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# Syntheses and Ethylene Polymerization Behavior of Supported Salicylaldimine-Based Neutral Nickel(II) Catalysts

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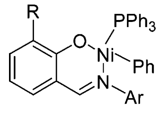
Two novel salicylaldimine-based neutral nickel(II) complexes, $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}{=}\text{CH}(2\text{-ArC}_6\text{H}_3\text{O})]\text{-Ni(PPh}_3\text{)Ph}$ (**6**, Ar = 2-(OH)$C_6H_4$; **8**, Ar = 2-OH-3-(2,6-$i\text{Pr}_2\text{C}_6\text{H}_3\text{N}{=}\text{CH}$)$C_6H_3$), have been synthesized, and their structures have also been confirmed by X-ray crystallography, elemental analysis, and $^1$H and $^{13}$C NMR spectra. An important structural feature of the two complexes is the free hydroxyl group, which allows them to react with silica pretreated with trimethylaluminum under immobilization by the formation of a covalent bond between the neutral nickel(II) complex and the pretreated silica. As active single-component catalysts, the two complexes exhibited high catalytic activities up to 1.14 and $1.47 \times 10^6$ g PE/$\text{mol}_{\text{Ni}}$·h for ethylene polymerization, respectively, and yielded branched polymers. Requiring no cocatalyst, the two supported catalysts also showed relatively high activities up to $4.0 \times 10^5$ g PE/$\text{mol}_{\text{Ni}}$·h and produced polyethylenes with high weight-average molecular weights of up to 120 kg/mol and a moderate degree of branching (ca. 13−26 branches per 1000 carbon atoms).

## Introduction

In the past few years, more and more attention has been concentrated on the late transition metal catalysts for olefin polymerization.[1−4] Due to their low electrophilicity and oxophilicity, the late transition metal catalysts can copolymerize ethylene and certain polar comonomers[5−12] and can even catalyze some polymerizations in water.[13−18] Remarkably, Grubbs and his co-workers found that the salicylaldimine-based neutral nickel(II) catalysts with bulky substituents *ortho* to a phenoxy group such as **1a−d** (Chart 1) not only showed high catalytic activities for ethylene polymerization without cocatalysts and produced polyethylenes (PEs) with high molecular weight but also could catalyze the copolymerization of ethylene and some functionalized olefins.[7−11,19−22] By avoiding hyperpurification of the monomer feed and the use of cocatalysts these readily available salicylaldimine-based neutral nickel(II) catalysts have been attracting the attention of many researchers.[23−33]

**Chart 1**



**1a-d**

**a**: R = $^t$Bu
**b**: R = Ph
**c**: R = 9-Anthrancenyl
**d**: R = 9-Phenanthrenyl
Ar = 2,6-$i\text{Pr}_2\text{C}_6\text{H}_3$

As we all know, homogeneous catalysts have to be supported on an innocuous carrier such as silica, alumina, or other

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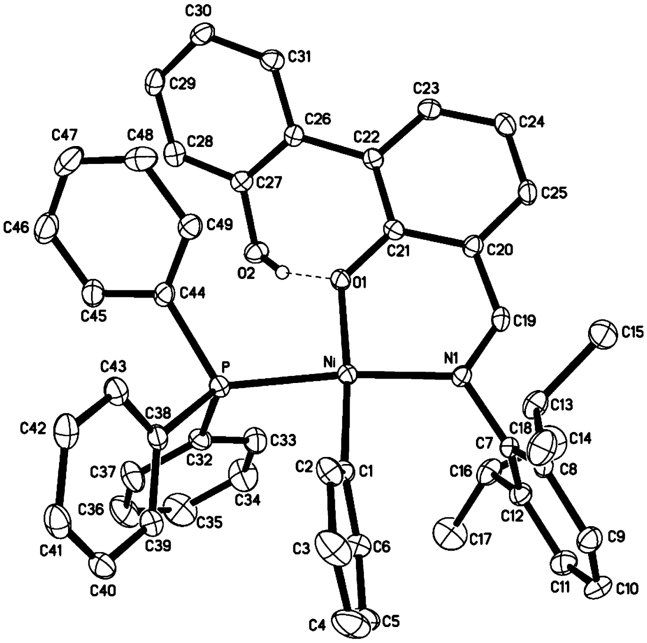


**Figure 1.** ORTEP view of complex **6**. Selected bond distances (Å) and angles (deg): Ni−C(1) 1.894(3), Ni−O(1) 1.9157(17), Ni−N(1) 1.947(2), Ni−P 2.1812(8), O(1)−C(21) 1.321(3), O(2)−C(27) 1.364(3), N−C(7) 1.456(3), N−C(19) 1.295(3), C(19)−C(20) 1.432(5), C(22)−C(26) 1.493(4), P−C(32) 1.825(3); N−Ni−P 170.89(7), C−Ni−P 84.90(8), C(1)−Ni−O(1) 174.45(10), C(1)−Ni−N 93.41(10), O(1)−Ni−P 90.25(6), O(1)−Ni−N 91.80(8).

