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Syntheses and catalytic properties of polystyrene supported nickel(II) carborane complexes

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Abstract

1-Methyl- and 1-phenyl-*ortho*-carborane functionalized polystyrenes (**1a**, **1b**) were synthesized by the reactions of pertinent carborane lithium salts and Merrifield's peptide resin (1%), in refluxing tetrahydrofuran (THF) solvent in 90 and 85% yield, respectively. Further reaction of dianions derived from the resulting **1a** and **1b** with dichloro bis(triphenylphosphine)nickel(+II) produced novel polystyrene supported neutral nickel(+II) carborane compounds (**2a**, **2b**). The polyethylene, polystyrene and polyvinyl chloride catalytic properties of the nickel complexes in THF and ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], of compounds **2a** and **2b** were tested.

Keywords: Carborane; Functionalized polystyrene; Nickel(+II) carborane complexes; Catalytic polymerization

1. Introduction

Recently, there have been significant efforts in the heterogenization of the Ziegler-Natta catalyst system by supporting the metallocene and cocatalyst onto an inorganic or organic support, in order to avoid the production of polymer dust that tends to agglomerate and stick to everything [1–10]. However, linking the metallocene catalyst onto silica or alumina-support is not a straightforward process. One attractive avenue in the research on catalysts for olefin polymerization is the discovery of the neutral nickel(+II) complexes of 'NO' chelate ligands that can be used as polyolefin catalysts, which was known as "Nickel effect" for a few decades. After modifying the classical shell higher olefin process (SHOP) catalyst [11], Younkin et al. [12] found a highly active polyolefin catalyst, which can tolerate heteroatoms, even without the presence of a cocatalyst. Although the true mechanism for the neutral nickel(+II) complexes is still unknown, they reported that the phosphine ligands and the increased reaction temperature (45–50 °C) play a key role in the process. In view of the development of exceptionally heat-resistant carborane elastomers (*ortho*-carborasiloxane polymer) by Olin Corporation, under the trade name Dexsil, the possibility of an alternative heterogeneous metallacarborane catalyst system has an obvious appeal. Moreover, the neutral icosahedral carborane cage can be heated to 600 °C without decomposition and its C_2B_9-cage ions can be recovered unchanged after several hours of heating in solution with aqueous acids and bases [13–15]. These properties of the carborane cage provide an incentive to explore the development of supported nickel(+II) carborane complexes and to investigate their potential as olefin polymerization catalysts. Here, we describe preliminary results on the synthesis and characterization of novel carborane-functionalized polystyrenes as well as the catalytic properties of nickel(+II) complexes derived from them.

2. Experimental

All synthetic procedures were carried out in inert atmosphere with standard Schlenk techniques. Tetrahydrofuran (THF) and *n*-hexane were heated over sodium and benzophenone until a dark blue color was obtained, and distilled under nitrogen just before use. Dichloromethane was dried over phosphorus pentoxide and distilled. *N*-Butyllithium in hexanes, Merrifield's peptide resin (1%) (contains 1.97 mmol Cl^-/g) and organic solvents were used as received from Aldrich. 1-Methyl- and 1-phenyl-*ortho*-

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$C_2B_{10}H_{11}$ were provided by Katchem Ltd. 1-Butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], was obtained from Solvent Innovation GmbH (Germany). Dichloro bis(triphenylphosphine)nickel(+II) was prepared according to a reported method [16]. Infrared (IR) spectra were measured using a BIO-RAD spectrophotometer with KBr pellets technique. TGA analyses were carried out on an SDT 2960 simultaneous DSC–TGA analyzer.

