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## Reductive deoxygenation of tertiary alcohols: a cobalt-catalyzed hydrosilylation approach

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Dehydrogenation of tertiary alcohols is both highly challenging and of notable importance in synthetic chemistry. We report a readily available  $\text{Co}_2(\text{CO})_8$  catalyzed hydrosilylation protocol for the reductive deoxygenation of tertiary alcohols involving a radical mechanism. Successful deoxygenation of various tertiary, secondary and primary alcohols demonstrated the broad applicability, including syntheses of fine chemicals. A plausible mechanistic path was proposed based on several control experiments.

### Introduction

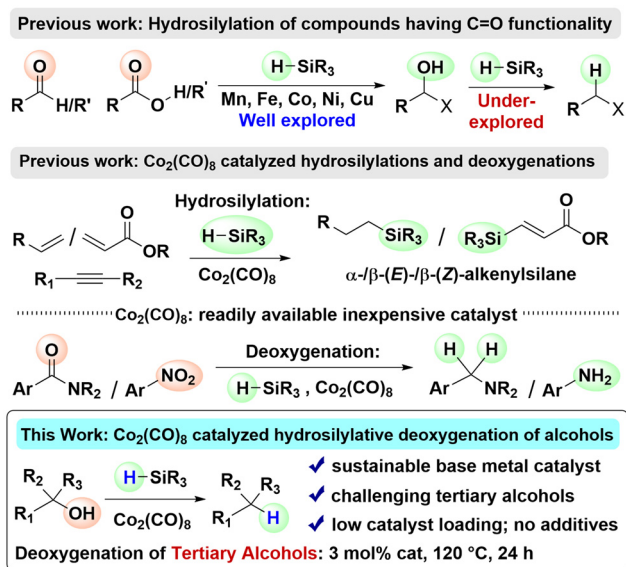
Deoxygenation of alcohols to alkanes is a key transformation for producing more stable, energy-dense, and versatile hydrocarbons, which are used as fuels, materials, and chemical intermediates.<sup>1</sup> It is an important industrial process, with applications ranging from biofuel production to synthetic chemistry and pharmaceutical applications. However, reductive deoxygenation of alcohols presents significant challenges due to the high bond dissociation energy of the C–OH bond and the poor leaving ability of the hydroxyl group.<sup>2</sup> Alcohol deoxygenation methods can be single-step and two-step strategies. The Barton–McCombie reaction, a classic method, involves a two-step process: first, conversion of the hydroxyl group into a better leaving group, followed by reduction with a stoichiometric amount of highly toxic  $\text{Bu}_3\text{SnH}$ .<sup>3</sup> Although modifications have been made, this two-step procedure still limits broader applicability. The search for sustainable and environmentally benign deoxygenation of alcohols has primarily focused on base metal catalysts<sup>4</sup> and silanes as hydrogen sources.<sup>5</sup> In 1988, the Chatgialiloglu group used  $(\text{Me}_3\text{Si})_3\text{SiH}$  as a free radical hydride donor, replacing  $\text{Bu}_3\text{SnH}$  with hydrosilane, a non-toxic hydrogen transfer reagent.<sup>6a</sup> In general, hydrosilanes offer advantages such as low toxicity, cost efficiency, and tunability through substituents on silicon.<sup>6</sup> In 1997, the Lopez group reported the first deoxygenation using silanes in a catalytic variant of the Barton–McCombie reaction, although it required organotin compounds and alcohol pre-functionalization.<sup>7</sup> This led to further exploration of silanes as hydride sources in catalytic systems with sustainable base metals. Titanium has been the most extensively investigated,

with numerous titanocene-mediated catalytic systems utilized for the reductive deoxygenation of alcohols.<sup>8</sup> In this context of using sustainable base metals, only a few research groups have reported progress. In 2014, Dang *et al.* employed a Cu-catalyst with  $\text{Me}_3\text{SiOSiMe}_3$  as a hydrogen donor.<sup>9</sup> However, this process proceeded *via* a two-step pathway involving a triflate intermediate. In 2017, Bauer *et al.* used a Mn–PNP pincer complex for this dehydrogenation, followed by Wolff–Kishner reduction utilizing hydrazine.<sup>10</sup> However, this approach has limitations, as hydrazine is a toxic and hazardous reagent and it requires prolonged reaction times. In 2021, the Newman group reported an excellent work on the deoxygenation of various C–O containing functional groups using  $\text{NiBr}_2$ -diglyme and  $\text{Me}_2\text{HSiSiHMe}_2$ .<sup>11</sup> However, this method required high catalyst loading and a stoichiometric amount of a base. Recently, the Gunanathan group used a Co–NNN pincer complex for the reductive deoxygenation of alcohols using  $\text{Et}_2\text{SiH}_2$ .<sup>12</sup> However, this method requires a strong base and was mostly effective for reducing primary alcohols.

