Synthesis of Salicylaldiminato-Functionalized N-Heterocyclic Carbene Complex of Nickel(II) and Its Catalytic Activity for Styrene Polymerization

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Received July 21, 2005

A novel potentially tridentate N-heterocyclic carbene (NHC) precursor, anionic salicylaldimine-functionalized imidazolium bromide, [3,5-^{t}Bu$_2$-2-(HO)C$_6$H$_2$CH=NCH$_2$CH$_2$(CH-{NCHCHN^{i}Pr})Br] (HL·HBr, **2**), was designed. The reaction of in situ-generated monoanionic tridentate salicylaldiminato-functionalized NHC LNa with Ni(PPh$_3$)$_2$Br$_2$ affords a novel mono-ligand Ni(II) bromide, [3,5-^{t}Bu$_2$-2-(O)C$_6$H$_2$CH=NCH$_2$CH$_2$(C{NCHCHN^{i}Pr})]NiBr (LNiBr, **3**), in good yield. Complex **3** can also be synthesized by the direct reaction of nickelocene (Cp)$_2$Ni or bis-indenyl Ni(II) complex (Ind)$_2$Ni with **2** in high yield via the cyclopentadiene or indene elimination reaction, respectively. Complex **3** has been fully characterized including X-ray structural determination. Preliminary study indicated that **3** shows good catalytic activity for the polymerization of styrene in the presence of NaBPh$_4$ at 80 °C.

Introduction

Free N-heterocyclic carbenes (NHCs), as appealing alternatives to traditional phosphine ligands, are being used increasingly in late transition metal-based organometallic catalysis such as C−C coupling,[1b,g] olefin metathesis,[1c] hydrogenation,[1d] hydroformylation,[1f] and many others.[1a,e] However, the application of this kind of NHC complexes in polymerization reactions has been quite limited.[2] This is due to its contribution to the decomposition of the active species; that is, the Pd(II)- or Ni(II)-based heterocyclic carbene complexes containing an alkyl group decomposed via the reductive elimination of the hydrocarbyl and carbene moiety, as free NHC tends to 1,2-alkyl migration.[2e] The problem might be solved by use of the pendant functionalized bidentate or polydentate NHC ligand developed recently, since these ligands could provide an opportunity to control the stability and reactivity of active centers more efficiently in a variety of homogeneous catalysis including the polymerization of olefins.[3−5] Thus, the Ni(II) complexes with pyridine-functionalized NHC ligands can act as the catalyst precursors for the copolymerization of CO and norbornene[5a] and the homopolymerization of norbornene or ethylene as well.[5b]

The salicylaldiminato framework, as a common motif in organometallic chemistry, has been extensively applied in transition metal-based, particularly Ni(II)-based, olefin catalyst systems,[6] such as the notable Grubbs' neutral salicylaldiminato phenyl Ni(II) complexes L′Ni(Ph)(PPh$_3$) (L′ = salicylaldiminato) for the polymerization of ethylene[7] and the bis-salicylaldiminato Ni(II) complexes L′$_2$Ni for the polymerization of norbornene.[8] However, mono-salicylaldiminato Ni(II) halide, which should be an important catalyst precursor, has not been synthesized yet, as this kind of complex tends to form a more stable one, i.e., bisalicylaldiminato Ni(II) complex, via a disproportionation reaction.[9]

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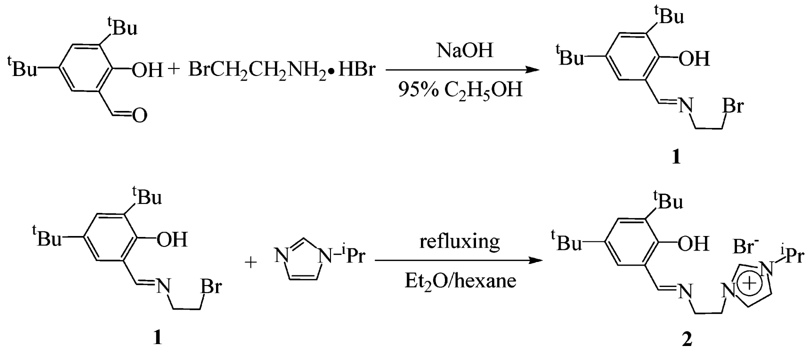
10.1021/om050612y CCC: $30.25

