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Hydrosilylation of carbonyl and carboxyl groups catalysed by Mn(I) complexes bearing triazole ligands†

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Manganese(I) complexes bearing triazole ligands are reported as catalysts for the hydrosilylation of carbonyl and carboxyl compounds. The desired reaction proceeds readily at 80 °C within 3 hours at catalyst loadings as low as 0.25 to 1 mol%. Hence, good to excellent yields of alcohols could be obtained for a wide range of substrates including ketones, esters, and carboxylic acids illustrating the versatility of the metal/ligand combination.

Introduction

The modern chemical industry mostly relies on catalysis for the synthesis of bulk materials and fine chemicals.[1] In the last three decades, industrial breakthroughs in homogeneous catalysis mainly involved catalysts based on second- and third-row transition metals, which are rare elements, whose mining generates waste, and is often associated with low abundance and high costs.[2] The excellent performance of the platinum group metals has overshadowed the potential of first-row transition metals, albeit they have been widely used in academia and industry at the early days of homogeneous catalysis. This interest is currently revitalized in particular for metals which can offer potential benefits such as biocompatibility, low toxicity, and high abundance, constituting greener alternatives towards more environmentally benign processes.[3] In this context, iron has arguably been the most studied candidate.[4] Most recently, manganese complexes are also gaining considerable importance in homogeneous catalysis defining an active area of current research.[5]

The hydrosilylation of C=O groups is a transformation of broad synthetic utility[6] and has recently been studied with manganese catalysts.[7] This reaction allows the one-step synthesis of protected silyl alcohols, which can be in a second step hydrolysed to the corresponding alcohols. The protocols represent an alternative to hydrogenation reactions where easy and safe-to-handle silanes replace the use of hydrogen.[8] Up to now, research in the area has focused mainly on carbonyl substrates using Mn(II) complexes,[9] and only a few studies have dealt with Mn(I) or Mn(0).[10] The hydrosilylation of carboxyl compounds is even less studied. For carboxylic acids, reduction with a Mn(0)-complex has been reported to yield aldehydes rather than alcohols as the preferred products.[10e] This lack of knowledge is surprising given that Mn(I) catalysts have already demonstrated a pronounced ability for the transfer of hydrides to substrates displaying electrophilic centres (*e.g.*, in the case of hydrogenation and hydroboration reactions).[11] In the previous studies, the Mn(I) complexes under scrutiny were composed mostly of cyclopentadienyl, carbene, or phosphine ligands (Chart 1).[10a–d] Nitrogen-based ligands can provide an attractive alternative, and triazole units have received attention as versatile donor units.[1a,12] Their synthesis takes advantage of the modularity of copper-catalysed azide–alkyne cycloaddition (*i.e.*, click-chemistry), which is convenient to access structurally different ligand frameworks *via* this atom- and step-economic robust synthetic method.[13] Hence, the stereoelectronic properties of the ligand architecture can be finely adjusted. Besides, their denticity can be controlled and thus, bidentate or tridentate variations are accessible, leading to neutral or cationic complexes respectively.[13d,e,14]

In the present study, we report the catalytic performance of Mn(I) complexes bearing triazol-based ligands for the hydrosilylation of carbonyl and in particular also for carboxyl derivatives. The new cationic complex 3 bearing a tridentate (PNN)-iminotriazole ligand and bidentate neutral complexes previously reported by our group[11b] were investigated. We found that the selected catalysts were able to convert a wide