Base metal catalysts with improved efficiency need to be developed for the hydrosilylative deoxygenation of alcohols. Cobalt is an important base metal, which is much cheaper and less toxic than its heavier analogues Rh and Ir (widely used as a catalyst). Along with other base metals, Co-catalysts have been extensively used in the hydrosilylation of various substrates such as alkynes, alkenes, allenes, amides, nitriles, aldehydes, ketones and esters (Scheme 1).<sup>13</sup> Notably, carbonyl and carboxyl groups were reduced to the corresponding alcohols; further reduction/deoxygenation was not achieved. In the context of Co-catalyzed hydrosilylations,  $\text{Co}_2(\text{CO})_8$  is particularly important (Scheme 1). The application of  $\text{Co}_2(\text{CO})_8$  in the hydrosilylation of diverse organic substrates such as alkenes, alkynes, nitriles and  $\alpha,\beta$ -unsaturated esters is well established.<sup>14</sup> Importantly,  $\text{Co}_2(\text{CO})_8$  was used for the hydrosilylative deoxygenation of amides to amines.<sup>14e</sup> We previously reported the efficient use of  $\text{Co}_2(\text{CO})_8$  for the deoxygenation of nitro-

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**Scheme 1** Base metal catalyzed hydrosilylation and hydrosilylative deoxygenation.

arenes to aromatic amines using  $\text{PhSiH}_3$  as a reducing agent.<sup>15</sup> However, hydrosilylative deoxygenation of alcohols to alkanes using  $\text{Co}_2(\text{CO})_8$  is not documented. With regard to the deoxygenation of alcohols, reduction of tertiary alcohols to alkanes is both highly challenging and of notable importance. Herein, we report  $\text{Co}_2(\text{CO})_8$  catalyzed hydrosilylative deoxygenation of tertiary alcohols to the corresponding alkanes (Scheme 1).

## Results and discussion

Unlike primary and secondary alcohols, tertiary alcohols lack a hydrogen atom on the carbon bearing the hydroxyl group,

making conventional  $\beta$ -hydride elimination pathways inaccessible. Moreover, tertiary alcohols are generally more sterically hindered, which can impede substrate-catalyst interactions. This structural limitation necessitates alternative reaction mechanisms, such as radical or hydride transfer processes. Thermodynamically, the transformation is often uphill, as alkanes are more reduced than alcohols, necessitating the use of potent reducing agents such as hydrosilanes under metal catalysis. Motivated by the successful use of  $\text{Co}_2(\text{CO})_8$  in various hydrosilylations, particularly in the challenging hydrosilylative deoxygenation of nitroarenes to anilines,<sup>15</sup> we selected  $\text{Co}_2(\text{CO})_8$  as a potential catalyst for the hydrosilylative deoxygenation of tertiary alcohols. In the presence of heat or light,  $\text{Co}_2(\text{CO})_8$  generates a reactive  $\text{Co}(\text{CO})_4$  radical, which might be well suited for the present purpose. Guided by this rationale,  $\text{Co}_2(\text{CO})_8$  was employed as a readily available catalyst for the hydrosilylative deoxygenation of 1,1-diphenylethanol (**A**<sub>1</sub>) as the standard substrate and  $\text{PhSiH}_3$  as the reducing agent (Table 1). Deoxygenation of tertiary alcohol **A**<sub>1</sub> was tested by using two equivalents of  $\text{PhSiH}_3$  and 5 mol% of  $\text{Co}_2(\text{CO})_8$  at 120 °C in THF as the solvent and the reaction was run for 24 h (entry 1). We observed complete conversion of **A**<sub>1</sub> to the desired deoxygenated product 2,2-diphenylethane (**B**<sub>1</sub>). When the catalyst loading was reduced to 3 mol%, complete deoxygenation of **A**<sub>1</sub> to **B**<sub>1</sub> (with an excellent isolated yield of 93%) was also achieved (entry 2). Further reduction of the catalyst loading to 2 mol% did not lead to complete deoxygenation of **A**<sub>1</sub> and a significant amount of unreacted **A**<sub>1</sub> was noted (entry 3). When the reaction time was reduced to 18 h, almost complete conversion of **A**<sub>1</sub> to **B**<sub>1</sub> was observed under 3 mol% catalyst loading (entry 4). However, a very small amount of **A**<sub>1</sub> was left unreacted. Similarly, a small amount of unreacted **A**<sub>1</sub> was also noted when the reaction was carried out at 100 °C for 24 h under 3 mol% catalyst loading (entry 6). Finally, we tested various silanes such as  $\text{Ph}_2\text{SiH}_2$ ,  $\text{Et}_3\text{SiH}$ , PHMS and TMDS;