2.1. Synthesis of carborane functionalized polystyrene 1a and 1b

Under argon atmosphere, 0.62 g (3.92 mmol) 1-Me-*ortho*-$C_2B_{10}H_{11}$ was added to a 250 mL two-necked round bottom flask, equipped with a magnetic stirring bar and 100 mL dry THF was added to dissolve the carborane compound to give a clear solution. The solution was cooled to −78 °C with liquid nitrogen–isopropanol cold bath, 2.7 mL (4.32 mmol) *n*-BuLi (1.6 M in hexanes) was added from a syringe under continuous stirring. After the addition, the mixture was kept at that temperature for 30 min followed by warming to room temperature, where it was reacted for further 4 h. The solvents were removed under reduced pressure, and the residue was washed with *n*-hexane (2 × 15 mL). It was then dissolved into 150 mL THF, and Merrifield's peptide resin (1%) 2.0 g (3.94 mmol Cl^-) was added and kept stirring at room temperature under argon for 2 days. At the end of the reaction process, the mixture was heated to reflux for 4 h before cooling down to room temperature and quenched with 3.0 mL methanol. The solvents were removed under reduced pressure, and the crude product was washed with deionized water (2 × 10 mL) and *n*-hexane (2 × 20 mL) to remove any trace of LiCl and starting material 1-Me-*ortho*-$C_2B_{10}H_{11}$, then dried in high vacuum for 2 days to lead a pale yellow solid 2.43 g **1a** in 90% yield. The collected aqueous solution was combined and concentrated to 5.0 mL and subjected to titration with $AgNO_3$ to detect the amount of the produced LiCl as 0.15 g. IR (KBr pellet, cm^{-1}): 3444, 3058, 3025, 2920, 2585, 1945, 1802, 1601, 1491, 1449, 1265, 1184, 1155, 1112, 1068, 1020, 907, 822, 756, 698, 542.

Compound **1b** was synthesized in 85% yield according to the procedure described above. IR (KBr pellet, cm^{-1}): 3429, 3061, 3026, 2927, 2852, 2591, 1944, 1871, 1802, 1748, 1647, 1601, 1491, 1447, 1371, 1264, 1182, 1109, 1070, 1020, 906, 818, 746, 675, 551.

2.2. Synthesis of polystyrene supported nickel(+II) carborane compounds 2a and 2b

2.33 g (contains carborane 3.40 mmol) **1a** was added to a clear solution of 2.50 g (37.87 mmol) potassium hydroxide in 150 mL ethanol, the mixture was stirred at room temperature for 30 min before refluxing for 30 h under argon atmosphere. Then the reaction mixture was cooled to room temperature and filtered. The resulting solid was washed with deionized water (3 × 10 mL) to removed any trace of EtOK, and dried in high vacuum for 2 days, then suspended in 200 mL dry THF. The suspended mixture was cooled to −78 °C and 2.5 mL (4.00 mmol) *n*-BuLi in hexanes was added under argon with continuous stirring. After reaction at −78 °C for 30 min, the mixture was warmed to room temperature and kept stirring for 18 h. The solvents were then removed under reduced pressure and the resulting residue was washed with *n*-hexane (2 × 15 mL) to remove any trace of unreacted *n*-BuLi. The residue was resuspended in 150 mL THF and dichloro bis(triphenylphosphine)nickel(+II) 2.23 g (3.41 mmol) was added at 0 °C. The colour of the reaction mixture changed quickly from deep green to light pink during the addition of the nickel complex. After the addition, the reaction was continued at room temperature for 52 h. During the last 2 h of reaction, the mixture was subjected to ultrasonic irradiation. Thereafter, the mixture was filtered, and the collected solid was washed with deionized water (2 × 15 mL), dichloromethane (2 × 20 mL) and *n*-hexane (3 × 20 mL) in turn, and dried in high vacuum to give an orange solid **2a** in 94% yield (4.15 g). The combined aqueous solutions were concentrated to 5.0 mL and subjected to titration with $AgNO_3$ to determine the amount of the produced LiCl as 0.27 g. IR (KBr pellet, cm^{-1}): 3433, 3026, 2924, 2853, 2518, 1636, 1603, 1491, 1449, 1371, 1170, 1096, 1020, 758, 699, 546.

Compound **2b** was synthesized in 83% yield through a similar process. IR (KBr pellet, cm^{-1}): 3601, 3140, 3059, 2925, 2523, 1493, 1870, 1802, 1747, 1597, 1474, 1067, 1027, 977, 907, 760, 700, 675, 527.

