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Hydrosilylation of Carbonyl Compounds Catalyzed by a Nickel Complex Bearing a PBP Ligand

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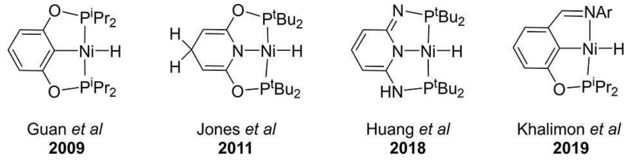
Dedicated to the memory of Professor Víctor Riera

The efficient catalytic hydrosilylation of ketones and aldehydes has been investigated using a nickel pincer hydride complex supported by a diphosphino-boryl ligand (PBP). It was found that the presence of the boryl group within the skeleton of the ligand has a beneficial effect on the catalytic activities observed for ketones compared to related pincer systems. The analysis of the reaction mechanism allows for the synthesis and characterization of a nickel alkoxide derivative by insertion of the carbonyl moiety into the Ni–H bond. Combined experimental and theoretical analysis (DFT) support a reaction mechanism that involves the initial formation of an alkoxide complex followed by reaction with the silane to release the corresponding silyl ether and regenerate the catalyst.

Introduction

Reduction of carbonyl compounds, mainly aldehydes and ketones, into their respective primary or secondary alcohols, is a fundamental reaction in organic chemistry that finds numerous applications in the pharmaceutical and cosmetic industries.[1] Consequently, in the last decades an intense search for different catalytic methodologies that effectively achieve this transformation has taken place.[2] Although the hydrogenation of C–O bonds using high pressure of H_2 gas or by means of hydrogen transfer reactions using alcohols as the source of hydrogen are the preferred procedures by industry,[3] the homogeneous catalytic hydrosilylation represents a valuable strategy for the synthesis of alcohols under milder reaction conditions. This two-step process allows the addition of a Si–H bond to a carbonyl group to generate a silyl ether that, after hydrolysis, provides the corresponding alcohol. Still, the silyl group may also behave as a protecting group that facilitate different protocols in organic synthesis.[4] To date, most reports on catalytic hydrosilylation have been focused on precious metals such as Ru, Rh, Ir or Pt;[2] however the scarcity and high cost of these metals press the need for cheaper and more abundant alternatives. Accordingly, over the past decade, we have witnessed the development of efficient catalysts based on first-row transition metals,[5] being iron the metal that dominates the field, whereas studies with other metals such as nickel are less common.[6–22]

In 2009 Guan et al. reported one of the first studies on nickel-catalyzed hydrosilylation of aldehydes employing a POCOP pincer hydride complex that, on the other hand, exhibited low catalytic activity and only partial hydrosilylation of ketones.[8] Shortly after, Mindiola and coworkers tested a nickel complex supported by an amido-phosphino ligand that demonstrated increased efficiency in the reduction of ketones.[9] In 2012, two different papers, by the groups of Royo and Ritleng, appeared simultaneously using N-Heterocyclic carbene complexes of nickel that are active for the reduction of both, aldehydes and ketones, with remarkable catalytic activity.[11,12] More recently, the family of carbene ligands employed in hydrosilylation reactions was expanded using a variety of systems based on triazolylidene bearing different hemilabile groups containing donor atoms (N, S, O or P) and two independent papers by Albrecht and Ritleng reported highly efficient nickel-based catalysts for the hydrosilylation of aldehydes with comparable catalytic activities at room temperature.[15,16] To our knowledge, apart from Guan's catalyst, only three nickel pincer complexes have been tested in the catalytic hydrosilylation of aldehydes or ketones (Figure 1).[8,10,21,22] It is worth mentioning that all these catalysts proved to be quite active for the hydrosilylation of aldehydes, being Guan's system the most active one, but showed very low (if any) catalytic activity with ketones.



Guan *et al* **2009** Jones *et al* **2011** Huang *et al* **2018** Khalimon *et al* **2019**

Figure 1. Previously reported nickel pincer catalysts for the hydrosilylation of aldehydes and ketones.

