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New Zinc Catalyst for Hydrosilylation of Carbonyl Compounds

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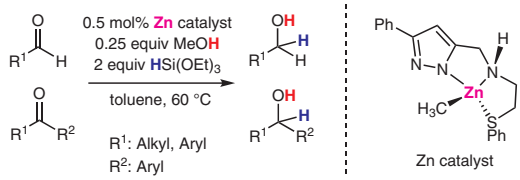

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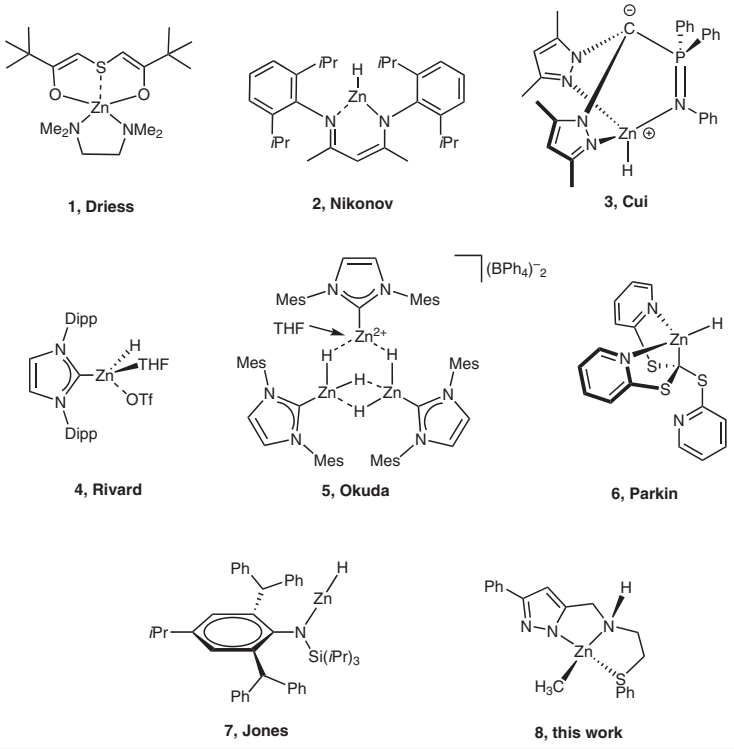
Abstract A new zinc complex was synthesized and applied in the catalytic hydrosilylation of carbonyl compounds. Optimization of the reaction conditions showed that the presence a substoichiometric amount of methanol accelerates the process significantly. The reaction can proceed at very low catalyst load (down to 0.1 mol%) under mild reaction conditions. The reaction tolerates the presence of C=C bonds, and thus can be useful for the synthesis of allylic alcohols from α,β-unsaturated aldehydes and ketones.

Key words zinc, catalysis, hydrosilylation, aldehydes, ketones, alcohols

Alcohols are important building blocks for pharmaceuticals, agrochemicals, polymers, in natural product syntheses, auxiliaries, and ligands.[1] The production of alcohols by the catalytic hydrogenation of carbonyls is attractive from an economic perspective, but faces issues with chemoselectivity in the case of multifunctional substrates because other functional groups can be reduced as well, of which the C=C bond is the most vulnerable. This problem can be circumvented by chemoselective hydrosilylation of aldehydes and ketones to afford alkoxysilanes that can be further hydrolyzed to afford primary and secondary alcohols. Furthermore, alkoxysilanes, on their own, have diverse applications as valuable reagents in organic synthesis[2] and material chemistry.[3] The catalytic hydrosilylation of carbonyl compounds can be now performed under mild reaction conditions and by using inexpensive hydrosilanes that are easy to handle.[1,4] Zinc has recently attracted increased attention as a rising star in catalysis, with many applications in the reduction of functional groups.[5] It is an inexpensive, nontoxic, and earth abundant post-transition metal.

The first applications of zinc compounds in the hydrosilylation of carbonyl compounds go back to the work of Calas and co-workers in the early 1960s.[6] But the modern chapter was opened in 1994 by Noyori and co-workers who generated a catalytically active zinc species in situ by the reaction of $Zn(OSO_2Me)_2$ with LiH.[7] In 1999, Mimoun[8] developed a procedure for zinc-catalyzed hydrosilylation with PMHS, utilizing Zn(2-ethylhexanoate)$_2$. Following the pioneering work of the Carpentier group,[9] chiral diamine ligands have been used for the zinc-catalyzed enantioselective hydrosilylation of ketones.[10] However, the procedures required either relatively high loads of zinc catalysts[10a–e] or large excess of hydrosilane reagents.[10f] Westerhausen and co-workers reported that bis(alkylzinc)-hydride-di(2-pyridylmethyl)amides can catalyze the hydrosilylation of aldehydes and ketone with mono- and diphenylsilanes. This reaction is sensitive to the sterics of reagents and no reaction occurred with triphenylsilane.[11] In 2010, Driess and co-workers reported a new zinc complex with the tridentate *O,S,O*-ligand **1** that showed high catalytic activity in the achiral hydrosilylation of ketones with triethoxysilane (Scheme 1).[12] Zinc complexes, synthesized in situ from diethylzinc and commercially available formamidine ligands, were also demonstrated to be highly efficient catalysts in the hydrosilylation of aryl and alkyl ketones with TOFs up to 1000 h^{-1}, albeit at 10% catalyst load.[13] Zinc hydride DippNacNacZnH **2** was shown to catalyze the hydrosilylation of aldehydes and ketones at 3 mol% load at room temperature and tolerated cyano, amino, nitro, and ester groups.[14] In 2015, a new type of heteroscorpionate zwitterionic terminal hydride zinc complex **3** was reported to catalyze the hydrosilylation of aldehydes with phenylsilane at room temperature at 1 mol% catalyst load.[15] Zinc hydride complexes **4**[16] and **5**[17] supported by N-heterocyclic carbenes have been also shown to act as efficient catalysts for the hydrosilylation of carbonyl compounds. Another zinc hydride catalyst [κ^3-Tptm]ZnH **6** was applied in multiple insertions of aldehydes and ketones into $PhSiH_3$ and Ph_2SiH_2, affording trialkoxy(aryl)silanes and dialkoxydiarylsilanes.[18] Zinc complex **7**, the first example of a two-coordinate zinc hydride complex, showed only moderate activity in the hydrosilylation of benzaldehyde and acetophenone and decomposed under the reaction conditions.[19]

