

A Highly Active Manganese Precatalyst for the Hydrosilylation of Ketones and Esters

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S Supporting Information

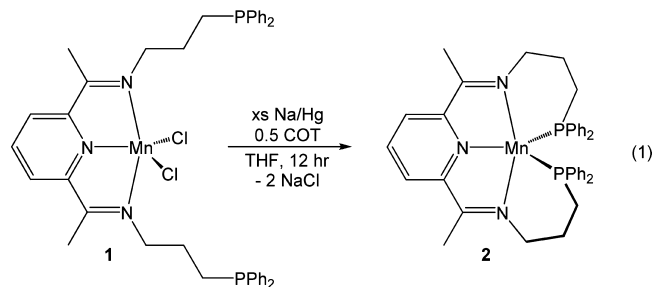
ABSTRACT: The reduction of $(\text{Ph}_2\text{PPrPDI})\text{MnCl}_2$ allowed the preparation of the formally zerovalent complex, $(\text{Ph}_2\text{PPrPDI})\text{Mn}$, which features a pentadentate bis(imino)pyridine chelate. This complex is a highly active precatalyst for the hydrosilylation of ketones, exhibiting TOFs of up to $76,800 \text{ h}^{-1}$ in the absence of solvent. Loadings as low as 0.01 mol % were employed, and $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ was found to mediate the atom-efficient utilization of Si–H bonds to form quaternary silane products. $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ was also shown to catalyze the dihydrosilylation of esters following cleavage of the substrate acyl C–O bond. Electronic structure investigation of $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ revealed that this complex possesses an unpaired electron on the metal center, rendering it likely that catalysis takes place following electron transfer to the incoming carbonyl substituent.

Hydrosilylation is conducted for the manufacture of silicone-based materials including coatings, adhesives, and cured rubbers.¹ Although this transformation has long relied on the use of precious metal catalysts,² the relative toxicity and cost of these metals has inspired the search for sustainable alternatives that exhibit comparable activity (or turnover frequency, TOF), selectivity, and stability (or turnover number, TON).³ Since traditional coordination compounds of Mn, Fe, and Co tend to participate in one-electron reaction pathways, rather than well-defined oxidative addition and reductive elimination cycles,⁴ the development of first-row metal hydrosilylation catalysts has only recently accelerated.^{5,6} The use of redox non-innocent ligands has emerged as a leading method to counteract this inconvenience.^{7,8} With the use of sterically demanding bis(imino)pyridine (or pyridine diimine, PDI) ligands, Fe catalysts that mediate the efficient hydrosilylation of olefins^{9–12} and ketones^{13,14} have been developed.

In contrast, Mn hydrosilylation catalyst design has yet to benefit from the use of redox-active chelates.¹⁵ Complexes of the general formula $(\text{CO})_5\text{Mn}(\text{X})$ ($\text{X} = \text{C}(\text{O})\text{Ph}$, $\text{C}(\text{O})\text{Me}$, Me, Br) have been found to hydrosilylate acetone, albeit with limited TOFs ($5\text{--}25 \text{ h}^{-1}$).¹⁶ Nonetheless, a phosphine-substituted derivative of this catalyst class, $(\text{Ph}_3\text{P})(\text{CO})_4\text{MnC}(\text{O})\text{Me}$, has emerged as the most active Mn-based ketone hydrosilylation catalyst to date, exhibiting TOFs of 27.2 min^{-1} ($1,632 \text{ h}^{-1}$) at ambient temperature.¹⁶ Furthermore, this complex catalyzes the dihydrosilylation of esters to form the corresponding ether and siloxane products.¹⁷ Although $(\eta^3\text{-1H-hydronaphthalene})\text{Mn}(\text{CO})_3\text{P}(\text{OMe})_3$ ¹⁸ and $[(\eta^6\text{-naphthalene})\text{Mn}(\text{CO})_3][\text{BF}_4]$ ¹⁹

have since been reported to mediate ketone hydrosilylation, both catalysts operate with modest TOFs (up to 40 h^{-1}).¹⁹ Recent studies have shown $(3,5\text{-}^t\text{Bu}_2\text{-salen})\text{MnN}$ to be an effective catalyst for the hydrosilylation of aldehydes and ketones at elevated temperatures²⁰ and that $\text{Mn}_2(\text{CO})_{10}$ can be irradiated with UV light to achieve the dihydrosilylation of carboxylic acids.²¹ In this report, we describe a redox-active, ligand-supported Mn complex that catalyzes ketone hydrosilylation at 25°C , with TOFs that are $45\times$ greater than those for $(\text{Ph}_3\text{P})(\text{CO})_4\text{MnC}(\text{O})\text{Me}$.¹⁶ Comparatively, the Mn complex described herein is roughly $3\times$ more active than the best Fe catalyst,^{6a} $1,500\times$ more active than the best Co catalyst,²² and $300\times$ more active than the best Ni catalyst²³ for carbonyl hydrosilylation under mild conditions. This catalyst has also been found to reductively cleave the acyl C–O bond of esters during their dihydrosilylation to yield a mixture of silyl ethers.

This study began with preparing $(\text{Ph}_2\text{PPrPDI})\text{MnCl}_2$ (**1**, eq 1), following the addition of Ph_2PPrPDI ²⁴ to $(\text{THF})_2\text{MnCl}_2$ in toluene solution. The complex was found to have a magnetic moment of $6.0 \mu_{\text{B}}$ at 23°C ($S_{\text{Mn}} = 5/2$), and single-crystal X-ray diffraction revealed that **1** possesses an unreduced $\kappa^3\text{-N}_3\text{-PDI}$ chelate²⁵ in the solid state (Figure S1 and Table S2 of Supporting Information [SI]). Reduction of **1** using excess Na/Hg in the presence of 1,3,5,7-cyclooctatetraene (COT) afforded the formally zerovalent complex, $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ (**2**, eq 1). This reaction was found to proceed at a slower rate in the absence of COT (completion at 60 h). Although **2** is paramagnetic ($2.2 \mu_{\text{B}}$ at 23°C), it was found to exhibit a ¹H NMR spectrum that features 10 broadened resonances that are shifted over a 200 ppm range.



The molecular structure of **2** (Figure 1) was determined so that information regarding PDI reduction could be obtained. The geometry about Mn in **2** is distorted trigonal bipyramidal with $\text{N}(2)\text{--Mn}(1)\text{--P}(1)$, $\text{N}(2)\text{--Mn}(1)\text{--P}(2)$, and $\text{N}(1)\text{--Mn}(1)\text{--N}(3)$ angles of $130.90(6)$, $123.14(6)$, and $157.54(9)^\circ$,

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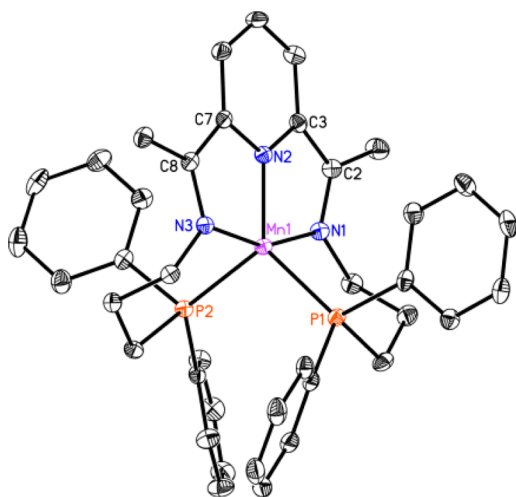


Figure 1. Molecular structure of **2** shown at 30% probability ellipsoids. H atoms omitted for clarity. Relevant distances and angles are discussed in the text and provided in Table S3 of the SI.

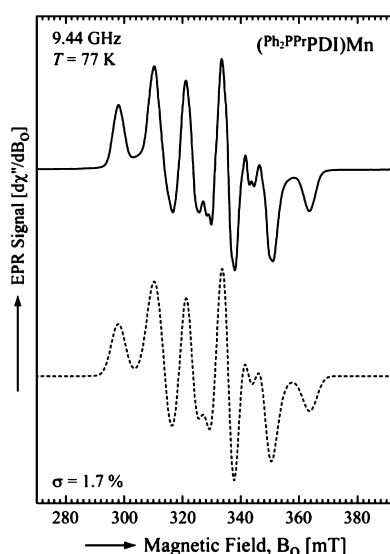


Figure 2. Experimental (solid line) and simulated (dashed line) X-band EPR spectra of **2** at 77 K.

respectively. The PDI chelate of **2** features significantly elongated N(1)–C(2) and N(3)–C(8) distances of 1.354(3) and 1.355(3) Å, along with contracted C(2)–C(3) and C(7)–C(8) distances of 1.416(4) and 1.414(3) Å, respectively. These bond lengths,²⁵ which are largely consistent with those reported for (2,6-*i*Pr₂Ph)PDI)Mn(THF)₂,²⁶ suggest that **2** contains a low-spin Mn(II) center ($S_{\text{Mn}} = 1/2$) that is supported by a singlet PDI dianion. To obtain supporting evidence for this electronic structure determination, the X-band (9.44 GHz) electron paramagnetic resonance (EPR) spectrum of **2** was recorded in a toluene glass at 77 K. Although a signal consistent with the presence of Mn(II) was observed (Figure 2), the spin state of the metal center and its hyperfine coupling interaction could not be determined by simple inspection of the spectrum. To obtain the EPR parameters, the respective spin Hamiltonian was fit to the data (Figure 2, dashed line). The spectral features observed for **2** were well-fit ($\sigma = 1.7\%$, see SI) considering a low-spin ⁵⁵Mn center ($S = 1/2$, $I = 5/2$) with anisotropic g values ($g_x = 2.079$, $g_y = 2.037$, $g_z = 2.017$) and large anisotropic hyperfine couplings

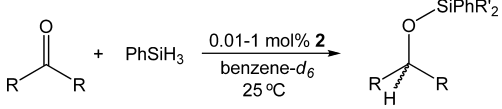
($|A_x| = 161.2$, $|A_y| = 375.4$, $|A_z| = 164.8$ MHz). Both properties are consistent with the crystallographically determined coordination environment about the Mn in **2** and are characteristic of a low-spin Mn(II) complex.²⁷

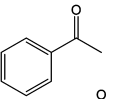
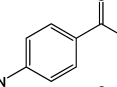
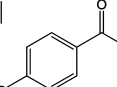
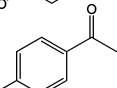
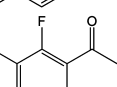
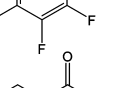
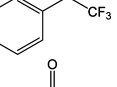
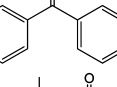
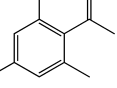
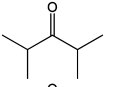
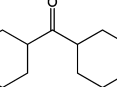
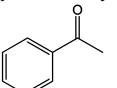
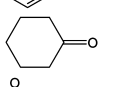
With **2** in hand, the ability of this complex to catalyze the hydrosilylation of ketones at 25 °C was evaluated. Adding 1 mol % of **2** to an equimolar solution of cyclohexanone and PhSiH₃ in benzene-*d*₆ afforded complete ketone reduction after 4 min (TOF = 1,485 h⁻¹). In addition to PhSiH(OCy)₂, a significant quantity of residual PhSiH₃ was identified by ¹H NMR spectroscopy. Since efficient hydrosilylation was achieved in the presence of PhSiH₃, the reductant was systematically varied to probe whether steric or electronic effects influence the rate of ketone reduction (Table S4, SI). While 26% conversion was observed after 4 min with Ph₂SiH₂, no reaction was observed over the same time period for tertiary silanes such as Ph₃SiH or Et₃SiH. In contrast, 28% conversion was achieved after 4 min in the presence of (EtO)₃SiH (TOF = 420 h⁻¹), confirming that quaternary silane products can be formed when using **2** as a catalyst. The activity noted for (EtO)₃SiH (compared with that for Ph₃SiH or Et₃SiH) suggests that the hydrosilylation of cyclohexanone with PhSiH₃ results in the formation of PhSiH(OCy)₂ rather than PhSiH₂(OCy) since the silyl ethers formed during ketone reduction enhance the reactivity of remaining Si–H bonds.

Encouraged, we investigated the scope of **2**-catalyzed ketone hydrosilylation (Table 1). By using an equimolar quantity of PhSiH₃ and 1 mol % of **2**, acetophenone was fully reduced after 4 min at 25 °C to yield a 3:1 ratio of PhSiH(OCH(Me)(Ph))₂ to PhSi(OCH(Me)(Ph))₃ (entry 1). Varying the phenyl group of acetophenone to include electron-donating (entries 2,3) or -withdrawing substituents (entries 4,5) greatly extended the time required to complete the reaction. A similar effect was observed for 2,2,2-trifluoroacetophenone (entry 6), but this reaction turned an uncharacteristic blue-green color upon adding **2**, and a delay in turnover onset was noticed (no reaction at 2 h). Steric bulk about the ketone functionality was also found to significantly influence turnover rates (entries 8–10).

Attempts to scale up this transformation were made to demonstrate the synthetic utility of **2**. Initially, the hydrosilylation of acetophenone with PhSiH₃ was conducted using 0.1 mol % of **2** in the absence of solvent (Table 1, entry 11). Exothermic in nature, the reaction reached completion after 4 min to yield a 5:1 mixture of PhSiH(OCH(Me)(Ph))₂ and PhSi(OCH(Me)(Ph))₃ (TOF = 14,850 h⁻¹). Although the silane products formed in this reaction proved difficult to separate, it was found that unhindered ketones such as cyclohexanone or 2-hexanone could be hydrosilylated after 4 min under these conditions to selectively yield either PhSiH(OCy)₂ or PhSiH(OCH(Me)(ⁿBu))₂, respectively. Thus, the catalyst loading was lowered to 0.01 mol %, and the **2**-catalyzed hydrosilylation of cyclohexanone or 2-hexanone with PhSiH₃ reached completion after 5 min (entries 12,13) as judged by ¹H NMR spectroscopy. Because a significant amount of heat was generated upon catalyst addition, it is believed that the isolated yields are lower than expected due to vaporization of the substrate [64% for PhSiH(OCy)₂, 62% for PhSiH(OCH(Me)(ⁿBu))₂]. Thus, the TOFs of these transformations are best calculated from the isolated yields (entry 12: TOF = 76,800 h⁻¹; entry 13: TOF = 74,400 h⁻¹), even though they represent the lower limit of what may have been achieved.

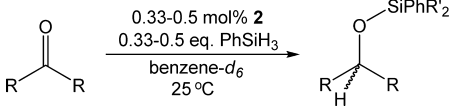
Since two hydrosilylation products were identified for many of the ketones in Table 1, efforts were made to improve the

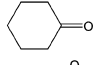
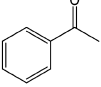
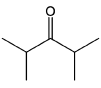
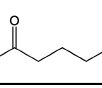
Table 1. Hydrosilylation of Ketones Using **2**^a


Entry	Substrate	Product(s) ^b (Ratio)	Time	% Conv. (Isol.) ^c
1		PhSiH(OCH(Me)(Ph)) ₂ PhSi(OCH(Me)(Ph)) ₃ (3:1)	4 min	>99
2		PhSiH(OCH(Me)(Ar)) ₂	6 h	>99
3		PhSiH(OCH(Me)(Ar)) ₂ PhSi(OCH(Me)(Ar)) ₃ (5:1)	25 min	>99
4		PhSiH(OCH(Me)(Ar)) ₂ PhSi(OCH(Me)(Ar)) ₃ (7:1)	4 h	>99
5		PhSiH(OCH(Me)(Ar)) ₂ PhSi(OCH(Me)(Ar)) ₃ (3:1)	3.5 h	>99
6		PhSi(OCH(CF ₃)(Ph)) ₃	12 h	>99
7		PhSiH(OCH(Ph)) ₂ PhSi(OCH(Ph)) ₃ (7:1)	20 min	>99
8		PhSiH(OCH(Me)(Ar)) ₂	5 d	80
9		PhSiH ₂ (OCH(ⁱ Pr)) ₂ PhSiH(OCH(ⁱ Pr)) ₂ (4:1)	36 min	>99
10		PhSiH(OCH(Cy)) ₂ PhSiH ₂ (OCH(Cy)) ₂ (3:1)	24 h	>99
11 ^d		PhSiH(OCH(Me)(Ph)) ₂ PhSi(OCH(Me)(Ph)) ₃ (5:1)	4 min	>99
12 ^e		PhSiH(OCy) ₂	5 min	>99(64)
13 ^e		PhSiH(OCH(Me)(ⁿ Bu)) ₂	5 min	>99(62)

^aReactions conducted in 0.7 mL of benzene-*d*₆ with ~0.0033 mmol of **2**, 0.33 mmol of PhSiH₃, and 0.33 mmol of substrate. ^bAryl groups designated as Ar. ^cConversion determined by ¹H NMR spectroscopy. ^dReaction conducted at 0.1 mol % of **2** in a neat solution of PhSiH₃ and substrate. ^eNeat reaction conducted at 0.01 mol % of **2**.

selectivity and atom efficiency of this transformation by decreasing the relative amount of PhSiH₃ added to the reaction. Adding 0.33 mol % of **2** to a benzene-*d*₆ solution containing 3 equiv of cyclohexanone or acetophenone per equiv of PhSiH₃ resulted in complete Si–H bond utilization and the selective formation of PhSi(OCy)₃ or PhSi(OCH(Me)(Ph))₃, respectively (Table 2, entries 1, 2). Likewise, the hydrosilylation of diisopropyl ketone to selectively yield PhSiH(OCH(ⁱPr))₂ was

Table 2. Atom-Efficient Hydrosilylation Reactions^a


Entry	Substrate	Product(s) (Ratio)	Time	% Conv.
1 ^b		PhSi(OCy) ₃	4 h	>99
2 ^b		PhSi(OCH(Me)(Ph)) ₃	6.5 h	>99
3 ^c		PhSiH(OCH(ⁱ Pr)) ₂ PhSiH ₂ (OCH(ⁱ Pr)) ₂ (9:1)	42 min	>99
4 ^b		PhSiH(OCH(Me)(ⁿ Bu)) ₂ PhSi(OCH(Me)(ⁿ Bu)) ₃ (3:1)	24 h	74

^aConversion determined by ¹H NMR spectroscopy. ^bReaction conducted in 0.7 mL of benzene-*d*₆ with ~0.0027 mmol of **2**, 0.27 mmol of silane, and 0.81 mmol of substrate. ^cReaction conducted in 0.7 mL of benzene-*d*₆ with 0.0036 mmol of **2**, 0.36 mmol of silane, and 0.72 mmol of substrate.

achieved within 42 min of adding **2** (TOF = 283 h⁻¹). When 3 equiv of 2-hexanone was added per PhSiH₃ equiv, the reaction did not reach completion after 24 h at 25 °C (entry 4), as PhSiH(OCH(Me)(ⁿBu))₂ reacted slowly under these conditions.

