Ethylene/Polar Norbornene Copolymerizations by Bimetallic Salicylaldimine−Nickel Catalysts

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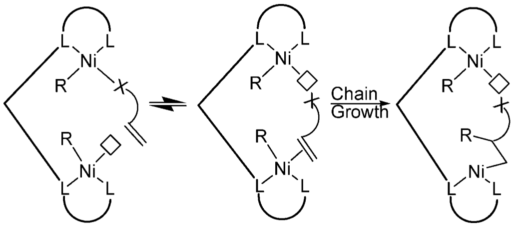
ABSTRACT: Bimetallic salicylaldimine−nickel complexes, bridge{[(2,6-iPr$_2$C$_6$H$_2$)-N=CH-(2-anthracenyl-C$_6$H$_3$-O)-κ^2-*N,O*]Ni(η^3-CH$_2$Ph)}$_2$ (bridge = *ortho*-C$_6$H$_4$, **10**; bridge = CH$_2$, **11**; bridge = *ortho*-C$_6$H$_4$(C$_6$H$_4$)$_2$, **12**), are prepared. The bimetallic complexes **10**−**12** show higher activities and higher polar monomer incorporations in the ethylene/2-(methoxycarbonyl)norbornene and ethylene/2-(acetoxymethyl)norbornene copolymerizations than the mononuclear complex, [(2,6-iPr$_2$C$_6$H$_3$)-N=CH-(2-anthracenyl-C$_6$H$_3$-O)-κ^2-*N,O*]-Ni(η^3-CH$_2$Ph) (**13**).

Introduction

The conventional Ziegler−Natta catalysts containing group 4 transition metals are not applicable for polymerization of polar monomers because of high oxophilicity of the early transition metals. Incorporation of polar monomers into nonpolar polyethylene backbone has been achieved only after protection of the polar functional groups.[1] Since late transition metals are less oxophilic than the early transition metals, the catalysts containing the late transition metals are more functional group tolerant and thus applicable to the polymerization of polar monomers.[2,3] Especially, neutral nickel complexes that do not require such an activator as methylaluminoxane (MAO) are attractive for the polymerization of polar monomers. Since Grubbs reported salicylaldimine-based neutral nickel complexes could serve as catalysts for ethylene/(functionalized norbornene) copolymerizations and ethylene homopolymerizations in the presence of polar impurities such as ether, ketone, esters, alcohol, or amine,[4,5] various neutral nickel catalysts have been prepared,[6] and some of them have been successfully applied for polymerization of the polar monomers.[7] Recently, ethylene polymerizations even in water phase have been achieved with the neutral nickel catalysts producing polyethylene latex.[8] However, addition of polar monomers or the presence of polar impurities leads to significant decrease of the activity, and the incorporations of the polar monomers are limited in some copolymerizations. Either the low activity or the low incorporation of the polar monomer is possibly attributed to the coordination of the polar group to the active metal center. Ziegler predicted that the O-bound species should be more favorable over the olefin-bound isomer in the case of vinyl acetate addition to the nickel catalyst and Grubbs proved it experimentally.[9] We envisioned that the shift from the polar group-bound species to the olefin-bound isomer, from which the chain growth occurs, can be efficiently triggered by using a bimetallic system, consequently leading to increase of either activity or the polar monomer incorporation (eq 1). Marks also reported bimetallic systems could incorporate significantly higher amount of styrene in the ethylene/styrene copolymerizations by cooperative action between the two metal centers.[10]



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Results and Discussion

Synthesis and Characterization. We recently reported the synthesis of diamino compound **1**, from which macrocyclic and acyclic dinuclear zinc complexes were successfully prepared for cyclohexene oxide/CO$_2$ copolymerizations.[11] The methylene-bridged compound **2** is prepared by the literature method,[12] and compound **3** is prepared by the similar method applied for the synthesis of **1** (eq 2). Schiff's base condensation between 3-anthracenylsalicylaldehyde and diamino compounds **1**−**3** affords bis(salicylaldimine) compounds **4**−**6** (Scheme 1). The bulky anthracenyl and isopropyl groups are attached in the ligand framework since it was reported that they are essential to acquire high activity and high molecular weight.[4,5] The characteristic feature of these ligand systems is that the N−N separations do not change by the conformational variations triggered by any allowed rotational movement around C−C bonds. That is, the bridging unit is rigid. The nickel−nickel separations in the prepared complexes can be modulated a little by the variation of the dihedral angle between the two chelating planes. The variation of the dihedral

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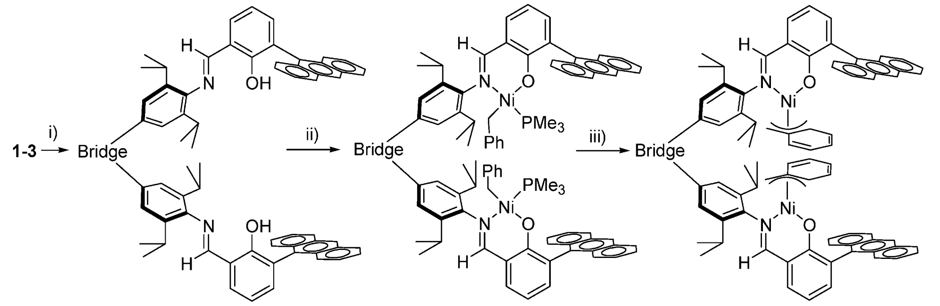
Scheme 1[a]



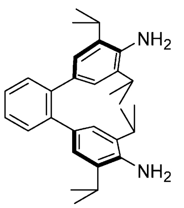
4: Bridge = *ortho*-C_6H_4
5: Bridge = CH_2
6: Bridge = *ortho*-$C_6H_4(C_6H_4)_2$

7: Bridge = *ortho*-C_6H_4
8: Bridge = CH_2
9: Bridge = *ortho*-$C_6H_4(C_6H_4)_2$

10: Bridge = *ortho*-C_6H_4
11: Bridge = CH_2
12: Bridge = *ortho*-$C_6H_4(C_6H_4)_2$

[a] Legend: (i) 3-anthracenylsalicylaldehyde, Dean−Stark; (ii) KH and then (η^3-$CH_2C_6H_5$)NiCl(PMe_3); (iii) $B(C_6F_5)_3$.

angle is triggered by the allowed rotation around the C−C bond(s) or C−N bond.[11b]



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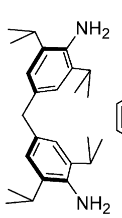

