Mechanism of Single-Site Molecule-Like Catalytic Ethylene Dimerization in Ni-MFU-4*l*
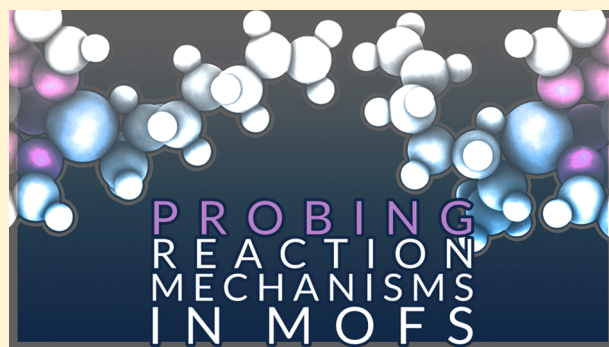
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S *Supporting Information*

ABSTRACT: A recently developed metal−organic framework (MOF) catalyst for the dimerization of ethylene has a combination of selectivity and activity that surpasses that of commercial homogeneous catalysts, which have dominated this important industrial process for nearly 50 years. The uniform catalytic sites available in MOFs provide a unique opportunity to directly study reaction mechanisms in heterogeneous catalysts, a problem typically intractable due to the multiplicity of coordination environments found in many solid catalysts. In this work, we use a combination of isotopic labeling studies, mechanistic probes, and DFT calculations to demonstrate that Ni-MFU-4*l* operates via the Cossee-Arlman mechanism, which has also been implicated in homogeneous late transition metal catalysts. These studies demonstrate that metal nodes in MOFs mimic homogeneous catalysts not just functionally, but also mechanistically. They provide a blueprint for the development of advanced heterogeneous catalysts with similar degrees of tunability to their homogeneous counterparts.

INTRODUCTION

Metal−organic frameworks (MOFs) have tremendous potential for heterogeneous catalysis due to their unparalleled tunability in the solid state. Indeed, numerous reports detail the development of catalytically active MOFs through the modification of either the organic ligands or inorganic clusters that define the materials,[1−9] although detailed mechanistic studies on MOF catalysts remain conspicuously absent. To fully leverage the unique tunability that these materials provide for the development of improved heterogeneous catalysts, rigorous mechanistic studies are necessary to enable rational catalyst design. In this work, we demonstrate that standard organometallic techniques can be translated to study the reaction mechanisms of catalytic MOFs by fully elucidating the mechanism of ethylene dimerization in Ni-MFU-4*l*.

The catalytic oligomerization of ethylene to form linear alpha olefins (LAOs) is one of the most commercially successful applications of catalysis in the petrochemical industry, with more than 1.1 million tons of oligomers produced annually.[10−12] Because the majority of oligomerization catalysts provide a wide distribution of products primarily consisting of C_{14}−C_{20} olefins, the advent of linear low-density polyethylene (LLDPE) has led to an increasing demand for just the short LAOs that are valuable as comonomers in LLDPE production.[13−16] With the growing interest in 1-butene, 1-hexene, and 1-octene, both academia and industry have expended considerable efforts on the development and study of catalysts for the *selective* dimerization, trimerization, and tetramerization of ethylene.[11,17−37]

