

Synthesis of New Phosphine Imine Ligands and Their Effects on the Thermal Stability of Late-Transition-Metal Olefin Polymerization Catalysts

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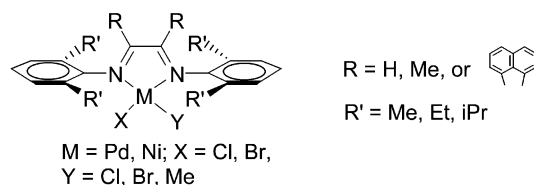
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A series of α -phosphine imine hybrid ligands was successfully synthesized by nucleophilic substitution of di-*tert*-butylchlorophosphine or diphenylchlorophosphine on imine anions. These ligands exist as α -phosphine enamines before complexation, which tautomerize to α -phosphine imines upon coordination to Ni(II) or Pd(II). The Ni(II) and Pd(II) complexes with these P \wedge N ligands were prepared and fully characterized by NMR, elemental analysis, and single-crystal X-ray crystallography. While all the Ni(II)–P \wedge N complexes assume tetrahedral coordination geometry, the Pd(II)–P \wedge N complexes are square planar. Upon activation with MAO, the Ni(II) complexes were active for ethylene polymerization. Whereas the Ni(II)–P \wedge N complexes are less productive than the Brookhart Ni(II)– α -bis(imine) complexes and form polyethylenes with relatively low molecular weight, the thermal stabilities of these complexes upon activation are significantly higher than those of the corresponding Ni(II)– α -bis(imine) complexes. ¹³C NMR shows that the polyethylenes are highly branched and have branch-on-branches. In contrast, the Pd(II)–P \wedge N complexes were inactive for ethylene polymerization.

Introduction

Transition-metal catalysts have played and will continue to play crucial roles in making important polymeric materials.^{1,2} Whereas early-transition-metal catalysts such as the Ziegler–Natta and single-site metallocene catalysts³ remain as the workhorse in olefin polymerization industry, significant advances have been made recently in late-transition-metal polymerization catalysts.^{4–6} Some exciting examples are the Ni(II)– and Pd(II)– α -bis(imine) complexes (Chart 1) reported by Brookhart and co-workers.^{7,8} These catalysts show activities comparable to those of the early-metal catalysts in polymerizing ethylene into high-molecular-weight polymers.⁹ The polyethylenes formed have branched microstructures in which the branching was proposed to be introduced by catalyst isomerization or

Chart 1



“walking” along the polyethylene backbone during the migratory insertion polymerization.^{7,8,10} By exploitation of this chain-walking feature, it was shown that polyethylenes with a broad spectrum of topology ranging from linear to hyperbranched to dendritic can be obtained from polymerization of ethylene by simply varying ethylene pressure.^{11–14}

Whereas the Ni(II)– and Pd(II)– α -bis(imine) catalysts exhibit excellent activity and good functional group tolerance, one severe limitation is their relatively low thermal stability. The catalysts decompose rapidly at temperatures about 50 °C for Pd(II)– α -bis(imine) and 70 °C for Ni(II)– α -bis(imine) catalysts,¹⁵ which is significantly lower than the decomposition temperatures of early-transition-metal species such as Ziegler–Natta and single-site metallocene catalysts.³ For practical

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† X-ray crystal structure determination of complexes **3a**, **b** and **4b**, **c**. Address: Experimental Station, DuPont Central Research and Development, Wilmington, DE 19880-0328.

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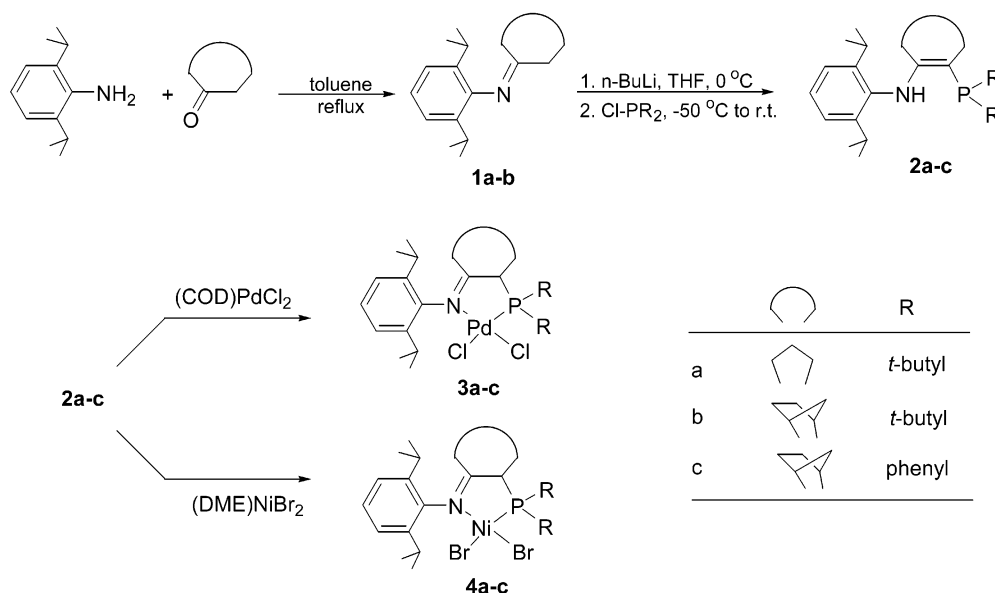
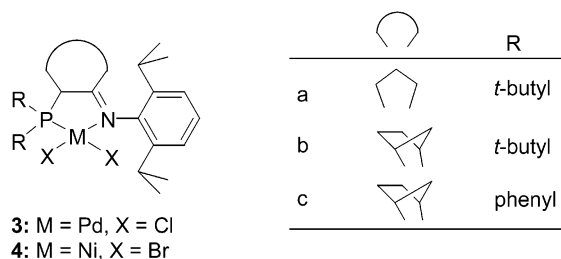
Scheme 1. Synthesis of P \wedge N Ligands and Their Ni(II) and Pd(II) Complexes

