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Synthesis and Ethylene Polymerization Activity of a Novel, Highly Active Single-Component Binuclear Neutral Nickel(II) Catalyst

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The novel binuclear neutral nickel(II) complex $[((2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{NCH})\mathrm{C}_6\mathrm{H}_3\mathrm{ONi}(\mathrm{PPh}_3)\mathrm{Ph}]_2$ (**5**), based on the 3,3′-bisalicylaldimine ligand, has been synthesized in high yield, and its structure has been confirmed by X-ray crystallography, elemental analysis, and ^{1}H NMR and ^{13}C NMR spectra. Used in the polymerization of ethylene as an active single-component catalyst, the complex exhibited a high catalytic activity of up to 4.55×10^5 g of PE/((mol of Ni) h), and polyethylenes with a weight-average molecular weight ($\bar{M}_\mathrm{w}$) of up to 487.7 kg/mol and relatively broad molecular weight distribution ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} = 2.8{-}3.8$) were produced.

Introduction

Over the past decade, interest in late-transition-metal olefin polymerization catalysts has mushroomed with a major advance which came with Brookhart's discovery of cationic Ni(II) and Pd(II) catalysts.[1−15] However, it is difficult for electrophilic cationic nickel catalysts to copolymerize olefins with polar monomers. Therefore, a number of neutral nickel catalysts (less electrophilic) have been developed to overcome this limitation. The most industrially relevant neutral nickel catalysts are the SHOP-type catalysts, developed for the conversion of ethylene to linear α-olefins.[16−20] Modified SHOP catalysts convert ethylene to high-molecular-weight polymers, but only under special conditions.[21−23] Recently, Grubbs and co-workers reported a series of highly active neutral single-component salicylaldimine-based nickel(II) catalysts (Grubbs catalysts) such as **1a−d** (Chart 1) for ethylene polymerization, which greatly stimulated research in this area.[24−27] Subsequently, a large number of neutral nickel(II) and palladium(II) catalysts which can homopolymerize olefins and copolymerize ethylene with polar monomers were reported.[28−39] They were so tolerant to the polar func-

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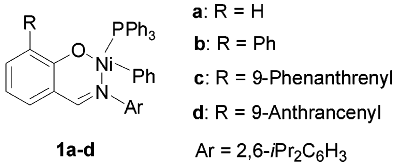
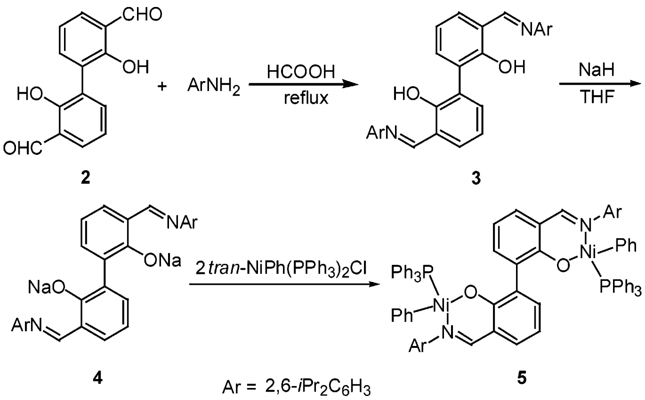
Chart 1



Scheme 1



tional groups that some polymerizations can be conducted in aqueous emulsion, affording stable polymer lattices.[40−43]

It has been reported that complex **1a** is not active for ethylene polymerization as a single-component catalyst because its deactivation easily occurs by a ligand disproportionation and dimerization.[24] Grubbs et al. found that the introduction of a bulky substituent at the ortho position of the phenoxy group not only blocks the axial faces of the nickel center and retards the rate of chain termination but also enhances the catalytic activity by accelerating PPh_3 dissociation and decreases the rate of catalyst deactivation.[24−27,44] For example, catalyst **1d**, with a bulky 9-anthracenyl at the ortho position of the phenoxy group, displays a high activity of up to 3.7 × 10^6 g of PE/((mol of Ni) h) under optimized conditions.[45] However, just as Mecking pointed out,[46] the syntheses of the ligands containing a bulky ortho-substituted group require multistep reactions in very low yields. Furthermore, the starting material 2-bromophenol is expensive.

In view of these, here we report the synthesis of the binuclear Ni(II) complex **5**, based on the 3,3′-bisalicylaldimine ligand, starting from the readily available 2,2′-biphenol (Scheme 1) and its catalytic activity as a single-component catalyst for ethylene polymerization. In this complex, each salicylaldimine unit plays the role of a bulky group at the C-3 position of the other unit.

