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Editor's Choice Paper

Role of $B(C_6F_5)_3$ in activating the nickel-methyl complex $(\eta^5\text{-}C_5H_5)Ni(CH_3)(PPh_3)$ to initiate the vinyl polymerization of norbornene

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ABSTRACT

The Ni-methyl complex $(\eta^5\text{-}C_5H_5)Ni(CH_3)(PPh_3)$ (**1**) reacted with $B(C_6F_5)_3$ to give an unstable contact ion-pair complex with a μ-methyl bridge between the Ni and B atoms. Formation of the B-CH_3 bond was confirmed by the reaction of this complex with PPh_3 to give $[(\eta^5\text{-}C_5H_5)Ni(PPh_3)_2][B(CH_3)(C_6F_5)_3]$ which was structurally characterized. Spontaneous decomposition of the contact ion-pair complex yielded $(\eta^5\text{-}C_5H_5)Ni(C_6F_5)(PPh_3)$ which is very stable and does not show any reactions with norbornene with or without added $B(C_6F_5)_3$. ^{19}F NMR study showed that the polynorbornene obtained by the catalysis of **1**/$B(C_6F_5)_3$ system has the C_6F_5 end-group. A series of reactions, which includes CH_3/C_6F_5 exchange between the Ni and B centers with concomitant dissociation of PPh_3 to accept coordination of a norbornene monomer, is proposed as the route to active species that can initiate vinyl polymerization of norbornene.

1. Introduction

The vinyl (co)polymerization, also termed addition (co) polymerization, of bicyclo[2,2,1]hept-2-ene (norbornene, NB) and its derivatives gives rise to polymers with attractive properties such as very high glass transition temperature, high optical transparency, low moisture absorption, and low dielectric constant [1]. Among effective catalysts for the vinyl polymerization of NB, the combinations of metallocene complexes of group 4 metals and methylalumoxane (MAO) are well known. As for the late transition metals, Ni(II) and Pd(II) complexes are the most frequently mentioned catalyst species. In many cases the precursor complexes have halogen, carboxylate, salen, acetylacetonate, etc. as the anionic ligands, which are often activated by MAO [1d]. Also reported are complexes with methyl, η^3-allyl, pentafluorophenyl, and 6-methoxybicyclo[2,2,1]hept-2-ene-5-yl ligands, which are expected to initiate the polymerization without the aid of co-catalysts since they have already a metal–C σ-bond, but in many cases borate or other salt having a large anion is added to generate vaunt coordination site while keeping the metal–C bond [2]. With few exceptions, common active species in these cases appears a cationic alkyl metal with weak or none coordinating counter ions. In particular, the neutral powerful Lewis acid $B(C_6F_5)_3$ can readily generate such species when the precursor complexes have two methyl groups, by abstracting one methide anion to form $[L_nMCH_3]^+[CH_3B(C_6F_5)_3]^-$ type active species. Although the abstraction of methide group by $B(C_6F_5)_3$ has been also observed in late transition metal complexes [3], the reactions of metallocene and half-metallocene dimethyl complexes of group 4 transition metals have been particularly well studied and intermediate complexes that lead to the methide abstraction have been observed by NMR spectroscopy or even isolated in some cases [4]. Such an "adduct" of the form M-(μ-CH_3)$B(C_6F_5)_3$ has not been observed, to the best of our knowledge, in the cases of late transition metal complexes where the metal–carbon σ-bond has more covalent nature compared to those of early transition metals.

We decided a few years ago to examine the reactivity of metallocene and half-metallocene type complexes of Ni and Pd as the catalysts for polymerization of NB. Although the cyclopentadienyl group has been well proved to be a useful ligand in early transition metal-catalyzed polymerization of olefins including NB, Ni and Pd complexes ligated by a cyclopentadienyl ligand had not been applied for the polymerization of NB. Recently, we reported that $CpNi(CH_3)(PPh_3)$ (**1**, Cp = $\eta^5\text{-}C_5H_5$) alone does not show any activity, but when activated with $B(C_6F_5)_3$, it turns into a very efficient catalyst for homo-polymerization of NB and co-polymerization of

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Table 1
Polymerization of NB by complex **1**/$B(C_6F_5)_3$ catalyst system.

Run	$[NB]_0/[Ni]$	$[B(C_6F_5)_3]/[Ni]$	[DTBP]/[Ni]	Time (h)	Yield (%)	Activity
1	500	3.0	0	2	99	2.34×10^4
2	500	3.0	10.0	2	97	2.30×10^4
3	500	3.0	37.6	2	88	1.88×10^4
4	1000	1.0	0	1	79	7.45×10^4
5	1000	1.0	0	24	84	

Complex **1**: 20 μmol, temperature: 25 °C, sovent: toluene 10 ml, DTBP = 2,6-di-*t*-butylpyridine, activity = polymer-g/cat-mol h.

