

Bifunctional Metal-Organic Layers for Tandem Catalytic Transformations Using Molecular Oxygen and Carbon Dioxide

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Supporting Information Placeholder

ABSTRACT: Tandem catalytic reactions improve atom- and step-economy over traditional synthesis but are limited by the incompatibility of the required catalysts. Herein we report the design of bifunctional metal-organic layers (MOLs), HfOTf-Fe and HfOTf-Mn, consisting of triflate (OTf)-capped Hf₆ SBUs as strong Lewis acidic centers and metalated TPY ligands as metal active sites for tandem catalytic transformations using O₂ and CO₂ as co-reactants. HfOTf-Fe effectively transforms hydrocarbons into cyanohydrins via tandem oxidation with O₂ and silylcyanation whereas HfOTf-Mn converts styrenes into styrene carbonates via tandem epoxidation and CO₂ insertion. Density functional theory (DFT) investigations were also performed to understand the mechanisms of these tandem catalytic transformations.

Introduction

By performing multiple organic transformations in one synthetic operation without separation and purification of the intermediates produced in each step, tandem reactions enhance resource utilization and reduce waste generation.¹⁻⁴ Despite their advantages in atom- and step-economy,⁵ tandem reactions are difficult to implement in catalytic fashion due to the incompatibility of different catalysts in the same solution. This incompatibility issue can be addressed if different catalysts can be hierarchically immobilized onto solid supports. However, most solid supports cannot anchor different catalysts in an ordered fashion to completely overcome catalyst incompatibility.

Metal-organic layers (MOLs) have recently been assembled from metal cluster secondary building units (SBUs) and polytopic organic linkers⁶⁻²⁴ to afford reusable single-site solid catalysts.²⁵⁻³⁰ The SBUs and linkers in MOLs can be individually functionalized to immobilize different catalysts in a fixed spacing. We surmise that MOLs can integrate synergistic catalytic sites to afford reusable solid catalysts for tandem reactions.

Herein we report the design of two new bifunctional MOLs, HfOTf-M (M=Fe^{II} or Mn^{II}), consisting of triflate (OTf)-capped Hf₆ SBUs as a strong Lewis acid and metalated TPY ligands {TPY is 4'-(4-carboxyphenyl)[2,2':6',2''-terpyridine]-5,5''-dicarboxylate} as the active metal site. HfOTf-Fe is highly effective for tandem oxidation with O₂ and cyanohydrination of

styrenes and aromatic alkanes whereas HfOTf-Mn is highly active in catalytic styrene carbonation via tandem epoxidation and CO₂ insertion (Figure 1). Spectroscopic and density functional theory (DFT) investigations were also performed to understand the mechanisms of these tandem catalytic transformations.

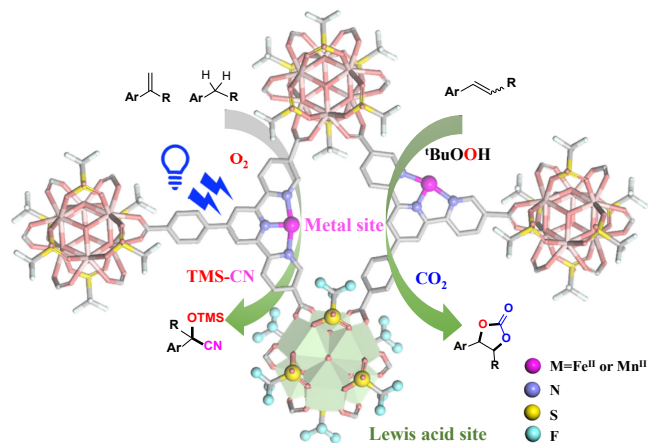


Figure 1. Bifunctional MOLs with Lewis acidic Hf₆ SBUs and TPY-M (M=Fe^{II} or Mn^{II}) ligands for tandem catalysis.