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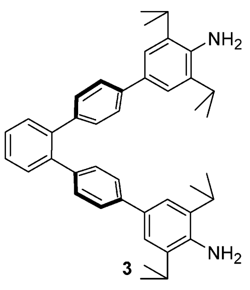

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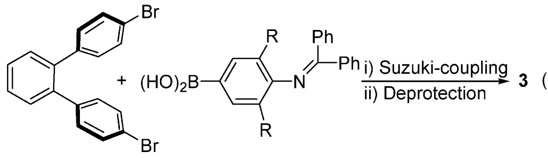


(2)

The η^1-benzyl-PMe_3−nickel(II) complexes **7**−**9** are prepared in 73−80% yields by reacting the potassium salt of **4**−**6** with (η^3-$CH_2C_6H_5$)NiCl(PMe_3) (Scheme 1).[13] The ^1H, ^{13}C, and ^{31}P NMR spectra are in agreement with the structures. The benzyl-CH_2 signal is observed at 0.84−0.90 ppm as a doublet by the coupling with phosphorus ($^3J_{PH}$ = 6.0−7.2 Hz) in the ^1H NMR spectra. The N=CH proton signal is also observed at 8.01−8.04 ppm as doublet by the coupling with phosphorus ($^4J_{PH}$ = 8.4 Hz). The number of signals in the ^{13}C NMR spectra is in agreement with the number of inequivalent carbons in the structure. Single signal is observed at 5.06−5.35 ppm in the ^{31}P NMR spectra.

$B(C_6F_5)_3$ has been effectively used for PMe_3-abstracting reagent to generate phosphine-free η^3-benzyl complexes which show fast initiation for olefin polymerizations.[14] Addition of equivalent amount of $B(C_6F_5)_3$ to the η^1-benzyl-PMe_3−nickel(II) complexes **7**−**9** affords a single clean complex. The ^1H and ^{13}C NMR spectra strongly support the formation of the PM_3-free η^3-benzyl complexes **10**−**12** (Scheme 1). In the ^1H NMR spectra, the PMe_3-methyl signal disappears completely, and the characteristic η^3-benzyl signals are observed upfield shifted at 6.03, (triplet, *meta*), 6.18 (doublet, *ortho*), and 6.27 ppm (triplet, *para*). Figure 1 shows the ^1H NMR spectrum of **11** and its assignment. The corresponding mononuclear complex [(2,6-$i$$Pr_2C_6H_3$)-N=CH-(2-anthracenyl-$C_6H_3$-O)-$\kappa^2$-$N$,$O$]Ni($\eta^3$-$CH_2Ph$) (**13**) is prepared by a similar method as a comparison catalyst for the polymerization studies. Grubbs reported preparation of the phosphine-free fast initiating system, (salicylaldimine)Ni(Me)($NCCH_3$), by reacting the neutral ligand with (tmeda)$NiMe_2$.[5] The advantage of the η^3-benzyl-(salicylaldimine)Ni complexes over the (salicylaldimine)-Ni(Me)($NCCH_3$) is that only a single isomer is formed for the η^3-benzyl complexes. For the (salicylaldimine)-Ni(Me)($NCCH_3$), two isomers were observed by the *cis*−*trans* isomerism. The presence of the *cis*−*trans* isomerism gives rise to three isomers in the case of the dinuclear complexes and a rather complex set of the ^1H NMR signals are observed when an equimolar amount of (tmeda)$NiMe_2$ is added to **4**−**6**.

Polymerization Studies. When the ethylene gas is added to complexes **10**−**12** in toluene under 100 psig pressure, temperature rises rapidly by exothermic reaction and viscous solution was obtained (Table 1). For complexes **10** and **12**, the temperature can be controlled in the range of 45−60 °C with an ice bath, and the obtained polymers show narrow molecular weight distributions (M_w/M_n, 3.0 and 3.5), indicating presence of a single active species (entries 1 and 4). However, the temperature cannot be controlled even with the ice bath and reaches up to 84 and 89 °C for methylene-bridged complex **11** and mononuclear complex **13**, respectively (entries 2 and 5). The polymers obtained from the uncontrolled batches show very broad molecular weight distributions (M_w/M_n, 16 and 15). Polymers of narrow molecular weight distributions are obtained by cutting the polymerization time to 5 min, at which time the temperature does not exceed 62 °C (entries 3 and 6). The activities of the dinuclear complexes (1900−3000 kg/(mol of Ni h)) are comparable to that of the mononuclear complex **13** (2400 kg/(mol of Ni h)). The DSC study of the polymers obtained by **10**, **12**, and **13** exhibits a sharp melting centered at 122, 117, and 120 °C, respectively, indicating the presence of some branches in the polyethylene backbone. Interestingly, the polymer obtained with CH_2-bridged dinuclear complex **11** exhibits two endothermic transitions: a broad one centered at ~94 °C and a sharp one centered at 114 °C (entry 3). Branch numbers calculated by the analysis of the ^1H NMR spectra of the polymers are in agreement with the DSC data. The higher the branches, the lower the melting temperature. The higher incorporation of branches observed for complexes **11** and **12** might be attributed to a cooperative action between the two metal centers. Marks has also reported that dinuclear CGC-type catalysts could generate some branches by feeding only ethylene gas by cooperative action of the two metal centers.[15] Molecular weights of the polymers obtained

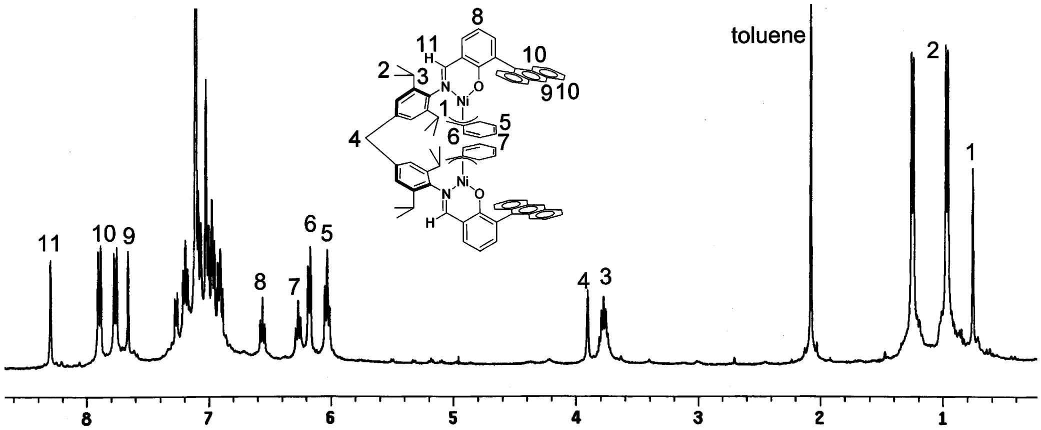


Figure 1. ^{1}H NMR spectrum of **11**.

