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Arene-Bridged Salicylaldimine-Based Binuclear Neutral Nickel(II) Complexes: Synthesis and Ethylene Polymerization Activities

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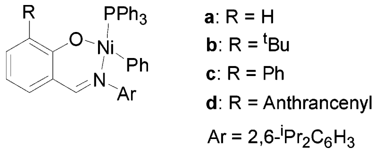
A series of novel *m*-arene-bridged salicylaldimine-based binuclear neutral nickel(II) complexes (2,4,6-$(R^2)_3C_6H$-1,3-$[N{=}CH\text{-}4\text{-}X\text{-}6\text{-}R^1C_6H_2ONi(Ph)(PPh_3)]_2$ (**3a**−**i**: R^1, R^2, X = Me, Me, H (**3a**), ^{t}Bu, Me, H (**3b**), Me, Et, H (**3c**), ^{t}Bu, Et, H (**3d**), H, ^{i}Pr, H (**3e**), Me, ^{i}Pr, H (**3f**), ^{t}Bu, ^{i}Pr, H (**3g**), Ph, ^{i}Pr, H (**3h**), NO_2, ^{i}Pr, NO_2 (**3i**), H, ^{i}Pr, NO_2 (**3j**)) are synthesized. The structure of complex **3h** is further confirmed by an X-ray diffraction study showing that the two Ni centers adopt an unsymmetrical, distorted square planar geometry. In the presence or absence of the phosphine scavenger $Ni(COD)_2$, complexes **3a**−**j** show high catalytic activities for ethylene polymerization. The effect of substituents on ethylene polymerization is significant. The introduction of an electron-withdrawing group to the ligand framework improves the catalytic activity significantly. The influence of polymerization temperature, polymerization time, and catalyst concentration on the activities of ethylene polymerization is also investigated. Highly branched polyethylenes (46−127 branches per 1000 carbon atoms) with moderate molecular weights ($M_\eta = (1.0-169) \times 10^4$) and narrow molecular weight distributions ($M_w/M_n = 2.3-2.4$) are obtained by using complexes **3a**−**j** as catalysts with or without a phosphine scavenger. In the presence of a polar solvent such as THF or Et_2O, complex **3h** polymerizes ethylene as a single-component catalyst. In comparison to the corresponding mononuclear Ni catalysts, the binuclear Ni catalysts generally show higher thermal stability, and complexes **3a**, **3c**, **3e**, and **3f**, which feature small R^1 substituents, are capable of acting as single-component ethylene polymerization catalysts.

Introduction

Due to their tolerance toward polar substrates, late-transition metal catalysts for α-olefin polymerization or oligomerization have received much attention.[1] In 1995, nickel and palladium complexes containing α-diimine ligands as olefin polymerization catalysts were reported by Brookhart and co-workers.[2] These complexes could not only polymerize ethylene to highly branched polymers but also copolymerize ethylene with polar-functionalized α-olefins.[3] In 1998, Brookhart's[4] and Gibson's[5] groups independently reported highly active cationic iron and cobalt olefin polymerization catalysts with bulky pyridinyldiimine ligands, and their catalytic activities were up to 10^7 g PE/(mol Fe•h). Among the numerous late-transition metal catalysts, neutral nickel complexes are considered to be very promising catalysts for α-olefin polymerization. As a highlight from the well-known Shell Higher Olefin Process (SHOP) catalysts,[6] Grubbs' group reported that neutral nickel(II) catalysts containing salicylaldimine ligands (Chart 1) exhibit high activities and efficiency for olefin polymerization in the presence of polar comonomers.[7] Recently, novel neutral nickel(II) complexes reported by Brookhart's group, based upon anilinotropone ligands, have been shown to be highly active ethylene polymerization catalysts.[8] As expected, these single-component catalysts can produce high molecular weight polyethylenes. Jin's group reported the self-immobilized neutral nickel(II) catalysts with an allyl functional group that can be used as a comonomer in the polymerization process.[9] More recently, Li's group reported that neutral nickel(II) complexes bearing β-ketoiminato chelate ligands copolymerize ethylene with methyl methacrylate.[10] In addition, such neutral nickel complexes can polymerize ethylene in an aqueous emulsion, affording stable polymer lattices with high molecular mass.[11]

Chart 1



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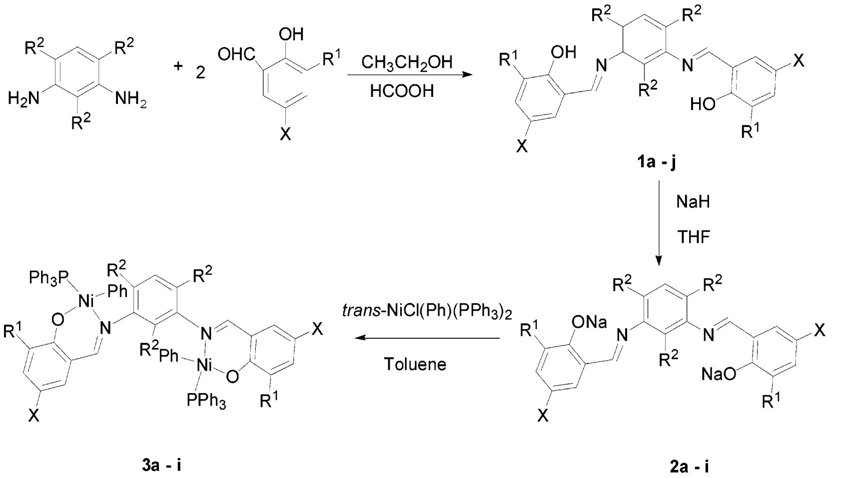
Scheme 1



a: R^1 = Me, R^2 = Me, X = H
b: R^1 = ^{t}Bu, R^2 = Me, X = H
c: R^1 = Me, R^2 = Et, X = H
d: R^1 = ^{t}Bu, R^2 = Et, X = H
e: R^1 = H, R^2 = ^{i}Pr, X = H
f: R^1 = Me, R^2 = ^{i}Pr, X= H
g: R^1 = ^{t}Bu, R^2 = ^{i}Pr, X = H
h: R^1 = Ph, R^2 = ^{i}Pr, X = H
i: R^1 = NO_2, R^2 = ^{i}Pr, X = NO_2
j: R^1 = H, R^2 = ^{i}Pr, X = NO_2

Considerable attention has lately been focused on binuclear organometallic compounds, based on expectations that their catalytic behavior may significantly differ from that of analogous mononuclear species.[12] Interactions between closely adjacent metal centers could potentially modify catalytic performance or provide alternative means for substrate activation. For example, Guo and Marks[13] have reported that binuclear titanocene complexes promote the copolymerization of ethylene with styrene. Although binuclear metallocenes for olefin polymerization have attracted much attention,[14] the binuclear neutral nickel catalysts received only a little attention.[15] We designed binuclear neutral nickel complexes that are connected via the conjugated π system of the bisalicylaldimine ligands and could provide attractive candidates to investigate the potential for cooperative effects during the ethylene polymerization reactions, which is a reaction of considerable interest in both academic and industrial sectors. The very rigid bisalicylaldimine ligands are now readily accessible and whose steric and electronic properties can be fine-tuned. In this contribution, we describe the synthesis and characterization of binuclear neutral nickel(II) complexes **3a**−**j**, $(2,4,6\text{-}(R^2)_3C_6H\text{-}1,3\text{-}[NCH\text{-}4\text{-}X\text{-}6\text{-}R^1C_6H_2ONi(Ph)(PPh_3)]_2$, R^1 = H, Me, ^{t}Bu, Ph, NO_2; R^2 = Me, Et, ^{i}Pr; X = H, NO_2), based on the rigid *m*-arene-bridged bisalicylaldimine ligands **1a**−**j** and their catalytic behavior of ethylene polymerization. Complexes **3a**−**j** are available as precursors to activator-free catalysts. The introduction of an electron-withdrawing group to the ligand framework improves the catalytic activity significantly, and very high molecular weight polyethylenes can be obtained.

Results and Discussion

Synthesis and Structure of Binuclear Neutral Nickel Complexes. In this study, we utilized nickel complexes that possess *m*-arene-bridged bisalicylaldimine chelate ligands. A general synthetic route for these complexes is shown in Scheme 1. 2,4,6-Trialkyl-*m*-phenylenediamines were obtained by performing the nitration of 1,3,5-trialkylbenzenes and sequential reduction.[16] The substituted salicylaldehyde was obtained by treatment of a phenol derivative with paraformaldehyde in the presence of anhydrous tin(IV) chloride in moderate yield.[17] However, phenols containing an electron-withdrawing group barely reacted. 5-Nitrosalicylaldehyde was isolated from a mixture of 5-nitrosalicylaldehyde and 3-nitrosalicylaldehyde.[18] 3,5-Dinitrosalicylaldehyde was obtained by performing the nitration of salicylaldehyde twice.[19]

All the bridged bisalicylaldimine ligands **1** were synthesized in moderate yields by condensation of *m*-phenylenediamine with 2 equiv of salicylaldehyde in ethanol with a catalytic amount of formic acid in order to minimize the amount of the monosalicylaldimine formed. It is clear that the excessive amount of amine would otherwise result in more mono-salicylaldimine ligand in our case.[20]

The general synthetic route for binuclear neutral nickel(II) complexes **3** is shown in Scheme 1. The deprotonation of free bisalicylaldimine ligands **1** proceeded readily with excess sodium hydride in dry THF at room temperature. Most sodium

