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Vinyl polymerization of norbornene with novel nickel (II) diphosphinoamine/methylaluminoxane catalytic system

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A new diphosphinoamine ligand [$Ph_2PN(p\text{-}C_6H_4OMe)PPh_2$] was prepared through aminolysis reaction of *p*-methoxyaniline with Ph_2PCl in the presence of NEt_3. Consequently, the corresponding nickel (II) diphosphinoamine complex [$(p\text{-}C_6H_4OMe)N(PPh_2)_2NiCl_2$] was synthesized and characterized. The solid-state structure of the complex was determined by single-crystal X-ray diffraction. As combined with methylaluminoxane (MAO), the complex displayed high catalytic activity for vinyl polymerization of norbornene. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: diphosphinoamine; nickel complex; polynorbornene; vinyl polymerization

INTRODUCTION

The design and synthesis of efficient transition metal complex catalysts directed for precise olefin polymerization and copolymerization have attracted considerable attention.[1,2] Recent progress has led to the development of a wide range of new high-performance polyolefin materials.[3,4] Cycloolefins (typically norbornene) are mainly used as monomers or comonomers. Norbornene (i.e. bicyclo[2.2.1]hept-2-ene; NBE) and its derivatives can be polymerized via ring-opening metathesis polymerization (ROMP), cationic (or radical) polymerization and vinyl (or addition) polymerization (see Scheme 1). Each route leads to its own polymer type that is different in structure and property from the other two, depending on the catalyst and mechanism.[5,6] The vinyl-type polynorbornene is of considerable interest as a special polymer because of its unique physical properties, including good mechanical strength and heat resistivity ($T_g > 350\,^{\circ}C$), and optical transparency for applications such as deep ultraviolet photoresists, excellent dielectrics in microelectronics applications, and as cover layers for liquid-crystal displays.[7] Catalysts described in the literature for the vinyl polymerization of norbornene are complexes of nickel,[8–14] cobalt,[15,16] palladium,[10,17–20] titanium,[21,22] zirconium,[23] iron,[24] and so on. The resulting norbornene polymers may be crystalline or amorphous, depending on the employed catalysts. While most of late metal catalysts contain ligands based on hard-donor atoms (N–N, N–O), or mixed hard–soft donors (P–O, P–N), reports on diphosphine-based Ni polymerization catalysts are scarce despite the crucial role that the latter ligands play in homogeneous catalysis.[15,25,26]

In recent years, the coordination chemistry of bis(phosphino) amines, $R'N(PR_2)_2$, has attracted considerable interest, due to the chemical and structural proximity to the widely used bis(diphenylphosphino)methane(dppm).[27–29] Compared with diphosphines with the P–C–P linkage, bis(phosphino)amines with P–N–P skeletons have proved to be much more versatile ligands, and varying the substituents on both the P- and N-centers gives rise to changes in the P–N–P angle and the conformation around the P-centers. Small variations in these ligands can cause significant changes in their coordination behaviors and the structural features of the resulting complexes. A structural characteristic of most of these ligands is that the electrons in the lone pair at the P-center point towards each other, indicating that these ligands prefer to adopt a bidentate-chelating bonding mode as opposed to adopting bridging coordination geometries.[30–32] This feature enables the synthesis of a wide range of four-membered ring systems containing transition metals such as Pd, Pt, Mo, Cu, Cr, Ni and Ru, which have potential uses in catalysis.[33–37] Wass and coworkers reported several bis(phosphino)methylamine

