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Journal of Organometallic Chemistry 673 (2003) 111–115

Journal of Organo metallic Chemistry

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The synthesis and catalytic activity of a first-generation poly(propylene imine) pyridylimine palladium metallodendrimer

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Received 20 November 2002; received in revised form 15 March 2003; accepted 19 March 2003

Abstract

The preparation of a new palladium metallodendrimer is described. The first generation poly(propylene imine) dendrimer [DAB(NH_2)$_4$] has been modified by the reaction of the amino end groups with 2-pyridinecarboxaldehyde. Complexation reactions with $PdCl_2$(COD) give rise to a metal-containing dendrimer with $PdCl_2$ moieties bound on the periphery. The new metallodendrimer was used as a catalyst precursor, activated by methylaluminoxane (MAO), for the polymerization of ethylene. High molecular weight, high density polyethylene was obtained.

Keywords: Poly(propylene imine); Metallodendrimer; Ethylene polymerization; Polyethylene

1. Introduction

The synthesis of metallodendrimers has in recent years, like the more linear metal-containing polymers, developed at a prolific rate. These materials show potential in a number of applications and are thought to possess interesting electronic, magnetic and catalytic properties [1–3]. These potential uses are in many instances ascribed to the incorporation of metal centers into the dendrimer. Essentially, the dendrimers consist of a central core and emanating from this are several branches leading to a number of successive, well-defined generations. As far as metallodendrimers are concerned, the introduction of metal centers may occur at various branching points within the dendrimer or they may be found on the periphery of the dendritic molecule.

In the case of terminal-functionalized dendrimers, a number of examples of metallodendrimers have been reported in recent times [3,4]. In addition several metallodendrimers have found application as catalysts or catalyst precursors [5–8]. Our interest in preparing catalytically active palladium metallodendrimers, prompted us to modify the end groups at the periphery of a commercially available first-generation poly(propyleneimine) dendrimer (DAB). One of the motivations for studying these multinuclear catalyst precursors is that these systems have high local concentrations of active sites within the same molecule. This we had hoped might lead to enhanced catalyst activity.

The DAB dendrimer employed as starting material, has a diaminobutane core and amino groups as termini. This compound was first synthesized by Meijer et al. [9] in 1993 and is now commercially available from the polymer company DSM©. Recently, Cuadrado and coworkers [10] functionalized the periphery of DAB with cobaltecenium moieties. They were able to prepare the first four generations and fully characterize the structures by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy and elemental analysis. Electrochemical studies were also performed using cyclic voltammetry and these showed that the metal centers undergo reversible redox processes. The same group also previously incorporated ferrocenyl units onto the periphery of the same dendrimer system [11].

The DAB structure can serve as a strongly complexing tridentate coordination site for various transition metals. Thus, by the addition of metal(II) chlorides (MCl_2, with M = Cu, Zn and Ni) in methanol to DAB, a number of metal ions have been incorporated onto the

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0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00173-6

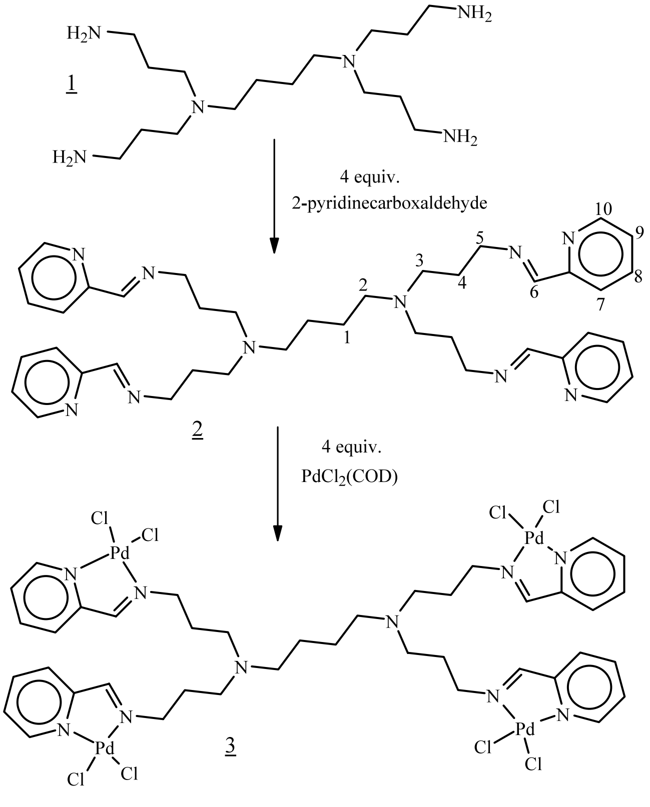
surface of the dendritic structure [12]. The work by Reetz et al. [13] presents one of the few examples where the DAB-dendrimer was used as a catalyst. Their efforts focussed on modifying the end groups of DAB through phosphinomethylation of the primary amino groups. Metallodendrimers were then formed through the reaction of terminal diphosphane ligands with [$PdCl_2(PhCN)_2$], [$Pd(CH_3)_3$(tmeda)], [$Ir(cod)_2BF_4$] or [$Rh(cod)_2BF_4$]. The use of the resulting complexes as catalysts in the Heck reaction was investigated and proved successful for the reaction of bromobenzene with styrene to produce stilbene.

