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Ketone hydrosilylation by Cu(I) diphosphine complexes: A kinetic study

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ABSTRACT

Diphosphine ligands are commonly used for the catalytic hydrosilylation of ketones using Cu(I) complexes. While some DFT studies on the suggested catalytic cycle have been reported, we present herein a complete kinetic study of the copper(I) catalyzed reaction to verify the plausibility of the proposed catalytic cycle from an experimental point of view. The rate constants of the two consecutives steps are determined for BDP (BDP = 1,2-bis(diphenylphosphino)benzene) and *rac*-BINAP ligands. The two constants are found not to differ significantly, *i.e.* no rate limiting step is identified. Depending on operation conditions, a switch between rate limiting steps is observed leading to either first order kinetics in silane or ketone.

1. Introduction

Carbonyl bond reduction, specifically of aldehydes and ketones, to the corresponding alcohol functionality via hydride transfer is a fundamental transformation in organic synthesis [1]. Transition-metal catalysis has been successfully applied in the reduction of many carbonyl compounds via hydrogenation or hydrosilylation [1]. Hydrogenation reactions proceed in good yields but require high pressure or elevated temperature. Moreover if the reaction is part of a multi-step synthesis, the resulting free alcohol can require protection prior to the next synthetic step. In contrast, the softer reactions conditions of hydrosilylation turned out to be a major advantage in addition to the fact that both the reduction and the protection steps are performed in a single atom-efficient step.

The first catalytic systems, based on rhodium, were developed in the early 1970s [2–4] after which other heavy metals were introduced, ranging from Re, Rh and Ru to Ir [5–14]. As the main drawback was the cost affiliated with these metals, efforts were made to find efficient, less expensive alternatives using titanium [15–22], iron [23–31], manganese [32–34] or zinc [35–43]. In 1984 Brunner and Miehling reported the first asymmetric hydrosilylation with a copper-diphosphine catalyst [44]. Since, many copper-diphosphine catalytic systems were developed [45–52]. Lipshutz et al. postulated the formation of a copper(I) hydride species as active catalyst for a system combining a catalytic quantity of CuCl/NaO*t*-Bu/diphosphine and a stoichiometric amount of hydrosilylant agent [53–57]. At the same time, Carreira and co-workers [58] as well as Riant and co-workers [49,59–61] reported CuF_2 systems as interesting precursors to copper hydride. Other air and moisture stable copper(II) salts, as $Cu(OAc)_2$, in combination with inexpensive and readily available diphosphines such as BINAP are used efficiently to catalyze the hydrosilylation of various ketones [47,62,63].

The generally accepted mechanism involves a σ-bond metathesis between the pre-catalyst and the hydrosilylating reagent to form a copper(I) hydride species **4**. The latter reacts with a ketone substrate **1** resulting in the formation of a copper alkoxide **5** (step 1) that subsequently undergoes a σ-bond metathesis with the organosilane **2** to afford the silyl ether **3** and regenerate the Cu–H catalyst (Step 2, see Scheme 1) [52,64–67]. Although computational studies [68–74] confirm this mechanism, little efforts were made to verify the mechanism experimentally. Considering our interest in ketone hydrosilylation by diphosphine-copper(I) catalysis [49,59–61], we decided to investigate this mechanism using chemical kinetics studies. To the best of our knowledge, the only kinetic studies performed were those by Issenhuth et al. [71] in which they use initial rate analysis based on NMR spectra to find a first order in ketone and silane and a 0.5 order in catalyst. However,