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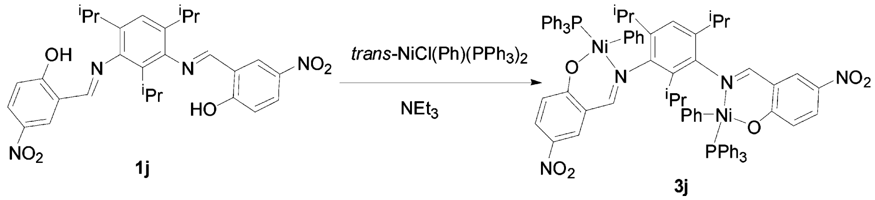
Scheme 2



salts of **1** are quite soluble in THF and are easily separated from residual NaH by filtration. After removal of the solvent, the sodium salts were treated with 2 equiv of *trans*-NiCl(Ph)(PPh$_3$)$_2$ in toluene to afford binuclear neutral nickel(II) complexes as analytically pure crystals after recrystallization from hydrocarbon solvents. However, the sodium salt of **1j** does not dissolve in THF, and the residual NaH is difficult to separate from the reaction system. In view of the acidity of the hydroxyl proton, ligand **1j** was reacted directly with *trans*-NiCl(Ph)(PPh$_3$)$_2$ in the presence of NEt$_3$ to afford the target complex **3j** in moderate yield (Scheme 2). The shift of the $\nu_{C=N}$ stretching absorption band to lower frequency is a consequence of the coordination through the nitrogen atom. For example, the IR spectrum of ligand **1h** shows a very strong absorption band at 1621 cm^{-1} attributed to $\nu_{C=N}$, while the $\nu_{C=N}$ band of complex **3h** is at 1597 cm^{-1}. The strong absorption bands at about 1435 (ν_{P-C}) and 693 (ν_{Ni-P}) cm^{-1} confirm the existence of PPh$_3$.[21]

A single crystal of binuclear neutral nickel(II) complex **3h** suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane into a benzene solution of complex **3h** at room temperature. Crystallographic data together with the collection and the refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. As depicted in Figure 1, complex **3h** possesses two unsymmetric nickel centers and exhibits C_1 symmetry in the solid state. The coordination geometry around each Ni atom is a distorted square plane with the triphenylphosphine ligand in the *trans*-position to the nitrogen donor of the bulky 2,4,6-triisopropylbenzimine moiety, as indicated by the very wide P(1)−Ni(1)−N(1) and P(2)−Ni(2)−N(1) angles of 162.84(12)° and 161.81(11)°, respectively. The phenyl ligand is located *trans* to the oxygen donor with O(1)−Ni(1)−C(29) and O(2)−Ni(2)−C(66) angles of 158.1(2)° and 157.49(17)°, respectively. The P−Ni−N and O−Ni−C bond angles in complex **3h** are somewhat smaller than those found in the mononuclear Grubbs' nickel complex (172.16(12)° and 166.2(2)°).[7] The bond distances of Ni(1)−O(1) (1.888(3) Å) and Ni(1)−N(1) (1.910(4) Å) are shorter than Ni(2)−O(2) (1.903(3) Å) and Ni(2)−N(2) (1.925(4) Å), respectively, which fall within the range observed for the related neutral nickel complexes (Ni−O, 1.885(3)−1.912(2) Å; Ni−N, 1.883(14)−1.937(4) Å).[7,9,10,20a] In contrast, the bond distance of Ni(1)−C(29) (1.902(4) Å) is longer than Ni(2)−C(66) (1.869(5) Å). Although the two segments in complex **3h** have seemingly identical chemical environments, the rigidity of the *m*-arene bridge and the steric hindrance among ligands and substituents most likely forces the unsymmetric orientation of the two moieties.

Table 1. Crystal Data and Structure Refinement Details for Complex 3h

empirical formula	$C_{89}H_{80}N_2Ni_2O_2P_2 \cdot 4C_6H_6$
fw	1701.34
temp (K)	293(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	11.3718(12)
b (Å)	20.898(2)
c (Å)	21.720(2)
α (deg)	66.805(2)
β (deg)	88.652(2)
γ (deg)	83.274(2)
volume (Å^3)	4710.4(8)
Z	2
calcd density (Mg/m^3)	1.200
absorp coeff (mm^{-1})	0.485
F(000)	1796
cryst size (mm)	0.510 × 0.490 × 0.139
θ range for data collection (deg)	1.74 to 26.00
limiting indices	$-14 \leq h \leq 13$, $-18 \leq k \leq 25$, $-25 \leq l \leq 26$
no. of reflns collected/unique	25 971/18 124 [*R*(int) = 0.1426]
completeness to θ = 26.00	98.1%
absorp corr	empirical
max. and min. transmn	1.00000 and 0.64310
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	18 124/26/1108
goodness-of-fit on F^2	0.841
final *R* indices [I > 2σ(I)]	$R_1 = 0.0742$, $wR_2 = 0.1630$
R indices (all data)	$R_1 = 0.1305$, $wR_2 = 0.1845$
largest diff peak and hole (e Å^{-3})	1.045 and −0.663

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Complex 3h

Ni(1)−O(1)	1.888(3)	Ni(2)−O(2)	1.903(3)
Ni(1)−C(29)	1.902(4)	Ni(2)−C(66)	1.869(5)
Ni(1)−N(1)	1.910(4)	Ni(2)−N(2)	1.925(4)
Ni(1)−P(1)	2.1709(13)	Ni(2)−P(2)	2.1868(14)
O(1)−C(22)	1.274(5)	O(2)−C(59)	1.300(5)
N(1)−C(16)	1.279(5)	N(2)−C(53)	1.283(5)
N(1)−C(1)	1.486(5)	N(2)−C(5)	1.459(5)
C(21)−C(23)	1.492(7)	C(58)−C(60)	1.466(7)
O(1)−Ni(1)−C(29)	158.1(2)	C(66)−Ni(2)−O(2)	157.49(17)
O(1)−Ni(1)−N(1)	92.44(14)	O(2)−Ni(2)−N(2)	93.01(15)
C(29)−Ni(1)−N(1)	98.07(16)	C(66)−Ni(2)−N(2)	96.22(17)
O(1)−Ni(1)−P(1)	89.05(10)	O(2)−Ni(2)−P(2)	88.75(11)
C(29)−Ni(1)−P(1)	86.51(13)	C(66)−Ni(2)−P(2)	88.82(13)
N(1)−Ni(1)−P(1)	162.84(12)	N(2)−Ni(2)−P(2)	161.81(11)

Ethylene Polymerizations Catalyzed by Binuclear Neutral Complexes 3a−j. Binuclear complexes are interesting candidates for catalytic reactions because they possess two potentially reactive sites susceptible to showing cooperative effects. One of our objectives was to determine whether cooperative effects resulting from electronic communication between the metal centers would lead to improved catalytic activity and/or broaden the molecular weight distribution.

First, complexes **3a−j** were tested as catalysts for ethylene polymerization in the presence of a phosphine scavenger, Ni(COD)$_2$. The results are summarized in Table 3. It was revealed

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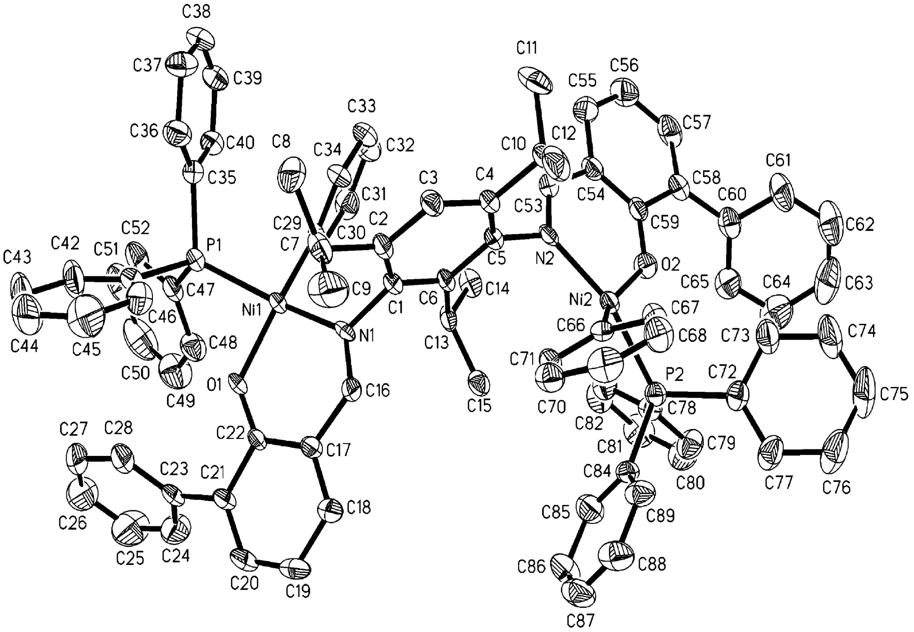

Figure 1. ORTEP diagram of complex **3h**. (Four benzene solvent molecules are present in the unit cell and all hydrogen atoms are omitted for clarity.)

