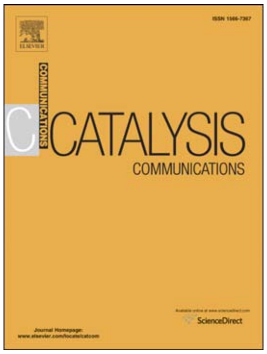

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PII: S1566-7367(16)30056-5
DOI: doi: 10.1016/j.catcom.2016.02.009
Reference: CATCOM 4590

To appear in: *Catalysis Communications*

Received date: 26 September 2015
Revised date: 20 January 2016
Accepted date: 8 February 2016

Please cite this article as: Adam Gorczyński, Maciej Zaranek, Samanta Witomska, Aleksandra Bocian, Artur R. Stefankiewicz, Maciej Kubicki, Violetta Patroniak, Piotr Pawluć, The cobalt(II) complex of a new tridentate Schiff-base ligand as a catalyst for hydrosilylation of olefins, *Catalysis Communications* (2016), doi: 10.1016/j.catcom.2016.02.009

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

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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.

Keywords: Schiff-base; Complex; Cobalt; Hydrosilylation; Catalysis; Dehydrogenative silylation

Dedicated to Professor Janusz Jurczak on the occasion of 75th birthday

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.[26, 27]

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)

Figure 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)

Figure 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**Cl_2](**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.

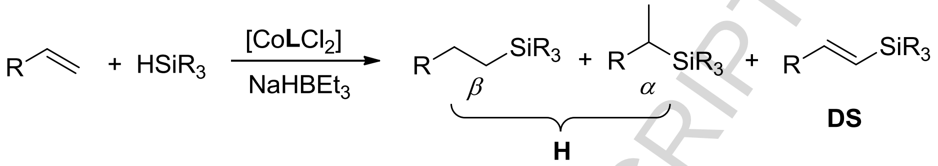
Figure 3

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 (β-α)/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)

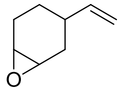
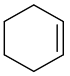
2.2 Catalytic hydrosilylation of alkenes

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**Cl_2] 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, 24h, $[HSiMe_2Ph]$:$[C_8H_{16}]$: [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**Cl_2] 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 [Co**L**Cl_2] were optimized *via* catalytic screening of the substrate conversion, together with evaluation of selectivity by GC and GC-MS methods. In a typical procedure, styrene, hydrosilane and the catalyst (1:1:0.03 molar ratio) were dissolved in dry toluene and heated in a Schlenk bomb flask fitted with a plug valve at 80°C for 30 min. Next, 0.12 equiv. of $NaHBEt_3$ was added and the reaction mixture was again heated for 2-24h at 80°C (Table 1).

Table 1. Results of hydrosilylation of olefins using Co(II)/$NaHBEt_3$ system.[a]



