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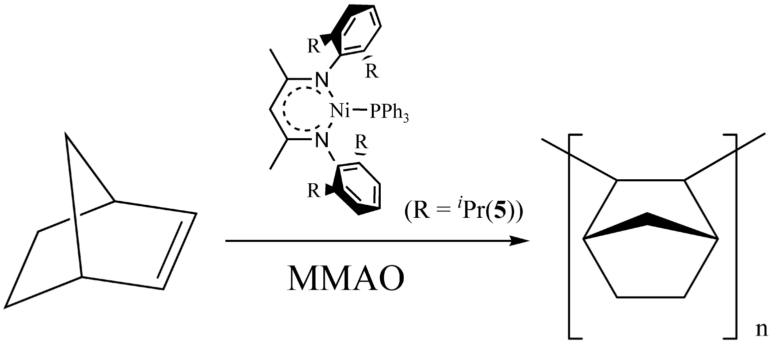

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Synthesis, Molecular Structures, and Norbornene Addition Polymerization Activity of the Neutral Nickel Catalysts Supported by β-Diketiminato [N, N], Ketiminato [N, O], and Schiff-Base [N, O] Ligands[⊥]

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A series of neutral nickel complexes [Ni(Ph)(PPh$_3$)(N, O)] with Schiff-base ligands (N, O) [N, O = 5-Me-3-*tert*-Bu-(Ar−N=CH)C$_6$H$_2$O (**1**, Ar = 2,6-Me$_2$C$_6$H$_3$; **2**, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$)], [Ni(Ph)(PPh$_3$)(N,O)], with β-ketiminato ligands (N, O) [N, O = CH$_3$COCHC=(CH$_3$)N−Ar (**3**, Ar = 2,6-Me$_2$C$_6$H$_3$; **4**, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$)] and [Ni(N, N)(PPh$_3$)], and with β-diketiminato ligands (N, N) [**5**, N, N = [2,6-*i*-Pr$_2$(C$_6$H$_3$)N=C(CH$_3$)]$_2$CH] have been synthesized and characterized. The molecular structures of complexes **1**, **4**, and **5** have been confirmed by X-ray single-crystal analyses. Although their ligands have similar structures, complex **4** possesses a structure similar to that of four-coordination nickel with complex **1**, while complex **5** reveals a rare three-coordination nickel geometry. These compounds show high catalytic activities of up to 3.16×10^7 g PNB mol^{-1} Ni h^{-1} for the addition polymerization of norbornene in the presence of modified methylaluminoxane (MMAO) as cocatalyst. Catalytic activities, polymer yield, molecular weights, and molecular weight distributions of polyborbornene have been investigated under various reaction conditions.

Introduction

Olefin polymerization based on late transition metal catalysts has been one of the most exciting developments in the area of catalysis, organometallic chemistry, and polymer science in recent years.[1] Ni-based catalysts are best known to oligomerize ethylene and dimerize propylene and higher α-olefins because nickel metal was usually thought to generally prefer β-hydride elimination followed by reductive elimination before 1995.[2] Now a large number of papers and patents published on this field show the intense exploration and commercialization of new polymerization technologies in both industrial and academic fields.[3]

Homo-polymer addition of polynorbornenes are of considerable interest because of their unique physical properties, including heat resistivity, good solubility in organic solvents, and excellent optical transparency. However, the addition polymerization is much less developed for norbornene than ROMP (ring-opening metathesis polymerization). Janiak et al.[4] gave a full literature and patent account on the work describing the addition polymerization to homo-polynorbornene. The olefin polymers of norbornene were obtained with early transition metals (titanium, zirconium, and chromium) and late transition metals (cobalt, nickel, and palladium). Deming and Novak introduced the first nickel complexes for the addition polymerization of norbornene in 1993[5] and recently several other catalyst systems were presented.[6]

During the past few years most of our effort has focused on neutral, single-component nickel ethylene-polymerization catalysts before we began our cycloolefin polymerization study. Several series of nickel catalysts supported by [**N**, **O**] monoanionic and bisanionic ligands, including salicylaldiminato phenyl nickel complexes[7] and binuclear 2,5-disubstituted amino-*p*-benzoquinone nickel(II) complexes,[8] were designed and synthesized on the basis of recent developments. These

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[⊥] Dedicated to Prof. Li-Xin Dai on the occasion of his 80th birthday.

