

Accepted Manuscript

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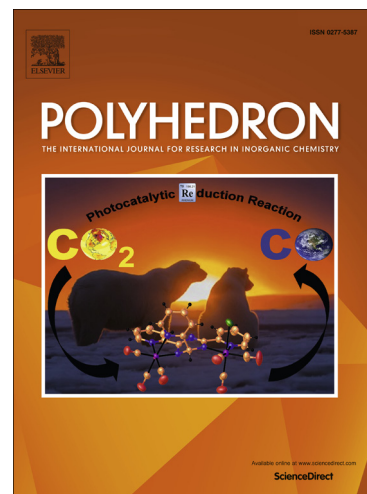
PII: S0277-5387(16)30449-1
DOI: <http://dx.doi.org/10.1016/j.poly.2016.09.021>
Reference: POLY 12209

To appear in: *Polyhedron*

Received Date: 18 April 2016
Revised Date: 10 September 2016
Accepted Date: 11 September 2016

Please cite this article as: C-T. Chen, M.E. Fischer, C. Windsor, I.C. Vei, D.G. Calatayud, M. L. H. Green, S.I. Pascu, Investigations into the reactivity of lithium indenyl with alpha diimines with chlorinated backbones and formation of related functional ligands and metal complexes I, *Polyhedron* (2016), doi: <http://dx.doi.org/10.1016/j.poly.2016.09.021>

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Proofs to Dr S. Pascu

Investigations into the reactivity of lithium indenyl with alpha diimines with chlorinated backbones and formation of related functional ligands and metal complexes¹

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Reaction between lithium indenyl and a chlorine substituted alpha diimine of the form $[\text{Cl}(\text{NPh})_2\text{C}]_2$ unexpectedly yielded the corresponding NH rearranged derivative $[\text{PhN}(\text{H})\text{C}(\text{C}_9\text{H}_6)]_2$ (**1**) rather than the predicted symmetrical α -diimine. This compound **1** was characterised by ¹H NMR, ¹³C{¹H} and mass spectrometry, and additionally by X-ray diffraction. It was found that **1** was the first indene-substituted and symmetric secondary amine which was also highly fluorescent in DMSO. The reactivity of **1** towards simple inorganic and organometallic transition metals precursors based on the MX_2 fragments, where M = Group 10 metals and X = halides or methyl groups, has been investigated. Surprisingly, the reaction with $[\text{PtMe}_2(\text{COD})]$ led to the coupling reaction between the indenyl groups incorporated at the C-C ligand backbone and a new ligand (**2**) was discovered, in an attempt to synthesise the metal-linked diamine. Single crystal X-ray diffraction studies confirm this compound **2** to feature coupled indenyl residues and delocalised C-C bonds in the solid state. Structural authentication by X-ray crystallography showed compound **2** to be a very rare example of flat and extended aromatic organic molecule and mass spectrometry, IR and NMR spectroscopy were carried out to gain further insight into the solid state and solution phase structures. Further experiments to synthesise analogues of $[\text{PhN}(\text{H})\text{C}(\text{Ind})]_2$ aiming to shift a likely equilibrium in favour the imine tautomer, by introducing bulky *ortho* substituents onto the benzene ring (R = Me, *i*Pr) showed the presence of the imine tautomer to be increasingly favoured in ¹H NMR spectra, with an increase in the steric bulk of the *ortho* substituents. However, the enamine tautomer is still observed to a minor extent even with isopropyl substituents and yields of these desired compounds were low on steric grounds.

INTRODUCTION

The discovery of the α -diimines led to the preparation of the Brookhart-type Group 10 catalysts, which constituted a paradigm shift in transition metals catalysis in the last decade of the 20th century [1-7]. Bis(imido)chloride, a versatile ligand incorporating both diimine and dichloride functionalities can be used as a starting material in the synthesis of diimine [8], heterocyclic [9, 10] or oxalamidine [11, 12] ligands when reacted with the suitable alkyl group, dianions or amines [13]. The steric and electronic effects of these versatile ligands are known to be programmable through the variations of the substituents on the nitrogen atoms [11] and to the groups attached to the carbon atoms. The diimine-containing ligands have attracted interest, mainly driven by the discovery that the late transition metal diimine complexes display efficient activity in catalysing the olefin polymerisation reaction [7, 14-24]. Furthermore, the well-known metallocene compounds also display excellent catalytic ability in olefin polymerisation reactions [25]. Therefore, studies to prepare ligands containing the two types of donor groups have been explored [26].

Tuning the electronic and structural properties of the ligand by changing its donor functionalities (in type and / or number), bite angle, bulkiness and chirality, has marked effects on transition metal catalysis [2, 3, 27, 28]. We describe here the synthesis and characterisation of a new class of ligands. These were designed such that they may held two pre-catalytic metallic centres in close proximity to the rigid framework reminiscent of an ansa-metallocene-derivatised bulky diimine. Such system might combine the different advantages of catalytic processes within early and late transition metal systems to generate new catalysts for coupling reactions, of interest for both academic and industrial research [29-31].

In spite of some significant advances in the chemistry of transition metals chemistry over the past decade [7, 25, 32-34], including the reports considered advances in ligand design for heterobimetallic chemistry [35-40], the quest for molecules and materials with

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