



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



Full paper/Mémoire

Synthesis, characterization and ethylene polymerization of 1-(2,6-dimethyl-4-fluorenylphenylimino)-2-aryliminoacenaphthylnickel bromides

Venkataramana Katla ^a, Erlin Yue ^a, Natesan Mannangatti Rajendran ^a,
Tongling Liang ^a, Wen-Hua Sun ^{a, b, *}

^a Key Laboratory of Engineering Plastics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

ARTICLE INFO

Article history:

Received 9 November 2015

Accepted 7 January 2016

Available online xxx

Keywords:

Acenaphthylene ligand

Ni(II) complex

Ethylene polymerization

Lesser branched polyethylene

ABSTRACT

A series of 1-(2,6-dimethyl-4-fluorenylphenylimino)-2-aryliminoacenaphthylene compounds (aryl = 2,6-di(Me)Ph (**L1**), 2,6-di(Et)Ph (**L2**), 2,6-di(*i*-Pr)Ph (**L3**), 2,4,6-tri(Me)Ph (**L4**), 2,6-di(Et)-4-MePh (**L5**)) was prepared and used to form their corresponding dibromonickel complexes (**D1–D5**). Both **L1–L5** and **D1–D5** were fully characterized by FT-IR and elemental analysis as well as NMR measurements in the case of ligands **L1–L5**. The molecular structure of the representative complex **D5** was confirmed by single crystal X-ray diffraction revealing a distorted trigonal bipyramidal geometry around the nickel center. On activation with either ethylaluminum sesquichloride (Et₃Al₂Cl₃, EASC) or methylaluminoxane (MAO), all nickel complexes exhibited high activities up to 9.82×10^6 g of PE (mol of Ni)⁻¹ h⁻¹ for ethylene polymerization. In comparison with the polyethylenes obtained with related Ni pre-catalysts, the polyethylenes obtained in this work possessed relatively higher molecular weights and lower levels of branching, highlighting the significant influence of the remote fluorenyl substituent.

© 2016 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

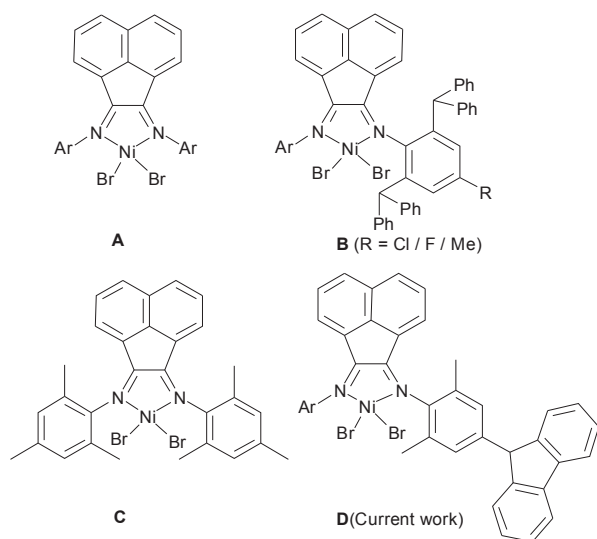
1. Introduction

The design of effective late-transition metal pre-catalysts for ethylene reactivity (polymerization vs. oligomerization) has been the subject of extensive exploration for twenty years or so [1]. The discovery of highly active α -diiminonickel complexes [2] (**A**, Scheme 1) resurrected the use of nickel as the metal centre following the pioneering SHOP process for ethylene oligomerization [3]. To enhance the catalytic performances of nickel-based pre-catalysts, two approaches have been followed: the fine tuning of existing

ligand types [4,5] and the design of alternative ligand sets [6,7]. The most promising pre-catalysts identified for a commercial process are those based on 1,2-bis(arylimino)acenaphthylnickel precursors (**B**, Scheme 1) [5], which exhibit high productivities and thermal stability. Moreover, the unique properties displayed by the resultant polyethylenes make these novel elastomeric materials worthy of note [8]. Among the reports dealing with ligand modifications [1,4,5], few have explored the influence of remote substituents [9], such as fluorenyl groups. Of these reports, most have focused on the effect of remote methyl substituents (e.g. on the *para*-position of N-aryl group) within late-transition metal complexes (**C**, Scheme 1) [10] due, in large part, to the availability of the anilines (with and without *para*-methyl substituents) involved in the ligand

* Corresponding author.

E-mail address: whsun@iccas.ac.cn (W.-H. Sun).