Table 1. Ethylene Polymerization Results[a]

entry	catalyst	temp (°C)[b]	activity (kg/ (mol of Ni h))	T_m (°C)	M_w	M_w/M_n	branches[c]
1	**10**	45−59	1900	122	44 000	3.0	16
2	**11**	45−84	3000		28 000	16	
3[d]	**11**	45−62	2400	114 (94)	55 000	3.6	51
4	**12**	45−59	2100	117	50 000	3.5	45
5	**13**[e]	45−89	2300		37 000	15	
6[d]	**13**	45−62	2400	120	72 000	4.2	23

[a] Polymerization conditions: 30 mL of toluene, 5 μmol of Ni, 100 psig of ethylene, 10 min. [b] Initial temperature − final temperature. [c] Determined by the ^{1}H NMR and corresponds to the number of branches/1000 carbons. [d] 5 min of polymerization time. [e] Mononuclear complex, $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{-N=CH-(2-anthracenyl-C}_6\text{H}_3\text{-O)-}\kappa^2\text{-}N,O]\text{Ni}(\eta^3\text{-CH}_2\text{Ph})$.

Table 2. Ethylene/2-(Methoxycarbonyl)norbornene Copolymerization Results[a]

entry	catalyst	f_M[b]	F_M[c]	activity (kg/ (mol of Ni h))	M_w	M_w/M_n
1	**10**	0.11	0.12	110	31 000	3.6
2	**10**	0.20	0.17	80	52 000	4.5
3	**10**	0.27	0.20	61	30 000	3.7
4	**10**	0.33	0.27	59	17 000	2.7
5	**11**	0.11	0.12	100	48 000	3.7
6	**11**	0.20	0.18	72	28 000	3.8
7	**11**	0.27	0.22	60	18 000	4.2
8	**11**	0.33	0.29	58	15 000	3.2
9	**12**	0.11	0.14	110	39 000	3.6
10	**12**	0.20	0.20	69	52 000	5.1
11	**12**	0.27	0.26	61	35 000	4.1
12	**12**	0.33	0.42	58	18 000	2.9
13	**13**[d]	0.11	0.076	83	54 000	4.2
14	**13**	0.20	0.099	41	31 000	4.2
15	**13**	0.27	0.12	36	31 000	4.0
16	**13**	0.33	0.15	33	29 000	4.5

[a] Polymerization conditions: 30 mL of toluene solution of 2-(methoxycarbonyl)norbornene (0.075, 0.15, 0.22, and 0.30 M), 20 μmol of Ni, 100 psig of ethylene (0.60 M), 45 °C, 15 min. [b] 2-(Methoxycarbonyl)norbornene mole fraction in the monomer feeding. [c] 2-(Methoxycarbonyl)norbornene mole fraction in the copolymer determined by the ^{1}H NMR. [d] Mononuclear complex, $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{-N=CH-(2-anthracenyl-C}_6\text{H}_3\text{-O)-}\kappa^2\text{-}N,O]\text{Ni}(\eta^3\text{-CH}_2\text{Ph})$.

by the bimetallic complexes **10**−**12** are slightly lower than that observed for the polymer obtained by the mononuclear complex **13**.

Some dramatic effects of the dinuclearity are observed in the ethylene/functionalized norbornene copolymerizations (eq 3).[16] The dinuclear complexes **10**−**12** show ~2 times higher activities than the mononuclear complex **13** under the same conditions in ethylene/2-(methoxycarbonyl)norbornene copolymerizations (Table 2). As expected, the dinuclear complexes exhibit much higher incorporation of 2-(methoxycarbonyl)norbornene under the same monomer feed ratio (Table 2 and Figure 2).

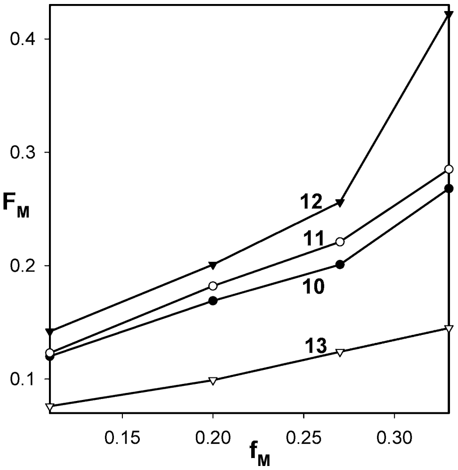
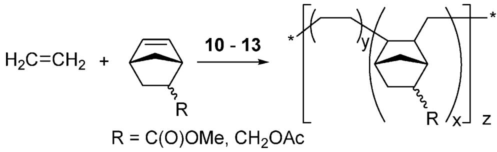


Figure 2. Relationship between the 2-(methoxycarbonyl)norbornene mole fraction in the monomer feeding (f_M) and that in the copolymers (F_M) prepared from **10**−**13**.

Among the three dinuclear complexes, *ortho*-C_6H_4-$(C_6H_4)_2$-bridged complex **12** exhibits the highest incorporation of the polar monomer (entries 9−12), and the mole fraction of 2-(methoxycarbonyl)norbornene in the copolymer is ~2 times higher than that observed for the copolymer obtained by the mononuclear complex **13** under the same monomer feed ratio (entries 13−16). Figure 2 shows the relationship between the 2-(methoxycarbonyl)norbornene mole fraction in the polymer (F_M) and that in the monomer feeding (f_M). Almost linear relationships between F_M and f_M are observed for all complexes, except the point at $f_M = 0.33$ of complex **12**. An attempt to evaluate the monomer reactivity ratio r_1 and r_2 by fitting the (f_A, F_A) data set to the Fineman−Ross plot is unsuccessful.[17] A straight line is not obtained at all in all cases.