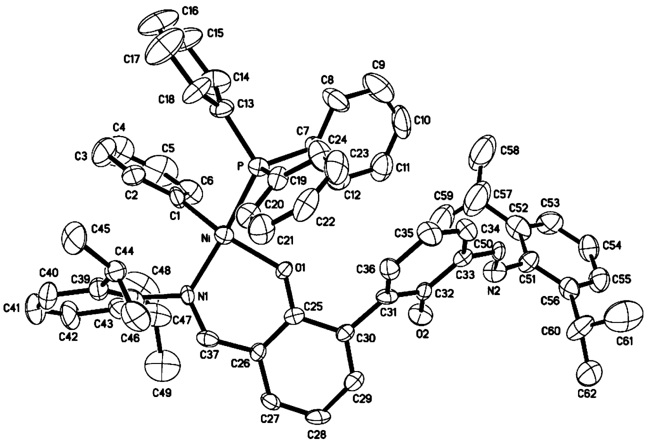
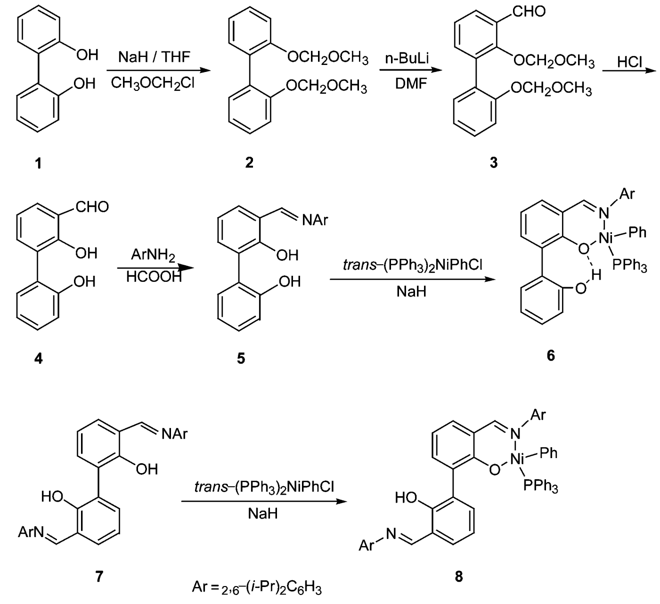


**Figure 2.** ORTEP view of catalyst **8**. Selected bond distances (Å) and angles (deg): Ni−C(1) 1.891(7), Ni−O(1) 1.920(4), Ni−N(1) 1.922(5), Ni−P 2.178(2), O(1)−C(25) 1.266(6), O(2)−C(32) 1.316(7), N(1)−C(37) 1.297(7), N(1)−C(38) 1.474(7), N(2)−C(50) 1.239(7), N(2)−C(51) 1.416(8), P−C(19) 1.839(7); N(1)−Ni−P 165.56(17), C(1)−Ni−P 91.0(2), C(1)−Ni−O(1) 163.9(3), C(1)−Ni−N(1) 92.7(3), O(1)−Ni−P 87.19(14), O(1)−Ni−N 93.0(2).

inorganic or organic supports in order to be applied in industrial gas-phase or slurry polymerization processes. Covalently attaching precatalysts to supports is a usual method that allows the precatalysts whose ligands contain a functionality to react with a second functional group on the surface of the support. Recently, covalently supported cationic Ni, Fe, and Co catalysts have been successfully used for ethylene polymerization;[34−38] however, the supported neutral nickel catalysts were seldom reported. This prompted us to explore the covalent supporting of neutral nickel catalysts and their catalytic behavior for ethylene polymerization so as to obtain PE with high molecular weight.

**Scheme 1**



For the covalent supporting of neutral catalysts, two factors must be considered in the design of catalysts: one is introduction of bulky substituents *ortho* to the phenoxy group in the backbone of the salicylaldimine ligand, which favors obtaining high catalytic activity and polyethylene with high molecular weight, and the other is introduction of an active functional group such as a hydroxyl or amino group in the salicylaldimine ligand, which can react with a second functional group on the surface of the support. Obviously, according to the conventional synthetic methods, the preparation of such ligands will require tedious multistep reactions with low yields.

Recently, we have developed a binuclear neutral Ni(II) catalyst based on the bis(salicylaldimine) ligand, which was derived from readily available 2,2′-biphenol, for the ethylene polymerization.[39] Here, we report the syntheses of two new neutral nickel(II) catalysts with free hydroxyl groups and attaching them covalently to silica as well as their catalytic behavior as homogeneous catalysts and their supported counterparts in ethylene polymerization.

## Results and Discussion

**Syntheses and Characterizations of Catalysts with a Free Hydroxyl Group.** The general synthetic route for neutral nickel(II) complexes **6** and **8** with a free hydroxyl group is shown in Scheme 1. Starting from 2,2′-biphenol, free ligands **5** and **7** were readily synthesized in good yields via a four-step reaction. The deprotonation of free ligands **5** and **7** with 1 equiv of sodium hydride in anhydrous THF gave yellow sodium salts at room temperature. Without further purification, the sodium salts were directly reacted with 1 equiv of *trans*-NiCl(Ph)$(PPh_3)_2$ for 14 h in benzene to afford the neutral nickel(II) complexes **6** and **8**

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**Table 1. Crystal Data and Structure Refinement for Catalysts 6 and 8**

| | catalyst **6** | catalyst **8** |
|---|---|---|
| empirical formula | $C_{49}H_{46}NNiO_2P$ | $C_{62}H_{63}N_2NiO_2P$ |
| fw | 770.55 | 957.82 |
| temperature (K) | 187(2) | 293(2) |
| cryst syst | monoclicic | monoclicic |
| space group | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 18.0911(9) | 10.109(3) |
| $b$ (Å) | 11.5610(6) | 34.169(10) |
| $c$ (Å) | 18.9745(10) | 15.642(4) |
| $V$ (Å$^3$) | 3927.5(4) | 5383(3) |
| α (deg) | 90 | 90 |
| $\beta$ (deg) | 98.2480(10) | 94.89(2) |
| $\gamma$ (deg) | 90 | 90 |
| $Z$ | 4 | 4 |
| $D_{calc}$ (Mg/m$^3$) | 1.303 | 1.182 |
| abs coeff (mm$^{-1}$) | 0.576 | 0.434 |
| $F$(000) | 1624 | 2032 |
| cryst size (mm) | 0.31 × 0.17 × 0.11 | 0.42 × 0.36 × 0.28 |
| $\theta$ range (deg) | 1.45 to 26.04 | 1.77 to 25.05 |
| no. of indep rflns | 7732 ($R_{int} = 0.0547$) | 8762 ($R_{int} = 0.0343$) |
| abs corr | semiempirical from equivalents | psi-scan |
| max. and min. transmn | 0.9383 and 0.8403 | 0.5989 and 0.5644 |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0508, wR2 = 0.1029 | R1 = 0.0511, wR2 = 0.0348 |
| $R$ indices (all data) | R1 = 0.0781, wR2 = 0.11152 | R1 = 0.2615, wR2 = 0.0510 |
| largest diff peak and hole (e Å$^{-3}$) | 0.451 and −0.241 | 0.435 and −0.275 |
| type of diffractometer | Bruker SMART | Bruker SMART |
| monochromator | graphite | graphite |

