



**HAL**  
open science

# Cobalt Complexes Supported by Phosphinoquinoline Ligands for the Catalyzed Hydrosilylation of Carbonyl Compounds

Pauline Schiltz, Nicolas Casaretto, Audrey Auffrant, Corinne Gosmini

► **To cite this version:**

Pauline Schiltz, Nicolas Casaretto, Audrey Auffrant, Corinne Gosmini. Cobalt Complexes Supported by Phosphinoquinoline Ligands for the Catalyzed Hydrosilylation of Carbonyl Compounds. *Chemistry - A European Journal*, 2022, 28 (32), pp.e202200437. 10.1002/chem.202200437 . hal-03800983

**HAL Id: hal-03800983**

**<https://hal.science/hal-03800983>**

Submitted on 6 Dec 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Cobalt Complexes supported by Phosphinoquinoline Ligands for the Catalyzed Hydrosilylation of Carbonyl Compounds

Pauline Schiltz,<sup>[a]</sup> Nicolas Casaretto,<sup>[a]</sup> Audrey Auffrant,<sup>\*,[a]</sup> and Corinne Gosmini<sup>\*,[a]</sup>

[a] P. Schiltz, Dr. N. Casaretto, Dr. A. Auffrant, Dr. C. Gosmini  
Laboratoire de Chimie Moléculaire (LCM),  
CNRS, Ecole Polytechnique, Institut Polytechnique de Paris  
Route de Saclay, 91120 Palaiseau, France  
E-mail: corinne.gosmini@polytechnique.edu

Supporting information for this article is given via a link at the end of the document.

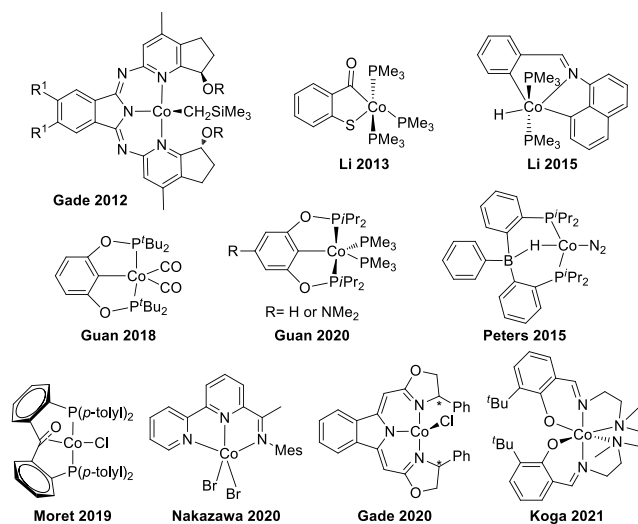
**Abstract:** *P,N* phosphinoquinoline based ligands differing by the nature of the phosphorus substituent (<sup>i</sup>Pr, Ph) were employed to synthesize a series of cobalt(II) complexes (**[LCoBr<sub>2</sub>]**, **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** and **[L'<sub>2</sub>CoBr](PF<sub>6</sub>)**). The latter were obtained in high yield and characterized among others by X-ray analysis and elemental analysis. Complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** showed a very good catalytic activity for the hydrosilylation of various ketones. The catalysis proceeds at a low catalytic loading (1 mol%) with only 1 equivalent of Ph<sub>2</sub>SiH<sub>2</sub> in mild conditions and was efficient with aliphatic or aromatic ketones giving moderate to excellent yields of the corresponding silylated ether.

## Introduction

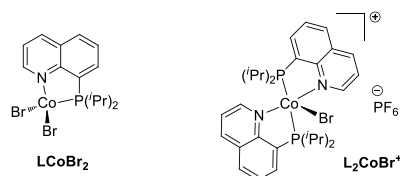
The reduction of double and triple bonds is one of the most useful reaction in organic chemistry. More specifically, the reduction of carbonyls into alcohols is particularly important in the synthesis of pharmaceuticals<sup>[1]</sup> and natural products.<sup>[2]</sup> Various methods have already been developed such as the reduction of carbonyls with metal hydrides,<sup>[3]</sup> the catalytic hydrogenation with molecular hydrogen<sup>[4]</sup> or with hydrogen transfer agents,<sup>[5]</sup> and the use of transition-metal hydride complexes.<sup>[6]</sup> Finally, an alternative strategy is the hydrofunctionalization<sup>[7]</sup> such as the hydrosilylation<sup>[8]</sup> which allows the simultaneously formation of C-H and Si-X (X=C, O, N,...) bonds under mild conditions. The use of non-noble transition metals such as manganese,<sup>[9]</sup> iron,<sup>[10]</sup> cobalt,<sup>[11]</sup> nickel<sup>[12]</sup> and copper<sup>[13]</sup> has become a major challenge these last years.<sup>[14]</sup> These metals are particularly interesting because of their higher abundance,<sup>[15]</sup> their cheaper price and lower toxicity<sup>[16]</sup> compared to noble metals from periods 5 and 6.<sup>[17]</sup> With this in mind, cobalt catalysis has become more and more attractive. It was shown to efficiently catalyze cross-coupling reactions,<sup>[18]</sup> cycloadditions,<sup>[19]</sup> hydrogen transfers<sup>[20]</sup> and the activation of unreactive chemical bonds.<sup>[21]</sup> For many years, the hydrosilylation of multiple bonds such as alkene and alkyne<sup>[22]</sup> via cobalt-catalyzed hydrogen transfer reactions has been well developed. However, cobalt<sup>[23]</sup> or nickel<sup>[23]</sup> catalyzed hydrosilylation of carbonyl remains underdeveloped compared to iron<sup>[24]</sup> and manganese<sup>[25]</sup> catalysis. Focusing on cobalt, more eco-compatible than nickel, the hydrosilylation of ketones was described with *in situ* formed cobalt complexes<sup>[26]</sup> while examples employing well-defined complexes are even rarer.<sup>[27]</sup> The majority

of them feature tridentate ligands with the exception of the (S,C) complex reported by Li in 2013 (Figure 1). Those examples exhibit generally phosphorus- or nitrogen-based ligands. Therefore, we wonder if bidentate Co complexes gathering these two functionalities would be interesting for this catalysis. Thus, this paper reports the synthesis and characterization of novel cobalt complexes bearing bidentate *P,N*-ligands and their performances in the catalytic hydrosilylation of ketones under mild and eco-friendly conditions.