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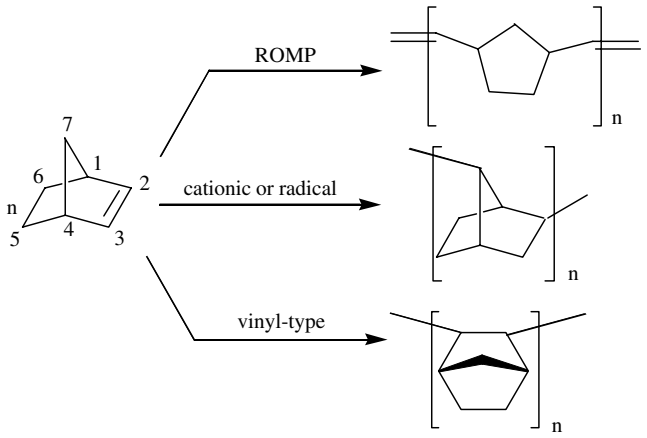


Scheme 1. Three different types of norbornene polymerization.

nickel (II) complexes that are highly active catalyst precursors for ethylene polymerization.[38,39] In this paper, we report a preliminary study of the norbornene polymerization with the new nickel (II) diphosphinoamine complex [(*p*-C_6H_4OMe)N(PPh_2)$_2NiCl_2$]/MAO catalytic system, and investigate the influence of polymerization conditions (such as temperature, Al : Ni molar ratio and catalyst concentration) on the catalyst activity.

EXPERIMENTAL

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk techniques.

Materials

Norbornene (Aldrich) was purified and dried using potassium at 60 °C for 8 h and distilled, then dissolved in toluene to make a 0.4 g mL^{-1} solution. Toluene was refluxed over sodium for 48 h and freshly distilled under a nitrogen atmosphere before use. Other solvents were purified using standard procedures. Methylaluminoxane (MAO) was prepared by the controlled hydrolysis reaction of trimethylaluminum (TMA) with $Al_2(SO_4)_3{\cdot}18H_2O$ in toluene. *p*-Methoxylaniline (Sinopharm Chemical Reagent Co., Ltd) was purified by recrystallization from methanol. Triethylamine (Guangzhou Chemical Reagent Co.) was distilled prior to use. $NiCl_2{\cdot}6H_2O$ (Guangzhou Chemical Reagent Co.) was dehydrated with $SOCl_2$ prior to use. Diphenylphosphine chloride (95%) was purchased from Acros and used without further purification.

Measurements

Elemental analysis (carbon, hydrogen and nitrogen) of ligand and complex was obtained using a Vario EL microanalyzer. IR spectra were recorded on a Nicolet 205FT-IR spectrophotometer in the region 4000–400 cm^{-1} in KBr pellets. ^1H NMR spectra were obtained using an Varian Mercury-plus 300 instrument at room temperature in $CDCl_3$ (for ligand and complex) or *o*-$C_6D_4Cl_2$ (for PNBE) solution using tetramethylsilane as internal standard, and 85% H_3PO_4 was used as external standard for $^{31}P\{^1H\}$NMR. GPC analysis of the molecular weight and molecular weight distribution of the polymers was performed on a Waters Breeze instrument using chlorobenzene as the eluent at 50 °C and standard polystyrene as the reference.

Crystal structure determination

Single-crystal X-ray diffraction data of the complex was collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.[40,41] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Synthesis of *N,N*-bis(diphenylphosphino)-*p*-methoxyaniline (ligand)

The ligand $Ph_2PN(p\text{-}C_6H_4OMe)PPh_2$ was synthesized by a similar published procedure.[30,31] The Ph_2PC1 (4.41 g, 20.0 mmol) was added slowly to a solution of *p*-methoxyaniline (1.23 g, 10.0 mmol) and Et_3N (2.53 g, 25 mmol) in CH_2C1_2 (50 ml) at 0 °C within 15 min. The resulting white suspension was stirred for 2 h at room temperature. After removal of the CH_2C1_2, the residue was washed with diethyl ether (4 × 30 ml). Removal of the solvent and recrystallization from CH_2C1_2/diethyl ether at −20 °C gave the ligand as a colorless solid. Yield 3.19g, 65%. Anal. found: C, 74.46; H, 5.30; N, 2.86. Calcd: $C_{31}H_{27}NOP_2$, C, 75.75; H, 5.54; N, 2.85. ^1H NMR ($CDCl_3$, δ): 3.72 (s, 3H,OCH_3), 6.60–6.82 (m, 4H, MeO-C_6H_4-), 7.20–7.63 [m, 20H, -P_2 ($C_{24}H_{20}$)]. Selected IR (KBr, cm^{-1}), 2834ν (OCH_3), 936ν (P-N).