Scheme 1. Synthesis of 2



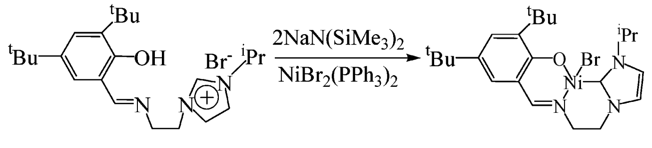
Taking advantage of an anionic functionalized NHC, where the anionic group acts as an anchor,[10] we designed a salicylaldiminato-functionalized NHC precursor, [3,5-$^tBu_2$-2-(HO)$C_6H_2CH{=}NCH_2CH_2$(CH-{NCHCHN^{i}Pr})Br] (HL·HBr, **2**), and successfully synthesized the corresponding salicylaldiminato-functionalized NHC Ni(II) bromide [3,5-$^tBu_2$-2-(O)$C_6H_2CH{=}NCH_2CH_2$(C{NCHCHN^{i}Pr})]NiBr (LNiBr, **3**) in good yield by the reaction of in situ-generated LNa with Ni-$(PPh_3)_2Br_2$. Complex **3** can also be synthesized in high yield by a one-pot synthetic route, i.e., the direct reaction of nickelocene $(Cp)_2Ni$ or bis-indenyl Ni(II) complex $(Ind)_2Ni$ with **2**. Preliminary study indicated that **3** exhibits good catalytic activity for the polymerization of styrene in the presence of $NaBPh_4$. Here we report the results.

Results and Discussion

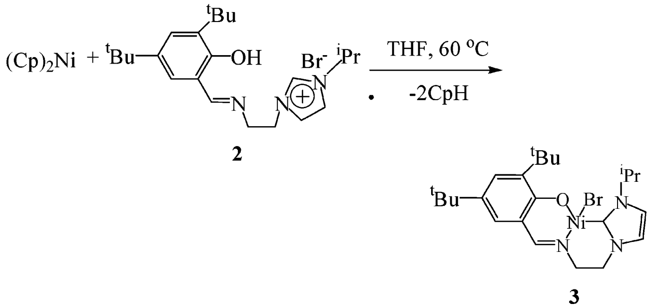
The synthetic route for a novel salicylaldimine-functionalized imidazolium bromide **2** was shown in Scheme 1. The reaction of salicylaldehyde [3,5-$^tBu_2$-2-(HO)C_6H_2-CHO] with 2-bromoethylamine hydrobromide gave the compound [3,5-$^tBu_2$-2-(HO)$C_6H_2CH{=}NCH_2CH_2Br$] (**1**) in ca. 80% yield. Treatment of **1** further with 1-isopropylimidazole afforded an almost quantitative yield of **2**. Compound **2** has been fully characterized. The ^1H NMR spectrum of **2** exhibits the characteristic signals of imidazolium $C_2{-}H$ at 10.80 ppm and of *tert*-butyl protons in the region of 1.29−1.42 ppm.

Indeed, the ligand designed can successfully stabilize the mono-ligand complex of Ni(II). Thus, the salicylaldimine-functionalized imidazolium bromide **2** reacted with 1 equiv of $Ni(PPh_3)_2Br_2$ in the presence of 2 equiv of $NaN(SiMe_3)_2$ at room temperature; after workup, the desired complex **3** was obtained in ca. 75% yield as a yellow-brown powder that was analytically pure (Scheme 2). Initial characterization of **3** was supported by elemental analysis and NMR spectroscopy. In the ^{13}C NMR spectrum, a singlet NHC carbon ($C_{carbene}$) signal appears at 165.9 ppm, which is very close to the values observed in nickel-based NHC complexes.[11] The further structural characterization of **3** was conducted by X-ray crystal structural determination.