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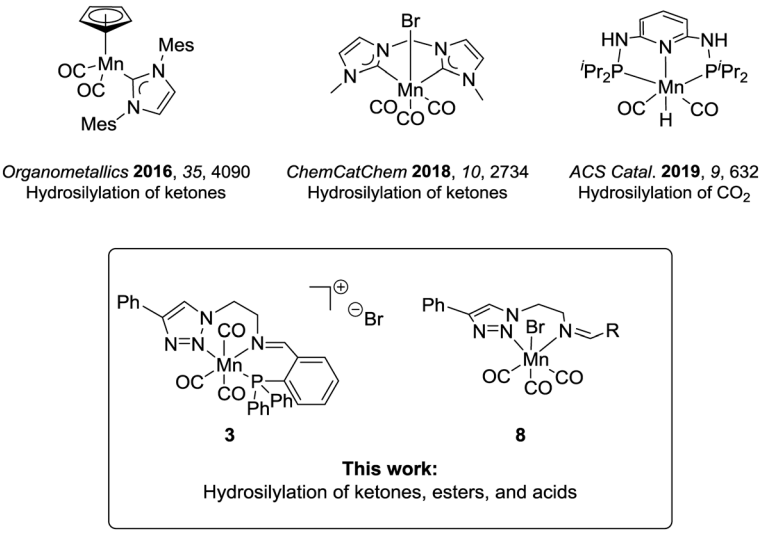


Chart 1 Examples of Mn(I) catalysts for hydrosilylation reactions.

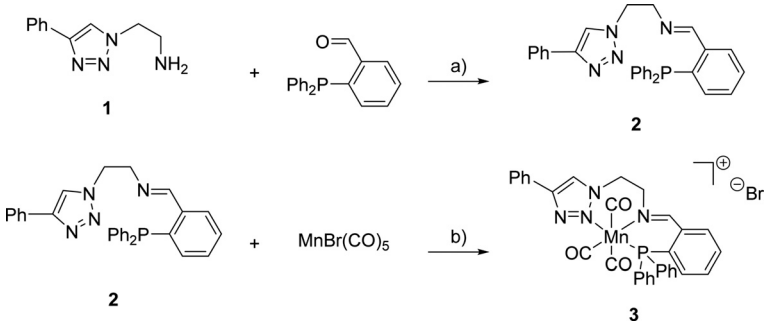
range of ketones to corresponding alcohols. Notably, the (PNN)-manganese(I) complex **3** showed promising results even in the reduction of ester and acid functionalities.

Results and discussion

The synthesis of (PNN)-ligand **2** and its cationic Mn(I) complex **3** was performed as summarised in Scheme 1. Triazole **1** and the corresponding aldehyde were reacted in dry toluene at 105 °C in the presence of $MgSO_4$ serving as a dehydrating agent. Under these reaction conditions, **2** was obtained in 99% yield. Subsequently, triazole **2** was treated with bromopentacarbonylmanganese(I) in toluene at room temperature to provide the desired complex **3** in 46% yield. High-resolution mass spectrometry confirmed the formation of the expected cationic complex with bromide as a counterion. Furthermore, ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy indicated the diamagnetic nature of the complex which agrees with a d^6-metal centre.

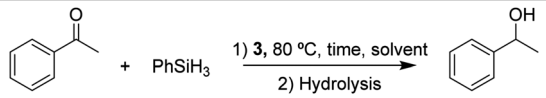
The catalytic activity of complex **3** was first studied for the hydrosilylation of ketones using acetophenone (**4a**) as a benchmark substrate (Table 1). Reacting **4a** with one equivalent of $PhSiH_3$ and 1 mol% of **3** under neat conditions at 80 °C for 20 h, produced alcohol **5a** after hydrolysis in 85% yield. In order to improve the efficiency of the reaction, a panel of different solvents were investigated. When the reaction was carried out in tetrahydrofuran (THF) or acetonitrile (MeCN), entry 2 and 3 respectively, yields up to 99% of **5a** were obtained. When the reaction time was reduced to 3 hours (entries 4–8), lower yields were obtained with apolar solvents (*e.g.*, 15% in toluene), but yields remained high in the polar solvents (*e.g.*, 99% in THF, 90% in MeCN).

For comparison, neutral triazole complexes **6–8** were prepared following previously described procedures,[11b] and tested also for the hydrosilylation of acetophenone (Fig. 1). Using 1 mol% of catalyst loading at 80 °C for 3 h, all the studied complexes were able to reduce **4a** to **5a** with yields up to 99%. To study more precisely the influence of the ligand, the reaction times were reduced to one hour while keeping the catalyst loading unchanged. Under these conditions, iminotriazole complexes **3** and **8** provided the best results, with yields reaching 99%. When complexes **6** and **7** were used, slightly lower yields were obtained (96%). Furthermore, when the catalyst loadings were reduced to 0.1 mol%, catalyst **8** exhibited the best performance. Finally, the activity of



Scheme 1 Reagents and conditions for the synthesis of **2** and **3**: a) $MgSO_4$, toluene, 105 °C, 16 h, 99%; b) toluene, r.t., 60 h, 46%.