**Table 1**  $\text{Co}_2(\text{CO})_8$  catalyzed reaction optimization for hydrosilylative deoxygenation<sup>a</sup>

Entry	$\text{Co}_2(\text{CO})_8$ (mol%)	Silane (2 eq.)	Temp. (°C)	Time (h)	Solv.	Yield <sup>b</sup> (%)
1	5/4	$\text{PhSiH}_3$	120	24	THF	>99
2	3	<b>PhSiH<sub>3</sub></b>	120	24	THF	>99 (93 <sup>c</sup> )
3	2	$\text{PhSiH}_3$	120	24	THF	84
4	3	$\text{PhSiH}_3$	120	18	THF	98
5	3	$\text{PhSiH}_3$	120	12	THF	90
6	3	$\text{PhSiH}_3$	100	24	THF	87
7	3	$\text{Ph}_2\text{SiH}_2$	120	24	THF	78
8	3	$\text{Et}_3\text{SiH}$	120	24	THF	80
9	3	PHMS	120	24	THF	36
10	3	TMDS	120	24	THF	42
11	3	$\text{PhSiH}_3$	120	24	Benzene	89
12	3	$\text{PhSiH}_3$	120	24	Toluene	75
13	3	$\text{PhSiH}_3$	120	24	MeCN	83
14	3	$\text{PhSiH}_3$	120	24	Anisole	90

<sup>a</sup> Reactions conducted with 0.5 mmol of **A**<sub>1</sub>, 1.0 mmol of silane and 2–5 mol% of  $\text{Co}_2(\text{CO})_8$  in 2 mL of solvent. <sup>b</sup> Yields were determined by GC using *p*-xylene as the internal standard. <sup>c</sup> Isolated yields.

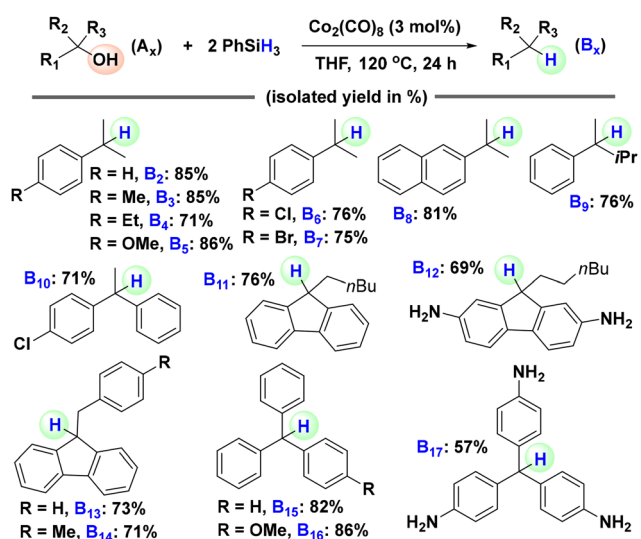


however, hydrosilylative deoxygenation of **A**<sub>1</sub> did not reach completion (entries 7–10). We also tested different solvents without any improvement in the outcome (entry 11). Therefore, the conditions shown in entry 2 (in bold) were identified as the optimal reaction conditions for the hydrosilylative deoxygenation of **A**<sub>1</sub> and a gram-scale reaction was also performed.

