

B(C₆F₅)₃ Promotes the catalytic activation of [N,S]-ferrocenyl nickel complexes in ethylene oligomerization

Bárbara Rodríguez^a, Diego Cortés-Arriagada^b, Elvia P. Sánchez-Rodríguez^c, R. Alfredo Toscano^c, M. Carmen Ortega-Alfaro^d, Jose G. López-Cortés^{c,*}, Alejandro Toro-Labbé^{b,*}, Rene S. Rojas^{a,*}

^a Nucleus Millennium Chemical Processes and Catalysis, Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

^b Nucleus Millennium Chemical Processes and Catalysis, Laboratorio de Química Teórica Computacional (QTC), Departamento de Química-Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

^c Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 Cd. Mx., Mexico

^d Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 Cd. Mx., Mexico

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ABSTRACT

The synthesis of new methallyl-ferrocenyl-thiazoline-nickel complexes [1-(2-thiazolin-2-yl)-2-(R-thio)-ferrocene-κ²N,S]-(η³-methallyl)nickel(II) [Y] (**1-3**, R = Me, *i*-Pr, Ph, Y = BF₄⁻; **4**, R = Me, Y = BAR'₄⁻) by reaction with 2-ferrocenyl-2-thiazoline ligands L1–3 with [Ni-(η³-(CH₂)₂CMe)Cl]₂ in presence of fluoroborate salts (Y = BAR'₄⁻; BF₄⁻) is reported. The complexes 1–4 were obtained in high yields, and characterized by ¹H, ¹³C, ¹⁹F and ¹¹B NMR, FTIR. The X-Ray diffraction analysis of **4** confirmed the formation of a single isomer containing a nickel center coordinated to L₁ in a bidentate [N,S] fashion and to a η³-methallyl ligand. These complexes catalyzed efficiently the ethylene oligomerization when tris(pentafluorophenyl)borane (BCF) was used as co-activator. All catalytic precursors produced C₄ and C₆ fractions. Complex **1** showed higher activity with TOF 3006 h⁻¹ at room temperature with selectivity of 86% to C₄ fraction. In contrast, catalyst **2** was more selective to the formation of 1-butene, but with low activity. DFT-Computational studies of complex-BCF adducts show that these species behave as frustrated Lewis pairs, mainly stabilized by long-range interactions enhancing the acceptor character of the complexes. Structural modifications over the sulfanyl group tune the acceptor character of Ni center, affecting their catalytic performance.

1. Introduction

Ethylene oligomerization for the manufacture of α-olefins is one of the most significant processes of homogenous transition-metal catalysis, inasmuch as they are extensively used as the starting materials for organic and polymer compounds [1]. Despite a significant historical record, the requirement of more efficient methods and the search for new macromolecular architectures continue to drive the development and design of new homogeneous transition-metal complexes, in both academic and industrial laboratories [2–4].

In this context, nickel-based olefin polymerization and oligomerization catalysts continue to attract considerable attention, a key feature of these catalysts lies in the electronic and steric control on the ligand motif, which can control the process of olefin polymerization [5–7]. Single-site nickel complexes bearing bidentate ligands are known to exhibit higher catalytic activities for ethylene oligomerization and polymerization reactions than those containing tridentate ligands [8].

These complexes include homo- or hetero-donor ligands such as [P,P], [P,N], [P,O], [N,O], and [N,N], and tend to catalyze the production of branched polymers [9–11].

Thus, a routine strategy for obtaining active nickel complexes for these catalytic applications involves the generation of cationic species by addition of strong Lewis acids cocatalyst, such as MAO, MMAO, TMA or B(C₆F₅)₃ [12–14]. In the case of cationic allyl Ni-complexes, although these are stable precursors for olefin polymerization, but the initiation process is generally inefficient, and only a few sites propagate rapidly, in agreement with reports of initiator systems containing π-allyl ligands [15,16]. However, recent studies have reported cationic methallyl nickel complexes able to produce since α-olefin such as butenes until polyethylenes, when they are activated with B(C₆F₅)₃ [17,18].

On the other hand, complexes containing ferrocenyl backbone-based ligands have been recognized as catalytically active in oligomerization and/or polymerization of ethylene (Fig. 1). For instance, the

* Corresponding authors.

