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Syntheses and catalytic activities of single-wall carbon nanotubes-supported nickel (II) metallacarboranes for olefin polymerization

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Abstract

Single-wall carbon nanotubes (SWCNTs)-supported nickel (II) carborane complex, ([*closo*-1-Ni$(PPh_3)_2$-2-Me-3-($(CH_2)_4$NH-)-η^5-2,3-$C_2B_9H_9$][OEt]$)_n$(SWCNT) (**3**) has been synthesized by the reaction of in situ prepared *nido*-C_2B_9-carborane-functionalized SWCNTs, ([Na^+][1-Me-2-($(CH_2)_4$NH-)-1,2-$C_2B_9H_{10}^-$][OEt]$)_n$(SWCNT) (**1**) with dichlorobis(triphenylphosphine)nickel (II) (**2**). Reaction of *closo*-1-Me-1,2-$C_2B_{10}H_{11}$ (**4**) with *n*-butyllithium followed by treatment with 1-bromopentane results in the formation of *closo*-1-Me-2-pentyl-1,2-$C_2B_{10}H_{10}$ (**5**) in 91% yield. After decapitation of (**5**) with sodium hydroxide in refluxing ethanol, the salt Na[*nido*-7-Me-8-pentyl-7,8-$C_2B_9H_{10}$] (**6**) has been obtained in 77% yield. For the purpose of comparison of catalytic activity, homogeneous analogue *closo*-1-Ni$(PPh_3)_2$-2-Me-3-Pentyl-η^5-2,3-$C_2B_9H_9$ (**7**) has been prepared in 83% from its *nido*-precursor (**6**). The above synthesized nickel complexes (**3**) and (**7**) have been tested as moderately active catalysts for olefin polymerization in the presence of the co-catalyst MAO.

Keywords: A. Nanostructures; A. Organometallic compounds; B. Chemical synthesis; D. Nuclear magnetic resonance (NMR)

1. Introduction

Due to their unique physical and chemical properties, as well as potentially important uses as nanomaterials, single-wall carbon nanotubes (SWCNTs) have attracted a great deal of research attention in recent years [1–5]. Although the detail mechanisms have not yet been disclosed, it has been found that carbon nanotubes are promising catalyst supports with improved catalytic activities after immobilization of homogeneous catalysts [6–9]. It is known that the existing Ziegler–Natta catalytic systems for olefin polymerization are not able to tolerate polar monomers such as vinyl chloride, acrylate, etc. It remains one of the main challenges of current polymer research to identify new generations of robust catalysts with unique properties. We found that carborane coordinated nickel (II) complexes are homogeneously polar groups sufferable polyolefin catalysts with moderate activity [10]. Motivated by the attractive properties of SWCNTs as catalyst supports, we began to explore the potentiality of chemical immobilization of the nickel (II) complexes to SWCNTs. Herein we report our initial results regarding the synthetic methodology to prepare SWCNTs-supported and unsupported nickel (II) metallacarboranes (Scheme 1), as well as their catalytic activities for ethylene and vinyl chloride polymerization.

2. Experimental

2.1. General comments

All synthetic procedures were carried out in an inert atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) and *n*-pentane were each heated over sodium and benzophenone until a dark blue color was obtained, and then distilled under argon prior to use. Dichloromethane was dried over phosphorus pentoxide and distilled. 1-Bromopentane, *n*-butyllithium (1.6 M in hexanes), and all other reagents were purchased from Aldrich and used as received. 1-Methyl-*closo*-1,2-$C_2B_{10}H_{11}$ (**4**) was obtained from Katchem Ltd, Methylaluminoxane (MAO, 10 wt% solution in toluene) was provided by Sigma-Aldrich. ([Na^+][1-Me-2-($(CH_2)_4$NH-)-1, 2-$C_2B_9H_{10}^-$][OEt]$)_n$(SWCNT) (**1**) [11] and Ni$(PPh_3)_2Cl_2$ (**2**) [12] were prepared according to literature. FT-IR spectra were measured using a BIO-RAD spectrophotometer with KBr pellets or organic solvent films. The Scanning Electron Microscopy (SEM) images were