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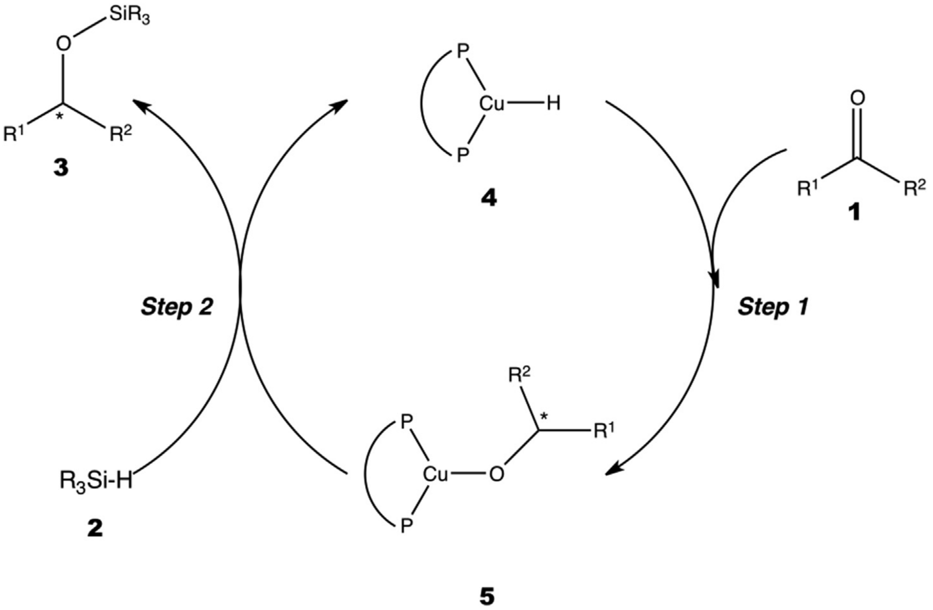

Scheme 1. Suggested catalytic cycle for the asymmetric hydrosilylation of ketones using diphosphine-copper(I) catalysts.

no efforts were placed in trying to fit these orders with the suggested catalytic scheme. Their observation of a rate limiting second step, furthermore, seems to contradict the observed first order kinetics with respect to the ketone species. In this paper, we want to apply kinetic studies to verify the plausibility of the suggested mechanism and investigate the apparent contradictions with respect to the nature of the rate limiting step [71].

2. Kinetic expressions

To verify the plausibility of the catalytic scheme one first needs to develop a corresponding rate expression. Within the Scheme shown above (Scheme 1), substrate **1** (ketone) adds to the catalytic species **4** in step 1. A second step consists of a reaction between species **5** and a second substrate **2** (the silane) to yield product **3** and species **4** (Scheme 2).

The rate equations for product appearance/reactant disappearance are given by:

$$v_{\mathbf{1}} = \frac{d[\mathbf{1}]}{dt} = -k_1[\mathbf{1}][\mathbf{4}] \tag{1a}$$

$$v_{\mathbf{3}} = \frac{d[\mathbf{3}]}{dt} = k_2[\mathbf{2}][\mathbf{5}] \tag{1b}$$

Although concentrations of species **1**, **2**, and **3** can easily be measured, those of copper containing species **4** and **5** are less easily accessible due to the small amount of species present. The overall rate Equations (1a) and (1b) will therefore be altered to depend solely on the major species present in solution. This is achieved assuming the steady state for species **4** and **5** (Equations (2a) and (2b)).

$$\mathbf{1} + \mathbf{4} \xrightarrow{k_1} \mathbf{5}$$

$$\mathbf{5} + \mathbf{2} \xrightarrow{k_2} \mathbf{3} + \mathbf{4}$$

Scheme 2. Consecutive elementary reactions corresponding to Scheme 1.

$$v_{\mathbf{4}} = \frac{d[\mathbf{4}]}{dt} = -k_1[\mathbf{1}][\mathbf{4}] + k_2[\mathbf{2}][\mathbf{5}] \cong 0 \tag{2a}$$

$$v_{\mathbf{5}} = \frac{d[\mathbf{5}]}{dt} = k_1[\mathbf{1}][\mathbf{4}] - k_2[\mathbf{2}][\mathbf{5}] \cong 0 \tag{2b}$$

Combining Equations (1) and (2) with the knowledge of the total amount of catalyst used:

$$[\mathbf{4}] + [\mathbf{5}] = [\mathrm{Cu}]^0 \tag{3}$$

The overall rate equation can be expressed based exclusively on experimentally readily accessible data ([**1**], [**2**] and $[\mathrm{Cu}]^0$)

$$v_{\mathbf{1}} = \frac{d[\mathbf{1}]}{dt} = -\frac{k_1 k_2[\mathbf{1}][\mathbf{2}][\mathrm{Cu}]^0}{k_1[\mathbf{1}] + k_2[\mathbf{2}]} = -\frac{d[\mathbf{3}]}{dt} = -v_{\mathbf{3}} \tag{4}$$

The overall rate expression contains a two-term denominator. In most two-step catalytic cycles, one of the two rate constants is dominating and one of these terms can be neglected, leading to two extremes. In a first case, the second step is rate limiting with $k_1[\mathbf{1}]$ outweighing $k_2[\mathbf{2}]$. This situation is commonly termed “saturation kinetics” in species **1**, with a simplified rate equation being first order with respect to the silane **2** (Equation (5) in Table 1).