Entry	Olefin	Silane	Time [h]	Silane Conversion [b] (isolated yield) [%]	%H [c](*β*/*α*)	%DS [c]
1.	$PhCH=CH_2$	H_3SiPh	2	82	98 (100/0)	2
2.	$PhCH=CH_2$	$HSiMe_2Ph$	24	79	96(100/0)	4
3	$PhCH=CH_2$	H_2SiPh_2	24	>99 (60)	100 (100/0)	0
4.	$PhCH=CH_2$	$HSiMe(OSiMe_3)_2$	24	34	21(100/0)	79
5.	$PhCH=CH_2$	$(HSiMe_2)_2O$[d]	24	98	1	99[e]
6.	$PhCH=CH_2$	$HSiEt_3$	24	0	-	-
7	3-$MeOC_6H_4CH=CH_2$	H_3SiPh	24	>99 (53)	98 (98/2)	2
8	4-$MeOC_6H_4CH=CH_2$	H_3SiPh	24	34	100 (94/6)	0
9	4-$MeOC_6H_4CH=CH_2$	$HSiMe(OSiMe_3)_2$	24	35	25	75
10	4-$MeC_6H_4CH=CH_2$	H_3SiPh	24	44	100 (94/6)	0
11	4-$MeC_6H_4CH=CH_2$	H_3SiPh	48	65	100 (63/37)	0
12	4-$ClC_6H_4CH=CH_2$	$HSiMe_2Ph$	24	37	89	11
13	4-$ClC_6H_4CH=CH_2$	H_3SiPh	24	>99 (81)	99[f, g]	1
14	4-$BrC_6H_4CH=CH_2$	H_3SiPh	24	>99	98[g, h]	2
15	2,4-$Me_2C_6H_3CH=CH_2$	H_3SiPh	24	46	100 (91/9)	0
16	$PhC(Me)=CH_2$	$HSiMe_2Ph$	24	0	-	-
17	*cis*-PhCH=CHPh	H_3SiPh	24	0	-	-
18	$Me_3SiCH=CH_2$	$HSiMe_2Ph$	24	41	85 (100/0)	15
19	$Me_3SiCH=CH_2$	H_2SiPh_2	24	97	98 (50/50)	2
20	$PhMe_2SiCH=CH_2$	H_3SiPh	24	68	100(90/10)	0

21	$PhMe_2SiCH=CH_2$	$HSiMe_2Ph$	24	>99 (78)	99 (99/1)	1
22	$PhMe_2SiCH=CH_2$	$HSiMe(OSiMe_3)_2$	24	55	54 (99/1)	46
23		$HSiMe_2Ph$	24	32	100[i]	0
24		H_3SiPh	24	21	15 (100/0)	85

[a] *0.5M hydrosilane in toluene, 80 °C, [HSi]:[styrene]:[Co]:[NaHBEt$_3$] = 1:2:0.03:0.12, 0.5 h of preactivation at 80 °C before addition of the borohydride;* [b] *calculated by GC analysis using decane as internal standard;* [c] *based on GC-MS analysis;* [d] *1:4 [HSi]:[styrene] ratio was applied;* [e] *42% of single and 63% of double addition products,* [f] *7% of single and 93% of double addition products;* [g] *single addition products were formed exclusively when equimolar amounts of styrene derivatives were used;* [h] *2% of single and 98% of double addition products;* [i]*mixture of isomers since the substrate consists of a mixture of isomers.*

The results show that [$CoLCl_2$] can be an active catalyst for hydrosilylation (H) and dehydrogenative silylation (DS) of styrene, depending on the hydrosilane substrate. Hydrosilanes with phenyl substituents undergo nearly exclusively hydrosilylation, while hydrosiloxanes give dehydrogenative silylation when a terminal alkene is used. Triethylsilane appears to be unreactive under the given conditions, presumably due to the electronic properties of its alkyl substituents. The products were selectively formed in an *anti-Markovnikov* manner. The structures of the selected reaction products were confirmed by the ^1H NMR spectra of the isolated compounds (see SI). Occurrence of dehydrogenative silylation was accompanied by formation of stoichiometric amounts of ethylbenzene or its derivative corresponding to used styrene detectable by both GC and GC-MS analyses, and no evolution of dihydrogen was observed. To our knowledge, such switching of the reaction product (H/DS), depending on the chosen hydrosilane, has not been seen earlier for alkenes in the presence of a cobalt catalyst. Similar behaviour has been demonstrated in the work of Li Yong et al. with respect to switching of regioselectivity but it was limited to terminal alkynes.[20] The products of dehydrogenative silylation were formed exclusively as *E* isomers. In the case of 1,1,3,3-tetramethyldisiloxane (Table 1, Entry 4), both single and double substitution products were formed (*cf.* Fig. S4). In general, substituted styrenes bearing functional groups such as –Me, –OMe, –Cl, and –Br, irrespective of the substituents' electronic character, reacted with phenyl-substituted silanes to give the corresponding hydrosilylation products (Table 1, entry 7-15). In contrast, reaction of 4-methoxystyrene with 1,1,1,3,5,5,5-heptamethyltrisiloxane in the presence of [Co**L**Cl$_2$] led to dehydrogenative silylation product as the predominant one (Table 1, entry 9). The influence of the temperature and catalyst loading has been investigated for the model hydrosilylation reaction involving styrene and dimethylphenylsilane. A decrease in the catalyst loading to 2 mol% lowered the conversion of $HSiMe_2Ph$ to 54% after 24h. The reaction performed at a lower temperature (50^{o}C) resulted in a decrease in silane conversion to 29% after 24h. An attempt to use 1,4-dioxane and THF as solvents failed, resulting in precipitation of grey metallic cobalt.