Chart 2



applications, significantly higher thermal stability is desired for process and economic considerations. We have been attempting to determine how ligand structure affects the thermal stability of the Ni(II) and Pd(II) complexes. In this paper, we wish to report the synthesis, structural characterization, and ethylene polymerization studies of a family of nickel and palladium complexes with a new class of phosphine imine (P \wedge N) ligands (Chart 2).¹⁶ In these P \wedge N ligands, we used a better σ -donating phosphine to replace one imine site of the bis(imine) ligands with the purpose of increasing the binding strength of the ligand to the metal center. The stronger binding ability of the phosphine may lead to an improvement of the catalyst thermal stability. Other complexes of late transition metals with various phosphine nitrogen,^{17–25} diphosphaalkene,²⁶ phosphi-

nosulfonamide,²⁷ and α -iminocarboxamidato²⁸ ligands have been reported for various studies.

Results and Discussion

Ligand and Complex Syntheses. Previous studies by Brookhart and co-workers on the Ni(II)– and Pd(II)– α -bis(imine) complexes have shown that the bulky ortho substituents on the aniline moieties and their orientation toward the axial positions of the square-planar complexes are crucial for obtaining high polymers (Chart 1). To maintain this steric requirement, bulky phosphines and aniline were used in the ligand synthesis. Monocyclic and bicyclic backbones were used to enhance the conformational rigidity of the P \wedge N ligands to improve the chelation with the metal center (Chart 2). A series of P \wedge N ligands with the structures shown in Scheme 1 were synthesized. Following standard procedures for imine preparation, imine precursors **1a,b** were synthesized by heating to reflux in toluene. A disubstituted phosphine was installed by nucleophilic substitution of the imine anion with a disubstituted chlorophosphine. The formation of **2a–c** was monitored by ³¹P NMR, and the products were analyzed by NMR, GC/MS, and elemental analysis. Solid products were purified by recrystallization, and liquid products were purified by flash column chromatography.

³¹P NMR showed single peaks for all the ligands, indicating that they are pure compounds. ¹H NMR showed that the products exist in the enamine tautomers (Scheme 2), which isomerize back to the imine tautomers upon coordination with Ni(II) or Pd(II) metal ions.

Pd(II) complexes **3a–c** and Ni(II) complexes **4a–c** were prepared by mixing the corresponding ligands with

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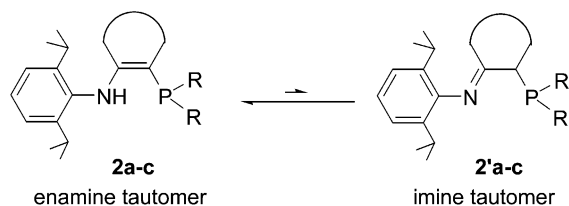
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Scheme 2. Tautomerization between Imine and Enamine



(COD)PdCl₂ or (DME)NiBr₂ in dichloromethane and purified by recrystallization in dichloromethane.

Single-Crystal X-ray Structure Analysis. Single crystals were grown from a dichloromethane solution for single-crystal X-ray crystallographic analysis. X-ray structures were obtained for the complexes **3a,b** and **4b,c**. As representative examples, the ORTEP plots for **3a** and **4b** are shown in Figure 1 and Figure 2, respectively.

Although some P \wedge N ligands were reported to form polynuclear complexes with Ni(II) or Pd(II),^{29,30} all our complexes between Ni(II) and Pd(II) and the P \wedge N ligands are mononuclear. Presumably the bulky substituents on the phosphine and on the aniline moiety prevent the polynuclear complexes from forming. The coordination geometry is tetrahedral for all the Ni(II) complexes and is square planar for all the Pd(II) complexes. The crystal, intensity collection, and refinement data for complexes **3a,b** and **4b,c** are presented in Table 1. The most relevant bond parameters for complexes **3a** and **4b** are summarized in Table 2.

The C1–N1 bond distances in complexes **3a** and **4b** are 1.276(4) and 1.274(9) Å, respectively, which agree with that of a carbon–nitrogen double bond, indicating that the enamines tautomerize to imines after coordinating to Ni(II) or Pd(II). The bond distances and bond angles in **3a** and **4b** are comparable to those in relevant complexes reported previously.^{17–25} Both **3a** and **4b** are chiral molecules, with the C5 carbon in **3a** and the C6 carbon in **4b** being chiral centers. Both enantiomers of **3a** were observed in the X-ray crystal analysis, which cocrystallize in the same unit cell (see Supporting Information). For **4b**, however, X-ray crystal analysis showed that the C6 carbon only exists in the *S* configuration (Figure 2), presumably because this is the thermodynamically more stable stereoisomer.

