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Functionalized pyridinyl–imine complexes of palladium as catalyst precursors for ethylene polymerization

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Abstract

Mononuclear pyridinyl–imine complexes of palladium containing functionalities attached to the alkyl or aromatic group bonded to the imino nitrogen were prepared and evaluated as potential catalyst precursors for ethylene polymerization. Activated by methylaluminoxane these complexes were found to be efficient ethylene polymerization catalysts. Complexes containing either allyl, styryl and phenol functionalities were found to be more active catalysts than a standard pyridinyl–imine complex containing an unfunctionalized aliphatic substituent.

Keywords: Functionalized imines; Pyridinyl–imine; Ethylene polymerization; Polyethylene; Palladium–imine complexes

1. Introduction

α-Diimine complexes have in recent years found increasing applicability as catalyst precursors in olefin polymerization. This has largely been due to the work of Brookhart and co-workers who developed Pd(II) and Ni(II) diimine catalyst systems, which showed high activity in ethylene polymerization [1,2]. Similar systems were also developed by Gibson and co-workers who focused largely on tridentate diimine systems of iron and cobalt [3,4].

Brookhart and Gibson's systems are to a large extent symmetrical in that the different imine nitrogens have the same substituents. There have been some studies on some asymmetrical diimines but these complexes have in the main not yielded polymerization catalysts [5–7].

We have, however, in recent years reported on pyridinyl–imine complexes of palladium containing long chain aliphatic substituents at the imino nitrogen, which were found to produce active ethylene polymerization catalysts when activated with methylaluminoxane (MAO) [8].

In this current paper we report on the preparation of functionalized pyridinyl–imine complexes of the type shown in Chart 1. These complexes were evaluated as polymerization catalysts after activation with MAO. The efficiency of these catalyst systems were compared against two standard pyridinyl–imine complexes having an unfunctionalized aliphatic chain and an unsubstituted phenyl group at the imino-nitrogen, respectively.

2. Experimental

2.1. General

All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Diethyl ether and THF were dried by distillation over sodium/benzophenone. Acetone was dried by distillation over anhydrous calcium chloride and CH_2Cl_2 was dried by distillation over phosphorous pentoxide. Methanol was dried by distilling it over a Grignard complex formed in situ by the addition of magnesium turnings in the presence of a small amount of iodine. Solvents (AR grade) were obtained from Kimix Chemicals (South Africa). The functionalized amines used as starting materials as well as the pyridine-2-carboxaldehyde were purchased from Aldrich Chemicals and used without further purification. $PdCl_2$ was purchased from Next Chimica (Pty) Ltd. (South Africa). $PdCl_2$(COD) and $PdCl_2(CH_3CN)$ were synthesized according to literature procedures[9].

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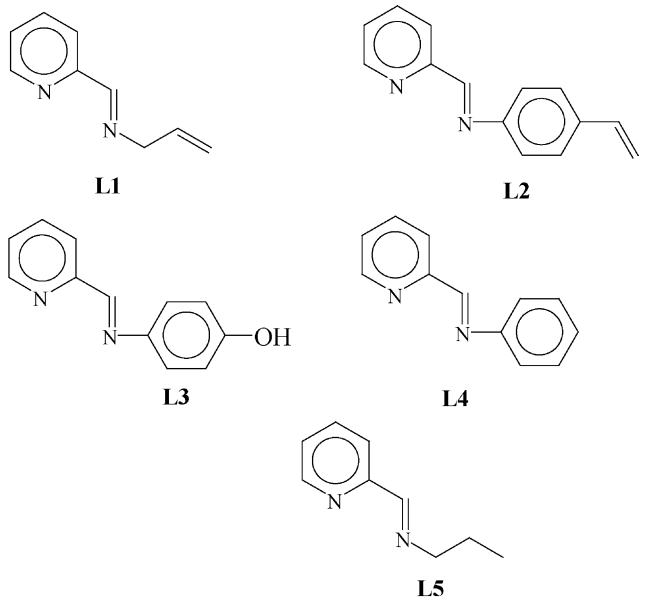


Chart 1.