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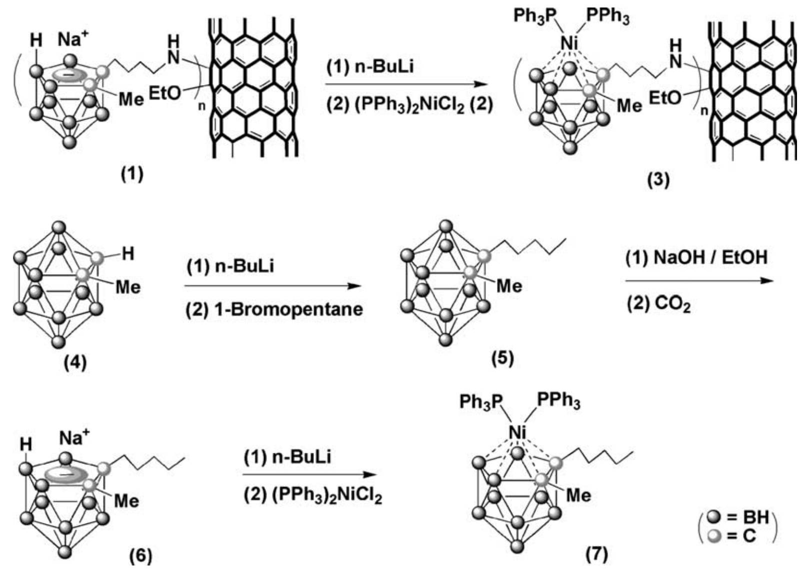

Scheme 1. Synthesis of carborane nickel (II) complexes.

obtained on a JSM-6700F field-emission microscope. Transmission Electron Microscopy (TEM) measurements were carried out on a JEOL Tecnai-G^2, FEI analyzer at 200 kV. The Elemental analyses were measured on a EURO EA. ^{1}H, ^{13}C, ^{11}B NMR spectra were recorded on a Bruker 400 analyzer at 400.13, 100.62 and 128.38 MHz, respectively.

2.2. Synthesis and characterization of **5**

A 2.00 g (12.64 mmol) sample of 1-Me-1,2-$C_2B_{10}H_{11}$ was placed in a 100 mL dry two-necked round bottom flask followed by dissolved with 30 mL THF to lead a colorless solution which was cooled to -78 °C. 8.30 mL (13.28 mmol) of *n*-butyllithium was slowly added via syringe. After addition, the mixture was kept reacting at that temperature for 40 min before warmed to room temperature spontaneously followed by further reaction of 4 h. The reaction mixture was then cooled to 0 °C and a solution of 2.00 g (13.11 mmol) 1-bromopentane in 10 mL THF was added drop-wise with addition funnel. After addition, the reaction mixture was stirred for 30 min at 0 °C, warmed to room temperature spontaneously, stirred for an additional 6 h and then refluxed for 4 h. Then the mixture was cooled to 0 °C and quenched with 10% aqueous HCl. The organic phase was separated and the aqueous layer was extracted with diethyl ether (2×20 mL), the extract was combined with the organic phase, dried with anhydrous $MgSO_4$, filtered and then the solvents removed leaving a pale yellow sticky residue. This residue was purified using thin-layer chromatography (SiO_2), developed with a mixture of *n*-pentane/ethyl acetate (v/v = 5/1), to give 2.63 g (91% yield) of (**5**) as a colorless sticky oil, which slowly solidified into wax during storage. Analytic data: Calcd for $C_8H_{24}B_{10}$: C, 42.07; H, 10.59. Found: C, 42.01; H, 10.63. ^{1}HNMR ($CDCl_3$, relative to $SiMe_4$, ppm): δ 3.11–1.05 (m, br, 10H, $B_{10}H_{10}$), 2.08 (t, 2H, $–C_{cage}–CH_2–$), 1.92 (s, 3H, $CH_3–C_{cage}$), 1.74 (m, 2H, $–C_{cage}–CH_2–CH_2–$), 1.26 (m, 4H, $–C_{cage}–CH_2–CH_2–CH_2–CH_2$-), 0.83 (t, 3H, $–CH_3$). ^{13}CNMR ($CDCl_3$, relative to $SiMe_4$, ppm): δ 78.41 and 74.70 for C_{cage}, 35.31, 31.23, 29.35, 23.10, 22.25 for $–(CH_2)_4–$ and $C_{cage}–CH_3$, 13.87 ($–CH_3$). ^{11}BNMR ($CDCl_3$, relative to $BF_3 \cdot OEt_2$, ppm): δ -4.47, -5.75, -8.75, -9.85, -10.75. IR (film on KBr, cm^{-1}): ν 2959 (s, s), 2934 (s, s), 2872 (m, s), 2586 (vs, s, ν_{BH}), 1956 (w, s), 1851 (w, s), 1685 (w, s), 1643 (w, s), 1460 (m, s), 1386 (m, s), 1313 (w, s), 1179 (m, s), 1118 (w, s), 1079 (w, s), 1030 (m, s), 983 (w, s), 949 (w, s), 921 (w, s), 790 (w, s), 729 (s, s), 678 (w, m), 483 (w, s).