Table 1 Optimization of reaction condition for acetophenone hydrosilylation



4a 5a

Entry	Solvent	T (h)	Yield[a] (%)
1	Neat	20	85
2	THF	20	99
3	MeCN	20	99
4	THF	3	99
5	MeCN	3	90
6	Toluene	3	15
7	1,4-Dioxane	3	36
8	Dimethoxyethane	3	95

0.5 mmol acetophenone, 0.5 mmol phenylsilane, 1 mol% **3**, 0.2 mL of solvent, 80 °C. [a] Quantified by ^{1}H NMR using mesitylene as an internal standard.

$Mn(CO)_5Br$ was also verified. When subjected to the standard set of conditions, 56% of conversion and 21% of the corresponding alcohol were obtained.

Based on the standard set of reaction conditions, we examined the substrate scope. These results are summarized in Scheme 2. For acetophenone derivatives, high yields were obtained for all studied *para*-substituted substrates **5b–e**. Only a minor impact related to the electronic properties was observed. The yields decreased slightly in the presence of electron donating groups where 95% and 93% of **5b** and **5c** were obtained, respectively. Introducing electron-donating groups in *meta*- and *para*-position of substrate **4h**, provided only 14% of **5h** when 0.25 mol% of catalyst loading was used. However, this could be increased to 73% yield with 1 mol% of catalyst loading under otherwise identical conditions. Low yields (2% of **5f** and 10% of **5g**) were observed also for the *ortho*-substituted compounds at low catalyst loading. Again, moderate yields (49% for **5g**) could be achieved when 1 mol% of catalyst **8** was used. It is conceivable that the lower yields are due to an increased steric hindrance around the carbonyl functionality for these substrates. The heteroaromatic ketone **4i** were not reduced under these conditions. The naphthyl derivatives **4j** and **4k** could be converted with good yields showing different reactivities depending on the relative position of the ketone. In the case of 2-acetonaphtone **4j**, 94% of isolated yield could be obtained with only 0.25 mol% of **8**. On the other hand, 1-acetonaphthone **4k**, required higher catalyst loadings (1 mol%) to furnish **5k** in 77% yield. This result can be rationalized by the *ortho*-substituted nature of ketone **4k** following the same trend as for **4f–i**. Benzophenone **4l** was