2.2. Synthesis of Compounds *L1–L5*

2.2.1. Preparation of *L1*

A slight excess of allylamine (1.87 ml, 25 mmol) was added drop-wise to a stirred solution of pyridine-2-carboxaldehyde (1.98 ml, 21 mmol) in dry, nitrogen-purged diethyl ether (10 ml). The reaction mixture was cooled in an ice-bath during the addition of the amine. Anhydrous magnesium sulfate (∼0.5 g) was added to the mixture and the resulting slurry was stirred for 2 h at room temperature. The magnesium sulphate was filtered off and the solvent removed from the filtrate yielding a bright yellow oil. The crude product was dissolved in hexane (20 ml) and the solution washed with water (3 × 20 ml). The organic layer was dried over anhydrous magnesium sulfate, after which the mixture was filtered and the solvent removed from the filtrate to yield the pure product (76%).

Anal. Calc. for $C_9H_{10}N_2$: C 73.94; H 6.89; N 19.19; found: C 73.72; H 6.69; N 19.22

^{1}H NMR ($CDCl_3$): δ 4.16 (d, 2H, CH_2–CH=CH_2), 5.04 (d, 2H, =CH_2), 5.90 (m, 1H, C*H*=), 7.18 (t, 1H, py-H4), 7.56 (t, 1H, py-H5), 7.87 (d, 1H, py-H3), 8.25 (s, 1H, C*H*=N), 8.51 (d, 1H, py-H6).

2.2.2. Preparation *L2*

Pyridine-2-carboxaldehyde (0.81 ml, 9 mmol) was added to 4-vinylaniline (1.0 ml, 9 mmol) in dry diethyl ether (5 ml) while stirring. Anhydrous magnesium sulfate (∼0.5 g) was added and the resultant slurry stirred at room temperature for 2 h. The mixture was then filtered and the solvent was removed from the filtrate leaving a yellow–brown oil. The crude product was dissolved in $CHCl_3$ (20 ml). The solution was then washed with water (3 × 20 ml). The organic layer was then dried over magnesium sulfate and the mixture filtered. The solvent was removed from the filtrate to yield a golden yellow oil (85%).

Anal. Calc. for $C_{14}H_{12}N_2$: C 80.74; H 5.81; N 13.45; found: C 80.72; H 5.69; N 13.22.

^{1}H NMR ($CDCl_3$): δ 5.20 (d, 2H, =CH_2), 5.71 (m, 1H, C*H*=), 7.27 (overlapping m, 3H, py-H4 and Ar of styryl), 7.71 (t, 1H, py-H5), 8.14 (m, 3H, py-H3 and Ar of styryl), 8.58 (s, 1H, C*H*=N), 8.65 (d, 1H, py-H6).

2.2.3. Preparation of *L3*

A solution of 4-aminophenol (2.73 g, 25 mmol) in dry THF (20 ml) was added slowly to a solution of pyridine-2-carboxaldehyde (1.98 ml, 21 mmol) in THF (10 ml). Anhydrous $MgSO_4$ (1 g) was added to the solution and the reaction mixture stirred at room temperature for 30 min. The mixture was filtered and the solvent removed from the filtrate to produce analytically pure product (81%).

Anal. Calc. for $C_{12}H_{10}N_2O$: C 72.71; H 5.08; N 14.13; found: C 72.67; H 5.18; N 14.11

^{1}H NMR ($CDCl_3$): δ 6.61 (d, 2H, Ar of styryl), δ 6.88 (d, 2H, Ar of styryl), 7.30 (1H, py-H4 and Ar of styryl), 7.80 (t, 1H, py-H5), 8.20 (d, 1H, py-H3), 8.62 (s, 1H, C*H*=N), 8.70 (d, 1H, py-H6).

The preparation of **L4** was similar to that of **L3**, while **L5** was prepared in the same way as **L1**.

L4: Anal. Calc. for $C_{12}H_{10}N_2$: C 79.10; H 5.53; N 15.37; found: C 79.34; H 5.35; N 15.14

^{1}H NMR ($CDCl_3$): δ 6.73 (d, 2H, Ar of styryl), 7.24 (m, 1H Ar of phenyl), 7.32 (t, 1H, py-H5), 7.73 (d, 2H, Ar of phenyl), 8.45 (d, 1H, py-H3), 8.50 (s, 1H, C*H*=N), 8.68 (d, 1H, py-H6).

