Nickel(II) Isocyanide Complexes as Ethylene Polymerization Catalysts

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Received March 4, 2004

Isocyanide complexes of nickel, $NiBr_2(CNAr)_2$, are found to be active catalysts for polymerization of ethylene in the presence of methylaluminoxane (MAO). The catalytic activity and properties of polyethylene formed vary with substituents on the aryl group, in particular, at the 2- or 2,6-positions. The nickel complexes having 2,6-diphenylphenylisocyanide and its analogues are catalysts showing moderate activity and giving high molecular weight polyethylene ($M_v > 10^6$), whereas those bearing 2-phenylphenylisocyanide and its analogues give polyethylene with $M_w = 10^3-10^4$.

Introduction

Isocyanides (CNR) are similar in their electronic structures to carbon monoxide (CO), but have stronger σ-donor and weaker π-acceptor properties as ligands of transition metal complexes.[1] Since their properties as a ligand depend on the steric and electronic factors of R groups in CNR, the ligand design of metal isocyanides as a key to controlling the catalysis may open an attractive research area in organometallic chemistry. However, high reactivity of CNR to metal-catalyzed self-polymerization[2] or insertion between O−H, N−H, and C−H bonds in certain organic molecules prevents studies using metal isocyanide complexes as catalysts for chemical transformation of organic molecules.[3] A notable exception is a report by Ito and co-workers, in which palladium complexes bearing certain bulky alkyl isocyanides are excellent catalysts for the activation of a Si−Si bond followed by intramolecular addition reaction of the resulting activated Si species to a carbon−carbon double or triple bond.[4] In other words, molecular catalysis of metal isocyanides may be discovered by appropriate design of the isocyanide ligands.

In this paper, we wish to report that Ni(II) isocyanide complexes unexpectedly behave as catalysts for ethylene polymerization in the presence of methylaluminoxane (MAO). Organonickel complexes had long been recognized as good catalysts for oligomerization of ethylene including industrial production of C4−C20 olefins[5,6] until Brookhart's discovery that judicious choice of the ligand structure in MX_2(α-diimine) (M = Ni, Pd) made it possible to obtain polyethylene with high molecular weight.[7,8] Since then, nickel complexes bearing analogues of bidentate diimine ligands,[9] bidentate phosphine ligands,[10] P∧O or P∧N chelate ligands,[11] N∧O chelate ligands,[12] and several carbon-based ligands[13]

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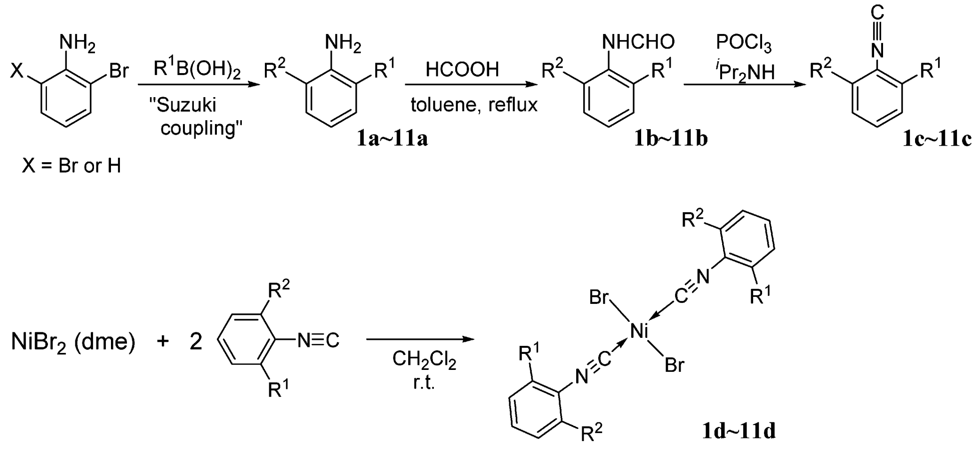
Scheme 1. Synthesis of Nickel Isocyanide Complexes



1d (85 %), **2d** (80 %), **3d** (82 %), **4d** (81 %),

5d (85 %), **6d** (83 %), **7d** (77 %), **8d** (98 %),

9d (69 %), **10d** (72 %), **11d** (54 %),

	R^1	R^2		R^1	R^2
1a ~ 1d	Me	Me	**7a ~ 7d**	4-*t*-BuC_6H_4	H
2a ~ 2d	Et	Et	**8a ~ 8d**	4-*t*-BuC_6H_4	4-*t*-BuC_6H_4
3a ~ 3d	*i*-Pr	*i*-Pr	**9a ~ 9d**	2-MeC_6H_4	H
4a ~ 4d	*i*-Pr	H	**10a ~ 10d**	2,6-MeC_6H_3	H
5a ~ 5d	Ph	H	**11a ~ 11d**	2,6-$Me_2C_6H_3$	2,6-$Me_2C_6H_3$
6a ~ 6d	Ph	Ph			