(3)

Higher activities and higher incorporations of polar norbornene are also observed for ethylene/2-(acetoxymethyl)norbornene copolymerizations (Table 3). Incorporation of 2-(acetoxymethyl)norbornene is much more difficult than that of 2-(methoxycarbonyl)norbornene, and thus higher feeding of the 2-(acetoxymethyl)norbornene is required to obtain a copolymer having similar composition. The order of the polar norbornene incorporation ability observed for ethylene/2-(acetoxymethyl)-norbornene copolymerizations is the same with that observed for the ethylene/2-(methoxycarbonyl)norbornene copolymerizations: **12** > **11** > **10** > **13**. The effect of dinuclearity is more dramatic in the ethylene/2-(acetoxymethyl)norbornene copolymerizations, and complex **12** shows almost 3 times higher incorporations of the 2-(acetoxymethyl)norbornene than the mononuclear complex **13** under the same feed ratio. Figure 3 shows the relationship between the 2-(acetoxymethyl)norbornene mole fraction in the polymer (F_A) and that in the monomer feeding (f_A). In the cases of **10** and **11**, an almost perfect linear relationship (R values, 0.9972 and 0.9996 for **10** and **11**, respectively) is observed with the steeper slope for complex **11**. In the case of **12**, three points except the point at $f_A = 0.33$ exhibit a linear relationship. The (f_A, F_A) data set for each complex does not give straight lines in the Fineman−Ross plot. Narrow molecular weight distributions (M_w/M_n, 2.1−2.9) are observed, indicating a single active species, and the molecular weights are not sensitive to the bridge structure (M_w, 20 000−30 000).

Theoretical Calculations. Geometry optimizations on the active species derived from complexes **10**−**12** were performed with Hartree−Fock theory to see whether the bimetallic mechanism proposed in eq 1 is fit for the complexes. The complexes were simplified by removing the anthracenyl groups and replacing the η^3-benzyl ligands with methyls, and full geometry optimizations were conducted on the initial structures where the carbonyl oxygen of the *endo*-2-(acetoxymethyl)-nobornene monomer was placed near a nickel center while the other nickel center is kept vacant. The optimized structures are shown in Figure 4. In all the three structures, the two metals are situated opposite each other, and the double bond on the norbornyl unit is directed toward the vacant site on the other nickel center, consequently supporting the possibility for the bimetallic mechanism proposed in eq 1. The Ni−Ni separation increases in the order of **10** (6.241 Å) < **12** (7.352 Å) < **11** (9.404 Å). The separation between the norbornyl double bond and the nickel center increases in the same order: **10** (the C−Ni distances, 2.469 and 2.544 Å) < **12** (the C−Ni distances, 3.563 and 3.813 Å) < **11** (the C−Ni distances, 5.668 and 6.753 Å). Because the double bond is situated more proximal to the nickel center for the structure derived from **12** than for the structure derived from **11**, the binding mode change from the oxygen to the double bond proposed in eq 1 is better expected for **12**, possibly leading to higher incorporation of the polar monomer with **12**, which is in agreement with the experimental results. An efficient binding mode change and consequently much higher incorporation of the polar monomer can be expected for **10** because the separation between the nickel center and the double bond is the shortest for the structure derived from **10**, but the lowest incorporation of the polar monomer is observed with **10**. This discrepancy might be explained by too short Ni−Ni separations. In the structure of **10**, there is not enough space between the nickels, and there may be severe steric repulsion when the methyl attached on the nickel is replaced with the

Table 3. Ethylene/2-(Acetoxymethyl)norbornene Copolymerization Results[a]

entry	catalyst	f_A[b]	F_A[c]	activity (kg/ (mol of Ni h))	M_w	M_w/M_n
1	**10**	0.33	0.064	59	27 000	2.7
2	**10**	0.43	0.094	40	22 000	2.6
3	**10**	0.50	0.11	32	22 000	2.4
4	**10**	0.56	0.13	31	20 000	2.0
5	**11**	0.33	0.071	61	27 000	2.6
6	**11**	0.43	0.11	41	22 000	2.9
7	**11**	0.50	0.14	31	17 000	2.2
8	**11**	0.56	0.17	28	22 000	2.3
9	**12**	0.33	0.099	61	30 000	2.6
10	**12**	0.43	0.12	43	30 000	2.6
11	**12**	0.50	0.16	35	24 000	2.2
12	**12**	0.56	0.19	29	20 000	2.5
13	**13**[d]	0.33	0.029	24	22 000	2.3
14	**13**	0.43	0.040	16	20 000	2.4
15	**13**	0.50	0.052	15	18 000	2.7
16	**13**	0.56	0.070	14	22 000	2.1

[a] Polymerization conditions: 30 mL of toluene solution of 2-(acetoxymethyl)norbornene (0.30, 0.45, 0.60, and 0.75 M), 20 μmol of Ni, 100 psig of ethylene (0.60 M), 45 °C, 15 min. [b] 2-(Acetoxymethyl)norbornene mole fraction in the monomer feeding. [c] 2-(Acetoxymethyl)norbornene mole fraction in the copolymer determined by the ^{1}H NMR. [d] Mononuclear complex, [(2,6-iPr$_2$C$_6$H$_3$)-N=CH-(2-anthracenyl-C$_6$H$_3$-O)-κ^2-N,O]Ni(η^3-CH$_2$Ph).

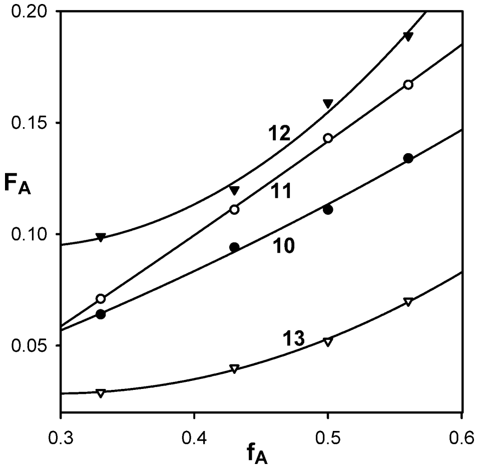


Figure 3. Relationship between the 2-(acetoxymethyl)-nobornene mole fractions in the monomer feeding (f_A) and that in the copolymers (F_A) prepared from **10**−**13**.

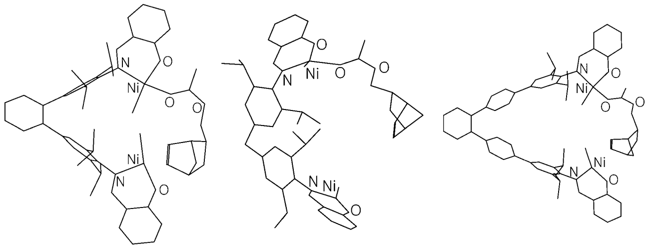


Figure 4. Calculated structures of *endo*-2-(acetoxymethyl)-nobornene coordinated active species derived from complexes **10**−**12**. Anthracenyl fragments are removed and the η^3-benzyl ligands are replaced with methyls for simplicity.

actual norbornyl group. In the structure derived from **10**, the separation between the two methyls is 4.637 Å, which implies that even the two methyls are situated almost in van der Waals contact.