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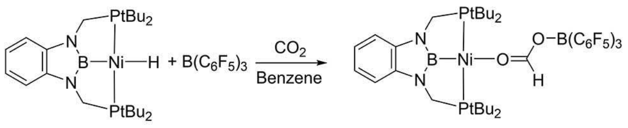
Recently, we have reported the synthesis of a nickel hydride complex supported by a pincer diphosphino-boryl ligand (**1**) that turned out to be a very efficient catalyst for the highly selective hydrosilylation of CO_2 to bis(silyl)acetal derivatives, using $B(C_6F_5)_3$ as co-catalyst (Scheme 1).[23] We reasoned that the strong σ-donor properties along with the high *trans*-influence of the boryl ligand in **1** could increase the nucleophilic character of the hydride group which might translate into a high catalytic efficiency for the reduction of C–O bonds.[24,25] In fact, the results reported by Guan et al[8] and Jones et al,[10] using POCOP- and PONOP-pincer nickel hydride complexes for the hydrosilylation of aldehydes support this hypothesis (Figure 1). In these systems, as expected, a high *trans*-influence ligand such as a carbon-based donor eases the insertion of the carbonyl functionality while the nitrogen-based ligand reacts slowly.

Results and Discussion

Bearing in mind these previous results, as a first approach to test the catalytic behavior of **1**, we analyzed the reduction of benzaldehyde under several experimental conditions (Scheme 2). We found the best catalyst performance using 5 mol% of **1** in C_6D_6, employing Ph_2SiH_2 as reductant at room temperature (Table 1). Different conditions such as triethylsilane, Me_2PhSiH or poly(methylhydrosiloxane) (PMHS) as reductants, or THF or pure silane as solvent did not translate into greater catalytic activity even at higher temperatures. $PhSiH_3$ leads to fast conversions (1 h at RT) but mixtures of $PhSiH_2(OBn)$ and $PhSiH(OBn)_2$ were obtained (product distribution 75:25). Reducing the amount of nickel to 2.5 or 1 mol% increased the reaction time to 12 and 24 h, respectively. Increasing the temperature to 50 °C decreases the reaction time to 3.5 h, however, since the catalytic studies reported by Guan were performed at room temperature, we decided to carry out this study at the same temperature to compare both systems.

Using the optimized reaction conditions, both aliphatic aldehydes as well as benzaldehydes having substituents with different electronic effects at the *para* position of the phenyl ring, were tested (Table 2). Cyclohexylcarbaldehyde was readily reduced to the hydrosilylated product after only 3.5 h (Table 2, entry 1). Benzaldehydes substituted with both electron-donating and electron-withdrawing groups are all reduced in excellent yields. Hydrosilylation of 4-dimethylaminobenzaldehyde was completed after 3.5 h while *p*-anisaldehyde and 4-chlorobenzaldehyde required 9 h and 24 h respectively for completion (Table 2, entries 3–5). The catalyst was not affected by using the halogenated derivative and no decomposition was observed. Similarly to the results reported by Guan, the substituents on the phenyl ring do affect the kinetics of the reaction, requiring longer reaction times when electro-withdrawing groups are used. A potential explanation



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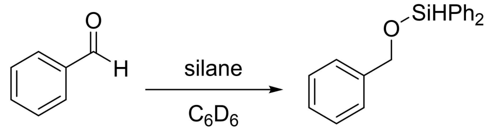
Scheme 1. Reactivity of complex **1** with CO_2.



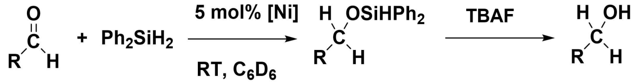
Scheme 2. Nickel catalyzed hydrosilylation of benzaldehyde.

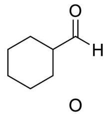
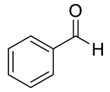
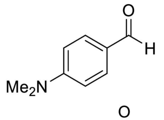
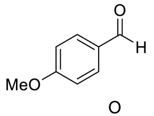
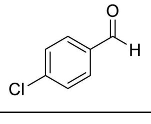
Table 1. Optimization of the reaction conditions for the hydrosilylation of benzaldehyde.

Entry[a]	Catalyst [mol%]	Silane	Time [h]	Conversion [%][b]
1	5	Ph_2SiH_2	9	>99
2	2.5	Ph_2SiH_2	12	>99
3	1	Ph_2SiH_2	24	>99
4[c]	5	Ph_2SiH_2	3.5	>99
5	5	Et_3SiH	15	0
6[c]	5	Et_3SiH	2	0
7[d]	5	Et_3SiH	2	0
8[d]	5	Me_2PhSiH	2	0
9[d]	5	PMHS	10	0
10	5	$PhSiH_3$	1	[e]

[a] Reaction conditions: benzaldehyde (1 mmol); silane (1 equivalent), C_6D_6 (0.4 ml), RT. [b] Conversions determined by crude ^1H NMR. [c] Reaction performed at 50 °C. [d] Reactions performed at 70 °C. [e] mixture of $PhSiH(OBn)_2$ and $PhSiH_2(OBn)$ was obtained (product distribution 75:25).

