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## Research Update: A hafnium-based metal-organic framework as a catalyst for regioselective ring-opening of epoxides with a mild hydride source

Casey J. Stephenson,<sup>1</sup> M. Hassan Beyzavi,<sup>1</sup> Rachel C. Klet,<sup>1</sup> Joseph T. Hupp,<sup>1,a</sup> and Omar K. Farha<sup>1,2,a</sup> <sup>1</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA <sup>2</sup>Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

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Reaction of styrene oxide with sodium cyanoborohydride and a catalytic amount of Hf-NU-1000 yields the anti-Markovnikov product, 2-phenylethanol, with over 98% regioselectivity. On the other hand, propylene oxide is ring opened in a Markovnikov fashion to form 2-propanol with 95% regioselectivity. Both styrene oxide and propylene oxide failed to react with sodium cyanoborohydride without the addition of Hf-NU-1000 indicative of the crucial role of Hf-NU-1000 as a catalyst in this reaction. To the best of our knowledge, this is the first report of the use of a metal-organic framework material as a catalyst for ring-opening of epoxides with hydrides. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4898359]

Metal-organic framework (MOF)<sup>1–4</sup> chemistry offers a bottom-up approach to the synthesis of new heterogeneous catalysts.<sup>5–7</sup> These crystalline, porous materials are composed of organic linkers with inorganic nodes. They offer almost endless synthetic tunability, the potential for large porosities,<sup>8–10</sup> and the prospect of well-defined, readily accessible catalytic sites. New catalytic MOFs can be synthesized: (a) *de novo*, (b) via post-synthetic modification of existing MOFs, or (c) solvent-assisted linker exchange, or other building-block-replacement chemistry.<sup>11–15</sup> There are two general approaches to engendering catalytic responses from MOFs: one is to incorporate a catalytic site into the linkers of the MOF,<sup>11,16,17</sup> while the other is to take advantage of open (or labile) metal-ion-coordination sites present at inorganic nodes—either by design or as a consequence of MOF structural defects such as missing linkers.<sup>18,19</sup>

Recently, we reported a Hf<sub>6</sub> based analogue of NU-1000,<sup>20</sup> Hf-NU-1000.<sup>21</sup> This MOF consists of eight-coordinate Hf atoms in a Hf<sub>6</sub> cluster, Hf<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>(OH)<sub>4</sub>(OH)<sub>2</sub>)<sub>4</sub>, linked to other clusters by 1,3,6,8-tetrakis(*p*-benzoate)pyrene (TBAPy<sup>4-</sup>). Together they define a 3-dimensional coordination polymer featuring large (ca. 31 Å diameter), one-dimensional channels (Figure 1). The combination of Brønsted acidic sites in conjunction with high surface area and large pore apertures led us to investigate Hf-NU-1000 as an acid catalyst for the cycloaddition of carbon dioxide to epoxides. The regioselective and enantioretentive epoxide activation in a solvolytic opening of epoxides with trimethylsilyl azide and methanol was also investigated. These reactions proceeded in high yield and with excellent regioselectivity regioselectivity.<sup>21</sup>

Ring-opening of epoxides with hydrides is one of the most fundamental reactions in organic chemistry and generally proceeds via an  $S_N 2$  type mechanism.<sup>22</sup> In the case of asymmetric molecules, hydride attack typically occurs at the most sterically accessible site to form the Markovnikov

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<sup>&</sup>lt;sup>a</sup>Authors to whom correspondence should be addressed. Electronic addresses: j-hupp@northwestern.edu and o-farha@northwestern.edu



FIG. 1. Molecular and structural features of Hf-NU-1000: (a)  $H_4$ TBAPy; (b) packing in the xy plane of Hf-NU-1000; (c) packing along z axis; (d)  $Hf_6$  core; (e) dehydrated-Hf-NU-1000 core.

product.<sup>23–25</sup> Anti-Markovnikov products of epoxide ring-opening, such as primary alcohols, are critical to the chemical and pharmaceutical industry and significant effort has gone into developing reagents and methodologies to obtain regioselective products.<sup>22</sup> With metal hydrides, Lewis acids, such as transition-metals,<sup>26</sup> AlCl<sub>3</sub>,<sup>27</sup> or BH<sub>3</sub>,<sup>28</sup> are added to the reaction to shift regioselectivity to the anti-Markovnikov product. While extremely effective, these reagents are added in stoichiometric amounts and, in most cases, lack functional-group tolerance.

