

# Productive Alkyne Metathesis with “Canopy Catalysts” Mandates Pseudorotation

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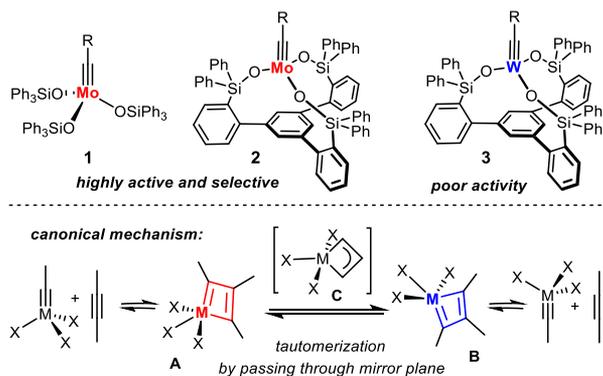
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**ABSTRACT:** Molybdenum alkylidyne complexes of the “canopy catalyst” series define new standards in the field of alkyne metathesis. The tripodal ligand framework lowers the symmetry of the metallacyclobutadiene complex formed by [2 + 2] cycloaddition with the substrate and imposes constraints onto the productive [2 + 2] cycloreversion; pseudorotation corrects this handicap and makes catalytic turnover possible. A combined spectroscopic, crystallographic, and computational study provides insights into this unorthodox mechanism and uncovers the role that metallatetrahedrane complexes play in certain cases.

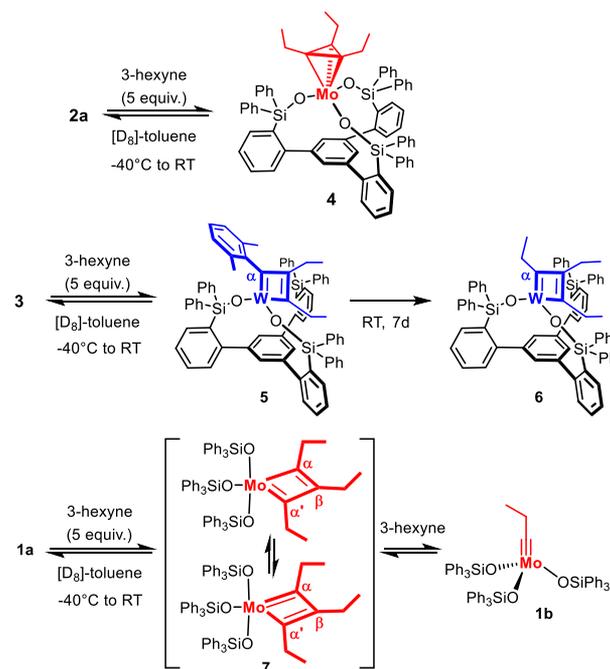
The discovery that molybdenum alkylidyne units synergize particularly well with triarylsilanolate ligands marked an important milestone in the development of alkyne metathesis in general.<sup>1–6</sup> Catalysts such as **1** and the derived bench-stable phenanthroline adducts combine high activity and unrivaled functional group tolerance with a previously unknown user-friendliness (Scheme 1).<sup>7–9</sup> A new generation of “canopy catalysts” of type **2** distinguished by a tripodal silanolate ligand framework shows an even better application profile.<sup>10–13</sup>

## Scheme 1. Overview



In consideration thereof, it was perplexing to find that addition of excess 3-hexyne to a solution of **2a** (R = 4-MeOC<sub>6</sub>H<sub>4</sub>-) in [D<sub>8</sub>]-toluene afforded the metallatetrahedrane **4** as the only detectable and isolable intermediate (Scheme 2).<sup>10–12</sup> Even though its formation is reversible, as shown by exchange NMR spectroscopy (EXSY), the generally accepted mechanism of alkyne metathesis does not involve an intermediate of this type; rather, it is believed to proceed via the two square-pyramidal metallacyclobutadiene tautomers **A** and **B** formed and disassembled by [2 + 2] cycloaddition/cycloreversion; they interconvert by passing through a trigonal-bipyramidal form **C** (Scheme 1);<sup>14–19</sup> metallatetrahedranes, in

## Scheme 2. Distinct Behavior of Different Alkylidyne Complexes



contrast, are considered to be unreactive sinks and/or gateways to catalyst decomposition.<sup>20–23</sup> The exclusive formation of **4** from one of the best available catalysts is therefore non-intuitive.<sup>10,11</sup> A veritable conundrum accrues when the behavior

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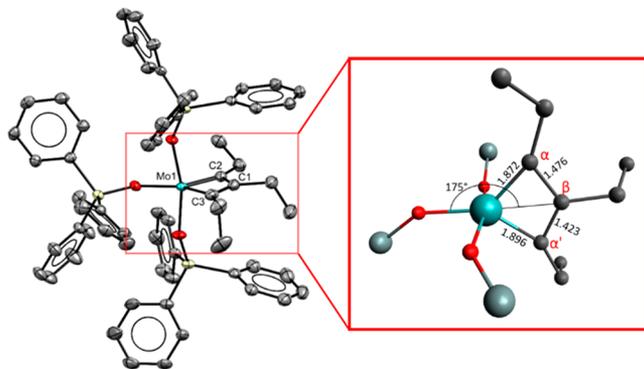


of the tungsten analogue **3** ( $R = 2,6\text{-Me}_2\text{C}_6\text{H}_3^-$ ) is also taken into consideration, which furnished the canonical metallacyclobutadiene **5** on reaction with 3-hexyne. It took 1 week for the latter to transform into **6** by what represents a single “turnover”; complex **3** is hence catalytically incompetent.<sup>24</sup> The question arises whether these perplexing observations challenge the consensus mechanism of alkyne metathesis or whether they can be consolidated with it. The answer is deemed critically important for further catalyst development.

In the first foray, we checked the behavior of the parent catalyst **1a** ( $R = 4\text{-MeOC}_6\text{H}_4^-$ ) endowed with *monodentate* silanolates, which had so far been tacitly assumed to follow the canonical mechanistic course. Indeed, treatment of a solution of **1a** with 3-hexyne (5 equiv) in  $[\text{D}_8]\text{-toluene}$  gave molybdenacyclobutadiene **7** exclusively (Scheme 2). Although **1a** and **2a** are both excellent catalysts and both carry silanolate ligands, they obviously afford distinct types of intermediates on reaction with the substrate. Complex **7** is  $C_{2v}$  symmetric in solution since only one signal is observed for the two  $C_{\alpha}$ -atoms ( $\delta_C = 248.8$  ppm); even at  $-90$  °C, the two tautomers of the metallacycle are not frozen out, which indicates an extremely low barrier for interconversion. EXSY-NMR data revealed the dynamic exchange of the ethyl substituents at the  $C_{\alpha}$ - and  $C_{\beta}$ -atoms with free 3-hexyne, thus implying that the product-forming (“productive”) and the substrate-regenerating (“unproductive”)  $[2 + 2]$  cycloreversions are equally likely.<sup>25</sup>

Highly sensitive steel-blue crystals suitable for X-ray diffraction could be grown from a solution of **7** in  $\text{Et}_2\text{O}$  at  $-85$  °C. This result is deemed rewarding since pertinent information about the structure of molybdenacyclobutadienes in the solid state is very limited.<sup>19,26–28</sup>

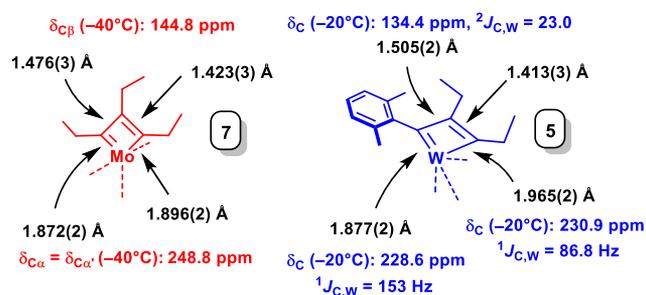
The Mo(+6) center of **7** adopts a coordination geometry in between trigonal-bipyramidal and square-pyramidal ( $\tau_5 = 0.37$ , Figure 1).<sup>29</sup> The bond lengths are uneven: whereas the Mo1–



