Synthesis and Characterization of Tridentate Nickel Complexes Bearing P∧N∧N and P∧N∧P Ligands and Their Catalytic Property in Ethylene Oligomerization

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Synthesis and Characterization of Tridentate Nickel Complexes Bearing P^N^N and P^N^P Ligands and Their Catalytic Property in Ethylene Oligomerization

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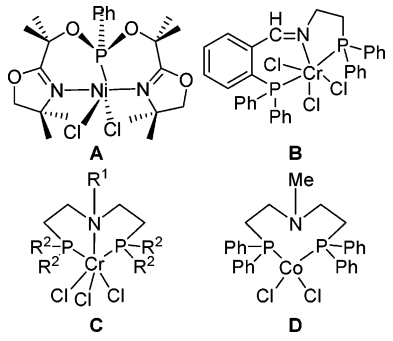
A series of nickel(II) complexes ligated by the *N*-(1-(2-(diarylphosphino)phenyl)methylidene)quinolin-8-amines (P^N^N) and 2-(diphenylphosphino)-*N*-[2-(diarylphosphino)benzylidene]anilines (P^N^P) were synthesized and characterized by elemental analysis, spectroscopy, and X-ray crystallography. X-ray crystallographic analyses reveal complexes **16** and **20** as having a five-coordinated distorted trigonal-bipyramidal geometry, while complex **12** displays a distorted square-pyramidal geometry and complex **13** is distorted square planar. Upon activation with MAO and $AlEtCl_2$, these complexes exhibited considerably high activity (up to 1.34×10^6 g·mol^{-1}(Ni)·h^{-1}) of ethylene oligomerization. It was found that ligand environment and reaction conditions significantly affect the activity of the catalysts. In addition, a cobalt analogue with a distorted tetrahedral coordination geometry was investigated, which showed low activity of ethylene oligomerization.

1. Introduction

Ethylene oligomerization represents a major industrial process for the production of linear α-olefins, which are extensively used in the preparation of detergents, plasticizers, and fine chemicals and as monomers for copolymerization with ethylene in the production of linear low-density polyethylene (LLDPE). The linear α-olefins were originally manufactured by the Ziegler (Alfen) process,[1] and current industrial catalysts include either alkylaluminum compounds or a combination of alkylaluminum compounds and early transition metal compounds or nickel(II) complexes containing bidentate monoanionic [P,O] ligands (the SHOP process).[2] The discovery of the cationic (diimino $NiCl_2$) complexes[3] as effective catalysts for ethylene oligomerization and polymerization resurrected interest in designing new catalysts of late-transition metal complexes with various ligands, such as diimine,[4] unsymmetrical pyridylimine,[5] salicylaldimine,[6] and 8-iminoquinoline.[7] Although only a few examples of the catalysts were found to be comparable to Brookhart's diimine-Ni(II) complexes in terms of their catalytic activities,[8] these numerous studies have enriched the knowledge of the effects of the ligand backbone on the catalysis behavior or mechanism of the catalysts.



Following the success of the SHOP process,[2] nickel complexes containing phosphine ligands have drawn much attention. These complexes contain either bridged bidentate ligands[9] or auxiliary ligands of PPh_3 and exhibit high catalytic activity for ethylene oligomerization.[5d,9h,10] The P^N^N nickel complexes (**A**) perform well as catalysts in the oligomerization of ethylene,[11] and the metal complexes containing various P^N^P

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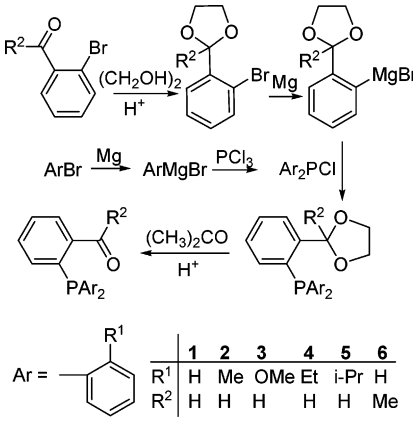
Scheme 1. Synthesis of 2-(Diarylphosphino)benzaldehyde (1−5) and 2-(Diphenylphosphino)acetophenone (6)



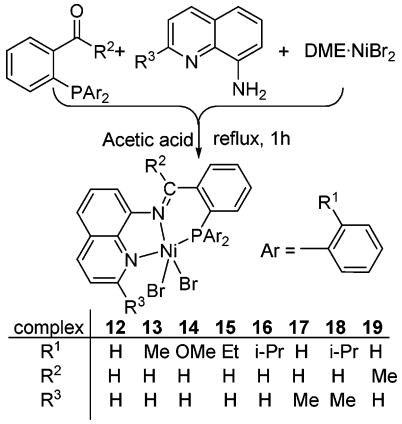
ligands such as the chromium (**B**[12] and **C**[13]) and cobalt analogues (**D**)[14] have also been developed as catalysts for oligomerization and polymerization of ethylene. To study [P^N^N] and [P^N^P] metal complexes for ethylene oligomerization and polymerization, one important research step is to design and synthesize various compounds that will provide the tridentate coordination sites in the complexes, such as the [P^N^N] or [P^N^P] ligands. In this study, nickel complexes containing *N*-(1-(2-(diarylphosphino)phenyl)methylidene)quinolin-8-amines (P^N^N) and 2-(diphenylphosphino)-*N*-[2-(diaryl-phosphino)benzylidene]-anilines (P^N^P) were synthesized, and their catalytic properties for ethylene activation were investigated under various reaction conditions.

2. Results and Discussion

2.1. Synthesis and Characterization. 2.1.1. Synthesis and Characterization of the Benzaldehydes and Ketone. The 2-(diarylphosphino)benzaldehydes (**1**−**5**) and 2-(diphenylphosphino)acetophenone (**6**) were prepared via a modified literature procedure (Scheme 1).[15] All compounds were fully confirmed with their analytic data. The compounds **1** and **6** were reported with basic analysis data without any NMR data of **6** and ^{31}P NMR of **1**.[15] The compounds **1**−**6** display a singlet in their ^{31}P NMR spectra at δ −11.2, −29.0, −36.8, −31.6, −32.9, and −2.3, respectively.

2.1.2. Synthesis and Characterization of the Nickel Complexes Containing the P^N^N Ligand. Much effort was spent in the synthesis of *N*-(1-(2-(diarylphosphino)phenyl)methylidene)-quinolin-8-amines as the P^N^N ligands. However, these compounds tend to decompose when separated by column chromatography. Therefore, the nickel complexes (**12**−**19**) were prepared through a one-pot template reaction, in which the central metal ion was introduced in situ in the condensation reaction of *o*-phosphinoaldehydes and 8-aminoquinolines (Scheme 2). Stoichiometric amounts of the *o*-phosphinoaldehydes, 8-aminoquinolines, and (DME)$NiBr_2$ were mixed and refluxed in acetic acid for 1 h, giving a dark red solution. The obtained complexes (**12**−**19**) were soluble in acetic acid, but did not dissolve in hexane. Therefore, the complexes were precipitated by the addition of hexane after the reaction solution was concentrated in vacuo to ca. 0.5 mL, and the complexes were obtained in high yields. All complexes were characterized with elemental analysis and IR spectroscopy. The NMR data were not obtained due to the paramagnetic nature of nickel complexes. Their structures were confirmed by single-crystal X-ray crystallography.

Scheme 2. Synthesis of Nickel Complexes 12−19



A crystal of **12** was grown by layering hexane on a methanol solution at room temperature under a nitrogen atmosphere. The single crystals of **13** and **16** suitable for X-ray crystallography were grown by layer diffusion of diethyl ether into their dichloromethane solutions. Complex **12** displays a distorted square-pyramidal geometry. The coordination geometry around the nickel atom for complex **13** is distorted square planar. The bromine atom in complexes **12** and **13** acts as a counterion relatively far from the nickel atom Ni(II) (Ni- - -Br distances are 2.891and 5.498 Å, respectively).

For complex **16** (Figure 3), the coordination geometry around the nickel can be described as distorted trigonal bipyramidal, in which the N(2)−Ni(1)−P angle is 151.85(10)° as a result of the strain imposed by the five-membered chelate rings. As noted, the distances between Ni and the two Br atoms are very close, at 2.4471(10) and 2.4789(9) Å, respectively, and the Ni−P bond length in **12** (2.1600(14) Å), **13** (2.1801(8) Å), and **16** (2.4108-(13) Å) increases in the same order as the bulky aryl group on the phosphorus atom.

2.1.3. Synthesis and Characterization of 2-(Diphenylphosphino)-*N*-[2-(diarylphosphino)benzylidene]anilines (P^N^P). The designed compounds (**7**−**11**) were synthesized in satisfactory yields (74.7−81.6%) through the Schiff-base condensation of (*o*-aminophenyl)diphenylphosphine with the corresponding *o*-phosphinoaldehydes in the presence of a catalytic amount of toluene-*p*-sulfonic acid (*p*-TsOH) in refluxing toluene (Scheme 3) as described above. All compounds were characterized and confirmed by elemental analysis, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and IR spectroscopy.