In the opposite case, the formation of intermediate **5** will be rate-limiting, and the unbound catalyst species **4** is the “resting state” of the catalyst. The rate equation is now first order with respect to the ketone **1** (Equation (6) in Table 1).

If none of the terms is dominating, the full rate Equation (4) needs to be considered. Significant amounts of both **4** and **5** are present in the system. However, it is possible to force the system to one of the two limiting situations working with an excess amount of one of the reactants.

The catalytic cycle shown in Scheme 1, suggests the copper-hydride to be monomeric. However, recent studies [71–73,75–80] postulate the copper hydride to be oligomeric with the monomer the only active form. This will not influence the overall expression (4) but will affect the rate order with respect to the catalyst and possibly explains the 0.5 order observed experimentally [71]. The goal of the current paper is to study the two steps of

Table 1
Full and simplified rate equations for the catalytic reaction shown in Scheme 1. Integrated rate expression; a^0 and b^0 represent the initial concentrations in ketone **1** and silane **2** respectively.

Major Cu species (Scheme 1)	Dominating term in denominator of Equation (4)	Observed rate equation	Integrated rate equation
5	$k_1[\mathbf{1}]$	$v = k_2[\mathbf{2}][\mathrm{Cu}]^0$ (5)	$\ln\left(\frac{b^0 - x}{b^0}\right) = -k_2[\mathrm{Cu}]^0 t$ (7)
4	$k_2[\mathbf{2}]$	$v = k_1[\mathbf{1}][\mathrm{Cu}]^0$ (6)	$\ln\left(\frac{a^0 - x}{a^0}\right) = -k_1[\mathrm{Cu}]^0 t$ (8)
None	All terms contribute	$v = \frac{k_1 k_2[\mathbf{1}][\mathbf{2}][\mathrm{Cu}]^0}{k_1[\mathbf{1}] + k_2[\mathbf{2}]}$ (4)	

Table 2
Experimental plan used working with an excess amount of silane.

	Ketone [1] (M)	Silane [2] (M)	[2]/[1]
BDP3	0.072	0.75	10
BDP4	0.068	0.75	11
BDP5	0.145	0.75	5
BDP6	0.145	0.75	5
BDP7	0.298	0.75	2.5
BDP8	0.303	0.75	2.5

the catalytic cycle, without focusing on the hydride equilibrium involved.

3. Results and discussion

Kinetic studies were conducted using $\mathrm{Cu(RCOO)_2}$/BDP (BDP = 1,2-bis(diphenylphosphino)benzene) and $\mathrm{Cu(RCOO)_2}$/(*rac*)-BINAP catalysts (2 mol%) as both lead to full conversion (>99%) of benzylacetone using $\mathrm{Me(OEt)_2Si{-}H}$[1] as a hydride source (Scheme 3). Concentrations of ketone and alcohol were monitored over time using gas chromatography. Reaction temperature was controlled and held constant at 298 K. Concentration profiles were constructed from calibration curves using an internal standard method (see Experimental section and Supporting material for more details). Kinetic orders with respect to reactants were obtained from an exponential fitting analysis of the concentration curves, varying the amounts of each component (ketone, silane). Rate constants were obtained through linearization of the obtained data.

3.1. Repeatability and standard conditions

For kinetic studies the quality of the obtained data is essential. For this reason, all conditions were repeated twice. Fig. 1 shows the repeatability of the obtained data for ketone reactant and alcohol product concentrations over time under standard conditions.[2]

Fig. 1 shows excellent repeatability between the two trials. This is also the case for all of the experimental conditions considered within the scope of this work. Quantitative analysis is performed both on ketone reactant **1** and alcohol product **3**, showing full conversion.

