

Highly Stereoselective Heterogeneous Diene Polymerization by Co-MFU-4l: A Single-Site Catalyst Prepared by Cation Exchange

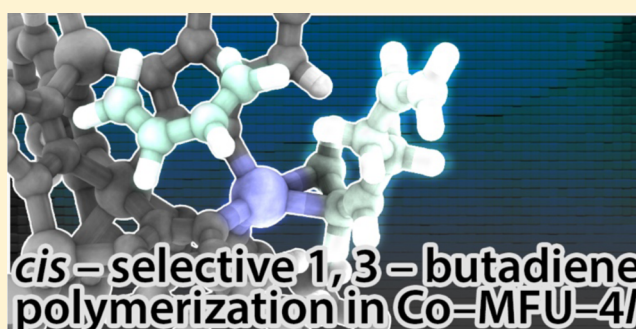
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S Supporting Information

ABSTRACT: Molecular catalysts offer tremendous advantages for stereoselective polymerization because their activity and selectivity can be optimized and understood mechanistically using the familiar tools of organometallic chemistry. Yet, this exquisite control over selectivity comes at an operational price that is generally not justifiable for the large-scale manufacture of polyolefins. In this report, we identify Co-MFU-4l, prepared by cation exchange in a metal–organic framework, as a solid catalyst for the polymerization of 1,3-butadiene with high stereoselectivity (>99% 1,4-*cis*). To our knowledge, this is the highest stereoselectivity achieved with a heterogeneous catalyst for this transformation. The polymer's low polydispersity (PDI \approx 2) and the catalyst's ready recovery and low leaching indicate that our material is a structurally resilient single-site heterogeneous catalyst. Further characterization of Co-MFU-4l by X-ray absorption spectroscopy provided evidence for discrete, tris-pyrazolylborate-like coordination of Co(II). With this information, we identify a soluble cobalt complex that mimics the structure and reactivity of Co-MFU-4l, thus providing a well-defined platform for studying the catalytic mechanism in the solution phase. This work underscores the capacity for small molecule-like tunability and mechanistic tractability available to transition metal catalysis in metal–organic frameworks.



■ INTRODUCTION

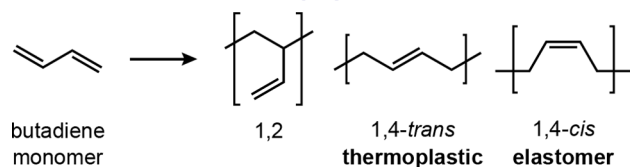
The development of single-site heterogeneous catalysts promises great improvements in selectivity and efficiency for large-scale chemical processes. In particular, the industrial polymerization of olefins continues to largely rely on solid catalysts for continuous throughput and efficient separation on a large scale.¹ Yet, conventional solid supports for polymerization are structurally inhomogeneous, which limits opportunities for catalyst design and optimization. By contrast, molecular polymerization catalysts are often capable of much finer catalytic selectivity.² The utility of molecular catalysts is highlighted in the production of highly stereoregular polymers, which feature improved mechanical properties. Because stereoselective polymerization relies on small differences in transition state energies as the basis for kinetic selectivity, it is highly sensitive to variations in a catalyst's steric and electronic environment.³ Consequently, soluble transition metal complexes with discrete and well-defined coordination structures have played a major role in the development of stereodefined polymers. Although stereoselective heterogeneous catalysts have been commercialized for a few polymers such as isotactic polypropylene,⁴ solid catalysts do not usually provide a sufficient degree of control.⁵