Scheme 2. Synthetic Route to 3 via Salt Exchange Reaction



Scheme 3. Synthetic Route to 3 via Cyclopentadiene Elimination Reaction



One-pot synthesis via the direct reaction of nickelocene $(Cp)_2Ni$ with imidazolium salt was reported to be a simple synthesis of the corresponding Ni(II) complex with a free NHC ligand.[12] We also found that the NHCs complexes of indenylnickel(II) could be easily synthesized by the analogous reaction of bis-indenyl Ni(II) complex $(Ind)_2Ni$ with the corresponding imidazolium salt.[11] The notable advantage of the one-pot synthetic approach is that the free NHC ligand does not need to be isolated and purified, especially the unstable NHC, and that without the formation of salt the target complex is easy to purify. Accordingly, it is of interest to extend the application of the method and/or to understand its generality. Thus, the one-pot synthesis for the preparation of **3**, a Ni(II) complex containing an anionic functionalized NHC ligand, was also tested. The reaction of **2** with $(Cp)_2Ni$ in THF at 60 °C went smoothly, and the color change of the reaction solution from dark green to red occurred concomitantly. After workup, **3** could be easily isolated as yellow-brown crystals in 90% yield (Scheme 3). A similar reaction of **2** with $(Ind)_2Ni$ in THF at 45 °C yields **3** in 92% yield (Scheme 4). Obviously, the yields of **3** for both the cyclopentadiene and indene elimination reactions are

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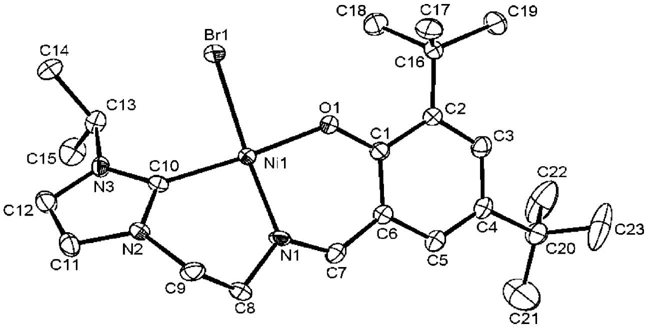
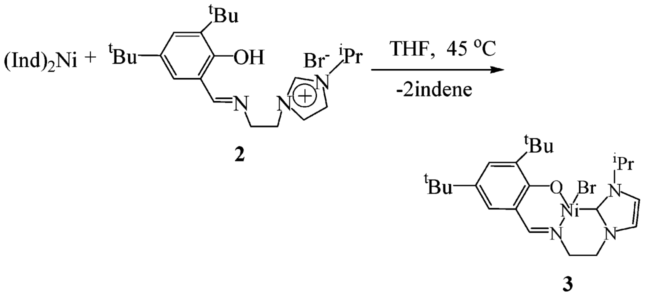


Figure 1. Crystal structure of **3** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Scheme 4. Synthetic Route to 3 via Indene Elimination Reaction



much higher than that obtained by the salt exchange reaction. These results indicated that the cyclopentadiene and indene elimination reactions both could be considered to be the popular synthetic approaches for the synthesis of Ni(II) NHC halides.

Complex **3** is sensitive to moisture, but much less sensitive to oxygen; it can even remain unchanged for several days in open dry air. Complex **3** is soluble in protic solvents $CHCl_3$, THF, DME, and toluene, sparingly soluble in diethyl ether, but insoluble in hexane. It is thermally stable and will melt at 160 °C without decomposition. Crystals of **3** suitable for X-ray structure determination were obtained by recrystallization from toluene/Et_2O at 0 °C. The molecular structure of **3** is shown in Figure 1. The crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively.

As seen from Figure 1, the nickel atom is bonded to Br, O, N, and the carbene carbon ($C_{carbene}$) to adopt a distorted square-planar geometry with angles in the range 86.4(2)–92.7(2)°. The bond lengths of Ni–Br, Ni–N, and Ni–O are equal to 2.353(1), 1.900(7), and 1.850(5) Å, respectively. The Ni–N and Ni–O bond distances are almost the same as the values in known salicylaldiminato phenyl Ni(II) complexes.[8] The Ni–Br bond distance is very close to that for a typical Ni(II)–Br bond.[13] The bond distance of Ni–$C_{carbene}$ in **3** is 1.882(7) Å, which falls within the range of previously reported values in Ni(II)-based NHC complexes.[11] The success in the synthesis of Ni(II) halide supported by a salicylaldiminato backbone indicated the potential of a tridentate anionic functionalized NHC ligand in the application of organometallic chemistry.

