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Bench-Stable Manganese NHC Complexes for the Selective Reduction of Esters to Alcohols with Silanes

Sara C. A. Sousa,[a†] Sara Realista,[a†] and Beatriz Royo[a]*

[a] Instituto de Tecnologia Química e Biológica António Xavier, ITQB NOVA, Universidade Nova de Lisboa, Oeiras, Portugal. E-mail: broyo@itqb.unl.pt
[for corresponding author(s) please include phone and fax number(s) and e-mail address(es)]

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Abstract. Selective reduction of esters to alcohols was accomplished through Mn(I)-mediated hydrosilylation reaction. The manganese tricarbonyl complex [Mn(bis-NHC)$(CO)_3$Br] resulted an active pre-catalyst for the reduction of a variety of esters using phenylsilane and the cheap and readily available polymethylhydrosiloxane. An *in situ* examination of the catalytic reaction using ^{55}Mn NMR spectroscopy allowed us to detect the formation of Mn(I) intermediate active species.

Keywords: Manganese; N-heterocyclic carbenes; reduction esters; hydrosilylation; PMHS

Introduction

The reduction of esters to alcohols is an important process for both laboratory organic synthesis and the chemical industry.[1] Although traditional methods involving the use of hazard and moisture-sensitive reducing agents such as $LiAlH_4$ and $NaBH_4$ are still applied,[2] the use of catalytic methods is much more attractive from an environmental point of view.[3] In particular, hydrogenation constitutes a very convenient method from the point of view of atom-economy.[3] However, direct reaction with hydrogen generally requires high pressure and temperature.[3] In this respect, hydrosilylation represents an interesting method, because allows milder conditions and simpler and safer manipulation, avoiding the use of hydrogen gas at high pressure.[4]

Metal-catalyzed systems for ester hydrosilylation have mainly relied on the use of noble metals (*eg.* Pt, Pd, Rh, Ir, Ru).[5] The use of earth-abundant 3d metals for the selective reduction of esters to alcohols through hydrosilylation remains a challenge.[6] Despite the enormous interest raised in Mn catalysis, hydrosilylation of esters mediated by Mn complexes has been scarcely studied.[7] To the best of our knowledge, apart from the initial studies reported in 1995 by Cutler with a manganese carbonyl acyl complex, that catalyzed ester deoxygenation to yield a mixture of siloxanes and their parent ethers,[8] only three additional reports can be found in the literature (Chart 1). In 2014, Trovitch´s group described a Mn(0) N,N,N-pincer complex that catalyzed the dihydrosilylation of esters to afford a mixture of alkoxysilane products.[9] The first Mn-mediated selective hydrosilylation of esters to alcohols, was disclosed three years later by Turculet and co-workers using a (*N*-phosphinoamidinate)Mn complex and $PhSiH_3$.[10] More recently, Leitner and co-workers described a Mn(I) tricarbonyl complex capable to efficiently reduce a variety of esters to a mixture of the corresponding alcohols and ethers.[11] Apart from these studies, Darcel and Sortais group successfully achieved the reduction of carboxylic acids with silanes mediated by $[Mn_2(CO)_{10}]$ under UV irradiation.[12] Despite these recent advances, further improvements are still needed, e.g. use of cheaper silanes, higher tolerance to functional groups, and development of operationally simple methodologies.

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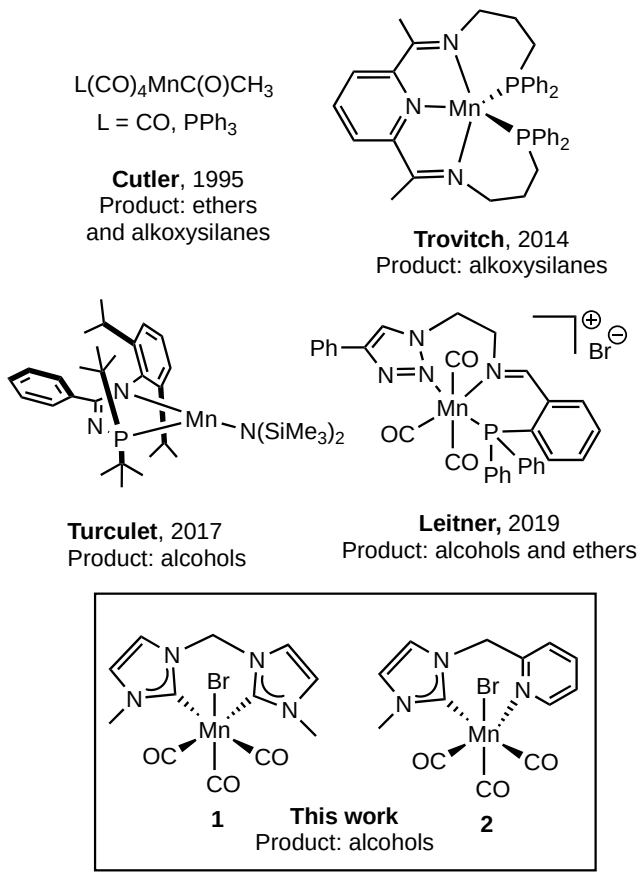
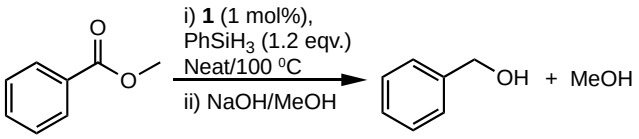


