



New POCOP-type pincer complexes of Nickel(II)

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ARTICLE INFO

Article history:

Received 1 September 2010

Received in revised form

4 October 2010

Accepted 6 October 2010

Available online 14 October 2010

Keywords:

Pincer complexes

Isonitrile nickel complexes

Cyano nickel complexes

Cyanato nickel complexes

Decomposition of isonitrile

ABSTRACT

The pincer complex $[(\text{POCOP})\text{Ni}(\text{NCMe})][\text{OSO}_2\text{CF}_3]$ (**1**: POCOP = $\{2,6-(i\text{-Pr}_2\text{PO})_2\text{C}_6\text{H}_3\}$) undergoes an acetonitrile substitution reaction in the presence of $\text{CN}(t\text{-Bu})$, KCN, and KOCN to give the new complexes $[(\text{POCOP})\text{Ni}\{\text{CN}(t\text{-Bu})\}][\text{O}_3\text{SCF}_3]$ and $(\text{POCOP})\text{Ni}(\text{X})$ ($\text{X} = \text{CN}$ and NCO). The Ni–CN derivative is also obtained from a gradual decomposition of the Ni–CN($t\text{-Bu}$) derivative, while the aquo derivative $[(\text{POCOP})\text{Ni}(\text{OH}_2)][\text{O}_3\text{SCF}_3]$ was obtained from slow hydrolysis of $(\text{POCOP})\text{Ni}(\text{OSO}_2\text{CF}_3)$. All new complexes have been characterized spectroscopically and by X-ray crystallography. IR and solid state structural data indicate that Ni–L/X interactions are dominated by ligand-to-metal σ -donation; presence of little or no π -backbonding is consistent with the electrophilicity of the cationic fragment $[(\text{POCOP})\text{Ni}]^+$.

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1. Introduction

Interest in pincer complexes has increased dramatically over the past decade as an increasing number of such complexes have been shown to possess unique reactivities that allow them to function as versatile catalysts and advanced materials [1]. In general, robust binding of metals by tridentate pincer ligands results in enhanced reactivity and thermal stability, thereby facilitating difficult reactions or allowing the isolation of rare reaction intermediates featuring unusual oxidation states or bonding patterns [2]. Moreover, the steric and electronic properties of pincer complexes can be modified readily by changes in ligand structure, thus allowing a wide-ranging modulation of chemical reactivities.

Our group has been interested in development of synthetic routes to pincer complexes of nickel and exploring their reactivities. In previous reports, we have described the chemistry of PCP-, POCOP-, and POCN-type complexes of Ni(II) and Ni(III) (Chart 1) [3]. We have also reported on the reactivities of these complexes in catalytic transformations such as Kumada–Corriu coupling, hydroamination and hydroalkoxylation of acrylonitrile derivatives, Kharasch additions to olefins, as well as oligomerization of PhSiH_3 and its addition to styrene [3d,f,g–i,k,l]. In the context of four-coordinate Ni^{II} derivatives, our current investigations are aimed at exploring the structural, bonding, and reactivity features that might arise from combinations of different pincer auxiliary and various

neutral (L) and anionic (X) ligands. We have found, for instance, that *N*-binding of acrylonitrile derivatives $\text{RCH}=\text{C}(\text{R}')\text{CN}$ ($\text{R}, \text{R}' = \text{H}$ or Me) to the cationic fragments $[(\text{PCP})\text{Ni}]^+$ or $[(\text{POCOP})\text{Ni}]^+$ leads to substantial activation (up to 100,000-fold) of the double bond moiety towards amine nucleophiles (Michael additions) [3g–i]. On the other hand, reaction of $\text{Ar}-\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$, or I) with the neutral derivatives $\text{LNi}(\text{alkyl})$ ($\text{L} = \text{PCP}$ or POCOP), generated in-situ from the Ni-halide precursors and Grignard reagents, promote C–C bond coupling reactions (Kumada–Corriu coupling) [3h].