Results and Discussion

Synthesis and Characterization of HfOTf-Fe and HfOTf-Mn

Hf-TPY MOL was synthesized by heating a mixture of HfCl₄, H₃TPY, and formic acid in N,N-dimethylformamide (DMF) and water at 120 °C (Scheme S1).³¹ Hf-TPY was metalated with FeBr₂ and MnCl₂ to afford Hf-Fe and Hf-Mn MOLs, respectively. The formate capping groups in Hf-Fe and Hf-Mn were then completely replaced by OTf groups via a metathesis reaction with trimethylsilyl triflate (TMS-OTf) to afford HfOTf-Fe and HfOTf-Mn, respectively (Figure 2a and Scheme S2), with a formula of Hf₆(μ₃-O)₄(μ₃-OH)₄(OTf)₆[TPY-M(OTf)₂]₂ (M=Fe or Mn) as established by inductively coupled plasma-mass spectrometric analysis (ICP-MS) and ¹H and ¹⁹F NMR analysis of digested HfOTf-M (M=Fe or Mn) MOLs (Figure S1-4). These analyses gave an OTf to Hf ratio of 1.4:1, which is slightly lower than the expected 1.67:1 ratio based on the proposed formula. Hf-TPY was also treated with HCl (pH=1) to afford HfOH-TPY, which was then treated with

TMS-OTf to yield HfOTf-TPY. ^1H NMR study indicated the generation of 1.83 equiv of $(\text{Me}_3\text{Si})_2\text{O}$ with respect to Hf (Figure S5).

