# Synthesis of Allylnickel Complexes with Phosphine Sulfonate Ligands and Their Application for Olefin Polymerization without Activators

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Summary: Phosphine sulfonate nickel complexes  $[(o-Ar_2-PC_6H_4SO_3)Ni(allyl)]$  (Ar = Ph,  $o-MeOC_6H_4$ ) are prepared and used as catalysts for ethylene polymerization. The products were low molecular weight polyethylenes possessing only methyl branches. The activity for ethylene polymerization with the phenyl-substituted complex was comparable to that of omethoxyphenyl-substituted complex in the absence of activator. Comparison with the corresponding allylpalladium complex revealed that the nickel catalysts produced polyethylenes with lower molecular weight and more branches than the palladium catalyst.

## Introduction

Transition-metal-catalyzed insertion polymerization of olefins has been studied and used considerably due to its great ability to control polymer microstructures. Particularly, early transition metal catalysts, such as Ziegler-Natta catalysts, are most widely utilized for olefin polymerization. Recent intensive studies have also developed the use of late-transition metals as catalysts for olefin polymerization.<sup>1</sup> One of the most elegant examples is Brookhart palladium/α-diimine catalysts used for copolymerization of ethylene with alkyl acrylates.<sup>2</sup> The palladium/ $\alpha$ -diimine catalysts produce unique amorphous-like highly branched polyethylenes with over 100 branches per 1000 carbon atoms via chain-walking. The catalysts were also successfully applied to copolymerization of ethylene/ $\alpha$ -olefins with alkyl acrylates for the first time. More recently, Drent and co-workers reported copolymerization of ethylene with alkyl acrylates<sup>3a</sup> using in situ generated palladium catalysts bearing phosphine sulfonate ligands.<sup>3</sup> Polymers produced by the catalysts have very few branches and acrylate units are incorporated into the polymer backbone. In recent years, the phosphine sulfonate palladium catalysts have been extensively studied<sup>4-7</sup> because linear copolymers of ethylene and polar vinyl monomers may provide control over important properties such as toughness and adhesion. Studies by many researchers, including our group, have revealed that in situ generated and isolated phosphine sulfonate palladium catalysts also copolymerize ethylene with other polar vinyl monomers, such as vinyl ethers,<sup>5a</sup> vinyl fluoride,<sup>5b</sup> acrylamides, vinyl pyrrolidone,<sup>6</sup> and acrylonitrile.<sup>7</sup> However, improvements in catalytic activity and molecular weight of produced polymers are still desired.

In contrast, several nickel catalysts have shown considerable catalytic activity and heteroatom tolerance. For example, Brookhart's nickel/ $\alpha$ -diimine catalysts display higher activity and produce polymers with higher molecular weight and fewer branches than the corresponding palladium catalysts. Grubbs and co-workers reported considerably active nickel catalysts bearing salicylaldiminato ligand for ethylene polymerization to generate high molecular weight polymers.<sup>8</sup>

Nickel catalysts bearing phosphine sulfonate ligands can be candidates for more desirable catalysts. Rieger and co-workers have reported the corresponding phenyl nickel catalysts with triphenylphosphine ligand and performed ethylene polymerization with or without activators, such as  $B(C_6F_5)_3$  or  $Ni(cod)_2$ .<sup>4d,9</sup> Although improvement in the activity is observed, molecular weights of the polymers are lower than those produced by the palladium catalysts. The possibility of triphenylphosphine or

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Figure 1. Molecular structure of 1. Selected bond distances (Å) and angles (deg): Ni(1)-P(1), 2.1845 (16); Ni(1)-O(1), 1.9235 (18); Ni(1)-C(19), 2.066 (2); Ni(1)-C(20), 1.9979 (19); Ni(1)-C(21), 1.981 (2); C(19)-C(20), 1.399 (3); C(20)-C(21), 1.413 (3); and C(19)-C(20)-C(21), 117.98 (16).



phosphine scavengers affecting polymerization lets us investigate activator- and additional phosphine-free phosphine sulfonate nickel catalysts. In this paper, we report the synthesis of allylnickel catalysts bearing phosphine sulfonate ligands and our examination on ethylene homopolymerization and copolymerization with polar vinyl monomers without any activators.