Among numerous ligands for transition metal complexes, compounds containing heterocyclic moieties (pyrazolyl, oxazolyl, imidazolyl, etc.) occupy a special position because of the potential non-innocent and cooperative behavior.[20] The pyrazolyl group, in particular, possesses an acidic pro-



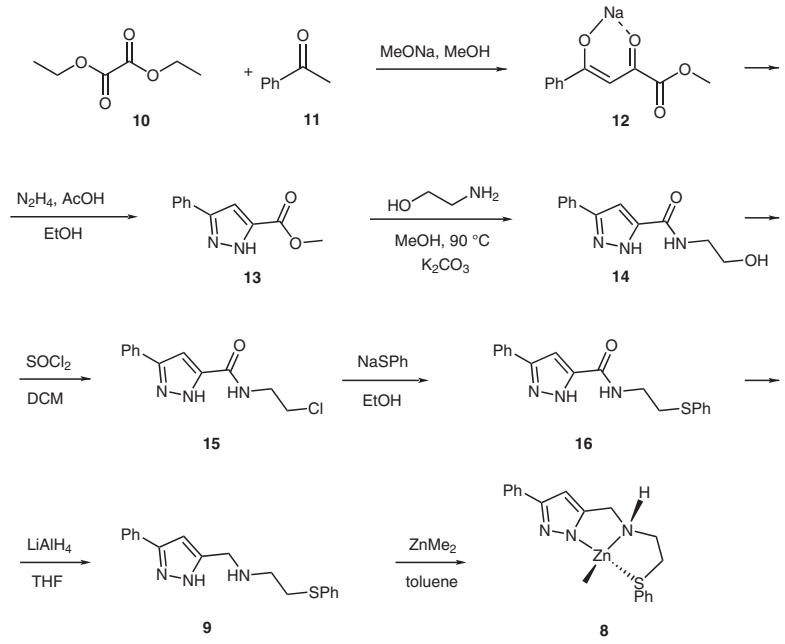
Scheme 1 Zinc catalysts for hydrosilylation of carbonyl compounds

ton on one of the nitrogen atoms, while the second nitrogen atom can coordinate to a metal center, which makes the proton even more acidic.[21] Meanwhile, the mutual affinity of zinc and sulfur is well-recognized not only in general chemistry and mineralogy, but also in biological systems. The coordination mode of zinc in hundreds of enzymes has proven to include not only nitrogen and oxygen (of amino acids), but also sulfur atoms, so that the Zn–S bond is as much frequently occurring phenomenon in the bioorganic world, as in the inorganic.[22] Combining these ideas from non-innocent chemistry and enzymology, we designed a new ligand to prepare zinc catalyst **8** for the hydrosilylation of aldehydes and ketones that operates under mild conditions and low catalyst load and tolerates C=C bonds.

The synthesis of ligand **9** is shown in Scheme 2. Claisen condensation of diethyl oxalate (**10**) with acetophenone (**11**) led to diketone **12**, which reacted with hydrazine to form the pyrazole **13**. Amide **14** was obtained by reacting **13** with 2-aminoethanol in the presence of K_2CO_3. Exchange of hydroxy for chloride in **14** led to compound **15**. Nucleophilic substitution in chloride **15** with sodium thiophenolate afforded sulfide **16** that was further reduced by $LiAlH_4$ to give the target *NNS* ligand **9** as a colorless semiliquid with an overall yield 55%. The ^{1}H NMR spectrum of **9** contains five sets of multiplets at lower field, corresponding to aromatic protons (δ = 7.18–7.77), as well as singlets at δ = 6.46 and 3.91 for the pyrazolyl proton and isolated methylene group, respectively, and two triplets at δ = 3.11 and 2.92 for the ethylene bridging group.

Zinc chloride was the first choice of a precursor for the preparation of the *NNS* Zn complex. Ligand **9** was deprotonated in situ by MeLi to create a driving force for the reaction with $ZnCl_2$ by elimination of LiCl. However, the experiment resulted in a complex mixture of products.

To circumvent this problem, dimethylzinc, a commercially available reagent, was reacted with compound **9** in toluene. Complex **8** and methane (as the only byproduct) formed almost instantly at room temperature. Under normal conditions, **8** is a colorless semiliquid, therefore growing crystals suitable for X-ray analysis was not possible. Nevertheless, the coordination of the *NNS* ligand **9** can be ascertained by ^{1}H NMR spectroscopy. Only one NH signal, significantly shifted upfield (δ = 1.18–1.92) can be observed in the NMR spectrum. The assignment of this signal to the NH proton was supported by ^{1}H-^{1}H COSY NMR that showed correlation of this signal with the nearby methylene protons. Disappearance of a broad IR signal at 3196 cm^{-1}, compared to the IR spectra of ligand **9**, also supports the coordination via amide formation. The reaction is also accompanied by evolution of gas, which could be assigned to methane based on appearance of a new ^{1}H NMR signal at δ = 0.17, suggesting that the pyrazolyl group was most like-



Scheme 2 The synthesis of ligand **9** and zinc complex **8**

ly deprotonated to give pyrazolide. The pyrazolyl CH signal (δ = 6.13), as well as the resonances for the methylene (δ = 3.09) and ethylene bridging groups (δ = 2.14 and 2.31), were also shifted to a stronger field relative to the free ligand. The zinc-bound methyl group gave rise to a high-field ^{1}H NMR signal at δ = –0.03. Furthermore, an NOE experiment showed a through space interaction between the methyl group and the protons of amine, methylene, ethylene, and phenyl units, which supports the tridentate coordination mode of the deprotonated *NNS* ligand.