### a) Recently reported Co complexes



### b) This work: Novel Co complexes bearing phosphinoquinoline ligands

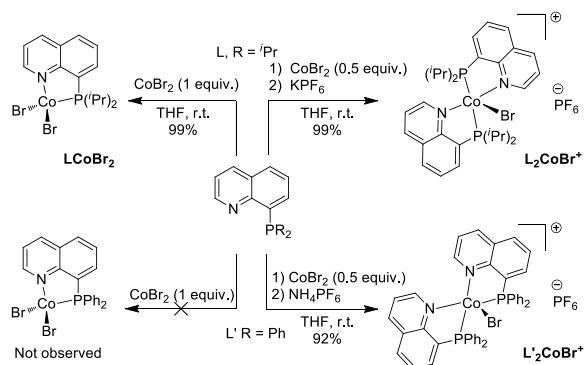


**Figure 1.** Some examples of Co-complexes catalytically active in the hydrosilylation of ketones.

## Results and Discussion

### I. Phosphinoquinoline based cobalt complexes synthesis

The phosphinoquinolines **L** (R = *i*Pr) and **L'** (R = Ph) were synthesized from 8-bromoquinoline as previously described.<sup>[28]</sup> They were reacted with CoBr<sub>2</sub> in THF (Scheme 1), the coordination induced the loss of the <sup>31</sup>P signal corresponding to the ligand. Reaction of **L** with one equivalent of metal precursor gave a neutral complex analyzed as [**L**CoBr<sub>2</sub>], while with half equivalent of cobalt salt a monocationic complex [**L**<sub>2</sub>CoBr](PF<sub>6</sub>) was isolated after salt metathesis. Both complexes were obtained in excellent yields. Because of their paramagnetism, no signal was observed in their <sup>31</sup>P{<sup>1</sup>H}v NMR spectrum, while their <sup>1</sup>H NMR spectrum showed broad signals between -12 and 200 ppm. The same coordination was conducted with the diphenylphosphino ligand **L'**. As with **L**, a monocationic complex was formed upon reaction with half an equivalent of CoBr<sub>2</sub>. [**L'**<sub>2</sub>CoBr](PF<sub>6</sub>) was isolated in 92% after salt metathesis. Its <sup>1</sup>H NMR spectrum did not show any resonance contrary to **L** cobalt complexes. Moreover, the stoichiometric reaction between **L'** and CoBr<sub>2</sub> did not lead to a neutral monoligated complex, rather [**L'**<sub>2</sub>CoBr](PF<sub>6</sub>) forms and some unreacted cobalt salt remained.



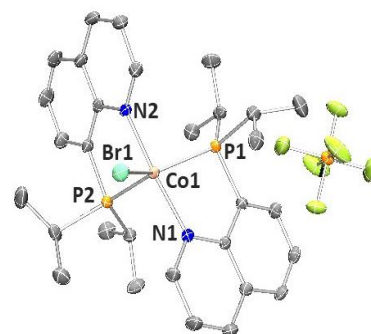
**Scheme 1.** Synthesis of novel cobalt complexes mono-substituted and di-substituted by 8-phosphinoquinoline ligands.

The magnetic moment of these 3 cobalt complexes was measured in solution.<sup>[29]</sup> The values measured for [**L**CoBr<sub>2</sub>], [**L**<sub>2</sub>CoBr](PF<sub>6</sub>), [**L'**<sub>2</sub>CoBr](PF<sub>6</sub>) were respectively 4.53, 2.19, and 1.91 μ<sub>B</sub>. Thus, the neutral cobalt is a high spin Co<sup>II</sup> complex (S=3/2) while the cationic ones are low-spin complexes (S=1/2). In addition, the obtained cobalt complexes were characterized by HR-mass spectroscopy; elemental analysis, and X-ray diffraction analysis. The structure of [**L**CoBr<sub>2</sub>] is shown in Figure 2. It exhibits a tetrahedral geometry around cobalt, all angles around the metal are in the range 108°-117° only N1-Co1-P1 is more acute because of the presence of the chelate ring. All other parameters do not deserve specific comments. The structures of complexes [**L**<sub>2</sub>CoBr](PF<sub>6</sub>) and [**L'**<sub>2</sub>CoBr](PF<sub>6</sub>) are very similar with a distorted square based pyramidal geometry (Figures 3 and 4). In the coordination plane, the angles around the cobalt atoms are slightly more acute than in [**L**CoBr<sub>2</sub>], with the smaller value measured for the P-Co-N angles corresponding to the chelate ligand. Noteworthy, the relative position of the phosphine groups are different in those two bis-ligated complexes: they are located *trans* in [**L**<sub>2</sub>CoBr](PF<sub>6</sub>) and *cis* in [**L'**<sub>2</sub>CoBr](PF<sub>6</sub>). π-π

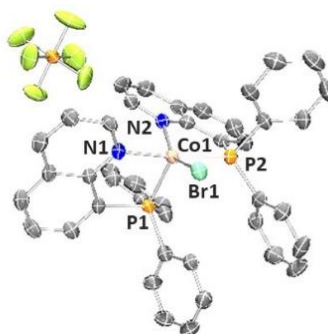
interactions between the aromatic rings may explain their *cis* position. In their absence, *trans* position is preferred probably because of steric hindrance. In both structures the two Co-N and Co-P bond lengths are slightly different. Moreover, the Co-Br bond length is longer with the dialkylphosphine than its diphenyl congener (2.4385(4) vs 2.385(1) Å). This may be ascribed to the better electron-donating properties of the diisopropylphosphine group.



**Figure 2.** ORTEP representation of complex [**L**CoBr<sub>2</sub>] (CCDC 2149630) with 50% ellipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-Br1 2.3813(6), Co1-Br2 2.3499(6), Co1-N1 2.036(2), Co1-P1 2.3489(9); N1-Co1-Br2 111.63(7), N1-Co1-P1 85.72(7), N1-Co1-Br1 108.21(7), Br2-Co1-Br1 115.71(2), Br2-Co1-P1 114.30(3), Br1-Co1-P1 117.05(3).



**Figure 3.** ORTEP representation of complex [**L**<sub>2</sub>CoBr](PF<sub>6</sub>) (CCDC 2149631) with 50% ellipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-Br1 2.4385(4), Co1-N1 1.983(2), Co1-N2 1.938(2), Co1-P1 2.2450(6), Co1-P2 2.2808(6); P1-Co1-N1 84.32(5), P2-Co1-N1 95.85(5), P2-Co1-N2 85.40(5), P1-Co1-N2 90.56(5), N1-Co1-Br1 94.53(5), P1-Co1-Br1 135.53(2), N2-Co1-Br1 89.56(5), P2-Co1-Br1 112.91(2).