The ability of **2** to catalyze the hydrosilylation of esters was also investigated (Table 3). To our surprise, adding 1 mol % of **2** to an equimolar solution of MeOAc and PhSiH₃ in benzene-*d*₆ afforded a mixture of quaternary silanes that included PhSi(OMe)₃, PhSi(OEt)₃, PhSi(OMe)₂(OEt), and PhSi(OEt)₂(OMe) (entry 1). ¹H and ²H NMR spectroscopy showed deuterium incorporation into the methylene position of each ethoxysilane product when this reaction was repeated using PhSiD₃, confirming that the ethoxide substituents arise from carbonyl reduction following reductive cleavage of the MeOAc acyl C–O bond. Although the reduction of MeOAc was not complete after 16 h at 25 °C, the dihydrosilylation of EtOAc to form a 9:1 mixture of PhSi(OEt)₃ to PhSiH(OEt)₂ took only 5.5 h to reach completion (entry 2). In contrast, the dihydrosilylation of ⁱPrOAc, PhOAc, or ^tBuOAc to tertiary and quaternary silane products required up to 10 d or heating to 80 °C to reach appreciable conversion (entries 3–5). On the basis of the results summarized in Table 3, it should be noted that the relative rates of ester dihydrosilylation do not closely correlate to the acyl C–O bond cleavage preferences reported for (^{2,6}-iPr₂PhPDI)Fe(N₂)₂.²⁸

In contrast to the commonly evoked Chalk–Harrod or modified Chalk–Harrod mechanisms for metal-catalyzed hydrosilylation,^{3,29} it is believed that **2** catalyzes this transformation by way of radical transfer to the incoming carbonyl moiety. This pathway is consistent with the electronic structure investigation of **2**, which has been found to possess a Mn-localized unpaired spin. For the hydrosilylation of ketones, radical transfer is likely followed by the abstraction of an H atom from silane, along with concomitant Si–O bond formation. It is believed that radical transfer and H atom abstraction also take place during ester hydrosilylation, but this substrate class may undergo β-alkoxide elimination to liberate an aldehyde that is ultimately converted to

Table 3. Reductive Cleavage and Dihydrosilylation of Esters Using **2**^a

Entry	Substrate	Product(s) (Ratio)	Time	% Conv. ^b
		$\xrightarrow[25-80\text{ }^\circ\text{C}]{1\text{ mol}\% \text{ 2, PhSiH}_3, \text{ benzene-}d_6}$		
		$\text{PhSi(H)}_x(\text{OCH}_2\text{R})_y(\text{OR}')_z$ x = 0 or 1; y = 0, 1, 2, or 3 z = 0, 1, 2, or 3		
1 ^c		PhSi(OEt) ₂ (OMe) PhSi(OMe) ₃ PhSi(OEt) ₃ PhSi(OMe) ₂ (OEt) (2:1.5:1.2:1)	24 h	>99
2 ^c		PhSi(OEt) ₃ PhSiH(OEt) ₂ (9:1)	5.5 h	>99
3 ^d		PhSi(OEt) ₃ PhSiH(O ⁱ Pr) ₂ PhSi(O ⁱ Pr) ₃ PhSiH(OEt) ₂ (2:1.5:1:1)	3 d	>99
4 ^c		PhSi(OPh) ₃ PhSi(OEt) ₃ PhSi(OEt) ₂ (OPh) (1.25:1.25:1)	10 d	95
5 ^d		PhSiH(O ^t Bu) ₂ PhSiH(OEt)(O ^t Bu) PhSi(OEt) ₃ (1.25:1.25:1)	10 d	85

^aReactions conducted in 0.7 mL of benzene-*d*₆ with ~0.003 mmol of **2**, 0.3 mmol of silane, and 0.3 mmol of substrate. ^bConversion determined by ¹H NMR spectroscopy. ^cReaction conducted at 25 °C. ^dReaction conducted at 80 °C.

the respective silyl ether. A comprehensive study to determine how the redox non-innocent Ph₂PP₂PDI ligand aids **2**-mediated ketone and ester hydrosilylation is underway.

In conclusion, the hydrosilylation of ketones and esters was achieved under mild conditions using a redox-active ligand-supported Mn catalyst. While excellent activities (TOFs up to 76,800 h⁻¹) and high atom efficiencies have been observed for the reduction of unhindered ketones, the dihydrosilylation of esters was found to proceed through a reductive acyl C–O bond cleavage pathway with relatively modest TOFs. Even though Mn-based reduction catalysts remain underexplored and underutilized, it is hoped that the transformations reported herein highlight the potential value of high-denticity, redox non-innocent chelates in catalyst design.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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