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Notes

Preparation, Structure, and Olefin Polymerization Behavior of a Picolyl-Functionalized Carborane Nickel(II) Complex

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Summary: The picolyl-functionalized o-carborane ligand Cab^N*H (**1**; Cab*^{N}*H = 1-(2′-picolyl)-o-carborane) was prepared from the monolithium carborane* $LiHC_2B_{10}H_{10}$ *(=LiCab) and picolyl chloride (2-*$CH_2ClC_5H_5N$*). **1** was lithiated with n-BuLi and then reacted with* $Ni(PPh_3)_2Cl_2$ *to give the mononuclear Ni complex* $[(Cab^N)_2]Ni$ *(**2**). **2** was characterized by IR and NMR spectroscopy and elemental analysis. In addition, an X-ray structure analysis was performed on the complex, where the potential C,N-chelate ligand **1** was found to coordinate in a bidentate mode. The carborane complex **2** shows moderate catalytic activities of up to* 3×10^6 *g of PNB (mol of Ni)*$^{-1}$ *h*$^{-1}$ *for the addition polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst. Catalytic activities, molecular weights, and molecular weight distributions of polynorbornene (PNB) have been investigated under the various reaction conditions.*

Introduction

In recent years, transition-metal complexes with ligands containing dissimilar donor atoms have been widely investigated, primarily for their applications in important homogeneous catalytic processes.[1−8] The coordinatively labile donor atom in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle; at the same time the strong donor moiety remains connected to the metal center. Therefore, the design of such ligand systems containing one functional group strongly bound to a late transition metal and another coordinatively labile group has been of considerable interest.[9−14]

Derivatives of the icosahedral carboranes have attracted considerable recent attention in both their fundamental properties and their wide-ranging potential applications.[15−17] N-functionalized carboranes are potential σ-bonded carboranyl ligands possessing a pendant nitrogen donor group.[18,19] It was therefore of interest to investigate the possibility of using such intramolecularly coordinated complexes containing the *o*-carboranyl C,N-chelating ligand system as catalysts for olefin polymerization.

Here we report the synthesis and characterization of an intramolecularly coordinated nickel complex. The method of preparing this compound is generally based on the addition of [picolyl-*o*-carboranyl]lithium to a suitable nickel complex. Preliminary studies show that the complex $[Cab^N]_2Ni$ is active toward the polymerization of norbornene.

Results and Discussion

Compound **1**, 1-(2′-picolyl)-*o*-carborane, was obtained by treating monolithium carborane with picolyl chloride (Scheme 1). IR and ^{1}H NMR spectroscopic data are consistent with the described picolyl-*o*-carborane structure.

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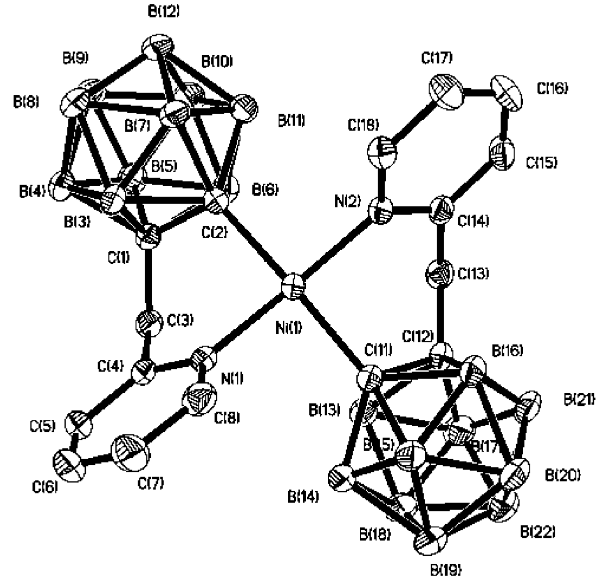

Figure 1. Molecular structure of complex **2**. The hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ni(1)−N(1) = 1.887(4), Ni(1)−N(2) = 1.892(4), Ni(1)−C(11) = 1.972(5), Ni(1)−C(2) = 1.973(5), C(1)−C(2) = 1.660(6); N(1)−Ni(1)−N(2) = 165.51(18), N(1)−Ni(1)−C(11) = 91.49(18), N(2)−Ni(1)−C(11) = 91.11(19), N(1)−Ni(1)−C(2) = 90.14(18), N(2)−Ni(1)−C(2) = 91.69(18), C(11)−Ni(1)−C(2) = 162.3(2), C(1)−C(2)−Ni(1) = 111.6(3), C(4)−N(1)−Ni(1) = 125.1(3).