Using the integrated rate expressions (Table 1), the data is checked with respect to the two extreme cases.[3] Fig. 2 shows the data following Equation (8). Although there is an excellent linear behavior indicative of first order kinetics, a change in slope at around $t = 50$ min is also observed. A similar observation can be made when considering the data under Equation (7) (Supporting information Fig. S.1). This change in slope can suggest a variation in mechanism or a change in rate limiting step, implying both steps to be governed by similar rate constants. As standard conditions are performed using 1 eq. of ketone and 1.2 eq. of silane, the relative importance of $k_1[\mathbf{1}]$ vs. $k_2[\mathbf{2}]$ would in this case depend on the relative concentrations [**1**] and [**2**], which in turn depends on reaction progress.

As the hypothesis implying a change in mechanism seems unlikely, we suspected both elementary steps to have comparable rate constants. To study both steps, we worked either with an excess amount of silane (rendering the first step rate limiting; Equations (6) and (8)) or an excess amount of ketone (rendering the second step rate limiting; Equations (5) and (7)).

3.2. Case 1: excess amount of silane

Under the hypothesis of comparable rate constants, working with an excess amount of silane **2**, the rate expression is first order with respect to the ketone **1** (Equation (6)). To verify this, an experimental plan was devised keeping the concentration in silane constant and in excess with respect to the amount of ketone (at least 2.5 times more important). The concentration of ketone was then varied from one experiment to the other (Fig. 3)

All curves show exponential decrease of the ketone concentration over time (Fig. 3). If the data corresponds to first order kinetics in ketone **1**, representing the conversion over time (Equation (8) $(a^0 - x)/a^0 = \exp(-k_1[\mathrm{Cu}]^0 t)$) should yield identical curves.[4] Fig. 4 confirms this type of behavior.

Taking the natural logarithm of this data (Fig. 5 and Figs S.2 to S.7), linear curves are obtained, once more highlighting first order kinetics in ketone. Considering the initial catalyst concentration $[\mathrm{Cu}]^0 = 0.004$ M, a value of $k_1 = 2.03 \pm 0.29\ \mathrm{M^{-1}\ s^{-1}}$ (confidence interval at 95%) is obtained (Table S.1).

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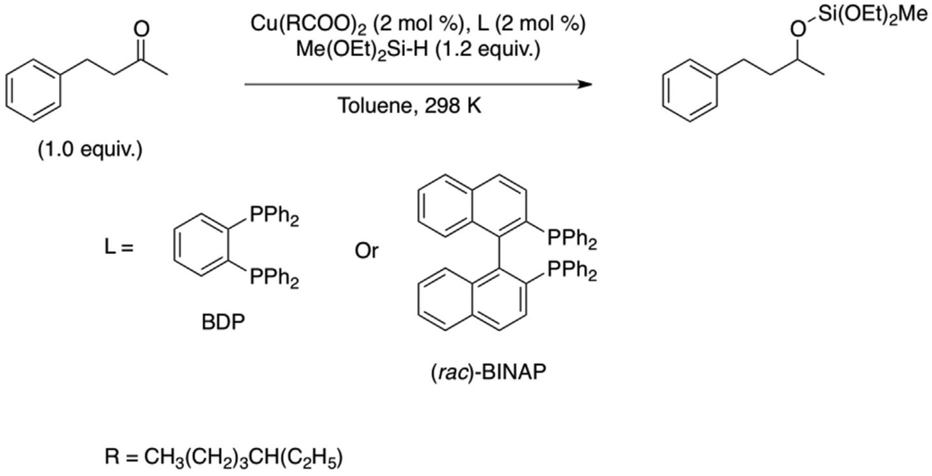
[1] The authors would like to emphasize that for other silane reactants the results obtained can strongly alter.

[2] Standard conditions, are those used in literature ($T = 25$ °C, $[\mathbf{1}] = \pm 0.2$ M; $[\mathbf{2}] = \pm 0.24$ M; 2 mol% catalyst, using the BDP ligand); The initial concentration in **1** is taken as the average value of the sum of **1** and **3** throughout the reaction. This sum is constant, as shown in Supporting information.

[3] As the silane concentration [**2**] is not measured directly, it is deduced from the initial amount of silane added with respect to the ketone **1**, and the concentration of alcohol [**3**] present.