Scheme 1. The variation of 1,2-bis(aryl-imino)acenaphthyl-nickel precatalysts.

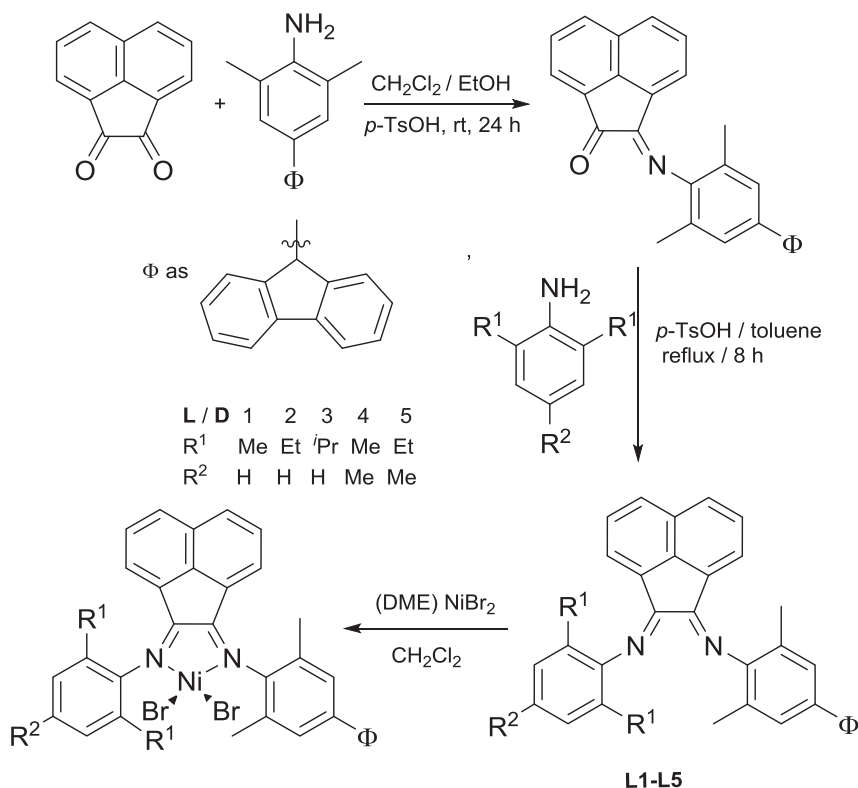
synthesis. To further investigate the influence of remote substituents, the 2,6-dimethyl-4-fluorenylphenylamine is designed and used to prepare 1-(2,6-dimethyl-4-fluorenylphenylimino)-2-aryliminoacenaphthylene derivatives and their nickel complexes (**D**, **Scheme 1**).

2. Results and discussion

2.1. Synthesis and characterization of 1-(2,6-dimethyl-4-fluorenylphenylimino)-2-aryliminoacenaphthylene derivatives (**L1–L5**) and their nickel bromide complexes (**D1–D5**)

According to a previous report [5], 2-(2,6-dimethyl-4-fluorenylphenylimino)acenaphthylene can be prepared by the stoichiometric condensation of acenaphthylene-1,2-dione with 2,6-dimethyl-4-fluorenylphenylamine. We have found that this compound can undergo further reactions with various anilines to form the corresponding 1-(2,6-dimethyl-4-fluorenylphenylimino)-2-aryliminoacenaphthylene derivatives (**L1–L5**, **Scheme 2**) in reasonable yields, respectively. These compounds were characterized by the FT-IR spectra, NMR spectroscopy and elemental analyses. Treatment of **L1–L5** with (DME)NiBr₂ in dichloromethane produces the corresponding nickel(II) bromide complexes **D1–D5** (**Scheme 2**) in good yields, which were characterized by FT-IR spectroscopy and elemental analyses.

With regard to the FT-IR spectra, the nickel bromide complexes **D1–D5** showed C=N stretching vibrations in the range of 1652 cm⁻¹–1609 cm⁻¹, which are at lower frequencies to those observed in the for free **L1–L5** (1677 cm⁻¹–1636 cm⁻¹) and of weaker intensity. This suggests effective coordination between N_{imino} atom and the nickel centre. In addition, the molecular structure of



Scheme 2. Synthesis of ligands **L1–L5** and their nickel complexes **D1–D5**.

Download English Version:

<https://daneshyari.com/en/article/10265137>

Download Persian Version:

<https://daneshyari.com/article/10265137>

[Daneshyari.com](https://daneshyari.com)