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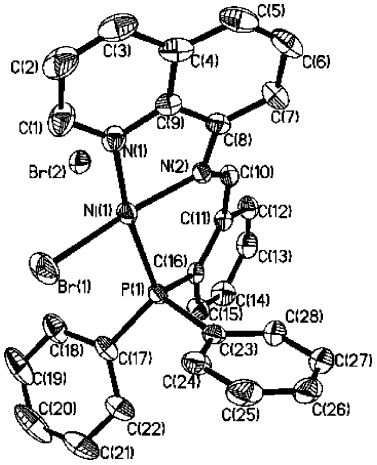


Figure 1. Molecular structure of **12** (thermal ellipsoids at 30% probability, hydrogen atoms and solvent have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−N(1) = 1.951(4), Ni(1)−N(2) = 1.931(3), Ni(1)−P(1) = 2.1600(14), Ni(1)−Br(1) = 2.3176(11); N(1)−Ni(1)−N(2) = 84.00(15); N(2)−Ni(1)−P(1) = 90.33(10), N(1)−Ni(1)−P(1) = 166.62(12), Br(1)−Ni(1)−N(1) = 92.77(12), Br(1)−Ni(1)−N(2) = 167.79(10), Br(1)−Ni(1)−P(1) = 90.24(4). The interaction distance of the Ni cation and bromide anion: Ni(1)- - -Br(2) = 2.891 Å.

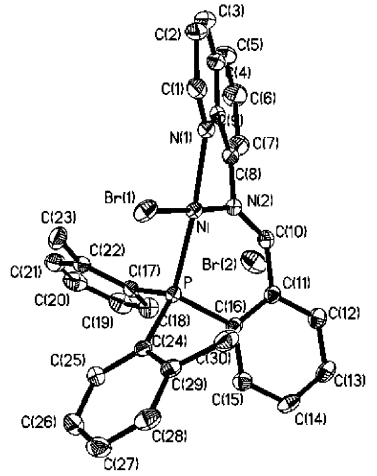


Figure 2. Molecular structure of **13** (thermal ellipsoids at 30% probability, hydrogen atoms and solvent have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni−N(1) = 1.979(2), Ni−N(2) = 1.899(2), Ni−P = 2.1801(8), Ni−Br(1) = 2.2885(5); N(1)−Ni−N(2) = 83.41(11), N(2)−Ni−P = 88.28(7), N(1)−Ni−P = 165.97(10), Br(1)−Ni−N(1) = 93.74(9), Br(1)−Ni−N(2) = 176.11(8), Br(1)−Ni−P = 95.03(3). The interaction distance of Ni cation and bromide anion: Ni- - -Br(2) = 5.498 Å.

2.1.4. Synthesis and Characterization of the Nickel Complexes Containing P^N^P Ligands. The nickel complexes **20**−**24** were easily prepared by combining a CH_2Cl_2 solution of (DME)$NiBr_2$ with 1 equiv of the corresponding P^N^P compounds (**7**−**11**) at room temperature (Scheme 3). The resulting nickel complexes were soluble in CH_2Cl_2, but did not dissolve in diethyl ether. Therefore, anhydrous diethyl ether was added to precipitate the nickel complexes. After washing with diethyl ether, the nickel complexes **20**−**24** were obtained as dark brown powders in good yields (typically 80.0−85.0%) and high purities. These complexes are air-stable in the solid state, but the solutions of these complexes turned from dark brown to red when exposed to air for a few days, most likely due to the oxidation of P(III) to P(V). The structures of these complexes

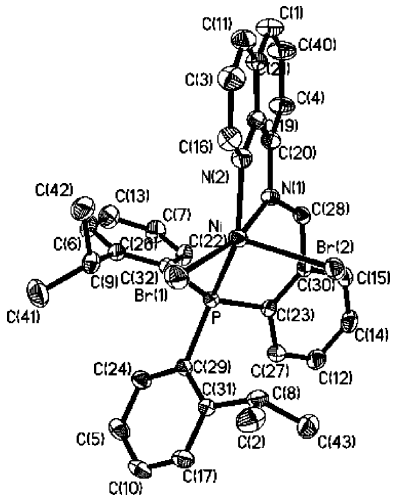
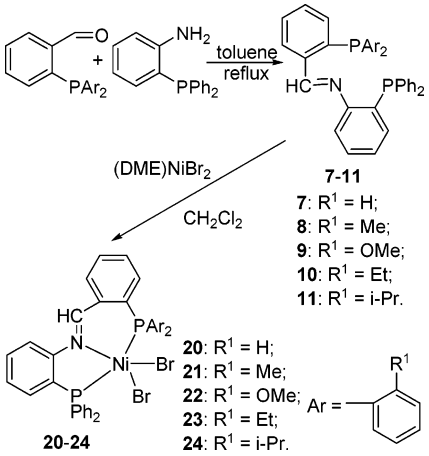


Figure 3. Molecular structure of **16** (thermal ellipsoids at 30% probability, hydrogen atoms and solvent have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni−N(2) = 2.054(3), Ni−N(1) = 2.103(3), Ni−P = 2.4108(13), Ni−Br(1) = 2.4471(10), Ni−Br(2) = 2.4789(9); N(2)−Ni−N(1) = 80.07(13), N(1)−Ni−P = 82.76(9), N(2)−Ni−P = 151.85(10), Br(1)−Ni−Br(2) = 102.68(4), Br(1)−Ni−N(2) = 94.14(10), Br(1)−Ni−N(1) = 166.47(9), Br(1)−Ni−P = 97.53(4), Br(2)−Ni−N(2) = 94.14-(10), Br(2)−Ni−N(1) = 90.20(9), Br(2)−Ni−P = 105.48(4).

Scheme 3. Synthesis of Nickel Complexes



were determined by elemental analysis and IR. The elemental analysis results reveal that the components of these complexes are in accord with the formula $MLBr_2$. The IR spectra of the ligands show that the CH═N stretching frequencies appear in the range 1619−1620 cm^{-1}, while the CH═N stretching vibrations in complexes **20**−**24** shift toward lower frequencies between 1575 and 1590 cm^{-1} with weak intensities, which indicate the effective coordination interaction between the imino nitrogen atoms and nickel center in the complexes.

Crystals of **20** suitable for X-ray crystallography were grown by layer diffusion of diethyl ether into their dichloromethane solutions. The molecular structure of **20** is depicted in Figure 4. In complex **20**, the coordination geometry around the nickel can be described as distorted trigonal bipyramidal, in which there is a *trans* arrangement of phosphorus atoms with the P(2)−Ni-(1)−P(1) angle 150.23(8)°. The C(20)−N(1), C(19)−N(1), and C(18)−C(19) bond lengths of 1.492(9), 1.275(9), and 1.441-(10) Å are typical of single and double bonds, respectively, and there is little electron delocalization through the imine system. The two Ni−P distances are very close (2.154(2) and 2.1972-(19) Å) despite the chemical inequivalence of the two P atoms.

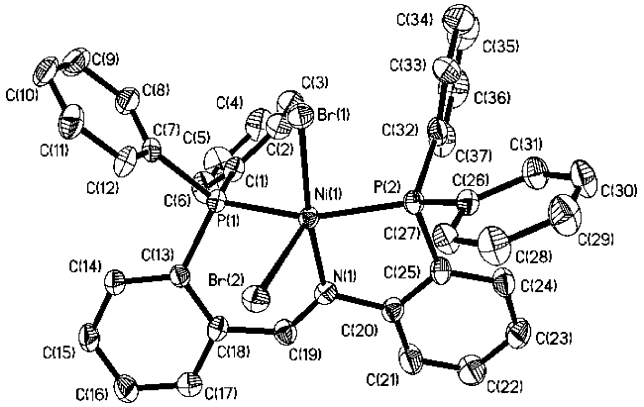


Figure 4. Molecular structure of **20** (thermal ellipsoids at 30% probability, hydrogen atoms and solvent have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ni(1)−P(1) = 2.1972(19), Ni(1)−P(2) = 2.154(2), Ni(1)−N(1) = 1.956(6), Ni(1)−Br(1) = 2.3222(11), Ni(1)−Br(2) = 2.7754(11); N(1)−Ni(1)−P(1) = 92.33(17), N(1)−Ni(1)−P(2) = 88.25(18), P(1)−Ni(1)−P(2) = 150.23(8), Br(1)−Ni(1)−Br(2) = 93.98(4), Br(1)−Ni(1)−P(1) = 91.56(6), Br(1)−Ni(1)−N(1) = 172.46(17), Br(1)−Ni(1)−P(2) = 85.17(6), Br(2)−Ni(1)−P(1) = 95.99(6), Br(2)−Ni(1)−N(1) = 92.05(16), Br(2)−Ni(1)−P(2) = 113.74(6).