Recently, we reported Ni-MFU-4*l*, a heterogeneous catalyst whose combined activity and selectivity for the production of 1-butene from ethylene surpasses analogous homogeneous catalysts and all other heterogeneous catalysts (Figure 1).[38] This highlighted the utility of MOFs in solving long-standing industrial challenges in heterogeneous catalysis. Indeed, despite decades of research devoted to displacing homogeneous catalysts for ethylene dimerization, solids tested for this process were either poorly active or unselective,[39] their performance plagued by the intractability and multiplicity of their active sites, a common problem in conventional heterogeneous catalysts. In contrast, MOFs provide well-defined platforms for reactivity, as inorganic clusters are held together by organic ligands to form periodic three-dimensional structures. MFU-4*l* is an ideal model system for investigating ethylene reactivity, because it is chemically robust and contains scorpionate-like coordination motifs that are known to activate small molecules.[40−43] Although we initially investigated Ni-MFU-4*l* due to the structural homology between the inorganic clusters and molecular $[Tp^{Mes}Ni]^+$ catalysts for ethylene dimerization (Tp^{Mes} = HB(3-mesitylpyrazolyl)$_3$), we found that the MOF's selectivity for 1-butene is considerably higher than that of the homogeneous system.[38,44] With Ni-MFU-4*l*, selectivities of up
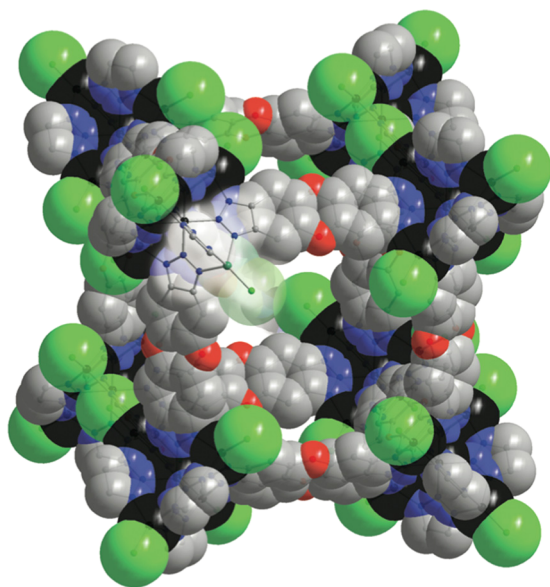
Figure 1. Structure of Ni-MFU-4*l*. Teal, nickel; green, chlorine; black, zinc; gray, carbon; blue, nitrogen; and red, oxygen. Hydrogens were omitted for clarity.

to 96.2% for 1-butene are obtained, although the molecular [Tp^{Mes}Ni]$^+$ catalyst is only 82.8% selective under identical conditions (Table S1). This was surprising because typical heterogenization techniques applied to homogeneous catalysts often lead to severe penalties in selectivity and/or activity.[45−47] Given the immense importance of selective heterogeneous catalysis, developing a detailed mechanistic understanding of ethylene dimerization in Ni-MFU-4*l* is of considerable fundamental interest and is crucial for ongoing efforts in catalyst development. Here, we elucidate this mechanism and demonstrate that methods common to molecular organo-metallic chemistry can similarly be applied to studying reaction mechanisms in well-defined heterogeneous materials such as MOFs. This study provides clear precedent and a blueprint for translating molecular design principles and applying the vast toolbox of mechanistic organometallic chemistry to this emerging class of heterogeneous catalysts.

Two mechanisms have commonly been invoked for ethylene dimerization. The Cossee-Arlman mechanism (Scheme 1A) involves the successive insertion of ethylene monomers into a growing metal alkyl chain prior to chain transfer, typically leading to an unselective distribution of higher oligomers determined by the relative rates of ethylene insertion and chain transfer.[13,48] In principle, however, catalysts operating by this mechanism can be selective for dimers if the rate of chain transfer is much faster than the rate of chain propagation. In contrast, the metallacyclic mechanism (Scheme 1B) involves the initial coordination of two ethylene molecules to a metal center followed by the reductive coupling of the olefin monomers to generate a metallacyclopentane.[11] The metalla-cycle subsequently decomposes in either a stepwise fashion or a concerted process to selectively release the desired 1-butene. Although the metallacyclic mechanism is most often proposed for early transition metals such as titanium,[24,25] chromi-um,[19−21,26,27,35,37] and tantalum,[22,23] nickel systems have also been shown to dimerize olefins through metallacyclic intermediates.[49,50] Furthermore, nickel-catalyzed reductive couplings are well established in organic synthesis.[51,52] In this

Scheme 1. Two Commonly Proposed Mechanisms for Ethylene Dimerization
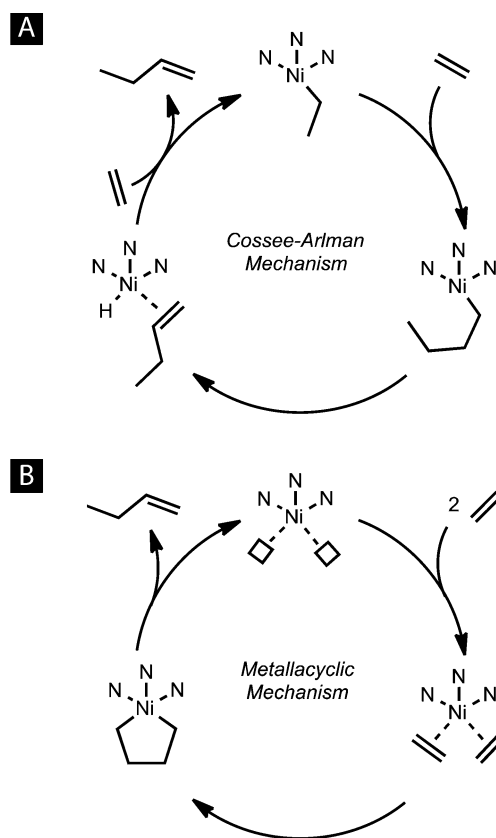
work, we report isotopic labeling experiments and reactions with mechanistic probes to conclusively determine the operative mechanistic pathway for ethylene dimerization in Ni-MFU-4*l*.