Table 1. Crystal Data and Structure Refinement for Complex 5

empirical formula	$C_{86}H_{82}N_2Ni_2O_2P_2$
fw	1354.90
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	14.685(2)
b (Å)	14.691(2)
c (Å)	20.695(4)
V (Å^3)	4171.6(12)
α (deg)	95.985(3)
β (deg)	101.920(3)
γ (deg)	104.487(3)
Z	2
D_{calcd} (Mg/m^3)	1.079
abs coeff (mm^{-1})	0.532
F(000)	1428
cryst size (mm)	0.34 × 0.21 × 0.09
θ range (deg)	1.63−26.09
no.of indep rflns	15 959 (R_{int} = 0.0186)
abs cor	semiempirical from equivalents
max and min transmn	0.9536 and 0.8397
refinement method	full-matrix least squares on F^2
final R indices ($I > 2\sigma(I)$)	R1 = 0.0647, wR2 = 0.1738
R indices (all data)	R1 = 0.0926, wR2 = 0.1967
largest diff peak and hole (e Å^{-3})	1.347 and −0.391
type of diffractometer	Bruker SMART
monochromator	graphite

Results and Discussion

Synthesis and Structure of the Binuclear Neutral Nickel(II) Catalyst 5. The synthetic route for the binuclear neutral nickel(II) catalyst **5** is shown in Scheme 1. The free ligand **3** was synthesized via the condensation reaction of the corresponding compound **2** and excess 2,6-diisopropylaniline in excellent yield. The deprotonation of the free ligand **3** readily proceeded with excess sodium hydride in anhydrous THF at room temperature. The isolated sodium salt **4** reacted with 2 equiv of *trans*-$NiCl(Ph)(PPh_3)_2$ for 14 h in benzene to afford the binuclear neutral nickel(II) catalyst **5**. Usually in the syntheses of salicylaldimine-based neutral Ni complexes, as the residual *trans*-$NiCl(Ph)(PPh_3)_2$ is difficult to remove from the reaction system, its starting quantity is slightly less than the stoichiometric amount.[27,32,36] In our case, however, it is clear that this approach would result in a mixture of the binuclear Ni complex and the mononuclear complex, and our multiple attempts to separate these two complexes have not been successful. Therefore, we found that it was critical that 2 equiv of *trans*-$NiCl(Ph)(PPh_3)_2$ should be used vs salicylaldimine sodium salt **4**. Nevertheless, multiple recrystallizations in benzene/pentane remained necessary to give brown-purple crystals of the binuclear Ni complex **5**. Surprisingly, the complex is so insensitive to moisture that it can be exposed to ambient atmosphere for several days without notable change.

Crystals of the binuclear neutral nickel(II) complex suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a benzene solution of **5**. The crystallographic data together with the collection parameters and the refinement parameters are summarized in Table 1. As shown in Figure 1, in the solid state, the molecule adopts a nearly square-planar coordination geometry with two Ni atoms displaced approximately 0.09 Å (Ni1) and 0.01 Å (Ni2) from the plane of their ligands, respectively. Although the two segments have almost the same Ni−P, Ni−N, Ni−O, and Ni−C bond lengths and seemingly identical chemical environments, the coordination geometries of the two

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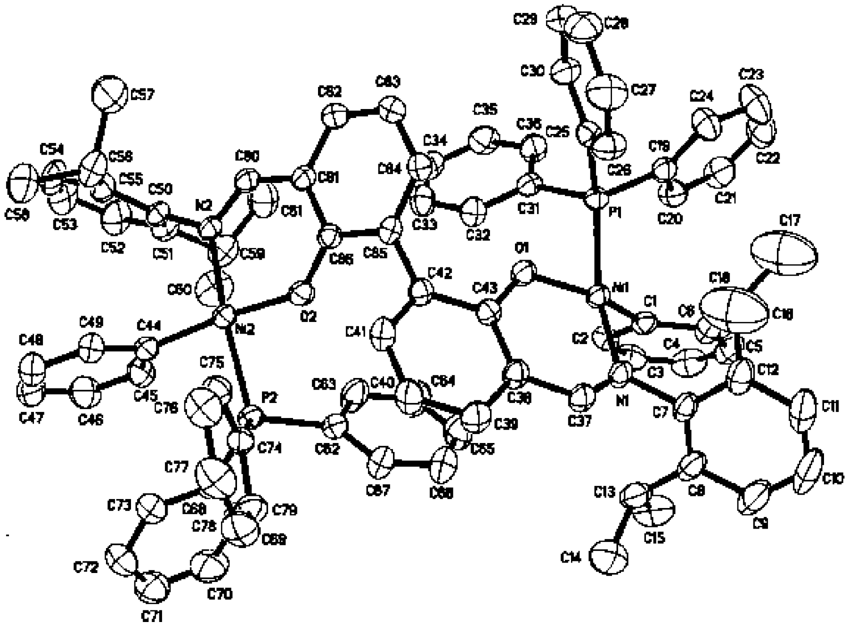