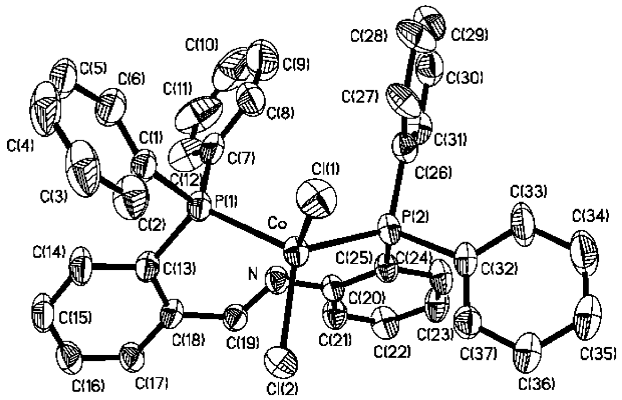


Figure 5. Molecular structure of **25** (thermal ellipsoids at 30% probability, hydrogen atoms and solvent have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Co−Cl(1) = 2.228(3), Co−Cl(2) = 2.237(3), Co−P(1)= 2.380(3), Co−P(2)= 2.367(3); Cl(1)−Co−Cl(2) = 110.24(13), Cl(1)−Co−P(1) = 107.05(12), Cl(1)−Co−P(2) = 103.67(12), Cl(2)−Co−P(1) = 109.04(11), Cl(2)−Co−P(2) = 111.99(11), P(1)−Co−P(2) = 114.59(11). The interaction distance of cobalt and nitrogen atoms: Co- - -N = 2.877 Å.

2.1.5. Synthesis and Characterization of the Cobalt Analogue Containing the P^N^P Ligand. To examine the influence of the metal cation on the catalytic properties of the resulting complex, cobalt analogues containing P^N^P ligands were explored, which showed low catalytic activities for ethylene activations. The cobalt complex **25** was studied in detail for the structural determination and analysis. The cobalt complex (L)$CoCl_2$ (**25**, L = **7**) was prepared by stirring equal amounts of **7** and $CoCl_2$ in EtOH at 25 °C for 2 h. After workup, the Co complex was isolated in 78.1% yield. The X-ray structural determination of **25** reveals that the cobalt(II) complex is four-coordinate with a distorted tetrahedral coordination geometry (Figure 5). The imine 2-PPh_2(C_6H_4N=CHC_6H_4)2-PPh_2 acts as a bidentate ligand through two phosphorus atoms, and the distance of Co- - -N (2.877 Å) is too long to be considered as a bond. The Co−P distances of 2.379(3) and 2.367(3) Å in **25** are significantly longer than the typical Co−P bond length (2.1−2.3 Å) reported for many cobalt(II) phosphine complexes.[16]

Table 1. Ethylene Oligomerization with 12−19 at 1 atm of Ethylene[a]

						oligomer distribution (%)			
entry	complex	Al/Ni[d]	temp (°C)	time (min)	activity[e]	$C_4/\sum C$	$C_6/\sum C$	$C_{\geq 8}/\sum C$	linear α-olefin
1	**12**[b]	1000	20	30	2.31	81.7	11.6	6.7	98
2	**13**[b]	1000	20	30	2.78	98.0	2.0	0	97
3	**14**[b]	1000	20	30	3.10	87.3	4.3	8.4	74
4	**15**[b]	1000	20	30	4.73	91.1	4.4	4.5	92
5	**16**[b]	250	20	30	4.01	94.2	3.2	2.6	92
6	**16**[b]	1000	20	30	5.24	97.0	1.8	1.2	93
7	**16**[b]	2000	20	30	2.07	96.8	1.6	1.6	98
8	**16**[c]	20	20	30	5.86	61.1	25.2	13.7	99
9	**17**[b]	1000	20	30	1.55	98.6	1.4	0	85
10	**18**[b]	1000	20	30	1.47	95.8	4.2	0	87
11	**19**[b]	150	20	30	8.37	23.3	23.5	53.2	69
12	**19**[b]	250	20	30	9.34	28.5	30.4	41.1	78
13	**19**[b]	1000	20	15	13.4	36.7	26.4	36.9	75
14	**19**[b]	1000	20	30	12.2	24.5	23.5	52.0	72
15	**19**[b]	1000	20	60	8.31	23.6	24.1	52.3	73
16	**19**[b]	1000	20	120	4.94	22.7	25.8	51.5	71
17	**19**[b]	1000	0	30	11.2	26.5	30.1	43.4	71
18	**19**[b]	1000	40	30	4.86	48.8	37.6	13.6	59
19	**19**[b]	2000	20	30	4.29	45.0	31.3	23.7	67
20	**19**[c]	10	20	30	7.52	67.6	18.4	14.0	64
21	**19**[c]	20	20	30	9.77	53.2	24.1	22.7	55

[a] General conditions: 5 μmol of catalyst, 30 mL of toluene, 0.5 h. [b] MAO as cocatalyst. [c] $AlEtCl_2$ as cocatalyst. [d] Ratio in moles. [e] 10^5g mol^{-1} h^{-1}.

2.2. Ethylene Oligomerization. 2.2.1. Ethylene Oligomerization Behavior of the Nickel Complexes Bearing P^N^N Ligands. The nickel(II) complexes **12**−**19** were systematically investigated for the oligomerization of ethylene by using MAO or $AlEtCl_2$ as cocatalyst. Various activators and experimental conditions were employed to improve the productivity and selectivity of the catalysts. In most cases, dimerization and trimerization of ethylene are the major reactions, and the selectivity of α-olefin products in total is modest to high according to GC and GC-MS analysis. The results with ambient pressure of ethylene are collected in Table 1.

Effect of Ligand Environment. As shown in Table 1, the bulkiness of the ligands in the complex affect the catalytic activity of ethylene oligomerization. Among complexes **12**−**16**, **16**, with the isopropyl group in the *ortho*-position of the phenyl ring, showed the highest activity, and the activity decreases in the order **16** > **15** > **14** > **13** > **12** under identical reaction conditions. Oligomerization results with **12**−**16** indicate that the introduction of steric hindrance on the phosphorus atom has little influence on the selectivity of α-olefin formation. Increased substitution at the carbon β to phosphorus leads to poor selectivities for α-olefin in the oligomerization of ethylene in the presence of 1000 equiv of MAO. For the purpose of increasing the ligand dimension furthermore, 2-methyl-8-aminoquinoline was introduced into the ligand backbone. Unexpectedly, the activities of the catalytic system with MAO of **17** and **18** are both lower than the analogues **12** and **16**, respectively. The ketimine-derived catalyst **19** was substantially more active than aldimine-derived catalysts **12**−**18**. Catalyst **19**/MAO produced oligomers ranging from C_6 to C_{22} with a low selectivity for α-olefins (50−80%).

Effects of Reaction Parameters. The influences of the Al/Ni molar ratio and the reaction temperature on ethylene oligomerization were investigated in detail with complex **19**. Variation of the Al/Ni molar ratio in the range 150−2000 significantly affects the oligomerization activity and oligomer distribution, and the highest oligomerization activity was

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Table 2. Ethylene Oligomerization of 12−19/MAO at 10 atm of Ethylene[a]

			oligomer distribution (%)			
entry	complex	activity (10^5 g mol^{-1} h^{-1})	$C_4/\sum C$	$C_6/\sum C$	$C_{\geq 8}/\sum C$	linear α-olefin
1	**12**	3.51	77.9	19.5	2.6	99
2	**13**	8.35	97.8	2.2	0	98
3	**14**	13.3	95.9	4.1	0	99
4	**15**	7.62	98.1	1.9	0	97
5	**16**	8.08	46.8	33.9	19.3	97
6	**17**	5.22	96.7	3.3	0	99
7	**18**	2.13	98.5	1.5	0	99
8	**19**	11.5	54.5	27.6	17.9	77

[a] Reaction conditions: 5 μmol of catalyst, Al/Ni = 1000, 20 °C, 120 mL of toluene, 0.5 h.

