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[2-(Alkylideneamino)benzoato]nickel(II) Complexes: Active Catalysts for Ethylene Polymerization

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The complexes $[RR'C{=}NC_6H_4C(O)O\text{-}\kappa^2N,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (R, R′ = −$(CH_2)_5$−, **6**; R = Et, R′ = Et, **7**; R = *t*Bu, R′ = H, **8**) are prepared by reaction of the corresponding potassium salts with $[(\eta^3\text{-}CH_2CMeCH_2)NiCl]_2$ in CH_3CN. Additions of 1 equiv of $B(C_6F_5)_3$ afford the zwitterionic complexes $[RR'C{=}NC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2N,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (R, R′ = −$(CH_2)_5$−, **9**; R = Et, R′ = Et, **10**; R = *t*Bu, R′ = H, **11**), which give poly(ethylene) when ethylene gas is added. This result is interesting in that the corresponding 2-(diphenylphosphino)benzoato and 2-(diphenylamino)benzoato complexes give mainly butene. Reactions of the potassium salts with $Ni(\eta^3\text{-}CH_2C_6H_5)Cl(PMe_3)$ afford benzyl complexes, $[RR'C{=}NC_6H_4C(O)O\text{-}\kappa^2N,O]Ni(\eta^1\text{-}CH_2C_6H_5)(PMe_3)$ (R, R′ = −$(CH_2)_5$−, **12**; R = Et, R′ = Et, **13**). Additions of 2 equiv of $B(C_6F_5)_3$ to **12** and **13** afford the zwitterionic η^3-benzyl complexes $[RR'C{=}NC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2N,O]Ni(\eta^3\text{-}CH_2C_6H_5)$ (R, R′ = −$(CH_2)_5$−, **14**; R = Et, R′ = Et, **15**). Complex **14** is rather unstable, and a bis ligand complex, $[(CH_2)_5C{=}NC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2N,O]_2Ni$ (**16**), is formed during recrystallization. Complexes **14** and **15** are highly active to ethylene polymerization, and activities reach 3000−4000 kg/((mol of Ni) h) at 75 psig pressure. Solid structures of **6**, **9**, **11**, **15**, and **16** were determined by X-ray crystallography.

Introduction

There has been a great deal of effort to develop late-transition-metal catalysts for polymerization or oligomerization of olefins in both academic and industrial fields.[1−4] Neutral nickel complexes with chelating κ^2P,O ligands are of industrial importance in the Shell Higher Olefin Process (SHOP) for ethylene oligomerization.[5] Notable in the recent progress are α-diimine Ni(II) and Pd(II) complexes,[6] diiminopyridine Fe(II) and Co(II) complexes,[7] and neutral salicylaldiminato Ni(II) complexes.[8] In those complexes, the molecular weight of the polymer can be modulated by the size of the substituents on pseudoaxial sites. Recently, Bazan, Lee, et al. have developed novel activation reaction of transition metal complexes containing carboxylate,[9−12] carboxamidate,[13,14]

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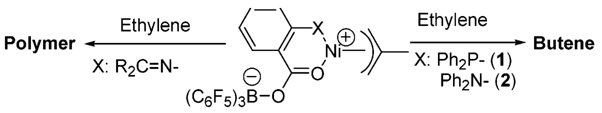
or enamide ligands.[15,16] Additions of $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ to the complexes afford zwitterionic complexes which are active for dimerization, oligomerization, and polymerization of ethylene. In those zwitterionic complexes, the molecular weight depends on the bulkiness on the pseudoaxial sites. In the cases of the carboxylato complexes $[(C_6H_5)_2PC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2 P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (**1**)[9] and $[(C_6H_5)_2NC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2 N,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (**2**),[11] in which steric bulkiness on the axial sites is not so great, the main product is butene by a rapid chain transfer reaction (eq 1). In the cases of the sterically more congested (pyridinecarboxamidato)nickel(II) complexes[14] and $[(H_3C)C({=}NC_6H_5)C\{OB(C_6F_5)_3\}({=}NC_6H_5)]Ni(\eta^3\text{-}CH_2C_6H_5)$,[12,13] oligomerization of ethylene was observed. A high molecular weight of poly(ethylene) was obtained only with complexes bearing the sterically bulky 2,6-diisopropylphenyl group, $[(H_3C)C\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}C\{OB(C_6F_5)_3\}\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}]Ni(\eta^3\text{-}CH_2C_6H_5)$[13] and $[(H_3C)C\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}C\{CH_2X(C_6F_5)_3\}\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}]Ni(\eta^3\text{-}CH_2C_6H_5)$ (X = B, Al).[15] Herein, we report an example showing that the electronic effect of the ligand also plays an important role in reducing the chain transfer reaction. When the diphenylphosphino or diphenylamino group in the dimerization catalyst **1** or **2** is simply replaced with an alkylideneamino group (imine functionality), the chain transfer reaction is reduced dramatically and polymerization is observed instead of dimerization (eq 1). Keim et al. also reported some examples showing ligand-induced changes from oligomerization catalyst to polymerization catalyst.[17] The (pyridinecarboxylato)nickel complex $(2\text{-}CO_2\text{-}C_5H_4N\text{-}\kappa^2 N,O)Ni(PPh_3)(\textit{o}\text{-tolyl})$ gave mainly liquid α-olefins, but a complex containing an electron-withdrawing nitro group in the ligand frame, $(2\text{-}CO_2\text{-}4\text{-}NO_2\text{-}C_5H_4N\text{-}\kappa^2 N,O)Ni(PPh_3)(\textit{o}\text{-tolyl})$, gave mainly high-density, high-molecular-weight polyethylene.

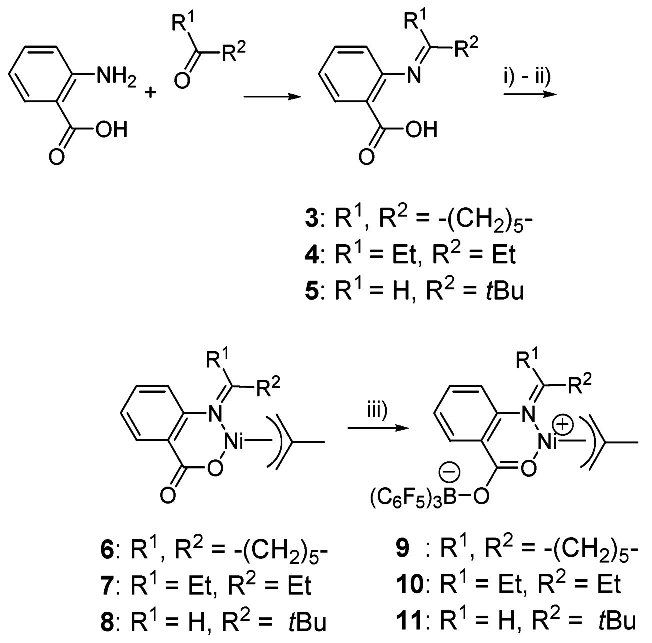


(1)

Results and Discussion

Synthesis and Characterization. Ligands **3**−**5** are simply synthesized by a conventional Schiff base condensation reaction (Scheme 1). Reactions of the acids with bis(methallyl)nickel(II), by which **1** and **2** were prepared, do not easily provide the desired methallylnickel complexes. The reaction is sluggish, which might be attributed to the lower acidity of the carboxylic acid due to a stronger hydrogen bond to the more basic nitrogen atom on the imine functionality. However, deprotonation of the acid with 1.0 equiv of KH and then addition, in CH_3CN, of $[(\eta^3\text{-}CH_2CMeCH_2)NiCl]_2$, which is prepared by the reaction of methallyl chloride with $Ni(COD)_2$,[18] afford the desired complexes **6**−**8** in nearly quantitative yield (Scheme 1). Acetonitrile solvent is crucial for the success of syntheses. In less polar solvents such as THF and benzene, the reaction is not clean. Signals for methylene protons on the methallyl ligand are broad at 2.70, 2.52, 2.41, and 2.23 ppm for **6** in the ^1H NMR spectrum (C_6D_6). The methyl proton signal on the methallyl ligand is observed at 1.87 ppm as a singlet. Similar ^1H NMR spectra are observed for **7** and **8**. Proton signals are rather broad in the ^1H NMR spectra, and methallyl $\textit{C}H_2$ signals in the ^{13}C NMR spectra, which are usually observed at 45−90 ppm for similar methallylnickel complexes, are not observed at all, presumably due to broadening of the signals by some fluxional motions. Metalations to more bulky ligands, $Ph_2C{=}NC_6H_4CO_2H$[19] and $(C_6H_{11})HC{=}NC_6H_4CO_2H$, were not successful.