have been reported as an active molecular catalyst for olefin polymerization, in which design of the ligand structure is crucially important for chain growth of polyethylene.[14] In our recent finding that treatment of $NiBr_2(CNAr)_2$ with MAO produces active species for the formation of polyethylene with $M_w = 10^3$ to $>10^6$ with $M_w/M_n = 1.8-3.2$ with moderate catalytic activity (1−633 g/mmol Ni·h), the ligand structures, particularly, substituents on the aryl group in the isocyanide ligands in the Ni(II) isocyanide complexes, apparently affect the catalytic activity and the molecular weight and number of methyl branches of the formed polymers. In other words, the nickel isocyanide complexes with appropriate ligand structures have made possible for the first time catalytic polymerization of ethylene, opening a new potential for metal isocyanides in molecular catalysis.

Results and Discussion

Although the synthesis of $NiX_2(CNR)_2$ was reportedly achieved by treatment of NiX_2 with CNR,[15,16c] we found that $NiBr_2$(dme) (dme = 1,2-dimethoxyethane) was a versatile precursor for preparation of $NiBr_2(CNAr)_2$ (**1d**−**11d**, Scheme 1) in CH_2Cl_2 in good yields. Structures of the isocyanide ligands, in particular, those having substituents at the 2- and/or 6-positions, are important for this study, and several novel aryl-substituted isocyanides are synthesized by the Suzuki coupling of bromoanilines with arylboronic acids followed by formylation and dehydration as shown in

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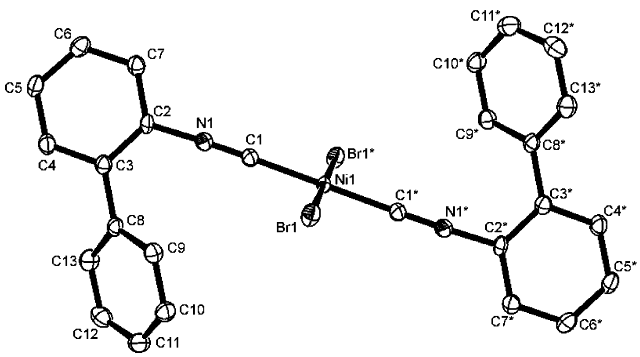

Figure 1. Molecular structure of **5d** in the crystal (ellipsoids represent 50% probability; hydrogen atoms are omitted for clarity). Selected bond length (Å), angles (deg), and dihedral angles (deg): Ni1−C1 = 1.846(2), C1−N1 = 1.141(3), Ni1−Br1 = 2.2978(3), C1−Ni1−Br1 = 90.4(1), N1−C1−Ni1 = 178.6(3), C1Ni1−C1* = 179.97, Br1−Ni1−C2−C3 = −68.0, C2−C3−C8−C9 = 49.2(4).

Scheme 1. A typical example is described in the Experimental Section, and details are summarized in the Supporting Information.

It was assigned from IR spectra in the literature[16] that nickel isocyanide complexes, $NiX_2(CNR)_2$, generally have a square-planar geometry with *trans*-configuration of two isocyanide ligands, which can be adopted to nickel complexes **1d**−**11d** showing a single $\nu_{C\equiv N}$ absorption at 2190−2202 cm^{-1}. The assigned structure is supported by X-ray crystallographic analysis of one of the compounds, **5d**, of which the ORTEP drawing is illustrated in Figure 1. Two bromine atoms and two carbons in the isocyanide ligands are bonded to the nickel center with bond distances of 2.2978(3) Å (Ni1−Br1) and 1.846(2) Å (Ni1−C1), respectively. The C≡N distances are 1.141(3) Å, which is similar to those of Pt(II), Pd(II), and Ni(0) complexes, *trans*-$[PdI_2(4\text{-}CN\text{-}3\text{-}C_2H_5C_6H_3CN)_2]$ [Pd−C = 1.941(6) Å, C≡N = 1.150(7) Å],[16a] *trans*-$[PtI_2(CN\text{-}C_6H_2\text{-}2,6\text{-}i\text{-}Pr_2\text{-}4\text{-}Br)_2]$ [Pt−C = 1.946(6) Å, C≡N = 1.146(8) Å],[16b] and $[Ni(4\text{-}Br\text{-}2,6\text{-}Me_2C_6H_3NC)_4HgI_2]_2$ [Ni−C = 1.936(19)−1.884(21) Å, C≡N = 1.145(26)−1.195(26) Å].[16c] ^1H and ^{13}C NMR data of nickel isocyanide complexes, **1d**−**11d**, are consistent with those deduced from *trans*-$NiX_2(CNR)_2$ as described in the Experimental Section.

