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Nickel and palladium complexes bearing *ortho*-phenoxy modified anilido-imine ligands: Drastic steric effect on coordinated geometry, and catalytic property toward olefin polymerization

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ABSTRACT

A series of new nickel complexes and palladium complexes bearing *ortho*-phenoxy modified anilido-imine ligands have been synthesized and characterized. X-ray diffraction analyses of the single crystal structures reveal that there are no direct metal–O interactions in all of the complexes. The steric hindrance of complexes has an importance influence on their coordinated geometries. The bulky complexes with 2,6-diisopropylphenyl substituent exist as a dimers with bromine-bridged structure while those with 2,6-dimethylphenyl or phenyl substituents adopt a distorted tetrahedral geometry with four nitrogen atoms of two anilido-imine ligands. The nickel complexes exhibited high activity up to 7.33×10^6 g/(mol of Ni · h) and palladium complexes showed very high activity up to 2.63×10^8 g/(mol of Pd · h) for norbornene polymerization with methylaluminoxane as cocatalyst. The nickel catalysts were attempted to polymerize ethylene at atmosphere pressure, however, only oligomers were produced.

1. Introduction

In transition metal olefin polymerization catalyst design, *ortho*-alkoxy-aryl substituents approach is proven to be an efficient strategy. A variety of transition metal complexes bearing *ortho*-alkoxy modified ligands exhibit interesting properties in olefin catalysis. Huang reported that zirconium complexes bearing mono-Cp and tridentate Schiff base [ONO$^-$] ligands exhibited high thermal stability and high catalytic activities for ethylene polymerization [1,2]. Gibson showed that titanium complexes containing phenoxy-amide ligands modified by phenoxy group exhibited low activity for ethylene polymerization [3]. Tang synthesized titanium (IV) complexes bearing monoanionic phenoxy modified salicylaldiminate ligand, and found they exhibited high activity for ethylene polymerization and excellent capability for copolymerization of ethylene with 1-hexene in the presence of modified methylaluminoxane (MMAO) [4]. Rare earth metal (yttrium and lanthanide) catalysts could also be stabilized by β-diiminato and anilido-iminato ligands modified by methoxy functional group, and showed good catalytic activity towards ring-opening polymerization of L-lactide [5,6]. Because of strong electrophilic metal center, the methoxy or phenoxy groups usually can coordinate to early transition metal and rare earth metals. Besides, Wass reported that chromium complexes of aminodiphosphine ligands containing *ortho*-methoxyaryl groups (PNP^{OMe}) are active and selective catalyst precursors for ethylene trimerization and tetramerization [7–11] and for the cotrimerization of ethylene and styrenic comonomers [12].

During the last decade, late transition metal catalysts for norbornene polymerization and ethylene oligomerization have been extensively studied and reviewed [13–19]. Late transition metal catalyst chelating a variety of *ortho*-alkoxy-aryl phosphine ligands also exhibited interesting properties in catalysis. Because of weak electrophilic metal center, the methoxy groups usually do not easily coordinate to late transition metal (Ni, Pd). Pd(II) catalysts containing {bis(*ortho*-alkoxyaryl)phosphino}arene sulfonate ligands (PO$^-$) could catalyze nonalternating ethylene/CO copolymerization to ethylene-enriched polyketones [20,21], ethylene/alkyl acrylate copolymerization to linear copolymers with in-chain acrylate incorporation [22], and other unusual copolymerizations [23–27]. Consiglio reported that palladium catalysts containing *ortho*-methoxysubstituted arylphosphine-oxazole ligands (PN) catalyze regioirregular alternating styrene/CO copolymerization [28]. Additionally, *in situ*-generated Ni(II) complexes containing PNP^{OMe} ligands exhibit better performance in ethylene polymerization and

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oligomerization than their nonsubstituted analogues [29]. Jordan reported the studies of synthesis, structures, dynamics, and ethylene reactivity of a series of nickel complexes containing a (PNP^{OMe}) aminodiphosphine ligand [30]. In several cases, the enhancements of catalytic activity and/or selectivity engendered by the *ortho*-methoxy groups in aryl phosphine ligands have been proposed to arise from steric effects [23], because similar enhancements were observed for analogous *ortho*-alkyl-substituted aryldiphosphines [25,28–31]. In other cases, it was proposed that the *ortho*-methoxy groups act as hemilabile ligands and reversibly coordinate to the metal center during catalysis [7,8].