In this paper, we report the synthesis and characterization of an iminopyridyl end group modified poly(propyleneimine) dendrimer and the subsequent complexation with palladium. The use of the metallodendrimer as a catalyst precursor for ethylene polymerization is also discussed.

2. Results and discussion

2.1. Synthesis and characterization of metallodendrimer

The synthesis of the new palladium metallodendrimer (**3**) was achieved in two steps. The first step entails synthesizing the organic ligand (**2**) via a Schiff-base condensation reaction (Scheme 1) of the commercially available 2-pyridinecarboxaldehyde with DAB-*dendr*-$(NH_2)_4$ (**1**). The dendrimer **2** was isolated as a stable orange oil in a yield of 76%. Copious washing with water is required to remove traces of excess 2-pyridinecarboxaldehyde. The functionalized dendrimer **2** was characterized by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy, MALDI-TOF and elemental analysis. Evidence of the condensation reaction is clearly seen in the ^{1}H-NMR by the absence of CH_2 signals adjacent to the NH_2 of the starting dendritic polyamine, as well as by the appearance of a new downfield signal due to the CH_2 group adjacent to the imine moiety. The MALDI-TOF mass spectrum shows the molecular ion peak and correlates well with the calculated monoisotopic molecular mass.



Scheme 1.

The second step in the synthesis was achieved cleanly through the complexation reaction of the dendritic polyimine **2** with $PdCl_2$(COD) in dry CH_2Cl_2. The peripherally bound Pd dendrimer (**3**) was isolated as a light orange, amorphous solid in 93% yield. The structure of this new metallodendrimer with $PdCl_2$ moieties bonded to pyridylimino units was established by ^{1}H-NMR spectroscopy in DMSO-d_6, solid-state IR spectroscopy and elemental analysis. The ^{1}H-NMR spectrum of **3** shows broadened peaks as compared with that of the ligand (Fig. 1). The aliphatic protons of the core and side arms occur at chemical shifts similar to those of the ligand. The peaks due to the aromatic protons of the pyridyl group are observed to be at lower chemical shifts, as a result of the complexation of the $PdCl_2$ moieties. The IR spectrum of **3** shows a characteristic peak at 1599 cm^{-1} due to the coordinated imine moiety (C=N). No absorption at 1650 cm^{-1}, which is a characteristic stretching frequency for the free uncomplexed imine system, is observed.

2.2. Catalytic evaluation

Ethylene polymerization studies were carried out in a stainless steel 300 ml Parr autoclave using the Pd dendrimer (**3**) as catalyst precursor. Preliminary results are summarized in Table 1.