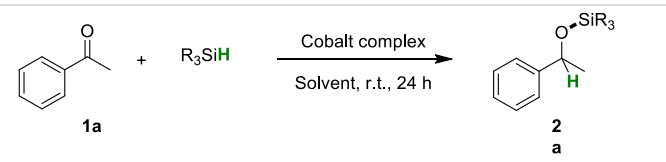


**Figure 4.** ORTEP representation of complex [**L'**<sub>2</sub>CoBr](PF<sub>6</sub>) (CCDC 2149631) with 50% ellipsoid probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-Br1 2.385(1), Co1-N1 1.971(4), Co1-N2 2.027(5), Co1-P1 2.281(2), Co1-P2 2.159(2); N1-Co1-N2 93.6(2), P1-Co1-N1

## II. Catalytic hydrosilylation of ketones

The catalytic activity of these novel Co complexes for the hydrosilylation of carbonyl compounds was investigated, with a special attention to deactivated/ electron-rich ketones. In order to optimize the experimental conditions, the catalytic hydrosilylation of acetophenone (**1a**), as a model compound and diphenylsilane, as the silane source, was first studied in acetonitrile at room temperature. The performances of the synthesized cobalt complexes were compared with those of the CoBr<sub>2</sub> salt (Table 1). We first observed that the use of complex **[LCoBr<sub>2</sub>]** and **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** gave encouraging results, respectively 61% and 78% yield of corresponding silyl ether (Table 1, Entry 1 and 2), whereas complex **[L'<sub>2</sub>CoBr](PF<sub>6</sub>)** or the simple CoBr<sub>2</sub> showed no catalytic activity (Table 1, Entry 3 and 4). Moreover, the CoBr<sub>2</sub> salt in presence of various commercial ligands such as bipyridine, phenanthroline or PCy<sub>3</sub>, showed no better results (see Table S2). When CoBr<sub>2</sub> was used with 1 or 2 equivalents of the synthesized ligand **L** without preformation of the complex, only 27% or 24% yields were observed respectively (Table 1, Entry 5 and 6) instead of 61% or 78% (Table 1, Entry 1 and 2). This result demonstrated the importance to use the well-defined complexes.

**Table 1.** Optimization of the hydrosilylation of acetophenone.



Entry	Silane (1 equiv)	Catalytic system	Solvent	<b>2a</b> (Yield %) <sup>[a]</sup>	Remaining <b>1</b> (%) <sup>[a]</sup>
1	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[LCoBr<sub>2</sub>]</b> 1 mol%	MeCN	61	39
2	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	MeCN	78(95) <sup>[b]</sup>	22(5) <sup>[b]</sup>
3	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L'<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	MeCN	0	100
4	Ph <sub>2</sub> SiH <sub>2</sub>	CoBr <sub>2</sub> 1 mol%	MeCN	0	100
5	Ph <sub>2</sub> SiH <sub>2</sub>	CoBr <sub>2</sub> 1 mol% <b>L</b> 1 mol%	MeCN	27	73
6	Ph <sub>2</sub> SiH <sub>2</sub>	CoBr <sub>2</sub> 1 mol% <b>L</b> 2 mol%	MeCN	24	76
7	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 2 mol%	MeCN	88	12
8	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 5 mol%	MeCN	97	3
9	(EtO) <sub>3</sub> SiH	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	MeCN	58	26
10	PhSiH <sub>3</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	MeCN	10	85
11	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	MeCN	90 <sup>[c]</sup>	10 <sup>[c]</sup>
12	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	THF	6	94
13	Ph <sub>2</sub> SiH <sub>2</sub>	<b>[L<sub>2</sub>CoBr](PF<sub>6</sub>)</b> 1 mol%	Toluene	0	0

Furthermore, various catalytic loadings were used and as expected, yields increased with it (Table 1, Entry 7 and 8): 78% yield was obtained using 1 mol% of complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)**, 88% yield using 2 mol% and 97% yield with 5 mol% of catalyst. Decreasing the catalytic loading to 0.5 mol% lowered the yield to 38% (see Table S3). However, giving the good activity observed with only 1 mol% of complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)**, we decided to pursue with this amount.

These first promising results encouraged us to continue the optimization of the experimental conditions. The nature and the quantity of silane were investigated. Various silanes were employed (see Table S4). Satisfactory results were obtained only with Ph<sub>2</sub>SiH<sub>2</sub> and (EtO)<sub>3</sub>SiH (Table 1, Entry 2 and 9). When the quantity of Ph<sub>2</sub>SiH<sub>2</sub> was increased to 1.5 equivalents, yields improved to 90% (Table 1, Entry 11). Even though better results were observed with a higher quantity of silane, we decided to carry out the reaction with only 1 equivalent of Ph<sub>2</sub>SiH<sub>2</sub> which is eco-friendlier. Finally, the temperature and the solvent were optimized. Similar yields were obtained when the reaction was carried out at room temperature, 40 °C or 80 °C (see Table S5). Furthermore, changing the solvent for THF or toluene did not improve the reaction yield, probably because of the low solubility of complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** in these solvents (Table 1, Entry 12 and 13). Finally, increasing the concentration from 1 M to 2 M improved the yield to 95% (Table 1, Entry 2). To conclude, the best experimental conditions were the use of 1 equivalent of acetophenone **1** with 1 equivalent of Ph<sub>2</sub>SiH<sub>2</sub> in presence of 1 mol% of **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** in MeCN (2 M).