NB with ester-substituted norbornenes [5]. The presence of the Cp ligand exerted unusual selectivity toward exo/endo isomers of ester-substituted monomers [6]. As is described in the present work, we have studied this catalyst system in more detail and found that an adduct between **1** and $B(C_6F_5)_3$ is initially formed. Its implication as the initiator for the vinyl type NB polymerization was also interesting, since successive simple abstraction of the methide group by $B(C_6F_5)_3$ would leave a cationic Ni complex of the type $[CpNi(PPh_3)]^+$, i.e. an intermediate having no Ni-alkyl σ-bond to which the first NB monomer should normally insert to start the polymerization.

2. Experimental part

2.1. General procedures and materials

All manipulations that involve air-sensitive compounds were performed under an atmosphere of argon or purified nitrogen using standard Schlenk or drybox techniques. Solvents were dried and deoxygenated by refluxing on sodium or CaH_2 under argon and distilled before use. NB was purchased from Tokyo Chemical Industrial Co., Ltd. and distilled from CaH_2 under argon. $B(C_6F_5)_3$ was purchased from Strem Co., Ltd. and used as received. $CpNi(CH_3)(PPh_3)$ and $CpNi(C_6F_5)(PPh_3)$ were prepared according to the literature methods [7,8].

^{1}H NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. ^{19}F NMR spectrum was recorded on a JEOL CMX400 spectrometer using $CFCl_3$ as the external standard. Molecular weights of poly(NB) were measured by TOSOH HLC-8220 GPC using an HZM-H column at 40 °C with THF eluent. Elemental analyses were performed by Chemical Analysis Team, D & S Center, RIKEN.

2.2. DFT calculations

Geometry optimizations of stationary points were performed by the B3LYP hybrid density functional methods using Gaussian 03 program [9] with CEP-31G effective core potential (ECP) for Ni, 4-31G* basis set for P, and 4-31G basis set for other atoms.

2.3. Typical polymerization procedure

Run 2 in Table 1 was carried out as follows: NB (0.942 g, 10 mmol), $B(C_6F_5)_3$ (0.031 g, 60 μmol), and 2,6-di-*tert*-butylpyridine (0.038 g, 200 μmol) were mixed in toluene (3 ml). A toluene solution (2 ml) of **1** (8 mg, 20 μmol) was added quickly under stirring. After 2 h, the viscous mixture was poured into a large amount of methanol. The precipitated colorless polymer was washed several times with methanol and vacuum dried at 80 °C. Yield 0.914 g (97%).

2.4. Polymerization procedure for soluble polymer sample

The soluble polymer sample for the ^{19}F and ^{11}B NMR measurements was obtained by using a large quantity of catalysts: to a mixture of **1** (0.200 g, 490 μmol) and NB (2.35 g, 25 mmol) in toluene (10 ml), was added a toluene solution (10 ml) of $B(C_6F_5)_3$ (0.511 g, 1.0 mmol) dropwise. After overnight stirring at room temperature, the polymer was precipitated with a large amount of methanol, filtered, and dried (2.34 g). The polymer sample (1.50 g) was suspended in CH_2Cl_2 (100 ml) and heated while ultra sonic vibration was being applied. The filtered solution was concentrated to ca. 10 ml and column chromatographed on alumina using hexane as eluent. The eluate (200 ml) was concentrated and poured into methanol to precipitate the polymer (0.106 g). GPC: $Mn = 4000$; $Mw/Mn = 2.1$. For ^{1}H NMR, see supplementary material.

2.5. Isolation of the red adduct (*2*) from *1* and $B(C_6F_5)_3$

To a CH_2Cl_2 solution (2 ml) of complex **1** (0.240 g, 0.60 mmol) cooled at −50 °C, a CH_2Cl_2 solution (3 ml) of $B(C_6F_5)_3$ (0.256 g, 0.5 mmol), pre-cooled to −50 °C, was slowly added with stirring. After 0.5 h, the solvent was evaporated at −10 °C leaving a red oily residue. Hexane, pre-cooled to −30 °C, was added with stirring. The supernatant hexane solution was removed with syringe and the red residue was pumped at −10 °C to give red powder. The powder was washed three times with cooled hexane and vacuum dried to give adduct $CpNi(PPh_3)(CH_3)B(C_6F_5)_3$ (**2**). Yield 0.426 g (93%). Elemental analysis calc. for $C_{42}H_{23}BF_{15}NiP$: C, 55.24; H, 2.54; F, 31.21; P, 3.39. Found: C, 55.22; H, 2.68; F, 30.85; P, 3.53%. ^{1}H NMR (toluene-d_8): $\delta = 0.19$ [s, 3H, CH_3], 4.45 [s, 5H, C_5H_5], 6.8–7.4 [m, 15H, P-C_6H_5].