Synthesis of diphosphinoamine nickel(II) complex

The diphosphinoamine nickel (II) complex was obtained using a similar published procedure.[42] A solution of Ph_2PN (*p*-C_6H_4OMe) PPh_2 (0.246 g, 0.5 mmol) in CH_2Cl_2 (10 ml) was added to $NiCl_2$ (0.065 g, 0.5 mmol) in CH_3OH (10 ml). The mixture was turned to dark red and stirred overnight. The volume was concentrated to *ca* 5 ml by evaporation under reduced pressure and addition of *n*-hexane (20 ml) gave a brick-red solid product. The product was collected by suction filtration and dried in *vacuo*. Yield: 0.171 g, 55%. The complex was dissolved in CH_2Cl_2–toluene at 40 °C, and then slow diffusion under nitrogen over one week gave crystals suitable for X-ray crystallography. ^1H NMR ($CDCl_3$, δ): 3.65 (s, 3H,OCH_3), 6.34–6.48 (m, 4H, MeO- C_6H_4-), 7.50–8.10 [m, 20H, -P_2 ($C_{24}H_{20}$)]. $^{31}P\{^1H\}$NMR: 47.6(s). Anal. found: C, 55.42; H, 4.59; N, 1.90. Calcd: $C_{31}H_{27}Cl_2NNiOP_2{\cdot}CH_2Cl_2$, C, 54.44; H, 4.14; N, 1.98.

NBE polymerization

The toluene (5–10 ml), 10 ml of NBE (4 g), and the appropriate amount of MAO solution were introduced into a 50 ml round-bottom glass flask in order, then an appropriate amount of nickel (II) complex in toluene solution was syringed into the well-stirred solution (total reaction volume is about 20 ml). The contents were continuously stirred for a certain time period at the polymerization temperature. The polymerization was stopped by addition of excess 10% HCl–EtOH. The resulting precipitated PNBE was collected and treated by filtering, washing with EtOH several times, and drying in vacuum at 60 °C to a constant weight.

RESULTS AND DISCUSSION

Syntheses of ligand and nickel (II) complex

Aminolysis reaction seems to be the most commonly used method for the synthesis of diphosphinoamines, and the solvent has a significant influence on the reaction rate and on the reaction product. In general, Et_2O or toluene is a very good solvent, but the reaction is very slow, especially for anilines and related compounds. It was found that CH_2Cl_2 is a more appropriate solvent.[30] Therefore we chose CH_2Cl_2 as the solvent in this synthesis process. In a typical reaction, 2 equivalents of Ph_2PCl were added slowly to a CH_2Cl_2 solution of *p*-methoxyaniline containing 2.2 equivalents of Et_3N to afford the bidentate diphosphinoamine ligand $Ph_2PN(p\text{-}C_6H_4OMe)PPh_2$. The subsequent reaction of the diphosphinoamine ligand with $NiCl_2$ in the mixed solvents of CH_2Cl_2–methanol (1 : 1 in volume) led to the formation of the corresponding nickel (II) diphosphinoamine complex in moderate yield (as shown in Scheme 2).

Crystal structure of nickel (II) complex

Crystals of the complex suitable for single-crystal X-ray diffraction analysis were grown from toluene–CH_2Cl_2 solution. The molecular structure of the complex is shown in Fig. 1. The crystallographic data are summarized in Table 1 and the selected bond lengths and bond angles are listed in Table 2.