Scheme 1. Synthesis of Complex 2

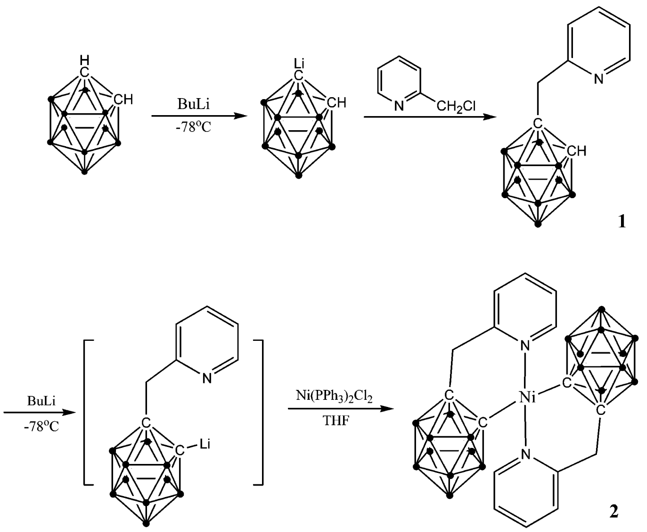

Table 1. Addition Polymerization of Norbornene with Nickel Complex 2 Activated by Methylaluminoxane (MAO)[a]

run	complex	Al/Ni	*T* (°C)	activity[b]	M_v[c]	M_w[d]	M_w/M_n[d]
1	2	3000	30	0.19	0.9		
2	2	6000	30	0.62	4.4		
3	2	8000	30	1.12	5.6		
4	2	10000	30	0.93	6.8		
5	2	8000	20	0.9	9.4		
6	2	8000	50	2.0	7.5	8.28	2.2
7	2	8000	60	3.0	6.0		
8	2	8000	80	2.3	7.3		
9[e]	2		30	0	0	0	0
10[f]			30	0	0	0	0

[a] Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex (**2**), 0.4 μmol; norbornene, 1.88 g (norbornene/Ni (molar) = 68 000); reaction time, 30 min. [b] In units of 10^6 g of PNB (mol of Ni^{-1}) h^{-1}. [c] M_v (10^{-5} g mol^{-1}) values were measured by the Ubbelohde calibrated viscosimeter technique.[d] M_w (10^{-5} g mol^{-1}) and M_w/M_n values were determined by GPC. [e] Without cocatalyst MAO. [f] Without nickel complex.

The intramolecularly stabilized tetracoordinated (*o*-carboranyl)nickel complex **2** was synthesized in THF from $Ni(PPh_3)_2Cl_2$ and the (picolyl-*o*-carboranyl)lithium compound $LiCab^N$ (Scheme 1). Complex **2** has been isolated as yellow, transparent crystals. A detailed analysis of the spectroscopic data (^1H NMR, ^{11}B NMR, ^{13}C NMR, and IR spectra) showed that the 1-(2′-picolyl)-*o*-carborane ligand **1** is coordinated to the nickel(II) through the carbon and nitrogen atoms.

The stabilization in complex **2** is due to the formation of a six-membered chelate ring. The nickel complex **2** is soluble in THF and CH_2Cl_2 and sparingly soluble in hexane. The complex **2** is moderately stable in air and shows only slow decomposition when in contact with moisture.