As a continuation of these studies, we are probing bonding and reactivities of neutral and cationic species featuring PCP-, POCOP-, and POCN-type pincer ligands and using insight gathered from such studies to develop interesting catalytic transformations such as nucleophilic additions to olefins and alkynes (e.g., hydroamination and hydroalkoxylation) and cyanation of aryl halides. The present report describes the preparation and characterization of neutral and cationic derivatives $[(\text{POCOP})\text{Ni}(\text{X}/\text{L})]^{n+}$ ($n = 1$: $\text{L} = \text{CN}(t\text{-Bu})$, and OH_2 ; $n = 0$: $\text{X} = \text{CN}$, and NCO).

2. Results and discussion

A previous report has shown that the triflate moiety in $(\text{POCOP})\text{Ni}(\text{OSO}_2\text{CF}_3)$ is very labile and allows this complex to serve as the synthetic equivalent of the coordinatively and electronically unsaturated species $[(\text{POCOP})\text{Ni}]^+$ [3g]. Thus, the neutral triflate derivative can serve as a suitable precursor for the preparation of various neutral and cationic derivatives $[(\text{POCOP})\text{Ni}(\text{X}/\text{L})]^{n+}$. On the other hand, the lability of the triflate moiety renders $(\text{POCOP})\text{Ni}$

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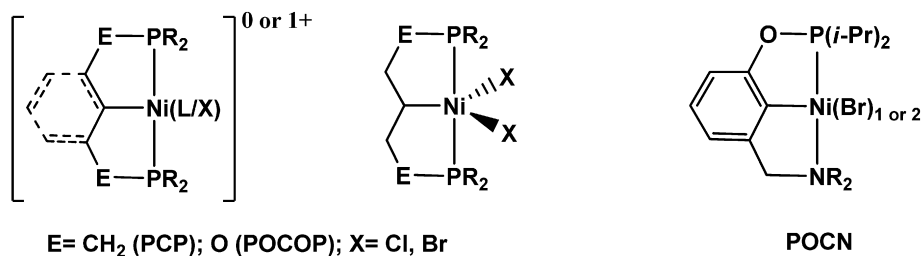


Chart 1.

(OSO₂CF₃) susceptible to side reactions such as hydrolysis. Indeed, samples of this compound often contain variable amounts of the aquo adduct [(POCOP)Ni(OH₂)] [OSO₂CF₃], which tends to complicate both stoichiometric and catalytic applications of the triflate derivative. Since formation of the aquo adduct could not be suppressed completely even when solid samples were stored in dry conditions, we sought more robust analogues that can serve as precursors for the preparation of new derivatives. The cationic acetonitrile adduct [(POCOP)Ni(NCMe)] [OSO₂CF₃], **1**, which is obtained readily by dissolving the triflate derivative in acetonitrile followed by evaporation [3g], is thermally stable and can be stored under ambient conditions for extended periods. This compound serves as a versatile precursor for the preparation of new derivatives of this family of complexes, as described below.

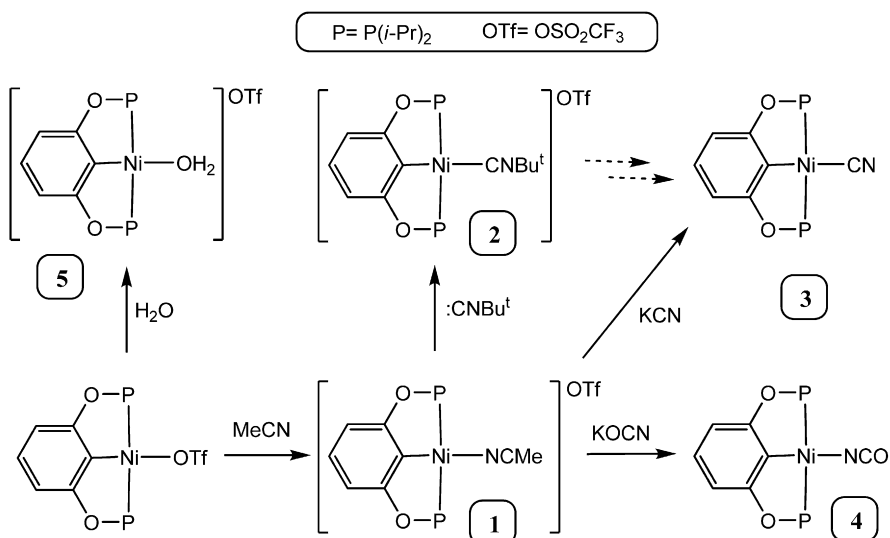
2.1. Preparation of [(POCOP)Ni{CN(*t*-Bu)}] [OSO₂CF₃] and (POCOP)Ni(X) (X = CN, NCO)