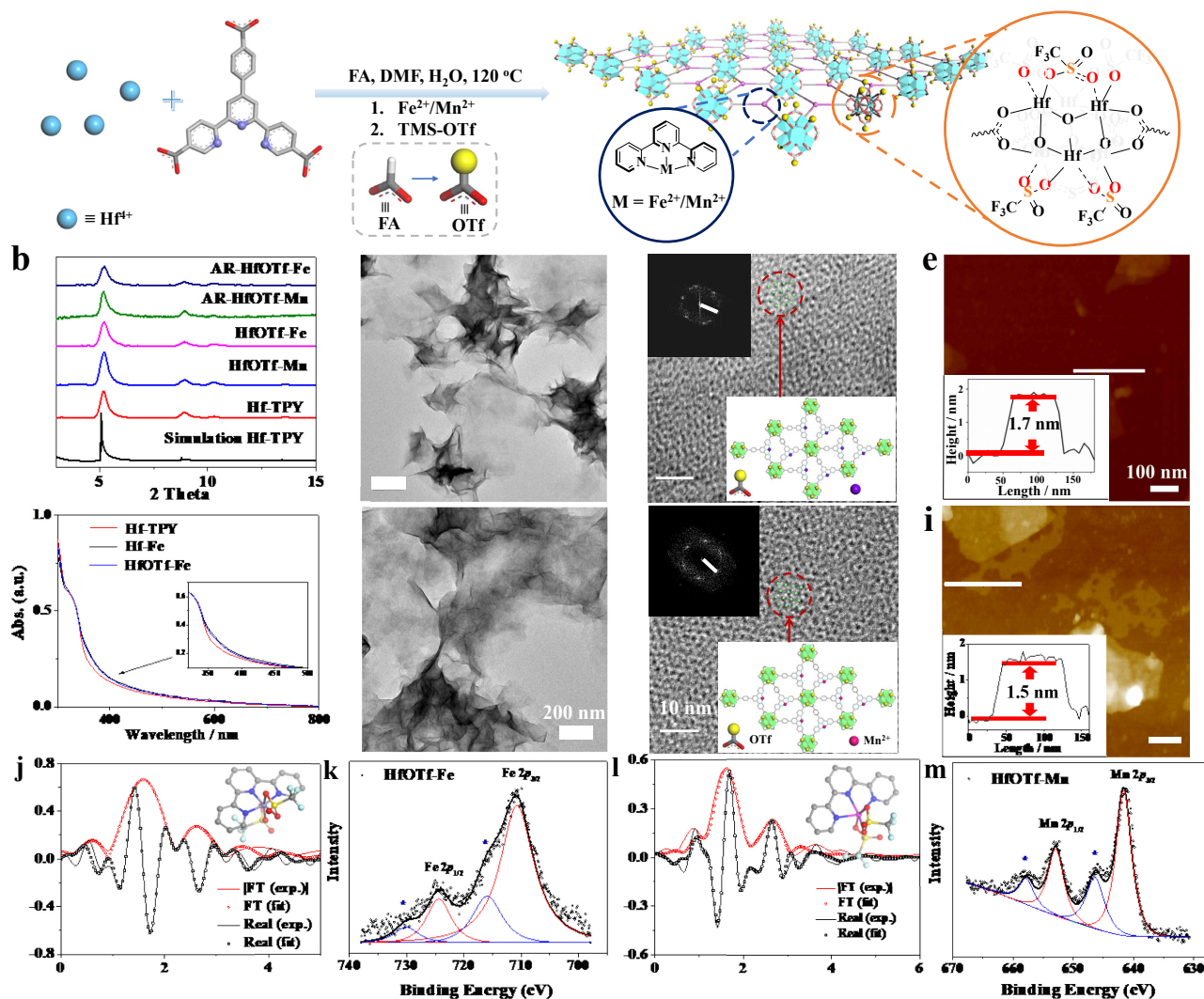


Figure 2. Synthesis and characterization of HfOTf-Fe and HfOTf-Mn MOLs. (a) Schematic showing the synthesis of HfOTf-Fe and HfOTf-Mn MOLs. (b) PXRD patterns of Hf-TPY, HfOTf-Mn, HfOTf-Fe, AR-HfOTf-Mn (after catalytic reaction), and AR-HfOTf-Fe (after catalytic reaction); TEM images of HfOTf-Fe (c) and HfOTf-Mn (g); HRTEM images and fast Fourier transform (FFT) patterns of AR-HfOTf-Fe (d) and AR-HfOTf-Mn (h); tapping-mode atomic-force microscope (AFM) topographic images and height profiles along the white lines of HfOTf-Fe (e) and HfOTf-Mn (i). UV-Vis spectra of $\text{H}_3\text{TPY-Fe}$ (black), Hf-TPY (red) and HfOTf-Fe (navy) (f). EXAFS fitting of HfOTf-Fe (j) and HfOTf-Mn (l); (k) Fe 2p XPS spectrum of HfOTf-Fe; (m) Mn 2p XPS spectrum of HfOTf-Mn. * in 2k and 2l represents the satellite peaks.

Thermogravimetric analysis (TGA) showed a weight loss of 50.4% for HfOTf-Fe at 220–600 °C, which matches the expected weight loss of 50.5% for the conversion of HfOTf-Fe to 6HfO_2 plus Fe_2O_3 . HfOTf-Mn showed a weight loss of 54.7% which is consistent with the expected weight loss of 54.6% for its conversion to 6HfO_2 plus Mn_2O_3 (Figure S6).

HfOTf-Fe and HfOTf-Mn retained the powder X-ray diffraction (PXRD) pattern of Hf-TPY that matched the simulated pattern based on the $(hk0)$ reflections characteristic of 2D MOL structures (Figure 2b). Transmission Electron Microscopy (TEM) images showed ultra-thin films of HfOTf-Fe (Figure 2c) and HfOTf-Mn (Figure 2g). Atomic force microscopy (AFM) measurements gave thicknesses of 1.7 and 1.5 nm for HfOTf-Fe and HfOTf-Mn, respectively (Figure 2e & 2i). UV-Vis

spectrum of HfOTf-Fe showed a tail extending to the visible wavelength, which covered the absorption peaks of $\text{TPY-Fe}^{\text{II}}$ (Figure 2f).