Summary. Dinuclear salicylaldimine neutral–nickel(II) complexes **10**–**12** with various bridge units are prepared (Scheme 1). Some dinuclear effects are observed in the ethylene homopolymerization and ethylene/functionalized norbornene copolymerizations. In the ethylene polymerization, higher branches are observed with methylene-bridged complex **11**. In the ethylene/2-(methoxycarbonyl)norbornene and in the ethylene/2-(acetoxymethyl)norbornene copolymerizations, the dinuclear complexes **10**–**12** show higher activities and higher polar norbornene incorporations than the mononuclear complex **13**. The polar norbornene incorporation is also dependent on the bridge structure, and the C_6H_4-$(C_6H_4)_2$-bridged complex **12** shows the highest incorporation of the polar norbornenes in both copolymerizations. We assume that the higher incorporations of the polar norbornenes are attributed to the cooperative action between the two metal centers.

Experimental Section

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, THF, and C_6D_6 were distilled from benzophenone ketyl. Toluene used for polymerization reaction was purchased from Aldrich (anhydrous grade) and purified further over Na/K alloy. Ethylene was purchased from Conley Gas (99.9%) and purified by contacting with molecular sieves and copper for several days under the pressure of 200 psig. 2-(Acetoxymethyl)norbornene was prepared according to the literature method.[18] The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Varian Mercury plus 400. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at 140 °C in trichlorobenzene using a Waters model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis 3100.

Compound 3. The boronic acid (2.60 g, 6.75 mmol), Na_2CO_3 (1.95 g, 10.2 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.068 mmol), and 4,4′-dibromoterphenyl were added into a Schlenk flask inside a glovebox. The flask was brought out, and degassed DME (35 mL) and water (10 mL) were added. The flask was sealed with screw-cap and heated at 100 °C overnight. The solution was cooled to room temperature, and the organic phase was extracted with ethyl acetate. Solvent was removed by rotary evaporator to give a residue which was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (10:1). The obtained solid was dissolved in THF (22 mL), and aqueous HCl (2 N, 11 mL) was added. After the solution was stirred at 60 °C for 2 h, solvent was removed by a rotary evaporator. White solid was thoroughly washed with diethyl ether until benzophenone is not detected in the ethereal solution. To a flask containing the white solid, diethyl ether (30 mL) and aqueous KOH solution (1.0 N, 35 mL) were added. Ethereal phases were collected, and the water phase was extracted with additional diethyl ether (30 mL). The ethereal phase was combined and dried over anhydrous $MgSO_4$. Solvent was removed with rotary evaporator to give a white crystalline solid which was pure by the analysis of the ^{1}H and ^{13}C NMR spectra, and it was used for the next reaction without further purification. Yield was 1.04 g (59%); mp 245 °C. IR (KBr): 3491 and 3401 cm^{-1} (N–H). ^{1}H NMR ($CDCl_3$): δ 1.40 (d, J = 7.2 Hz, 12H, CH3), 3.05 (septet, J = 7.2 Hz, 2H, CH), 3.99 (br s, 2H, NH), 7.28–7.64 ppm (m, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.58 (CH_3), 28.12 (CH), 121.31, 125.79, 127.17, 129.94, 130.49, 130.59, 132.59, 139.04, 139.39, 139.74, 140.02 ppm. Anal. Calcd ($C_{42}H_{48}N_2$): C, 86.85; H, 8.33; N, 4.82%. Found: C, 86.79; H, 8.31; N 4.78, %.

Compound 4. Compound **1** (0.20 g, 0.47 mmol), 3-anthracenylsalicylaldehyde (0.35 g, 1.17 mmol), and *p*-toluenesulfonic acid (0.005 g, 0.0234 mmol) were added into a flask (50 mL), and benzene (8 mL) was added. The flask was connected to a Dean–Stark apparatus, and the solution was refluxed overnight. After the solution was cooled to room temperature, solvent was removed by rotary evaporator to give a residue which was triturated in hexane for 5 h. Yield was 0.422 g (91%); mp 228 °C. IR (KBr): 3413 (OH) and 1630 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ 1.04 (d, J = 7.2 Hz, 12H, CH_3), 2.98 (septet, J = 7.2 Hz, 2H, CH), 6.98 (s, 2H, *i*Pr_2C_6-H), 7.21 (t, J = 7.2 Hz, 1H, phenol-*p*H), 7.36–7.64 (m, 8H), 7.80 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.11 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.40 (s, 1H, anthracenyl-H10 or N=CH), 8.59 ppm (s, 1H, anthracenyl-H^{10} or N=CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.76 (CH_3), 27.90 (CH), 118.69, 118.78, 124.94, 125.03, 125.41, 126.36, 126.66, 126.98, 127.20, 128.45, 129.83, 130.15, 131.31, 132.04, 132.22, 136.43, 138.19, 138.37, 140.98, 144.23, 159.15, 166.47 ppm. Anal. Calcd ($C_{72}H_{64}N_2O_2$): C, 87.41; H, 6.52; N, 2.83. Found: C, 87.25; H, 6.83; N, 3.11%.

Compound 5. The compound was synthesized according to same conditions and procedure as for **4** using **2**. Yield was 57%; mp 209 °C. IR (KBr): 3401 (OH) and 1631 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ 1.18 (d, J = 7.2 Hz, 12H, CH_3), 3.05 (septet, J = 7.2 Hz, 2H, CH), 4.02 (s, 1H, CH_2), 7.03 (s, 2H, *i*Pr_2C_6-H), 7.21 (t, J = 7.2 Hz, 1H, phenol-*p*H), 7.38–7.56 (m, 7H), 7.61 (d, J = 7.2 Hz, 1H, phenol-*m*H), 7.79 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.09 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.49 (s, 1H, anthracenyl-H10 or N=CH), 8.56 ppm (s, 1H, antracenyl-H10 or N=CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.82 (CH_3), 28.14 (CH), 29.81 (CH_2), 118.72, 118.78, 123.65, 124.94, 125.41, 126.39, 126.70, 127.01, 128.46, 130.17, 131.34, 132.00, 132.11, 136.50, 137.71, 138.73, 143.81, 159.26, 166.51 ppm. Anal. Calcd ($C_{79}H_{70}N_2O_2$): C, 87.90; H, 6.54; N, 2.60. Found: C, 88.23; H, 6.66; N, 2.59%.