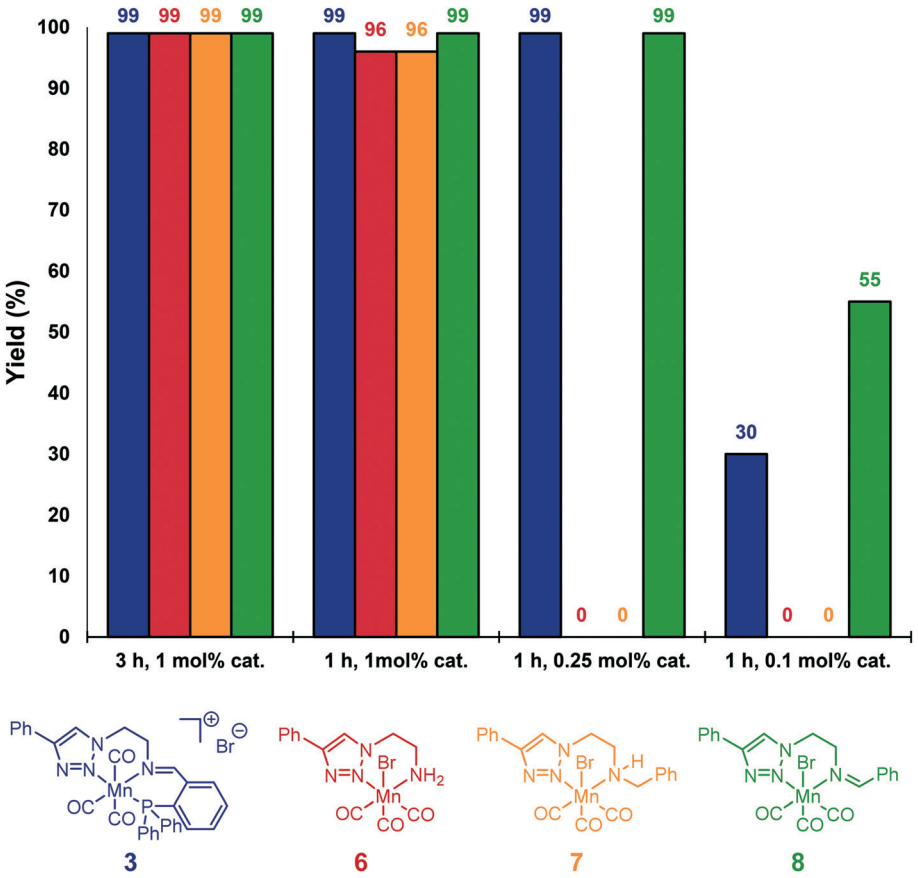
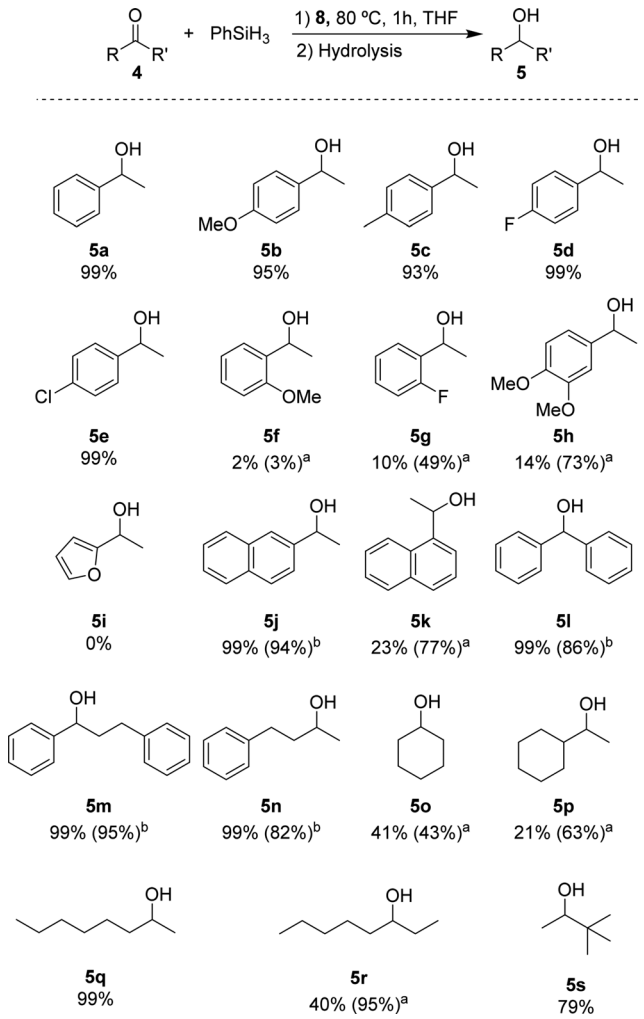


Fig. 1 Screening of reaction times and Mn(I) complexes for the hydrosilylation of **4a**. Reaction conditions: 0.5 mmol acetophenone, 0.5 mmol phenylsilane, 0.2 mL THF, 80 °C. Quantified by 1H NMR using mesitylene as internal standard.



Scheme 2 Substrate screening for the hydrosilylation of ketones catalysed by **8**. Reaction conditions: 0.5 mmol substrate, 0.25 mol% of **8**, 1 mmol of silane, 0.2 mL THF, 80 °C, 1 h. Quantified by ^{1}H NMR using mesitylene or tetradecane (0.5 mmol) as the internal standard. [a]1 mol% catalyst loading. [b]Isolated yield.