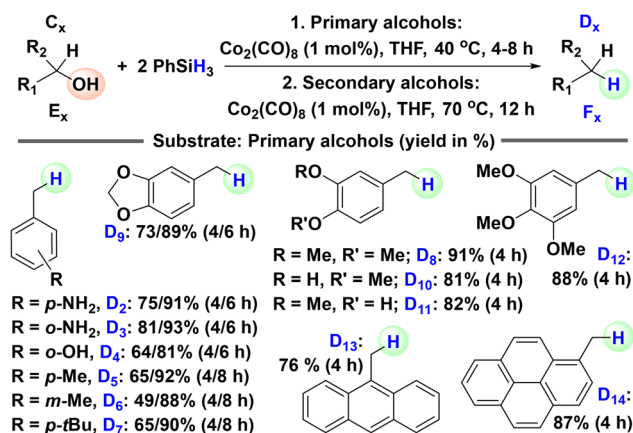
With the optimized conditions for the hydrosilylative deoxygenation of 1,1-diphenylethanol in hand, we set out to explore the generality of this reduction protocol by applying it to the deoxygenation of various tertiary alcohols (Scheme 2). We started with 2-phenylpropan-2-ol and its derivatives with various electron-donating and electron-withdrawing functionalities attached to the phenyl ring. 2-Phenylpropan-2-ol was effectively reduced to the corresponding alkane, cumene (**B**<sub>2</sub>: 85%), with a good isolated yield. The derivatives having electron-donating groups such as methyl, ethyl and methoxy were also subjected to the optimized reaction conditions and efficient deoxygenations to the corresponding alkanes (**B**<sub>3</sub>: 85%, **B**<sub>4</sub>: 71%, and **B**<sub>5</sub>: 86%) were observed. *o*-Amino substituted 2-phenylpropan-2-ol was not compatible. Analogous compounds with weak electron-withdrawing groups such as chloro and bromo gave the corresponding alkanes (**B**<sub>6</sub>: 76% and **B**<sub>7</sub>: 75%) in decent yields. Then, we tested bulkier tertiary alcohols such as 2-(2-naphthyl)-2-propanol and 2-phenylpentan-2-ol and they were also effectively reduced to 2-isopropyl-naphthalene (**B**<sub>8</sub>: 81%) and pentan-2-ylbenzene (**B**<sub>9</sub>: 76%), respectively. Similar to the hydrosilylation of the model substrate 1,1-diphenylethanol (**A**<sub>1</sub>), the hydrosilylation of 2-(4-chlorophenyl)-2-phenylethanol gave the desired product 2-(4-chlorophenyl)-2-phenylethane (**B**<sub>10</sub>: 71%) in a decent yield. Subsequently, we turned our attention to structurally more complex alcohols, focusing on cases where the deoxygenated products have potential practical applications. Four 9-alkyl-9-fluorenol with various functionalities were subjected to the optimized hydrosilylation conditions. All four were effectively

deoxygenated to the corresponding 9-alkyl-9H-fluorenes (**B**<sub>11</sub>: 76%, **B**<sub>12</sub>: 69%, **B**<sub>13</sub>: 73%, and **B**<sub>14</sub>: 71%) with potential applications in pharmaceuticals, optoelectronics, semiconductors, and solar cells.<sup>16</sup> Finally, we examined triphenylmethanol and two substituted derivatives. Under the optimized conditions, all of them were reduced to the corresponding triphenylmethane derivatives (**B**<sub>15</sub>: 82%, **B**<sub>16</sub>: 86%, and **B**<sub>17</sub>: 57%) with functional relevance. Leucoparosaniline (**B**<sub>18</sub>), in particular, finds diverse applications such as use as a radiochromic dye, an HCV helicase inhibitor, and a synthetic precursor for 3D COFs and polyisocyanate adhesives.<sup>17</sup>

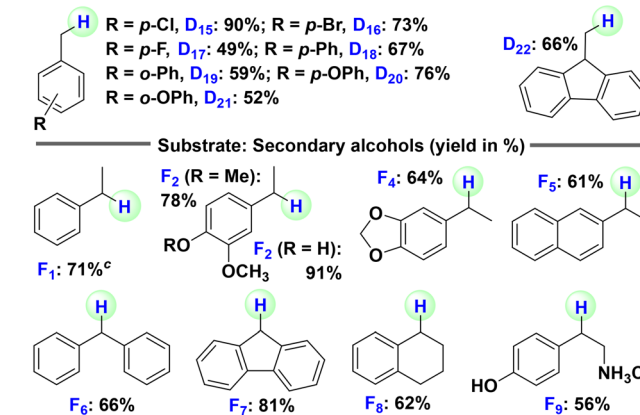
Successful hydrosilylative deoxygenation of tertiary alcohols motivated us to turn our attention to relatively easier primary and secondary alcohols. We initiated the reaction optimization for the reduction of primary alcohols using 4-methoxybenzyl alcohol (**C**<sub>1</sub>) as the model substrate (see the SI for details). The optimized reduction conditions for the deoxygenation of the primary alcohol **C**<sub>1</sub> were as follows: 2 eq. of PhSiH<sub>3</sub>, 1 mol% of Co<sub>2</sub>(CO)<sub>8</sub>, THF, 40 °C, and 4 h. Similarly, the optimized conditions for the dehydrogenation of secondary alcohols were as follows: 2 eq. of PhSiH<sub>3</sub>, 1 mol% of Co<sub>2</sub>(CO)<sub>8</sub>, THF, 70 °C, and 12 h (see the SI for details). Next, we aimed to expand the substrate scope for both primary and secondary alcohols (Scheme 3). First, we targeted primary alcohols. Various substi-



Scheme 2 Hydrosilylative deoxygenation of tertiary alcohols.