Compound 6. The compound was synthesized according to the same conditions and procedure as for **4** using **3**. Yield was 92%; mp 222 °C. IR (KBr): 3394 (OH) and 1634 cm^{-1} (C=N). ^{1}H NMR ($CDCl_3$): δ 1.23 (d, J = 6.8 Hz, 12H, CH_3), 3.08 (septet, J = 6.8 Hz, 2H, CH), 7.23 (t, J = 7.6 Hz, 1H, phenol-*p*H), 7.27 (s, 2H, *i*Pr_2C_6–H), 7.29 (d, J = 8 Hz, 2H, C_6H_4–H), 7.34–7.60 (m, 9H), 7.64 (d, J = 7.2 Hz, 1H, phenol-*m*H), 7.77 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.09 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.50 (s, 1H, anthracenyl-H^{10} or N=CH), 8.56 ppm (s, 1H, anthracenyl-H^{10} or N=CH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.84 (CH_3), 28.31 (CH), 118.72, 118.84, 121.88, 124.95, 125.42, 126.36, 126.76, 127.02, 127.45, 128.47, 130.15, 130.57, 131.32, 131.99, 132.20, 136.57, 137.50, 139.16, 139.91, 140.05, 145.34, 159.24, 166.55 ppm. Anal. Calcd ($C_{84}H_{72}N_2O_2$): C, 88.38; H, 6.36; N, 2.45. Found: C, 88.25; H, 6.52; N, 2.54%.

Compound 7. To a flask containing compound **4** (0.200 g, 0.202 mmol) in THF (2 mL) was added KH (0.17 g, 0.44 mmol), and the solution was stirred overnight. The solution was filtered, and solvent was removed under vacuum to give a yellow residue. To a flask containing the residue was added a solution of (η^3-$CH_2C_6H_5$)NiCl(PMe_3) (0.218 g, 0.202 mmol) in toluene (4 mL). After the resulting solution was stirred for 1.5 h at room temperature, it was filtered over Celite, and solvent was removed under vacuum to yield a light brown powder. In case that THF signals were observed in the NMR spectra, the complex was dissolved in a minimum amount of toluene and then evacuated once again to remove the residual THF. THF should be completely removed for the next reaction. Yield was 0.244 g (76%). ^{1}H NMR (C_6D_6): δ −0.20 (d, $^2J_{PH}$ = 10 Hz, 9H, PMe_3), 0.90 (d, $^3J_{PH}$ = 7.2 Hz, 2H, benzyl-CH_2), 1.07 (d, J = 6.8 Hz, 6H, CH_3), 1.23 (d, J = 6.8 Hz, 6H, CH_3), 4.29 (septet, J = 6.8 Hz, 2H, CH), 6.77 (t, J = 7.6 Hz, 1H, phenol-*p*H), 6.97 (t, J = 7.2 Hz, 1H, benzyl-*p*H), 7.04 (t, J = 7.2 Hz, 2H, benzyl-*m*H), 7.07 (s, 2H, *i*Pr_2C_6–H), 7.09–7.26 (m, 5H), 7.27 (dd, J = 7.6, 2.0 Hz, 1H, phenol-*m*H), 7.33 (AA′BB′, C_6H_4–H), 7.38 (dd, J = 6.8, 1.6 Hz, 1H, phenol-*m*H), 7.80 (d, J = 7.6 Hz, 2H, benzyl-*o*H), 7.84 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.03 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.14 (d, $^4J_{PH}$ = 8.4 Hz, 1H, N=CH), 8.20 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR

(C$_6$D$_6$): δ 8.59 (d, $^2J_{PC}$ = 33.4 Hz, benzyl-CH$_2$), 11.08 (d, $^1J_{PC}$ = 25.8 Hz, PMe$_3$), 23.89 (CH$_3$), 25.62 (CH$_3$), 28.90 (CH), 114.21, 120.37, 123.42, 125.22, 125.28, 125.54, 125.86, 127.49, 127.64, 128.17, 128.54, 129.61, 130.91, 131.26, 131.85, 131.99, 134.52, 136.81, 137.05, 140.20, 141.27, 141.48, 147.93, 150.29, 165.52 ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 5.35 ppm. Anal. Calcd (C$_{92}$H$_{94}$N$_2$Ni$_2$O$_2$P$_2$): C, 76.78; H, 6.58; N, 1.95. Found: C, 76.92; H, 6.85; N, 2.25%.

Compound 8. The compound was synthesized according to the same conditions and procedure as for **7** using **5**. Yield was 80%. ^{1}H NMR (C$_6$D$_6$): δ −0.22 (d, $^2J_{PH}$ = 10.4 Hz, 9H, PMe$_3$), 0.89 (d, $^3J_{PH}$ = 6.0 Hz, 2H, benzyl-CH$_2$), 1.13 (d, J = 6.8 Hz, ^{6}H, CH$_3$), 1.27 (d, J = 6.8 Hz, 6H, CH$_3$), 3.82 (s, 1H, CH$_2$), 4.24 (septet, J = 6.8 Hz, 2H, CH), 6.69 (t, J = 6.8 Hz, 1H, phenol-*p*H), 6.93 (t, J = 7.2 Hz, 1H, benzyl-*p*H), 7.01 (s, 2H, *i*Pr$_2$C$_6$−H), 7.96−7.28 (m, 7H), 7.33 (dd, J = 6.8, 1H, phenol-*m*H), 7.77 (d, J = 7.2 Hz, 2H, benzyl-*o*H), 7.82 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.01 (d, J = 8.4 Hz, 3H, N═CH and anthracenyl-H), 8.19 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 8.58 (d, $^2J_{PC}$ = 33.4 Hz, benzyl-CH$_2$), 11.05 (d, $^1J_{PC}$ = 25.8 Hz, PMe$_3$), 22.91 (CH$_3$), 23.82 (CH$_3$), 25.42 (CH), 28.94 (CH$_2$), 113.98, 120.30, 123.33, 124.19, 125.17, 125.25, 125.65, 125.81, 127.51, 128.51, 129.27, 129.67, 131.24, 131.68, 131.97, 134.43, 136.64, 137.11, 139.14, 141.69, 147.48, 150.47, 165.42 ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 5.06 ppm. Anal. Calcd (C$_{87}$H$_{92}$N$_2$Ni$_2$O$_2$P$_2$): C, 75.88; H, 6.73; N, 2.03. Found: C, 76.21; H, 6.95; N, 2.10%.