[4] A same amount of catalyst is used from one experiment to the other, so the term $k_1[\mathrm{Cu}]^0$ is constant.



Scheme 3. Copper-catalyzed hydrosilylation of benzylacetone.

The data is shown not to correspond to first order kinetics with respect to silane **2** (Equation (7)). Working with an excess amount of silane, the first step is found to be rate limiting, or in other words the copper-hydrate species **4** to correspond to the resting state of the catalyst.

3.3. *Case 2: excess amount of ketone*

Working with an excess amount of ketone **1**, we expect the rate expression to be given by Equations (5) and (7), being first order with respect to the silane **2**. An experimental plan (Table 3) was

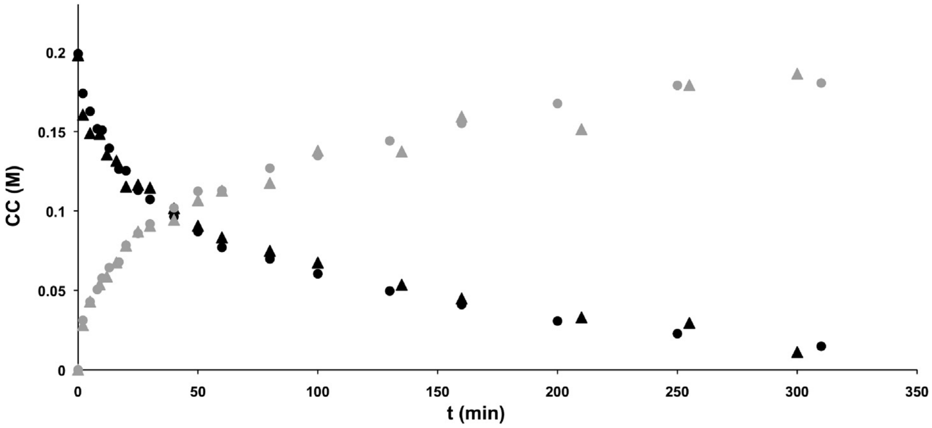


Fig. 1. Concentration of reactant **1** (black) and product **3** (gray) over time under standard conditions (round and triangle points respectively correspond to two independent trials BDP1 and BDP2).

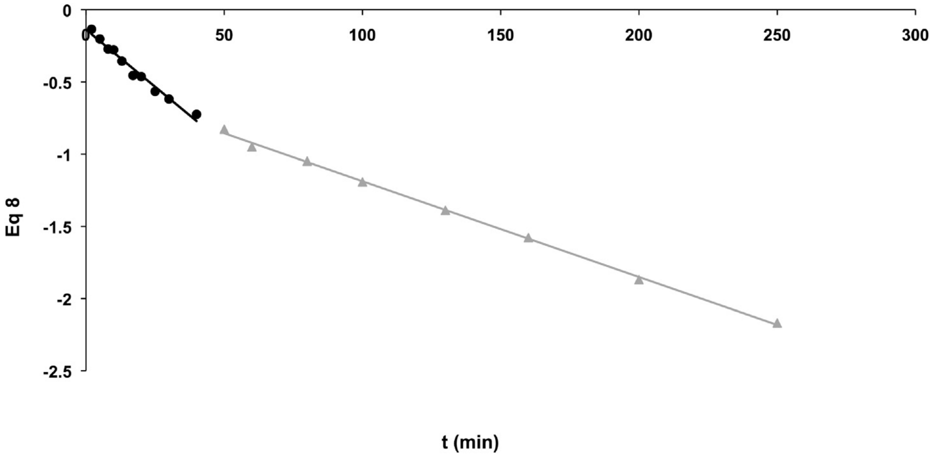


Fig. 2. Transformation of the data presented in Fig. 1 according to the expression of Equation (8) (data represented for experiment BDP1).