Because complex **8** is a viscous semiliquid, for simplicity of operations, it is easier to generate it in situ from stock solutions of $ZnMe_2$ and ligand **9**, prior to applications in catalysis. The formation of **8** was confirmed by ^{1}H NMR spectroscopy, after that a substrate and a hydrosilane were added. For the optimization of catalytic conditions acetophenone was chosen as a model substrate, and different hydrosilanes, containing alkyl, aryl, and/or alkoxy groups, were investigated for their reducing ability (Table 1). Triethoxysilane was found to have the best activity, providing full conversion of the substrate within 10 hours at room temperature and in 1.5 hours when heated at 60 °C (Table 1, entries 5 and 7, respectively). To confirm the positive effect of **9**, the reaction was performed under the same conditions as in entry 5, but in the absence of the ligand, which resulted in a very low yield of the hydrosilylation product (Table 1, entry 6).

Table 1 Hydrosilylation of Acetophenone with **8** Formed In Situ[a]

Entry	Hydrosilane	Temp (°C)	Time	Conv.[b] (%)
1	$PhMe_2SiH$	rt	22 h	–
2	$PhMeSiH_2$	rt	3 d	60
3	PMHS	rt	3 d	9
4	$(EtO)_2MeSiH$	rt	5 d	100
5	$(EtO)_3SiH$	rt	10 h	100
6[c]	$(EtO)_3SiH$	rt	22 h	12
7	$(EtO)_3SiH$	60	1.5 h	97

[a] Reaction conditions: acetophenone (50 μL, 0.429 mmol), $ZnMe_2$ (5 mol%, 0.022 mmol), ligand **9** (5 mol%, 0.022 mmol), hydrosilane (2 equiv), toluene (1 mL).
[b] Conversions were determined by ^{1}H NMR analysis.
[c] No ligand added.

The Carpentier group previously reported that zinc-catalyzed hydrosilylation of carbonyl compounds can be accelerated in methanol/toluene (v/v = 80:20) medium and attributed this effect to the formation of a reactive zinc methoxide intermediate. The same idea was applied to the hydrosilylation with catalyst **8** (Table 2). When 10 equivalents of methanol (relative to the substrate) were added, 27% conversion was reached almost instantly at room temperature, however, no further conversion was observed. Instead, all triethoxysilane was consumed by methanol in a concurrent alcoholysis reaction to give triethoxy(methoxy)silane (Table 2, entry 2).[23] Nevertheless, the high initial rate of hydrosilylation under these conditions served as

a proof of principle. Further optimization showed that if one equivalent of methanol is added to the reaction mixture, almost full conversion of acetophenone can be reached within 5.5 hours at room temperature (Table 2, entry 3), which is about twice as fast as the reaction without addition of methanol (Table 2, entry 1). Further decrease of the amount of methanol down to 0.25 equivalents leads to further increase of the reaction rate, with a nearly full conversion achieved in 2.5 hours (Table 2, entry 6). However, when an even smaller amount of methanol is used, the reaction slows down (Table 2, entry 7 and 8).

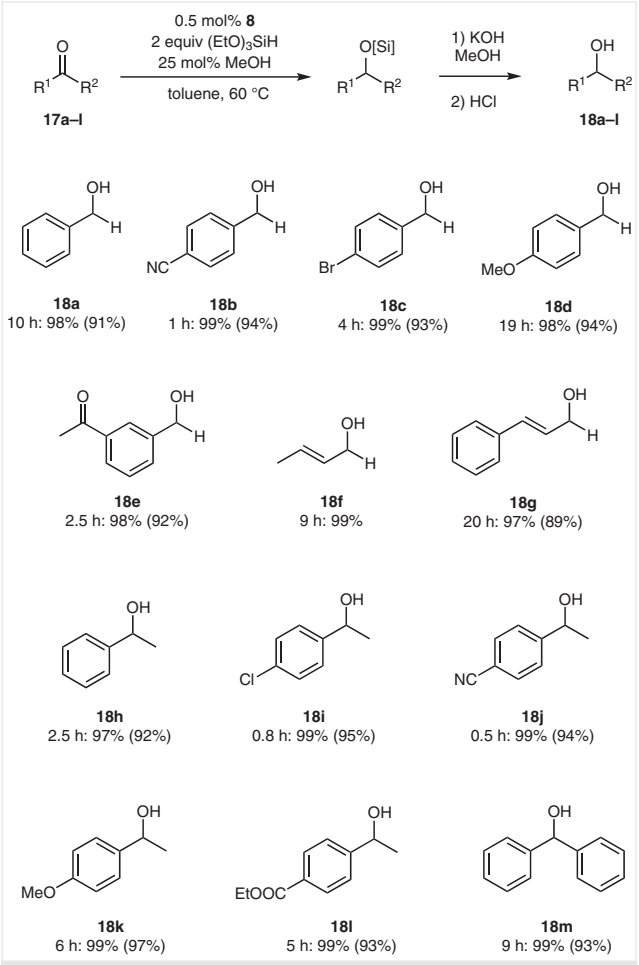
Table 2 Hydrosilylation of Acetophenone with **8** with Various Amounts of Methanol[a]

Entry	Catalyst (mol%)	MeOH (equiv)	Temp (°C)	Time (h)	Conv.[b] (%)
1	5	–	rt	10	100
2	5	10	rt	0.5	27[c]
3	5	1.0	rt	5.5	98
4	5	0.75	rt	4.5	100
5	5	0.50	rt	3	99
6	5	0.25	rt	2.5	98
7	5	0.10	rt	4	100
8	5	0.05	rt	8.5	96
9	2	0.25	rt	10	100
10	2	0.25	60	0.5	98
11	1	0.25	60	1	96
12	0.5	0.25	60	2.5	97
13	0.1	0.25	60	5	84

[a] Reaction conditions: acetophenone (50 µL, 0.429 mmol), $ZnMe_2$, ligand **9**, triethoxysilane (158 µL, 0.858 mmol), toluene (1 mL).
[b] Determined by ^1H NMR analysis.
[c] No further conversion.