Following products need harsh condition: 1 mol% catalyst, 120 °C, 24 h



Scheme 3 Hydrosilylative deoxygenation of primary and secondary alcohols.

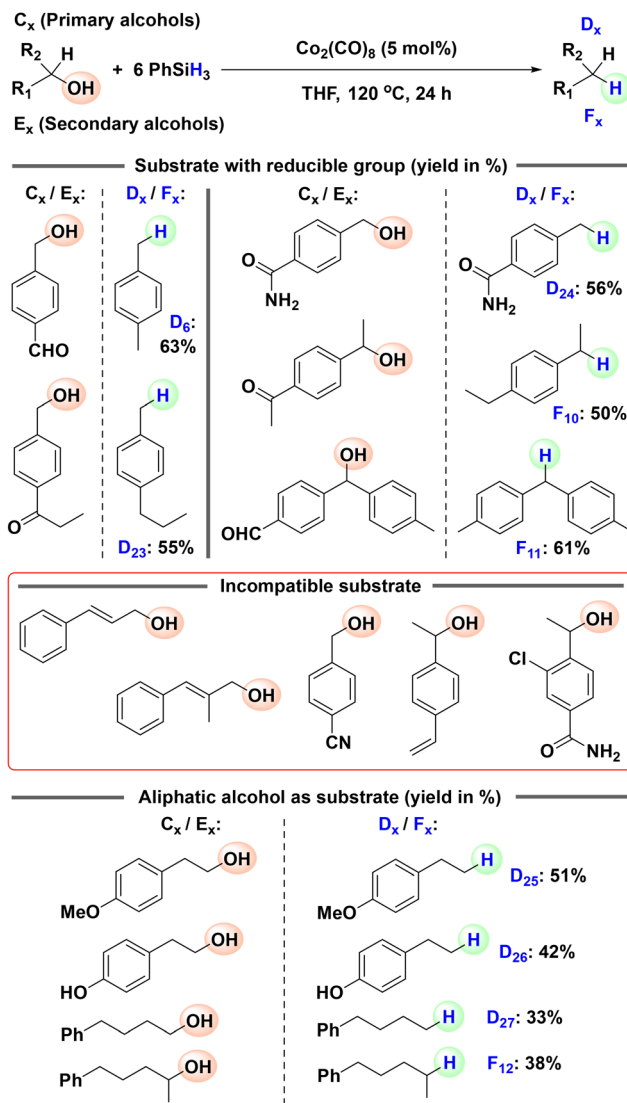


tuted benzyl alcohols with electron-donating groups were deoxygenated to the corresponding toluene derivatives ( $D_2$ – $D_{12}$ ) in good yields. More complex alcohols such as 9-anthracenemethanol and 1-pyrenemethanol were also easily reduced to 9-methylanthracene ( $D_{13}$ ) and 1-methylpyrene ( $D_{14}$ ), respectively, commonly used as photoluminescent materials and OLEDs. A longer reaction time (24 h) and higher temperature (120 °C) were required for the reduction of benzyl alcohols with electron-withdrawing groups to the corresponding products ( $D_{15}$ – $D_{21}$ ). Similarly, 9-fluorenylmethanol was reduced to 9-methyl-9H-fluorene, which is used in optoelectronics. Then, we tested a few secondary alcohols, starting with 1-phenylethanol and its substituted derivatives. They were reduced to the corresponding ethylbenzene derivatives ( $F_1$ – $F_5$ ) in decent to good yields. Diphenylmethanol ( $F_6$ ), fluorene ( $F_7$ ) and 1-tetralol ( $F_8$ ) were also successfully deoxygenated. Finally, octopamine hydrochloride was deoxygenated to tyramine ( $F_9$ ), a naturally occurring trace monoamine that helps regulate blood pressure.