Activities for the precursor (**3**) ranged from 0.87 to 118 kg mol^{-1} h^{-1}, using Al–Pd ratios between 500 and 1500. It was found that a ratio of Pd:Al = 1:1000 gave the optimum activity. This was found to be higher than activities for analogous mononuclear and binuclear palladium diimine systems, which we reported recently [14,15]. The higher activity could possibly be ascribed to the increased local concentration of catalytic sites within the multinuclear precursors. The overall activity is, however, lower than the highly bulky catalyst precursors reported by Brookhart [16,17]. High molecular weight polyethylene was obtained ($M_w = 14.07 \times 10^5$) at this ratio, and is comparable with catalytically active metallocenes and certain Pd-containing complexes. The

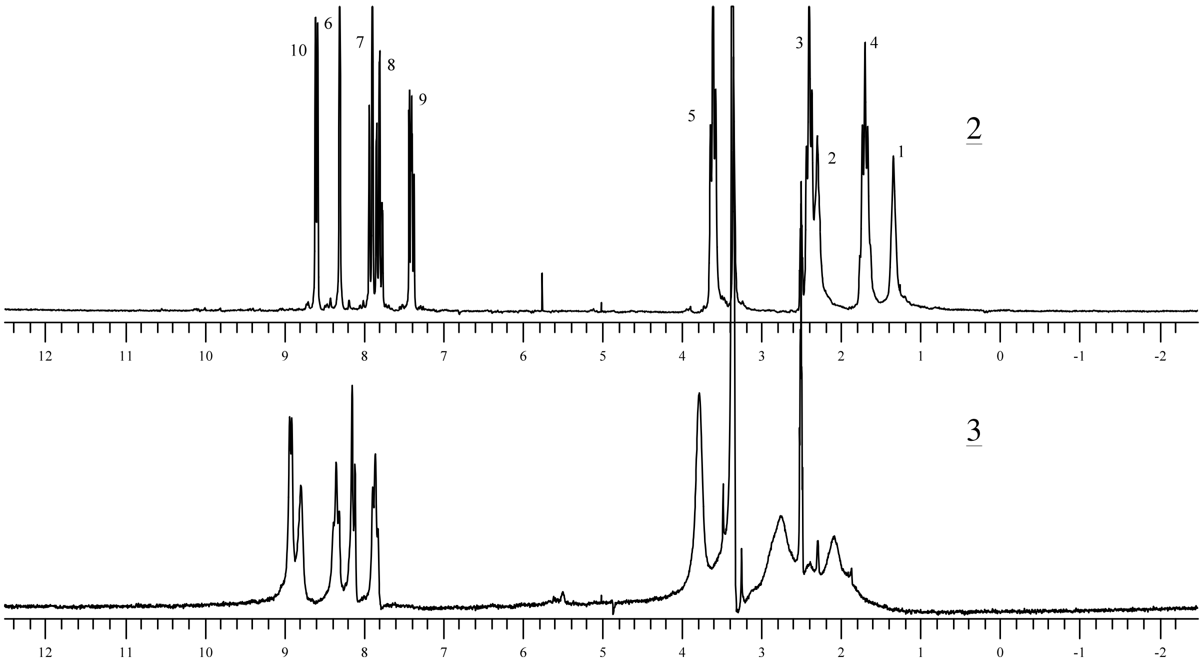


Fig. 1. ^{1}H-NMR spectra (DMSO-d_6) of the ligand **2** and the palladium metallodendrimer **3**.

polydispersity indices for these polymers were found to average around 2.7, slightly higher than other transition metal catalysts that average around 2.2. In all cases, a unimodal molecular weight distribution was observed. The melting point temperatures (T_m) as determined by DSC average around 137 °C. This indicates that the polymers are highly linear and allude to the formation of high-density polyethylene. High temperature NMR shows the polymeric material to be linear in nature with no evidence of any branching.

We are currently preparing higher generation Pd-containing metallodendrimers and are further investigating their use as catalyst precursors for ethylene polymerization.

3. Conclusion

In summary, a new peripherally bound palladium dendrimer was synthesized, with four $PdCl_2$ moieties situated on the dendritic surface. This complex has shown catalytic activity in producing high molecular weight polyethylene. Further studies are underway to prepare higher generation metallodendrimers.

