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Supported Single-Site Ti(IV) on a Metal–Organic Framework for the Hydroboration of Carbonyl Compounds

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Supporting Information

ABSTRACT: A stable and structurally well-defined titanium alkoxide catalyst supported on a metal-organic-framework (MOF) of UiO-67 topology $(ANL1-Ti(O'Pr)_2)$ was synthesized and fully characterized by a variety of analytical and spectroscopic techniques, including BET, TGA, PXRD, XAS, DRIFT, SEM, and DFT computations. The Tifunctionalized MOF was demonstrated active for the catalytic hydroboration of a wide range of aldehydes and ketones with HBpin as the boron source. Compared to traditional homogeneous and supported hydroboration catalysts, ANL1-Ti(O'Pr), is completely recyclable and reusable, making it a promising hydroboration catalyst alternative for green and sustainable chemical synthesis. In addition, ANL1-Ti(O^{*i*}Pr)₂ catalyst exhibits remarkable hydroboration selectivity toward aldehydes vs ketone in competitive study. DFT calculations suggest that the catalytic hydroboration proceeds via a



(1) hydride transfer between the active Ti-hydride species and a carbonyl moiety (rate-determining step) and (2) alkoxide transfer (intramolecular σ -bond metathesis) to generate the borate ester product.

INTRODUCTION

The reduction of aldehydes and ketones to functionalized alcohols is an important tool for the synthesis of natural products and fine chemicals.¹ Because of its importance, various stoichiometric and catalytic carbonyl reduction strategies have been established.² Most approaches employ stoichiometric amounts of reducing agents, e.g., LiAlH₄ and NaBH₄, which, in general, effect poor selectivity (over-reduction) and functional group tolerance, modest reaction rates, and often require harsh conditions.³ Several molecular and supported catalysts for carbonyl hydroboration have been shown effective and selective for the synthesis of functionalized alcohols.⁴ Less expensive and abundant s-, p-, and f-block precatalysts, e.g., Mg,⁵ Ga,⁶ Sn,⁷ and La⁸ (Chart 1), have been used for hydroboration of aldehydes and ketones.⁹ These systems are proposed to function through an active metal-hydride that forms in situ from the reaction between an H-BR₂ species, i.e., HBpin and HBcat, and the precatalyst. Other examples of molecular hydroboration catalysts include base and precious transition metals such as $Ti(O^{i}Pr)_{4}^{10}$ Shvo's catalyst (Ru),¹¹ (IPr)CuO'Bu (IPr = N_iN' -bis(2,6-diisopropylphenyl)imidazol-2-ylidene),¹² and Zn- $(iminooxazoline)(OTf)_2^{13}$ (Chart 1). For the systems mentioned, carbonyl (and pyridine) hydroboration proceeds through a σ -bond metathesis mechanism.^{5c,14} The reaction is commonly first-order in HBpin and the catalyst and zero-order in the carbonyl substrate, suggesting that the rate-determining step is σ bond metathesis between HBpin and the alkoxide intermediate. In addition, other mechanisms have been proposed, including a Ti(II) η^2 -carbonyl/Ti(IV) metallacycle scenario¹⁵ and a Mg(II)catalyzed hydroboration of esters via a zwitterionic alkoxyborate reaction pathway.^{5a}

Despite the growing scope of homogeneous hydroboration catalysts, these systems are generally plagued with deactivation processes arising from irreversible ligand redistribution pathways. Such catalyst deactivation mechanisms can be prevented via kinetic stabilization of the active site using sterically encumbered ligands. However, this approach results in lower activity since the increased steric constraints renders the active site inaccessible for substrate binding and activation.

Alternatively, stabilization of highly reactive intermediates has been achieved via surface organometallic chemistry (SOMC).¹⁶ Supported organometallic catalysts have garnered significant attention in the past 25 years as a result of the ever increasing

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Chart 1. Examples of Homogenous and Supported Hydroboration Catalysts



demand for enhanced catalyst efficiencies and amenability to spectroscopic characterization.¹⁷ The latter has drastically contributed to understanding of structure-property relationships, which is a key tool enabling the rational design of more efficient catalysts. In this context, Pruski, Sadow, and coworkers¹⁸ have successfully developed well-defined, isolated amidozirconium(IV) sites on mesoporous silica (Chart 1) for the catalytic hydroboration of a range of carbonyl compounds. Recently, Lin and co-workers¹⁹ have shown that single-site magnesium alkyl sites supported on a node of a metal-organic framework (TPHN-MOF of UiO-69 topology; TPHN = 4,4bis(carboxyphenyl)-2-nitro-1,1'biphenyl, Chart 1) are catalytically active for hydroboration of ketones, aldehydes, and imines. Our catalyst (vide infra) shows some notable advantages to the prior works referenced above, including higher activity than the homogeneous counterpart and the use of commercially available, nonpyrophoric starting material.

MOFs are 3D, atomically periodic, chemically and thermally robust porous materials composed of inorganic nodes and organic linkers.²⁰ In contrast to the irregular surfaces of bulk inorganic oxides, i.e., SiO₂ or Al₂O₃, MOFs have intrinsically uniform surface structures, making them an ideal support platform for supported-but-homogeneous-in-function catalysts.²¹ Two strategies are commonly employed for incorporating catalytic active site into MOFs: (1) covalent attachment via functionalized organic linkers²² or (2) grafting to inorganic node groups.²³ Given the periodicity of MOFs, we consider them a promising underexplored platform for supporting molecular catalysts. Here, we report the synthesis and detailed characterization of a stable and well-defined titanium alkoxide catalyst supported on a MOF of UiO-67²⁴ topology (ANL1-Ti($O^{i}Pr$)₂). It is seen that ANL1-Ti(O'Pr), is an efficient and recyclable catalyst for hydroboration of a diverse scope of carbonyl compounds using HBpin as reductant. Additionally, computational and mechanistic studies suggest that the catalytic hydroboration proceeds via (1) hydride transfer between the active Ti-hydride species and a carbonyl moiety (ratedetermining step) and (2) alkoxide transfer (intramolecular σ bond metathesis) to generate the borate ester product.