Table 3. Ethylene Oligomerization Using the 20−24/MAO Systems[a]

					oligomer distribution (%)			
entry	complex	Al/Ni	temp (°C)	activity (10^4 g mol^{-1} h^{-1})	$C_4/\sum C$	$C_6/\sum C$	$C_{\geq 8}/\sum C$	linear α-olefin
1	**20**	1000	20	3.16	85.9	11.1	3.0	98
2	**21**	1000	20	3.94	85.1	9.6	5.3	97
3	**22**	1000	20	5.58	50.4	35.1	14.5	94
4	**23**	1000	20	7.72	84.5	11.3	4.2	98
5	**24**	250	20	10.2	80.1	14.3	5.6	98
6	**24**	500	20	11.4	83.8	10.1	6.1	98
7	**24**	500	0	7.44	87.8	12.2	0	96
8	**24**	500	40	3.52	92.1	7.9	0	97
9	**24**	1000	20	9.33	81.6	11.2	7.2	98

[a] Reaction condition: 5 μmol of catalyst, 30 mL of toluene, 0.5 h, 1 atm ethylene.

observed at the Al/Ni molar ratio of 1000. The catalyst **19** showed higher oligomerization activity at lower temperature, and elevating the reaction temperature to 40 °C led to the remarkable reduction in activity (entry 18, Table 1), which may be attributable to the decomposition of the active catalytic sites and lower ethylene solubility at higher temperature. The oligomerization activity progressively decreased when the reaction was prolonged from 15 to 60 min and finally to 120 min, which indicates that the catalyst lifetime is relative short.

Recently Braunstein's group reported that N^P-coordinated nickel complexes show high ethylene oligomerization activity upon activation with a slight excess of $AlEtCl_2$.[9d−f,11] Therefore, oligomerization with complexes **16** and **19** was investigated by using $AlEtCl_2$ instead of MAO as cocatalyst. It was observed that complex **19** displays high activity with only 20 molar equiv of $AlEtCl_2$ as the cocatalyst (entry 21, Table 1).

Effects of Ethylene Pressure. The complexes **12**−**19** were also examined for ethylene oligomerization at 10 atm of ethylene pressure, and the results are summarized in Table 2. These data suggest that increased ethylene pressure results in slightly higher catalytic activity, and the effect of the ligand environments on the oligomerization activity is similar to that observed at 1 atm. In addition, the percentages of the higher carbon number olefins in the oligomers are much lower than those obtained at 1 atm of ethylene pressure, while the similar tendency of selectivity for α-olefin was observed at elevated ethylene pressure.

2.2.2. Ethylene Oligomerization Behavior of the Nickel Complexes Bearing P^N^P Ligands. The complexes **20**−**25** were investigated for their ethylene oligomerization behavior upon activation with MAO and $AlEtCl_2$, and the results are listed in Tables 3 and 4, respectively. In all cases, dimers and trimers of ethylene are the main products. According to GC and GC-MS results, the selectivity of α-olefins in total olefins is high.

Effect of Ligand Environment. The bulkiness of the ligand in the nickel complex slightly affects the ethylene oligomerization activity. The selectivity of α-olefins with the catalytic system of complexes **20**−**24**/MAO is generally high. The main products formed during the oligomerization reactions were C_4 and C_6. **24**, with an isopropyl substituent on the phenyl ring, showed the highest activity under identical reaction conditions. Precatalyst **22** generated a large quantity of octenes, while the selectivity for α-olefins was poor. As shown in Table 3, the activity increases in the order of increased ligand bulk: **24** > **23** > **22** > **21** > **20**. These results resemble the catalytic activities obtained with four-membered diphosphine nickel(II) chelates.[17]

Table 4. Ethylene Oligomerization Using the 20−24/$AlEtCl_2$ Systems[a]

			oligomer distribution (%)			
entry	complex	activity (10^5 g mol^{-1} h^{-1})	$C_4/\sum C$	$C_6/\sum C$	$C_{\geq 8}/\sum C$	linear α-olefin
1	**20**	1.04	66.7	21.2	12.1	98
2	**21**	2.78	72.2	24.3	3.5	99
3	**22**	3.33	79.1	19.7	1.2	99
4	**23**	3.24	76.9	14.3	8.8	98
5	**24**	3.74	69.6	25.4	5.0	99

[a] Reaction conditions: 5 μmol of catalyst, Al/Ni = 20, 20 °C, 30 mL of toluene, 0.5 h, 1 atm ethylene.

Effects of Reaction Parameters. The influences of the Al/Ni molar ratio and the reaction temperature on ethylene oligomerization were investigated in detail with complex **24**. Varying the Al/Ni molar ratio in the range 250−1000 had little effect on the oligomerization activity and oligomer distribution, and the highest oligomerization activity was observed when the Al/Ni molar ratio is 500.

When $AlEtCl_2$ was used as the cocatalyst, all nickel complexes performed well as catalysts for ethylene oligomerization, with high selectivity of α-olefins and considerably high activity. Collected in Table 4 are the results obtained with complexes **20**−**24** as the catalysts and 20 equiv of $AlEtCl_2$.

2.2.3. Test of Ethylene Activation on the Cobalt Complex Bearing a P^N^P Ligand. General scanning work has been done to test cobalt complexes bearing various PNP ligands; however, all the cobalt complexes were inactive in the presence of MAO or $AlEt_3$. In the presence of 20 equiv of $AlEtCl_2$, precatalyst **25** showed an activity of 7.4×10^4 g mol^{-1} h^{-1}. Dimerization (92.1%) and trimerization (7.9%) of ethylene dominated, and a selectivity for 1-butene within the C_4 fraction of 94% was observed. Therefore there is less interest for the Co(II) complexes for ethylene activity. That might be caused by the ligand being bidentate instead of tridentate.

3. Conclusion

A series of nickel(II) complexes ligated by *N*-(1-(2-(diarylphosphino)phenyl)methylidene)quinolin-8-amines (P^N^N) and 2-(diphenylphosphino)-*N*-[2-(diarylphosphino)benzylidene]-anilines (P^N^P) were synthesized and characterized. The P^N^N ligands are not stable, and their complexes were synthesized through metal-induced template reaction. Activated by MAO and $AlEtCl_2$, all nickel complexes exhibited considerably high catalytic activity for ethylene oligomerization, with the dimers and trimers of ethylene as the major products. In the presence of 1000 equiv of MAO, complex **19** showed an

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activity of 1.34×10^6 g·mol^{-1}(Ni)·h^{-1}. Interestingly, the selectivities of α-olefins are modest to high, which will be further investigated. The ethylene oligomerization activity was found to be affected by the substituents in the ligands' framework. Incorporation of bulky groups of ligands led to an increase in catalytic activity of ethylene oligomerization.

4. Experimental Section

General Considerations. All manipulations involving air- or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All solvents were dried and distilled using common techniques unless otherwise stated. All Grignard reagents were prepared by slow addition of the corresponding aryl bromides or chlorides to a suspension of magnesium in THF. The magnesium was activated by adding some iodine crystals. (DME)$NiBr_2$,[18] 2-(diphenylphosphino)benzaldehyde (**1**) (^{31}P NMR ($CDCl_3$) δ: −11.2 (s)),[15] 2-(2-bromophenyl)-1,3-dioxolane,[15] 2-{bis(2-methylphenyl)}chlorophosphine,[19a] and (*o*-aminophenyl)diphenylphosphine (^{31}P NMR ($CDCl_3$) δ: −19.9 (s))[19b] were prepared according to the literature methods. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.4 M toluene solution. $AlEtCl_2$ was purchased from Fluka as a 1.0 M hexane solution. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. The chemical shifts of the NMR spectra were measured with a Bruker BMX-300 MHz instrument and were referenced against residual solvent peaks (^{1}H, ^{13}C) or H_3PO_4 (^{31}P). Elemental analysis was performed by using a HP-MOD 1106 microanalyzer. GC analyses were performed with a Carlo Erba Strumentazione gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) DM-1 silica capillary column.

4.1. Synthesis of the *o*-Phosphinoaldehydes. 2-(Di-*o*-tolylphosphino)benzaldehyde (2). Magnesium (0.15 mol) and 200 mL of THF were placed into a 1000 mL, three-neck flask equipped with a mechanical stirrer, a condenser, and a pressure-equalizing addition funnel. The addition funnel was charged with 27.5 g (0.12 mol) 2-(2-bromophenyl)-1,3-dioxolane. The reaction was initiated with a crystal of I_2 and a few milliliters of the dioxolane. The remaining dioxolane was added slowly in 3 mL aliquots from the addition funnel, and the reaction was then heated to reflux for 30 min. The clear, brownish solution was cooled in an ice bath while a solution of chloro-di(*o*-tolyl)phosphine (0.12 mol) in 200 mL of anhydrous THF was prepared in the addition funnel. The phosphine was added dropwise to the stirred Grignard reagent while the temperature was maintained at ca. 5 °C. After the addition was complete, the reaction was heated to reflux for 10 h. The cooled reaction was cautiously quenched with 75 mL of 10% aqueous NH_4Cl, and the nonaqueous extracts was further extracted with 100 mL of saturated aqueous NaCl. The combined aqueous extracts were washed with 200 mL of diethyl ether. The combined nonaqueous extracts were dried over anhydrous Na_2SO_4 and then concentrated to an oily liquid on a rotary evaporator. The produced mixture was separated by column chromatography over silica gel (petroleum ether/ethyl acetate, 8/1) to give (2-(1,3-dioxolan-2-yl)phenyl)di-*o*-tolylphosphine (19.4 g, 44.6%). R_f (petroleum ether/ethyl acetate, 2/1): 0.81. ^{1}H NMR ($CDCl_3$) δ: 2.36 (s, 6H, CH_3), 3.96−4.10 (m, 4H, O−CH_2CH_2−O), 6.45−6.47 (m, 1H, PhC*H*), 6.72−6.74 (m, 2H, Ph), 6.86−6.89 (m, 1H, Ph), 7.08−7.11 (m, 2H, Ph), 7.23−7.25 (m, 5H, Ph), 7.40−7.45 (m, 1H, Ph), 7.71−7.72 (m, 1H, Ph).

