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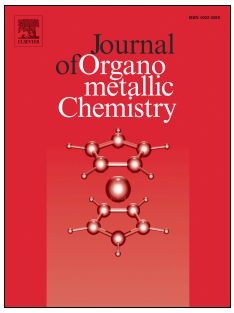

Chemistry of Hume-Rothery inspired organometallics: Selective functionalization of $[M(ZnCp^*)_4(ZnCH_3)_4]$ (M = Ni, Pd, Pt) with terminal alkynes to yield $[M(ZnCp^*)_4(ZnCCSi^iPr)_4]$

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ACCEPTED MANUSCRIPT

Chemistry of Hume-Rothery Inspired Organometallics: Selective Functionalization of $[M(ZnCp^*)_4(ZnCH_3)_4]$ (M = Ni, Pd, Pt) with Terminal Alkynes to yield $[M(ZnCp^*)_4(ZnCCSi^iPr)_4]$.

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Dedicated to Prof. Dr. Dr. h.c. mult. Wolfgang A. Herrmann on the occasion of his 70th birthday.

Abstract

The all-zinc coordinated group-8 metal complexes $[M(ZnCp^*)_4(ZnCCSi(^iPr)_3)_4]$ (M = Ni (**1**), Pd (**2**), Pt (**3**)) were obtained by selective functionalization of the protecting organic ligand shell starting out from the organometallic MZn_8-complexes $[M(ZnCp^*)_4(ZnMe)_4]$. The reaction with excess $HC{\equiv}CSi(^iPr)_3$ leads to a stepwise exchange of the methyl to alkynyl groups under liberation of methane over very long reaction times at elevated temperatures. All complexes **1**-**3** were isolated in pure form an in good yields and were fully characterized by ^1H, ^{13}C NMR as well as by liquid injection field desorption (LIFDI) mass spectrometry. In addition, single crystal structure analysis of **1** and **3** were performed showing that the bimetallic dodecahedral $[MZn_8]$ core of the starting complexes remains intact in the product complexes.

Introduction

Heterometallic complexes and clusters with direct covalent bonds between transition metals and the main group metals Al, Ga, In and Zn have been in the focus of our research for quite some time - since starting the independent academic career at TU Munich in 1990 with the support of Wolfgang A. Herrmann as a most generous mentor.[1] [2] H.-G. Schnöckel's discovery of the compounds ECp* (E = Al,[3a] Ga[3b]) did not only invaluably stimulate main group metal chemistry, but by recognizing the potentially rich coordination chemistry of these compounds bonded to transition metals (TM), we and other groups systematically developed a family of compounds of the general formula $[TM_a(ECp^*)_bL_c]$ (L = CO, CN^tBu, PR_3, etc.). Important early reports were the synthesis and

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