Redox Non-Innocent Ligand Supported Vanadium Catalysts for the Chemoselective Reduction of C=X (X = O, N) Functionalities

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Supporting Information Placeholder

ABSTRACT: Molecular complexes of vanadium (V) are particularly useful and efficient catalysts for oxidation processes; however, their ability to catalyze reductive transformations has yet to be fully explored. Here we report the first examples of polar organic functionality reduction mediated by V. Open-shell V^{III} complexes that feature a π -radical monoanionic 2,2':6',2"-terpyridine ligand (Rtpy·)^{1–} functionalized at the 4'-position (R = (CH₃)₃SiCH₂ or C₆H₅) catalyze mild and chemoselective hydroboration and hydrosilylation of functionalized ketones, aldehydes, imines, esters and carboxamides with turnover numbers (TONs) of up to ~1,000 and turnover frequencies (TOFs) of up to ~500 h⁻¹. Computational evaluation of the precatalyst synthesis and activation has revealed underappreciated complexity associated with the redox active tpy chelate.

1. INTRODUCTION

Homogeneous catalysis using structurally well-defined transition metal complexes was an integral part of the scientific-technological revolution in the 20th century.¹ The properties of these complexes result from the interaction between the metal center and its surrounding ligands. Ligands do not only control the electronic and steric properties of a molecular catalyst, but can also be directly involved in the catalytic reaction via the cleavage or formation of bonds, the gain or loss of electrons, or the stabilization of transition states via non-covalent interactions.² The last decade of homogeneous catalysis has been marked by the extensive development of transition metal complexes featuring so-called "redox non-innocent" ligands.³ The main concept of such catalysis relies on temporary electron storage in the ligand, and this property can affect a catalytic reaction in several ways.^{2c,3d} The ability to mediate multi-electron transformations while avoiding uncommon oxidation states via temporary electron storage in redox noninnocent ligands is a particular feature of many 1st-row transition metal catalysts.3c,3h,4

Vanadium (V) is the 20th most abundant element in the Earth's crust and 6th most abundant among the transition metals.⁵ Catalysis is the second largest application for V after its use as an additive to improve steel production. It has found several uses in catalytic homogeneous transformations, most notably in polymerization and oxidation reactions.⁶ In contrast, applications of V in catalytic reductions remain extremely rare. Only three examples, all involving H₂ as the reductant, have been reported under homogeneous conditions, **Scheme 1**.⁷ Specifically, the first example of catalytic hydrogenation involving V was reported in the 1970s, where a VCl4-Mg-AlCl₃ system was found to hydrogenate

cyclohexene.^{7c} In 2001, Gambarotta and coworkers described a dimeric vanadium hydride catalyst for the hydrogenation of styrene.^{7b} A decade later, Arnold & Toste reported a Z-selective semihydrogenation of alkynes to afford *cis*-alkenes using a well-defined vanadium bis(imido) complex.^{7a}

Scheme 1. Reported examples of catalytic reduction using homogeneous vanadium complexes.⁷



This paper describes redox non-innocent ligand supported compounds of $V^{\rm III}$ and their use in the chemoselective hydroboration

and hydrosilylation of ketones, aldehydes, imines, esters and carboxamides leading to alcohols, amines and nitriles. Computational analysis also reveals that the one-electron reduced terpyridine (tpy) supporting ligand exhibits chemical non-innocence during precatalyst formation and activation with either PhSiH₃ or HBpin.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of V^{III} Complexes 1, 1H. and 2. The reaction oftpy ligand L1⁸ with VCl₃ in THF followed by treatment with 3 equiv. of LiCH₂SiMe₃ in diethyl ether (Et₂O) afforded dark-brown crystals composed of two separate complexes, 1 and 1H, Scheme 2. The crystal selected for X-ray diffraction analysis contained 1 and 1H in a ~55:45 ratio. Specifically, 1 was found to be a distorted trigonal bipyramidal vanadium complex possessing two inner-sphere (CH₃)₃SiCH₂⁻ anions and a tridentate L1 ligand that underwent 4'-functionalization.9 The N1-C45 [1.35(2) Å], N3-C65 [1.392(14) Å], C45-C51 [1.459(15) Å], and C55-C65 [1.460(14) Å] distances in 1 (Figure 1) are consistent with a one-electron reduction of the terpyridine chelate,¹⁰ as expected to balance the charge of a VIII center, with the electron delocalized on the central pyridine ring. Co-crystallized 1H was also found to possess a distorted trigonal bipyramidal geometry; however, the ligand L1 is dearomatized, featuring H-atom and -CH₂Si(CH₃)₃ substituents at the 4'-position. The anionic nature of the central ring of 1H is evidenced by the relatively short V1-N2A bond distance of 1.86(2) Å (Figure 1). This can be compared to the dative V1–N2 interaction of 2.004(16) Å in 1. The dearomative functionalization at the 4'-position of tpy was only scarcely addressed previously.8c The combined 1/1H product was isolated in ~63% yield, which was reproduced over five independent trials. The same reaction with ligand L2 gave solely complex 2, in which no functionalization of the ligand took place (Scheme 2). Product 2, featuring the radical monoanionic ligand $(4'-C_6H_5tpy)^{1^-}$, was isolated in 45% yield and characterized by single crystal X-ray diffraction. Complexes 1/1H and 2 were also characterized by elemental analysis, IR spectroscopy in the solid state and electron paramagnetic resonance (EPR) spectroscopy, as described in the following section.