### **Results and Discussion**

First, preparation of allylnickel complex bearing a phosphine sulfonate ligand (1) was examined (Scheme 1). When phenylsubstituted phosphine 2 was treated with NaH in THF, deprotonation proceeded smoothly to afford the corresponding sodium salt of the phosphine sulfonate ligand 3, which is soluble in THF. A THF solution of 3 was obtained by filtration and directly used to form a nickel complex. Addition of this THF solution of **3** to a toluene solution of  $[(allyl)NiBr]_2$  gave allylnickel complex 1, which was isolated in 81% yield. The structure of complex 1 was confirmed by X-ray crystallography (Figure 1). As expected, the phosphine sulfonate ligand is bound to the nickel atom via one of the three oxygen atoms of the sulfonate group and the phosphorus atom to form a six-membered chelate. The allyl group binds to nickel in a  $\eta^3$  fashion. The two terminal allyl carbons, the coordinating phosphorus and the oxygen, and the nickel are all placed in a single plane. The distance between the terminal carbon and the nickel is longer for the bond located trans to the phosphorus from that trans to the oxygen, reflecting the stronger trans influence of the phosphine than that of the sulfonate.

Synthesis of allylnickel complex with an *o*-methoxyphenylsubstituted ligand (4) was then investigated. However, treatment of sulfonic acid 5 with NaH in THF resulted in formation of Scheme 2



the insoluble sodium salt of the ligand, which is difficult to separate from excess NaH. Therefore, sodium carbonate was used as an alternative weaker base. Sulfonic acid **5** was treated with sodium carbonate in  $CH_2Cl_2$ , followed by the addition of a toluene solution of [(allyl)NiBr]<sub>2</sub> to give the corresponding nickel complex **4**, which was isolated in 74% yield after recrystallization (Scheme 2). The structure of complex **5** was also confirmed by X-ray diffraction analysis.

Ethylene polymerization by the allylnickel complexes 1 and 4 was examined, and the results are summarized in Table 1. When the polymerization was performed at 80 °C, only a trace amount of polyethylene was generated (Table 1, entries 1 and 4). However, raising the reaction temperature to 100 °C led to formation of low molecular weight polymers  $(M_n)$ 1400-1700) with activities of 7-9 g·mmol<sup>-1</sup>·h<sup>-1</sup>(= 2-3  $g \cdot mmol^{-1} \cdot h^{-1} \cdot MPa^{-1}$ ) and with relatively narrow polydispersities  $(M_w/M_n = 1.5-2.0)$  (entries 3 and 5). These results show ethylene polymerization with the allylnickel complexes can be performed in the absence of activators. The observed dramatic increase in the activity indicates that a higher reaction temperature is required for initiation than for propagation. Almost no product was given by in a shorter reaction time (entry 2). It indicates slow initiation with the allyl nickel complex. Rieger and co-workers reported that in the presence of  $B(C_6F_5)_3$  as an activator, phenylnickel/PPh3 complex of o-methoxyphenylsubstituted 5 catalyzed ethylene polymerization with high activities but that only a trace amount of polyethylene was obtained with the phenyl-substituted ligand 2.4d The importance of the o-methoxy group was emphasized. Therefore, it is noteworthy that, here in this study, phenyl-substituted complex 1 actually catalyzes ethylene polymerization with activity comparable to the methoxyphenyl-substituted catalyst 4, both in the absence of activators. All obtained polymers had certain branches with 8-13 branches per 1000 carbon atoms. The number of branches is measured by <sup>13</sup>C NMR using inversegated decoupling.<sup>10</sup> The generated polyethylenes possess only methyl branches, and there are no longer side chains, such as ethyl, propyl, or butyl groups. It indicates that  $\beta$ -hydride elimination and reinsertion of the resulting olefin often occurs, but it occurs mostly at the chain end, and chain-walking further into the polymer chain does not proceed at a significant rate. Copolymerization with methyl acrylate is also examined, but as the result, only poly(methyl acrylate) is obtained.