2.6. Reaction of adduct *2* with PPh_3

Complex **1** (0.400 g, 1.0 mmol) in toluene (3 ml) and $B(C_6F_5)_3$ (0.512 g, 1.0 mmol) in toluene (3 ml) were mixed at −50 °C to give a red solution. After 0.5 h, a toluene solution (3 ml) of PPh_3 (0.262 g, 1.0 mmol), pre-cooled to −50 °C, was added slowly under stirring and this temperature was kept overnight. The greenish yellow solution was allowed to warm to room temperature. The solvent was evaporated and the residue was chromatographed on alumina (deactivated with 5 wt% of water). Elution of a yellow band with CH_2Cl_2 and concentration of the eluate followed by slow addition of hexane gave dark-green crystals of $[CpNi(PPh_3)_2][B(CH_3)(C_6F_5)_3]$ (**3**). Yield 1.05 g (89%). Elemental analysis calc. for $C_{60}H_{38}BF15NiP_2$: C, 61.31; H, 3.26; F, 24.25; P, 5.27. Found: C, 60.89; H, 3.63; F, 24.88; P, 5.15%. ^{1}H NMR (C_6D_6): $\delta = 1.49$ [s, 3H, CH_3], 4.69 [s, 5H, C_5H_5], 6.8-7.2 [m, 30H, P-C_6H_5].

2.7. Product isolation from decomposed solution of adduct *2*

Complex **1** (0.200 g, 0.5 mmol) in toluene (5 ml) and $B(C_6F_5)_3$ (0.250 g, 0.6 mmol) in toluene (10 ml) were mixed at room temperature to give a red solution, color of which rapidly turned yellow brown. After 5 h, the mixture was concentrated and column chromatographed on alumina (deactivated with 5 wt% of water). A green band was eluted with hexane/benzene (1:1). Concentration of the eluate and addition of hexane gave crystals of $CpNi(C_6F_5)(PPh_3)$ (**4**). Yield 78 mg (28%). From a second yellow fraction which was eluted with CH_2Cl_2, an 8% yield of complex **3** was obtained.

2.8. X-ray crystallographic study

Single crystals of **3** suitable for X-ray analysis were obtained as described in the preparations. The crystals were sealed in thin-walled glass capillaries under a microscope in the glove box. Data collections were performed at 100 K on a Rigaku AFC-8 diffractometer with a Saturn 70 CCD area detector using confocal-mirror monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was carried out using the program CrystalClear [10], The structures were solved by using SHELXTL program [11]. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystallographic data for **3** can be found in the CIF file: CCDC reference number 699721.

Crystallographic data for **3**: $C_{60}H_{38}Ni_1P_2B_1F_{15}$, $M = 1175.36$, $T = 100(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.1193(19)$, $b = 29.635(6)$, $c = 14.701(2)$ Å; $\beta = 102.625(3)^\circ$, $V = 5152.5(15)$ Å^3, $Z = 4$, Dc = 1.515 g cm^3, $\mu = 0.534$ mm^{-1}, reflections collected: 57,894, independent reflections: 16,230, ($R_{int} = 0.0800$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0656$, $wR_2 = 0.1541$, R indices (all data): $R_1 = 0.1039$, $wR_2 = 0.1797$.

3. Results and discussion

3.1. Polymerization of norbornene initiated by the $CpNi(CH_3)(PPh_3)/B(C_6F_5)_3$ system

The polymerization of NB catalyzed by **1**/$B(C_6F_5)_3$ was briefly reported as a part of our previous communication [5]. The nickel complex **1** does not show any activity itself but addition of equimolar mixture of **1** and $B(C_6F_5)_3$ to a toluene solution of NB at room temperature gave poly(NB) in 47% yield when $[NB]_0/[\mathbf{1}]$ was 5000 [5] and in 84% yield when $[NB]_0/[\mathbf{1}]$ was 1000. Some typical polymerization data are presented in Table 1, though the activities reported were not optimized, particularly concerning the reaction time. The poly(NB) obtained in this way was insoluble in organic solvents even at elevated temperatures and no soluble portion could be extracted from it. To obtain a soluble sample, a large amount of catalyst ($[NB]_0/[\mathbf{1}] \approx 50$) was used and the soluble polymer fraction was extracted with CH_2Cl_2. The CH_2Cl_2-soluble portion was purified by passing through an alumina column to remove any Ni fragment and unreacted $B(C_6F_5)_3$. The polymer sample thus obtained was confirmed by proton NMR spectrum to contain no CpNi or aromatic (PPh_3) residues. The ^{1}H NMR of this poly(NB) (supplementary material) was similar to the one reported by Rhodes and coworkers [12], which was assigned by them to have exo-enriched sequences with low diisotacticity.