RESULTS AND DISCUSSION

Synthesis and Characterization of ANL1 and ANL1-Ti(O'Pr)₂. ANL1, a MOF of UiO-67 topology, was synthesized via direct solvothermal reaction of **bpdcOAc** (2,2'-bis(acetoxy)-1,1'-biphenyl-4,4'-dicarboxylic acid) and H₂bpdc (1,1'-biphenyl-4,4'-dicarboxylic acid) ligands (molar ratio of 1.5:1) with ZrCl₄ in N,N'-dimethylformamide (DMF) and acetic acid (HOAc, as a modulator) at 120 °C for 24 h. Notably, solvothermal synthesis from bpdcOAc ligand under the same conditions failed. The resulting white microcrystalline powder was washed with DMF and methanol, then dried at 150 °C under vacuum for 2 h to give ANL1 in ~83% yield (based on H_2 bpdc). ¹H NMR spectroscopy upon digestion of ANL1 with D_2SO_4/d_6 -DMSO solution confirmed the complete deprotection of the acetylated **bpdcOAc** ligand, with a molar ratio between the two ligands determined to be $\sim 1:1$ (Figure S3). Powder X-ray diffraction (PXRD) analysis reveals the classic isoreticular nature of ANL-1 and high crystallinity typical of the UiO-67 topology (Figure 1). Meanwhile, scanning electron microscopy (SEM)



Figure 1. PXRD of UiO-67-bpdc, ANL1, ANL1-Ti $(O^{i}Pr)_{2}$, and ANL1-Ti $(O^{i}Pr)_{2}$ post-catalysis.

analysis shows octahedral-shaped, phase-pure products with homogeneous particle morphology and crystal sizes of $\sim 1 \ \mu m$ (Figure S9). Gas adsorption analysis of ANL1 gives a BET surface area of 1876 m² g⁻¹ (N₂ gas at 77 K), lower than the typical UiO-67-bpdc (2411 m² g⁻¹); this is attributable to the presence of OH groups (Table S1). In addition, N₂ adsorption isotherm confirms that mesoporosity is maintained in ANL1, with an average pore-size distribution of 10.9 Å (Figures S1 and S2). Also, thermogravimetric analysis (TGA) shows that ANL1 is stable up to 400 °C (Figure S4). The diffuse reflectance FT-IR (DRIFTS) spectrum of ANL1 exhibits characteristic stretching frequencies of the node $-OH/-OH_2$ groups at 3673 cm⁻¹ and the 2,2-biphenyldiol (BIPHENOL) linker –OH at 3582 cm⁻¹ respectively (Figure 2). Accessibility of the BIPHENOL chelating sites in ANL1 to early transition metals was evidenced by postsynthetic metalation with a molecular Ti(IV) precursor. A toluene solution of $Ti(O'Pr)_4$ (1.05 mmol, 0.128 g) was added to a toluene slurry of microcrystalline ANL1 (0.30 mmol equiv of bpdcOH, 0.220 g) at 25 °C for 30 h in a N₂ glovebox. The airsensitive yellow product ANL1-Ti(O'Pr)₂ was washed repeatedly with toluene to remove the excess, unreacted $Ti(O'Pr)_4$, and the toluene supernatant exchanged with Et₂O to facilitate solvent removal from the functionalized MOF.



Figure 2. Diffuse reflectance FT-IR (DRIFTS) of **ANL1**, **ANL1**-**Ti**(**O**[']**Pr**)₂, **UiO-67-bpdc**, and **Ti-UiO-67-bpdc**. See Figure S8 for full spectra.

¹H NMR scale metalation experiments reveal the complete consumption of the $Ti(O^{i}Pr)_{4}$ precursor, along with the generation of a substoichiometric amount (1.75 equiv) of isopropanol (Figures S6 and S7). This suggests that each ANL1-based Ti(IV) is stabilized by a dianionic BIPHENOL unit, two anionic isopropoxy groups.²⁵

X-ray absorption spectroscopy (XAS) reveal hexacoordination of the Ti(IV) centers (*vide infra*), suggesting that the Ti(IV) center is datively bound to neutral donor ligands, consistent with a precatalyst formula unit of $[(BIPHENOL)Ti(O^{i}Pr)_{2}(L)_{2}]$, where L is a residual isopropanol or Et₂O molecule. The presence of labile donor groups was confirmed through thermogravimetric analysis (TGA) showing a weight loss of 1.4% (1.2% theoretical) upon heating **ANL1-Ti(O^{i}Pr)**₂ between 110 and 200 °C, corresponding to the departure of two isopropanol/Et₂O molecules (Figure S5).

