

## Accepted Manuscript

Synthesis and characterisation of cobalt, nickel and copper complexes with tripodal 4N ligands as novel catalysts for the homogeneous partial oxidation of alkanes

Elisa Tordin, Manuela List, Uwe Monkowius, Siegfried Schindler, Günther Knör

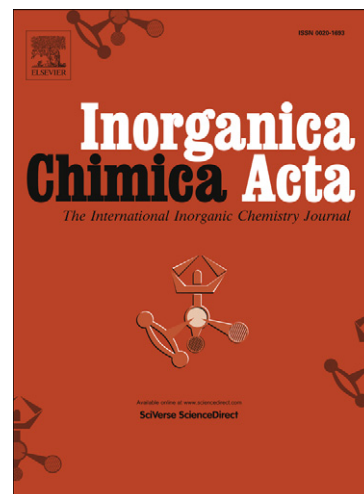
PII: S0020-1693(13)00169-2  
DOI: <http://dx.doi.org/10.1016/j.ica.2013.03.034>  
Reference: ICA 15393

To appear in: *Inorganica Chimica Acta*

Received Date: 16 January 2013  
Revised Date: 19 March 2013  
Accepted Date: 20 March 2013

Please cite this article as: E. Tordin, M. List, U. Monkowius, S. Schindler, G. Knör, Synthesis and characterisation of cobalt, nickel and copper complexes with tripodal 4N ligands as novel catalysts for the homogeneous partial oxidation of alkanes, *Inorganica Chimica Acta* (2013), doi: <http://dx.doi.org/10.1016/j.ica.2013.03.034>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



# Synthesis and characterisation of cobalt, nickel and copper complexes with tripodal 4N ligands as novel catalysts for the homogeneous partial oxidation of alkanes

Elisa Tordin <sup>a</sup>, Manuela List <sup>b</sup>, Uwe Monkowius <sup>a</sup>, Siegfried Schindler <sup>c</sup> and Günther Knör <sup>\*a</sup>

<sup>a</sup> Institut für Anorganische Chemie, Johannes Kepler Universität Linz (JKU), Altenbergerstr. 69, A-4040 Linz, Austria.

<sup>b</sup> Institut für Chemische Technologie Organischer Stoffe, Johannes Kepler Universität Linz (JKU), Altenbergerstr. 69, A-4040 Linz, Austria.

<sup>c</sup> Institut für Anorganische und Analytische Chemie, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany.

\* Corresponding author

E-mail address: E-mail: Guenther.Knoer@jku.at

† Electronic Supplementary Information (ESI) available. CCDC reference numbers 913118 - 913121: For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

## ABSTRACT

Four new compounds of the general formula  $[M(L)(CH_3COO)](PF_6)$ , where L is a tetradentate tripodal ligand such as tris[2-(dimethylamino)ethyl]amine (L1) or (2-aminoethyl)bis(2-pyridylmethyl)amine (L2) and M is Co(II), Ni(II) or Cu(II), have been prepared employing a simple two-step synthesis. The compounds have been characterised by elemental analysis, mass spectroscopy, IR spectroscopy and X-ray diffraction. The catalytic properties of the derivatives containing the aliphatic ligand L1 have been investigated in particular toward the oxidation of cyclohexane and adamantane in the presence of the sacrificial oxidant *m*-CPBA (*meta*-chloroperbenzoic acid). Good TONs and selectivity have been determined for the cobalt and nickel compounds.

**Keywords:** Homogeneous Catalysis, C-H Activation, Alkane Oxidation, Tripodal Ligands, Earth-abundant Elements (Co, Ni, Cu).

## 1 INTRODUCTION

The development of efficient non-precious metal catalysts capable of oxidizing saturated hydrocarbons under mild reaction conditions is a challenging goal in both synthetic and industrial organic chemistry. In nature, redox processes such as the selective hydroxylation of C-H bonds are catalysed at the active sites of iron or copper containing enzymes including methane monooxygenases and proteins of the cytochrome P450 family.<sup>1</sup> First-row transition metal complexes are therefore promising candidates in the search for new homogeneous alkane oxidation catalysts. In this field, tripodal tetradentate ligands, such as tris(2-pyridylmethyl)amine (TPA) and its derivatives,<sup>2</sup> containing both  $\sigma$ -donating tertiary amine and  $\pi$ -accepting pyridyl groups are versatile ligands and have been used for the preparation of various transition-metal complexes containing the group 5-11 elements, lanthanides, and an actinide.<sup>3</sup> These ligands have been employed for the design of structural and/or functional model complexes of mono- and dinuclear metalloenzymes<sup>4</sup> containing different metal sites as dioxygen activation centres. Even though iron complexes might be considered as the most promising candidates for biomimetic C-H bond hydroxylation, several other catalysts for alkane oxidation containing transition metals such as Mn, Co, Cu, Ru and Os instead of iron have also been successfully investigated.<sup>5 6 7 8 9 10</sup> Recently, a few publications showed that nickel chemistry could also be employed as a valid alternative to iron systems.<sup>11</sup> In particular, Itoh *et al.* have demonstrated that the Ni(II) complex  $[Ni(TPA)(CH_3COO)(H_2O)](BPh_4)$  is a very efficient and robust catalyst showing a high alcohol selectivity for alkane hydroxylation with *m*-chloroperbenzoic acid (*m*-CPBA) as an oxidant. These experiments also showed that the total TON (turnover number) of the Ni(II) complex was higher than that of Fe(II), Mn(II) and Co(II) complexes of the same ligand, and the alcohol-product selectivity of the Ni(II) complex was much better than that of the Fe(II) and Mn(II) complexes. Notably, orders of the catalytic activity (TON) (Ni > Fe > Co > Mn) and the alcohol-product selectivity (Co > Ni > Fe > Mn) of the complexes in the TPA-system were similar to the orders of the efficiency and alcohol-product selectivity in the gas phase reaction of methane with the first-row metal-oxo species  $[MO]^+$  (M = Ni, Co, Fe, Mn) reported by Schwarz and co-workers.<sup>10</sup> The same group also pointed out recently that copper-based intermediates of the type  $[CuO\bullet]^+$  with a Cu(II) oxyl radical character show an excellent reactivity and selectivity toward hydrogen atom abstraction from inert hydrocarbons such as methane.<sup>12</sup> Later, Itoh and co-workers isolated a series of Ni(II) complexes of 3N, tripodal 4N and 3NO ligands and studied the effect of ligand and counter anion on the catalytic oxidation of cyclohexane with *m*-CPBA and

Download English Version:

<https://daneshyari.com/en/article/7751740>

Download Persian Version:

<https://daneshyari.com/article/7751740>

[Daneshyari.com](https://daneshyari.com)