Figure 1 and Table 1 show that the complex is monoclinic, Cc symmetric with distorted square-planar coordination at nickel atom and a near-planar four-membered chelate ring (NiP_2N). It is reflected by the bond angles [P(1)–Ni(1)–P(2) 73.99°(5), P(1)–Ni(1)–Cl(1) 92.01°(6), P(2)–Ni(1)–Cl(2) 94.96°(6), Cl(1)–Ni(1)–Cl(2) 99.14°(6), P(1)–N(1)–P(2) 96.3°(2)]. Moreover, the smaller P–Ni–P angle may afford more space for NBE and the polymer chain on the active species Ni during polymerization, which may explain why this nickel (II) diphosphinoamine complex is an effectively catalyst precursor for NBE polymerization.[26]

NBE polymerization

The use of bulky and substituted chelating ligands is a prerequisite for achieving polymeric products in late transition metal-catalyzed ethylene polymerization reactions. In addition, chain termination induced by β–H elimination is thermodynamically unfavorable when using norbornene. Therefore, we chose norbornene as the monomer to verify the polymerization capability of this new nickel complex. This nickel (II) diphosphinoamine complex could effectively catalyze NBE polymerization in the presence of MAO. The PNBE was white solid and all polymers were soluble in chlorobenzene, *o*-dichlorobenzene and cyclohexane at room temperature, which indicated that the PNBE was low stereoregularity. The M_n of all PNBEs was between 10^5 and 10^6 g mol^{-1}, and the resulting PNBEs were very stable up to about 400 °C, determined by TGA under nitrogen. Moreover, according to the polymerization results, the polymerization

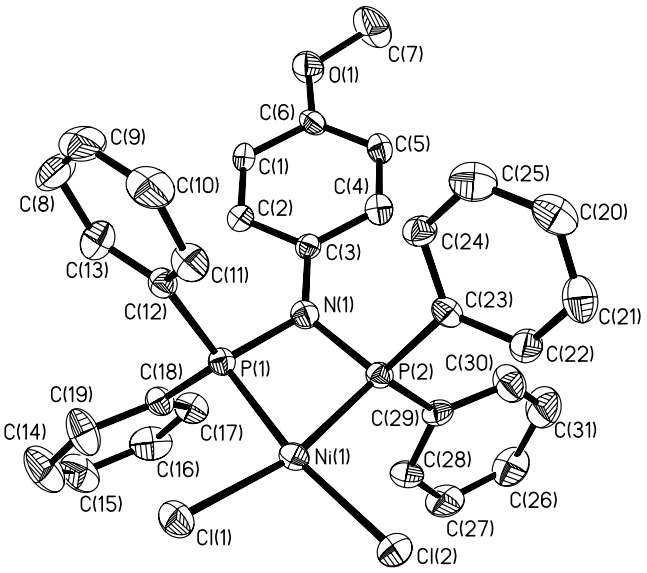
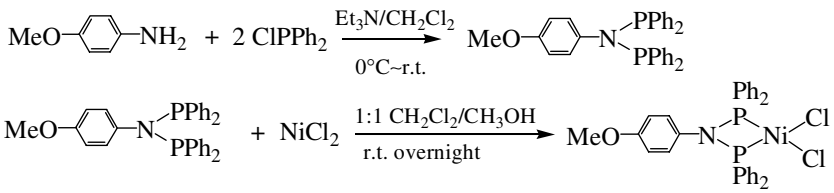


Figure 1. Molecular structure of the Ni(II) complex.



Scheme 2. Synthesis of bis(diphenylphosphino)amine and nickel (II) complex.

yield, molecular weight and molecular weight distribution (MWD), as well as catalytic activity, depended significantly on the polymerization parameters, such as polymerization temperature, Al : Ni molar ratio, and the amount of the catalyst.