Table 2. Nickel catalyzed hydrosilylation of aldehydes.



Entry[a]	Substrate		Time [h]	Conversion [%][b]	Yield [%]
1		a	3.5	>99	68
2		b	9	>99	64
3		c	3.5	>99	81
4		d	9	>99	60
5		e	24	>99	63

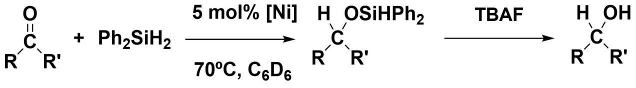
[a] Reaction conditions: aldehyde (0.196 mmol); silane (1 equivalent), C_6D_6 (0.4 ml), RT. [b] Conversions determined by ^1H NMR of the reaction mixture.

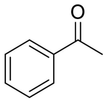
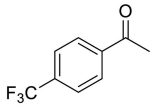
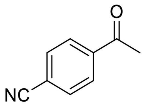
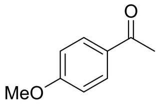
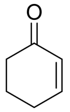
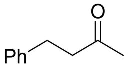
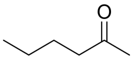
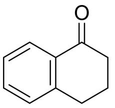
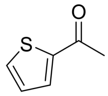
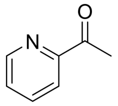
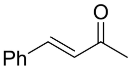
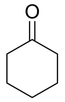
to this phenomenon may lie on the stabilization of some intermediate species (*vide infra*).

However, comparison of **1** with Guan's catalyst revealed a superior catalytic activity in hydrosilylation of aldehydes for the latter (0.2 mol% catalyst loading and 2 h at RT for the reduction of benzaldehyde to obtain the corresponding alcohol in 79% yield vs 68% yield in 3.5 h using 5 mol% of catalyst loading with our system).[8] Other systems, for example the Royo's catalyst, yields 89% of the alcohol at room temperature in 5 minutes using 1 mol% of catalyst. Although, our results in the hydrosilylation of aldehydes were not remarkable, we considered of interest to explore the hydrosilylation of ketones. Usually, ketones are viewed as more challenging substrates due to the greater steric hindrance around the carbonyl group compared to aldehydes. For instance, the nickel catalyst reported by Albrecht *et al.* has no catalytic activity towards ketones but is extremely active towards aldehydes.[15] In line with this, harsher reaction conditions and/or lower catalytic activities compared to those for the reduction of aldehydes, were reported for all of the nickel catalysts previously described.

Gratifyingly, reduction of acetophenone was readily completed in 6 h at 70 °C using 5 mol% of catalyst (Table 3, entry 1). It must be mentioned that the same catalytic reaction using Guan's nickel catalyst required extended reaction times to obtain a conversion of 18% (24 h at 70 °C) with 1 mol% catalyst loading.[8c] In our case, 92% conversion was obtained after 13 h at 70 °C using 1 mol% catalyst loading. The substrate scope of this reaction was then investigated, and the results are presented on Table 3. We analyzed a variety of acetophenone derivatives presenting different substituents on the *para*-position of the phenyl ring. We found that while 4'-methoxyacetophenone was rapidly reduced in 5 h, the CF_3 substituted analogue required longer reaction times (Table 3, entries 2–4). Only 50% conversion was observed after 24 hours at 70 °C when 4-acetylbenzonitrile was employed. In addition, other aliphatic (2-hexanone; 4-phenylbutan-2-one), cyclic (cyclohexanone; α-tetralone) and heteroaromatic ketones (2-acetylthiophene; 2-acetylpyridine) were also studied under the same conditions. Cyclohexanone was hydrosilylated in only 1 h (Table 3, entry 5) while the reduction of α-tetralone, 2-hexanone and 4-phenylbutan-2-one (Table 3, entries 6–8) required from 4.5 to 10 hours to reach completion. The reduction of 2-acetylthiophene proceeded slowly and only 50% of the corresponding silyl ether was obtained after 24 h at 70 °C (Table 3, entry 9). No hydrosilylation was observed for 2-acetylpyridine (Table 3, entry 10). Finally, analysis of α,β-unsaturated ketones (*trans*-4-phenyl-3-buten-1-one and 2- cyclohexen-1-one) ended up giving a mixture of reduction products of both alkene and carbonyl functionalities (Table 3, entries 11–12*)*.[26] A comparative analysis of the data previously reported positioned our catalyst among the most active nickel catalysts for hydrosilylation of ketones in terms of conversions but, in general, the isolated yields of the corresponding alcohols are lower that what has been observed using other well defined nickel catalysts.'[11][12] However, it is important to mention that many variables have to be considered when comparing two different catalytic systems (temperature, catalyst loading, reaction time, …..) so an accurate comparison cannot be made.