that these complexes exhibited high catalytic activities for ethylene polymerization, and the highest activity, 314 kg PE/(mol Ni·h), was observed for the **3j**/Ni(COD)$_2$ (R^1 = H, X = NO_2, R^2 = ^{i}Pr) catalytic system (entry 38). In general, these binuclear neutral nickel complexes show similar catalytic activities to Grubbs' analogous mononuclear nickel complexes.[7] Binuclear nickel complexes **3a**−**j** were synthesized in an effort to explore the effects of varying the *ortho*-substituents on phenol and N-aryl moieties of ligands **1a**−**j** on ethylene polymerization. Complexes **3a**, **3c**, **3e**, and **3f** (R^1 = H or Me), with small substituents at the *ortho*-position of the phenolic ring, are less active at low temperature (25 °C). The phosphine scavenger Ni(COD)$_2$ binds PPh$_3$ more strongly than the nickel(II) complex and removes phosphine from the nickel complex. Less sterically hindered *ortho*-substituents disfavor the dissociation of PPh$_3$ to form a vacant coordination site at low temperature and therefore extend the induction period of generating the active "Ni−H" species. It has been proposed for the SHOP system that the induction period is due to the slow coordination and insertion of ethylene into the Ni−Ph bond, followed by β-hydride elimination to generate the active "Ni−H" species.[22] Increasing the polymerization temperature to 70 °C accelerates the abstraction of PPh$_3$ from the Ni center. Due to the same effect, the complexes containing bulky *ortho*-substituents (^{t}Bu or Ph) reach optimal activities at relatively lower temperatures (25 or 50 °C) than those with smaller *ortho*-substituents. Complexes **3i** and **3j**, containing the electron-withdrawing nitro groups, show enhanced catalytic activities and produce polyethylenes with higher molecular weights. Compared with complex **3j**, complex **3i**, bearing 4-nitro groups, shows lower catalytic activity. It was observed that the polymer was rapidly precipitated at the beginning of the polymerization in the case of complex **3i**, which would lead to the occlusion of the catalytic active center in the precipitated polymer and disfavor the mass transport of ethylene.

The polymerization runs were carried out at different temperatures (25−90 °C) to study the thermal stability of all catalysts. The polymerization temperature has a remarkable effect on the catalytic behavior, as demonstrated in Table 3. When the polymerization temperature is elevated from 25 to 70 °C, the activity of complex **3a** rises from 32.8 to 203 kg PE/(mol Ni·h) (entries 1−3, Table 3). For complexes **3d** and **3i**, it is found that the catalytic activities decrease gradually with elevating the temperature from 25 to 90 °C. A higher temperature is favorable for the abstraction of PPh$_3$, which decreases the induction period and generates the active "Ni−H" species faster. At the same time, the deactivation of active species and the β-hydride elimination reaction also become more significant at high temperature. The optimal polymerization temperature for individual systems depends on the balance between the propagation rate and the thermal stability. In comparison to the analogous mononuclear nickel catalysts, which usually are deactivated above 80 °C under polymerization conditions, our binuclear nickel catalysts are more stable and still show moderate catalytic activities even at 90 °C.[7,9]

Highly branched polyethylenes were obtained by using complexes **3a**−**j**/Ni(COD)$_2$ systems. The degree of branching, determined by ^{1}H NMR spectroscopy, varies from 46 to 127 branches per 1000 carbon atoms. Complexes with small substituents at the *ortho*-position of the phenolic ring produce polyethylene with a low number of branches, which is in contrast to the mononuclear nickel catalytic system. A branch in the polymer is introduced by β-hydride elimination of a growing polymer chain followed by olefin rotation and reinsertion with opposite regiochemistry. The high-temperature ^{13}C NMR spectrum of the polymer (entry 18, Table 3) shows there are few ethyl and longer branches besides methyl ones in the resulting PE chains. Analysis of the more highly branched polymer (entry 26, Table 3) shows that no other types of short branches are observed besides methyl branches. The polyethylenes obtained using complex **3g** display a relatively narrow molecular weight distribution (M_w/M_n = 2.43); a possible reason is that binuclear nickel complexes may possess a symmetric structure in solution (entry 26, Table 3). Increasing the polymerization temperature, the molecular weights of the obtained polymer are decreased, which could be attributed to the much faster β-hydride elimination and chain transfer rate caused by raising the polymerization

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Table 3. Ethylene Polymerization by Binuclear Nickel Complexes 3a−j with Scavenger Ni(COD)$_2$[a]

entry	complex (μmol)	temp (°C)	yield PE (g)	activity[b]	M_η[c] (10^4 g mol^{-1})	branches[e]/1000C
1	**3a** (2.0)	25	0.0875	32.8	15.4	
2	**3a** (2.0)	50	0.2105	78.9	5.70	65
3	**3a** (2.0)	70	0.5425	203	1.95	
4	**3a** (2.0)	90	0.2824	106	1.80	
5	**3b** (2.0)	0	0.1147	43.0	3.05	
6	**3b** (2.0)	25	0.5272	198	1.96	
7	**3b** (2.0)	50	0.3020	113	1.78	
8	**3b** (2.0)	70	0.1524	57.2	1.23	
9	**3c** (2.0)	25	0.0539	20.2		
10	**3c** (2.0)	50	0.1595	59.8	5.94	
11	**3c** (2.0)	70	0.3662	137	2.88	
12	**3c** (2.0)	90	0.2790	105	2.81	
13	**3d** (2.0)	25	0.5910	221	3.19	
14	**3d** (2.0)	50	0.4532	170	6.11	
15	**3d** (2.0)	70	0.2179	81.7	5.17	
16	**3d** (2.0)	90	0.1280	48.6		
17	**3e** (2.0)	25	0.1668	62.6	15.3	
18	**3e** (2.0)	50	0.2340	87.8	6.71	46
19	**3e** (2.0)	70	0.3769	141	4.12	
20	**3e** (2.0)	90	0.2724	102	1.08	
21	**3f** (2.0)	25	0.1089	40.8	16.7	
22	**3f** (2.0)	50	0.1184	44.4	8.61	
23	**3f** (2.0)	70	0.3144	117	5.46	
24	**3f** (2.0)	90	0.1824	68.4	3.44	
25	**3g** (2.0)	25	0.3877	145	4.56	
26	**3g** (2.0)	50	0.4624	173	3.11	87[d]
27	**3g** (2.0)	70	0.2367	88.8	2.07	
28	**3g** (2.0)	90	0.1772	66.3	1.89	
29	**3h** (2.0)	25	0.5035	189	15.7	
30	**3h** (2.0)	50	0.3350	126	20.9	127
31	**3h** (2.0)	70	0.2735	102	5.30	
32	**3h** (2.0)	90	0.2232	88.7	2.43	
33	**3i** (2.0)	25	0.5965	224		
34	**3i** (2.0)	50	0.5086	191	169	
35	**3i** (2.0)	70	0.4434	166		
36	**3i** (2.0)	90	0.2730	102	60.5	
37	**3j** (2.0)	25	0.6751	253	82.3	
38	**3j** (2.0)	50	0.8360	314	66.1	
39	**3j** (2.0)	70	0.4925	185	13.6	
40	**3j** (2.0)	90	0.2847	109	6.56	

[a] Conditions: solvent, toluene 25 mL; pressure, 10 atm; polymerization time, 40 min; Ni(COD)$_2$/**3** = 2. [b]kg PE/(mol Ni·h). [c]Molecular weights were determined by intrinsic viscosity. [d]$M_w = 2.93 \times 10^4$, $M_w/M_n = 2.43$, M_w and M_w/M_n were determined by GPC. [e]Determinted by ^{1}H NMR.

temperature. The polyethylenes produced by complexes **3i** and **3j** containing the nitro groups show very high molecular weights; an M_η value as high as 169×10^4 g/mol is detected (entry 34, Table 3). The electron-withdrawing nitro groups decrease the ethylene insertion barrier.[23] The acceleration of chain propagation results in an increase in molecular weights.

The effect of the catalyst concentration on polymerization by complex **3g** was investigated (Table 4). High catalyst concentration results in the decrease of catalytic activity, which could be interpreted as a mass-transport effect. More polymer is produced at higher catalyst concentration, and the viscosity of the reaction mixture is increased. In particular, the reaction mixture becomes a paste at high catalyst concentration, which inhibits ethylene from reaching the active center.

We further investigated the effect of polymerization time on the ethylene polymerization. The data in Table 5 show that the activity decreases gradually when the polymerization time is prolonged from 10 to 80 min. The slight reduction of activity may be attributed to the deactivation of the active centers or the occlusion of part of the catalyst in the precipitated polymer.

Table 4. Ethylene Polymerization by Binuclear Nickel Complex 3g with Scavenger Ni(COD)$_2$ under Different Catalyst Concentrations[a]

entry	complex (μmol)	temp (°C)	yield PE (g)	activity[b]	M_η[c] (10^4 g mol^{-1})
1	**3g** (1.0)	50	0.2373	178	3.96
2	**3g** (2.0)	50	0.4624	173	3.11
3	**3g** (4.0)	50	0.8428	158	4.56
4	**3g** (6.0)	50	0.9360	117	2.83

[a] Conditions: solvent, toluene 25 mL; pressure, 10 atm; polymerization time, 40 min; Ni(COD)$_2$/**3g** = 2. [b]kg PE/(mol Ni·h). [c]Molecular weights were determined by intrinsic viscosity.

Table 5. Ethylene Polymerization by Binuclear Nickel Complex 3g with Scavenger Ni(COD)$_2$ under Different Polymerization Times[a]

entry	complex (μmol)	temp (°C)	time (min)	yield PE (g)	activity[b]
1	**3g** (2.0)	50	10	0.1853	278
2	**3g** (2.0)	50	20	0.2961	222
3	**3g** (2.0)	50	40	0.4624	173
4	**3g** (2.0)	50	60	0.6240	156
5	**3g** (2.0)	50	80	0.6773	127

[a] Conditions: solvent, toluene 25 mL; pressure, 10 atm; Ni(COD)$_2$/**3g** = 2. [b]kg PE/(mol Ni·h).