The present hydrosilylative deoxygenation protocols can tolerate halide, phenolic, alkoxy and amine functional groups. We wanted to check if this hydrosilylation is selective in the presence of reducible functional groups. Therefore, several alcohols having reducible functionalities such as aldehyde, ketone, alkene, cyano and amide groups were subjected to cobalt catalyzed hydrosilylation in the presence of excess phenylsilane (Scheme 4). First, primary and secondary alcohols with aldehyde, ketone and amide groups were tested. We did not observe any chemoselectivity; the aldehyde, ketone and amide groups were also reduced along with the deoxygenation of the alcohol moieties and the completely reduced products ( $D_6$ ,  $D_{23}$ ,  $D_{23}$ ,  $F_{10}$  and  $F_{11}$ ) were isolated in decent yields. Primary and secondary alcohols with alkene and cyano groups gave a complex mixture of products that could not be separated. We also tested challenging aliphatic alcohols (Scheme 4). When subjected to cobalt catalyzed hydrosilylation, partial deoxygenation (40–70%) of the aliphatic alcohols was noted and the corresponding reduced products ( $D_{25}$ ,  $D_{26}$ ,  $D_{27}$  and  $F_{12}$ ) were isolated in poor yields.

Finally, we investigated the plausible catalytic reaction path (Scheme 5). We carried out some control experiments to gain insight into this hydrosilylative dehydrogenation process (see the SI for details).

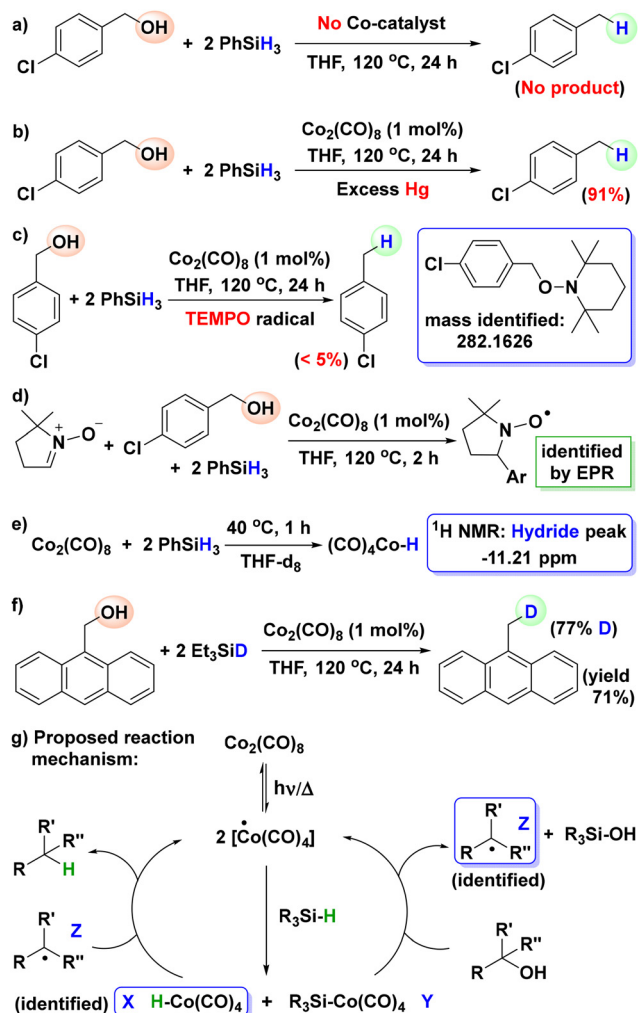
First, deoxygenation of 4-chlorobenzyl alcohol under the standard optimized conditions was carried out in the absence of  $Co_2(CO)_8$  (Scheme 5a). No conversion to the desired product  $D_{15}$  was observed, suggesting the active role of  $Co_2(CO)_8$  as the catalyst. Next, the reduction of 4-chlorobenzyl alcohol under the optimized conditions was performed in the presence of excess mercury. Successful reduction to the desired product  $D_{15}$  was observed, indicative of a homogeneous pathway (Scheme 5b). Dehydrogenation of 4-chlorobenzyl alcohol under the optimized conditions was also performed in the presence of TEMPO as the radical scavenger (Scheme 5c). Extremely poor reduction (<5%) of the substrate was noted, hinting at a likely radical pathway for this process. The corres-