Table 3. Nickel catalyzed hydrosilylation of ketones.

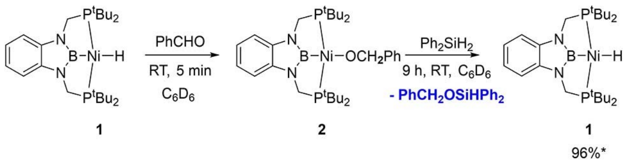


Entry[a]	Substrate		Time [h]	Conversion [%][b]	Yield [%]
1		f	6	> 99	56
2		g	6.5	> 99	50
3		h	24	50	37
4		i	5	> 99	67
5		j	1	> 99	54
6		k	10	> 99	72
7		l	4.5	> 99	47
8		m	6	> 99	46
9		n	24	50	–
10		o	12	–	–
11[c,d]		p	2	Mixture[d]	–
12[c,d]		q	5	Mixture[d]	–

[a] Reaction conditions: ketone (0.196 mmol); Ph_2SiH_2 (1 equivalent), C_6D_6 (0.4 ml), 70 °C. [b] Conversions determined by ^1H NMR of the reaction mixture. [c] 2 equivalents of Ph_2SiH_2 were used. [d] > 99% conversion by ^1H NMR. See ref. [26].

With these experimental results in hand, we were interested on the mechanism of this reaction. Different pathways that can be operative in metal-catalyzed aldehyde and ketone hydrosilylation reactions have been described. In most of the cases, a *metal hydride mechanism*, based on the initial carbonyl insertion into the metal-hydride bond to give an alkoxide, is postulated. However, other possibilities based on a *non-hydride mechanism* have also been demonstrated. Recently, Nikonov and co-workers reported a series of labeling experiments to certainly discriminate between the *hydride mechanism* (commonly accepted) *and* the *non-hydride* one.[27] To find experimental evidence to distinguish between different pathways, we studied the stoichiometric reaction between complex **1** and benzaldehyde (Scheme 3).

We observed the rapid insertion of the carbonyl group into the Ni–H bond to form a new complex **2** that shows a signal at 4.7 ppm in the ^{1}H NMR spectrum that correlates with a signal in the ^{13}C NMR spectrum at 72.9 ppm, attributable to the methylene fragment of a benzyloxide group.[8] The ^{31}P and ^{11}B NMR spectra exhibit signals (δ^{31}P 82.1 ppm; δ^{11}B 38 ppm) at a higher field than those observed for **1** (See Experimental Section). This result, in accordance with a hydride mechanism, is not surprising considering the strong σ-donor properties and high *trans*-influence of the boryl group that renders the hydride group very nucleophilic.[25] Furthermore, treatment of a solution of the nickel deuteride complex [(PBP)Ni–D] (**1-D**) (prepared by reaction of ^{tBu}(PBP)NiMe with 2 bar of D_2) with 4 equivalents of benzaldehyde leads to the formation of a mixture (1:2) of complex [(PBP)Ni-OCH_2Ph] (**2**) and [(PBP)Ni-OCHDPh] (**2-D**) proving the existence of an equilibrium that interconverts the benzyloxide and the hydride nickel complexes. In fact, β-hydrogen elimination processes are frequently observed in nickel alkoxide complexes and constitutes a common decomposition pathway, however the stability of these species seems to be associated to the reactivity of the nickel hydride complex more than to the β-hydrogen elimination process itself.[28] Then, we confirmed that complex **2** reacts slowly with Ph_2SiH_2 at room temperature to produce $PhCH_2OSiHPh_2$ and nickel hydride complex **1** (Scheme 3). Additionally, we conducted a second experiment consisting of the stoichiometric reaction of benzaldehyde with Ph_2SiH_2 and **1** in a 1:1:1 ratio. Monitoring the progress of this reaction by ^{1}H and ^{31}P NMR allowed us to observe, initially, the formation of **2** followed by the slow release of the silyl ether and formation of **1** (See ESI). In order to get more information about this catalytic process, we performed a DFT analysis of the hydrosilylation of benzaldehyde catalyzed by **1** using the PBE0/def2TZVP/def2QZVP level of theory, including Grimme's D3 (PBE0-D3) dispersion correction (see ESI for more information and references).[29] The overall Gibbs free energy profile is represented on Figure 2, using complex **1**, benzaldehyde and diphenylsilane as energy reference. The first step of the catalytic cycle involves the insertion of the aldehyde C=O group into the nickel-hydride bond via TS1 (18.9 kcal mol^{-1}) to afford nickel alkoxide complex **2** which



Scheme 3. Reactivity studies of **1** with benzaldehyde and Ph_2SiH_2; * conversion determined by ^{1}H NMR spectroscopy.