2.3. Synthesis of and characterization of **6**

A 1.20 g (5.25 mmol) sample of (**5**) was added to a prepared solution of 2.50 g sodium hydroxide dissolved in 80 mL 95% ethanol with constant stirring. The resulting mixture was heated to reflux for 1 day, cooled to 0 °C and saturated with CO_2 gas for about 4 h to neutralize unreacted sodium hydroxide. After filtration, the obtained filtrate was dried under reduced pressure to produce 0.97 g waxy solid (**6**) in 77% yield. Analytic data: Calcd for $C_8H_{24}B_9Na$: C, 39.94; H, 10.06. Found: C, 39.89; H, 10.10. ^{1}HNMR (MeOD-d_4, relative to $SiMe_4$, ppm): δ 2.38- -0.98 (m, br, 9H, B_9H_9), 1.45 (t, 2H, $–C_{cage}–CH_2–$), 1.29 (s, 3H, $CH_3–C_{cage}$), 1.25 (m, 2H, $–C_{cage}–CH_2–CH_2–$), 1.17 (m, 4H, $–C_{cage}$-$CH_2–CH_2–CH_2–CH_2$-), 0.69 (t, 3H, $–CH_3$), -2.95 (s, br, 1H, BH_{bridge}). ^{13}CNMR (MeOD-d_4, relative to $SiMe_4$, ppm): δ 63.98 and 58.80 for C_{cage}, 36.92, 34.02, 31.72, 23.74, 22.48 for $–(CH_2)_4–$ and C_{cage}-CH_3, 14.84 ($–CH_3$). ^{11}BNMR (MeOD-d_4, relative to $BF_3 \cdot OEt_2$, ppm): δ -9.92, -11.60, -18.02, -19.55, -34.82, -37.50. IR (film on KBr, cm^{-1}): ν 3572 (s, s), 3235 (m, s), 3185 (m, s), 3135 (m, br), 2957 (vs, s), 2933 (vs, s), 2871 (s, s), 2517 (vs, s, ν_{BH}), 1997 (w, br), 1849 (w, s), 1615 (s, s), 1537 (m, s), 1487 (s, s), 1458 (s, s), 1379 (m, s), 1328 (w, s), 1261 (w, s), 1200 (w, s), 1038 (s, s), 876 (w, s), 738 (s, s), 669 (s, s), 437 (m, s).