Studies on the polymerization of ethylene were carried out in a 100 mL stainless steel autoclave in the presence of MAO (Al/Ni ratio = 100/1) as the cocatalyst ($P_{ethylene}$ = 0.8 MPa). Our initial examinations using 2,6-dialkylphenylisocyanide as the ligand led to successful polymerization of ethylene as shown in entries 1−3. Although the activity was low (1−3 g/mmol Ni·h), these complexes act as polymerization catalysts; this is apparent in comparison with the complete lack of activity of $NiBr_2(CNR)_2$ (R = *t*-Bu, cyclohexyl) under the conditions used. An interesting observation of these polymerizations is the properties of polyethylene formed, in which increase in the steric bulkiness of the *ortho*-substituents of the phenylisocyanide ligands tended to give a polymer with higher molecular weight and many methyl branches (entries 1−3). In sharp contrast to the fact that polymerization with the diisopropyl derivative **3d** gave polyethylene with M_w = 960 000, use of **4d** as the catalyst afforded polyethylene with magnitudes of smaller molecular weight with somewhat higher catalytic activity (entries 3 and 4). A similar change in the molecular weight of the product dependent on the aryl group of the ligand is also seen in the polymerization with the Brookhart catalyst.[9] In all cases, polyethylene formed has a relatively narrow molecular weight distribution (M_w/M_n = 2.1−3.2).

A remarkable increase in the catalytic activity was discovered when 2-aryl or 2,6-diarylphenyl isocyanides were used as the ligand of Ni(II) complexes. As shown in Table 1, entries 5 and 6, 2-phenyl-substituted complex **5d** showed relatively high catalytic activity [223 g/mmol Ni·h by 10 μmol of the catalyst (Al/Ni = 100/1)] to produce the polymer with M_w = 2200 (M_w/M_n = 1.8). Use of 1 μmol of the catalyst (Al/Ni = 1000/1) resulted in production of polyethylene with 633 g/mmol Ni·h of activity. The higher Al/Ni ratio somewhat increased the catalytic activity. For example, the *tert*-butylphenyl anologue of **5d**, **7d**, showed an activity of 80.0 and 198 g/mmolNi·h with the Al/Ni ratio of 100/1 and 1000/1, respectively. The 2,6-disubstituted complex **6d** showed lower catalytic activity (47 g/mmol Ni·h with 10 μmol of the catalyst) than **3d**. Although the catalytic activity was lower, it was surprising that the molecular weight of formed polyethylene was too large to be determined by our GPC system. The viscosity average molecular weight (M_v) of polyethylene formed by the catalyst **6d** was estimated by the intrinsic viscosity [η] measurement to be 6 100 000. Since M_w is higher than M_v, existence of two phenyl group at *ortho*-positions in the phenylisocyanide ligand in **6d** caused production of polyethylene of M_w > ca. 6 × 10^6. In both of the catalysts, the formed polyethylene has a small number of methyl branches.[17] In particular, polymer obtained by **6d** is almost linear.

To look at further aspects of the substituent effects of the isocyanide ligands, we prepared a series of Ni(II) complexes having 2-aryl and 2,6-diarylphenylisocyanide ligands, shown in Chart 1. The results of polymerization of ethylene using these catalysts are summarized in Table 1, entries 5−15. Introduction of a *t*-Bu group at the 4′-position of the aryl moiety (**5d** vs **7d**, **6d** vs **8d**) led to some decrease of the catalytic activity, but the molecular weight and M_w/M_n of the polyethylene formed were similar. Interestingly, introduction of a 2-tolyl group of the aryl group of the isocyanide in **5d** caused a dramatic decrease of the catalytic activity (entry 13, using **9d**), whereas that of a 2,6-xylyl derivative (**10d**) completely inhibited the reaction. Similarly, 2,6-dixylyl-substituted derivative **11d** showed no catalytic activity. There is a striking difference in the molecular structure of **10d** (Figure 2) from that of **5d**: the two methyl groups in the *ortho*-aryl group prohibit the rotation, which may be related to the inhibition mechanism by the methyl groups at the 2- or 2,6-positions described above.The above clearly showed that the polymerization behavior is very sensitive to the ligand structure of Ni(II) isocyanide complexes; in particular, 2- and 2,6-substituents of the aryl group in $NiBr_2(CNAr)_2$ play key roles in both catalyst efficiency and the molecular weight control of the polyethylene formed. Use of alkyl isocyanides or introduction of certain aryl substituents to the aryl isocyanides inhibited the polymerization. These features

