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Communication

Ring Contraction of a Tungstacyclopentane Supported on Silica: Direct Conversion of Ethylene to Propylene

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ABSTRACT: The reaction of $W(NAr)(^{13}C_4H_8)(OSiPh_3)_2$ (**1**) (NAr = 2,6-diisopropylphenylimido) with silica partially dehydroxylated at 700 °C ($SiO_{2\text{-}700}$) is highly dependent on the reaction conditions. The primary product of this reaction is $W(NAr)(^{13}C_4H_8)(OSiPh_3)(OSi(O-)_3)$ (**2**) when the reaction is carried out in the dark. Grafting **1** onto $SiO_{2\text{-}700}$ in ambient lab light results in the formation of **2**, $W(NAr)(^{13}CH_2{}^{13}CH_2)(OSiPh_3)(OSi(O-)_3)$ (**4**), and one isomer of square-pyramidal $W(NAr)(^{13}CH_2{}^{13}CH(^{13}Me)^{13}CH_2)(OSiPh_3)(OSi(O-)_3)$ (**3**). Heating **2** to 85 °C for 6 h results in the formation of **3**, **4**, $W(NAr)(^{13}CH(^{13}Me)^{13}CH_2{}^{13}CH_2)(OSiPh_3)(OSi(O-)_3)$ (**5**), and $W(NAr)((^{13}CH_2)_2{}^{13}CH(^{13}Me)(^{13}CH_2)_2)(OSiPh_3)(OSi(O-)_3)$ (**6**). Photolysis of **2** with blue LEDs (λ_{max} = 450 nm) produces 4, both isomers of 3, **5**, and free ethylene. In the presence of excess ethylene and blue LED irradiation at 85 °C, **1**/$SiO_{2\text{-}700}$ catalyzes the direct conversion of ethylene to propylene.

Propylene is a vital small-molecule feedstock that is produced on large scale by energy-intensive and unselective steam cracking of propane. Catalytic methods used to generate propylene and the thermodynamic parameters associated with these reactions are shown in Figure 1. Catalytic propane dehydrogenation operates at high temperatures because this reaction is enthalpically demanding (ΔH_{rxn} = 29.9 kcal mol^{-1}).[1] Ethenolysis of 2-butene is essentially thermoneutral at 25 °C (ΔH_{rxn} = −0.2 kcal mol^{-1}), but typical WO_3/SiO_2 catalysts for this reaction operate at ~400 °C.[2] This discrepancy between a thermoneutral olefin metathesis reaction and catalytic reality is likely a consequence of the sequence of events necessary to form the tungsten alkylidene active site. Indeed, the formation of well-defined alkylidenes on oxides[3] or treatment of WO_3/SiO_2 catalysts with two-electron-reducing reagents results in metathesis catalysts that are active at or near room temperature.[4]

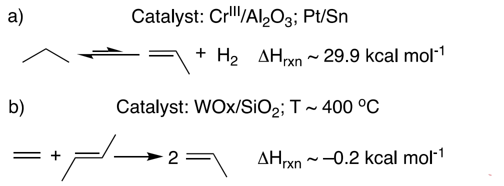

Figure 1. Catalytic reactions for the synthesis of propylene and their associated calculated enthalpies: (a) propane dehydrogenation; (b) ethenolysis of 2-butene.

In this contribution, we propose that the mechanism shown in Figure 2a generates propylene directly from ethylene. Direct conversion of ethylene to propylene is significantly more enthalpically favorable than ethenolysis of 2-butene (ΔH = −27.8 kcal mol^{-1}; Figure 2b). Previously reported examples of the direct conversion of ethylene to propylene involve dimerization of ethylene to form 2-butene followed by ethenolysis or cracking reactions to generate propylene.[5]

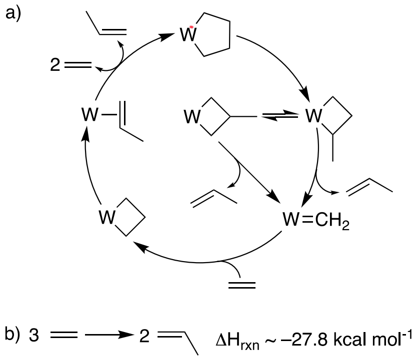

Figure 2. (a) Proposed catalytic cycle for direct conversion of ethylene to propylene and (b) enthalpy of this reaction.

