The final publication is available at

https://doi.org/10.1002/ejic.201801068

Additional Information

EurJIC

European Journal of Inorganic Chemistry

Accepted Article

FULL PAPER

WILEY-VCH

Cobalt catalysts for alkene hydrosilylation under aerobic conditions without dry solvents or additives.

Silvia Gutiérrez-Tarriño[a], Patricia Concepción[a] and Pascual Oña-Burgos*[a]

Abstract: Alkene hydrosilylation is typically performed with Pt catalysts, but inexpensive base-metal catalysts would be preferred. Here, we report a simple method for the use of air stable cobalt catalysts for anti-Markovnikov alkene hydrosilylation that can be used under aerobic conditions without dry solvents or additives. These catalysts can be generated from low-cost commercially available materials. In addition, these catalysts possess good catalytic ability for both hydrosilanes and hydroalcoxysilanes. Finally, a mechanistic study demonstrates the silane and the catalyst generates a Co-H species in the course of the reaction, which has been observed by in-situ Raman spectroscopy.

Introduction

Hydrosilylation of alkenes catalyzed by transition metals is a well-known reaction to provide organosilanes due to two main advantages: straightforward and atom-economic. In the industry, organosilanes are employed as precursor of alcohols or as building blocks for the production of silicon-based polymers.[1] Catalysts based on platinum, due to their effectiveness and high selectivity, are the highlighted ones for hydrosilylation of alkenes.[2] However, the main disadvantage of these catalysts is its high and volatile price, which is directly correlated with its shortage in the Earth´s crust. In addition, platinum extraction has associated a high environmental footprint.[3] All these points have inspired the discovery of a new generation of catalysts based on earth-abundant transition metals.

Then, catalysts based on abundant first-road transition metals such as Fe,[4-11] Co,[4,6,12–14] and Ni[15] have been developed for the catalytic hydrosilylation of alkenes with a good catalytic ability. However, these catalysts are limited to silanes such as $PhSiH_3$ or Ph_2SiH_2; in fact, only a few studies have achieved alkene hydrosilylation with silanes containing polar functional groups such as hydroalcoxysilanes and hydrosiloxanes. In this sense, catalysts which are useful for both $PhSiH_3$ and Ph_2SiH_2 are often inactive or less efficient for hydrosilylation using hydrosiloxanes. Moreover, another limitation of these catalysts is their high sensitivity toward air and moisture, which implies a careful preparation and usage. Thus, the active species can be generated in situ in order to face this disadvantage, by treating stable well-defined Fe(II) or Co(II) coordination compounds with an organometallic co-catalyst like $EtMgBr$, $BuLi$, $NaEt_3BH$ or $NaOtBu$.[16-18] However, this strategy

implies three main disadvantages: 1) these activators are also moisture sensitive; 2) these activators are stronger nucleophiles, which could potentially provide the cleave the Si−O bonds in the alkoxysilanes and siloxanes; 3) the Li, Mg, or B metal from the activator could be incorporated in the final product. All of these are potential risk, which are more remarkable in the case of the synthesis of silicone polymers. In summary, a desirable catalyst should be air and moisture stable and operate under aerobic conditions without requiring co-catalysts.

Although, Nagashima[19a] and Chirik[19b] groups have reported the employment of air-stable cobalt catalysts in this process they have never used aerobic conditions and non-dry solvents. Herein the catalytic hydrosilylation of alkenes under aerobic conditions and without dry solvents or additives is shown, where the development of air stable cobalt-aquo complexes is pivotal. The developed catalysts are based on terpyridine (tpy) ligand and commercial cobalt precursors. Cobalt(II) carboxylates have been selected as cobalt precursors because these are stable and inexpensive sources of cobalt and offer structural diversity.

Results and Discussion

We used cobalt(II) acetate tetrahydrate (**1a**), cobalt(II) acetylacetonate hydrate (**2a**), cobalt(II) naphthenate (10% Co) (**3a**) and cobalt(II) octanate (8% Co) (**4a**) as precursors. For catalyst screening, 4-vinylcyclohexene was reacted with $PhSiH_3$ as the hydrosilane at room temperature under optimized conditions: 0.1% mol cobalt precursor and 0.1 % mol of tpy ligand in THF (see Table S1 in SI). In all cases, the anti-Markovnikov product was exclusively observed.

Table 1. Evaluation of cobalt precatalysts for the Hydrosilylation of 4-vinylcyclohexene with $PhSiH_3$.[a]

Entry	Co(II) precursor	Time (min)	Conversion (%)[b]	TOF(min^{-1})
1	**1a**	240	72	7.00[c]
2	**2a**	240	99	21.66[d]
3	**3a**	180	99	22.33[d]
4	**4a**	240	99	12.10[d]
5	**1a**[e]	240	92	8.33[c]
6	**2a**[e]	240	90	7.88[c]

[a] All reactions were performed on 0.89 mmol scale using a 1:1 silane-olefin mixture under aerobic conditions, where the mixture Co-precursors/tpy was previously prepared. [b] Determined by ^1H NMR analysis of the crude reaction mixture. [c] Calculated after 60 min from the beginning of the reaction. [d] TOF calculated after 30 min from the beginning of the reaction. [e] Employing isolated species. The reaction without the presence of the tpy ligand does NOT take place.

For the evaluation of cobalt precursors, we monitored the of the catalysis by ^1H NMR (Figure 2). A catalyst loading of 0.1%

[a]   Miss. S. Gutiérrez Tarriño, Dr. P. Concepción and Dr. P. Oña-Burgos
       Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain.
       http://itq.upv-csic.es/

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

WILEY-VCH

mol in THF was used and the reactions were monitored at several times during four hours. This allowed us to calculate TOF after 30 min. Also, this reaction was studied by NMR *in situ* (Figure S1 and S2), where both results are consistent. In general, all precursors have shown high TOFs values (entries 1-4, table 1), but precursor **3a** (entry 3) is the most active for this reaction (TOF = 22.33 min^{-1}).
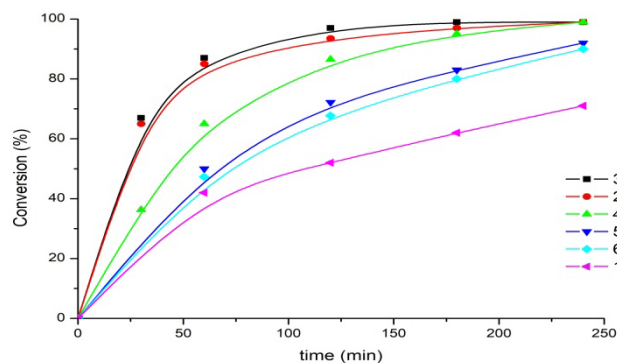

Figure 1. Kinetic study of 4-vinylciclohexene hydrosilylation with PhSiH$_3$ for the evaluation of cobalt precatalysts. The numbers in the figure correspond to entries in Table 1.