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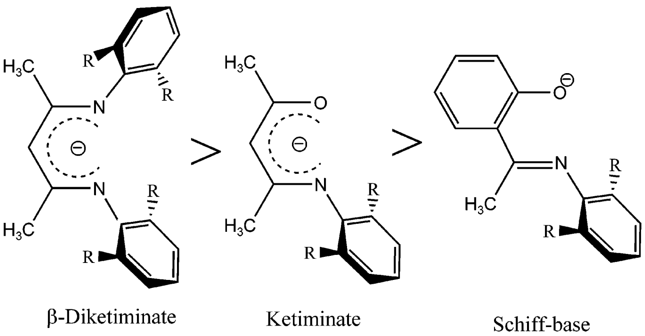
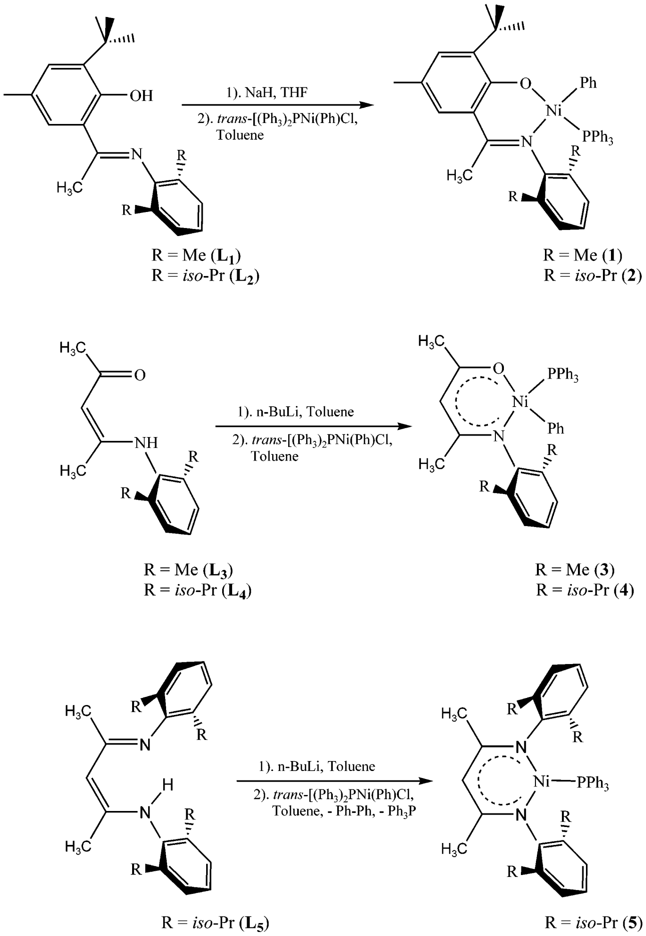
Scheme 1



Scheme 2. Synthesis of Nickel Complexes 1−5



neutral nickel complexes based on anion ligands are very reactive toward ethylene.

Our goal was to study nickel catalysts supported by monoanionic ligands whose steric and electronic properties can be easily modified. Since β-ketiminato and β-diketiminato ligands with bulky substitutes not only have stronger π-bonding tendencies to the same acceptor (Scheme 1) than Schiff-base ligands we have used but also are able to stabilize metal complexes, we have been examining some nickel compounds stabilized by these ligands. Polymerization experiments show that these nickel complexes are not reactive to ethylene or α-olefins but display very high *cyclo*-olefin polymerization activities. The focus of this article is the synthesis of a series of neutral nickel(II) complexes bearing Schiff-base ligands [**N**, **O**], β-ketiminato ligands [**N**, **O**], and β-diketiminato [**N**, **N**] ligands and the polymerization of norbornene upon activation with modified methylaluminoxane (MMAO) (Scheme 2). Three typical molecular structures of nickel catalysts were characterized by an X-ray crystallographic study.

Results and Discussion

The syntheses of the nickel complexes as catalytic precursors are shown in Scheme 2. The ligands of salicylaldimines, $\mathbf{L_1}$ and $\mathbf{L_2}$, were synthesized as yellow oils via the condensation reaction of salicylaldehydes and anilines in good yield as we previously reported.[7] The β-ketoamine ligands $\mathbf{L_3}$ and $\mathbf{L_4}$ were also efficiently obtained as white solids by the condensation reaction of β-diketone and corresponding anilines.[9] The β-ketoamine ligand $\mathbf{L_4}$ continuously reacted with substituted aniline hydrochloride to afford white β-iminoamine ligand $\mathbf{L_5}$ as reported.[10] The obtained organic ligands were treated with *n*-BuLi in toluene (NaH in THF for $\mathbf{L_1}$ and $\mathbf{L_2}$) and then reacted with *trans*-chloro(phenyl) bis(triphenylphosphine) nickel(II) to give their corresponding complexes **1**−**5**. The [**N**, **O**] and [**N**, **N**] ligands and corresponding complexes were characterized by ^{1}H NMR spectra and elemental analyses. Single crystals of nickel complexes **1**, **4**, and **5** suitable for X-ray structure determination were recrystallized from toluene at lower temperature. The collection data and refinement data of the analyses are summarized in Table 1. The ORTEP diagrams are shown in Figures 1, 2 and 3.

