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Novel, Highly Active Binuclear 2,5-Disubstituted Amino-*p*-benzoquinone−Nickel(II) Ethylene Polymerization Catalysts[†]

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Reaction of salts of the 2,5-disubstituted amino-*p*-benzoquinone bridging ligand (**1a**−**e**) with *trans*-bis(triphenylphosphane)phenylnickel(II) chloride results in the binuclear complexes **2a**−**e**, which show high activities for ethylene polymerization without any cocatalysts. High-molecular-weight, moderately branched polyethylene of broad molecular-weight distribution was obtained.

Over the past decade, late-transition-metal catalysts for olefin polymerization have received increasing attraction, for they are much less oxophilic and more tolerant of polar functional groups than the catalysts ordinarily used.[1] Among the numerous catalysts, neutral nickel catalysts play an important role and now are considered to be very promising catalysts for olefin polymerization and copolymerization.[2−6] In the 1960s, Keim et al. developed neutral nickel(II) complexes bearing bidentate phosphoro keto-ylide P,O ligands $[(\mathrm{P}{\wedge}\mathrm{O})\mathrm{Ni^{II}R(L)}]$, which are the basis for the Shell high olefin process (SHOP) for ethylene oligomerization to form linear α-olefins.[2] Two years ago, Grubbs et al. developed the neutral, single-component salicylaldimine-based nickel(II) complexes $[(\mathrm{N}{\wedge}\mathrm{O})\mathrm{Ni^{II}R(L)}]$ catalysts for polyolefin.[5] More recently, a new neutral nickel(II) complex reported by the Brookhart group, $[(\mathrm{N}{\wedge}\mathrm{O})\mathrm{Ni^{II}R(L)}]$, based upon an anilinotropone ligand has been shown to be a highly active ethylene polymerization catalyst.[6] As expected, these single-component catalysts can produce high-molecular-weight polyethylene. They also can polymerize functionalized olefins and require no cocatalyst. In addition, such neutral complexes can polymerize ethylene in an aqueous emulsion, affording stable polymer lattices with high molecular mass.[7]

To date, the quest for novel polymerization catalysts involves the search for new ligand structures. The well-known late-transition-metal systems, such as catalysts bearing P−O, N−O, and N−N ligands for ethylene polymerizations affording high-molecular-weight polymers with high activities, are based on variations in the ligands. However, in the course of our studies on the late-transition-metal catalysts,[8] we found this search to be empirical in nature; recent developments have provided somewhat more comprehensive guidelines for catalyst design. We report here ethylene polymerization by a series of new, neutral binuclear nickel(II) complexes of bridging ligands comprising 2,5-disubstituted amino-*p*-benzoquinones without any cocatalysts and the properties of polymer obtained. To the best of our knowledge, neutral, single-component binuclear nickel(II) complexes for olefin polymerization have not been reported.[9]

The free ligands **1a**−**e** were prepared from a substituted amine and 2,5-dihydroxy-*p*-benzoquinone by vinylogous nucleophilic substitution in *m*-cresol.[10] By using trifuoroacetic acid as a catalyst, almost all ligands were obtained in good yield. A single crystal of **1a** suitable for an X-ray structure determination was obtained from acetic acid. The crystal structure of **1a** (Figure 1)[11] shows a symmetrical framework and two

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[†] Dedicated to Prof. E. O. Fischer on the occasion of his 85th birthday.

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(10) Ueda, M.; Sakai, N.; Imai, Y. *Macromol. Chem.* **1979**, *180*, 2813−2818.

(11) Crystal data for **1a**: triclinic, $P\bar{1}$, $a = 8.417(3)$ Å, $b = 8.827(3)$ Å, $c = 12.86(4)$ Å, $\alpha = 75.3(3)°$, $\beta = 80.48(3)°$, $\gamma = 67.92(3)°$, $V = 854.6(5)$ Å^3, $Z = 1$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 0.0497 and wR2 = 0.0493 for 3339 independent reflections.