Among stereodefined polymers, those of conjugated dienes represent one of the largest and most structurally diverse categories. These polymers offer both a commercially significant target and an important proving ground for new strategies in single-site heterogeneous catalysis. As a prototypical diene monomer, 1,3-butadiene inserts with either 1,2- or 1,4-regiochemistry; the 1,4-units have either *cis*- or *trans*-geometry (Figure 1).⁶ The configuration and stereopurity of polybutadienes define both their mechanical properties and their commercial applications. For instance, polymers featuring primarily 1,4-*trans* units are thermoplastics, whereas those featuring primarily 1,4-*cis* units are elastomers. The latter are desirable in high stereopurity (>98%) because they exhibit improved wear resistance and impact resilience.⁷ Interest in these high-performance elastomers has created a demand for catalysts with high stereoselectivity and molecular weight control (PDI \approx 2), typically achieved only by homogeneous catalysts.⁸ Transferring the high selectivity of these catalysts into the solid state remains challenging because insoluble metal halide-based precatalysts show a strong tendency to form

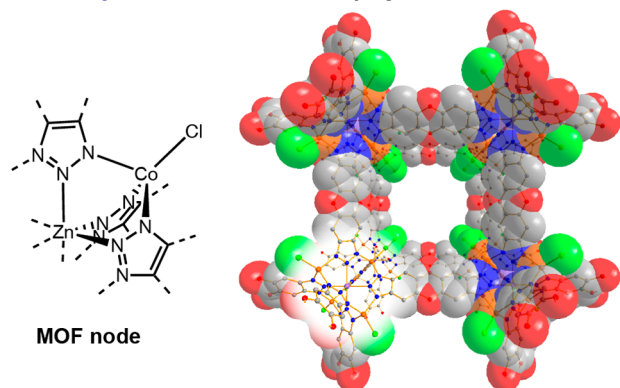
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Commercial stereoselective polymerization of 1,3-butadiene:



This study: Stereoselective diene polymerization in MOFs



Co-MFU-4l (1): a single-site heterogeneous catalyst

Figure 1. Design plan for stereoselective polymerization of 1,3-butadiene with a solid catalyst.

soluble active catalysts in the presence of diene and alkylaluminum cocatalysts.⁹ Although more robust surface immobilization techniques have been proposed to address this challenge,¹⁰ none of these catalysts preserve the low PDI and high 1,4-*cis* selectivity of their soluble counterparts.

Because of their monodisperse and well-defined transition metal coordination environments, porous metal–organic frameworks (MOFs) offer unique opportunities for single-site heterogeneous catalysis.¹¹ The inorganic nodes, or secondary building units (SBUs), are particularly attractive targets as site-isolated platforms for small-molecule like transition metal catalysis in a high surface area solid support. Many SBUs are capable of cation exchange, which occurs with preservation of local coordination structure and offers a predictable strategy to incorporate transition metals in a desired coordination geometry, an important design feature for organometallic catalysis.¹²

To address the challenge of designing a heterogeneous stereoselective butadiene polymerization catalyst, we were inspired by molecular cyclopentadienyl (Cp) catalysts.¹³ On the basis of the established isolobal analogy between Cp and tris-pyrazolylborate (Tp) complexes, we reasoned that the material known as MFU-4l ($Zn_5Cl_4(BTDD)_3$, $H_2BTDD = \text{bis}(1H\text{-}1,2,3\text{-triazolo}[4,5\text{-}b],[4',5'\text{-}i])\text{dibenzo}[1,4]\text{dioxin}$),¹⁴ which features exchangeable Zn^{2+} cations in a Tp-like coordination environment, would serve as an excellent support for addressing this challenge (Figure 1).¹⁵ Through this approach, we identified Co-MFU-4l (1) as a highly selective catalyst for the 1,4-*cis*-polymerization (>99%) of 1,3-butadiene. To our knowledge, this stereoselectivity is the highest reported for 1,3-butadiene polymerization with a heterogeneous catalyst. We further present evidence for the single-site structure of 1 as well as a molecular model for interrogating the mechanistic basis for *cis*-selectivity in this catalyst.