In order to elucidate the structure of the active species the reaction between the four cobalt precursors **1a-4a** and the tpy ligand was studied, where the formation of the complexes **1b-4b** is expected (Scheme 1) based on the employed stoichiometry metal to ligand.

Scheme 1. General illustration of the synthesis of cobalt (II) complexes **1b-4b**.
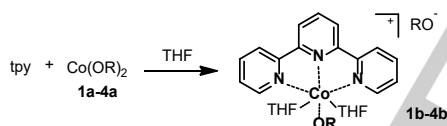
The reaction between cobalt precursor **1a** and tpy yielded mostly the complex **1b** with a small amount of the homoleptic complex, which was determined by NMR despite its paramagnetism (see Figure S3 in the SI).[20] On the other hand, the reaction with cobalt precursor **2a** affords exclusively the homoleptic complex **2c**,(**2b** was not observed). The NMR spectra obtained with from the reaction of tpy with precursors **3a** and **4a** show also the formation of complexes **3b** and **4b**, but the presence of homoleptic complex is also detected. These data suggest that acetylacetonate is more labile than carboxylates under these conditions. These data obtained by NMR spectroscopy were consistent with UV-Vis studies (see Figures S8-S12) where the band at 350 cm^{-1} clearly supports the coordination of the tpy ligand to the metal. [21] In this sense, the differences between the proposed structure and homoleptic ones are associated to the molar absorbtivity, which will be bigger for the homoleptic complexes. The amount of precursor employed for 2a was a 25% respect to the others three.

On the other hand, the reactions with precursors **3a** and **4a** cannot be studied using ESI-MS and X-ray techniques since the naphthenate and otanate precursors are a mixture of several isomers. In addition, these are provided in solution in mineral oils, but at the same time both represent the main cobalt species industrially used, for instance in alkane oxidation. In this sense, ESI-MS analysis for the reactions with **1a** and **2a** are also consistent with the proposed structures by the other techniques (see figures S4-S7).

Moreover, EPR spectroscopy at *rt* and 77 K was employed to characterize the reaction with precursors **1a** and **2a** (see Figure S13), where both reactions show a unique signal with *S*=1/2. The observed *g* value (*g* =2.09) is consistent with a low spin homoleptic complex [Co(tpy)$_2$]$^{2+}$,[22] but not with the heteroleptic complexes, **1b** or **2b** which are expected to be *S*=3/2 species. However, Co (II) species with *S*=3/2 could be EPR silent.[23] Then, quantitative EPR[24] was employing in order to measure the formation of homoleptic species with both precursors. The reaction with precursor **1a** provided a signal with an intensity corresponding to only 1.3% of cobalt this implying that the homoleptic species is not preferred. On the other hand, this experiment with precursor **2a** showed 9% of the S=1/2 signal, which is consistent with the exclusive formation of homoleptic complex. In fact, solution magnetic moment measurements (method of Evans[25] in MeOD-d$_4$, 23 °C, Figure S14) on **1b** and **2c** established an average effective magnetic susceptibility (μ$_{eff}$) of 3.7 and 1.7, respectively, consistent with 3 and 1 unpaired electrons, respectively. Therefore **1b** is a high-spin Co(II) electronic configuration, while **2c** is a low-spin Co(II) electronic configuration.

Crystallization of **1b** revealed a structure consistent with the molecular formula, [Co(OAc)(H$_2$O)$_2$(tpy)]OAc, (by single crystal XRD) whereby the THF ligands are replaced with water.[26a-b] In addition, the homoleptic complex **2c** was confirmed by single crystal x-ray diffraction.[26a,c] Thus, under non-inert atmosphere, the acetylacetonate anions from the reaction forming **2c** are replaced by chloride anions (derived from CHCl$_3$). The X-ray study revealed that both **1b** and **2c** complexes are six-coordinate cobalt complexes. The first one, [Co(OAc)(H$_2$O)$_2$(tpy)]OAc, shows that carboxylate ligand adopts κ^{1}binding mode with two water molecules coordinated to the metal centre. While in the second one, [Co(tpy)$_2$]Cl$_2$·6H$_2$O, the six-nitrogens of the two ligands are coordinated to the metal centre, fact which could make this complex less active as catalyst since the metal centre is less accessible than for complex **1b**. In addition, it is observed that the central nitrogen of the tpy ligand in **1b** is closer to the Co(II) compared to the other two nitrogens of this ligand, as observed in the case of complex **2c** (see tables S4 and S5).
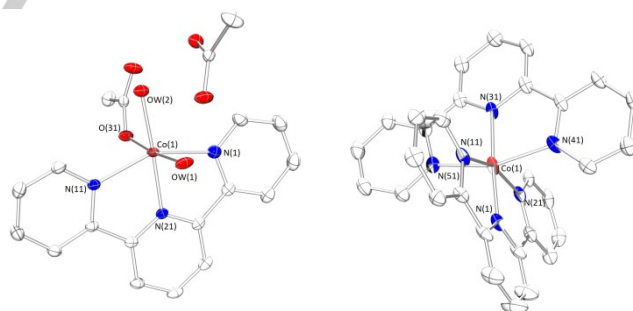

Figure 2. Molecular structures of complexes [Co(OAc)(H$_2$O)$_2$(tpy)]OAc, **1b** (left) and [Co(tpy)$_2$]Cl$_2$·6H$_2$O, **2c** (right). Thermal ellipsoids shown at 30% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Gray = C, blue = N, red = O, brown = Co. Chloride anions of complex **2c** are also omitted for clarity.