This positive effect of methanol allowed us to reduce the load of the catalyst. Thus, if the reaction is performed in the presence of 2 mol% of **8**, it requires about 10 hours at room temperature for the quantitative conversion of the substrate (Table 2, entry 9). When heated with the same amount of the catalyst, the reaction time drops significantly to 0.5 hour (Table 2, entry 10). If the catalyst load is reduced further, the process slows down accordingly. Thus, considering the catalyst economy and time efficiency, the conditions in entry 12 were chosen as optimal.

Next, the catalytic system was studied for its applicability and limitations. It was observed that the reaction rate is highly dependent on the substrate (Scheme 3). Thus, the hydrosilylation of benzaldehyde (**17a**) under the optimized conditions was significantly slower than in the case of acetophenone (**17h**), which is opposite to the usually observed trend for these substrates, but nevertheless finds precedents in the literature.[7] However, when both an aldehyde and ketone groups were present in the molecule, e.g. **17e**, the aldehyde is the first to be reduced. Overall, a tendency for faster reduction of benzaldehydes containing electron-withdrawing groups was observed. Thus, 4-cyanobenzaldehyde (**17b**) and 4-bromobenzaldehyde (**17c**) were fully converted into the primary alcohols **17d** and **17c** in 1 and 4 hours, respectively, with the retention of cyano and bromo groups. However, 4-methoxybenzaldehyde (**17d**) requires a much longer time, 19 hours. These observations suggest that the reduced reactivity of aldehydes under these catalytic conditions may be caused by the increased stability of the corresponding primary alcoholates of zinc relative to secondary alcoholates. Importantly, the reaction tolerates the C=C bonds in α,β-unsaturated aldehydes **17f** and **17g**, leading to primary allylic alcohols **18f** and **18g**, respectively, in excellent yields. Here, cinnamaldehyde (**17g**) contains a more electron-donating group in the γ-position, as com-



Scheme 3 *Reagents and conditions*: substrate **17** (0.429 mmol), $ZnMe_2$ (0.5 mol%), ligand **9** (0.5 mol%), MeOH (4.4 µL, 25 mol%), triethoxysilane (158 µL, 0.858 mmol), toluene (1 mL). Conversions were determined by ^1H NMR spectroscopy by relative integration of the corresponding ^1H NMR signals of substrate and product, isolated yields are shown in parentheses.

pared to crotonaldehyde (**17f**), and requires about twice as much time as **17f** for full conversion. Acetophenones **17i** and **17j**, containing electron-withdrawing groups, can be reduced in less than 1 hour, while the substrate with a methoxy substituent in the *para*-position, **17k**, requires 6 hours for full conversion into the product. In addition to the cyano group in **17j**, the reaction tolerates the ester group (substrate **17l**), which remains unhydrolyzed despite isolation under basic conditions. Benzophenone (**17m**) can be fully reduced within 9 hours, which is significantly longer compared to acetophenone (**17h**); this can be explained by increased steric hindrance of **17m**, as well as by the presence of two electron-donating phenyl groups.

The mechanism of the hydrosilylation with **8** and the exact role of methanol in the reaction acceleration remain unclear. No distinctive zinc species could be isolated or determined in the ^{1}H NMR spectrum when alcohol was added to a solution of **8**. For their zinc catalytic system, the Carpentier group previously proposed a mechanism based on the formation of a zinc–methoxy species, which reacts fast with a hydrosilane, producing a zinc hydride complex.[9a] We believe that a similar process can occur in our system, with the only difference being that a much reduced amount of methanol (25 mol%) is the most beneficial for the catalytic system $ZnMe_2$/**9**, and in fact stoichiometric amounts of alcohol impede the reaction completely. Thus, the role of methanol is likely to help convert **8** into alkoxide **19** (Scheme 4) that is more reactive towards the hydrosilane to produce the active zinc hydride species **20**. Subsequent insertion of a carbonyl compound into the Zn–H bond results in a new zinc alkoxide **21**. Further reaction with hydrosilane completes the catalytic cycle.

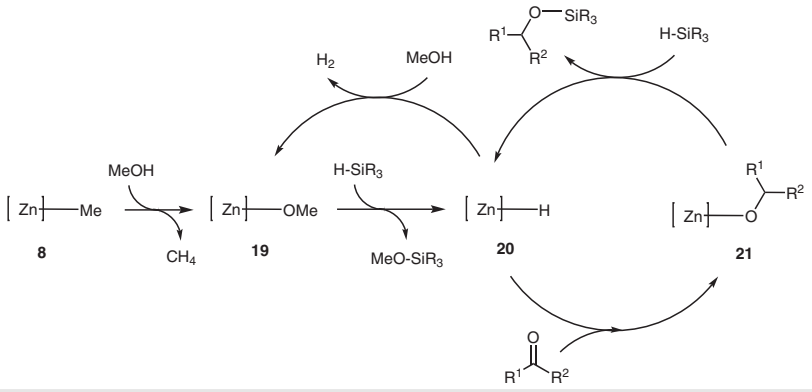
The suggested mechanism implies that ligand **9** acts as an innocent ligand and is not involved in the reaction process. Although transition metal catalysts bearing acidic amine ligands are often considered to act via a bifunctional mechanism (the NH effect),[24] recent DFT calculations showed that the role of the N–H functionality in close proximity to the metal center is to stabilize the rate-determining transition state by N–H···O hydrogen-bonding interactions rather than by a reversible proton transfer.[25] Considering this finding, we believe that ligand **9** operates as a directing moiety, as well as by stabilizing the zinc alkoxide intermediate **21**.