Ethylene polymerization with the corresponding Pd complex bearing a phosphine sulfonate ligand was also examined. The use of allylpalladium complex [(o-Ar<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)Pd(allyl)] (Ar = o-MeOC<sub>6</sub>H<sub>4</sub>) (**6**)<sup>4j</sup> produced polyethylene with a higher molecular weight ( $M_n = 11500$ ) and higher linearity (less than 1 branch per 1000 carbon atoms) but lower reactivity than nickel complexes under the same conditions (entry 6). The higher molecular weight and linearity indicate that allylpalladium complex **6** bearing phosphine sulfonate ligand has less tendency to undergo  $\beta$ -hydride elimination than the corresponding nickel

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		temp time		vield	productivity				branches
entry	catalyst	(°C)	(h)	(g)	$(g \cdot mmol^{-1} \cdot h^{-1})$	$(\mathbf{g} \boldsymbol{\cdot} \mathbf{mmol}^{-1} \boldsymbol{\cdot} \mathbf{h}^{-1} \boldsymbol{\cdot} \mathbf{MPa}^{-1})$	$M_{ m n}$	$M_{\rm w}/M_{\rm n}$	(/1000C)
1	1	80	15	trace	trace	trace	$ND^b$	ND	ND
2	1	100	1	ND	ND	ND	ND	ND	ND
3	1	100	15	1.3	8.9	2.9	1400	1.5	8
4	4	80	15	trace	trace	trace	ND	ND	ND
5	4	100	15	1.0	6.8	2.2	1700	2.0	13
6	6	100	15	0.35	2.2	0.7	11600	2.3	<1

<sup>a</sup> Conditions: 0.010 mmol of catalyst, ethylene pressure = 3.0 MPa, 2.5 mL of toluene. <sup>b</sup> Not determined.

complexes 1 and 4. It is of interest to compare the difference between nickel complex 4 and palladium complex 6 in relation to the Brookhart's  $\alpha$ -diimine complexes. The result that the nickel/phosphine sulfonate complexes produce polyethylenes with lower molecular weight and more branches than palladium/ phosphine sulfonate is in sharp contrast to that the nickel/ $\alpha$ diimine complexes are considered to produce more linear polyethylene with higher molecular weight than the corresponding palladium complexes. The origin of the difference is not clear at this moment.

The polymerization activity initiated by the allylpalladium **6** is lower than that by alkylpalladium complex: alkyl complex  $(o\text{-Ar}_2\text{PC}_6\text{H}_4\text{SO}_3)\text{PdCH}_3(2,6\text{-lutidine})$  produced polyethylene with 15.0 g · mmol<sup>-1</sup> · h<sup>-1</sup>(= 5.0 g · mmol<sup>-1</sup> Pd · h<sup>-1</sup> · MPa<sup>-1</sup>),  $M_n$  = 75 700,  $M_w/M_n$  2.2, <1 branches over 1000 carbons at 80 °C.<sup>7</sup> The lower activity with  $\pi$ -allyl complex **6** may originate from the higher activation energy requested for the olefin insertion into the Pd–C bond in the  $\eta^3$ -complex when compared to methylpalladium complex.<sup>4</sup>

## Conclusion

Phosphine sulfonate nickel complexes are prepared and used as catalysts for ethylene polymerization without addition of any activator. Structures of the obtained low molecular weight polyethylene were analyzed to detect only methyl branches. The activity for ethylene polymerization with 1 was comparable to that with 4. Comparison with the corresponding allylpalladium complex 6 revealed that the nickel catalysts produced polyethylenes with lower molecular weight and more branches than the palladium catalyst.