As depicted in Figure 1, complex **1** has a crystal structure similar to the analogue complexes we previously reported.[4] Complex **1** contains a chelating [**N**, **O**] ligand, a triphenylphosphine group (PPh_3), and a phenyl group. The bulky [2,6-$Me_2(C_6H_3)$-N] moiety occupies the position *trans* to PPh_3 with a nearly linear N(1)−Ni(1)−P(4) angle (177.67°), and the phenyl group bonded to Ni(1) also lies in a position *trans* to O(1) with an

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Table 1. Crystal Data and Summary of Data Collection and Refinement Detail for 1, 4, and 5

	1	**4**	**5**
formula	$C_{44}H_{44}NNiOP$	$C_{41}H_{44}NNiOP$	$C_{47}H_{56}N_2NiP$
cryst size (mm)	0.40 × 0.30 × 0.30	0.45 × 0.25 × 0.20	0.20 × 0.15 × 0.10
fw	692.48	656.45	738.62
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a, Å	8.7839(16)	9.252(2)	11.9854(15)
b, Å	9.7859(18)	9.611(2)	20.481(3)
c, Å	22.642(4)	21.215(5)	18.536(2)
α, deg	98.765(2)	84.184(3)	90
β, deg	97.512(3)	80.258(3)	108.381(2)
γ, deg	103.571(2	69.734(3)	90
V, $Å^3$	1841.5(6)	1742.2(7)	4318.0(10)
Z	2	2	4
D_{calcd}, Mg/m^3	1.249	1.251	1.136
radition (λ), Å	M*o* Kα (0.71073)	M*o* Kα (0.71073)	M*o* Kα (0.71073)
2θ range, deg	1.84 to 50.02	3.90 to 52.02	3.06 to 54.02
μ, mm^{-1}	0.604	0.635	0.518
$F(000)$	732	696	1580
no. of obsd reflns	6396	6667	9351
no. of params refnd	439	412	470
goodness of fit	0.946	0.882	0.801
$R_1[I > 2\sigma(I)]$	0.0416	0.0538	0.0566
wR_2(all data)	0.0955	0.0975	0.1006

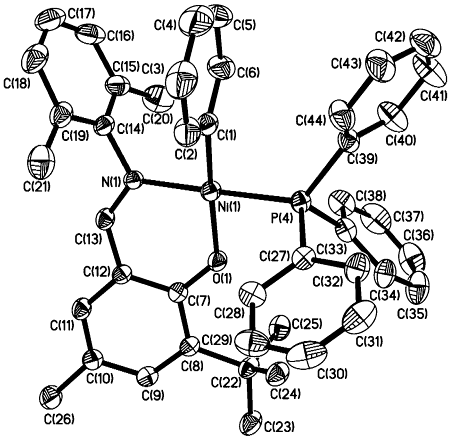

Figure 1. Molecular structure of complex **1**. Selected bond lengths [Å] and angles [deg]: Ni(1)−C(1) = 1.887(3), Ni(1)−O(1) = 1.9126(18), Ni(1)−N(1) = 1.920(2), Ni(1)−P(4) = 2.1731(8), C(1)−Ni(1)−O(1) = 171.43(10), C(1)−Ni(1)−N(1) = 92.62(10), O(1)−Ni(1)−N(1) = 92.25(8), C(1)−Ni(1)−P(4) 85.24(8), O(1)−Ni(1)−P(4) = 89.75(6).

O(1)−Ni(1)−C(1) angle of 171.43(10)°. The *cis* angles at nickel are in the range 85.24−92.62°. Thus the four-coordinate atoms [P(4), O(1), N(1), and C(1)] have an almost exactly square-planar geometry with the Ni(1) approximately 0.03 Å from the plane in complex **1**.

Because of the obvious structural similarity between β-ketoamine and salicylaldimine, particularly with respect to steric disposition, complex **4** has a molecular structure (Figure 2) similar to complex **1**, although seemingly there are many differences between the two kinds of ligands. The four-coordinate atoms [N(1), O(1), P(1), and C(1)] and the central Ni atom are also almost in the same planar. The *trans* N(1)−Ni(1)−P(1) [C(1)−Ni(1)−O(1)] angle and *cis* C(1)−Ni(1)−N(1) [C(1)−Ni(1)−P(1)] angle are 176.81(10) [170.69(15)]° and 95.82(14) [87.24(14)]°. Moreover, the bond lengths of C(7)−C(8) [1.356(5) Å] and C(8)−C(9) [1.400(5) Å] are shorter than that of a normal C−C single bond, which suggests the significant delocalization within the π-system of the β-enaminoketonato ligand.