with a free hydroxyl group. In order to protect 2′-OH from deprotonation, the sequence of adding reactants is important in the deprotonation of the ligands. The stoichiometric amount of NaH should be added slowly to the ligands so that the ligands are always in excess prior to the end of the reaction, and thus the corresponding monosodium salts were obtained.

The molecular structures of complexes **6** and **8** were confirmed by single-crystal X-ray structure analyses. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a concentrated solution of catalysts **6** and **8** in benzene, respectively. The crystallographic data including the collection and refinement parameters are summarized in Table 1, and their ORTEP diagrams are shown in Figures 1 and 2. In the solid state, the square-planar coordination around nickel is only slightly distorted and the six-membered $\overline{\mathrm{Ni{-}N{-}C{-}C{-}C{-}O}}$ ring is nearly planar owing to electron delocalization. The deviations of Ni atoms from the plane of their ligands are approximately 0.0483 and 0.0023 Å for **6** and **8**, respectively. The bulky 2,6-diisopropylbenzimine occupies the position *trans* to the triphenylphosphine ligand with a nearly linear P−Ni−N angle, and the phenyl group attached to the Ni atom lies *trans* to the O atom, similar to the binuclear neutral nickel(II) complex $[((2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NCH})\mathrm{C}_6\mathrm{H}_3\mathrm{ONi}(\mathrm{PPh}_3)\mathrm{Ph}]_2$ based on the 3,3′-bisalicylaldimine ligand reported previously.[39] The dihedral angles between the plane defined by the atoms of the salicylideniminato fragment and the planes of the phenyl ring *ortho* to the phenoxy group of the salicylideniminato fragment are 44.3° and 58.3° for **6** and **8**, respectively, and that for the corresponding binuclear complex is 53.6°. The Ni−O bond lengths of complexes **6** (1.9157(17) Å) and **8** (1.920(4) Å) are both longer than that (1.903(2) Å) found in the binuclear complex reported previously. The other way round, the (Ni)O−C bond lengths of complexes **6** (1.321(2) Å) and **8** (1.266(6) Å) are both much shorter than that (1.903(2) Å) observed in the binuclear complex. In addition, a great difference between the Ni−N bond lengths of single-nuclear complexes **6** (1.947(2) Å) and **8** (1.922(5) Å) and the corresponding binuclear complex (1.932(3) Å) is also observed.

Complex **6** shows a strong intramolecular O−H···O hydrogen bonding between the free hydroxyl group and the oxygen atom of the salicylideniminato ligand in the solid state. The O(2)H hydrogen atom is located 1.82 Å from the oxygen atom O(1) of the salicylideniminato ligand and 0.84 Å from the oxygen atom O(2) of the free hydroxyl group, as shown in Figure 1. The distance between the oxygen atom of the free hydroxyl group and that of the salicylideniminato ligand is 2.62 Å, and the O−H···O bond angle is 158°. These values are very close to those found for the intermolecular O−H···O bond in the phenoxo complex $[\mathrm{NiMe(OPh)(HOPh)(PMe_3)_2}]$ with free phenol.[40] However, as shown in Figure 2, the analogous hydrogen bonding does not exist in catalyst **8** because the free hydroxyl group is very far from the oxygen atom of the salicylideniminato ligand, which results from the steric effect of the bulky (2,6-diisopropylphenyl)iminomethylene *ortho* to the free hydroxyl group.

**Preparations of Supported Catalysts SC-6 and SC-8.** The hydroxyl group on the surface of silica reacted with excess $AlMe_3$, which afforded the modified silica containing 4.26 wt % Al. In order to covalently attach catalysts **6** and **8** to the silica, their toluene solutions were combined with the modified silica (Scheme 2). Via this procedure, only methane was generated as a byproduct and the unreacted nickel(II) catalysts could be easily washed off, while the pale yellow supported catalyst was successfully obtained. During the immobilization process, no obvious color changes occurred, and the supported catalyst was stable both in the solid state and in the solvent; therefore we presumed that the nickel(II) catalysts were not significantly activated by the aluminum species on the surface of the silica. In other words, the immobilization procedure does not change the coordination structure of the Ni center. Accordingly, the structures of **SC-6** and **SC-8** may be used to describe the supported forms of catalysts **6** and **8**. As shown in Figure 3, FTIR spectra of the free neutral catalysts and the corresponding

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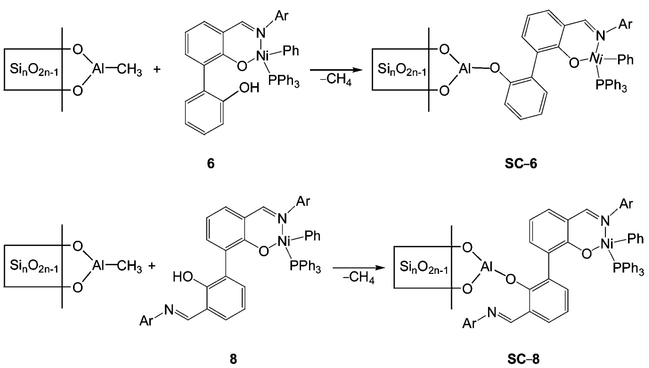
**Scheme 2**