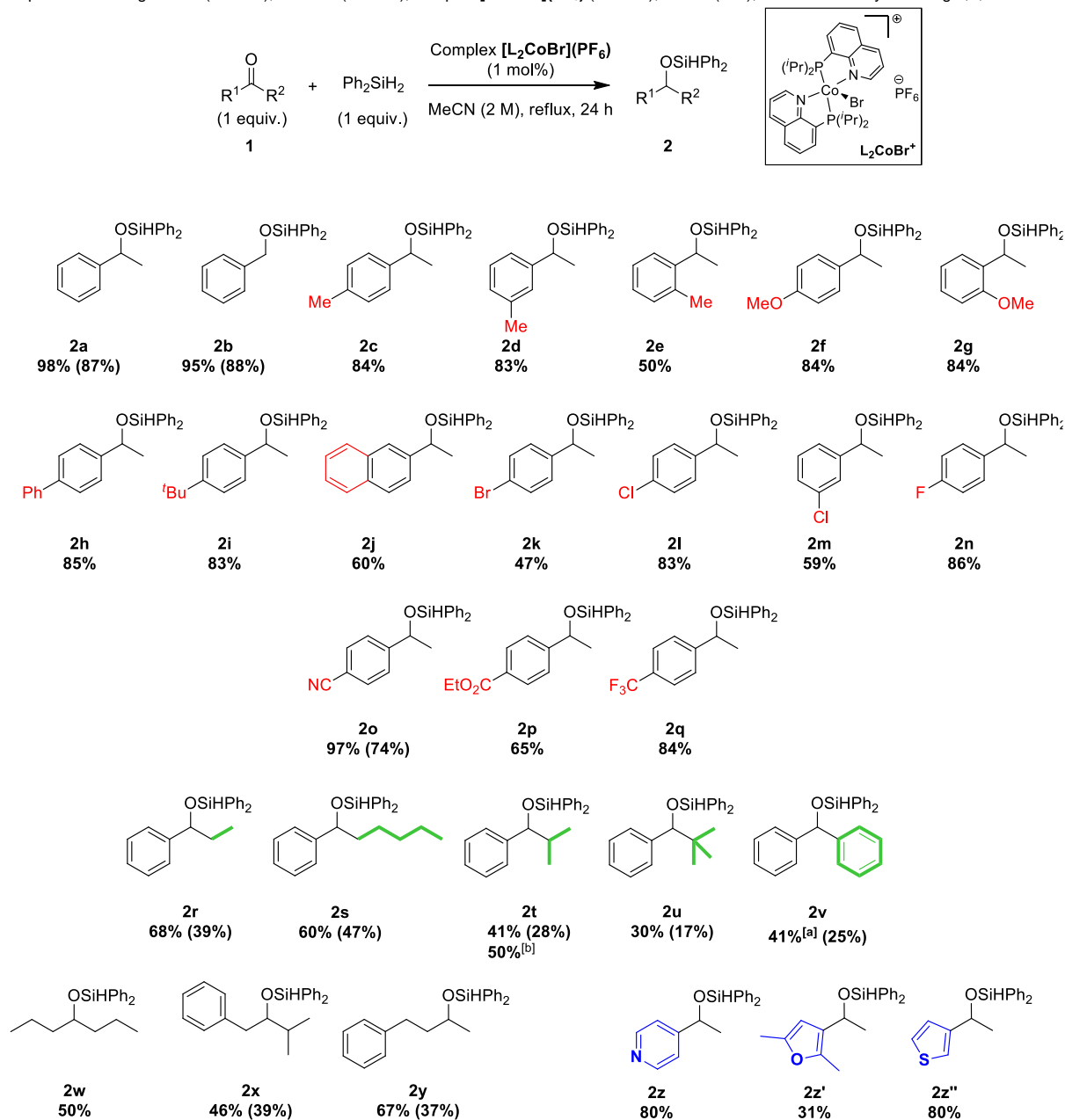
To confirm that the reaction is also feasible with the more reactive aldehyde, benzaldehyde was tested and showed with no surprise an excellent reactivity yielding 95% of product **2b**. With the optimized conditions in hands, this hydrosilylation protocol was applied to variously substituted ketones (Scheme 2). In order to increase the reaction rate, the reaction was carried out at 80 °C without loss of performance. When methyl substituent was in *para* or *meta* position (**2c** and **2d**), excellent yields were obtained, respectively 84% and 83%. However, when methyl group was located in *ortho* position (**2e**), the yield decreased to 50%. This may be the sign of a sensitivity to steric hindrance. But for the methoxy group no change in yield was observed between *o*- and *p*- substituted substrate (84% yield for **2f** and **2g**). These results showed the good tolerance to electron-donating groups. The use of more bulky substituents in *para* position such as a phenyl or a tertbutyl had no influence on the yield (**2h**, 85% and **2i**, 83%). However, naphthalene derivative was obtained in moderate yield (**2j**, 60%). Furthermore, halogen groups were also well tolerated. Moderate to excellent yield were obtained using *p*-chloro (**2l**, 82%), *p*-fluoro (**2n**, 86%), *p*-bromo (**2k**, 47%) and *m*-chloro (**2m**, 59%). Additionally, various electron-withdrawing groups were well tolerated, such as *p*-nitrile (**2o**), *p*-ester (**2p**) and *p*-trifluoromethyl (**2q**).

Hydrosilylation of other alkyl substituted ketones was achieved. With a primary alkyl group on the ketone such as ethyl (**2r**) or hexyl (**2s**) moderate yields were obtained (68% and 60%). However, when the steric hindrance of this substituent increased such as isopropyl (**2t**) or tertbutyl (**2u**), poor yields were obtained. Benzophenone also led to a low conversion (**2v**). These results

confirmed the sensitivity of this reaction to steric hindrance. Furthermore, other dialkyl ketones gave moderate yields (**2w**, **2x** and **2y**). In order to push further the conversion, as a test reaction, hydrosilylation of **1t** was also performed using an excess of silane under different conditions. However, the increasing amount of hydrosilane failed to promote the reactivity, similar yields were obtained. Only the reaction with 3 mol% cobalt catalyst for longer

time at room temperature gave a slightly better yield. Finally, hydrosilylation of heterocyclic containing ketones was attempted. 4-Acetylpyridine and 3-acetylthiophen led to very good yields (80%, **2z** and **2z'**), while the furan analogue gave a moderated one (31%, **2z''**).

Reaction performed using ketone (1 mmol), Ph<sub>2</sub>SiH<sub>2</sub> (1 mmol), complex [L<sub>2</sub>CoBr](PF<sub>6</sub>) (1 mol%), MeCN (2 M), reflux, 1H NMR yield using 1,3,5-trimethoxybenzene

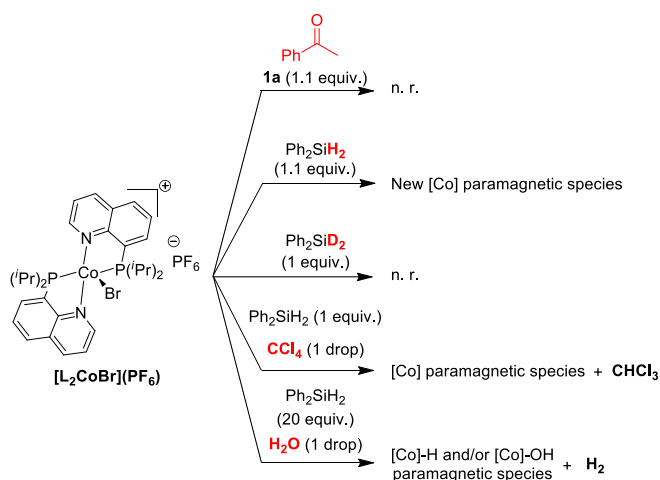


as internal standard. Isolated yields of corresponding alcohol in bracket (4 mmol scale reaction). [a] GC yield, [b] yield obtained after 5 days at room temperature with 3 mol% of catalyst.

**Scheme 2.** Scope of the reaction.

### III. Mechanistic investigations

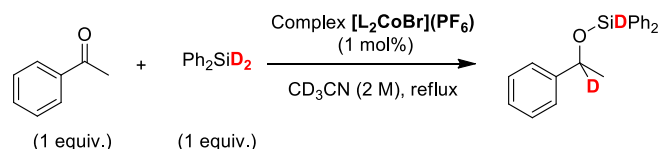
Few experiments were conducted to shed light on the reaction mechanism (Scheme 3). First, we checked if there is an interaction between the ketone and the precatalyst in the absence of silane, no change was observed by  $^1\text{H}$  NMR spectroscopy even after heating (see Figure S30). When the cobalt complex  $[\text{L}_2\text{CoBr}](\text{PF}_6)$  is reacted in an NMR tube with the silane, no reaction occurs at room temperature while a new species forms upon heating. We observed that the reactions in NMR tube are slower because of the absence of stirring (see Figure S31). This explains, in our opinion while it was necessary to heat to observe a change while the catalytic reactions in vials under stirring can proceed at room temperature. Our repeated attempts to grow single crystals from this reaction have failed. Therefore, in order to evidence the formation of a Co-H complex that should be the active species in this reaction, two electrophiles were added.<sup>[30]</sup> Reaction with  $\text{CCl}_4$  led to the formation of chloroform ( $\delta_{\text{H}} = 7.58$  ppm) while the addition of water produced hydrogen ( $\delta_{\text{H}} = 4.57$  ppm) (see Figures S33 and S34). Such results are in agreement with the involvement of a Co-H species. The Co-H complex supported by **L** should present a better hydride donor ability<sup>[31]</sup> than the one formed from  $[\text{L}'_2\text{CoBr}](\text{PF}_6)$ . As M-H complexes involving first row metals are generally less reactive than their noble congeners, the use of electron rich ligands are particularly important to enhance their reactivity.<sup>[32]</sup> However, the observed difference may also result from the difference in geometry of these complexes which may have consequences on the generation of the active species or its reactivity.