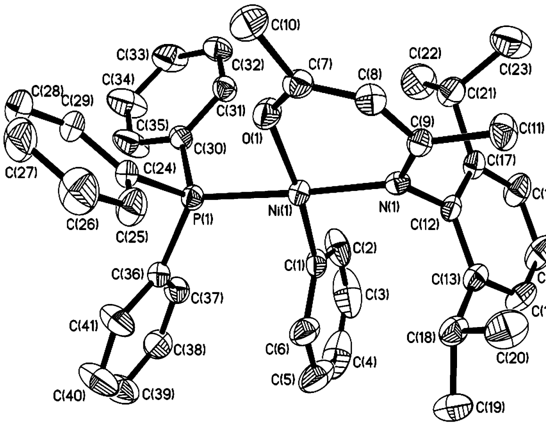

Figure 2. Molecular structure of complex **4**. Selected bond lengths [Å] and angles [deg]: Ni(1)−C(1) = 1.881(4), Ni(1)−O(1) = 1.881(3), Ni(1)−N(1) = 1.951(3), Ni(1)−P(1) = 2.1868(12), C(7)−C(8) = 1.356(5), C(8)−C(9) = 1.400(5), C(7)−C(10) = 1.506(5), C(9)−C(11) = 1.513(5), C(1)−Ni(1)−O(1) = 170.69(15), C(1)−Ni(1)−N(1) = 95.82(14), O(1)−Ni(1)−N(1) = 92.78(12), C(1)−Ni(1)−P(1) = 87.24(12), O(1)−Ni(1)−P(1) = 84.12(9), N(1)−Ni(1)−P(1) = 176.81(10).

Bond length distances in complexes **1** and **4** are not significant, although they have different steric congestions due to the replacement of *tert*-butyl and methyl of the phenyliminophenolato ligand $\mathbf{L_1}$ by the methyl and isopropyl groups of the β-enaminoketonato ligand $\mathbf{L_4}$. The Ni(1)−C(1) and Ni(1)−O(1) bond distances [1.887(3) and 1.9126(18) Å] in complex **1** are similar to those found in complex **4** [1.881(4) and 1.881(3) Å, respectively], and Ni(1)−N(1) and Ni(1)−P(4) bond lengths [1.920(2), 2.1731(8) Å] are slightly shorter than those in complex **4** [Ni(1)−N(1) 1.951(3) Å; Ni(1)−P(1) 2.1868(12) Å].

As given in the Experimental Section, after the ligands $\mathbf{L_3}$−$\mathbf{L_5}$ were treated with 1 equiv of BuLi in toluene the mixture was not isolated but continuously reacted with *trans*-[chloro(phenyl)bis(triphenylphosphine)nickel(II)]. However, the obtained complex **5** no longer contains a phenyl group like complex **4** described above under the same reaction conditions. The crystal-

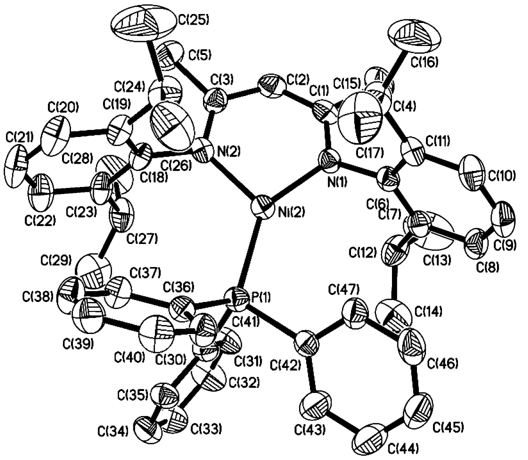

Figure 3. Molecular structure of complex **5**. Selected bond lengths [Å] and angles [deg]: Ni(2)−N(1) = 1.889(3), Ni(2)−N(2) = 1.911(3), Ni(2)−P(1) = 2.2044(12), C(1)−N(1) = 1.324(5), C(3)−N(2) = 1.331(5), C(1)−C(2) = 1.392(5), C(2)−C(3) = 1.397(5), C(1)−C(4) = 1.514(5), C(3)−C(5) = 1.520(5); N(1)−Ni(2)−N(2) = 96.77(14), N(1)−Ni(2)−P(1) = 142.53(11), N(2)−Ni(2)−P(1) = 120.60(10).