(2-(1,3-Dioxolan-2-yl)phenyl)di-*o*-tolylphosphine (19.4 g, 53.5 mmol) was added to 400 mL of acetone in a 1000 mL, round-bottomed flask equipped with a magnetic stirrer and a condenser. *p*-Toluenesulfonic acid monohydrate (0.57 g, 3.0 mmol) was added, and the solution was refluxed for 8 h. During this time, the yellow color of the final product developed. The product mixture was separated by column chromatography over silica gel (petroleum ether/ethyl acetate, 8/1). R_f (petroleum ether/ethyl acetate, 2/1): 0.86. To obtain pure product, the yellow crystals were recrystallized from petroleum ether/ethyl acetate, affording 2-(di-*o*-tolylphosphino)benzaldehyde (13.4 g, 42.1 mmol, 78.7%). Mp: 120.0−120.5 °C. ^{1}H NMR ($CDCl_3$) δ: 2.43 (s, 6H, CH_3), 6.68−6.72 (m, 2H, Ph), 6.92−6.96 (m, 1H, Ph), 7.07 (t, 2H, Ph, J = 7.5 Hz), 7.22−7.30 (m, 4H, Ph), 7.43−7.53 (m, 2H, Ph), 7.99−8.02 (m, 1H, Ph), 10.58 (d, 1H, C*H*O, J(PH) = 6.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 55.5, 110.2, 121.0, 123.5, 123.6, 128.3, 128.6, 130.5, 133.3, 134.0, 138.7, 138.9, 140.7, 141.0, 161.0, 161.2, 191.7, 192.0. Anal. Calcd for $C_{21}H_{19}OP$: C, 79.23; H, 6.02. Found: C, 79.09; H, 6.27. ^{31}P NMR ($CDCl_3$) δ: −29.0 (s). IR (KBr): 1696 ($\nu_{C=O}$), 1648, 1584, 1562, 1451, 1391, 1288, 1264, 1200, 1166, 1120, 1066, 1037 cm^{-1}.

2-(Bis(2-methoxyphenyl)phosphino)benzaldehyde (3). The 2-(bis(2-methoxyphenyl)phosphino)benzaldehyde was prepared according to a literature method.[20] Mp: 176.0−176.5 °C. ^{1}H NMR ($CDCl_3$) δ: 3.74 (s, 6H, CH_3), 6.68−6.71 (m, 2H, Ph), 6.84−6.93 (m, 4H, Ph), 7.01−7.03 (m, 1H, Ph), 7.33−7.45 (m, 4H, Ph), 7.98−8.00 (m, 1H, Ph), 10.78 (d, 1H, C*H*O, J(PH) = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 52.2, 54.4, 108.9, 116.3, 119.9, 122.5, 122.6, 124.7, 125.9, 126.0, 127.0, 127.1, 127.5, 128.3, 129.2, 129.4, 131.1, 131.5, 131.6, 132.1, 132.7, 133.0, 135.8, 135.9, 136.3, 136.5, 138.4, 138.6, 152.6, 152.8, 157.1, 157.5, 159.9, 160.1. Anal. Calcd for $C_{21}H_{19}O_3P$: C, 71.99; H, 5.47. Found: C, 71.86; H, 5.36. ^{31}P NMR ($CDCl_3$) δ: −36.8 (s). IR (KBr): 1692 ($\nu_{C=O}$), 1645, 1579, 1463, 1428, 1393, 1275, 1242, 1196, 1172, 1132, 1070, 1017 cm^{-1}.

2-(Bis(2-ethylphenyl)phosphino)benzaldehyde (4). The 2-ethylphenyl Grignard reagent was prepared by the dropwise addition of 22.15 g (0.120 mol) of 1-bromo-2-ethylbenzene in 60 mL of anhydrous THF to 3.38 g (0.139 mol) of magnesium turnings in 40 mL of THF under reflux conditions (in a 250 mL three-neck flask fitted with a pressure-equalizing dropping funnel, magnetic stirrer, and condenser). After the addition was complete (ca. 1 h) the solution was refluxed for a further 1 h, at which stage little magnesium metal still remained. At this time the Grignard was cooled in an ice bath. To a three-neck 1 L flask was added 7.83 g (0.057 mol) of phosphorus trichloride in 120 mL of anhydrous THF. The solution was cooled in a dry ice/acetone bath. The Grignard solution was then transferred under nitrogen through a tube into a pressure-equalizing dropping funnel. Then the Grignard solution was added slowly in a dropwise manner over a 1 h period to the solution of phosphorus trichloride with the aid of a magnetic stirrer. After the addition was complete, the solution was slowly warmed to room temperature overnight. The solution was then heated to reflux for 1 h. The solvent was removed by distillation, and the product extracted with hexane. Distillation of the extracts gave a light yellow liquid that solidified overnight. The phosphine was added dropwise to the stirred solution of 2-(2-bromophenyl)-1,3-dioxolane Grignard reagent (0.05 mol) in THF (100 mL) while the temperature was maintained at ca. 5 °C. After the addition was complete, the reaction was heated to reflux for 10 h. The cooled reaction was cautiously quenched with 30 mL of 10% aqueous NH_4Cl, and the nonaqueous extracts were further extracted with 35 mL of saturated aqueous NaCl. The combined aqueous extracts were washed with 100 mL of diethyl ether. The combined nonaqueous extracts were dried over anhydrous Na_2SO_4 and then concentrated to an oily liquid on a rotary evaporator. The mixture was separated by column chromatography over silica gel (petroleum ether/ethyl acetate, 10/1) to give (2-(1,3-dioxolan-2-yl)phenyl)bis(2-ethylphenyl)phosphine (13.0 g, 66.6%). R_f (petroleum ether/ethyl acetate, 3/1): 0.78. ^{1}H NMR ($CDCl_3$) δ: 1.13 (t, 6H, CH_3, J = 7.6 Hz,),

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2.75−2.83 (q, 4H, CH_2, J = 7.4 Hz), 3.89−4.13 (m, 4H, O−CH_2CH_2−O), 6.41 (d, 1H, Ph−CH, J = 5.5 Hz), 6.74−6.78 (m, 2H, Ph), 6.86−6.88 (m, 1H, Ph), 7.06 (t, 2H, Ph, J = 7.3 Hz), 7.22−7.29 (m, 4H, Ph), 7.36−7.38 (m, 2H, Ph), 7.67−7.69 (m, 1H, Ph).

(2-(1,3-Dioxolan-2-yl)phenyl)-bis(2-ethylphenyl)phosphine (13.0 g, 33.3 mmol) was added to 250 mL of acetone in a 500 mL, round-bottomed flask equipped with a magnetic stirrer and a condenser. *p*-Toluenesulfonic acid monohydrate, 0.38 g (2.0 mmol), was added, and the solution was refluxed for 8 h. During this time, the yellow color of the final product developed. The warm solution was diluted with 50 mL of H_2O, concentrated to 60 mL, and cooled overnight at −20 °C. The precipitated yellow crystals were filtered from the cold solution. To obtain pure product, the yellow crystals were recrystallized from CH_2Cl_2/MeOH, affording 2-(bis(2-ethylphenyl)-phosphino)benzaldehyde (8.08 g, 70.0%). Mp: 82.0−82.5 °C. ^{1}H NMR ($CDCl_3$) δ: 1.14 (t, 6H, CH_3, J = 7.2 Hz), 2.81−2.86 (q, 4H, CH_2, J = 7.4 Hz), 6.70−6.73 (m, 2H, Ph), 6.87−6.90 (m, 1H, Ph), 7.03 (t, 2H, Ph, J = 7.6 Hz), 7.23−7.30 (m, 4H, Ph), 7.38−7.46 (m, 2H, Ph), 7.93−7.96 (m, 1H, Ph), 10.52 (d, 1H, CHO, J(PH) = 6.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.3, 27.5, 27.8, 126.3, 128.5, 128.8, 129.4, 129.8, 129.9, 133.7, 133.9, 134.0, 134.2, 138.4, 138.5, 141.2, 141.4, 148.6, 148.8, 191.6, 191.8. Anal. Calcd for $C_{23}H_{23}OP$: C, 79.75; H, 6.69. Found: C, 79.41; H, 6.86. ^{31}P NMR ($CDCl_3$) δ: −31.6 (s). IR (KBr): 1696 ($\nu_{C=O}$), 1642, 1580, 1463, 1436, 1388, 1286, 1259, 1197, 1161, 1131, 1112, 1027 cm^{-1}.