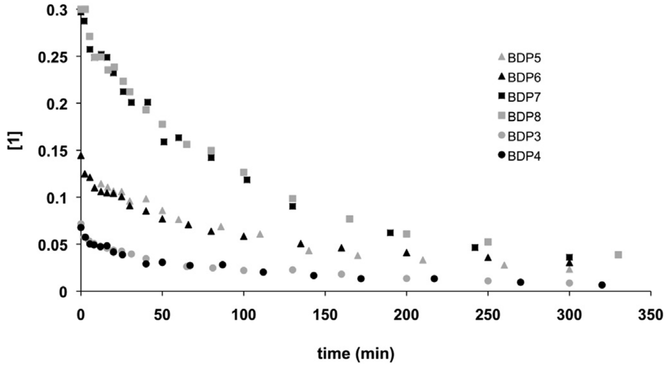


Fig. 3. Concentration of [**1**] over time, for experiments of Table 2.

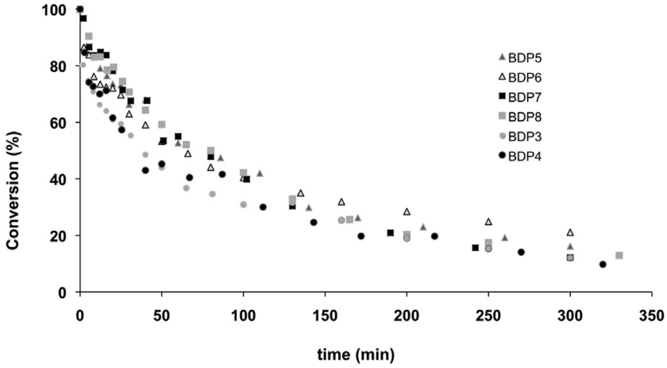


Fig. 4. Conversion over time, for experiments from Table 2.

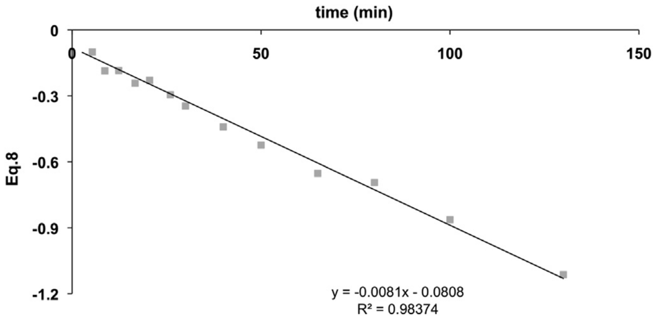


Fig. 5. Linearization of the data of experiment BDP8 according to Equation (8).

devised in a similar spirit as above, keeping the concentration in ketone constant and in excess and varying the concentration of silane. Exponential decrease of reactant concentration is once more observed (Fig. 6). Representing the conversion over time (Equation (7) $(b^0 - x)/b^0 = \exp(-k_2[\mathrm{Cu}]^0 t)$) yields identical curves, as expected (Fig. 7).

Linearizing the data, a first order kinetics in silane **2** is confirmed (Figs S.9 to S.13). This implies the second step to be rate limiting or in other words the copper-alkoxyde species **5** to correspond to the resting state of the catalyst. A value of $k_1 = 2.41 \pm 0.62\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ can be extracted from the data (Table S.1).

A pooled *t*-test does not show a significant difference between the values of k_1 and k_2, validating the hypothesis of comparable rate constants for both elementary steps of the catalytic cycle.

Table 3
Experimental plan used when working with an excess amount of ketone.

	Ketone [1] (M)	Silane [2] (M)	[1]/[2]
BDP9	0.919	0.092	10
BDP10	0.922	0.092	10
BDP11	0.928	0.223	4.2
BDP12	0.944	0.228	4.2
BDP13	0.847	0.339	2.5

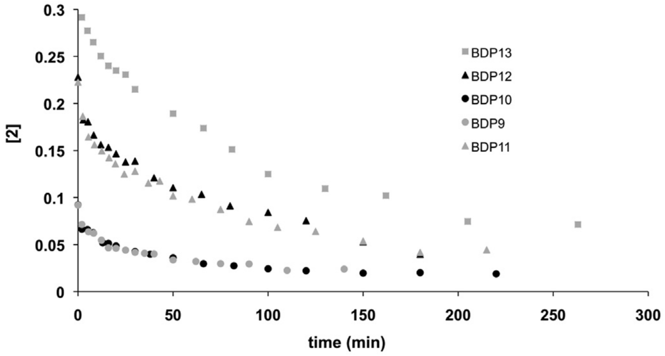


Fig. 6. Concentration of [**2**] over time, for experiments from Table 3.