To control the molecular weight of poly(NB) more efficiently, a similar reaction as above ($[NB]_0/[\mathbf{1}] \approx 10$) was carried out in toluene saturated with ethene. The resulting soluble fraction of the polymer (65% yield, $Mn = 2030$, $Mw/Mn = 1.54$) showed ^{1}H NMR resonances at 4.88 and 5.70 ppm as broad singlets with relative intensities of 2:1 (NMR chart in supplementary material). Thus the presence of terminal vinyl group is apparent.

When carrying out these polymerization experiments, care was taken because the Lewis acidic $B(C_6F_5)_3$ itself can polymerize NB by a cationic mechanism if a trace amount of moisture is present. The adduct with water, $B(C_6F_5)_3{\cdot}3H_2O$, has been known to work as a Brϕnsted acid [13]. In our dry toluene solvent freshly distilled from sodium, $B(C_6F_5)_3$ did not active for the NB polymerization. It was further confirmed that the polymerization by **1**/$B(C_6F_5)_3$ catalyst system in toluene was not retarded by addition of 10–13 equiv. (per **1**) of the cationic inhibitor, 2,6-di-*tert*-butylpyridine (DTBP) (Table 1, runs 2 and 3). Indeed when the commercially available solvent was not dried, $B(C_6F_5)_3$ alone did catalyze the polymerization of NB, but that was inhibited completely by the addition of a small excess DTBP. It is thus obvious that the polymerization of NB effected by the combination of **1** and $B(C_6F_5)_3$ in the dried solvent is a coordination polymerization taking place on Ni(II). Another difference between this coordination polymerization and the cationic polymerization by $B(C_6F_5)_3$ is that only the former can co-polymerize NB with ester-substituted NB derivatives, which greatly improves undesired properties of the NB homopolymer [5].

One notable observation about the present polymerization system is obvious color change; the green color of a toluene solution of **1** changes immediately to red upon addition of $B(C_6F_5)_3$. When the monomer solution is added, the red color disappears quickly and turns pale-brown as the polymerization starts.

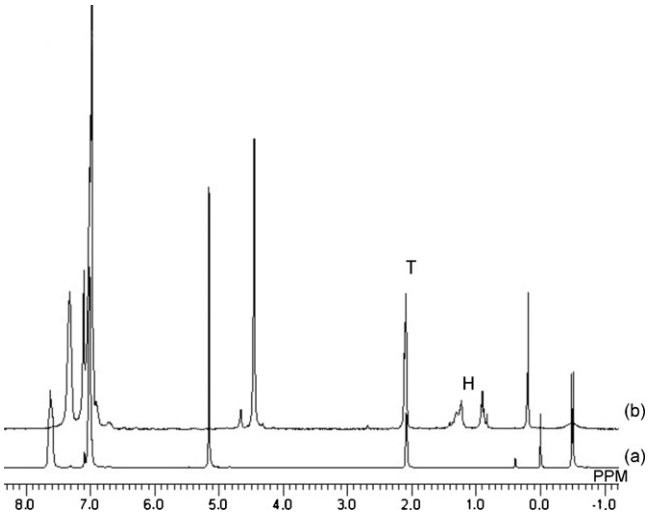


Fig. 1. ^{1}H NMR spectra of (a): $CpNi(CH_3)(PPh_3)$ (**1**, toluene-d_8, 25 °C), and (b): adduct $CpNi(CH_3)(PPh_3)B(C_6F_5)_3$ (**2**, toluenen-d_8, −10 °C). Peaks marked T and H are those of toluene and hexane, respectively.

3.2. Adduct formation of $CpNi(CH_3)(PPh_3)$ with $B(C_6F_5)_3$

The red-colored 1:1 mixture of **1** and $B(C_6F_5)_3$ (*vide supra*) was prepared in dichloromethane at −50 °C. Subsequent reduction of the volume of the solution at −10 °C in vacuum and slow addition of cold hexane to the oily residue gave red powder in almost quantitative yield. Unfortunately, the red complex was unstable at room temperature and efforts to get single crystals at low temperatures were unsuccessful. Elemental analysis of the powder was consistent with the composition for a 1:1 adduct (**2**) between **1** and $B(C_6F_5)_3$. The proton NMR spectra for complexes **1** and **2** are compared in Fig. 1. The spectrum of **2** measured at low temperature showed the Cp proton absorption at 4.42 ppm, a large up-field shift from that of **1** at 5.16 ppm. The methyl resonance was observed at 0.19 ppm as a singlet, in contrast to the sharp doublet peak for the methyl protons of **1** (−0.49 ppm, $J_{PH} = 8$ Hz).