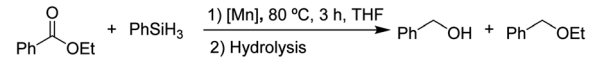
reduced to the corresponding alcohol **5l** in high yield, similar to other substrates containing unsubstituted phenyl rings (**4m**, **n**). For the aliphatic substrate cyclohexanone **4o** and 1-cyclohexylethanone **4p**, good yields (43% and 63% respectively) could be achieved with 1 mol% of catalyst loading. The linear aliphatic ketones 2- and 3-octanone (**4q** and **4r**) were hydrosilylated in high yields, whereby **4q** required again higher catalyst loading (1 mol%). Even the sterically congested *tert*-butyl methyl ketone **4s** was readily reduced providing **5s** in good yields (79%).

After the successful hydrosilylation of ketones, the catalytic competence of the Mn(I) catalysts was probed for the hydrosilylation of more challenging carboxyl groups in esters and acids. In the case of esters as substrates, the reduction and hydrolysis can lead to either the corresponding alcohols or ethers as products. Ethyl benzoate **9** was chosen as prototypical substrate for the screening of catalysts and reaction conditions (Table 2). Reacting **9** with 2 equivalents of $PhSiH_3$ and 2 mol% of complex **8** in THF at 80 °C for 3 hours led to moderate conversions (53%), with preferential formation of ethyl benzyl ether **11** (94%) relative to benzyl alcohol **10** (6%, entry 1). Catalyst **6** gave slightly higher conversion than **8** forming a nearly 1 : 1 mixture of ether and alcohol (entry 2). When complex **7** was used, only 18% conversion was obtained with alcohol **10** being the preferred product in this case (entry 3). The highest activity for reduction was observed with complex **3** that fully converted **9** to a roughly 60 : 40 mixture of **10** and **11** under the given conditions (entry 4).

To investigate whether the two products **10** and **11** are interconverted under the given reaction conditions, two control experiments were carried out (Scheme S1†). Firstly, reductive ether cleavage was investigated. Only 1% of **11** was converted to alcohol **10** under the optimized reaction conditions established for the hydrosilylation of **9** in presence of excess phenylsilane. Similarly, no etherification was observed when alcohol **10** was reacted with ethanol in the presence of **3** and phenylsilane. These results indicate that the selectivity is controlled through competing pathways, presumable branching from a common intermediate $RC(OR')(OSiH_2Ph)$, rather than by secondary interconversion.

Having established the principle ability for carboxyl reduction, the variation of reaction conditions was investigated (Table 2). The rate of reduction increased at elevated temperatures reaching full conversion above 120 °C for catalysts **8** (entries 1, 5–7). The ether **11** remained the preferred product, but selectivity decreased from 94% to *ca.* 70% at higher temperature. For catalyst **3**, the selectivity towards the alcohol product **10** also increased with decreasing temperature, albeit at the expense of conversion (entry 4, 8–10). The reaction was not very solvent dependent

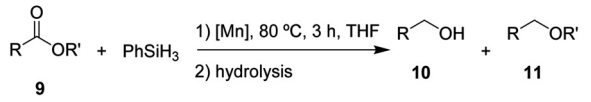
Table 2 Optimization of the catalyst loading and temperature for the hydrosilylation of ethyl benzoate

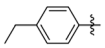
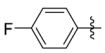


Entry	t (°C)	Cat. (mol%)	Conv.[a] (%)	Sel. **10**[a] (%)	Sel. **11**[a] (%)
1	80	**8** (2)	53	6	94
2	80	**6** (2)	67	48	52
3	80	**7** (2)	18	67	33
4	80	**3** (2)	100	62	38
5	105	**8** (2)	88	35	65
6	120	**8** (2)	100	32	68
7	140	**8** (2)	100	25	75
8	r.t.	**3** (2)	18	83	17
9	60	**3** (2)	64	77	23
10	100	**3** (2)	100	57	43
11[b]	80	**3** (2)	81	84	16
12[c]	80	**3** (2)	78[d]	—	100

0.5 mmol ethyl benzoate, 1 mmol phenylsilane, 3 h, 0.2 mL of THF. [a] Quantified by ^{1}H NMR using tetradecane as an internal standard. [b] Slow addition of phenyl silane, 0.33 mmol per hour. [c] Hydrolysis with Me_4NF, and further addition of 10 equivalents of sodium hydride and 5 equivalents of ethyl bromide. [d] Yield after workup.