E-mail addresses: jglcvdw@unam.mx, jglcvdw@gmail.com (J.G. López-Cortés), atola@puc.cl (A. Toro-Labbé), rrojasg@uc.cl (R.S. Rojas).

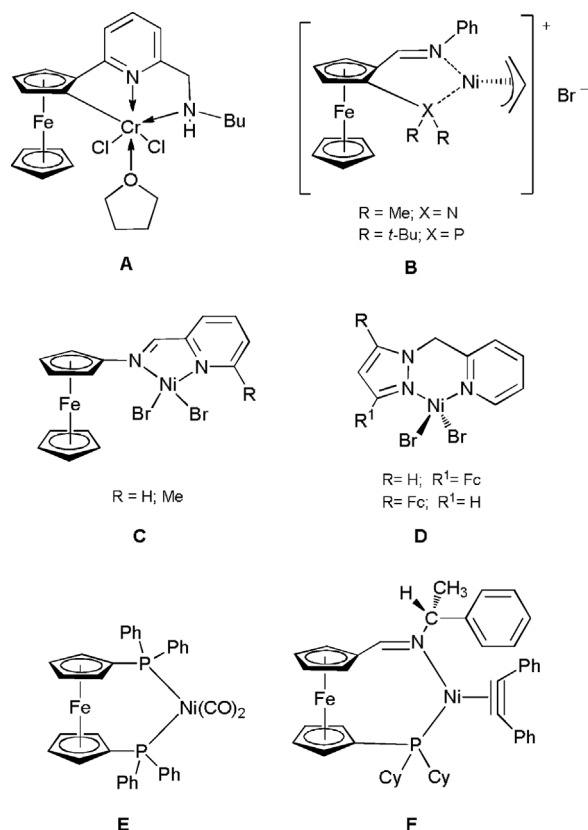


Fig. 1. Cr and Ni complexes containing a ferrocenyl framework used in the oligomerization of ethylene.

chromium complex (A) showed 80% higher selectivity for the oligomerization of ethylene to 1-hexene, with 9213 TOF (h^{-1}) in the presence of 600 equivalents of MAO (Fig. 1a) [19]. Additionally, ferrocenylimine allyl nickel complexes (B) containing [N,N] or [P,N] arms have been reported as active catalysts for ethylene polymerization, in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ as a co-activator [20]. Gibson et al. reported the efficiency of ferrocenyliminopyridines nickel complexes (C) for catalyzing the ethylene dimerization but produced traces of longer chains (C6 and C8), exhibiting TONs between 16.43 and 1.64×10^3 (mol ethylene/mol cat) [21].

Likewise, ferrocenylpyrazolyl nickel(II) (D) [22], ferrocenyl phosphane nickel carbonyls (E) [23], and ferroceneiminophosphine nickel complexes (F) [24] have also been reported in literature for these catalytic applications, using MAO or EtAlCl_2 as co-catalysts.

Despite of several studies involving ferrocenyl ligands in homogeneous catalysis [25–27], to best our knowledge, there is no precedent in the literature about the use of 2-ferrocenyl-2-thiazoline ligands in ethylene oligomerization, which can be due to the difficulty of introducing the 2-thiazoline motif tethered to ferrocene. Recently, our group reported the synthesis of bidentate ligands based on ferrocenyl thiazolines and their applications in palladium catalyzed asymmetric allylic alkylation and Heck coupling reaction [28,29]. We have envisaged to explore the reactivity of a new catalytic system which allows us to combine the methallyl nickel properties [30–32] with the 1-(2-thiazolin-2-yl)-2-(R-thio)-ferrocene ligand features [29], taking as advantage of the possible double activation through the action of an appropriated Lewis acid [33–35]. In this context, we herein report the synthesis and the catalytic applications of a new family of cationic methallyl-nickel complexes with 1-alkylthio-2-thiazoline ferrocene ligands. These Nickel complexes were used as catalysts in the ethylene oligomerization using $\text{B}(\text{C}_6\text{F}_5)_3$ to promote the double activation of the active specie.

2. Experimental

2.1. General considerations

All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk-line techniques. All reagents were used as received from Aldrich, unless otherwise specified. Toluene and pentane were distilled from benzophenone under a nitrogen atmosphere. The ligands L_1 , L_2 and L_3 , were prepared as described in literature [29]. Tris(pentafluorophenyl)borane (BCF) was doubly sublimed at 65 °C under static vacuum and stored in the glovebox.