The ORTEP diagram of $[Cab^N]_2Ni$ is presented in Figure 1. Crystallographic data and processing parameters are given in Table 2. The molecular structure reveals that the geometry at the nickel atom is distorted square planar, the two chelates $[Cab^N]$ adopt a trans arrangement around the nickel atom, and there is a C_2 symmetry. The angles of C(1)−C(2)−Ni(1) and C(12)−C(11)−Ni(1) within the two six-membered rings are smaller (111.6(3) and 111.8(3)°, respectively) than the expected 120°. The Ni−N distances in **2** (1.887(4) and 1.892(4) Å) are much smaller than that in the corresponding pyridine-ligated system $[\{bpa(CH_2)_2O(CH_2)_2OH\}Ni(NO_3)](NO_3)$ (bpa = bis(2-picolyl)amine; 2.0708(13) and 2.0765(12) Å)[20] and $[Ni(2\text{-}\{1'\text{-}(diphenylphosphanyl)\text{-}1'\text{-}methyl\}ethylpyridine)Cl_2]$ (1.950(3) Å).[21] The two six-membered Ni−C−C−C−C−N rings are folded with the dihedral angle between the planes [Ni(1), C(2), C(1), C(3)] and [Ni(1), N(1), C(4), C(3)] being 59.9° and that between [Ni(1), C(11), C(12), C(13)] and [Ni(1), N(2), C(14), C(13)] being 57.9°. The bond lengths and angles associated with pyridine and *o*-carboranyl groups are normal with respect to the other *o*-carboranyl substituted compounds.[14,19,22]

Preliminary experiments indicated that the nickel complex **2** can be activated for norbornene polymerization by treatment with MAO to afford addition-type polynorbornene (PNB) with moderate activity (10^6 g of PNB (mol of Ni)$^{-1}$ h^{-1}), high molecular weight ($M_w = 10^5$ g mol^{-1}), and moderate molecular weight distribution ($M_w/M_n = 2.2$). Under the same conditions, however, the complex itself and MAO did not produce polymers (runs 9 and 10). The norbornene polymerization results are collected in Table 1. It was revealed that MAO was essential for this polymerization, and the catalytic activity was dependent upon the Al/Ni molar ratio, as shown in Table 1 (runs 1−4). The optimized Al/Ni molar ratio for the activity was 8000, and the activity decreased for both lower and higher molar ratios. Intrinsic

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Table 2. Summary of Crystallographic Data for 2

chem formula	$C_{18}H_{36}B_{20}Cl_4N_2Ni$
formula wt	697.20
temp (K)	293(2)
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	
a (Å)	11.095(4)
b (Å)	21.883(8)
c (Å)	14.564(5)
β (deg)	90.213(5)
V (Å^3)	3536(2)
Z	4
D_{calcd} (Mg/m^3)	1.310
abs coeff (mm^{-1})	0.869
F(000)	1416
cryst size (mm)	0.40 × 0.25 × 0.20
θ range for data collecn (deg)	1.68−25.01
limiting indices	$-13 \leq h \leq 13$, $-22 \leq k \leq 26$, $-17 \leq l \leq 16$
no. of rflns collected	14 683
no. of indep rflns	6214 (R(int) = 0.0346)
completeness to θ (deg)	25.01 (99.7%)
max and min transmissn	0.8454 and 0.7225
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	6214/4/396

viscosity molecular weights M_v of polymers increased due to an increase in the Al/Ni molar ratio. We found that the complex **2** showed the highest activity at 60 °C (3×10^6). The activity of **2** increased when the temperature of polymerization rose from 20 to 60 °C. This is because the concentration of the active center activated by MAO increases as the temperature rises. At the same time **2** usually becomes unstable at high temperature. The highest activity at 60 °C is the result of the compromise of two factors. The decomposition of the active center increased and the activity dropped at 80 °C. It is clear that the M_v value was lower at higher temperature. A molecular weight of 9.4×10^5 was obtained at a reaction time of 20 °C.