To get structural information for adduct **2**, the reaction with an equal molar amount of PPh_3 was examined. After mixing the toluene solution of the two reactants at −50 °C, the temperature was allowed to warm to room temperature during which time the color changed from red to greenish yellow. Work-up of the resulting solution gave crystals, that was analyzed to have the composition $[CpNi(PPh_3)_2(CH_3)B(C_6F_5)_3]$, in 89% yield. Single crystal X-ray analysis revealed the ionic molecular structure $[CpNi(PPh_3)_2]^+[B(CH_3)(C_6F_5)_3]^-$ (**3**) as shown in Fig. 2. Facile formation of **3** by the reaction with PPh_3 strongly suggests that the structure of the red complex **2** is of the methyl bridged type, or the

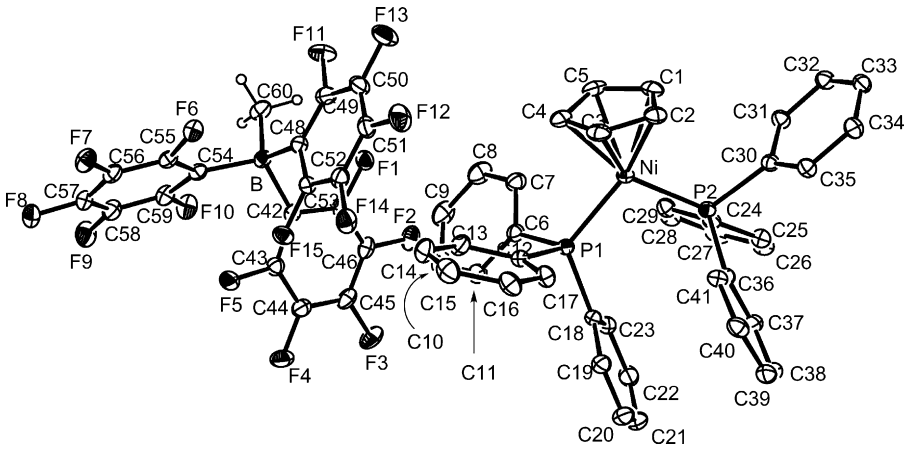


Fig. 2. Molecular structure and numbering scheme of $[CpNi(PPh_3)_2][CH_3B(C_6F_5)_3]$ (**3**). Hydrogen atoms are omitted for clarity. For atomic coordinates, see supplementary material.