Figure 1. ORTEP diagram of **5**. (Two benzene solvent molecules of crystallization are omitted.) Selected bond distances (Å) and angles (deg): Ni(1)−C(1) = 1.896(3), Ni(1)−O(1) = 1.903(2), Ni(1)−N(1) = 1.932(3), Ni(1)−P(1) = 2.1846(10), O(1)−C(43) = 1.309(4), N(1)−C(7) = 1.449(4), N(1)−C(37) = 1.305(4), C(37)−C(38) = 1.420(5), P(1)−C(25) = 1.841(4); N(1)−Ni(1)−P(1) = 162.45(9), N(2)−Ni(2)−P(2) = 173.12(9), C(1)−Ni(1)−O(1) = 158.61(13), C(44)−Ni(2)−O(2) = 168.70(14), O(1)−Ni(1)−P(1) = 88.42(7), O(2)−Ni(2)−P(2) = 84.97(8).

Table 2. Ethylene Polymerization Results Catalyzed by Catalyst 5[a]

entry	reacn temp (°C)	time (min)	pressure (atm)	yield (g)	10^{-5}(activity)[b]	$10^{-3}\bar{M}_w$	PDI ($\bar{M}_w/\bar{M}_n$)	T_m (°C)[c]	branches[d]/1000C
1	42	60	7	1.5	0.75	335.6	3.75	122	15
2	43	60	14	4.7	2.35	462.3	2.92	124	12
3	43	60	21	9.1	4.55	487.7	2.82	123	11
4	54	60	21	6.6	3.30	314.2	2.87	123	14
5	64	60	21	3.6	1.80	128.2	2.78	120	17
6[e]	43	60	14	6.1	3.05	353.7	2.76	124	15
7[f]	43	60	21	7.9	3.95	438.6	3.46	123	16
8	43	30	14	2.1	2.10	421.4	3.01	124	14
9	43	90	14	6.7	2.23	447.1	2.91	123	12
10	43	120	14	8.4	2.10	451.8	2.87	122	13

[a] Polymerizations run using 10 μmol of catalyst in 60 mL of toluene with a maximum exotherm of 2 °C. [b] In units of g of PE/((mol of Ni) h). [c] Melting temperature is determined by DSC. [d] Determined by ^{1}H NMR. [e] A 4.5 equiv portion of $(COD)_2Ni$ was used as phosphine scavenger. [f] Without efficient cooling, exotherm from 43 to 55 °C.

Ni atoms are different. The bond angles of N(1)−Ni(1)−P(1), C(1)−Ni(1)−O(1), and O(1)−Ni(1)−P(1) are all different from the corresponding bond angles for Ni(2), and the coplanarity of Ni(1) atom and the atoms around it is not identical with that of Ni(2). The root-mean-square (RMS) deviations from the planes for the atoms Ni(1), O(1), N(1), C(37), C(38), C(43) and the atoms Ni(1), O(1), N(1), P(1), C(1) are 0.0710 and 0.2631 Å, respectively, while those for the atoms Ni(2), O(2), N(2), C(80), C(81), C(86) and the atoms Ni(2), O(2), N(2), P(2), C(44) are 0.0112 and 0.1018 Å, respectively.

Ethylene Polymerization Behavior of the Binuclear Neutral Nickel(II) Catalyst 5. According to literature reports,[24,25] in the absence of other added activators, complex **1a** exhibited no activity for ethylene polymerization. Even when $(COD)_2Ni$ or $B(C_6F_5)_3$ was used as a phosphine acceptor, only a low catalytic activity was observed.[24−27] Interestingly, the binuclear Ni complex **5**, which may be treated as the product of the two **1a** molecules coupled at the ortho position of the phenoxy group, is capable of polymerizing ethylene with an activity of up to 4.55 × 10^5 g of PE/((mol of Ni) h) without any cocatalyst. This activity is higher than that of the sterically modified Grubbs catalysts reported, such as **1b** (1.0 × 10^5 g of PE/((mol of Ni) h)) and **1c** (3.1 × 10^5 g of PE/((mol of Ni) h)).[24−27] Furthermore, in comparison with the binuclear single-component neutral nickel catalysts reported earlier, whose catalytic activities were up to 8.5 × 10^4 g of PE/((mol of Ni) h),[39] catalyst **5** also has much higher activity. These results clearly indicate that two separate Ni complex units act as the mutual bulky ortho-substituted steric groups for each other, which leads to the excellent catalytic performance.