In addition, the isolated homoleptic complex **2c** (entry 6) has also shown activity for this reaction, although its TOF value is smaller than the freshly prepared (entry 2). This fact supports that one tpy ligand is enough to activate cobalt precursors, and that the formation of homoleptic species have a negative influence in the process and reaction rate. Finally, respect to the catalytic activity for precatalyst **1b**, freshly and isolated (both lightly soluble in the solvent, which is a technical limitation), the TOF values are in the same order but the efficiency is higher for the isolated one. The discovery of highly active selective and
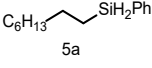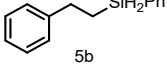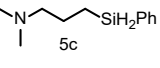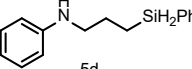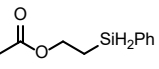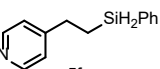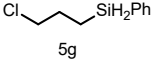
FULL PAPER

bench-stable cobalt precatalysts enabled exploration of the scope of the alkene substrates in the hydrosilylation reaction.

As presented in Table 2, freshly prepared cobalt precursors **2a**, **3a** and **4a** with tpy were effective for the hydrosilylation of a range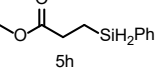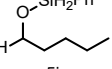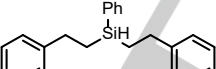 of terminal alkenes bearing functional groups using $PhSiH_3$. High to excellent conversions were obtained between 0.5 and 8h of reaction time at 23 °C using 0.1% mol of the cobalt precatalyst.

Table 2. Functionalized hydrosilylation products from $PhSiH_3$ using the cobalt precursors **2a**, **3a** and **4a** with tpy.[a,b]
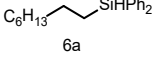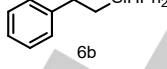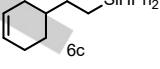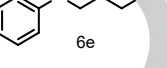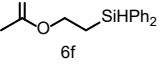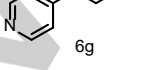

C6H13 ~ SiH2Ph 5a	~ SiH2Ph 5b	N(Me) ~ SiH2Ph 5c
2b. 93% (6h) 3b. > 99% (3h) 4b. > 99% (20h)	> 99% (3h)[c]	> 99% (3h)
(H)N-Ph ~ SiH2Ph 5d	O=C-O ~ SiH2Ph 5e	pyridyl ~ SiH2Ph 5f
2b. 97% (1h) 3b. >99% (1h) 4b. 95% (1h)	2b. 99% (8h) 3b. 99% (8h) 4b. 96% (8h)	2b. <1% (16h) 3b. >99% (3h) 4b. >99% (3h)
Cl ~ SiH2Ph 5g	O=C ~ SiH2Ph 5h	O-SiH2Ph 5i
< 1% (16h)	2b. 25% (0.5h)[c] 3b. >99% (0.5h)[c] 4b. 88% (0.5h)[c]	<1 % (16h)[d]
O-SiH2Ph / H 5j	Ph-Si-H (phenethyl) 5k	
<1% (16h)[d]	>99% (3h)[e]	

[a]All reactions were performed on 0.89 mmol scale using a 1:1 silane-olefin mixture under aerobic conditions. [b]Conversions were determined by ^1H NMR analysis of the crude reaction mixture. [c]Addition of silane at 0°C. [d]Reaction performed at 50°C. [e]Reaction performed using a 2:1 silane-olefin mixture.

Notable findings include tolerance of tertiary and secondary amine functional groups (5c, 5d). Styrene a challenging substrate for regioselective hydrosilylation[27] yielded exclusively the anti-Markovnikov product (5b). On the other hand, oxygen-based functional groups such as esters (5e, 5h) were also well-tolerated by the cobalt precatalyst. In addition, these precatalysts are chemoselective: they are not reactive with carbonyl groups such as aldehydes (5k), ketones (5j), or internal alkenes. Finally, a controlled reaction provides mono- or bi-functionalized products 5b or 5l when 1 or 2 equivalents of styrene are used, respectively.

Reaction of these olefins with the secondary silane Ph_2SiH_2 was also performed using **2a**, **3a** and **4a** cobalt precursors with tpy in order to give, after a few hours, moderate to high conversions with an excellent selectivity at room temperature (Table 3). In this study with Ph_2SiH_2 the regio- and chemo-selectivity has also been studied with successful results for the several alkenes used, although the reaction rates are slower than in the case of $PhSiH_3$.

Table 3. Functionalized hydrosilylation products from Ph_2SiH_2 using the cobalt precursors **2a**, **3a** and **4a** with tpy.[a,b]
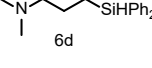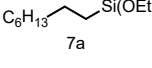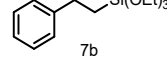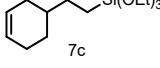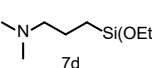

C6H13 ~ SiHPh2 6a	~ SiHPh2 6b	cyclohexenyl ~ SiHPh2 6c
2b. 60% (6h) 3b. >99% (3h) 4b. >99% (3h)	2b. >99%(3h) 3b. 97% (3h) 4b. 91% (3h)	2b. >99% (16h) 3b. >99% (16h) 4b. 40% (16h)
N(Me) ~ SiHPh2 6d	(H)N-Ph ~ SiHPh2 6e	O=C-O ~ SiHPh2 6f
2b. 70% (1h) 3b. 90% (1h) 4b. 80% (1h)	2b. >99% (8h) 3b.90% (8h) 4b. 82% (8h)	<1% (16h)
pyridyl ~ SiHPh2 6g		
2b. <1% (8h) 3b. > 99% (8h) 4b. 89% (8h)		

[a]All reactions were performed on 0.89 mmol scale using a 1:1 silane-olefin mixture under aerobic conditions. [b]Conversions were determined by ^1H NMR analysis of the crude reaction mixture.