RESULTS AND DISCUSSION

Stereoselective catalysis often relies upon systematic variation as a means to optimize small differences in activation energy, which can be difficult to anticipate a priori but nevertheless underlie significant differences in stereoselectivity. In analogy to metalloligand-based catalysis, cation exchange provides a unique opportunity to compare the reactivity of a range of transition metal cations with equivalent coordination geometry in the solid state. By contrast, conventional heterogeneous supports do not show equivalent support–catalyst interaction across a broad range of transition metals, highlighting the advantage that the well-defined, modular structure of MOFs holds for heterogeneous catalyst design.

Given the variety of transition metals used for stereoselective diene polymerization in Cp complexes, we initiated our catalyst development by evaluating a variety of 3d metals. Thus, MFU-4l samples exchanged with Ti, Cr, Fe, Co, and Ni¹⁶ were treated with 1,3-butadiene and modified methylaluminoxane-12 (MMAO-12) under semibatch conditions. The results evidenced considerable variation in activity and selectivity based on both the choice of transition metal and its oxidation state (Table 1). In all cases, the exchanged transition metals

Table 1. Evaluation of Transition Metal and Activator for the Heterogeneous Polymerization of 1,3-Butadiene

| entry | precatalyst | activator | TOF ^a | % 1,4- <i>cis</i> ^b |
|-----------------|----------------|---------------------------------|------------------|--------------------------------|
| 1 ^c | MFU-4l | MMAO-12 | 0 | |
| 2 ^c | Ti(IV)-MFU-4l | MMAO-12 | 1000 | 23% |
| 3 ^c | Ti(III)-MFU-4l | MMAO-12 | <20 | |
| 4 ^c | Cr(II)-MFU-4l | MMAO-12 | 44 | |
| 5 ^c | Cr(III)-MFU-4l | MMAO-12 | 62 | 92% |
| 6 ^c | Fe(II)-MFU-4l | MMAO-12 | 140 | 68% |
| 7 ^c | Co(II)-MFU-4l | MMAO-12 | 270 | 99.3% |
| 8 ^c | Ni(II)-MFU-4l | MMAO-12 | 1500 | 96% |
| 9 ^d | Co(II)-MFU-4l | MMAO-12 | 270 | 99.3% |
| 10 ^d | Co(II)-MFU-4l | AlEt ₂ Cl | 200 | 89% |
| 11 ^d | Co(II)-MFU-4l | AlMe ₃ | <20 | |
| 12 ^d | Co(II)-MFU-4l | AlEt ₃ | <20 | |
| 13 ^d | Co(II)-MFU-4l | Al ⁱ Bu ₃ | <20 | |

^aTurnover frequency (h^{-1}) determined by isolated yield. ^b1,4-*cis* content determined by ¹³C NMR. ^cSemibatch conditions, 6 h, 21 °C. ^dBatch conditions for 2 h, 21 °C, 3.5 M monomer.

were responsible for catalysis, the all-zinc MFU-4l parent MOF showing no background reactivity for this reaction. Surprisingly, the metal-exchanged MFU-4l catalysts previously reported to be most active for ethylene polymerization (i.e., Ti- and Cr-exchanged MFU-4l)¹⁷ were found to be least effective for 1,3-butadiene polymerization (Table 1, entries 2–5, 8). Thus, although Ti(IV)-MFU-4l showed promising activity for 1,3-butadiene polymerization, the resulting polymer is predominantly *trans* and exhibits modest stereopurity (Table 1, entry 2). This observation contrasts with the well-documented 1,4-*cis*

selectivity of CpTiCl_3 , underscoring the somewhat empirical nature of stereoselective catalysis. MFU-4l samples exchanged with late transition metals show contrasting reactivity with both olefins and dienes: whereas Fe(II)-MFU-4l is unreactive toward ethylene and produces polybutadiene with only modest stereoselectivity (68% 1,4-*cis*), Ni(II)-MFU-4l is a selective ethylene dimerization catalyst¹⁸ and a very active 1,3-butadiene polymerization catalyst, providing a polymer with promising stereoselectivity (96% 1,4-*cis*). However, Co(II)-MFU-4l (**1**) provides polybutadiene with the highest stereoselectivity, greater than 99% 1,4-*cis* content (Table 1, entry 7). This selectivity is exceptional among heterogeneous catalysts and is relevant for high-performance elastomer applications, prompting a more in-depth study of the nature of the Co site in this catalyst.

