# COMMUNICATIONS

# Cobalt Carbonyl-Based Catalyst for Hydrosilylation of Carboxamides

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**Abstract:** The cobalt carbonyl $[Co_2(CO)_8]$ complex is employed as a useful catalyst for the reduction of tertiary amides to the corresponding tertiary amines using 1,1,3,3-tetramethyldisiloxane (TMDS) and poly(methylhydrosiloxane) (PMHS) as silane reagents under thermal (100°C) or photo-assisted conditions (UV, 350 nm at room temperature). Of particular interest, a low catalytic amount (0.5 mol%) of $[Co_2(CO)_8]$ is used to perform the reaction with 2.2 equiv. of PMHS at 100°C for 3 h. This reaction is the first example of a cobalt-catalyzed hydrosilylation of amides.

**Keywords:** amides; amines; cobalt; hydrosilylation; reduction

The development of an efficient synthetic methodology towards amines is still attracting the constant interest of chemists as they are an important class of products in the pharmaceutical, natural product, and agrochemical areas. Among the numerous ways to synthesise amines,[1] the reduction of the corresponding amide or imine derivatives and the reductive amination of aldehydes are among the most documented strategies, using stoichiometric amounts of reactive alkali hydrides.[2] Alternatively, during the last decades, reduction protocols catalysed by transition metals to prepare amines have been widely developed.[3] Numerous transition metals including platinum,[4] ruthenium,[5] rhodium,[6] iridium,[7] titanium,[8] zinc,[9] indium,[10] gold,[11] and even iron[12] have been used as catalysts in the hydrosilylation of amides.

Nowadays, the substitution of expensive and rare transition metals by less expensive and environmentally benign first row transition metals as catalysts has become a topical area of research. In the field of hy-

drosilylation reactions, cobalt was efficiently used in the hydrosilylation of unsaturated C−C bonds.[13] Murai et al. developed in the early 1990s catalytic transformations using $Co_2(CO)_8$ as the catalyst in the presence of hydrosilane under an atmospheric pressure of CO resulting in the introduction of a siloxymethyl group with concomitant cleavage of a C−O bond in various substrates such as cyclic ethers, aromatic aldehydes, benzylic esters and cyclic orthoesters.[14] However, in comparison to other transition metals, examples of the cobalt-catalyzed hydrosilylation of carbonyl derivatives are scarce.[15]

As a part of our current interest in first row transition metal-catalysed hydrosilylation,[5g,12c,16] we now report the use of the $Co_2(CO)_8$ complex as a precatalyst for the hydrosilylation of amides.

In initial catalytic experiments on the hydrosilylation of N,N-dimethylbenzamide **1** to N,N-dimethylbenzamine **2**, $[Co_2(CO)_8]$ (1 mol%) was used in the presence of 2.2 equiv. of 1,1,3,3-tetramethyldisiloxane (TMDS) under UV activation (350 nm) at room temperature for 15 h; the amine **2** was selectively obtained as a single product. (Table 1, entry 1) The catalytic loading can be reduced to 0.5 mol% without alteration of the activity under similar conditions (entry 2). But when decreasing the loading to 0.1 mol%, even if a full conversion was observed, only 31% of amine **2** was detected in a mixture with 66% of benzaldehyde (entry 3). The reaction can also be performed under thermal conditions at 100°C: using 1 mol% of $[Co_2(CO)_8]$, a full conversion was obtained in 15 min (entries 4 and 5). Using 0.5 mol% of precatalyst, a longer reaction time was required to obtain a full conversion of the amide **1** (3 h, entries 6 vs. 7 and 8). The decrease of the temperature to 50°C or of the catalytic loading to 0.05 mol% did not allow similar results to be obtained (entries 9–11). Notably, the conversion of the N,N-dimethylbenzamide **1** was complete at 100°C for 3 h in the presence of