On the other hand, catalysts useful for $PhSiH_3$ or Ph_2SiH_2 often are inactive or less efficient for hydrosilylation using hydroalkoxysilanes or hydrosiloxanes. Therefore, we evaluated these precatalysts in the activation of this type of silanes. In this way, we have used $(EtO)_3SiH$ to evaluate the activity of precursors **2a**, **3a** and **4a** with tpy (Table 4). The reactions were performed at 50°C to activate the $(EtO)_3SiH$. In this case, cobalt naphthenate has shown the best results for the desired products for the selected alkenes. However, this reaction with this catalyst has been more sensitive to the presence of some functional groups in the alkenes such as esters and alcohols. The addition of thrietoxysilane to 1-octene was conducted on 10g scale as the resulting $^noctylsilane$ product is manufactured annually on >6000 ton scale and finds commercial applications in coatings such as weatherproofing for masonry products, metal oxides and glass.[19b] The conversion for this 10g scale reaction was >99% in three hours.
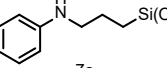
Table 4. Functionalized hydrosilylation products from $(EtO)_3SiH$ using the cobalt precursors **2a**, **3a** and **4a** with tpy.[a,b]

C6H13 ~ Si(OEt)3 7a	~ Si(OEt)3 7b	cyclohexenyl ~ Si(OEt)3 7c
2b. >99% (1h) 3b. >99% (10 min) 4b. >99% (1h)	2b. 66% (3h) 3b. >99% (3h) 4b. 94% (3h)	2b. 79% (6h) 3b. >99% (6h) 4b. 85% (6h)
N(Me) ~ Si(OEt)3 7d	(H)N-Ph ~ Si(OEt)3 7e	
>99% (6h)	>99% (6h)	

[a]All reactions were performed on 0.89 mmol scale using a 1:1 silane-olefin mixture under aerobic conditions. [b]Conversions were determined by ^1H NMR analysis of the crude reaction mixture.

FULL PAPER

In addition, pentamethyldisiloxane has also been used to evaluate the pre-catalysts mentioned (Table 5). In this case 80°C were required to activate this hydrosiloxane to provide product 8a with excellent yield in 8 hours. This reaction is the first step in the formation of silicone fluid crosslinking.

Table 5. Functionalized hydrosilylation product from $(CH_3)_3SiOSi(CH_3)_2H$ using the cobalt precursors **2a**, **3a** and **4a** with tpy.[a,b]

$$\text{R} + (CH_3)_3SiOSiH(CH_3)_2 \xrightarrow[\text{THF, 80ºC}]{\text{0.1 mol% [Co]/tpy}} \text{R} \diagdown Si(CH_3)_2OSi(CH_3)_3$$
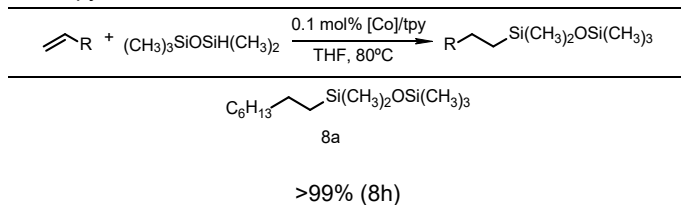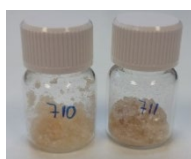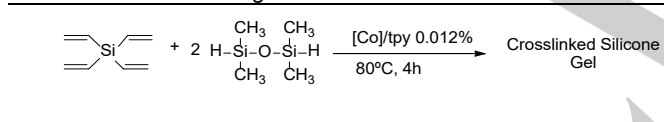
$$C_6H_{13} \diagdown Si(CH_3)_2OSi(CH_3)_3$$
8a

>99% (8h)

[a]All reactions were performed on 0.89 mmol scale using a 1:1 silane-olefin mixture under aerobic conditions.[b]Conversions were determined by ^1H NMR analysis of the crude reaction mixture.

The cross-linking of silicone fluids by platinum-catalyzed hydrosilylation produces silicone products, which have applications in release coatings. Due to the high viscosity of the final product, the platinum catalyst becomes trapped in the final silicone and is not recovered, accounting for approximately 30% of the final silicone cost.[19b] Commercial standards require this curing process to proceed rapidly with low catalyst loadings and without leaving the product coloured in any way.[21] The cross-linking activity of **2a**, **3a** and **4a** precursors with tpy was examined at different catalyst loadings (Scheme 2). It can be observed a gel formation in each case, and an effective silicon cross-linking. The catalyst loading used related to the silane was 0.0125% mol, while Chirik and coworkers used 0.0625% mol related to the silane when they said "1ppm of cobalt" in their study.[19b] Therefore, this result is in the range of Chirik´s system.

Scheme 2. Crosslinking of Silicone Fluids.[a]

$$\text{Si} + 2\ H{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}H \xrightarrow[\text{80ºC, 4h}]{\text{[Co]/tpy 0.012\%}} \text{Crosslinked Silicone Gel}$$

[a]Top: Cure reaction performed on 1.78 mmol scale using 1:2 silane-olefin mixture to obtain cross-linked silicone gel. Bottom: Isolated gels from cross-linking reactions with cobalt precursors **2a**, **3a** and **4a.**

Mechanistic study. The first approach was focused on the rate law of the reaction. In order to face it, we varied the concentration of each component of the reaction, following a similar methodology than the one described by Bleith and Gade.[28] For the hydrosilylation of 4-vinylcyclohexene with $PhSiH_3$ with catalyst **3b**, we found that the initial rate of the reaction was not appreciably affected as a function of 4-vinylcyclohexene concentration, indicating a zeroth order dependence on alkene concentration (Figure S15). The same effect was observed when the concentration of $PhSiH_3$ is varied, indicating a zeroth order dependence on silane concentration,

as well (Figure S16). Finally, the initial rate depends linearly on the catalyst loading when this is altered in the range of 0.5 to 0.05 mol % (see Figure 3). This first order dependence on the concentration of the catalyst implies that no induction time is required and the cobalt center is not aggregate with this range of concentration.
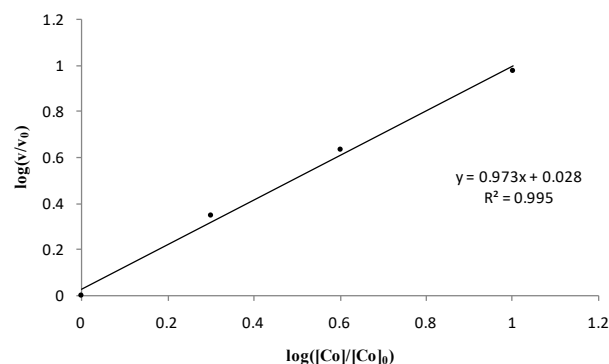
Figure 3. Initial rate depending on the catalyst loading.