2.3. Evaluation of the catalytic activity

The polymerization of ethylene, styrene and vinyl chloride catalyzed by compounds **2a** and **2b** has been performed in THF or ionic liquid [BMIM][BF_4] solvents without the presence of a cocatalyst. The polymerization conditions were: catalysts (**2a**, **2b**) 2.5×10^{-4} mol based on nickel carborane species, solvents (THF and [BMIM][BF_4]) 20 mL, reaction temperature 80 °C for polyethylene and polyvinyl chloride, and 25 °C for polystyrene, the reaction pressure was 1.5 bar for polyethylene and 1.2 bar for polyvinyl chloride, the reaction time was 4 h. After polymerization, the polymers were collected by filtration and washed with *n*-hexane (2 × 20 mL) and dried in high vacuum for 2 days to constant weight. Polymerization results are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of polystyrene supported nickel(+II) complexes

The immobile process from commercially available *ortho*-carborane and Merrifield's peptide resin (1%) is based on Scheme 1. Deprotonation of 1-R-*ortho*-$C_2B_{10}H_{11}$ (R = Me, Ph) with *n*-butyllithium in THF results in a

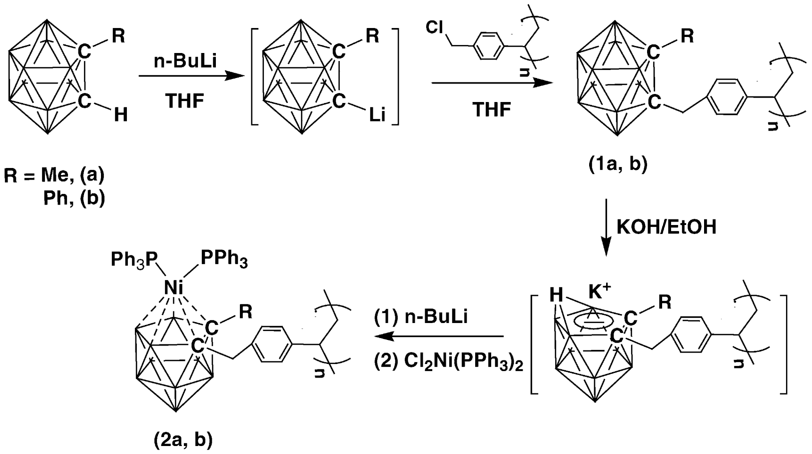
Table 1
Polymerization of ethylene, styrene and vinyl chloride with **2a** and **2b**

Polymer[a]	Activity[b]	M_w ($\times 10^3$ g/mol)[c]	M_w/M_n
Polyethylene	28A, 34B, 25C, 30D	2.5A, 4.7B, 3.2C, 5.1D	1.6A, 1.3B, 2.3C, 1.8D
Polystyrene	43A, 52B, 38C, 49D	2.8A, 3.6B, 3.0C, 4.7D	1.9A, 1.5B, 1.7C, 1.9D
Polyvinyl chloride	36A, 44B, 33C, 41D	4.6A, 5.8B, 4.2C, 5.4D	1.3A, 1.2B, 1.6C, 1.4D

[a] All catalytic processes were operated under inert atmosphere in dry vessel without cocatalyst. A = 2a in THF, B = 2a in [BMIM][BF_4], C = 2b in THF, D = 2b in [BMIM][BF_4].

[b] Activity = kg polymer per mol catalyst per h per bar.

[c] Molecular weight and molecular weight distribution of the polymers were determined by means of gel-permeation chromatography (GPC: Waters 150 °C) at 145 °C using 1,2,4-trichlorobene as a solvent. The weight average molecular weight and polydispersity index (M_w and M_w/M_n, respectively) were calculated on the basis of polystyrene standards.



Scheme 1. Synthesis of polystyrene supported nickel(+II) carboranes.