All reactivity olefin studies were carried out in a J. Young NMR tube. NMR spectra were recorded on NMR Varian Inova 500 MHz, Bruker Unity Plus 600 MHz and Bruker AV 400. Chemical shifts are given in parts per million relative to TMS [^1H and ^{13}C , $\delta(\text{SiMe}_4) = 0$] or an external standard [$\delta(\text{BF}_3\text{OEt}_2) = 0$ for ^{11}B NMR, $\delta(\text{CFCl}_3) = 0$ for ^{19}F NMR]. Most NMR assignments were supported by additional 2D experiments.

FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets. MS – FAB spectrum was obtained JEOL JMS – SX102A using nitrobenzyl alcohol as a matrix. For X-ray crystal structure analysis, data sets were collected with a Bruker SMART APEX CCD diffractometer; full details can be found in the independently deposited crystallography information files (cif). Graphics show thermal ellipsoids at the 30% probability level.

Results of the oligomerization reactions were assessed by GC–MS for reaction mixture composition. Gas chromatography of oligomeric products was conducted on a GC Perkin Elmer equipment, model Clarus 680 with Phenomenex column model Zebron ZB-5MS and MS detector model Clarus SQ8T.

2.2. General procedure for the synthesis of ferrocenylmethallyl nickel complexes with BF_4^- anion (1–3)

1 equivalent of 1-(2-thiazolin-2-yl)-2-(R-thio)-ferrocene ligand (L) and 1 equivalent of AgBF_4 were dissolved in dry dichloromethane (5 mL). The solution was stirred vigorously and a solution of 0.5 equivalent of methallyl nickel chloride dimer in dichloromethane was added. The mixture was stirred for 22 h at room temperature. The resulting suspension was filtered through a pad of celite and the solvent was evaporated *in-vacuo*. After that, pentane (10 mL) was added and the solid was washed and dried *in-vacuo* to give the corresponding nickel complex.

2.2.1. Compound 1

This compound was obtained as a red powder in 81% yield (95 mg; 0.182 mmol). ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 4.93$ (s, 1H, subst Cp, H9), 4.75 (s, 1H, subst Cp, H7), 4.67 (s, 1H, subst Cp, H8), 4.40 (br s, 7H, Cp ring, H16; $-\text{CH}_2-\text{N}$, H2), 3.75 (br s, 1H, $-\text{CH}_2-\text{S}$, H3), 3.46 (br s, 2H, $-\text{CH}_2-\text{S}$, H3, = H_2 -allyl, H17), 3.18 (br s, 2H, = H_2 -allyl, H19), 2.69 (br s, 3H, S- CH_3 , H12), 2.31 (br s, 3H, allyl- CH_3 , H20). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 178.8$ (C5), 86.5 (C6), 76.5 (C10), 76.0 (C9), 73.4 (C7), 73.2 (C8), 72.9 (C16), 70.1 (C2, C18), 65.8 (C17, C19), 31.5 (C3), 27.3 (C12), 23.4 (C20). ^{19}F NMR (376 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = \text{s}$, -151.77 . ^{11}B NMR (128 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = \text{s}$, -0.68 . FT-IR (KBr): $\nu/\text{cm}^{-1} = 2925$, 2848, 1560, 1434, 1241, 1049, 835, 501. HR-MS (FAB +) m/z for $\text{C}_{18}\text{H}_{22}\text{NS}_2\text{FeNi} [\text{M}]^+$: calculated 429.9897, found 429.9894.

2.2.2. Compound 2

This compound was obtained as a red powder in 88% yield (74 mg; 0.134 mmol). ^1H NMR (400 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 4.89$ (s, 1H, subst Cp/ H9), 4.79 (s, 1H, subst Cp, H7), 4.72 (s, 1H, subst Cp, H8), 4.54 (br m, 1H, $-\text{CH}_2-\text{N}$, H2), 4.39–4.43 (m, 6H, $-\text{CH}_2-\text{N}$, H2; Cp ring, H16), 3.73 (br s, 1H, $-\text{CH}_2$ -allyl, H19), 3.45–3.50 (br m, 3H, $-\text{CH}_2-\text{S}$, H3; $-\text{CH}_2$ -allyl, H19), 3.21 (br s, 1H, *i*-Pr-CH, H12), 2.90 (br s,

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