Chart 1. Hydrosilylation of esters mediated by Mn-based catalysts.

As part of our interest in hydrosilylation of functional groups with 3d metal compounds supported by N-heterocyclic carbene ligands (NHC),[13] we recently focused our attention on Mn-based catalysis.[14] We report in this work an efficient catalytic system for the selective reduction of esters to alcohols using polymethylhydrosiloxane (PMHS) or phenylsilane in the presence of [Mn(bis-NHC)$(CO)_3$Br] (**1**). To the best of our knowledge, this work represents the first Mn-mediated reduction of esters using the cheap and readily available PMHS as reducing agent. Notable, our catalytic system operates under air atmosphere, without addition of any auxiliary additives.

Results and Discussion

Initial experiments were performed using methyl benzoate as a model substrate in the presence of [Mn(bis-NHC)$(CO)_3$Br] (**1**) (1 mol%) as catalyst and $PhSiH_3$ (1.2 eqv.) as reducing agent, in neat conditions at 100 ºC. Gratifyingly, after 3 h of reaction, quantitative conversion of methyl benzoate to benzyl alcohol was obtained (98% yield determined by gas chromatography (GC), 83% isolated yield, Scheme 1). When lower amount of **1** (0.75 mol%) was used, longer reaction time (6 h) was needed to afford high conversion (Table 1, entries 3 and 4). Lowering the temperature to 90 ºC has also a significant impact in the catalytic reaction; the conversion of methyl benzoate dropped to 57 % after 6 h (Table 1, entry 2). Next, the influence of different solvents was evaluated. As shown in Table 1, quantitative yield was attained when the reaction was carried out in THF, but negligible conversions were obtained in chloroform, acetonitrile, or toluene (<10%). A slight drop in the conversion was observed when the amount of $PhSiH_3$ was reduced to 1 equivalent (95% yield, Table 2, entry 2).



98% yield

Scheme 1. Reduction of methyl benzoate with $PhSiH_3$ mediated by **1**.

Table 1. Optimization of catalytic conditions using **1** with $PhSiH_3$ [a]

Entry	Solvent	Catalyst loading (mol%)	Temp. (ºC)	Time (h)	Conv.[b]
1	Neat	1	100	3	>99
2	Neat	1	90	6	57
3	Neat	0.75	100	3	<5
4	Neat	0.75	100	6	95
5	CH_3CN	1	100	16	<10
6	$CHCl_3$	1	100	16	0
7	Toluene	1	100	16	<10
8	THF	1	100	3	98

[a] Reaction conditions: methyl benzoate (1 mmol), complex **1**, $PhSiH_3$ (1.2 eqv.), solvent (0.4 mL).
[b] Conversions determined by GC employing *n*-tetradecane as internal standard (Figures S6-S13).

It is worth noting that in the absence of **1** or using [Mn$(CO)_5$Br] as catalyst, no reaction took place. When complex **2** (Chart 1) bearing a mixed NHC-pyridine ligand, was applied as catalyst, longer reaction time (6 h) was needed to afford high conversion under similar reaction conditions (Table S1). The courses of the hydrosilylation reaction using complexes **1** and **2** were investigated by GC. The catalytic reactions were performed in small reaction vessels (5 mL); reagents were mixed in air and then the vessels were closed and heated to 100 ºC. We observed that when the vessels were opened to take the aliquots for the monitoring of the reaction, the catalytic reaction was altered, and the data obtained was not reproducible. Therefore, to obtain information about the profile of the reaction, several vessels loaded with complex **1** (1 mol%), methyl benzoate (1 mmol) and $PhSiH_3$ (1.2 mmol) in neat conditions were heated at 100 ºC, and the reactions were stopped at different times. As shown in Table S1, during the first hours of reaction (2 h 45 min for **1**