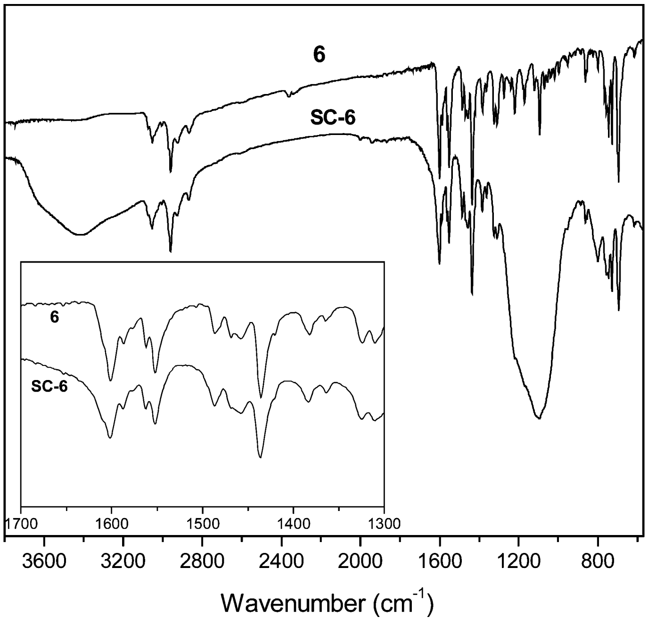


**Figure 3.** FTIR spectra of catalyst **6** and **SC-6**.

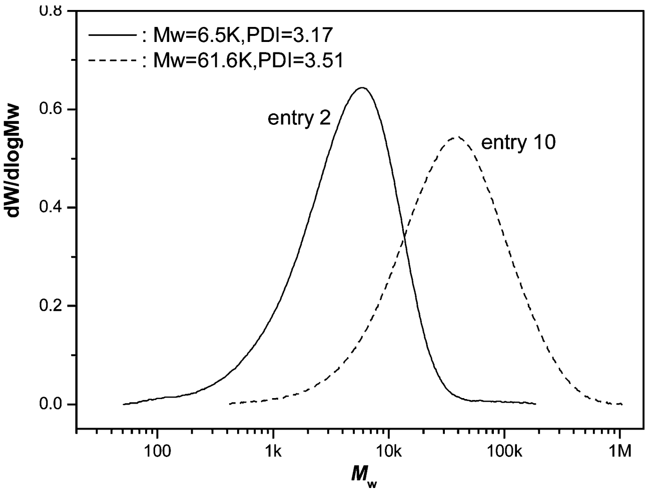


**Figure 4.** Molecular weight distributions of PEs synthesized by catalyst **6** (entry 2) and **SC-6** (entry 10).

supported ones indicate that the aluminum species on the surface of the silica did not change the coordination structure of the Ni center.

**Polymerization of Ethylene Using Catalysts 6 and 8.** In the absence of cocatalysts, complexes **6** and **8** were used to catalyze ethylene polymerization under ethylene pressures between 7 and 21 atms and at temperatures between 25 and 60 °C. The typical experimental results are summarized in Table 2. Catalysts **6** and **8** displayed high activities up to 1.47 × $10^6$ g PE/$mol_{Ni}$·h, which is comparable to that of neutral nickel(II) catalyst **1c**.[20] Grubbs reported that catalyst **1b** showed a catalytic activity of only 1.0 × $10^5$ g PE/$mol_{Ni}$·h for ethylene polymerization under similar conditions,[20] which is 1 order of magnitude lower than that of catalyst **6**. This difference may result from the intramolecular O−H···O hydrogen bonding in catalyst **6**. As for catalyst **8**, the more bulky (2,6-diisopropylphenyl)-iminomethylene at the C-3′ position accelerates $PPh_3$ dissociation. Therefore, catalyst **8** also exhibited much higher catalytic activity than neutral nickel(II) catalyst **1b**.

Interestingly, the molecular weights of the PEs produced by catalyst **6** are relatively low. The weight-average molecular weight ($M_w$) usually achieves only 5−6 kg/mol, which is not only lower than those of the PEs produced using catalyst **8**, but also much lower than those of the PEs reported by neutral nickel(II) catalyst **1b**. This indicates that the intramolecular O−H···O hydrogen bond in catalyst **6**, which decreases the electronic density at the Ni center, favors the $\beta$-hydride elimination. Consequently, the ratio of chain transfer speed to chain propagation speed increased during ethylene polymerization, and the low molecular weight PEs were obtained. Braunstein and co-workers also found that the analogous intramolecular hydrogen bonding in the SHOP-type catalysts dramatically influenced the molecular weight distribution of the ethylene oligomers and aided in obtaining products with low molecular weights.[41]

It is noteworthy that the PEs produced by catalyst **6** exhibited high branching degrees, which are higher than 80 branches per 1000 carbon atoms.[42] Compared with catalyst **6**, catalyst **8** produced PEs with lower branching degrees, which were usually lower than 45 branches per 1000 carbon atoms.