New zinc complex **8** was synthesized and applied in catalytic hydrosilylation of carbonyl compounds. The optimization of reaction conditions revealed that the presence of a substoichiometric amount of methanol significantly accelerates catalysis. This behavior was explained by fast formation of a zinc alkoxide species, which is believed to be more active towards hydrosilanes in the production of a zinc hydride intermediate. The reaction can proceed at low catalyst load (down to 0.1 mol%) under relatively mild reaction conditions. The substrate scope analysis showed the tolerance to C–Br, C≡N, and CO_2Et functionalities, and in particular to the reactive C=C bond. Thus, this procedure can be useful for the syntheses of allylic alcohols from α,β-unsaturated aldehydes and ketones.

All manipulations, required inert atmosphere, were carried out using conventional atmosphere glove-box or N_2-line Schlenk techniques. Benzene, toluene, and THF were dried and purified using a Grubbs-type solvent purification system. All organic substrates were purchased from Sigma-Aldrich and Alfa Aesar. These reagents were used without further purification. NMR spectra were obtained with a Bruker DPX-300, AVANCE III HD 400 MHz, and DPX-600 spectrometers (^{1}H, 400 MHz; ^{13}C, 101 MHz) at rt, then processed and analyzed with MestReNova software (v10.0.2–15465). IR spectra were measured on a Perkin-Elmer 1600 FT-IR spectrophotometer. HRMS analysis was carried out on Thermo Scientific DFS (Double Focusing Sector) mass spectrometer.

Sodium 4-Methoxy-3,4-dioxo-1-phenylbut-1-enolate (12)

Solid Na (2.53 g, 0.110 mol) was dissolved in MeOH (100 mL, cooled by ice bath) in a 500-mL round-bottomed flask equipped with a condenser. Acetophenone (**11**; 11.7 mL, 0.100 mol) was added to this solution, followed by diethyl oxalate (**10**; 13.6 mL, 0.100 mol). The mixture was stirred for 12 h to produce a yellow precipitate, which was filtered, washed with water (2 × 20 mL), and dried; yield: 22.1 g (98%).



Scheme 4 Proposed mechanism of hydrosilylation of carbonyl compounds with **8** in the presence of a substoichiometric amount of methanol

IR (KBr): 1712.8 (C=O), 1633.1 (C=O), 1245.2 cm^{-1} (C–O).

^1H NMR ($CDCl_3$, 400 MHz): δ = 8.00–8.07 (m, 2 H, *o*-ArH), 7.60–7.68 (m, 1 H, *p*-ArH), 7.50–7.57 (m, 2 H, *m*-ArH), 7.12 (s, 1 H, CH), 3.97 (s, 3 H, OCH_3).

^{13}C {^1H} NMR ($CDCl_3$, 105 MHz): δ = 179.7 (*C*=O or CH=*C*O), 178.1 (*C*=O or CH=*C*O), 165.7 ($COOCH_3$), 137.0 (C_{Ar}), 133.1 (C_{Ar}), 128.6 (C_{Ar}), 128.4 (C_{Ar}), 92.5 [(C=O)*C*H=(C–O)], 52.8 (OCH_3).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{11}H_9NaO_4$: 228.1765; found: 228.1738.

Methyl 3-Phenyl-1*H*-pyrazole-5-carboxylate (13)

Compound **12** (10.0 g, 43.8 mmol) was dissolved in EtOH (200 mL) then AcOH (3.00 mL) was added. A solution of hydrazine monohydrate (3.76 mL, 96.0 mmol) in EtOH (20.0 mL) was gently added dropwise with stirring. The mixture was stirred for 1 d, and then it was concentrated under reduced pressure. Toluene (100 mL) was added and the mixture was dried again under vacuum to remove the residual hydrazine monohydrate. Sat. aq $NaHCO_3$ soln was added to the residue to remove AcOH and the white solid obtained was filtered and dried under vacuum; yield: 8.50 g (96%).

IR (KBr): 3282.9 (N–H), 1736.1 (C=O), 1255.9 cm^{-1} (C–O).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.73–7.81 (m, 2 H, *o*-ArH), 7.44–7.51 (m, 2 H, *m*-ArH), 7.37–7.44 (m, 1 H, *p*-ArH), 7.15 (s, 1 H, CH), 3.98 (s, 3 H, OCH_3).

^{13}C {^1H} NMR ($CDCl_3$, 105 MHz): δ = 16.3 ($COOCH_3$), 149.5 (C_{pyr}), 139.5 (C_{pyr}), 129.0 (C_{Ar}), 128.7 (C_{Ar}), 126.9 (C_{Ar}), 125.7 (C_{Ar}), 105.7 (CH_{pyr}), 52.2 (OCH_3).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{11}H_{10}N_2O_2$: 202.2093; found: 202.2049.

N-(2-Hydroxyethyl)-3-phenyl-1*H*-pyrazole-5-carboxamide (14)

Compound **13** (5 g, 24.7 mmol) was dissolved in MeOH (100 mL). 2-Aminoethanol (7.48 mL, 137 mmol) and K_2CO_3 (1.71 g, 13.7 mmol) were added to the solution. The mixture was refluxed (90 °C) for 24 h. Then volatiles were removed on a rotavap, and the oily residue was treated with brine. The product precipitated from the solution as a creamy solid and was separated and dried; yield: 4.97 g (87%).