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and 5 h 45 min for **2**) no reaction occurred. After the induction period, the reaction suddenly accelerated, reaching full conversion of methyl benzoate in few minutes. These findings indicate that complexes **1** and **2** are pre-catalysts for the hydrosilylation reaction. Complex **1** resulted less active than Turculet´s Mn pre-catalyst, [(k^2-P,N)Mn(N($SiMe_3$)$_2$], which can selectively reduce esters to alcohols at 25 ºC.[10] However, in contrast to Turculet´s catalyst, **1** do not require inert atmosphere for its manipulation and can operate under air and moisture conditions.

Next, we explored the reuse of **1** by adding new charges of substrate, methyl benzoate, and $PhSiH_3$ under the optimized conditions (1 mol% of **1**, 1.2 eqv. of $PhSiH_3$, 100 °C, neat conditions). Interestingly, when the reaction vessels were opened and new charges of substrate and $PhSiH_3$ were added, the reaction resumed. In this way, 5 cycles were completed, reaching an overall TON number of 485 after several days (Figure S1).

Then, we explored the activity of less expensive silanes, such as Ph_2SiH_2, PMHS, and 1,1,3,3-tetramethyldisiloxane (TMDS). Interestingly, the readily available PMHS afforded 88% conversion of methyl benzoate in 24 h, while Ph_2SiH_2 and TMDS resulted inactive (Table 2, entries 3-5).

Table 2. Screening of various silanes in the reduction of methyl benzoate with **1** [a]

Entry	Silane	Amount silane (eqv.)	Solvent	Time (h)	Conversion [b]
1	$PhSiH_3$	1.2	Neat	3	>99
2	$PhSiH_3$	1.0	Neat	3	95
3	Ph_2SiH_2	3	Neat	24	<8
4	PMHS	3	THF	24	88
5	TMDS	3	THF	24	<2

[a] Reaction conditions: methyl benzoate (1 mmol), complex **1** (1 mol%), silane, neat or THF (0.4 mL), at 100 ºC.
[b] Conversions determined by GC employing *n*-tetradecane as internal standard (Figures S15-S19).

Having selected the optimised conditions (1 mol% of complex **1**, 100 ºC), the applicability of this catalytic system was assessed with $PhSiH_3$ (under neat conditions, Table 3) and PMHS (in THF, Table 4). Ethyl benzoate and the acetates, methyl phenylacetate and methyl 2-(naphthalen-2-yl)acetate were quantitatively reduced to the corresponding alcohols in high yields (82-89%) using $PhSiH_3$ (Table 3, entries 2-4). In addition, the reduction of the cyclic aliphatic methyl cyclohexane carboxylate (entry 5) and the linear aliphatic methyl octanoate (entry 6) yielded the corresponding alcohols in high yields. Methyl acetates bearing a heteroaromatic substituent such as methyl nicotinate (Table 3, entry 7), afforded a complex mixture of products which could not be identified. To evaluate the tolerance of the catalytic system to functional groups, the reduction of a variety of benzoates bearing electron donating and electron withdrawing substituents was investigated. Benzoates bearing groups such as CF_3, Cl, and OMe were well tolerated, and the corresponding alcohols were obtained in good to high yields (71-91%) (Table 3, entries 8-10). Notable limitations were detected in the reduction of benzoates bearing the NO_2, NH_2, and CN groups. Methyl 4-nitrobenzoate and methyl 3-aminobenzoate were fully converted into a complex product mixture. In the case of methyl 3-aminobenzoate, the formation of several silylated compounds was detected by ^{29}Si NMR (Figure S2), but after basic hydrolysis the target reduction product, 3-aminobenzyl alcohol was not obtained. In addition, reduction of conjugated systems such as the methyl cinnamate gave a complex mixture of products. Substrate limitations have also been encountered by Turculet and co-workers using the manganese complex [(k^2-P,N)Mn(N($SiMe_3$)$_2$],[10] and have been described with iron-based catalysts.[6e,6g]

Table 3. Scope of the reduction of esters using **1** with $PhSiH_3$[a]