Some of the most elegant studies on selective ethylene oligomerization have analyzed the isotopomer distribution resulting from the oligomerization of a 1:1 mixture of ethylene and perdeuteroethylene.[27,35,53,54] When coloading C_2H_4 and C_2D_4 over a catalyst that operates via the metallacyclic mechanism, only C_4H_8, $C_4H_4D_4$, and C_4D_8 should be present, in a 1:2:1 ratio (Figure S1). In contrast, β-hydride crossover that accompanies chain transfer causes H/D scrambling for catalysts operating via the Cossee-Arlman mechanism, yielding C_4H_8, C_4H_7D, $C_4H_5D_3$ $C_4H_4D_4$, $C_4H_3D_5$, C_4HD_7, and C_4D_8 in a 1:1:1:2:1:1:1 ratio (Figure S2). However, the mass fragmentation pattern of 1-butene shows substantial C−H bond fragmentation, giving rise to ions over the range 49−57 m/z (Figure S3), substantially complicating the isotopomer analysis.[54] Previous studies have modeled hydrocarbon fragmentation whereby the probability of H or D loss via EI ionization is proportional to the ratio of H and D in the isotopomer.[53−55] Building upon this prior work, we added corrections to account for the natural abundance of ^{13}C in ethylene and C_2D_4, as the fragmentation pattern shows a substantial spectral ion at $m/z = 57$ that is due to ^{13}C incorporation in 1-butene (Figures S3−S17). Once these corrections are applied, it is facile to analyze the product mixture by gas chromatography/mass spectrometry to distinguish between the two mechanisms.

■ RESULTS AND DISCUSSION

We initially sought to dimerize an equimolar mixture of C_2D_4/C_2H_4 with Ni-MFU-4l and modified methylaluminoxane (MMAO-12)[56] for 1 h, mimicking our previously reported conditions. Although the resulting mass fragmentation pattern fits the Cossee-Arlman mechanism better than the metallacyclic mechanism, the observed intensities at m/z = 58 and 62 are both higher than expected (Figure S19). This slight mismatch between the experimental results and the theoretical distribution suggests that some secondary H/D scrambling occurs, generating additional isotopomers such as $C_4H_6D_2$ and $C_4H_2D_6$ and leading to an enrichment of observable species at these m/z values. Indeed, GC/MS analysis of the leftover ethylene/perdeuteroethylene mixture after 1 h dimerization experiments show substantial H/D scrambling between C_2H_4 and C_2D_4 (Figure 2). This H/D scrambling among ethylene monomers
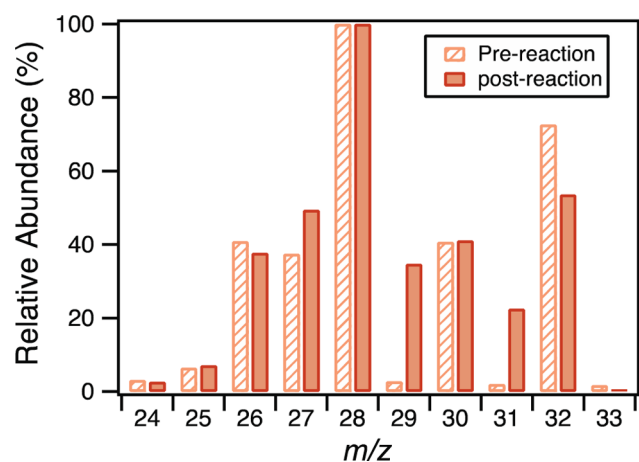

Figure 2. Mass fragmentation pattern of a mixture of ethylene/d_4-ethylene before and after a 1 h reaction with Ni-MFU-4l/MMAO-12. Note the increased relative abundance of spectral ions 29 and 31 after the reaction, indicative of H/D scrambling.

accounts for the perceived mismatch between experimental results and theoretical predictions; theoretical isotopomer distributions for both mechanisms assume all starting monomers to be either pure C_2H_4 or C_2D_4, with no contribution from C_2H_3D, $C_2H_2D_2$, or C_2HD_3. The scrambled ethylenes are nevertheless clearly present by the end of the reaction. Together, these results suggest that ethylene dimerization with Ni-MFU-4l occurs via the Cossee-Arlman mechanism. Importantly, high selectivity is only possible with the Cossee-Arlman mechanism if the rate of ethylene insertion is slower than the rate of chain termination via β-hydride elimination. Because high selectivity is indeed observed with our catalyst, it implies that the rate of ethylene insertion is slow relative to chain termination, which necessarily leads to H/D scrambling between C_2D_4 and C_2H_4.

Although the isotope labeling studies strongly suggested a Cossee-Arlman mechanism, we nonetheless sought to make a more conclusive determination by shortening the reaction time to obtain the initial isotopomer distribution prior to extensive H/D scrambling. As expected, when dimerization experiments under a C_2H_4/C_2D_4 atmosphere were quenched after only 3 minutes (Figure 3A), much less H/D scrambling among the ethylene monomers was observed, making the assumption that all of the monomeric species participating in dimerization were unscrambled C_2H_4 or C_2D_4 much more accurate. Indeed, a
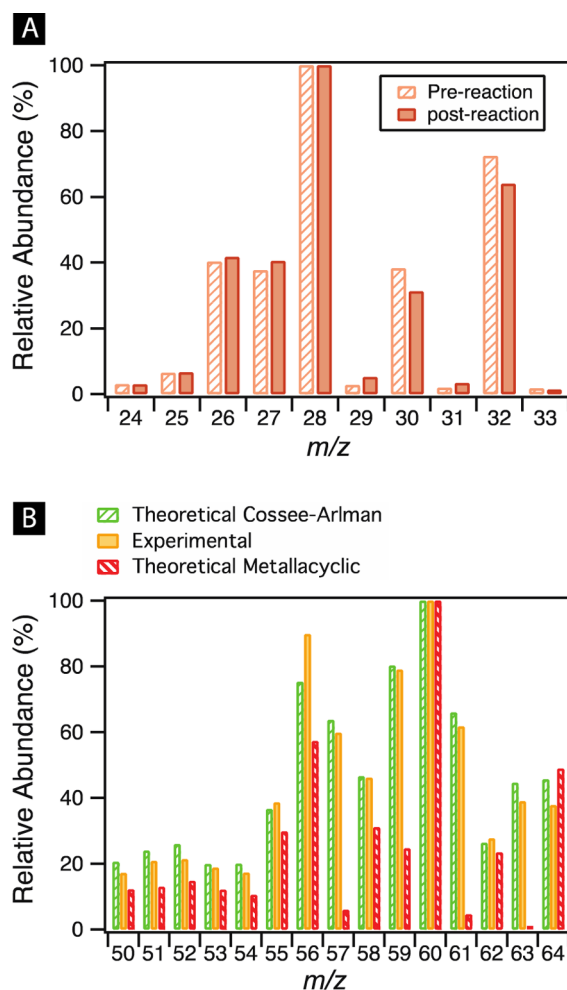

Figure 3. (A) The mass fragmentation pattern of a mixture of ethylene/d_4-ethylene before and after a 3 min reaction with Ni-MFU-4l/MMAO-12. (B) The mass fragmentation pattern of the 1-butene resulting from a mixture of ethylene/d_4-ethylene after a 3 min reaction.

close match is observed between the experimental mass fragmentation pattern for dimerized products and the predicted mass fragmentation pattern for products resulting from the Cossee−Arlman mechanism (Figure 3B), providing additional evidence that Ni-MFU-4l operates via this mechanism. At these short reaction times, we also observe increased abundance at m/z = 56. This is due to trace decomposition products from quenched MMAO-12 that coelute with 1-butene (Figures S21 and S22), and which naturally become more prominent components of the overall reaction mixture as the reaction time decreases. Further validation of the Cossee-Arlman mechanism comes from an analysis of the 2-butenes produced, which do not suffer from issues of coelution with MMAO-12 decomposition products. Indeed, when H/D scrambling among olefins is limited by reducing the reaction time, the mass fragmentation pattern of the resulting 2-butenes is nearly identical to the theoretical distribution for the Cossee-Arlman mechanism (Figure S23).