Lewis Acidity of HfOTf-Fe and HfOTf-Mn was probed by *N*-methylacridone (NMA) fluorescence.^{32–33} HfOTf-M ($\text{M}=\text{Fe}$ and Mn) was shown to be more Lewis acidic than HfOH-MOL and ZrOTf-M ($\text{M}=\text{Fe}$ and Mn). Free NMA has an emission maximum (λ_{max}) at 433.0 nm (Figure S7a). Upon coordination to HfOTf-Fe and HfOTf-Mn, the Hf-bound NMA displayed a λ_{max} at 472 nm (Figure S7a). This red-shift of NMA emission suggests comparable Lewis acidity between HfOTf-M ($\text{M}=\text{Fe}$ and Mn) and $\text{Sc}(\text{OTf})_3$.³³ In comparison, ZrOTf-M has slightly lower Lewis acidity than HfOTf-M, with a measured λ_{max} at 470 nm. The nontriflated HfOH-TPY only shifted the NMA

emission λ_{max} to 468 nm, suggesting lower Lewis acidity compared to HfOTf-M. The Lewis acidic sites of the MOL catalysts were further probed by FT-IR but no conclusive evidence was obtained due to the interference of TPY ligands (Figure S8). We also calculated adsorption of ammonia on the active metal sites of HfOTf-TPY and ZrOTf-TPY to characterize their Lewis acidity. Ammonia interaction energy is a well-established method for comparing Lewis acidity of different catalysts.³⁴ The optimized structures and binding energies are shown in Figure S7b-c. The N-Hf bond length in $\text{NH}_3\text{-HfOTf-TPY}$ (2.335 Å) is shorter than that in $\text{NH}_3\text{-ZrOTf-TPY}$ (2.343 Å). HfOTf-TPY also has a stronger ammonia adsorption with a ΔG of -9.97 kcal/mol compared that of ZrOTf-TPY (ΔG = -8.15 kcal/mol). These results indicate that HfOTf-TPY has stronger Lewis acidity than ZrOTf-TPY.³⁵

X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) were used to determine the Fe and Mn oxidation states in HfOTf-Fe and HfOTf-Mn. The XPS spectrum of HfOTf-Fe showed Fe 2p_{3/2} peak at 710.9 eV and Fe 2p_{1/2} peak at 724.5 eV (2p_{1/2}) along with their corresponding satellite peaks that are characteristic of the Fe²⁺ oxidation state (Figure 2k and Figure S10).³⁶ Similarly, HfOTf-Mn showed Mn 2p_{3/2} peak at 641.2 eV and Mn 2p_{1/2} peak at 653.0 eV along with their corresponding satellite peaks that are characteristic of the Mn²⁺ oxidation state (Figure 2m and Figure S10).³⁷ The assignment of Fe²⁺ and Mn²⁺ oxidation states in HfOTf-M were supported by XANES analyses: HfOTf-Fe showed a similar pre-edge peak at 7114.0 eV to Fe(OTf)₂ (7114.2 eV, Figure S9a), whereas HfOTf-Mn showed a slightly weaker feature at ~6540 eV than MnCl₂ (Figure S9b).³⁸⁻³⁹ Extended X-ray absorption fine structure (EXAFS) fitting indicated the coordination of Fe²⁺ and Mn²⁺ to the three N atoms of TPY and two OTf ligands in HfOTf-Fe and HfOTf-Mn, respectively (Figure 2j and 2l, Table S1 and S2).

HfOTf-Fe catalyzed tandem cyanohydration of hydrocarbons with O₂

Cyanohydrins are of great synthetic value as they can be elaborated into different functional intermediates.⁴⁰ While aldehydes,⁴¹ ketones,⁴¹ and acetals⁴² can be readily converted to cyanohydrins, direct cyanohydration of hydrocarbons remains underdeveloped.⁴³ We became interested in developing a tandem process for direct cyanohydration of hydrocarbons using a combination of transition metal and Lewis acid catalysts. We hypothesized that the Fe centers in HfOTf-Fe could catalyze the oxidation of hydrocarbons to generate the corresponding ketones while the Lewis acidic SBUs could catalyze silylcyanation of the ketone intermediates.