^1H NMR (CD_3CN, 400 MHz): δ = 7.73–7.81 (m, 2 H, *o*-ArH), 7.47–7.54 (m, 2 H, *m*-ArH), 7.39–7.47 (m, 1 H, *p*-ArH), 7.06 (s, 1 H, CH), 3.69 (t, *J* = 5.49 Hz, 2 H, CH_2), 3.50 (dt, *J* = 5.49, 5.67 Hz, 2 H, CH_2), 2.36 (br s, NH, OH).

^{13}C {^1H} NMR (CD_3CN, 101 MHz): δ = 161.4 ($CONHCH_2$), 146.0 (C_{pyr}), 142.3 (C_{pyr}), 134.9 (C_{Ar}), 134.4 (C_{Ar}), 133.9 (C_{Ar}), 130.9 (C_{Ar}), 107.6 (CH_{pyr}), 66.2 ($NHCH_2CH_2OH$), 46.9 ($NHCH_2CH_2OH$).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{13}N_3O_2$: 231.2505; found: 231.2512.

N-(2-Chloroethyl)-3-phenyl-1*H*-pyrazole-5-carboxamide (15)

$SOCl_2$ (1.62 mL, 22.7 mmol) was added to a suspension of **14** (3.5 g, 15.1 mmol) in DCM (100 mL). The mixture was stirred at rt for 24 h. Then the solution was filtered and neutralized with sat. aq $NaHCO_3$ solution. The organic phase was separated and dried ($MgSO_4$); the solvent was removed under reduced pressure to give a white solid; yield: 3.39 g (90%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 8.89 (br s, 1 H, NH), 7.95–8.02 (m, 2 H, *o*-ArH), 7.48–7.62 (m, 3 H, *m*- and *p*-ArH), 7.44 (s, 1 H, CH), 3.83–3.91 (m, 2 H, CH_2), 3.74–3.82 (m, 2 H, CH_2).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 155.7 ($CONH-CH_2$), 147.1 (C_{pyr}), 143.0 (C_{pyr}), 132.3 (C_{Ar}), 130.1 (C_{Ar}), 129.5 (C_{Ar}), 127.0 (C_{Ar}), 106.9 (CH_{pyr}), 42.4 ($NHCH_2CH_2Cl$), 41.7 ($NHCH_2CH_2Cl$).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{12}ClN_3O$: 249.6962; found: 249.6957.

3-Phenyl-*N*-[2-(phenylthio)ethyl]-1*H*-pyrazole-5-carboxamide (16)

The reaction was performed under a N_2 atmosphere. A solution of NaSPh (1.07 g, 8.10 mmol) in EtOH (50 mL) was carefully added to a solution of **15** (2 g, 8.01 mmol) in EtOH (50 mL). The mixture instantly turned dark grey, and was stirred at rt for 24 h until the color became pale yellow. Then the solution was filtered and EtOH was removed under reduced pressure to give a creamy solid; yield: (2.49 g (96%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 11.43 (br s, 1 H, NH), 7.65 (d, *J* = 7.3 Hz, 2 H, *o*-ArH), 7.36–7.50 (m, 5 H, ArH), 7.26–7.34 (m, 2 H, *m*-ArH), 7.17–7.24 (m, 1 H, *p*-ArH), 7.05 (s, 1 H, CH), 3.69 (q, *J* = 6.41 Hz, 2 H, CH_2), 3.19 (t, *J* = 6.56 Hz, 2 H, CH_2).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 161.7 ($CONHCH_2$), 146.5 (C_{pyr}), 146.1 (C_{pyr}), 135.0 (C_{Ar}), 130.0 (C_{Ar}), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (C_{Ar}), 128.7 (C_{Ar}), 126.5 (C_{Ar}), 125.6 (C_{Ar}), 103.1 (CH_{pyr}), 38.5 (CH_2), 33.6 (CH_2).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{17}N_3OS$: 323.4121; found: 323.4128.

3-Phenyl-*N*-[2-(phenylthio)ethyl]-1*H*-pyrazole-5-methanamine (9)

The reaction was performed under a N_2 atmosphere. Compound **16** (1.00 g, 3.09 mmol) was dispersed in dry THF and the mixture was cooled with an ice bath. $LiAlH_4$ (0.153 g, 4.00 mmol) was added carefully in two potions. The mixture was allowed to warm to rt and stirred for 16 h. Excess $LiAlH_4$ was quenched with EtOH. The solution was filtered and the solvent was removed under reduced pressure. The product was purified by treatment with aq HCl. The crystalline product was filtered, washed with hexane and dried. Then it was suspended in DCM and the solution was treated with sat. aq $NaHCO_3$ solution. The organic phase was separated and dried ($MgSO_4$), and the volatiles were removed under reduced pressure to give a pale yellow semi-liquid; yield: 0.746 g (78%).

IR (Nujol): 3196, 3055, 1469, 1444, 1415, 1377, 1310, 1259, 1193, 1155, 1087, 1074, 1024, 966, 802, 759, 734, 688 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.70–7.77 (m, 2 H, *o*-ArH), 7.39–7.45 (m, 2 H, ArH), 7.32–7.38 (m, 3 H, ArH), 7.25–7.31 (m, 2 H, *m*-ArH), 7.18–7.23 (m, 1 H, *p*-ArH), 6.46 (s, 1 H, CH), 3.91 (s, 2 H, CH_2), 3.11 (t, *J* = 6.34 Hz, 2 H, CH_2), 2.92 (t, *J* = 6.34 Hz, 2 H, CH_2).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 149.4 (C_{pyr}), 145.8 (C_{pyr}), 135.4 (C_{Ar}), 132.3 (C_{Ar}), 129.8 (C_{Ar}), 129.0 (C_{Ar}), 128.8 (C_{Ar}), 128.0 (C_{Ar}), 126.4 (C_{Ar}), 125.6 (C_{Ar}), 101.5 (CH_{pyr}), 47.6 (CH_2), 45.0 (CH_2), 34.1 (CH_2).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{19}N_3S$: 309.4286; found: 309.4278.