Reaction of **1** with two equivalents of CN(*t*-Bu) led to facile substitution of acetonitrile at room temperature and gave the corresponding cationic adduct [(POCOP)Ni{CN(*t*-Bu)}] [OSO₂CF₃], **2**, as a dark yellow powder in 94% yield (Scheme 1). This new derivative is thermally stable in the solid state, but in solution it undergoes a gradual decomposition to a new nickel complex and other, unidentified fragments. We were surprised to find that the product of this decomposition was the neutral Ni–CN species (POCOP)Ni(CN), **3**. This assignment was confirmed by direct synthesis of the Ni–CN derivative from the reaction of **1** with KCN, which allowed us to isolate and fully characterize this new complex. A similarly facile reaction was observed between **1** and potassium cyanate,

which led to the corresponding neutral Ni–NCO derivative **4** as a yellow powder.

A few literature precedents exist for the decomposition of transition metal-coordinated CN(*t*-Bu) ligands to cyanide or other ligands, especially in cationic complexes. The first report of such a transformation, which appeared in 1914 [4], involved the conversion of [Pt{CN(*t*-Bu)}₄]²⁺ to (CN)₂Pt(CN Bu^t)₂. A later report on transalkylation of [(CN)Fe(CNR)₅]⁺ by R'Br raised the possibility of dealkylation in coordinated isocyanide ligands [5], and dealkylation was also inferred in the decomposition of M{CN(*t*-Bu)}_x(CO)_{6-x} (x = 1–3; M = Cr, Mo, or W) [6]. These early reports were somewhat lacking in details as far as characterization of the decomposition products was concerned, but reports appearing in the 1980's and later have provided many concrete examples for isonitrile decomposition, including the following thermal decompositions: [M{CN(*t*-Bu)}₇]²⁺ to [(CN)M{CN(*t*-Bu)}₆]⁺ (M = Mo or W) [7], [M{CN(*t*-Bu)}₆]²⁺ to [(CN)M{CN(*t*-Bu)}₅]⁺ (M = Ru, Os) [8], and [M{CN(*t*-Bu)}₆X]²⁺ to [(CN)M{CN(*t*-Bu)}₅X]⁺ (M = Tc, X = Cl, Br; M = Re, X = Br) [9]. Other cases involved the reaction of [Mo{CN(*t*-Bu)}₇]²⁺ with 2,2'-bipyridine (bpy) to give [Mo{CN(*t*-Bu)}₄(bpy)₂(μ-CN)]³⁺ [10], reaction of RNC with Cp*₂V to give Cp*₂V(CN) (CNR) or with Cp*₂V(CO) to give Cp*₂V(CN) and Cp*₂V(CO)(CN) [11], and thermolysis of Ru(dmpe)(naphthyl)(H) with CN(*t*-Bu) to give (dmpe)Ru(CN)₂ and (dmpe)Ru(CN)(H) (dmpe = bis(dimethylphosphino)ethane) [12].

In the case of cationic complexes bearing CN(*t*-Bu), it is possible that a heterolytic cleavage of the N–(*t*-Bu) bond takes place to generate a cyano group and release the carbonium ion [CMe₃]⁺; the latter decomposes in-situ while the CN moiety remains coordinated to the metal (Scheme 2). We suspect that such a process is



Scheme 1.

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