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Table 1. Polymerization of Ethylene[a]

entry	complex (amount of catalyst)	yield (g)	activity (g/mmol·h)	M_w	M_w/M_n	M_v	T_m (°C)	branch[b] (1/1000C)
1	**1d** (100)	0.181	1.81	200 000	2.1	180 000	118.1	13.7
2	**2d** (100)	0.192	1.92	580 000	2.3		107.8	15.7
3	**3d** (100)	0.088	0.88	960 000	3.2	310 000	78.8	41.3
4	**4d** (100)	0.353	3.53	4200	2.3		128.0	5.1
5	**5d** (10)	2.23	223	2200	1.8		120.8	5.5
6[c]	**5d** (1)	0.633	633					
7	**6d** (100)	0.746	7.46	N.D.	N.D.	6 100 000	132.5	(<5)
8	**6d** (10)	0.466	46.6					
9	**7d** (10)	0.80	80.0	2900	2.4		128.9	1.3
10[c]	**7d** (10)	1.98	198					
11[c]	**7d** (1)	0.267	267					
12	**8d**	0.344	34.4			5 620 000	132.0	(<5)
13	**9d**	0.210	21.0	3000	3.1			
14	**10d**	0	N.R.					
15	**11d**	0	N.R.					

[a] All reactions were carried out in a 100 mL stainless steel autoclave in the presence of MAO (Al/Ni = 100/1 unless otherwise noted) at room temperature for 1 h. Ethylene (0.8 MPa) was applied. [b] Type and amounts of branching were determined by ^{13}C NMR according to the assignment reported by Galland and co-workers.[17] [c] The Al/Ni ratio was 1000/1.

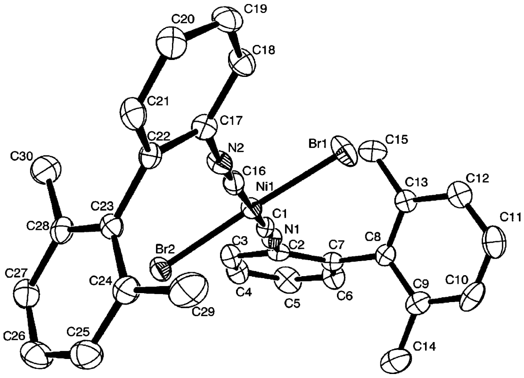

Figure 2. Molecular structure of **10d** in the crystal (ellipsoids represent 50% probability; hydrogen atoms are omitted for clarity). Selected bond length (Å), angles (deg), and dihedral angles (deg): Ni1−C1 = 1.843(3), C1−N1 = 1.145(4), Ni1−Br1 = 2.2857(4), C1−Ni1−Br1 = 89.96(8), N1−C1−Ni1 = 178.6(3), C1−Ni1−C16 = 176.8(1), Br1−Ni1−C2−C7 = 37.3, C2−C7−C8−C13 = −72.3(4).

as well as the relatively narrow molecular weight distribution strongly suggest that a single molecular catalyst species is produced by the reaction of $NiBr_2(CNAr)_2$ with MAO. Further studies including a search for more active catalysts as well as elucidation of mechanism[18] are in progress in our laboratory.

Experimental Section

General Procedures. All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Diethyl ether, THF, benzene, toluene, heptane, hexane, and benzene-d_6 were distilled from benzophenone ketyl and stored under an argon atmosphere. Other reagents and solvents were used as received. The ^{1}H NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer. Chemical shifts were recorded in ppm from the internal standard (^{1}H, ^{13}C: solvent). IR spectra were recorded in cm^{-1} on a JASCO FT/IR-550 spectrometer. Molecular weights of the formed polyethylene were deterimined by gel permeation chromatography (TOSOH HLC-8121GPC/HT) using *o*-dichlorobenzene as a solvent at 140 °C. The intrinsic viscosity [η] measurements were carried out on an Automatic Viscometer (Shibayama Scientific Co., Ltd. SS-201H-2T) in *o*-dichlorobenzene at 135 °C. Viscosity average molecular weights (M_v) of the formed polyethylene were calculated by the following equation: $[\eta] = 4.77 \times 10^{-4} M_v^{0.7}$. Transition melting temperatures of the formed polyethylene were determined by differential scanning calorimetory (Seiko DSC-200) at a heating rate of 10 °C/min. Analysis of type and amounts of branching of the polymer obtained was carried out by ^{13}C NMR according to the assignment in the literature.[17] As a representative example, an actual ^{13}C NMR chart of polyethylene formed by the experiment shown in Table 1, entry 1, is shown in the Supporting Information (p S-23).