lographic analysis shows clearly that reduction occurred to give a nickel(I) complex with PPh_3 as the second ligand. The X-ray structure of **5** (Figure 3) contains only a chelating β-diketiminato ligand and a triphenylphosphine ligand and reveals rare trigonal-planar coordination at nickel. The Ni(2)−P(1) distance [2.2044(12) Å] is slightly longer than that in either complex **1** [2.1731(8) Å] or **4** [2.1868(12) Å]. Consistent with a lower coordination number at nickel(I) just reported, the β-diketiminate Ni−N distances (1.889(3)−1.911(3) Å) in **5** are slightly longer than those in the three-coordinate complexes $[2,4,6\text{-}Me_3NN]Ni^{I}(NO)]$ [1.883(2) and 1.885(2)Å] $\{2,4,6\text{-}Me_3NN = (2,4,6\text{-}Me_3(C_6H_2)N{=}C(CH_3))_2CH\}$[11] and $[LNi^{I}(THF)]$ [1.876(1) and 1.882(1) Å] $\{L = (2,6\text{-}i\text{-}Pr_2(C_6H_3)N{=}C(t\text{-}Bu))_2CH\}$,[12] while the N−Ni−N angle of complex **5** [96.77(14)°] lies in the range of 95.79(10)° of $[2,4,6\text{-}Me_3NN]Ni^{I}(NO)]$[11] and 100.46(6)° of $[[LNi^{I}(THF)]$.[12] However, compared with other three-coordinate nickel(II) complexes, the Ni−N distances of complex **5** are much longer than that in $[LNi^{II}Cl]$ [1.81(5) Å] $\{L = (2,6\text{-}i\text{-}Pr_2(C_6H_3)N{=}C(t\text{-}Bu))_2CH\}$[12] but shorter than those in $[L^{Me}Ni^{II}N(SiMe_3)_2]$ [1.911(2) and 1.953(2) Å] $\{L^{Me} = (2,6\text{-}i\text{-}Pr_2(C_6H_3)N{=}C(CH_3))_2CH\}$.[13] It has been reported that attempted alkylation gives reduction of the Ni(II) complex to Ni(I).[12] Another support for the nickel(I) oxidation state comes from the ESR spectra of the nickel complex **5** both in toluene and in the solid state. An investigation to understand the mechanism of reduction is still in progress.

Preliminary experiments indicated that complexes **1**−**5** are not able to catalyze ethylene polymerization with or without modified methylaluminuoxane (MMAO) as cocatalyst at 1 atm pressure of ethylene. However, after being activated with MMAO these catalytic precursors **1**−**5** could polymerize norbornene to afford addition-type polynorbornene (PNB) with high activities (10^7 g PNB mol^{-1} Ni h^{-1}), high molecular weight M_w (10^6 g mol^{-1}), narrow molecular weight distribution M_w/M_n (from 2.31 to 3.45), and high glass transition temperature T_g (≈400 °C), while under the same conditions, the complexes themselves and MMAO did not produce polymer (runs 7, 15, 22, and 23). These values of PNB productivity were below 59%, which is different from other reported results.[5,6]

Table 2. Addition Polymerization of Norbornene with Nickel Complexes 1−5 Activated by Modified Methylaluminoxane (MMAO)[a]

run	complex	T (°C)	yield (%)	activity[b]	M_w[c]	M_w/M_n[c]
1	**1**	30	59	3.35	13.56	2.48
2	**2**	30	49	2.75	11.42	2.39
3[d]	**2**	30	48	2.74	15.18	2.14
4	**2**	0	45	2.53	12.66	2.26
5	**2**	60	50	2.84	9.32	2.58
6[e]	**2**	30	59	1.66	12.12	2.33
7[f]	**2**	30	0	0		
8	**3**	30	54	3.02	14.23	2.40
9[g]	**4**	30	59	1.67	13.24	2.29
10	**4**	30	46	2.60	12.48	2.32
11[d]	**4**	30	37	2.11	14.99	2.53
12	**4**	0	38	2.13	17.50	2.31
13	**4**	60	50	2.80	10.95	2.90
14[e]	**4**	30	53	1.49	13.40	2.59
15[f]	**5**	30	0	0		
16	**5**	30	42	2.36	13.16	2.63
17[d]	**5**	30	35	1.97	13.46	3.45
18[g]	**5**	30	62	1.75	15.22	2.32
19[e]	**5**	30	55	1.54	12.73	2.61
20	**5**	0	52	2.93	18.91	2.39
21	**5**	60	56	3.16	12.54	2.67
22[f]	**5**	30	0	0		
23[h]	-	30	0	0		

[a] Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex, 0.20 μmol; 1.0 mL of MMAO (2.2 M) [Al/Ni(molar) = 11 000]; norbornene, 1.88 g [nornorene/Ni(molar) = 136 000]; reaction time, 10 min. [b] 10^7 g PNB mol^{-1} Ni h^{-1}. [c] M_w (10^{-5} g mol^{-1}) and M_w/M_n values were determined by GPC. [d] 0.5 mL of MMAO (2.2 M). [e] Reaction time, 20 min. [f] Without cocatalyst MMAO. [g] Nickel complex, 0.40 μmol. [h] Without nickel complex.