The catalytic performance of binuclear neutral nickel complexes **3a−j** is also evaluated as single-component catalysts for ethylene polymerization. The results are summarized in Table 6. In the absence of Ni(COD)$_2$ as a phosphine scavenger, these complexes still exhibit high catalytic activities for ethylene polymerization. Although a decrease of the catalytic activity is observed for most complexes when compared with complexes **3a−j**/Ni(COD)$_2$ catalytic systems. It is worth noting that **3i** shows greater activity as a single-component catalyst and exhibits the highest activity, 298 kg PE/(mol Ni·h) (entry 33). Obviously, complex **3i** is much more suitable for use as a single-component catalyst for ethylene polymerization. As can be seen in Table 6, when the catalyst concentration and polymerization time decrease at the same time, the catalytic activity of **3i** rises from 271 to 710 kg PE/(mol Ni·h) (entries 34 and 35). The strong electron-withdrawing substituent and bulky *ortho*-substituents essentially promote the dissociation of PPh$_3$ from the nickel center under the polymerization conditions.

It has been reported that the structure analogous Grubbs' catalysts **a** and **b** (Chart 1) were not active for ethylene polymerization as single-component catalysts, because the deactivation of catalysts easily occurs via ligand dimerization. Computational work by Ziegler and co-workers supports the proposal that the bulky *ortho*-substituent is primarily responsible for the high catalytic activity by promoting PPh$_3$ dissociation.[23] In our case, complexes containing less bulky substituents, such as hydrogen or methyl, can still polymerize ethylene as single-component catalysts. The two metal centers in these binuclear nickel complexes are connected through the *m*-arene bridge and are located in *trans*-position. The interaction between two Ni centers seems weak, and the *m*-arene bridge may play an important role in raising the activity and thermal stability by the unique steric bulkiness and electronic effect.

Polymerization temperature has a dramatic effect on the catalytic activities of complexes **3a−j** employed as single-component catalysts for ethylene polymerization trials. When the polymerization temperature is elevated from 25 to 70 °C, the activity of complex **3a** increases more than 6-fold. For complexes **3i** and **3j**, the catalytic activities decrease gradually with increasing temperature from 25 to 90 °C. The polymerization behavior is similar to that using Ni(COD)$_2$ as a scavenger

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(23) Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallis* **2000**, *19*, 2741.

Table 6. Ethylene Polymerization by Binuclear Nickel Complexes 3a−j as Single-Component Catalysts

entry	complex (μmol)	temp (°C)	yield PE (g)	activity[b]	M_η[c] (10^4 g mol^{-1})
1	**3a** (4.0)	25	0.0754	14.2	6.21
2	**3a** (4.0)	50	0.2259	42.4	1.98
3	**3a** (4.0)	70	0.4744	89.0	1.72
4	**3a** (4.0)	90	0.2395	44.7	1.21
5	**3b** (4.0)	0	0.1936	36.3	4.22
6	**3b** (4.0)	25	0.5362	101	2.45
7	**3b** (4.0)	50	0.2216	41.2	1.92
8	**3b** (4.0)	70	0.1454	27.3	1.40
9	**3c** (4.0)	25	trace		
10	**3c** (4.0)	50	0.1081	20.3	9.72
11	**3c** (4.0)	70	0.1942	36.4	2.38
12	**3c** (4.0)	90	0.0856	16.0	1.47
13	**3d** (4.0)	25	0.1244	23.3	9.78
14	**3d** (4.0)	50	0.2190	82.1	6.56
15	**3d** (4.0)	70	0.2050	76.9	2.59
16	**3d** (4.0)	90	0.0698	13.1	
17	**3e** (4.0)	25	0.1344	25.2	25.1
18	**3e** (4.0)	50	0.1459	27.4	6.52
19	**3e** (4.0)	70	0.1673	31.4	4.15
20	**3e** (4.0)	90	0.1956	36.6	2.63
21	**3f** (4.0)	25	0.0996	18.7	15.4
22	**3f** (4.0)	50	0.1143	21.4	10.5
23	**3f** (4.0)	70	0.1775	33.3	7.71
24	**3f** (4.0)	90	0.1620	30.4	6.91
25	**3g** (4.0)	25	0.6513	122	6.17
26	**3g** (4.0)	50	0.3875	72.7	2.15[d]
27	**3g** (4.0)	70	0.1570	29.4	1.58
28	**3g** (4.0)	90	0.0833	15.6	1.16
29	**3h** (4.0)	25	0.5264	98.7	19.7
30	**3h** (4.0)	50	0.6631	124	16.3
31	**3h** (4.0)	70	0.2591	48.6	1.74
32	**3h** (4.0)	90	0.2170	40.7	1.60
33	**3i** (4.0)	25	1.591	298	40.5
34	**3i** (4.0)	50	1.448	271	29.7
35	**3i** (1.0)[e]	50	0.2365	710	25.8
36	**3i** (4.0)	70	0.8299	156	27.5
37	**3i** (4.0)	90	0.6646	125	11.0
38	**3j** (4.0)	25	0.7412	139	56.6
39	**3j** (4.0)	50	0.6126	115	47.2
40	**3j** (4.0)	70	0.4050	75.9	27.0
41	**3j** (4.0)	90	0.3106	58.1	12.4

[a] Conditions: solvent, toluene 25 mL; pressure, 10 atm; polymerization time, 40 min. [b] kg PE/(mol Ni·h). [c] Molecular weights were determined by intrinsic viscosity. [d] M_w = 1.84 × 10^4, M_w/M_n = 2.36, the number of branches = 111 per 1000 C. [e] Polymerization time, 10 min.

at different polymerization temperatures for all complexes **3a**−**j**. The resultant polymer obtained by using complex **3g** as a single-component catalyst has a moderate molecular weight (M_w = 1.84 × 10^4) with a relatively narrow molecular weight distribution (M_w/M_n = 2.36), which is similar to that using Ni(COD)$_2$ as a scavenger. The number of branches is 111 per 1000 carbon atoms, which is higher than that produced in the presence of Ni(COD)$_2$ as a scavenger. The M_η value of the resultant polymer increases with increasing steric hindrance on the N-aryl ligands. The steric hindrance on the axial site is important in controlling the molecular weight of polyethylenes by increasing the chain termination barrier.[23]

As mentioned previously, late-transition metal catalysts are tolerant toward functional groups. Therefore, complex **3h** was selected as an example to investigate the tolerance of these binuclear Ni catalysts to functional group as a single-component catalyst for ethylene polymerization. The results are listed in Table 7. These results demonstrate that the polymerizations can still be carried out successfully in the presence of polar substances, but the impact varies significantly across the various polar species. Binuclear neutral catalysts show similar tolerance for functional groups to Grubbs' mononuclear Ni catalysts. The degree of the impact decreases in the following order: THF > DME > CH_2Cl_2 > Et_2O. The binuclear neutral nickel complex can tolerate polar functional groups, so complexes **3g**−**j** were tested as catalysts for ethylene/MMA copolymerization in the presence of a phosphine scavenger, Ni(COD)$_2$. To our disappointment, complexes **3g**−**j** do not exhibit MMA incorporation ability from the analysis of the high-temperature ^{13}C NMR spectrum of the resultant polymer.

Table 7. Ethylene Polymerization by Binuclear Nickel Complex 3h as a Single-Component Catalyst in the Presence of Polar Additives[a]

entry	complex (μmol)	temp (°C)	polar additive[b]	yield PE (g)	activity[c]
1	**3h** (4.0)	50	no additive	0.6631	124
2	**3h** (4.0)	50	tetrahydrofuran	0.1598	29.9
3	**3h** (4.0)	50	1,2-dimethoxyethane	0.1674	31.3
4	**3h** (4.0)	50	diethyl ether	0.5182	95.7
5	**3h** (4.0)	50	dichloromethane	0.4274	79.9

[a] Conditions: solvent, toluene 25 mL; pressure, 10 atm; polymerization time, 40 min. [b] Quantity of additive, 0.5 mL. [c] kg PE/(mol Ni·h).

Conclusions

Ten new binuclear neutral Ni(II) complexes bearing a chelating bisalicylaldimine ligand have been synthesized. The binuclear molecular structure of complex **3h** was confirmed by X-ray diffraction analysis. In the presence of the phosphine scavenger Ni(COD)$_2$, complexes **3a**−**j** prove to be efficient catalytic systems for the polymerization of ethylene. In addition, when employed as single-component ethylene polymerization catalysts, these complexes show high catalytic activities and yield polyethylene products with moderate molecular weights (M_η = (1.0−169) × 10^4), narrow molecular weight distributions (M_w/M_n = 2.3−2.4), and a high degree branching (ca. 46−127 branches per 1000 carbon atoms). The variation of substituents on the *ortho*-positions of the phenyl rings and arene bridge of the ligand dramatically influences the polymerization behavior of these binuclear nickel complexes. The introduction of an electron-withdrawing group to the ligand framework improves the catalytic activity significantly, and very high molecular weight polyethylenes can be obtained by complexes **3i** and **3j** with nitro groups. The binuclear neutral nickel complexes show much higher thermal stability and can tolerate polar functional groups.