Scheme 1[a]



3: R^1, R^2 = -$(CH_2)_5$-
4: R^1 = Et, R^2 = Et
5: R^1 = H, R^2 = *t*Bu

6: R^1, R^2 = -$(CH_2)_5$-
7: R^1 = Et, R^2 = Et
8: R^1 = H, R^2 = *t*Bu

9 : R^1, R^2 = -$(CH_2)_5$-
10: R^1 = Et, R^2 = Et
11: R^1 = H, R^2 = *t*Bu

[a] Legend: (i) KH; (ii) $[Ni(\eta^3\text{-}CH_2CMeCH_2)Cl]_2$; (iii) $B(C_6F_5)_3$.

Single crystals of **6** suitable for X-ray crystallography were grown from a toluene solution at −30 °C, and the results of the X-ray crystallographic studies are shown in Figure 1. A square-planar coordination geometry is observed. The two axial sites are not equivalent to each other. The cyclohexylidene group is situated on an axial site, and phenyl ring is directed toward the other site. The NiOC−O distance (1.232(2) Å) is strongly indicative of a double bond, while the NiO−C distance is 1.290(2) Å. Ni−O and Ni−N distances are 1.9401(17) and 1.9426(13) Å, respectively. The bite angle of O−Ni−N is 88.83(5)°.

Addition of 0.9 equiv of $B(C_6F_5)_3$ to **6**−**8** in benzene and slow layer diffusion of pentane into the solution afford analytically pure single crystals in 69%, 78% and 75% yields, respectively. ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR

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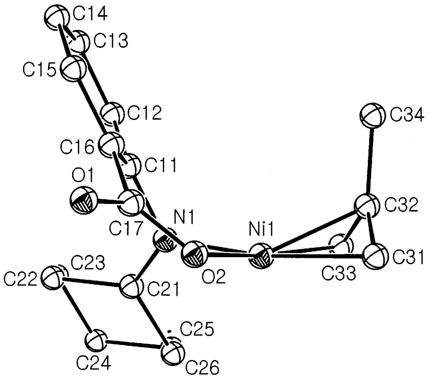


Figure 1. Thermal ellipsoid plot (30% probability level) of the structure of **6**. Selected bond distances (Å) and angles (deg): Ni(1)−O(2), 1.9401(11); Ni(1)−N(1), 1.9426(13); Ni(1)−C(31), 2.008(2); Ni(1)−C(33), 1.985(2); Ni(1)−C(32), 1.943(2); O(2)−C(17), 1.290(2); O(1)−C(17), 1.232(2); N(1)−C(21), 1.289(2); N(1)−C(11), 1.441(2); N(1)−Ni(1)−O(2), 88.83(5); O(1)−C(17)−O(2), 123.2(2); C(21)−N(1)−Ni(1), 129.64(11); C(26)−C(21)−N(1), 120.40(14); Ni(1)−O(2)−C(17), 124.59(10).

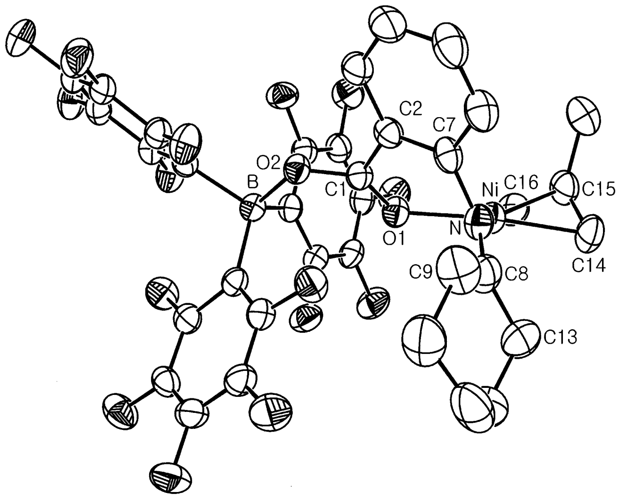


Figure 2. Thermal ellipsoid plot (30% probability level) of the structure of **9**. Selected bond distances (Å) and angles (deg): Ni−C(14), 2.000(5); Ni−C(16), 1.994(5); Ni−C(15), 1.986(5); N−C(8), 1.294(6); N−C(7), 1.438(6); N−Ni−O(1), 87.45(13); O(1)−C(1)−O(2), 124.7(4); C(8)−N−Ni, 132.4(4); N−C(8)−C(9), 123.1(5); C(1)−O(1)−Ni, 121.9(3). See Table 1 also.

spectra and elemental analyses are in agreement with the structures of zwitterionic complexes **9**−**11** (Scheme 1). ^{1}H NMR signals are rather broad, indicating the complex is under some fluxional motion. The proton signals of **11** are broader than those of **9**, while the signals of **10** are sharper.

X-ray crystallographic studies confirm the solid structure of **9**. Figure 2 shows the Ortep drawing with selected bond lengths and angles, and the bond distances within the NNiOCOB fragment are compared with those observed for similar complexes in Table 1. The methyl group on the methallyl ligand is directed opposite to the cyclohexylidene group. Metrical parameters within the NiOCOB fragment strongly support the zwitterionic structure depicted in Scheme 1. The Ni−N distance observed for **9** is shorter than that observed for **2**. Solid structures of **9** and **2** are compared in Figure 3 to see if there is any steric difference in the axial sites.

Table 1. Comparison of the Bond Distances (Å) within the N−Ni−O−C−O−B Fragment in 1, 2, 9, 11, 15, and 16

	1	2	9	11	15	16
Ni−OCOB	1.909(3)	1.899(3)	1.946(3)	1.931(3)	1.940(5)	1.887(4)
NiO−COB	1.240(5)	1.229(4)	1.237(5)	1.251(4)	1.259(8)	1.257(7)
NiOC−OB	1.289(5)	1.297(4)	1.271(5)	1.279(4)	1.279(8)	1.268(7)
NiOCO−B	1.541(5)	1.546(5)	1.539(5)	1.534(4)	1.542(9)	1.550(8)
Ni−N		2.059(3)	1.946(3)	1.929(3)	1.905(7)	1.902(5)

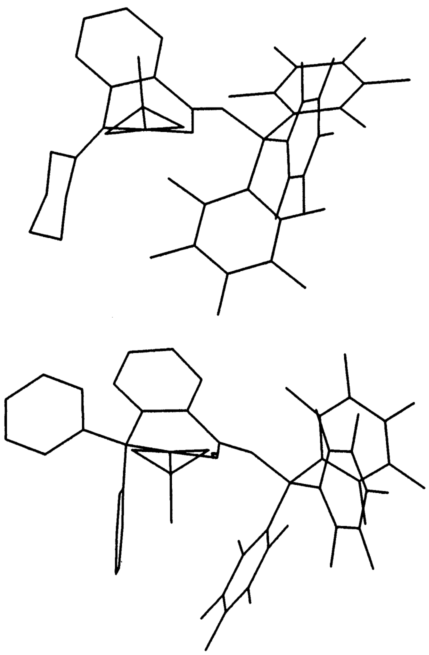


Figure 3. Comparison of the structures of **9** (polymerization catalyst) and $[(C_6H_5)_2NC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2 N,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ (dimerization catalyst).

In the structure of dimerization catalyst **2**, one observes a slight shielding of one axial site by a phenyl group and a pentafluorophenyl group. One of the N−C^{ipso} (on C_6H_5) vectors is nearly perpendicular to the square plane (dihedral angle of O$^{\kappa}$NiNC^{ipso} 71.1°), but the phenyl ring is situated almost parallel to a side of the square so as not to impose any great steric bulkiness on the axial site. The other N−C^{ipso} (on C_6H_5) vector is almost on the plane (dihedral angle of O$^{\kappa}$NiNC^{ipso} −169.1°), and hence, steric imposition by the ring is small. One of the pentafuorophenyl rings slightly blocks the axial site, even though the boron atom is located far from the nickel center. In the structure of **9**, somewhat less steric bulkiness on the axial site is observed as compared to that observed for **2**. The cyclohexylidene group is not as perpendicular to the square plane as one phenyl group is in **2** (dihedral angle of O$^{\kappa}$NiNC^{cy} 107.1°), and a pentafluorophenyl ring located at the nickel side is situated almost parallel to a side of the square, not imposing any steric bulkiness on the axial site.