Compound 9. The compound was synthesized according to the same conditions and procedure as for **7** using **6**. Yield was 73%. ^{1}H NMR (C$_6$D$_6$): δ −0.27 (d, $^2J_{PH}$ = 9.6 Hz, 9H, PMe$_3$), 0.84 (d, $^3J_{PH}$ = 6.0 Hz, 2H, benzyl-CH$_2$), 1.07 (d, J = 6.8 Hz, 6H, CH$_3$), 1.18 (d, J = 6.8 Hz, 6H, CH$_3$), 4.25 (septet, J = 6.8 Hz, 2H, CH), 6.68 (t, J = 7.2 Hz, 1H, phenol-*p*H), 6.88 (t, J = 6.8 Hz, 1H, benzyl-*p*H), 6.95 (t, J = 6.8 Hz, 2H, benzyl-*m*H), 7.01−7.47 (m, 8H), 7.11 (s, 2H, *i*Pr$_2$C$_6$−H), 7.70 (d, J = 6.8 Hz, 2H, benzyl-*o*H), 7.78 (d, J = 8.4 Hz, 2H, anthracenyl-H), 7.97 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.04 (d, $^4J_{PH}$ = 8.4 Hz, 1H, N═CH), 8.15 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 8.34 (d, $^2J_{PC}$ = 33.3 Hz, benzyl-CH$_2$), 10.90 (d, $^1J_{PC}$ = 26.6 Hz, PMe$_3$), 23.50 (CH$_3$), 25.20 (CH$_3$), 28.93 (CH), 113.94, 120.12, 122.45, 123.23, 125.05, 125.11, 125.50, 125.69, 127.11, 127.42, 127.98, 128.36, 129.12, 129.51, 130.54, 131.10, 131.64, 131.82, 134.28, 136.63, 136.88, 137.65, 138.86, 139.99, 140.47, 140.72, 141.97, 145.75, 150.19 (J = 4.5 Hz), 165.28 (J = 12.9 Hz) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 5.32 ppm. Anal. Calcd (C$_{104}$H$_{102}$N$_2$Ni$_2$O$_2$P$_2$): C, 78.50; H, 6.46; N, 1.76. Found: C, 78.35; H, 6.65; N, 1.90%.

Compound 10. To a flask containing compound **7** (0.132 g, 0.096 mmol) and B(C$_6$F$_5$)$_3$ (0.103 g, 0.201 mmol) was added toluene (2 mL) at room temperature. The solution was stirred for 1.5 h. The white precipitates of B(C$_6$F$_5$)$_3$·PMe$_3$ were removed by filtration. Solvent was removed to give red powder which was pure by the analysis of the ^{1}H and ^{13}C NMR spectra. Yield was 0.097 g (77%). ^{1}H NMR (C$_6$D$_6$): δ 0.78 (s, 2H, benzyl-CH$_2$), 0.89 (d, J = 6.8 Hz, 6H, CH$_3$), 1.19 (d, J = 6.8 Hz, 6H, CH$_3$), 3.76 (septet, J = 6.8 Hz, 2H, CH), 6.03 (t, J = 7.6 Hz, 2H, benzyl-*m*H), 6.18 (d, J = 7.6 Hz, 2H, benzyl-*o*H), 6.27 (t, J = 8.4 Hz, 1H, benzyl-*p*H), 6.62 (t, J = 7.6 Hz, 1H, phenol-*p*H), 7.00 (s, 2H, *i*Pr$_2$C$_6$−H), 6.84−7.26 (m, 6H), 7.30 (d, J = 6.0 Hz, 1H, phenol-*m*H), 7.42 (AA′BB′, C6H4−H), 7.77 (d, J = 8.4 Hz, 2H, anthracenyl-H), 7.85 (s, 1H, N═CH), 7.90 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.31 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 23.33 (CH$_3$), 25.78 (CH$_3$), 28.23 (CH), 28.45 (benzyl −CH$_2$), 106.77, 114.43, 116.14, 119.39, 124.94, 125.20, 125.32, 125.65, 126.00, 126.89, 128.51, 129.27, 130.89, 131.25, 131.76, 131.98, 133.70, 134.53, 136.38, 137.08, 139.66, 140.00, 141.36, 150.80, 164.63, 165.25 ppm.

Compound 11. The compound was synthesized according to the same conditions and procedure as for **10** using **8**. Yield was 73%. ^{1}H NMR (C$_6$D$_6$): δ 0.76 (s, 2H, benzyl-CH$_2$), 0.97 (d, J = 6.8 Hz, 6H, CH$_3$), 1.25 (d, J = 6.8 Hz, 6H, CH$_3$), 3.78 (septet, J = 6.8 Hz, 2H, CH), 3.91 (s, 1H, CH$_2$), 6.02 (t, J = 7.6 Hz, 2H, benzyl-*m*H), 6.18 (d, J = 7.6 Hz, 2H, benzyl-*o*H), 6.26 (t, J = 7.6 Hz, 1H, benzyl-*p*H), 6.56 (t, J = 6.8 Hz, 1H, phenol-*p*H), 7.02 (s, 2H, ^{i}Pr$_2$C$_6$-H), 6.86−7.24 (m, 5H), 7.26 (dd, J = 7.2, 1.2 Hz, 1H, phenol-*m*H), 7.67 (s, 1H, N═CH), 7.76 (d, J = 8.4 Hz, 2H, anthracenyl-H), 7.90 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.31 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 23.34 (CH$_3$), 25.46 (CH$_3$), 27.87 (CH), 28.55 (benzyl-CH$_2$), 42.09(CH$_2$), 106.73, 114.20, 116.15, 119.41, 124.02, 124.90, 125.17, 125.65, 125.93, 125.82, 128.44, 131.23, 131.73, 131.97, 133.80, 134.47, 136.48, 136.94, 138.95, 139.95, 150.77, 164.77, 165.12 ppm.

Compound 12. The compound was synthesized according to the same conditions and procedure as for **10** using **9**. Yield was 74%. ^{1}H NMR (C$_6$D$_6$): δ 0.70 (s, 2H, benzyl-CH$_2$), 0.95 (d, J = 6.8 Hz, 6H, CH$_3$), 1.20 (d, J = 6.8 Hz, 6H, CH$_3$), 3.79 (septet, J = 6.8 Hz, 2H, CH), 6.03 (t, J = 7.6 Hz, 2H, benzyl-*m*H), 6.18 (d, J = 6.8 Hz, 2H, benzyl-*o*H), 6.28 (t, J = 7.2 Hz, 1H, benzyl-*p*H), 6.59 (t, J = 7.2 Hz, 1H, phenol-*p*H), 6.92 (t, J = 6.4 Hz 2H, anthracenyl-H), 7.18−7.40 (m, 10H), 7.46 (t, J = 6.4, 2H, anthracenyl-H), 7.74 (d, J = 4.8 Hz, 2H, anthracenyl-H), 7.76 (s, 1H, N═CH), 7.90 (d, J = 8.4 Hz, 2H, anthracenyl-H), 8.31 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 23.02 (CH$_3$), 25.20 (CH$_3$), 27.92 (CH), 28.50 (benzyl −CH$_2$), 106.60, 114.09, 115.97, 119.22, 122.26, 124.73, 125.02, 125.79, 126.70, 127.06, 127.60, 128.84, 130.66, 130.87, 131.08, 131.58, 131.68, 131.83, 133.62, 134.31, 136.29, 136.85, 138.54, 139.89, 140.14, 140.39, 140.87, 151.64, 164.46, 165.07 ppm.