In our initial ethylene polymerization experiments using **5** as a catalyst, the temperature increases were not as rapid as those when highly active catalysts were used, such as cationic Ni and Fe catalysts. For example, using 10 μmol of catalyst loading, a polymerization starting at 43 °C and 21 atm can heat up to 55 °C within 1 h without temperature control (Table 2 entry 7), and the reaction temperature can continue to increase after 1 h. To accurately compare activities and lifetimes under various reaction conditions, it is critical to control reaction temperature for a highly active catalyst. Thus, an autoclave with cooling water coils was used to control the temperature of the reaction solutions. With circulating cooling water, the temperature increase can be controlled to within 2 °C of the initial temperature as the autoclave was pressurized and throughout the polymerization runs.

In a series of ethylene polymerization trials, the temperature and ethylene pressure were found to have a dramatic effect on catalyst activity. As can be seen in Table 2, when the ethylene pressure increases from 7 to 21 atm, the catalyst activity rises from 0.75×10^5 to 4.55×10^5 g of PE/((mol of Ni) h) (entries 1−3). It is also found that the catalyst activity decreases gradually with temperature, increasing from 43 to 64 °C, and the highest activity comes at 43 °C (entries 3−5). Moreover, using $(COD)_2Ni$ as a phosphine scavenger increases the catalyst activity and decreases the molecular weight of the resultant polymer (entry 6), which is consistent with what was found for Grubbs catalysts **1b**−**d**. Additionally, the activity of the catalyst remains essentially same at 0.5, 1, 1.5, and 2 h runs under the same conditions (entries 2 and 8−10), indicating that the lifetime of catalyst **5** is longer than 2 h.

It is noteworthy that the PEs obtained using catalyst **5** display a molecular weight distribution (PDI > 2.8) slightly broader than that for the PEs reported by Grubbs using their catalysts (PDI < 2.2) under similar conditions. A possible reason for this is that complex **5** is asymmetric in structure, as mentioned above. The two Ni units are not identical, which may result in two slightly different active sites during the polymerization. The two different active species then lead to the broadening of the molecular weight distribution, in comparison to the scenario where there is only one active species present. In addition, the binuclear Ni complex **5** produces PEs of higher molecular weight than Grubbs catalysts under similar conditions. With the ethylene pressure increasing, weight-average molecular weights of the polymers display an increasing trend and are usually higher than 400 kg/mol, which are generally higher than those of the PEs produced, employing Grubbs catalysts.[24−27] This suggests that the rate of chain transfer for catalyst **5** is quite slow relative to the rate of chain propagation.

High-temperature ^{13}C NMR spectra show there are few ethyl and longer branches besides methyl ones in the resulting PE chains (cf. Figure 2 in the Supporting Information). On the basis of Mandelken's protocol,[47] all of the corresponding carbon resonances can be assigned unambiguously. Furthermore, in the high-temperature ^{1}H NMR spectrum (cf. Figure 3 in the Supporting Information), the methyl resonance at δ 0.93 ppm splits into a doublet, which again indicates that the branches in the polyethylenes are mainly CH_3 branches. According to the ^{1}H NMR result, the average branching content of the PEs is around 10−15 branches per 1000 carbon atoms,[48] which is slightly higher than those of the PEs produced using Grubbs catalysts (5−8 branches per 1000 carbon atoms) under similar conditions. This may be the reason the melting temperatures of our PEs are slightly lower ($T_m = 122{-}124$ °C, vs 129.5 °C reported by Grubbs).

In conclusion, a new binuclear 3,3′-bisalicylaldimine-based neutral nickel(II) complex, derived from the readily available 2,2′-biphenol, has been developed. Employed as a single-component catalyst for ethylene polymerization, this well-defined complex displayed a high catalytic activity and produced high-molecular-weight polyethylenes with broad molecular weight distribution and moderate branching degree of ca. 10−15 methyl branches per 1000 carbon atoms.