Since the active cationic catalytic species during polymerization adopt square-planar geometry at the metal center for both Ni(II) and Pd(II) complexes, it would be interesting to examine the square-planar palladium complex **3a** more carefully. Similar to the Brookhart Pd(II)– α -bis(imine) complexes,^{7,15} the aniline phenyl ring in **3a** is almost perpendicular to the coordination plane. The angle between the coordination mean plane defined by P1–N1–Pd–Cl1–Cl2 and the phenyl ring is 78.75°. This orients the two *o*-isopropyl substituents on the aniline moiety to the axial positions of the complex. The two *tert*-butyl groups on the phosphine are also oriented toward the axial positions of the coordination center. The angle between the same coord-

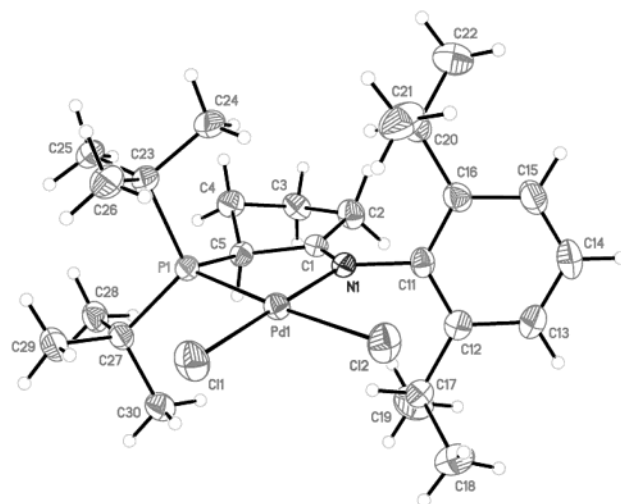


Figure 1. ORTEP drawing for **3a**.

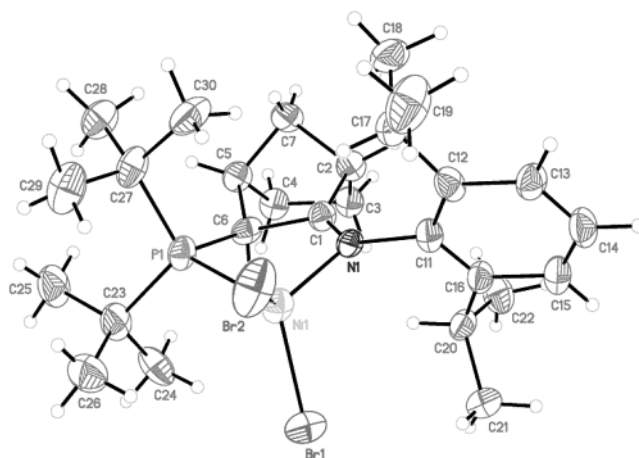


Figure 2. ORTEP drawing for **4b**.

ination mean plane and the plane defined by C23–P1–C27 is 83.35°. As shown by Brookhart and co-workers^{7,15} in previous studies of Ni(II)– and Pd(II)– α -bis(imine) complexes, blocking axial faces of the coordination site with bulky substituents of the aniline moieties is critical for shutting off the associative chain transfer process in order to obtain polymers with high molecular weight. In complex **3a**, the orientation of both the *tert*-butyl groups from phosphine and the isopropyl groups from aniline to the axial positions should partially reduce the chain transfer process. However, the steric bulkiness for **3a** is unsymmetrical for the axial faces above and below the coordination plane. This can be better viewed in the space-filling model of **3a**. Figure 3 shows the space-filling models of the complex **3a** viewed from the front, the top, and the bottom. The top axial face is much more open than the bottom one. The openness at the top axial face makes the metal center susceptible to ethylene associative chain transfer, which is presumably the cause for the formation of polyethylenes with relatively low molecular weight in the ethylene polymerization catalyzed by the Ni(II)–P \wedge N complexes (vide infra).

Ethylene Polymerization by the Complexes. Surprisingly, all the Pd(II)–P \wedge N complexes (**3a–c**) upon activation with MAO were inactive to polymerize ethylene. We are not exactly sure why the Pd(II)–P \wedge N complexes are inactive in ethylene polymerization but

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Table 1. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters for Complexes 3a,b and 4b,c

	3a	3b	4b	4c
formula	C ₂₆ H ₄₄ PdCl ₄ PN	C ₂₉ H ₄₈ PdCl ₆ PN	C ₂₇ H ₄₄ Br ₂ NiPN	C ₃₁ H ₃₆ Br ₂ NiPN
fw	649.83	760.80	632.16	672.14
temp (K)	173	173	173	173
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ (No. 4)	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	20.556(2)	9.996(1)	9.053(1)	16.939(1)
<i>b</i> (Å)	14.819(1)	19.452(1)	14.751(2)	32.804(1)
<i>c</i> (Å)	21.382(2)	19.352(1)	11.194(1)	10.554(1)
β (deg)	109.31(1)	110.96(1)	104.49(1)	
<i>V</i> , Å ³	6147.1	3513.9	1447.3	5864.5
<i>Z</i>	8	4	2	8
μ (Mo K α), cm ⁻¹	10.13	10.46	34.77	34.38
ρ_{calcd} (g cm ⁻³)	1.404	1.438	1.450	1.522
cryst size (mm)	0.35 × 0.39 × 0.43	0.28 × 0.37 × 0.41	0.08 × 0.28 × 0.38	0.02 × 0.44 × 0.50
2 θ range (deg)	3.4–48.2	3.1–48.2	5.2–48.2	4.6–48.2
total no. of rflns	32 097	18 571	7884	21 820
no. of unique data, <i>I</i> = 3.0 σ (<i>I</i>)	7603	3821	3080	2741
<i>R</i> _{merge}	0.018	0.019	0.021	0.044
no. of params	595	338	288	325
<i>R</i> ₁	0.032	0.076	0.054	0.036
w <i>R</i> ₂	0.037	0.089	0.062	0.035
goodness of fit	1.89	4.58	3.20	1.43