The key steps shown in Figure 2a have not been established at a single metal center but resemble those proposed for the homologation of vinyltributyltin catalyzed by a Mo(IV) olefin complex.[6] Recent results showed that high-oxidation-state W(VI) metallacyclopentanes undergo photochemical ring contraction to form substituted W(VI) metallacyclobutanes.[7] In the presence of excess ethylene, the substituted W(VI) metallacyclobutane releases a stoichiometric amount of

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propylene and forms the unsubstituted W(C_3H_6) metallacyclobutane. Under certain conditions, W(C_3H_6) rearranges to the W(IV) propylene adduct.[8] This reaction probably occurs through β-H elimination to form the allyl−hydride intermediate and is a decomposition pathway for metathesis-inactive square-pyramidal (SP) metallacyclobutanes.[9] Reaction of the propylene adduct with ethylene regenerates the W(VI) metallacyclopentane and closes the catalytic cycle.

This paper describes the reaction of W(NAr)($^{13}C_4H_8$)($OSiPh_3$)$_2$ (**1**) with silica partially dehydroxylated at 700 °C ($SiO_{2\text{-}700}$) (0.26 ± 0.01 $mmol_{OH}$ g^{-1}). The primary product of this reaction is W(NAr)($^{13}C_4H_8$)($OSiPh_3$)(OSi(O−)$_3$) (**2**), which evolves to form a mixture of products specific to the reaction conditions (Scheme 1). In the rigorous absence of light, **1** reacts with $SiO_{2\text{-}700}$ to form **2** (major) and SP W(NAr)($CH_2CH(Me)CH_2$)($OSiPh_3$)(OSi(O−)$_3$) (**3**) (minor). **2** is a primary product of the reaction of **1** and $SiO_{2\text{-}700}$. Thermal or photomediated ring contraction of **2** followed by cycloreversion and cycloaddition steps form **3** (vide infra). In ambient lab light **1** reacts with $SiO_{2\text{-}700}$ to form **2**, **3**, and W(NAr)($^{13}CH_2{}^{13}CH_2$)($OSiPh_3$)(OSi(O−)$_3$) (**4**). **4** is formed by the loss of ethylene from **2**. Elemental analysis of **1**/SiO_2 gives 1.90% W (0.10 $mmol_W$ g^{-1}). Monitoring this reaction by solution ^1H NMR spectroscopy in C_6D_6 showed that free $HOSiPh_3$ does not form in this reaction. However, the FTIR spectrum of **1**/SiO_2 contains ν_{CH} and $\nu_{C=C}$ bands, as expected, and a broad ν_{OH} band centered at 3611 cm^{-1} characteristic of hydrogen-bonded silanols (Figure S2). This is consistent with grafting of **1** onto $SiO_{2\text{-}700}$ to form **2** and reaction of released $HOSiPh_3$ with unreacted silanols to form $Ph_3SiOSi(O-)_3$ and water, which adsorbs onto silica to form hydrogen-bonded silanols. Control experiments showed that $HOSiPh_3$ adsorbs onto silica from pentane solutions, and the resulting FTIR data of $HOSiPh_3$-contacted silica also contain the broad ν_{OH} band centered at 3611 cm^{-1} (Figure S6).