The norbornene polymerization results are collected in Table 2. In general, the steric structure and bulky group in nickel complexes slightly influence their catalytic activities. For example, complexes **1** and **2**, bearing phenyliminophenolato, have higher activities than complexes **3** and **4**, bearing β-enaminoketonato, at same polymerization conditions due to the unpliant framework of the former ligands. Complex **5**, having two big steric groups $[2,6\text{-}i\text{-}Pr_2(C_6H_3)N]$, is the least active among all five catalysts. Recently, the addition mechanism of norbornene using neutral nickel complexes was hypothesized as the insertion of norbornene into the Ni−C bond.[6i,l] If so, we can easily explain that the higher activaties for complexes **1** and **2** than those for **3** and **4** is because the former have less rigid ligand frameworks and norbornene inserts into the Ni−C bond more easily after the precatalyst is activated with MMAO to afford an empty site.

MMAO was essential for the polymerization of norborene catalyzed by **1**−**5**. Variation of the ratio of MMAO:complex (**1**−**5**), which is expressed here as Al:Ni ratio, showed considerable effects on molecular weight but barely any effect on catalyst activity and polymer yield (runs 2 and 3). Like other nickel catalytic systems for norbornene polymerization,[6] when the total reaction volume was kept constant, an increase of monomer concentration (the molar ratio of norbornene:Ni) caused a dramatic increase of activity combined with

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a slight decrease of molecular weight (runs 9 and 10). The polymerization seems independent of temperature, and the polymerization reaction showed a higher activity tendency with increasing reaction temperature from 0 to 60 °C (runs 4, 2, and 5). As shown in Table 2, the yields of PNB increase and the molecular weights of the polymer decrease slightly with longer reaction time (runs 10 and 14).

The polymers obtained were characterized by ^{1}H NMR, IR, and GPC analyses. The ^{1}H NMR spectra of six PNB products are similar to each other. The resonances of PNB appear at 2.6−0.9 (m, maxima at 1.2, 1.4, 1.6, 2.3 ppm), and the absence of bands at 1680−1620 cm^{-1} in the IR spectra indicated no double bonds, which was different from the polymers of norbornene ring-opening metathesis polymerization.[14] The GPC molecular weights M_w of five polymers were very high, up to near 2 000 000, indicating that the normal mode of chain transfer (β-hydride elimination) was not possible in PNB given the geometry of the active growing center. From XRD data of these polymers, only very weak signals could be observed. The DSC study of obtained PNB did not gave an endothermic signal upon heating to the decomposition temperature (above 450 °C), and the TGA scans suggested these polymers are very stable up to 400 °C.

Conclusion

We have synthesized nickel complexes of bulky monoanionic β-diketiminato, ketiminato, and Shiff-base ligands and examined their catalytic behavior for the addition polymerization of norbornene. β-Ketiminato nickel complexes can be conveniently prepared by the same synthetic method as Shiff-base phenyl nickel complexes, and they all share the four-coordination binding mode around nickel(II). The steric protection of the β-diketiminato ligand can stabilize highly electronically unsaturated organometallic complexes, and thus it has been possible to synthesize a rare three-coordinate nickel(I) complex (**5**) in the presence of PPh$_3$. All these nickel complexes show extremely high activities for the addition polymerization of norbornene with the MMAO as cocatalyst. A mechanistic study of the formation of the nickel(I) from nickel(II) as well as the steric effects of the substituents is our current investigation.

Experimental Section

General Considerations. All experiments with metal complexes and ligands were carried out under argon using standard Schlenk and vacuum-line techniques. Solvents were dried by refluxing with appropriate drying agents and distilled under argon prior to use. 2,6-Dimethylaniline, 2,6-diisopropylaniline, 2-*tert*-butyl-4-methylphenol, NaH (60%), and *n*-BuLi (1.6 M) were obtained from Acros Chem. Co. Norbornene (bicyclo[2.2.1]hept-2-ene, Fluka) was purified by sublimation under reduced pressure and used as a solution in chlorobenzene. Modified methylaluminoxane (MMAO) [(AlMeO)$_n$/(AliBuO)$_m$ = 3:1] was purchased from Acros Organics as 10% weight of a toluene solution and used without further purification. The starting materials 3-*tert*-butyl-5-methylbenzaldehyde[15] and *trans*-[Ni(PPh$_3$)$_2$(Ph)Cl][16] were prepared according to literature procedures. Schiff-base [**N**, **O**] ligands 3-*t*-Bu-5-Me-(2,6-Me$_2$(C$_6$H$_3$)N=CH)C$_6$H$_2$OH (**L$_1$**) and 3-*t*-Bu-5-Me-(2,6-*i*-Pr$_2$(C$_6$H$_3$)N=CH)C$_6$H$_2$OH (**L$_2$**) were synthesized as we previously reported.[7] β-Diketiminato [**N**, **O**] ligands (2,6-Me$_2$(C$_6$H$_3$)N=C(CH$_3$)CH=C(CH$_3$)OH (**L$_3$**)[9] and (2,6-*i*-Pr$_2$(C$_6$H$_3$)N=C(CH$_3$)CH=C(CH$_3$)OH (**L$_4$**) and β-diketiminato [**N**, **N**] ligand (2,6-*i*-Pr$_2$(C$_6$H$_3$)N=C(CH$_3$))$_2$CH$_2$ (**L$_5$**)[10] were obtained according to literature methods or using analogous methods reported. All five ligands were characterized by ^{1}H NMR spectra. Other commercially available reagents were purchased and used without purification.

