

Selective Dimerization of Propylene with Ni-MFU-4l

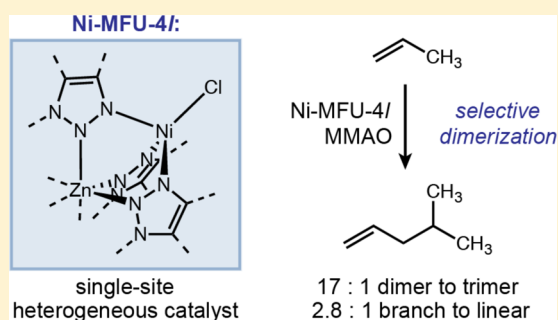
Robert J. Comito,[†] Eric D. Metzger,[†] Zhenwei Wu,[‡] Guanghui Zhang,[‡] Christopher H. Hendon,[†] Jeffrey T. Miller,[‡] and Mircea Dinca^{*,†}

[†]Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

[‡]Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, Indiana 47907, United States

Supporting Information

ABSTRACT: We report the selective dimerization of propylene to branched hexenes using Ni-MFU-4l, a solid catalyst prepared by cation exchange. Analysis of the resulting product distribution demonstrates that the selectivity arises from 2,1-insertion and slow product reinsertion, mechanistic features reproduced by a molecular nickel tris-pyrazolylborate catalyst. Characterization of Ni-MFU-4l by X-ray absorption spectroscopy provides evidence for discrete, tris-pyrazolylborate-like coordination of nickel, underscoring the small-molecule analogy that can be made at metal–organic framework nodes.



The nodes of metal–organic frameworks (MOFs) represent promising targets for industrially significant single-site heterogeneous catalysis. These secondary building units (SBUs) are often capable of cation exchange with preservation of their local coordination structure,^{1,2} offering a predictable strategy for installing a discrete active site in a solid, high-surface-area medium. Along these lines, we recently reported the selective dimerization of ethylene to 1-butene using Ni-MFU-4l (**1**),³ prepared by replacing Zn²⁺ ions with Ni²⁺ in Zn₅Cl₄(BTDD)₃ (MFU-4l, H₂BTDD = bis(1*H*-1,2,3-triazolo[4,5-*b*][4',5'-*i*])dibenzo[1,4]dioxin)).⁴ The cation exchange, performed by soaking MFU-4l in a Ni²⁺ solution at room temperature, preserves the crystallinity and high surface area of the parent material, suggesting that Ni²⁺ has been incorporated into an SBU with an otherwise preserved structure.⁴

Here, we evaluate **1** as a heterogeneous catalyst for the selective dimerization of propylene, a reaction for which molecular complexes provide the best chain selectivity and regioselectivity.^{5–7} Industrially, this process continues to rely on soluble nickel catalysts, despite the large reactor volumes and challenging catalyst recovery associated with homogeneous catalysis.^{8–11} We reasoned that Ni-MFU-4l would be a selective catalyst for this reaction on the basis of the proposed structural analogy between **1** and molecular tris-pyrazolylborate (Tp) complexes, given the selective olefin dimerization activity of catalysts such as Tp^{Mes}NiCl (**2**).¹² Because MFU-4l coordinates Zn²⁺ tetrahedrally with three azolate nitrogens, it serves as a good template for scorpionate-like coordination of Ni²⁺ ions, installed through cation exchange (Figure 1).¹³ Indeed, computational modeling of Ni-MFU-4l within the Kohn–Sham DFT construct (DFT-1, Figure 1) and comparison of the

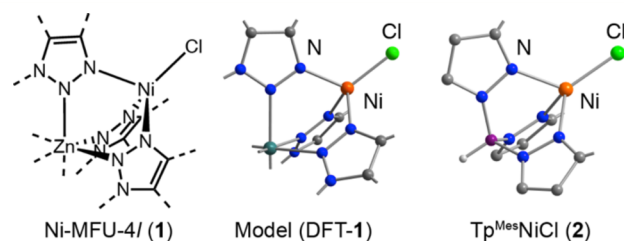


Figure 1. Structural analogy between Ni-MFU-4l and Tp^{Mes}NiCl (structures abbreviated for clarity).

model with the reported crystal structure of scorpionate **2** confirmed a close structural analogy between **1** and **2** (Table S3.1 in the Supporting Information): both feature a pseudotetrahedral arrangement of three nitrogen atoms and one chloride. The most significant difference is a slightly wider bite angle for DFT-1, with $\angle\text{N–Ni–N} = 97.06^\circ$ versus 92.88° for **2**. Notably, the porous structure of MFU-4l is well preserved in DFT-1 (Figure S3.1 in the Supporting Information).

