



Unsymmetrical pyrazole-based PCN pincer Ni^{II} halides: Reactivity and catalytic activity in ethylene oligomerization

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ABSTRACT

The reactivity of unsymmetrical pyrazole-based PCN pincer Ni(II) halides has been tested in the presence of copper(II) halides as an oxidizing agent as well as with NaBH₄ and LiAlH₄ as a hydride source. While the reaction with CuX₂ resulted into the generation of metastable PCN pincer Ni(III) species, the treatment of (t^{Bu}PCN)NiCl with NaBH₄ led to the preparation and isolation of the borohydride complex (t^{Bu}PCN)Ni(BH₄). Attempts to isolate nickel-hydride species upon treatment of (t^{Bu}PCN)NiCl with either NaBH₄ or LiAlH₄ invariably led to the formation of free PCN(H) ligand and metallic Ni(0) nanoparticles after an *in situ* reductive elimination from the (metastable) hydride derivative (t^{Bu}PCN)NiH. Finally, the halide complexes (pre-activated by MMAO) have been tested as homogeneous catalysts in ethylene oligomerization showing moderate activity (~ 14 × 10³ mol_{C₂H₄}·mol_{Ni}⁻¹·h⁻¹) with the formation of even-numbered olefins (mainly C₄–C₁₀ fractions) as products.

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1. Introduction

The control of the steric and electronic properties of transition metal complexes is one of the main tasks of modern organometallic chemistry [1,2]. Their structural features, reactivity and stability can be deeply tuned and adapted to their downstream application in catalysis through a judicious design of their organic ligands with different donor-atom sets [3]. On this regard, the use of pincer-ligated transition metal complexes as catalysts for organic transformations is steadily growing in recent years [4–11]. Pincer ligands have general formula E¹YE², where E is typically a neutral two-electron donor group, while Y is represented by an anionic

carbon atom of a 2,6-disubstituted aryl moiety [12–16]. Accordingly, they commonly participate to the metal coordination sphere as tridentate monoanionic ligands. PCP type nickel complexes have been firstly reported as an example of nickel pincer systems [17], followed by their NCN counterparts [18–25]. These two types of pincer ligands have shown different influence on the properties of the corresponding organometallics. For example, the use of NCN ligands has allowed to stabilize nickel (III) species [19–21], while nickel complexes with P(E)C(E)P ligands (E = O, S) have been successfully engaged in the activation of small molecules [26–33]. In contrast to these more common symmetric ligands [34,35], recent years have witnessed an increasing interest towards the development of new complexes based on unsymmetrical pincer-type donors (POCN, PNN, PCO, PCS, etc.) [36–49]. PCN ligands are particularly intriguing because their nickel complexes can be easily prepared by direct C–H bond activation at the central aryl moiety and (unlike their PCP analogues) they can stabilize nickel (III) species [50].

Following our interest for this class of organometallics [51,52],

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