The catalytic activity of **3** for the polymerization of styrene was examined.

Table 1. X-ray Crystallographic Data for 3

empirical formula	$C_{23}H_{34}BrN_3NiO\cdot 0.5(C_7H_8)\cdot C_4H_{10}O$
fw	627.34
temperature (K)	193(2)
λ(Mo Kα) (Å)	0.71070
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	8.527(2)
b (Å)	11.504(2)
c (Å)	18.451(4)
α (deg)	80.97(2)
β (deg)	79.34(2)
γ (deg)	64.36(1)
V (Å^3)	1597.5(6)
Z	2
D_{calcd} (g/cm^3)	1.304
absorp coff (mm^{-1})	1.891
F(000)	662.00
cryst size (mm)	0.05 × 0.38 × 0.19
$2\theta_{max}$(deg)	54.9
no. of reflns collected	36 298
no. of indep reflns	7196 (R_{int} = 0.068)
goodness-of-fit on F^2	1.003
final R indices [$I > 2\sigma(I)$]	0.074

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

Br(1)–Ni(1)	2.353(1)	Ni(1)–O(1)	1.850(5)
Ni(1)–N(1)	1.900(7)	Ni(1)–C(10)	1.882(7)
O(1)–Ni(1)–N(1)	92.7(2)	O(1)–Ni(1)–C(10)	172.7(2)
O(1)–Ni(1)–Br(1)	86.4(2)	N(1)–Ni(1)–C(10)	91.5(3)
N(1)–Ni(1)Br(1)	167.0(2)	C(10)–Ni(1)–Br(1)	90.9(2)

The preliminary results showed that complex **3** alone is inactive and inert toward the insertion of styrene. However, it exhibited good activity in the presence of $NaBPh_4$ for the polymerization of styrene. For example, when styrene polymerization was carried out under the conditions of styrene/$NaBPh_4$/**3** = 500:7:1 (molar ratio) in toluene at 80 °C, the polystyrene of ca. 100% yield with number-average molecular weight of 17 600 (PDI = 1.97) could be obtained after 12 h. The activity is higher than those of the Ni(II) halides supported by PPh_3 or IPr [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] and the indenyl group as well.[14a] Furthermore, it was noteworthy that the later systems yielded polymers with very low molecular weights, indicating that the active species are unstable and tend toward deactivation,[14b] while the system containing **3** yielded polymers with much higher number-average molecular weights. The results demonstrated that the introduction of a salicylaldiminato-functionalized NHC ligand could improve the stability of the active species and prevent their deactivation.[2e] The details of the polymerization mechanism and its polymerization behavior together with other cocatalysts are being studied in our laboratory.

Conclusions

A novel potentially tridentate salicylaldimine-functionalized imidazolium bromide, **2**, was designed and its corresponding mono-ligand Ni(II) bromide **3** has been synthesized both by the reaction of in situ-generated monoanionic tridentate salicylaldiminato-functionalized N-heterocyclic carbene LNa with $Ni(PPh_3)_2Br_2$ and by the direct reaction of $(Cp)_2Ni$ or $(Ind)_2Ni$ with **2** for the

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first time. Complex **3** shows good catalytic activity for the polymerization of styrene in the presence of $NaBPh_4$. Further investigation on the applications of the functionalized NHC ligands in other metals and the catalytic behavior of **3** for the polymerization of other olefins is in progress.

Experimental Section

General Considerations. All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. $Ni(PPh_3)_2Br_2$,[15] $Ni(IPr)_2Cl_2$,[2i] and $(Ind)_2Ni$[16] were prepared by published methods; all other chemicals were obtained commercially and used as received unless stated otherwise. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. Molecular weight and molecular weight distribution were determined against a polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-3, HR-4). NMR spectra were measured on a Unity Inova-400 spectrometer at 25 °C.