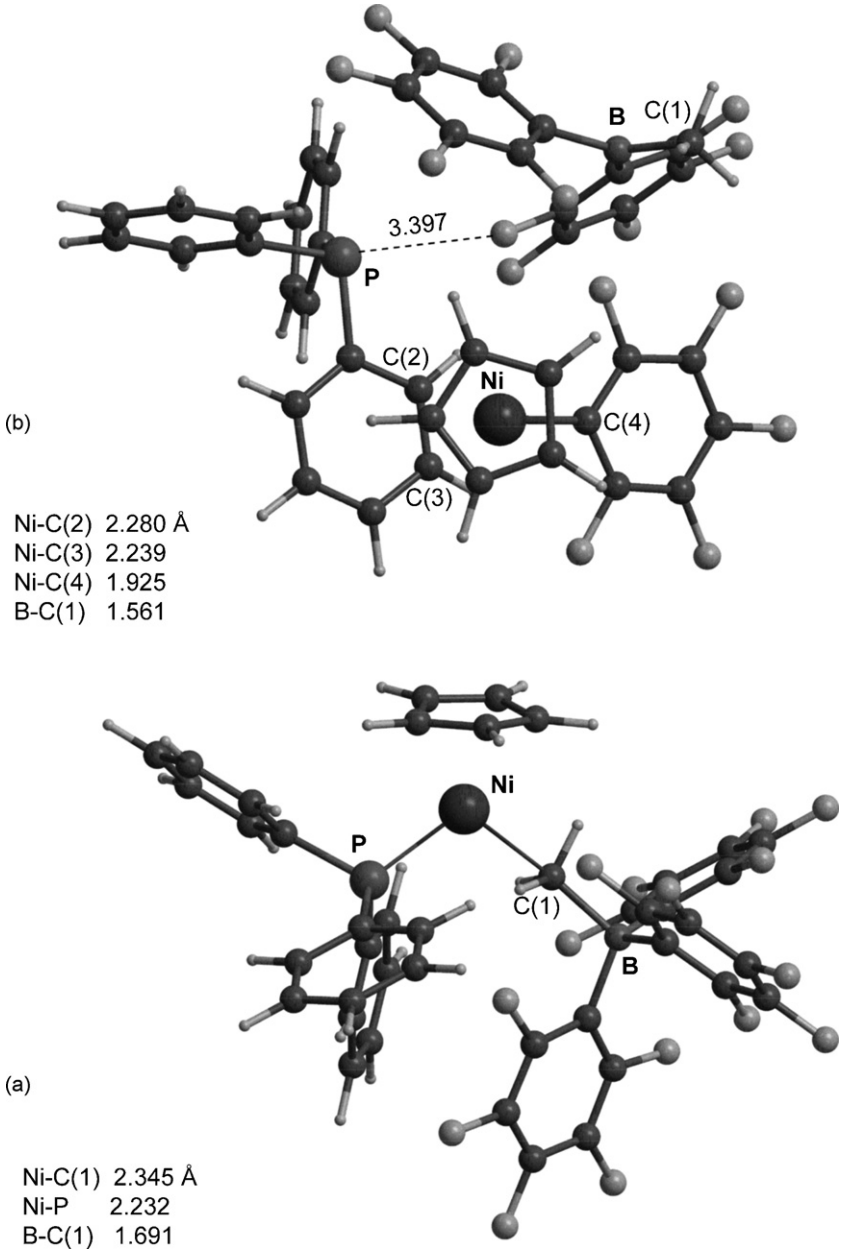


Fig. 3. The DFT-optimized structures for (a): contact ion-pair **2**, and (b): a proposed intermediate for the borane-assisted dissociation of PPh_3.

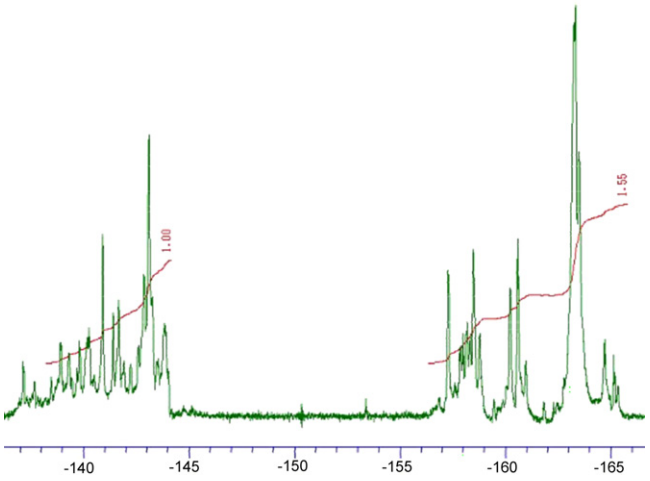


Fig. 4. ^{19}F NMR (in $CDCl_3$, $CFCl_3$ as external standard) of the soluble fraction of poly(NB) prepared by **1**/$B(C_6F_5)_3$ catalyst.

contact ion structure, $Cp(PPh_3)Ni$-(μ-CH_3)$B(C_6F_5)_3$ (Eq. (1)).

$$\underset{\mathbf{2}}{CpNi(PPh_3)-(\mu\text{-}CH_3)B(C_6F_5)_3} + PPh_3 \rightarrow \underset{\mathbf{3}}{[CpNi(PPh_3)_2]^+[B(CH_3)(C_6F_5)_3]^-} \quad (1)$$

In the cases of Ti and Zr metallocene complexes, single crystal X-ray analyses of contact ion-pair of the type $Cp_2M(CH_3)$-(μ-CH_3)$B(C_6F_5)_3$ (M = Ti, Zr) were reported, which revealed that the M–CH_3 distance is much longer than the CH_3–B bond and hence partial charge separation $M(\delta+)\cdots B(\delta-)$ occurs [4a,4b].