The solid structure of **11** was determined by X-ray crystallography as well (Figure 4). The geometric parameters are similar to those of **9**. The *tert*-butyl group and nickel atom have a cis relationship, and the methallyl CH_3 group is situated opposite to the *tert*-butyl group. Slight contractions of Ni−O and Ni−N bond distances and elongation of NiO−C distance are observed when the parameters are compared with those observed for **9** (Table 1).

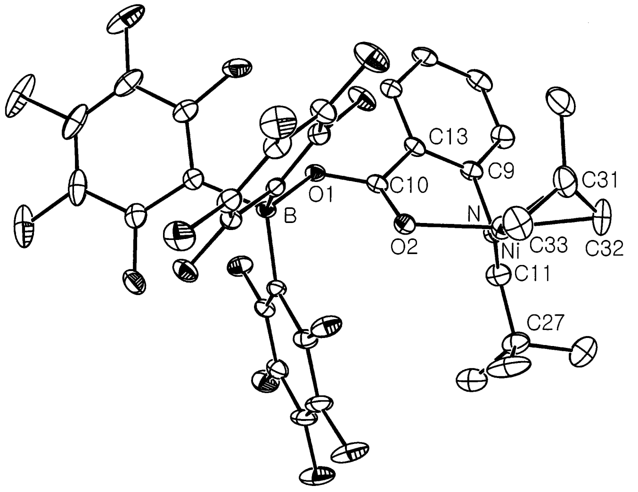
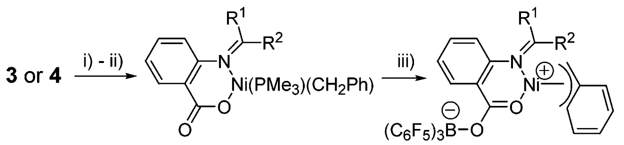


Figure 4. Thermal ellipsoid plot (30% probability level) of the structure of **11**. Selected bond distances (Å) and angles (deg): Ni−C(31), 1.969(4); Ni−C(32), 1.989(4); Ni−C(33), 1.998(4); N−C(11), 1.280(5); N−C(9), 1.436(5); N−Ni−O(2), 86.87(12); O(1)−C(10)−O(2), 122.5(3); C(9)−N-Ni, 105.2(2); N−C(11)−C(27), 105.2(2); C(10)−O(2)−Ni, 118.9(2). See Table 1 also.

Scheme 2[a]



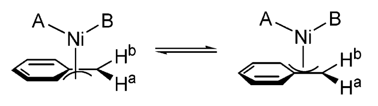
12: $R^1, R^2 = -(CH_2)_5-$ **14**: $R^1, R^2 = -(CH_2)_5-$

13: $R^1 = Et, R^2 = Et$ **15**: $R^1 = Et, R^2 = Et$

[a] Legend: (i) KH; (ii) (η^3-$CH_2C_6H_5$)NiCl(PMe_3); (iii) $B(C_6F_5)_3$ (2.0 equiv).

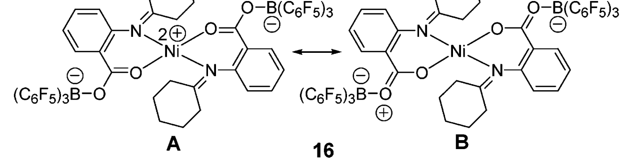
We attempted to synthesize the corresponding η^3-benzyl complexes, because they display faster rates of initiation than methallyl complexes.[10] Reaction of the potassium salt of **3** with (η^3-$CH_2C_6H_6$)NiCl(PMe_3)[20] cleanly affords the desired complex **12** (Scheme 2). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra and elemental analyses are in agreement with the structure. Because the two axial sites are not equivalent, two benzyl CH_2 hydrogens are diastereotopic with each other and consequently proton signals are observed separately at 3.6 and 2.8 ppm as broad signals. The benzyl CH_2 signal is observed as a doublet ($^2J_{PC} = 25$ Hz) at 6.41 ppm in the $^{13}C\{^1H\}$ NMR spectrum (C_6D_6) by coupling with the phosphorus atom. A very broad signal is observed at −8.2 ppm in the $^{31}P\{^1H\}$ NMR (C_6D_6) spectrum. Similarly, complex **13** is obtained from ligand **4.** The phosphorus signal is relatively sharp at −6.5 ppm. Reaction with **5** does not provide a clean complex. Three sets of signals are observed in the ^1H NMR spectrum, and three signals are observed at −7.2, −10.3, and −15.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

When 2 equiv of $B(C_6F_5)_3$ is added to **12** and **13,** one observes immediate formation of white precipitates, $PMe_3{\cdot}B(C_6F_5)_3$. Removal of the precipitates by filtration and trituration of the residue in pentane give a brownish red powder. NMR studies support that η^3-benzyl complexes **14** and **15** are formed (Scheme 2). The signal patterns are somewhat different from those observed for (pyridinecarboxamidoato)nickel(II)[14] and (α-iminocarboxamidato)nickel(II)[13] complexes in ^1H NMR spectra. In those cases, two ortho protons and two methylene protons on the benzyl ligand are equivalent, respectively, and hence, a relatively sharp doublet signal for the ortho protons and a singlet signal for the methylene protons are observed in the ^1H NMR spectra. The equivalency results from not only a rapid suprafacial shift[21]



but also equivalency of the two axial sites. For **14** and **15**, two ortho protons are separately observed at 6.2 and 6.0 ppm as broad signals. Two meta protons are separately observed at 6.9 and 6.7 ppm as broad signals as well. The signal of the para proton is relatively sharp at 7.27 ppm as a triplet. Two methylene protons are also separately observed at 1.0 and 0.7 ppm as doublets. These observations are attributed to inequivalency of the two axial sites. Even if the rapid suprafacial shift is underway, the two protons attached on ortho carbons, meta carbons, or the methylene carbon are not equivalent to each other, respectively, and hence signals are observed separately.

Recrystallization by layer diffusion of pentane into a benzene solution of **14** at room temperature gives crystals. Inspection of the crystals through a microscope reveals that there are two kinds of crystals. One type is pale red and rectangular, which is suitable for X-ray crystallography, and the other type is an orange plate. X-ray crystallographic studies of the pale red rectangular crystlas reveal the structure of the bis ligand complex **16** (Figure 5). Formations of similar types of bis ligand complexes were frequently observed in the SHOP complexes, and these turned out to be the main modes of the inactivation process.[22] A square-planar geometry is observed with a trans relationship between the two nitrogen atoms. Metrical parameters within the NNiOCOB fragment (Table 1) suggest a significant contribution of the resonance structure **B**. The NiO−C bond distance observed for **16** is relatively long and the NiOC−O distance is relatively short when the distances are compared with those observed for **1** and **2**. The longest B−O distance and the shortest Ni−O and Ni−N distances are observed for **16** among those tabulated in Table 1.



16

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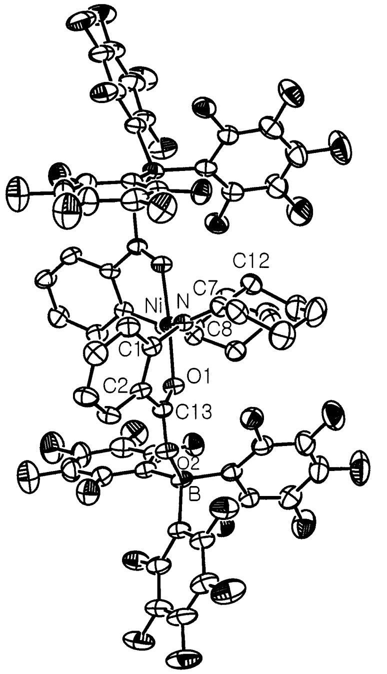

Figure 5. Thermal ellipsoid plot (30% probability level) of the structure of **16**. Selected bond distances (Å) and angles (deg): N−C(7), 1.284(8); N−Ni−O(1), 88.81(19); O(1)−C(13)−O(2), 122.2(6); C(7)−N−Ni, 124.7(5); N−C(7)−C(8), 126.4(7); C(13)−O(1)−Ni, 123.6(4). See Table 1 also.