Structure Determination. A suitable single crystal of **3** was sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(2) K. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively. Crystal data and collection and main refinement parameters are given in Table 1. Selected bond lengths (Å) and angles (deg) for **3** are given in Table 2.

Synthesis of [3,5-^{t}Bu$_2$-2-(HO)C$_6$H$_2$CH=NCH$_2$CH$_2$Br] (1). Following a procedure similar to the reported method,[17] to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (6.10 g, 50.0 mmol) in 20 mL of 95% alcohol was added 2-bromoethylamine hydrobromide (10.80 g, 52.7 mmol) in 20 mL of H_2O. When the solution was heated to 50 °C, NaOH (2.20 g, 55.0 mmol) in 2 mL of H_2O was added with stirring. Recrystallization from 95% alcohol afforded the target product **1** as yellow crystals in ca. 80% yield (13.50 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 13.36 (1H, s, O*H*), 8.39 (1H, s, C*H*=N), 7.41 (1H, s, Ph-*H*), 7.12 (1H, s, Ph-*H*), 3.99 (2H, m, NC*H*$_2$), 3.66 (2H, m, C*H*$_2$Br), 1.38 (9H, s, CH(C*H*$_3$)$_3$), 1.36(9H, s, CH(C*H*$_3$)$_3$). Anal. Calcd for $C_{17}H_{26}BrNO$: C, 60.00; H, 7.70; N, 4.12. Found: C, 60.08; H, 7.73; N, 4.14.

Synthesis of HL·HBr (2). To a solution of **1** (10.20 g, 30.0 mmol) in 20 mL of hexane was added 1-isopropylimidazole (3.30 g, 30.0 mmol) in 20 mL of Et_2O. After refluxing for 4 days, the suspension solution was cooled to room temperature and filtered. The product **2** was obtained as a pale yellow powder in ca. 95% yield (12.84 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 13.02 (1H, s, O*H*), 10.80 (1H, s, NC*H*N), 8.45 (1H, s, C*H*=N), 7.39−7.42 (2H, m, Ph-*H*), 7.22 (1H, s, NC*H*), 7.09 (1H, d, NC*H*), 4.86 (2H, m, NC*H*$_2$), 4.78 (1H, m, C*H*(CH$_3$)$_2$), 4.23 (2H, m, NC*H*$_2$), 1.62 (6H, m, CH(C*H*$_3$)$_2$), 1.42 (9H, s, CH(C*H*$_3$)$_3$), 1.29 (9H, s, CH(C*H*$_3$)$_3$). Anal. Calcd for $C_{23}H_{36}BrN_3O$: C, 61.32; H, 8.06; N, 9.32. Found: C, 61.26; H, 8.08; N, 9.35.

Synthesis of LNiBr (3). A Schlenk flask was charged with **2** (0.62 g, 1.38 mmol), THF (20 mL), and a stir bar. To this suspension solution was added dropwise the solution of $NaN(SiMe_3)_2$ (0.84 M, 3.30 mL) in THF at −78 °C. The reaction was stirred for 30 min and gradually warmed to room temperature for an additional 30 min. Then a solution of $Ni(PPh_3)_2Br_2$ (1.03 g, 1.38 mmol) in 20 mL of THF was added slowly to the reaction system under stirring at −78 °C. The color of the solution immediately changed from green to red. The resulting solution was allowed to warm to room temperature and then stirred for an additional 12 h, filtered, and evaporated to dryness. The residue was extracted with toluene. The toluene solution was combined and concentrated, and a drop of ether was added. The obtained crystals by cooling the concentrated solution at −30 °C were pumped off to give the product as a yellow-brown powder (0.52 g, 75%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 9.22 (1H, s, C*H*=N), 7.40 (1H, s, Ph-*H*), 7.31 (1H, s, Ph-*H*), 6.91 (1H, s, NC*H*), 6.86 (1H, s, NC*H*), 5.77 (1H, m, C*H*(CH$_3$)$_2$), 4.53 (2H, m, NC*H*$_2$), 3.72 (2H, m, NC*H*$_2$), 1.53 (6H, s, CH(C*H*$_3$)$_2$), 1.16−1.44 ppm (18H, m, CH(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 165.91 (N*C*N, s). Anal. Calcd for $C_{23}H_{34}BrN_3ONi$: C, 55.38; H, 7.24; N, 8.46. Found: C, 55.35; H, 7.21; N, 8.49.