All measurements were carried out at the Analysis Center of Changchun Institute of Applied Chemistry, The Chinese Academy of Sciences. ^{1}H NMR spectra were recorded with a Varian Unity-400 spectrometer. Elemental analyses were performed with a Perkin-Elmer Series II CHN/O analyzer 2400. Average molecular weight (M_w) and molecular weight distribution (M_w/M_n) values of PNB products were determined using a PL GPC-220 gel permeation chromatograph at 150 °C using a narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 m MIXED-B LS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL/min. IR spectra were measured with a Bio-Rad FTS 135 spectrometer.

Preparation of [3-*t*-Bu-5-Me-(2,6-Me$_2$(C$_6$H$_3$)N=CH)-C$_6$H$_2$O](PPh$_3$)(Ph)Ni](1). The suspension solution of sodium hydride (0.2 g, 5 mmol) in THF (20 mL) was channeled into a 100 mL flask with a solution of the ligand **L$_1$** (0.596 g, 1.5 mmol) in THF (20 mL). After stirring at room temperature for 2 h, the mixture was centrifuged and the upper clear solution was transferred and concentrated in vacuo to afford a pale yellow solid residue. The residue was washed with hexane (20 mL), and the resulting sodium salt of **L$_1$** was used for the next step without any other purification. A solution containing the sodium salt of **L$_1$** (0.443 g, 1.5 mmol) and *trans*-[Ni(PPh$_3$)$_2$(Ph)Cl] (1.0 g, 1.44 mmol) in benzene (50 mL) was stirred at room temperature. After 6 h, the reaction mixture was separated by centrifugaton to remove NaCl. The upper clear solution was evaporated to about 5 mL in a vacuum, and then hexane (30 mL) was slowly added. Complex **1** was obtained as a yellow solid. Yield: 0.81 g (78%). Single crystals were obtained from hexane/toluene. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.98 (d, 1 H, N=CH), 7.85−6.44 (m, 25 H, Ar−H), 2.50 (s, 6 H, CH$_3$−Ar), 2.31 (s, 3 H, CH$_3$−Ar), 1.01 (s, 9 H, CH$_3$ of *t*-Bu). Anal. Calcd for C$_{44}$H$_{44}$NNiOP (692.507): C 76.31, H 6.40, N 2.02. Found: C 76.31, H 6.45, N 2.12.

Preparation of [3-*t*-Bu-5-Me-(2,6-*i*-Pr$_2$(C$_6$H$_3$)N=CH)-C$_6$H$_2$O](PPh$_3$)(Ph)Ni](2). Complex **2** was obtained as a yellow solid. Yield: 0.92 g (81%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 8.07 (d, 1 H, N=CH), 7.90−6.51 (m, 25 H, Ar−H), 4.31 (m, 2 H, CH of *i*-Pr), 2.32 (s, 3 H, CH$_3$−Ar), 1.24 (d, 6 H, CH$_3$ of *i*-Pr), 1.10 (d, 6 H, CH$_3$ of *i*-Pr), 0.98 (s, 9 H, CH$_3$ of *t*-Bu). Anal. Calcd for C$_{48}$H$_{52}$NNiOP (748.614): C 77.01, H 7.00, N 1.87. Found: C 77.90, H 7.03, N 1.88.

Preparation of [(2,6-Me$_2$(C$_6$H$_3$)NC(CH$_3$)=CHCOCH$_3$)-(PPh$_3$)(Ph)Ni] (3). Ligand **L$_3$** was obtained as a white solid in 61% yield by using the analogous method according to ref 9. ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.03 (s, 1 H, NH), 7.30−7.14 (m, 3 H, Ar−H), 5.19 (m, 1 H, CH$_{\text{backbone}}$), 2.33 (s, 6 H, CH$_3$−Ar), 2.13 (s, 3 H, CH$_3$−Ar), 1.64 (d, 3 H, CH$_3$).

n-BuLi (0.95 mL, 1.6 M, 1.52 mmol) in a solution of toluene and hexane was slowly added to a solution of the ligand **L$_3$** (0.305 g, 1.5 mmol) in toluene (20 mL) at −78 °C. The mixture was warmed to room temperature by itself and stirred for