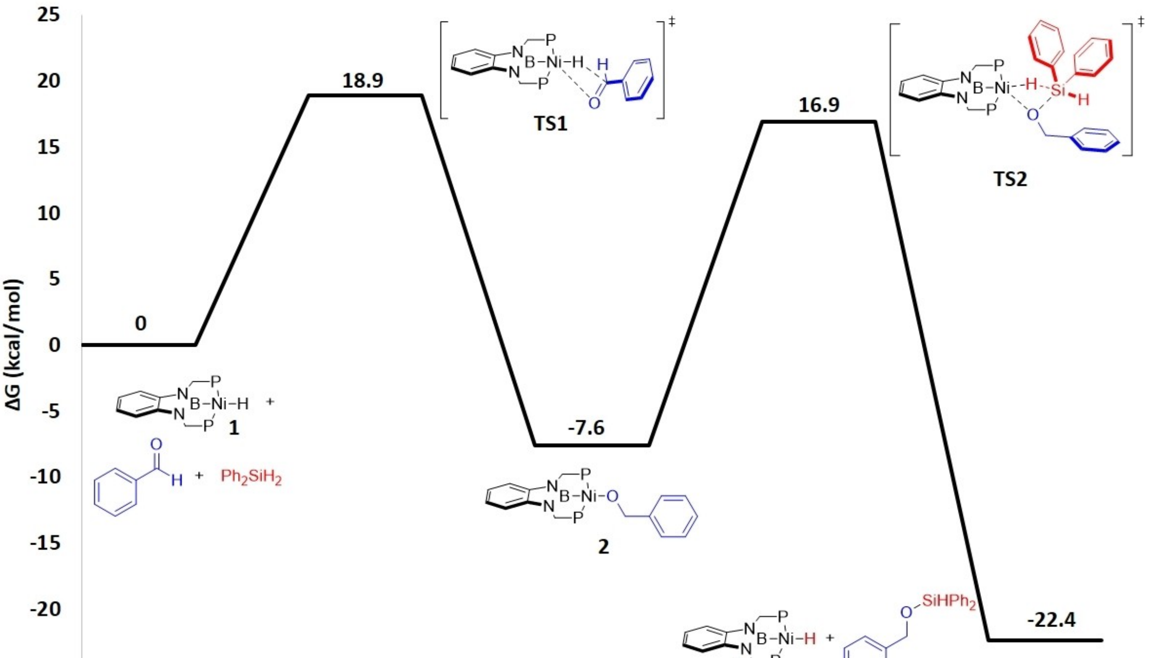


Figure 2. Gibbs energy profile in benzene for the reaction of 1 with Ph_2SiH_2 and benzaldehyde. Relative Gibbs energies at 298 K and 1 M in kcal mol^{-1}. The phosphine groups (P^{t}Bu$_2$) have been abbreviated as P for clarity.

is 7.6 kcal mol^{-1} more stable than the origin. Then, Ph_2SiH_2 interacts with **2** through TS2 (16.9 kcal mol^{-1}), and this step is associated to the highest energy barrier (24.5 kcal mol^{-1}) of the whole process. Lastly, from TS2, the resulting silyl ether product is released, and the nickel hydride complex is regenerated, closing the catalytic cycle. The values extracted from this theoretical analysis are consistent with the experimental observations: i) during the catalytic reaction **2** was the only nickel species observed by NMR spectroscopy at room temperature; ii) the formation of **2** is instantaneous at room temperature while the hydrosilylation step requires several hours to reach completion.

Finally, we have investigated the electronic effect of the substituents in the *para* position of the aryl fragment calculating the energy profile for this reaction with *p*-NO_2-benzaldehyde and *p*-NMe_2-benzaldehyde (See ESI).The insertion of the C–O bond into the Ni–H bond to form the corresponding alkoxide complex is exergonic in both cases ($\Delta G = -12.7$ and -1.4 kcal mol^{-1} respectively) and the activation energy is lower for the aldehyde bearing the more electrophilic carbonyl carbon ($E_a(NO_2) = 15.4$ vs $E_a(NMe_2) = 25.6$ kcal mol^{-1}) which is in accordance with a mechanism involving a nucleophilic hydride addition. The second step, the hydrosilylation of the alkoxide complex, requires higher activation barriers than the first step, as observed for benzaldehyde, though the reaction is facilitated by electron-donor substituents on the *para* position ($E_a(NMe_2) = 23.5$ vs $E_a(NO_2) = 25.3$ kcal mol^{-1}) that increase the nucleophilic character of the alkoxide species easing the reaction towards Ph_2SiH_2. These numbers are consistent with the experimental observations (See Table 2 and Table 3).