First, to determine the kinetic nature of our catalyst, the polymer's molecular weight distribution was examined by gel permeation chromatography (GPC, section S4.1). For the polymers produced by both Ni(II)- and Co(II)-MFU-4l (**1**), the number-average molecular weights (M_N) were high, significant for elastomer applications, while the polydispersity index (PDI) was low, indicative of single-site activity. By both metrics, **1** displayed superior selectivity; while Ni(II)-MFU-4l provided a polymer with $M_N = 71\,000$ and PDI = 2.12, that of Co(II)-MFU-4l displayed $M_N = 200\,000$ and PDI = 1.26.

To further substantiate the single-site activity in **1**, we evaluated the integrity of the catalyst under conditions relevant to polymerization. After treatment with MMAO-12 for 7 h, the powder X-ray diffraction (PXRD) pattern of **1** did not change noticeably, suggesting that the crystallinity of the material was preserved. Likewise, PXRD analysis indicated minimal decomposition for samples of **1** recovered after polymerization at 21 °C (Figure 2A) and at 60 °C (Figure S3.2). Moreover, scanning electron microscopy (SEM) analysis demonstrated that the block-shaped crystallite morphology of pristine **1** is retained in

the recovered catalyst (Figure 2B and C). The lack of particle fracturing or surface restructuring suggests that polymerization largely takes place at or near the surface of the MOF particles.

To assess the heterogeneity of our catalyst system under reaction conditions, we evaluated possible leaching of soluble catalytically competent Co(II) species. Thus, the filtrate obtained by catalyst recovery after 1 h of polymerization was treated with supplemental monomer. Negligible polymerization in the presence of this filtrate solution provides evidence against leaching of a soluble active catalyst (Figure S5.1). Indeed, elemental analysis of this filtrate solution confirmed low cobalt concentration corresponding to less than 1% leaching.¹⁹

Having shown that **1** and MMAO-12 provide a highly stereoselective heterogeneous catalyst for 1,3-butadiene polymerization, we sought to further optimize its activity by systematically changing the nature of the cocatalyst and the reaction temperature. Among the various alkylaluminum cocatalysts explored in Table 1, MMAO-12 provides the best yield and stereoselectivity (entry 9). Although similar in activity, diethylaluminum chloride leads to a considerable reduction in stereoselectivity (entry 10). Trialkylaluminum reagents yielded the lowest reactivity (entries 11–13), likely due to reductive deactivation of **1**, which occurs faster for Co(II) polymerization catalysts in combination with trialkylaluminum reagents than with methylaluminoxane.²⁰ Time and temperature studies showed that at 40 °C the catalyst is active for 2 h, after which the yield remains constant even upon addition of excess monomer (Figure 3A). In contrast, M_N levels off at $\sim 700\,000$ g/mol after only 1 h. Together, these data suggest that the polymerization occurs with rapid chain transfer and is therefore not likely to be a living polymerization, except possibly at short reaction times and reduced temperature. This is in line with what is observed for homogeneous transition metal catalysts for this reaction; living polymerization in this system is more characteristic of main group catalysts.²¹ Importantly, **1** exhibits good thermal stability: its catalytic activity increases with temperature up to 65 °C (Figure 3B), albeit at the expense of a slight reduction in stereoselectivity, which decreases to >96% at elevated temperatures. Stereoselectivity is optimized at low temperature and reaches 99.4% 1,4-*cis* at 0 °C.

Initial mechanistic insight into the activity of **1** came from systematic investigations of the Al:Co ratio. Thus, at constant loading of Co in **1**, the activity correlated positively with increasing Al:Co ratio (Figure 4). In contrast, increasing the Co loading while keeping the Al:Co ratio constant had little effect on the overall turnover frequency or selectivity (Table S4.2). M_N did not depend on the Al:Co ratio, remaining generally high ($\sim 700\,000$ g/mol). Together, these results indicate that MMAO-12 does not play a kinetically significant role in chain transfer. Nevertheless, both M_N and turnover frequency have a first-order dependence on monomer concentration (Figure S6.37). This concentration effect represents a handle for molecular weight control and provides evidence for a unimolecular mechanism for chain transfer or termination. By contrast, a weak or inverse dependence of M_N on monomer concentration would be expected in the case of chain transfer to monomer, observed for ethylene polymerization with Cr- and Ti-MFU-4l and for ethylene dimerization with Ni-MFU-4l. As a plausible explanation, we propose chain transfer by hydride elimination followed by monomer insertion, drawing a parallel with the reported behavior of single-site Ni(II) catalysts for 1,4-*cis*-selective polymerization.²²

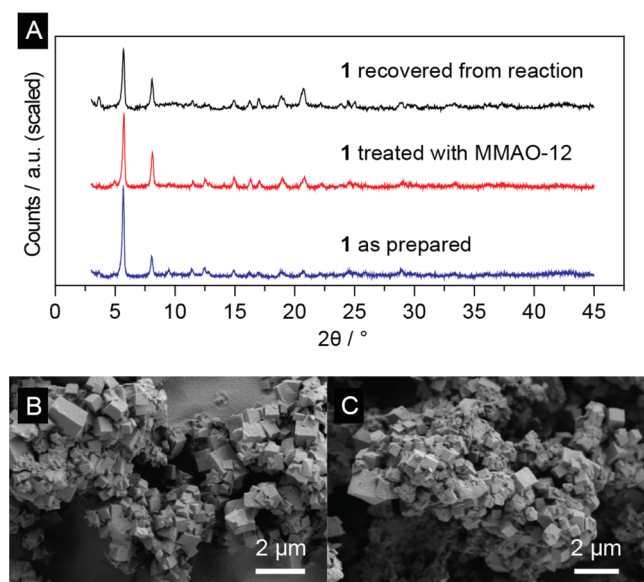


Figure 2. Characterizing the integrity of **1**. (A) PXRD analysis of **1** recovered from the polymerization reaction, after treatment with MMAO-12, and as prepared. (B) SEM image of pristine **1**. (C) SEM image of **1** recovered from the polymerization reaction. Recovered samples were rinsed with toluene to remove residual polymer, activator, and monomer.