Since Hf-NU-1000 acted as such a remarkable catalyst for regioselective ring-openings of epoxides with other mentioned nucleophiles,<sup>21</sup> we sought to use Hf-NU-1000 as a catalyst to ring-open epoxides with hydrides to form 1° alcohols. Since a strong hydride would preferentially react with the acidic protons on the  $Hf_6$  node, a mild hydride reagent is needed to prevent non-productive formation of hydrogen. Unlike other more reactive hydrides, cyanoborohydride is stable in water at pH 7 and above, but is unreactive toward epoxides.<sup>29</sup> Indeed, ring-opening of epoxides with cyanoborohydride has been carried out at low pHs (pH 3-4), by the addition of BF<sub>3</sub> · etherate,<sup>30</sup> ZSM-5,<sup>31</sup> or by carrying out the reaction in neat acetic acid.<sup>32</sup> Therefore, sodium cyanoborohydride was selected as our hydride source for the ring-opening of styrene oxide. Combining four equivalents of sodium cyanoborohydride with styrene oxide at room temperature in the presence of a catalytic amount (10 mol. %) of Hf-NU-1000 produces the anti-Markovnikov product, 2-phenylenthanol, in 60% yield with over 98% selectivity (Table I, entry 1). (See Figure 2 for a proposed mechanism.) In the absence of Hf-NU-1000, no product was obtained (Table I, entry 2) indicating that Hf-NU-1000 is a necessary component of the reaction. The catalyst was reused three times without decrease in activity or loss of crystallinity as shown by powder X-ray diffraction (PXRD) measurements (Figure S6).<sup>33</sup> To gauge the importance of the Brønsted acid sites in this reaction, we also investigated a dehydrated form of



SCHEME 1. Ring-opening of styrene oxide (top) and propylene oxide (bottom) catalyzed by Hf-NU-1000.

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Entry <sup>a</sup>	Catalyst	Hydride	Substrate	Product yield (A:B) (%)
1	Hf-NU-1000	NaBH <sub>3</sub> CN	Styrene oxide	60 (98:2) <sup>b</sup>
2		NaBH <sub>3</sub> CN	Styrene oxide	0 <sup>b</sup>
3	Hf-NU-1000-dehydrated <sup>c</sup>	NaBH <sub>3</sub> CN	Styrene oxide	0 <sup>b</sup>
4 <sup>d</sup>	Hf-NU-1000	NaBH <sub>3</sub> CN	Styrene oxide	40 (48:52) <sup>e</sup>
5	Hf-NU-1000	NaBH <sub>3</sub> CN	Propylene oxide	65 (5:95) <sup>b</sup>
6		NaBH <sub>3</sub> CN	Propylene oxide	0 <sup>b</sup>

TABLE I. Results from the Hf-NU-1000 catalyzed reactions of epoxides with various hydride sources.

<sup>a</sup>General reaction conditions: 0.2 mmol substrate, 0.8 mmol hydride, and 0.02 mmol catalyst were stirred for 24 h at room temperature under a  $N_2$  atmosphere in 1.9 ml dry tetrahydrofuran (THF).

<sup>b</sup>Determined by <sup>1</sup>H NMR.

<sup>c</sup>See Ref. 21 for details of its preparation and characterization.

<sup>d</sup>Carried out in refluxing tetrahydrofuran.