Scheme 3. Experiments for the study of mechanism.

The catalytic hydrosilylation of acetophenone was also conducted with  $\text{Ph}_2\text{SiD}_2$  to ascertain the origin of the H atoms. The formation of bis-deuterated silyl ether was observed by  $^1\text{H}$  NMR spectroscopy (Scheme 4). Because of the presence of a deuterium alpha to the methyl, those 3 protons resonate as a singlet ( $\delta = 1.40$  ppm) and not a doublet as in **2a** (see Figure S28). Additionally, no signal corresponding to  $\text{SiHPh}_2$  was observed indicating that the other deuterium is linked to the Si atom and the absence of H/D scrambling during the course of the reaction. The kinetics of the reaction with  $\text{Ph}_2\text{SiD}_2$  differs markedly. First, we did not observe any change in the NMR spectrum of  $[\text{L}_2\text{CoBr}](\text{PF}_6)$  upon mixing with  $\text{Ph}_2\text{SiD}_2$  in an NMR tube, even

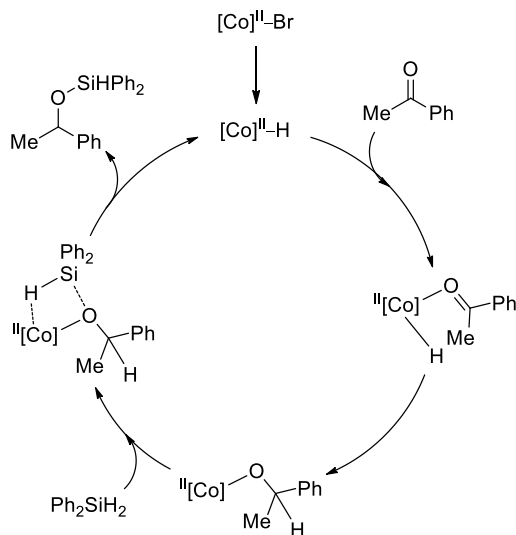
after 24 h heating (Scheme 3, see Figure S32). For the catalytic reaction, 10% conversion was observed with  $\text{Ph}_2\text{SiD}_2$  after 5 h reaction, to compare with 90% conversion using  $\text{Ph}_2\text{SiH}_2$ . Comparison of reaction rates using  $\text{Ph}_2\text{SiH}_2$  and  $\text{Ph}_2\text{SiD}_2$  led to a kinetic isotopic effect (KIE) of 17 ( $k_{\text{H}}/k_{\text{D}}$ ), meaning that H is involved in a rate determining bond forming/breaking step (see Figure S29 and Table S6).<sup>[33]</sup>



Scheme 4. Deuterium-labelling experiment using  $\text{Ph}_2\text{SiD}_2$  with acetophenone.

The catalytic reaction conducted in presence of Hg showed no significant difference since the silyl ether was formed in 80% yield (see Figure S35). This confirms that the reaction is catalysed by the molecular cobalt catalyst.

The experiments conducted are in favour of a classical mechanism involving a cobalt-hydride as the active catalyst. In our case as for others<sup>[26c, 27a, 27f, 27i, j]</sup> the hydrosilylation catalytic reaction works without any hydride additive, therefore the formation of the active Co-H species may result from  $\sigma$ -bonds interchange at the metal center by the so-called sigma-bond metathesis.<sup>[34]</sup> Coordination of the ketone and its insertion into the Co-H bond leads to an alkoxo complex which upon reaction with the silane regenerates the active Co-H complex and releases the silyl ether (Scheme 5). Given the observed isotopic effect, the rate determining step is either the ketone insertion or the regeneration of the active species. The driving force of this last step being the formation of the Si-O bonds.<sup>[24b]</sup> Along the process the oxidation state of the metal should not be modified, suggesting sigma-bond metathesis.



Scheme 5. Proposed catalytic cycle.

## Conclusion

Cobalt complexes featuring phosphinoquinoline based ligands were synthesized in high yield and characterized. Differences in their coordination chemistry and catalytic performances were evidenced with the change in the P-substituent. Cationic bis-liganded diisopropylphosphino complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** presents the best catalytic performances in the hydrosilylation of ketones. The reaction was tolerant to electron-withdrawing or releasing substituents giving satisfactory to high yields of the corresponding silyl ether. The proposed mechanism suggests a cobalt hydride complex as active species. This study shows that bidentate ligands can be an interesting option for cobalt catalysts in that reaction. Nevertheless, the reaction seems to be sensitive to the presence of sterically hindered groups next to the keto group, this may be overcome by the use of a more flexible ligand structure. A direction that we wish to pursue in the future.