Experimental Section

General Remarks. All operations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were distilled from sodium wire prior to use, and chemicals were obtained from commercial suppliers. Methylene dichloride was distilled from drying CaH_2 under argon. ^{1}H NMR and ^{31}P NMR spectra were recorded on a Bruker Avance-500 spectrometer with $CDCl_3$ or C_6D_6 as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance-300 spectrometer with $CDCl_3$ or C_6D_6 as the solvent. Chemical shifts were referenced internally using the residual solvent resonances or reported relative to tetramethylsilane. Elemental analysis data were obtained with an EA-1106 spectrometer. Infrared spectra using KBr pellets were collected on a Nicolet Magna-IR 550 spectrophotometer. ESI-MS spectra were recorded on a Micromass LCT mass instrument. Polymer grade ethylene was directly used for polymerization without further purification. The starting materials 2,4,6-trialkyl-*m*-phenylenediamine,[16] 3-methylsalicylaldehyde, 3-*tert*-butylsalicylaldehyde, 3-phenylsalicylaldehyde,[17] 3,5-dinitrosalicylaldehyde,[18] 5-nitrosalicylaldehyde,[19] *trans*-NiCl(Ph)(PPh$_3$)$_2$,[24] and bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$)[25] were prepared according to the literature procedures.

^{1}H NMR and ^{13}C NMR spectra of polyethylenes were recorded on a Bruker Avance-500 spectrometer with $C_6D_4Cl_2$ at 110 °C. The formula used to calculate branching was $[CH_3/3]/[(CH + CH_2 + CH_3)/2] \times 1000$ = branches per 1000 carbons.[8b] CH_3, CH_2, and CH refer to the integration obtained for the methyl, methylene, and methane resonances, respectively. The intrinsic viscosities $[\eta]$ of polyethylenes (PE) in decahydronaphthrene were measured with a Ubbelohde viscometer at 135 °C. The viscosity average molecular weights (M_η) were calculated as follows: $[\eta] = 6.77 \times 10^{-4} M_\eta^{0.67}$. The gel permeation chromatography (GPC) performed on a Waters 150 ALC/GPC system in a 1,2,4-trichlorobenzene solution at 135 °C was used to determine the weight-average molecular weights (M_w) and the molecular weight distributions (M_w/M_n) of the polymer.

Synthesis of Binuclear Nickel Complex 3a. The ligand **1a** was prepared by the following procedure. To an ethanol (25 mL) solution of 3-methylsalicylaldehyde (1.36 g, 10.0 mmol) were added formic acid (0.5 mL) and 2,4,6-trimethyl-*m*-phenylenediamine (0.75 g, 5.0 mmol). The resulting mixture was refluxed for 4 h and then cooled to room temperature. A precipitate was formed, which was recrystallized from ethyl acetate to afford yellow crystals in 64% yield (1.23 g). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (s, 2H, CH═N), 7.28 (d, J = 7.4 Hz, 2H, ArH), 7.20 (d, J = 7.4 Hz, 2H, ArH), 7.02 (s, 1H, ArH), 6.87 (t, J = 7.4 Hz, 2H, ArH), 2.34 (s, 6H, Me), 2.18 (s, 6H, Me), 2.05 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.5, 159.6, 146.7, 134.6, 130.1, 126.5, 125.1, 119.7, 118.7, 117.9, 18.3, 15.6, 14.1. IR (cm^{-1}, KBr) ν: 3052w, 3002m, 2958m, 2915w, 1619vs, 1583s, 1490m, 1461s, 1435s, 1376m, 1354w, 1319w, 1302w, 1268s, 1251m, 1235m, 1210s, 1162w, 1090s, 1074m, 1031s, 1010m, 984w, 963w, 861w, 829m, 808s, 773s, 746vs, 683w.

To a suspension of sodium hydride (0.060 g, 0.20 mmol) in THF (10 mL) was added a solution of ligand **1a** (0.290 g, 0.750 mmol) in THF (20 mL). The resulting mixture was stirred for 4 h at ambient temperature. After filtration, the solvent of the filtrate was removed under vacuum. The solid residue was washed with *n*-hexane (10 mL) and dried under vacuum. The sodium salt of ligand **1a** was immediately used in the next step without further purification. The sodium salt obtained above and *trans*-NiCl(Ph)(PPh_3)$_2$ (1.00 g, 1.44 mmol) were dissolved in toluene (30 mL) and stirred for 14 h at room temperature. After filtration to remove the formed sodium chloride, the clear solution was concentrated to ca. 10 mL under vacuum, and *n*-hexane (20 mL) was added to the solution. A yellow solid precipitated from solution was isolated by filtration. The crude product was recrystallized from toluene and *n*-hexane to give yellow needle crystals as complex **3a** in 65% yield based on ligand **1a**. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.67−7.63 (m, 14H, CH═N and ArH), 7.36 (d, J = 7.5 Hz, 2H, ArH), 7.20 (d, J = 8.0 Hz, 3H, ArH), 6.98−6.95 (m, 6H, ArH), 6.90−6.86 (m, 13H, ArH), 6.67 (d, J = 7.5 Hz, 2H, ArH), 6.55 (t, J = 7.4 Hz, 2H, ArH), 6.40 (t, J = 7.1 Hz, 3H, ArH), 6.25 (t, J = 6.3 Hz, 2H, ArH), 6.17 (t, J = 7.4 Hz, 2H, ArH), 2.48 (s, 5H, Me), 2.21 (s, 2H, Me), 1.55 (s, 2H, Me), 1.44 (s, 6H, Me). ^{13}C NMR (C_6D_6, 300 MHz): 166.2, 164.6, 150.1, 149.1, 148.4, 138.0, 137.2, 134.7, 134.5, 133.8, 132.3, 131.9, 131.7, 130.9, 129.6, 127.8, 127.7, 127.5, 126.4, 125.3, 121.1, 119.0, 113.9, 19.2, 16.3, 15.8. ^{31}P NMR (C_6D_6, 202.5 MHz): δ 30.1 (s). IR (cm^{-1}, KBr): 3048m, 3019w, 3003w, 2986w, 2942w, 1606vs, 1586s, 1560s, 1544vs, 1478m, 1449vs, 1433vs, 1377s, 1330s, 1286w, 1238s 1216s, 1198m, 1185w, 1160w, 1121w, 1096vs, 1075s, 1053w, 1017w, 997w, 973w, 890w, 866w, 748s, 734s, 694vs, 649w, 614w, 530vs, 510s, 498m, 469w. Anal. Calcd for $C_{73}H_{64}N_2Ni_2O_2P_2$: C, 74.26; H, 5.46; N, 2.37. Found: C, 74.49; H, 5.63; N, 2.22.

Synthesis of Binuclear Nickel Complex 3b. Ligand **1b** was prepared using the same procedure for ligand **1a**. A 1.78 g (10.0 mmol) sample of 3-*tert*-butylsalicylaldehyde and 0.75 g (5.0 mmol) of 2,4,6-trimethyl-*m*-phenylenediamine were used to give 1.43 g (yield, 74%) of yellow needle crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.34 (s, 2H, CH═N), 7.43 (m, 2H, ArH), 7.20 (d, J = 7.5 Hz, 2H, ArH), 7.02 (s, 1H, ArH), 6.90 (t, J = 7.5 Hz, 2H, ArH), 2.20 (s, 6H, Me), 2.08 (s, 3H, Me), 1.49 (d, J = 7.6 Hz, 18H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 300 MHz): 167.8, 160.7, 147.0, 137.8, 130.6, 130.4, 130.0, 124.9, 119.6, 118.7, 118.2, 35.0, 29.4, 18.4, 14.2.

Complex **3b** was prepared using the same procedure for complex **3a**. A 0.060 g (0.20 mmol) amount of sodium hydride, 0.353 g (0.750 mmol) of ligand **1b**, and 1.00 g (1.44 mmol) of *trans*-NiCl-(Ph)(PPh_3)$_2$ were used to give 0.557 g (yield, 59%) of yellow crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.94 (d, J = 8.8 Hz, 2H, CH═N), 7.77 (d, J = 8.8 Hz, 12H, ArH), 7.58 (d, J = 9.1 Hz, 3H, ArH), 7.42 (d, J = 7.3 Hz, 2H, ArH), 7.24 (d, J = 7.6 Hz, 2H, ArH), 7.02−6.90 (m, 17H, ArH), 6.62 (t, J = 7.6 Hz, 2H, ArH), 6.44 (s, 1H, ArH), 6.35 (t, J = 7.1 Hz, 2H, ArH), 6.29−6.24 (m, 4H, ArH), 6.00 (t, J = 7.1 Hz, 2H, Ar), 2.67 (s, 5H, Me), 2.11 (s, 2H, Me), 2.01 (s, 2H, Me), 0.91 (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6, 300 MHz): 166.7, 166.1, 150.0, 141.9, 138.3, 136.8, 136.3, 135.1, 134.9, 133.4, 132.4, 131.9, 131.2, 129.7, 127.8, 127.5, 126.9, 125.2, 123.6, 121.8, 121.0, 115.8, 34.6, 29.8, 19.5, 15.5. IR (cm^{-1}, KBr): 3045m, 3004w, 2949m, 2855m, 1596vs, 1561m, 1535vs, 1481m, 1466m, 1435s, 1416vs, 1387m, 1142m, 1096s, 1083m, 1055w, 1018w, 998w, 981w, 863w, 749s, 730s, 694vs, 646w, 618w, 606w, 531s, 511s, 493m, 449w. Anal. Calcd for $C_{79}H_{76}N_2Ni_2O_2P_2$: C, 75.02; H, 6.06; N, 2.21. Found: C, 75.00; H, 6.24; N, 2.10.