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3a and 4b

	3a		4b
Bond Lengths			
Pd1–N1	2.056(2)	Ni1–N1	2.043(6)
Pd1–P1	2.2545(8)	Ni1–P1	2.338(2)
Pd1–Cl1	2.2934(7)	Br1–Ni1	2.359(1)
Pd1–Cl2	2.3615(8)	Br2–Ni1	2.341(1)
N1–C1	1.276(4)	N1–C1	1.274(9)
P1–C5	1.856(3)	P1–C6	1.861(8)
N1–C11	1.464(4)	N1–C11	1.470(9)
P1–C23	1.866(3)	P1–C23	1.896(8)
P1–C27	1.863(3)	P1–C27	1.870(9)
Bond Angles			
P1–Pd1–N1	85.07(7)	P1–Ni1–N1	87.4(2)
N1–Pd1–Cl1	177.7(1)	Br1–Ni1–Br2	119.01(5)
N1–Pd1–Cl2	91.78(7)	Br1–Ni1–N1	100.6(2)
Cl1–Pd1–P1	93.72(3)	Br2–Ni1–N1	124.3(2)
Cl2–Pd1–P1	176.25(7)	Br1–Ni1–P1	110.08(7)
Cl1–Pd1–Cl2	89.49(3)	Br2–Ni1–P1	110.91(6)
Pd1–N1–C1	119.3(2)	Ni1–N1–C1	116.4(5)
Pd1–N1–C11	123.9(2)	Ni1–N1–C11	119.7(4)
Pd1–P1–C5	99.1(1)	Ni1–P1–C6	92.8(2)
Pd1–P1–C23	112.0(1)	Ni1–P1–C23	114.5(2)
Pd1–P1–C27	117.2(1)	Ni1–P1–C27	116.7(2)

tentatively attribute this to the electronic structure of the Pd(II)–P \wedge N complexes.³¹ Low activity was also observed by Rieger and co-workers for ethylene polymerization catalyzed by Pd(II) complexes with some special bis(imine) ligands in which the catalysts decomposed rapidly.³²

All the Ni complexes are active to polymerize ethylene upon activation with MAO. Some of the ethylene polymerization results are summarized in Table 3. Whereas the activities of these catalysts are less than those of the Ni(II)– α -bis(imine) complexes and the molecular weights of the polyethylenes are generally low, one

(31) Pd black was observed for some polymerization of Pd(II)–P \wedge N complexes activated with MAO. Presumably, this could be either due to the low thermal stability of the activated catalysts or due to reduction of the Pd(II) by MAO to Pd(0). P \wedge N–Pd(Me)Cl complexes were also prepared and tested for ethylene polymerization. Upon activation with 2 equiv of Na⁺BAF⁻ (where BAF⁻ = [B{3,5-C₆H₃(CF₃)₂]₄]⁻), the complexes were also inactive in polymerizing ethylene.

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striking feature of the Ni(II)–P \wedge N complexes is their relatively high thermal stability. The catalysts remained active to polymerize ethylene after polymerization at 70 °C for many hours. Comparison of polymerization with **4b** for 3 and 7 h (runs 2 and 3) indicates that the catalyst remains active after polymerizing ethylene for up to 7 h. For comparison, the Ni(II)– α -bis(imine) catalysts usually decompose within 1/2 h for ethylene polymerization at 70 °C. The enhanced thermal stability is ascribed to the stronger binding ability of the phosphine site introduced into the ligands.

The ligand structure influences both the catalyst activity and the molecular weight of the polymer formed (comparing runs 1, 2, and 6). Complex **4c** is much more active than **4a,b**. This is presumably due to the difference of electronic structure between **4c** and **4a,b**. The phosphine in **4a,b** is much more electron rich than the phosphine in **4c** because the *tert*-butyl group has a stronger electron donating ability than the phenyl group has. The lower molecular weight for polyethylene obtained with complex **4c** is attributed to the decreased steric bulkiness of the diphenylphosphine in **4c** as compared to the di-*tert*-butylphosphine in **4a,b**. To examine the influence of polymerization conditions on the catalyst performance, complex **4b** was studied for ethylene polymerization at different temperatures and pressures. Polymerization at lower ethylene pressure (comparing runs 3 and 4) resulted in a lower turnover rate and lower molecular weight for the polymer. The catalyst was more active at higher temperature but afforded short oligomers as the major product (run 5, at 110 °C).

The molecular weights of the polyethylenes obtained with these three complexes are generally low compared to those obtained with the Ni(II)– α -bis(imine) catalysts. Whereas the exact cause for this warrants further investigation, it is tentatively attributed to the unsymmetrical geometry of the complexes, which causes one side of the axial face to be susceptible to ethylene associative chain transfer (*vide supra*).