## Experimental Section

### General information

All air and moisture sensitive reactions were performed under inert atmosphere using a vacuum line, inert Schlenk techniques (N<sub>2</sub>) and a glove box (Ar, <0.1 ppm H<sub>2</sub>O, <0.1 ppm O<sub>2</sub>) with oven-dried glassware unless otherwise notified. 8-(diisopropylphosphino)quinoline and 8-(diphenylphosphino)quinoline were synthesized following reported procedures.<sup>[28]</sup> All other reagents were used as received from commercial available suppliers (Acros Organics, Alfa Aesar, Fluorochem and Sigma Aldrich) without further purification unless otherwise noticed. THF, CH<sub>2</sub>Cl<sub>2</sub>, pentane, ether and toluene were taken from solvent purification system (MBraun-SPS). Acetonitrile was distilled and degassed using freeze-pump technique. CD<sub>2</sub>Cl<sub>2</sub> was degassed using freeze-pump technique. Flash chromatography was performed using an Isolera Prime Biotage preparative chromatography machine equipped with UV detector and using pre-packaged Biotage silica column of 50 μm particle size. TLC were realized using TCL silica gel plates from Merck (60 F254) and visualized by UV detector and permanganate solution heated as developing agent. NMR spectra were recorded on a Bruker AC-300 SY spectrometer at 300 MHz for <sup>1</sup>H, 120 MHz for <sup>31</sup>P and 75 MHz for <sup>13</sup>C. Solvent peaks were used as internal references for <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm). <sup>31</sup>P{<sup>1</sup>H} NMR spectra are relative to an 85% H<sub>3</sub>PO<sub>4</sub> external reference. Unless otherwise mentioned, NMR spectra were recorded at 300 K. The abbreviations used to indicate the multiplicity of signals are: s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), m (multiple) or a combination of the above. The coupling constants *J* were expressed in hertz. The spectra were analyzed with MestReNova software. Gas chromatography (GC) was performed on a Perichrom PR2100 2317 Series chromatogram equipped with a split mode, capillary injection system, flame ionization detector and an IDBP5 apolar SGE column (25 m x 0.33 mm). Mass spectrometry experiments were performed on a Tims-TOF mass spectrometer (Bruker, France). Electrospray source has been used in positive and negative modes. Samples are prepared in acetonitrile with 0.1 % formic acid at μM concentration. 2 to 10 μL were introduced without separation with Elute UHPLC module (Bruker) at a 100 μL min<sup>-1</sup> flow rate into the interface of the instrument. Capillary and end plate voltages were set at 4.5 kV and 0.5 kV for ESI experiments. Nitrogen was used as the nebulizer and drying gas at 2 bar and 8 L min<sup>-1</sup>, respectively, with a drying temperature of 220 °C for ESI source. Tuning mix (Agilent, France) was used for calibration. The elemental compositions of all ions were determined with the instrument software Data Analysis, the precision of mass measurement was less than 3 ppm. Elemental analyses were performed to the School of Human Sciences, Science Center, London Metropolitan University. X-ray crystallography data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo-κ (λ=0.71069Å) X-ray source and a graphite monochromator. The crystal structures were solved using Shelxtl<sup>[35]</sup> or olex<sup>[36]</sup> and refined using Shelxl-97 or Shelxl-2014.<sup>[35]</sup> ORTEP drawings

were made using ORTEP III<sup>[37]</sup> for Windows or Mercury. Details of crystal data and structure refinements are summarized in table S1.

### General procedures for Co complexes synthesis

**[LCoBr<sub>2</sub>]**: A yellow solution of 8-(diisopropylphosphino)quinoline (540 mg, 2.2 mmol, 1.1 equiv.) in THF (20 mL) was added by cannula to a blue solution of cobalt bromide (437 mg, 2 mmol, 1 equiv.) in THF (20 mL) at room temperature. The mixture was stirred at room temperature overnight. Volatiles were removed under vacuum and the green emerald solid was washed with ether (3x10 mL). After drying, **[LCoBr<sub>2</sub>]** was obtained as a green emerald solid (921 mg, 1.98 mmol, 99%). Single crystals were grown in CH<sub>2</sub>Cl<sub>2</sub>/pentane layering at room temperature and afforded emerald crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 25 °C): δ = 198.87 (s, 1.7H), 120.06 (s, 0.7H), 39.34 (s, 1H), 28.80 (d, *J* = 8.0 Hz, 1H), 17.61 (s, 1H), 14.01 (s, 1H), 9.78 (s, 6H), -6.99 (s, 6H), -11.63 (s, 1H) ppm. HRMS (ESI<sup>+</sup>): calculated for [C<sub>15</sub>H<sub>20</sub>BrCoNP]<sup>+</sup> ([M-Br]<sup>+</sup>): 382.9843; found: 382.9850. Elemental analysis for C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>CoNP: calc (%) C 38.82; H 4.34; N 3.02; found C 38.62; H 4.31; N 2.93. Evans method (C = 0.027 mM, CD<sub>2</sub>Cl<sub>2</sub>) μeff: 4.53 μ<sub>B</sub>, S=3/2.

**[L<sub>2</sub>CoBr](PF<sub>6</sub>)**: A yellow solution of 8-(diisopropylphosphino)quinoline (741 mg, 3.02 mmol, 2 equiv.) in THF (20 mL) was introduced by cannula to a blue solution of cobalt bromide (330 mg, 1 mmol, 1 equiv.) in THF (20 mL) at room temperature. The mixture was stirred at this temperature for 3 days. Volatiles were removed under vacuum and the brown solid was washed with ether (3x10 mL). After drying, KPF<sub>6</sub> (465 mg, 2.53 mmol, 5 equiv.) and CH<sub>2</sub>Cl<sub>2</sub> (30 mL) were introduced. The mixture was stirred at room temperature for 3 days. The mixture was let to settle and filtered. Volatiles were removed under vacuum leading to **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** as a brown solid (657 mg, 0.85 mmol, >99%). Single crystals were grown in CH<sub>2</sub>Cl<sub>2</sub>/pentane layering at room temperature and afforded brown crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, 25 °C): δ = 200.78 (s, 3.4H), 121.69 (s, 0.4H), 39.78 (s, 2H), 29.21 (s, 2H), 17.89 (s, 2H), 14.38 (s, 2H), 9.67 (s, 12H), -7.24 (s, 12H), -11.46 (s, 2H) ppm. <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 120 MHz, 25 °C): δ = -138.85 (quint, *J*<sub>P,F</sub> = 715 Hz) ppm. HRMS (ESI<sup>+</sup>): calculated for [C<sub>30</sub>H<sub>40</sub>CoN<sub>2</sub>P<sub>2</sub>]<sup>+</sup> ([M-2Br]<sup>+</sup>): 382.9843; found: 382.9850. Elemental analysis for C<sub>23</sub>H<sub>18</sub>Br<sub>2</sub>CoNP: calc (%) C 46.53; H 5.21; N 3.62; found C 46.75; H 5.22; N 3.35. Evans method (C = 0.012 mM, CD<sub>2</sub>Cl<sub>2</sub>) μeff: 2.19 μ<sub>B</sub>, S=1/2.

**[L'<sub>2</sub>CoBr](PF<sub>6</sub>)**: Same procedure as for complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** was used. MeCN and NH<sub>4</sub>PF<sub>6</sub> (2.8 mmol, 6.6 equiv.) were used instead for the salt metathesis. **[L'<sub>2</sub>CoBr](PF<sub>6</sub>)** was obtained as a brown solid (352 mg, 0.39 mmol, 92%). Single crystals were grown in CH<sub>2</sub>Cl<sub>2</sub>/pentane layering at room temperature and afforded brown crystals. HRMS (ESI<sup>+</sup>): calculated for [C<sub>42</sub>H<sub>32</sub>BrCoN<sub>2</sub>P<sub>2</sub>]<sup>2+</sup> ([M-Br]<sup>+</sup>): 549.2002; found: 549.1993. Elemental analysis for [C<sub>42</sub>H<sub>32</sub>BrCoN<sub>2</sub>P<sub>2</sub>].PF<sub>6</sub> 2(CH<sub>2</sub>Cl<sub>2</sub>) 0.8(CH<sub>3</sub>CN): calc (%) C 49.16; H 3.45; N 3.52; found C 48.78; H 3.56; N 3.93. Evans method (C = 0.012 mM, CD<sub>2</sub>Cl<sub>2</sub>) μeff: 1.91 μ<sub>B</sub>, S=1/2.