Synthesis of 2-Arylanilines and 2,6-Diarylanilines. A typical procedure is as follows: In a 300 mL flask were placed 2,6-dibromoaniline (25.3 mmol, 6.35 g), $Pd(PPh_3)_4$ (4.0 mmol, 4.62 g), and toluene (350 mL). To this flask were added an ethanol solution of $PhB(OH)_2$ (100 mL, 0.76 M, 76 mmol) and an aqueous solution of Na_2CO_3 (200 mL, 1.9 M, 379 mmol). The mixture was stirred at 80 °C for 3 days and then poured into water. Organic products were extracted with ether. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatograpy (silica gel) eluted with ether to give 2,6-diphenylaniline (**6a**) in 88% yield (5.47 g). **6a**: mp 71.5 °C. ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.54 (d, $J = 8.0$ Hz, 4H, Ar), 7.48 (dd, $J = 8.0$ Hz, 4H, Ar), 7.38 (t, $J = 7.3$ Hz, 2H, Ar), 7.16 (d, $J = 7.5$ Hz, 2H, Ar), 6.92 (t, $J = 7.5$ Hz, 1H, Ar), 3.75 (br, 2H, NH_2). ^{13}C NMR (99 MHz, $CDCl_3$): δ140.01, 141.00, 130.02, 129.58, 129.10, 128.18, 127.51, 118.40. IR: ν_{N-H} 3398, 3376, 1603. HRMS: calcd 245.1204, found 245.1207. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.87; H, 6.23; N, 5.75. In a similar fashion, a coupling reaction of other arylboronic acids with 2-bromoaniline or 2,6-dibromoaniline affords the corresponding aniline derivatives in 70−95% yield. Spectral data are described in the Supporting Information.

Synthesis of 2-Arylphenyl Isocyanides and 2,6-Diarylphenyl Isocyanides. A typical procedure is as follows: A mixture of aniline (10 mmol), formic acid (130 mmol, 5.0 mL, 6.1 g), and toluene (50 mL) was heated under reflux. During

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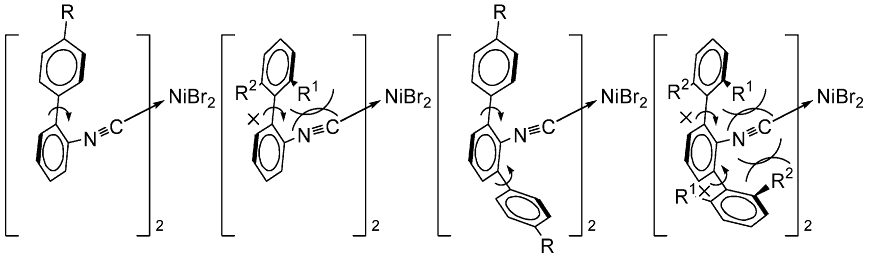
(18) Although further detailed investigation to detect the reactive catalyst species should be awaited, it seems worthwhile to point out that there are two possibilities for the net catalyst species: One is the case that the isocyanide behaves as a unique ligand to produce the catalytic species. The cationic species, *cis*-$(ArNC)_2NiMe^+$, is its candidate, and MAO promotes *trans*- to *cis*-isomerization and methylation of *trans*-$(ArNC)_2NiBr_2$ followed by generation of cationic species. The other is the case that MAO-promoted oligomerization of isocyanides on the nickel produces new nickel species. The paper reporting that $(Me_3P)_2Ni(R)X$ reacted with *t*-BuNC to give a metallacyclic compound may indicate the involvement of oligomerization of isocyanides on the nickel atom for the production of net catalyst species.[19] We have recently found that metallacyclic compounds analogous to that reported in ref 19 are a good catalyst for ethylene polymerization in the presence of MAO (Tanabiki, M.; Matsubara, K.; Motoyama, Y.; Nagashima, H., manuscript in preparation); this supports the mechanism involving oligomerization of isocyanides on the nickel atom.

Chart 1



5d (R = H)
7d (R = ^{t}Bu)

9d (R^1=Me, R^2=H)
10d (R^1=R^2=Me)

6d (R = H)
8d (R = ^{t}Bu)

11d (R^1=R^2=Me)

the reaction, formed water was removed from the reaction mixture by a Dean−Stark apparatus. After 24 h, the reaction mixture was evaporated to dryness, and the resulting white solids were washed with ether to remove excess formic acid and with hexane to get rid of trace amounts of aniline. Then, the resulting solid was dried in vacuo at room temperature. The crude product was used for the next step without further purification. **6b**: mp 175 °C. ^{1}H NMR (395 MHz, $CDCl_3$), two isomers: δ 7.85 (d, J = 0.97 Hz) and 7.78 (d, J = 11.6 Hz) (1H, CHO), 7.36−7.47 (m, 13H, Ar), 6.76 (d, J = 11. 6 Hz) and 6.62 (bs) (1H, NH). ^{13}C NMR (99 MHz, $CDCl_3$): δ 164.47, 159.91, 140.75, 139.52, 138.47, 136.90, 130.67, 130.60, 130.01, 129.35, 129.01, 128.81, 128.26, 127.92, 127.80, 127.44, 126.54. IR: ν_{N-H} = 3233, $\nu_{C=O}$ = 1653. HRMS: calcd 273.1154, found 273.1154. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.29; H, 5.57; N, 5.06. The formanilide prepared by the above procedure (1.0 mmol) and diisopropylamine (350 mg, 3.5 mmol) were dissolved in CH_2Cl_2 (3.0 mL). The mixture was cooled to 0 °C, and $POCl_3$ (1.1 mmol) was added dropwise. After stirring at 0 °C for 2 h, the solution was treated with Na_2CO_3 (0.5 g) dissolved in H_2O (3.0 mL) at a rate so that the temperature was maintained at 25−30 °C. The mixture was stirred for 12 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 three times. The organic layer and the extracts combined were washed with Et_2O, dried over $MgSO_4$, and evaporated to dryness. In all of the reactions, the desired product was obtained as a single product (no byproduct was observed in NMR and IR spectroscopy), which can be used in the next step without further purification. The analytically pure product can be obtained by recrystallization from ether and hexane. **6c**: mp 175 °C. ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.37−7.56 (m, 13H, Ar). ^{13}C NMR (99 MHz, $CDCl_3$): δ 169.23, 140.01, 137.56, 129.48, 129.34, 129.11, 129.02, 128.50, 128.32. IR: $\nu_{C\equiv N}$ 2121. HRMS: calcd 256.1126, found 256.1125.