Other olefins exhibited a relatively low reactivity in the reaction with silanes. Vinylsilanes underwent a hydrosilylation with phenyl-substituted silanes (Table 1, entry 17-20) with moderate to high conversion (41-99%) to yield mostly hydrosilylation products. Reactions of simple 1-alkenes such as 1-hexene and 1-octene led only to the isomerisation of alkenes and no conversion to the silane was observed. The hydrosilylation of cyclohexene by phenylsilane in the presence of Co/borohydride system yielded predominantly the dehydrogenative silylation product.

To show that the catalyst was actually necessary for the reaction, we performed a blank experiment under similar reaction conditions without cobalt complex. The reaction of styrene with silanes in the presence of $NaHBEt_3$ ([HSi]:[styrene]:[NaHBEt$_3$] = 1:2:0.12) confirmed that cobalt complex was essential to achieve high conversion of silane and to promote the hydrosilylation process. No conversion of 1,1,3,3-tetramethyldisiloxane was observed after 24h but small amounts of hydrosilylation products were detected when $HSiMe_2Ph$ (16% conversion of silane) was used as a reagent. Such observations seem to be consistent with the results reported by Crabtree and co-workers [34] and Nikonov [35], who showed that borohydrides e.g. $LiHBEt_3$ and $NaBH_4$ as well as simple bases can be active catalysts in hydrosilylation of C=O and C=N bonds.

We believe that cobalt hydride complexes are probably the true catalysts but the paramagnetism of [Co**L**Cl_2] precluded NMR experiments to establish the nature of catalytically active system as was possible with related Fe-based systems[12]. Co nanoparticles are not formed under the reaction conditions (no dynamic light scattering was observed in the region of: 0.6 nm-6 μm as established with Zetasizer analyzer), so that catalysis by decomplexated metallic cobalt species may be discounted. The related 'open species' (i.e. those that are susceptible to the effect of external environment) iron(III) [Fe**L**Cl_3] complex was found to be inactive under similar reaction conditions.

Conclusions

The facile synthesis of a new Schiff-base ligand **L** has enabled the preparation of its Co(II) complex that shows activity as a homogeneous catalyst. Preliminary results show that upon *in situ* reduction with $NaBHEt_3$, we are able to isolate the products of hydrosilylation and/or dehydrogenative silylation of alkenes depending upon the nature of the hydrosilane. Our further aim is to broaden the scope of our new system, with respect to both the ligand framework (electronic and steric factors) and the use of other non-precious-metals such as iron or nickel, so as to improve the reactivity and selectivity of investigated process.

Acknowledgements

This research was carried out as a part of a National Science Center project (Grant No. 2011/03/B/ST5/01036). A.G. declares that he is a scholarship holder within the project "Scholarship support for Ph.D. students specializing in majors strategic for Wielkopolska's development", Submeasure 8.2.2 Human Capital Operational Programme, cofinanced by the European Union under the European Social Fund as well as a scholarship holder of The Adam Mickiewicz University Foundation in Poznań, 2014/2015 year edition

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Fig. 1. Synthetic protocol for new Schiff-base ligand **L** utilized in formation of cobalt hydrosilylation catalyst.