Table 3 Mn(I) catalysed hydrosilylation of esters



Entry	R	R′	Conv.[a] (%)	Sel. 10[a] (%)	Sel. 11[a] (%)
1	Ph	Me	97	69	31
2	Ph	Et	100	62	38
3	Ph	Bn	100	70	30
4	Ph	^{t}Bu	14	40	60
5	Ph	Ph	80	82	18
6	C_6H_{13}	Et	100	40	60
7		Me	100	73	27
8		Me	100	78	22

0.5 mmol ethyl benzoate, 2 mol% of **3**, 1 mmol phenylsilane, 0.2 mL of THF. [a] Quantified by ^{1}H NMR using tetradecane or mesitylene as an internal standard.

and toluene, as well as neat conditions, provide potential alternatives to THF (Fig. S1†). The reactivity of silanes followed the hydricity strength in the order $PhSiH_3$ > Ph_2SiH_2 ≫ Ph_3SiH with only moderate influence on product distribution (Table S1†). A significant improvement could be achieved when $PhSiH_3$ was added slowly (0.33 mmol per hour) to the reaction mixture at 80 °C. This protocol combined high conversion (81%) with good selectivity towards the alcohol **10** (84%) (entry 11).

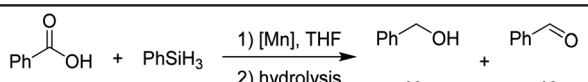
Examples for the synthesis of ethers *via* hydrosilylation of esters are limited and ample scope prevails for further development.[10e,g] We, therefore, investigated the possibility to combine the reduction step directly with a workup under etherification conditions to provide access to **11** from **9**. After reduction of **9** with $PhSiH_3$ using catalyst **3** under standard conditions, the reaction mixture was treated with tetramethylammonium fluoride to remove the silyl group, followed by addition of ethyl bromide and base. The ether **11** was isolated in 78% yield directly from this method after standard workup procedure (Table 2, entry 12).

Subsequently, various esters were hydrosilylated using cationic catalyst **3** under the standard set of reaction conditions to assess the scope and limitation of the reduction (Table 3). When benzoates were used as substrates, comparable results in yield and selectivity for methyl-, ethyl- and benzyl-benzoates were observed (entry 1–3, Table 3). For the bulky *tert*-butyl ester a low conversion was obtained (14%) with the selectivity favouring formation of ether-type product **11** over the alcohol **10** (60% *versus* 40%, entry 4). Interestingly, phenyl benzoate (entry 5), provided satisfactory results with 80% conversion and high selectivity 82% for corresponding benzyl alcohol. When ethyl heptanoate was used as substrate we observed a full reduction of the ester, with the ether being the major product (60%, entry 6). Finally, *para*-substituted methyl-benzoates substrates could be fully converted to the alcohols as the major product (entry 7–8).

Then, we explored the hydrosilylation of acids with leading complexes **3** and **8** and benzoic acid as the benchmark substrate (Table 4). Gratifyingly, conversion of 50% with 98% selectivity towards the corresponding alcohol was observed with catalyst **3** at 80 °C (entry 2). At lower (60 °C, entry 1) as well as higher temperatures (140 °C, entry 3) the conversions towards **10** decreased to 26% and 31% respectively. At 60 °C (entry 1), significant amounts of aldehyde **13** were formed (38%). Control experiments at 80 °C for 2 hours in absence of catalyst **3** in solution (entry 8) and neat (entry 9) revealed no conversion. The neutral complex **8** showed lower catalytic activity than **3** (entries 4–6). When catalyst loading for **3** was increased to 2 mol%, 94% conversion (entry 7) with nearly perfect selectivity for the alcohol could be obtained even with lower reaction time of 2 h, setting these conditions as standard conditions for exploring the substrate scope.