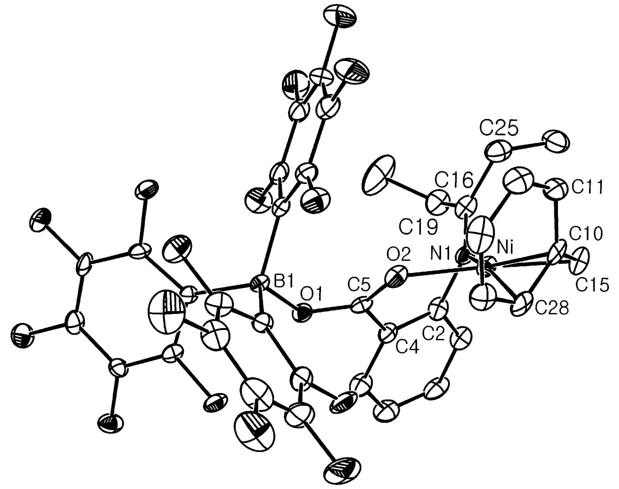

Figure 6. Thermal ellipsoid plot (30% probability level) of the structure of **15**. Selected bond distances (Å) and angles (deg): Ni−C(28), 2.128(8); Ni−C(10), 1.976(7); Ni−C(15), 1.940(8); N(1)−C(2), 1.431(10); N(1)−C(16), 1.305(10); N(1)−Ni−O(2), 88.2(2); O(1)−C(5)−O(2), 123.4(7); C(2)−N(1)−Ni, 108.4(5); N(1)−C(16)−C(19), 124.9(8); C(5)−O(2)−Ni, 122.3(5). See Table 1 also.

In the case of **15**, recrystallization by layer diffusion of pentane into a benzene solution gives single crystals, which are analytically pure and suitable for X-ray crystallography. Inspection through a microscope shows the presence of only one kind of crystal. NMR studies support that the crystals are pure η^3-benzyl complexes **15**, and X-ray crystallographic studies confirm the structure (Figure 6). The (1-ethylpropylidene)amino group in $Et_2C{=}NC_6H_4C(O)O$ is bulkier than the cyclohexylideneamino group in $(CH_2)_5C{=}NC_6H_4C(O)O$ and, hence, might prevent the formation of the bis ligand complex. The occurrence of the inactive bis ligand complex was also successfully prevented in the (salicylaldiminato)nickel(II) complex by introducing a bulky substituent on the ligand frame.[8]

Table 2. Ethylene Reactivity[a]

entry	complex	temp[b] (°C)	*P* (Psig)	A[c]	M_w	M_w/M_n	branches[d]
1	**14**	50−80−75	25	1000	7800	2.0	50
2	**14**	50−88−85	50	1700	7300	2.0	43
3	**14**	50−98−68	75	1300			
4[e]	**14**	50−103−73	75	3200	9300	2.7	35
5	**14**	25	100	190			
6[e]	**15**	50−104−94	75	4100	12000	2.5	47
7	comp 1[f]	room temp	100	850	349000	2.3	104
8	comp 2[g]	80	100	800	495000	2.5	104
9	comp 3[h]	80	100	550	729000	2.9	82

[a] Polymerization conditions: 30 mL of toluene, 10 μmol of complex, 25 μmol of $B(C_6F_5)_3$ as a scavenger, 15 min. [b] Initial temperature−maximum temperature−final temperature. [c] Activity in kg/((mol of Ni) h). [d] Determined by ^{1}H NMR and corresponds to the number of branches/1000 carbons. [e] 5.0 μmol of complex + 12 μmol of $B(C_6F_5)_3$ as a scavenger. [f] $[(H_3C)C\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}C\{OB(C_6F_5)_3\}\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}]Ni(\eta^3\text{-}CH_2C_6H_5)$. [g] $[(H_3C)C\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}C\{CH_2B(C_6F_5)_3\}\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}]Ni(\eta^3\text{-}CH_2C_6H_5)$. [h] $[(H_3C)C\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}C\{CH_2Al(C_6F_5)_3\}\{{=}N(2,6\text{-}(Me_2CH)_2C_6H_3)\}]Ni(\eta^3\text{-}CH_2C_6H_5)$.

Ethylene Reactivity Studies. When ethylene gas is added to a NMR cell containing **9** in C_6D_6, no consumption of ethylene is initially observed. An ethylene proton signal is observed around 5.2 ppm, and one cannot observe any changes for the signals originally observed for **9**. However, one observes, after the mixture stands overnight, the appearance of polymer particles along with the disappearance of the ethylene signal. A soluble poly(ethylene) signal is also observed at 1.0−1.5 ppm in the ^{1}H NMR spectrum, but signals of the end vinyl group are not detected, which implies that the molecular weight of even the soluble part of the obtained poly(ethylene) is fairly high. When the molecular weight of poly(ethylene) is not as high (below several thousands), the end vinyl groups are usually detected in the ^{1}H NMR spectrum and the number-average molecular weight can be calculated by integration of the signals.[14] One also observes proton signals of **9** almost untouched, which suggests that only a small fraction of **9** is initiated, followed by very fast propagation and chain growth. Slow initiations of allyl- or methallylnickel complexes were reported with other nickel complexes.[4,9,14,15] Similar slow formations of polyethylene are observed in NMR cells with the methallyl complexes **10** and **11**.

When ethylene gas is added to a NMR cell containing the η^3-benzyl complex **14** in C_6D_6, rapid consumption of ethylene gas and immediate formation of polymer particles are observed. Ethylene polymerization reactivity was studied with a 60 mL glass reactor under ethylene pressure. The results are summarized in Table 2. Activity is not as high at room temperature (entry 5), but high activity is observed when the polymerization is initiated in a heating bath (50 °C). Solution temperatures rise rapidly and reach 80−100 °C in several minutes by heat of polymerization. In the cases of 25 and 50 psig, the temperatures reach 80 and 88 °C, respectively, and the temperatures do not decay severely through the polymerization time (entry 1 and 2). These observations imply that the active species is thermally stable at 80 and 88 °C.[3] At 75 psig, however, the temperature reaches 98 °C in 2 min and then rapid decay of the temperature is observed, resulting in lower activity (entry 3). This result indicates that the catalyst is deactivated at the high temperature of 98 °C. When the catalyst amount is reduced to half under a pressure of 75 psig (entry 4), the temperature increases rather slowly but reaches still 103 °C in 6 min. Rapid decay of the temperature is observed after that point also. The activity is calculated to be 3200 kg/((mol of Ni) h), which is higher than those activities observed for (α-iminocarboxamido)-[12] and (α-iminoenamido)nickel(II)[14] complexes (entries 7−9). One observes a similar rise of the temperature to 104 °C with **15**, but the temperature does not decay as rapidly, implying that the active species derived from **15** is thermally stable even at 104 °C. The activity is calculated to be 4100 kg/((mol of Ni) h) under these conditions.

The obtained poly(ethylene)s are branched ones, and the branch numbers are in the range of 35−50 branches/1000 carbons. The branch number decreases slightly with increase of the pressure. Examination by ^{13}C NMR spectroscopy using established pulse sequences[23] shows a similar distribution of branching to other nickel catalysts.[13] For the polymer in entry 6 in Table 2, one observes a majority of methyl branches (∼50%) and a minor component of approximately equal quantities of ethyl, propyl, butyl, amyl, and long-chain branches. Recently, Bazan demonstrated a synthesis of branched polyethylene by tandem catalysis.[12] Molecular weights of the poly(ethylene) are rather low ($M_w \approx 10\,000$). The molecular weight distribution is narrow ($M_w/M_n = 2.0-2.7$), indicating that a single active species is present in the polymerization solution.