### General procedure for the hydrosilylation of ketones

In the glovebox, Co complex **[L<sub>2</sub>CoBr](PF<sub>6</sub>)** (8 mg, 0.01 mmol, 1 mol%) was introduced in a 20 mL catalytic vial and the vial was capped. Ph<sub>2</sub>SiH<sub>2</sub> (0.19 mL, 1 mmol, 1 equiv.) and ketone derivative (1 mmol, 1 equiv.) were added followed by MeCN (2M). After stirring 24 h at reflux, 1,3,5-trimethoxybenzene (55 mg, 0.33 mmol) was added and volatiles removed under vacuum. Reaction mixture was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C).

## Acknowledgements

The authors thank Dr. Sophie Bourcier for mass spectrometry measurements. Ecole polytechnique and CNRS are acknowledged for financial support.

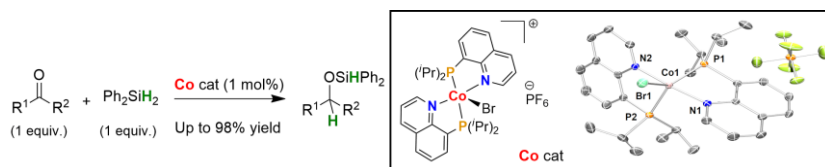
**Keywords:** Cobalt Complexes • Catalysis • Hydrosilylation • *P,N* Ligand • Phosphinoquinoline