Having established that ethylene dimerization with Ni-MFU-4l proceeds by the Cossee-Arlman mechanism, we next focused upon the mechanism of initiation. When ethylene dimerization reactions are run under low conversion, substoichiometric amounts of propylene are detected (Figures S24−S26 and S21). This suggests the formation of an initial

nickel methyl species, which subsequently undergoes ethylene insertion. Deuterium labeling studies confirm that the observed propylene is not attributable to quenched MMAO-12 products formed after the reaction, but indeed to reaction with ethylene substrate. Interestingly, the amount of propylene detected increases with increasing equivalents of MMAO-12, following a similar trend to that observed for turnover frequency versus equivalents of MMAO-12. This suggests that the large excess of MMAO-12 is in part necessary to activate all of the nickel sites dispersed throughout the MOF. Given that methylaluminoxane exists in toluene as a set of dynamic oligomers with sizes similar to the MOF's pore window, we hypothesize that the large excess of MMAO-12 is necessary to support the formation of a sufficiently large concentration of small aluminoxane oligomers to allow these to diffuse into the MOF and activate internal nickel sites.[57−59]

Our isotopic labeling experiments clearly demonstrate dynamic binding and release of olefins at the nickel sites in Ni-MFU-4l. We sought to gain further insight into this process by utilizing substrates whose dynamic binding to the active site is trapped with a subsequent irreversible step that affords structurally distinct products. Nonconjugated dienes such as 1,6-heptadiene are ideal mechanistic probes for this purpose, as the irreversible insertion of the pendant alkene into either the primary or secondary alkyl species leads to different cyclic products (Scheme 2). Indeed, literature examples show that when zirconocene catalysts are treated with 1,6-heptadiene, the tethered alkene solely inserts into the primary Zr alkyl species, selectively producing methylenecyclohexane.[60] In contrast, the cyclopolymerization of 1,6-heptadiene with cobalt and iron catalysts yields exclusively 1,2-cyclopentanediyl rings,[61] demonstrating that late transition metal catalysts prone to chain walking can selectively insert alkenes into secondary alkyls. Given previous results with molecular catalysts demonstrating olefin insertion into primary and secondary nickel alkyls in roughly equivalent amounts,[16] we anticipated observing a mixture of methylenecyclohexane and 1-methyl-2-methylene-cyclopentane upon treatment of Ni-MFU-4l with 1,6-heptadiene. Surprisingly, we observed only the latter along with isomerized linear dienes (Scheme 2), indicating that the tethered alkene selectively inserts into the secondary nickel alkyl species.

DFT calculations provide further insight into the selective insertion of the pendant alkene into the secondary nickel alkyl species. Experimentally, the presence of isomerized dienes implies a highly dynamic nickel alkyl in Ni-MFU-4l, as the formation of internal olefins requires the formation of a secondary nickel alkyl species prior to β-hydride elimination (Scheme 2). Calculations reveal that the primary nickel alkyl species is in fact more stable than the secondary alkyl by 3.5 kcal/mol, and that the Ni−C bond is elongated by 2% in the latter (Figure S29). These results are consistent with literature examples of group 10 metal alkyl complexes, which show that secondary metal alkyl complexes are commonly less stable than primary metal alkyls, with a slight elongation of the M−C bond for the secondary alkyl species.[62−64] This elongation suggests that the Ni−C bond is weaker in the secondary Ni-alkyl species, which therefore favors olefin insertion and the formation of 1-methyl-2-methylenecyclopentane. Furthermore, 5-exo ring closures are often kinetically favored,[65] providing additional kinetic selectivity for 1-methyl-2-methylenecyclopentane. Thus, we propose that the selectivity for 1-methyl-2-methylenecyclopentane results from the kinetically favored alkene insertion