Scheme 2. Synthesis of V^{III} complexes 1/1H and 2.



2.2. EPR Spectroscopy of V^{III} Complexes 1 and 2. The X-band (9.40 GHz) EPR spectra of 1/1H and 2 (toluene glass, T = 123 and 118 K, respectively) showed signals consistent with the presence of a quartet state S = 3/2 (black lines in Figure 2).^{11,12} To ascertain whether these spectra correspond to $V^{III}(d^2, S_V = 1)$ centers that are ferromagnetically coupled to a (4'-Rtpy)¹⁻ ligand radical or to V^{II} $(d^3, S_V = 3/2)$ centers supported by a neutral 4'-Rtpy ligand, the respective spin Hamiltonians were fit to the data (red lines in Figure 2). The spectral features observed for 1 and 2 were well-fit ($\sigma =$ 1.1% and 0.9%, respectively, see SI) considering a quartet state with rhombic g-values ($g_x = 2.047$, $g_y = 1.884$, and $g_z = 1.991$ for 1 and $g_x = 2.017$, $g_y = 1.914$, and $g_z = 1.994$ for **2**; see **Table 1** for all fitting parameters) and rhombic hyperfine coupling (hfc) interactions ($A_x = 165.2$, $A_y = 148.1$, and $A_z = 77.7$ MHz for 1 and $A_x =$ 164.2, $A_y = 152.5$, and $A_z = 76.2$ MHz for **2**) with a ⁵¹V (I = 7/2) nucleus. These parameters differ from the axial g-values and axial ⁵¹V hfc interactions reported for vanadocene, which is a well-defined and thoroughly-studied V^{II} (d^3 , $S_V = 3/2$) system (**Table 1**).¹³ The rhombic distortion of the g-values indicates that delocalization of the unpaired electrons in both 1 and 2 is not restricted to the molecular orbitals of V^{III} and extends throughout the plane of the ligand. Furthermore, the rhombic distortion of the ⁵¹V hfc interactions is due to the dipole-dipole interaction between the magnetic moment of the unpaired electron system and the magnetic moment of the ⁵¹V nucleus. The larger values observed for A_x and A_y (**Table** 1) are consistent with the presence of a ligand-based radical, and we therefore assign the EPR spectra of **1** and **2** to V^{III} (d^2 , $S_V = 1$) centers that are ferromagnetically coupled to (4'-Rtpy·)¹⁻ ligand radicals.

Figure 2. Experimental (black) and simulated (red) EPR spectra of **1/1H** (top) and **2** (bottom) using a conventional X-band (9.4 GHz) spectrometer.¹¹ The small lines around 320 mT (marked with asterisks) belong to a minor impurity, V(CH₂Si(CH₃)₃)₄.¹⁴



Figure 1. The solid state structures of 1 (left), 1H (middle), and 2 (right) with ellipsoids at 30% probability.



Table 1. Parameters used to fit the X-band EPR spectra of 1/1H and 2 in toluene at low temperature.

	V(III) coupled to a	V(II)	
	$(S_{\rm T} = 3)$	(S = 3/2)	
Parameter ^a	1/1H (T = 123 K)	2 (<i>T</i> = 118 K)	VCp2 ¹³
g_x	2.047	2.017	1.991
g_y	1.884	1.914	1.991
g_z	1.991	1.994	2.010
D (cm ⁻¹)	> 2.671	> 2.671	2.836
E (cm ⁻¹)	0.00	0.00	0.00
A_x (MHz)	165.2	164.2	62
A_y (MHz)	148.1	152.5	62
A_z (MHz)	77.7	76.2	108
ΔB_x (MHz)	187.7	186.0	
ΔB_y (MHz)	200.5	192.3	
ΔB_z (MHz)	52.0	44.1	

^{*a*}The fitting parameters were the following: the principal components of g (*i.e.* g_x , g_y , and g_z), the zero-field splitting parameters, D and E, the principal components of the hfc tensor A (*i.e.* A_x , A_y , and A_z) and the peak-to-peak linewidths (ΔB_x , ΔB_y , and ΔB_z).

2.3. Electronic Structure of 1: Metal-Ligand Ferro- vs Antiferromagnetic Coupling. In a diethyl ether continuum, unrestricted density functional theory (UDFT) calculations of a VII (d^3) center supported by a neutral 4'-(CH₃)₃SiCH₂tpy ligand (initial guess for the wave function) converged to quartet ⁴1, in which a V^{III} (d^2 , $S_V = 1$) center is ferromagnetically coupled with the unpaired electron of $(4'-(CH_3)_3SiCH_2tpy)^{1-}$ to yield a $|\uparrow>_L|\uparrow\uparrow>_V$ state. Broken-symmetry (BS) UDFT calculations converged to a spin-contaminated doublet ²1 as a result of antiferromagnetic coupling between one of two VIII alpha- electrons and the betaelectron of the π -radical monoanionic ligand ($|\downarrow>_L|\uparrow\uparrow>_V$ state). Both calculated structures displayed similar geometrical parameters to the X-ray structure of 1 (see SI for details). The value of spin-contamination in ²1 determined by the eigenvalue of the spin-squared operator $\langle S^2 \rangle = \sim 1.8$ does not depend on the identity of functional (meta-GGA vs hybrid, range-separated or dispersion corrected hybrid), percent of Hartree-Fock exchange term and/or the basis set (Figure 3). Application of the Yamaguchi correction¹⁵ revealed that ⁴1 is on average 3-6 kcal·mol⁻¹ more favorable than ²1, consistent with the experimental EPR measurements. Mulliken spin density plots suggest the electron is delocalized largely at the central pyridine ring for both spin states (Figure 3), in agreement with the X-ray diffraction data.

2.4. Computed Reaction Profile Leading to 1/1H. Experimental Isolation of Pure 1. A mixture of 1 and 1H was consistently found when collecting data for randomly picked crystals from two independent syntheses and analyzing the unit cell parameters of a third. Increasing the reaction time to 6 h did not influence crystal composition; the same dark-brown crystals of 1/1H were obtained, indicating that the solution still contained both products. One could reasonably assume that an H-atom can be abstracted from 1H to form 1. The singly reduced ligand (4'-(CH₃)₃SiCH₂tpy·)¹⁻ in 1 can in turn act a radical to remove an H-atom from a substrate to produce 1H. In an attempt to generate pure 1, the reaction shown for L1 in Scheme 2 was undertaken in the presence of TEMPO (0.5 eq.). Unfortunately, the resulting solution was a different color, suggesting that TEMPO reacts with the catalyst. Based on the experimental procedure in Scheme 2, we propose the reaction profile leading to 1/1H as shown in Scheme 3.

Figure 3. Influence of different UDFT/SMD(Et₂O) functionals/basis sets on the energy difference between the doublet and quartet spin states for 1. Mulliken spin density plots (yellow: α -spin; Blue: β -spin) for the quartet and spin-contaminated doublet of 1 optimized at the ω B97XD/def2-SVP level; non-critical H-atoms are omitted for clarity.

	Functional /basis set	Δ(²E − ⁴ E), kcal·mol ^{_1}	Δ(²G –⁴G), kcal·mol ⁻¹
	M06L/def2-SVP	6.4	6.5
	ωB97XD/def2-SVP	3.0	3.5
	ωB97XD/def2-TZVP	3.2	2.7
	ωB97XD/6-311++G**/ECP10MDF(V)	2.7	3.9
	M06-D3/def2-SVP	7.3	8.0
	M062X-D3/def2-SVP	4.3	7.0
	M06HF-D3/def2-SVP	4.1	4.8
	⁴ 1, $ \uparrow>_L \uparrow\uparrow>_V$ state ⟨S ² ⟩ = 3.80	² 1 , ↓> _L ↑↑> _V ⟨S²⟩ = 1.7	state 79

This path to 1/1H formation is rationalized by computational analysis at the wB97XD/def2-SVP/SMD(Et2O) level. As expected, the addition of tpy to VCl₃ affords (tpy)VCl₃ (A), where triplet ³A is 7.6 kcal·mol⁻¹ more favorable than singlet ¹A. The reaction of ³A with 3 equiv. of (CH₃)₃SiCH₂Li results in the formation of **B**, which is a combination of "free" $[(tpy)V^{III}(CH_2Si(CH_3)_3)_2]^+$ cation (d^2, S_V) = 1) and "free" (CH₃)₃SiCH₂⁻ anion ($\Delta G^{\circ}_{298K} = -2.5 \text{ kcal} \cdot \text{mol}^{-1}$). Numerous attempts to optimize contact ion-pair [V^{III}(CH₂Si(CH₃)₃)₂(tpy)]⁺(CH₃)₃SiCH₂⁻ failed and the solution always converged to one of two spin-isomers of C (Scheme 3), which are thermodynamically preferred ($\Delta G^{\circ}_{298K} \sim -33 \text{ kcal} \cdot \text{mol}^{-1}$ ¹). Complex C represents a contact radical-pair consisting of [V^{III}(CH₂Si(CH₃)₃)₂(tpy·)] and (CH₃)₃SiCH₂· (the spin states, $|\downarrow\rangle_R|\uparrow\rangle_L|\uparrow\uparrow\rangle_V$ and $|\uparrow\rangle_R|\downarrow\rangle_L|\uparrow\uparrow\rangle_V$, are almost isoenergetic; $\langle S^2 \rangle =$

~3.0 for each case as expected). The recombination of these radical pairs (light-blue and blue-dotted lines in **Scheme 3**) affords complex **1H** (where triplet ³**1H** is favored by 11.6 kcal·mol⁻¹ over singlet ¹**1H**), and the reaction is even more thermodynamically favorable, $\Delta G^{\circ}_{298K} = -72.0 \text{ kcal·mol}^{-1}$. Notably, the activation barrier for both processes is extremely small (~3 kcal·mol⁻¹; transition states **ts0a** and **ts0b** in **Scheme 3**). The alternative process, recombination of (CH₃)₃SiCH₂· radicals to generate (CH₃)₃SiCH₂CH₂Si(CH₃)₃ and putative complex ⁴**4**, is barrierless according to the constrained potential surface scan. However, the

kinetics of this step should be controlled by the diffusion of $(CH_3)_3SiCH_2$ · radicals and/or magnetic effects.¹⁶ Since ⁴4 is not observed experimentally (at least in the solid state), the kinetics of $(CH_3)_3SiCH_2$ · radical recombination are likely to be slower than the kinetics of recombination between $[V^{III}(CH_2Si(CH_3)_3)_2(tpy)]$ and $(CH_3)_3SiCH_2$ · to afford ³1H.

Scheme 3. The reaction profile leading to ${}^{4}\mathbf{1} + (CH_3)_4Si + LiH vs. {}^{4}\mathbf{4} + (CH_3)_3SiCH_2CH_2Si(CH_3)_3$ computed at the $\omega B97XD/def2-SVP/SMD(diethyl ether)$ level. Mulliken spin density plots (Yellow: α -spin; Blue: β -spin) are shown for selected stationary points; non-critical H-atoms are omitted for clarity.



To obtain experimentally observed ⁴1, complex ³1H should lose a hydrogen atom radical. We suggest this happens upon reaction with $(CH_3)_3SiCH_2$ radical to afford $(CH_3)_4Si$. Where does this $(CH_3)_3SiCH_2$ come from? In one scenario, this radical comes from complex C. In this case, the reaction would produce a mixture of ⁴1, ⁴4 and ³1H, the relative composition of which would largely be determined by kinetic control. In contrast to the recombination of $(CH_3)_3SiCH_2$ to give $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$, in which the kinetics are controlled solely by diffusion and/or magnetic effects,¹⁶ the kinetics of the reaction between C and ³1H should be determined by the barrier to hydrogen atom abstraction from ³1H. The corresponding transition state, ts1, is located only 7.1 kcal·mol⁻¹ higher in energy than (CH₃)₃SiCH₂· and ³1H. However, taking into account our crystallized yields of 1/1H (~60%), we believe that (CH₃)₃SiCH₂· does not originate from C, but instead from the reagent (CH₃)₃SiCH₂Li as suggested for similar bases.¹⁷ Computationally, hydrogen atom abstraction from ³1H by (CH₃)₃SiCH₂· takes place with a relative activaton barrier of 16.3 kcal·mol⁻¹, taking into account the thermodynamics of the following reaction:

$$[^{3}1H] + \frac{1}{2}[(CH_{3})_{3}SiCH_{2}Li] = \frac{1}{2}[ts1] + \frac{1}{2}[^{4}D$$

where ⁴**D** is the product of one-electron transfer from Li· radical to ³**1H**. Attempts to optimize the contact radical [³**1H**]·Li pair failed; the calculations converged to complex ⁴**D** ($\langle S^2 \rangle = 3.79$ as expected for three alpha electrons), which represents a contact cation– π ion pair between Li⁺ and one-electron reduced ³**1H**. According to Mulliken spin-density analysis, the electron in ⁴**D** is localized on one side of the tridentate ligand, based on the located minumum (**Scheme 3**, bottom). Complex ³**1H** can also react with (CH₃)₃SiCH₂· radical via homolytic (S_H2) substitution through transition state **ts2** to afford ⁴**4** and (CH₃)₃SiCH₂CH₂Si(CH₃)₃. This process is unfavorable according to a relative activation barrier of 35.1 kcal·mol⁻¹, taking into account the thermodynamics of the same reaction ([³**1H**] + $\frac{1}{2}$ [(CH₃)₃SiCH₂Li] = $\frac{1}{2}$ [**ts2**] + $\frac{1}{2}$ [**4D**]). To complete the reaction, ⁴**D** transfers a hydride via **ts3** to afford ⁴**1** (the relative barrier is computed as 26.4 kcal·mol⁻¹, **Scheme 3**).

Computations explain why 1/1H is obtained as a mixture, despite 1 being thermodynamically favored over 1H by 5.7 kcal·mol⁻¹. A 100% theoretical yield of 1 is possible when there are at least 3.5 equiv. of (CH₃)₃SiCH₂Li according to the stoichiometry. Under the conditions of Scheme 2, there is not enough (CH₃)₃SiCH₂Li to react with 1H, and therefore the reaction does not proceed further. Independent attempts to carry out the same reaction with 3.5 – 4.0 equiv. of (CH₃)₃SiCH₂Li and a longer reaction time (48 h) afforded well-shaped dark-brown crystals of pure 1 according to X-ray crystallographic analysis, see SI.¹⁸ Although the isolation of 1 was reproducible across three independent syntheses, the bulk samples contained a significant quantity of V(CH₂Si(CH₃)₃)₄ based on EPR analysis,¹⁴ previously observed as a small impurity in the 1/1H bulk sample shown in Figure 1 (marked with asterisks).

2.5. VIII-Catalyzed Reduction of Ketones and Aldehydes. Next, we examined the possible catalytic activity of precatalyst complexes 1/1H, 1 and 2 for the reduction of ketones and aldehydes with pinacolborane (HBpin) and C6H5SiH3 (PhSiH3). Ketones and aldehydes are important raw materials, and their chemoselective reduction is an effective and convenient synthetic route to functionalized alcohols.¹⁹ Hydrogen gas is the ideal reducing agent in terms of cost and atom efficiency, and has very broad applicability.²⁰ However, H₂ is flammable and can require the use of specialized reaction vessels. Catalytic hydroboration and hydrosilylation are alternative methods that avoid these disadvantages.²¹ Benchmark studies were first performed for acetophenone hydroboration with HBpin, Table 2. While the reaction does not occur in the absence of a catalyst or with VCl₃, and barely with a putative (tpy)VCl₃ complex (entries 1–3, Table 2), 1/1H, 1 and 2 catalyze the reaction to give the corresponding product in >99% yield under identical conditions (entries 4-6). Although 2 and manually-isolated crystals of 1 are equally efficient, the easily-accessed 1/1H precatalyst mixture was further broadly evaluated for catalytic reduction activity due to the commerical availability of tpy.²² Solvent tests (entries 4, 6-9) indicate that diethyl ether is the solvent of choice for 1/1H; additionally, the reaction can proceed under higher substrate-to-catalyst ratios (S/C's) of 500 and even 1,000, providing the product in >99% yield at 25 °C in 2 h (TONs of up to 990, TOFs of up to 495 h⁻¹). Scheme 4 provides further information on the ketone/aldehyde substrate scope using precatalyst 1/1H under the optimized hydroboration conditions (diethyl ether, 25 °C, S/C = 1,000).

 Table 2. Condition screening for V-catalyzed hydroboration of acetophenone with HBpin.^a

ORPin

		+ HBpin <u>[V]</u> solvent, 25 ⁰C		
entry	catalyst	loading (mol%)	solvent	% yield ^b
1	-	-	Et ₂ O	0
2	VCl ₃	2.0	Et_2O	0
3	(tpy)VCl ₃	2.0	Et_2O	5
4	1/1H	2.0	Et ₂ O	>99
5°	1	1.0	Et_2O	>99
6	2	1.0	Et_2O	>99
7	1/1H	1.0	THF	99
8	1/1H	1.0	C_6H_6	86
9	1/1H	1.0	toluene	92
10	1/1H	1.0	pentane	84
11	1/1H	0.5	Et_2O	>99
12	1/1H	0.1	Et ₂ O	99

^aConditions: acetophenone (1.0 mmol), HBpin (1.1 mmol), [V] (0.1-1 mol%) and solvent (1 mL), 25 $^{\circ}$ C, 2 h, N₂. ^bDetermined by GC analysis with hexamethylbenzene as an internal standard. ^cManually-isolated crystals of 1 were used.





^aConditions: 1/1H (0.1 mol%), ketone or aldehyde (1.0 mmol), HBpin (1.1 mmol) and Et₂O (1 mL), 25 °C, 2 h, N₂. Yields of isolated alcohol products (GC yields of borate esters are shown in parentheses).

Based on thirty-five tested substrates, under the optimized conditions, the hydroboration of ketones and aldehydes exhibits excellent C=O vs. C=C chemoselectivity as well as tolerance of various functional groups (Cl, CF₃, NO₂, OMe, SMe, CO₂Me) as shown in **Scheme 4**. As expected, aldehydes are hydroborated faster than ketones, as evidenced by the isolation of product **4q**. Replacement of HBpin with PhSiH₃ allowed for comparable ketone reduction; however, the reaction failed for aldehydes at room temperature (<5% yield for the four substrates tested, **Scheme 5**), while a reasonable yield can be reached at elevated temperature for 4-methoxybenzaldehyde.

Scheme 5. Hydrosilylation of ketones and aldehydes with 1/1H.^a



^aConditions: 1/1H (0.1 mol%), ketone or aldehyde (1.0 mmol), PhSiH₃ (1.1 mmol) and Et₂O (1 mL), 25 °C, 2 h, N₂. Yields of isolated alcohol products. ^bGC yield at 25 °C. ^cGC yield at 50 °C.

2.6. Imine Hydroboration Using 1/1H. Imines are readily accessible from the condensation of ketones or aldehydes with primary amines, and imine reduction represents a common synthetic method to generate secondary amines. The hydroboration of N-benzylideneaniline under the conditions of Scheme 4 or 5 was slow; after 16 h only 18% conversion to the corresponding amine 5a was noted. However, the hydroboration of imines using 1/1H proceeded smoothly under gentle warming in THF, affording secondary amines with 72–90% yield (Scheme 6, TOFs of up to 62 h^{-1}). Interestingly, the hydrosilylation of N-benzylideneaniline using PhSiH₃ was unsuccessful under the conditions of Scheme 6. In a control experiment, the reaction of a 1:1 mixture of acetophenone and N-benzylideneaniline with 1 equiv. of HBpin (Et2O, 25 °C, S/C \approx 1,000) resulted in quantitative reduction of the ketone, which implies that 1/1H-catalyzed hydroboration is chemoselective for C=O over C=N bonds.

Scheme 6. Reduction of imines with 1/1H.^a



^aConditions: 1/1H (0.1 mol%), imine (1.0 mmol), HBpin (1.1 mmol) and THF (1 mL), 50 °C, 16 h, N₂. Yields of isolated amine products. ^b GC yield.