**Scheme 4** Hydrosilylative deoxygenation of aliphatic alcohols and alcohols with reducible groups.

ponding benzylic radical was trapped by TEMPO in this process and the trapped species was identified by mass analysis. To further verify the possibility of a radical pathway, we performed the catalytic hydrosilylative deoxygenation of 4-chlorobenzyl alcohol in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), a well-known radical trapping agent. When a reaction proceeds through a radical route involving transient radical intermediates, DMPO can capture these species to generate a DMPO–radical adduct, which can be detected by EPR spectroscopy (Scheme 5d).<sup>18</sup> This method has previously been employed to confirm radical mechanisms in various reactions.<sup>19</sup> In our study, the cobalt-catalyzed hydrosilylative deoxygenation of 4-chlorobenzyl alcohol conducted with DMPO produced a distinct EPR signal corresponding to the DMPO–radical adduct, providing strong evidence for a radical pathway in this transformation. TM catalyzed hydrosilylations often generate metal-hydrides as reactive intermedi-





Scheme 5 Control experiments and the proposed mechanism for Co-catalyzed hydrosilylative deoxygenation of alcohol.

ates. The formation of  $(\text{CO})_4\text{CoH}$  from  $\text{Co}_2(\text{CO})_8$  in hydrosilylations is well known.<sup>18</sup> To check this possibility, we performed a stoichiometric reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{PhSiH}_3$  in the absence of an alcohol substrate in  $\text{THF-d}_8$  (Scheme 5e).  $^1\text{H}$  NMR measurement of the reaction mixture showed the presence of cobalt-hydride resonance at  $-11.21$  ppm. Next, we performed a deuterium labelling test with deuterated silane ( $\text{Et}_3\text{SiD}$ , *ca.* 90% D) to confirm hydride transfer in this hydrosilylative deoxygenation (Scheme 5f). The deoxygenation of 9-anthracenemethanol to high deuterium enriched 9-methylanthracene provides direct evidence for hydride transfer in the present hydrosilylative deoxygenation. Based on the control experiments and previous reports,<sup>13–15</sup> we proposed a plausible reaction pathway that begins with the formation of two  $\text{Co}(\text{CO})_4$  radicals by homolytic bond cleavage of the Co–Co bond in  $\text{Co}_2(\text{CO})_8$  (Scheme 5g). Then  $\text{Co}(\text{CO})_4$  radicals react with silane to form the cobalt-hydride and cobalt-silyl species **X** and **Y**, respectively. The cobalt-silyl intermediate **Y** reacts with alcohol to form silanol and the carbon-centered radical **Z** and

regenerates a  $\text{Co}(\text{CO})_4$  radical. The transfer of the hydrogen radical from the cobalt-hydride intermediate **X** to the carbon-centered radical **Z** yields the expected deoxygenated alkane product with the regeneration of the other  $\text{Co}(\text{CO})_4$  radical.

## Conclusions

In conclusion, we have developed an efficient Co-catalyzed hydrosilylation protocol for the reductive deoxygenation of alcohols to alkanes using readily available  $\text{Co}_2(\text{CO})_8$ . This method is effective for tertiary alcohols, offering a rare yet highly selective transformation under additive-free conditions. This catalytic reaction also accommodates a broad range of primary and secondary alcohols, highlighting the versatility and generality of the protocol. The reaction proceeds under relatively mild conditions, exhibits good functional group tolerance, and delivers high yields of the corresponding alkanes. Several fine chemicals with applications in materials science have also been synthesized. Mechanistic studies, including plausible pathway involving cobalt-centered radicals and hydride species. Operational simplicity, scalability, and use of an Earth-abundant base metal catalyst make this strategy an attractive alternative to traditional deoxygenation approaches that often rely on prefunctionalized substrates or toxic reagents. This work not only provides a valuable tool for synthetic organic chemistry but also contributes to the growing field of sustainable base metal catalysis.

## Experimental

### General experimental procedure for the deoxygenation of tertiary alcohols

In a dried pressure tube fitted with a magnetic stir bar,  $\text{Co}_2(\text{CO})_8$  (3–5 mol%), 1,1-diphenyl ethanol (0.099 g, 0.50 mmol), silane (1.00 mmol) and solvent (2 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at the appropriate temperature (100/120 °C) in a preheated oil bath for 12 to 24 h. After cooling to r.t., *p*-xylene (62  $\mu\text{L}$ , 0.50 mmol) was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of 1,1-diphenyl ethanol to 1,1-diphenylethane. Thereafter, water (3 mL) was added to the mixture and the mixture was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 5$  mL). The organic layer was collected and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Thereafter, all volatiles were removed to give a crude product. When necessary, the crude product was purified by column chromatography using silica gel as the stationary phase and a mixture of hexane and ethyl acetate as the eluent.