Table 1. Crystal data and structure refinement for the complex

	$Ni(PPh_2)_2NPhO$ $MeCl_2 \cdot CH_2Cl_2$
Empirical formula	$C_{32}H_{29}Cl_4NNiOP_2$
Formula weight	706.01
Temperature (K)	293(2)
Wavelength (Å)	0.71073 A
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions	
a (Å)	10.114(4)
b (Å)	15.038(6)
c (Å)	21.251(8)
α (deg)	90
β (deg)	95.311(7)
γ (deg)	90
Volume ($Å^3$)	3218(2)
Z, calculated density (Mg/m^3)	4, 1.457
Absorption coefficient (mm^{-1})	1.061
F(000)	1448
θ range for data collection (deg)	1.92–27.08
Limiting indices	$-12 \le h \le 9$, $-16 \le k \le 19$, $-27 \le l \le 25$
Reflections collected/unique	9452/5321 [R(int) = 0.0240]
Completeness to $\theta = 27.08$	99.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5321/2/363
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0452$, $\omega R_2 = 0.1043$
R indices (all data)	$R_1 = 0.0698$, $\omega R_2 = 0.1163$
Largest difference peak and hole ($e^- Å^{-3}$)	0.620 and −0.509

Polymerization temperature had a remarkable effect on activity and MWD of PNBE. As shown in Table 3, this catalytic system showed higher activity over a wide temperature range. The polymerization yield was more than 30%. In the range of the experimental temperature, the IR spectra of the resulting polymers proved the absence of a double bond at 1620–1680 cm^{-1}, and also the ^1H NMR spectrum of the resulting PNBE indicates that all protons appeared in $\delta = 0$–3 and no vinyl hydrogen atoms ($\delta > 4$) were observed (as shown in Fig. 2). This ensured the occurrence of vinyl-type polymerization rather than ROMP. Moreover, the highest catalyst activity was 7.63×10^5 g PNBE mol^{-1} Ni h^{-1} at 20 °C. Meanwhile, with increasing temperature, the M_n decreased and MWD increased.

MAO combines the function of alkyl-transfer agent, activator and scavenger in olefin coordination polymerization.[26,43]

Table 2. Selected bond lengths (Å) and angles (deg) for the complex

Bond length	Bond angle
Ni(1)–P(1) 2.1148(17)	P(1)–Ni(1)–P(2) 73.99(5)
Ni(1)–P(2) 2.1232(15)	P(1)–N(1)–P(2) 96.3(2)
Ni(1)–Cl(2) 2.1904(18)	Cl(1)–Ni(1)–Cl(2) 99.14(6)
Ni(1)–Cl(1) 2.1920(17)	P(1)–Ni(1)–Cl(1) 92.01(6)
P(1)–N(1) 1.711(4)	P(2)–Ni(1)–Cl(2) 94.96(6)
P(2)–N(1) 1.712(5)	N(1)–P(1)–Ni(1) 94.99(16)
P(1)···P(2) 2.5501(18)	N(1)–P(2)–Ni(1) 94.63(14)

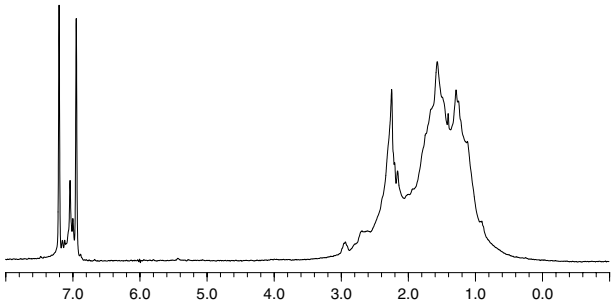


Figure 2. ^1H NMR spectrum of PNBE catalyzed by Ni(II) complex/MAO.

