

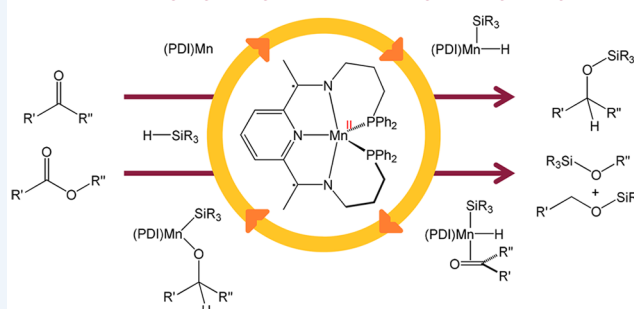
The Emergence of Manganese-Based Carbonyl Hydrosilylation Catalysts

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CONSPECTUS: In recent years, interest in homogeneous manganese catalyst development has intensified because of the earth-abundant and nontoxic nature of this metal. Although compounds of Mn have largely been utilized for epoxidation reactions, recent efforts have revealed that Mn catalysts can mediate a broad range of reductive transformations. Low-valent Mn compounds have proven to be particularly effective for the hydrosilylation of carbonyl- and carboxylate-containing substrates, and this Account aims to highlight my research group's contributions to this field. In our initial 2014 communication, we reported that the bis(imino)pyridine-supported compound $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{Mn}$ mediates ketone hydrosilylation with exceptional activity under solvent-free conditions. Silanes including Ph_2SiH_2 , $(\text{EtO})_3\text{SiH}$, $(\text{EtO})_2\text{MeSiH}$, and $(\text{EtO})\text{Me}_2\text{SiH}$ were found to partially reduce cyclohexanone in the presence of $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{Mn}$, while turnover frequencies of up to 1280 min^{-1} were observed using PhSiH_3 . This led us to evaluate the hydrosilylation of 11 additional ketones and allowed for the atom-efficient preparation of tertiary and quaternary silanes. At that time, it was also discovered that $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{Mn}$ catalyzes the dihydrosilylation of esters (by way of acyl C–O bond hydrosilylation) to yield a mixture of silyl ethers with modest activity. Earlier this year, the scope of these transformations was extended to aldehydes and formates, and the observed hydrosilylation activities are among the highest obtained for any transition-metal catalyst. The effectiveness of three related catalysts has also been evaluated: $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{MnH}$, $(^{\text{PyEt}}\text{PDEA})\text{Mn}$, and $[(^{\text{Ph}_2\text{PEt}}\text{PDI})\text{Mn}]_2$. To our surprise, $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{MnH}$ was found to exhibit higher carboxylate dihydrosilylation activity than $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{Mn}$, while $(^{\text{PyEt}}\text{PDEA})\text{Mn}$ demonstrated remarkable carbonyl hydrosilylation activity considering that it lacks a redox-active supporting ligand. The evaluation of $[(^{\text{Ph}_2\text{PEt}}\text{PDI})\text{Mn}]_2$ revealed competitive aldehyde hydrosilylation and formate dihydrosilylation turnover frequencies; however, this catalyst is significantly inhibited by pyridine and alkene donor groups. In our efforts to fully understand how $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{Mn}$ operates, a thorough electronic structure evaluation was conducted, and the ground-state doublet calculated for this compound was found to exhibit nonclassical features consistent with a low-spin Mn(II) center supported by a singlet PDI dianion and an intermediate-spin Mn(II) configuration featuring antiferromagnetic coupling to PDI diradical dianion. A comprehensive mechanistic investigation of $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{Mn}$ - and $(^{\text{Ph}_2\text{PPr}}\text{PDI})\text{MnH}$ -mediated hydrosilylation has revealed two operable pathways, a modified Ojima pathway that is more active for carbonyl hydrosilylation and an insertion pathway that is more effective for carboxylate reduction. Although these efforts represent a small fraction of the recent advances made in Mn catalysis, this work has proven to be influential for the development of Mn-based reduction catalysts and is likely to inform future efforts to develop Mn catalysts that can be used to prepare silicones.

Efficient Carbonyl Hydrosilylation and Carboxylate Dihydrosilylation



INTRODUCTION

Manganese is no longer the black sheep among first-row transition metals. A decade ago, Layfield described alkyl compounds of Mn(II) as “the black sheep of the organometallic family” because of the ionic character of their Mn–C bonds.¹ At that time, it could have been broadly stated that the propensity of Mn to participate in radical chemistry was causing it to be passed over in favor of Fe,² Co,³ and Ni⁴ for homogeneous catalytic applications. In fact, prior to 2008, breakthroughs in homogeneous Mn catalysis were largely limited to the initiation of free-radical alkylation⁵ or cyclization⁶ reactions and the development of (salen)Mn olefin epoxidation catalysts by Kochi⁷ and Jacobsen⁸ (which operate through a radical mechanism).^{7,9} Given that Mn is nontoxic and readily abundant within the earth's crust (950 mg/kg),¹⁰ researchers have sought to unlock

its full potential. A tidal wave of reports featuring Mn catalyst development have inundated leading chemistry journals in recent years, many of which have been featured in a pair of 2016 reviews.¹¹ Our research group has been fortunate to contribute to this surge, and this Account aims to highlight our recent efforts to explore the utility of Mn-based hydrosilylation catalysts.

HISTORY OF MANGANESE-BASED HYDROSILYLATION

Alcohols have long been prepared by reduction of carbonyl-containing substrates in the presence of inorganic hydrides¹² or

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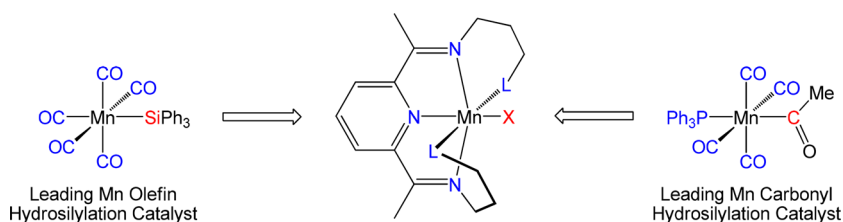


Figure 1. Mimicking the neutral donors of leading Mn hydrosilylation catalysts with a modular κ^5 -PDI chelate.

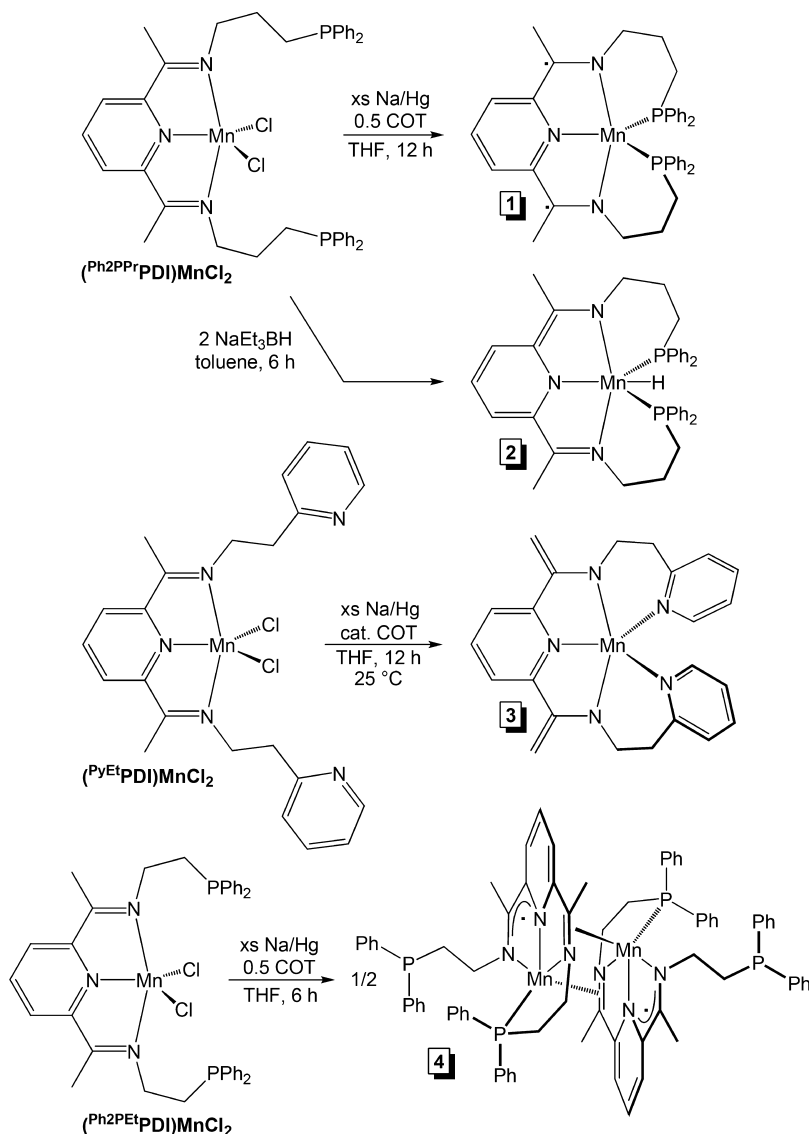


Figure 2. Preparation of compounds **1**,³² **2**,³⁴ **3**,³⁸ and **4**.³⁹

pressurized hydrogen.¹³ However, the inherent flammability of these reductants has inspired the search for mild and operationally simple synthetic approaches for carbonyl reduction. In 1972, Ojima and co-workers discovered that Wilkinson's catalyst mediates the hydrosilylation of carbonyls to yield the respective silyl ethers, which can be hydrolyzed to yield alcohols.¹⁴ Given the cost and toxicity associated with precious-metal catalysts, researchers have been seeking to develop sustainable alternatives ever since. At the beginning of this century, phosphine-coordinated copper catalysts were widely investigated for carbonyl hydrosilylation and were found to exhibit impressive turnover frequencies (TOFs) of up to 660 min⁻¹.¹⁵ In recent

years, focus has shifted to the development of Fe (TOFs of up to 393 min⁻¹),¹⁶ Co (49.5 min⁻¹),¹⁷ and Ni (38.4 min⁻¹)¹⁸ catalysts for this transformation. Main-group compounds have also been shown to mediate carbonyl hydrosilylation, albeit with lower activity.¹⁹

Prior to our efforts, manganese catalysts had been comparatively underutilized for carbonyl hydrosilylation. Pioneering work by the Cutler group demonstrated that Mn(I) alkyl, silyl, and acyl compounds are active for the catalytic hydrosilylation of metal–acyl complexes.²⁰ Some of these catalysts, most notably $(\text{Ph}_3\text{P})(\text{CO})_4\text{Mn}(\text{C}(\text{O})\text{CH}_3)$, were screened for the hydrosilylation of ketones and found to exhibit impressive TOFs of

up to 27.2 min^{-1} .²¹ Over the subsequent years, several Mn(0)²² and Mn(I)²³ compounds were found to mediate carbonyl hydrosilylation; however, this level of activity was not matched until 2013, when Chidara and Du²⁴ reported that (3,5-*t*-Bu-Salen)MnN hydrosilylates aldehydes with TOFs of up to 196 min^{-1} when heated to 80°C (modest activity was noted at ambient temperature). In the presence of silane reductant, related Mn-catalyzed transformations, including hydrosilylation of olefins,²⁵ deoxygenative conversion of esters to ethers²⁶ and amides to amines,²⁷ and dehydrogenative silylation of alcohols,²⁸ had also been reported prior to our foray into this field.

LIGAND DESIGN

When starting out, we were drawn to the use of neutral and π -acidic pentadentate chelates to mimic the ligand field of the leading olefin and carbonyl hydrosilylation catalysts, $(\text{CO})_5\text{MnSiPh}_3$ and $(\text{Ph}_3\text{P})(\text{CO})_4\text{MnC}(\text{O})\text{CH}_3$, respectively.²⁹ It was anticipated that ligands of this type would stabilize low-valent Mn and afford us the opportunity to tune the chelate rigidity, sterics, and electronics to achieve improved hydrosilylation activity (Figure 1). Given the propensity of Mn to participate in one-electron chemistry, we also sought to incorporate a redox-noninnocent moiety within the ligand, allowing the metal to remain in a persistent oxidation state throughout catalysis.³⁰ Therefore, we decided to prepare donor-functionalized bis(imino)pyridine (or pyridinediimine (PDI)) ligands and evaluate their complexes of Mn for hydrosilylation activity. We reasoned that it should be possible to synthesize six-coordinate Mn(I) compounds analogous to $(\text{CO})_5\text{MnSiPh}_3$ and $(\text{Ph}_3\text{P})(\text{CO})_4\text{MnC}(\text{O})\text{CH}_3$ (Figure 1, middle). Furthermore, we wanted to target ligand-reduced species that lack a monodentate X ligand, leaving a coordination site open for substrate binding.

CATALYST PREPARATION AND CHARACTERIZATION

We began by refluxing the propylene-bridged chelate Ph_2PPrPDI ³¹ with $(\text{THF})_2\text{MnCl}_2$, which afforded the κ^3 -PDI dihalide precursor $(\text{Ph}_2\text{PPrPDI})\text{MnCl}_2$ (Figure 2, top left). When the precursor was subjected to excess Na/Hg, reduction over 60 h yielded the formal Mn(0) complex $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ (**1**) (Figure 2).³² This transformation was optimized by adding 0.5 equiv of 1,3,5,7-cyclooctatetraene (COT), allowing for completion within 12 h. Although **1** exhibits a magnetic moment of $2.2\mu_{\text{B}}$ at ambient temperature, its ^1H NMR spectrum features broadened resonances over a 200 ppm range, which has aided our study of this compound. Furthermore, the electron paramagnetic resonance (EPR) spectrum of **1** in toluene at 77 K was effectively modeled by treating Mn as a low-spin ^{55}Mn center ($S = 1/2$, $I = 5/2$) with anisotropic g values and hyperfine couplings.³²

To gain additional insight, the solid-state structure of **1** was determined by single-crystal X-ray diffraction (Figure 3). Notably, the PDI chelate was found to feature significantly elongated N(1)–C(2) and N(3)–C(8) distances of 1.354(3) and 1.355(3) Å, respectively, along with shortened C(2)–C(3) and C(7)–C(8) contacts of 1.416(4) and 1.414(3) Å, respectively. When a PDI is coordinated to a low-valent first-row transition metal, bond lengths such as these signify two-electron chelate reduction.³³ In our initial 2014 communication,³² it was suggested that **1** possesses a low-spin Mn(II) center ($S_{\text{Mn}} = 1/2$) and a singlet PDI dianion. Earlier this year, density

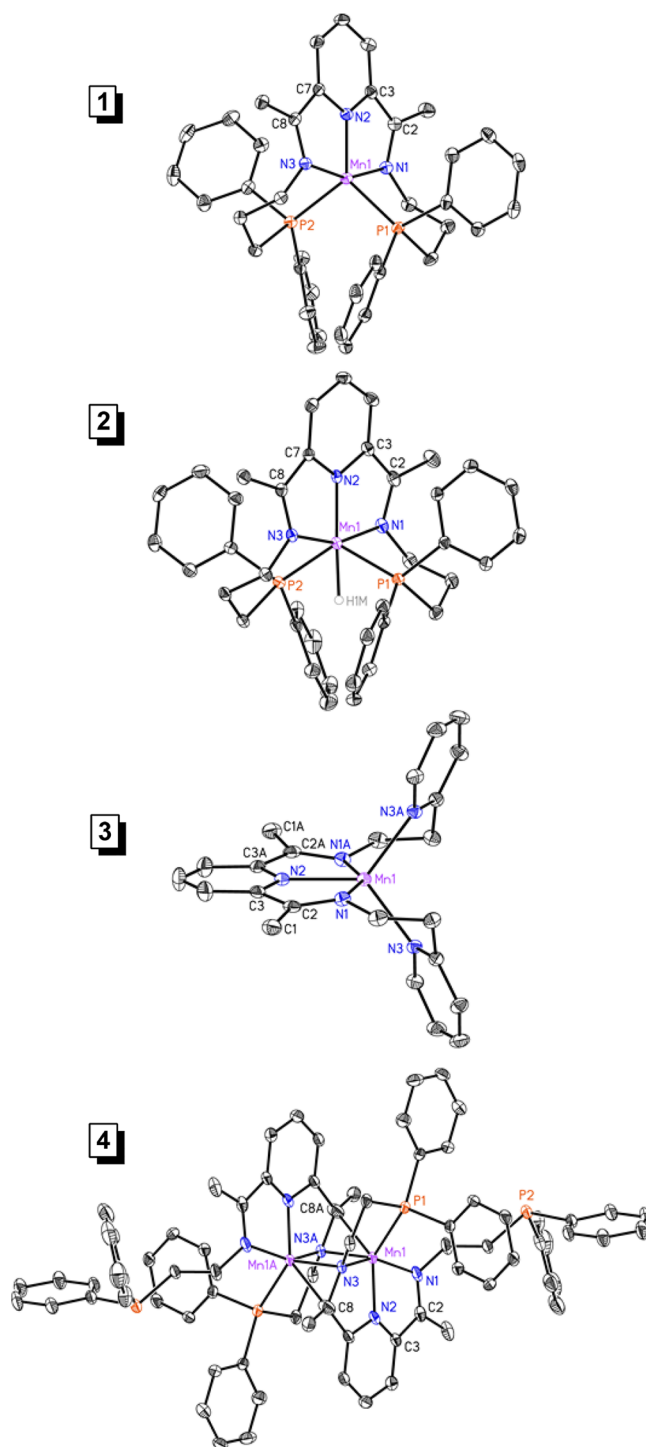
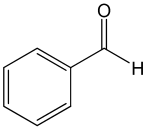
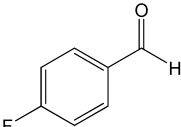
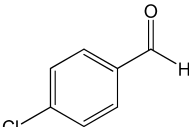
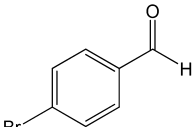
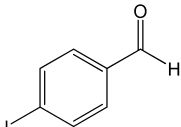
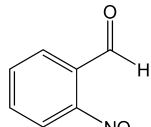
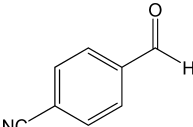
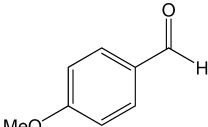
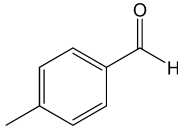
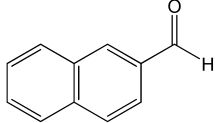
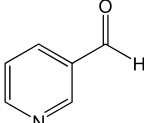
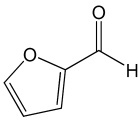
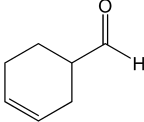
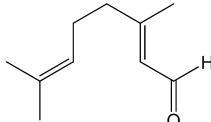
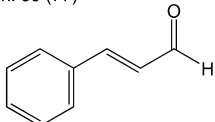
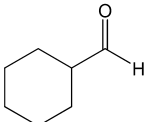


Figure 3. Solid-state structures of **1**,³² **2**,³⁴ **3**,³⁸ and **4**.³⁹

functional theory (DFT) calculations were performed to confirm this electronic structure assignment.³⁴ To our surprise, the ground-state doublet was found to exhibit nonclassical features revealing a superposition of two electronic structures: a low-spin Mn(II) center supported by a singlet PDI dianion (as proposed) and an intermediate-spin Mn(II) configuration in which two Mn-based electrons are antiferromagnetically coupled to a triplet PDI dianion.

Attempts were also made to prepare compounds having the formula $(\text{Ph}_2\text{PPrPDI})\text{MnX}$. Although a monochloride complex could not be isolated by modifying the reduction conditions,

Table 1. Hydrosilylation of Aldehydes with PhSiH₃ at 25 °C Using 1, 3, and 4^a

$(1a-1p) \quad R-\text{CHO} + \text{PhSiH}_3 \xrightarrow[\text{(ii) 10\% aq. NaOH, 25 °C, 2 h}]{\text{(i) 0.01-1.0 mol\% cat, neat, 25 °C}} R-\text{CH}_2\text{OH}$		
 1a1 - 0.1 mol% 1, 2 min: 99 (94) 1a2 - 0.01 mol% 1, 2 min: 99 (92) 1a3 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1a4 - 0.02 mol% 3, 2 min: 99 (99) 1a5 - 0.1 mol% 4, ^d 2 min: 99 (93) 1a6 - 0.01 mol% 4, ^d 2 min: 99 (92)	 1b1 - 0.1 mol% 1, 2 min: 99 (93) 1b2 - 0.01 mol% 1, 2 min: 99 (87) 1b3 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1b4 - 0.02 mol% 3, 2 min: 99 (71) 1b5 - 0.1 mol% 4, ^d 2 min: 99 (90) 1b6 - 0.01 mol% 4, ^d 2 min: 18 (-)	 1c1 - 0.1 mol% 1, 2 min: 99 (88) 1c2 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1c3 - 0.1 mol% 4, ^d 2 min: 99 (83)
 1d1 - 0.1 mol% 1, 2 min: 99 (91) 1d2 - 0.1 mol% 4, ^d 2 min: 99 (83)	 1e1 - 0.1 mol% 1, 2 min: 32 (-) 1e2 - 0.1 mol% 4, ^d 2 min: 0 (-)	 1f1 - 0.1 mol% 1, 2 min: 99 (74) 1f2 - 0.1 mol% 4, ^d 2 min: 99 (79)
 1g1 - 0.1 mol% 1, 2 min: 99 (78) 1g2 - 0.1 mol% 4, ^d 2 min: 99 (71)	 1h1 - 0.1 mol% 1, 2 min: 99 (81) 1h2 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1h3 - 0.1 mol% 4, ^d 2 min: 99 (86)	 1i1 - 0.1 mol% 1, 2 min: 99 (90) 1i2 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1i3 - 0.1 mol% 4, ^d 2 min: 99 (88)
 1j1 - 0.1 mol% 1, 2 min: 99 (81) 1j2 - 0.01 mol% 1, 2 min: 99 (87) 1j3 - 0.1 mol% 4, ^d 2 min: 99 (93)	 1k1 - 0.1 mol% 1, 2 min: 99 (27) 1k2 - 0.1 mol% 4, ^d 2 min: 88 (21)	
 1l1 - 0.1 mol% 1, 2 min: 99 (89) 1l2 - 0.01 mol% 1, 2 min: 99 (57) 1l3 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1l4 - 0.1 mol% 4, ^d 2 min: 99 (77)	 1m1 - 0.1 mol% 1, 2 min: 99 (88) 1m2 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c 1m3 - 0.1 mol% 4, ^d 2 min: 32 (-)	 1n1 - 0.1 mol% 1, 2 min: 99 (82) 1n2 - 0.1 mol% 4, ^d 2 min: 18 (-)
 1o1 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c	 1p1 - 1.0 mol% 3, ^b 1 h: 99 (-) ^c	

^aThe percent conversion for each trial is given, followed by the isolated yield of the alcohol (in parentheses). ^bConducted in benzene-*d*₆. ^cComplete conversion to a mixture of silyl ethers. ^dLoading relative to Mn, not dimer.

refluxing ^{Ph}2PP^rPDI in the presence of (CO)₅MnBr afforded (κ⁴-^{Ph}2PP^rPDI)MnBr.³⁵ Notably, the ambient-temperature magnetic susceptibility of (κ⁴-^{Ph}2PP^rPDI)MnBr was found to be 4.4μ_B at ambient temperature, indicating a high-spin configuration.³⁵ Therefore, to prepare formal Mn(I) complexes featuring a κ⁵-PDI ligand, stronger-field X ligands were considered. Adding 2 equiv of NaEt₃BH to (Ph₂PP^rPDI)MnCl₂ produced a new diamagnetic complex featuring an ¹H NMR triplet at -2.98 ppm and a ³¹P NMR singlet at 69.19 ppm.³⁴ A single crystal was obtained, and X-ray diffraction analysis revealed it to be the six-coordinate monohydride (Ph₂PP^rPDI)MnH (**2**) (Figure 2). The

chelate of **2** coordinates in a trigonal-bipyramidal fashion about Mn, and the hydride ligand is located in the pocket between the phosphine donors (Figure 3). As with **1**, compound **2** was found to exhibit PDI distances that are suggestive of two-electron chelate reduction [N(1)–C(2) = 1.351(3) Å; N(3)–C(8) = 1.342(3) Å; C(2)–C(3) = 1.424(4) Å; C(7)–C(8) = 1.418(3) Å].³⁶ DFT calculations performed on **2** revealed a Mn(III) center that is supported by a singlet PDI dianion, as illustrated in Figure 2.

In addition to our efforts with ^{Ph}2PP^rPDI, we have modified the chelate donor substituents and arm rigidity. Moving from

Table 2. Hydrosilylation of Ketones at 25 °C Using 1, 3, and 4^a

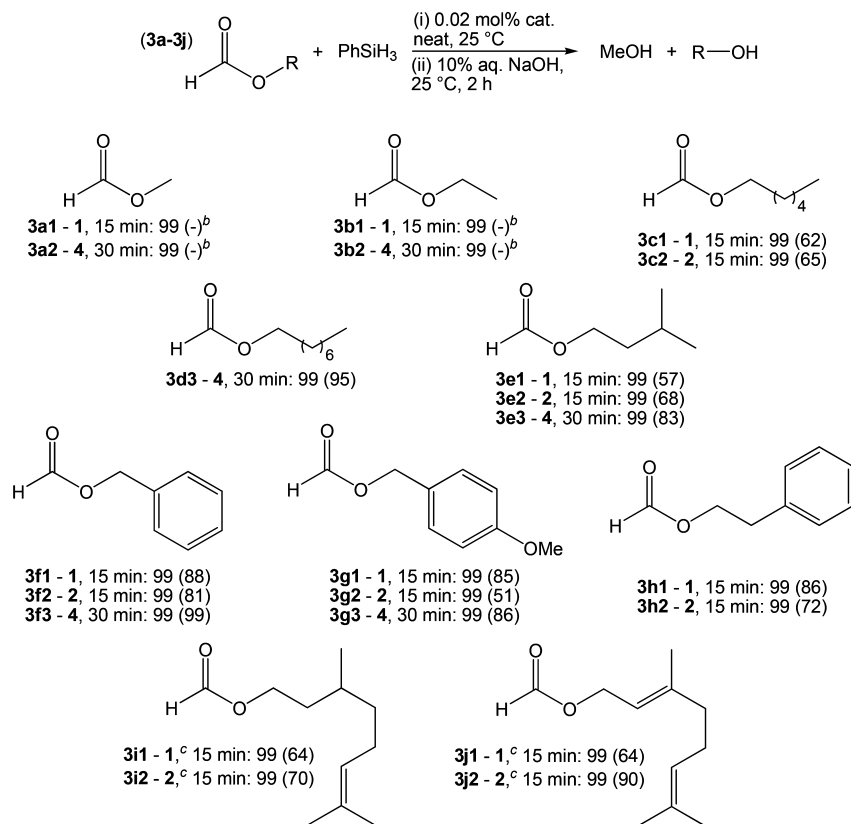
	2a1 - 1.0 mol% 1 , PhSiH ₃ , 4 min: 99 (-) ^b 2a2 - 1.0 mol% 1 , (EtO) ₃ SiH, 4 min: 28 (-) 2a3 - 1.0 mol% 1 , Ph ₂ SiH ₂ , 4 min: 26 (-) 2a4 - 1.0 mol% 1 , (EtO) ₂ MeSiH, 4 min: 5 (-) 2a5 - 1.0 mol% 1 , (EtO)Me ₂ SiH, 4 min: 3 (-)	2a6 - 0.01 mol% 1 , ^c 5 min: 99 (64 ^d) 2a7 - 0.33 mol% 1 , 0.33 PhSiH ₃ , 4 h: 99 (-) ^e 2a8 - 1.0 mol% 3 , 1 h: 99 (-) ^b 2a9 - 0.02 mol% 3 , ^c 5 min: 99 (55 ^d /99 ^f) 2a10 - 0.1 mol% 4 , ^{c,g} 4 min, 99 (-) ^b
	2b1 - 1.0 mol% 1 , 6 h: 99 (-) ^e 2b2 - 1.0 mol% 3 , 1 h: 99 (-) ^e	
	2c1 - 1.0 mol% 1 , 25 min: 99 (-) ^b 2c2 - 1.0 mol% 3 , 1 h: 99 (-) ^b	
2e1 - 1.0 mol% 1 , 3.5 h: 99 (-) ^b		
	2f1 - 1.0 mol% 1 , 12 h: 99 (-) ^e 2g1 - 1.0 mol% 1 , 20 min: 99 (-) ^b 2g2 - 1.0 mol% 3 , 1 h: 99 (-) ^b	
2h1 - 1.0 mol% 1 , 5 d: 80 (-) ^e	2i1 - 1.0 mol% 1 , 36 min: 99 (-) ^b 2i2 - 0.5 mol% 1 , 0.5 PhSiH ₃ , 42 min: 99 (-) ^b 2i3 - 1.0 mol% 3 , 1 h: 99 (-) ^b	2j1 - 1.0 mol% 1 , 24 h: 99 (-) ^b
2k1 - 1.0 mol% 1 , PhSiH ₃ , 4 min: 99 (-) ^b 2k2 - 0.1 mol% 1 , ^c PhSiH ₃ , 4 min: 99 (-) ^b 2k3 - 0.33 mol% 1 , 0.33 PhSiH ₃ , 6.5 h: 99 (-) ^e 2k4 - 1.0 mol% 3 , PhSiH ₃ , 1 h: 99 (-) ^b 2k5 - 0.1 mol% 4 , ^{c,g} PhSiH ₃ , 4 min: 99 (-) ^b	2l1 - 0.01 mol% 1 , ^c 5 min: 99 (62 ^d) 2l2 - 0.33 mol% 1 , 0.33 PhSiH ₃ , 24 h: 74 (-) ^b 2l3 - 1.0 mol% 3 , 1 h: 99 (-) ^b 2l4 - 0.02 mol% 3 , ^c 5 min: 99 (63 ^d /72 ^f)	

^aThe percent conversion is provided for each trial. For entries other than **2a2**–**2a5**, PhSiH₃ was used as the reductant. ^bA mixture of silyl ethers was observed. ^cNeat reaction. ^dIsolated yield of tertiary silane. ^eConversion to a single silyl ether product. ^fIsolated yield of the alcohol following hydrolysis. ^gLoading relative to Mn, not dimer.

phosphine codonors to the pyridine-substituted ligand ^{PyEt}PDI³⁷ also yielded a κ^3 -PDI dichloride precursor, (^{PyEt}PDI)MnCl₂ (Figure 2).³⁸ However, upon addition of excess Na/Hg and a catalytic quantity of COT, deprotonation of both PDI backbone methyl substituents was observed, affording (^{PyEt}PDEA)Mn (**3**) (Figure 2). The ambient-temperature magnetic susceptibility of **3** was determined to be 3.8 μ_B , and the EPR spectrum of this complex featured multiline signals at 330 mT ($g_{\text{eff}} = 2.0$) and 150 mT ($g_{\text{eff}} = 4.3$), consistent with an intermediate-spin Mn(II) center ($S_{\text{Mn}} = 3/2$). The solid-state structure of **3** (Figure 3) was determined by single-crystal X-ray diffraction, and metrical parameters consistent with disruption of the PDI π system were observed [$C(1)$ – $C(2)$ = 1.363(3) Å; $N(1)$ – $C(2)$ = 1.369(3) Å].³⁸

Knowing that the weak-field pyridine codonors of ^{PyEt}PDI lead to deprotonation and loss of chelate redox noninnocence upon (^{PyEt}PDI)MnCl₂ reduction, our recent efforts have involved evaluating the influence of the chain length between the imine and phosphine donors. As with ^{Ph2PPr}PDI and ^{PyEt}PDI, isolation

of a dichloride precursor was achieved upon addition of ethylene-bridged ^{Ph2PEt}PDI³¹ to (THF)₂MnCl₂. However, subsequent reduction with excess Na/Hg and 0.5 equiv of COT did not afford a monomeric product. Single-crystal X-ray diffraction data revealed a dimer, **4**, in which each Mn center is supported by a κ^4 -*P,N,N,N*-PDI chelate (Figure 2).³⁹ Since the rigidity of ^{Ph2PEt}PDI disfavors ligation of both phosphine donors to Mn, the coordination sphere of each metal is completed by η^2 -imine binding of the neighboring (PDI)Mn moiety (Figure 3). Inspection of the chelate metrical parameters also revealed a $N(1)$ – $C(2)$ distance of 1.338(6) Å and a $C(2)$ – $C(3)$ distance of 1.425(7) Å, which are consistent with single-electron reduction of the unbridged α -diimine portion of ^{Ph2PEt}PDI.⁴⁰ To gain additional insight, an EPR spectrum of this complex was collected at 107 K, and the spectral features were consistent with hyperfine coupling interactions between two neighboring $S = 1/2$ Mn nuclei. Moreover, the magnetic susceptibility of this complex was found to be 3.3 μ_B at 25 °C. Taken together, these data suggest that **4** possesses two intermediate-spin Mn(I)

Table 3. Dihydrosilylation of Formates at 25 °C Using 0.02–0.1 mol % 1, 2, and 4^a

^aThe percent conversion is provided for each trial, followed by the isolated yield of the higher-molecular-weight alcohol (in parentheses). For 4, loading is relative to Mn, not dimer. ^bA mixture of silyl ethers was observed. ^cThe trial was conducted with 0.1 mol % catalyst.

centers that are antiferromagnetically coupled to singly reduced $\text{Ph}_2\text{PE}^+\text{PDI}$ chelates.

■ ALDEHYDE AND KETONE HYDROSILYLATION

After synthesizing and evaluating the electronic structures of compounds 1–4, we screened them for carbonyl hydrosilylation activity. Starting with aldehydes (Table 1, aldehydes begin with “1”), we have demonstrated a broad hydrosilylation scope for 1, 3, and 4 in the presence of PhSiH_3 at 25 °C. Using 0.1–0.01 mol % 1 in the absence of solvent results in complete aldehyde hydrosilylation after 2 min to yield a mixture of silyl ethers, which were hydrolyzed to give the respective alcohols in good yield (1a1–n1, 1a2–b2, 1j2, and 1l2; TOFs up to 4900 min^{-1} , turnover numbers (TONs) up to 31 000).³⁴ Although 3 exhibits lower activity at 1.0 mol % when monitored in benzene- d_6 , using a 0.02 mol % loading of this complex for benzaldehyde or 4-fluorobenzaldehyde hydrosilylation under neat conditions also resulted in complete conversion after 2 min (1a4–b4; TOF = 2475 min^{-1} , TONs up to 14 170).³⁸ These reactions could not be achieved at a 0.01 mol % loading, as 3 is more sensitive to substrate impurities than 1; however, we found it surprising that such activity could be realized for a Mn complex that lacks chelate redox noninnocence. At a loading of 0.005 mol % (0.01 mol % relative to Mn), dimer 4 has also been shown to complete benzaldehyde hydrosilylation after 2 min in the absence of solvent (1a6). However, attempts to extend these conditions to other substrates, including 4-fluorobenzaldehyde, were unsuccessful (1b6, 18% conversion).³⁹ Precatalyst 4 was effectively employed for 10 different substrates at 0.05 mol % (0.1 mol % relative to Mn); however, this complex is more susceptible to

donor group inhibition than 1 (1k2, 1m3, and 1n2). The neat hydrosilylation reactions in Table 1 that reached completion were highly exothermic, resulting in nearly instantaneous boiling of the reaction mixture upon catalyst addition (the exotherm required several additional seconds when 4 was used).³⁹ Generally, compounds 1, 3, and 4 exhibit good functional group tolerance but are not effective for 4-iodobenzaldehyde hydrosilylation (1e). Moreover, 1, 3, and 4 are chemoselective for aldehyde hydrosilylation over alkene hydrosilylation (entries 1m–o), and attempts to hydrosilylate α -olefins such as 1-hexene were completely unsuccessful, even at temperatures up to 120 °C.^{38,39}

Catalysts 1–4 have also been shown to hydrosilylate ketones (Table 2). In our initial communication of 1-mediated hydrosilylation,³² seven different silanes were screened for cyclohexanone reduction in benzene- d_6 at 25 °C. When using 1.0 mol % 1 and PhSiH_3 , complete conversion to a mixture of silyl ethers was noted within 4 min (TOF = 25 min^{-1} , 2a1). Lower rates of cyclohexanone hydrosilylation were observed in the presence of $(\text{EtO})_3\text{SiH}$ (TOF = 7 min^{-1} , 2a2), Ph_2SiH_2 (TOF = 6.5 min^{-1} , 2a3), $(\text{EtO})_2\text{MeSiH}$ (TOF = 1.3 min^{-1} , 2a4), and $(\text{EtO})\text{Me}_2\text{SiH}$ (TOF = 0.8 min^{-1} , 2a5), while no reaction was observed after 4 min using Ph_3SiH or Et_3SiH . For this reason, our hydrosilylation efforts have overwhelmingly been performed using PhSiH_3 . Compound 1 hydrosilylated a broad scope of ketones at 1.0 mol % loading in benzene- d_6 , and under neat conditions the catalyst loading was first lowered to 0.1 mol % (2k2) and finally to 0.01 mol % (2a6, 2l1) to obtain the tertiary silane products $\text{PhSiH}(\text{OCy})_2$ and $\text{PhSiH}(\text{OCH}(\text{Me})(^n\text{Bu}))_2$ (TOF = 1280 and 1240 min^{-1} , respectively, based on isolated

yields of 64% and 62%). At that time, we also demonstrated that **1** fully utilizes 0.33 equiv of PhSiH_3 to generate quaternary silane products at extended reaction times (**2a7**, **2k3**). In our follow-up mechanistic study, compound **2** was found to be slightly less active for diisopropyl ketone hydrosilylation (rate = 4.48×10^{-4} and 3.87×10^{-4} M/s for **1** and **2**, respectively);³⁴ therefore, we have not performed a comprehensive aldehyde or ketone hydrosilylation study using **2**. At 1.0 mol % loading, **3** has been found to mediate ketone hydrosilylation after 1 h at 25 °C in benzene- d_6 .³⁸ Under neat conditions, 0.02 mol % **3** catalyzes the complete hydrosilylation of cyclohexanone and 2-hexanone within 5 min (TOF = 990 min^{-1}), affording either tertiary silanes or alcohols in good yield. Likewise, at 0.1 mol % catalyst loading relative to Mn, **4** has been shown to catalyze the hydrosilylation of acetophenone and cyclohexanone within 4 min (TOF = 248 min^{-1}) using PhSiH_3 .³⁹

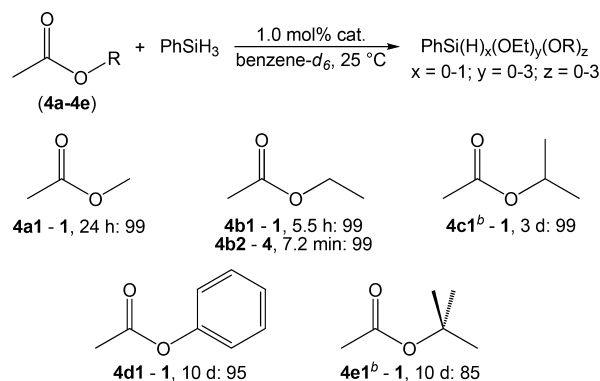
Given recent interest in base-metal catalyst development, comparison of **1**–**4** to leading catalysts for this transformation is warranted. Relative to the ketone hydrosilylation TOFs of 27.2 min^{-1} reported by Cutler and co-workers,²¹ the TOFs of 1280 and 990 min^{-1} demonstrated for **1** and **3**, respectively, are considerably higher. While aldehydes are easier to reduce, the maximum aldehyde hydrosilylation TOFs observed for **1** (4900 min^{-1}), **3** (2475 min^{-1}), and **4** (4950 min^{-1}) are 2 orders of magnitude better than those of all other Mn-catalyzed examples conducted under ambient conditions. These activities also compare favorably with those reported for the leading Fe (393 min^{-1}),^{16b} Co (49.5 min^{-1}),^{17b} and Ni (38.4 min^{-1})^{18c} carbonyl hydrosilylation catalysts.

■ FORMATE AND ESTER DIHYDROSILYLATION

Additionally, compounds **1**, **2**, and **4** have been shown to mediate carboxylate dihydrosilylation. Since our efforts have been guided by TOF optimization, we have predominantly focused on the reduction of formates (Table 3). Adding 0.02 mol % **1** to an equimolar mixture of PhSiH_3 and methyl formate or ethyl formate in the absence of solvent results in an exothermic reaction and complete dihydrosilylation within 15 min to yield a mixture of silyl ethers (**3a**, **3b**). Analogous results were achieved using either **1** or **2** for eight additional formates (**3c**, **3e**–**j**), and the resulting product mixtures were hydrolyzed in aqueous NaOH to afford the higher-molecular-weight alcohols in modest yield (51–90%).³⁴ A similar set of substrates was found to undergo dihydrosilylation using 0.02 mol % **4** relative to Mn; however, these transformations required 30 min to reach completion (**3a**, **3b**, **3d**–**g**).³⁹ The formate dihydrosilylation activities observed for **1** and **2** (TOF = 330 min^{-1}) are orders of magnitude faster than those reported for leading carboxylate dihydrosilylation catalysts.⁴¹

In our initial communication, we also reported that **1** exhibits activity for the dihydrosilylation of esters (Table 4).³² Using 1.0 mol % **1** and an equimolar quantity of PhSiH_3 , methyl acetate was converted into a mixture of silyl ethers after 24 h at 25 °C. Although ethyl acetate dihydrosilylation reached completion within 5.5 h (TOF = 18 h^{-1}), isopropyl acetate reduction required 3 days of heating at 80 °C. Moreover, the conversion of phenyl acetate to silyl ethers reached 95% conversion after 10 days at 25 °C, while *tert*-butyl acetate dihydrosilylation was not fully achieved even after heating to 80 °C for 10 days. During our mechanistic investigation of (PDI)Mn-catalyzed carboxylate reduction, we determined that **2** is considerably more efficient for ethyl acetate dihydrosilylation than **1** (rate = 0.41×10^{-4} and 0.16×10^{-4} M/s for **2** and **1**, respectively, in benzene- d_6 at 25

Table 4. Dihydrosilylation of Esters Using **1** and **4**^a



^aThe percent conversion is provided for each trial. ^bThe reaction was conducted at 80 °C.

°C). This improved ester dihydrosilylation activity has yet to be extended to additional substrates; however, we are hopeful that improved TOFs for this transformation will be achieved by comparing the effectiveness of **1**–**4** under neat conditions.

■ MECHANISTIC CONSIDERATIONS

Throughout these studies, several observations were made that hint at the mechanism of **1**-mediated hydrosilylation. Post-catalysis, a significant quantity of unreacted PhSiH_3 was observed, coupled silanes and substrates were not observed, and spectroscopic analysis of the Mn-containing species revealed a mixture of **1** and a ligand-modified hydride compound reminiscent of **2**. Control experiments employing AIBN, Mn^0 , $(\text{THF})_2\text{MnCl}_2$, and $(\text{Ph}_2\text{PPr})\text{PDI}\text{MnCl}_2$ did not result in carbonyl hydrosilylation. Hydrosilylation was not inhibited by exogenous PPh_3 , and the phosphine-free κ^3 -PDI complex $(^{2,6\text{-iPr}_2\text{Ph}}\text{PDI})\text{Mn}(\text{THF})_2$ was found to exhibit carbonyl hydrosilylation activity, indicating that the phosphine donors of **1** may dissociate during catalysis.³⁴ The rate laws for **1**-mediated carbonyl hydrosilylation and carboxylate dihydrosilylation were also found to be first-order with respect to catalyst, substrate, and silane, and a kinetic isotope effect (KIE) of 2.2 ± 0.1 was observed for **1**-mediated diisopropyl ketone hydrosilylation using $\text{PhSiH}_3/\text{PhSiD}_3$.

Considering this and other evidence, we proposed that **1** achieves carbonyl and carboxylate hydrosilylation through the modified Ojima mechanism shown in Figure 4.³⁴ The initial step involves phosphine dissociation and Si–H oxidative addition to generate a five-coordinate silyl hydride intermediate. Upon substrate coordination, insertion into the Mn–H bond is believed to be the rate-determining step, consistent with a first-order dependence on both the substrate and the silane. Once formed, the resulting silyl alkoxide undergoes reductive elimination to yield the silyl ether product. For carboxylates, β -alkoxide elimination occurs before reductive elimination to eliminate aldehyde, which may re-enter the catalytic cycle. It is believed that Mn remains divalent throughout this process as a result of the redox activity of Ph_2PPr -PDI. Dimer **4** is believed to operate via the same mechanism upon dissociation into monomeric $(\text{Ph}_2\text{PEt})\text{PDI}\text{Mn}$; however, this catalyst is far more susceptible to donor group inhibition.³⁹

Notably, **2** is less active than **1** for carbonyl hydrosilylation but more active for carboxylate dihydrosilylation. Catalyst **2** was also found to exhibit a KIE of 4.1 ± 0.6 for diisopropyl ketone hydrosilylation, indicating that it operates through a competing

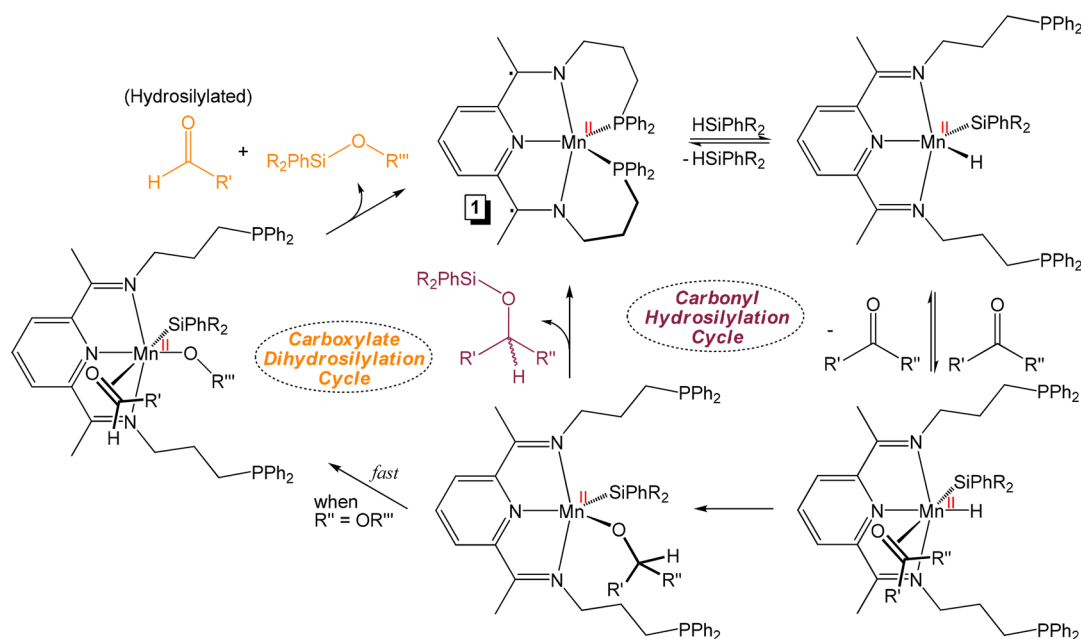


Figure 4. Modified Ojima mechanism proposed for 1-catalyzed carbonyl and carboxylate hydrosilylation.³⁴