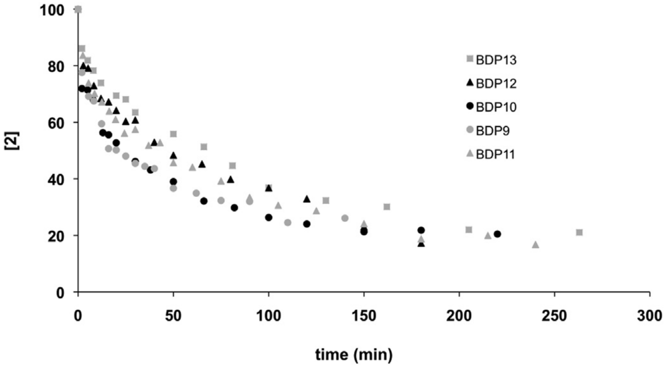


Fig. 7. Conversion over time, for experiments from Table 3.

3.4. Changing the ligand – (rac)-BINAP

To study the effect of different ligands on reaction kinetics, studies were performed using the (*rac*)-BINAP ligand. Under standard conditions, a similar observation is made to that mentioned above, with the data corresponding to first order kinetics and showing a change in rate limiting step (Supporting information, data BIN1 and BIN2). Table 4 shows the experimental plan used, working either with an excess amount of silane **2** (BIN3 to BIN7) or ketone **1** (BIN8 to BIN11) (Fig. 8).

Plotting the conversion over time, confirms first order behavior (Fig. S.22). Linearizing the data according to Equations (7) or (8),

Table 4
Experimental plan used for the mechanistic study involving the BINAP ligand.

	Ketone [1] (M)	Silane [2] (M)	[1]/[2]
BIN3	0.075	1.00	13
BIN4	0.133	1.00	7.5
BIN5	0.134	1.00	7.5
BIN6	0.270	1.00	3.7
BIN7	0.266	1.00	3.7
	Ketone [1] (M)	Silane [2] (M)	[2]/[1]
BIN8	0.752	0.180	4.2
BIN9	0.772	0.185	4.2
BIN10	0.705	0.338	2.1
BIN11	0.676	0.324	2.1

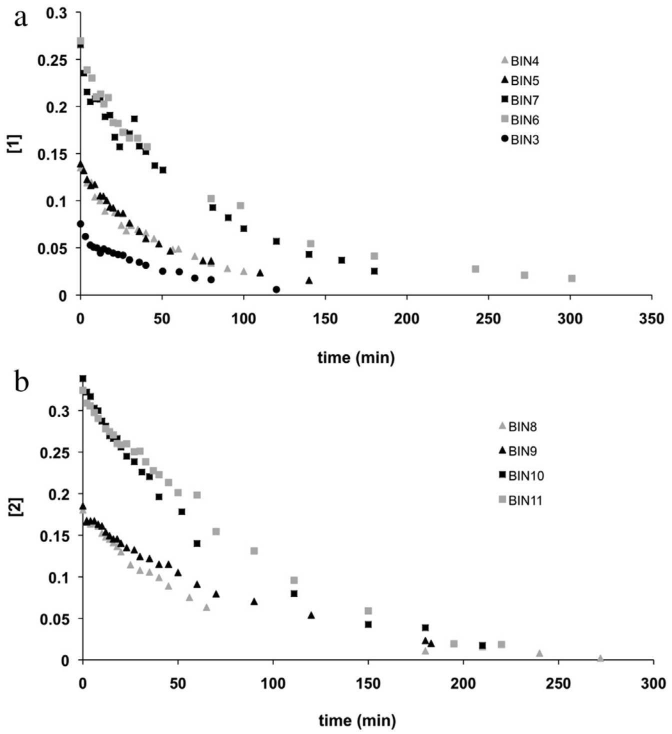


Fig. 8. a) Concentration of [**1**] over time, for experiments BIN3 to BIN7 from Table 4. b) Concentration of [**2**] over time, for experiments BIN8 to BIN11 from Table 4.

Table 5
Rate constants obtained within this study.