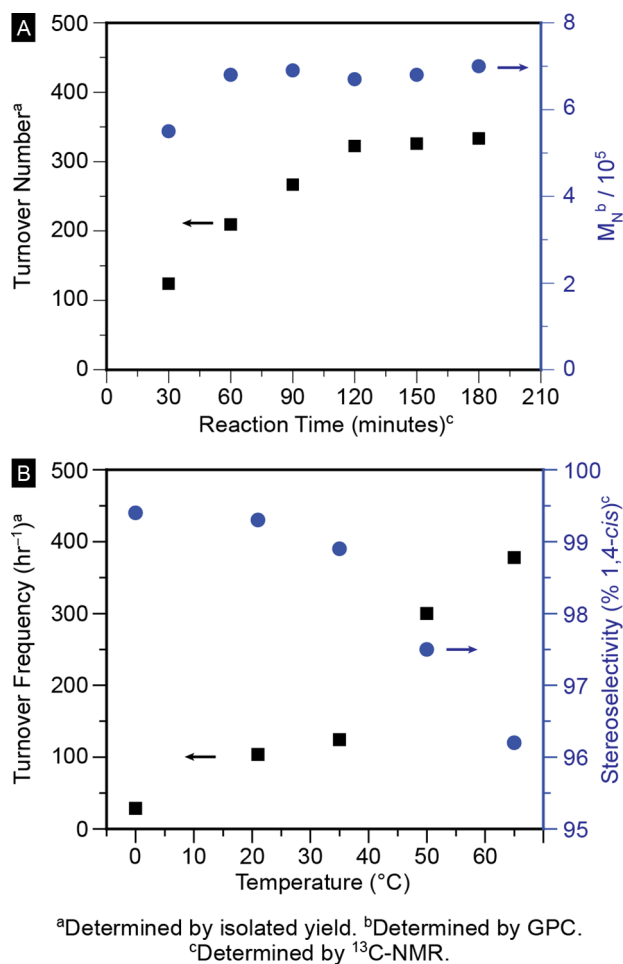


Figure 3. (A) Time study (performed at 40 °C). (B) Temperature study. Performed in separate batches with an initial monomer concentration of 2.25 M.

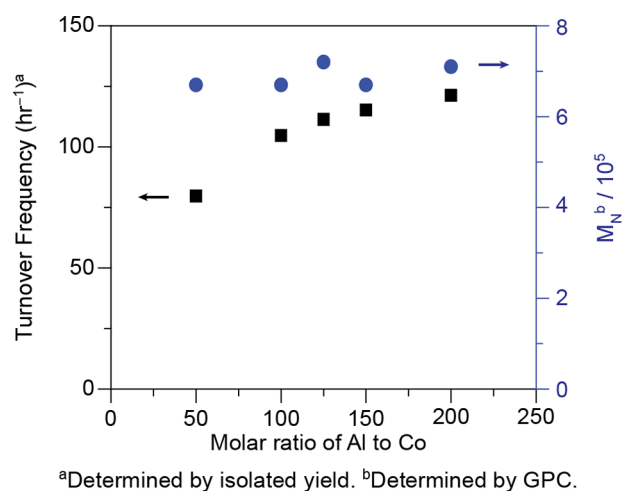
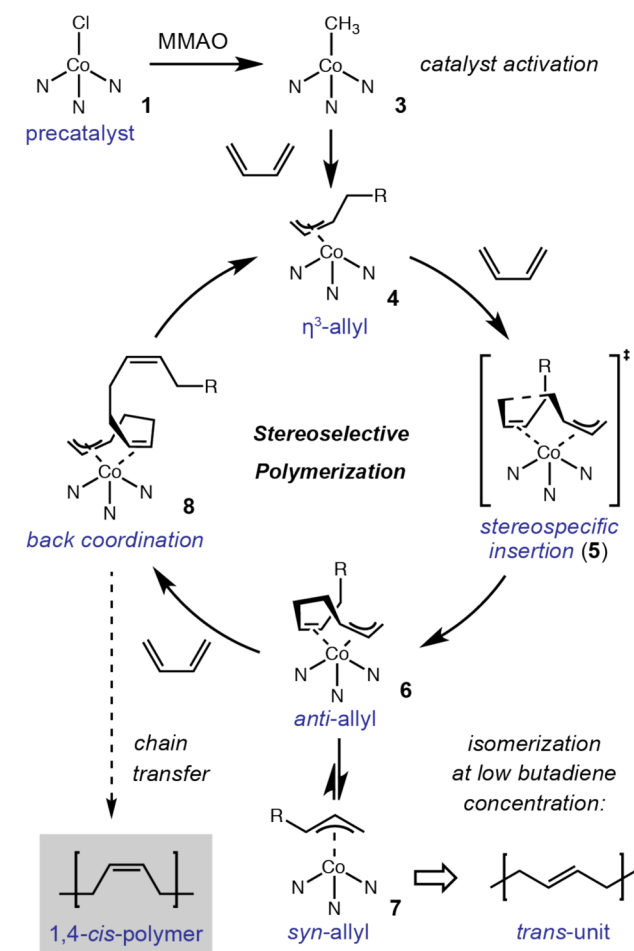


Figure 4. Evaluating cocatalyst loading. Data points are from 2 h reactions performed at 21 °C.

To elucidate the origin of stereoselectivity in **1**, we took inspiration from mechanistic studies on single-site molecular catalysts. These reports have established the role of olefin back coordination and the stereospecific insertion of dienes to form η^3 -allyl intermediates (steps **6** and **5**, respectively, in Scheme 1).²³ In analogy to this work, we propose a mechanism for the

Scheme 1. Proposed Mechanism for the 1,4-cis-Selective Polymerization of 1,3-Butadiene with **1**



1,4-cis-selective polymerization with **1**: alkylation of a cobalt site by MMAO-12 generates an alkyl cobalt intermediate (**3**).²⁴ Direct insertion of 1,3-butadiene forms η^3 -allyl complex **4**, initiating the catalytic cycle. Stereospecific insertion of 1,3-butadiene through transition state **5** would provide an *anti*- η^3 -allyl **6**, whose configuration gives rise to the *cis*-geometry of the resulting olefin. Continued insertion of butadiene would lead to chain growth, while chain transfer at this stage would furnish the 1,4-cis polymer. In contrast, isomerization of **6** to the *syn*- η^3 -allyl **7** would provide a *trans*-unit in the growing polymer. Consistent with this slow equilibrium, reduced monomer concentration leads to increased 1,4-*trans* content, which nevertheless remains low overall (Figure S6.37). Back-coordination of the previously inserted monomer unit would presumably stabilize intermediates such as **6** toward this isomerization, a unimolecular process that competes with bimolecular insertion.

To evaluate the proposed mechanism in **1**, we first sought to characterize the structure of our catalyst and the key reactive intermediates. First, the structure of precatalyst **1** was confirmed by X-ray absorption spectroscopy (XAS) in conjunction with an optimized structure under the Kohn–Sham density functional theory (DFT) construct. Consistent with the proposed Co²⁺ oxidation state, **1** displayed a Co K-edge energy similar to those of two Co²⁺ standards: Tp₂Co and anhydrous CoCl₂ (Table S10.1). Precatalyst **1** also exhibits a higher intensity pre-edge feature than the two standards,

consistent with the lower symmetry pseudotetrahedral coordination environment of Co observed in the DFT-optimized structure of **1** (DFT-1, Figure 5). Fitting the X-ray

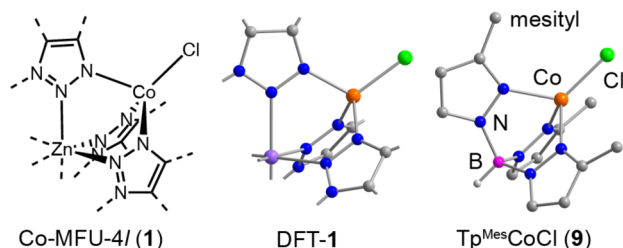


Figure 5. A comparison of the coordination environment between catalyst **1** and molecular model **9**.

absorption fine structure (EXAFS) data resulted in three N–Co (2.02 Å) and one Cl–Co (2.15 Å) bonds (Table 2). These

Table 2. Fitting Results of the EXAFS Spectra^a

| sample | scattering pair | coordination number | bond length | σ^2 (Å ²) |
|--------------------|-----------------|---------------------|-------------|------------------------------|
| Tp ₂ Co | Co–N | 6 | 2.14 | 0.007 |
| CoCl ₂ | Co–Cl | 6 | 2.42 | 0.010 |
| Co-MFU-4l | Co–N | 3 | 2.02 | 0.011 |
| | Co–Cl | 1 | 2.15 | 0.007 |

^aThe average error in bond length is 0.02 Å and in σ^2 is 0.003 Å². The fitting ranges for Tp₂Co and Co-MFU-4l are $\Delta k = 3.0\text{--}11.0$ Å⁻¹ and $\Delta R = 1.0\text{--}2.0$ Å. For CoCl₂, the ranges are $\Delta k = 3.2\text{--}10.6$ Å⁻¹ and $\Delta R = 1.3\text{--}2.4$ Å.

bond lengths are in excellent agreement with those of DFT-1 (1.915 and 2.134 Å, respectively). Moreover, all models with different coordination numbers or choice of scattering pairs provided quantitatively worse fits. Together with the kinetic observations, these data provide good evidence for the discrete, single-site structure of precatalyst **1**.