The presence of Ti in ANL1-Ti(OⁱPr)₂ (Scheme 1) was confirmed by ICP-atomic emission spectroscopy. The elemental composition suggests that on average there are 2.3 Ti atoms for every Zr_6 node. This ratio translates to ~80% metalation of the BIPHENOL linkers. This degree of metalation is consistent with results of DRIFTS measurements where significant attenuation of the O-H vibration at 3583 cm⁻¹, along with the detection of evident alkyl C-H stretching vibration of the isopropoxy groups (Figure 2, blue line vs red line), was observed. Additionally, the DRIFTS spectra suggest that node

-OH groups of **ANL1** at 3673 cm⁻¹ remain intact after the metalation reaction (Figure 2, purple line vs green line). Note that negligible reaction occurs between the Ti(IV) precursor and the Zr_6 nodes in **UiO-67-bpdc**, as suggested by DRIFT spectroscopy (**Ti-UiO-67-bpdc**, Figure 2C-D).²⁶

Results of the PXRD analysis of $ANL1-Ti(O^{i}Pr)_{2}$ confirm retention of the MOF crystallinity after Ti incorporation (Figure 1). This was further confirmed by SEM–EDX analysis where retention of the MOF crystallinity was observed (Figure S9). Notably, although the BET surface area of $ANL1-Ti(O^{i}Pr)_{2}$ slightly decreased to $1554 \text{ m}^{2} \text{ g}^{-1}$ after metalation (Table S1), the N₂ adsorption isotherms reveal that mesoporosity is maintained (Figure S1 and S2).

The XAS pre-edge and edge energies of ANL1-Ti(O[']Pr)₂ (a, Figure 3) are consistent with the Ti⁴⁺ standard TiO₂ (Anatase).²⁷



Figure 3. (a) X-ray absorption near edge structure (XANES) and (b) EXAFS spectra of Ti(0) foil (green), TiO_2 (Anatase) (blue), and ANL1- $Ti(O^iPr)_2$ (red).





Specifically, the pre-edge energy feature at 4970.8 eV, observed at a normalized height of 0.21, is attributable to a 6-fold coordination. The X-ray absorption fine structure (EXAFS) spectra further confirm the 6-fold coordination number (Figures S10-S12). Three Ti–O distances were observed (1.79, 1.94, and 2.44 Å, Table 1), indicative of the presence of three different

Table 1. EXAFS-Based Bonding Parameters for ANL1- $Ti(O^{i}Pr)_{2}^{a}$

bonds	CN	bond length (Å)	computed bond length (Å)			
Ti-O ₁	2	1.79	1.82			
Ti-O ₂	2	1.94	1.98			
Ti-O ₃	2	2.44	2.13			
^{<i>a</i>} Fitting range: k-range = $3.2-12$ Å ⁻¹ ; <i>R</i> -range = $0.95-2.23$ Å.						

donor groups around the Ti(IV) center and consistent with the results of the ¹H NMR-scale metalation experiments (*vide supra*). Altogether, these spectroscopic features are consistent with a precatalyst structure where each isolated Ti(IV) center is stabilized by a anionic BIPHENOL unit, two anionic isopropoxide groups, and two datively bound neutral donor molecules.

Catalytic Hydroboration of Carbonyl Compounds. ANL1-Ti(OⁱPr)₂ exhibits excellent reactivity in the hydroboration of benzaldehyde with 1.5 equiv of HBpin.²⁸ At 2 mol % Ti loading, benzaldehyde is quantitatively converted to the corresponding benzyl alcohol borate ester at room temperature within 5 h (Table 2, entry 1; isolated yield = 98%). Under the

Table 2. Hydroboration of Benzaldehyde with HBpin in thePresence of Different Catalysts a

Phro 0.4 mmol	+ HB 1.5 equiv + HB + HB - + HB - + HB - + HB - + + HB - + + + HB - + + + + + + + + + + + + + + + + + + +	Ph~o-B-o
entry	catalyst	yield (%) ^b
1	ANL1-Ti(O ⁱ Pr) ₂	>99 (98) ^c
2	ANL1	20
3	Ti-UiO-67-bpdc	22
4	$Ti(O^iPr)_4$	46
5	_	1

^{*a*}Reaction conditions: benzaldehyde (0.4 mmol, 42.4 mg), HBpin (0.6 mmol, 76.8 mg), toluene/hexane (1.5/0.5 mL), 25 °C, N₂, 5 h. ^{*b*}Yield was determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard. ^{*c*}Isolated yield.

same conditions, less than 1% of the product was generated in the absence of the catalyst, confirming the catalytic role of ANL1-Ti(OⁱPr)₂ for this transformation (Table 2, entry 4). Meanwhile, unfunctionalized ANL1 and Ti-UiO-67-bpdc effected 20 and 22% conversion, respectively (Table 2, entries 2 and 3), suggesting that the observed quantitative conversion in Entry 1 mainly mediated by the supported Ti(IV) center. Markedly, when molecular Ti(OⁱPr)₄ was used as the catalyst, 46% yield of the product was obtained. This result further supports the advantage of heterogenizing the catalytic sites for this transformation. Furthermore, the ANL1-Ti(OⁱPr)₂-catalyzed hydroboration of benzaldehyde can be scaled up (>1 g) successfully without significant loss in efficiency, and the borate-ester product is isolated by simple filtration in 99% yield after 5 days (Figure S42).