L5: Anal. Calc. for $C_9H_{12}N_2$: C 72.94; H 8.16; N 18.90; found: C 72.66; H 8.06; N 18.97

^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, CH_3), 1.67 (m, 2H, $CH_2CH_2CH_3$), 3.56 (t, 2H, $CH_2CH_2CH_3$), 7.22 (t, 1H, py-H4), 7.65 (t, 1H, py-H5), 7.91 (d, 1H, py-H3), 8.30 (s, 1H, C*H*=N), 8.56 (d, 1H, py-H6).

2.3. Synthesis of complexes

Complexes **1**–**5** were prepared by reaction of the appropriate ligand with a molar equivalent of either $PdCl_2(CH_3CN)_2$ or $PdCl_2$(COD) as the palladium precursor. In the case of $PdCl_2(CH_3CN)_2$, acetone was used as the solvent while in the case of $PdCl_2$(COD), CH_2Cl_2 was used as solvent. A general procedure for complex formation is illustrated for complex **1**.

$PdCl_2(CH_3CN)_2$ (0.08 g, 0.3 mmol) was dissolved in dry acetone (10 ml) in a 100 ml nitrogen purged Schlenk tube. A solution of the ligand **L1** in acetone (5 ml) was added to the $PdCl_2(CH_3CN)_2$ solution. This resulted in the formation of a yellow precipitate. The mixture was stirred at room temperature for 24 h. The yellow solid was allowed to settle and the supernatant liquid syringed off. The precipitate was washed with dry acetone (3 × 5 ml) and the mother liquors syringed off after each washing. The yellow solid was then dried in vacuo (63% yield).

1. Anal. Calc. for $C_9H_{10}N_2PdCl_2$: C 33.41; H 3.12; N 8.66; found: C 33.99; H 2.99; N 8.52

^{1}H NMR (DMSO-d_6): δ 4.42 (d, 2H, CH_2-CH=CH_2), 5.35 (d, 2H, =CH_2), 6.18 (m, 1H, C*H*=), 7.87 (t, 1H, py-H4), 8.14 (d,

1H, py-H3), 8.35 (t, 1H, py-H5), 8.62 (s, 1H, C*H*=N), 8.97 (d, 1H, py-H6).

2. Anal. Calc. for $C_{14}H_{12}N_2PdCl_2$: C 43.61; H 3.14; N 7.27; found: C 43.91; H 2.89; N 6.89

^{1}H NMR (DMSO-d_6): δ 5.36–5.94 (dd, 2H, =CH_2), 6.80 (m, 1H, C*H*=), 7.41 (overlapping d, 2H, Ar of styryl), 7.57 (d, 2H, Ar of styryl), 7.94 (t, 1H, py-H4), 8.22 (d, 1H, py-H2), 8.41(t, 1H, py-H5), 8.74 (s, 1H, C*H*=N), 9.06 (d, 1H, py-H6).

3. $C_{12}H_{10}N_2OPdCl_2$: C 38.38; H 2.68; N 7.46; found: C 3.33; H 2.25; N 6.93

^{1}H NMR (CD_3COCD_3): δ 6.88 (d, 2H, Ar of phenyl), δ 7.39 (d, 2H, Ar of phenyl), 7.89 (1H, py-H4), 8.23 (d, 1H, py-H3), 8.40 (t, 1H, py-H5), 8.64 (s, 1H, C*H*=N), 9.23 (d, 1H, py-H6).

4. Anal. Calc. for $C_{12}H_{10}N_2PdCl_2$: C 40.05; H 2.78; N 7.79; found: C 39.97; H 2.65; N 7.53

^{1}H NMR (DMSO-d_6): δ 6.93 (d, 2H, Ar of styryl), 7.44 (m, 1H Ar of phenyl), 7.92 (t, 1H, py-H5), 8.23 (d, 2H, Ar of phenyl), 8.48 (d, 1H, py-H3), 8.52 (s, 1H, C*H*=N), 9.21 (d, 1H, py-H6).