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another 2 h to afford the lithium salt of the ligand **L₃**. The solution containing the lithium salt of **L₃** was slowly channeled into a 100 mL flask with 1.0 g of *trans*-[Ni(PPh_3)$_2$(Ph)Cl] (1.44 mmol) in toluene (20 mL) and continuously stirred overnight at room temperature. The reaction mixture was separated by centrifugation to remove LiCl. After the upper clear, dark red solution was concentrated to about 5 mL, 30 mL of hexane was added to the top of the solution. Complex **3** was obtained as yellow-orange crystals. Yield: 0.95 g (83%). Anal. Calcd for $C_{37}H_{36}NNiOP$ (600.366): C 74.02, H 6.04, N 2.33. Found: C 73.88, H 6.22, N 2.47.

Preparation of [(2,6-*i*-Pr$_2$(C_6H_3)NC(CH_3)=CHCOCH$_3$)-(PPh$_3$)(Ph)Ni] (4). Ligand **L₄** was obtained as a white solid by using a method similar to **L₃** in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.07 (s, 1 H, NH), 7.32−7.17 (m, 3 H, Ar−H), 5.20 (m, 1 H, $CH_{backbone}$), 3.03 (m, 2 H, CH of *i*-Pr), 2.13 (s, 3 H, CH_3), 1.64 (d, 3 H, CH_3), 1.20 (d, 6 H, CH_3 of *i*-Pr), 1.15 (d, 6 H, CH_3 of *i*-Pr). Complex **4** was synthesized as a yellow-orange solid. Yield: 0.92 g (81%). Orange single crystals were obtained from toluene at −30 °C. Anal. Calcd for $C_{41}H_{44}NNiOP$ (656.474): C 75.01, H 6.76, N 2.13. Found: C 74.92, H 6.91, N 2.15.

Preparation of [((2,6-*i*-Pr$_2$(C_6H_3)N=C(CH_3))$_2$CH)(PPh$_3$)-Ni] (5). *n*-BuLi (0.95 mL, 1.6 M, 1.52 mmol) in a solution of toluene and hexane was slowly added to a solution of the ligand **L₅** (0.605 g, 1.5 mmol) in toluene (20 mL) at −78 °C. The mixture was warmed to room temperature by itself and stirred for another 2 h to afford the lithium salt of the ligand **L₅**. The solution containing the lithium salt of **L₅** was slowly channeled into a 100 mL flask with 1.0 g of *trans*-[Ni(PPh_3)$_2$-(Ph)Cl] (1.44 mmol) in toluene (20 mL) and continuously stirred overnight at room temperature. The reaction mixture was separated by centrifugation to remove LiCl. After the upper clear, dark red solution was concentrated to about 5 mL, 30 mL of hexane was added. Complex **3** was obtained as a red-orange solid. Yield: 0.56 g (53%). Red-orange single crystals suitable for X-ray were recrystallized from toluene at −30 °C. Anal. Calcd for $C_{47}H_{56}N_2NiOP$ (738.64): C 76.43, H 7.64, N 3.79. Found: C 76.60, H 7.53, N 3.88. EPR (9.4280 GHz, 298 K, toluene): $g = 2.0202$.

Structure Solution and Refinement for Complexes 1, 4, and 5. For complexes **1**, **4**, and **5**, a single crystal suitable for X-ray analysis was sealed into a glass capillary, and the intensity data of the single crystal were collected on the CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in Table 1.

Polymerization of Norbornene. In a typical procedure (run 4, Table 2), 0.2 μmol of nickel complex **4** in 2.0 mL of chlorobenzene, 1.88 g of norbornene in 4.0 of mL chorobenzene, and another 3.0 mL of fresh chlorobenzene were added into a special polymerization bottle (20 mL) with a strong stirrer under Ar atmosphere. After the mixture was kept at 30 °C for 10 min, 1.0 mL of MMAO (10%) was charged into the polymerization system via syringe, and the reaction was started. Ten minutes later, the acidic ethanol ($V_{methanol}$:$V_{concd.HCl}$ = 20:1) was added to terminate the reaction. The PNB was isolated, washed with methanol, and dried at 80 °C for 48 h under vacuum. For all the polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by variation of the amount of chlorobenzene when necessary. IR (KBr): 2947, 2866, 1475, 1453, 1295, 1223, 1190, 1147, 1108, 1043, 942, 892 cm^{-1}. ^{1}H NMR (*o*-dichlorobenzene-d_4, 400 Hz): δ 0.9−2.6 (m, maxima at 1.2 1.4, 1.6 2.3).

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Supporting Information Available: CIF data of **1**, **4**, and **5** are available free of charge via the Internet at http://pubs.acs.org.

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