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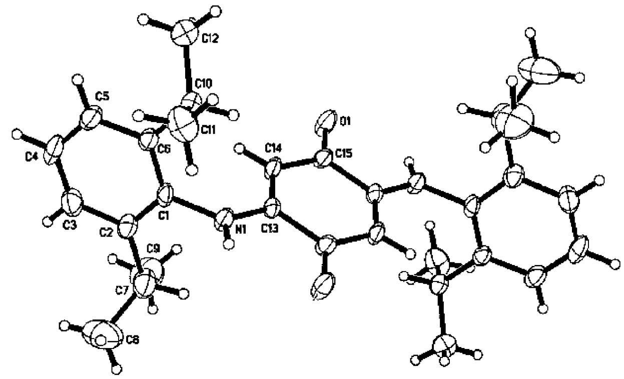
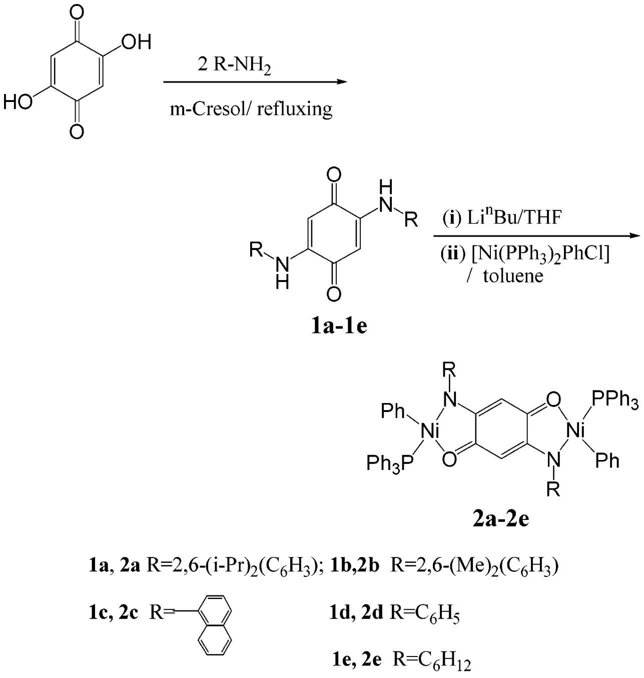


Figure 1. Crystal structure of **1a** (with acetic acid solvent molecules omitted). Selected distances (Å) and angles (deg): O(1)−C(15) = 1.236(2), C(14)−C(15) = 1.420(3), C(13)−C(14) = 1.359(3), N(1)−C(1) = 1.451(3), N(1)−C(13) = 1.340(2), C(1)−C(2) = 1.385(3), C(1)−C(6) = 1.403(3); O(1)−C(15)−C(14) = 123.4(2), C(13)−C(14)−C(15) = 120.9(2), N(1)−C(13)−C(14) = 125.2(2), C(1)−N(1)−C(13) = 124.5(2), N(1)−C(1)−C(2) = 118.7(2).

Scheme 1. Synthesis of Binuclear Nickel Complexes 2a−e



hydrogen-bonded acetic acid molecules. A band at 1720 cm^{-1} in the IR spectrum is also indicative of **1a**.

Binuclear nickel(II) complexes **2a**−**e** were obtained by the reaction of *trans*-[Ni(PPh$_3$)$_2$(Ph)Cl] with $^1/_2$ equiv of the lithium salts of the free ligands, which were obtained via deprotonation (Scheme 1). Most of the complexes were isolated as blue powders. To date, we have not obtained crystals suitable for an X-ray structure determination. However, the high activities for ethylene polymerization and spectral characterizations of **2a**−**e** suggest that they have a square-planar structure, as in other comparable nickel(II) [N,O] complexes.[5−8]

Table 1. Polymerization of Ethylene by Complexes 2a−e[a]

	reacn conditions			results			
entry no.	catalyst (amt, μmol)	T, (°C)	amt of PE (g)	activity[b]	M_w[c]	M_w/M_n[c]	T_m[d]
1	**2a** (27)	40	2.82	104	43.1	3.5	128.8
2	**2a** (22)	60	3.31	148	41.2	5.0	125.8
3	**2a** (22)	80	3.81	170	6.7	3.7	121.1, 70.0
4	**2a** (22)	100	2.97	133	1.7	3.2	103.9, 71.1
5	**2b** (41)	80	2.60	64	53.5	8.2	125.6
6[e]	**2c** (15)	80	0.24	23	6.0	48.2	123.7
7	**2d** (41)	80	0.04	1	n.d.[f]	n.d.[f]	n.d.[f]
8	**2e** (131)	80	trace				

[a] Conditions: ethylene pressure, 0.4 Mpa; polymerization time, 1 h; total volume of toluene, 120 mL; 800 rpm; PE = polyethylene. [b] In units of 10^3 g of PE (mol of Ni)$^{-1}$ h^{-1}. [c] M_w ($\times 10^{-4}$) and M_w/M_n values were determined by GPC. [d] T_m values were determined by DSC with second heat curves. [e] Polymerization time: 40 min. [f] Not determined.