Another unusual feature of ethylene polymerization by the Ni(II)–P \wedge N complexes is that the polyethylenes

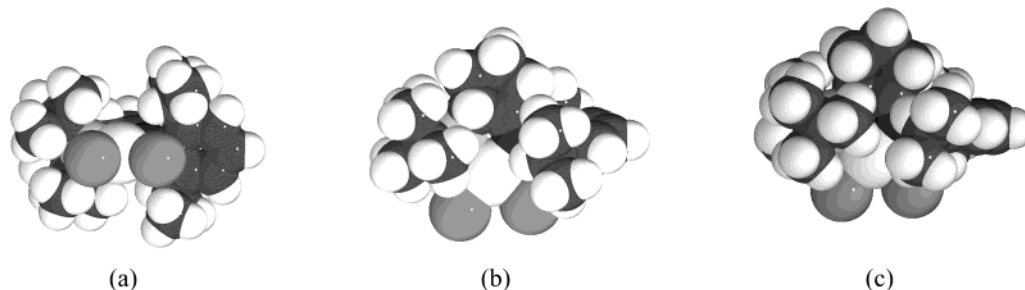


Figure 3. Space-filling models of the complex **3a** based on its X-ray structure: (a) front view; (b) top view; (c) bottom view.

Table 3. Ethylene Polymerization Results with the Ni^{II}-P \wedge N Complexes^a

run no.	catalyst	temp (°C)	pressure (psi)	time (h)	TO ^b	TO/h ^c	M _n ^d	M _w /M _n
1	4a	70	500	7	6700	960	2000	1.4
2	4b	70	500	3	5020	1670	1450	1.2
3	4b	70	500	7	10800	1540	1400	1.2
4	4b	70	350	5	5880	1180	1290	1.3
5	4b	110	500	4	13390	3350	^e	^e
6	4c	70	500	2.7	46500	17200	800	1.3

^a Polymerizations were run with 20 mg of catalyst loading in 100 mL chlorobenzene. ^b TO = turnover, which is the ratio of moles of ethylene polymerized by 1 mol of catalyst. ^c TO/h is the average turnover per hour. ^d In units of g/mol. ^e The GPC trace of the product showed bimodal distribution with the major peak with peak molecular weight of 430 and a very small peak at very high mass (M_n = 59 500, M_w/M_n = 2.8).

Table 4. Short-Chain Branching Distribution Obtained from Quantitative ¹³C NMR^a

catalyst	total Me	Me	Et	Pr	Bu	Am	Hex+	1B2%
4a	55	23	3.2	0.5	1.1	7.0	20.3	53
4b	58	22	3.0	0.6	1.6	8.9	22	58
4c	65	22	4.5	1.1	3.7	11.9	22	55

^a The data are for polyethylenes obtained at 500 psi and 70 °C with different complexes. The data are expressed as the number of branches per 1000 CH₂ units. The abbreviations used in the table are as follows: total Me = total branches including chain ends, Me = methyl branches, Et = ethyl branches, Pr = propyl branches, Bu = butyl branches, Am = amyl branches, Hex+ = hexyl and longer branches, 1B2% = percentage of ethyl branches existing in isobutyl branches.

formed are much more branched than the polyethylenes made by the Ni(II)- α -bis(imine) complexes at similar polymerization conditions. The short-chain branches measured by quantitative ¹³C NMR analyses^{33,34} were summarized in Table 4, which indicates that the polymers formed were highly branched with branching densities in the range of 50–60 total branches per 1000 methylenes. Significant amounts of the branches are relatively long (such as amyl and hexyl). Short branch-on-branches also exist in the polyethylenes, as evidenced by the presence of ethyl in isobutyl groups. This is in great contrast to the polyethylenes formed by Ni(II)- α -bis(imine) complexes. The polyethylenes obtained by the Brookhart Ni(II)- α -bis(imine) complexes under similar polymerization conditions usually only have about 20 total branches per 1000 methylenes, with most

of the branches being simple methyl and ethyl branches.⁹ The short-chain branches in Ni(II)-P \wedge N catalyzed ethylene polymerization is presumably formed by the chain-walking mechanism proposed by Brookhart⁷ and Fink¹⁰ for the Ni(II)- and Pd(II)- α -bis(imine) catalyst systems. The observed higher branching density, longer short-chain branches, and significant amount of branch-on-branches for polyethylenes made by our Ni(II)-P \wedge N complexes suggest that chain walking is more competitive in our system than in the Ni(II)- α -bis(imine) system.

Conclusions

A series of new phosphine imine hybrid ligands were successfully synthesized. Ni(II) and Pd(II) complexes with these P \wedge N ligands were prepared and fully characterized by NMR, elemental analysis, and single crystal X-ray crystallography. Whereas the Ni(II)-P \wedge N complexes assume a tetrahedral coordination geometry, the Pd(II)-P \wedge N complexes are all square planar. Upon activation with MAO, the Ni(II) complexes were active for ethylene polymerization. The Ni(II)-P \wedge N complexes are significantly more stable than the corresponding Ni(II)- α -bis(imine) complexes, which is ascribed to the stronger binding ability of the phosphine binding site. The molecular weights of the polyethylenes are relatively low, which is presumably caused by facile chain transfer at one axial face that is relatively open. ¹³C NMR shows that the polyethylenes are highly branched and have branch-on-branches. In contrast, the Pd(II)-P \wedge N complexes were inactive for ethylene polymerization.

Experimental Section

Materials. All the starting materials and reagents were purchased from Aldrich and Strem and used without further purification. Ethylene (99.9%) was purchased from MG Industries. All dry solvents were purified by passing through solvent purification columns following the method introduced by Grubbs.³⁵ Deuterated solvents were dried using standard procedures and stored over freshly calcined molecular sieves (4 Å) in the glovebox. Methyl aluminoxane (MAO) was purchased from Aldrich as a 10 wt % solution in toluene.