Summary and Discussion

In summary, syntheses and characterization of some (2-(alkylideneamino)benzoato)nickel complexes have been demonstrated. The zwitterionic η^3-benzyl complexes $[RR'C{=}NC_6H_4C\{OB(C_6F_5)_3\}O\text{-}\kappa^2N,O]Ni(\eta^3\text{-}CH_2C_6H_5)$ (R, R′ = −(CH$_2$)$_5$−, **14**; R = Et, R′ = Et, **15**) are active in the polymerization of ethylene. Molecular weights of the obtained poly(ethylenes) are rather low ($M_w \approx 10\,000$), but this result is interesting when considering that the corresponding (2-(diphenylphosphino)benzoato)- and (2-(diphenylamino)benzoato)nickel complexes give mainly butene by a rapid chain transfer reaction. The chain transfer process is usually reduced by an increase of steric bulkiness on the axial sites, but no increase of the steric bulkiness on the axial sites is observed when the solid structure of the (2-(cyclohexylideneamino)benzoato)nickel complex is compared with that of the (2-(diphenylamino)benzoato)nickel complex (Figure 3). Thus, reduction of the chain transfer process in (2-(alkylideneamino)benzoato)nickel complexes might be explained by a change of electronic effect.

Experimental Section

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, pentane, and C_6D_6 were distilled from benzophenone ketyl. Acetonitrile was distilled over CaH_2. Toluene used for the 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 a pressure of 150 psig. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz), ^{11}B NMR (128 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Varian Mercury Plus 400. ^{19}F NMR, ^{11}B NMR, and ^{31}P NMR spectra were calibrated and reported downfield from external $CFCl_3$, $BF_3{\cdot}OEt_2$, and PPh_3, respectively. 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 Waters Model 150-C+ GPC, and the data were analyzed using a polystyrene analyzing curve.

2-(Cyclohexylideneamino)benzoic Acid (3). Anthranilic acid (2.00 g, 14.6 mmol) and cyclohexanone (7.2 g, 73 mmol) were weighed in a flask, and benzene (60 mL) was added. A condensation reaction was carried out by azeotropic removal of water using the Dean−Stark apparatus overnight. After solvent and excess cyclohexanone were removed under vacuum, the residue was sublimed at 150 °C to give a white solid (2.73 g, 86%). ^{1}H NMR (CDCl$_3$): δ 7.91 (dd, J = 8.0, 1.6 Hz, 1 H, Ph $H^{3\text{ or }6}$), 7.39 (ddd, J = 8.0, 7.2, 1.6 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.88 (ddd, J = 8.0, 7.2, 1.2 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.75 (ddd, J = 8.0, 1.2, 0.4 Hz, 1 H, Ph $H^{3\text{ or }4}$), 4.66 (br s, 1 H, CO$_2$$H$), 2.14−2.20 (m, 2 H, Cy H), 1.86−1.70 (m, 4 H, Cy H), 1.62−1.40 (m, 4 H, Cy H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 163.74, 145.21, 135.14, 129.92, 119.55, 116.10, 113.02, 90.14, 35.61, 24.90, 22.09 ppm. IR (neat): 3350, 3294 (br, OH), 1688 (carbonyl) cm^{-1}.

2-((1-Ethylpropylidene)amino)benzoic Acid (4). The compound was prepared according to the same procedure and conditions for **3**, except for a reaction time of 5 days. Removal of all volatiles gave a white solid (100%) that was pure by the analysis of ^{1}H and ^{13}C NMR spectra and was used for the next reaction without further purification. ^{1}H NMR (CDCl$_3$): δ 7.88 (dd, J = 7.6, 1.2 Hz, 1 H, Ph $H^{3\text{ or }6}$), 7.36 (ddd, J = 8.0, 6.8, 1.6 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.83 (td, J = 8.0, 0.8 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.72 (d, J = 8.0 Hz, 1 H, Ph $H^{3\text{ or }6}$), 4.64 (br s, 1 H, CO$_2$$H$), 1.93 (m, 4 H, C$H_2CH_3$), 0.99 (t, J = 7.2 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 163.74, 145.59, 135.21, 129.98, 119.30, 115.62, 112.38, 93.86, 29.56, 8.02 ppm. IR (neat): 3450−1690 (br, OH), 1690 (carbonyl) cm^{-1}.

2-((2,2-Dimethylpropylidene)amino)benzoic Acid (5). Anthranilic acid (1.06 g, 7.74 mmol) and molecular sieves (3.9 g) were weighed into a flask, and then CHCl$_3$ (40 mL) and trimethylacetaldehyde (1.00 g, 11.6 mmol) were added successively. The solution was stirred overnight. The solution was filtered over Celite, and the residual product on the molecular sieves was washed with THF. Evaporation of solvent gave a white powder, which was pure by the analysis of ^{1}H and ^{13}C NMR spectra and was used for the next reaction without further purification (1.05 g, 95%). ^{1}H NMR (CDCl$_3$): δ 7.94 (dd, J = 8.0, 1.6 Hz, 1 H, Ph $H^{3\text{ or }6}$), 7.40 (ddd, J = 8.4, 7.6, 1.6 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.93 (td, J = 8.0, 0.8 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.80 (d, J = 8.0, 1 H, Ph $H^{3\text{ or }6}$), 4.86 (d, J = 2.8 Hz, 1 H, C=NH), 4.54 (br s, 1 H, CO$_2$$H$), 1.12 (s, 9 H, tBu) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 164.87, 147.61, 134.87, 130.66, 120.59, 115.86, 113.74, 92.23, 34.14, 24.91 ppm. IR (neat): 3320 (br, OH), 1685 (carbonyl) cm^{-1}.

Bis(μ-chloro)bis(η^3-methallyl)dinickel(II). Ni(COD)$_2$ (0.912, 3.32 mmol) and methallyl chloride (0.46 g, 0.51 mmol) were dissolved in 7.0 and 3.0 g of THF, respectively. Both solutions were cooled in a freezer (−30 °C) and combined rapidly while being cooled. The solution was stirred overnight at room temperature. The solvent was removed, and the complex was dissolved in toluene. Filtration and evaporation of the solvent under vacuum gave a red solid, which was pure by the analysis of ^{1}H and ^{13}C NMR spectra and was used for the next reaction without further purification. The yield was 80% (0.390 g). ^{1}H NMR (C$_6$D$_6$): δ 2.53 (s, 2 H, CH_2), 1.89 (s, 3 H, CH_3), 1.64 (s, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 120.07 (C(CH$_3$)), 54.42 (CH$_2$), 22.48 (CH$_3$) ppm.

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[2-(Cyclohexylideneamino)benzoato-κ^2N,O](η^3-methallyl)nickel(II) (6). 2-(Cyclohexylideneamino)benzoic acid (54.3 mg, 0.250 mmol) and KH (10.0 mg, 0.250 mmol) were weighed into a vial inside a glovebox, and THF (1.0 g) was added. The mixture was stirred for 1 h at room temperature, upon which a white thick slurry was formed. Acetonitrile (1.0 g) was added, and the mixture was stirred further for 30 min. Bis(μ-chloro)bis(η^3-methallyl)dinickel(II) (37.3 mg, 0.125 mmol) was added, and the solution was stirred for 30 min. Solvent was removed under vacuum, and the product was extracted with THF. Removal of the solvent gave a red crystalline complex (83 mg, 100%) which was pure by the analysis of ^{1}H and ^{13}C NMR spectra. Single crystals suitable for X-ray crystallography and elemental analysis were grown from toluene solution at −30 °C overnight. ^{1}H NMR (C_6D_6): δ 8.50 (d, $J = 7.2$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 7.07 (t, $J = 7.2$ Hz, 1 H, Ph $H^{4\text{ or }5}$), 7.02 (t, $J = 7.2$ Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.34 (d, $J = 7.2$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 2.70 (br, 1 H, methallyl CH_2), 2.52 (br, 1 H, methallyl CH_2), 2.41 (br, 1 H, methallyl CH_2), 2.23 (br, 1 H, methallyl CH_2), 1.87 (s, 3 H, methallyl CH_3), 1.80−0.80 (m, 10 H, Cy H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 184.04 (carbonyl or imine), 168.24 (carbonyl or imine), 142.29, 135.40, 131.90, 129.30, 127.06, 123.37, 120.11, 42.19, 32.37, 27.86, 27.69, 25.39, 22.84 ppm. Anal. Calcd for $C_{17}H_{22}NNiO_2$: C, 61.7; H, 6.71; N, 4.23. Found: C, 61.6; H, 7.01; N, 4.55.