Complexes **2a**−**e** were catalytically active in ethylene polymerization (Table 1). Complex **2a**, comprising a bulky substituted aryl group bound to the anilino function (R = 2,6-$^iPr_2$-C_6H_5), has a high potential for olefin polymerization. Its activity was comparable to that of the Grubbs catalyst ([3-phenyl phenolate-2′,6′-diisopropylphenylimine](triphenylphosphine)phenylnickel(II))[5a] under the same conditions. A reduction in steric bulk resulted in a marked decrease from 1.7 × 10^5 g of PE (mol of Ni)$^{-1}$ h^{-1} for **2a** to 6.4 × 10^4 g of PE (mol of Ni)$^{-1}$ h^{-1} for **2b** (R = 2,6-Me_2-C_6H_5). For complexes **2c** (R = naphthyl) and **2d** (R = phenyl), activities decreased to 2.3 × 10^4 and 1.0 × 10^3 g of polymer/(mol of cat)$^{-1}$ h^{-1}, respectively. However, the replacement of the aryl at the R position with cyclohexyl afforded only traces of polymer with complex **2e**. This different catalytic behavior clearly suggests that the change of bulky substituents at the R position influences the polymerization activity, as in other late-transition-metal catalyst systems.

In a series of ethylene polymerization experiments, reaction temperatures have some effect on the activities of catalysts. For complex **2a**, 80 °C represents the optimum (entry 3). At a lower or higher temperature, the catalytic performance decreased.

GPC analysis of polyethylene obtained employing complexes **2a**−**c** revealed molecular weights of typically M_w = 4.31 × 10^5, 5.35 × 10^5, and 6.03 × 10^4, respectively. The relatively wide molecular weight distributions of 3.21−48.24 were quite different from those of well-behaved single-site catalysts.[12] The mononuclear nickel catalyst with an anilinotropone ligand reported by Brookhart afforded polyethylene with a narrower molecular weight distribution of 1.68−2.81. Figure 2 shows the evidence for a bimodal distribution of polyethylene obtained by catalyst **2a** (Table 1, entry 2). The observed effects on very wide molecular weight distribution can also be explained on the basis of electronic effects and cooperative interactions of the two adjacent nickel centers in binuclear complexes. These two metal centers are electronically coupled through the ligand bridge. When one of the centers was activated by removing phosphane at a given time, it had an electron-withdrawing effect on another center. The interaction between two metals made it possible to create more than one kind of active species during the polymerization. Moreover, with an increase in temperature the effect

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(12) For metallocenes, a similar phenomenon was observed. The molecular weight distributions of polyethylene produced by binuclear group IV metallocene−MAO catalysts are usually broad compared with those of polyethylene produced by mononuclear compounds.[9]

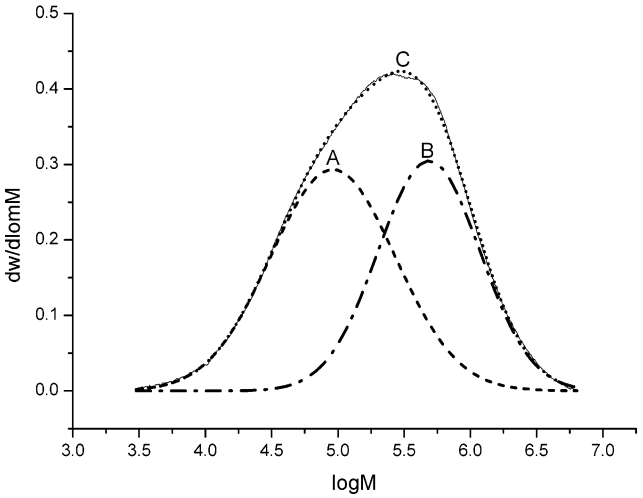

Figure 2. GPC spectra of polyethylene produced by catalyst **1a** (Table 1, entry 2). The spectral components of the pattern (curves A and B) were obtained by deconvolution of the observed spectrum. Curve C represents the sum of the components.

of molecular weight declining became remarkable because of the higher rate of β-hydrogen elimination.