In a series of ethylene polymerization experiments, temperature and ethylene pressure were found to dramatically affect catalytic activities and properties of the resultant polymers. When the temperature was increased from 25 to 60 °C, at a constant pressure of 21 atm, the activity of catalyst **6** increased, and the highest value, 1.14 × $10^6$ g PE/$mol_{Ni}$·h, was observed at 40 °C followed by a gradual decrease (Table 2, entries 1−4). Meanwhile, $M_w$ of the PE decreased from 11.5 to 2.7 kg/mol and the degree of branching increased from 81 to 127 branches per 1000 carbon atoms. On the basis of our experimental results and the literature,[20] we found that 40−50 °C was the most suitable reaction temperature range for the two neutral nickel catalyst for ethylene polymerization. As ethylene pressure was increased from 7 to 21 atms, at 40 °C, the activity of catalyst **8** increased from 5.2 to 14.7 × $10^5$ g PE/$mol_{Ni}$·h (Table 2, entries 5−7). Simultaneously, $M_w$ of the PEs increased from 36.3 to 72.6 kg/mol and the branching degrees of the polymers decreased from 43 to 25 branches per 1000 carbon atoms.

**Ethylene Polymerizations Using Supported Catalysts SC-6 and SC-8.** Under 21 atm of ethylene pressure and at temperatures between 40 and 50 °C, supported catalysts **SC-6** and **SC-8** were used to catalyze ethylene polymerization without cocatalysts, and the typical experimental results are also summarized in Table 2. The immobilized catalysts exhibited activities up to 4.0 × $10^5$ g PE/$mol_{Ni}$·h for ethylene polymerization. Compared

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(42) The branching numbers for polyethylene were determined by $^1H$ NMR spectroscopy using the ratio of the number of methyl groups to the overall number of carbons (e.g., methyl + methylene + methine), and reported as branches per one thousand carbon atoms. See the following reference: Gates, D. P.; Svejda, S. A.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.

**Table 2. Ethylene Polymerization Results**[a]

| entry | cat. | wt % Ni | react temp (°C) | pressure (atm) | react time (min) | yield (g) | activity[b] $\times 10^{-5}$ | $M_w$[c] $\times 10^{-3}$ | PDI ($M_w$/$M_n$)[c] | $T_m$ (°C)[d] | branches[e]/1000C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **6** | | 25 | 21 | 60 | 0.7 | 0.7 | 11.5 | 2.32 | 72 | 81 |
| 2 | **6** | | 40 | 21 | 60 | 11.4 | 11.4 | 6.5 | 3.17 | 81 | 90 |
| 3 | **6** | | 50 | 21 | 60 | 10.7 | 10.7 | 3.6 | 2.57 | 68 | 112 |
| 4 | **6** | | 60 | 21 | 60 | 9.1 | 9.1 | 2.7 | 2.53 | 63 | 127 |
| 5 | **8** | | 40 | 7 | 60 | 5.2 | 5.2 | 36.3 | 3.15 | 100 | 43 |
| 6 | **8** | | 40 | 14 | 60 | 9.1 | 9.1 | 59.3 | 3.57 | 99 | 32 |
| 7 | **8** | | 40 | 21 | 60 | 14.7 | 14.7 | 72.6 | 3.22 | 102 | 25 |
| 8 | **SC-6** | 0.81 | 40 | 21 | 60 | 2.9 | 3.0 | 53.4 | 2.66 | 131 | 21 |
| 9 | **SC-6** | 0.81 | 50 | 21 | 60 | 2.4 | 2.4 | 47.5 | 3.45 | 130 | 26 |
| 10 | **SC-6** | 0.59 | 40 | 21 | 60 | 1.4 | 1.9 | 61.6 | 3.51 | 132 | 19 |
| 11 | **SC-6** | 0.59 | 50 | 21 | 60 | 1.3 | 1.7 | 55.6 | 3.03 | 120 | 24 |
| 12 | **SC-8** | 0.66 | 40 | 21 | 60 | 3.2 | 4.0 | 120.8 | 4.93 | 122 | 13 |
| 13 | **SC-8** | 0.66 | 60 | 21 | 60 | 2.9 | 3.5 | 86.1 | 4.25 | 121 | 19 |
| 14 | **6** | | 40 | 21 | 40 | 7.3 | 11.0 | 6.3 | 2.79 | 79 | 93 |
| 15 | **8** | | 40 | 14 | 40 | 6.0 | 9.0 | 60.1 | 3.41 | 99 | 33 |
| 16 | **8** | | 40 | 14 | 90 | 12.6 | 8.7 | 61.4 | 3.46 | 100 | 31 |
| 17 | **SC-6** | 0.59 | 40 | 21 | 90 | 2.2 | 2.0 | 62.9 | 3.56 | 132 | 21 |
| 18 | **SC-8** | 0.66 | 40 | 21 | 90 | 4.6 | 3.8 | 125.8 | 4.67 | 124 | 14 |

[a] Polymerizations run in 60 mL of toluene and 10 $\mu$mol of catalysts were used for entries 1−7. [b] In units of g PE/mol$_{Ni}$·h. [c] Determined by GPC. [d] Melting temperature is determined by DSC. [e] Determined by $^1$H NMR.

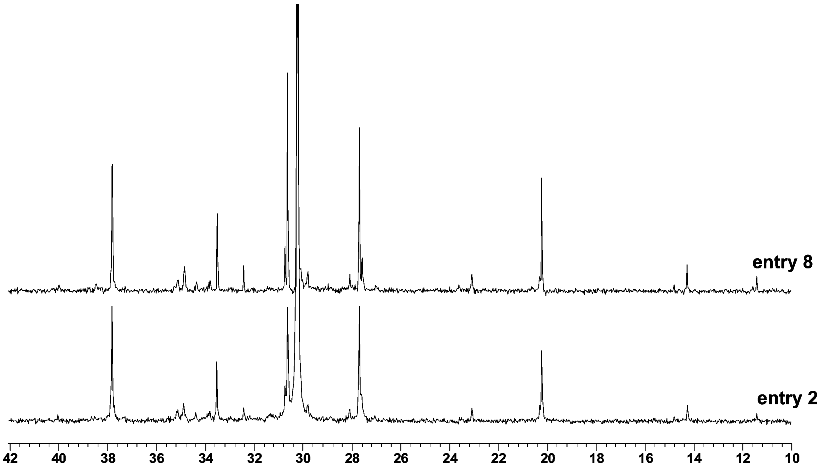

**Figure 5.** High-temperature $^{13}$C NMR spectra of the PEs by catalyst **6** (entry 2) and **SC-6** (entry 8).

with catalysts **6** and **8**, the activities of supported catalysts **SC-6** and **SC-8** decreased by more than half. The data of entries 8−13 of Table 2 indicate that supported catalyst **SC-8** showed slightly higher activity than supported catalyst **SC-6**, which is in accordance with the scenario of the corresponding homogeneous catalysts.