$y = 0.973x + 0.028$
$R^2 = 0.995$

I*n-situ* Raman spectroscopy was employed to study the intermediate species formed during the reaction between the catalyst and the two reagents. First, the three isolated components catalyst, $PhSiH_3$ and 4-vinylcyclohexene were studied. Then, catalyst and silane mixture was studied where bubbles are observed that may be due to hydrogen formation. Indeed, the catalytic reaction is veryfast with $PhSiH_3$ (Table 2), so when the catalyst:silane ratio is 1:2, the process is more exothermic, in addition to heating due to irradiation from the Raman laser. This high temperature can promote other process, so therefore this is not the best method to elucidate the mechanism. In order to make the process less exothermic and slower the $PhSiH_3$ were substituted by $(EtO)_3SiH$ and the same procedure was employed. In this case, the reaction with this silane needed higher temperatures (Table 4). Under these conditions, a strong band at 2251 cm^{-1} was detected (Figure 4 in black), and this band was clearly shifted respect to the Si-H bond of the silane (Figure 4 in green). This band was observed for a long period of time and disappeared when the alkene was added (Figure 4 in red). Based on this behaviour, this signal was assigned to a Co-H bond.[29] Moreover, an additional band of Si-O bond was identified at 465 cm^{-1}.[30]

FULL PAPER

Figure 4. Spectrum of the *in-situ* Raman experiment: in blue the catalyst **3b**, in green (EtO)$_3$SiH, in black the reaction mixture between **3b** and (EtO)$_3$SiH, and in red after addition of the alkene.

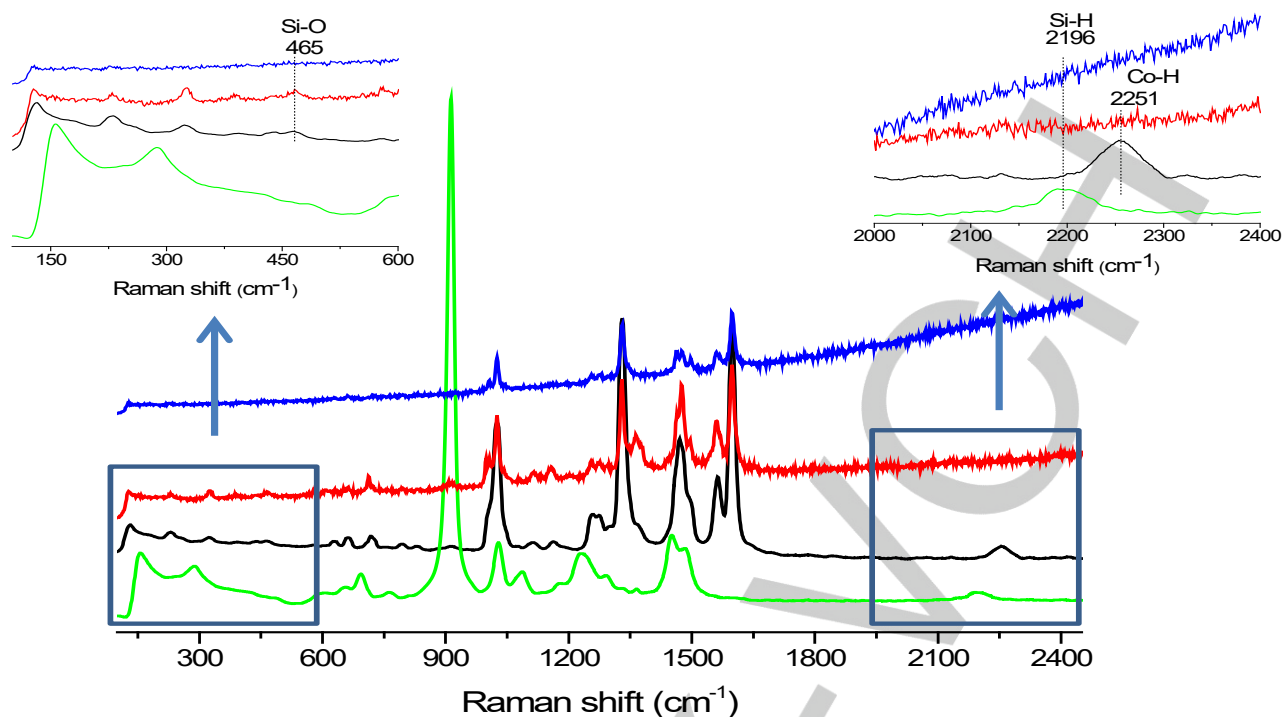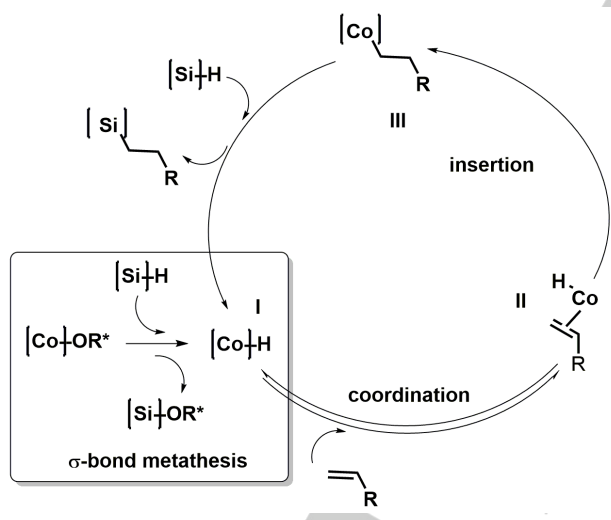**Scheme 3.** Mechanistic proposal for the cobalt-catalyzed hydrosilylation of alkenes.

