

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

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Abstract

The synthesis of new methallyl-ferrocenyl-thiazoline-nickel complexes [1-(2-thiazolin-2-yl)-2-(R-thio)-ferrocene- κ^2 N,S]-(η^3 -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-(η^3 -(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 η^3 -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.