Under blue LED irradiation and oxygen atmosphere, HfOTf-Fe competently catalyzed tandem transformations of styrenes to give trimethylsiloxybenzyl cyanide derivatives. Upon silica gel column chromatography, the trimethylsiloxybenzyl cyanide derivatives were hydrolyzed, and the corresponding α -hydroxybenzyl cyanide derivatives were obtained in up to 95% isolated yields with turnover numbers of up to 190 (Table 1). α -Methylstyrenes bearing different functional groups of -F, -Cl, -Me and -CF₃ were well tolerated with no obvious electronic effects observed. 2-Isopropenylnaphthalene and α -ethylstyrene worked well to afford **6c** and **7c** in 70% and 78% isolated yields, respectively. 2-Bromostyrene also underwent the tandem transformation effectively to produce **8c** in 86% yield. This tandem reaction did not proceed in the absence of light (Scheme S3a) or light sources with longer wavelengths (Scheme S3d). The

control catalyst ZrOTf-Fe only provided 45% yield (Scheme S3e), consistent with its lower Lewis acidity than HfOTf-Fe.⁴⁴ Mixed catalysts Hf-Fe and ZrOTf-BTC produced **1c** in 26% yield (Scheme S3f), suggesting that the proximity of Lewis acid and Mn²⁺/Fe²⁺ active sites is important for the tandem reactions.

HfOTf-Fe was successfully used to catalyze tandem silylcyanation of prop-1-en-2-ylbenzene below 25% conversion in three times (Figure S14a), indicating recycle and reuse of the HfOTf-Fe catalyst. After the catalytic reaction, only trace amount of OTf was detected in the supernatant but these OTf ligands were quantitatively detected in the digested solution of the recovered catalyst AR-HfOTf-Fe (Figure S13). PXRD studies indicated that the catalyst recovered from the reactions, AR-HfOTf-Fe, maintained the framework structure of Hf-TPY (Figure 2b). High resolution TEM (HRTEM) image of AR-HfOTf-Fe exhibited clear lattices with dark spots corresponding to Hf₆ clusters, supporting that the Hf-TPY structure was maintained. The Fourier transforms of the HRTEM image gave a hexagonal pattern of the reciprocal lattice with a d(100) spacing of 1.7 nm, which corresponds to an inter-SBU distance of 2.0 nm in the structure model (Figure 2d).

Table 1. HfOTf-Fe catalyzed cyanohydration via tandem oxidation of hydrocarbons and trimethylsilylcyanation of the ketone intermediates^a

 1c (90%, 180)	 2c (89%, 178)	 3c (91%, 182)	 4c (95%, 190)
 5c (70%, 140)	 6c (70%, 140)	 7c (78%, 156)	 8c (86%, 172)

 1c (81%, 162)	 4c (77%, 154)	 7c (76%, 152)	 9c (85%, 170)
 10c (72%, 144)	 11c (74%, 148)	 12c (70%, 140)	

^aReactions were conducted at 0.1 mmol scale with yields of isolated products.

Interestingly, HfOTf-Fe effectively catalyzed the oxidation of aromatic alkanes with O₂ upon light irradiation, followed by silylcyanation with TMSCN to give the corresponding trimethylsiloxybenzyl cyanide or α -hydroxybenzyl cyanide products (after column chromatography). Ethyl- and propyl-arenes underwent tandem transformations to afford **1c**, **4c** and **7c** in 81%, 77%, and 76% isolated yields, respectively, after silica gel column chromatography. Cyclic indan and fluorene substrates worked well to afford products **10c** and **11c** in 72% and 74% yields, respectively, after flash column chromatography with diatomite (Table 1). Substrates containing thiophene and