4. Experimental

All reactions and manipulations were carried out using a dual vacuum/nitrogen line and standard Schlenk techniques. All solvents were dried over the appropriate drying agent and distilled prior to use. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000PC FTIR spectrophotometer, using either solution cells with NaCl windows or diffuse reflectance infrared transmission spectroscopy (DRIFTS) in a KBr matrix. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. MALDI-TOF analyses were carried out on a Perseptive Biosystems-Voyager-DE STR mass spectrometer, equipped with a nitrogen laser (337 nm) and operated in reflector mode. Irradi-

Table 1
Ethylene polymerization using compound **3** as precatalyst

Run [a]	[MAO]–[Pd]	PE yield (g)	Activity (kg mol^{-1} h^{-1})	10^{-5} M_n [b]	10^{-5} M_w [b]	M_w/M_n	T_m (°C) [c]
1	500	0.0221	0.87	4.21	10.91	2.59	137.18
2	866	2.7764	60.34	4.91	13.56	2.76	137.95
3	1000	3.1761	118.01	4.87	14.07	2.89	137.59
4	1500	2.3938	83.55	4.95	12.41	2.51	137.30

[a] Polymerization performed in dry toluene at 3 atm of ethylene, 25 °C, 3 h, using ~2.0 μmol palladium complex activated with MAO.

[b] Molecular weight data was determined by high temperature (160 °C) GPC vs. polystyrene standards.

[c] Determined by differential scanning calorimetry (DSC).

ance intensity and accelerating voltage were at 20 kV for the sample. DSC data were obtained at the University of Cape Town on a Perkin–Elmer PC7 Series Thermal Analysis System, at a scanning rate of 10 °C min^{-1} under N_2 gas-purge with a flow rate of 30 ml min^{-1}.

4.1. Synthesis of iminopyridyl ligand 2

A round-bottomed flask was charged with dry toluene (60 ml). Anhydrous $MgSO_4$ (~ 5 g) was transferred to the flask. 2-Pyridinecarboxaldehyde (0.2709 g, 2.5316 mmol) was syringed into the round-bottomed flask and the mixture stirred at room temperature (r.t.). A sample of the DAB-*dendr*-$(NH_2)_4$ (0.2000 g, 0.6329 mmol) was dissolved in 5 ml of dry toluene. The toluene solution was added dropwise to the stirring mixture of the aldehyde and $MgSO_4$, and the reaction allowed to proceed at r.t. for 2 days. The reaction mixture was filtered by gravity and the solvent removed from the filtrate by rotary evaporation with gentle heating (~ 40 °C). The residual oil was extracted with hot MeOH and the solvent removed from the extract. The remaining oil obtained from the extract was dissolved in CH_2Cl_2 (20 ml) and washed copiously with water (7 × 50 ml). The organic layer was collected, dried over anhydrous $MgSO_4$ and filtered by gravity. Removal of the solvent by rotary evaporation yielded the desired product as an orange oil. Yield = 76%. Anal. Found: C, 70.44; H, 8.16; N, 20.55. Calc. for $C_{40}H_{52}N_{10}$: C, 70.40; H, 7.79; N, 20.82%. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.40 (br m, 4H, H-1; 1.84 (qn, 8H, H-4); 2.40 (br t, 4H, H-2); 2.51 (t, 8H, H-3); 3.67 (t, 8H, H-5); 7.28 (t, 4H, H-9); 7.70 (t, 4H, H-8); 7.92 (d, 4H, H-7); 8.36 (s, 4H, H-6); 8.60 (d, 4H, H-10) (see Scheme 1 for numbering system).

^{13}C-NMR ($CDCl_3$): δ 24.7, 27.8, 51.2, 53.6, 59.1 ($CH_{2,\ \mathrm{aliphatic}}$); 120.7, 124.0, 136.0, 148.9, 161.4 (CH_{aromatic}); 154.1 (CH_{imine}).

IR (neat oil, NaCl plates): $\nu = 1648.8, 1587.6, 1567.4$ cm^{-1} (C=N).

MS (MALDI-TOF) Calc. ($C_{40}H_{52}N_{10}$) $[M]^+$ at 672.80.