**Table 1.** Optimisation of the reaction conditions for the reduction of *N,N*-dimethylbenzamide.[a]
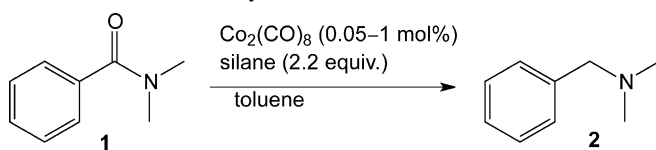


| Entry | Co₂(CO)₈ (mol%) | Silane | Conditions | Conv. [%][b] |
|---|---|---|---|---|
| 1 | 1 | TMDS | UV, 15 h | > 97 |
| 2 | 0.5 | TMDS | UV, 15 h | > 97 |
| 3 | 0.1 | TMDS | UV, 15 h | > 97[c] |
| 4 | 1 | TMDS | 100 °C, 1 h | > 97 |
| 5 | 1 | TMDS | 100 °C, 15 min | > 97 |
| 6 | 0.5 | TMDS | 100 °C, 3 h | > 97 |
| 7 | 0.5 | TMDS | 100 °C, 1 h | 87 |
| 8 | 0.5 | TMDS | 100 °C, 15 min | 16 |
| 9 | 0.5 | TMDS | 75 °C, 8 h | 46 |
| 10 | 0.5 | TMDS | 50 °C, 24 h | 6 |
| 11 | 0.05 | TMDS | 75 °C, 24 h | 15[d] |
| 12 | 0.5 | PMHS | 100 °C, 3 h | > 97 |

[a] *N,N*-Dimethylbenzamide (1 mmol), silane (2.2 equiv.), Co₂(CO)₈ (0.05–1 mol%), toluene (2 mL). For photo-assisted conditions: UV Rayonet apparatus, 350 nm.
[b] Conversions determined by GC and ¹H NMR.
[c] 31% of amine **2** and 66% of benzaldehyde were obtained.
[d] 8% of amine **2** and 7% of benzaldehyde were observed.

2.2 equiv. of poly(methylhydrosiloxane) (PMHS) as the hydrosilane, and 0.5 mol% of [Co₂(CO)₈] (entry 12).

Encouraged by these results, we then examined the scope of the hydrosilylation of amides under thermal conditions (Table 2). Various *N,N*-dibenzylbenzamide derivatives were reduced in high yields. Both electron-withdrawing and electron-donating substituents on the aromatic ring of the benzamide moieties had a low influence on the activity as the obtained yields were very good (86–98%) (Table 3, entries 2, 3, and 6–8). It is noteworthy that with *p*-nitro- and *p*-chloro-substituted *N,N*-dibenzylbenzamides, no or low activities were observed under standard conditions using PMHS as the hydrosilane (entries 9 and 11). Nevertheless, using a more reactive silane, namely phenylsilane (1 equiv.), a full conversion could be obtained in the presence of 1 mol% of catalyst at 100 °C after 16 h and the corresponding amine was isolated in 92% yield (entry 10). When the reaction was performed with benzamides bearing a methyl group in *meta*- and *ortho*-positions, even if a full conversion was observed for the *meta*-substituted substrate (entry 3), only 16% conversion was observed in the case of the *ortho*-substituted derivative which shows

that an *ortho* substituent hampers the reaction (entry 4). Nevertheless, the use of phenylsilane (1 equiv.) at 100 °C for 16 h with 1 mol% of Co₂(CO)₈ complex allowed the reaction to reach full conversion and an excellent isolated yield (98%) was obtained (entry 5). It must be underlined that reductive dehalogenation was not observed in the reaction of *N,N*-dibenzyl-*p*-chlorobenzamide and *N,N*-dibenzyl-*p*-bromobenzamide (entries 8–10). Furthermore, heteroaromatic amides such as *N,N*-dibenzyl-2-pyridylamide and *N,N*-dibenzyl-2-furylamide could also be efficiently reduced using PMHS as the silane and the corresponding tertiary amines were obtained with 60 and 92% yields, respectively (entries 12 and 13).