Li[1-R-*ortho*-$C_2B_{10}H_{10}$] intermediate, which further reacts with Merrifield's peptide resin (1%) resulting in carborane ligand functionalized polystyrenes **1a** and **1b**. After decapitation process with potassium hydroxide in refluxing ethanol followed by further deprotonation with *n*-butyllithium and metathesis reaction with dichloro bis(triphenylphosphine)nickel(+II) in situ, polystyrene supported nickel(+II) carborane complexes **2a** and **2b** were obtained in satisfiying yields. The yields of **1a**, **1b**, **2a** and **2b** are based on the analysis of produced lithium chloride, which is determined by titration with $AgNO_3$.

The IR spectra of all carborane functionalized polystyrene exhibit typical ν_{B-H} absorption in the range of 2510–2595 cm^{-1}, which confirms the successful immobilization of the carborane cage to polystyrene. An example of the change in the FT-IR spectra from Merrifield's peptide resin to **1a** and **2a** is presented in Fig. 1.

In the simultaneous DSC–TGA analysis, the residue weight of **1a**, **1b**, **2a** and **2b** increases noticeably as compared to that of Merrifield's peptide resin (1%), which is burnt completely between 200 and 600 °C in air. These results confirm further the attachment of carborane to Merrifield's peptide resin. Unlike other polymerization processes, the amounts of immobilized carborane cannot be determined by calculation from the changes of the residual weight, because both the starting material 1-R-*ortho*-$C_2B_{10}H_{11}$ (R = Me, Ph) and Merrifield's peptide resin (1%) burnt completely in air above 900 °C (see Fig. 2). In addition, carborane compounds 1-R-*ortho*-$C_2B_{10}H_{11}$ (R = Me, Ph) sublime when heated and this property also makes it impossible for the quantitative determination of carborane attached Merrifield's peptide resin even under nitrogen atmosphere by the simultaneous DSC–TGA analysis. Hence we determined the amount of anchored carborane by titrating the lithium chloride produced in the reaction with $AgNO_3$.

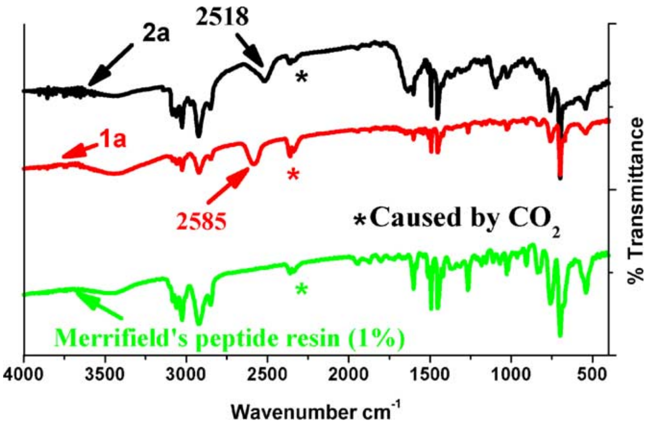


Fig. 1. FT-IR spectra of Merrifield's peptide resin (1%), 1a and 2a.

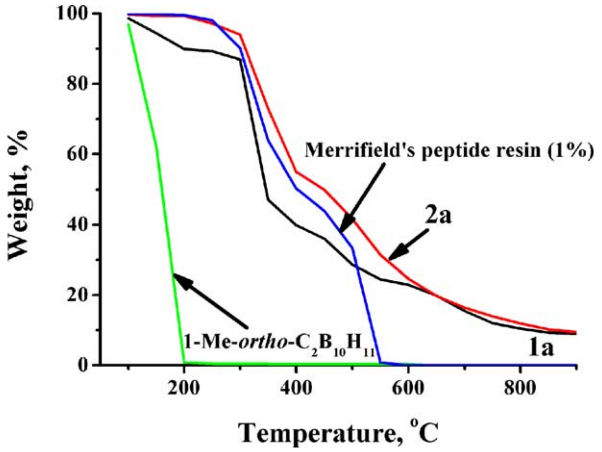


Fig. 2. TGA curves of Merrifield's peptide resin, 1-me-*ortho*-$C_2B_{10}H_{11}$, 1a and 2a.

