

Comparing Well-Defined Manganese, Iron, Cobalt, and Nickel Ketone Hydrosilylation Catalysts

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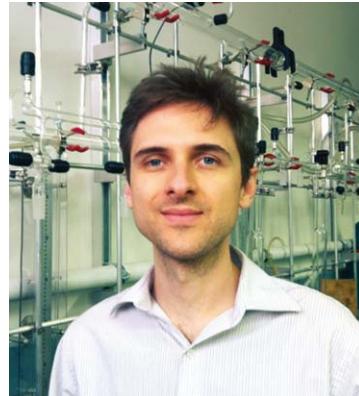
Abstract: A brief review of manganese-catalyzed hydrosilylation is presented along with a personal account of how the design for the highly active catalyst, $(^{Ph_2PPr}PDI)Mn$, was conceived. The reductive transformations achieved using this catalyst are described and put into further context by comparing the observed activities with those attained for leading late first-row transition-metal catalysts.

Key words: catalysis, hydrosilylation, ketones, manganese, ligands

Due to the cost and relative toxicity associated with homogeneous precious metal catalysts,¹ the search for sustainable alternatives that operate with competitive activities, selectivities, and lifetimes has continued to intensify.² Much of this effort has centered around the development of late first-row transition-metal (Mn, Fe, Co, and Ni) catalysts,³ as these metals are earth-abundant and far less expensive than their precious metal counterparts.⁴ While a wide range of organic transformations have been targeted,⁵ the development of first-row metal hydrosilylation catalysts remains of interest to the polysilane industry^{2b} since platinum catalysts have long been used to prepare silicone coatings and elastomers.⁶ With this in mind, my colleagues and I recently reported the development of a well-defined manganese complex that is capable of mediating ketone hydrosilylation with turnover frequencies (TOF) of up to 76,800 h⁻¹ at ambient temperature.⁷

To put our discovery into perspective, a comparison of manganese-based hydrosilylation catalysts reported to date is essential. The initial mention of manganese-mediated hydrosilylation was published in 1983 by Pratt and Faltynek,⁸ more than 25 years after Speier and co-workers reported H₂PtCl₆ to be an effective olefin hydrosilylation catalyst.^{6a} In this work, (CO)₅MnSiPh₃ was found to catalyze the reduction of 1-pentene following irradiation with 350 nm light or heating to 180 °C.⁸ A few years later, Hilal and co-workers reported that Mn₂(CO)₁₀ effectively mediates the hydrosilylation of 1-hexene with tertiary silanes under relatively mild conditions (40 °C).⁹

Since these reports, manganese-based hydrosilylation chemistry has dealt exclusively with the reduction of carbonyl containing substrates (Table 1). In 1995, the Cutler group reported (PPh₃)(CO)₄MnC(O)Me to be an effective



Ryan J. Trovitch received a BSc degree from the Honors Program at King's College (PA) in 2004, where he worked with Prof. Robert L. LaDuc to prepare metal-organic frameworks. After spending a summer at the University of Michigan learning the craft of air-free synthesis from Prof. Mark M. Banaszak-Holl, he went on to receive a PhD in inorganic chemistry from Cornell University under the direction of Prof. Paul J. Chirik. In 2008, he joined Los Alamos National Laboratory as a postdoctoral research associate and was later appointed as a Glenn T. Seaborg Postdoctoral Fellow. While at LANL, Ryan worked with Dr. Kevin D. John, Dr. John C. Gordon, Dr. Alfred P. Sattleberger (ANL), and Prof. R. Tom Baker (University of Ottawa) to develop transition-metal catalysts for a broad range of organic transformations. Ryan joined the Department of Chemistry & Biochemistry at Arizona State University as an assistant professor in 2012, and his group is currently designing sustainable transition-metal catalysts that operate efficiently under mild conditions.