Methyl[3-phenyl-5-({[2-(phenylthio-κ*S*)ethyl]amino-κ*N*}methyl)-1*H*-pyrazol-1-yl]zinc (8)

The reaction was performed under the N_2 atmosphere. Stock solutions of 1.0 M **9** in dry toluene (0.400 mL, 0.100 g, 0.320 mmol) and 1.2 M $ZnMe_2$ in toluene (0.267 mL, 0.320 mmol) were combined in toluene (2 mL). The solution was stirred at rt in the glovebox for 20 min. When the reaction was complete, the solvent was removed under reduced pressure to give a colorless semiliquid; yield: 0.123 g (99%).

IR (Nujol): 3057, 1631, 1602, 1556, 1496, 1462, 1438, 1415, 1377, 1350, 1338, 1327, 1301, 1288, 1155, 1085, 1070, 1055, 1024, 1001, 981, 914, 893, 804, 759, 738, 690, 659 cm^{-1}.

^1H NMR (C_6D_6, 400 MHz): δ = 7.99–7.87 (m, 2 H, *o*-ArH), 7.20–7.33 (m, 2 H, *o*-ArH), 7.06–7.15 (m, 1 H, *p*-ArH), 6.85–7.06 (m, 5 H, ArH), 6.13 (s, 1 H, CH), 3.09 (d, J_{HH} = 6.9 Hz, 2 H, CH_2), 2.31 (br s, 2 H, CH_2), 2.14 (br s, 2 H, CH_2), 1.18–1.92 (m, 1 H, NH), –0.03 (s, 3 H, CH_3).

^{13}C {^1H} NMR (C_6D_6, 101 MHz): δ = 214.2 ($ZnCH_3$), 153.3 (C_{pyr}), 148.7 (C_{pyr}), 135.0 (C_{Ar}), 134.7 (C_{Ar}), 129.7 (C_{Ar}), 128.9 (C_{Ar}), 128.2 (C_{Ar}), 127.8 (C_{Ar}), 126.9 (C_{Ar}), 126.3 (C_{Ar}), 98.9 (CH_{pyr}) , 47.7 (CH_2), 46.1 (CH_2), 31.5 (CH_2).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{21}N_3SZn$: 388.8641; found: 388.8613.

Hydrosilylation; General Procedure

All manipulations were performed under a N_2 atmosphere. Stock solutions of 1.2 M $ZnMe_2$ in toluene (1.8 μL) and a stock solution of 1 M ligand **9** in toluene (2.2 μL) were added to benzene (1 mL) in a low pressure NMR sample tube. After 1 min, aldehyde or ketone (0.429 mmol) was injected into the toluene solution, followed by silane (0.858 mmol) and MeOH (4.4 μL, 0.107 mmol). The sealed NMR tube was heated at 60 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy.

Product isolation: All operations were performed in air. A 0.5 M KOH in MeOH solution (1 mL) was added to the reaction solution. The mixture was stirred at rt for 20 min, and then the solvent was removed under reduced pressure. 1 M Aq HCl (2 mL) was added to the residue, and product was extracted with DCM (2 × 1 mL). The combined organic solutions were dried ($MgSO_4$) and the solvent was removed on a rotavap. The purity of the products was confirmed by NMR spectroscopy.

Benzyl Alcohol (18a)

Full conversion was reached in 10 h; yield: 42.2 mg (91%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.85–7.93 (m, 4 H, *o*- and *m*-ArH), 7.79–7.84 (m, 1 H, *p*-ArH), 5.22 (s, 2 H, C*H*$_2$OH), 2.78 (s, 1 H, OH).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 141.0 (C_{Ar}), 128.5 (C_{Ar}), 127.6 (C_{Ar}), 127.0 (C_{Ar}), 65.3 (CH_2OH).

4-Cyanobenzyl Alcohol (18b)

Full conversion was reached in 1 h; yield: 53.6 mg (94%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.63 (d, *J* = 7.9 Hz, 2 H, ArH), 7.47 (d, *J* = 7.8 Hz, 2 H, ArH), 4.76 (s, 2 H, CH_2OH), 1.88 (s, 1 H, OH).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 146.3 (C_{Ar}), 132.3 (C_{Ar}), 127.0 (C_{Ar}), 118.8 (CN), 111.1 (C_{Ar}), 64.2 (CH_2-OH).

4-Bromobenzyl Alcohol (18c)

Full conversion was reached in 4 h; yield: 74.6 mg (93%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.47 (d, *J* = 8.4 Hz, 2 H, ArH), 7.23 (d, *J* = 8.3 Hz, 2 H, ArH), 4.63 (s, 2 H, C*H*$_2$OH), 1.88 (s, 3 H, OH).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 139.8 (C_{Ar}), 131.6 (C_{Ar}), 128.6 (C_{Ar}), 121.5 (C_{Ar}), 64.6 (CH_2OH).

4-Methoxybenzyl Alcohol (18d)

Full conversion was reached in 19 h; yield: 55.7 mg (94%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.30 (d, *J* = 8.7 Hz, 2 H, ArH), 6.87 (d, *J* = 8.7 Hz, 2 H, ArH), 4.56 (s, 2 H, C*H*$_2$OH), 3.80 (s, 3 H, OCH_3), 2.20 (s, 1 H, OH).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 159.7 (C_{Ar}), 130.0 (C_{Ar}), 129.3 (C_{Ar}), 114.1 (C_{Ar}), 55.2 (CH_2OH), 46.2 (OCH_3).