3.2. *Catalytic property evaluation of polystyrene supported nickel (+II) complexes*

In order to evaluate the catalytic properties of **2a** and **2b** for polymerizing olefins, commercially available ethylene, styrene and vinyl chloride are chosen as test monomers for polymerization with **2a** and **2b** in THF or [BMIM][BF_4]. Table 1 summarizes that (1) both of the nickel(+II) carborane complexes are active for polymerization reaction in THF and [BMIM][BF_4] without the presence of cocatalyst, an observation consistent with results reported by Younkin et al. who showed that nickel complexes could be active polyolefin catalysts that can tolerate heteroatoms even in the absence of a cocatalyst [12] and comparable with the catalytic activity of the analogous unsupported catalyst, homogeneous nickel(+II) carborane catalyst [17], (2) the activities of **2a** and **2b** are influenced by solvents, improved catalytic activity has been observed in ionic liquid [BMIM][BF_4] as compared to THF, (3) in same solvent, the activity of the two nickel(+II) complexes for three monomers are in the order: ethylene $<$ vinyl chloride $<$ styrene. Detailed mechanistic studies and optimization of the catalytic polymerization conditions with respect to molecular structure modification, use of suitable cocatalysts, and reaction temperature are currently undertaken in our laboratory.

4. Conclusions

Carborane functionalized polystyrenes have been synthesized by the reaction of the lithium salts of 1-R-*closo*-1,2-$C_2B_{10}H_{11}$ (R = Me, Ph) with Merrifield's peptide resin. The attached carboranes were found to undergo standard decapitation reactions to yield the corresponding *nido*-carboranes, which, in turn, could be metallated to give supported Ni(+II) metallacarboranes. These polymer supported nickel(+II) carborane complexes were found to be active olefin polymerization catalysts, their activities are greater for substituted olefins, such as vinyl chloride and styrene, than for unsubstituted ones.

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References

[1] M. Kwanten, B.A.M. Carriere, P.J. Grobet, P.A. Jacobs, Chem. Commun. (Cambridge) 13 (2003) 1508–1509.
[2] G.J.M. Gruter, A. Graham, B. McKay, F. Gilardoni, Macromol. Rapid Commun. 24 (2003) 73–80.
[3] M.deF.V. Marques, C.C. Pombo, R.A. Silva, A. Conte, Eur. Polym. J. 39 (2003) 561–567.
[4] M. De Fatima, V. Marques, A. Conte, J. Appl. Polym. Sci. 86 (2002) 2054–2061.
[5] C.C. Pombo, A. Conte, M.deF.V. Marques, Annual Technical Conference—Society of Plastics Engineers 60 (2002) 4033–4038.
[6] H.C.L. Abbenhuis, Angew. Chem. Int. Ed. 38 (1999) 1058–1060.
[7] J.H. Zimnoch dos Santos, A.E. Gerbase, K.C. Rodenbusch, G.P. Pires, M. Martinelli, K.M. Bichinho, J. Mol. Catal. A: Chem. 184 (2002) 167–173.
[8] A.M. Uusitalo, T.T. Pakkanen, E.I. Iskola, J. Mol. Catal. A: Chem. 177 (2002) 179–194.
[9] M.L. Ferreira, P.P. Greco, J.H.Z. dos Santos, D.E. Damiani, J. Mol. Catal. A: Chem. 172 (2001) 97–116.
[10] M. Galan-Fereres, T. Koch, E. Hey-Hawkins, M.S. Eisen, J. Organomet. Chem. 580 (1999) 145–155.
[11] E.N. Jacobsen, R. Breinbauer, Science 287 (2000) 437–438.
[12] T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460–462.
[13] A.M. Thayer, Chem. Eng. News 11 (1995) 15–20.
[14] H.A. Schroeder, Inorg. Macromol. Rev. 1 (1970) 45–73.
[15] G.S. Henrice-Olive, S. Olive, Angew. Chem. Int. Ed. 6 (1967) 790–798.
[16] F.A. Cotton, O.D. Faut, D.M.L. Goodgame, J. Am. Chem. Soc. 83 (1961) 344–351.
[17] Y. Zhu, Advances in Petrochemicals and Polymers in the New Millennium, Bangkok, Thailand, 23–25 July 2003, p. 105.