Synthesis of Binuclear Nickel Complex 3c. Ligand **1c** was prepared using the same procedure for ligand **1a**. A 1.36 g (10.0 mmol) sample of 3-methylsalicylaldehyde and 0.96 g (5.0 mmol) of 2,4,6-triethyl-*m*-phenylenediamine were used to give 1.47 g (yield, 68%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36 (s, 2H, CH═N), 7.29 (d, J = 7.5 Hz, 2H, ArH), 7.21 (d, J = 7.5 Hz, 2H, ArH), 7.04 (s, 1H, ArH), 6.88 (t, J = 7.5 Hz, 2H, ArH), 2.51 (m, 6H, CH_2), 2.34 (s, 6H, Me), 1.17 (t, J = 7.5 Hz, 6H, Me), 0.99 (t, J = 7.5 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): 167.4, 160.8, 146.1, 137.8, 131.0, 130.6, 130.4, 126.9, 125.7, 118.6, 118.2, 35.0, 29.4. 24.7, 20.6. 15.0, 14.6.

Complex **3c** was prepared using the same procedure for complex **3a**. A 0.060 g (0.20 mmol) amount of sodium hydride, 0.321 g (0.750 mmol) of ligand **1c**, and 1.00 g (1.44 mmol) of *trans*-NiCl-(Ph)(PPh_3)$_2$ were used to give 0.664 g (yield, 72%) of yellow crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.96 (d, J = 9.1 Hz, 2H, CH═N), 7.65 (t, J = 8.6 Hz, 12H, ArH), 7.02 (d, J = 6.7 Hz, 4H, ArH), 6.97−6.90 (m, 27H, ArH), 6.52 (t, J = 7.4 Hz, 2H, ArH), 6.41 (t, J = 7.1 Hz, 2H, ArH), 6.28−6.24 (m, 4H, ArH), 6.13 (s, 1H, ArH), 3.42 (m, 1H, CH_2), 3.03 (m, 2H, CH_2), 2.57 (m, 1H, CH_2), 2.40 (m, 5H, CH_2 and Me), 2.10 (s, 3H, Me), 1.44 (s, 6H, Me), 1.00 (t, J = 7.5 Hz, 6H, Me). ^{13}C NMR (C_6D_6, 300 MHz): 166.2, 164.8, 148.8, 148.7, 137.9, 137.8, 134.7, 134.5, 134.0, 133.0, 132.2, 131.7, 131.0, 130.2, 129.6, 127.7, 124.7, 123.6, 123.2, 121.0, 118.4, 114.0, 25.8, 22.7, 16.3, 15.5, 15.2. IR (cm^{-1}, KBr): 3045m, 3018m, 2960s, 2926m, 2864m, 1605vs, 1583s, 1563s, 1543vs, 1449s, 1431vs, 1375m, 1331s, 1236m, 1214s, 1189m, 1160m, 1095s, 1078s, 1053m, 1020m, 996m, 970m, 872s, 746s, 728s, 692vs, 529s, 509s, 493s, 441m, 419m. Anal. Calcd for $C_{76}H_{70}N_2Ni_2O_2P_2 \cdot C_6H_5CH_3$: C, 75.82; H, 5.98; N, 2.13. Found: C, 75.69; H, 5.86; N, 2.19.

Synthesis of Binuclear Nickel Complex 3d. Ligand **1d** was prepared using the same procedure for ligand **1a**. A 1.78 g (10.0 mmol) portion of 3-*tert*-butylsalicylaldehyde and 0.96 g (5.0 mmol) of 2,4,6-triethyl-*m*-phenylenediamine were used to give 1.80 g (yield, 70%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.37 (s, 2H, CH═N), 7.43 (dd, J = 7.6 Hz, J = 0.9 Hz, 2H, ArH), 7.21 (dd, J = 7.6 Hz, J = 0.9 Hz, 2H, ArH), 7.04 (s, 1H, ArH),

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6.89 (t, J = 7.6 Hz, 2H, ArH), 2.51 (m, 6H, CH_2), 1.48 (s, 18H, ^{t}Bu), 1.18 (t, J = 7.5 Hz, 6H, Me), 1.00 (t, J = 7.5 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.4, 160.7, 146.0, 137.8, 131.0, 130.6, 130.5, 126.8, 125.8, 118.6, 118.2, 35.0, 29.4, 24.8, 20.6, 15.1, 14.6. Anal. Calcd for $C_{34}H_{44}N_2O_2$: C, 79.65; H, 8.65; N, 5.46. Found: C, 79.34; H, 8.65; N, 5.34.

Complex **3d** was prepared using the same procedure for complex **3a**. A 0.060 g (0.20 mmol) sample of sodium hydride, 0.385 g (0.75o mmol) of ligand **1d**, and 1.00 g (1.44 mmol) of *trans*-NiCl(Ph)(PPh_3)$_2$ were used to give 0.811 g (yield, 83%) of yellow-brown crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.98 (d, J = 9.2 Hz, 2H, CH═N), 7.78 (t, J = 8.7 Hz, 12H, ArH), 7.43 (d, J = 7.4 Hz, 2H, ArH), 7.10 (d, J = 7.6 Hz, 2H, ArH), 7.05−6.91 (m, 21H, ArH), 6.77 (d, J = 7.6 Hz, 2H, ArH), 6.61 (t, J = 7.4 Hz, 2H, ArH), 6.32 (t, J = 7.0 Hz, 2H, ArH), 6.18 (t, J = 7.4 Hz, 2H, ArH), 6.12 (t, J = 7.0 Hz, 2H, ArH), 3.51 (m, 1H, CH_2), 3.08 (m, 2H, CH_2), 2.68 (m, 1H, CH_2), 2.51 (t, J = 7.5 Hz, 3H, Me), 2.42 (m, 2H, CH_2), 1.00 (t, J = 7.5 Hz, 6H, Me), 0.92(s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6, 300 MHz): 167.1, 166.4, 148.9,147.5, 146.3, 141.9, 137.4, 137.2, 135.1, 134.9, 133.6, 133.3, 132.4, 131.8, 131.4, 129.7, 126.1, 124.7, 124.2, 120.9, 120.4, 113.9, 34.6, 29.8, 25.8, 22.8, 15.7, 15.5. IR (cm^{-1}, KBr): 3046m, 3004w, 2961s, 2867m, 1601vs, 1587vs, 1563s, 1536vs, 1481m, 1461s, 1435s, 1417s, 1386s, 1337s, 1317s, 1222w, 1187s, 1144s, 1092s, 1056w, 1018w, 996w, 965w, 871m, 859w, 749s, 729s, 693vs, 530s, 511s, 490s, 450w, 438w, 421w. Anal. Calcd for $C_{82}H_{82}N_2Ni_2O_2P_2$: C, 75.36; H, 6.32; N, 2.14. Found: C, 75.12; H, 6.50; N, 1.98.

Synthesis of Binuclear Nickel Complex 3e. Ligand **1e** was prepared using the same procedure for ligand **1a**. A 1.22 g (10.0 mmol) amount of salicylaldehyde and 1.17 g (5.00 mmol) of 2,4,6-triisopropyl-*m*-phenylenediamine were used to give 1.83 g (yield, 82%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (s, 2H, CH═N), 7.43 (t, J = 7.4 Hz, 2H, ArH), 7.36 (d, J = 8.1 Hz, 2H, ArH), 7.18 (s, 1H, ArH), 7.08 (d, J = 8.1 Hz, 2H, ArH), 6.97 (t, J = 7.4 Hz, 2H, ArH), 3.19 (m, 1H, CH), 2.94 (m, 2H, CH), 1.20 (d, J = 6.9 Hz, 12H, Me), 1.17 (d, J = 7.1 Hz, 6H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.2, 161.4, 144.9, 136.2, 133.9, 132.5, 128.8, 121.2, 119.3, 118.3, 117.5, 28.2, 28.0, 23.7, 22.2. IR (cm^{-1}, KBr) ν: 3061m, 2957s, 2927m, 2784m, 1626vs, 1576s, 1495s, 1463s, 1409m, 1383w, 1316m, 1327w, 1273vs, 1242w, 1224w, 1191s, 1152s, 1115w, 1090w, 1059w, 1033m, 1013m, 992w, 947w, 908s, 887m, 816s, 756vs, 736m, 708w. Anal. Calcd for $C_{29}H_{34}N_2O_2$: C, 78.70; H, 7.74; N, 6.33. Found: C, 78.64; H, 7.54; N, 6.19.

Complex **3e** was prepared using the same procedure for complex **3a**. A 0.060 g (0.20 mmol) amount of sodium hydride, 0.332 g (0.750 mmol) of ligand **1e**, and 1.00 g (1.44 mmol) of *trans*-NiCl(Ph)(PPh_3)$_2$ were used to give 0.818 g (yield, 88%) of yellow crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.02 (d, J = 8.6 Hz, 2H, CH═N), 7.64 (m, 12H, ArH), 7.42−6.93 (m, 26H, ArH), 6.51−6.29 (m, 11H, ArH), 4.15 (m, 1H, CH), 2.73 (m, 2H, CH), 1.35 (d, J = 7.1 Hz, 3H, Me), 0.94 (d, J = 7.2 Hz, 12H, Me), 0.84 (d, J = 7.1 Hz, 3H, Me). ^{13}C NMR (C_6D_6, 300 MHz): 166.6, 160.0, 148.2, 146.8, 138.3, 138.0, 134.5, 134.4, 134.0, 131.9, 131.4, 129.9, 127.8, 127.5, 125.2, 124.7, 122.8, 121.1, 119.4, 114.3, 30.0, 28.5, 26.0, 25.2, 24.8, 22.2. IR (cm^{-1}, KBr): 3047w, 2957m, 2869w, 1606vs, 1582s, 1561m, 1531s, 1465m, 1444vs, 1374w, 1358m, 1327m, 1251w, 1199w, 1146m, 1127w, 1095m, 1057w, 1018w, 925w, 743m, 731s, 694vs, 530s, 512s, 494m, 454w. Anal. Calcd for $C_{77}H_{72}N_2Ni_2O_2P_2$: C, 74.78; H, 5.87; N, 2.27. Found: C, 75.08; H, 6.14; N, 2.07.