For catalysts **2b**,**c**, polymer crystallinity amounts to ca. 47% and 42% and the melt peaks occur at ca. 126 and 124 °C. From the DSC curves of polymers produced by catalyst **2a** at different temperatures something different could be found. When the polymerization temperature was increased to 80 °C, a bimodal distribution of DSC appeared (for figures giving DSC curves, see the Supporting Information). The results showed that the interaction between two metals created more than one kind of active species during the polymerization. Another reason for this was that, at higher reaction temperatures, branching polyethylene increases and the polymer molecular weight and melting point decrease.[1c]

High-temperature ^{13}C NMR spectra showed that the polymers are moderately branched (see Supporting Information).[13] Methyl branches predominate with ca. 10 methyl branches per 1000 carbon atoms. Additional weak signals suggested that higher branches, such as butyl, are also present. The polymer microstructure is similar to that obtained with other single-component nickel(II) complexes.

In conclusion, binuclear nickel(II) 2,5-disubstituted amino-*p*-benzoquinone complexes represent new types of homogeneous neutral, single-component catalysts containing two catalytically active or dormant sites. High-molecular-weight, moderately branched polymers are accessible at reasonable rates by employing bulky substituted ligands.

Experimental Section

General Considerations. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Toluene, benzene, hexane, and tetrahydrofuran were dried by refluxing these solvents with appropriate drying agents (sodium/benzophenone) and distillation under argon prior to use. Commercial reagents, namely *n*-BuLi (1.6 M), hydroquinone, 2,6-diisopropylaniline, 2,6-dimethylaniline, naphthylamine, aniline, and cyclohexanylamine, were used as purchased from Acros Co. *m*-Cresol was purified by vacuum distillation and stored over 4 Å molecular sieves. 2,5-Dihydroxy-*p*-benzoquinone[14] and *trans*-[Ni(PPh$_3$)$_2$PhCl][15] were prepared according to the analogous methods reported. For compounds **1a**−**e** and complexes **2a**−**e**, ^{1}H NMR spectra were recorded on a Unity-400 spectrometer; ESI-MS spectra were recorded on a Finigan MAT 8500 spectrometer (70 eV), and elemental analysis was performed on a Perkin-Elmer Series II CHN/O analyzer 2400. For polyethylene, ^{13}C NMR spectra were obtained using *o*-dichlorobenzene as a solvent on an FX-100 NMR spectrometer at 130 °C. Molecular weight distribution (M_w/M_n) values of polyethylene were determined using a PL GPC-220 gel permeation chromatograph at 150 °C using narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 μm MIXED-B LS); 1,2,4-trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL min^{-1}.

[μ-*p*-Benzoquinone-2,5-bis(2,6-diisopropylanilino)]bis[(triphenylphosphane)phenylnickel(II)] (2a). (a) Free Ligand Synthesis.[10] A 1.4 g (10 mmol) amount of 2,5-dihydroxy-*p*-benzoquinone were added to a stirred solution of 2,6-diisopropylaniline (3.85 g, 20 mmol) in *m*-cresol (40 mL). After 0.40 g (3.2 mmol) of trifuoroacetic acid as a catalyst was charged into the reaction mixture, the mixture was heated with stirring at 100 °C for 1.5 h under an argon atmosphere. The resulting reaction mixture was poured into 5% aqueous sodium hydroxide (1.2 L). The precipitate was collected by filtration, washed with water, and dried in vacuo at 80 °C for 8 h. Yield: 3.88 g (84.8%). ^{1}H NMR (CDCl$_3$): δ 1.17 (d, ^3J = 6.8 Hz, 12H, CH$_3$(iPr)), 1.25 (d, ^3J = 6.8 Hz, 12H, CH$_3$(iPr)), 2.97 (septet, ^3J = 6.8 Hz, CH(iPr)), 5.05 (s, 2H, H(*p*-benzoquinone)), 7.24 (d, 4H, H(arom)), 7.36 (t, 2H, H(arom)), 7.64 (s, 1H, NH). IR (KBr): 3245 (vs; N−H), 1570 cm^{-1} (vs; C═O). Anal. Calcd for $C_{30}H_{38}N_2O_2$ (458.64): C, 78.56; H, 8.35; N, 6.11. Found: C, 78.54; H, 8.30; N, 6.15. EI-MS (*m*/*e* (relative abundance, %)): 458 (M$^+$, 24). The 2,5-bis(2,6-diisopropylaniline)-*p*-benzoquinone (**1a**) obtained was crystallized from acetic acid to afford red single crystals suitable for X-ray determination. IR (KBr): 3245 (vs; N−H), 1720 (vs; C═O(acetic acid)), 1570 cm^{-1} (vs; C═O).