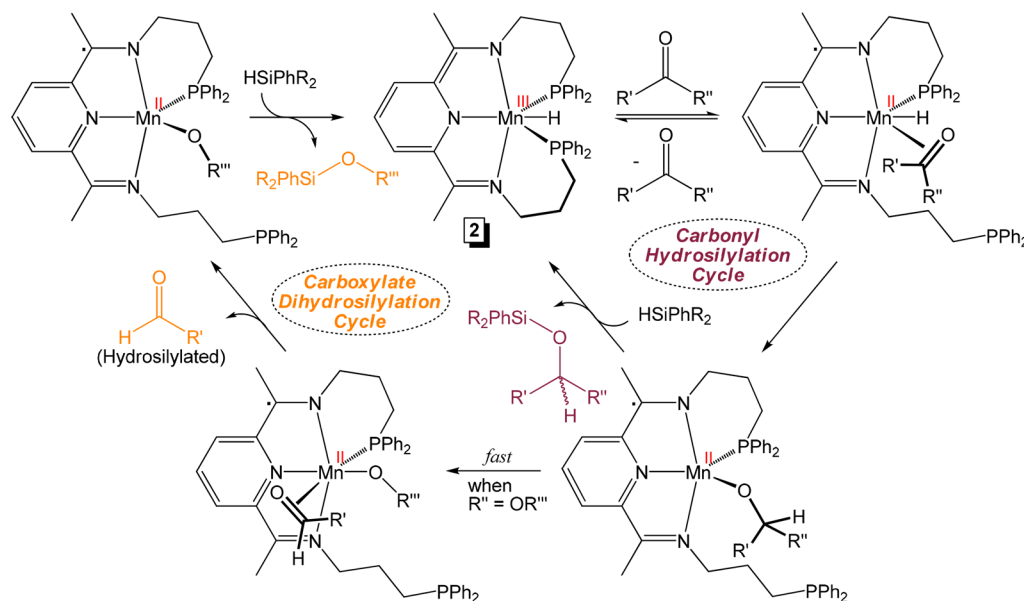


Figure 5. Hydride insertion mechanism for 2-catalyzed hydrosilylation.³⁴

mechanism (Figure 5). It has been proposed that phosphine displacement by the substrate allows for direct insertion into the Mn–H moiety of **2**, generating an alkoxide intermediate. This intermediate can then undergo rate-determining σ -bond meta-thesis with the silane to yield the silyl ether and generate **2** or, in the case of carboxylates, undergo fast β -alkoxide elimination. Although the electronic structure of **2** is consistent with a Mn(III) center supported by a PDI dianion, Mn is believed to remain divalent throughout the remainder of the cycle as a result of chelate redox flexibility.³⁴ The mechanism of **3**-mediated carbonyl hydrosilylation has not been thoroughly investigated; however, the nature of the supporting PDEA ligand suggests that redox activity is not a requirement for the development of highly active Mn hydrosilylation catalysts.³⁸

OUTLOOK

It remains an exciting time to study homogeneous manganese catalysis. Since our 2014 communication, tremendous progress has been made in the development of Mn catalysts for the hydrogenation,⁴² transfer hydrogenation,⁴³ and hydroboration⁴⁴ of carbonyl-containing substrates. Our reports on PDI-supported Mn hydrosilylation also inspired Huang and co-workers to develop iminopyridine oxazoline manganese dichloride precatalysts that mediate asymmetric ketone hydrosilylation when activated with NaEt_3BH .⁴⁵ Although good enantioselectivity was observed, it is fair to predict that this will not be the last report that covers Mn-catalyzed asymmetric hydrosilylation.

Although **1**–**4** are very effective for carbonyl hydrosilylation, it was disappointing to learn that these compounds are inactive for

olefin hydrosilylation. Silicones are prepared on an industrial scale using Pt catalysts,⁴⁶ and there remains a desire to prepare Mn variants that exhibit comparable olefin hydrosilylation activity. Earlier this year, Du and co-workers revealed new synthetic protocols for silicone formation that rely on Mn-catalyzed dehydrogenative silylation of diols or hydrosilylation of dicarbonyls.⁴⁷ We believe that compounds **1–4** may prove to be particularly useful for these alternative silicone preparation methods. Moreover, it is hoped that the work described herein will guide future development of Mn olefin hydrosilylation catalysts that can replace Pt in existing formulations.

CONCLUSION

By employing donor-substituted bis(imino)pyridine ligands, our group has successfully prepared a family of manganese catalysts that exhibit excellent carbonyl hydrosilylation activity (TOFs up to 4950 min⁻¹) and carboxylate dihydrosilylation activity (TOFs up to 330 min⁻¹). Electronic structure analysis has revealed that chelate redox noninnocence stabilizes **1**, **2**, and **4**, and mechanistic evidence suggests that redox activity allows Mn to remain divalent throughout catalysis. Even though **3** possesses a redox-innocent PDEA ligand, it has also been found to exhibit impressive aldehyde and ketone hydrosilylation activity. Taking this work into account alongside the tidal wave of recent Mn-focused reports from other research groups,^{11,42–45,47} it should be clear to the casual observer that this metal has yet to reveal its full synthetic utility. It is about time for Mn to join the flock.

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Notes

The author declares the following competing financial interest(s): R.J.T. retains rights to the catalysts described herein through U.S. Patent 9,708,355. Compound **1** has been commercialized by Sigma-Aldrich Corporation (a subsidiary of Merck KGaA).

Biography

Ryan J. Trovitch grew up outside of Hazleton, PA, and attended MMI Preparatory School in nearby Freeland, PA. He received a B.S. in Chemistry from King's College (PA) in 2004 and a Ph.D. in Inorganic Chemistry from Cornell University in 2009 and was a postdoctoral research associate at Los Alamos National Laboratory from 2008 to 2011. He joined the Department of Chemistry and Biochemistry (now School of Molecular Sciences) at Arizona State University in 2012 and currently holds the rank of Assistant Professor.

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