Scheme 1. Evolution of Products in the Reaction of 1 with $SiO_{2\text{-}700}$

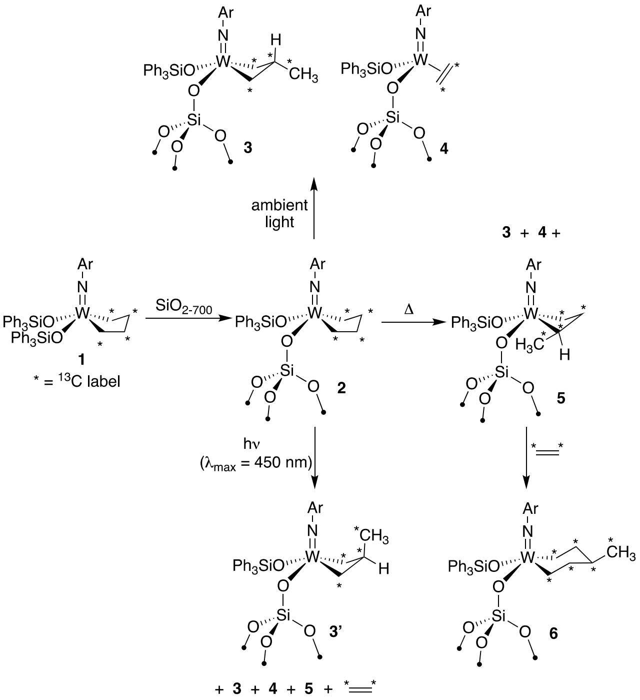


Figure 3a shows the 2D $^{13}C-{}^{13}C$ chemical shift correlation spectrum acquired with dipolar-assisted rotational resonance (DARR) mixing[10] of **2** (major) and **3** (minor) prepared from **1** and $SiO_{2\text{-}700}$ in the absence of light. In a $^{13}C-{}^{13}C$ DARR experiment, cross-polarization from protons to nearby ^{13}C spins is followed by magnetization transfer to neighboring ^{13}C spins that are dipolar-coupled (i.e., close to one another in space),[10a] resulting in cross-peaks that are symmetrical about the diagonal in the 2D DARR spectrum. Expected cross-peaks for the various metallacycles formed in Scheme 1 are shown in Figure 3d. The DARR spectrum in Figure 3a contains intense cross-peaks between ^{13}C NMR signals at 71.5 and 34.1 ppm that are from Cα and Cβ of the W(C_4H_8) moiety in **2**. The minor set of cross-peaks from **3** are at 63.8 (Cα), 27.5 (Cβ), and 11.7 (Me) for the β-methyl species W($^{13}CH_2{}^{13}CH$(^{13}Me)$^{13}CH_2$). When **1** and $SiO_{2\text{-}700}$ react the presence of ambient light, the $^{13}C-{}^{13}C$ DARR spectrum contains characteristic signals for **2** and **3** and cross-peaks at 60.2 and 51.8 assigned to W($^{13}CH_2{}^{13}CH_2$) in **4** (Figure S8); two signals are expected for a slowly rotating ethylene coordinated the unsymmetrical W center in **4**.[8b] The chemical shift for Cα in **3** is consistent with the formation of the SP isomer, which we assume to be the isomer of **3** with the β-Me pointed away from the NAr group as shown in Scheme 1 because all metallacyclobutanes containing substituents at Cβ characterized by X-ray crystallography adopt this conformation to reduce steric interactions with the bulky imido group.[11]

Heating material prepared from **1** and $SiO_{2\text{-}700}$ in the absence of light at 85 °C for 6 h results in complete consumption of **2** to form a mixture of **3**, **4**, and SP W(NAr)(^{13}CH(^{13}Me)$^{13}CH_2{}^{13}CH_2$)($OSiPh_3$)(OSi(O−)$_3$) (**5**). Gas chromatography analysis of the gas phase after heating showed that no volatile products (e.g., ethylene, propylene, or butenes) formed during thermolysis. The $^{13}C-{}^{13}C$ DARR spectrum after heating is shown in Figure 3b. The resonances in W(^{13}CH(^{13}Me)$^{13}CH_2{}^{13}CH_2$) in **5** appear at 69.0 (Cα-Me), 63.1 (Cα), 28.7 (Cβ), and 23.7 (Me). This spectrum also contains minor cross-peaks at 63.0 (Cα), 32.7 (Cβ), 17.2 (Cγ), and 10.9 (Me) assigned to the γ-methyltungstacyclohexane W(NAr)(($^{13}CH_2$)$_2{}^{13}CH$(^{13}Me)($^{13}CH_2$)$_2$)($OSiPh_3$)(OSi(O−)$_3$) (**6**). To our knowledge, tunstacyclohexanes have not been reported in the literature.[12]

Photolyzing material prepared from **1** and $SiO_{2\text{-}700}$ in the absence of light with blue LEDs (λ_{max} = 450 nm) at 37.5 °C results in complete consumption of **2** and the formation of **3**, **4**, and **5** (Figure 3c). Propylene, butenes, and **6** are not formed in this reaction, but ethylene is formed. The $^{13}C-{}^{13}C$ DARR spectrum of photolyzed material shown in Figure 3c is qualitatively similar to the $^{13}C-{}^{13}C$ DARR spectrum shown in Figure 3b. However, there are clearly two signals for the Cα in **3**, indicating that both **3** and **3′** are generated during photolysis. The signals for the SP β-methyl moiety W($^{13}CH_2{}^{13}CH$(^{13}Me)$^{13}CH_2$) in **3′** appear at 66.3 (Cα), 28.8 (Cβ), and 11.7 (Me).