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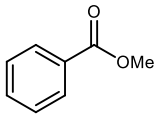
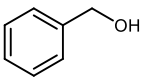
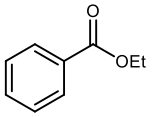
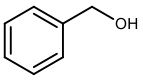
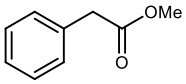
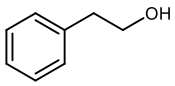
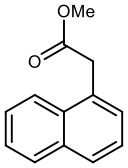
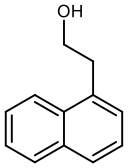
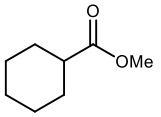
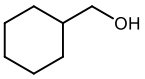
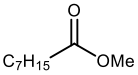
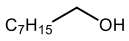
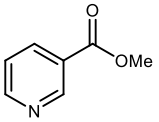
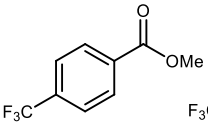
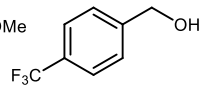
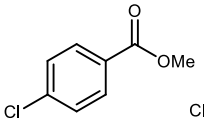
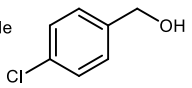
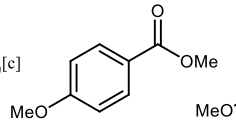
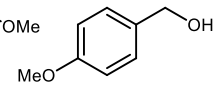
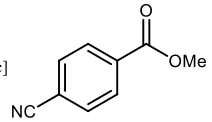
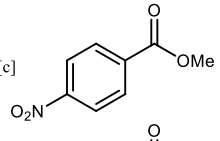
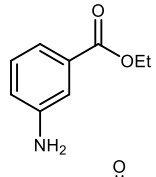
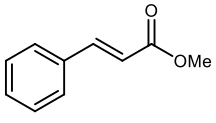
Entry	Substrate	Product	Time (h)	Conv./ yield (%) [b]
1			3	>99/98 (83)
2			16	>99/84 (82)
3			16	94/89
4			3	>99/82 (80)
5			24	>99/85
6			16	>99/79
7[c,d]		-----	24	>99/0
8			6	>99/80 (71)
9[c]			16	93/91
10[c]			6	>99/77
11[c]		-----	24	58/0
12[c]		-----	24	93/0
13[c]		-----	24	89/0
14		-----	24	>99/0

[a] Reaction conditions: substrate (1 mmol), catalyst (1 mol%), $PhSiH_3$ (1.2 mmol), *n*-tetradecane (0.5 mmol), 100 ºC, neat conditions.
[b] Conversions and yields determined by GC (Figures S20-S27). Isolated yields in parenthesis.
[c] Reaction performed in THF (0.5 mL).

Next, we explored the scope of the catalytic reaction using PMHS as a reducing agent. A variety of esters were efficiently reduced with **1** using PMHS (3 eqv.) in THF at 100 °C affording the corresponding alcohols in high yields (66-88% yield, Table 4, entries 1-9). Notably, ethyl benzoate, methyl phenylacetate and methyl 2-(naphthalen-2-yl)acetate were quantitatively reduced affording the corresponding alcohols in high yields (82-88%). Both the aliphatic linear and cyclic esters, methyl octanoate and methyl cyclohexane carboxylate, were also successfully reduced (Table 4, entries 5 and 6). Finally, *para*-substituted methyl benzoates containing CF_3, Cl, and MeO functional groups were converted to the corresponding alcohols in good yields (Table 4, entries 7-9), while NO_2 and NH_2 groups were not tolerated (Table 4, entries 10 and 11).

To the best of our knowledge, this work represents the first Mn-catalyzed reduction of esters through hydrosilylation using PMHS. Hydrosilylation of esters using 3d metals as catalysts and PMHS as reducing agent is rare.[6d,f,g,13d] One of the few examples reported in the literature was described by Adolfsson and co-workers using $ZnEt_2$ in the presence of LiCl.[6f] This catalytic system displayed high functional group tolerance and provided a facile access to a wide range of alcohols. Broad substrate scope was also exhibited by the iron-based catalytic system, $Fe(stearate)_2/NCH_2CH_2NH_2$ and PMHS, described by Beller.[6d] Recently, Findlater and co-workers reported an iron-based catalytic system capable to convert esters to alcohols using PMHS in the presence of *n*-BuLi (30 mol%), although in this case substrate limitations were encountered.[6g] In contrast to these reports, no auxiliary reagents (LiCl, *n*-BuLi) were required using complex **1**.