[2-(1-(Ethylpropylidene)amino)benzoato-κ^2N,O](η^3-methallyl)nickel(II) (7). Compound **4** (1.00 g, 4.87 mmol) and KH (195 mg, 4.87 mmol) were weighed into a flask inside a glovebox, and THF (20 mL) was added. The mixture was stirred overnight at room temperature, upon which a white thick slurry was formed. Solvent was removed under vacuum. The potassium salt was triturated in pentane. Pentane was removed by decantation, and the solid was dried under vacuum (1.00 g, 85%). The potassium salt (245 mg, 1.01 mmol) and bis(μ-chloro)bis(η^3-methallyl)dinickel(II) (150 mg, 0.500 mmol) were weighed into a vial, and acetonitrile (5.0 mL) was added. The solution was stirred overnight. Solvent was removed under vacuum, and the product was extracted with toluene. Removal of the solvent gave a red solid, which was purified by triturating in pentane to give a light yellow solid. The solid was pure by the analysis of ^{1}H and ^{13}C NMR spectra. The yield was 84% (270 mg). Single crystals suitable for elemental analysis were grown by layer diffusion of pentane into a benzene solution at room temperature overnight. ^{1}H NMR (C_6D_6): δ 8.46 (br d, $J = 6.4$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 7.06 (t, $J = 7.2$ Hz, 1 H, Ph $H^{4\text{ or }5}$), 7.02 (td, $J = 7.6$, 1.6 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.34 (br d, $J = 7.2$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 2.51 (br s, 2 H, methallyl CH_2), 2.36 (br, 2 H, methallyl CH_2), 1.85 (s, 3 H, methallyl CH_3), 1.78 (br q, $J = 7$ Hz, 2 H, CH_2CH$_3$), 1.68 (br q, $J = 7$ Hz, 2 H, CH_2CH$_3$), 1.12 (t, $J = 7.6$ Hz, 3 H, CH$_2$CH_3), 0.47 (t, $J = 7.6$ Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 187.51 (carbonyl or imine), 168.14 (carbonyl or imine), 142.55, 134.89, 131.65, 129.53, 127.01, 123.43, 119.65, 34.73, 26.20, 22.76, 12.51, 11.42 ppm. Anal. Calcd for $C_{16}H_{21}NNiO_2$: C, 60.4; H, 6.66; N, 4.40. Found: C, 60.0; H, 6.49; N, 4.19.

[2-((2,2-Dimethylpropylidene)amino)benzoato-κ^2N,O](η^3-methallyl)nickel(II) (8). The compound was prepared under conditions and by procedures similar to those for **7**. The reaction time was 2 h, and the product was extracted with THF. The yield was 90%. Single crystals suitable for elemental analysis were grown by layer diffusion of pentane into a benzene solution at room temperature overnight. ^{1}H NMR (CD_3CN/C_6D_6 (v/v, 1:1)): δ 7.89 (br t, $J = 7.6$ Hz, 1 H, Ph $H^{4\text{ or }5}$), 7.75 (s, 1 H, CH═N), 7.51 (br t, $J = 7.6$ Hz, 1 H, Ph $H^{4\text{ or }5}$), 7.42 (br d, $J = 7.2$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 6.98 (br d, $J = 7.2$ Hz, 1 H, Ph $H^{4\text{ or }6}$), 2.65 (br s, 2 H, methallyl CH_2), 2.13 (s, 3 H, methallyl CH_3), 1.94 (br s, 2 H, methallyl CH_2), 1.56 (s, 9 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (CD_3CN/C_6D_6 (v/v, 1:1)): δ 184.53 (carbonyl or imine), 168.42 (carbonyl or imine), 146.48, 133.38, 131.69, 129.99, 127.55, 124.88, 119.09, 36.72, 27.14, 22.29 ppm. Anal. Calcd for $C_{16}H_{21}NNiO_2$: C, 60.4; H, 6.66; N, 4.40. Found: C, 60.0; H, 6.64, N; 4.36.

[(2-(Cyclohexylideneamino)benzoato)tris(pentafluorophenyl)borato-κ^2N,O](η^3-methallyl)nickel(II) (9). When 1 equiv of $B(C_6F_5)_3$ is added to **6** in C_6D_6, two sets of signals are observed in the ^{1}H NMR spectrum, but a set of clean ^{1}H NMR signals is observed when only 0.9 equiv of $B(C_6F_5)_3$ (23.0 mg, 0.0450) is added to **6** (16.5 mg, 0.0500 mmol). Analytically pure single crystals, which were suitable for X-ray crystallography, were obtained by layer diffusion of pentane into the C_6D_6 solution in the NMR cell. Light yellow crystals were isolated (16 mg, 69%). ^{1}H NMR (C_6D_6): δ 8.29 (br d, $J = 7.6$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 6.86 (br t, $J = 8.8$, 1 H, Ph $H^{4\text{ or }5}$), 6.82 (br t, $J = 8.8$ Hz, 1 H, Ph $H^{4\text{ or }5}$), 5.96 (br d, $J = 7.6$ Hz, Ph $H^{3\text{ or }6}$), 2.54−2.26 (br, 2 H, methallyl CH_2 and Cy H), 2.24−1.88 (br, 1 H, methallyl CH_2), 1.59 (s, 3 H, methallyl CH_3), 1.8−0.65 (m, 11 H, methallyl CH_2 and Cy H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 189.15 (carbonyl or imine), 173.04 (carbonyl or imine), 148.7 (dm, $^1J_{CF} = 240$ Hz), 143.10, 139.7 (dm, $^1J_{CF} = 245$ Hz), 137.4 (dm, $^1J_{CF} = 245$ Hz), 133.18, 132.34, 128.53, 127.23, 126.53, 121.34, 42.54, 33.00, 28.48, 27.98, 25.09, 22.22 ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −134 (d, $^3J_{FF} = 18$ Hz), −159 (t, $^3J_{FF} = 18$ Hz), −165 (t, $^3J_{FF} = 18$ Hz) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ −3.4 ppm. Anal. Calcd for $C_{35}H_{21}BF_{15}NNiO_2$: C, 49.9; H, 2.52; N, 1.66. Found: C, 50.2; H, 2.95; N, 2.03.

[(2-((1-Ethylpropylidene)amino)benzoato)tris(pentafluorophenyl)borato-κ^2N,O](η^3-methallyl)nickel(II) (10). The complex was prepared according to the same procedure and conditions for **9** from **7**. The isolated yield was 78%. ^{1}H NMR (C_6D_6): δ 8.31 (d, $J = 7.6$ Hz, 1 H, Ph $H^{3\text{ or }6}$), 6.91 (td, $J = 7.6$, 1.6 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.85 (td, $J = 7.6$, 0.8 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.10 (br d, $J = 7.6$ Hz, Ph $H^{3\text{ or }6}$), 2.35 (br s, 1 H, methallyl CH_2), 2.07 (br s, 1 H, methallyl CH_2), 2.03 (q, $J = 7.6$ Hz, 2 H, CH_2CH$_3$), 1.62 (br s, 1 H, methallyl CH_3), 1.54 (q, $J = 7.6$ Hz, 2 H, CH_2CH$_3$), 1.31 (br s, 1 H, methallyl CH_2), 1.13 (br s, 1 H, methallyl CH_2), 0.97 (t, $J = 7.6$ Hz, 3 H, CH$_2$CH_3), 0.35 (t, $J = 7.6$ Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 192.37 (carbonyl or imine), 172.74 (carbonyl or imine), 148.7 (dm, $^1J_{CF} = 250$ Hz), 143.59, 139.7 (dm, $^1J_{CF} = 230$ Hz), 137.5 (dm, $^1J_{CF} = 240$ Hz), 133.33, 132.32, 127.01, 126.51, 121.02, 34.72, 26.87, 22.29, 12.72, 11.00 ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −134 (d, $J = 18$ Hz), −159 (t, $^3J_{FF} = 18$ Hz), −165 (t, $^3J_{FF} = 18$ Hz) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ −2.7 ppm. Anal. Calcd for $C_{34}H_{21}BF_{15}NNiO_2$: C, 49.2; H, 2.55; N, 1.69. Found: C, 49.6; H, 2.68; N, 1.65.