**Figure 1.** Structure of complex **7** in the solid state; H atoms and the solvent are omitted for clarity.

C2 bond is only slightly shorter than the Mo1–C3 bond, the difference is more pronounced for C1–C2 versus C1–C3 (Figure 2).<sup>30,31</sup> It is remarkable that the metallacyclobutadiene forms A/B surface in the X-ray structure of **7** even though it is fairly close to the trigonal-bipyramidal rendition C where the tautomers converge (Scheme 1);<sup>18</sup> this peculiar situation may explain why their interconversion in solution is fast even at  $-90$  °C as manifested in the spectra of  $C_{2v}$  symmetry.<sup>32,33</sup>

The comparison of **7** with the structure of tungstenacyclobutadiene **5**<sup>24</sup> derived from the catalytically incompetent tungsten alkyldiene **3** is also informative, as it allows the effect of the tripodal “canopy” ligand architecture to be assessed



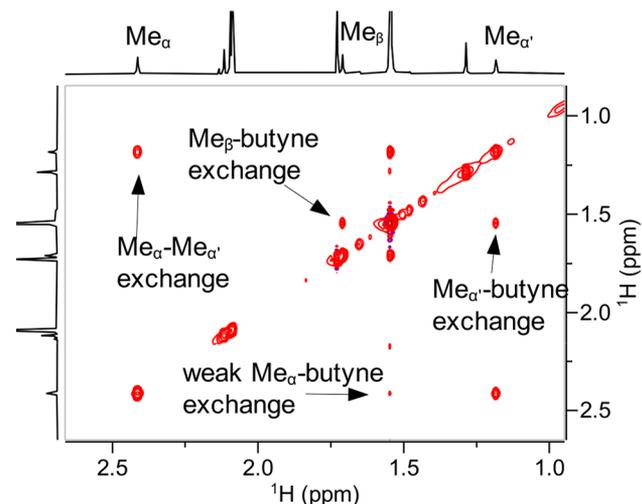
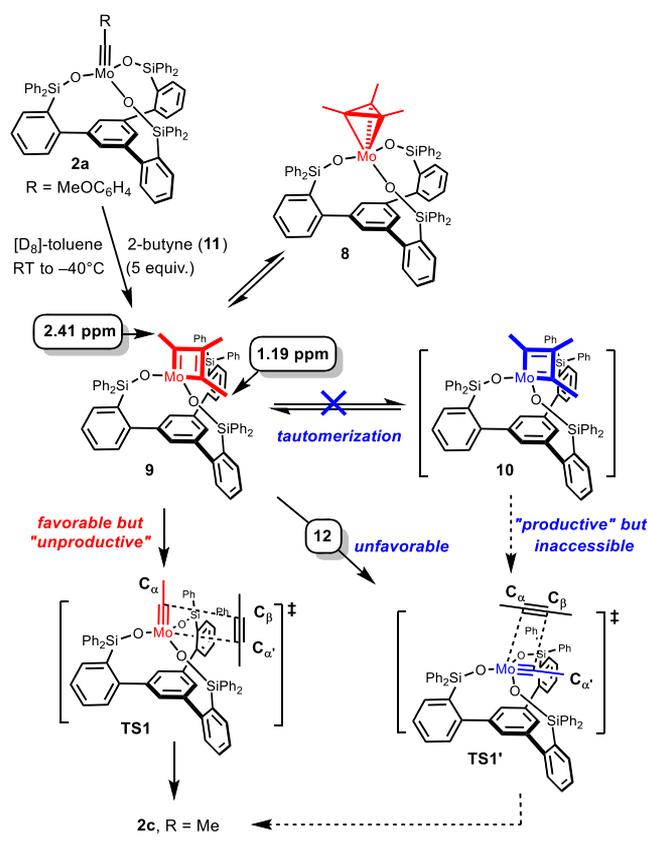
**Figure 2.** Comparison of the metallacyclobutadiene cores of complexes **7** and **5**.

(Figure 2). In contrast to **7**, complex **5** is closer to square-pyramidal than trigonal-bipyramidal ( $\tau_5 \approx 0.14$ ).<sup>29</sup> The metallacyclic core is much more distorted in all bond distances;<sup>24,34</sup> this distortion persists in solution in that the  $C_{\alpha}/C_{\alpha}$ -atoms of **5** are inequivalent as manifested in discrete shifts and notably different  $^1J_{C,W}$  coupling constants indicative of substantial “double” bond character for the short W– $C_{\alpha}$  bond but “single” bond character for the longer W– $C_{\alpha}$ .<sup>24</sup> The fact that a single tautomer of **5** is detected in solution explains why EXSY-NMR experiments show only the dynamic exchange between the ethyl substituents at  $C_{\alpha}$  and  $C_{\beta}$  with free 3-hexyne by “unproductive”  $[2 + 2]$  cycloreversion that regenerates the starting materials. The obviously much higher barrier of the “productive” cycloreversion is in line with the overly long reaction time of 1 week for **5** to transform into the all-ethyl-substituted tungstenacyclobutadiene **6**.<sup>24</sup> The core of **6** must be similarly distorted since the  $C_{\alpha}/C_{\alpha}$ -atoms and their ethyl substituents are inequivalent. However, mutual interconversion of these positions is observed on the NMR time scale: for favorable circumstances, the activation parameters could be deduced.<sup>35</sup>

As mentioned above, the reaction of the molybdenum alkyldiene **2** with 3-hexyne gave metallatetrahedrane **4** exclusively. A more systematic study, however, showed that the outcome is substrate-dependent: thus, treatment of **2a** with 2-butyne gave a mixture of metallatetrahedrane **8** and the corresponding metallacyclobutadiene **9** (Scheme 3).<sup>36</sup> Only for the latter, a dynamic exchange with 2-butyne by  $[2 + 2]$  cycloreversion was observed by EXSY-NMR, whereas the metallatetrahedrane **8** is static at  $-40$  °C. The mixture had to be warmed to  $0$  °C for **8** and **9** to mutually interconvert and for **8** to commence exchanging with 2-butyne (see the SI).

The shifts of the methyl groups at the  $C_{\alpha}$  and  $C_{\alpha}$  positions of **9** are strikingly different, which implies a complex of low symmetry: on the NMR time scale, only one of these methyl substituents resides in the anisotropy cone of a neighboring phenyl ring.<sup>39,40</sup> Equally informative are the EXSY data, which show two different dynamic processes: First, the methyl groups at  $C_{\alpha}/C_{\beta}$  exchange with 2-butyne (**11**) much more readily than that at  $C_{\alpha}$  (Figure 3). This finding proves that the “unproductive” and the “productive”  $[2 + 2]$  cycloreversion both proceed even at  $-40$  °C but are not equally facile.<sup>25</sup> Second, interconversion of the methyl substituents at the  $C_{\alpha}/C_{\alpha}$  positions is observed: this effect, however, is unlikely to be caused by formation of the second canonical tautomer: the tripodal ligand scaffold renders the second canonical tautomer (Scheme 1) inaccessible on steric grounds. Retention of the geometry of **9** but shuffling of the  $\pi$ -bonds with formation of a hypothetical tautomer **10** is equally excluded,<sup>41</sup> even if **10** were

## Scheme 3. Formation and Fate of Intermediates Carrying a Tripodal Ligand Framework

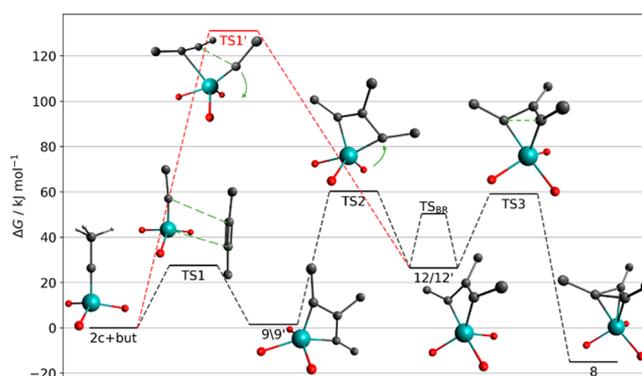


**Figure 3.** Dynamic exchange processes of **9** manifested in cross peaks in the EASY-ROESY spectrum ( $[D_8]$ -toluene,  $-40^\circ\text{C}$ , spin-lock time: 200 ms).<sup>37,38</sup>

reached, release of the product would be strongly disfavored by the clash of the incipient alkyldiene with the ligand framework (Scheme 3). DFT calculations confirmed the notion of two massively different barriers for the disintegration of the metallacyclobutadiene (TS1/TS1', see below). It is therefore safe to conclude that canopy catalysts do *not* operate by the generally accepted mechanism because the second required canonical metallacyclobutadiene tautomer is beyond reach, and its productive deconvolution is disfavored. Yet, complexes of type **2** are very powerful catalysts; therefore, some process must

be operative that corrects this situation and renders turnover facile.

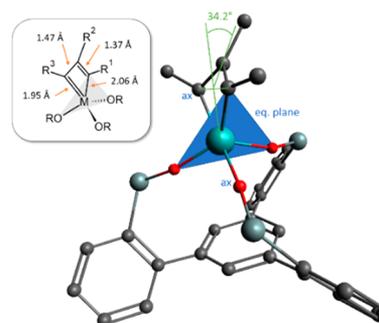
DFT calculations were used to probe this missing piece of the mechanism.<sup>42,43</sup> The minimum and transition state geometries as well as the obtained minimum energy pathways for the reaction of **2c** (R = Me) with 2-butyne and the interplay of **8** and **9** are available in the SI as well as Cartesian coordinates and video files A and B. Figure 4 summarizes the essentials: focusing



**Figure 4.** Thermochemistry of the reaction of **2c** with 2-butyne.

on the black data first, all barriers along the path are thermally accessible, including the interconversion of **9** and **8**. Moreover, the Gibbs free energy of the dissociated reactants is similar to that of these intermediates. Therefore, a mixture of both intermediates should be formed in the presence of excess alkyne, whereas the starting alkyldiene complex gets depleted. This conclusion is in excellent agreement with experiment (NMR) and hence gives confidence in the accuracy of the chosen DFT level of theory.

Complexes **9** to **8** were computationally found to interconvert via an intermediate **12**, which is higher in energy and hence not observed by NMR. A priori, **12** shows the proper  $\pi$ -bonding for productive cycloreversion. However, the metallacyclobutadiene ring is no longer flat as in **9**, but the three Mo–C distances are not yet equal as in **8** (Figure 5); it adopts a trigonal-bipyramidal

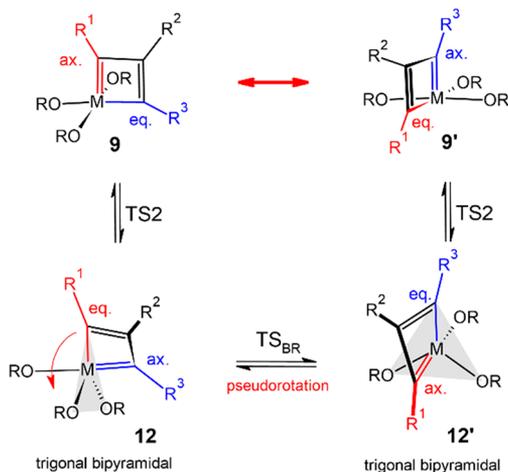


**Figure 5.** Computed structure of **12**; lateral phenyl groups and H-atoms are omitted for clarity.

geometry with two oxygen atoms and the former  $C_\alpha$ -atom occupying equatorial positions, whereas the third oxygen and the former  $C_{\alpha'}$  are axially disposed. Related metallacyclobutadienes are known in the literature,<sup>19</sup> the arguably most relevant one is a rhenacycle, in which  $C_\beta$  is tilted out of the M– $C_\alpha$ – $C_{\alpha'}$  plane by no less than  $34^\circ$ ; importantly, however, this complex does not undergo  $[2 + 2]$  cycloreversion and is hence catalytically incompetent.<sup>44,45</sup>