Experimental Section

General Considerations. 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, and tetrahydrofuran were refluxed with sodium/benzophenone ketyl and were distilled under nitrogen prior to use. Methylene dichloride was distilled from drying CaH_2 under nitrogen. Commercial ethylene was directly used for polymerization without further purification. 2,6-Diisopropylaniline and NaH were purchased from Acros. *trans*-$[Ni(PPh_3)_2PhCl]$[49] and $(COD)_2Ni$ (bis(1,5-cyclooctadiene)nickel)[50] were prepared according to the analogous methods reported, respectively.

The NMR spectra of the polyethylenes were recorded on a Varian Unity 400 MHz spectrometer with *o*-dichlorobenzene as the solvent at 120 °C. The other NMR data of the ligands and the complex were obtained on a Bruker 300 MHz spectrometer at ambient temperature, with $CDCl_3$ or C_6D_6 as the solvent. The IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a heating rate of 10 °C/min. The weight-average molecular weight ($\bar{M}_w$) and the polydispersity index (PDI) of the polyethylene samples were determined via high-temperature GPC according to the procedure reported previously.[51] Elemental analyses were performed on a Perkin-Elmer Series II CHN/O analyzer 2400.

Synthesis of Compound 2. In accordance with the reported method,[52] compound **2** was prepared from 2,2-biphenol. ^{1}H NMR ($CDCl_3$): δ 7.07 (t, 2H, Ar H), 7.56 (m, 4H, Ar H), 9.89 (s, 2H, =CHO), 11.3 (s, 2H, OH). IR (KBr) ν 3435 (OH), 1633 (CH=O), 1613, 1477, 1456 cm^{-1} (Ph). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.36; H, 4.11.

Synthesis of Compound 3. To a stirred solution of compound **2** (2.42 g, 10 mmol) in dried methylene dichloride (40 mL) were added 2,6-diisopropylaniline (4.43 g, 25 mmol) and formic acid (0.3 mL) as a catalyst. The mixture was refluxed and stirred for 24 h. During the stirring period, a yellow solution was formed. The evaporation of solvent gave a yellow solid powder. The crude product was washed with ethanol and dried. Yield: 5.1 g, 91%. ^{1}H NMR ($CDCl_3$): δ 1.09 (d, $^3J = 6.8$ Hz, 12H, CH_3), 1.11 (d, $^3J = 6.8$ Hz, 12H, CH_3), 2.97 (sept, $^3J = 6.8$ Hz, 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). 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.

Sodium Salt of Compound 3. A solution of **3** (0.43 g, 0.76 mmol) in anhydrous THF (15 mL) was added to sodium hydride (46 mg, 1.9 mmol). The resultant mixture was stirred at room temperature for 4 h and then filtered and evaporated. The solid residue was immediately used in the next step without further purification.

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Synthesis of Complex 5. The Na salt of **3** obtained above and *trans*-[Ni(PPh_3)$_2$PhCl] (1.06 g, 1.52 mmol) were dissolved in benzene (45 mL) in a Schlenk flask and stirred at room temperature for 14 h. The resultant mixture was filtered, and the filtrate was concentrated under vacuum to ca. 6 mL. Pentane (30 mL) was added to the reaction mixture. A brown-purple solid crystallized from solution and was isolated by filtration to give **5**. Yield: 0.73 g (71%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.32 (d, J_{HH} = 6.6 Hz, 12H, CH_3), 1.40 (d, J_{HH} = 6.3 Hz, 12H, CH_3), 4.46 (m, 4H, CH), 5.54−7.81 (m, 52H, Ar H), 7.93 (d, 2H, J_{HP} = 9.3 Hz, N=CH). ^{13}C NMR (C_6D_6): δ 23.2, 26.2, 29.3, 114.0, 119.9, 121.6, 123.2, 125.5, 126.4, 129.8, 130.5, 132.4, 132.8 (m), 134.8 (d, J_{CP} = 39 Hz), 137.2, 138.5, 141.3, 150.4, 164.0, 166.6. Anal. Calcd for $C_{86}H_{82}N_2Ni_2O_2P_2$: C, 76.23; H, 6.10; N, 2.07. Found: C, 76.32; H, 6.06; N, 2.11.

Ethylene Polymerization. A 100 mL autoclave was heated under vacuum up 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 three times with ethylene and then was charged with toluene (50 mL) under vacuum. A 10 μmol amount of catalyst dissolved in 10 mL of toluene was added into the autoclave by 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, 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 10 h under vacuum.

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Supporting Information Available: A CIF file giving crystallographic data and a figure giving a crystal cell diagram of complex **5** and figures giving the GPC and ^{1}H NMR and ^{13}C NMR spectra of a typical PE sample (entry 3). This material is available free of charge via the Internet at http://pubs.acs.org.

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