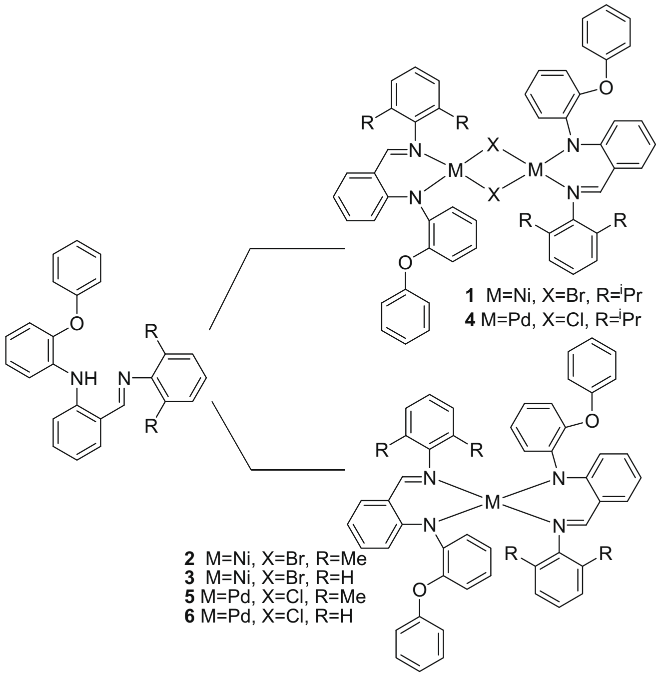
Therefore, a understanding of the properties of ortho-alkoxy(or phenoxy)-aryl is interesting and enable new opportunities in catalysis. During the past few years, our groups have focused our attention on anilido-imino nickel complexes due to their easily modified features. From the view points of ligand steric and electronic, we previously synthesized a series of bulky anilido-imino nickel complexes and investigated their catalytic behaviors toward olefin polymerization [32–37]. Herein we reported the initial studies of the synthesis and structure of a series of phenoxy-modified anilido-imine nickel and palladium complexes, as well as their catalytic properties toward norbornene polymerization and ethylene oligomerization.

2. Results and discussion

2.1. Ligand and complex synthesis

Three phenoxy-modified anilido-imine ligands with various sterically hindered substituents were synthesized. The general synthetic route for the ligands was shown in Scheme 1. Condensation of 2-fluorobenzaldehyde with corresponding anilines afforded the imines (**1a**–**c**) in high yields. The corresponding ligands **HL** can be obtained *via* a nucleophilic aromatic displacement of fluorine in the imines using 2-phenoxyaniline lithium salt (Ph–O–2-C_6H_4NHLi). Pure products were obtained as yellow crystals by recrystallization from ethanol in 43–57% yields. All of the ligands had been confirmed by ^1H NMR, ^{13}C NMR and elemental analyses (EA).

The general synthetic route for the complexes was shown in Scheme 2. After the ligands **HL** were deprotonated by 1.0 equiv. of *n*-butyllithium in toluene, certain amount of (1,2-dimethoxyethane) nickel(II) bromide ((DME)$NiBr_2$) or (1,5-cyclooctadiene) chloromethylpalladium ((COD)PdMeCl) was added to the solutions. Nickel complexes **1**–**3** and palladium complexes **4**–**6** were obtained in moderate yields. Surprisingly, the complexes with different aryl substituents showed different colors. The nickel and palladium complexes with 2,6-diisopropylphenyl substituents (**1** and **4**) are grass green, those with 2,6- dimethylphenyl substituents (**2** and **5**) are brown, while those with phenyl substituent (**3** and **6**) is dark red. This indicated that steric hindrance of aryl substituents played an importance role in coordination geometries of these complexes. Elemental analyses (EA) and mass spectrometry (MS) proved the nickel and palladium complexes with 2,6-diisopropylphenyl substituents (**1** and **4**) are in the form of a dimers and bromine-bridged structure (LM-μBr_2-ML), while those with 2,6-dimethylphenyl or phenyl substituents are mononuclear chelating two ligands (L_2M). ^1H NMR spectra of palladium complexes **4**–**6** could be assigned accurately, but nickel complexes **1**–**3** were hardly analyzed due to their paramagnetism.

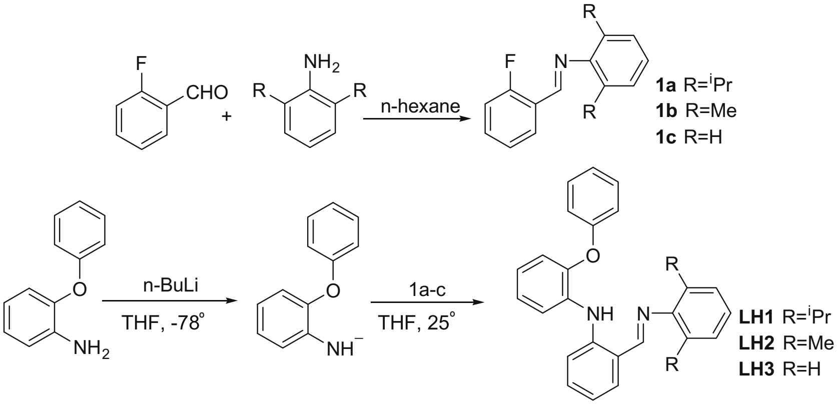

1 M=Ni, X=Br, R=^{i}Pr
4 M=Pd, X=Cl, R=^{i}Pr

2 M=Ni, X=Br, R=Me
3 M=Ni, X=Br, R=H
5 M=Pd, X=Cl, R=Me
6 M=Pd, X=Cl, R=H

Scheme 2. Synthesis of the complexes **1**–**6**.

2.2. Molecular structures

The single crystals of nickel complexes **2**, **3** and palladium complex **4** were grown in toluene/hexane solutions. The crystal data, together with the data collection and structure refinement parameters are presented in Table 1, and the selected bond lengths and


1a R=^{i}Pr
1b R=Me
1c R=H

LH1 R=^{i}Pr
LH2 R=Me
LH3 R=H

Scheme 1. Synthesis of the ligands **LH1**–**LH3**.