To demonstrate the utility of our catalytic system, we performed the scale up of the hydrosilylation reaction; 0.7 g of methyl benzoate were reacted with PMHS in the presence of **1** (5 mol%) and THF (1 mL) at 100 ºC. After 24 h of reaction, benzyl alcohol was obtained in 90 % yield.

Table 4. Scope of the reduction of esters using **1** with PMHS [a]

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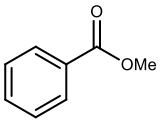
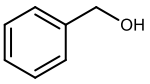
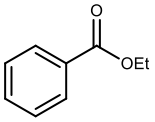
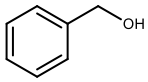
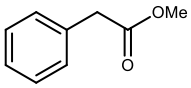
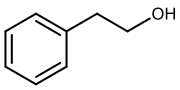
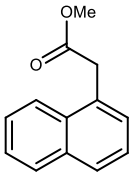
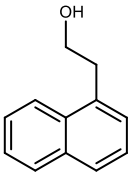
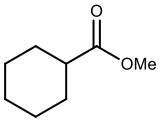
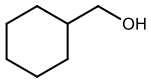
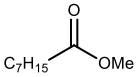
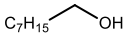
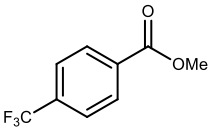
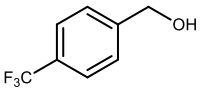
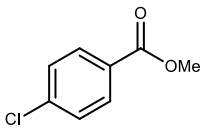
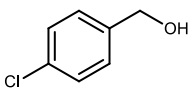
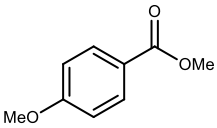
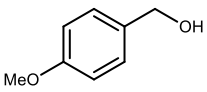
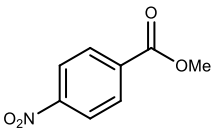
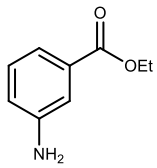
Entry	Substrate	Product	Conv./ yield (%)[b]
1			88/83 (60)
2			99/84 (64)
3			>99/88
4			>99/88 (55)
5			>99/85
6			>99/81
7			84/66 (55)
8[c]			81/71
9			>99/83
10[c]		----	66/0
11[c]		----	94/0

[a] Reaction conditions: substrate (1 mmol), catalyst (1 mol%), PMHS (3 mmol), *n*-tetradecane (0.5 mmol), 100 ºC, in THF (0.4 mL), 24 h.

[b] Conversions and yields determined by GC (Figures S28-S36). Isolated yields in parenthesis.

[c] 3 mol% of catalyst **1** and 5 mmol of PMHS.

In order to gain information on the mechanism of the catalytic reaction, an *in situ* examination of the catalytic reaction using ^{55}Mn NMR spectroscopy allow us to detect the formation of Mn(I) intermediate active species. First, we recorded the ^{55}Mn NMR spectrum of **1** in THF-d_8, which showed a resonance at -1684 ppm (Fig. S3a), shifted to lower frequency than those observed for tricarbonyl Mn complexes bearing bidentate phosphines [Mn(CO)$_3$Br(P-P)] (δ -890 to -1254).[15a] This observation is consistent with the stronger donating character of the NHC ligand versus phosphines. Then, three J- Young valve NMR tubes loaded with methyl benzoate (0.75 mmol), complex **1** (0.75 mol%), $PhSiH_3$ (0.9 mmol) and THF-d_8 (0.4 mL) were heated to 100 °C for 1, 3 and 6 h, respectively, and their ^{55}Mn NMR spectra recorded at 25 °C. The ^{55}Mn NMR spectrum of the sample that was heated for 1 h showed the loss of the peak at -1684 ppm and the formation of one new resonance at -2185 ppm (Figure S3b). After 3 h of heating, the resonance at -2185 ppm remained in the spectrum as the major peak, and the appearance of a new signal at -2230 ppm was observed (Figure S3c). The ^{55}Mn NMR spectrum recorded after 6 h of heating displayed a new resonance at -2124 ppm along with the peaks at -2185 and -2230 ppm. These three signals remained in the spectrum until completion of the reaction. It must be noted that the catalytic reactions performed in J-Young valve NMR tubes (without stirring) took longer reaction times than those performed in 5 mL vessels.