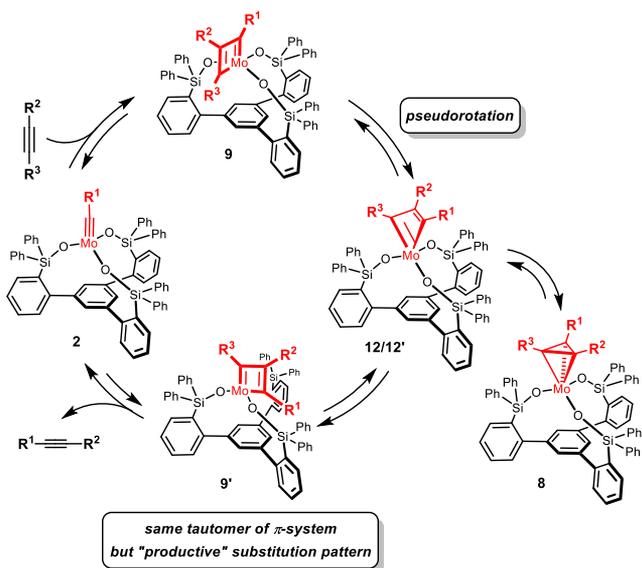
Intermediate **12** is not static but succumbs to Berry pseudorotation<sup>46</sup> about the adjacent M–O bond,<sup>47</sup> which exchanges the axial and equatorial  $C_\alpha$  positions via  $TS_{BR}$ ; **12**/**12'**, in turn, connect to two distinct metallacyclobutadienes **9**/**9'**, in which the  $C_\alpha/C_\alpha'$  atoms and their substituents  $R^1/R^3$  are mutually exchanged, whereas  $C_\beta$  remains in place (Scheme 4).<sup>48,49</sup>

Scheme 4. Crucial Berry Pseudorotation



Because of the lost  $C_{2v}$  symmetry, only the “unproductive” cycloreversion is facile for metallacyclobutadiene **9** via the low-lying  $TS_1$ .<sup>50,51</sup> “Productive” cleavage would either require isomer **10**, which is not within reach, or the highly distorted metallacycle **12**, for which DFT predicts an unfavorably high barrier ( $TS_1'$ ) (Figure 4). The fact that **9** is, after all, not a dead end but a truly competent catalytic intermediate is solely due to its dynamic behavior: the pseudorotation that interconverts **9**/**9'** via **12**/**12'** entails exchange of the  $R^1$  and  $R^3$  substituents on one and the same tautomeric form of the  $\pi$ -system (Scheme 5). The small barrier  $TS_{BR}$  can be overcome at (or even below) room temperature, where the canopy catalysts are usually fully operative. Hence, we conclude that catalysts of type **2** operate

Scheme 5. Turnover Enabled by Pseudorotation



by an unprecedented mechanism that involves a *single tautomeric form of the metallacyclobutadiene which appears in two differently substituted formats (9/9')*. Pseudorotation is the quintessential link in between them, without which product formation and catalyst turnover would not take place. The need to pass through this higher-lying intermediate and the accumulation of **8** off the actual cycle (see below) might be construed as an inherent kinetic disadvantage: indeed, **2** reacts more slowly than **1**. Importantly, however, canopy catalysts comprising smaller lateral  $R_2Si-$  groups allow this handicap to be counterbalanced.<sup>10</sup>

Finally, one needs to consider that the interconversion of **9** and **9'** could pass through **8**. Yet, several pieces of evidence speak against this assumption. As discussed above, EXSY-NMR experiments showed the exchange of **9** with 2-butyne at  $-40^\circ C$ , whereas **8** was static; productive and unproductive [2 + 2] cycloreversions are obviously ongoing, but the metallatetrahdrene is not engaged. The new mechanism allows this observation to be readily explained, since the barrier  $TS_{BR}$  for pseudorotation is lower than  $TS_3$  connecting **9** and **8**.

Moreover, if a metallatetrahdrene were to connect **9/9'**, all three C atoms would eventually get scrambled. However, the EXSY-NMR experiments showed only exchange of  $C_\alpha/C_\alpha'$  but no exchange of  $C_\alpha/C_\beta$ . For the tungstenacyclobutadiene **6**, which exhibits an analogous dynamic behavior, such a process can also be firmly excluded: only the NMR signals of the  $C_\alpha/R^1$  and  $C_\alpha'/R^3$  are broadened, whereas the resonances of  $C_\beta/R^2$  remain sharp.