### General experimental procedure for the deoxygenation of primary alcohols

In a dried pressure tube fitted with a magnetic stir bar,  $\text{Co}_2(\text{CO})_8$  (1/2/3 mol%), 4-methoxy benzylic alcohol (0.068 g,



0.50 mmol), silane (1.00 mmol) and solvent (2 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at the appropriate temperature (40–120 °C) in a preheated oil bath for 4 to 24 h. After cooling to r.t., *p*-xylene (62 μL, 0.50 mmol) was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of 4-methoxy benzylic alcohol to 4-methylanisole. Thereafter, water (3 mL) was added to the mixture and the mixture was extracted with Et<sub>2</sub>O (3 × 5 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Thereafter, all volatiles were removed to give a crude product. When necessary, the crude product was purified by column chromatography using silica gel as the stationary phase and a mixture of hexane and ethyl acetate as the eluent.

#### General experimental procedure for the deoxygenation of secondary alcohols

In a dried pressure tube fitted with a magnetic stir bar, Co<sub>2</sub>(CO)<sub>8</sub> (1/2/3 mol%), 4-(1-hydroxyethyl)-2-methoxyphenol (0.076 g, 0.50 mmol), phenylsilane (124 μL, 1.00 mmol) and THF (2 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at the appropriate temperature (40–120 °C) in a preheated oil bath for 6 to 24 h. After cooling to r.t., *p*-xylene (62 μL, 0.50 mmol) was added to the resultant mixture. The mixture was then analyzed by GC to determine the conversion of 4-(1-hydroxyethyl)-2-methoxyphenol to 4-ethyl-2-methoxyphenol. Thereafter, water (3 mL) was added to the mixture and the mixture was extracted with Et<sub>2</sub>O (3 × 5 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Thereafter, all volatiles were removed to give a crude product. When necessary, the crude product was purified by column chromatography using silica gel as the stationary phase and a mixture of hexane and ethyl acetate as the eluent.

#### General conditions for the substrate screening of primary, secondary, and tertiary alcohols

In a dried pressure tube fitted with a magnetic stir bar, Co<sub>2</sub>(CO)<sub>8</sub> (1–5 mol%), alcohol substrates (0.50 mmol), phenylsilane (124 μL, 1.00 mmol) and THF (2 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 40–120 °C in a preheated oil bath for 4 to 24 h. After cooling to r.t., water (3 mL) was added to the mixture and the mixture was extracted with Et<sub>2</sub>O (3 × 5 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Thereafter, all volatiles were removed to give a crude product. The crude product was purified by column chromatography using silica gel as the stationary phase and a mixture of hexane and ethyl acetate as the eluent. When necessary, in the case of volatile alkane products, the <sup>1</sup>H NMR yield was used to calculate the yield using 1,3,5-trimethoxybenzene as the standard (1/3 equiv.).

#### Gram-scale synthesis of B<sub>1</sub>

In a dried pressure tube fitted with a magnetic stir bar, Co<sub>2</sub>(CO)<sub>8</sub> (3 mol%), 1,1-diphenylethanol (1.98 g, 10 mmol),

phenylsilane (2.48 mL, 20 mmol), and THF (20 mL) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 120 °C in a preheated oil bath for 24 h. After cooling to r.t., water (30 mL) was added to the reaction mixture and the mixture was extracted with Et<sub>2</sub>O (3 × 50 mL). The organic layer was collected and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Thereafter, all volatiles were removed and the crude product was purified by column chromatography using silica gel as the stationary phase and hexane as the eluent to give pure 1,1-biphenylethane (1.58 g, 87%).

#### Reaction conditions for the deoxygenation of octapamine hydrochloride to tyramine

In a dried pressure tube fitted with a magnetic stir bar, Co<sub>2</sub>(CO)<sub>8</sub> (10 mol%), the corresponding octapamine hydrochloride (0.50 mmol), phenylsilane (124 μL, 1.00 mmol) and THF : EtOH (2 mL; 1 : 1) were added successively under a nitrogen atmosphere. The reaction mixture was heated at 90 °C in a preheated oil bath for 48 h. Thereafter, volatiles were removed and the crude product was purified by column chromatography using silica gel as the stationary phase and a mixture of DCM/MeOH/diethylamine = 20/1/1 as the eluent.

#### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Conflicts of interest

The authors declare no competing financial interest.

#### Data availability

The data underlying this study are available in the published article and its supplementary information (SI). Supplementary information: experimental procedures, characterization data and spectra, and mechanistic analysis. See DOI: <https://doi.org/10.1039/d5ob01788b>.

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