General Considerations. Manipulation of organometallic compounds was performed in a nitrogen-filled Vacuum Atmospheres drybox. NMR spectra were obtained with a Bruker Avance 500 spectrometer. Quantitative ¹³C NMR spectra were obtained in a 10 mm probe on 10–20 wt % solutions of the polymers and 0.05 M CrAcAc in 1,2,4-trichlorobenzene (TCB)

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unlocked at 120–140 °C using a 90° pulse of 17.8 μ s, a spectral width of 35 kHz, a relaxation delay of 5 s, an acquisition time of 0.64 s, and inverse gated decoupling.^{33,34} Spectra are referenced to the solvent TCB high-field resonance at 127.9 ppm. GC-MS analysis was carried out with a Hewlett-Packard 6890 series instrument. Molecular weights of polyethylenes were measured by gel permeation chromatography (GPC) using trichlorobenzene as eluent on an Agilent GPC equipped with a polystyryl gel mixed bed column. The molecular weight was obtained by calibration using polystyrene as standard.

Single-Crystal X-ray Structure Analysis. X-ray diffraction data for all of the structures, **3a**, **b** and **4b**, **c**, were collected using Mo K α radiation on a Rigaku RU300 diffractometer modified with an R-Axis image plate area detector. For each structure 45 frames of data were collected, each having an ω oscillation of 4° and exposure times of 8–20 min. All structures were solved by direct methods using teXsan³⁶ (SIR-92) and were refined using the Z program suite (Calabrese).³⁷ Refinement was by full-matrix least squares on F . Scattering factors, including anomalous terms for Pd, Br, Cl, and P, were taken from refs 38 and 39. All of the hydrogen atoms have been idealized close to their previously refined positions. The enantiomeric setting for noncentrosymmetric **4b** was chosen on the basis of the r factors. Inverting to the opposite enantiomer raised the R1 value significantly from 5.47 to 6.57. Table 1 provides information on the data collection and refinement parameters for complexes **3a**, **b** and **4b**, **c** reported in this paper. The pertinent bond parameters for complexes **3a** and **4b** are summarized in Table 2.

General Procedure for the Synthesis of P \wedge N Ligands.

Step 1. An appropriate amount of cyclopentanone or norcamphor was mixed with 1.5 equiv of 2,6-diisopropylaniline in toluene followed by addition of a small amount of *p*-toluenesulfonic acid as the catalyst. The solution was heated to reflux for 2 days, and a Dean–Stark trap was used to remove water constantly. After the completion of the reaction as monitored by GC, the solvent was removed by vacuum to leave an oily mixture. The imine intermediate was obtained by recrystallization or flash column separation.

Step 2. To a solution of lithium diisopropylamide (LDA, 1.15 equiv) in THF at 0 °C, one of the imine intermediates from the first step dissolved in THF was added dropwise. After being stirred at 0 °C for 4 h, the mixture was cooled to –100 °C by using an ether/dry ice cold bath. Di-*tert*-butylchlorophosphine or diphenylchlorophosphine (1.0 equiv) in THF was syringed into the reaction mixture dropwise. After addition was completed, the mixture was stirred at –50 °C overnight and then at room temperature and finally heated if necessary until the reaction was completed, as monitored by ³¹P NMR. After removal of solvent, the residue was dissolved in diethyl ether, and this solution was subsequently poured into 1 N NH₄-Cl aqueous solution. The organic layer was collected, and the aqueous layer was extracted with diethyl ether. The organic phases were combined, washed with water, and dried with MgSO₄, and finally the solvent was removed. The final product was purified either by recrystallization or flash column separation.

Synthesis of 2a. Step 1: cyclopentanone (8.00 g, 0.095 mol), 2,6-diisopropylaniline (25.29 g, 0.14 mol), 50.0 mL of toluene, flash column separation (basic alumina, 40:1 hexane/chloroform), yield 13.8 g (60%). Step 2: imine **1a** (1.0 g, 4.12 mmol) in THF (10 mL), LDA (1.5 M in cyclohexane, 3.1 mL, 4.65 mmol), di-*tert*-butylchlorophosphine (0.744 g, 4.12 mmol) in

THF (10 mL), –50 °C overnight and 35 °C for 18 h, flash column separation (basic alumina, 40:1 hexane/chloroform), yield 0.40 g white powder (26%). ¹H NMR (CDCl₃): δ 1.02 (d, J = 6.8 Hz, 6H, CHMe₂), 1.11 (d, J = 6.8, 6H, C'HMe₂), 1.19 (d, J_{P-H} = 13.0, 18H, Bu^t), 1.66 (quint, J = 7.0, 2H, CH₂CH₂-CH₂), 1.90 (t, J = 7.0, 2H, CH₂CH₂CH₂), 2.62 (t, J = 7.0, 2H, CH₂CH₂CH₂), 3.21 (sep, J = 6.8, 2H, CHMe₂ and C'HMe₂), 6.23 (b, 1H, NH), 7.02 (d, J = 8.6, 2H, Ar *m*-H), 7.12 (t, J = 8.6, 1H, Ar *p*-H). ³¹P NMR (CDCl₃): δ 6.08 (s). Anal. Calcd for C₂₅H₄₂NP: C, 77.47; H, 10.92; N, 3.61. Found: C, 77.36; H, 10.78; N, 3.63.