[(2-((2,2-Dimethylpropylidene)amino)benzoato)tris(pentafluorophenyl)borato-κ^2N,O](η^3-methallyl)nickel(II) (11). The complex was prepared according to the same procedure and conditions for **9** from **8**. The isolated yield was 75%. ^{1}H NMR (C_6D_6): δ 8.32 (br, 1 H), 6.93 (br, 2 H), 6.54 (s, 1 H, CH═N), 6.40 (br, 1 H), 2.43 (br, 1 H, methallyl CH_2), 1.85 (br, 1 H, methallyl CH_2), 1.54 (s, 3 H, methallyl CH_3), 1.1−0.5 (br, 11 H, *t*Bu H and methallyl CH_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 187.25 (carbonyl or imine), 172.83 (carbonyl or imine), 148.6 (dm, $^1J_{CF} = 240$ Hz), 138.8 (dm, $^1J_{CF} = 250$ Hz), 137.3 (dm, $^1J_{CF} = 240$ Hz), 134.74, 131.73, 128.96, 127.04, 26.75, 22.07 ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −134 (d, $J = 18$ Hz), −159 (t, $^3J_{FF} = 18$ Hz), −165 (t, $^3J_{FF} = 18$ Hz) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ 0.0 ppm. Anal. Calcd for $C_{34}H_{21}BF_{15}NNiO_2$: C, 49.2; H, 2.55; N, 1.69. Found: C, 49.0; H, 2.56; N, 1.63.

(η^3-Benzyl)chloro(trimethylphosphine)nickel(II). The compound was reported and can be synthesized according to the reported procedure and conditions.[20] We have developed a more convenient procedure. Thus, Ni(COD)$_2$ (2.74 g, 10.0 mmol) was dissolved in THF (20 g). Benzyl chloride (1.27 g, 10.0 mmol) and PMe$_3$ (0.76 g) were added rapidly and successively. The solution was stirred for 1 h at room temperature. The solvent was removed, and the residue was dissolved in toluene (10 mL). The solution was filtered over Celite and

Table 3. Crystallographic Parameters of 6,[a] 9,[b] 11,[a] 15,[a] and 16[b]

	6	**9**	**11**	**15**	**16**
formula	$C_{17}H_{22}NNiO_2$	$C_{35}H_{21}BF_{15}NNiO_2$	$C_{34}H_{19}BF_{15}NNiO_2$	$C_{37}H_{23}BF_{15}NNiO_2$	$C_{34}H_{17}BF_{15}NNi_{0.5}O_2$
fw	331.07	842.05	828.02	868.08	796.65
color	red	light yellow	red-brown	red	Pale red
shape	plate	polyhedral	polyhedral	needle	rectangular
size, mm^3	0.53 × 0.21 × 0.07	0.85 × 0.70 × 0.56	0.90 × 0.74 × 0.54	0.90 × 0.24 × 0.12	0.2 × 0.2 × 0.2
a, Å	9.4241(8)	12.4931(3)	14.255(9)	19.276(12)	23.3070(8)
b, Å	9.8557(8)	19.2695(4)	22.582(13)	18.250(12)	21.6187(8)
c, Å	10.2580(8)	14.7536(6)	11.208(7)	9.935(7)	14.3394(4)
α, deg	93.6100(10)	90	90	90	90
β, deg	111.6960(10)	108.0172(12)	108.98(5)	96.60(5)	90
γ, deg	114.8280(10)	90	90	90	90
V, Å^3	776.09(11)	3377.56(17)	3411(4)	3472(4)	7225.2(4)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/a$	$Pbcn$
D(calcd), g cm^{-3}	1.417	1.656	1.612	1.661	1.465
Z	2	4	4	4	8
μ, mm^{-1}	1.253	0.693	0.684	0.677	0.393
no. of data collected	8093	18619	5795	5214	9813
no. of unique data	3469	6150	5517	4922	5183
no. of variables	207	497	491	516	483
R (%)	0.0281	0.0423	0.0502	0.0781	0.0662
R_w (%)	0.0826	0.1136	0.1335	0.1640	0.2049
goodness of fit	1.262	0.954	1.050	0.979	1.003

[a] Data collected at 150 K with Mo Kα radiation ($\lambda(K\alpha) = 0.7107$Å). $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 2.0\sigma(I)$; $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$. [b] Data collected at 293(2) K.

stored in a freezer (−30 °C) for 2 days to give crystals, which were pure by the analysis of ^{1}H and ^{13}C NMR spectra (1.56 g, 60%).

[2-(Cyclohexylideneamino)benzoato-κ^2N,O](η^1-benzyl)(trimethylphosphine)nickel(II) (12). 2-(Cyclohexylideneamino)benzoic acid (100 mg, 0.460 mmol) and KH (18.5 mg, 0.460 mmol) were weighed into a vial inside a glovebox, and THF (3.0 g) was added. The mixture was stirred overnight at room temperature, upon which a thick white slurry was formed. Ni(η^3-$CH_2C_6H_5$)Cl(PMe$_3$) (120.3 mg, 0.460 mmol) was added in one portion, and the solution was stirred for 1 h. The solvent was removed under vacuum, and the product was dissolved in toluene. The solution was filtered over Celite, and the solvent was removed. The product was triturated in pentane. A brownish red powder was obtained, which was pure by the analysis of ^{1}H and ^{13}C NMR spectra (178 mg, 87%). Analytically pure crystals were obtained by layer diffusion of pentane into a benzene solution at room temperature overnight. ^{1}H NMR (C_6D_6): δ 8.52 (d, J = 7.6 Hz, 1 H, Ph $H^{3 \text{ or } 6}$), 7.26−6.98 (m, 6 H), 6.94 (t, J = 7.6 Hz, 1 H), 5.76 (d, J = 7.6 Hz, 1 H, Ph $H^{3 \text{ or } 6}$), 3.5−3.65 (br m, 1 H, CH_2Ph), 2.75−2.85 (br m, 1 H, CH_2Ph), 1.83−0.80 (m, 10 H), 0.73 (d, $^2J_{PH}$ = 9.6 Hz, 9 H, PCH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 182.04 (carbonyl or imine), 168.01 (carbonyl or imine), 156.63, 150.70, 142.56, 133.84, 131.50, 129.22, 128.39, 126.53, 122.74, 120.40, 40.96, 32.26, 28.11, 27.28, 25.57, 11.67 (d, $^1J_{PC}$ = 28 Hz), 6.41 (d, $^2J_{PC}$ = 25 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −8.2 (br) ppm. Anal. Calcd for $C_{23}H_{30}NO_2PNi$: C, 62.5; H, 6.84; N, 3.17. Found: C, 62.4; H, 6.78; N, 3.17.

[2-((1-Ethylpropylidene)amino)benzoato-κ^2N,O](η^1-benzyl)(trimethylphosphine)nickel(II) (13). The potassium salt of **4** (279 mg, 1.15 mmol) and Ni(η^3-$CH_2C_6H_5$)Cl(PMe$_3$) (300 mg, 1.15 mmol) were weighed into a vial inside a glovebox, and toluene (5.0 mL) was added. The solution was stirred for 3 h. The solution was filtered over Celite, and the solvent was removed. The residue was triturated in a mixture of pentane and toluene (v/v, 4:1). A light brown powder was obtained, which was pure by the analysis of ^{1}H and ^{13}C NMR spectra (472 mg, 96%). Single crystals suitable for elemental analysis were grown by layer diffusion of pentane into a benzene solution at room temperature overnight. ^{1}H NMR (C_6D_6): δ 8.49 (d, J = 7.6 Hz, 1 H, Ph $H^{3 \text{ or } 6}$), 7.2−7.0 (m, 6 H), 6.94 (t, J = 7.6 Hz, 1 H), 5.73 (d, J = 7.6 Hz, 1 H, Ph $H^{3 \text{ or } 6}$), 3.40 (br, 1 H, CH_2Ph), 2.60 (br, 1 H, CH_2Ph), 1.64−1.18 (br, 4 H, CH_2CH$_3$), 1.42 (t, J = 7.6 Hz, 3 H, CH$_2$CH_3), 0.73 (d, $^2J_{PH}$ = 10 Hz, 9 H, PCH_3), 0.43 (t, J = 7.6 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 185.05 (carbonyl or imine), 167.95 (carbonyl or imine), 150.87, 142.80, 133.47, 131.38, 129.24, 127.77, 127.30, 126.51, 122.65, 119.97, 33.69, 25.57, 12.72, 11.71, 11.52 (d, $^1J_{PC}$ = 19 Hz), 6.00 (d, $^2J_{PC}$ = 27 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −6.50 ppm. Anal. Calcd for $C_{22}H_{30}NO_2PNi$: C, 61.4; H, 7.03; N, 3.26. Found: C, 61.1; H, 6.95; N, 3.08.