ANL1-Ti $(O^{i}Pr)_{2}$ was also demonstrated efficient for the hydroboration of a wide range of carbonyl compounds with excellent functional group tolerance. Table 4 summarizes the

Table 3. Hydroboration of Acetophenone with HBpin in the Presence of Different Catalysts a

Ph+O 0.4 mmol	+ HB 1.5 equiv + HB 	Ti) Me O H Ph O B O
entry	catalyst	yield (%) ^b
1	ANL1-Ti(O ⁱ Pr) ₂	78 $(65)^c$
2	ANL1	0
3	$Ti(O^{i}Pr)_{4}$	14
4	_	0

^{*a*}Reaction conditions: acetophenone (0.4 mmol, 48.1 mg); HBpin (0.6 mmol, 76.8 mg), toluene/hexane (1.5/0.5 mL), 25 °C, N_2 , 24 h. ^{*b*}Yield was determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard. ^{*c*}Isolated yield.

scope of functionalized aldehydes reduced to the corresponding Bpin borate esters. ANL1-Ti(O^{*i*}Pr)₂ quantitatively converts arylfunctionalized aldehydes (Table 4) to the corresponding borate ester products in good to quantitative yields with good functional group tolerance (phenyl, naphthyl, C₆H₄CH₃, C₆H₄CF₃, C_6H_4Br , C_6H_4F , C_6F_5 , and OMe). Notably, aldehydes with a heteroaromatic substituent such as pyridyl could be quantitatively reduced with complete tolerance of the heteroaryl functionality (entry 4). Less electrophilic, linear, and cyclic alkyl-substituted aldehydes are reduced in good yields at slower rates (entries 5 and 6). In addition, trans-cinnamaldehyde, an α_{β} -unsaturated aldehyde, is selectively reduced at the carbonyl position, leaving the vinylic C=C bond intact (entry 7). The slower rates of hydroboration for *n*-hexyl- and styryl-substituted aldehydes (entries 6 and 7) are attributed to active pore blockage by the bulkier borate ester product. The same is observed in the case of bulkier ketone substrates (vide infra).

The reactivity of ketones (Table 5) is, in general, slightly lower compared to aldehydes, likely rates due to the formation of bulkier borate esters that could block the catalytic pore, and they require higher catalyst loadings (7.5 mol % Ti) and prolonged reaction time (24 h). Importantly, under the same conditions (Table 3), homogeneous $Ti(O^{i}Pr)_{4}$ catalyst converts acetophenone with a total yield of only 14%, whereas $ANL1-Ti(O'Pr)_2$ gives rise to the corresponding hydroborate product as a racemic mixture with an NMR yield of 78% (65% isolated yield). Notably, negligible conversion is observed in the absence of the catalyst, confirming again the catalytic role of $ANL1-Ti(O^{i}Pr)_{2}$. In general, ketone hydroboration rates appear to be mainly influenced by steric effects. Electron-donating and withdrawing groups (-CH₃, -OCH₃, C₁₀H₇, -CF₃, I, and NO₂; Table 5, entries 2-7) do not affect acetophenone hydroboration rates. In addition, ketones bearing a heteroaromatic substituent such as pyridyl are converted with remarkably yield. Cyclic and linear aliphatic ketones such as cyclopentanone and 2-pentanone generate the corresponding products at comparable yields, 77 and 80%, respectively (entries 9 and 10). Notably, the sterically encumbered carbonyl group in benzophenone undergoes slower hydroboration, giving moderate yield of the borate ester

R 个 O 0.4 mmol	+	$HB_0 + 1.5 equiv$	5 mol% [Ti] tol/hex (3:1) rt, N ₂ , 24 h	R~0-B.0×
entry			yield ^b (%)	
1 ^c		Ph	0 ^{.8} .0	>99
2			0. [₿] .0×	>99
3			о. в. о.	79
4 ^d			0.₿.0×	>99
5		∽ cy∕	0 0. ⁸ .0	88
6 ^d		<i>n</i> -Hex	0.B.0X	67
7		\bigcirc		66
8		Ĺ	To B.ot	84
9		F F F F		83
10		₽Û		91
11		F ₃ C		92
12		Ph	Toto	83
13			, et al	86

Table 4. ANL1-Ti(OⁱPr)₂-Catalyzed Hydroboration of Aldehydes^a



Table 5. ANL1-Ti(OⁱPr)₂-Catalyzed Hydroboration of

Ketones⁴

^{*a*}Reaction conditions: 5 mol % **ANL1-Ti**(**O**^{*i*}**Pr**)₂ (8.6 or 21.5 mg), aldehydes (0.4 mmol), HBpin (0.6 mmol, 76.8 mg), toluene/hexane (1.5/0.5 mL), 25 °C. ^{*b*}Yield was determined by ¹H NMR with 1,3,5 trimethoxybenzene as the internal standard (Figures \$14-\$26). ^{*c*}Using 2% catalyst loading, 5 h. ^{*d*}Using 2% catalyst loading, 24 h

derivative (entry 11), compared to less sterically demanding acetone (entry 12). Moreover, hydroboration of α , β -unsaturated ketones proceeds selectively the carbonyl group without detectable reduction of the C=C bond (entries 13 and 14).

^{*a*}Reaction conditions: 7.5 mol % **ANL1-Ti**(**O**^{*i*}**Pr**)₂ (32.3 mg), ketones (0.4 mmol), HBpin (0.6 mmol, 76.8 mg), toluene/hexane (1.5/0.5 mL), 25 °C. ^{*b*}Yield was determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard (Figures S17–S40).