2-(Bis(2-isopropylphenyl)phosphino)benzaldehyde (5). The 2-isopropylphenyl Grignard reagent was prepared by the dropwise addition of 59.73 g (0.300 mol) of 1-bromo-2-isopropylbenzene in 120 mL of anhydrous THF to 8.51 g (0.350 mol) of magnesium turnings in 60 mL of THF under reflux conditions in a 500 mL three-neck flask fitted with a pressure-equalizing dropping funnel, magnetic stirrer, and condenser. After the addition was complete (ca. 1 h) the solution was refluxed for a further 1 h, at which stage little magnesium metal still remained. At this time the Grignard was cooled in an ice bath. To a three-neck 1000 mL flask was added 19.61 g (0.143 mol) of phosphorus trichloride in 200 mL of anhydrous THF. The solution was cooled in a dry ice/acetone bath. The Grignard solution was then transferred under nitrogen through a tube into a pressure-equalizing dropping funnel. Then the Grignard solution was added slowly in a dropwise manner over a 1 h period to the solution of phosphorus trichloride with the aid of a magnetic stirrer. After the addition was complete, the solution was slowly warmed to room temperature overnight. The solution was then heated to reflux for 1 h. The solvent was removed by distillation, and the product extracted with hexane. Distillation of the extracts gave a light yellow liquid that solidified overnight. The phosphine was added dropwise to the stirred solution of 2-(2-bromophenyl)-1,3-dioxolane Grignard reagent (0.10 mol) in THF (200 mL) while the temperature was maintained at ca. 5 °C. After the addition was complete, the reaction was heated to reflux for 10 h. The cooled reaction was cautiously quenched with 60 mL of 10% aqueous NH_4-Cl, and the nonaqueous extracts was further extracted with 70 mL of saturated aqueous NaCl. The combined aqueous extracts were washed with 200 mL of diethyl ether. The combined nonaqueous extracts were dried over anhydrous Na_2SO_4 and then concentrated to an oily liquid on a rotary evaporator. The mixture was separated by column chromatography over silica gel (petroleum ether/ethyl acetate, 8/1) to give (2-(1,3-dioxolan-2-yl)phenyl)bis(2-isopropy-lphenyl)phosphine (11.4 g, 27.2%). R_f (petroleum ether/ethyl acetate, 10/1): 0.52. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (d, 6H, J = 6.8 Hz, CH_3), 1.19 (d, 6H, J = 7.2 Hz, CH_3), 3.63−3.76 (m, 2H, CH(CH_3)$_2$), 3.92−4.12 (m, 4H, O−CH_2CH_2−O), 6.39 (s, 1H, Ph-CH), 6.70−6.74 (m, 2H, Ph), 6.93−6.96 (m, 1H, Ph), 7.00−7.03-(m, 2H, Ph, J = 7 Hz), 7.31−7.42 (m, 6H, Ph), 7.68−7.71 (m, 1H).

(2-(1,3-Dioxolan-2-yl)phenyl)bis(2-isopropylphenyl)phosphine (11.4 g, 27.2 mmol) was added to 250 mL of acetone in a 500 mL, round-bottomed flask equipped with a magnetic stirrer and a condenser. *p*-Toluenesulfonic acid monohydrate, 0.38 g (2.0 mmol), was added, and the solution was refluxed for 8 h. During this time, the yellow color of the final product developed. The product mixture was separated by column chromatography over silica gel (petroleum ether/ethyl acetate, 20/1). R_f (petroleum ether/ethyl acetate, 6/1): 0.64. To obtain pure product, the yellow crystals were recrystallized from petroleum ether/ethyl acetate, affording 2-(bis(2-isopropyl-phenyl)phosphino)benzaldehyde (6.34 g, 62.1%). Mp: 158.0−158.5 °C. ^{1}H NMR ($CDCl_3$) δ: 1.11 (d, 6H, CH_3, J = 6.5 Hz), 1.19 (d, 6H, CH_3, J = 6.7 Hz), 3.67−3.73 (m, 2H, CH(CH_3)$_2$), 6.75−6.77 (m, 2H, Ph), 6.93−6.96 (m, 1H, Ph), 7.04 (t, 2H, Ph, J = 7.3 Hz), 7.31−7.36 (m, 4H, Ph), 7.44−7.48 (m, 2H, Ph), 7.97−8.00 (m, 1H, Ph), 10.54 (d, 1H, CHO, J(PH) = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.8, 24.0, 31.4, 31.6, 125.6, 126.3, 128.8, 129.7, 130.0, 133.7, 134.2, 134.4, 138.3, 138.4, 141.8, 141.9, 153.3, 153.5, 191.6, 191.8. Anal. Calcd for $C_{25}H_{27}OP$: C, 80.19; H, 7.27. Found: C, 79.95; H, 7.24. ^{31}P NMR ($CDCl_3$) δ: −32.9 (s). IR (KBr): 1697 ($\nu_{C=O}$), 1647, 1583, 1469, 1435, 1384, 1290, 1259, 1201, 1163, 1113, 1054, 1029 cm^{-1}.

2-(Diphenylphosphino)acetophenone (6). The 2-(diphenylphos-phino)acetophenone was prepared according to a literature method,[15a] but without the detailed analysis data in the literature. Mp: 137.0−137.5 °C. ^{1}H NMR ($CDCl_3$) δ: 2.59 (s, 3H, CH_3), 7.01−7.04 (m, 1H, Ph), 7.26−7.47 (m, 12H, Ph), 7.94−7.97 (m, 1H, Ph). ^{31}P NMR ($CDCl_3$) δ: −2.3 (s). IR (KBr): 1668 ($\nu_{C=O}$), 1585, 1559, 1477, 1431, 1355, 1252, 1204, 1092, 1022 cm^{-1}.

4.2. Synthesis of the Nickel Complexes Containing P^N^N Ligands (12−19). Complexes **12**−**19** were prepared with the same method, and the typical procedure is described as follows. An orange suspension of aldehyde **7** (0.5806 g, 2.00 mmol), 8-aminoquinoline (0.2884 g, 2.00 mmol), and (DME)$NiBr_2$ (0.6180 g, 2.00 mmol) in glacial acetic acid (12 mL) was refluxed for 2 h, giving a dark red solution. The solution was concentrated in vacuo to ca. 1 mL. Hexane (10 mL) was added to precipitate the complex. After filtration and washing with hexane, **12** was obtained as a purple powder in 89.7% yield. Mp: 218 °C (dec). IR (KBr): 1603, 1556, 1507, 1480, 1434, 1406, 1315, 1231, 1187, 1136, 1098, 1050 cm^{-1}. Anal. Calcd for $C_{28}H_{21}Br_2N_2NiP$: C, 52.96; H, 3.33; N, 4.41. Found: C, 52.51; H, 3.60; N, 4.37.

Complex **13** was obtained as an orange powder in 94.2% yield. Mp: 259 °C (dec). IR (KBr): 1605, 1558, 1504, 1435, 1407, 1311, 1230, 1202, 1130, 1076, 1030 cm^{-1}. Anal. Calcd for $C_{30}H_{25}Br_2N_2$-NiP·2H_2O: C, 51.55; H, 4.18; N, 4.01. Found: C, 51.29; H, 3.92; N, 4.19.

Complex **14** was obtained as an orange powder in 90.4% yield. Mp: 257 °C (dec). IR (KBr): 1603, 1585, 1506, 1475, 1431, 1280, 1244, 1165, 1135, 1075, 1013 cm^{-1}. Anal. Calcd for $C_{30}H_{25}Br_2N_2$-NiO_2P·2H_2O: C, 49.29; H, 4.00; N, 3.83. Found: C, 49.48; H, 4.03; N, 3.86.

Complex **15** was obtained as an orange powder in 87.1% yield. Mp: 220 °C (dec). IR (KBr): 1602, 1558, 1506, 1467, 1435, 1377, 1316, 1236, 1168, 1075, 1049 cm^{-1}. Anal. Calcd for $C_{32}H_{29}Br_2N_2$-NiP·2H_2O: C, 52.86; H, 4.57; N, 3.85. Found: C, 51.93; H, 4.48; N, 4.21.

Complex **16** was obtained as an orange powder in 90.7% yield. Mp: 238 °C (dec). IR (KBr): 1600, 1557, 1506, 1471, 1434, 1408, 1382, 1317, 1269, 1237, 1213, 1165, 1088, 1032 cm^{-1}. Anal. Calcd for $C_{34}H_{33}Br_2N_2NiP$: C, 56.79; H, 4.63; N, 3.90. Found: C, 56.71; H, 4.29; N, 3.51.