It is noteworthy that immobilized catalysts **SC-6** and **SC-8** produce PEs with much higher molecular weight and much lower degree of branching under the same conditions, compared with homogeneous catalysts **6** and **8**. Especially for catalyst **6** and immobilized catalyst **SC-6**, the molecular weight of the PE increased from 6.5 to 61.6 kg/mol, a magnitude enhancement as shown in Figure 4, and the degree of branching decreased from 90 to 19 branches per 1000 carbon atoms, a decrease of about 75%. Without doubt, these differences result from the changes in the structure of the ligands. Silica bound to catalyst **6** increased the steric bulk at the *ortho* position of the phenoxy group in the salicylideniminato fragment, which aided in inhibiting the chain migration and transfer to some extent, during ethylene polymerization. Accordingly, catalyst **SC-6** favors the production of PE with high molecular weight and low branching content.

As shown in Figure 5, high-temperature $^{13}$C NMR spectra show that all the PEs obtained are mainly branched by methyl. On the basis of Mandelkern's protocol,[43] all of the carbon resonances can be unambiguously assigned. Furthermore, the intensity of the peak corresponding to the methyl branch and the nearby carbon at $\delta = 20.35$, 27.62, and 37.83 in the high-temperature $^{13}$C NMR spectra indicates that methyl branches predominate in the resulting PE chains. DSC analyses display that the melting temperatures ($T_m$'s) of the PEs produced using supported catalysts are 120−132 °C, which are much higher than those (63−102 °C) of the PEs produced using catalysts **6** and **8**. The reason is that the molecular weight of the resulting PE significantly increased and the degree of branching dramatically decreased after the immobilization of homogeneous catalysts.

## Conclusions

Two new salicylideneiminato-based neutral Ni catalysts with free hydroxyl groups have been synthesized, and the corresponding supported neutral nickel catalysts have also been prepared. Remarkably, both bulky substituent and active hydroxyl functional group were introduced into the *ortho* position of the phenoxy group in the backbone of the salicylideniminato

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[43] Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41.

ligand at the same time, which avoided using complicated multistep reactions in the process of respectively introducing them on the ligand. By reaction of their free hydroxyl group with activated silica, these two neutral Ni catalysts were covalently bound to the support. Without cocatalyst, the two immobilized catalysts can be used to polymerize ethylene with high activity and produce PEs with high molecular weight. To our best knowledge, they are the first covalently supported neutral Ni catalysts that can produce PEs with high molecular weight.

## Experimental Section

**General Procedures and Materials.** All manipulations of air- and/or water-sensitive compounds were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Toluene, benzene, *n*-pentane, diethyl ether, methane dichloride, and tetrahydrofuran were purified by a solvent purification system (SPS, M.Braun Inertgas-Systeme GmbH). Commercial ethylene was directly used for polymerization without further purification. Trimethylaluminum was purchased from Akzo Nobel Chemical Inc. Silica was purchased from Aldrich Chemicals (200 mesh, surface area: 480 $m^2/g$) and pretreated by heating under vacuum at 150 °C for 12 h to remove the water absorbed before use. 2,6-Diisopropylaniline and NaH were purchased from Acros. *trans*-$[Ni(PPh_3)_2PhCl]$ was prepared according to the method reported.[44]

NMR spectra of the polyethylenes were recorded on a Varian Unity 400 spectrometer at 400 MHz with *o*-dichlorobenzene as a solvent at 120 °C. NMR data of the compounds and the complexes were obtained on a Bruker Avance 300 spectrometer at 300 MHz at ambient temperature. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter. Melting temperatures were recorded in the second heating run at a heating rate of 10 °C/min. High-temperature GPC was performed in 1,2,4-tirchlorobenzene at 140 °C using a PL-GPC 220 instrument equipped with three PL gel 10 $\mu$m mixed-B LS columns. A calibration curve was established with polystyrene standards. Aluminum contents of silica pretreated with trimethyaluminum and nickel contents of supported catalysts were determined by a TJA-POEMS-I inductively coupled plasma optical emission spectrometer (ICP-OES). Elemental analyses were performed on a Perkin-Elmer Series II CHN/O 2400 analyzer.

**Synthesis of Compound 2.** According to the reported method,[45] compound **2** was prepared from 2,2-biphenol and was isolated as a colorless, sticky liquid. $^1H$ NMR ($CDCl_3$): $\delta$ 3.25 (s, 6H, $CH_3$), 4.98 (d, 4H, $CH_2O$), 6.98 (m, 2H, Ar−H), 7.12−7.25 (m, 6H, Ar−H).

**Synthesis of Compound 3.** Under nitrogen, *n*-BuLi (1.6 M in hexane, 17.8 mL, 28.4 mmol) was added to a solution of compound **2** (7.63 g, 27.8 mmol) in ether (300 mL) at room temperature over 15 min. The mixture was stirred for 4 h and gave a meat-red suspension. After the mixture was cooled to 0 °C, *N,N*-dimethylformamide (2.37 mL, 30.5 mmol) was added dropwise over 10 min. The reaction mixture was warmed to room temperature and stirred overnight. Saturated $NH_4Cl$ (50 mL) was then added to the resulting milk-white solution to quench the reaction. The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (60 mL × 3). The combined organic phase was washed with water and brine and then dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to give compound **3** as colorless crystals in 48% yield. $^1H$ NMR ($CDCl_3$): $\delta$ 3.12 (s, 3H, $CH_3$), 3.28 (s, 3H, $CH_3$), 4.63 (s, 2H, $CH_2$), 5.04 (s, 2H, $CH_2$), 6.99 (m, 1H), 7.22 (m, 4H), 7.48 (d, 1H), 7.79 (d, 1H), 10.39 (s, 1H, CHO). FTIR (KBr, $cm^{-1}$): 1153[$\nu$(C−O−C)], 1602, 1584, 1496[$\nu$(C═C)], 1689[$\nu$(C═O)], 2849, 2828[$\nu$(C−H, −CHO)], 2959[$\nu$(C−H, $-CH_3$)]. Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.78; H, 6.93.

**Synthesis of Compound 4.** To a stirred solution of compound **3** (4.0 g, 13.2 mmol) in methane dichloride (10 mL) were added ethanol (50 mL) and hydrochloric acid (6 M, 40 mL). Under nitrogen, the mixture was refluxed at 60 °C for about 8 h. After the mixture was cooled to room temperature, the organic phase was separated and saturated $NaHCO_3$ solution was added to the aqueous layer up to pH = 7−8. The aqueous phase was extracted with methane dichloride (30 mL × 3), and the combined organic phase was washed with water and then dried over $Na_2SO_4$. Concentration with a rotary evaporator gave compound **4** as colorless crystals in 99% yield. $^1H$ NMR ($CDCl_3$): $\delta$ 6.20 (s, 1H, 2′-OH), 7.00 (m, 2H), 7.11−7.21 (m, 3H), 7.61 (d, 2H), 9.92 (s, 1H, CHO), 12.05 (s, 1H, 2-OH). FTIR (KBr, $cm^{-1}$): 1607, 1590, 1507[$\nu$(C═C)], 1638[$\nu$(C═O)], 2847, 2756[$\nu$(C−H, −CHO)], 3324[$\nu$(O−H)]. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 67.92; H, 6.07.

**Synthesis of Compound 5.** To a stirred solution of compound **4** (1.61 g, 7.66 mmol) in ethanol (45 mL) were added 2,6-diisopropylaniline (2.06 g, 10.72 mmol) and formic acid (0.05 mL) as a catalyst. The mixture was refluxed under nitrogen for 24 h. The resultant yellow solution was concentrated with a rotary evaporator, and the excess 2,6-diisopropylaniline was evaporated under reduced pressure. After recrystallizing the residue from petroleum ether at −20 °C ligand **5** was isolated as orange crystals in 76% yield. $^1H$ NMR ($CDCl_3$): $\delta$ 1.22 (d, $^3J$ = 6.6 Hz, 12H, $CH_3$), 3.02 (sept, $^3J$ = 6.6 Hz, 2H, CH), 7.09−7.17 (dd, 3H, Ar−H), 7.24 (d, 3H, Ar−H), 7.35−7.47 (m, 3H, Ar−H), 7.53 (s, 1H, 2′-OH), 7.61 (dd, 1H, Ar−H), 8.40 (s, 1H, CH═N), 15.25 (s, 1H, 2-OH). $^{13}C$ NMR ($CDCl_3$): 24.03, 28.40, 116.43, 117.25, 118.93, 122.93, 123.64, 124.17, 125.65, 128.31, 129.07, 132.35, 135.83, 136.89, 139.30, 146.47, 158.28, 160.81, 167.11. FTIR (KBr, $cm^{-1}$) $\nu$: 3432 (OH), 1643 (CH═N), 1616, 1473, 1458 $cm^{-1}$ (Ph). Anal. Calcd for $C_{26}H_{31}NO_2$: C, 80.17; H, 8.02; N, 3.60. Found: C, 80.03; H, 8.07; N, 3.65.

**Synthesis of Complex 6.** To a solution of ligand **5** (0.47 g, 1.26 mmol) in anhydrous THF (10 mL) was added sodium hydride (30.2 mg, 1.26 mmol) in THF (10 mL). The resultant mixture was stirred at room temperature for 4 h, then filtered and evaporated. The pale yellow solid residue and *trans*-$[Ni(PPh_3)_2PhCl]$ (0.88 g, 1.26 mmol) were dissolved in benzene (35 mL) and stirred overnight at room temperature. The resultant mixture was filtered, and the filtrate was concentrated under vacuum to ca. 5 mL. Pentane (8 mL) was added to the residue. The resultant yellow precipitate was recrystallized with benzene/pentane to give **6** as a yellow powder in 72% yield. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 1.17 (d, $J_{HH}$ = 6.6 Hz, 6H, $CH_3$), 1.33 (d, $J_{HH}$ = 6.3 Hz, 6H, $CH_3$), 4.32 (bs, 2H, CH), 6.25 (t, 2H, Ar−H), 6.35 (t, 1H, Ar−H), 6.48 (dd, 1H, Ar−H), 6.71 (t, 1H, Ar−H), 6.86−6.94 (m, 3H, Ar−H), 6.96−7.09 (m, 15H, Ar−H), 7.49 (dd, 2H, Ar−H), 7.69 (m, 5H, Ar−H), 8.01 (d, 1H, $J_{HP}$ = 6.3 Hz, N═CH), 8.06 (s, 1H, 2′-OH). $^{13}C$ NMR ($C_6D_6$): $\delta$ 23.0, 25.8, 29.3, 106.4, 116.8,118.8, 119.8, 121.7, 123.2, 123.5, 125.6, 126.6, 130.0, 130.7, 131.0, 131.6, 133.4, 134.2, 134.5, 137.4, 138.2, 140.8, 149.8, 156.5, 167.6. Anal. Calcd for $C_{49}H_{46}NNiO_2P$: C, 76.38; H, 6.02; N, 1.82. Found: C, 76.53; H, 6.08; N, 1.91.

**Synthesis of Compound 7.** Compound **7** was prepared according to the procedure reported previously.[39] $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 1.09 (d, 12H, $CH_3$), 1.11 (d, 12H, $CH_3$), 2.97 (sept, 4H, CH), 7.01 (t, 2H, Ar−H), 7.13 (s, 6H, Ar−H), 7.47 (d, 2H, Ar−H), 7.53 (d, 2H, Ar), 8.33 (s, 2H, Ar−H). $^{13}C$ NMR (300 MHz, $CDCl_3$): $\delta$ 24.04, 28.49, 118.92, 119.49, 123.65, 125.86, 132.49, 136.09, 139.30, 146.59, 159.20, 167.29. FTIR (KBr, $cm^{-1}$): 1581, 1460[$\nu$(C═C)], 1615[$\nu$(C═N)], 2962[$\nu$(C−H, $-CH_3$)], 3408[$\nu$(O−

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[44] Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279.

[45] Zhang, H. C.; Huang, W. S.; Pu, L. *J. Org. Chem.* **2001**, *66*, 481.

H)]. Anal. Calcd for $C_{38}H_{44}N_2O_2$: C, 81.39; H, 7.91; N, 5.00. Found: C, 81.52; H, 7.86; N, 4.97.

**Synthesis of Complex 8.** Starting from compound **7**, which was prepared according to our previous method, complex **8** was isolated as a brown powder in 59% yield following the procedure analogous to the synthesis of catalyst **6**. $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 1.09 (d, $J_{HH}$ = 6.6 Hz, 12H, $CH_3$), 1.30 (d, $J_{HH}$ = 6.9 Hz, 6H, $CH_3$), 1.39 (d, $J_{HH}$ = 6.9 Hz, 6H, $CH_3$), 3.06 (sept, 2H, CH), 4.27 (sept, 2H, CH), 6.33−7.91 (m, 32H, Ar−H), 8.02 (d, 1H, $J_{HP}$ = 5.7 Hz, N═CH), 8.21 (s, 1H, 2′-OH), 8.30 (s, 1H, N═CH). $^{13}C$ NMR ($C_6D_6$): $\delta$ 22.6, 25.3, 25.5, 28.8, 107.1, 115.8, 117.4, 117.8, 118.7, 120.7, 122.3, 122.6, 122.8, 123.2, 123.5, 125.1, 125.8, 126.1, 128.3, 128.7, 129.4, 130.3, 131.2, 132.7, 134.9, 137.3, 140.1, 141.3, 149.0, 166.3, 169.6. Anal. Calcd for $C_{62}H_{63}N_2NiO_2P$: C, 77.74; H, 6.63; N, 2.92. Found: C, 78.02; H, 6.58; N, 2.81.

**Pretreatment of the Silica.** To a suspension of silica (3.2 g) in toluene (40 mL) was added $AlMe_3$ (0.92 mL, 9.6 mmol) over 5 min at room temperature. The mixture was stirred for 4 h and then was filtered. The filter cake was washed with toluene (3 mL × 5) and hexane (3 mL × 3) and then was dried to give the modified silica as a white powder. Elemental analysis: 4.26 wt % Al.

**Preparation of Supported Catalyst SC-6.** To a solution of complex **6** (34.8 mg, 45.2 mmol) in toluene (10 mL) was added a suspension of the above modified silica (194 mg) in toluene (10 mL) over 10 min at room temperature. The mixture was stirred for 2 h and then was filtered. The filter cake was washed with toluene (3 mL × 3) at 50 °C and then was dried to give the supported catalyst **SC-6** as a pale yellow powder.

**Preparation of Supported Catalyst SC-8.** Supported catalyst **SC-8** was prepared following the method analogous to that for the synthesis of supported catalyst **SC-6**.

**General Procedure for Ethylene Polymerization.** A 100 mL autoclave was heated under vacuum to 140 °C for 10 h and then was cooled to the desired reaction temperature in an oil bath with constant temperature. The vessel was purged by ethylene three times and then was charged with toluene (35 mL) under vacuum. A solution of catalyst **6** or **8** (10 $\mu$mol) in toluene (15 mL) or a suspension of supported catalyst (ca. 70 mg) in toluene (15 mL) was added into the autoclave by a syringe. The reactor was sealed and pressurized to the desired level, and the stirring motor was engaged. Temperature control was maintained by internal cooling water coils with temperature increases within 2 °C in every case. After the prescribed reaction time, the stirring motor was stopped and the reactor was vented, and the polymer was isolated via precipitation from ethanol and dilute HCl (10%). The solid polyethylene was filtered, washed with ethanol, and dried at 60 °C for 15 h under vacuum.

**Crystallographic Studies.** The X-ray crystallographic analyses were performed using crystal **6** with the size 0.31 × 0.17 × 0.11 mm and **8** with the size 0.42 × 0.36 × 0.28 mm, obtained by slow diffusion of pentane into a concentrated solution of catalysts **6** and **8** in benzene, respectively. The intensity data were collected with the $\omega$ scan mode (293 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Lorentz, polarization factors were made for the intensity data, and absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least-squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

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**Supporting Information Available:** Figures and tables giving crystallographic data and crystal cell diagrams of catalysts **6** and **8**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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