We sought to examine the mechanistic basis for stereoselectivity and single-site reactivity in **1** with an analogous molecular complex, an attractive strategy for overcoming the inherent difficulty of characterizing reaction intermediates in the solid state that nevertheless suffers from the lack of reliable models for typical heterogeneous catalysts. By contrast, the single-site structure of **1** provided an excellent opportunity for structural modeling with Tp complexes. Although simple Tp ligands tend to form homoleptic complexes with Co(II) (e.g., Tp₂Co²⁵), we identified pyrazole-substituted Tp^{Mes}CoCl (**9**, Tp^{Mes} = HB(3-mesityl-1-pyrazolyl)₃) as a close structural analogue accessible by metal metathesis with Tp^{Mes}Tl.²⁶ Indeed, X-ray diffraction analysis of a single crystal of **9** indicated a primary coordination sphere nearly identical to that of DFT-1, with bond distances (Co–N = 2.023(2) Å; Co–Cl = 2.175(9) Å) that also agreed with those fit from the EXAFS analysis of **1**.

The close structural homology between **9** and **1** suggested that the former would serve as an excellent molecular model for investigating the stereoselection in 1,3-butadiene polymerization with **1** (Scheme 1). Toward this end, we chose symmetrical allyl complex **10**, available by treating **9** with allylmagnesium bromide, as a stable, crystallizable model for proposed intermediates such as **4**. Single-crystal diffraction analysis of **10** (Figure 6) showed near-symmetric η^3 -

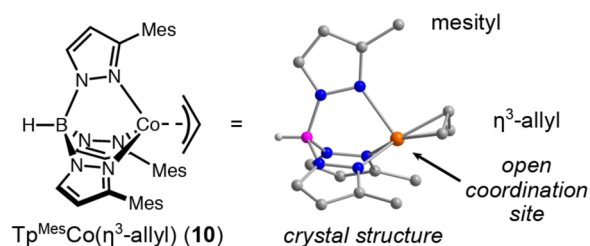


Figure 6. Structure of TpMesCo(η^3 -allyl) (**10**).

coordination of the allyl group, as would be required for the stereodefined diene insertion proposed in our mechanism (transition state **5** in Scheme 1). Notably, the crystal structure of **10** reveals a clear open coordination site at Co, as would be required for direct insertion into an η^3 -allyl or for olefin back coordination, the mechanistic bases for *cis*-selectivity in the proposed mechanism.

Finally, the validity of molecular complexes **9** and **10** as mechanistic models for **1** was verified by subjecting **1**, **9**, and **10** to analogous polymerization conditions (Table S4.6). All three precatalysts provided polymers with >98% 1,4-*cis* selectivity. This reinforces the concept that the proposed SBU-based reactivity is consistent with the close correspondence in molecular selectivity between **1** and **9**, with the 17-fold increase in activity for **9** versus **1** suggesting an increase in substrate accessibility in the solution phase.

CONCLUSION

We have shown that **1** is a robust heterogeneous single-site catalyst for 1,3-butadiene polymerization, whose mechanism of stereoselection can be understood in fine detail by small molecule analogy. Both the control over the local structure of the catalyst and its stereoselectivity (>99% 1,4-*cis*) are exceptional among solid catalysts for olefin polymerization and highlight the utility of MOFs beyond reactions typically studied with these catalysts. Indeed, the results herein stand out among all heterogeneous catalysts and should stimulate interest for the manufacture of advanced polyolefins using heterogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06841.

Experimental details, IR spectra, NMR spectra, PXRD spectra, N₂ adsorption isotherms, GPC elution curves, SEM pictures, XAS spectra, and fitting results (PDF)
X-ray crystallographic data for Tp^{Mes}CoCl (CIF)
X-ray crystallographic data for Tp^{Mes}Co-allyl (CIF)

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Notes

The authors declare no competing financial interest.

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