Moreover, based on the *in-situ* Raman and kinetic experiments, a plausible mechanism has been proposed in the scheme 3. First, the cobalt pre-catalysts Co-OR dissociation takes places to provide [Co]$^+$ and [OR]$^-$, which would have to be the rate-determining step since the reaction rate respect to the silane is zero-order as has been observed in the kinetic study. Then, [Co]$^+$ specie reacts with the corresponding silane to provide the Co-H intermediate **I**. This is the first order reaction, which is based on σ-bond metathesis. In addition, the species **I** are in equilibrium with species **II**. Then species **II** react with the alkene to form the alkyl complex **III**, which is converted to hydride complex **I** upon the reaction with silane, accompanied by the formation of the linear alkylsilane.

Conclusions

In summary, we have developed new families of cobalt(II) complexes which are air- and moisture-stable, and work as catalysts for the hydrosilylation of alkenes with several silane precursors, avoiding the use of external activators. In addition, it is the first case where these reactions are carried out under aerobic conditions with first row transition metal complexes. Finally, a mechanistic study was performed where the reaction between the silane and the catalyst provides the Co-H species which has been observed by in-situ Raman spectroscopy. This is a main insight into the mechanism of this process. Based on that, a new catalyst design for the hydrosilylation of alkenes under aerobic conditions is ongoing.

Experimental Section

Instrumentation information and crystallographic details (CCDC 1817714 and CCDC 1817709) are given in the Supporting Information.

New hydrosilylation products obtained were characterized by GC-MS, ^{1}H- and ^{13}C-NMR. When available, characterization given in the literature was used for comparison. Isolated catalysts were characterized by elemental analysis, ^{1}H-NMR, monocrystal X-Ray Diffraction, Electron Paramagnetic Resonance (EPR) and HR-MS. Freshly prepared catalysts were characterized by EPR, UV/Vis absorption and HR-MS.

FULL PAPER

Chemicals

All reagents and solvents were purchased from commercial suppliers and used without further purification.

Synthesis

A. Preparation of Cobalt Complexes.

Reaction of tpy ligand with Co(OAc)₂ precursor (1b). 5.5 mg of terpyridine (0.022 mmol) and 5.2 mg of Cobalt (II) acetate tetrahydrate (0.022 mmol) was dissolved in 5 mL of THF and stirred for 1 hour. In addition, we prepared the same mixture in $CD_3CN:CDCl_3$ containing a few drops of CD_3OD in an NMR tube and the ^{1}H-NMR spectra shown in Figure S1 (up) shows that we form mainly the 1:1 paramagnetic complex 1b. ^{1}H NMR (300 MHz): δ = 169.42 (bs), 105.75 (bs), 83.27 (bs), 42.50 (bs), 36.92(bs) and 12.72 (bs).[1] In addition, a small amount the homoleptic complex 1c is also obtained. (300 MHz): δ= 97.05 (bs), 55.75 (bs), 45.80 (bs), 33.91 (bs), 21.98 (bs), and 9.22 (bs).

Reaction of tpy ligand with Co(acac)₂ precursor (2b). 5.2 mg of terpyridine (0.022 mmol) and 5.7 mg of Cobalt (II) acetylacetonate hydrate (0.022 mmol) was dissolved in 5 mL of THF and stirred for 5 minutes. In the same way, we prepared the same mixture in $CD_3CN:CDCl_3$ containing a few drops of CD_3OD in an NMR tube and the ^{1}H-NMR spectra shown in Figure S1 (bottom) shows that we only form the homoleptic complex 2c. ^{1}H NMR (300 MHz): δ= 96.07 (bs), 55.57 (bs), 45.73 (bs), 33.78 (bs), 21.87 (bs), and 9.48 (bs).

Reaction of tpy ligand with Co(naphth)₂ precursor (3b). 5.2 mg of terpyridine (0.022 mmol) and 13.11 mg of Cobalt (II) naphtenate (10% Co, 0.022 mmol) was dissolved in 5 mL of THF and stirred for 5 minutes.

Reaction of tpy ligand with Co(oct)₂ precursor (4b). 5.2 mg of terpyridine (0.022 mmol) and 16.4 mg of Cobalt (II) octanate (8% Co, 0.022 mmol) was dissolved in 5 mL of THF and stirred for 5 minutes.

Preparation of [Co(OAc)(H₂O)₂(tpy)]OAc (1b'). 100 mg of terpyridine (0.428 mmol) and 106.6 mg of Co(II) acetate tetrahydrate (0.428 mmol) were dissolved in 50 mL of a mixture of acetonitrile:chloroform (1:1) with some drops of methanol. An immediate color change to orange was observed. Single crystals were obtained by slow evaporation of the solvent. Anal. For $C_{19}H_{21}CoN_3O_6$: calc. = C, 51.131; H, 4.743; N, 9.415. Found = C, 51.048; H, 4.667; N, 9.543.

Preparation of [Co(tpy)₂]Cl₂·6H₂O (2c). 100 mg of terpyridine (0.428 mmol) and 110 mg of Cobalt (II) acetylacetonate hydrate

(0.428 mmol) were dissolved in 50 mL of a mixture of acetonitrile:chloroform (1:1) with some drops of methanol. An inmediate color change to orange was observed. Single crystals were obtained by slow evaporation of the solvent. Anal. For $C_{30}H_{26}Cl_2CoN_6O_6$: calc. = C, 51.745; H, 3.764; N, 12.069. Found = C, 51.899; H, 3.876; N, 11.698.

B. General Procedure for Catalytic Hydrosilylation Reactions

Method A: 0.2 mL of freshly catalyst solution (0.001 equiv.) were taken and added to a vial equipped with a stir bar, followed by olefin (1 equiv.) and Silane (1 equiv.) resulting in formation of a dark reaction mixture. The vial was sealed with a cap and stirred at pertinent temperature. N-Hexane was added and the catalyst was filtered. Then, n-hexane was rotaevaporated and an aliquot was analyzed by ^{1}H NMR in $CDCl_3$.

