10% v/v water. [e] Run terminated after 30 min; after this time the polymer produced hindered stirring. [f] 0.02 mmol catalyst used. [g] 0.04 mmol catalyst used. [h] Mpeak: Bimodal distribution obtained with additional low molecular peak at 300. [i] 5 ml 1-hexene added. [j] Butyl branches; 4.2 methyl branches also present.

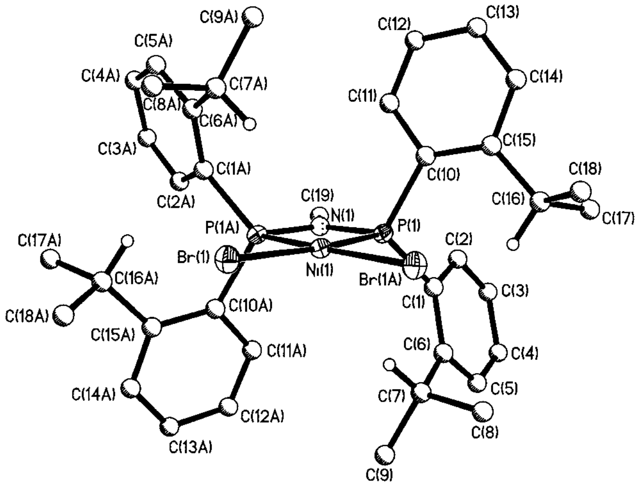

Figure 1. Molecular structure and numbering scheme for **2a**. All but the tertiary isopropyl hydrogen atoms have been omitted for clarity. Important molecular dimensions: bond lengths (Å) Ni(1)−P(1) 2.1611(6), Ni(1)−Br(1) 2.3276(4); bond angles (deg) P(1)−Ni(1)−P(1a) 74.07(3), P(1)−N(1)−P(1a) 92.49(7).

NiP_2N chelate ring. As a consequence, the aryl groups are isoclinal, and two have *ortho* isopropyl groups orientated so as to block the axial sites at nickel. The conformation of the other aryls (at C10 and C10A) is such as to provide some blocking of the freedom of ligands (or polymer chain) bound in the equatorial coordination plane of the nickel. Steric bulk is important in reducing chain transfer rates, as described for other nickel polymerization catalysts.[1] In this case, we propose the sterically encumbered chelates may also prevent the formation of dimeric nickel species, often observed with one-atom backbone diphosphines.[12]

Treatment of **2a** with MAO (methyl alumoxane) cocatalyst yielded a highly active polymerization catalyst. However, the reactivity observed is very dependent on the free trimethyl aluminum content of the MAO used;[13] active catalyst systems are formed only with cocatalyst batches containing no free trimethyl aluminum.[14] Furthermore, addition of trimethyl aluminum to an ongoing polymerization inhibits further activity.[15] Using a MAO activation procedure results in higher activity compared to the [Ni(COD)$_2$]/H(Et$_2$O)$_2$BAF method (compare entries 1 and 5), although the structure of the polyethylene obtained is very similar.

The effects of temperature and pressure have been investigated. As temperature is increased from 25 °C to 50 °C, the rate of polymerization increased and the molecular weight of the resultant polymer decreased. The catalysts show some deactivation with time;[16] initial activity for entry 7, measured over the first 10 min of the polymerization run, is as high as 6000 g mmol^{-1} h^{-1}. Polymerization rate and molecular weight have a zeroth-order dependence on ethylene pressure (entries 7 and 8), as observed with other nickel polymerization catalysts.[1]

Catalyst systems may be formed using a MAO-treated silica cocatalyst (eq 1, method iv).[17] This procedure provides a method for generating MAO-based cocatalysts that are free of trimethyl aluminum. Supported catalysts may also be conveniently obtained by mixing [Ni(acac)$_2$] (acac = acetylacetonate), ligand, and MAO-silica in situ (eq 1, method v); the results obtained with either method are the same (compare entries 9 and 10). As is usual, the supported catalysts investigated show somewhat lower activity compared to unsupported analogues (entries 7 and 9), although it is interesting to note that the product polymer properties remain largely unchanged. Reducing the steric bulk of the ligand again leads to a reduction in polymer molecular weight and a considerable reduction in the activity observed. Introduction of 1-hexene comonomer to a

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(11) **2a**: $C_{37}H_{47}Br_2NNiP_2$, $M = 786.23$, monoclinic, space group $C2/c$ (no. 15), $a = 16.6700(17)$ Å, $b = 8.9444(10)$ Å, $c = 24.614(4)$ Å, $\beta = 102.024(8)°$, $U = 3589.4(8)$ Å^3, $Z = 4$, $\mu = 2.882$ mm^{-1}, $T = 173$ K, 4119 unique data, R1 = 0.0280. Molecules of **2a** have exact crystallographic C_2 symmetry.

(12) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(13) Similar effects have been observed for metallocene-type catalysts. For a discussion of this and a recent review of MAO cocatalysts in general, see: Chen, E. Y.-X.; Marks, T. J. *Chem Rev.* **2000**, *100*, 1391.

(14) Addition of an excess of Lewis base, in this case 1,4-dioxane, to MAO solutions allows the free trimethyl aluminium content to be quantified using ^{1}H NMR spectroscopy (see Supporting Information).

(15) See Supporting Information.

(16) A typical profile is included in the Supporting Information.

(17) For a recent review of support strategies, mainly in the metallocene area, see: Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.

polymerization leads to incorporation of this higher 1-olefin (entry 14), as shown by an increase in polymer butyl branches.

In conclusion, these new nickel compounds are highly active and poison-tolerant catalysts for the polymerization of ethylene. Catalyst performance approaches that of the best existing nickel-based systems.[1,10b] Given the great array of related chelates that are synthetically accessible and widely used in other areas of catalysis, it seems likely that yet more active and selective phosphorus ligands for this application await discovery.

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Supporting Information Available: Experimental details. Typical polymerization gas-uptake profile. Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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