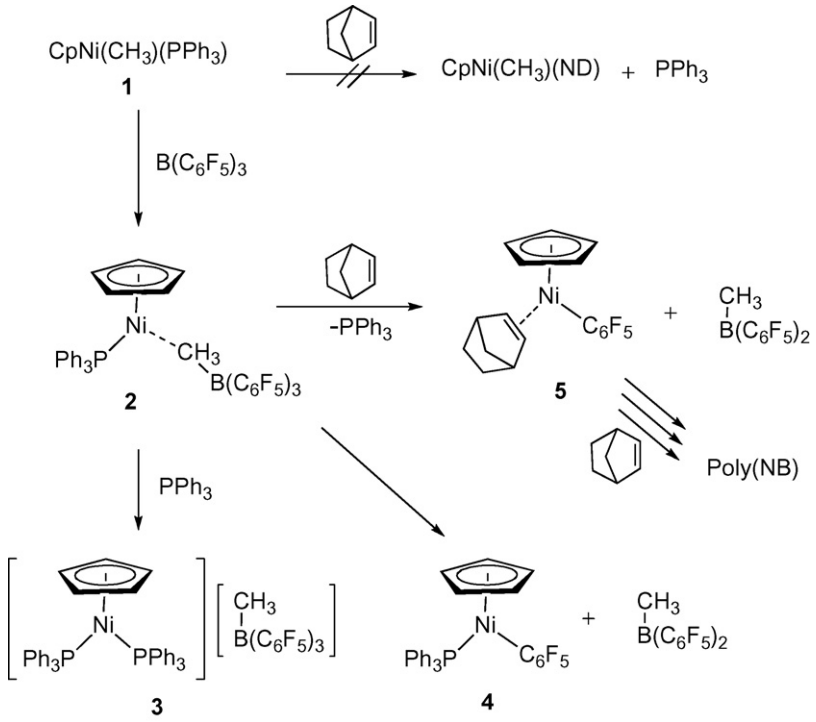
The Ni–C_{Me} distances in complex **1** and in adduct **2** were compared based on DFT studies. The interaction of the methyl group in **1** with $B(C_6F_5)_3$ to form **2** gives rise to considerable elongation of the Ni–C_{Me} distance (Fig. 3(a), calculated values; **1**, 1.944 Å, **2**, 2.345 Å). The B–C_{Me} bond length is 1.691 Å, only a little longer than the value calculated for the free $[B(CH_3)(C_6F_5)_3]^-$ anion (1.559 Å). Thus, adduct **2** has a "contact ion-pair" structure primarily comparable to those found in $B(C_6F_5)_3$ adduct of group IV metallocenes. The Ni–C_{Me}–B vector is not straight but bent (154.3°). The degree of bent of the Ni–C_{Me}–B vector computed for **2** is much pronounced than those for the Ti and Zr complexes (170–178°). Judging from the direction of the bending, this may be attributable to steric repulsion between the C_5H_5 ring and $B(C_6F_5)_3$ unit. Another marked difference between early and late transition metal analogs is their energetics: the calculated enthalpy gain on forming adduct **2** from **1** and $B(C_6F_5)_3$ is 9.4 kcal/mol, while the DFT computed values of 13–19 kcal/mol were reported [14] for $CpM(CH_3)_3$, $H_2SiCp(NH)M(CH_3)_2$, and $Cp_2M(CH_3)_2$ complexes (M = Ti, Zr), probably because the methide character of the CH_3 group is more enhanced in early transition metal complexes.

When adduct **2** and 5000 equiv. NB were mixed in toluene at room temperature, poly(NB) was obtained in 10% yield, i.e. **2** could initiate polymerization of 500 equiv. NB, in spite of its instability at room temperature.

3.3. Formation of $CpNi(C_6F_5)(PPh_3)$ on spontaneous decomposition of **2**

When a toluene solution of **2** was prepared at room temperature, the red color changed to yellow-brown in a short time. After 5 h, column chromatographic work-up of the solution yielded a known complex, $CpNi(C_6F_5)(PPh_3)$ (**4**), in 28% yield, which was confirmed by comparing with the authentic sample [8].

The spontaneous decomposition of a C_6D_6 solution of **2** carried out in a tube lead to rather simple ^1H NMR pattern. Beside the singlet peaks due to **3** (4.71 (C_5H_5) and 1.48 (CH_3-$B(C_6F_5)_4^-$) ppm) and **4** (5.13 ppm (C_5H_5)), a resonance assignable to CH_3-$B(C_6F_5)_2$ was observed at 1.34 ppm (supplementary material). Origin of a set of small peaks at 4.88 and 3.42 ppm is not known but tentatively assigned to C_5H_5 and CH_3 protons of an intermediate shown in Fig. 3(b) (*vide infra*). All other resonances observed were those for phenyl protons. It is thus obvious that a part of the spontaneous



Scheme 1. Proposed reaction pathways.

decomposition of **2** is the transfer of the C_6F_5 group from B to Ni (Eq. (2)).

$$\underset{\mathbf{2}}{CpNi(PPh_3)-(\mu\text{-}CH_3)B(C_6F_5)_3} \rightarrow \underset{\mathbf{4}}{CpNi(C_6F_5)(PPh_3)} + (CH_3)B(C_6F_5)_2 \quad (2)$$