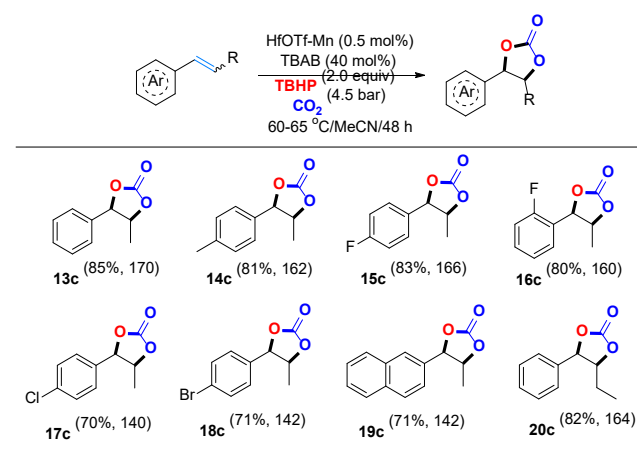
naphthalene rings also underwent tandem transformations, leading to **9c** and **12c** in 85% and 70% yields, respectively, after flash column chromatography with diatomite (Table 1). This represents the first example of efficient synthesis of cyanohydrins from aromatic alkanes via challenging sp^3 C-H oxidation (Table S3). HfOTf-TPY did not catalyze the cyanohydration of ethylbenzene (Scheme S3c) but converted phenylacetaldehyde into **1c** in >99% yield (Scheme S3g). On the other hand, Hf-TPY-Fe(OTf)₂ only catalyzed C-H oxidation of ethylbenzene but not the subsequent silylcyanation (Scheme S3b).

Hf-OTf-Mn-MOL catalyzed tandem styrene carbonation with CO₂

We next examined the use of HfOTf-Mn in tandem styrene epoxidation and CO₂ insertion to form styrene carbonate. Direct incorporation of CO₂, a greenhouse gas,⁴⁵ as a C1 building block for the synthesis of high-value chemicals is of great interest.⁴⁶ While metal-catalyzed insertion of CO₂ into epoxides provides an efficient synthetic route to cyclic organic carbonates (COCs),⁴⁷⁻⁴⁸ efficient synthesis of COCs directly from alkenes remains a challenge.⁴⁹⁻⁵⁰ We carried out one-pot synthesis of styrene carbonates from styrenes and CO₂ using HfOTf-Mn as a dual catalyst.

Under CO₂ environment (4.5 bar), treatment of styrenes, *tert*-butyl hydroperoxide (TBHP), and tetra-*n*-butylammonium bromide (TBAB) in the presence of HfOTf-Mn (0.5 mol%) in dry CH₃CN at 60–65 °C for 48 h gave styrene carbonates in 70% to 85% isolated yields, with turnover up to 190 (Table 2). Styrenes bearing halo groups including -F, -Cl, and -Br were compatible. 2-Vinyl naphthalene underwent the tandem transformation smoothly to generate **19c** in 71% yield. The use of β -ethylstyrene as the feedstock afforded **20c** in 82% isolated yield. HfOTf-Mn was recycled and used in three consecutive reactions of 1-methyl-4-(prop-1-en-1-yl)benzene without a significant drop in catalytic activity (Figure S14b). PXRD and HRTEM studies indicated that AR-HfOTf-Mn maintained the framework structure of Hf-TPY (Figure 2b and 2h).

Table 2. HfOTf-Mn catalyzed tandem epoxidation and CO₂ insertion of styrenes



Hf-TPY-Mn(OTf)₂ with only Mn catalytic centers and HfOTf-TPY with only Lewis acid sites were also prepared as control catalysts. HfOTf-TPY afforded only a trace amount of **13c** (Scheme S4a), while Hf-TPY-Mn(OTf)₂ generated **13c** in 37% yield (Scheme S4b). These control experiments demonstrated the synergistic actions of both metal and Lewis acid catalysts in MOL-catalyzed tandem transformations. Catalytic reaction

with *trans*-stilbene as substrate produced the stilbene oxide intermediate in 27% yield (Scheme S4c), which supports the tandem catalytic pathway.