Synthesis of Binuclear Nickel Complex 3f. Ligand **1f** was prepared using the same procedure for ligand **1a**. A 1.36 g (10.0 mmol) amount of 3-methylsalicylaldehyde and 1.17 g (5.00 mmol) of 2,4,6-triisopropyl-*m*-phenylenediamine were used to give 1.81 g (yield, 77%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.31 (s, 2H, CH═N), 7.30 (d, J = 7.5 Hz, 2H, ArH), 7.20 (d, J = 7.5 Hz, 2H, ArH), 7.17 (s, 1H, ArH), 6.88 (t, J = 7.5 Hz, 2H, ArH), 3.20 (m, 1H, CH), 2.95 (m, 2H, CH), 2.35 (s, 6H, Me), 1.19 (d, J = 6.8 Hz, 12H, Me), 1.16 (d, J = 7.2 Hz, 6H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): 167.2, 159.5, 145.8, 135.7, 134.4, 130.0, 128.5, 126.4, 120.9, 118.7, 117.9, 28.2, 28.0, 23.8, 22.3, 14.3. Anal. Calcd for $C_{31}H_{38}N_2O_2$: C, 79.11; H, 8.14; N, 5.95. Found: C, 78.93; H, 8.17; N, 5.86.

Complex **3f** was prepared using the same procedure for complex **3a**. A 0.060 g (0.20 mmol) portion of sodium hydride, 0.353 g (0.750 mmol) of ligand **1f**, and 1.00 g (1.44 mmol) of *trans*-NiCl(Ph)(PPh_3)$_2$ were used to give 0.624 g (yield, 66%) of yellow crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.06 (d, J = 9.1 Hz, 2H, CH═N), 7.66 (m, 12H, ArH), 6.97−6.78 (m, 26H, ArH), 6.52−6.34 (m, 9H, ArH), 4.13 (m, 1H, CH), 3.64 (m, 2H, CH), 1.50 (s, 6H, Me), 1.02−0.87 (m, 18H, Me). IR (cm^{-1}, KBr): 3049m, 2956s, 2926m, 2865m, 1605vs, 1583s, 1561m, 1542vs, 1481m, 1466m, 1448s, 1433vs, 1376s, 1360m, 1329s, 1240m, 1217s, 1191m, 1163m, 1095s, 1083m, 1052m, 1018m, 998w, 969w, 868m, 747s, 729s, 693vs, 640w, 529s, 511s, 492m, 453w, 420w. Anal. Calcd for $C_{79}H_{76}N_2Ni_2O_2P_2$: C, 75.02; H, 6.06; N, 2.21. Found: C, 75.26; H, 6.32; N, 1.82.

Synthesis of Binuclear Nickel Complex 3g. Ligand **1g** was prepared using the same procedure for ligand **1a**. A 1.78 g (10.0 mmol) amount of 3-*tert*-butylsalicylaldehyde and 1.17 g (5.00 mmol) of 2,4,6-triisopropyl-*m*-phenylenediamine were used to give 2.09 g (yield, 71%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (s, 2H, CH═N), 7.44 (d, J = 7.5 Hz, 2H, ArH), 7.20 (d, J = 7.5 Hz, 2H, ArH), 7.17 (s, 1H, ArH), 6.90 (t, J = 7.5 Hz, 2H, ArH), 3.21 (m, 1H, CH), 2.96 (m, 2H, CH), 1.49 (s, 18H, ^{t}Bu), 1.20 (d, J = 6.7 Hz, 12H, Me), 1.17 (d, J = 6.9 Hz, 6H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.6, 160.7, 145.6, 137.9, 135.7, 130.6, 130.5, 128.7, 120.9, 118.5, 118.2, 35.0, 29.4, 28.2, 27.9, 23.8, 22.2. Anal. Calcd for $C_{37}H_{50}N_2O_2$: C, 80.10; H, 9.08; N, 5.05. Found: C, 80.12; H, 8.64; N, 4.95.

Complex **3g** was prepared using the same procedure for complex **3a**. A 0.060 g (0.20 mmol) sample of sodium hydride, 0.416 g (0.750 mmol) of ligand **1g**, and 1.00 g (1.44 mmol) of *trans*-NiCl(Ph)(PPh_3)$_2$ were used to give 0.821 g (yield, 81%) of yellow-brown crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.07 (d, J = 8.9 Hz, 2H, CH═N), 7.76 (m, 12H, ArH), 7.44−7.39 (m, 4H, ArH), 7.02−6.93 (m, 21H, ArH), 6.63−6.59 (m, 4H, ArH), 6.33−6.17 (m, 6H, ArH), 4.31 (m, 1H, CH), 2.95 (m, 2H, CH), 1.31(d, J = 5.3 Hz, 6H, Me), 1.03(d, J = 5.3 Hz, 12H, Me), 0.95 (s, 18H, ^{t}Bu). ^{13}C NMR (C_6D_6, 300 MHz): 167.6, 166.1, 148.6, 142.1, 138.8, 137.2, 135.0, 134.9, 133.5, 132.1, 131.5, 130.4, 129.7, 127.5, 125.4, 124.6, 120.9, 120.0, 119.2, 113.9, 34.6, 30.3, 29.9, 28.6, 26.2, 25.6, 24.9, 22.5. IR (cm^{-1}, KBr): 3049m, 3003w, 2956s, 2906m, 2876m, 1600vs, 1562m, 1536vs, 1481w, 1466m, 1436s, 1417s, 1384m, 1360w, 1338m, 1319m, 1265w, 1246w, 1224w, 1187m, 1143m, 1098s, 1057w, 1020w, 997w, 869w, 748s, 729m, 693vs, 657w, 636w, 530s, 511m, 492m. ESI-MS (*m/e*): 1349 (M^+). Anal. Calcd for $C_{85}H_{88}N_2Ni_2O_2P_2$: C, 75.68; H, 6.58; N, 2.08. Found: C, 75.77; H, 6.56; N, 1.82.

Synthesis of Binuclear Nickel Complex 3h. Ligand **1h** was prepared using the same procedure for ligand **1a**. 3-Phenylsalicylaldehyde (1.98 g, 10.0 mmol) and 1.17 g (5.00 mmol) of 2,4,6-triisopropyl-*m*-phenylenediamine were used to give 2.12 g (yield, 71%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.38 (s, 2H, CH═N), 7.70 (d, J = 7.4 Hz, 4H, ArH), 7.52 (d, J = 7.5 Hz, 2H, ArH), 7.47 (t, J = 7.5 Hz, 4H, ArH), 7.37 (t, J = 7.4 Hz, 4H, ArH), 7.17 (s, 1H, ArH), 7.05 (t, J = 7.5 Hz, 2H, ArH), 3.21 (m, 1H, CH), 2.96 (m, 2H, CH), 1.12−1.17 (m, 18H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 167.3, 158.3, 145.5, 137.4, 135.9, 134.4, 131.8, 130.1, 129.4, 128.6, 128.2, 127.3, 121.0, 119.1, 118.7, 28.3, 28.0, 23.8, 22.3. IR (cm^{-1}, KBr) ν: 3051w, 2960s, 2925m, 2867m, 2786w, 2718w, 1621vs, 1585s, 1526w, 1492w, 1453s, 1432s, 1383w, 1362m, 1322m, 1280m, 1220w, 1204m, 1169w, 1099s, 1071m, 1015m, 933m, 905w, 882w, 851w, 831m, 797w, 754s, 696s, 640w, 617w, 579w. Anal. Calcd for $C_{41}H_{40}N_2O_2$: C, 82.79; H, 7.12; N, 4.71. Found: C, 82.82; H, 6.89; N, 4.57.

Complex **3h** was prepared using the same procedure for complex **3a**. Sodium hydride (0.060 g, 0.20 mmol), 0.476 g (0.750 mmol) of ligand **1h**, and 1.00 g (1.44 mmol) of *trans*-NiCl(Ph)$(PPh_3)_2$ were used to give 0.857 g (yield, 77%) of yellow-brown crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.95 (d, $J = 8.6$ Hz, 2H, CH═N), 7.52 (m, 12H, ArH), 7.37 (dd, $J = 7.2$ Hz, $J = 1.9$ Hz, 2H, ArH), 7.09 (d, $J = 7.6$ Hz, 1H, ArH), 7.02−6.91 (m, 16H, ArH), 6.82 (t, $J = 7.0$ Hz, 15H, ArH), 6.72 (t, $J = 7.3$ Hz, 3H, ArH), 6.64 (t, $J = 7.5$ Hz, 4H, ArH), 6.60 (s, 1H, Ar−H), 6.55 (t, $J = 7.5$ Hz, 2H, ArH), 6.39 (t, $J = 7.0$ Hz, 2H, ArH), 6.26 (t, $J = 7.2$ Hz, 4H, ArH), 3.94 (m, 1H, CH), 2.68 (m, 2H, CH), 2.08 (s, 3H, Me), 1.00−0.79 (m, 18H, Me). ^{13}C NMR (C_6D_6, 300 MHz): 167.2, 163.6, 148.3, 140.1, 139.2, 135.2, 134.7, 134.5, 134.1, 132.0, 131.5, 129.7, 128.1, 127.8, 127.5, 127.2, 125.4, 121.0, 119.6, 118.8, 114.4, 30.1, 28.6, 26.0, 25.2, 24.8, 22.3, 21.2. IR (cm^{-1}, KBr): 3049m, 2958s, 2930m, 2867w, 1597vs, 1561m, 1540vs, 1466m, 1423vs, 1380m, 1361w, 1328s, 1282m, 1244w, 1217s, 1192m, 1162w, 1095s, 1072m, 1021m, 998w, 948w, 907w, 884w, 854m, 750s, 731s, 693vs, 616w, 599w, 575w, 529s, 512s, 494m, 453w, 418w. ESI-MS (*m/e*): 1389.3 $[M + H]^+$. Anal. Calcd for $C_{89}H_{80}N_2Ni_2O_2P_2{\cdot}C_6H_5CH_3$: C, 77.85; H, 5.99; N, 1.89. Found: C, 77.67; H, 6.02; N, 1.66.

Synthesis of Binuclear Nickel Complex 3i. Ligand **1i** was prepared using the same procedure for ligand **1a**. 3,5-Dinitrosalicylaldehyde (2.12 g, 10.0 mmol) and 1.17 g (5.00 mmol) of 2,4,6-triisopropyl-*m*-phenylenediamine were used to give 2.43 g (yield, 78%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.09 (d, $J = 2.6$ Hz, 2H, ArH), 8.61 (s, 2H, ArH), 8.42 (s, 2H, CH═N), 7.33 (s, 1H, ArH), 3.15 (m, 1H, CH), 2.88 (m, 2H, CH), 1.26 (d, $J = 6.9$ Hz, 12H, Me), 1.23 (d, $J = 7.0$ Hz, 6H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): 165.8, 164.6, 140.1, 136.7, 133.0, 131.5, 130.7, 126.6, 124.4, 122.7, 119.0, 28.5, 27.3, 23.7, 22.3. Anal. Calcd for $C_{29}H_{30}N_6O_{10}$: C, 55.95; H, 4.86; N, 13.50. Found: C, 55.86; H, 4.47; N, 13.26.

Complex **3i** was prepared using the same procedure for complex **3a**. Sodium hydride (0.060 g, 0.20 mmol), 0.467 g (0.750 mmol) of ligand **1i**, and 1.00 g (1.44 mmol) of *trans*-NiCl(Ph)$(PPh_3)_2$ were used to give 0.586 g (yield, 52%) of yellow-brown crystals. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.26 (d, $J = 2.8$ Hz, 2H, ArH), 7.93 (d, $J = 2.8$ Hz, 2H, ArH), 7.78 (d, $J = 7.9$ Hz, 2H, CH═N), 7.49 (t, $J = 9.1$ Hz, 12H, ArH), 7.13−7.01 (m, 27H, ArH), 6.59 (s, 1H, ArH), 6.43 (t, $J = 7.1$ Hz, 2H, ArH), 6.25−6.20 (m, 4H, ArH), 3.84 (m, 1H, CH), 2.56 (m, 2H, CH), 2.10 (s, 3H, Me), 1.11 (d, $J = 7.0$ Hz, 3H, Me), 0.97 (d, $J = 6.8$ Hz, 6H, Me), 0.90 (d, $J = 6.8$ Hz, 9H, Me). ^{13}C NMR (C_6D_6, 300 MHz): 165.5, 161.5, 147.0, 142.7, 138.9, 136.9, 134.2, 134.1, 133.9, 133.0, 130.4, 129.9, 128.1, 127.8, 127.5, 124.8, 122.0, 121.5, 120.0, 29.2, 27.8, 26.0, 25.1, 24.9, 22.1, 21.2. IR (cm^{-1}, KBr): 3051w, 2958w, 2868w, 1612vs, 1557s, 1530m, 1507w, 1474m, 1434s, 1334vs, 1222w, 1185w, 1096s, 1018w, 1185w, 1096s, 1018w, 995w, 909w, 732m, 692s, 529m, 509m. Anal. Calcd for $C_{77}H_{68}N_6Ni_2O_{10}P_2{\cdot}C_6H_5CH_3$: C, 66.86; H, 5.08; N, 5.57. Found: C, 66.62; H, 5.33; N, 5.18.

Synthesis of Binuclear Nickel Complex 3j. Ligand **1j** was prepared using the same procedure for ligand **1a**. A 1.67 g (10.0 mmol) amount of 5-nitrosalicylaldehyde and 1.17 g (5.00 mmol) of 2,4,6-triisopropyl-*m*-phenylenediamine were used to give 2.34 g (yield, 88%) of yellow crystals. ^{1}H NMR($CDCl_3$, 500 MHz): δ 8.40 (s, 2H, CH═N), 8.35 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.15 (d, $J = 8.8$ Hz, 2H, ArH), 3.13 (m, 1H, CH−H), 2.88 (m, 2H, CH), 1.22 (d, $J = 6.8$ Hz, 12H, Me), 1.16 (d, $J = 7.0$ Hz, 6H, Me). ^{13}C NMR ($CDCl_3$, 300 MHz): 166.8, 165.9, 144.3, 140.1, 136.5, 128.8, 128.4, 121.6, 118.6, 117.4, 28.3, 28.1, 23.7, 22.3. Anal. Calcd for $C_{29}H_{31}N_4O_6$: C, 65.40; H, 6.06; N, 10.52. Found: C, 65.29; H, 5.61; N, 10.41.

To a suspension of *trans*-NiCl(Ph)$(PPh_3)_2$ (1.04 g, 1.50 mmol) and NEt_3 (0.175 g, 1.73 mmol) in toluene (15 mL) was added dropwise a toluene solution (20 mL) of ligand **1j** (0.400 g, 0.750 mmol). This reaction mixture was allowed to stir for 12 h at ambient temperature. After filtration, the filtrate was concentrated to ca. 10 mL under vacuum, and *n*-hexane (20 mL) was added to the solution. A yellow solid precipitated from solution was isolated by filtration. The crude product was recrystallized from toluene and *n*-hexane to give yellow crystals as complex **3j** in 52% yield. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.25 (d, $J = 2.6$ Hz, 2H, ArH), 7.94−7.89 (m, 4H, CH═N and ArH), 7.50 (t, $J = 8.9$ Hz, 12H, ArH), 7.05−6.93 (m, 26H, ArH), 6.60 (m, 1H, ArH), 6.47 (s, 1H, ArH), 6.38 (t, $J = 7.1$ Hz, 2H, ArH), 6.23 (t, $J = 7.1$ Hz, 2H, ArH), 6.18 (t, $J = 7.3$ Hz, 2H, ArH), 5.98 (t, $J = 7.3$ Hz, 2H, ArH), 3.95 (m, 1H, CH), 2.64 (m, 2H, CH), 2.10 (s, 3H, Me), 1.22 (d, $J = 7.0$ Hz, 3H, Me), 0.93 (d, $J = 6.6$ Hz, 6H, Me), 0.85 (d, $J = 6.6$ Hz, 9H, Me). ^{13}C NMR (C_6D_6, 300 MHz): 170.2, 166.3, 147.3, 144.4, 138.5, 137.8, 137.3, 136.7, 134.3, 131.3, 131.0, 130.4, 130.0, 127.9, 125.7, 125.4, 125.0, 123.0, 121.7, 119.5, 118.2, 31.7, 30.0, 26.1, 25.2, 25.0, 22.1, 21.2. IR (cm^{-1}, KBr): 3049w, 2959m, 2918w, 2867w, 1606vs, 1561m, 1543s, 1468s, 1433s, 1379m, 1322vs, 1243w, 1186m, 1095s, 1019w, 996w, 950m, 834m, 730s, 693s, 649w, 528m, 510m, 458w. Anal. Calcd for $C_{77}H_{70}N_4Ni_2O_6P_2{\cdot}C_6H_5CH_3$: C, 71.11; H, 5.54; N, 3.95. Found: C, 71.12; H, 5.68; N, 3.92.

Ethylene Polymerization Procedure. A 100 mL autoclave, equipped with a magnetic stirrer bar, was heated at 100 °C under vacuum for 30 min and then cooled to the required temperature. Toluene was injected into the reactor and pressurized with ethylene to 1 atm. After equilibrating for 3 min, an appropriate volume of catalyst solution and $Ni(COD)_2$ solution were injected to start the reaction. The ethylene pressure was kept constant at 10 atm during the polymerization. After the desired run time, the reactor was vented and the reaction mixture was quenched with 3% HCl in ethanol. The precipitated polymer was filtered, washed to neutral with ethanol, and then dried overnight in a vacuum oven at 80 °C.

X-ray Crystallography of Complex 3h. A yellow-brown crystal of complex **3h** was sealed in a capillary under an argon atmosphere. All measurements were made on a Bruker AXSD8 diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. All data were collected at 20 °C using the scan techniques. The structure of **3h** was solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.[26] All non-hydrogen atoms were refined by full-matrix least-squares on F^2 using the SHELXTL program package.[27] Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done by Bruker SAINT.[28] The structure solution and refinement were performed by SHELXS-97[29] and SHELXL-97,[30] respectively. For further crystal data and details of measurements see Table 1.

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Supporting Information Available: Data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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