The polymers obtained were characterized by IR, ^1H NMR, ^{13}C NMR, and GPC analyses. The resonances of PNB appear at 0.9−3.03 ppm (m, maxima at 1.52, 1.87, 2.23, 2.59 ppm) in the ^1H NMR, and the absence of bands at 1680∼1620 cm^{-1} in the IR spectra indicated no double bonds, which was different from the polymers of norbornene ring-opening metathesis polymerization.[23] The ^{13}C NMR spectrum of PNB shows the main resonances at δ 30.0−48.8 ppm (m, maxima at 32.43, 39.12, 48.39, 48.77 ppm), attributed to the vinyl-addition polymer structure of polynorbornene, bridge carbon, bridgehead carbon, and the backbone carbon.[24] Furthermore, the product of cationic or free-radical polymerization of norbornene is usually formed with low molecular weight (molecular weight <1000) and low yield because of the rearrangements and transfer reactions.[25] The GPC molecular weights M_w and intrinsic viscosity molecular weights M_v of polymers were very high, indicating that the normal mode of chain transfer (β-hydride elimination) was not possible in PNB, given the geometry of the active growing center. Therefore, the polymerization took place in a vinyl addition manner. The DSC study of obtained PNB did not give an endothermic signal upon heating to the decomposition temperature (above 450 °C).

Conclusion

This report provides the first report of an intramolecularly coordinated nickel complex containing an *o*-carboranyl C,N-chelating ligand system. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of this nickel complex. A preliminary study shows that the new nickel complex **2** is moderately active as a catalyst precursor in norbornene polymerization. To the best of our knowledge, this is the first report that this kind of N-functionalized *o*-carboranyl late-transition-metal complex exhibits activity toward vinyl addition polymerization of norbornene. Further investigations into the polymerization mechanism are ongoing.

Experimental Section

General Procedures. All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. CH_2Cl_2 and chlorobenzene were dried over CaH_2 and THF, diethyl ether, hexane, and norbornene over Na and then distilled under nitrogen immediately prior to use. Methylaluminoxane (MAO) and 2-picolyl chloride hydrochloride were purchased from Witco and Acros, respectively. Other solvents were used as received as technical grade solvents. $Ni(PPh_3)_2Cl_2$[26] was prepared according to the literature. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker VAVCE-DMX 500 spectrometer in $CDCl_3$ or *o*-dichlorobenzene-d_4. Elemental analysis was performed on an Elementar Vario EL III analyzer. Average molecular weight (M_w) and molecular weight distribution (M_w/M_n) values of PBN products were determined with a PL GPC-220 permeation chromatograph at 150 °C, using a narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10m MIXED-BLS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL/min. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer.

1-(2′-Picolyl)-*o*-carborane (1). To a solution of *o*-carborane (288 mg, 2 mmol) in dry Et_2O (20 mL) at −78 °C was added 2.5 M of n-BuLi in hexane (0.8 mL, 2 mmol), and the reaction mixture was stirred for 1 h at −78 °C. Then 2-picolyl chloride (255 mg, 2 mmol; prepared by neutralizing picolyl chloride hydrochloride[18]) was added at −78 °C, and the stirred reaction mixture was warmed to room temperature for 1 h. Addition of water (30 cm^3) dissolved the nascent LiCl, and the separated Et_2O layer was further washed with water (2 × 30 mL) before being isolated and dried over Na_2SO_4. Filtration, followed by removal of the solvent in vacuo, gave a white solid. Unreacted *o*-carborane was removed by slow vacuum sublimation (40 °C, 0.01 mmHg) to give analytically pure **1** (250 mg, 57% yield). IR (KBr, cm^{-1}): 3069, 3020 m (br) (carborane CH), 2916 w, 2848 w (pyridyl/CH_2 str), 2596 vs, 2575 s (BH); 1593 s, 1570 m, 1476 s, 1438 s (pyridyl skel), 1095 m, 1063 m, 1017 m, 769 s, 751 m (CH oop and carborane skel), 719 s (br) (BH wag). ^1H NMR (500 MHz, $CDCl_3$): δ 8.56 (1H, d, pyridyl), 7.70 (1H, m, pyridyl), 7.26 (1H, m, pyridyl), 7.18 (1H, d, pyridyl), 4.08 (1H, s, C2H), 3.66 (1H, m, CH_2), 3.55 (1H, m, CH_2).