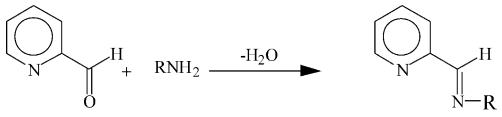
5. Anal. Calc. for $C_9H_{12}N_2PdCl_2$: C 33.18; H 3.69; N 8.60; found: C 33.63; H 3.41; N 8.37

^{1}H NMR (DMSO-d_6): δ 0.94 (t, 3H, CH_3), 1.92 (m, 2H, $CH_2CH_2CH_3$), 3.83 (t, 2H, $CH_2CH_2CH_3$), 7.89 (t, 1H, py-H4), 8.15 (d, 1H, py-H3), 8.38 (t, 1H, py-H5), 8.63 (s, 1H, C*H*=N), 9.15 (d, 1H, py-H6).

3. Results and discussion

3.1. Ligand preparation

Ligands **L1**–**L5** were prepared using the general approach as depicted in Eq. (1).



L1: R = -$CH_2CH{=}CH_2$

L2: R = -$C_6H_4CH{=}CH_2$

L3: R = -C_6H_4OH

L4: R = -C_6H_5

L5: R = C_3H_7 (1)

All products were isolated as orange yellow oils, which show some decomposition if left for prolonged periods of time at room temperature. However, no decomposition is noted when the oils are stored at −5 °C for extended periods. All the ligands except **L3** are soluble in common organic solvents. **L3** is soluble in only polar solvents such as CH_2Cl_2 and THF. The ligands were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as mass spectrometry.

3.2. Preparation of complexes

Complexes **1**–**5** (Chart 2) were prepared by reaction of equimolar amounts of the appropriate ligand with either $Pd(CH_3CN)_2Cl_2$ or $Pd(COD)Cl_2$. In all cases air stable yellow solids were obtained in moderate to good yields. Complexes **1**, **2**, **4** and **5** were insoluble in common organic solvents with the exception of dimethyl sulphoxide. Complex **3** was however soluble in acetone and sparingly soluble in CH_2Cl_2. All complexes prepared were characterized by IR and ^{1}H NMR spectroscopy as well as micro-analysis (elemental analysis).

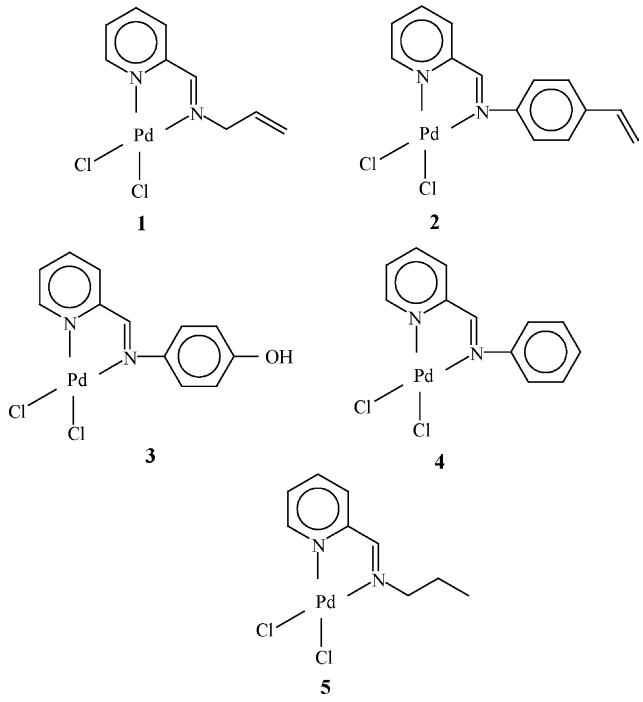


Chart 2.

3.2.1. ^{1}H NMR of complexes

The NMR spectra of all complexes show similar trends especially in the aromatic region. There is a distinct shift of the signals of the aromatic groups of the imine system including the pyridine ring on complexing of the ligand to the metal centre. A rearrangement of the aromatic signals as compared to the ligand spectra. In all cases there is a shift of the doublet found around 8.50 ppm assigned to H-6 (see Fig. 1) and the singlet found around 8.25 ppm assigned to H-7 in the ligand spectra. These two signals shift to around 8.97 and 8.62 ppm, respectively, in the spectrum of the metal complex. Thus these two signals also

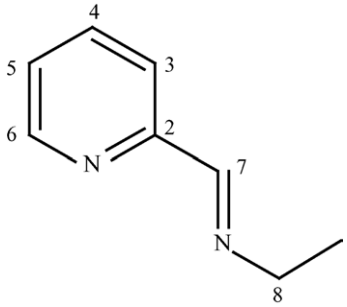


Fig. 1. Numbering scheme for pyridinyl–imine group.