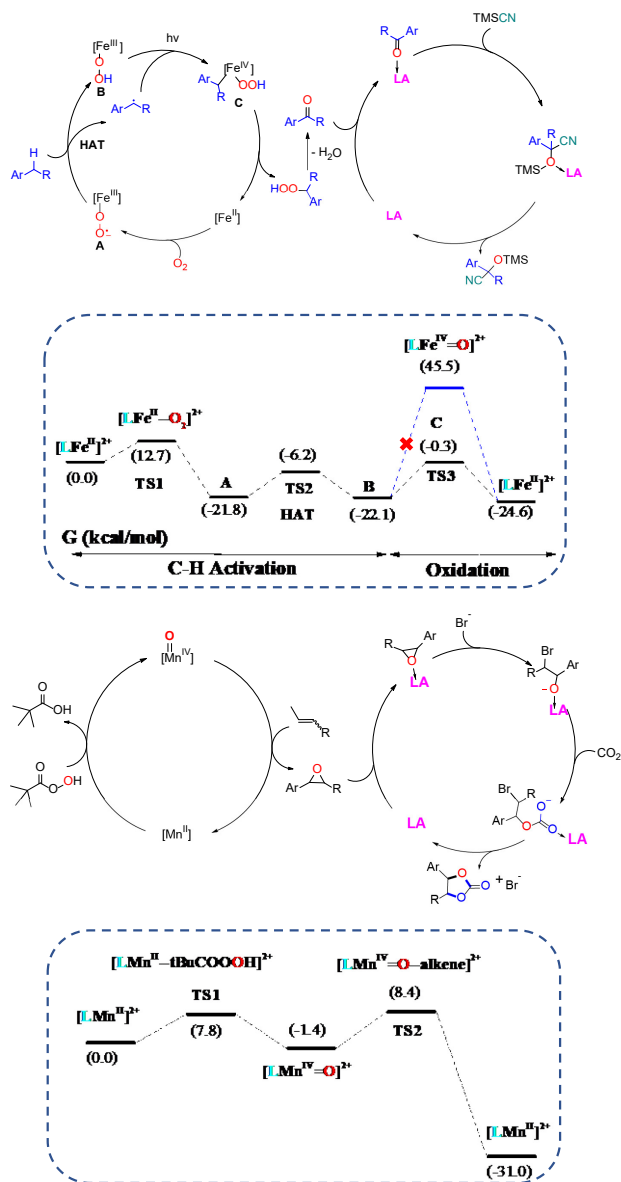
Mechanistic studies of Hf-OTf-Fe and Hf-OTf-Mn catalyzed tandem reactions

Scheme 1a shows a plausible mechanism for HfOTf-Fe catalyzed transformation of aromatic alkanes to cyanohydrins via tandem oxidation with O₂ and silylcyanation. DFT calculations with the PBE functional were carried out to understand C-H oxidation with O₂.⁵¹ The oxidation reaction consists of C-H activation and subsequent hydroperoxidation. The C-H activation is initiated through hydrogen atom transfer (HAT) with an Fe^{III}-superoxo species ([LFe^{III}-OO•]²⁺), which may result from the electron transfer (ET) between O₂ and TPY-Fe^{II} ([LFe^{II}]²⁺) species through the transition state **TS1**.⁵² This process is akin to O₂ activation by metalloenzymes such as nonheme iron oxygenases and copper-containing oxygenases and oxidases.⁵³ The energy barrier for this process was calculated to be 12.7 kcal/mol. The HAT of LFe^{III}-OO• with C-H bond forms Fe^{III}-hydroperoxo species ([LFe^{III}-OOH]²⁺) through the LFe^{III}-(OO•)(-Ar) species (**TS2**) and the open-shell carbon radical species. The energy barrier of this process is endergonic by 15.6 kcal/mol.