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Bis[1-(2′-picolyl)-*o*-carborane]nickel (2). To a stirred solution of **1** (235 mg, 1 mmol) in 20 mL of THF, which was cooled to −78 °C, was added 2.5 M n-BuLi (0.4 mL, 1 mmol) via a syringe. The resulting pale yellow solution was stirred at −78 °C for 1 h and then transferred through a cannula to a suspension of $Ni(PPh_3)_2Cl_2$ (654 mg, 1 mmol) in 20 mL of THF. After the mixture was stirred for 16 h, the solvent was removed under vacuum, and the resulting residue was taken up in a minimum of THF and then recrystallized by slow diffusion of hexane into this solution. Yield: 163 mg (62%). IR (KBr, cm^{-1}): 3057 m (br) (carborane CH), 2924 w, 2850 w (pyridyl/CH_2 str), 2561 vs (BH), 1593 m, 1560 m, 1437 s (pyridyl skel), 1119 vs, 1098 s, 1073 m, 1023 m, 749 m (CH oop and carborane skel), 723 s, 694 s (br) (BH wag). ^1H NMR (500 MHz, $CDCl_3$): δ 9.64 (1H, d, pyridyl), 7.98 (1H, m, pyridyl), 7.59 (2H, m, pyridyl), 4.33 (1H, d, CH_2), 4.01 (1H, d, CH_2) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ 156.6 (pyridyl, C_2), 151.9 (pyridyl, C_6), 139.1 (pyridyl, C_4), 126.0 (pyridyl, C_5), 123.5 (pyridyl, C_3), 71.3 (C1), 52.0 (C2) ppm. ^{11}B NMR (500 MHz, $CDCl_3$): δ −2.15, −5.71, −8.78, −9.62, −10.88 ppm. Anal. Calcd for $C_{16}B_{20}H_{32}N_2Ni{\cdot}0.5C_4H_8O$: C, 38.39; H, 6.39; N, 4.97. Found: C, 38.62; H, 6.01; N, 4.69.

X-ray Crystallography. Suitable crystals for X-ray analysis of **2** were obtained by slow diffusion of hexane into CH_2Cl_2 solutions of the corresponding compound. None showed signals of decomposition during X-ray data collection, which was carried out at room temperature. Details of the data collection and refinement are summarized in Table 2. Selected bond lengths and angles are given in Figure 1. The structure was solved by direct methods using SHELX-97 and refined by full-matrix least-squares calculations, using the program system SHELXTL-97.

Norbornene Polymerization. In a typical procedure, 0.4 μmol of nickel complex **2** in 2.0 mL of chlorobenzene, 1.88 g of norbornene in 4.0 mL of chlorobenzene, and another 3.0 mL of fresh chlorobenzene were added into a special polymerization bottle (20 mL) with a strong stirrer under an Ar atmosphere. After the mixture was kept at the desired temperature for 10 min, the desired MAO (10%) was charged into the polymerization system via syringe, and the reaction was started. Thirty minutes later, acidic ethanol (V_{methanol}:$V_{\mathrm{concd\ HCl}} = 20{:}1$) was added to terminate the reaction. The PNB was isolated, washed with methanol, and dried at 80 °C for 48 h under vacuum. For all the polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by variation of chlorobenzene when necessary. IR (KBr, cm^{-1}): 2946 vs, 2869 vs, 1473 m, 1451 s, 1375 m, 1295 m, 1258 m, 1222 m, 1148 m, 1108 m, 1040 w, 943 w, 893 m. ^1H NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 0.9−3.03 ppm (m, maxima at 1.52, 1.87, 2.23, 2.59). ^{13}C NMR (*o*-dichlorobenzene-d_4, 500 MHz): δ 30.0−48.8 ppm (m, maxima at 32.43, 39.12, 48.39, 48.77).

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Supporting Information Available: Crystallographic data for **2** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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