Short communication

# The cobalt(II) complex of a new tridentate Schiff-base ligand as a catalyst for hydrosilylation of olefins ☆

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## ARTICLE INFO

## ABSTRACT

Condensation of 1-methyl-2-imidazolecarboxaldehyde with 2-(1-methylhydrazinyl)pyridine results in the synthesis of new, tridentate Schiff-base ligand **L**, which readily reacts with CoCl$_2$ to form a monometallic [Co**L**Cl$_2$] complex that, upon reduction, functions as active hydrosilylation catalyst. The ligand and the [Co**L**Cl$_2$] catalyst have been characterized spectroscopically (MS, NMR, FTIR) and by single crystal X-ray diffraction techniques. The results of preliminary catalytic experimentation show that the cobalt complex can induce hydrosilylation and dehydrogenative silylation of olefins, depending upon the hydrosilane substrate used.

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## 1. Introduction

Hydrosilylation is believed to be one of the most straightforward and efficient catalytic processes, important from both academic and industrial points of view, that enables the synthesis of functionalized organosilicon compounds [1]. Since its first description in 1947 by Sommer and coworkers [2] considerable attention and effort has been given towards broadening the scope of the reaction involving the addition of Si-H unit to C-C multiple bonds, carbonyl and imine moieties, with much improved tolerance of various functional groups [1,3]. Of particular importance as substrates are olefins and alkynes due to the fact that the organosilicon products, functionalized silanes or siloxanes and their alkenyl-tailored counterparts, are valuable and attractive scaffolds from the perspective of their further synthetic transformations [4–7] or have direct industrial applications such as in silane-modified polymers.

Meridional tridentate ligands have been found to be useful scaffolds for transition metal ions and studies on catalytic systems containing N,N,N chelating groups involving oxazoline [8–10], (poly)pyridine [11–13] or bis(imino)pyridine [13–15] moieties are frequently performed. Even though the quest for cheaper and environmentally sustainable catalysts progresses [3], much still needs to be done in order to outperform low oxidation state, platinum group metal complexes. These are particularly important for industry, in processes such as the production of organofunctional silanes. [16] For economic reasons, iron is the most popular alternative metal and, there have been numerous reports of its complexes' activity [17],the most recent ones focusing on asymmetric hydrosilylation of alkenes and carbonyl compounds [9, 18]. Conversely, complexes of cobalt are mostly recognized as catalysts for hydrosilylation of alkynes [19–21]and they are likely to promote dehydrogenative silylation when used with alkenes [22]. For this reason, cobalt has not been a focus of recent research [3] and any reports of its use in alkene hydrosilylation were relatively scarce. The most recent ones are the works of Deng et al. utilising silyl-donor-functionalised NHC–cobalt complexes in the hydrosilylation of 1-octene [23], and of Holland et al. on β-diketiminate-supported cobalt catalysts [24]. An excellent review on all recent advances in this field is given by Sun. and Deng [25].

Motivated by such reports of the applications of environmentally benign non-precious-metal-based catalysts in hydrosilylation reactions, we have synthesized a new ligand and its Co(II) complex, so as to utilize the latter for studies of hydrosilylation of alkenes, rarely undertaken due to the abovementioned reasons. It is noteworthy, that iron(0) bis(dinitrogen) complexes with this type of ligand were successfully used by Chirik et al. as hydrosilylation catalysts [14,26,27].
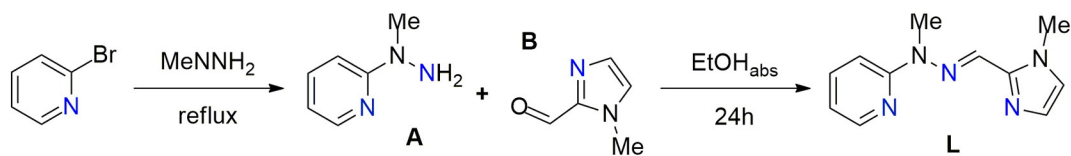
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**Fig. 1.** Synthetic protocol for new Schiff-base ligand **L** utilized in formation of cobalt hydrosilylation catalyst.

## 2. Results and discussion

### 2.1. Synthesis and characterization of the Schiff-base ligand and its cobalt(II) complex

The new Schiff-base scaffold was synthesized *via* a condensation reaction between two building blocks: 2-(1-methylhydrazinyl)pyridine **A** and 1-methyl-2-imidazolecarboxaldehyde **B**. (Fig. 1).

**A** has been recognized as moiety that effectively coordinates variety of transition metal ions, in particular having been applied within helical nanomechanical molecular motors [28,29], metal sensors [30], artificial model DNA nucleobases [31] and for enantiodiscrimination of chiral organic products [32]. Its reaction with **B** enabled us to form an $N_3$ tridentate Schiff-base ligand **L**, with a meridional coordination motif, analogous to the classical ter- or bis(imino)pyridine ligands [3,12,13]. We also envisaged that lack of steric hindrance in the *o*-positions of the pyridine/imidazole terminal coordinating rings should facilitate the overall activity and selectivity of the system, as shown in the works of Chirik and co-workers [13,14]. The new coordinating agent was characterized by spectroscopic and analytical methods, as well as by single crystal X-ray analysis upon transformation to its hydrochloride salt. (**1**).

The ligand cation (**1**) is almost flat and the dihedral angle between the mean planes of rings is 4.98(9)°. (Fig. 2).