Conclusion

Our catalytic studies indicate that, by using a pincer ligand with a boryl group at the central atom, the enhanced nucleophilic character of the hydride group *trans* to it facilitates the hydrosilylation of ketones compared to other analogous pincer systems. On the contrary, our system proved to be less active for the hydrosilylation of aldehydes. We observed that both aromatic and aliphatic substrates are easily reduced to the corresponding silyl ether being the latter more efficiently reduced that the former. Electron-donating groups on the *para* position of the aryl ring increase the rate of the reaction while no conversion was observed with ketones bearing heteroaromatic substituents such as pyridine or thiophene. Both DFT analysis and the experimental observations point to a hydride mechanism for the hydrosilylation of aldehydes and ketones.

Experimental Section

General: All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of argon or of high purity nitrogen, respectively. All solvents were dried and degassed prior to use. Benzene-*d*$_6$ (C_6D_6) was distilled under argon over sodium and then degassed and dried over 4 Å molecular sieves. All other compounds were commercially available and were used as received. Solution NMR spectra were recorded on Bruker DRX-400 spectrometer and they were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standard (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). ^{11}B NMR spectra were referenced to an external standard of $BF_3 \cdot Et_2O$. ^{31}P NMR chemical shifts were referenced to an external 85% solution of H_3PO_4 in the adequate solvent. $NiBr_2$(dme) was purchased from Aldrich and used as received. [(^{tBu}PBP)NiBr], [(^{tBu}PBP)NiMe] and [(^{tBu}PBP)NiH] (**1**) were prepared as previously described.[21]

Synthetic procedures

Catalytic reactions and Spectroscopic Characterization Data for the Alcohol Products

In a glove box, the corresponding aldehyde or ketone and Ph_2SiH_2 were added (first the carbonyl derivative (0.196 mmol) followed by the silane (0.196 mmol) to a J. Young NMR tube containing a solution of **1** (0.0098 mmol) in 400 μL of C_6D_6. Then, the tube was sealed, and the reaction progress was monitored by ^1H NMR spectroscopy. The catalytic hydrosilylation reaction was performed at room temperature for aldehydes and at 70 °C for ketones. The conversion was determined by ^1H NMR. Once the reaction was completed, the solution was treated with a THF solution of TBAF (200 μl, 0.2 mmol) and stirred at room temperature for 15 minutes. Then, the volatiles were removed under vacuum and 5 mL of water were added. The organic product was extracted with diethyl ether (2 x 6 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduce pressure. The alcohol products with high boiling points were purified by short silica gel column chromatography using ethyl acetate-hexanes mixtures (5 to 10%). Those alcohols with low boiling points were purified by distillation. All the alcohol products have been characterized by ^1H NMR and the spectroscopic data were identical to previously reported data (See ESI for details).

Synthesis and NMR characterization of [^{tBu}(PBP)Ni(OCH_2Ph)] (2)

Complex **2** was prepared following a slightly modified procedure to that previously reported by our group: (11 mg, 0.02 mmol) of [^{tBu}(PBP)NiMe] were dissolved in 400 μL of C_6D_6 in a J. Young valve NMR tube, then the tube was degassed via three freeze-pump-thaw cycles, charged with H_2 (4 bar) and heated at 70 °C for 4 hours. After checking by ^1H and ^{31}P {^1H} NMR spectroscopy that the reaction was completed, the tube was degassed again and 2.2 μL (0.02 mmol) of benzaldehyde were added at room temperature. ^1H and $^{31}P\{^1H\}$ NMR spectra confirmed the instantaneous and clean formation of complex **2**. Attempts to purify it or isolate it led to its decomposition. ^1H NMR (400 MHz, C_6D_6): 1.28 (t, $^3J_{HP} = 6.4$ Hz, 36H, ^{t}Bu); 3.49 (s, 4H, NCH_2); 5.35 (s, 2H, OCH_2); 6.87 (dd, ($^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz, CH aromatic); 7.09 (dd, ($^3J_{HH} = 6$ Hz, $^4J_{HH} = 3$ Hz, CH aromatic); 7.18 (t, $^3J_{HH} = 8$ Hz; *p*-CH phenyl); 7.40 (t, $^3J_{HH} = 8$ Hz; *m*-CH phenyl); 7.80 (t, $^3J_{HH} = 8$ Hz; *o*-CH phenyl). $^{31}P\{^1H\}$ (162 MHz, C_6D_6): 82.1 ppm; $^{11}B\{^1H\}$ (128 MHz, C_6D_6): 38 ppm; $^{13}C\{^1H\}$ (100 MHz, C_6D_6): 29.3 (s, ^{t}Bu-CH_3); 34.4 (t, $^3J_{CP} = 4.5$ Hz, ^{t}Bu–Cq); 39.8 (t, $^3J_{CP} = 18.5$ Hz, NCH_2); 72.9 (s, OCH_2); 107.9 (s, CH aromatic-PBP); 118.2 (s, CH aromatic-PBP); 124.8 (s, CH aromatic-Ph); 126.2 (s, CH aromatic-Ph); 133.5 (s, Cq–Ph); 139.2 (s, Cq aromatic-PBP).