For *N,N*-dialkylamides, steric hindrance can have an influence on the reactivity: with *N,N*-di-*n*-propylbenzamide, or *N*-methyl-*N*-benzylbenzamide a full conversion was obtained under standard conditions. The corresponding amines were then isolated with yields of 58 and 94%, respectively (entries 14 and 24). In contrast, with more hindered *N,N*-diisopropylbenzamide and *N,N*-dicyclohexylbenzamide, only 10% conversion was observed, which confirms that hindrance seems to inhibit the reactivity when PHMS is the reductant. In contrast, using phenylsilane as the hydrosilane permitted us to reach 98 and 54% conversions, respectively and obtain the amine with 86 and 50% isolated yields, respectively (entries 15–18). Similarly, benzamides derived from pyrrolidine, piperidine and morpholine were also reduced using 2.2 equiv. of PMHS to afford the corresponding benzylamine derivatives in 65–92% isolated yields (entries 21–23). For *N*-phenyl-substituted benzamides, the reduction also proved to be more difficult. For example, *N,N*-diphenylbenzamide and *N*-phenyl-*N*-ethylbenzamide led to low conversions in the presence of PMHS, whereas with the more reactive phenylsilane, full conversions and good yields can be obtained. (entries 19, 20 and 25, 26)

On the other hand, aliphatic amides such as *N,N*-dibenzylhexanamide or *N*-benzyl-ε-caprolactam can also successfully lead to the corresponding amines with moderate yields (50–73%) (entries 27 and 28). It must be underlined, in the case of *N,N*-dibenzylhexanamide, that the reduction led also to 40% of Bn₂NH resulting from hydrogenolysis of the amide.

Notably, the reduction of secondary amides such as *N*-benzylbenzamide could also be performed using 1 equiv. of PhSiH₃ and a higher loading of catalyst (1 mol%), leading to the corresponding secondary dibenzylamine in 68% conversion and 48% isolated yield (entries 29 and 30).

Finally, attempts to differentiate the selectivity between a tertiary and a secondary amide failed as the reaction of a 1:1 mixture of *N,N*-dibenzylbenzamide and *N*-benzylbenzamide using 5 mol% of Co₂(CO)₈ in the presence of 2.2 equiv. of PMHS at 100 °C for 18 h

**Table 2.** Scope of the hydrosilylation of amides catalysed by [Co$_2$(CO)$_8$].[a]

Co$_2$(CO)$_8$ (0.5 mol%)
silane (2.2 equiv.)
toluene, 100 °C, 3 h

| Entry | Substrate | Silane | Conv. [%][b] | Yield [%][c] |
|---|---|---|---|---|
| 1 | | PMHS | > 98 | |
| 2 | | PMHS | > 98 | 90 |
| 3 | R = m-Me | PMHS | > 98 | 86 |
| 4 | R = o-Me | PMHS | 16 | 16 |
| 5 | | PhSiH$_3$[d] | 99 | 98 |
| 6 | R = CF$_3$ | PMHS | > 98 | 94 |
| 7 | R = OMe | PMHS | > 98 | 98 |
| 8 | R = Br | PMHS | > 98 | 93 |
| 9 | R = Cl | PMHS | 13 | - |
| 10 | R = NO$_2$ | PhSiH$_3$[d] | > 98 | 92 |
| 11 | | PMHS | 0 | - |
| 12 | | PMHS | > 98 | 60 |
| 13 | | PMHS | > 98 | 92 |
| 14 | R' = n-Pr | PMHS | > 98 | 58 |
| 15 | R' = i-Pr | PMHS | 0 | - |
| 16 | | PhSiH$_3$[d] | > 98 | 86 |
| 17 | R = Cy | PMHS | 10 | 10 |
| 18 | | PhSiH$_3$[d] | 54 | 50 |
| 19 | R = Ph | PMHS | 6 | 6 |
| 20 | | PhSiH$_3$[d] | > 98 | 70 |
| 21 | n = 1 | PMHS | > 98 | 72 |
| 22 | n = 2 | PMHS | > 98 | 92 |
| 23 | | PMHS | > 98 | 65 |
| 24 | | PMHS | > 98 | 94 |
| 25 | | PMHS | 35 | 33 |
| 26 | | PhSiH$_3$[d] | > 98 | 82 |
| 27 | | PMHS | > 98 | 50[e] |

**Table 2.** (Continued)

| Entry | Substrate | Silane | Conv. [%][b] | Yield [%][c] |
|---|---|---|---|---|
| 28 | | PMHS | > 98 | 73 |
| 29 | | PMHS | 10 | - |
| 30 | | PhSiH$_3$[d] | 68 | 48 |

[a] Amide (1 mmol), PMHS (2.2 mmol, 2.2 equiv.), Co$_2$(CO)$_8$ (0.5 mol%), toluene (2 mL), 100 °C, 3 h.
[b] Conversion by $^1$H NMR.
[c] Isolated yield.
[d] Amide (1 mmol), PhSiH$_3$ (1 mmol), Co$_2$(CO)$_8$ (1 mol%), toluene (2 mL), 100 °C, 16 h.
[e] 40% of Bn$_2$NH was detected on GC.