Scheme 2. Formation of 1-Methyl-2-methylenecyclopentane from 1,6-Heptadiene in Ni-MFU-4l
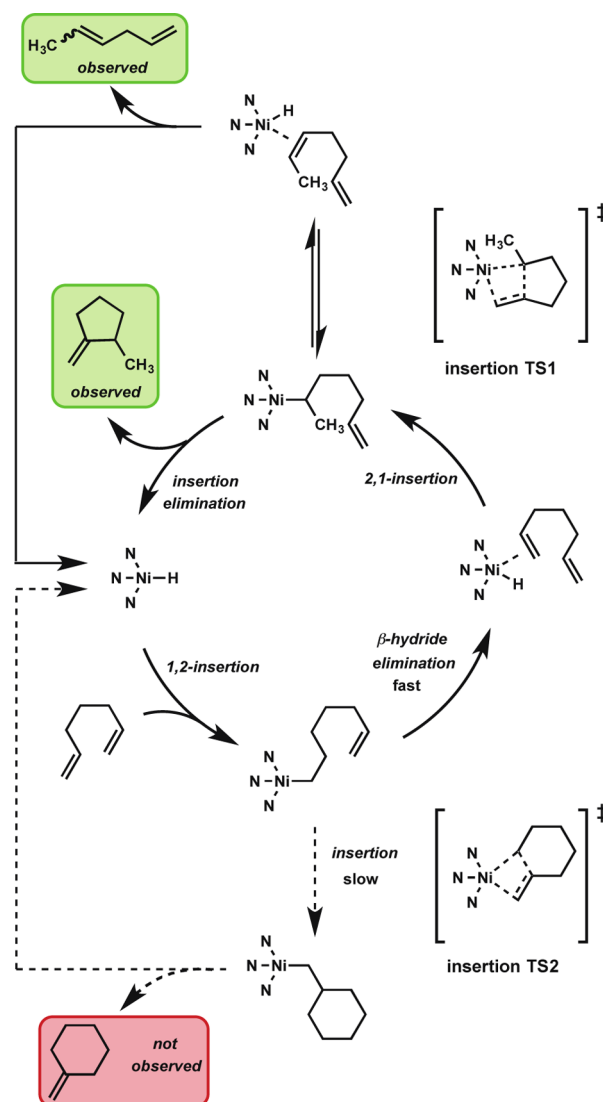
into the less thermodynamically stable secondary nickel alkyl species. Indeed, when the molecular Cossee-Arlman catalyst (2,2′-bipyridine)nickel bromide/MMAO-12[15] was treated with 1,6-heptadiene, the resulting product mixture was similar to that obtained with Ni-MFU-4l: isomerized dienes and 1-methyl-2-methylenecyclopentane. This provides further confirmation that our MOF catalyst operates by the Cossee-Arlman mechanism and suggests that the selectivity for 1-methyl-2-methylenecyclopentane results from the kinetically favorable 5-exo ring closure relative to the 6-exo ring closure.[66]

Control experiments further ruled out the formation of 1-methyl-2-methylenecyclopentane by a metallacyclic mechanism. When a prototypical system for reductive coupling via metallacyclic intermediates—Ni(cod)₂ with two equivalents of triphenylphosphine[49,50,52]—was allowed to react with 1,6-heptadiene, the starting material was recovered quantitatively, despite noticeable color changes indicating the formation of a nickel alkene complex. This, in tandem with the results obtained with (2,2-bipyridine)nickel bromide/MMAO-12 (see above), strongly suggests that Ni-MFU-4l forms 1-methyl-2-methylenecyclopentane via the Cossee-Arlman mechanism.

CONCLUSIONS

Due to the tremendous utility of short linear alpha olefins and the recent development of a heterogeneous catalyst that can selectively dimerize ethylene, determining the catalyst's mechanism of operation is a question of fundamental interest with substantial practical implications. In this study, we have conclusively shown that Ni-MFU-4*l* selectively dimerizes ethylene via the Cossee-Arlman mechanism with a combination of isotopic labeling experiments, molecular probes, and DFT calculations. Importantly, we have shown that the toolbox of homogeneous organometallic chemistry can be applied to rigorously elucidate catalytic mechanisms in MOFs. Continued research in MOF catalysis should leverage the unique opportunities afforded by these materials to address unsolved challenges in heterogeneous catalysis and exploit the molecular nature of active sites to provide insight into the fundamental chemistry that enables the catalytic transformation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10300.

> Experimental details, gas chromatograms, and mass fragmentation patterns (PDF)
> 1-Butene isotopomer analysis (XLSX)

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Notes

The authors declare no competing financial interest.

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(66) An alternative hypothesis is the selective 2,1-insertion of 1,6-heptadiene into the Ni−H species followed by a 1,2-insertion of the tethered alkene. This is also consistent with the data and has some literature support (for example, see Widenhoefer, R. A. *Acc. Chem. Res.* **2002**, *35*, 905 and references therein). However, we support the hypothesis presented in the main text due to the well established chain walking behavior of Ni alkyl complexes.