3-(Hydroxymethyl)acetophenone (18e)

98% Conversion was reached in 2.5 h; yield: 59.3 mg (92%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (s, 1 H, ArH), 7.86 (d, *J* = 7.7 Hz, 1 H, ArH), 7.56 (d, *J* = 7.6 Hz, 1 H, ArH), 7.44 (t, *J* = 7.7 Hz, 1 H, ArH), 4.74 (s, 2 H, C*H*$_2$OH), 2.59 (s, 3 H, CH_3), 2.21 (s, 1 H, OH).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 198.3 (C=O), 141.6 (C_{Ar}), 137.3 (C_{Ar}), 131.6 (C_{Ar}), 128.8 (C_{Ar}), 127.5 (C_{Ar}), 126.6 (C_{Ar}), 64.6 (CH_2OH), 26.7 (CH_3).

(2*E*)-But-2-enol (18f)

Full conversion was reached in 9 h. Due to the high volatility of the product, it was not isolated. ^1H NMR signals of the product in the reaction mixture are reported below.

^1H NMR (C_6H_6/D_2O, 400 MHz): δ = 5.50–5.74 (m, 2 H, CH=CH), 4.31–4.40 (m, 1 H, CH_2OSi), 4.22–4.31 (m, 1 H, CH_2OSi), 1.49–1.63 (m, 3 H, CH_3).

(*E*)-Cinnamyl Alcohol (18g)

97% Conversion was reached in 20 h; yield: 50.8 mg (89%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.96–7.26 (m, 5 H, ArH), 6.42 (d, *J* = 15.6 Hz, 1 H, CH), 6.09 (dt, *J* = 14.8, 7.2 Hz, 1 H, CH), 4.01 (d, *J* = 7.2 Hz, 2 H, C*H*$_2$OH), 2.38 (s, 1 H, OH).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 135.8 (C_{Ar}), 134.0 (CH), 128.6 (C_{Ar}), 128.2 (C_{Ar}), 126.6 (C_{Ar}), 124.9 (CH), 45.2 (CH_2OH).

1-Phenylethanol (18h)

97% Conversion was reached in 2.5 h; yield: 48.2 mg (92%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.26–7.46 (m, 5 H, ArH), 4.84–4.97 (m, C*H*OH), 2.16 (s, OH), 1.52 (d, *J* = 6.5 Hz, CH_3).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 146.0 (C_{Ar}), 128.6 (C_{Ar}), 127.6 (C_{Ar}), 125.5 (C_{Ar}), 70.5 (CHOH), 25.2 (CH_3).

1-(4-Chlorophenyl)ethanol (18i)

99% conversion was reached in 0.8 h; yield: 63.8 mg (95%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.18–7.25 (m, 4 H, ArH), 4.77 (q, *J* = 6.5 Hz, C*H*OH), 3.56 (s, 1 H, OH), 1.38 (d, *J* = 6.5 Hz, CH_3).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 144.4 (C_{Ar}), 132.7 (C_{Ar}), 128.3 (C_{Ar}), 126.9 (C_{Ar}), 69.26 (CH-OH), 25.17 (CH_3).

1-(4-Cyanophenyl)ethanol (18j)

99% Conversion was reached in 0.5 h; yield: 59.3 mg (94%).

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, *J* = 8.2 Hz, 2 H, ArH), 7.45 (d, *J* = 8.2 Hz, 2 H, ArH), 4.90 (q, *J* = 6.4 Hz, C*H*OH), 2.64 (s, 1 H), 1.44 (d, *J* = 6.5 Hz, CH_3).

^{13}C {^1H} NMR ($CDCl_3$, 101 MHz): δ = 151.5 (C_{Ar}), 132.3 (C_{Ar}), 126.1 (C_{Ar}), 118.9 (CN), 110.8 (C_{Ar}), 69.4 (CHOH), 25.4 (CH_3).

1-(4-Methoxyphenyl)ethanol (18k)

99% Conversion was reached in 6 h; yield: 63.3 mg (97%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.30 (d, *J* = 8.6 Hz, 2 H, ArH), 6.88 (d, *J* = 8.6 Hz, 2 H, ArH), 4.85 (q, *J* = 6.4 Hz, 1 H, C*H*OH), 3.80 (s, 3 H, OCH_3), 1.47 (d, *J* = 6.4 Hz, 3 H, CH_3).

^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 159.1 (C_{Ar}), 138.1 (C_{Ar}), 126.8 (C_{Ar}), 113.8 (C_{Ar}), 69.9 (CHOH), 55.4 (OCH_3), 25.1 (CH_3).

Ethyl 4-(1-Hydroxyethyl)benzoate (18l)

99% Conversion was reached in 5 h; yield: 77.5 mg (93%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (d, *J* = 8.2 Hz, 2 H, ArH), 7.44 (d, *J* = 8.2 Hz, 2 H, ArH), 4.96 (q, *J* = 6.5 Hz, 1 H, C*H*OH), 4.37 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 1.50 (d, *J* = 6.5 Hz, 3 H, CH_3), 1.39 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3).

^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 166.6 (COOEt), 150.7 (C_{Ar}), 129.7 (C_{Ar}), 128.3 (C_{Ar}), 125.1 (C_{Ar}), 70.1 (CHOH), 60.9 (OCH_2), 25.3 (CH_3), 14.3 (CH_3).

Diphenylmethanol (18m)

Full conversion was reached in 9 h; yield: 79.1 mg (93%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (d, *J* = 7.5 Hz, 4 H, *o*-ArH), 7.64–7.54 (m, 6 H, ArH), 6.42 (s, 1 H, CH_2OH).

^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ = 141.1 (C_{Ar}), 128.6 (C_{Ar}), 128.1 (C_{Ar}), 127.8 (C_{Ar}), 64.3 (CHOH).

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Supporting Information

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