Method B: 0.2 mL of freshly catalyst solution (0.001 equiv.) were taken and added to a vial equipped with a stir bar, followed by olefin (2 equiv.) and Silane (1 equiv.) resulting in formation of a dark reaction mixture. The vial was sealed with a cap and stirred at pertinent temperature. n-Hexane was added and the catalyst was filtered. Then, n-hexane was rotaevaporated and an aliquot was analyzed by ^{1}H NMR in $CDCl_3$.

C. Kinetic study for hydrosilylation of 4-vinylcyclohexene with PhSiH₃

Method A: The isolated catalyst (0.001 equiv.) was dissolved in 0.2 mL of THF and added to a vial equipped with a stir bar, followed by 4-vinylcyclohexene (96.3 mg, 0.89 mmol) and phenylsilane (96.3 mg, 0.89 mmol) and mesitylene (107 mg, 0.89 mmol) resulting in formation of a dark reaction mixture. The vial was sealed with a cap and stirred at room temperature. An aliquot of crude reaction was taken each 30 minutes and analized by ^{1}H NMR in $CDCl_3$.

Method B: 0.2 mL of freshly catalyst solution (0.001 equiv.) were taken and added to a vial equipped with a stir bar, followed by 4-vinylcyclohexene (96.3 mg, 0.89 mmol) and phenylsilane (96.3 mg, 0.89 mmol) and mesitylene (107 mg, 0.89 mmol) resulting in formation of a dark reaction mixture. The vial was sealed with a cap and stirred at room temperature. An aliquot of crude reaction was taken each 30 minutes and analized by ^{1}H NMR in $CDCl_3$.

Method C: To a NMR tube were added 0.2 mL of a catalyst's solution in THF-d^8 followed by 4-vinylcyclohexene (96.3 mg, 0.89 mmol), phenylsilane (96.3 mg, 0.89 mmol) and mesitylene (107 mg, 0.89 mmol) resulting in formation of dark reaction mixture. The reaction was carried out inside the NMR Spectrometer.

FULL PAPER

WILEY-VCH

D. Procedure for 10g Scale Hydosilylation of 1-octene with (EtO)₃SiH.

20 mL of freshly catalyst solution (0.001 equiv.) were taken and added to a 100 mL flask equipped with a stir bar, followed by 1-octene (10 g, 89 mmol) and triethoxysilane (14.62 g, 89 mmol). The flask was sealed with a cap and stirred for 3 hours at 50 ºC, resulting in formation of a dark reaction mixture. In order to calculate the isolated yield, first, THF was rotaevaporated. When n-hexane was added, the precatalyst precipitated and this allowed us to filter it. Finally, the solvent was evaporated (Yield: 97%).

E. Synthesis of Crosslinking Silicone Fluids

In order to synthesize Crosslinking Silicone Fluids, 0.1 mL of freshly catalyst solution (0.00025 equiv.) were taken and added to a vial equipped with a stir bar, followed by tetravinylsilane (1 equiv., 250.1 mg, 1.78 mmol) and 1,1,3,3-Tetramethyldisiloxane (2 equiv., 478.2 mg, 3.56 mmol). The vial was sealed with a cap and stirred at 80 ºC. After 4 hours, gel formation occurred. The resulting clear, colorless gel was opened and broken up with a spatula to assess the color and consistency of the product obtained.

Acknowledgements

Conflict of interest

The authors declare no competing financial interest.

Keywords: Homogeneous catalysis, cobalt, alkene, hydrosilylation, mechanism.

[1] (a) B. Marciniec, J. Gulinski, W. Urbaniac, Z. W. Kornetka in *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, U.K., **1992**. (b) B. Marciniec, *Applied Homogeneous Catalysis with Organometallic Compounds*; Wiley−VCH: Weinheim, Germany, **1996**. (c) B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluć in *Hydrosilyaltion: A Comprehensive Review on Recent Advances*; Marciniec, B., Ed.; Springer: Berlin, **2009**; pp 3−51. (d) Y. Nakajima, S. Shimada, *RSC Adv.* **2015**, *5,* 20603−20616. (e) J. Sun, L. Deng, *ACS Catal.* **2016**, *6*, 290−300. (f) C. Wang, W. J. Teo, S. Ge. *ACS Catal.* **2017**, *7*, 855-863.

[2] (a) B. D. Karstedt, Platinum Complexes of Unsaturated Siloxanes and Platinum Containing Organopolysiloxanes. U.S. Patent 3775452A, Nov. 27, **1973**. (b) L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn, G. Hutchins, *Platinum. Met. Rev.* **1997**, *41*, 66−75. (c) I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J-P. Declercq, *Science* **2002**, *298*, 204−206. (d) I. E. Markó, S. Stérin, O. Buisine, G. Berthon, G. Michaud, B. Tinant, J-P. Declercq, *Adv. Synth. Catal.* **2004,** *346*, 1429−1434. (e) B. Marciniec, K. Posała, I. Kownacki, M. Kubicki, R. Taylor, *ChemCatChem* **2012**, *4*, 1935−1937. (f) J. C. Bernhammer, H. V. Huynh, *Organometallics* **2014**, *33*, 172−180.

[3] For example, one kilo of platinum requires 210 tons of ore, see: Hilliard, H. E. U.S. Geological Survey, Platinum-Group Metals Mineral Commodity Summary (January 2003) (minerals.usgs.gov/minerals/pubs/commodity/platinum/.

[4] X. Du, Z. Huang, ACS Catal. **2017,** *7*, 1227.

[5] A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P-J. Chirik, *Science* **2012**, *335*, 567-570.

[6] Earlier reports: (a) J. C. Mitchener, M. S. Wrighton, *J. Am. Chem. Soc.* **1981**, *103*, 975-977. (b) J. F. Harrod, A. J. Chalk, *J. Am. Chem. Soc.* **1967**, *89*, 1640-1647. (c) M. A. Schroeder, M. S. Wrighton, *J. Organomet. Chem.* **1977,** *128,* 345-358. (d) C. L. Reichel, M. S. Wrighton, *Inorg. Chem.* **1980**, *19*, 3858-3860. (e) F. Seitz, M. S. Wrighton, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289-291.