Experimental procedure for the NMR tube reaction of 2 with Ph_2SiH_2

2.2⊥⊥μL (0.02 mmol) of benzaldehyde were added at room temperature to a solution of 0.02 mmol of complex **1** in 400 μL of C_6D_6 in a J. Young NMR tube (prepared as indicated in the previous section). ^1H and $^{31}P\{^1H\}$ NMR spectra confirmed the instantaneous and clean formation of complex **2**. Then 4 μL (0.02 mmol) of Ph_2SiH_2 were added and the reaction progress was monitored by ^1H NMR. After 4 hours at room temperature, the ^1H NMR spectrum showed the formation of the corresponding silyl ether ($PhCH_2OSiPh_2H$) along with nickel hydride complex **1** (40%). After 9 hours at room temperature **2** was completely transformed into **1**.

Stoichiometric reaction between 1 and an equimolar mixture of Ph_2SiH_2 and benzaldehyde

A solution of an equimolar mixture of Ph_2SiH_2 and benzaldehyde in 100 μL of C_6D_6 [4 μL of Ph_2SiH_2 (0.02 mmol) and 2.2 μL of benzaldehyde (0.02 mmol)] were added at room temperature to a solution of 0.02 mmol of complex **1** in 400 μl of C_6D_6 in a NMR J. Young tube (prepared as indicated in the previous section). The reaction progress was followed by ^1H NMR. After 5 minutes **1** was fully transformed into complex **2** and the formation of a very small amount of the corresponding silyl ether ($Ph_2HSiOCH_2Ph$) was observed along with the presence of unreacted Ph_2SiH_2. After 9 hours at room temperature, Ph_2SiH_2 was completely consumed and complex **2** was transformed into **1**.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals, Beller, M., Bolm, Eds., Vol. 1, 2nd Edition, Wiley-VCH: Weinheim, **2008**.

[2] a) B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluc in *Hydrosilylation: A Comprehensive Review on Recent Advances*, (Eds.: B. Marciniec), Springer, Berlin, **2009**; b) S. Díez-González, S. Nolan, *Org. Prep. Proced. Int.* **2007**, *39*, 523; c) A. K. Roy, *Adv. in Organomet. Chem., Vol. 55*, (Eds.: R. C. West, A. F. Hill, M. J. Fink), Elsevier, Oxford, **2008**, pp. 1–53; d) I. Ojima, Z. Li, J. Zhu in *The Chemistry of Organic Silicon Compound, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**; e) I. Ojima in *The Chemistry of Organic Silicon Compound*, (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1989**.

[3] H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103.

[4] a) R. D. Crouch, *Synth. Commun.* **2013**, 43, 2265–2279; b) R. D. Crouch, *Tetrahedron* **2013**, *69*, 2383–2417.

[5] For selected reviews, see: hydrosilylation with Mn: a) R. J. Trovitch, *Acc. Chem. Res.* **2017**, *50*, 2842; b) *X. Yang, C. Wang, Chem. Asian J.* **2018**, *13*, 2307. Hydrosilylation with Fe: c) A. Raya-Baron, P. Oña-Burgos, I. Fernández, *ACS Catal.* **2019**, *9*, 5400; d) D. Wei, C. Darcel, *Chem. Rev.* **2019**, *119*, 2550; General reviews about catalytic hydrosilylation with First Row Transition Metals: e) M. Bhunia, S. P. S. K. Mandal, *Coord. Chem. Rev.* **2020**, *405*, 213110; f) B. Royo, *Advances in Organometallic Chemistry*, *Vol. 72*, (Ed.: P. J. Pérez), Elsevier, Oxford**, 2019**, pp. *50–102*.