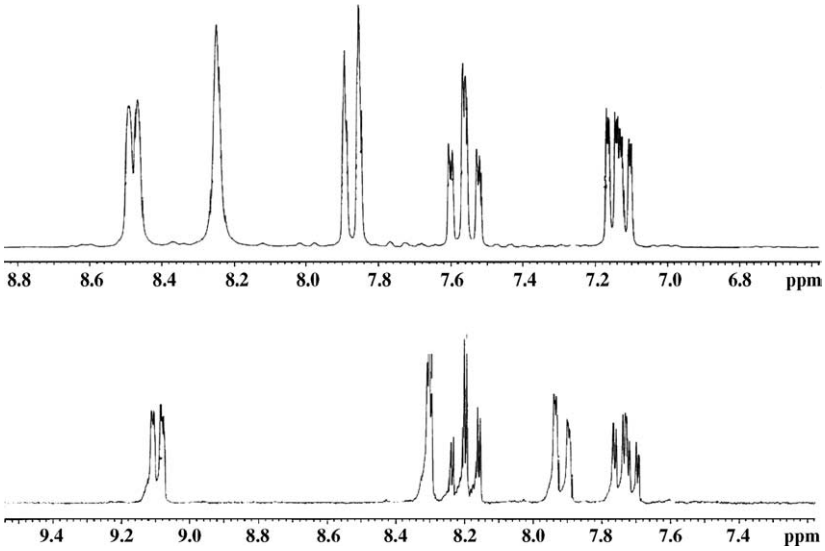


Fig. 2. Ligand **L1** (top) and complex **1** (bottom) ^{1}H NMR spectra showing shifts in signals after complexation.

exhibit a greater separation between each other when complexation takes place.

Furthermore, the two triplets, which occur at 7.18 ppm (H-4) and 7.56 ppm (H-5) in the ligand spectrum and move significantly downfield to 7.87 and 8.35 ppm during complexation. These shifts are illustrated in Fig. 2.

3.2.2. *Infra-red spectroscopy*

The infra-red spectra of all the complexes show a shift of the ν(C=N) band which normally occurs around 1650 cm^{-1} in the free ligand and around 1600 cm^{-1} in the complexes.

3.3. *Evaluation of complexes as catalyst precursors for ethylene polymerization*

Complexes **1**–**3** were evaluated as catalyst precursors in ethylene polymerization. Their efficiency was compared against the known complexes **4** and **5** to evaluate the effect of the functionalized imino N substituents on the polymerization process. In all cases the palladium complexes were activated using methylaluminoxane (MAO) in toluene. Polymerization of ethylene was conducted at various Al:Pd ratios in order to ascertain the optimum activity. All polymerizations were conducted at 25 °C and under 5 atm of pressure of ethylene. The main polymerization results are collected in Table 1.

None of the catalysts evaluated showed activity at Al:Pd ratios lower than 500:1. Of the catalysts evaluated the one containing the hydroxy phenyl substituent, complex **3** shows the highest activity. The optimal activity for this catalyst occurs however at relatively higher Al:Pd ratios when compared to the other catalyst systems. The highest activity (133.8 kg PE mol^{-1} Pd atm^{-1} h^{-1}) occurs at Al:Pd ratio of 2000:1. The catalyst based on complex **2** on the other hand reaches optimal activity at Al:Pd of 1500:1. A possible reason why complex **3** requires a much higher amount of MAO to activate it could be the fact that the hydroxy functionality on the aromatic ring undergoes some reaction with MAO to form an Al phenoxide adduct. The existence of aluminium phenoxides is well known [10].

The reaction of MAO with the phenol substituent would necessitate the requirement of additional (excess) MAO before the Pd centre is sufficiently activated for ethylene polymerization.