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**Cl$_2$] complex; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

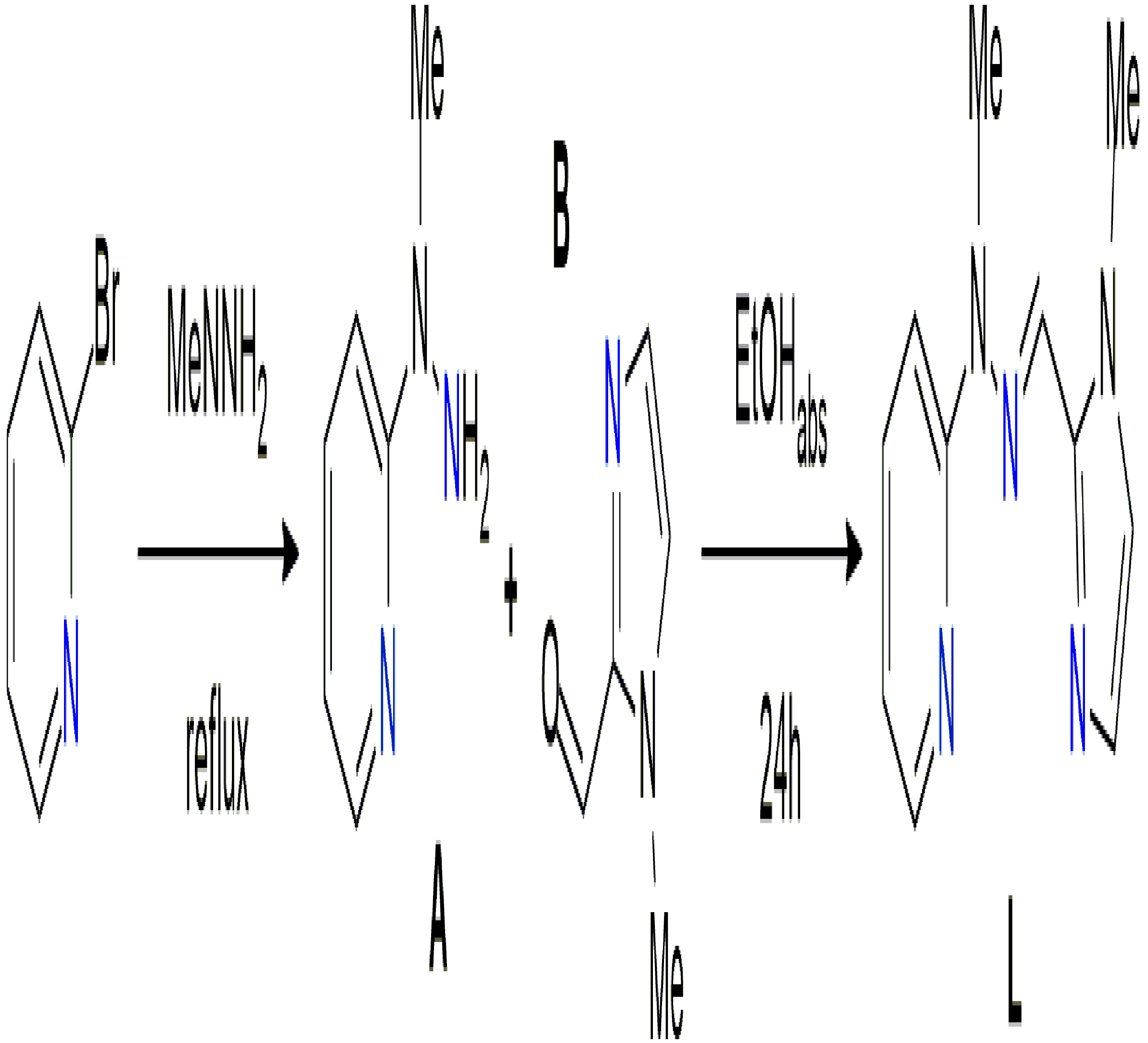


Figure 1