In a similar fashion, 2-substituted phenylisocyanides and 2,6-disubstituted phenylisocyanides were synthesized via the corresponding formanilides. Spectral data of the formanilides and isocyanides synthesized are described in the Supporting Information.

Synthesis of Ni(II) Isocyanide Complexes. A typical example is given below. A solution of the isocyanide **6c** (216 mg, 0.84 mmol) dissolved in CH_2Cl_2 (3.0 mL) synthesized by the above procedure was added to a suspension of (1,2-dimethoxyethane)$NiBr_2$ (123 mg, 0.4 mmol) in CH_2Cl_2 (7.0 mL), and the mixture was stirred for 24 h at room temperature. The resulting suspension was filtered through a short pad of Celite. The resulting dark brown filtrate was concentrated in vacuo, and the residue was washed with Et_2O. Recrystallization of this crude product from dichloromethane−hexane gave the desired complex **6d** in 83% yield (232 mg). With similar procedures, nickel complexes **1d**−**5d** and **7d**−**11d** were synthesized in 54−98% yield.

Dibromobis[2-(isocyano-κC)-1,3-diphenylbenzene]nickel (6d): mp 203 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.49 (bs, 26H, Ar). ^{13}C NMR (99 MHz, $CDCl_3$): δ 140.42, 136.02, 130.39, 129.49, 129.28, 128.91, 128.65, 122.31. IR: $\nu_{C\equiv N}$ 2190. Anal. Calcd for $C_{54}H_{58}Br_2N_2Ni$: C, 62.59; H, 3.59; N, 3.84. Found: C, 62.52; H, 3.52; N, 3.81.

Dibromobis[2-(isocyano-κC)-1,3-dimethylbenzene]nickel (1d): mp 180 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, 2H, J = 7.59 Hz, *para*-H-Ar), 7.10 (d, 4H, J = 7.59 Hz, *meta*-H-Ar), 2.44 (s, 12H, *ortho*-Me-Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.44, 130.24, 128.00, and 125.59(Ar), 18.55 (Me-Ar). IR: $\nu_{C\equiv N}$ 2198. Anal. Calcd for $C_{18}H_{18}Br_2N_2Ni$: C, 44.96; H, 3.77; N, 5.83. Found: C, 44.95; H, 3.79; N, 5.81.

Dibromobis[2-(isocyano-κC)-1,3-diethylbenzene]nickel (2d): mp 193 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, 2H, J = 7.99 Hz, *para*-H-Ar), 7.12 (d, 4H, J = 7.99 Hz, *meta*-H-Ar), 2.79 (q, 8H, J = 7.59 Hz, C*H*$_2$-Et), 1.27 (t, 12H, J = 7.59 Hz, C*H*$_3$-Et). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.36, 130.69, 126.51, and 124.19 (Ar), 25.40 (C*H*$_2$-CH$_3$) 14.22 (CH$_2$-C*H*$_3$). IR: $\nu_{C\equiv N}$ 2194. Anal. Calcd for $C_{22}H_{26}Br_2N_2Ni$: C, 49.21; H, 4.88; N, 5.22. Found: C, 49.25; H, 4.89; N, 5.21.

Dibromobis[2-(isocyano-κC)-1,3-diisopropylbenzene]nickel (3d): mp 224 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, 2H, J = 7.99 Hz, *para*-Ar), 7.18 (d, 4H, J = 7.99 Hz, *meta*-Ar), 3.35 (sept, 4H, J = 6.79 Hz, C*H* of *i*Pr), 1.28 (d, 24H, J = 6.79 Hz, *Me* of *i*Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.61, 130.88, 134.55, 123.53 (Ar), 29.43 (*C*HMe$_2$), 22.73 (CH*Me*$_2$). IR: $\nu_{C\equiv N}$ 2192. Anal. Calcd for $C_{26}H_{34}Br_2N_2Ni$: C, 52.66; H, 5.78; N, 4.72. Found: C, 52.66; H, 5.75; N, 4.71.