Due to the markedly different rates of reduction of aldehydes and ketones exhibited by ANL1- $Ti(O^{i}Pr)_{2}$, competition experiment was carried out to directly probe hydroboration selectivity. In the reaction of 4-acetylbenzaldehyde (Scheme 2, Figure S41) with 1.5 equiv of HBpin at 94% conversion (5 mol % Ti, 5 h), the aldehyde-only hydroboration product is obtained in 99% yield, with only 1% of the dihydroborated and ketone-only hydro-

Scheme 2. Competitive Experiment: Aldehyde/Ketone Hydroboration Selectivity in 4-Acetylbenzaldehyde



boration products. Such remarkable selectivity for the hydroboration of aldehyde versus ketone with HBpin has only been shown before few times using homogeneous catalysts, such as $La(N(TMS)_2)_3$,^{8a} [Ru(p-cymene)Cl₂]₂,²⁹ and [{(2,4,6-Me₃-C₆H₂)NC(Me)}₂(Me)(H)]AlH.^{9b}

To test the heterogeneity of ANL1-Ti $(O^{i}Pr)_{2}$, a hot filtration experiment was carried out after 0.5 h of hydroboration of benzaldehyde with HBpin (conversion = 27%), after which no further conversion of the substrate was observed. Furthermore, neither significant leaching (<0.1 ppm Ti) of titanium nor any change in Zr/Ti ratio (2.3 Ti/Zr₆ node) were observed, as evidenced by ICP-OES analysis of the filtrate and the MOF after catalysis. ANL1-Ti(OⁱPr), also displayed remarkable recyclability (vide supra), forming the borate ester derivative in excellent vields (>99%) and selectivity (100%) over five cycles. Between each run, the catalyst was recovered and directly used for the next reaction. The crystallinity was maintained after each cycle. confirmed by PXRD (Figure 1), showing the robust nature of ANL1-Ti(OⁱPr), under catalytic conditions and stirring required for these reaction. SEM analysis of the MOF after hydroboration (Figure S9) also indicates that crystallites are largely undamaged and N₂ adsorption isotherms reveal that mesoporosity is maintained (Figure S1). However, BET surface area of ANL1- $Ti(O^{i}Pr)_{2}$ slightly decreased to 1329 m² g⁻¹ (Table S1 and Figure S2), likely due the blocking of some active pores.

DFT Calculations and Reaction Mechanisms. The fragment of the support with the catalyst that was used in the calculations is shown in Table S3. Benzaldehyde and

acetophenone were chosen to represent, respectively, the aldehyde and the ketone families studied. Two plausible mechanistic scenarios for the hydroboration of carbonyl groups were taken into account and probed by DFT calculations.³⁰

In the first scenario (Figure 4), which mimics more closely the experimental conditions, both reagents (HBpin and benzaldehyde or HBpin and acetophenone) were added simultaneously to the active titanium(IV) dihydride (TiH₂) center, which is formed in situ from the reaction between the HBpin and the precatalyst.^{5–9} Note that ¹H NMR-scale reaction of ANL1- $Ti(O^{i}Pr)_{2}$ with HBpin shows the formation of iPrOBpin, suggesting the formation of the Ti-hydride species (Figure S43). The full cycle of the catalytic hydroboration in this scenario is depicted in Figure 4B, whereas the Gibbs free energies corresponding to all the intermediates and transition states involved are shown in Figure 4C (1, catalytic center; 2, HBpin; 3a, benzaldehyde; 3b, acetophenone). The intermediacy of metal hydrides has been previously demonstrated in metal-catalyzed hydroelementation of carbonyl and N-heterocycle compounds.^{4,8,31} Our results obtained within the natural bond orbital (NBO)³² analysis scheme are consistent with a hydridic active species (1), where each titanium-bound hydrogen has a charge of -0.3 (see Table S3). The DFT calculations indicate a barrierless coadsorption of the reactants on 1 to give intermediate 4, followed by 1,2-addition of a Ti-H moiety across a C=O moiety (intramolecular hydride transfer) to give monoalkoxy monohydride titanium(IV) intermediate 5. Intermediate 5 then undergoes σ -bond metathesis between the Ti-O(alkoxy) and B-H moieties to regenerate the TiH₂ fragment and a Ti-bound borate ester (7). Ultimately, barrierless desorption of the hydroborated product regenerates the active TiH_2 species (1). The overall hydroboration reaction is exothermic with the hydride transfer from Ti to the carbonyl moiety as the rate-limiting step. The hydroboration of acetophenone follows an energy profile, which is similar to that of benzaldehyde, albeit with an overall upward shift in energy. Interestingly, this shift is most significant for the transition state TS1 that defines the rate-limiting step. This finding is consistent



Figure 4. Calculated catalytic pathway for **ANL1-Ti**($O^{i}Pr$)₂-mediated hydroboration of benzaldehyde (a) and acetophenone (b). (A) Formation of TiH₂ active species. (B) Proposed hydroboration mechanistic summary. (C) Corresponding energetic profile (the zero of energy is defined as the sum of Gibbs free energies of noninteracting species 1, 2, and 3).



Figure 5. Calculated energetic profile (in term of Gibbs free energies) for the first half of the catalytic cycle along the second scenario for the hydroboration of benzaldehyde (the zero of energy is defined as the sum of Gibbs free energies of noninteracting species 1, two benzaldehydes, and one HBpin). "1" denotes the catalyst (the same as in Figure 4).

with experimental observations where hydroboration of aldehydes is more favored than that of ketones.

The second scenario assumes concomitant addition of two molecules of a carbonyl compound, i.e., benzaldehyde or acetophenone, to the Ti(IV) dihydride (TiH₂) center, followed by Ti–H insertions into the carbonyls to yield $[Ti(O-CR_2H)_2]$ and subsequent σ -bond metathesis with HBpin, which leads to transfer of H to Ti and formation of a hydroborated carbonyl as a product of the first half of the full catalytic cycle (Figure 5). Similarly to the first scenario, the first half of the second scenario is overall exothermic with the rate-limiting step also being a hydride transfer, in this case the transfer of the second hydride. The energy (21.7 kcal/mol) of the transition state for this transfer (TS2 in Figure 5) is slightly higher than the energy (21.1)kcal/mol) of the transition state for the hydride transfer in the first scenario (TS1 on Figure 4C). The second half of the full catalytic cycle of the second scenario, which leads to the second hydroborated carbonyl product and regeneration of the titanium(IV) dihydride (TiH_2) catalyst, is then completed by adding the second HBpin reagent and following or closely mimicking the part of the first scenario after step 5 (Figure 4).

Overall, the two mechanistic scenarios explored here can be viewed as energetically competitive, with the first scenario being slightly more facile. In addition, the first scenario, as mentioned above, more closely corresponds to our experimental conditions. The 1.5:1 ratio of the concentrations of the HBpin to carbonyl reagents, together with the higher or comparable binding energy of HBpin (28.6 kcal/mol) as compared to those of the carbonyls (24.9 kcal/mol for benzaldehyde and 29.6 kcal/mol for acetophenone) to the catalytic center, favor initial coadsorption of a HBpin/carbonyl pair, rather than that of a pair of carbonyls.

CONCLUSIONS

A new, structurally well-defined MOF-based catalyst for hydroboration of carbonyl groups was synthesized by integration of a Ti-alkoxide complex into the BIPHENOL linkers of ANL1. Compared to traditional homogeneous catalyst, purposeful site isolation of active Ti centers in ANL1-Ti($O^{i}Pr$)₂ enabled the stabilization of highly active, robust, and reusable catalyst. This makes it an attractive hydroboration catalyst for green and sustainable chemical synthesis. High selectivity for aldehyde hydroboration over ketones and good functional group tolerance for many other groups is observed. In addition, DFT calculations suggest that the catalytic hydroboration proceeds via (1) hydride transfer between the active Ti-hydride species and a carbonyl moiety (rate-determining step), and (2) alkoxide transfer (intramolecular σ -bond metathesis) to generate the borate ester product.

EXPERIMENTAL SECTION

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of O_2 and moisture in oven-dried Schlenk-type glassware on a dual manifold Schlenk line and in a N₂-filled atmosphere glovebox with a high capacity recirculator (<1 ppm of O_2). Toluene and diethyl ether were sparged with N₂, dried using activated alumina columns according to the method described by Grubbs,³³ transferred into the glovebox, and stored over 4 Å molecular sieves prior to use. Unless specified, all chemicals and other solvents were purchased and used as received from Sigma-Aldrich, Acros Organics, Strem Chemicals, TCI America. 2,2'-Bis(acetoxy)-1,1'-biphenyl-4,4'-dicarboxylic acid (**bpdcOAc**) was prepared according to a previous report.³⁴ 1,1'-Biphenyl-4,4'-dicarboxylic acid (**H₂bpdc**) were purchased from TCI America.

Nuclear magnetic resonance (NMR) spectra (¹H and ¹³C) were recorded using a Bruker UltraShield 500 MHz spectrometer (¹H = 500 MHz, ¹³C = 125 MHz) and analyzed using MestReNova (v11.0.1, MestreLab Research S. L., Santiago de Compostela, Spain) software. Chemical shifts for ¹H and ¹³C spectra were referenced using internal solvent resonances and reported relative to tetramethylsilane (TMS). Gas chromatography mass spectrometry (GC-MS) and flame ionization detection (GC-FID) data were collected using a Thermo Scientific Trace GC Ultra Gas Chromograph system equipped with a Tri Plus RSH autosampler, a Thermo Scientific ISQ GC-MS detector, and a FID detector. The data was analyzed using the Themo Xcalibur 2.2 SP1.48 software. Elemental analysis (% C, H, Zr, Ti) was conducted by Galbraith Laboratories, Inc. (Knoxville, TN). Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) data were collected on a Thermo Scientific iCAP 600 spectrometer with errors within 5%.

Digestion and Analysis by ¹H NMR. Approximately 3 mg of dried MOF material was digested with sonication in 500 μ L of d_6 -DMSO with 35 μ L of D₂SO₄ (96–98 wt % in D₂O).

Powder X-ray Diffraction Analysis. Approximately 20–30 mg of MOF samples were dried under vacuum before PXRD analysis. PXRD data were collected at ambient temperature on a Bruker Diffractometer D8 Advance operating with the following parameters: Cu K α radiation of 40 mA, 40 kV, K λ = 0.15418 nm, 2 θ scanning range of 2–40°, a scan step size of 0.02° and a time of 3 s per step. The samples were grinded to smaller particles and placed on a zero-background silicon holder (MTI Corp.) for analysis.

Brunauer–Emmett–Teller (BET) Surface Area Analysis. Approximately 50-100 mg of the MOF sample was dried under vacuum line for 2 h at 150 °C. The sample was then transferred to a preweighed sample tube and degassed at 150 °C using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics, Norcross, GA) overnight or until the outgas rate was <5 mmHg. The sample tube was then cooled to room temperature and reweighed to obtain a consistent weight. BET surface area (m²/g) measurements and full isotherm data were collected at 77 K with N₂ on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer employing the volumetric technique.

Thermogravimetric Analysis. Approximately 10 mg of the MOF material was used for TGA measurements. Samples were analyzed under a stream of N_2 using a Mettler Toledo TGA 851 unit, running from room temperature to 600 °C at a scan rate of 5 °C/min.