[7] (a) C. C. H. Atienza, A. M.Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis, P.J. Chirik, *ACS Catal.* **2012**, *2*, 2169-2172. (b) S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004,** *126*, 13794- 13807.

[8] J. Y. Wu B. N. Stanzl, T. Ritter, *J. Am. Chem. Soc.* **2010,** *132*, 13214-13216.

[9] B. Marciniec, A. Kownacka, I. Kownacki, R. Taylor, *Appl. Catal. A,* **2014**, *486*, 230-238.

[10] J. Chen, B. Cheng, M. Cao, Z. Lu, Angew. Chem. Int. Ed. **2015**, 54, 4661-4664.

[11] B. Cheng, W. Liu, Z. Lu, J. Am. Chem. Soc. **2018**, 140, 5014-5017.

[12] C.C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy, P. J. Chirik, *J. Am. Chem. Soc.* **2014,** *136*, 12108- 12118.

[13] Z. Mo, Y. Liu, L. Deng, *Angew. Chem., Int. Ed.* **2013**, *52*, 10845-10849.

[14] C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2015**, *137*, 13244-13247.

[15] (a) M. Lipschutz, T. D. Tilley, *Chem. Commun.* **2012**, *48*, 7146-7148. (b) I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, X. Hu, *Angew. Chem., Int. Ed.* **2015,** *54*, 14523-14526.

[16] M. D. Greenhalgh, D. J. Frank, D. J.; Thomas, S. P.; Iron-Catalysed Chemo-, Regio-, and Stereoselective Hydrosilylation of Alkenes and Alkynes using a Bench-Stable Iron(II) Pre-Catalyst. *Adv. Synth. Catal.* **2014**, 356, 584-590.

[17] Dow Corning applied for patents for hydrosilylation catalyzed by metal salts and ligands with the aid of various activators, such as organometallic reagents. Examples include Co- and Fe-catalyzed hydrosilylation with MD′M, which were limited to reaction of 1-hexene by complexes containing multidentate heteroatom ligands. Automatic screening of the metal compounds and the ligand was performed to show whether the reaction took place. K. Brandstadt, S. Cook, B. T. Nguyen, A. Surgenor, R. Taylor, M. Tzou, WOPatent Appl. 2013043846, **2013.**

[18] J. H. Docherty, J. Peng, A. P. Dominey, S. P. Thomas, Nature Chem. **2017**, 9, 595-600.

[19] (a) D. Noda, A. Tahara, Y. Sunada, H. Nagashima, *J. Am. Chem. Soc.* **2016**, *138*, 2480-2483. (b) C. H. Schuster, T. Diao, I. Pappas, P. J. Chirik, *ACS Catal.* **2016**, *6*, 2632-2636.

[20] E. C. Constable, C. E. Housecroft, V. Jullien, M. Neuburger, S. Schaffner, *Inorg. Chem. Commun.* **2006**, *9,* 504-506.

[21] R. Indumathy, S. Radhika, M. Kanthimathi, T. Weyhermuller, B.U. Nair, *J. Inorg. Biochem.* **2007**, *101*, 434-443.

[22] K. Mizuno, S. Imamura, J. H. Lunsford, *Inorg. Chem.* **1984**, **23**, 3510-3514.

WILEY-VCH

[23] M. Cibian, G. S. Hana, *Chem. Eur. J.* **2015**, *21*, 9474-9481.

[24] G. R. Eaton, S. S. Eaton, D. P. Barr, R. T. Weber, in *Quantitative EPR*. Springer-Verlag Wien, Austria, **2010.**

[25] (a) D. F. Evans, *J. Chem. Soc.* **1959**, 2003–2005; (b) D. F. Evans, G. V. Fazakerley, R. F. Phillips, *J. Chem. Soc. A*, **1971**, 1931–1934. (c) C. W. Garland, J. W. Nibler, D. P. Shoemaker, *Experiments in Physical Chemistry*, 8th Ed.; McGraw-Hill; New York: **2003**, p. 371-379.

[26] (a) The crystals suitable for X-ray measurements were grown under aerobic. (b) THF was replaces by water in complex **1b**. (c) acetylcateonate was replaces by chlorine in complex **2c**, which is provided from the chloroform used in the crystallization process.

[27] J. W. Sprengers, M. de Greef, M. A. Duin, C. J. Elsevier, *Eur. J. Inorg. Chem.* **2003**, *2003,* 3811-3819.

[28] T. Bleith, L. H. Gade, *J. Am. Chem. Soc.* **2016**, *138*, 4972-4983.

[29] G. Socrates,*Infrared and Raman Characteristic Group Frequencies*. John Wiley & Sons Ltd, Chichester, UK, **2001**.

[30] E. S. Park, H. W. Ro, C. V. Nguyen, R. L. Jaffe, D. Y.Yoon, *Chem. Mater.* **2008**, *20*, 1548–1554.

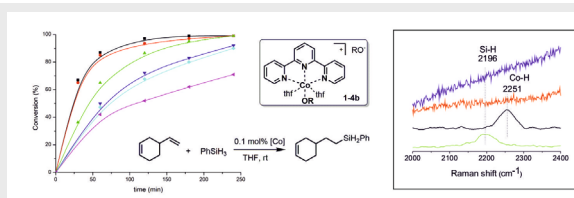**Entry for the Table of Contents** (Please choose one layout)

Layout 2:

FULL PAPER

Silvia Gutiérrez-Tarriño, Patricia Concepción and Pascual Oña-Burgos*

Page No. – Page No.

Cobalt catalysts for alkene hydrosilylation under aerobic conditions without dry solvents or additives.

Text for Table of Contents
Alkene hydrosilylation catalyzed by cobalt (II) complexes under aerobic conditions without dry solvent or external activators. In addition, a mechanistic study based on kinetics experiments and *in-situ* Raman spectroscopy has been carried out, where a Co-H specie has been identified.

Keywords: Hydrosilylation catalysis, cobalt complexes and mechanistic study