Dibromobis[2-(isocyano-κC)-1-isopropylbenzene]nickel (4d): mp 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.41 (m, 6H, Ar), 7.26−7.22 (m, 2H, Ar), 3.35 (sept, 2H, J = 6.79 Hz, C*H* of *i*Pr), 1.29 (d, 12H, J = 6.79 Hz, *Me* of *i*Pr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.32, 131.20, 127.07, 126.70, 126.47, and 126.61 (Ar), 29.28 (*C*HMe$_2$), 22.65 (CH*Me*$_2$). IR: $\nu_{C\equiv N}$ 2190. Anal. Calcd for $C_{20}H_{22}Br_2 N_2Ni$: C, 47.20; H, 4.36; N, 5.50. Found: C, 47.63; H, 4.39; N, 5.56.

Dibromobis[2-(isocyano-κC)-1,1′-biphenyl]nickel (5d): mp 202 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.50−7.40 (m, 18H, Ar). ^{13}C NMR (99 MHz, $CDCl_3$): δ 139.20, 135.51, 131.05, 130.63, 129.04, 128.97, 128.78, 128.13, 128.01, 124.07. IR: $\nu_{C\equiv N}$2202. Anal. Calcd for $C_{54}H_{58}Br_2N_2Ni$: C, 54.13; H, 3.14; N, 4.86. Found: C, 54.08; H, 3.15; N, 4.81.

Dibromobis[2-(isocyano-κC)-1,3-diphenylbenzene]nickel (6d): mp 203 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.48−7.41 (m, 26H, Ar). ^{13}C NMR (99 MHz, $CDCl_3$): δ 140.42, 136.02, 130.39, 129.49, 129.28, 128.91, 128.65, 122.31. IR: $\nu_{C\equiv N}$ 2190. Anal. Calcd for $C_{54}H_{58}Br_2N_2Ni$: C, 62.59; H, 3.59; N, 3.84. Found: C, 62.52; H, 3.52; N, 3.84.

Dibromobis[2-(isocyano-κC)-4′-tert-buthylbiphenyl]nickel (7d): mp 241 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ7.34−7.52 (m, Ar, 16H), 1.38 (s, *t*-Bu, 18H). ^{13}C NMR (99 MHz, $CDCl_3$): δ151.76, 139.16, 132.63, 130.94, 130.54, 128.71, 128.14, 127.85, 125.98, 125.19, 34.71, 31.30. IR: $\nu_{C\equiv N}$ 2197. Anal. Calcd for $C_{34}H_{34}Br_2N_2Ni$: C, 59.26; H, 4.97; N, 4.07. Found: C, 58.87; H, 5.00; N, 4.01.

Dibromobis[2-(isocyano-κC)-1,3-bis(4-*tert*-butylphenyl)benzene]nickel (8d): mp 255 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.35−7.51 (m, 22H, Ar), 1.39 (s, *t*-Bu, 36H). ^{13}C NMR (99 MHz, $CDCl_3$): δ 151.43, 145.25, 140.44, 133.25, 130.16, 129.37, 128.95, 125.91, 34.68, 31.35. IR: $\nu_{C\equiv N}$ 2172. Anal. Calcd for $C_{54}H_{58}Br_2N_2Ni$: C, 68.02; H, 6.13. N, 2.94. Found: C, 67.41; H, 6.13; N, 2.93.

Dibromobis[2-(isocyano-*κ*C)-2′-methyl-1,1′-biphenyl]nickel (9d): mp 180 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.19−7.23 (m, 6H, Ar), 7.00−6.96 (m, 2H, Ar), 6.82−6.77 (m, 6H, Ar), 6.66−6.61 (m, 2H, Ar), 2.13 (s, 6H, CH_3). ^{13}C NMR (99 MHz, $CDCl_3$): δ 139.77, 135.87, 135.41, 131.00, 130.64, 130.62, 129.43, 128.87, 128.18, 127.08, 126.06 and 125.31 (Ar), 20.60 (Me). IR: $\nu_{C\equiv N}$ 2201. Anal. Calcd for $C_{28}H_{22}Br_2N_2Ni$: C, 55.59; H, 3.67; N, 4.63. Found: C, 55.57; H, 3.68; N, 4.62.

Dibromobis[2-(isocyano-*κ*C)-2′,6′-dimethyl-1,1′-biphenyl]nickel (10d): mp 206 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.52−7.38 (m, 3H, Ar), 7.25−7.13 (m, 4H, Ar), 1.97 (s, 6H, CH_3). ^{13}C NMR (99 MHz, $CDCl_3$): δ 139.18, 135.79, 135.02, 130.92, 130.83, 128.55, 128.14, 127.81, 127.05, 125.42 (Ar), 20.27. IR: $\nu_{C\equiv N}$ 2198. Anal. Calcd for $C_{30}H_{26}Br_2N_2Ni$: C, 56.92; H, 4.14; N, 4.43. Found: C, 56.65; H, 4.20; N, 4.46.