<sup>e</sup>Determined by GC-TOF.

the MOF, Hf-NU-1000-dehydrated (Table I, entry 3). The dehydrated MOF is structurally identical to Hf-NU-1000 with the exception that there are no metal bound  $H_2O$  or OH molecules; only linker carboxylate groups and bridging oxo ligands are found at the Hf core. With the dehydrated MOF as the candidate catalyst, no conversion of styrene oxide was obtained, thereby illustrating the importance of Brønsted acid sites for activation of cyanoborohydride.

A dramatic loss in both yield and selectivity occurred when the reaction was carried out in refluxing tetrahydrofuran (Table I, entry 4). We attribute this loss to the deprotonation of Hf-bound acid sites by the hydride to generate  $H_2$ . Therefore, a <sup>1</sup>H NMR experiment was conducted to assess the stability of Hf-NU-1000 under conditions that simulated reaction conditions in the presence of sodium cyanoborohydride, both at room temperature and at elevated temperatures. Under a  $N_2$ 



FIG. 2. Proposed catalytic cycle for ring-opening of styrene oxide with sodium cyanoborohydride, catalyzed by Hf-NU-1000. The epoxide is activated by H-bonding with the acidic protons of the  $Hf_6$  core. The hydride attacks the benzylic carbon in a  $S_N2$  fashion. The alkoxide then attacks BH<sub>2</sub>CN moiety. The catalytic cycle is complete when a new molecule of styrene oxide H-bonds with Hf-NU-1000. For clarity, the bottom third of the hafnium core and the ligand carboxylate groups have been omitted.

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We also investigated the ring-opening of propylene oxide (Table I, entries 5 and 6). A yield similar to that for styrene oxide was obtained for propylene oxide, but the regioselectivity of the reaction was reversed, with 2-propanol as the only product. Based on literature precedent<sup>30</sup> and our results with styrene oxide, we expected instead to see 1-propanol as the dominant product. This is an intriguing result since cyanoborohydride is generally unreactive to epoxides; Hf-NU-1000 clearly is required for the ring opening to occur. Identification and validation of the mechanism responsible for exclusive formation of 2-propanol is a focus of ongoing work.

In conclusion, Hf-NU-1000 serves as a catalyst for ring-opening epoxides with sodium cyanoborohydride. Although the product yields are modest, the regioselectivities obtained for both substrates are excellent. Hf-coordinated Brønsted acid groups appear to be important to the catalytic function of Hf-NU-1000, as a dehydrated version of the MOF is ineffective as a catalyst. Hf-NU-1000 is reusable as a catalyst for ring-opening, with no loss of activity and no evidence for structural deterioration after three cycles of reuse. These promising results warrant further investigation of MOFs as catalysts for hydride based ring-opening reactions and related reactions.