To verify the Ni²⁺ coordination environment, **1** was examined by X-ray absorption spectroscopy (XAS). The XAS spectra of Tp₂Ni and anhydrous NiCl₂ were also collected for comparison. The edge energy obtained for Ni-MFU-4l agrees well with both of these standards (Table S2 in the Supporting Information), consistent with a Ni(II) oxidation state in **1**. Furthermore, Ni-MFU-4l displays a more intense pre-edge feature in comparison to either NiCl₂ or Tp₂Ni, consistent with

Received: March 7, 2017

Published: April 25, 2017

a lower-symmetry, pseudotetrahedral coordination environment (Figure S4.2 in the Supporting Information). Fitting the X-ray absorption fine structure (EXAFS) data resulted in three Ni–N bonds (1.99 Å, Table S4.2 in the Supporting Information) and one Ni–Cl bond (2.14 Å), similar in length to those of DFT-1 (1.95 and 2.12 Å, respectively) (Table 1).

Table 1. Fitting Results of the EXAFS Spectra^a

sample	scattering pair	coordination no.	bond length (Å)	σ^2 (Å ²)
Tp ₂ Ni	Ni–N	6	2.06	0.006
NiCl ₂	Ni–Cl	6	2.40	0.009
Ni-MFU-4l	Ni–N	3	1.99	0.006
	Ni–Cl	1	2.14	0.003

^aThe average error in bond length is 0.01 Å and in σ^2 is 0.002 Å². The fitting ranges for Tp₂Ni and Ni-MFU-4l are $\Delta k = 3.0\text{--}11.0 \text{ \AA}^{-1}$ and $\Delta R = 1.0\text{--}2.0 \text{ \AA}$. For NiCl₂, the ranges are $\Delta k = 3.0\text{--}10.0 \text{ \AA}^{-1}$ and $\Delta R = 1.4\text{--}2.4 \text{ \AA}$.

Fitting a different coordination number and a different combination of scattering atoms both gave significantly worse fits, allowing us to rule out other potential coordination modes for Ni²⁺ in **1**.

The competence of **1** and **2** as propylene dimerization catalysts was evaluated in the presence of modified methylaluminoxane-12 (MMAO-12) and 6 bar of applied propylene pressure, under slurry-phase and semibatch conditions as in the ethylene dimerization with **1**.³ On a total Ni basis, **1** is less active than **2** (490 versus 2000 (mol of product)/(mol of Ni) h), respectively), and both catalysts are considerably less active toward propylene than toward ethylene.^{12,14} These differences in reactivity can be explained on the basis of the greater steric hindrance of propylene in comparison to ethylene and the differences in the steric environment of the active sites in **1** and **2**. Nevertheless, the dimer to trimer ratios (C₆:C₉) are high and nearly identical for the two catalysts (17:1). Neither MFU-4l nor MMAO-12 shows oligomerization activity in the absence of nickel.

To gain insight into the C₆ regioselectivity, propylene dimerization was repeated using C₆D₆ as solvent, so that the

resulting product distribution could be analyzed by quantitative ¹³C NMR. This analysis reveals a modest selectivity for branched products, which are valuable as antiknock additives for gasoline,^{8–11} with a 2.8:1 ratio of dimers **3**, **4**, and **6** to **5** (Scheme 1). The low overall concentration of chain-walking products suggests that reinsertion of the products is slow, also consistent with the high C₆:C₉ selectivity. Consequently, the resulting product distribution can be analyzed as a product of primary insertion selectivity.^{15–17} Indeed, we recently showed that ethylene dimerization with **1** proceeds through such a coordination–insertion mechanism.¹⁴ Parsing the product distribution into an insertion tree indicates a mechanistic preference for 2,1- over 1,2-insertion of propylene (Scheme 1). In this analysis, regioselectivity increases with the steric size of the alkyl group on nickel (H < 1-propyl < 2-propyl). Significantly, this branch distribution is well reproduced by **2** under analogous conditions, including a comparable step-specific 2,1-insertion selectivity and low isomerization rate (Figure S6.1 in the Supporting Information).

In summary, we have shown that Ni-MFU-4l serves as a selective propylene dimerization catalyst whose selectivity can be understood by structural and mechanistic analogy to molecular Ni(II) tris-pyrazolylborate complexes. This work underscores the molecule-like reactivity and tunability of MOF nodes that underlie catalyst development and selectivity for α -olefin dimerization, which represents a longstanding goal of heterogeneous catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00178.