catalyst for the dihydrosilylation of esters to yield the parent ether and siloxane products.¹⁰ Importantly, this catalyst was found to operate at 24 °C with TOF of up to 227 h⁻¹. Cutler and co-workers later demonstrated that (PPh₃)(CO)₄MnC(O)Me catalyzes the hydrosilylation of ketone-containing substrates with TOF of up to 1,632 h⁻¹.¹¹ Moreover, this complex has been found to mediate the hydrosilylation of transition-metal acyl complexes.^{12–14} In 1999, Chung and co-workers reported that (η⁵-C₁₀H₉)Mn(CO)₃ catalyzes the ambient-temperature hydrosilylation of ketones when employing Ph₂SiH₂ as the reductant.¹⁵ Soon after, this investigation was extended to the utilization of the naphthalene-supported complex, [(η⁶-C₁₀H₈)Mn(CO)₃][BF₄]⁻, which was found to exhibit improved, yet limited, TOF for ketone reduction of up to 99 h⁻¹.¹⁶

More recently, researchers have investigated the ability of Mn₂(CO)₁₀ to catalyze the reduction of *N*-acetyl piperidine to *N*-ethyl piperidine^{17,18} and the hydrosilylation of car-

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Table 1 Carbonyl Hydrosilylation Activities Reported for Well-Defined Manganese Catalysts

Catalyst	mol%	Temp (°C)	Substrate class	Product class	Silane used	Highest TOF (h ⁻¹)
$(\text{PPh}_3)(\text{CO})_4\text{MnC(O)Me}$	1.5–3.0	24	esters	ethers	PhSiH_3	22710
	2.4	24	ketones	silyl ethers	PhMe_2SiH	1,63211
$(\eta^5\text{-C}_{10}\text{H}_9)\text{Mn}(\text{CO})_3$	5.0	25	ketones	silyl ethers	Ph_2SiH_2	715
$[(\eta^6\text{-C}_{10}\text{H}_8)\text{Mn}(\text{CO})_3][\text{BF}_4]$	0.5–5.0	25	ketones	silyl ethers	PhMe_2SiH	9916
$\text{Mn}_2(\text{CO})_{10}$	1.0	100	amides	amines	Et_3SiH	617
	5.0	25	carboxylic acids	disilylacetals	Et_3SiH	619
$(3,5\text{-}t\text{-Bu}_2\text{-salen})\text{MnN}$	0.5	80	aldehydes	alcohols	PhSiH_3	11,76020
	0.5	80	ketones	alcohols	PhSiH_3	58220
$(\text{Ph}^2\text{PPrPDI})\text{Mn}$	0.01–1.0	25	ketones	silyl ethers	PhSiH_3	76,8007
	1.0	25–80	esters	silyl ethers	PhSiH_3	187

boxylic acids to yield disilylacetals or their related aldehydes;¹⁹ however, relatively modest TOF have been realized for both transformations. Chidara and Du have also reported that $(3,5\text{-}t\text{-Bu}_2\text{-salen})\text{MnN}$ is capable of mediating the hydrosilylation of 4-nitrobenzaldehyde with a TOF of 11,760 h⁻¹; however, this transformation required heating to 80 °C.²⁰ Further attempts to catalyze the hydrosilylation of benzaldehyde using 1 mol% of $(3,5\text{-}t\text{-Bu}_2\text{-salen})\text{MnN}$ at room temperature have taken either 22 hours (in CDCl_3) or 47 hours (in C_6D_6) to reach completion.²⁰

When we first became interested in developing a manganese-based hydrosilylation catalyst, we hoped to design one that could operate with exceptional activities at mild temperatures. Considering the data in Table 1, along with the benzaldehyde hydrosilylation experiments reported for $(3,5\text{-}t\text{-Bu}_2\text{-salen})\text{MnN}$,²⁰ it became clear that $(\text{PPh}_3)(\text{CO})_4\text{MnC(O)Me}$ remained the best-performing carbonyl hydrosilylation catalyst at ambient temperature.¹¹ It has been found that a bulky $\kappa^3\text{-}N,N,N$ -bis(imino)pyridine (or pyridine diimine, PDI) ligand could be used to mimic the coordination environment of *mer*-car-

bonyl ligands,²¹ allowing the preparation of an iron-based hydrogenation catalyst that operates efficiently under mild thermal conditions (Figure 1, a).^{22,23} With this in mind, we believed that a pentadentate PDI chelate could mimic the five neutral ligands of $(\text{PPh}_3)(\text{CO})_4\text{MnC(O)Me}$ and allow for the preparation of a manganese hydrosilylation catalyst with the general formula $(\kappa^5\text{-PDI})\text{MnX}$, where X is an anionic ligand (Figure 1, b).