[(2-(Cyclohexylideneamino)benzoato)tris(pentafluorophenyl)borato-κ^2N,O](η^3-benzyl)nickel(II) (14). Complex **4** (0.221 g, 0.500 mmol) and B(C_6F_5)$_3$ (0.512 g, 1.00 mmol) were weighed into a vial inside a glovebox, and cold toluene (ca. 5 mL, −30 °C) was added. The solution was stirred for 30 min. A white solid of PMe$_3$·B(C_6F_5)$_3$ was filtered over Celite. The solvent was removed, and the residue was triturated in pentane overnight. A red solid was filtered and washed with pentane several times. Drying under vacuum gave a red powder (370 g, 85%). Fairly clean NMR spectra, which can be assigned to **14**, were obtained. An analytically pure complex was not obtained by the formation of the bis ligand complex **16** during recrystallization. ^{1}H NMR (C_6D_6): δ 8.23 (d, J = 7.6, 1 H, Ph $H^{3 \text{ or } 6}$), 7.27 (t, J = 7.6 Hz, benzyl H^p), 6.86 (t, J = 7.6 Hz, 1 H, Ph $H^{4 \text{ or } 5}$), 6.80 (t, J = 7.6 Hz, 1 H, Ph $H^{4 \text{ or } 5}$), 6.90 (br, 1 H, benzyl H^m), 6.68 (br, 1 H, benzyl H^m), 6.24 (br, 1 H, benzyl H^o), 6.03 (d, J = 7.6 Hz, 1 H, Ph $H^{3 \text{ or } 6}$), 5.40 (br, 1 H, benzyl H^o), 2.96−2.82 (m, 1 H, Cy H), 1.98 (ddd, J = 13, 11, 3.6 Hz, 1 H, Cy H), 1.78−1.52 (m, 2 H, Cy H), 1.09 (d, J = 2.0 Hz, 1 H, benzyl CH_2), 0.74 (d, J = 2.0 Hz, 1 H, benzyl CH_2), 1.46−0.60 (m, 6 H, Cy H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 190.27 (carbonyl or imine), 172.34 (carbonyl or imine), 148.6 (dm, $^1J_{CF}$ = 240 Hz), 142.83, 139.7 (dm, $^1J_{CF}$ = 260 Hz), 137.2 (dm, $^1J_{CF}$ = 250 Hz), 129.61, 132.87, 132.35, 120.72, 113.10, 42.17 (Cy C), 33.30 (Cy C), 28.63 (Cy C), 28.11 (Cy C), 25.18 (Cy C), 23.31 (benzyl CH_2) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −134 (d, J = 18 Hz), −159 (t, $^3J_{FF}$ = 18 Hz), −165 (t, $^3J_{FF}$ = 18 Hz) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ −3.3 ppm.

[(2-((1-Ethylpropylidene)amino)benzoato)tris(pentafluorophenyl)borato-κ^2N,O](η^3-benzyl)nickel(II) (15). The complex was prepared according to the same conditions and procedures for **14**. A red powder was obtained, which was fairly pure by the analysis of ^{1}H and ^{13}C NMR spectra (89%). Single crystals suitable for X-ray crystallography and elemental analysis were grown by layer diffusion of pentane into a benzene solution at room temperature overnight. ^{1}H NMR (C_6D_6): δ 8.26 (dd, J = 7.6, 2.0 Hz, 1 H, Ph $H^{3\text{ or }6}$), 7.27 (t, J = 7.6 Hz, benzyl H^p), 6.83 (td, J = 7.6, 2.0 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.79 (td, J = 7.6, 2.0 Hz, 1 H, Ph $H^{4\text{ or }5}$), 6.90 (br, 1 H, benzyl H^m), 6.72 (br, 1 H, benzyl H^m), 6.26 (br, 1 H, benzyl H^o), 6.01 (d, J = 7.2, 1.2 Hz, 1 H, Ph $H^{3\text{ or }6}$), 5.39 (br, 1 H, benzyl H^o), 2.23–2.09 (m, 2 H, CH_2CH_3), 1.51 (dq, J = 13.6, 7.6 Hz, 1 H, CH_2CH_3), 1.21 (dq, J = 13.6, 7.6 Hz, 1 H, CH_2CH_3), 1.08 (d, J = 2.8 Hz, 1 H, benzyl CH_2), 0.99 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 0.68 (d, J = 2.8 Hz, 1 H, benzyl CH_2), 0.27 (t, J = 7.6 Hz, 3 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 193.32 (carbonyl or imine), 172.26 (carbonyl or imine), 148.5 (dm, $^1J_{CF}$ = 240 Hz), 143.08, 139.7 (dm, $^1J_{CF}$ = 260 Hz), 137.2 (dm, $^1J_{CF}$ = 250 Hz), 133.02, 132.32, 129.75, 120.22, 113.00, 34.67, 27.06, 22.89, 12.87, 10.91 ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ −134 (d, J = 18 Hz), −159 (t, $^3J_{FF}$ = 18 Hz), −165 (t, $^3J_{FF}$ = 18 Hz) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ −3.3 ppm. Anal. Calcd for $C_{37}H_{21}BF_{15}NO_2Ni$: C, 51.3; H, 2.44; N, 1.62. Found: C, 51.4; H, 2.44; N, 1.40.

Ethylene Polymerization in an NMR Cell. Catalyst (5 μmol) dissolved in C_6D_6 (ca. 0.5 mL) was added inside a glovebox into an NMR cell (5 mm) with J. Young valves. The cell was brought out from the box and assembled on a Schlenk line. The cell was frozen in a dry ice/acetone bath, and the nitrogen gas was evacuated. Ethylene gas was charged through the Schlenk line, and the J. Young valve was closed. ^{1}H NMR spectra were recorded at that time.

Ethylene Polymerization in a Reactor. Toluene (30 mL) and $B(C_6F_5)_3$ (25 or 12 μmol) were added into a 60 mL glass reactor containing a stirring bar inside a glovebox. The reactor was assembled and brought out of the glovebox. The reactor was then immersed in an oil bath, the temperature of which had been set to 50 °C. The solution was stirred for 15 min, at which time the temperature of the solution reached the bath temperature. A solution of complex **14** or **15** (10 or 5.0 μmol) in toluene (1.0 mL) was injected with syringe into the reactor. Ethylene was fed continuously for 15 min under pressure. The temperature of the solution was monitored. The reaction was quenched by release of ethylene pressure, and the reaction mixture was poured into a flask containing 100 mL of acetone. White precipitates were collected by filtration and dried under vacuum. Branch numbers were calculated from the integration value of methyl, methylene, and methine proton regions in the ^{1}H NMR spectra. NMR spectra of the polymers were obtained at 100 °C in benzene-d_6 and 1,2,4-trichlorobenzene (v/v, 4:1).

Crystallographic Studies. Crystals of **9** and **16** coated with grease (Apiezon N) were mounted inside a thin glass tube with epoxy glue and placed on an Enraf-Nonius CCD single-crystal X-ray diffractometer. The crystal of **6** was mounted onto a thin glass fiber with Paratone and immediately placed in a cold nitrogen stream at 150 K on a Bruker SMART CCD diffractometer. Crystals of **11** and **15** were mounted on a MXC3 diffractometer (Mac Science) with Paratone under cold nitrogen at 150 K. The structures were solved by direct methods (SHELXS-97)[24] and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results are summarized in Table 3.

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Note Added after ASAP: The version published on the Web 9/17/2003 contained a misspelling in an author name. The final Web version published 9/23/2003 and print version are correct.

Supporting Information Available: Complete details for the crystallographic studies of **6**, **9**, **11**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.