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Manganese N-Heterocyclic Carbene Complexes for Catalytic Reduction of Ketones with Silanes

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Well-defined manganese(I) carbonyl complexes bearing bis-N-heterocyclic carbene (NHC) ligands are shown to be effective catalysts for the reduction of carbonyl groups through hydrosilylation reactions. A wide variety of ketones are selectively reduced to the corresponding alcohols by using phenylsilane, and the cheap and readily abundant polymethylhydrosiloxane (PMHS) in the presence of catalytic amounts of Mn^{I} organometallic complexes. Interestingly, α,β-unsaturated ketones and dialkyl ketones are selectively reduced. Mechanistic studies based on radical scavengers suggest the involvement of radical species in the catalytic reaction.

Introduction

In recent years, the development of catalysts based on abundant first-row transition metals has become a central topic in catalysis.[1] Among the 3d metals, iron and manganese are particularly attractive candidates for catalysis owing to their natural abundance, and their useful features of being non-toxic and biocompatible metals. In comparison with the spectacular growth of catalysis based on iron,[2] manganese has remained relatively unexploited. However, the last few years have witnessed a remarkable growth of interest in manganese-based catalysis.[3,4] In particular, a number of efficient manganese catalysts have been reported for the reduction of carbonyl compounds through hydrosilylation reactions.[4,5] The hydrosilylation reaction represents a fundamental method for the preparation of silyl ethers, and can be employed as a convenient alternative to hydrogenation when combined with a hydrolysis protocol.[6] So far, the majority of the Mn complexes developed for catalytic reduction of carbonyl groups are coordination compounds bearing N-, O-, and P- ligands;[3a,4,5,7–9] pure organometallic Mn-based catalysts are scarce.[3d,f]

N-Heterocyclic carbenes (NHCs) are a fundamental class of ligands in organometallic chemistry and catalysis. It is well recognized that their use as supporting ligands in transition-metal chemistry can provide metal complexes with enhanced catalytic performances and higher stability.[10] However, until now, catalysis with Mn-NHC has been poorly explored.[11] In particular, in hydrosilylation reactions, the only examples of well-defined Mn-NHC complexes were recently reported by Lugan, Sortais, and co-workers.[5g,h]

In line with our interest in developing the organometallic chemistry and catalysis of 3d metals with NHC ligands,[12] we decided to develop a new family of manganese carbonyl complexes bearing bis-NHCs and explore their potential in catalysis. In a recent work, we demonstrated the high catalytic efficiency of the manganese complex $MnBr(CO)_3(bis\text{-}NHC^{Me})$ for the electrocatalytic reduction of CO_2 to CO.[13] Here, we report our studies on the reduction of ketones by using manganese(I) compounds bearing bis-NHC, mixed NHC-pyridyl, and bipyridyl ligands, aiming to explore the effect of the introduction of NHCs in the first coordination sphere of the metal.

Results and Discussion

The synthesis of the manganese bis-NHC complexes *fac*-$[Mn(bis\text{-}NHC^{R})(CO)_3Br]$ [R = Me (**1**); Mes (**2**)] was achieved by treatment of $Mn(CO)_5Br$ with the corresponding imidazolium salts in the presence of potassium *tert*-butoxide (Figure 1 and Scheme 1). Complexes **1** and **2** are air stable; they can be stored in air for weeks without noticeable decomposition. Complexes $[Mn(NHC\text{-}py)(CO)_3Br]$ (**3**) and $[Mn(bpy)(CO)_3Br]$ (**4**) were prepared by following the procedure reported in the literature.[14,15] The identity of all complexes was established by analytical and spectroscopic methods. The synthesis and characterization of complex **1**, including the X-ray diffraction studies, has been recently described by us.[13] The ^{13}C NMR spectrum of **2** shows a resonance at 191 ppm, indicative of a Mn–$C_{carbene}$ bond, confirming that coordination of the NHC has occurred. The IR spectrum of **2** displays characteristic carbonyl stretching bands (at 2007, 1923, and 1887 cm^{-1}) for three CO

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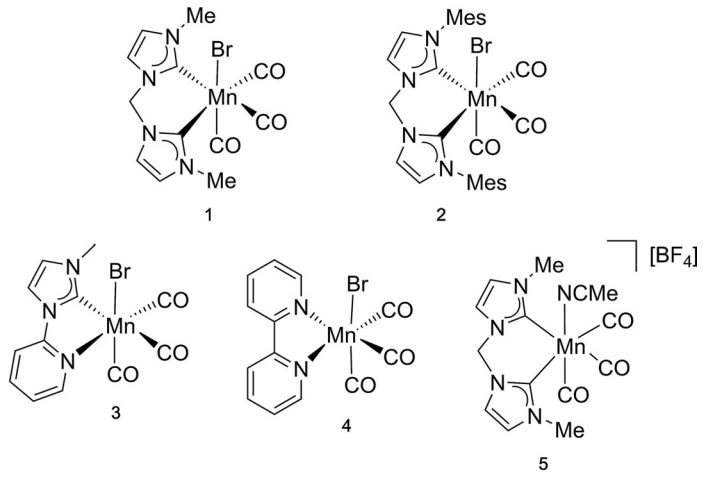
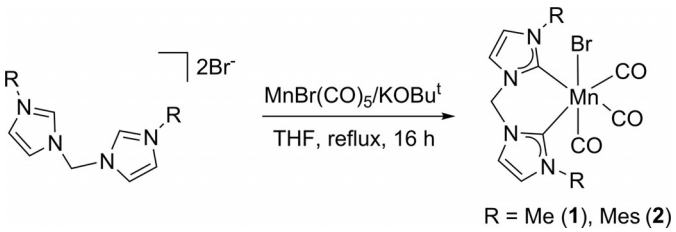


Figure 1. Manganese NHC complexes **1**–**5** explored as catalysts in the hydrosilylation of carbonyl groups.



Scheme 1. Synthesis of manganese NHC complexes **1** and **2**.

ligands coordinated to Mn in a facial fashion, two carbonyls located *trans* to the NHC ligands, and the third CO situated *trans* to the bromide ligand.[16] As expected, complex **2** exhibited lower energy carbonyl bands than those of **3** and **4**, consistent with the expected effect of the strong donating NHC ligand versus the mixed pyridyl-NHC and the bipyridyl ligand. In addition, the weaker donating character of the NHC bearing a mesityl wingtip in **2** compared with the methyl group in **1** is reflected in their IR spectra (2004, 1912, and 1881 cm^{-1}).

The hydrosilylation of benzaldehyde was selected as a benchmark reaction for an initial screening of the Mn^{I} catalysts **1**–**4** by using phenylsilane as reducing agent. Initially, reactions were performed in benzene at 80 °C by using 1 mol% of catalyst. Conversion of benzaldehyde to the corresponding silyl ether was monitored by ^{1}H NMR spectroscopy. When the reaction was completed, hydrolysis with aqueous NaOH (2 M) solutions, followed by extraction with dichloromethane allowed the isolation of the corresponding alcohols. Results are summarized in Table 1. Excellent aldehyde conversions were achieved for complexes **1**–**3** bearing NHC ligands (entries 2, 4, 6, Table 1). Interestingly, the presence of the strong donating NHC ligands improves the catalytic efficiency (**1**–**3** versus **4**). Complex **4**, bearing a bipyridyl ligand, resulted in the least active catalyst, affording a moderate yield of benzyl alcohol (53%) after 24 h (entry 8, Table 1). Complexes **1**–**3** displayed comparable activity, achieving high yields of benzyl alcohol in 16 h; although a slight decrease in activity in the series **1** > **2** > **3** was observed after 6 h of reaction (entries 1, 3, 5, 7, Table 1). These results suggest that increasing the donor properties of the chelating C_{NHC},C_{NHC}/C_{NHC},N_{byp} fragment in [$LMn(CO)_3Br$] (L = bis-NHC, NHC-py) complexes, makes the manganese(I) center more electron rich, facilitating the activation of silane. A blank experiment in the absence of a manganese complex under identical conditions did not yield any detectable conversion of benzaldehyde (entry 9, Table 1).

Encouraged by the efficiency of complex **1** in the hydrosilylation of benzaldehyde, we decided to investigate its catalytic activity in the reduction of acetophenone and evaluate the effect of the solvent on the catalysis. Full conversion of acetophenone was observed when using **1** and $PhSiH_3$ in benzene after 20 h at 80 °C (entry 1, Table 2). Interestingly, the reaction proceeded similarly in THF and neat conditions (entries 2 and 3, Table 2), but a dramatic increase in the reaction rate was observed when the reaction was performed in acetonitrile, affording quantitative yield in 5 h. Attempts to reduce the temperature of the reaction and catalyst loading resulted in a decrease in the yield of 1-phenylethanol (53% yield at 60 °C, and 37% yield when using 0.5 mol% of **1** in 5 h).

Taking into consideration our previous results on iron-based hydrosilylation reactions, in which we observed that addition of catalytic amounts of silver tetrafluoroborate activated the

Table 1. Hydrosilylation of benzaldehyde catalyzed by complexes **1**–**4**.[a]

Entry	Catalyst	*t* [h]	Yield [%][b]
1	**1**	6	78
2		16	98
3	**2**	6	62
4		16	86
5	**3**	6	56
6		16	96
7	**4**	6	31
8		24	53
9	–	24	0

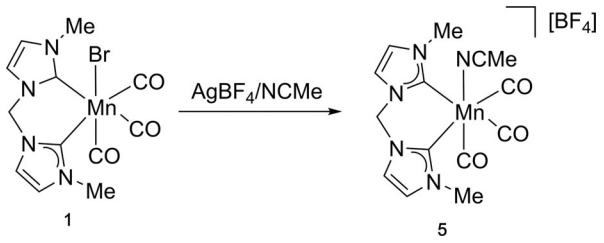
[a] All reactions were performed with 1 mmol of benzaldehyde and 1.2 mmol of phenylsilane by using 1 mol% of catalysts **1**–**4** at 80 °C in benzene (0.4 mL). [b] Yields were determined by ^{1}H NMR spectroscopy by using *n*-tetradecane as an internal standard after basic hydrolysis.

Table 2. Hydrosilylation of acetophenone catalyzed by **1**.[a]

Entry	Solvent	*t* [h]	Yield [%][b]
1	benzene	20	93
2	THF	20	94
3	neat	24	83
4	acetonitrile	5	99

[a] All reactions were performed with 1 mmol of acetophenone and 1.2 mmol of phenylsilane by using 1 mol% of catalyst **1** at 80 °C in 0.4 mL of solvent. [b] Yields were determined by ^{1}H NMR spectroscopy by using *n*-tetradecane as an internal standard after basic hydrolysis.

catalyst,[12d] we decided to explore the reaction of **1** with $AgBF_4$. Treatment of **1** with one equivalent of $AgBF_4$ in acetonitrile resulted in abstraction of the bromide ligand and formation of the cationic species $[Mn(CO)_3(bis\text{-}NHC^{Me})(NCMe)][BF_4]$ (**5**; Scheme 2). Complex **5** was isolated as a brown, stable solid,



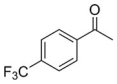
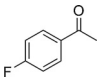
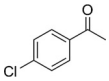
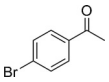
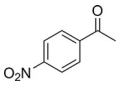
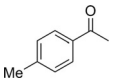
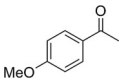
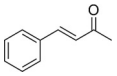
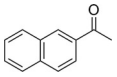
Scheme 2. Synthesis of the cationic complex **5**.

which can be handled in air. As expected, the infrared spectrum of **5** shows the characteristic pattern of a tricarbonyl complex, displaying the symmetric CO stretching frequency at 2020 cm^{-1}, at a higher value than that displayed by the neutral complex **1** (2004 cm^{-1}).[13]

As anticipated, complex **5** displayed higher catalytic activity than **1** in the hydrosilylation of acetophenone when using phenylsilane as a reducing agent. Under similar conditions, quantitative conversion of acetophenone was obtained after 1 h, whereas 5 h were needed for complex **1** to reach full conversion (entries 1 and 2, Table 3). To determine the highest attainable turnover frequencies (TOFs) and turnover numbers (TONs) for **5**-catalyzed ketone hydrosilylation, the catalyst loading was reduced to 0.1 mol%, reaching a TOF number of 320 h^{-1} (calculated at 90 min of reaction, kinetic profile in the Supporting Information, Figure S8), and a TON of 1000 (in acetonitrile at 80 °C). The TON value is comparable to those obtained by the scarce Mn-NHC complexes known to catalyze this reaction (TON up to 960 reported in the literature for $[CpMn(CO)_2(NHC)]$),[5h] but is lower than the best performing Mn catalysts reported in the literature (TOF of up to 76800 h^{-1} reported by Trovitch and co-workers).[4]

The scope of the reaction was explored by using complexes **1** and **5**. All ketone substrates were converted within 1–5 h when using **5**, whereas **1** needed slightly longer reaction times (2–8 h), depending on the substrates. Both catalysts **1** and **5** tolerated fluoro, chloro, and bromo functionalities (entries 3–10, Table 3), in contrast with other Mn-based catalysts, reported to be inactive in the presence of chloro- and bromo-substituents.[5g] For the *p*-iodo-benzaldehyde, reductive dehalogenation occurred and formation of 1-phenyethanol was detected by NMR spectroscopy. Ketones bearing electron-donating substituents such as methoxy and methyl groups in the *para* position were fully reduced and the corresponding alcohols obtained in high yields (entries 15–18, Table 3). Reduction of 4-nitro-acetophenone was also selective, achieving a good yield of the corresponding alcohol after 3–4 h. Interestingly, both **1** and **5** were capable of reducing aliphatic ketones, cyclic and linear, including the selective reduction of *trans*-4-phenyl-3-buten-2-one (entries 19–28, Table 3). All yields were consistently very good to excellent, ranging between 72 and 99% isolated yields. Unfortunately, our catalytic system was inactive towards the reduction of esters under similar reaction conditions.

Table 3. Hydrosilylation of ketones catalyzed by **1** and **5** with $PhSiH_3$.[a]

Entry	Substrate	Catalyst	*t* [h]	Yield [%][b]
1		**1**	5	97 (92)
2		**5**	1	93
3		**1**	5	97
4		**5**	1	85
5		**1**	3	96
6		**5**	2	97 (93)
7		**1**	2	96
8		**5**	2	95
9		**1**	8	78
10		**5**	5	90
11		**1**	24	0
12		**5**	24	0
13		**1**	4	91
14		**5**	3	83
15		**1**	4	93
16		**5**	3	95
17		**1**	6	72
18		**5**	3	86
19		**1**	5	72
20		**5**	4	92 (85)
21		**1**	8	91
22		**5**	5	93 (93)
23		**1**	5	94
24		**5**	2	99
25		**1**	8	93
26		**5**	5	91 (88)
27		**1**	8	89
28		**5**	4	93

[a] All reactions were perfomed with 1.0 mmol of substrate and 1.2 mmol of $PhSiH_3$ in acetonitrile (0.4 mL) at 80 °C and with 1 mol% of catalyst. [b] Yields were determined by ^1H NMR spectroscopy by using *n*-tetradecane as an internal standard after basic hydrolysis. Isolated yields are indicated in parenthesis.

We have also explored the applicability of the method by using other silanes, such as Ph_2SiH_2 and Ph_3SiH. Both silanes afforded the reduction of acetophenone in good yields, 94% and 89%, respectively, in 8 h in the presence of catalyst **5**. Gratifyingly, we observed that hydrosilylation could be performed by using the cheap and readily available polymethylhydrosiloxane (PMHS) as a reducing agent. When the reactions were done with PMHS, catalyst **1** displayed higher activity than **5** (80% versus 64% yield of 1-phenylethanol in 8 h, when using **1** and **5**, respectively), achieving moderate to good yields and selectivities for the reduction of a wide variety of

substrates, including both aromatic and aliphatic ketones. Results are summarized in Table 4.

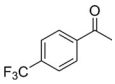
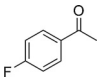
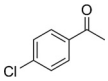
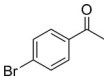
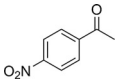
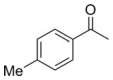
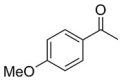
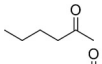
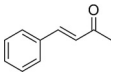
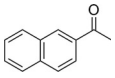
Prompted by the observation that acetonitrile accelerates the hydrosilylation reaction rate, we decided to investigate the influence of radical traps on the catalytic rates. The catalytic reduction of acetophenone with $PhSiH_3$ (1.2 equiv) when using **5** (1 mol%) was performed in the presence of a variety of spin-traps. Interestingly, the presence of Ph_2NH, $CBrCl_3$, and 2,2,6,6-tetramethylpiperidin *N*-oxide (TEMPO) radical scavengers of oxygen, carbon, and silyl, respectively,[17] strongly inhibited the reaction. As shown in Table 5, hydrosilylation of acetophenone in the presence of 1 mol% of Ph_2NH, $CBrCl_3$, and TEMPO afforded only 11, 14, and 26% conversion in 1 h, respectively, whereas in the absence of radical scavengers, full conversion was obtained (entries 1, 4, 7, 10, Table 5). However, the reaction resumed and reached quantitative conversions after 8 h when TEMPO and Ph_2NH were present, and it afforded 44% conversion in the presence of $CBrCl_3$. These observations indicated the involvement of radical species as intermediates in the catalytic reaction.

Table 5. Effect of addition of spin-traps in the hydrosilylation of acetophenone catalyzed by **5**.[a]

Entry	Spin-trap	*t* [h]	Yield [%][b]
1		1	11
2	Ph_2NH	3	30
3		8	>99
4		1	14
5	$CBrCl_3$	3	28
6		24	44
7		1	26
8	TEMPO	3	64
9		8	93
10	–	1	>99

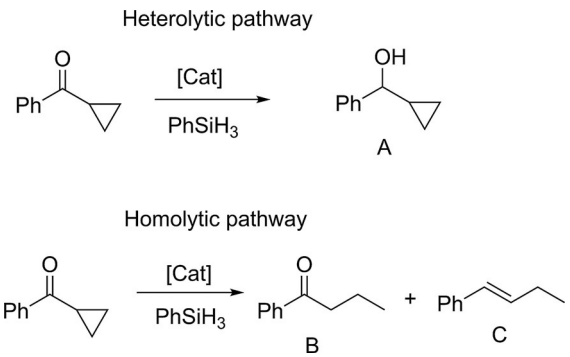
[a] All reactions were performed with 1 mmol of acetophenone and 1.2 mmol of phenylsilane by using 1 mol% of catalyst **5**, and 1 mol% of radical scavenger at 80 °C in acetonitrile (0.4 mL). [b] Yields were determined by ^{1}H NMR spectroscopy by using *n*-tetradecane as an internal standard after basic hydrolysis.

Table 4. Hydrosilylation of ketones catalyzed by **1** with PMHS.[a]

Entry	Substrate	Yield [%][b]
1		80
2		88 (82)
3		57
4		65 (58)
5		56
6		0
7		75 (72)
8		53
9		69
10		69
11		65
12		91 (88)
13		63
14		64 (58)

[a] All reactions were performed with 1.0 mmol of substrate and 1.2 mmol of $PhSiH_3$ by using 1 mol% of **1** in acetonitrile at 80 °C for 8 h. [b] Yields were determined by ^{1}H NMR spectroscopy by using *n*-tetradecane as an internal standard after basic hydrolysis. Isolated yields are indicated in parenthesis.

In addition to the spin-trap experiments, cyclopropyl phenyl ketone was employed as a mechanistic probe of intermediate radical species involvement. In fact, formation of the cyclopropyl ring-opening products would indicate a radical mechanism, allowing us to differentiate between heterolytic and homolytic pathways for reduction.[18] If cyclopropyl phenyl ketone is reduced by the hydride transfer mechanism, it yields phenylcyclopropylcarbonol **A** (Scheme 3), whereas the homolytic pathway, based on the formation of a ketyl intermediate, would provide the open-chain phenyl propyl ketones **B** and **C** as final products (Scheme 3). In our studies with complex **5**, the hydrosilylation reaction of cyclopropyl phenyl ketone afforded, after hydrolysis, a complex mixture in which the ring-opening product β-ethyl styrene (**C**) and cyclopropyl phenyl methanol (**A**) were detected in a **C**/**A** ratio of 1:2.8 (Figure S9 in the Supporting Information). The presence of **C**, unequivocally indicates the involvement of a radical pathway. Our findings differ from the Mn-based catalysts reported in the litera-



Scheme 3. Heterolytic and homolytic pathways for the reduction of cyclopropyl phenyl ketone with phenylsilane.

ture, in which the classical Ojima-like mechanism has been proposed to be operative.[5a,d,e] Trovitch and colleagues elegantly proved that the concurrent modified Ojima and Mn–H insertion mechanisms were responsible for catalysis with a Mn^0 catalyst.[5a,d] Identification of Mn–H species was also achieved by Lugan, Sortais, and co-workers with $CpMn(NHC)(CO)_2$ systems.[5g,h] In contrast, a radical transfer mechanism has been proposed by Trovitch and co-workers with a Mn complex bearing a redox-active ligand.[5f]

Further experiments were performed to get an insight into the mode of activation of the Mn-NHC catalyst. The stoichiometric reaction of **5** and acetophenone in a molar ratio 1:1 did not display any observable change, neither by NMR nor by UV/Vis spectroscopy. Treatment of complex **5** with two equivalents of $PhSiH_3$ in acetonitrile at 80 °C over 2 h, produced a rapid color change from brownish to grey. Formation of a new Mn complex featuring a ^1H NMR signal at −6.8 ppm was detected (Figure S10 in the Supporting Information). The signal at −6.8 ppm could be indicative of the formation of Mn–H or $Mn(\eta^2\text{-H-}SiH_2Ph)$ species.[5g,h] In an attempt to characterize Mn–H species, the reaction of **5** with $LiEt_3BH_4$ was performed without success. Finally, the stoichiometric reaction of **5** with phenylsilane in THF was monitored in a high-pressure sealed reactor by FTIR spectroscopy. The temperature of the reactor was controlled externally with a thermocouple and progressively increased. At room temperature (20 °C), the typical CO stretches of **5** at 2025, 1935, 1925 cm^{-1} are observed in the spectrum, together with the ν_{Si-H} band at 2158 cm^{-1} and a new set of signals (2007, 1925, 1879 cm^{-1}), most likely corresponding to a new carbonyl Mn species. Increasing the temperature favors the formation of the new species at the expense of **5** being predominant at 80 °C. The new compound showed the typical pattern of a facial tricarbonyl compound without loss of any CO ligand. This finding contrasts with $CpMn(NHC)(CO)_2$ compounds, in which dissociation of a CO ligand precedes activation of silane.[5g,h]

Conclusions

We have reported Mn^I N-heterocyclic carbene (NHC) complexes for the effective catalytic reduction of ketones groups by using silanes as reducing agents, including polymethylhydrosiloxane, which is an inexpensive, easy to handle, and environmentally friendly byproduct of the silicone industry. Interestingly, the Mn-NHC complexes are air stable and catalytic experiments are performed under atmospheric air. The reduction reaction is compatible with aromatic and aliphatic ketones bearing a wide variety of functional groups. We have demonstrated that the presence of NHC ligands in the coordination sphere of Mn produces an enhancement of the catalyst performance. It is expected that the enormous flexibility of NHC ligands will allow a significant optimization of these promising catalysts. Ongoing studies in our group are focusing on the synthesis of Mn-NHC compounds with improved catalytic efficiencies, and further development of the methodology to other applications.

Experimental Section

General methods

The synthesis of manganese complexes was performed under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were purified from appropriate drying agents and distilled under nitrogen. Deuterated solvents were degassed and stored over molecular sieves. The imidazolium salt 1,1′-methylene-3,3′-di-mesitylimidazolium dibromide,[19] and the manganese complexes $[Mn(bpy)(CO)_3Br]$,[15] $[Mn(NHC\text{-}py)(CO)_3Br]$,[14] and $[Mn(bis\text{-}NHC^{Me})(CO)_3Br]$[13] were synthesized according to the methods described in the literature. All other reagents were purchased from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 MHz. Assignment of resonances was made from HMQC and HMBC experiments. Electrospray mass spectra (ESI-MS) were recorded with a Micromass Quatro LC instrument; nitrogen was employed as a drying and nebulizing gas. Elemental analyses were performed in our laboratories at ITQB.

Preparation and characterization of 2

Solid $MnBr(CO)_5$ (0.19 g, 0.7 mmol) was suspended in THF (15 mL) and potassium *tert*-butoxide (0.14 g, 1.2 mmol) was added first, followed by addition of 1,1′-methylene-3,3′-di-mesitylimidazolium dibromide (0.30 g, 0.55 mmol) at 60 °C. The resulting suspension was heated at 60 °C for 16 h under stirring. All volatiles were removed under vacuum and the resulting residue was washed with Et_2O (4× 15 mL) and dissolved in dichloromethane (80 mL). The dichloromethane solution was washed with water (80 mL) and the organic extract was dried with Na_2SO_4. The solution was filtered and concentrated to dryness under vacuum to yield a yellow crystalline powder. Yield: 0.15 g (45% yield). ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 7.83 (s, 2H, CH_{imid}), 7.36 (s, 2H, CH_{imid}), 7.01 (s, 2H, *CH*Ph), 6.96 (s, 2H, *CH*Ph), 6.78 (d, $^2J_{H\text{-}H}$ = 12 Hz, 1H, NCH_2N), 6.43, (d, $^2J_{H\text{-}H}$ = 12 Hz, ^1H, NCH_2N), 2.28 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 1.82 ppm (s, 6H, CH_3); ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 223.99 (*CO*), 217.91 (*CO*), 191.63 (Mn-$C_{carbene}$), 138.32 (C_{ipso}), 136.64 (C_{ipso}), 136.00 (C_{ipso}), 135.16 (C_{ipso}), 128.69 (C_{Ph}), 128.50 (C_{Ph}), 123.33 (CH_{imid}), 123.04 (CH_{imid}), 61.79 (NCH_2N), 20.64 (CH_3), 18.03 (CH_3), 17.46 ppm (CH_3); IR (KBr): $\tilde{\nu}$(CO) = 2007 (s), 1923 (s), 1887 cm^{-1} (s); HRMS ESI-MS (positive mode): 523 $[M-Br]^+$; elemental analysis calcd (%) for $C_{28}H_{28}MnBrN_4O_3Br$: C 55.73, H 4.68, N 9.28; found: C 55.40, H 4.61, N 8.90.

Preparation and characterization of 5

$AgBF_4$ (0.14 g, 0.73 mmol) was added to a solution of **1** (0.26 g, 0.66 mmol) in NCMe (15 mL), and the reaction mixture was stirred at room temperature overnight. The solution was filtered, and the filtrate was concentrated to dryness under vacuum. The residue was washed with diethyl ether and dried under vacuum to afford 0.20 g (72% yield) of crystalline brown solid. ^1H NMR (CD_3CN, 25 °C): δ = 7.41 (s, 2H, CH_{imid}), 7.21 (s, 2H, CH_{imid}), 6.11 (d, $^2J_{H\text{-}H}$ = 12 Hz, 1H, NCH_2N), 6.01 (d, $^2J_{H\text{-}H}$ = 12 Hz, 1H, NCH_2N), 3.93 ppm (s, 6H, NCH_3); ^{13}C NMR (CD_3CN, 25 °C): δ = 220.99 (*CO*), 218.29 (*CO*), 188.28 (Mn-$C_{carbene}$), 124.93 (CH_{imid}), 123.13 (CH_{imid}), 63.07 (NCH_2N), 38.37 ppm (NCH_3); IR (KBr): $\tilde{\nu}$(CO) = 2020 (s), 1928 cm^{-1} (s); HRMS ESI-MS (positive mode): 356.0 $[M-BF_4]^+$ and 315.0 $[M-NCMe\text{-}BF_4]^+$; elemental analysis calcd (%) for $C_{14}H_{15}MnN_5O_3$: C 37.95, H 3.41, N 15.81; found: C 37.81, H 3.21, N 15.90.

Typical procedure for the hydrosilylation of benzaldehyde and ketones catalyzed by complexes 1–5

An open-air flask was charged with catalyst (1 mol%) and solvent (0.4 mL). Then, silane (1.2 equiv) and the corresponding substrate (1 mmol) were added. The reaction mixture was stirred and heated at 80 °C. The progress of the reactions was monitored by taking aliquots of the reaction mixtures and subjecting them to ^{1}H NMR spectroscopy in chloroform-d. Conversion was determined by ^{1}H NMR spectroscopy by using *n*-tetradecane as an internal standard. At the end of the reaction, MeOH (1 mL) and 2 M NaOH (10 mL) were added consecutively under vigorous stirring. The reaction mixture was stirred overnight at room temperature and was extracted with dichloromethane (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to afford the isolated product. For some representative samples, the final products were isolated by following same experimental procedure (reactions were performed in the absence of internal standard), dried, and weight to calculate the isolated yields.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbonyl reduction · hydrosilylation · manganese · N-heterocyclic carbenes

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