- [1] a) E. H. Demont, S. Arpino, R. A. Bit, C. A. Campbell, N. Deeks, S. Desai, S. J. Dowell, P. Gaskin, J. R. J. Gray, L. A. Harrison, A. Haynes, T. D. Heightman, D. S. Holmes, P. G. Humphreys, U. Kumar, M. A. Morse, G. J. Osborne, T. Panchal, K. L. Philpott, S. Taylor, R. Watson, R. Willis, J. Witherington, *J. Med. Chem.* **2011**, *54*, 6724-6733; b) T. F. Schäberle, F. Lohr, A. Schmitz, G. M. König, *Nat. Prod. Rep.* **2014**, *31*, 953-972.
- [2] a) L. Chen, Y. Fang, T. Zhu, Q. Gu, W. Zhu, *J. Nat. Prod.* **2008**, *71*, 66-70; b) R. M. Friedrich, G. K. Friestad, *Nat. Prod. Rep.* **2020**, *37*, 1229-1261.
- [3] a) E. Ashby, J. R. Boone, *J. Am. Chem. Soc.* **1976**, *98*, 5524-5531; b) H. C. Brown, S. Narasimhan, Y. M. Choi, *J. Org. Chem.* **1982**, *47*, 4702-4708.
- [4] a) J. Pritchard, G. A. Filonenko, R. Van Putten, E. J. Hensen, E. A. Pidko, *Chem. Soc. Rev.* **2015**, *44*, 3808-3833; b) S. Sandl, T. M. Maier, N. P. van Leest, S. Kröncke, U. Chakraborty, S. Demeshko, K. Koszinowski, B. de Bruin, F. Meyer, M. Bodensteiner, *ACS Catal.* **2019**, *9*, 7596-7606; c) L. Alig, M. Fritz, S. Schneider, *Chem. Rev.* **2019**, *119*, 2681-2751.
- [5] a) D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621-6686; b) S. Werkmeister, J. Neumann, K. Junge, M. Beller, *Chem. Eur. J.* **2015**, *21*, 12226-12250; c) Y.-Y. Li, S.-L. Yu, W.-Y. Shen, J.-X. Gao, *Acc. Chem. Res.* **2015**, *48*, 2587-2598.
- [6] a) J. M. Simoes, J. Beauchamp, *Chem. Rev.* **1990**, *90*, 629-688; b) A. Maity, T. S. Teets, *Chem. Rev.* **2016**, *116*, 8873-8911; c) R. P. Herrera, *Top. Curr. Chem.* **2016**, *374*, 1-40.
- [7] a) J. Chen, J. Guo, Z. Lu, *Chin. J. Chem.* **2018**, *36*, 1075-1109; b) J. Guo, Z. Cheng, J. Chen, X. Chen, Z. Lu, *Acc. Chem. Res.* **2021**, *54*, 2701-2716.
- [8] a) B. Marciniak, in *Hydrosilylation: a comprehensive review on recent advances*, Springer, Dordrecht, **2008**, p. 408; b) J. Y. Corey, *Chem. Rev.* **2011**, *111*, 863-1071.
- [9] J. B. Sortais, R. Buhaibeh, Y. Canac in *Manganese - Catalyzed Hydrogenation and Hydrogen Transfer Reactions*, Vol. (Ed. J.-B. Sortais), Wiley-VCH, Weinheim, **2021**, pp. 39-66.
- [10] C. Darcel, J.-B. Sortais in *Iron-Catalyzed Reduction and Hydroelementation Reactions*, Vol. (Ed. E. Bauer), Springer, **2015**, pp. 173-216.
- [11] M. Hapke, G. Hilt, in *Cobalt Catalysis in Organic Synthesis: Methods and Reactions*, Wiley - VCH, **2020**, p. 480.
- [12] S. Ogoshi, in *Nickel Catalysis in Organic Synthesis: Methods and Reactions*, Wiley - VCH, Weinheim **2020**, p. 352.
- [13] G. Anilkumar, S. Saranya, in *Copper Catalysis in Organic Synthesis*, Wiley - VCH, **2020**, p. 504.
- [14] a) R. J. K. Gebbink, M.-E. Moret, in *Non-Noble Metal Catalysis: Molecular Approaches and Reactions*, Wiley - VCH, **2019**, p. 616; b) M. C. Haibach, A. R. Ickes, A. M. Wilders, S. Shekhar, *Org. Process Res. Dev.* **2020**, *24*, 2428-2444.
- [15] N. N. Greenwood, A. Earnshaw, in *Chemistry of the Elements 2nd Edition*, Butterworth-Heinemann, **1997**, p. 1364.
- [16] a) P. J. Chirik, *Acc. Chem. Res.* **2015**, *48*, 1687-1695; b) R. H. Morris, *Acc. Chem. Res.* **2015**, *48*, 1494-1502.
- [17] P. Chirik, R. Morris, *Acc. Chem. Res.* **2015**, *48*, 2495-2495.
- [18] a) C. Gosmini, J.-M. Bégouin, A. Moncombe, *Chem. Commun.* **2008**, 3221-3233; b) G. Cahiez, A. Moyeux, *Chem. Rev.* **2010**, *110*, 1435-1462.
- [19] a) P. Gandeepan, C.-H. Cheng, *Acc. Chem. Res.* **2015**, *48*, 1194-1206; b) G. Domínguez, J. Pérez - Castells, *Chem. Eur. J.* **2016**, *22*, 6720-6739; c) A. Anand, P. Singh, V. Kumar, G. Bhargava, *RSC Adv.* **2019**, *9*, 25554-25568.
- [20] a) F. Kallmeier, R. Kempe, *Angew. Chem. Int. Ed.* **2018**, *57*, 46-60; b) W. Ai, R. Zhong, X. Liu, Q. Liu, *Chem. Rev.* **2019**, *119*, 2876-2953.
- [21] a) B. Su, Z.-C. Cao, Z.-J. Shi, *Acc. Chem. Res.* **2015**, *48*, 886-896; b) C. Dorval, M. Tricoire, J.-M. Bégouin, V. Gandon, C. Gosmini, *ACS Catal.* **2020**, *10*, 12819-12827.
- [22] a) J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290-300; b) X. Du, Z. Huang, *ACS Catal.* **2017**, *7*, 1227-1243; c) J. V. Obligation, P. J. Chirik, *Nat. Rev. Chem.* **2018**, *2*, 15-34; d) D. Lu, P. Lu, Z. Lu, *Eur. J. Org. Chem.* **2021**, *2021*, 4861-4864.
- [23] a) B. Royo in *Recent advances in catalytic hydrosilylation of carbonyl groups mediated by well-defined first-row late transition metals*, Vol. 72 (Ed. P. J. Pérez), Elsevier **2019**, pp. 59-102; b) M. Bhunia, P. Sreejyothi, S. K. Mandal, *Coord. Chem. Rev.* **2020**, *405*, 213110.
- [24] a) M. Zhang, A. Zhang, *Appl. Organomet. Chem.* **2010**, *24*, 751-757; b) A. Raya-Baron, P. Ona-Burgos, I. Fernandez, *ACS Catal.* **2019**, *9*, 5400-5417.
- [25] R. J. Trovitch, *Acc. Chem. Res.* **2017**, *50*, 2842-2852.
- [26] See for examples: a) H. Brunner, F. Prester, *J. Organomet. Chem.* **1991**, *414*, 401-409; b) T. Inagaki, L. T. Phong, A. Furuta, J. i. Ito, H. Nishiyama, *Chem. Eur. J.* **2010**, *16*, 3090-3096; c) F. Yu, X.-C. Zhang, F.-F. Wu, J.-N. Zhou, W. Fang, J. Wu, A. S. Chan, *Org. Biomol. Chem.* **2011**, *9*, 5652-5654; d) T. Dombay, C. Helleu, C. Darcel, J. B. Sortais, *Adv. Synth. Catal.* **2013**, *355*, 3358-3362; e) X. Chen, Z. Lu, *Org. Lett.* **2016**, *18*, 4658-4661; f) T. Kumon, S. A. B. M. Sari, S. Yamada, T. Konno, *J. Fluor. Chem.* **2018**, *206*, 8-18; g) V. Rysak, A. Descamps-Mandine, P. Simon, F. Blanchard, L. Burylo, M. Trentesaux, M. Vandewalle, V. Collière, F. Agbossou-Niedercorn, C. Michon, *Catal. Sci. Technol.* **2018**, *8*, 3504-3512.
- [27] a) D. s. e. C. Sauer, H. Wadeh, L. H. Gade, *Inorg. Chem.* **2012**, *51*, 12948-12958; b) Q. Niu, H. Sun, X. Li, H.-F. Klein, U. Flörke, *Organometallics* **2013**, *32*, 5235-5238; c) H. Zhou, H. Sun, S. Zhang, X. Li, *Organometallics* **2015**, *34*, 1479-1486; d) M. A. Nesbit, D. L. Suess, J. C. Peters, *Organometallics* **2015**, *34*, 4741-4752; e) Y. Li, J. A. Krause, H. Guan, *Organometallics* **2018**, *37*, 2147-2158; f) D. G. Verhoeven, J. Kwakernaak, M. A. Van Wiggen, M. Lutz, M. E. Moret, *Eur. J. Inorg. Chem.* **2019**, *2019*, 660; g) K. Kobayashi, D. Taguchi, T. Moriuchi, H. Nakazawa, *ChemCatChem* **2020**, *12*, 736-739; h) Y. Li, J. A. Krause, H. Guan, *Organometallics* **2020**, *39*, 3721-3730; i) C. K. Blasius, H. Wadeh, L. H. Gade, *Eur. J. Inorg. Chem.* **2020**, *2020*, 2335-2342; j) K. Matsubara, T. Mitsuyama, S. Shin, M. Hori, R. Ishikawa, Y. Koga, *Organometallics* **2021**, *40*, 1379-1387.
- [28] D. Basu, R. Gilbert-Wilson, D. L. Gray, T. B. Rauchfuss, A. K. Dash, *Organometallics* **2018**, *37*, 2760-2768.
- [29] a) E. M. Schubert, *J. Chem. Educ.* **1992**, *69*, 62; b) C. Piguet, *J. Chem. Educ.* **1997**, *74*, 815.
- [30] a) For an example of previous use of water see ref [26]; For an example using a chloroalkane see: b) G. Zhang, B. L. Scott, S. K. Hanson, *Angew. Chem. Int. Ed.* **2012**, *51*, 12102-12106.
- [31] A. Kumar, S. Semwal, J. Choudhury, *Chem. Eur. J.* **2021**, *27*, 5842-5857.
- [32] M. S. Jeletic, E. B. Hulley, M. L. Helm, M. T. Mock, A. M. Appel, E. S. Wiedner, J. C. Linehan, *ACS Catal.* **2017**, *7*, 6008-6017.
- [33] a) N. Schneider, M. Finger, C. Haferkemper, S. Bellemin - Laponnaz, P. Hofmann, L. H. Gade, *Chem. Eur. J.* **2009**, *15*, 11515-11529; b) T. Bleith, L. H. Gade, *J. Am. Chem. Soc.* **2016**, *138*, 4972-4983.
- [34] R. N. Perutz, S. Sabo - Etienne, *Angew. Chem. Int. Ed.* **2007**, *46*, 2578-2592.
- [35] G. M. Sheldrick, *Acta Crystallogr. A: Found. Adv.* **2015**, *71*, 3-8.
- [36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
- [37] L. Farrugia in *ORTEP-3 program*, Department of Chemistry, University of Glasgow, **2001**.



---

## Entry for the Table of Contents



Phosphinoquinoline cobalt(II) complexes were used for the hydrosilylation of ketones. The diisopropylphosphino containing bisliganded complex was the most efficient allowing the transformation of variously substituted aliphatic or aromatic ketones at low catalyst loading and under mild conditions. The involvement of a Co-H complex as the active species was experimentally ascertained.

Institute and/or researcher Twitter usernames: