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Manganese Salan Complexes as Catalysts for Hydrosilylation of Aldehydes and Ketones

Nora Almutairi, Srikanth Vijjamarri and Guodong Du *

Department of Chemistry, University of North Dakota, 151 Cornell Street Stop 9024, Grand Forks, ND 58202, USA
* Correspondence: guodong.du@und.edu; Tel.: +1-701-7772241

Abstract: Manganese has attracted significant recent attention due to its abundance, low toxicity, and versatility in catalysis. In the present study, a series of manganese (III) complexes supported by salan ligands have been synthesized and characterized, and their activity as catalysts in the hydrosilylation of carbonyl compounds was examined. While manganese (III) chloride complexes exhibited minimal catalytic efficacy without activation of silver perchlorate, manganese (III) azide complexes showed good activity in the hydrosilylation of carbonyl compounds. Under optimized reaction conditions, several types of aldehydes and ketones could be reduced with good yields and tolerance to a variety of functional groups. The possible mechanisms of silane activation and hydrosilylation were discussed in light of relevant experimental observations.

Keywords: manganese; catalysis; hydrosilylation; aldehydes and ketones; salan

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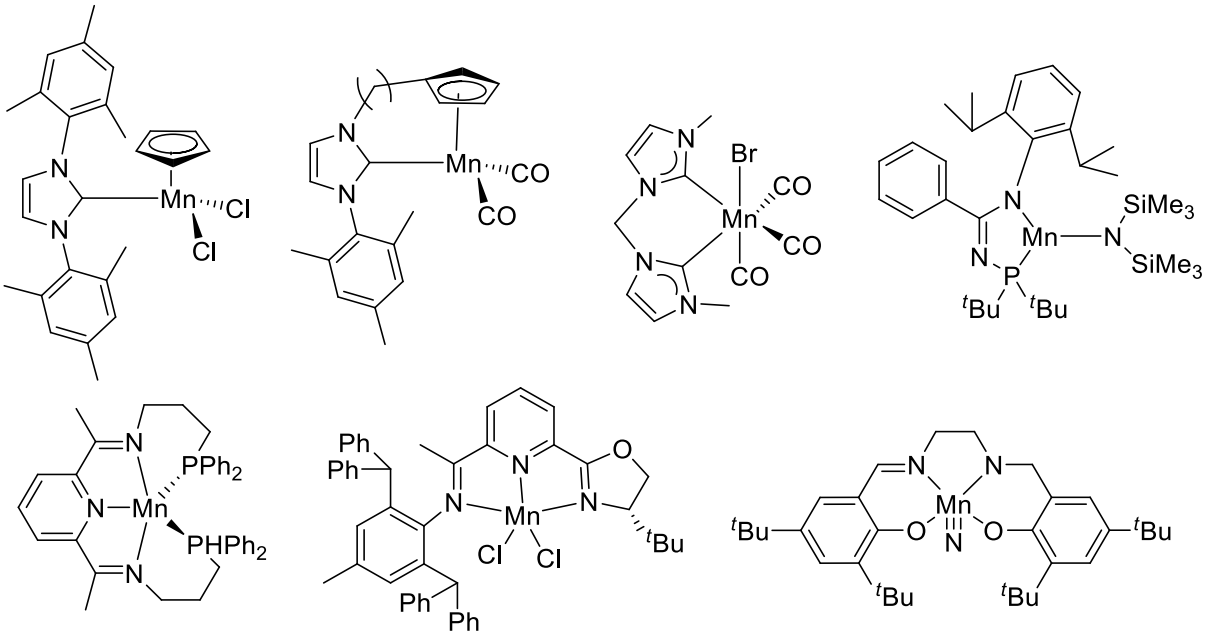
1. Introduction

There has been an emerging shift towards first-row transition metals in catalysis [1–4]. Conventionally, the precious metal-based catalysts, represented by palladium, have been a dominating force, particularly in the pharmaceutical industry. However, the toxicity and the increasing scarcity of these elements have raised health and sustainability concerns and stimulated the search for alternative catalytic systems. Consequently, first-row metals such as Fe [5–8], Cu [9,10], and Zn [11–14] have attracted growing interest in various catalytic reactions due to their abundance and low toxicity. The distinct reactivity of the first-row metals may enable new transformations inaccessible with the second- and third-row metals. As one of the most abundant transition metals, Mn has seen a recent resurgence of research beyond traditional oxidation/oxygenation catalysis [15,16]. A wide variety of chemical transformations have been achieved with manganese catalysis, such as hydrogenation of alkenes [17], CO_2, esters, ketones, nitriles [18–24], hydroboration of carbonyls, nitriles carboxylic acids and CO_2 [25–30], electrochemical hydrogen production [31], dehydrogenative olefination of alkyl-substituted heteroarenes and sulfones with alcohols [32–35], alkylation of nitriles, esters, and amides [36,37], dehydrogenation of alcohols [38–40] and its application in the synthesis of pyrroles and imides from amines and diols [41,42], and dehydrogenative cross-coupling of hydrosilanes and alcohols [43–46].

Among these developments, manganese-catalyzed hydrosilylation occupies a special place, thanks to the early work by the Cutler group, showing that simple manganese carbonyl complexes were effective catalysts for the hydrosilylation of various unsaturated substrates [47–52]. Hydrosilylation of C=O-containing compounds represents a mild and versatile approach for the reduction of these compounds and various metal and nonmetal-catalyzed reactions have been reported using commercial hydrosilane reagents [53–56]. Not surprisingly, recent research in manganese also provides a wide range of catalysts for the hydrosilylation of aldehydes, ketones, esters, amides, and carboxylic acids [57–70]. Efficient hydrosilylation of C=C double bonds by manganese catalysts has also been reported [71,72]. A few representative examples of manganese (pre)catalysts for hydrosilylation are shown

in Scheme 1. Although a direct comparison of the catalytic activity of these catalysts across different groups is difficult due to the varied reaction conditions and the choice of substrates, a brief summary of typical carbonyl substrates is compiled in Table S1.



Scheme 1. Selected examples of Mn (pre)catalysts for hydrosilylation.

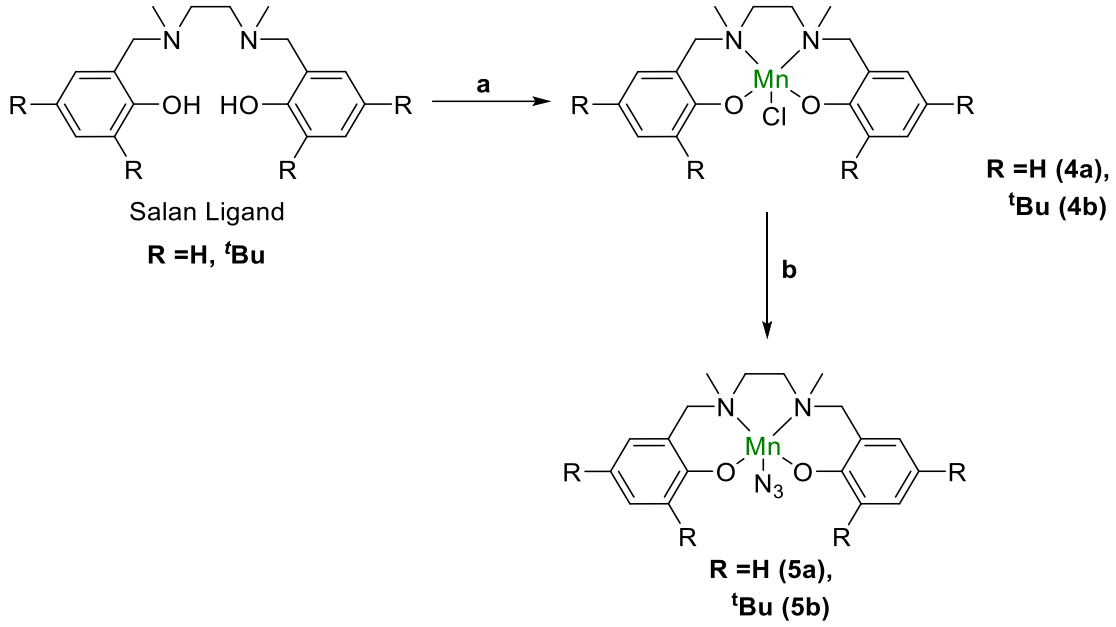
Metals supported by salen ligands have been widely reported as catalysts in different transformations. Our previous work has shown a manganese salen complex is highly efficient in catalyzing the hydrosilylation and hydroboration of carbonyl groups with high yields and broad tolerance of functional groups [28,68]. Mechanistic investigations suggest that the availability of two cis-coordination sites at the Mn center is important for the catalytic activity. Although such a cis-coordination mode has been observed with salen complexes [73], it is conceivably difficult to achieve without some transformation on the salen ligand, since such ligands typically need four planar coordination sites on the metal center. Thus our attention has turned to the reduced salen, or salan ligands (where H_2salan = N,N′-dimethyl-N,N′-bis(o-hydroxybenzyl)-1,2-diaminoethane), which are derived from the hydrogenation of the imine bonds in salen. The replacement of the C=N double bonds by the C-N single bonds provides a more flexible coordination environment around the metal center, and this may allow ready access to the cis-coordination mode and facilitate the catalytic reaction. It has been illustrated that salan ligands are a good platform that could support various transition metals and provide catalytic reactivity as well as selectivity [74–76]. Herein we report our studies of manganese salan complexes for catalytic hydrosilylation of carbonyl compounds.

2. Results and Discussion

2.1. Synthesis and Characterization of (Salan)Mn Complexes

The salan ligands were obtained by following the literature procedures [77]. Briefly, the reaction of salicyaldehyde derivatives with diamine afforded the parent H_2salen ligand, which was first reduced with excess $NaBH_4$ and subsequently methylated by reductive amination with $NaBH_4/CH_2O$. The metallation was carried out with $MnCl_2$ or $Mn(OAc)_2/LiCl$ to first obtain the chloride compounds. The substitution with NaN_3 in the presence of $AgClO_4$ afforded the azido complex (Scheme 2) [78]. The presence of the azido ligand in (salan-^{t}Bu$_2$)Mn(N_3) (**5b**) was confirmed by the peak at 2050 cm^{-1} in the FT-IR spectrum (Figure 1). Similarly, the parent (salan)Mn(N_3) (**5a**) featured an azide-stretching peak at 2037 cm^{-1}. For comparison, the starting NaN_3 shows an IR peak at 2104 cm^{-1}. The known

salen analogue, (salen-$^{t}Bu_2$)Mn(N_3) (**6**) [79], was also obtained in a similar procedure, and the IR peak for the azido ligand as a thin film is observed at 2063 cm^{-1}. The vibrational mode of a series of (salen)Mn(N_3) derivatives appeared in the range of 2046–2048 cm^{-1} in a solution phase determination, typical for the apical azido group in five-coordinate square pyramidal Mn(III) complexes. Efforts were made to prepare the nitrido manganese salan complexes since this would offer a direct comparison with the salen analogue [68]. However, experimental attempts, either by photolysis [80–84] of the azido precursor (salan-$^{t}Bu_2$)Mn(N_3) or by bleach oxidation of (salan-$^{t}Bu_2$)MnCl in the presence of NH_4OH [85], were not successful. Thus, we focused on the (salan)Mn(N_3) complexes which showed reasonable activity in the hydrosilylation reaction.



Scheme 2. Synthesis of salan Mn complexes. (a) $MnCl_2$ or $Mn(OAc)_2$/LiCl; (b) $AgClO_4$/NaN_3.

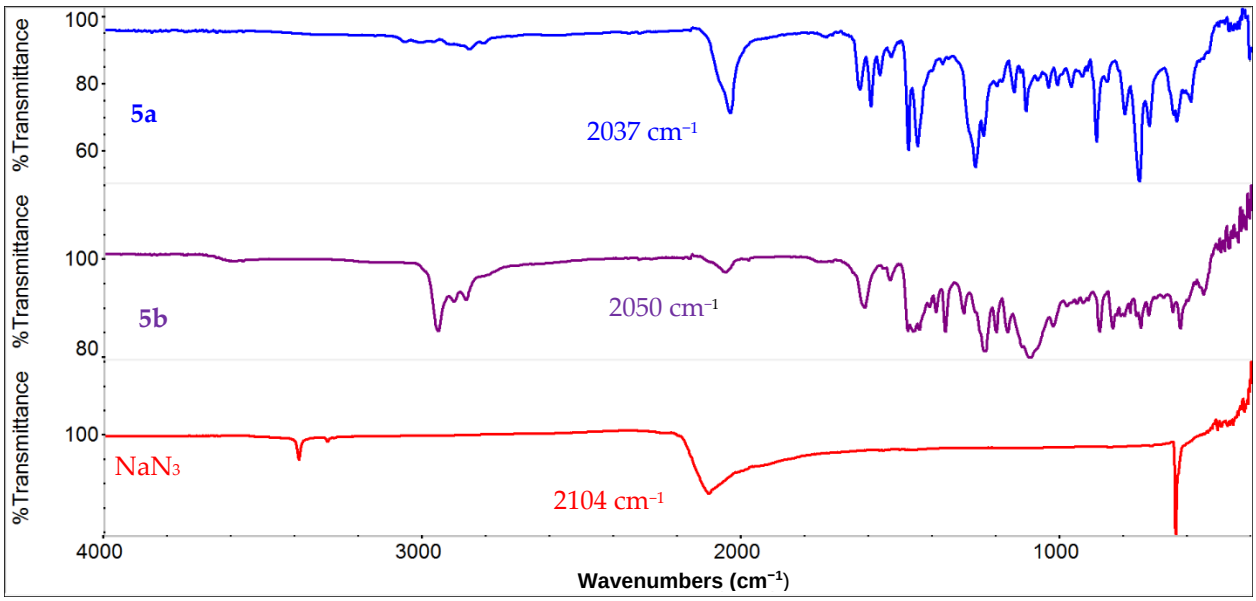
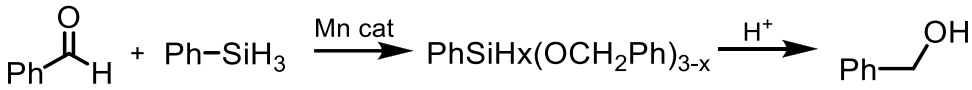


Figure 1. Comparison of FT-IR spectra of (salan)Mn(N_3) (**5a**) (**top**), (salan-$^{t}Bu_2$)Mn(N_3) (**5b**) (**middle**), and NaN_3 (**bottom**).

2.2. Catalytic Hydrosilylation

Having a series of manganese (III) complexes in hand, we first examined the efficacy of complex **5b** in the hydrosilylation under a variety of reaction conditions, with benzaldehyde PhCHO as a model substrate and phenylsilane $PhSiH_3$ as the hydrogen source, and the results are compiled in Table 1. Screening different solvents in the reaction illustrated that benzene was an optimal solvent in this system, while the hydrosilylation in other common solvents such as CD_3CN and $CDCl_3$ was slower or with low conversions. The reaction with benzene as a solvent at elevated temperature exhibited a high conversion of >99 % in less than 1 h with 0.5 mol % loading of the catalyst (entry 1, Table 1). Reaction in CD_3CN under identical conditions resulted in a 94 % conversion within 6.5 h (entry 2). Unlike C_6D_6 and CD_3CN, $CDCl_3$ as a solvent showed negligible conversion after a long reaction time (entry 4), though increasing the catalyst loading to 1 mol % at a longer reaction time did lead to some conversion of PhCHO (entry 5). Reaction in toluene-d_8 showed comparable reactivity, as in benzene, reaching a >99% conversion within 40 min (entry 3). Other reaction parameters were also explored. The reaction with C_6D_6 could be carried out at a lower temperature (80 °C or at room temperature), and longer reaction times were needed for reasonable conversion (entries 6 & 7). For example, the reaction could still reach a 90% conversion after a few days at 80 °C. However, when the reaction was run under air, only minimal conversion was obtained within 5 h (entry 8), which was less active than the (salen)MnN system in the presence of air [68]. So the rest of the reactions were carried out under N_2. Among other common hydrosilanes, a tertiary hydrosilane, triethoxysilane, was also active for the hydrosilylation in CD_3CN, and a 54% conversion of PhCHO was observed after 8 h of reaction (entry 9). At this point, the triethoxysilane was completely consumed, though the side reaction product was not identified. When the loading of the triethoxysilane was increased to two equivalents of PhCHO, the complete conversion of PhCHO could be achieved within 8 h (entry 10). Under the same conditions, a reaction with a ketone, acetophenone, was slower but reached a 99% conversion within 25 h (entry 11). Secondary silanes, such as Ph_2SiH_2, showed lower activity than $PhSiH_3$ and tertiary silanes such as Et_3SiH showed no activity.

Table 1. Hydrosilylation of PhCHO under different conditions [a].



Entry	Cat (Equiv.)	Silane (Equiv.)	Solvent	Temp (°C)	Time	Convn (%)
1	**5b** (0.5%)	$PhSiH_3$(1)	C_6D_6	120	40 min	>99%
2	**5b** (0.5%)	$PhSiH_3$(1)	CD_3CN	120	6.5 h	94%
3	**5b** (0.5%)	$PhSiH_3$(1)	C_7D_8	120	40 min	>99%
4	**5b** (0.5%)	$PhSiH_3$(1)	$CDCl_3$	120	3 d	<1%
5	**5b** (1%)	$PhSiH_3$(1)	$CDCl_3$	120	4 d	10%
6	**5b** (1%)	$PhSiH_3$(1)	C_6D_6	RT	67 h	20%
7	**5b** (1%)	$PhSiH_3$(1)	C_6D_6	80	13 h	90%
8 [b]	**5b** (1%)	$PhSiH_3$(1)	C_6D_6	120	3 h	4.8%
9	**5b** (0.5%)	$(EtO)_3SiH$(1)	CD_3CN	120	8 h	53.6%
10	**5b** (0.5%)	$(EtO)_3SiH$(2)	CD_3CN	120	8 h	>99%
11 [c]	**5b** (0.5%)	$(EtO)_3SiH$(2)	CD_3CN	120	25 h	>99%
12 [d]	**4b** (0.5%)	$PhSiH_3$(1)	C_6D_6	120	48 h	9%
13 [e]	**4b** (0.5%)	$PhSiH_3$(1)	C_6D_6	120	48 h	87%
14 [f]	**5a** (0.5%)	$PhSiH_3$(1)	C_6D_6	120	2.3 h	99%
15 [g]	**6** (0.5%)	$PhSiH_3$(1)	C_6D_6	120	12 h	>99%

[a] Reaction conditions: PhCHO (1 equivalent). The temperature refers to the heating bath temperature. [b] The reaction was run under air. [c] Acetophenone as substrate. [d] Reaction with complex **4b**. [e] Combination of **4b** with $AgClO_4$ (1:1 ratio). [f] Reaction with complex **5a**. [g] Reaction using (salen-^{t}Bu$_2$)Mn(N_3) **6**.

After exploration of the reaction conditions, we examined the hydrosilyation of PhCHO with different salan Mn(III) complexes (entries 12–15, Table 1). The parent salen azido complex **5a** was capable of catalyzing the reaction, though with somewhat lower activity

(entry 14). On the other hand, the chloride complex **4b** on its own showed little activity in the hydrosilylation of PhCHO (entry 12). However, it could be activated by treatment with an equimolar amount of $AgClO_4$. The hydrosilylation of PhCHO took place after an induction period and up to 90% conversion was achieved after 48 h (entry 13). Figure 2 depicts the conversion-time profiles of these catalytic systems and it is notable that the (salan-^{t}Bu$_2$)Mn(N_3) complex (**5b**) was the most active among these complexes. For further comparison, the salen analogue (salen-^{t}Bu$_2$)Mn(N_3) (**6**) was also tested under the same conditions, though it displayed lower activity than **5a** and **5b** (entry 15).

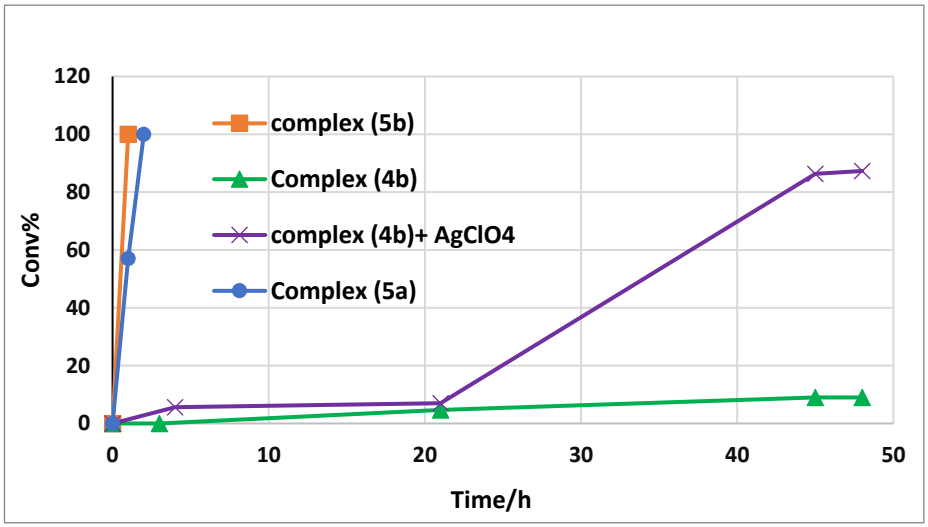
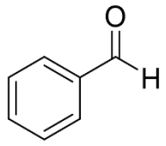
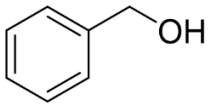
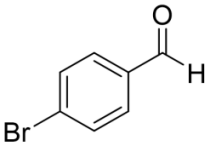
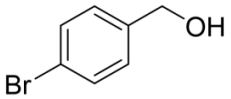
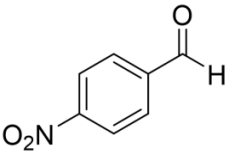
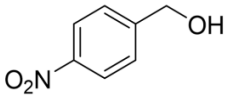
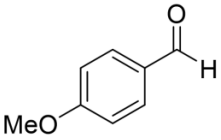
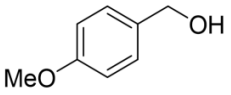
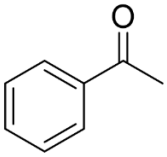
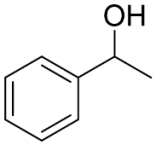
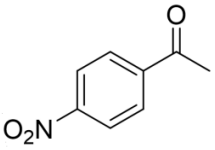
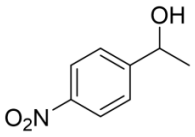
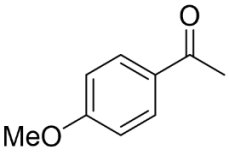
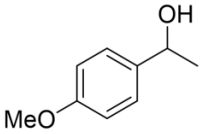
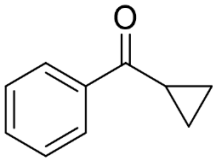
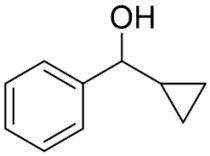
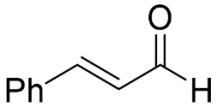
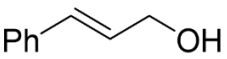
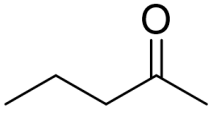
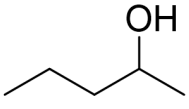
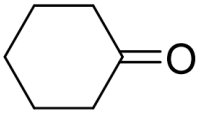
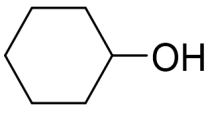


Figure 2. The conversion-time profile with different catalysts (0.5 mol%) in the hydrosilylation of PhCHO.

With the reaction condition established above, we next examined the scope of carbonyl substrates with **5b**. Hydrosilylations of a variety of aldehydes and ketones occurred at 120 °C with low loadings of the catalyst **5b** (0.5 mol %) in benzene-d_6 (as it is cheaper than toluene-d_8) in the presence of $PhSiH_3$ (Table 2). The purified corresponding alcohols were obtained after an acidic workup of the reaction mixtures. High conversions and good isolated yields were observed in most cases. The reaction generally proceeded faster with aldehydes when compared to ketones, as typically observed in the hydrosilylation of carbonyl compounds [53–56]. In an intermolecular competition reaction between PhCHO and PhCOMe with $PhSiH_3$ (1:1:1 molar ratio), PhCHO conversion reached 89% within 3 h while only <5% PhCOMe reacted. Common functional groups, including halides, nitro, and methoxy, were tolerated under the reaction conditions. The benzaldehyde derivatives bearing the electron-withdrawing groups Br and NO_2 tended to react more rapidly than those with electron-donating OMe (entries 2–3 vs. 4). The progress of the reaction of 4-methoxyacetophenone (entry 7, Table 2) monitored by ^{1}H NMR spectroscopy was shown in Figure S5. In addition, the reaction of 4-nitroacetophenone was peculiar under this condition in that no further conversion was observed at 76% after 72 h (entry 6, Table 2). The reaction of cinnamaldehyde led to the reduction of the carbonyl group without any reduction of the C=C double bond, suggesting that the reaction was selective toward carbonyl groups over alkenes (entry 9). The nearly exclusive 1,2-hydrosilylation of the α,β-unsaturated carbonyl substrates was different from that of the (salen)MnN-catalyzed reaction, in which the 1,4-addition product seemed to dominate [68]. Furthermore, aliphatic carbonyl substrates also underwent hydrosilylation reactions under the same conditions (entries 10–11), and the conversions were generally high (>95%).

Table 2. Hydrosilylation of Aldehydes and Ketones Catalyzed by (salan)MnN_3 [a].

Entry	Substrate	Time (h)	%Conv (Yield)	Product
1		0.67	100 (76)	
2		5.3	100 (60)	
3		2.3	100 (70)	
4		61	100 (95)	
5		41	93 (73)	
6		72	76	
7		40	100 (62)	
8		15	100 (49)	
9		13	100 (97)	
10		36	>95 (88)	
11		18	>96 (94)	

[a] Reaction conditions: the reactions were performed with ~1 mmol of the substrates, 1.0 equivalent of $PhSiH_3$ 0.5 mol% of catalyst **5b** in benzene heated at ~120 °C. The conversions were estimated from the ^1H NMR spectroscopy, and the yields in parentheses were isolated yields of alcohols after acidic workup.

In a reusability test of catalyst **5b**, we carried out the hydrosilylation of PhCHO with $PhSiH_3$ under standard conditions. After the complete consumption of PhCHO, a second batch of PhCHO and $PhSiH_3$ (1:1 molar ratio) was added and the complete reaction of PhCHO was observed within 2 h. A third and a fourth batch were added in the subsequent runs and gave comparable results. These observations indicated that the catalyst could be reused without much loss of reactivity. At a practical level, a gram-scale reaction with PhCHO was carried out with 0.5 mol% of **5b** under solvent-free conditions, and >97% conversion of PhCHO was observed in 4 h. After hydrolysis and purification, a benzyl alcohol product was obtained in good yield.

2.3. Mechanistic Consideration

In our previous study with a (salen)$Mn^{V}N$ catalyst, [68] it was observed that the reduction of $Mn^{V}N$ by hydrosilanes, as indicated by the color change and the NMR observations, was the first step of catalysis. Though the exact nature of the reduced Mn species was not confirmed, it was thought to be a Mn(II) or Mn(III) species that could interact with and activate hydrosilanes for the subsequent reactions. There was also evidence that the salen ligand might have undergone some transformation. In the current study, we employed Mn(III)-salan species as the (pre)catalyst so the reduction of Mn might not be necessary, though the reduction to a Mn(II) species as the active catalyst was possible under the current conditions. It has been shown that several manganese(III) catalysts could be efficient catalysts in hydrosilylation reactions [61–70]. However, (salan)MnCl **4b** showed minimum catalytic activity in the hydrosilylation of PhCHO, indicating that Mn(III) alone was not a determining factor. Activation of **4b** by $AgClO_4$ suggested that it was critical to open up the coordination site around the metal center for catalysis. The comparatively higher activity of **5b** (salan)Mn(N_3) vs. **4b** (salan)MnCl could be attributed to the weaker azido-metal interaction than M-Cl due to the larger size of N_3^-. In an analogous case, (salan)Cr(N_3) was active in the ring-opening reaction of epoxides, while (salan)CrCl was considered a precatalyst that required further activation [79]. By the same consideration, the reduction of $Mn^{V}N$ was supposedly required to open up the coordination site in the (salen)MnN catalysis. It should also be pointed out that the metal center in (salen)MnN and (salan)MnCl presumably adopts a square pyramidal geometry with an open site *trans* to the nitrido or chloride ligands. This indicated that a second open site, preferably *cis* to the first one, around the metal center, might be needed for hydrosilylation, i.e. to accommodate the coordination of both hydrosilane (or a hydride) and the carbonyl substrate. The observation that (salan-$^{t}Bu_2$)Mn(N_3) is more active than (salen-$^{t}Bu_2$)Mn(N_3) in catalysis (Table 1, entry 1 vs. 13) lends support to this notion since the salan ligands are more flexible to accommodate two *cis* open sites. As to the further activation of the hydrosilanes, a radical mechanism seems unlikely, since no ring-opening product was observed with cyclopropyl phenyl ketone [86,87]. The reaction progress of the cyclopropyl phenyl ketone monitored by the NMR spectroscopy was shown in Figure 3, and the straight conversion of the ketone to silyl ethers could be noted with the cyclopropyl ring intact during the process. The electronic effect of 4-substituted benzaldehydes indicated that the electron-withdrawing groups tended to give faster reactions than the electron-donating groups, which was comparable to the (salen)MnN-catalyzed hydrosilylation reactions [68], suggesting a similar activation mechanism. Taken together, we speculated a reaction pathway involving the formation of a hydrosilane-Mn adduct that generated an electrophilic silicon center, the coordination of a carbonyl substrate *cis* to the silane, followed by a subsequent nucleophilic attack of oxygen on the silicon for a silyl ether bond, though further details may vary.

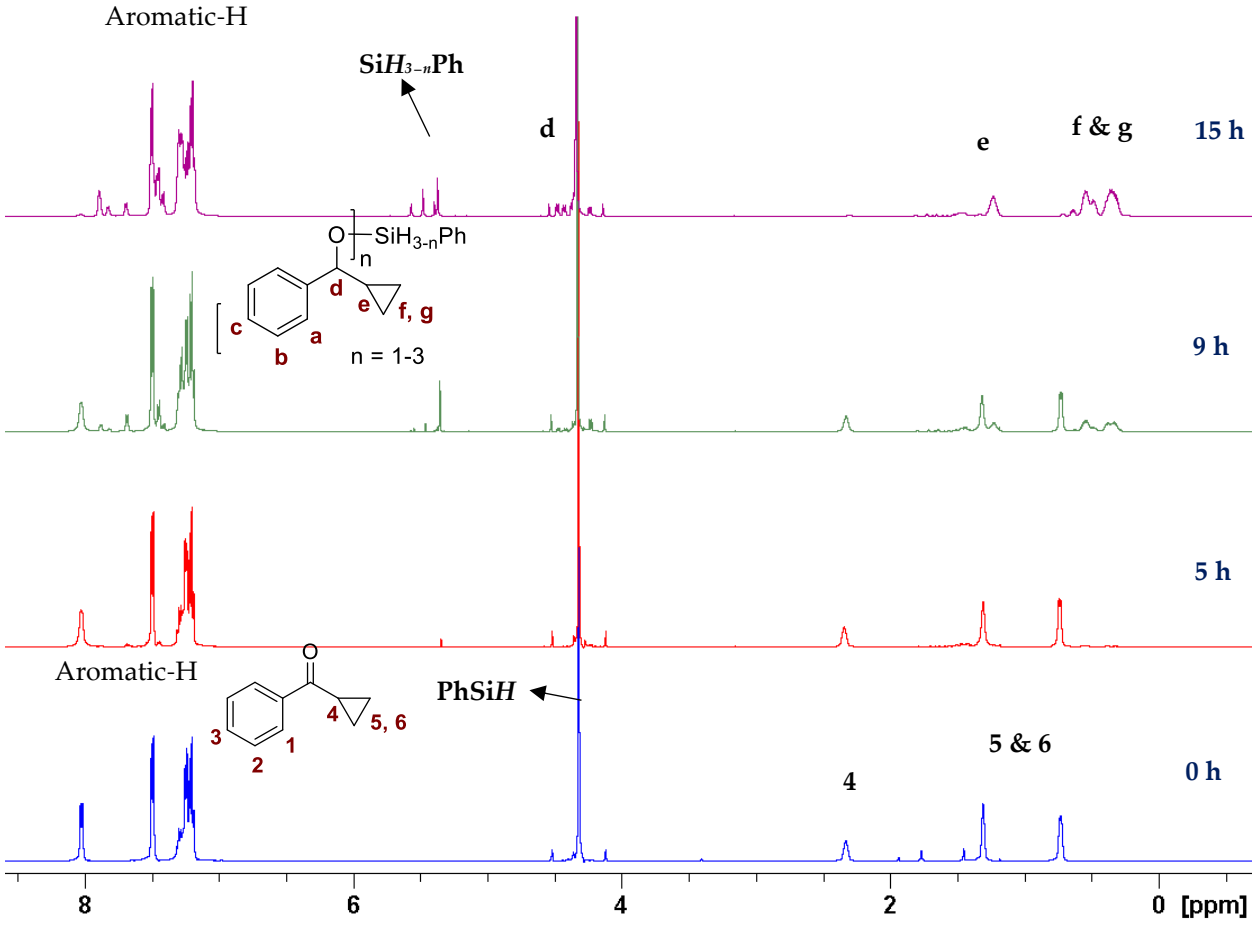


Figure 3. Hydrosilylation of cyclopropyl phenyl ketone monitored by the NMR spectroscopy.

3. Materials and Methods

All the substrates and reagents were obtained commercially, and the liquid substrates were degasified and dried over activated molecular sieves (4 Å) prior to the reaction. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 (Billerica, MA, USA) or AVANCE NEO 400 (Billerica, MA, USA) NMR spectrometer and referenced to the residue peaks in $CDCl_3$ (7.26), CD_3CN (1.94), or C_6D_6 (7.16).

General procedures for hydrosilylation. To a J Young NMR tube, the catalyst (0.5 mol %), substrate (one equivalent), C_6D_6 (0.35 mL), and $PhSiH_3$ (one equivalent) were added in order under nitrogen in a glovebox. The sealed tube was heated in an oil heating bath preset at 120 °C and the reaction was monitored by the NMR spectroscopy. When the reaction was completed, the reaction mixture was transferred to a vial with diethyl ether (2 mL). The mixture was then hydrolyzed using HCl (2 mL, 1 M) and extracted with diethyl ether. The organic phase was combined and dried over anhydrous Na_2SO_4. After the removal of the solvent, the alcohol product was isolated by column chromatography using silica with hexane-EtOAc as an eluent. The final products were confirmed by ^{1}H NMR and comparison with the literature's data.

4. Conclusions

A series of well-defined manganese salan complexes have been synthesized and shown to exhibit catalytic activity in the hydrosilylation of various aldehydes and ketones. Decent-to-high yields of the corresponding alcohols were obtained after an acidic workup, and a variety of functional groups in the carbonyl compounds, such as the methoxy, halides, and nitro groups, were tolerated. Future efforts will focus on the mechanistic elucidation

of the silane activation and on additional ligand systems that may improve the catalytic activity of manganese compounds.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13040665/s1, Detailed experimental procedural, and characterization data for catalysts and the hydrosilylation products; Figures S1–S5: ^{1}H NMR spectra of catalytic hydrosilylation reactions of selected substrates with $PhSiH_3$. Table S1: Comparison of catalytic activity of selective Mn complexes [76,77,88–92].

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Data Availability Statement: The data that support the findings of this study are available in the Supporting Information of this article.

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