In some reactions of methyl complexes of Ti and Zr, transfer of a C_6F_5 group from the co-catalyst $B(C_6F_5)_3$, *via* the initially formed contact ion-pair M-(μ-CH_3)$B(C_6F_5)_3$, has been observed and are considered to be a deactivation process of these catalyst systems for olefin polymerizations [15]. A similar migration of the C_6F_5 group from borane to late transition metals has been reported for Ni, i.e. from the reaction mixture of the dimeric complex $[Ni(Ph)(PPh_2CH{=}C(O)Ph)]_2$ with $B(C_6F_5)_3{\cdot}3H_2O$, $(C_6F_5)_2Ni(PPh_2CH{=}C(O)Ph)$ was isolated in a moderate yield [13b]. Unlike the cases of early transition metal complexes, intermediate in this reaction was proposed to be $(PPh_2CH_2$-$C(O)Ph)(Ph)Ni \leftarrow O(H)$-$B(C_6F_5)_3$. Therefore, the proton from the hydrated water plays an important role. The resulting complex with the Ni–C_6F_5 bond showed activity for the vinyl polymerization of NB [13a]. In contrast, the transfer of C_6F_5 group from $B(C_6F_5)_3$ to Ni found in the present study is remarkably parallel to the chemistry of early transition metals.

3.4. Identification of the polymer end-group by ^{19}F NMR

The formal exchange of the methyl group in **1** with a C_6F_5 group of borane to give **4**, as described in the preceding sections, suggests a possibility that the polymerization starts by the insertion of NB into a Ni–C_6F_5 bond. Therefore, the soluble polymer fraction described in Section 3.1 was subjected to ^{19}F NMR analysis in $CDCl_3$ (Fig. 4).

By comparing the spectrum with that of a similar NB vinyl polymer having the C_6F_5 end-group reported by Jang et al. [16], we can assign the resonances for *o*-F (−143 to −144 ppm), *m*-F (−156 to −162 ppm), and *p*-F (−163 to −165 ppm) of the C_6F_5 group, which were rather complex multiplets owing to the measurement using a concentrated and viscous solution of the polymer. Measurement of the same sample with the ^{11}B NMR did not give any signals, indicating that the resonances observed in the ^{19}F NMR do not arise from contaminated boron derivatives, but from polymer-bound C_6F_5 unit. A similar ^{19}F NMR (supplementary material) was observed for the polymer sample prepared in the presence of ethene (see Section 3.1).

3.5. Reactivity of $CpNi(C_6F_5)(PPh_3)$ toward NB

Although we knew already that methyl complex **1** itself is unable to initiate polymerization of NB, reactivity of C_6F_5 analog **4** was carefully examined since polymer chain appeared to have a C_6F_5 group at its end. However, inertness of **4** was confirmed by heating a catalytic amount of **4** with NB at 80 °C, which resulted in no polymer formation. In the presence of proton scavenger DTBP, the combination **4**/$B(C_6F_5)_3$ could not conduct polymerization of NB either. In contrast to the combination **1**/$B(C_6F_5)_3$, a mixture of **4** and $B(C_6F_5)_3$ (1:3) in C_6D_6 was quite stable and proton NMR did not show any change after 20 days at room temperature. All of these observations indicate that **4** is quite stable once formed, in spite of the suggestion from the polymer end study that a Ni-C_6F_5 species is involved in the initiation step of the polymerization.

4. Conclusions

When the Lewis acid $B(C_6F_5)_3$ is added to a solution of complex **1**, it firstly attacks CH_3 group of **1** to form adduct **2**. Isolation of the cationic complex **3** having the $[CH_3B(C_6F_5)_3]^-$ anion supports the structure proposed in Fig. 3(a) on the basis of DFT calculations. That complex **4** was isolated as a spontaneous decomposition product of **2** indicates the presence of a facile C_6F_5 transfer route from the borane to Ni center. In the presence of NB too, the C_6F_5 migration to Ni appears to take place since the resulting poly(NB) contains the C_6F_5 unit presumably at the chain end. Thus, it is reasonable to assume $[CpNi(C_6F_5)(NB)]$ (**5**) as the starting species of the polymerization. Because complex **4** is too stable to start the polymerization, substitution of NB for PPh_3 to give **5** must occur kinetically during the CH_3/C_6F_5 exchange process between Ni and B centers. As a plausible candidate for such intermediate species, the stationary state shown in Fig. 3(b), where the phosphine is weakly interacting with the $B(Me)(C_6F_5)_2$ moiety in the vicinity of Ni, was calculated to be only 2.1 kcal/mol above the energy of complex **2**. The proposed reaction pathways are summarized in Scheme 1.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.11.037.

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