Table 3. Influence of temperature on polymerization of NBE catalyzed by Ni (II) complex/MAO[a]

Entry	T (°C)	t_p (min)	Yield (%)	Activity/10^5 g PNBE (mol Ni h)$^{-1}$	M_w (kg mol^{-1})	M_n (kg mol^{-1})	M_w/M_n
1	0	20	31.5	5.78	1421	573	2.48
2	20	20	41.0	7.63	1036	191	5.42
3	30	20	33.1	6.17	902	175	5.15
4	50	20	30.2	5.61	683	120	5.69

[a] Polymerization conditions: [Ni] = 0.32 mmol l^{-1}; Al : Ni = 500; [NBE] = 2.13 mol l^{-1}; V_{total} = 20 ml.

Table 4. Influence of Al/Ni ratio on polymerization of NBE catalyzed by Ni(II) complex/MAO[a]

Entry	Al : Ni	t_p (min)	Yield(%)	Activity (10^5 g) PNBE (mol Ni h)$^{-1}$	M_w (kg mol^{-1})	M_n (kg mol^{-1})	M_w/M_n
5	200	60	trace	~0	—	—	—
6	300	20	24.7	4.60	1156	274	4.22
2	500	20	41.0	7.63	1036	191	5.42
7	700	20	29.3	5.46	980	166	5.90

[a] Polymerization conditions: [Ni] = 0.32 mmol l^{-1}; T_p = 20 °C; [NBE] = 2.13 mol l^{-1}; V_{total} = 20 ml.

Table 5. Influence of catalyst concentration on polymerization of NBE catalyzed by Ni(II) complex/MAO[a]

Entry	[Ni]/mmol L^{-1}	t_p/min	Yield/%	Activity/10^5 g PNBE (mol Ni h)$^{-1}$	Mw/kg mol^{-1}	Mn/kg mol^{-1}	Mw/Mn
8	0.16	60	18.7	2.32	1160	202	5.74
9	0.24	20	26.4	6.56	1176	250	4.70
2	0.32	20	41.0	7.63	1036	191	5.42
10	0.40	20	38.2	5.69	—	—	—

[a] Polymerization conditions: T_p = 20 °C; Al : Ni = 500; [NBE] = 2.13 mol l^{-1}; V_{total} = 20 ml.

The amounts of MAO are essential for this polymerization. As shown in Table 4, variations in the Al : Ni molar ratio resulted in different catalytic activities. The optimized Al : Ni ratio was 500. Higher or lower Al : Ni led to decreases in the catalytic activity. In addition, the Al : Ni molar ratio also affected the molecular weight and MWD of the PNBE. GPC results showed lower M_n values and higher MWD with increasing the Al : Ni ratio.

The data in Table 5 show that the catalyst concentration had a considerable effect on the polymerization reaction under certain reaction conditions. With an increasing amount of the catalyst, the catalytic activity increased first and then declined. The optimized concentration of nickel was 0.32 mmol l^{-1} for the highest catalytic activity in this polymerization. The reason perhaps was that a higher catalyst concentration could speed up polymerization and result in high viscosity in a very short time (shorter gel time), and high viscosity could stunt the chain propagation reaction by slowing down the diffusion of the monomer to the catalytically active nickel active species. In addition, the catalyst concentration had a slight effect on the M_n and the MWD.

CONCLUSIONS

A new bidentate diphosphinoamine ligand and the corresponding nickel (II) diphosphinoamine complex were synthesized and characterized. The catalytic behavior of the complex for norbornene polymerization was investigated. The complex exhibited relatively higher activity promoted by cocatalyst MAO. The structure characterization of polynorbornene indicated that the norbornene polymerization is vinyl-type polymerization rather than ROMP. Under appropriate conditions, the catalytic activity could be up to 7.63 × 10^5 g PNBE (mol Ni h)$^{-1}$, and could obtain the polynorbornene with high molecular weight and broad molecular weight distribution. The catalytic activity, polymerization yield and the polymer molecular weight could be controlled over a wide range by variation of the polymerization parameters. Studies on α-olefin and norbornene copolymerization are currently under investigation.

Supplementary materials

CCDC 286709 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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