#### **Experimental Section**

**General Methods.** All manipulations were carried out using the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. <sup>1</sup>H (500 MHz), <sup>13</sup>C (126 MHz), and <sup>31</sup>P NMR (202 MHz) spectra were recorded on a JEOL JNM-ECP-500 spectrometer. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, the University of Tokyo. Size exclusion chromatography analyses at 145 °C were carried out with a Tosoh instrument (HLC-8121) equipped with three columns (Tosoh TSKgel GMHhr-H(20)HT) by eluting the columns with *o*-dichlorobenzene at 1 mL/min.

Dichloromethane, toluene, THF, and hexanes were purified by the method of Pangborn et al.<sup>11</sup> 2-(Diphenylphosphino)benzenesulfonic acid (2) and 2-{di(2-methoxyphenyl)phosphino}benzenesulfonic acid (5) were prepared according to literature procedures.  $^{3b,4b}$  Phosphine sulfonate palladium complex  ${\bf 6}$  was prepared according to literature method.  $^{4j}$ 

**Preparation of** [(*o*-**Ph**<sub>2</sub>**PC**<sub>6</sub>**H**<sub>4</sub>**SO**<sub>3</sub>)**Ni**(allyl)] (1). To a suspension of 50 mg of sodium hydride (2.05 mmol) in 20 mL of THF was added 205 mg of **2** (0.60 mmol), and the resulting mixture was stirred for 1 h at rt. The mixture was filtered and slowly added to a solution of 115 mg of [(allyl)NiBr]<sub>2</sub> (0.32 mmol) in 10 mL of toluene and stirred for 20 h at rt. The resulting mixture was filtered through Celite and evaporated to dryness. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Slow diffusion of hexane into the concentrated CH<sub>2</sub>Cl<sub>2</sub> solution afforded nickel complex **1** (128.3 mg, 0.29 mmol, 48% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.21–8.18 (m, 1H), 7.56–7.38 (m, 12H), 7.08 (t, *J* = 8.4 Hz, 1H), 5.70–5.29 (m, 1H), 4.80–0.98 (br m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, -50 °C): δ 48.8 (CH<sub>2</sub>, allyl), 116.2 (ArC), 119.7 (CH, allyl), 129.4, 129.8, 131.1, 131.9, 133.2, 135.3, 136.6, 148.7 (ArC, ArCH). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 8.6. Anal. Calcd for C<sub>21</sub>H<sub>19</sub>NiO<sub>3</sub>PS: C, 57.18; H, 4.34. Found: C, 56.96; H, 4.48.

**Preparation of** [{(*o*-(*o*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>**P**)C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]NiCH<sub>2</sub>CHCH<sub>2</sub>] (4). To a solution of 436 mg of **5** (1.08 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 230 mg of sodium carbonate (2.17 mmol), and the reaction mixture was stirred for 4 h at rt. Then a solution of 210 mg of allylnickel bromide (0.584 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the mixture and stirred for 3 h at rt. The resulting mixture was filtered through Celite. Slow diffusion of hexane into the concentrated CH<sub>2</sub>Cl<sub>2</sub> solution afforded nickel complex **4** as a redbrown powder (405 mg, 0.808 mmol, 74% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.20–8.17 (m, 1H), 7.52–7.46 (m, 3H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.01–6.92 (m, 7H), 5.59–5.49 (m, 1H), 3.78 (s, 6H), 4.74–0.53 (br m, 4H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  41.7. Anal. Calcd for C<sub>23</sub>H<sub>23</sub>NiO<sub>5</sub>PS: C, 55.12; H, 4.63. Found: C, 54.96; H, 4.64.

**Ethylene Polymerization.** To a 50 mL autoclave containing 0.010 mmol of metal complex and a stir bar was transferred 2.5 mL of toluene under argon atmosphere. The mixture was stirred at rt for 10 min and charged with 3.0 MPa of ethylene. The autoclave was heated, and the mixture was stirred for 15 h. After the reaction, MeOH was added to the cooled contents of the autoclave. Precipitated materials were collected by filtration and washed several times with MeOH. The remaining solid was dried under vacuum at 80 °C to afford polyethylene, which was analyzed without further purification.

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**Supporting Information Available:** X-ray crystallographic data of **1** and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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