Synthesis of 2b. Step 1: norcamphor (8.00 g, 0.073 mol), 2,6-diisopropylaniline (21.6 g, 0.12 mol), 60.0 mL of toluene, recrystallized from Et₂O, yield 11.0 g (56%). Step 2: imine **1b** (2.0 g, 7.42 mmol) in THF (10 mL), LDA (1.5 M in cyclohexane, 5.5 mL, 8.25 mmol), di-*tert*-butylchlorophosphine (1.34 g, 7.42 mmol) in THF (20 mL), –50 °C overnight and room temperature for 2 days, recrystallized from hexane twice, yield 0.75 g (24%). ¹H NMR (CDCl₃): δ 1.00 (d, J = 6.8 Hz, 3H, CHMeMe'), 1.03 (d, J = 6.8, 3H, CHMeMe'), 1.11 (d, J = 6.8, 3H, C'HMeMe'), 1.15 (d, J = 6.8, 3H, C'HMeMe'), 1.27 (d, J_{P-H} = 13.0, 18H, Bu^t), 1.35–1.47 (b, 3H), 1.66–1.73 (b, 1H), 1.88 (b, 1H), 2.45 (b, 1H), 2.54 (b, 1H), 2.67 (sep, J = 6.8, 1H, CHMeMe'), 2.79 (b, 1H), 2.85 (sep, J = 6.8, 1H, C'HMeMe'), 6.94 (t, J = 8.6, 1H, Ar *p*-H), 6.99 (d, J = 8.6, 1H, Ar *m*-H), 7.02 (d, J = 8.6, 1H, Ar *m'*-H). ¹³C NMR (CDCl₃): δ 21.88, 22.92, 23.91, 24.48, 24.75, 24.51, 28.45, 30.84, 30.89, 30.99, 31.10, 31.12, 31.24, 33.22, 37.03, 41.88, 42.92, 43.03, 48.94, 49.26, 122.30, 122.82, 122.96, 135.90, 137.03, 147.34, 181.44. ³¹P NMR (CDCl₃): δ 53.47 (s). Anal. Calcd for C₂₇H₄₄NP: C, 78.40; H, 10.72; N, 3.39. Found: C, 78.29; H, 10.70; N, 3.35.

Synthesis of 2c. Step 1: same as above. Step 2: imine **1b** (2.0 g, 7.42 mmol) in THF (10 mL), LDA (1.5 M in cyclohexane, 5.5 mL, 8.25 mmol), diphenylchlorophosphine (1.65 g, 7.42 mmol) in THF (20 mL), –50 °C overnight and 45 °C for 6 h, recrystallized from hexane twice, yield 1.15 g (35%). ¹H NMR (CDCl₃): δ 0.89 (d, J = 6.8 Hz, 3H, CHMeMe'), 1.04 (d, J = 6.8, 3H, CHMeMe'), 1.10–1.20 (m, 6H, C'HMe₂), 1.29–1.51 (m, 3H), 1.58–1.74 (m, 1H), 1.99 (b, 1H), 2.18 (m, 1H), 2.60 (b, 1H), 2.73 (sep, J = 6.8, 1H, CHMeMe'), 2.82 (sep, J = 6.8, 1H, C'HMe₂), 3.15 (m, 1H), 6.84–7.05 (m, 3H, Ar H), 7.15 (m, 3H, Ar' H), 7.30 (m, 3H, Ar' H), 7.49 (m, 2H, Ar' H), 7.67 (m, 2H, Ar' H). ³¹P NMR (CDCl₃): δ –7.44 (s). Anal. Calcd for C₃₁H₃₆-NP: C, 82.08; H, 8.00; N, 3.09. Found: C, 82.02; H, 7.94; N, 3.11.

General Procedures for the Synthesis of Pd and Ni Complexes. Into a suspension of dichloro(1,5-cyclooctadiene)-palladium ((COD)PdCl₂) or dibromo(1,2-dimethoxyethane)-nickel ((DME)NiBr₂) in dichloromethane was added one of the P \wedge N ligands. The mixture was stirred at room temperature for 2–3 days. The solution was passed through Celite to remove any insoluble materials. After the solution was concentrated, a large excess of hexane was added to precipitate the complex. The complex was filtered, washed with hexane, and recrystallized from dichloromethane or a mixture of dichloromethane and hexane.

Synthesis of 3a: (COD)PdCl₂ (60 mg, 0.21 mmol), **2a** (87 mg, 0.22 mmol), 10 mL of CH₂Cl₂, 2 days, recrystallized from dichloromethane, yield 59 mg (50%). ¹H NMR (CDCl₃): δ 1.12 (d, J = 6.8 Hz, 3H, CHMeMe'), 1.20 (d, J = 6.8, 3H, CHMeMe'), 1.44 (d, J = 6.8, 3H, C'HMeMe'), 1.51 (d, J = 6.8, 3H, C'HMeMe'), 1.70 (d, J_{P-H} = 13.0, 9H, Bu^t), 1.79 (d, J_{P-H} = 13.0, 9H, Bu^t), 1.85–2.5 (m, 6H, CH₂CH₂CH₂), 3.04 (sep, J = 6.8, 1H, CHMeMe'), 3.23 (sep, J = 6.8, 1H, C'HMeMe'), 3.68 (dt, J_{P-H} = 14.0, J_{H-H} = 7.0, 1H, CHP), 7.13 (d, J = 8.6, 2H, Ar *m*-H), 7.25 (t, J = 8.6, 1H, Ar *p*-H). ³¹P NMR (CDCl₃): δ 77.17 (s). Anal. Calcd for C₂₅H₄₂NPPdCl₂: C, 53.15; H, 7.49; N, 2.48. Found: C, 53.06; H, 7.44; N, 2.43.

