

N-Arylcyano-beta-diketimate Methallyl Nickel Complexes : Synthesis, Adduct Formation, and Reactivity toward Ethylene

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Abstract

The syntheses and structures of new bis-N-phenyl-4-cyano- β -diketimate, bis-N-phenyl-2-cyano- β -diketimate, N-phenyl-4-cyano-N-phenyl-2-cyano- β -diketimate, N-phenyl-4-cyano-N-2,6-diisopropylphenyl- β -diketimate, N-phenyl-2-cyano-N-2,6-diisopropylphenyl- β -diketimate, and methallyl nickel complexes [L1Ni(η^3 -methallyl)], [L2Ni(η^3 -methallyl)], [L4Ni(η^3 -methallyl)], and [L5Ni(η^3 -methallyl)] from the reaction of deprotonated ligands 1/2, 4/5, and methallylnickel chloride dimer are reported. Subsequent reactions of complexes 6–9 with tris(pentafluorophenyl)boron give rise to new adducts [L1Ni(η^3 -methallyl)]·2B(C6F5)3, [L2Ni(η^3 -methallyl)]·2B(C6F5)3, [L4Ni(η^3 -methallyl)]·B(C6F5)3, and [L5Ni(η^3 -methallyl)]·B(C6F5)3, where B(C6F5)3 is coordinated to the cyano group. New compounds are characterized by NMR, IR, and mass spectrometry techniques, and crystal structures of most compounds are obtained and described. Complexes 6–9, adducts 10–13, and adducts 10–13 with 5 equiv of B(C6F5)3 have been investigated toward ethylene activation. Complexes 6–9 were inactive toward ethylene even at 60 °C, while adducts 10–13 showed reactivity toward ethylene; adding 5 equiv of B(C6F5)3 to adducts 10–13 leads to an increase in reactivity toward ethylene. Adducts 10 and 11 alone and with 5 equiv of B(C6F5)3 catalyze the oligomer formation, while adducts 12 and 13 by the same conditions catalyze the polyethylene formation. Adduct 13 activity is five times higher with respect to 12 at 50 °C and two times higher at 70 °C. The formation of branched moderate molecular weight PE by 12/B(C6F5)3 and 13/B(C6F5)3 is observed..

Keywords

Hydrocarbons, Adducts, Ligands, Polyethylene, Nickel.