2.7. VIII-Catalyzed Reduction of Esters and Carboxamides. In the next step, we focused on the more challenging^{20a} catalytic reduction of esters and carboxamides with 1/1H (Schemes 7 and 8). These are ubiquitous compounds and can be easily accessed, for example, by coupling biorenewable carboxylic acids to alcohols and amines, respectively. Similar to ketones, aldehydes and imines, H₂ is the ideal reducing agent for these substrates,^{20a} but hydroboration and hydrosilylation could benefit the reaction in several ways. In particular, the reduction of carboxamides may follow up to three different pathways23 and the nature of the reducing reagent and/or catalyst could be crucial in terms of selectivity. Hydroboration and hydrosilylation of esters²⁴ and carboxamides^{24a, 24b, 25} are relatively underexplored with molecular catalysts, and most of these systems exhibit low TONs. It was found that 1/1H hydroborated a variety of esters and carboxamides with TONs of ~1,000 and ~ 200 (TOFs of 62 and 12.5 h⁻¹), respectively. For esters, the products (after work-up) were primary alcohols 4 as expected, whereas for secondary and tertiary carboxamides, the reaction products were secondary and tertiary amines 6, i.e. the later catalytic process represents deoxygenative reduction. For the primary benzamide, however, the reaction product was benzonitrile (7), similar to the pattern established for other molecular catalysts.^{25d,25e} The hydrosilylation of methyl benzoate proceeded equally well under the same conditions (Scheme 7), affording 4a in 80% yield. In contrast, the 1/1H-catalyzed hydrosilylation of carboxamides with PhSiH3 was found to be less effective; only 11% of 6c was detected for the reduction of N-methylbenzamide under the conditions described in Scheme 8. Competition experiments have revealed good chemoselectivity for hydroborative ketone over ester reduction and amide over ester reduction (see SI for details).





^aConditions: 1/1H (0.1 mol%), ester (1.0 mmol), HBpin (2.0 mmol) and THF (1 mL), 50 °C, 16 h, N₂. Yields of isolated products (GC yields of borate esters are shown in parentheses).

Scheme 8. Reduction of Carboxamides with 1/1H.^a



^aConditions: 1/1H (0.5 mol%), amide (0.5 mmol), HBpin (1.0 mmol) and THF (1 mL) or neat, 60 $^{\circ}$ C, 16 h, N₂. Yields of isolated products (GC yields are shown in parentheses). ^bIsolated as 6c HCl. ^cIsolated as a HCl salt (X-ray structure is shown at the 30% probability level). ^dReaction run with ben-zamide.

2.8. Preliminary Mechanistic Insights: Identification of Possible Active Species and Ligand Chemical Non-Innocence in the Presence of Excess Reductant. Adding 2.2 equiv. of HBpin or PhSiH₃ to 1/1H (diethyl ether, 1 h) afforded pinBCH₂Si(CH₃)₃ or PhSiH₂CH₂Si(CH₃)₃ in 75% (65% isolated) or 44% yield, respectively (Scheme 9A).^{26,27} Similarly, reacting complex 2 with 2.2 equiv. of HBpin also afforded pinBCH₂Si(CH₃)₃ in 73% yield, after column chromatography.²⁸ These results suggest that V monohydride and/or dihydride compounds could be relevant catalytic species,^{8c,29} given that hydrides are known intermediates in catalytic hydroboration and hydrosilylation reactions.²¹ Unfortunately, attempts to isolate or characterize such hydride species by ¹H NMR spectroscopy have been unsuccessful, as have efforts to trap these compounds in the presence of 4,4-dimethylaminopyrdine.

To gain additional mechanistic insight, UDFT/BSUDFT calculations were performed at the ωB97X-D/def2-SVP/SMD(diethyl ether) level. The results demonstrate that the hydroborative transformation of $1 \rightarrow$ monohydride $1a \rightarrow$ dihydride 1b is thermodynamically favorable, with a ΔG°_{298K} of -3.94kcal·mol⁻¹ and -7.11 kcal·mol⁻¹ for the first and second steps, respectively (Scheme 9B).³⁰ The generated species 1a/1b are quartets in their ground state. The calculated structures are similar for ⁴1a/²1a, likely due to spin-contamination for the former, whereas the structures are different for ⁴1b/²1b. State ⁴1b represents a distorted trigonal bipyramidal V complex, whereas the geometry of doublet ²1b is square pyramidal. Interestingly, if HBpin is replaced by PhSiH₃, the same transformation ${}^{4}1 \rightarrow$ monohydride ${}^{4}1a \rightarrow \text{dihydride} {}^{4}1b$ becomes slightly thermodynamically unfavorable, but still accesible (taking into account accuracy of DFT and basis set choice), with a ΔG°_{298K} of 1.70 kcal·mol⁻¹ and 4.10 kcal·mol⁻¹ for the first and second steps, respectively.

Scheme 9. Experimental reactions between 1/1H or 2 with 2.2 equiv. of HBpin or PhSiH₃ (A). ω B97X-D/def2-SVP/SMD(Et₂O) thermodynamics of the reactions: ⁴1 \rightarrow 1a \rightarrow 1b (B; spin-contaminated energies for ²1a/²1b were corrected by the Yamaguchi Correction¹⁵), ΔG°_{298K} /kcal·mol⁻¹ (1M).



Although the redox non-innocent ligand in 1b stabilizes VIII, it can also be involved in the catalyst activation process (Scheme 10). In a "chemically non-innocent" fashion,^{3d} one could imagine Hatom abstraction from HBpin or PhSiH₃ by ⁴1b, leading to complex ³1c (assuming ferromagnetic coupling is more favorable, as found for 1b) and \cdot Bpin (or PhSiH₂ \cdot) (Scheme 10A). The resultant contact radical pairs $[{}^{3}1c] \cdot Z$ ($\cdot Z = \cdot Bpin$, PhSiH₂ \cdot and CH₃CH(\cdot)OCH₂CH₃, derived from diethyl ether for comparison) are too high in energy (>40 kcal·mol⁻¹); however, ³1c becomes accesible (~16 kcal·mol⁻ ¹) when ·Z undergoes dimerization, Scheme 9B. Interestingly, in attempts to model various isomers of $[{}^{3}1c] \cdot Z$ ($\cdot Z = \cdot Bpin$, PhSiH₂·), several calculations converged to ⁴1d-⁴1g (Scheme 10B). These are products of B-H or Si-H bond addition across the central pyridine ring of ⁴1b and Mulliken spin density plots (yellow: αspin; blue: β -spin) are shown for ⁴1d and ⁴1e in Scheme 10B. According to these calculations, the central pyridine ring in ⁴1b is susceptible to the addition of B-H or Si-H bonds (especially in the absence of substrate), which can lead to a mixture of activated species, complicating their observation or isolation. Similar tpybased reactivity has been described for related Al complexes.8c

Scheme 10. H-atom abstraction from three substrates by the *para*-C atom of the central pyridine ring of ⁴**1b** (**A**). Addition of B–H or Si–H bonds across the central pyridine ring in ⁴**1b** (**B**). Calculations performed at the ω B97X-D/def2-SVP/SMD(Et₂O) level, ΔG°_{298K} /kcal·mol⁻¹ (1M).



Further elucidation of the active species, the role or roles that the redox (and chemically) non-innocent ligand plays in these reactions, and the possible radical nature of the catalytic reactions requires a separate contribution featuring in depth experimental and computational studies.

3. CONCLUSION

This paper reports the first examples of vanadium-catalyzed ketone, aldehyde, imine, ester and carboxamide reduction through hydroboration and/or hydrosilylation. Whereas the catalytic reduction of ketones, aldehydes and imines has been well-explored with molecular catalysts over the last few decades, the catalytic conversion of esters and amides to alcohols and amines or nitriles described herein is a notable conceptual advance. The reductive transformations described herein are chemoselective, tolerant of various functional groups, and have been achieved with reasonable TONs of up to ~1000 (and TOFs of up to ~500 h⁻¹). Based on these findings, it is believed that homogeneous vanadium catalysts have been considerably underutilized in reductive transformations. In addition to our catalytic results, our computational findings highlight the multiple roles that redox non-innocent ligands can play in precatalyst formation and activation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.xxx. Detailed experimental procedures, characterization data, X-ray crystallographic data (CIF) and computational details (PDF).

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Notes

The authors declare no competing financial interests.

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26. The yields were determined by GC using hexamethylbenzene as an internal standard. Colorless oil of pinBCH₂Si(CH₃)₃ was isolated in 65% yield and characterized by multinuclear NMR spectroscopy, as reported in reference 28. ¹H NMR (600 MHz, CDCl₃) δ 1.24 (s, 12H), 0.10 (s, 2H), 0.05 (s, 9H) ppm; ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 82.85, 25.08, 0.51 ppm. See SI for details.

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28. For details, see the SI.

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30. Preliminary computational analysis shows that the reaction of **1** with 2 equiv. of HBpin is more complicated, in particular several stable adducts

are located following intrinsic reaction coordinate path calculations. Further complication may arise from the reactivity of the central pyridine ring as described in the text. This might explain relatively moderate yield of pinBCH₂Si(CH₃)₃ in the experimental reaction and also our unsuccesfull attempts to isolate the V product. Additional effort and a separate contribution is warranted.