Diffuse Reflectance Infrared Fourier Transform Measurements. Infrared (IR) spectra were collected under nitrogen atmosphere in a glovebox using a Bruker Alpha FTIR spectrometer (Bruker Optics, Billerica, MA) with a single-reflection diamond ATR setup. Samples were activated at 150 °C under vacuum for 4 h and mixed with dry KBr (chromatographically pure) before each measurement (sample content, ca. 10% in KBr). A sample of solid KBr was utilized as the background. Spectra were collected at 4 cm⁻¹ resolution over 64 scans. All IR data were normalized, baseline corrected, and analyzed using OPUS (v7.0, Bruker Optics, Billerica, MA) software.

Scanning Electron Microscopy. Approximately 2–5 mg of dried MOF sample was suspended in 3 mL of acetone, and the mixture was sonicated to make a slurry. Two drops of the slurry was transferred to a conductive carbon tape on a sample holder disk and air-dried. A Phenomworld SEM instrument was used for acquiring images using a 10 kV energy source under vacuum.

X-ray Absorption Spectroscopy. XAS experiments were conducted in the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS), Argonne National Laboratory. XAS data were acquired in transmission step scan mode with photon energies selected using a water-cooled, double-crystal Si(111) monochromator. The monochromator was detuned by approximately 50%, reducing harmonic reflections. The ionization chambers were optimized for the maximum current with linear response (~10¹⁰ photons detected/sec) with 10% absorption (30% N₂ and 70% He) in the incident ion chamber and 70% absorption (90% N₂ and 10% Ar) in the transmission detector. A Ti foil spectrum (edge energy 4966 eV) was acquired simultaneously with each measurement for energy calibration.

Each sample $(TiO_2; anatase, and ANL1-Ti(O'Pr)_2)$ was mixed with boron nitride to a weight ratio of about 4% with Ti under inert and moisture-free atmosphere. The mixture was mixed well with a mortar and pestle, and 10 mg of the mixture then was pressed into a cylindrical sample holder consisting of six wells with a radius of 2.0 mm, forming a self-supporting wafer. The sample holder was placed in a quartz tube (1 in. OD, 10 in. length) sealed with Kapton windows by two Ultra-Torr fittings and used for transmission mode measurement.

The edge energy of the XANES spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak. Standard procedures based on Demeter 0.9.24 software package were used to extract the extended X-ray absorption fine structure (EXAFS) data. The coordination parameters were obtained by a least-square fit in *R*-space using k1-, k2-, and k3-weighted Fourier transformed data.

Electron Paramagnetic Resonance Spectroscopy (EPR). Continuous wave (CW) X-band (9–10 GHz) EPR experiments were carried out with a Bruker ELEXSYS II E500 EPR spectrometer (Bruker Biospin, Rheinstetten, Germany), equipped with a TE₁₀₂ rectangular EPR resonator (Bruker ER 4102ST). A He gas-flow cryostat (ICE Oxford, UK) and an intelligent temperature controller (ITC503, Oxford Instruments, UK) were used for measurements at cryogenic temperatures (T = 30 K). Data processing was done using Xepr (Bruker BioSpin, Rheinstetten) and Matlab 7.11.2 (The MathWorks, Inc., Natick) environment.

Synthesis of UiO-67-bpdcOH/bpdc (ANL1). A Schlenk flask (100 mL) branched with a Teflon adaptor equipped with pressure relief was charged with bpdcOAc (0.226 g, 0.63 mmol), H₂bpdc (0.102 g, 0.42 mmol), and DMF (40 mL). The resulting mixture was sonicated for ~5 min, followed by the addition of $ZrCl_4$ (0.245 g, 1.05 mmol) and glacial acetic acid (1.8 mL, 31.5 mmol). The reaction mixture was further sonicated for ~5 min, sealed with a greased glass stopper, and incubated at 120 °C for 24 h. After cooling, the solid was collected by filtration, washed with DMF (10 mL \times 2), MeOH (10 mL \times 2), and dried under vacuum at 150 °C for 2 h (258 mg, white powder, yield: 83% based on H_2 bpdc). Anal. Calcd for $Zr_6O_4(OH)_4[bpdcOH]_3[bpdc]_3$ $(Zr_6C_{84}H_{64}O_{38}, M_w = 2227.65)$: C, 45.25; H, 2.90, Zr, 24.57. Found: C, 39.70; H, 2.39, Zr, 25.3. Satisfactory C% and H% were not obtained, likely due to the presence of defects in the MOF. However, digestion and analysis by ¹H NMR and PXRD suggest acceptable purity of the material.

Chemisorption of Ti(O'Pr)₄ Complex on ANL1. In a glovebox, ANL1 (220 mg, 0.30 mmol equiv of bpdcOH) was added to a solution of $Ti(O^{i}Pr)_{4}$ (0.128 g, 0.45 mmol) in anhydrous toluene (4 mL). Upon addition of Ti(O'Pr)₄, the MOF immediately turned from white to yellow. The suspension was allowed to stand for 30 h at room temperature. The resulting yellow solid of ANL1-Ti(O'Pr)2 was soaked first with anhydrous toluene $(2 \times 5 \text{ mL in } 12 \text{ h intervals})$ followed by anhydrous Et₂O (5 mL \times 2 in 12 h intervals) to remove all uncoordinated Ti(OⁱPr)₄. The obtained ANL1-Ti(OⁱPr)₂ was activated by heating at 150 °C in vacuo for 2 h. The extent of titanium uptake was estimated through the Ti/Zr ratio based on ICP-OES analysis (atomic ratio Ti/Zr₆ = 2.3). Anal. Calcd for $Zr_6O_4(OH)_4[bpdcOTi(i OPr)_{2]_{3}}[bpdc]_{3}$ ($Zr_{6}Ti_{3}C_{108}H_{118}O_{44}$, M_{w} = 2809.64): C, 46.13; H, 4.23; Ti, 5.11, Zr, 19.48. Found: C, 36.33; H, 2.64; Ti, 4.36; Zr, 21.83. Satisfactory C% and H% were not obtained, likely due to the presence of defects in the MOF. However, digestion and analysis by ¹H NMR and PXRD suggest acceptable purity of the material.