In the oxidation step, the carbon radical is photochemically oxidized by LFe^{III}-OOH. Upon light irradiation, LFe^{III}-OOH is excited and undergoes MLCT to give L•-Fe^{IV}-OOH. Nucleophilic carbon radical attack on the Fe^{IV} center followed by the back electron transfer from the L• radical anion to the Fe center forms the LFe^{IV}(-Ar)(-OOH) species (**TS3**), which possesses a high spin Fe^{IV} (S=2) center by natural bond order (NBO) analysis (Figure S11). The subsequent reductive elimination affords 1-hydroperoxyethyl-arene and the Fe^{II} species to finish the catalytic cycle which is exergonic by 24.3 kcal/mol. We rule out the involvement of the Fe^{IV}=O intermediate because this pathway has a much higher energy barrier (67.6 kcal/mol) than **TS2** (21.8 kcal/mol).

These steps were further confirmed by the X-band electron paramagnetic resonance (EPR) spectroscopy. The starting high-spin HfOTf-Fe complex was ESR-silent with S=2. After the addition of oxygen, the ESR spectrum showed a rhombic peak with g=5.02, g=4.23 and g=2.04, typical of high-spin Fe^{III} centers with S=5/2.⁵⁴⁻⁵⁵ The ESR signal retained after styrene was added, suggesting that the catalyst center was still a high-spin Fe^{III} center. With light irradiation, the ESR signal of Fe^{III} species disappeared (Figure S15), consistent with the oxidation proposal. After light irradiation, the reaction turnover occurred to form ESR-silent Fe^{IV} and Fe^{II} species.

Finally, 1-hydroperoxyethyl-arene is converted to the corresponding ketone,⁴³ which undergoes silylcyanation at the Lewis acid site to afford the cyanohydrin product.



Scheme 1. (a) Proposed mechanism for cyanohydration of aromatic alkanes via C-H oxidation with O₂ (top) and free energy profiles for HfOTf-Fe catalyzed benzylic C-H bond oxidation of ethylbenzene (bottom). (b) Proposed mechanism of tandem styrene carbonation catalyzed by HfOTf-Mn (top) and free energy profiles for HfOTf-Mn catalyzed styrene epoxidation (bottom).

The plausible mechanism for the one-pot synthesis of styrene carbonates from styrenes and CO₂ is given in the top of Scheme 1b and DFT calculation of the epoxidation step is shown in the bottom of Scheme 1b. It involves the in-situ formation of styrene oxide from the epoxidation of styrene catalyzed by the TPY-Mn^{IV} center in HfOTf-Mn in the presence of TBHP as an oxidant, the energy barrier was only 7.8 kcal/mol. The Lewis acid site effectively activates the styrene oxide due to its proximity (8.3 Å) to the metal center (Figure S12). Nucleophilic attack of the Br⁻ anion of TBAB leads to the ring opening of the epoxide and formation of nucleophilic oxygen anion. Subsequent insertion of CO₂ and the intramolecular ring-closure reaction afford styrene carbonate. An incoming styrene oxide releases the styrene carbonate product and restarts the catalytic cycle on the right.

Conclusion

In this work, we designed two bifunctional MOLs for highly effective tandem catalytic reactions. HfOTf-Fe converted hydrocarbons into cyanohydrins via tandem oxidation with O₂ and silylcyanation whereas HfOTf-Mn transformed styrenes into styrene carbonates via tandem epoxidation and CO₂ insertion by combined actions of adjacent active sites on the MOLs. Our work represents the first example of cyanohydrin synthesis from aromatic alkanes. DFT calculations showed the oxidation of aromatic alkanes went through a high spin Fe^{IV}-hydropreox-ide transition state with an energy barrier of 21.8 kcal/mol. This work demonstrates the potential of building multifunctional MOLs for the synthesis of fine chemicals via tandem catalysis.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis and characterization of Hf-TPY, HfOTf-Fe, and HfOTf-Mn, synergistically catalytic reactions, and mechanistic study (PDF)

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Notes

The authors declare no competing financial interests.

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TOC Graphic:

