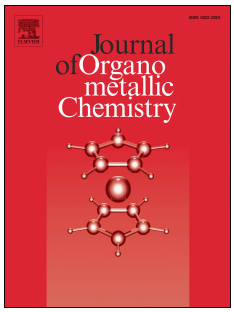
Accepted Manuscript



Indenyl rhodium complexes. Synthesis and catalytic activity in reductive amination using carbon monoxide as a reducing agent

Sofiya A. Runikhina, Mikhail A. Arsenov, Vladimir B. Kharitonov, Elizaveta R. Sovdagarova, Olga Chusova, Yulia V. Nelyubina, Gleb L. Denisov, Dmitry L. Usanov, Denis Chusov, Dmitry A. Loginov

PII: S0022-328X(17)30635-6

DOI: 10.1016/j.jorganchem.2017.11.003

Reference: JOM 20168

To appear in: *Journal of Organometallic Chemistry*

Received Date: 15 August 2017

Revised Date: 2 November 2017

Accepted Date: 2 November 2017

Please cite this article as: S.A. Runikhina, M.A. Arsenov, V.B. Kharitonov, E.R. Sovdagarova, O. Chusova, Y.V. Nelyubina, G.L. Denisov, D.L. Usanov, D. Chusov, D.A. Loginov, Indenyl rhodium complexes. Synthesis and catalytic activity in reductive amination using carbon monoxide as a reducing agent, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.11.003.

Indenyl rhodium complexes. Synthesis and catalytic activity in reductive amination using carbon monoxide as a reducing agent

Sofiya A. Runikhina,[a] Mikhail A. Arsenov,[a] Vladimir B. Kharitonov,[a] Elizaveta R. Sovdagarova,[a] Olga Chusova,[b] Yulia V. Nelyubina,[a] Gleb L. Denisov,[a] Dmitry L. Usanov,[c] Denis Chusov,*[a,b] Dmitry A. Loginov*[a]

[a]A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova st. 28, Moscow 119991, Russian Federation.

[b]Faculty of Science, RUDN University, 6 Miklukho-Maklaya St., Moscow 117198, Russian Federation

[c]c/a: Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138, United States

E-mail: Chusov@ineos.ac.ru or dloginov@ineos.ac.ru

Dedicated to 85th anniversary of Prof. Irina P. Beletskaya in recognition of her great contribution to the development of catalysis with metal complexes.

Abstract: Indenyl-ligated rhodium(III) catalyst $[(\eta^5\text{-indenyl})RhX_2]_n$ (**1**) is reported for the synthesis of alkylated amines via catalytic reductive amination using carbon monoxide as a reducing agent. Water as a solvent was found to be the best media for the reaction. Complex **1** was synthesized via a high-yielding procedure based on the reaction of bis(ethylene) derivative $(\eta^5\text{-indenyl})Rh(C_2H_4)_2$ with iodine.

Introduction

N-alkylated amines are important synthetic intermediates for pharmaceuticals and fine chemicals and considerable efforts have been focused on the development of general and efficient methodologies for the generation of alkylated amines[1]. Some of those include traditional coupling of amines with halogenated molecules, reductive amination of aldehydes or ketones[2–8], as well as hydroamination[9–17] and N-alkylation of alcohols[18–20]. Recently, we described an atom- and step-economical approach to the synthesis of amines without an external hydrogen source[21,22]. This methodology uses carbon monoxide[23–28] as a reducing agent and tolerates various functional groups, including aromatic and aliphatic nitriles[29], esters[30], phenols[31] and cyclopropanes[32], such moieties as Cbz- [31], trifluoroacetamido-[31], N-benzyl-[33], O-benzyl-[22], aromatic fluoro-[29], chloro-[22], bromo-[33] and even aromatic nitro-[31]. Experimental data consistently demonstrated that the presence of water leads to decreased catalytic activity. On the contrary, herein we describe new indenyl rhodium complexes with highest catalytic activity observed in water, which constitutes a desirable feature in the context of economic and ecological impacts.

Results