**Table 3.** Competition reaction of the hydrosilylation with tertiary benzamide catalyzed by [Co$_2$(CO)$_8$].[a]

| Entry | Substrate mixture | | Conv. [%][b] |
|---|---|---|---|
| | Amide | Competing substrate | |
| 1 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | p-MeO<o-C$_6$H$_4$-CO-Me | 50/50 |
| 2 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | p-Me-C$_6$H$_4$-CO$_2$Me | > 99/< 1 |
| 3 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | | > 99/< 1 |
| 4 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | | > 99/< 1 |
| 5 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | p-Me-C$_6$H$_4$-CN | 10/< 1 |
| 6 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | p-Me-C$_6$H$_4$-NO$_2$ | 0/0 |
| 7 | m-Me-C$_6$H$_4$-CO-NBn$_2$ | Ph-CO-NH$_2$ | 0/0 |

[a] Amide (1 mmol), competing substrate (1 mmol), PMHS (2.2 mmol, 2.2 equiv.), Co$_2$(CO)$_8$ (0.5 mol%), toluene (2 mL), 100 °C, 3 h.
[b] Conversion by $^1$H NMR.

led to 50% of conversion and a 1:1 ratio of tribenzyl-amine/dibenzylamine.

In order to have more insights on the chemoselectivity of this cobalt-catalysed hydrosilylation, a combination of derivatives bearing potent reductive functional groups with N,N-dibenzyl-m-methylbenzamide was reacted with 0.5 mol% of Co$_2$(CO)$_8$ in toluene at 100 °C for 3 h in the presence of 2.2 equiv. of PMHS. (Table 3) Excellent chemoselectivities (>99%) in favour of the reduction of the benzamide were obtained with esters and alkenes (entries 2–4). By contrast, with p-methoxyacetophenone, 50% conversions for both compounds were obtained (entry 1). Noteworthy, in presence of p-tolyl nitrile, p-nitrotoluene and primary benzamide, low or no conversions were observed. (entries 5–7).

Interestingly, the present transformation catalysed by a cobalt complex is quite comparable to the iron-catalysed hydrosilylation reaction: both systems are efficient with inexpensive siloxanes and can be activated under UV irradiation or thermal conditions. The main difference lies in the lower loading of cobalt (0.5 mol%) compared to iron carbonyl complexes (typically 5 mol%).

In conclusion, we have demonstrated that the commercially available $Co_2(CO)_8$ complex can be used in low catalytic loading for the chemoselective reduction of tertiary amides in the presence of the inexpensive PMHS as the reductant.

## Experimental Section

### Typical Procedure for Cobalt-Catalysed Hydrosilylation of Amides (Table 2)

A 10-mL oven-dried Schlenk tube containing a stirring bar, was charged with $[Co_2(CO)_8]$ (1.7 mg, 0.5 mol%). After purging with argon (argon-vacuum three cycles), the amide derivative (1 mmol) was added followed by PMHS (130 μL, 2.2 mmol) and toluene (2 mL). The reaction mixture was stirred in a preheated oil bath at 100°C for 3 h. Then 1 mL of MeOH was added followed by 1 mL of 2 M NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 1 hour at room temperature and was extracted with diethyl ether (2×10 mL). The combined organic layers were washed with brine (3×10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The conversion was determined by $^1$H NMR. The residue was then purified by silica gel column chromatography using ethyl acetate-petroleum ether mixture (0 to 10%) to afford the desired amine.

## Acknowledgements

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[18] Notably, under the optimised conditions used (4.4 equiv. of PMHS, toluene, 100 °C for 3 h), the use of 5 mol% of $Zn(OAc)_2$, $Pd(OAc)_2$, $PdCl_2$, $Fe(CO)_5$, led to no reaction. With $Fe_2(CO)_8$ and $Fe_3(CO)_{12}$ (5 mol%), low conversions (6 and 18%, respectively) were obtained (see the Supporting Information).