Furthermore, due to the redox noninnocent nature of PDI ligands,²⁴ we recognized that it might be possible to improve upon $(\text{PPh}_3)(\text{CO})_4\text{MnC(O)Me}$ by designing a formally zerovalent manganese complex that had one or more electrons stored in the π -system of the ligand (Figure 2, a). This approach would obviate the need for a dedicated anionic ligand within the catalyst structure, while providing an open site for substrate binding. In order to prepare such a complex, the metalation of $\text{Ph}^2\text{PPrPDI}^{25}$ with $(\text{THF})_2\text{MnCl}_2$ was conducted, allowing the isolation of $(\kappa^3\text{-}N,N,N\text{-Ph}^2\text{PPrPDI})\text{MnCl}_2$. Reduction of this compound in the presence of excess Na/Hg (with or without 1,3,5,7-cyclooctatetraene present) enabled the preparation of $(\text{Ph}^2\text{PPrPDI})\text{Mn}$ (Figure 2, b).⁷ The characterization of this complex by X-ray diffraction, ¹H NMR and EPR spec-

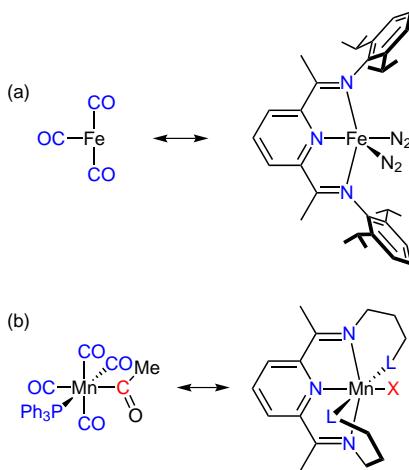


Figure 1 (a) Using a PDI ligand framework to mimic $\text{Fe}(\text{CO})_3$. (b) Designing a Mn-based hydrosilylation catalyst with a $\kappa^5\text{-PDI}$ ligand.

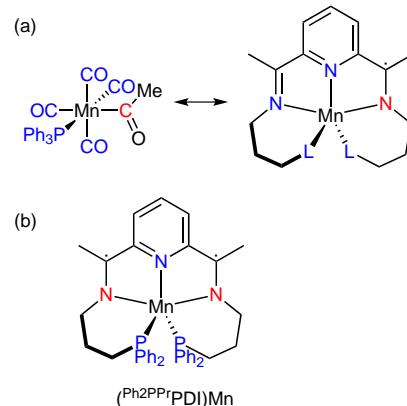
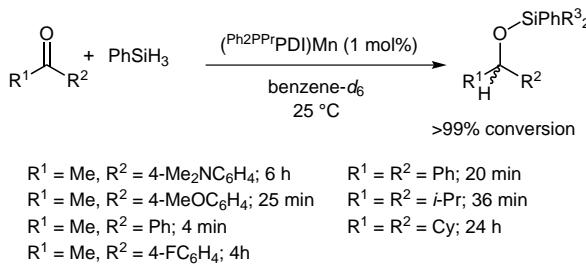


Figure 2 (a) A PDI radical monoanion imitating the ligand field of $(\text{PPh}_3)(\text{CO})_4\text{MnC(O)Me}$. (b) Electronic structure representation of $(\text{Ph}^2\text{PPrPDI})\text{Mn}$.

troscopy revealed that (^{Ph₂PP_r}PDI)Mn likely consists of a low-spin, divalent manganese center that is coordinated to a singlet PDI dianion. However, the possibility that (^{Ph₂PP_r}PDI)Mn possesses a PDI radical monoanion that is antiferromagnetically coupled to an intermediate-spin manganese(I) center has yet to be ruled out computationally.