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- <sup>1</sup> O. K. Farha and J. T. Hupp, Acc. Chem. Res. 43, 1166–1175 (2010).
- <sup>2</sup> H.-C. Zhou, J. R. Long, and O. M. Yaghi, Chem. Rev. 112, 673-674 (2012).
- <sup>3</sup> J. R. Long and O. M. Yaghi, Chem. Soc. Rev. **38**, 1213–1214 (2009).
- <sup>4</sup> H. Furukawa, K. E. Cordova, M. O'Keeffe, and O. M. Yaghi, Science **341**, 1230444-1–1230444-12 (2013).
- <sup>5</sup> J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, and J. T. Hupp, Chem. Soc. Rev. 38, 1450–1459 (2009).
- <sup>6</sup> M. Zhao, S. Ou, and C.-D. Wu, Acc. Chem. Res. 47, 1199–1207 (2014).
- <sup>7</sup> D. Farrusseng, S. Aguado, and C. Pinel, Angew. Chem., Int. Ed. 48, 7502–7513 (2009).
- <sup>8</sup> H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim, and O. M. Yaghi, Science **329**, 424–428 (2010).
- <sup>9</sup> D. Fairen-Jimenez, Y. J. Colon, O. K. Farha, Y.-S. Bae, J. T. Hupp, and R. Q. Snurr, Chem. Commun. **48**, 10496–10498 (2012).
- <sup>10</sup> O. K. Farha, A. Özgür Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr, and J. T. Hupp, Nat. Chem. 2, 944–948 (2010).
- <sup>11</sup> A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp, and S. T. Nguyen, J. Am. Chem. Soc. **133**, 13252–13255 (2011).
- <sup>12</sup> M. Lalonde, W. Bury, O. Karagiaridi, Z. Brown, J. T. Hupp, and O. K. Farha, J. Mat. Chem. A **1**, 5453–5468 (2013).
- <sup>13</sup> P. Deria, J. E. Mondloch, O. Karagiaridi, W. Bury, J. T. Hupp, and O. K. Farha, Chem. Soc. Rev. 43, 5896–5912 (2014).
- <sup>14</sup> J. D. Evans, C. J. Sumby, and C. J. Doonan, Chem. Soc. Rev. **43**, 5933–5951 (2014).
- <sup>15</sup> Y. Han, J.-R. Li, Y. Xie, and G. Guo, Chem. Soc. Rev. **43**, 5952–5981 (2014).
- <sup>16</sup> O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen, and J. T. Hupp, J. Am. Chem. Soc. 133, 5652–5655 (2011).
- <sup>17</sup> L. Ma, J. M. Falkowski, C. Abney, and W. Lin, Nat. Chem. 2, 838–846 (2010).
- <sup>18</sup> F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, and D. E. De Vos, J. Am. Chem. Soc. **135**, 11465–11468 (2013).
- <sup>19</sup> A. Dhakshinamoorthy, M. Alvaro, and H. Garcia, Chem. Eur. J. 16, 8530-8536 (2010).
- <sup>20</sup> J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha, and J. T. Hupp, J. Am. Chem. Soc. **135**, 10294–10297 (2013).
- <sup>21</sup> M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp, and O. K. Farha, "A Hafnium-Based Metal–Organic Framework as an Efficient and Multifunctional Catalyst for Facile CO<sub>2</sub> Fixation and Regioselective and Enantioretentive Epoxide Activation," J. Am. Chem. Soc. (in press).
- <sup>22</sup> S. Murai, T. Murai, and S. Kato, "Reduction of epoxides," in *Comprehensive Organic Synthesis*, 5th ed., edited by B. M. Trost and I. Fleming (Elsevier, Oxford, UK, 1993), Vol. 8, pp. 871–893.
- <sup>23</sup> J. J. Eisch, Z. R. Liu, and M. Singh, J. Org. Chem. 57, 1618–1621 (1992).
- <sup>24</sup> E. L. Eliel and D. W. Delmonte, J. Am. Chem. Soc. 78, 3226–3226 (1956).
- <sup>25</sup> E. L. Eliel and D. W. Delmonte, J. Am. Chem. Soc. **80**, 1744–1752 (1958).

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- <sup>26</sup> S. Kano, Y. Tanaka, E. Sugino, and S. Hibino, Synthesis **1980**, 695–697 (1980).

- <sup>27</sup> H. C. Brown and B. C. S. Rao, J. Am. Chem. Soc. **78**, 2582–2588 (1956).
  <sup>28</sup> H. C. Brown and N. M. Yoon, J. Am. Chem. Soc. **79**, 2686–2688 (1968).
  <sup>29</sup> R. O. Hutchins, D. Kandasamy, C. A. Maryanoff, D. Masilamani, and B. E. Maryanoff, J. Org. Chem. **42**, 82–91 (1977).
  <sup>30</sup> R. O. Hutchins, I. M. Taffer, and W. Burgoyne, J. Org. Chem. **46**, 5214–5215 (1981).
- <sup>31</sup> A. Gupta and Y. D. Vankar, Tetrahedron Lett. **40**, 1369–1372 (1999).
- <sup>32</sup> M. D. Chappell, S. J. Stachel, C. B. Lee, and S. J. Danishefsky, Org. Lett. 2, 1633–1636 (2000).
  <sup>33</sup> See supplementary material at http://dx.doi.org/10.1063/1.4898359 for details of the experimental and spectra (NMR, GC-TOF, and PXRD).