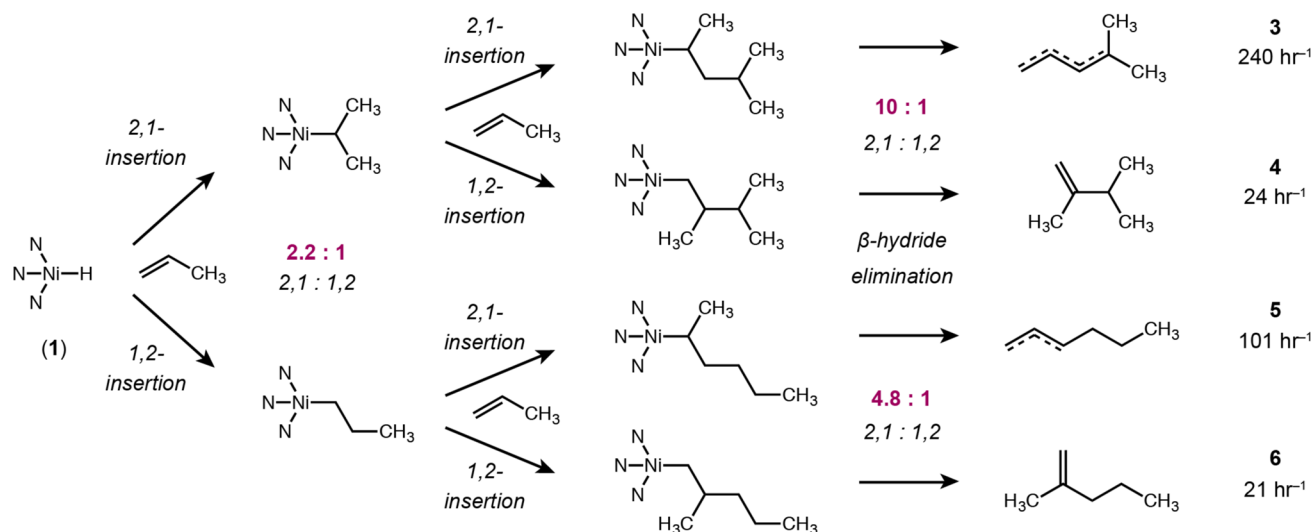
Experimental details, gas chromatograms, NMR data, computational methods, and XAS data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for M.D.: mdinca@mit.edu.

Scheme 1. Product Distribution and Insertion Tree for the Dimerization of Propylene by **1^a**



^aYields were determined by NMR.

ORCID 

Eric D. Metzger: 0000-0001-6597-1981

Christopher H. Hendon: 0000-0002-7132-768X

Mircea Dincă: 0000-0002-1262-1264

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported through a Research Agreement with Saudi Aramco, a Founding Member of the MIT Energy Initiative. Fundamental studies of cation exchange in MOFs were supported through a CAREER award to M.D. from the National Science Foundation (DMR-1452612). E.D.M. acknowledges the Department of Defense (DoD) for support through the National Defense Science and Engineering Fellowship (NDSEG) Program. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357. MRCAT operations, beamline 10-BM, are supported by the Department of Energy and the MRCAT member institutions.

■ REFERENCES

- (1) Brozek, C. K.; Dincă, M. *Chem. Sci.* **2012**, *3*, 2110.
- (2) Brozek, C. K.; Dincă, M. *Chem. Soc. Rev.* **2014**, *43*, 5456–5467.
- (3) Metzger, E. D.; Brozek, C. K.; Comito, R. J.; Dincă, M. *ACS Cent. Sci.* **2016**, *2*, 148–153.
- (4) Denysenko, D.; Grzywa, M.; Tonigold, M.; Streppel, B.; Krkljus, I.; Hirscher, M.; Mugnaioli, E.; Kolb, U.; Hanss, J.; Volkmer, D. *Chem. - Eur. J.* **2011**, *17*, 1837–1848.
- (5) Kaminsky, W. *Macromol. Symp.* **1995**, *89*, 203–219.
- (6) Janiak, C. *Coord. Chem. Rev.* **2006**, *250*, 66–94.
- (7) Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86* (1), 353–399.
- (8) Gaillard, J. *Pétrole Technol.* **1985**, *314*, 20–27.
- (9) Favre, F.; Olivier-Bourbigou, H.; Forestière, A.; Chodorge, J. A. In *DGMK-Conference "C4/CS-Hydrocarbons: Routes to Higher Value-Added products"*; Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle: Munich, Germany, 2004; pp 153–160.
- (10) Favre, F.; Forestière, A.; Hugues, F.; Olivier-Bourbigou, H.; Chodorge, J. A. *Oil Gas Eur. Mag.* **2005**, *31*, 83–86.
- (11) Olivier-Bourbigou, H.; Favre, F.; Forestière, A.; Hugues, F. In *Handbook of Green Chemistry*; Crabtree, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2009; Vol. 1, pp 101–126.
- (12) Kunrath, F. A.; de Souza, R. F.; Casagrande, O. L.; Brooks, N. R.; Young, V. G. *Organometallics* **2003**, *22*, 4739–4743.
- (13) Denysenko, D.; Grzywa, M.; Jelic, J.; Reuter, K.; Volkmer, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 5832–5836.
- (14) Metzger, E. D.; Comito, R. J.; Hendon, C. H.; Dincă, M. *J. Am. Chem. Soc.* **2017**, *139*, 757–762.
- (15) Svejda, S. A.; Brookhart, M. S. *Organometallics* **1999**, *18*, 65–74.
- (16) Vicente, I.; Bernardo-Gusmão, K.; De Souza, M. O.; De Souza, R. F. *Braz. Chem. Soc.* **2014**, *25*, 2151–2156.
- (17) Nelkenbaum, E.; Kapon, M.; Eisen, M. S. *Organometallics* **2005**, *24*, 2645–2659.