Interestingly, the ^{55}Mn NMR spectrum of the reaction of complex **1** with $PhSiH_3$ (in 1:100 ratio), recorded after 3 h of heating at 100 °C (in the absence of substrate) showed a single peak at -2185 ppm (Figure S4). These findings indicate that the resonance observed at -2185 ppm corresponds to a Mn species (**A**) formed upon reaction of **1** with $PhSiH_3$, while the resonances at -2124 and -2230 ppm, might be formed by interaction of **A** with the substrate (methyl benzoate), affording two new Mn intermediate species, **B** (at -2230 ppm) and **C** (at -2124 ppm). The ^{55}Mn chemical shifts of **A**, **B** and **C** species lie in the range of those resonances observed for other Mn(I) complexes reported in the literature.[15] The shifting of the ^{55}Mn signals to lower frequencies reflects the shielding of the manganese nucleus, which is in accord with the formation of Mn-H or Mn(η^2-H-SiH_2Ph) species that have been proposed by us based on stochiometric reactions of **1** with $PhSiH_3$.[14b] Interestingly, when the J- Young valve NMR tube was opened, the three resonances at -2124, -2185 and -2230 ppm rapidly disappeared from the spectrum (Figure S5b), but if a new charge of $PhSiH_3$ was added, the three resonances appeared again (Figure S5c). These results indicate that the Mn active species are regenerated by addition of new charges of silane.

We speculate that the reaction occurs through an outer-sphere mechanism.[16,6a] This hypothesis was supported by our *in situ* IR spectroscopy study of the stochiometric reaction of **1** with $PhSiH_3$ in which no CO dissociate Mn intermediate was observed.[14b] The

outer-sphere mechanism has also been proposed for **1** in the selective *N*-alkylation of anilines and α-alkylation of ketones with alcohols.[17]

Conclusion

In summary, we have described the first manganese-catalyzed reduction of esters to alcohols using the cheap and readily available PMHS as reducing agent. The reduction of a variety of esters with $PhSiH_3$ or PMHS afforded the corresponding alcohols in good to excellent yields. Further investigation of the reaction mechanism employing computational methods are currently ongoing in our laboratory. Future research in our group aims to develop new Mn-NHC catalysts with improved activities.

Experimental Section

General Procedure for the Reduction of Esters with Phenysilane Catalyzed by 1: A 5 mL sealed cap flask with a stirring bar was loaded with complex **1** (1 mol%, 0.01 mmol) and ester (1 mmol). Then, $PhSiH_3$ (1.2 eqv. , 1.2 mmol) and the internal standard (*n*-tetradecane, 0.5 mmol) were added. The mixture was stirred at 100 ºC for 3-24 h. Then, the reaction mixture was diluted with 4 mL of chloroform and quenched with 0.3 mL of 25% NaOH in MeOH at room temperature. An aliquot (1 mL) was taken, filtered through celite and subjected to GC-FID analysis.
To obtain the isolated products, all the volatiles were evaporated after the quenching. The crude residue was dissolved in ethyl acetate and washed with water 3 x 20 mL, dried with Na_2SO_4, filtered and evaporated. The crude was purified by using silica gel column chromatography with the appropriate mixture of *n*-hexane and ethyl acetate to afford the alcohol.

General Procedure for the Reduction of Esters with PMHS Catalyzed by 1: A 5 mL sealed cap flask with a stirring bar was loaded with complex **1** (1-3 mol%, 0.01 – 0.03 mmol), ester (1 mmol) and THF (0.4 mL). Then, PMHS (3-5 eqv , 3 - 5 mmol) and the internal standard (*n*-tetradecane, 0.5 mmol) were added. The mixture was stirred at 100 ºC for 24 h. Then, the reaction mixture was diluted with 4 mL of chloroform and quenched with 0.3 mL of 25% NaOH in MeOH at room temperature. An aliquot (1 mL) was taken, filtered through celite and subjected to GC-FID analysis.
To obtain the isolated products, all the volatiles were evaporated after the quenching. The crude residue was stirred with diethyl ether for 1 h at room temperature. Then, the organic phase was washed with water (3 x 20 mL), dried over anhydrous Na_2SO_4, filtered and evaporated. The crude was purified by using silica gel column chromatography with the appropriate mixture of *n*-hexane and ethyl acetate to afford the alcohol.

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†S. C. A. Sousa and S. Realista contributed equally to this work.

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FULL PAPER

Bench-Stable Manganese NHC Complexes for the Selective Reduction of Esters to Alcohols with Silanes

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Sara C. A. Sousa, Sara Realista, Beatriz Royo*