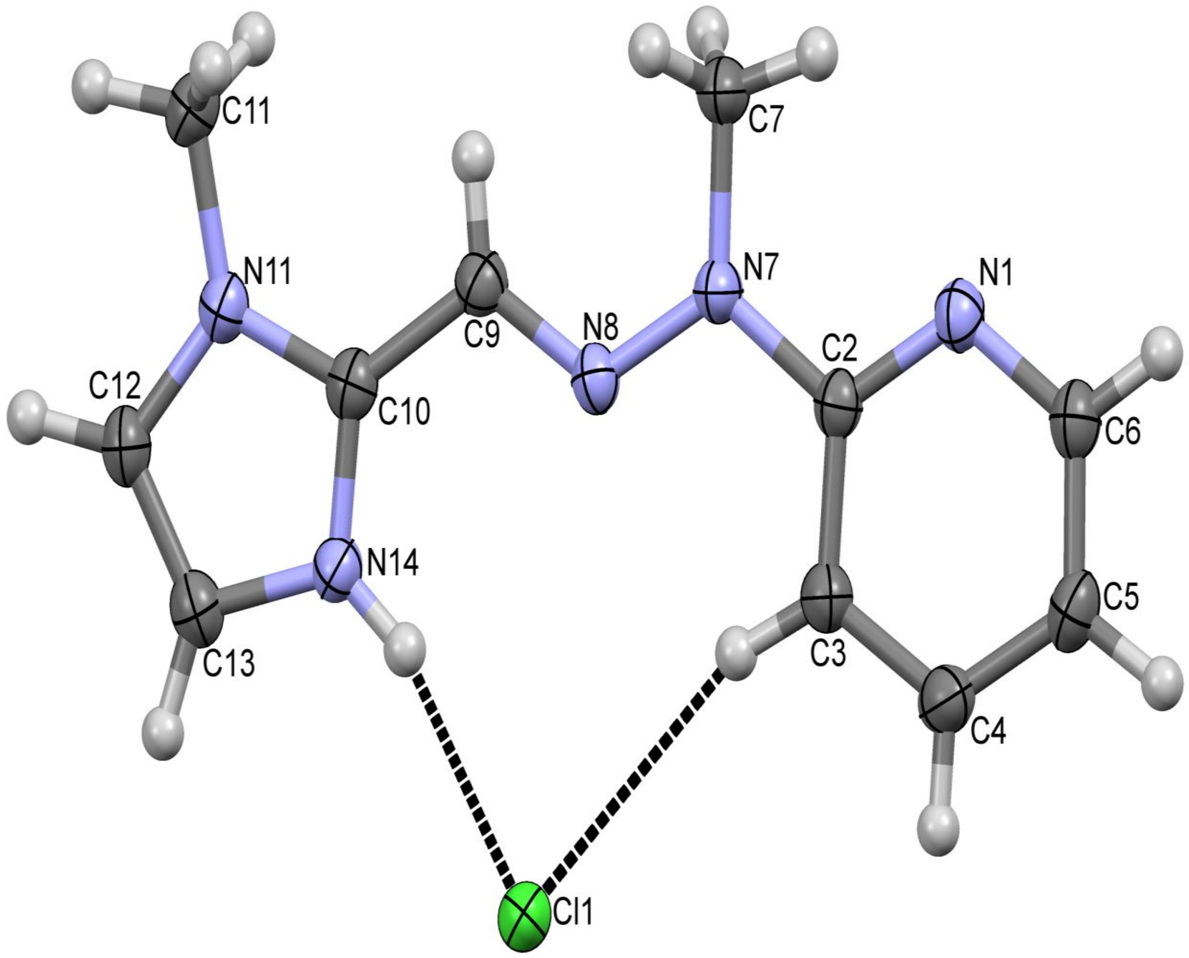
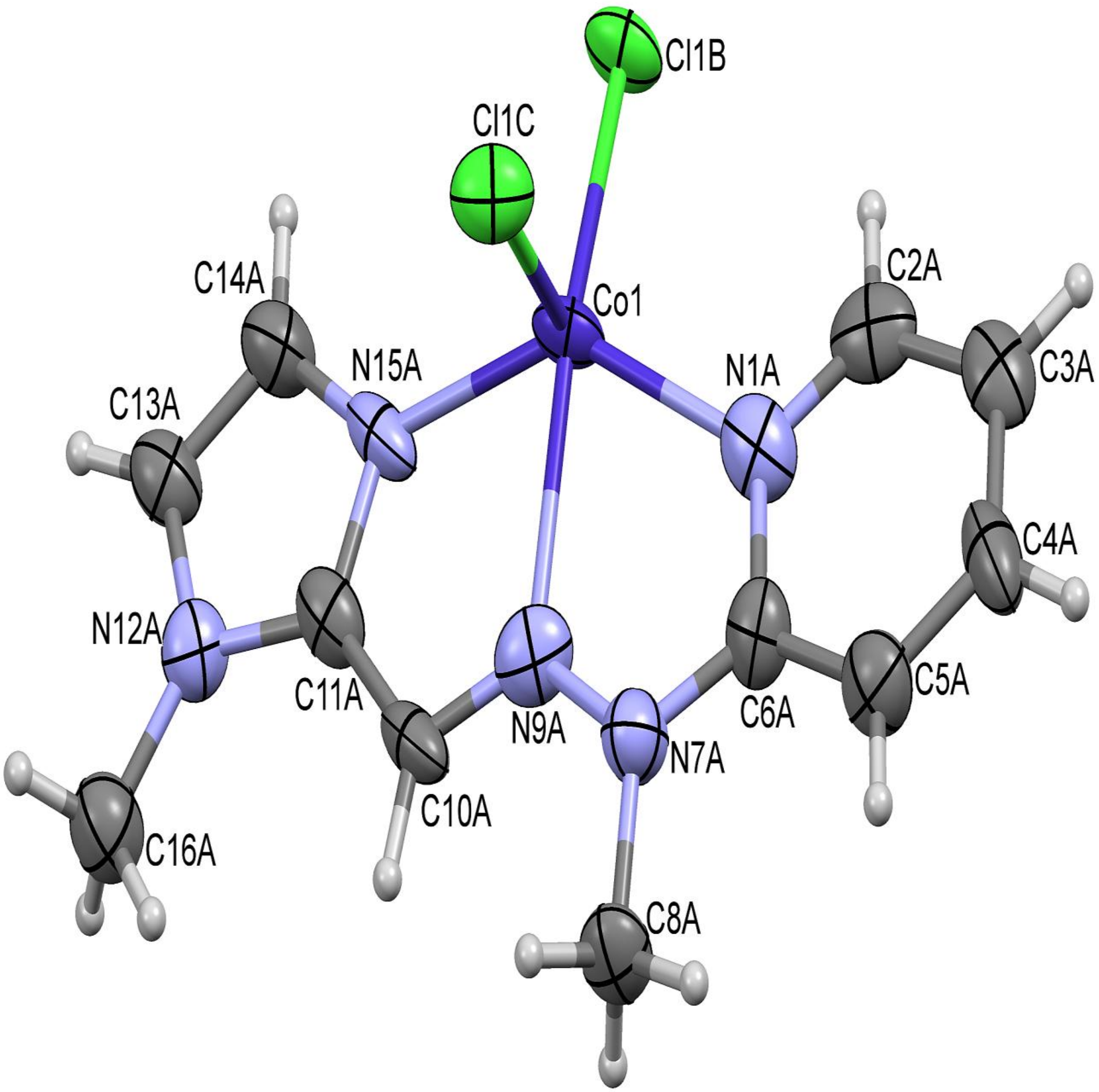


Figure 2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Cl1C
C14A
Co1
C2A
N15A
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C3A
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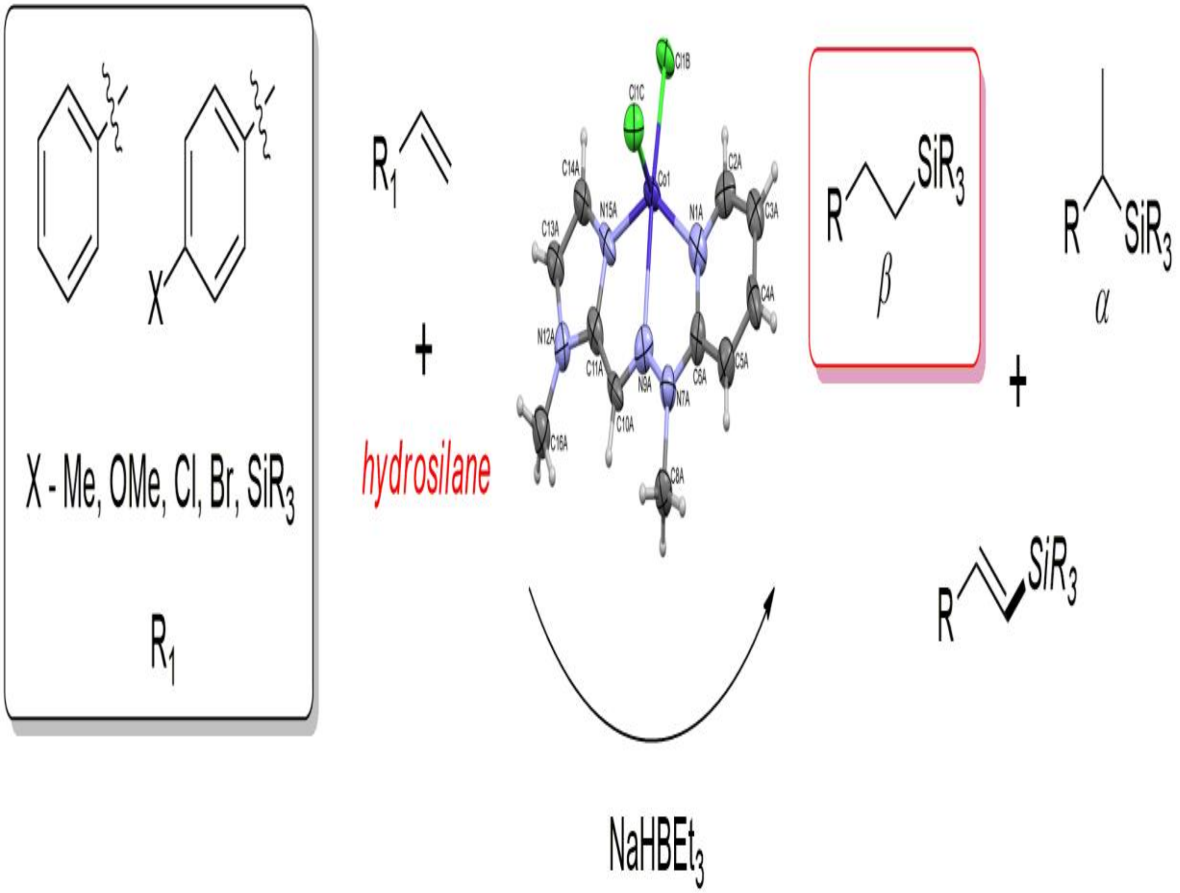
Figure 3



Graphical abstract

Highlights:

- Synthesis of new Schiff-base ligand and its cobalt(II) complex are reported
- Crystallographic structures of ligand **L** and [Co**L**Cl$_2$] complex are presented
- Cobalt complex induces hydrosilylation and dehydrogenative silylation of alkenes