4.2. Synthesis of metallodendrimer 3

A Schlenk tube was evacuated and then filled with nitrogen. $PdCl_2(COD)$ (0.1704 g, 0.5968 mmol) was transferred to the Schlenk tube. This was dissolved in dry CH_2Cl_2 (15 ml). The iminopyridyl ligand **2** (93.4 mg, 0.1388 mmol) was dissolved separately in dry CH_2Cl_2 (5 ml). This solution was added to the Schlenk tube and the mixture stirred at r.t. under nitrogen. After a few minutes, an orange precipitate formed. The reaction was allowed to proceed for 2 days, and the solid collected on a Hirsch funnel. The solid was washed with CH_2Cl_2 and dried under vacuum, yielding an amorphous, light orange solid (93%).

Elemental analysis Calc. for $C_{40}H_{52}N_{10}Pd_4Cl_8$: C = 34.76%, H = 3.79%, N = 10.13%. Found: C = 34.48%, H = 3.99%, N = 9.90%.

^{1}H-NMR (DMSO-d_6): 2.29–2.78 (br signals, core), 3.78 (br t, 8H, $-CH_2-N=$), 7.85, 8.20, 8.35, 8.90 (br, pyridine), 8.76 (br s, $-N=CH-$).

IR (Nujol between NaCl plates): $\nu = 1598.6$ cm^{-1} (C=N).

4.3. Polymerization procedure

The loading of the autoclave took place in a nitrogen-purged glove-box. The catalyst precursor **3** (~ 2.00 μmol) was suspended in dry, degassed toluene (50 ml) in a 300 ml stainless steel Parr autoclave. The appropriate amount of methylaluminoxane (10% w/v toluene solution of MAO) was added and an additional 50 ml of toluene added to the solution. The autoclave was sealed, removed from the glovebox and flushed with ethylene. Ethylene was introduced to a pressure of 3 atm and maintained at this pressure throughout the polymerization. Polymerization was conducted at 25 °C for 3 h. At the end of the polymerization, the unreacted ethylene was vented and the reaction quenched with ethanol (20 ml). The resulting polymer suspension was poured into 245 ml of ethanol–HCl (7:1) to remove any palladium residues and left to stand overnight. After filtration, the polymer was washed with ethanol and dried at 80 °C in a vacuum oven to constant weight.

Acknowledgements

We thank the Institutional Research Development Programme of the National Research Foundation of South Africa and the Research Committee of the University of the Western Cape for financial support. Ms. Valerie Grumel, Stellenbosch University is thanked for assisting with GPC measurements.

References

[1] C. Gorman, Adv. Mater. 4 (1998) 295.

[2] I. Cuadrado, M. Moran, C.M. Casado, B. Alonso, J. Losada, Coord. Chem. Rev. 193–195 (1999) 395.

[3] G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. 99 (1999) 1689.

[4] A. Salmon, P. Jutzi, J. Organomet. Chem. 637–639 (2001) 595.

[5] J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, Nature 372 (1994) 659.

[6] K. Vassilev, J. Kreider, P.D. Miller, W.T. Ford, React. Funct. Polym. 41 (1999) 205.

[7] R. Van Heerbeek, P.C.J. Kramer, P.W.N.M. Van Leeuwen, J.N.H. Reek, Chem. Rev. 102 (2002) 3717.

[8] L. Twyman, A.S.H. King, I.K. Martin, Chem. Soc. Rev. 31 (2002) 69.

[9] E.M.N. de Brabander-van den Berg, E.W. Meijer, Angew. Chem. Int. Ed. Engl. 32 (1993) 1308.

[10] K. Takada, D.J. Diaz, H.D. Abruna, I. Cuadrado, B. Gonzalez, C.M. Casado, B. Alonso, M. Moran, J. Losada, Chem. Eur. J. 7 (2001) 1109.

[11] I. Cuadrado, M. Moran, C.M. Casado, B. Alonso, F. Lobete, B. Garcia, M. Ibisate, J. Losada, Organometallics 15 (1996) 5278.

[12] A.W. Bosman, A.P.H.J. Schenning, R.A.J. Janssen, E.W. Meijer, Chem. Ber. 130 (1997) 725.

[13] M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem. Int. Ed. Engl. 36 (1997) 1526.

[14] R. Chen, J. Bacsa, S.F. Mapolie, Inorg. Chem. Commun. 5 (2002) 724.

[15] R. Chen, S.F. Mapolie, J. Mol. Catal. 193 (2003) 33.

[16] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.

[17] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.