(b) Complex Synthesis. Complex **2a** was synthesized by a similar method reported by Brookhart[6] and Grubbs.[5] The sodium salt of **1a** was obtained by treating **1a** with 2 equiv of NaH or BuLi in THF solution. *trans*-Bis(triphenylphosphane)phenylnickel(II) chloride (1.5 mmol) reacted with $^1/_2$ equiv of the lithium salt of **1a** (0.72 mmol) in toluene to afford the dark blue binuclear nickel(II) complex **2a**. Yield: 0.47 g (52.5%). ^{1}H NMR (C$_6$D$_6$CD$_3$): δ 1.00 (d, ^3J = 6.8 Hz, 12H, CH$_3$(iPr)), 1.25 (d, ^3J = 6.8 Hz, 12H, CH$_3$(iPr)), 3.38 (m, ^3J = 6.4 Hz, CH(iPr)), 5.31 (s, 2H, H(*p*-benzoquinone)), 6.45−7.86 (m, 46H, H(arom)). Anal. Calcd for $C_{78}H_{76}N_2Ni_2O_2P_2$ (1252.80): C, 74.78; H, 6.11; N, 2.24. Found: C, 74.54; H, 6.08; N, 2.32. EI-MS (*m*/*e* (relative abundance, %)): 651 (M$^+$ − 2PPh$_3$ − Ph, 5), 574 (M$^+$ − 2PPh$_3$ − 2Ph, 17).

[μ-*p*-Benzoquinone-2,5-bis(2,6-dimethylanilino)]bis[(triphenylphosphane)phenylnickel(II)] (2b). 2,5-Bis(2,6-dimethylaniline)-*p*-benzoquinone (**1b**) was obtained as a pale pink solid in 91% yield. ^{1}H NMR (CDCl$_3$): δ 2.22 (s, 12H, CH$_3$), 5.03 (s, 2H, H(*p*-benzoquinone)), 7.14 (d, 4H, H(arom)), 7.21 (t, 2H, H(arom)), 7.65 (s, 2H, NH). IR (KBr): 3253 (vs; N−H), 1563 cm^{-1} (vs; C═O). Anal. Calcd for $C_{22}H_{22}N_2O_2$ (346.43): C, 76.28; H, 6.40; N, 8.09. Found: C, 76.28; H, 6.38; N, 8.12. EI-MS (*m*/*e* (relative abundance, %)): 346 (M$^+$, 40). **2b** was obtained as a blue powder. Yield: 0.54 g (65.7%). Anal. Calcd

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[13] Branching structure assigned according to: (a) Randall, J. C. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201−317. (b) Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41−52.

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for $C_{70}H_{60}N_2Ni_2O_2P_2$ (1140.58): C, 73.71; H, 5.30; N, 2.46. Found: C, 73.38; H, 5.12; N, 2.76. EI-MS (*m*/*e* (relative abundance, %)): 538 ($M^+ - 2PPh_3 - Ph$, 18). No satisfying ^1H NMR data for the complexes were obtained due to their insolubility.

[*μ*-*p*-Benzoquinone-2,5-bis(naphthylamino)]bis[(triphenylphosphane)phenylnickel(II)] (2c). 2,5-Bis(naphthylamino)-*p*-benzoquinone (**1c**) was obtained as a brown powder in 94% yield. ^1H NMR ($CDCl_3$): δ 5.77 (s, 2H, H(*p*-benzoquinone)), 7.50−7.58 (m, 8H, H(naphthylene)), 7.83 (d, 2H, H(naphthylene)), 7.90−7.94 (m, 4H, H(naphthylene)), 8.36 (s, 2H, NH). IR (KBr): 3284 (vs; N−H), 1594, 1573 cm^{-1} (vs; C═O). Anal. Calcd for $C_{26}H_{18}N_2O_2$ (390.44): C, 79.98; H, 4.65; N, 7.18. Found: C, 80.01; H, 4.63; N, 7.20. EI-MS (*m*/*e* (relative abundance, %)): 390 (M^+, 100). **2c** was obtained as a blue powder. Yield: 0.48 g (56.3%). Anal. Calcd for $C_{74}H_{56}N_2Ni_2O_2P_2$ (1184.60): C, 75.03; H, 4.76; N, 2.36. Found: C, 74.31; H, 4.85; N, 2.49. EI-MS (*m*/*e* (relative abundance, %)): 583 ($M^+ - 2PPh_3 - Ph$, 3%).

