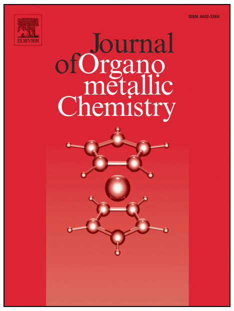

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Structural analysis of imino- and amino-pyridine ligands for Ni(II): Precatalysts for the polymerization of ethylene

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ABSTRACT

Imino- and amino-pyridine ligands are versatile scaffolds to probe how ligand sterics influence polymerization outcomes for nickel(II) ethylene polymerization catalysts. Six imino- and one amino-pyridine nickel(II) complexes with varied imino/amino-carbon substitution (R_1 = methyl, ethyl, isopropyl or *tert*-butyl) were synthesized (**1-7**). Five of these complexes were analyzed crystallographically: dimeric {[2-[(2,6-Me_2-C_6H_3)N=C(R_1)]C_5H_4N]$NiBr_2$}$_2$ (R_1 = Et **2**; R_1 = *t*-Bu **4**), monomeric [2-[(2,6-Me_2-C_6H_3)N=C(R_1)]C_5H_4N]$NiBr_2NCCH_3$ (R_1 = Me **5**; R_1 = *t*-Bu **6**), and monomeric [2-[(2,6-Me_2-C_6H_3)NHCH(*t*-Bu)]C_5H_4N]$NiBr_2$ (**7**). Complexes **1-7** are competent ethylene polymerization precatalysts at 0°C, and *tert*-butyl substituted imino-pyridine precatalysts **4** and **6** and amino-pyridine precatalyst **7** display the best activity, highest polyethylene molecular weight, and narrowest dispersity values of the series. ^{13}C-NMR analyses of polyethylene samples reveal a lightly branched morphology with a modest amount of methyl branching; polymer T_m values are consistent with this assessment. Ongoing work includes further exploration of precatalysts **4**, **6**, and **7** in attempt to maximize polyethylene molecular weight and achieve living polymerization.

1. Introduction

For over fifteen years, imino-pyridine nickel(II) complexes have been examined as precatalysts for ethylene polymerization.[1-3] This field of inquiry developed as a natural progression based on successes of Brookhart's[4-7] α-diimine Ni(II) and Pd(II) complexes for formation of hyperbranched polyethylene (PE) and Brookhart[8-10] and Gibson's[11-13] bis(imino)-pyridine Fe(II) and Co(II) complexes for formation of linear, high molecular weight polyethylene. A growing family of imino-pyridine Ni(II) complexes have been reported (Chart 1, left) where *N*-aryl, R_2, and R_1 substituents are varied to explore structure/activity relationships in catalytic ethylene polymerization.[14-21] Amino-pyridine nickel(II) complexes (Chart 1, right) are a more recent development and also show promise for catalysis (vide infra).[22] Researchers have also explored more elaborate scaffolds based on the imino-pyridine ligand core; some of the most active precatalysts for ethylene polymerization appear in Chart 2.[23-27]

Modification of the *N*-aryl substitution pattern is common; for example, enhanced steric bulk of *ortho*-aryl substituents (i.e. from methyl to isopropyl) can increase polyethylene molecular weight at the expense of diminished catalyst activity; these trends mirror results for bis(imino)pyridine Fe(II) precatalysts.[12] Halide *N*-aryl substituents may be incorporated to enhance catalyst activity.[23] Replacement of *N*-aryl with an 8-arylnaphthyl substituent provides additional steric shielding for nickel, retarding chain transfer and thus increasing polyethylene molecular weight substantially (up to one million with optimized substitution).[26, 27] Notably, catalyst activity is moderate to high for these catalysts (see Chart 2).

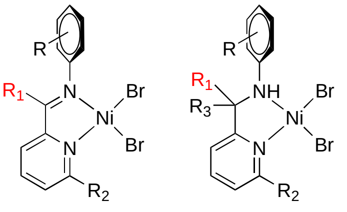

Chart 1. Reported imino- and amino-pyridine Ni(II) catalysts. Most commonly, where R_1 = H, Me, or aryl; R_2 = H, Me, or aryl; R_3 = H or Me; and R-aryl = 2,6-*i*-Pr_2-C_6H_3, 2,6-Me_2-C_6H_3, or 2,4,6-Me_3-C_6H_2. More elaborate substitution patterns appear in Chart 2, top right and bottom left.

Ortho-aryl substituents are proposed to provide steric protection to the metal and hinder chain transfer during ethylene polymerization; the more limited steric protection of an imino-pyridine (as compared to α-diimines or bis(imino)pyridines) is used to explain the tendency of many imino-pyridine nickel(II)