[6] F.-G. Fontaine, R.-V. Nguyen, D. Zargarian, *Can. J. Chem.* **2003**, *81*, 1299.

[7] T. Irrgang, T. Schareina, R. Kemp, *Journal of Molecular Catalysis A: Chemica*l **2006**, *257*, 48.

[8] a) S. Chakraborty, J. A. Krause, H. Guan, *Organometallics* **2009**, *28*, 582; b) S. Chakraborty, H. Guan, *Dalton Trans.* **2010**, *39*, 7427. For a related work, see: c) J. Chang, F. Fang, C. Tu, J. Zhang, N. Ma, X. Chen, *Inorg. Chim. Acta* **2021**, *515*, 120088; d) Hydrosilylation of cyclohexanone (60% conversion) and benzophenone (6% conversion) were also reported by Guan. See ref. [8a]

[9] B. L. Tran, M. Pink, D. Mindiola, *Organometallics* **2009**, *28*, 2234.

[10] S. Kundu, W. W. Brennessel, W. D. Jones, *Inorg. Chem.* **2011**, *50*, 9443.

[11] L. Postigo, B. Royo, *Adv. Synth. Catal.* **2012**, *354*, 2613.

[12] L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J.-B. Sortais, V. Ritleng, *Adv. Synth. Catal.* **2012**, *354*, 2619. See also: J. Zheng, C. Darcel, J.-B. Sortais, *Catal. Sci. Technol.* **2013**, *3*, 81.

[13] S. N. MacMillan, W. H. Harman, J. C. Peters, *Chem. Sci.* **2014**, *5*, 590.

[14] L. Wang, H. Sun, X. Li, *Organometallics* **2015**, *34*, 5175.

[15] Y. Wei, S.-X. Liu, H. Mueller-Bunz, M. Albrecht, *ACS Catal.* **2016**, 6, 8192.

[16] F. Ulm, A. I. Poblador-Bahamonde, S. Choppin, S. Bellemin-Laponnaz, M. J. Chetcuti, T. A. V. Ritleng, *Dalton Trans.* **2018**, *47*, 17134.

[17] M. Henrion, B. P. Cardoso, V. César, M. J. Chetcuti, V. Ritleng, *Organometallics* **2017**, *36*, 1113

[18] H. Tafazolian, R. Yoxtheimer, R. S. Thakuri, J. A. R. Schmidt, *Dalton Trans.* **2017**, *46*, 5431.

[19] C. L. Rock, T. L. Groy, R. J. Trovitch, *Dalton Trans.* **2018**, *47*, 8807

[20] M. C. Neary, P. J. Quinlivan, G. Parkin, *Inorg. Chem.* **2018**, *57*, 374.

[21] H. Li, T. P. Gonçalves, J. Hu, Q. Zhao, D. Gong, Z. Lai, Z. Wang, J. Zheng, K.-W. Huang, *J. Org. Chem.* **2018**, *83*, 14969.

[22] K. A. Gudun, M. Segizbayev, A. Adamov, P. N. Plessow, K. A. Lyssenko, M. P. Balanay, A. Y. Khalimon, *Dalton Trans.* **2019**, *48*, 1732.

[23] a) P. Ríos, N. Curado, J López-Serrano, A. Rodríguez, *Chem. Commun.* **2016**, *52*, 2114; b) P. Ríos, J. López-Serrano, A. Rodríguez, *ACS Catal.* **2016**, *6*, 5715.

[24] a) H.-W Suh, T. J. Schmeier, N. Hazari, R. A. Kemp, M. K. Takase, *Organometallics* **2012**, *31*, 8225; b) S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, *Acc. Chem. Res.* **2015**, *48*, 1995.

[25] J. Zhu, Z. Lin, T. B. Marder, *Inorg. Chem.* **2005**, *44*, 9384.

[26] For substrate **p** and **q:** A mixture of products was obtained and the disappearance of the characteristic olefinic resonances and those corresponding to the starting materials was observed but not further purification was done.

[27] O. G. Shirobokov, L. G. Kuzmina, G. I. Nikonov, *J. Am. Chem. Soc.* **2011**, *133*, 6487.

[28] a) L. M. Martínez-Prieto, E. Ávila, P. Palma, E. Álvarez, J. Cámpora, *Chem. Eur. J.* **2015**, 21, 9833; b) L. M. Martínez-Prieto, J. Cámpora, *Isr. J. Chem.* **2020**, *60*, 373.

[29] The calculations were performed with the Gaussian 09 program: Gaussian 09, Revision E.01, Gaussian, Inc, Wallingford CT, 2013, the full Gaussian citation can be found in the ESI.

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