[*μ*-*p*-Benzoquinone-2,5-bis(anilino)]bis[(triphenylphosphane)phenylnickel(II)] (2d). The ligand 2,5-bis(anilino)-*p*-benzoquinone (**1d**) was obtained as a pale pink solid in 98% yield. ^1H NMR ($CDCl_3$): δ 5.03 (s, 2H, H(*p*-benzoquinone)), 7.14 (d, 4H, H(arom)), 7.21 (t, 2H, H(arom)), 7.65(s, 2H, NH). IR (KBr): 3230 (vs; N−H), 1566 cm^{-1} (vs; C═O). Anal. Calcd for $C_{18}H_{14}N_2O_2$ (290.32): C, 74.47; H, 4.86; N, 9.65. Found: C, 74.49; H, 4.84; N, 9.67. EI-MS (*m*/*e* (relative abundance, %)): 290 (M^+, 100%). **2d** was obtained as a pale blue powder. Yield: 0.57 g (72.3%). Anal. Calcd for $C_{66}H_{52}N_2Ni_2O_2P_2$ (1084.48): C, 73.10; H, 4.83; N, 2.58. Found: C, 72.41; H, 4.75; N, 2.73. EI-MS (*m*/*e* (relative abundance, %)): 560 ($M^+ - 2PPh_3$, 11%), 483 ($M^+ - 2PPh_3 - Ph$, 6%).

[*μ*-*p*-Benzoquinone-2,5-bis(cyclohexanylamino)]bis[(triphenylphosphane)phenylnickel(II)] (2e). 2,5-Bis(cyclohexanylamino)-*p*-benzoquinone (**1e**) was prepared as a pale pink solid in 99% yield. ^1H NMR ($CDCl_3$): δ 1.23−1.41 (m, 10H, CH_2(cyclohexanylamine)), 1.63−1.67 (m, 2H, CH_2(cyclohexanylamine)), 1.76−1.81 (m, 4H, CH_2(cyclohexanylamine)), 1.96−1.99 (m, 10H, CH_2(cyclohexanylamine)), 3.27(m, 2H, CH-(cyclohexanylamine)), 5.33 (s, 2H, H(*p*-benzoquinone)), 6.58 (d, $^3J = 6.8$ Hz, 2H, NH). IR (KBr): 3272 (vs; N−H), 1562 cm^{-1} (vs; C═O). Anal. Calcd for $C_{18}H_{26}N_2O_2$ (302.42): C, 71.49; H, 8.66; N, 9.26. Found: C, 71.49; H, 8.67; N, 9.27. EI-MS (*m*/*e* (relative abundance, %)): 302 (M^+, 100). **2e** was obtained as a yellowish powder. Yield: 0.64 g (80.6%). Anal. Calcd for $C_{66}H_{64}N_2Ni_2O_2P_2$ (1096.57): C, 73.29; H, 5.88; N, 2.55. Found: C, 73.28; H, 5.87; N, 2.59. EI-MS (*m*/*e* (relative abundance, %)): 495 ($M^+ - 2PPh_3 - Ph$, 7).

Ethylene Polymerization. A 500 mL autoclave was charged with 100 mL of toluene under an atmosphere of argon. The catalyst was weighed and added to the polymerization system. After three cycles of ethylene gas exchange, the ethylene pressure was raised to the specified value and maintained for a certain time. The polymerization was terminated by the addition of methanol and dilute HCl (10%). The solid polyethylene was filtered, washed with methanol, and dried at 40 °C for 10 h under vacuum.

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Supporting Information Available: Figures giving three DSC curves and ^{13}C NMR spectra of polyethylene prepared and tables and figures giving complete details of the crystallographic study of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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