Having characterized (^{Ph₂PP_r}PDI)Mn, we set out to determine whether or not this complex was capable of mediating ketone hydrosilylation. Adding a 1:1 ratio of acetophenone and phenylsilane to 1 mol% of (^{Ph₂PP_r}PDI)Mn in benzene-*d*₆ solution resulted in complete ketone reduction after only four minutes at 25 °C.⁷ After comparing the activities observed for different silanes, we decided to continue our study with PhSiH₃, which enabled the fastest reaction times. We then sought to determine how the electronic and steric properties of the substrate would influence their relative ease of hydrosilylation. Several of the ketones investigated are shown in Scheme 1,⁷ along with the time needed to achieve >99% conversion at 25 °C.

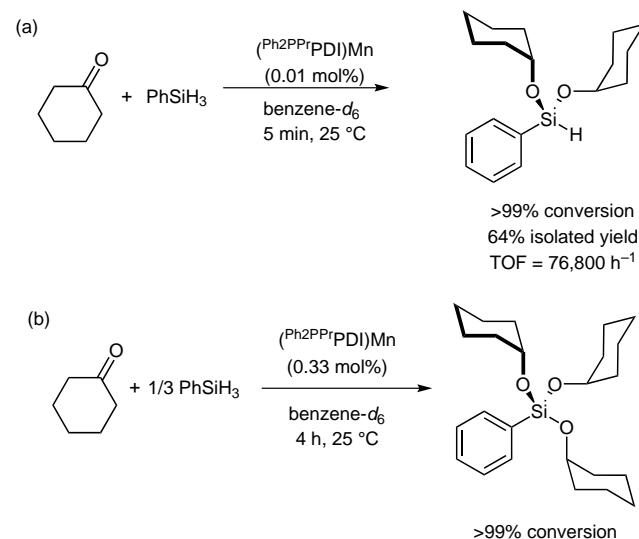


Scheme 1 The time required to achieve >99% hydrosilylation for series of acetophenones and symmetric ketones (as judged by ¹H NMR spectroscopy).

As displayed in Scheme 1, varying the *para* position of acetophenone significantly extended the time it took for the reaction to reach completion, regardless of whether the substituent was electron donating or electron withdrawing in nature. Extended reaction times were also encountered when investigating the hydrosilylation of sterically demanding substrates such as dicyclohexyl ketone.

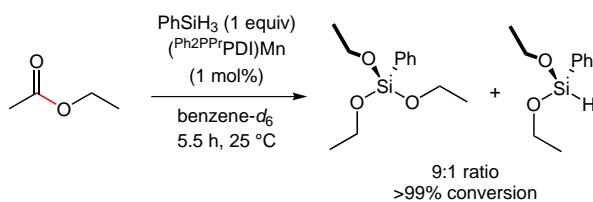
Realizing that the activity of (^{Ph₂PP_r}PDI)Mn appeared highly substrate dependent, efforts were made to scale up the hydrosilylation of readily reduced substrates to demonstrate the synthetic utility of our work. In the process, we also sought to enhance the desirability of this transformation by using lower catalyst loadings, eliminating the requirement for solvent, and by adding a stoichiometric amount of PhSiH₃ in order to improve atom-efficiency. These efforts are best summarized for the cyclohexanone reductions shown in Scheme 2.⁷ When the catalyst loading was lowered to 0.01 mol% in the absence of solvent, the hydrosilylation of cyclohexanone reached completion

within five minutes (Scheme 2, a). Although the reagents were mixed at 25 °C, significant heat was generated due to the exothermic nature of the reaction. In turn, the isolated yield was a fairly low 64% due to evaporation of the reactants, equating to a TOF of 76,800 h⁻¹ (based on product recovery). When a 3:1 ratio of cyclohexanone to phenylsilane was added to 0.33 mol% of (^{Ph₂PP_r}PDI)Mn, complete utilization of the Si–H bonds was achieved within four hours to yield PhSi(OCy)₃, demonstrating that hydrosilylation could be conducted in an atom-efficient manner at ambient temperature (Scheme 2, b).



Scheme 2 The hydrosilylation of cyclohexanone (a) at 0.01 mol% catalyst loading and (b) at 0.33 mol% with 0.33 equiv of PhSiH₃.