	BDP		BINAP	
k_1	2.03	[1.72;2.33]	3.51	[2.58;4.44]
k_2	2.41	[1.78;3.03]	3.04	[2.00;4.07]

respectively for the experiments with an excess amount of ketone **1** or silane **2**, a value of $k_1 = 3.51 \pm 0.93$ M^{-1} s^{-1} and $k_2 = 3.04 \pm 1.03$ M^{-1} s^{-1} is obtained (Figs S.14 to S.22, Table S.1). Once more a pooled *t*-test does not show any significant difference between both rate constants.

Table 5 sums up the rate constants obtained within this study. The k_1 value of the BDP system is significantly different from the k_1 value of the (*rac*)-BINAP system. Nevertheless, the values remain extremely close and one can conclude that the diphosphine complexes show comparable reactivity. For both systems, no significant difference is obtained between k_1 and k_2 values. This implies that working with an excess amount of silane **2**, renders the first step rate limiting and the copper hydride species **4** the resting state of the catalyst. Working with an excess amount of ketone, implies the second step to be rate limiting and the alkoxide species **5** to be the catalyst resting state. These findings are in agreement with the earlier results [71], showing a first order with respect to ketone and silane respectively, as both orders were determined under conditions favoring this outcome.

4. Conclusions

In this paper, we experimentally confirm the validity of the suggested catalytic cycle for the hydrosilylation of ketones using copper(I) diphosphine complexes. The kinetics studies show comparable rate constants for the two successive steps of the cycle, with the rate-limiting step depending on the relative importance of reactant concentrations. The full rate equation should be considered when working with equal amounts of reactants. Similar results are obtained using either BDP or BINAP as a ligand.

5. Experimental section

5.1. Instrumentation and chemicals

Unless otherwise noted, all manipulations were performed under an argon atmosphere using standard Schlenk-type glassware. Toluene was distilled on sodium under an argon atmosphere. Solvents used for work-up were of technical grade. Commercial reagents were purchased from Acros, Sigma–Aldrich, ABCR, TCI or Apollo scientific and used as received unless stated otherwise. GC analyses were recorded on a ThermoFinnigan Trace GC apparatus with a CHIRALSIL-DEX CB (25 m, 0.25 mm, 25 μm) column. Column chromatography was carried out on silica gel (ROCC 60, 40–63 μm). TLC analyses were performed on commercial aluminum plates bearing a 0.25 mm layer of Merck Silica gel $60F_{254}$.

5.2. Representative procedure for the hydrosilylation of benzylacetone

A flame-dried Schlenk was sequentially charged with a magnetic stirrer, copper(II) 2-ethylhexanoate (0.02 eq.), and the diphosphine ligand (0.02 eq.). Freshly distilled toluene (4 ml per mmol) was added under argon, and the solution was stirred for 15 min at room temperature. The silane ($Me(OEt)_2SiH$, 1.2 eq.) was added drop wise, followed by the benzylacetone (1.0 eq.) and the mixture was allowed to stir at room temperature. After total consumption of the starting material as indicated by TLC, a solution of NaOH in methanol (5% in MeOH) was added (1.5 ml per mmol) and the solution was stirred for 30 min at room temperature. The light gray mixture was filtered on a plug silica gel (eluting with P.E./AcOEt: 7/3). Concentration *in vacuo* of the filtrate provided the desired alcohol (95–98 %yield).

5.3. Representative procedure for the kinetic studies

Hydrosilylation studies were carried out at 298 K. The general procedure was followed, with the ketone being added at t_0. The reaction was monitored by withdrawing 100 μL samples of the reaction media at specific time ($t_1, t_2, \ldots, t_n > t_0$). 400 μL of Et_2O and 500 μL of a solution of NaOH 5% in MeOH were added to each of the samples, for hydrolysis. After 1 h at room temperature, the sample mixture is filtered on a capillary plug silica gel mixed with $MgSO_4$ (eluting with 600 μL of Et_2O). If necessary, the filtrate can be kept in a freezer at 255 K for a couple of days without any loss. To each sample, 400 μL of anisole (internal standard, solution of 7500 ppm in Et_2O) was then added, bringing the final volume to 2 ml. The latter were analyzed by GC, giving the ketone and silane concentration through the calibration curves. The initial rates of the various reactions were determined from an exponential fitting analysis of the concentration curves.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.054.

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