Compound 13. The η^1-benzyl PMe$_3$ nickel(II) complex was synthesized according to the same conditions and procedure as for **7** using 2-anthracen-9-yl-6-[(2,6-diisopropylphenyl)-iminomethyl]phenol. Yield was 96%. Data for the η^1-benzyl PMe$_3$ nickel(II) complex: ^{1}H NMR (C$_6$D$_6$): δ −0.28 (d, $^2J_{PH}$ = 10.0 Hz, 9H, PMe$_3$), 0.80 (d, $^3J_{PH}$ = 6.0 Hz, 2H, benzyl-CH$_2$), 1.10 (d, J = 7.2 Hz, 6H, CH$_3$), 1.22 (d, J = 7.2 Hz, 6H, CH$_3$), 4.23 (septet, J = 7.2 Hz, 2H, CH), 6.66 (t, J = 7.2 Hz, 1H, phenol-*p*H), 6.88 (t, J = 7.6 Hz, 1H, benzyl-*p*H), 6.94 (t, J = 7.6 Hz, 2H, benzyl-*m*H) 6.98−7.24 (m, 8H), 7.29 (dd, J = 6.8, 1.6 Hz, 1H, phenol-*m*H), 7.70 (d, J = 7.2 Hz, 2H, benzyl-*o*H), 7.78 (d, J = 8.0 Hz, 2H, anthracenyl-H), 7.97 (d, J = 8.0 Hz, 2H, anthracenyl-H), 8.03 (d, $^4J_{PH}$ = 8.4 Hz, 1H, N═CH), 8.15 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 8.30 (d, $^2J_{PC}$ = 33.3 Hz, benzyl-CH$_2$), 11.07 (d, $^1J_{PC}$ = 25.8 Hz, PMe$_3$), 23.71, 25.40, 28.90, 114.02, 120.24, 123.05, 123.36, 123.69, 125.18, 125.24, 125.81, 126.63, 127.54, 128.12, 128.41, 129.62, 131.25, 131.72, 131.97, 134.42, 136.71, 137.08, 141.61, 149.42, 150.40 (d, J = 4.6 Hz), 165.39 ppm (d, J = 15.2 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 5.15 ppm. Anal. Calcd (C$_{43}$H$_{46}$NOPNi): C, 75.67; H, 6.79; N, 2.05%. Found: C, 75.95; H, 6.82; N, 2.42%. The PMe$_3$-free η^3-benzyl−nickel(II) complex **13** was synthesized according to the same conditions and procedure as for **10** from the η^1-benzyl-PMe$_3$−nickel(II) complex. Data for **13**: ^{1}H NMR (C$_6$D$_6$): δ 0.74 (s, 2H, benzyl-CH$_2$), 0.99 (d, J = 6.8 Hz, 6H, CH$_3$), 1.25 (d, J = 6.8 Hz, 6H, CH$_3$), 3.81 (septet, J = 7.2 Hz, 2H, CH), 6.09 (t, J = 7.6 Hz, 2H, benzyl-*m*H), 6.20 (d, J = 7.6 Hz, 2H, benzyl-*o*H), 6.32 (t, J = 7.6 Hz, 1H, benzyl-*p*H), 6.62 (t, J = 6.8 Hz, 1H, phenol-*p*H), 6.96 (t, J = 6.8 Hz, 2H, anthracenyl-H), 7.00−7.08 (m, 3H, *i*Pr$_2$C$_6$−H), 7.10 (dd, J = 7.2, 1.2 Hz, 1H, phenol-*m*H), 7.25 (t, J = 6.8 Hz, 2H, anthracenyl-H), 7.33 (dd, J = 7.2, 1.2 Hz, 1H, phenol-*m*H), 7.74 (s, 1H, N═CH), 7.83 (d, J = 8.8 Hz, 2H, anthracenyl-H), 7.95 (d, J = 8.8 Hz, 2H, anthracenyl-H), 8.35 ppm (s, 1H, anthracenyl-H^{10}). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 23.23, 25.41, 28.49, 106.67, 114.12, 116.12, 119.33, 123.58, 124.84, 125.15, 125.89, 126.34, 126.82, 128.52, 131.27, 131.80, 132.00, 133.79, 134.26, 134.46, 136.59, 136.89, 139.77, 152.41, 164.54, 165.19 ppm.

Polymerization. To a 60 mL glass reactor containing a stirring bar was added toluene or toluene solution of the functionalized norbornene (30 mL). The reactor was assembled and brought out of the glovebox. The reactor was immersed in an oil bath, the temperature of which had been set to 45 °C. The solution was stirred until the temperature reached that of the oil bath. The nickel complex dissolved in toluene (2 mL) was injected to the reactor via a syringe, and ethylene was fed continuously for a given time under the pressure of 100 psig. The temperature of the solution was monitored. In the ethylene polymerization, the oil bath was replaced with an ice bath right after the ethylene charge. After release of ethylene pressure, acetone (60 mL) was added to the reactor to obtain white precipitates, which were collected by filtration and dried under vacuum. In the case of ethylene/functionalized norbornene copolymerizations, solvent was removed under vacuum and methanol (20 mL) and a few drops of HCl were added. The solution was stirred for 30 min to obtain white precipitates, which were filtered and washed with methanol (50 mL). The mole fractions in the ethylene/functionalized norbornene copolymers were calculated by the analysis of the ^{1}H NMR spectra. Branch numbers of the polyethylenes were calculated from the integration value of methyl, methylene, and methine proton regions in the ^{1}H NMR spectra. The NMR spectra of the polyethylene were obtained at 100 °C in benzene-d_6 and 1,2,4-trichlorobenzene (v/v, 4:1). The NMR spectra of the ethylene/functionalized norbornene copolymers were obtained at 70 °C in benzene-d_6. Ethylene concentration in toluene at 45 °C (0.60 M) was measured with mass flow controller.

Theoretical Calculations. Geometry optimizations were performed with Hartree−Fock theory in combination with the 3-21G basis set. The GAMESS (general atomic and molecular electronic structure system) program was used for the computations.[19]

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References and Notes

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