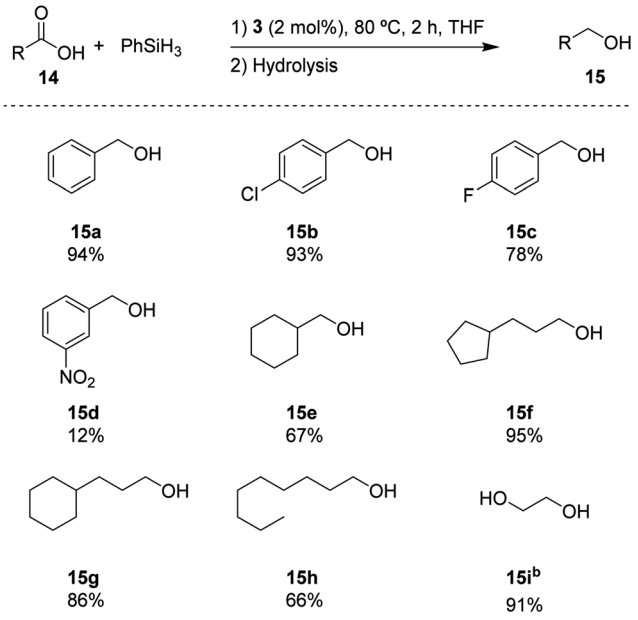
Based on the standard set of reaction conditions, we examined the substrate scope of carboxylic acids as reported in Scheme 3. It is shown that the *para*-substituted substrates **15b** and **15c** could be converted in high yields, albeit with a noticeable influence of the electron-withdrawing substituents. Introducing a NO_2 group in the *meta*-position in substrate

Table 4 Optimization of the catalyst loading, time and temperature for the hydrosilylation of benzoic acid



Entry	t (°C)	Time (h)	Cat. (mol%)	Conv.[a] (%)	Sel. 10[a] (%)	Sel. 13[a] (%)
1	60	3	**3** (1)	26	62	38
2	80	3	**3** (1)	50	98	<1
3	140	3	**3** (1)	31	100	—
4	80	3	**8** (1)	28	100	—
5	120	3	**8** (1)	10	80	20
6	140	3	**8** (1)	2	100	—
7	80	2	**3** (2)	94	100	—
8[b]	80	2	—	0	—	—
9[c]	80	2	—	0	—	—

0.5 mmol acid, 1 mmol phenylsilane, 0.2 mL of THF. [a] Quantified by ^{1}H NMR using mesitylene or tetradecane as an internal standard. [b] Reaction was performed in the absence of catalyst. [c] Reaction was performed in absence of catalyst under neat condition.