The bond length and angles establish the double-bond character of the N8-C9 bond (1.289(2)Å); the protonation site (N14) is confirmed by the localization of the hydrogen atom in the difference Fourier map and the successful refinement of this atom and the bond angles pattern around N14. In the crystal structure – besides the obvious Coulombic interactions between charged species – hydrogen bonds involving the hydration water molecule are also present and play an important role in the determination of the internal crystal architecture. (Fig. S1).

Direct reaction of $CoCl_2 \cdot 6H_2O$ salt with ligand **L** resulted in the synthesis of the monometallic [Co**L**Cl₂](**2**) complex characterized by means of an X-ray structure determination. The Co(II) atoms are five-coordinated by three nitrogen atoms from **L** (meridional binding mode) and two chlorides (Fig. 3). The latter is desirable from the catalytic point of view, bearing in mind the lability and stereochemical

flexibility of Co(II) including the possibility of adopting an octahedral binding mode.

The ligand has an almost flat *cisoidal* conformation, with dihedral angles between the main planes of terminal rings being only 3.8(6)°. The coordination of Co is best described as closer to square-pyramidal (three N atoms and Cl1B in one plane within 0.076(4) Å, Co out of this plane by 0.406(3) Å and Cl1C at apex, 2.698(3) Å) than to trigonal bipyramidal (Co placed almost exactly in the plane formed by Cl1B, Cl1C and N9A atoms, and two remaining N atoms at equal distances from this plane: N1A 1.959(9) Å, N15A -1.965(8) Å). This observation is confirmed by the value of the parameter tau [33], defined as $(\beta-\alpha)/60$ [where beta and alpha are the largest X-Co-Y angles)]. In ideal cases it is equal 0 in regular square-base pyramid, and 1 in regular trigonal bipyramid. In **1** the value of this parameter is 0.35. Relevant geometrical parameters are listed in Table S2. In the crystal structure small voids are filled by disordered (over the twofold axis) methanol molecules, which take part in weak O-H···Cl hydrogen bonds. (Fig. S2).

### 2.2. Catalytic hydrosilylation of alkenes

ESI-MS of a solution of the complex provides no evidence of disproportionation to give a $[CoL_2]^{2+}$ species which would be expected to be catalytically inactive, thus indicating that the potentially active 'open' coordination mode present in the solid state of [Co**L**Cl₂] is retained in the solution. Thus, due to its similarity to the active catalysts described by Chirik et al. [22], the new cobalt complex was expected to act as hydrosilylation catalyst. However, the first attempts to hydrosilylate 1-octene with dimethylphenylsilane under the conditions used by Chirik et al. [22] (neat, RT, 24 h, $[HSiMe_2Ph]:[C_8H_{16}]:[Co] = 1:10:0.02$) did not lead to any changes and neither did heating of the reaction mixture. Considering that the chloride complex might be a catalyst precursor, its activation was performed in accordance with the protocol of Nakazawa et al. [12] using sodium triethylborohydride. We expected that the key to activation might be reduction at the metal centre but a preliminary study using [Co**L**Cl₂] in the presence of $NaBHEt_3$, dimethylphenylsilane and 1-hexene resulted only in isomerisation of the alkene. Seeing some activity, we switched to an olefin unable to isomerise – styrene. The conditions for an effective addition of hydrosilanes to styrene in the presence of the cobalt(II) complex
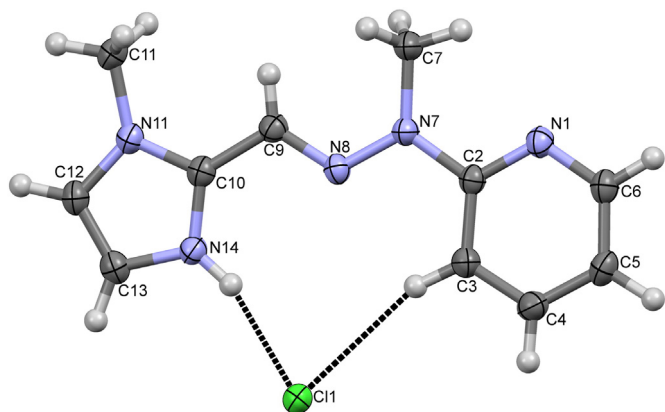


**Fig. 2.** Anisotropic ellipsoid representation of the ligand cation **1**; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.
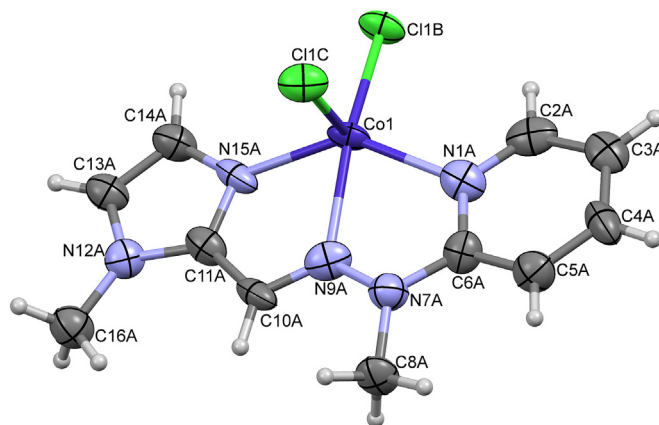


**Fig. 3.** Anisotropic ellipsoid representation of the [Co**L**Cl₂] complex; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.