Synthesis of 3b: (COD)PdCl₂ (70 mg, 0.25 mmol), **2b** (111 mg, 0.27 mmol), 10 mL of CH₂Cl₂, 3 days, recrystallized from CH₂Cl₂/hexane, yield 85 mg (58%). ¹H NMR (CDCl₃): δ 1.04

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(d, $J = 6.8$ Hz, 3H, CHMeMe'), 1.16 (d, $J = 6.8$, 3H, CHMeMe'), 1.37 (d, $J = 6.8$, 3H, C'HMeMe'), 1.42 (d, $J = 6.8$, 3H, C'HMeMe'), 1.60 (d, $J_{P-H} = 13.0$, 9H, Bu^t), 1.65 (d, $J_{P-H} = 13.0$, 9H, Bu^t), 1.69–1.93 (b, 4H), 2.05 (b, 1H), 2.58 (sep, $J = 6.8$, 1H, CHMeMe'), 2.71–2.87 (b, 2H), 3.02 (b, 2H), 3.34 (sep, $J = 6.8$, 1H, C'HMeMe'), 7.00–7.20 (m, 3H, Ar H). ³¹P NMR (CDCl₃): δ 97.73 (s). Anal. Calcd for C₂₇H₄₄NPPdCl₂: C, 54.88; H, 7.50; N, 2.37. Found: C, 54.81; H, 7.46; N, 2.35.

Synthesis of 3c: (COD)PdCl₂ (70 mg, 0.25 mmol), **2c** (122 mg, 0.27 mmol), 10 mL of CH₂Cl₂, 2 days, recrystallized from CH₂Cl₂/hexane, yield 95 mg (60%). ¹H NMR (CDCl₃): δ 0.73 (d, $J = 6.8$ Hz, 3H, CHMeMe'), 0.90 (b, 1H), 1.09 (d, $J = 6.8$, 3H, CHMeMe'), 1.29–1.35 (m, 1H), 1.38 (d, $J = 6.8$, 3H, C'HMeMe'), 1.55 (d, $J = 6.8$, 3H, C'HMeMe'), 1.55–1.65 (m, 1H), 1.63–1.77 (m, 2H), 1.80–1.92 (m, 1H), 2.49 (b, 1H), 2.72 (sep, $J = 6.8$, 1H, CHMeMe'), 2.91 (b, 1H), 3.15 (sep, $J = 6.8$, 1H, C'HMeMe'), 3.86 (dd, $J_{P-H} = 14.0$, $J_{H-H} = 3.2$, 1H, CHP), 7.00–7.22 (m, 3H, Ar H), 7.38–7.78 (m, 8H, Ar' H), 8.20–8.31 (m, 2H, Ar' H). ³¹P NMR (CDCl₃): δ 49.69 (s). Anal. Calcd for C₃₁H₃₆NPPdCl₂: C, 59.01; H, 5.75; N, 2.22. Found: C, 58.92; H, 5.69; N, 2.24.

Synthesis of 4a: (DME)NiBr₂ (110 mg, 0.36 mmol), **2a** (87 mg, 0.38 mmol), 10 mL of CH₂Cl₂, overnight, recrystallized from CH₂Cl₂/hexane, yield 98 mg (45%). Anal. Calcd for C₂₅H₄₂-NPNiBr₂: C, 49.54; H, 6.98; N, 2.31. Found: C, 49.46; H, 6.88; N, 2.30.

Synthesis of 4b: (DME)NiBr₂ (90 mg, 0.29 mmol), **2b** (121 mg, 0.29 mmol), 10 mL of CH₂Cl₂, 3 days, recrystallized from CH₂Cl₂/hexane, yield 85 mg (46%). Anal. Calcd for C₂₇H₄₄-NPNiBr₂: C, 51.30; H, 7.02; N, 2.22. Found: C, 51.23; H, 6.94; N, 2.19.

Synthesis of 4c: (DME)NiBr₂ (90 mg, 0.29 mmol), **2c** (136 mg, 0.30 mmol), 10 mL of CH₂Cl₂, overnight, recrystallized from CH₂Cl₂/hexane, yield 81 mg (44%). Anal. Calcd for C₃₁H₃₆-NPNiBr₂: C, 55.40; H, 5.40; N, 2.08. Found: C, 55.30; H, 5.32; N, 2.04.

Procedure for Ethylene Polymerization. An evacuated 600 mL Parr pressure reactor was charged with a solution of one of the complexes (20 mg) in 100 mL of chlorobenzene under nitrogen. After the reactor was flushed with ethylene, methyl aluminoxane (MAO) (4 mL in 4.14 M toluene solution, 16 mmol) was charged to the above solution under 100 psi of ethylene. The resulting mixture was stirred under 500 psi of ethylene at 70 °C for 2–7 h. Ethylene pressure was vented and the reaction mixture quenched by the addition of 50 mL of 2-propanol. Water (200 mL) was added into the mixture, and the organic layer was separated. The aqueous layer was extracted with hexane (4 × 40 mL), and all the organic phases were combined and dried with MgSO₄. Polyethylene oils were obtained by solvent removal.

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Supporting Information Available: Tables of crystallographic data, bond distances, bond angles, anisotropic displacement parameters, and all atom coordinates and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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