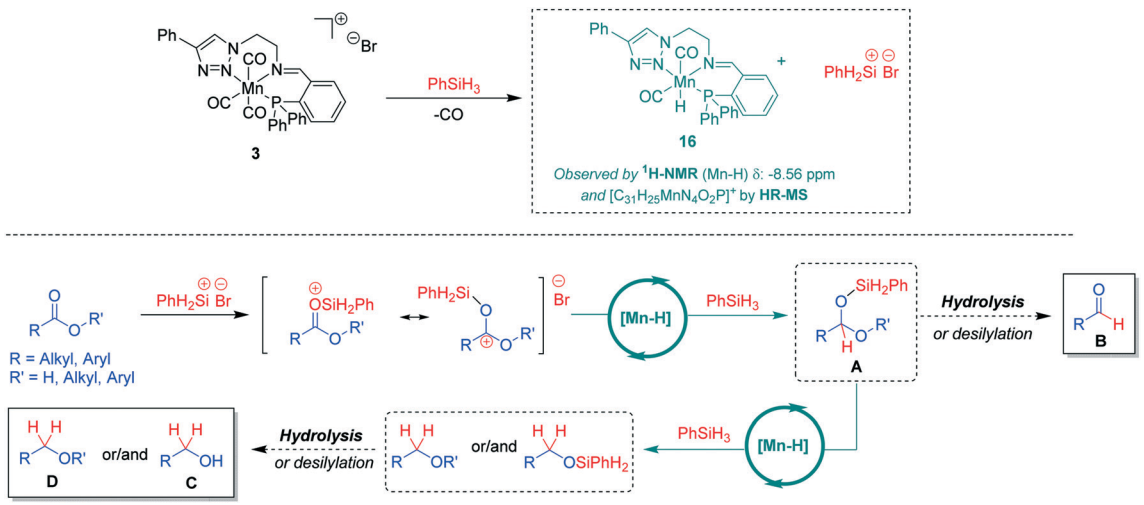


Scheme 3 Substrate screening for the hydrosilylation of carboxylic acids catalysed by **3**. Reaction conditions: 0.5 mmol substrate, 2 mol% of **3**, 1 mmol of silane, 0.2 mL THF, 80 °C, 2 h. Quantified by ^{1}H NMR using mesitylene as an internal standard. [b]2 mmol of silane.

14d, reduced the yield to 12% for **15d**. The aliphatic substrates **14e–h** could be converted in good yields (67% and 66% for **14e** and **14h**, respectively) to excellent yields (95% and 86% for **14f** and **14g**, respectively). In addition, oxalic acid **14i** remarkably provided the corresponding diol (**15i**) with a high yield of 91%. These results indicate a broad portfolio of potential target substrates.

On the basis of the experimental observations and current reports in the literature,[7b,15] a tentative mechanism for the hydrosilylation of the carboxylic C=O units using Mn(I) complexes can be proposed (Scheme 4). In the presence of phenylsilane, a catalytically active neutral hydride complex [**Mn-H**] may be formed under concomitant formation of a silyl cation.[16] This mode of activation is supported by *ex situ* reaction of complex **3** with $PhSiH_3$. Analysis of the reaction mixture revealed the formation of a hydride complex **16** based on HR-MS data indicating a molecular formula $[C_{31}H_{25}MnN_4O_2P]^+$ and a hydride signal in the ^{1}H-NMR spectrum at −8.56 ppm (see ESI† for further details). The [**Mn-H**] species are expected to catalyse hydride transfer from $PhSiH_3$ to the silyl-activated substrate. The resulting intermediate **A** can be converted by hydrolysis or desilylation to aldehyde **B** or it is reduced further *via* a second Mn-catalysed hydride transfer to the alkyl- or silyl-ether derivatives affording after hydrolysis the corresponding organic product alcohol **C** or ether **D**. While the exact nature of the catalytically active [**Mn-H**] species and how it enables the hydride transfer still needs to be elucidated, the proposed pathway is in line with the currently available experimental data and may thus serve as a working hypothesis for future studies.

In summary, we have shown that manganese(I) complexes based on iminotriazole ligands constitute efficient catalysts for the hydrosilylation of carbonyl and carboxyl groups. Aromatic and aliphatic ketones can be reduced with good to excellent yields at low catalyst loadings within 1 h reaction time, using either neutral or cationic complexes comprising bidentate or tridentated ligands, respectively. Extending the reaction to carboxyl groups, esters were reduced with very high conversions, whereby the bidentate-ligated complex **8** favoured formation of ether products while in complex **3** bearing a tridentate (PNN)-iminotriazole ligand lead preferentially to alcohols. Most significantly, complex **3** provides the first example for effective manganese(I) catalysed hydrosilylation of carboxylic acids to alcohols, we believe that the insights provided herein will encourage further investigations into the dynamic field of manganese(I) catalysis in the prospect of finding greener alternatives to existing catalytic methodologies.



Scheme 4 A tentative reaction mechanism for Mn(I)-catalysed hydrosilylation of carboxylic groups in acids or esters.

Experimental section

General procedure for the catalytic hydrosilylation of carbonyl and carboxyl substrates

Selected ketone/ester/acid (0.5 mmol), phenylsilane (0.5 mmol for ketone and 1–2 mmol for ester/acid), and mesitylene or tetradecane (0.5 mmol) were added to a stock solution (0.2 mL) of the Mn(I) catalyst. The reaction mixture was stirred at 80 °C for the required time (1 to 3 h). After this time, the reaction was cooled to room temperature and the corresponding hydrolysis was performed (see ESI†). After hydrolysis, the sample was diluted with $CDCl_3$ (0.6 mL), and subjected to ^{1}H-NMR spectroscopy to determine the yield of the product.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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