Dibromobis[2-(isocyano-*κ*C)-1,3-bis(2,6-dimethylphenyl)benzene]nickel (11d): mp 262 °C (dec). ^{1}H NMR (395 MHz, $CDCl_3$): δ 7.52 (m, 2H, Ar), 7.25 (m, 16H, Ar), 1.98 (s, 24H, CH_3). ^{13}C NMR (99 MHz, $CDCl_3$): δ 139.64, 135.68, 135.47, 130.50, 129.35, 128.39, 127.87 and 127.41 (Ar), 20.34 (Me). IR: $\nu_{C\equiv N}$ 2195. Anal. Calcd for $C_{46}H_{42}Br_2N_2Ni$: C, 65.67; H, 5.03; N, 3.33. Found: C, 65.69; H, 5.03; N, 3.34.

Ethylene Polymerization. In a typical example, toluene (50 mL) and MAO (1.0 mmol, 0.42 mL in 7.5 wt % toluene solution) were measured into a 100 mL Schlenk tube, and the mixture was stirred for 15 min. The nickel complex (10 μmol) prepared by the method described above was added, and the solution was stirred for 1 h. The resulting catalyst/cocatalyst solution was loaded into a 100 mL stainless steel autoclave, and ethylene was introduced (0.8 MPa) at room temperature. A continuous supply of ethylene kept the gas pressure at 0.8 MPa during the polymerization. The polymerization was terminated by the release of ethylene and subsequent addition of methanol (10 mL). The product was added to a mixture of methanol (200 mL) and concentrated HCl (12 mL) to remove aluminum compounds. Polyethylene precipitated was isolated by filtration, washed with methanol, and dried in vacuo for 12 h.

X-ray Structure Determination and Details of Refinement. X-ray-quality crystals of **5d** and **10d** were grown from a mixture of CH_2Cl_2 and hexane and mounted in glass capillaries. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation; $\lambda = 0.71075$ Å. The data were collected at 123(1) K using a ω scan technique to a maximum 2θ value of 55°. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods[20] for **5d** and by direct methods[21] for **10d**, and expanded using Fourier techniques.[22] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 2546 observed reflections and 152 variable parameters for **5d** and on 6365 observed reflections and 343 variable parameters for **10d**. Neutral atom scattering factors were taken from Cromer and Waber.[23] All calculations were performed using the CrystalStructure[24,25] crystallographic software package. Details of final refinement are summarized in Table 2, and the numbering schemes employed are shown in Figures 1 and 2, which were drawn with ORTEP with 50% probability ellipsoids.

Table 2. X-ray Crystallographic Data for 5d and 10d

	5d	**10d**
empirical formula	$C_{26}H_{18}N_2Br_2Ni$	$C_{30}H_{26}Br_2N_2Ni$
fw	576.95	633.06
temperature, K	123(1)	123(1)
wavelength, Å	0.71075	0.71075
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P21/n$
a, Å	8.588(5)	12.08(2) Å
b, Å	8.740(5)	14.76(3)
c, Å	9.090(4)	16.46(3)
α, deg	67.70(4)	90
β, deg	73.47(4)	108.1(1)
γ, deg	64.02(4)	90
V, Å^3	561.7(5)	2790(8)
Z	1	4
density(calcd), Mg/m^3	1.705	1.507
abs coeff, cm^{-1}	44.47	35.88
F(000)	286.00	1272
cryst size, mm	0.40 × 0.25 × 0.08	0.40 × 0.40 × 0.10
θ range for data collection, deg	3.0−30.0	3.0−30.0
index ranges	$-11 \leq h \leq 11$; $-11 \leq k \leq 11$; $-11 \leq l \leq 11$	$-15 \leq h \leq 15$; $-19 \leq k \leq 18$; $-19 \leq l \leq 21$
no. of reflns collected	2552	6632
no. of indep reflns	2552 [R(int) = 0.053]	6632 [R(int) = 0.050]
no. of reflns obsd (>2σ)	2546	6365
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	2546/0/152	6365/0/343
goodness-of-fit on F^2	1.009	1.008
final R indices [I>2σ(I)]	R1 = 0.030	R_1 = 0.031
R indices (all data)	wR2 = 0.080	wR_2 = 0.059
largest diff peak and hole, e Å^{-3}	0.65 and −0.98	0.80 and −0.76

Acknowledgment. We appreciate the financial support provided by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, and Technology, Japan. A part of this study was supported by CREST (JST, Japan Science and Technology Coorporation).

Supporting Information Available: Characterization of **6a**−**6c**, **7a**−**7c**, **8a**−**8c**, **9a**−**9c**, **10a**−**10c**, and **11a**−**11c**, crystallographic data of **5d** and **10d**, and a ^{13}C NMR chart of polyethylene. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0498394

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