Complex **17** was obtained as a green powder in 90.7% yield. Mp: 300 °C (dec). IR (KBr): 1593, 1557, 1505, 1478, 1432, 1408, 1373, 1320, 1295, 1242, 1213, 1147, 1093, 1029 cm^{-1}. Anal. Calcd for $C_{29}H_{23}Br_2N_2NiP$: C, 53.67; H, 3.57; N, 4.32. Found: C, 53.44; H, 3.62; N, 4.22.

Complex **18** was obtained as a green-gray powder in 91.5% yield. Mp: 282 °C (dec). IR (KBr): 1607, 1560, 1503, 1468, 1433, 1377, 1326, 1292, 1242, 1210, 1164, 1114, 1073, 1029 cm^{-1}. Anal. Calcd for $C_{35}H_{35}Br_2N_2NiP\cdot 0.5H_2O$: C, 56.64; H, 4.89; N, 3.77. Found: C, 56.62; H, 4.87; N, 3.81.

Complex **19** was obtained as an orange powder in 84.4% yield. Mp: 244 °C (dec). IR (KBr): 1628, 1571, 1504, 1473, 1393, 1318, 1260, 1210, 1168, 1134, 1076, 1021 cm^{-1}. Anal. Calcd for $C_{29}H_{23}Br_2N_2NiP$: C, 53.67; H, 3.57; N, 4.32. Found: C, 53.47; H, 3.71; N, 4.16.

4.3. Synthesis of the Nickel Complexes Containing P^N^P Ligands (20−24). 2-(Diphenylphosphino)-*N*-[2-(diphenylphosphino)benzylidene]aniline (7). This compound was prepared according to a literature method.[21] Mp: 185.0−185.5 °C. ^{1}H NMR ($CDCl_3$) δ: 6.45−6.49 (m, 1H, Ph), 6.73−6.85 (m, 2H, Ph), 7.06 (t, 1H, J = 7.4 Hz, Ph), 7.21−7.36 (m, 23H, Ph), 7.94−7.98 (m, 1H, Ph), 8.93 (d, 1H, C*H*═N, J = 5.5 Hz). ^{31}P NMR ($CDCl_3$) δ: −14.5 (s), −13.8 (s). IR (KBr): 1619 ($\nu_{CH=N}$), 1561, 1469, 1431, 1361, 1307, 1266, 1229, 1186, 1157, 1091, 1069, 1025 cm^{-1}.

2-(Diphenylphosphino)-*N*-[2-(di(*o*-methylphenyl)phosphino)-benzylidene]aniline (8). A solution of (*o*-aminophenyl)diphenylphosphine (0.555 g, 2.0 mmol), 2-(di-*o*-tolylphosphino)benzaldehyde (0.634 g, 2.0 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (60 mL) was refluxed for 10 h. After solvent evaporation, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15/1) as eluent to afford a yellow oil. This was dissolved in a minimum amount of dichloromethane, then methanol was added until crystallization began. The pale yellow crystals were isolated and dried in vacuo. Yield: 0.739 g (64.0%). Mp: 82.0−82.5 °C. ^{1}H NMR ($CDCl_3$) δ: 2.37 (s, 6H, C*H*$_3$), 6.46−6.49 (m, 1H, Ph), 6.71−6.77 (m, 4H, Ph), 7.05−7.08 (m, 3H, Ph), 7.22−7.34 (m, 17H, Ph), 7.97−8.00 (m, 1H, Ph), 8.93 (d, 1H, C*H*═N, J = 5.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.2, 21.5, 117.3, 126.0, 126.4, 127.6, 128.3, 128.4, 128.5, 129.1, 129.8, 130.2, 131.1, 132.5, 132.7, 132.9, 133.4, 133.7, 133.9, 134.0, 134.1, 134.3, 136.7, 136.9, 137.1, 139.6, 139.9, 142.3, 142.7, 154.0, 154.3, 158.1, 158.5. Anal. Calcd for $C_{39}H_{33}NP_2\cdot H_2O$: C, 78.64; H, 5.92; N, 2.35. Found: C, 78.50; H, 5.85; N, 2.54. ^{31}P NMR ($CDCl_3$) δ: −31.1 (s), −13.8(s). IR (KBr): 1619 ($\nu_{CH=N}$), 1564, 1464, 1433, 1361, 1307, 1267, 1191, 1160, 1123, 1092, 1065, 1028 cm^{-1}.

2-(Diphenylphosphino)-*N*-[2-(di(*o*-methoxyphenyl)phosphino)-benzylidene]aniline (9). Using the same procedure as for the synthesis of **8**, **9** was obtained as yellow crystals in 71.4% yield. Mp: 206.0−206.5 °C. ^{1}H NMR ($CDCl_3$) δ: 3.71 (s, 6H, C*H*$_3$), 6.64−6.74 (m, 4H, Ph), 6.81−6.91 (m, 5H, Ph), 7.04 (t, 1H, Ph, J = 7.2 Hz), 7.19−7.36 (m, 15H, Ph), 7.95−7.99 (m, 1H, Ph), 9.11 (d, 1H, C*H*═N, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.2, 21.5, 117.3, 126.0, 126.4, 127.6, 128.3, 128.4, 128.5, 129.1, 129.8, 130.2, 131.1, 132.5, 132.7, 132.9, 133.4, 133.7, 133.9, 134.0, 134.1, 134.3, 136.7, 136.9, 137.1, 139.6, 139.9, 142.3, 142.7, 154.0, 154.3, 158.1, 158.5. Anal. Calcd for $C_{39}H_{33}NO_2P_2\cdot H_2O$: C, 74.63; H, 5.62; N, 2.23. Found: C, 74.55; H, 5.41; N, 2.06. ^{31}P NMR ($CDCl_3$): δ −37.7 (s), −14.1(s). IR (KBr): 1620 ($\nu_{CH=N}$), 1578, 1461, 1427, 1393, 1242, 1196, 1172, 1132, 1070, 1016 cm^{-1}.

2-(Diphenylphosphino)-*N*-[2-(di(*o*-ethylphenyl)phosphino)-benzylidene]aniline (10). A solution of (*o*-aminophenyl)diphenylphosphine (0.555 g, 2.0 mmol), 2-(di(*o*-ethylphenyl)phosphino)-benzaldehyde (0.693 g, 2.0 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (60 mL) was refluxed for 10 h. After solvent evaporation, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10/1) as eluent to afford a yellow powder. Yield: 0.756 g (62.4%). Mp: 163.0−163.5 °C. ^{1}H NMR ($CDCl_3$) δ: 1.19 (t, 6H, CH_3, J = 7.5 Hz), 2.85(q, 4H, C*H*$_2$, J = 7.4 Hz), 6.34−6.37 (m, 1H, Ph), 6.75−6.82 (m, 4H, Ph), 7.04−7.10 (m, 3H, Ph), 7.19−7.36 (m, 17H, Ph), 7.95−7.97 (m, 1H, Ph), 8.91 (d, 1H, C*H*═N, J = 5.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.4, 27.6, 27.8, 117.3, 125.9, 126.4, 127.5, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.4, 129.7, 130.9, 132.5, 132.7, 132.8, 133.2, 133.6, 133.7, 133.8, 134.0, 134.3, 134.6, 137.0, 137.1, 138.0, 138.1, 139.1, 139.2, 148.5, 148.8, 154.1, 154.3, 158.3, 158.6. Anal. Calcd for $C_{41}H_{37}NP_2\cdot 0.5H_2O$: C, 80.11; H, 6.23; N, 2.28. Found: C, 80.21; H, 6.43; N, 2.57. ^{31}P NMR ($CDCl_3$): δ −33.4 (s), −13.9(s). IR (KBr): 1621 ($\nu_{CH=N}$), 1565, 1464, 1433, 1366, 1264, 1191, 1160, 1092, 1025 cm^{-1}.

2-(Diphenylphosphino)-*N*-[2-(di(*o*-isopropylphenyl)phosphino)benzylidene]aniline (11). Using the same procedure as for the synthesis of **10**, **11** was obtained as a yellow powder in 67.7% yield. Mp: 166.0−166.5 °C. ^{1}H NMR ($CDCl_3$) δ: 1.11 (d, 6H, C*H*$_3$, J = 5.8 Hz), 1.20 (d, 6H, C*H*$_3$, J = 6.5 Hz), 3.62−3.71 (m, 2H, C*H*), 6.19−6.23 (m, 1H, Ph), 6.71−6.80 (m, 4H, Ph), 7.00−7.07 (m, 3H, Ph), 7.13−7.40 (m, 17H, Ph), 7.88−7.92 (m, 1H, Ph), 8.86 (d, 1H, C*H*═N, J = 5.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.8, 24.1, 31.4, 31.6, 53.5, 117.3, 125.4, 125.5, 125.9, 126.4, 127.4, 128.3, 128.4, 128.5, 128.7, 129.6, 130.8, 132.4, 132.6, 132.7, 133.1, 133.3, 134.0, 134.2, 134.7, 136.9, 137.1, 138.6, 138.7, 138.9, 153.3, 153.5, 154.1, 154.3, 158.4, 158.7. Anal. Calcd for $C_{43}H_{41}NP_2$: C, 81.49; H, 6.52; N, 2.21. Found: C, 81.21; H, 6.80; N, 2.29. ^{31}P NMR ($CDCl_3$) δ: −34.3 (s), −13.3 (s). IR (KBr): 1617 ($\nu_{CH=N}$), 1564, 1467, 1433, 1361, 1264, 1190, 1163, 1113, 1094, 1059, 1027 cm^{-1}.

Complexes **20**−**24** were prepared with the same method, and the typical procedure is described as follows. Compound **7** (0.3297 g, 0.60 mmol) and (DME)$NiBr_2$ (0.1852 g, 0.60 mmol) were added to a Schlenk tube under nitrogen, followed by the addition of freshly distilled dichloromethane (20 mL) with rapid stirring at room temperature. The solution turned dark red immediately. The reaction mixture was stirred for 5 h at room temperature and then concentrated to ca. 4 mL. Hexane (10 mL) was added to precipitate the complex. After filtration and washing with hexane, **20** was obtained as a purple powder in 75.6% yield. Mp: 190 °C (dec). IR (KBr): 1575, 1550, 1479, 1432, 1307, 1270, 1220, 1184, 1154, 1097, 1069, 1026 cm^{-1}. Anal. Calcd for $C_{37}H_{29}Br_2NNiP_2$: C, 57.86; H, 3.81; N, 1.82. Found: C, 57.95; H, 3.83; N, 1.73.

Complex **21** was obtained as an orange powder in 83.2% yield. Mp: 192 °C (dec). IR (KBr): 1555, 1469, 1436, 1383, 1302, 1275, 1234, 1200, 1183, 1164, 1133, 1099, 1068, 1027 cm^{-1}. Anal. Calcd for $C_{39}H_{33}Br_2NNiP_2\cdot 0.5CH_2Cl_2$: C, 56.57; H, 4.09; N, 1.67. Found: C, 56.76; H, 4.21; N, 1.76.

Complex **22** was obtained as a purple powder in 79.5% yield. Mp: 191 °C (dec). IR (KBr): 1583, 1553, 1472, 1432, 1337, 1277, 1245, 1164, 1134, 1099, 1073, 1012 cm^{-1}. Anal. Calcd for $C_{39}H_{33}Br_2NNiO_2P_2\cdot 0.75CH_2Cl_2$: C, 53.53; H, 3.90; N, 1.57. Found: C, 53.61; H, 4.07; N, 1.62.

Complex **23** was obtained as an orange powder in 77.1% yield. Mp: 167 °C (dec). IR (KBr): 1589, 1553, 1468, 1435, 1376, 1304, 1266, 1231, 1165, 1133, 1098, 1068, 1025 cm^{-1}. Anal. Calcd for $C_{41}H_{37}Br_2NNiP_2\cdot 0.75CH_2Cl_2$: C, 56.48; H, 4.37; N, 1.58. Found: C, 56.27; H, 4.66; N, 1.47.

Complex **24** was obtained as a purple powder in 70.4% yield. Mp: 180 °C (dec). IR (KBr): 1589, 1555, 1471, 1435, 1386, 1305, 1269, 1230, 1164, 1137, 1099, 1068, 1027 cm^{-1}. Anal. Calcd for $C_{43}H_{41}Br_2NNiP_2\cdot 0.5CH_2Cl_2$: C, 58.40; H, 4.73; N, 1.57. Found: C, 58.04; H, 5.05; N, 1.57.

4.4. Synthesis of the Cobalt Analogue Containing the P^N^P Ligand (25). To a solution of compound **7** (0.3297 g, 0.60 mmol) in degassed ethanol (10 mL) was added $CoCl_2$ (0.0774 g, 0.60 mmol), and the solution was stirred for 2 h at room temperature. After 3 min, a color change from purple to blue was observed. The solvent was evaporated under reduced pressure. The blue residue was dissolved in CH_2Cl_2 (10 mL), and this solution was filtered. The filtrate was evaporated, giving the product as a blue

(21) Ainscough, E. W.; Brodie, A. M.; Buckley, P. D.; Burrell, A. K.; Kennedy, S. M. F.; Waters, J. M. *Dalton* **2000**, 2663.

Table 5. Crystallographic Data of Complexes 12, 13, 16, 20, and 25

	12·CH_3OH	**13**·H_2O	**16**·CH_2Cl_2	**20**·$0.5CH_2Cl_2$·$0.5Et_2O$	**25**·CH_2Cl_2
formula	$C_{29}H_{25}Br_2N_2NiOP$	$C_{30}H_{27}Br_2N_2NiOP$	$C_{35}H_{35}Br_2Cl_2N_2NiP$	$C_{39.50}H_{35}Br_2ClNNiO_{0.50}P_2$	$C_{38}H_{31}Cl_4CoNP_2$
fw	667.01	681.04	804.05	847.61	764.31
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
a (Å)	10.109(2)	16.5092(4)	11.298(2)	11.4617(17)	10.475(2)
b (Å)	11.233(2)	10.1035(2)	11.879(2)	28.609(4)	13.575(3)
c (Å)	13.541(3)	16.9507(5)	14.045(3)	12.1638(18)	13.657(3)
α (deg)	82.68(3)	90.00	91.99(3)	90	75.02(3)
β (deg)	70.56(3)	104.7810(10)	97.91(3)	94.501(3)	73.06(3)
γ (deg)	63.38(3)	90.00	114.07(3)	90	88.40(3)
V (Å^3)	1295.8(4)	2733.82(12)	1696.1(6)	3976.3(10)	1792.3(6)
Z	2	4	2	4	2
D_{calc}, (g cm^{-3})	1.710	1.655	1.574	1.416	1.416
abs coeff, μ (mm^{-1})	3.921	3.718	3.160	2.674	0.895
F(000)	668	1368	812	1712	782
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
θ range (deg)	1.60 to 27.48	1.54 to 28.28	1.47 to 27.48	1.42 to 25.01	1.55 to 25.49
no. of data collected	5887	6753	6896	20 121	5978
no. of unique data	3891	4192	4970	7014	3562
R	0.0509	0.0383	0.0506	0.0572	0.0986
R_w	0.1181	0.0845	0.1115	0.1527	0.2645
goodness of fit	1.099	1.096	0.966	1.065	1.097

powder in 78.1% yield. Mp: 179 °C. IR (KBr): 1616 ($\nu_{CH=N}$), 1577, 1559, 1474, 1433, 1394, 1301, 1265, 1184, 1163, 1095, 1068, 1026 cm^{-1}. Anal. Calcd for $C_{37}H_{29}Cl_2CoNP_2$: C, 65.41; H, 4.30; N, 2.06. Found: C, 65.25; H, 4.30; N, 1.96.

4.5. X-ray Crystallographic Studies. Single-crystal X-ray diffraction for complexes **12**, **16**, and **25** was carried out on a Rigaku R-AXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Intensity data of crystal **13** were collected on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Intensity data of crystal **20** were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and processing parameters for complexes **12**, **13**, **16**, **20**, and **25** are summarized in Table 5.

4.6. Procedure for Ethylene Oligomerization. The oligomerization with 1 atm of ethylene was carried out as follows. Complex (5 μmol) was added to a Schlenk type flask under nitrogen. The flask was back-filled three times with N_2 and twice with ethylene and then charged with toluene and cocatalyst solution in turn under ethylene atmosphere. Under the prescribed temperature, the reaction solution was vigorously stirred under 1 atm of ethylene for the desired period of time. The oligomerization reaction was quenched by the addition 60 mL of 10% HCl solution. About 1 mL of organic solution was dried by anhydrous Na_2SO_4 for GC analysis. No polyethylene formation was observed after pouring the remaining solution into 100 mL of ethanol.

The oligomerization with 10 atmospheric pressure of ethylene was performed in a stainless steel autoclave (0.25 L capacity) equipped with gas ballast through a solenoid clave for continuous feeding of ethylene at constant pressure. A 137 mL amount of toluene containing the catalyst precursor was transferred to the fully dried reactor under nitrogen atmosphere, and 13 mL of MAO in toluene solution was then injected into the reactor using a syringe. As the prescribed temperature was reached, the reactor was pressurized to 10 atm. After stirring for 30 min, the reaction was quenched and worked up using the same method as described above for the 1 atm reaction.

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Supporting Information Available: Crystallographic data for **12**, **13**, **16**, **20**, and **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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