Synthesis of LNiBr (3) via Cyclopendiene Elimination. A Schlenk flask was charged with **2** (0.45 g, 1.00 mmol) and a stir bar. To this solution was added $(Cp)_2Ni$ (0.19 g, 1.00 mmol) in 20 mL of THF at room temperature. The solution was stirred overnight at 60 °C, filtered, and evaporated to dryness. The residue was extracted with hot toluene and crystallized from concentrated toluene/Et_2O at −30 °C, yielding yellow-brown crystals (0.46 g, 90%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 9.22 (1H, s, C*H*=N), 7.40 (1H, s, Ph-*H*), 7.31 (1H, s, Ph-*H*), 6.91 (1H, s, NC*H*), 6.86 (1H, s, NC*H*), 5.77 (1H, m, C*H*(CH$_3$)$_2$), 4.53 (2H, m, NC*H*$_2$), 3.72 (2H, m, NC*H*$_2$), 1.53 (6H, s, CH(C*H*$_3$)$_2$), 1.16−1.44 ppm (18H, m, CH(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 165.91 (N*C*N, s). Anal. Calcd for $C_{23}H_{34}BrN_3ONi$: C, 55.38; H, 7.24; N, 8.46. Found: C, 55.40; H, 7.26; N, 8.35.

Synthesis of LNiBr (3) via Indene Elimination. A Schlenk flask was charged with **2** (0.45 g, 1.00 mmol) and a stir bar. To this solution was added $(Ind)_2Ni$ (0.29 g, 1.00 mmol) in 20 mL of THF at room temperature. The solution was stirred overnight at 45 °C, filtered, and evaporated to dryness. The residue was extracted with hot toluene and crystallized from concentrated toluene/Et_2O at −30 °C, yielding crystals (0.47 g, 92%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 9.22 (1H, s, C*H*=N), 7.40 (1H, s, Ph-*H*), 7.31 (1H, s, Ph-*H*), 6.91 (1H, s, NC*H*), 6.86 (1H, s, NC*H*), 5.77 (1H, m, C*H*(CH$_3$)$_2$), 4.53 (2H, m, NC*H*$_2$), 3.72 (2H, m, NC*H*$_2$), 1.53 (6H, s, CH(C*H*$_3$)$_2$), 1.16−1.44 ppm (18H, m, CH(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 165.91 (N*C*N, s). Anal. Calcd for $C_{23}H_{34}BrN_3ONi$: C, 55.38; H, 7.24; N, 8.46. Found: C, 55.34; H, 7.20; N, 8.42.

A Typical Procedure for the Polymerization of Styrene. A typical procedure for the polymerization of styrene is given as follows. Under dry argon, the solid initiator **3** (10.1 mg, 0.02 mmol), $NaBPh_4$ (47.9 mg, 0.14 mmol), toluene (0.2 mL), and styrene (1.2 mL, 0.01 mol) were added into a dry glass ampule in turn. Then, the sealed ampule was placed in a water bath held at 80 °C. After a definite reaction time, the polymerization was stopped by adding 1 mL of 5% HCl/ethanol. After evaporation of solvent and unreacted monomer, the resulted polymer was dissolved in THF, followed by precipitation in 95% ethanol. After filtration, the white polymer was dried in vacuo at room temperature overnight. The polymer yield was determined gravimetrically.

Acknowledgment. We are grateful to the Ph.D. Foundation of the Department of Education, the Department of Education of China and Key Laboratory of Organic Chemistry, Jiangsu Province, for financial support.

Supporting Information Available: Crystallographic data, in CIF format, for the structure analysis of **3**, and a figure of the crystal structure of complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050612Y

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