Finally, we investigated ester hydrosilylation using (^{Ph₂PP_r}PDI)Mn since (PPh₃)(CO)₄MnC(O)Me had been reported to catalyze ester deoxygenation to yield siloxane and the parent ether.¹⁰ Surprisingly, adding 1 mol% of (^{Ph₂PP_r}PDI)Mn to a benzene-*d*₆ solution containing a 1:1 ratio of MeOAc and PhSiH₃ resulted in the formation of four different quaternary silanes after 24 hours at 25 °C: PhSi(OMe)₃, PhSi(OEt)₃, PhSi(OMe)₂(OEt), and PhSi(OEt)₂(OMe).⁷ Repeating the experiment with PhSiD₃ confirmed that each ethoxide substituent was formed following reductive cleavage of the acyl C–O bond and carbonyl reduction. Although much longer reaction times (and/or heating to 80 °C) were required to achieve appreciable dihydrosilylation conversions for *i*-PrOAc, PhOAc, and *t*-BuOAc, the reduction of EtOAc into a 9:1 ratio of PhSi(OEt)₃ and PhSiH(OEt)₂ had reached completion after 5.5 hours (Scheme 3).⁷ Although this reaction proceeded much slower (TOF = 18 h⁻¹) than the ester dihydrosilylation reactions reported by Cutler and co-workers (TOF up to 227 h⁻¹),¹⁰ it should be noted that (PPh₃)(CO)₄MnC(O)Me has not been found to catalyze the cleavage of ester acyl C–O bonds.



Scheme 3 The $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ -catalyzed dihydrosilylation of ethyl acetate; the reductively cleaved ester C–O bond is shown in red

While the ambient temperature ester dihydrosilylation activities achieved for $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ are relatively modest, this complex remains the most active manganese-based ketone hydrosilylation catalyst described to date (Table 1). Furthermore, the ketone hydrosilylation activities achieved for $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ (TOF up to $76,800 \text{ h}^{-1}$) favorably compare to those reported for other late first-row metal hydrosilylation catalysts. Many iron-based precatalysts that mediate this transformation operate efficiently at 23°C and those featuring the most impressive reported activities include $[\text{k}^2\text{-N-phosphinoamidinate}]\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2$ (TOF up to $23,600 \text{ h}^{-1}$),²⁶ $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$ (TOF up to $2,400 \text{ h}^{-1}$),²⁷ $(\text{CyPDI})\text{Fe}(\text{Ns})_2$ (Ns = neosilyl; TOF up to 333 h^{-1}),²⁸ $(\text{iPrPybox})\text{Fe}(\text{Ns})_2$ and $(\text{iPrBox})\text{Fe}(\text{Ns})_2$ (TOF up to 333 h^{-1}).²⁹ In contrast, cobalt-based carbonyl hydrosilylation catalysts have been found to operate with relatively poor TOF. For example, $[\text{Co}(\text{py})_6]\text{[BPh}_4]$ remains the most active cobalt catalyst for ketone hydrosilylation at low temperatures ($0\text{--}20^\circ\text{C}$; TOF of 11 h^{-1})³⁰ while attaining aldehyde hydrosilylation TOF of up to 50 h^{-1} with a cobalt(III) hydride complex required heating to 40°C .³¹ Nickel catalysts have achieved carbonyl hydrosilylation TOF of 225 h^{-1} (for a PCP-supported nickel hydride complex)³² and 388 h^{-1} [for $(\text{Cp})\text{NiH}(\text{NHC})$]³³ at $23\text{--}25^\circ\text{C}$; however, both catalysts are significantly more effective for aldehyde reduction than ketone reduction.

In summary, my colleagues and I have found that $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ catalyzes the ambient-temperature hydrosilylation of carbonyl groups with activities that are ca. $3\times$ higher than the most active iron catalyst,²⁶ $>1500\times$ higher than the most active cobalt catalysts,^{30,31} and ca. $200\times$ higher than the most active nickel catalyst reported to date.³³ We are currently working to determine the mechanism of this transformation while seeking to expand upon the range of substrates that can be effectively reduced. Additionally, we hope to determine how the redox noninnocence and pentadentate coordination of Ph_2PPrPDI allows for efficient manganese-mediated ketone hydrosilylation so that these design characteristics can be applied to a number of first-row-metal-mediated transformations.³⁴

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Graphical Abstract