Catalytic Hydroboration of Carbonyl Compounds. All hydroboration experiments were carried out inside a N₂-atmosphere glovebox. In a typical experiment, **ANL1-Ti(OⁱPr)**₂ (Ti loading: 2 or 5 mol % for aldehydes and 7.5 mol % for ketones) was added to 20 mL vial charged with dry toluene (1.5 mL). A solution of the carbonyl compound (0.4 mmol) and HBpin (0.6 mmol, 88 μ L) in 0.5 mL of hexane was then added to the catalyst–toluene suspension. The resulting mixture was shaken at room temperature under N₂ atmosphere until completion (confirmed by TLC analysis). The solid was then filtered off and washed with hexane (3 × 2 mL). The solvent fraction was removed in vacuo to yield the borate ester product. Hydroborated products were identified based on comparison of ¹H NMR data with the literature.^{3–13}

Preparative-Scale Reaction Procedure. In a glovebox, ANL1-Ti(OⁱPr)₂ (0.215 g, 0.2 mmol) was added to an oven-dried 50 mL Schlenk flask and suspended in dry toluene (10 mL). Then, a solution of benzaldehyde (1.06 g, 10 mmol) and HBpin (2.2 mL, 15 mmol) in 37.5 mL of dry toluene and 12.5 mL of hexane were transferred to the flask using syringe. The flask was shaken at room temperature for 5 days. Then, the mixture was filtered, and the solid was washed multiple times with ethyl acetate. The solutions were combined in a preweighed Schlenk flask and the volatiles were removed in vacuo, yielding 2-

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(benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (99% yield; Figure S42).

Recycling Experiment. A series of catalyst recyclability tests were carried out with benzaldehyde as test substrate. After each catalyst testing cycle, the recovered catalyst was dried under vacuum for 1 h. The dried catalyst was then added to an oven-dried 20 mL vial and suspended in dry toluene (1.5 mL). A solution of benzaldehyde (0.4 mmol, 41 μ L) and HBpin (0.6 mmol, 88 μ L) in 0.5 mL of hexane was then transferred to the catalyst–toluene suspension. The resultant mixture was shaken at room temperature for 5 h. The spent catalyst was then filtered off and washed with hexane (3 × 2 mL). The solvent fraction was removed in vacuo to yield the borate ester product.

Hot Filtration Test. In a glovebox, ANL1-Ti($O^{i}Pr$)₂ (2 mol %, 8.6 mg) was added to an oven-dried 20 mL vial and suspended in dry toluene (1.5 mL). Then, a solution of benzaldehyde (0.4 mmol, 41 μ L) and HBpin (0.6 mmol, 88 μ L) in 0.5 mL of hexane was transferred to the vial using syringe. The resultant mixture was shaken at room temperature under nitrogen atmosphere for 0.5 h. Then, the reaction mixture was quickly filtered in glovebox. The filtrate was analyzed by ¹H NMR (1,3,5-trimethoxybenzene as the internal standard), shaken at room temperature under nitrogen atmosphere for 4.5 h, and analyzed by ¹H NMR.

Computational Methods. The computations were performed using the spin-unrestricted formalism of the density functional theory (DFT) as implemented in the NWChem package.³⁵ We employed the meta-generalized gradient approximation (meta-GGA) with the M06-L exchange-correlation functional³⁶ and all-electron double- ζ (LANL2DZ) basis sets³⁷ for all the elements involved, except Ti. The latter was characterized by an effective core potential, which incorporates the 10 inner electrons in the ionic core, in combination with the LANL2DZ basis set for the 12 valence electrons (3s²3p⁶4s²4d²). This computational framework has been shown in earlier studies to provide adequate accuracy for systems similar to those studied here.⁸ Our tests on reactions involving Ti⁺, C₆H₆, and C₇H₆O, for which experimental data are available and which are species akin to those forming our supported catalyst, provide further corroboration of the accuracy of the calculations (see Table S11). The structural optimizations of all the reactants and products involved in the elementary reaction steps were performed using gradient-based techniques with no symmetry constraints imposed. The nudged elastic band (NEB) technique was employed to identify the transition state geometries and their energies. The identities of the reactants and the products connected via a given transition state were confirmed via a small distortion of the transition state configuration along the eigenmode corresponding to the imaginary frequency in the positive and negative directions and optimization of the distorted structures. Results of ab initio molecular dynamics (AIMD) trajectories run under the conditions of constant energy or constant temperature were analyzed to visualize and understand the mechanism of interaction of the reactants with the ANL1-Ti(H)₂ catalyst.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00544.

Calculated vs measured reaction enthalpies, BET surface area measurements, N₂ isotherms, pore-size distributions, ¹H NMR spectrum of digested ANL1, TGA analysis, ¹H NMR stack plot of $Ti(O^{i}Pr)_{4}$ + ANL1, DRIFTS spectra, SEM images, X-band EPR spectra, ¹H NMR spectra of hydroborated carbonyl compounds, calculated structures, Gibbs free energies, and NBO charge analyses (PDF)

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Notes

The authors declare no competing financial interest.

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