A plausible mechanism accounting for the products formed from **2** is shown in Scheme 2. Thermolysis results in β-H elimination from W(C_4H_8) to generate W(4-butenyl)H, which inserts the olefin into the W−H bond at the more substituted carbon to form key α-Me-substituted metallacyclobutane **5** that is responsible for the formation of β-Me-substituted metallacyclobutanes **3** and **3′** and γ-Me-substituted tungstacy-

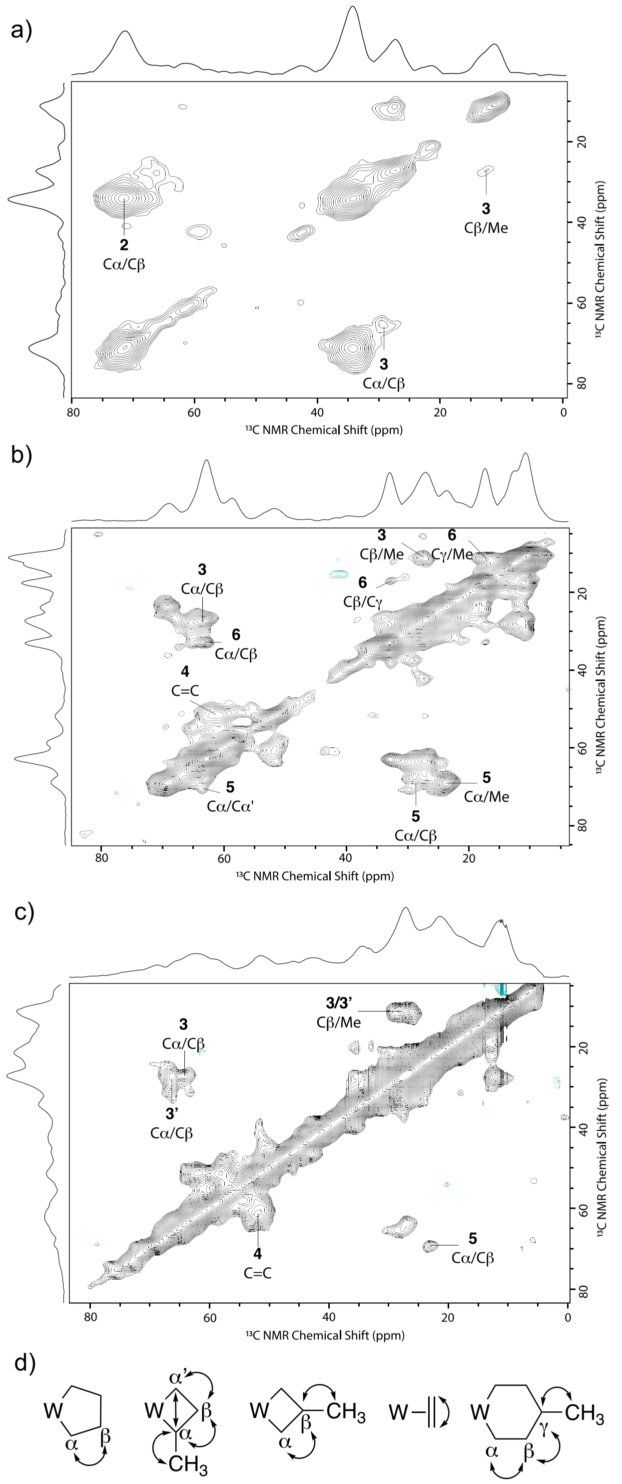
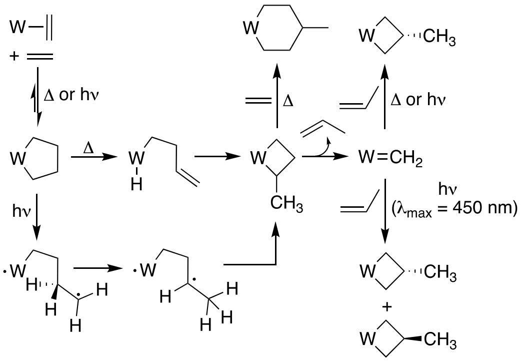


Figure 3. (a−c) 2D ^{13}C−^{13}C chemical shift correlation spectrum with DARR mixing of **2** (major) and **3** (minor) prepared from **1** and $SiO_{2\text{-}700}$ in the absence of light (a), after thermolysis at 85 °C for 6 h (b), and after photolysis with LEDs (λ_{max} = 450 nm) for 6 h at 37.5 °C (c). (d) Arrows showing cross-peaks expected based on the structures of **2**−**6**. The cross-peak for Cα'−Cβ in **5** overlaps with signals for **3**.

Scheme 2. Thermal or Photomediated Rearrangement of 2 to Form Ring-Contracted Products



clohexane **6**. Cycloreversion of **5** forms W═CH_2 and propylene. Neither of these products was observed experimentally because fast cycloaddition forms the β-Me-substituted metallacyclobutane, which thermally forms one isomer of **3** but in the presence of blue LEDs forms both isomers of **3**. Complete conversion of W(C_4H_8) to **3** and **5** indicates that the ring-contracted metallacyclobutanes are more stable than **2**.

Under thermolytic conditions, W(C_4H_8) also releases ethylene to form **4**. Free ethylene was not detected in the gas phase after ring contraction, indicating that ethylene is consumed during thermolysis. The product of this reaction is γ-Me-substituted tungstacyclohexane **6**, which apparently forms through insertion of ethylene into the more substituted W−C bond in **5**.

Photochemical ring contraction was recently observed in **1** and W($NCPh_3$)(C_4H_8)($OSiPh_3$)$_2$ in solution.[7] This reaction was proposed to involve either thermal or photomediated Berry pseudorotation to isomerize the SP isomer to the unobserved trigonal-bipyramidal (TBP) W(C_4H_8) followed by homolysis of a W−C bond, H atom migration, and recombination. This process generates α-Me-substituted metallacyclobutane **5**. Similar to thermolytic conditions, W(C_4H_8) also forms **3** in the presence of blue LEDs. However, photolytic conditions result in free ethylene, and the characteristic correlations in the ^{13}C−^{13}C DARR NMR spectrum of **6** are not present, indicating that the reaction of **5** and ethylene to form **6** is a thermal reaction.

Irradiation of **1**/$SiO_{2\text{-}700}$ with blue LEDs in the presence of excess ethylene (1900 equiv per W) generates propylene at elevated temperatures (Figure 4a). At 85 °C, **1**/$SiO_{2\text{-}700}$ generates 22 $mol_{C_3H_6}$ mol_W^{-1} over 48 h, corresponding to 11 turnovers of the catalytic cycle shown in Figure 2a. Decreasing or increasing the reaction temperature results in a lower turnover number in this reaction. Heating **1**/$SiO_{2\text{-}700}$ to 85 °C in the absence of light forms only traces of propylene (0.25 $mol_{C_3H_6}$ mol_W^{-1}). Figure 4b shows a GC trace of the gas phase after maximum turnover at 85 °C. Neither this GC trace nor GC traces taken at intermediate time points during this reaction contain butenes, indicating that ethenolysis of 2-butene intermediates is unlikely in this reaction. Indeed, **2** does metathesize propylene to 2-butenes and ethylene, but this reaction is slow, suggesting that 2-butenes would be observed under ethylene to propylene conditions (see the Supporting Information).

Irradiating **1**/$SiO_{2\text{-}700}$ with blue LEDs at 85 °C in the presence of ^{13}C-labeled ethylene (190 equiv per W) for 2 h gives five equivalents of ^{13}C-propylene per W (2.5 TON). This shorter reaction time was chosen because under these conditions **1**/SiO_2 will continue to form propylene from

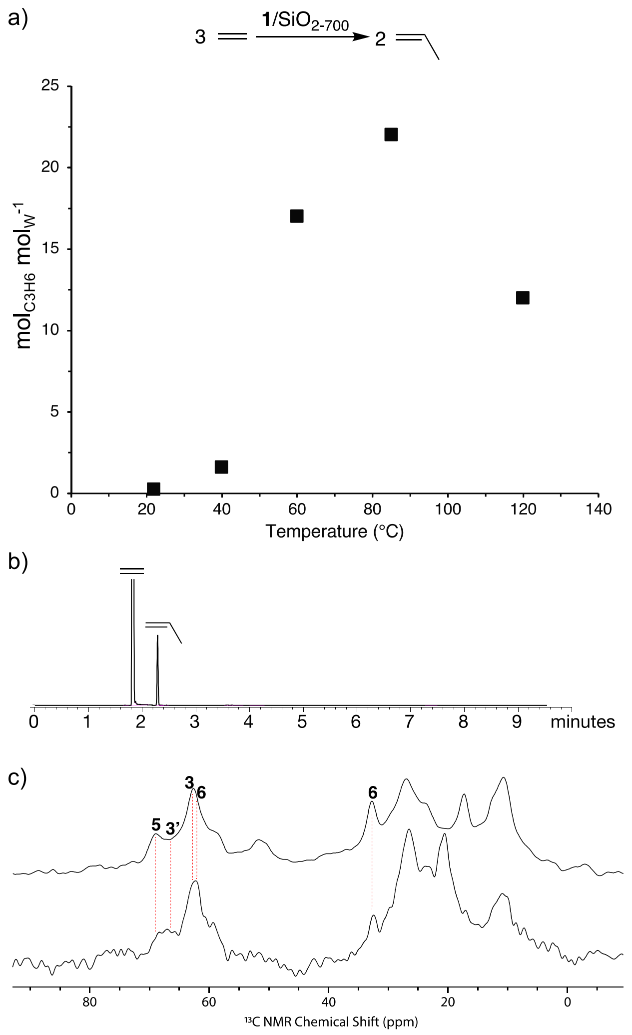


Figure 4. (a) Turnover numbers (TONs) for ethylene to propylene at different temperatures under blue LED irradiation. (b) Gas chromatography trace after maximum TON for the reaction performed at 85 °C. (c) $^{13}C\{^1H\}$ CPMAS NMR spectra of $1/SiO_{2\text{-}700}/^{13}CH_2{}^{13}CH_2$ (bottom) and thermolyzed **2**/**3** (top). Assignments from $^{13}C-^{13}C$ DARR experiments for key resonances are given above the top spectrum.

ethylene. The ^{13}C cross-polarization magic angle spinning (CPMAS) NMR spectrum of $\mathbf{1}/SiO_{2\text{-}700}/^{13}CH_2{}^{13}CH_2$ is shown in Figure 4c (bottom spectrum) and contains characteristic signals for **3**, **3′**, **5**, and **6**. For comparison, the 1D $^{13}C\{^1H\}$ CPMAS NMR spectrum of **2**/**3** heated at 85 °C for 6 h is also shown in Figure 4c (top spectrum).

There are several implications of the data shown in Figures 3 and 4. The observed metallacyclobutanes are SP, which are not metathesis-active,[13] indicating that **3**, **3′**, or **5** requires thermal or photomediated isomerization to the TBP isomer prior to loss of propylene. The formation of **6** in thermolyzed **2** and $\mathbf{1}/SiO_{2\text{-}700}/^{13}CH_2{}^{13}CH_2$ was unexpected, but this species appears to be a deactivation product because $\mathbf{1}/SiO_{2\text{-}700}$ does not form products with higher molecular weight than propylene in the presence of ethylene. The formation of **6** may also explain why $\mathbf{1}/SiO_{2\text{-}700}$ does not thermally convert ethylene to propylene even though the $W(C_4H_8)$ ring contracts at 85 °C in the absence of light. This behavior suggests that loss of propylene from **3** is slower than insertion of ethylene to form **6** under thermal conditions. This scenario is supported by the spectrum shown in Figure 4c, which contains **6**. $W(C_4H_8)$ species that undergo ring contraction to form TBP metallacyclobutanes should be more active in this reaction by avoiding formation of tungstacyclohexanes in the presence of ethylene.

The reaction of **1** with $SiO_{2\text{-}700}$ is surprisingly complex. The thermal ring contraction of **2** contrasts with solution studies of **1** and $W(NCPh_3)(C_4H_8)(OSiPh_3)_2$, in which blue light was required to form metallacyclobutanes.[7] Supporting **1** on $SiO_{2\text{-}700}$ results in a sterically open $W(C_4H_8)$ in **2**, suggesting that steric modification of the ligands in homogeneous $W(C_4H_8)$ species may also result in ring contraction under thermal conditions. Avoiding SP substituted metallacyclobutanes appears to be critical to promote the conversion of ethylene to propylene and to avoid the formation of inactive tungstacyclohexanes. We are currently exploring strategies to form catalysts that are more robust than **2** for the conversion of ethylene to propylene.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07934.

Experimental methods, solid-state NMR spectra, and gas chromatograph traces (PDF)

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Notes

The authors declare the following competing financial interest(s): A provisional patent describing these findings was submitted.

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