Table 1
Results of ethylene polymerization catalyzed by complexes **1**, **2**, **3** and **5**

Catalysts	Al/Pd	Activity kg PE (mol Pd atm h)$^{-1}$	$M_n \times 10^{-5}$[a]	$M_w \times 10^{-5}$[a]	PDI[b]
1	250	0	–	–	–
1	500	74.0	3.99	10.33	2.59
1	1000	67.6	4.29	11.67	2.72
1	1500	36.2	6.28	15.07	2.40
1	2000	0	–	–	–
2	250	0	–	–	–
2	500	13.5	5.94	14.67	2.47
2	1000	21.6	6.90	17.59	2.55
2	1500	54.2	5.65	12.94	2.29
2	2000	26.4	6.84	15.74	2.31
3	500	0	–	–	–
3	1000	8.1	4.14	12.63	3.05
3	1500	42.3	4.36	13.30	2.82
3	2000	133.8	3.42	8.97	2.63
3	3000	53.8	4.58	12.05	2.63
3	3500	0	–	–	–
4	250	0	–	–	–
4	500	3.2	3.60	9.42	2.62
4	1000	12.8	3.79	10.46	2.76
4	1500	33.2	4.81	11.74	2.44
4	2000	8.3	5.22	12.32	2.36
5	250	0	–	–	–
5	500	58.3	2.24	6.54	2.24
5	1000	46.3	2.46	6.05	2.47
5	1500	27.1	2.63	6.26	2.38
5	2000	0	–	–	–

[a] Determined by gel permeation chromatography.
[b] PDI = M_w/M_n.

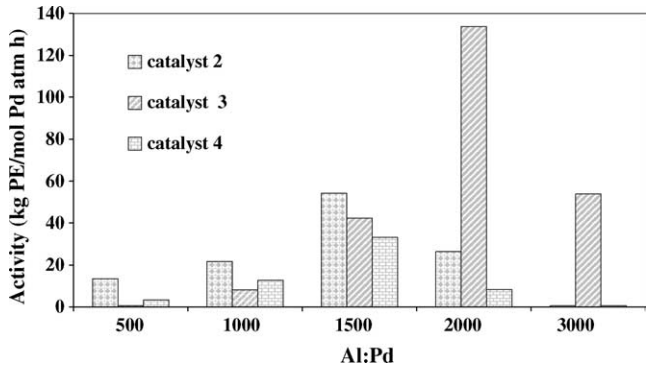


Fig. 3. Catalyst activity for catalysts **2**–**4**.

A comparison of complexes **1** and **5** in terms of their activity as well as a comparison of the activity of complexes **2**–**4**, clearly shows that the introduction of the electron withdrawing functionalities on the substituents at the imine nitrogen has an activity enhancing effect. This is quite marked in the case of complexes **3** and **4** (Fig. 3) where the activity of hydroxy functionalized complex is substantially greater than that of the unfunctionalized complex **4**. The enhanced activity of complex **3** could also be due to previously discussed Al adduct formation. Such an adduct would enhance the electron-withdrawing capability of the ligand, thus making the metal electron deficient. This would enhance alkene coordination thus accelerating the polymerization process. Attempts to isolate a MAO adduct of complex **3** were not successful as the product appears to be highly unstable. We have previously noted similar enhancement of catalyst activity in a catalyst system containing oxygen donor atoms [11].

In all cases, the catalysts employed, produced high molecular weight polyethylene with Mw ranging from $\sim 6 \times 10^5$ to 12×10^5. The polydispersity indices of the polymers obtained have values averaging around 2.5, which is typical of high-density polyethylene produced using single site catalysts [12].

Thermal analysis of the polymers produced by DSC shows melting points in the range 135–137 °C. These melting points are similar to linear high-density polyethylene.

Polymers were also analyzed by high temperature NMR. In all cases the NMR spectrum shows only a single peak around 30 ppm, confirming that we have only linear high-density polyethylene.

The activities of these functionalized pyridinyl–imine complexes are also higher than previously studied simple mononuclear pyridinyl–imine complexes without functionalities at the imino substituents [8].

4. Conclusions

We have successfully prepared three new palladium complexes containing functionalized substituents at the imino nitrogen. These substituents were shown to have a marked effect on the catalyst activity of the complexes. All complexes tested were effective as catalysts in the production of high-density polyethylene.

Acknowledgements

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