Taken together, these data suggest that the metallatetrahdrene is off-cycle (Scheme 5). The question as to whether this conclusion applies to any substrate/catalyst combination can currently not be answered. In the present case, however, it is clear that intermediate **12** brokers the interconversion of the metallacyclobutadiene isomers **9/9'** and connects them with the metallatetrahdrene **8**; since  $TS_2$  and  $TS_3$  are of similar magnitude, a metallatetrahdrene can—but must not—be present in high concentration.

In summary, a combined spectroscopic/theoretical investigation advocates the notion that the performant canopy catalysts for alkyne metathesis operate by a mechanism that is notably different from that of earlier catalyst generations. The tripod ligand framework lifts the degeneracy of the [2 + 2] cycloreversions and makes the classical pathway unattainable: pseudorotation, however, clears this handicap. This conclusion needs to be closely considered in future catalyst development exercises.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c01404>.

Experimental part (procedures, characterization data, and supporting crystallographic information) and computational part (energies and geometries of stable structures computed as well as energy paths of isomerization reactions) (PDF)

Pseudorotation video A (ZIP)

Pseudorotation video B (ZIP)

### Accession Codes

CCDC 1987916 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_](mailto:data_)

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§A.H. and J.H. contributed equally.

### Notes

The authors declare no competing financial interest.

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(25) For symmetrical alkynes such as 2-butyne or 3-hexyne used to facilitate the NMR investigation, the “productive” (that is, product-forming) and the “unproductive” (that is, substrate-regenerating) cycloreversions are degenerate; these denominations are used to illustrate the fate of a putative unsymmetrical substrate.

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(27) Bittner, C.; Ehrhorn, H.; Bockfeld, D.; Brandhorst, K.; Tamm, M. Tuning the Catalytic Alkyne Metathesis Activity of Molybdenum and Tungsten 2,4,6-Trimethylbenzylidyne Complexes with Fluoroalkoxide Ligands  $\text{OC}(\text{CF}_3)_n\text{Me}_{3-n}$  ( $n = 0-3$ ). *Organometallics* **2017**, *36*, 3398–3406.

(28) A compilation of the few molybdenacyclobutadienes that have been crystallographically characterized so far is contained in the SI. The example derived from the catalytically most competent molybdenum alkylidyne endowed with hexafluoro-*tert*-butoxide ligands did not diffract well, thus preventing a discussion of bond lengths and angles, see: Ehrhorn, H.; Bockfeld, D.; Freytag, M.; Bannenberg, T.; Kefalidis, C. E.; Maron, C.; Tamm, M. Studies on Molybdena- and Tungstenacyclobutadiene Complexes Supported by Fluoroalkoxy Ligands as Intermediates of Alkyne Metathesis. *Organometallics* **2019**, *38*, 1627–1639.

(29) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen-Sulfur Donor Ligands: The Crystal and Molecular Structures of Aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

(30) With 2.117(2) Å, the Mo1–C1 distance across the almost perfectly planar metallacycle is also short; for a discussion of possible “transannular” bonding, see: Suresh, C. H.; Frenking, G. Direct 1–3 Metal–Carbon Bonding and Planar Tetracoordinated Carbon in Group 6 Metallacyclobutadienes. *Organometallics* **2010**, *29*, 4766–4769.

(31) Suresh, C. H.; Frenking, G. 1,3-Metal–Carbon Bonding and Alkyne Metathesis: DFT Investigations on Model Complexes of Group 4, 5, and 6 Transition Metals. *Organometallics* **2012**, *31*, 7171–7180.

(32) This result is somewhat reminiscent of the DFT analysis of a truncated [Mo]-model system, which found only a single intermediate that averages the square-pyramidal and trigonal-bipyramidal forms, see ref 18.

(33) For a catalytically active canonical tungsten catalyst, the barrier for the interconversion of the square-pyramidal tautomers A/B via a trigonal-bipyramidal transition state C was also computed to be very low (1.5 kcal·mol<sup>-1</sup>), see: Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. Efficient Room-Temperature Alkyne Metathesis with Well-Defined Imidazolin-2-iminato Tungsten Alkylidyne Complexes. *Angew. Chem., Int. Ed.* **2007**, *46*, 8890–8894.

(34) Moreover, the *trans*-O–W–C<sub>β</sub> angle (166°) is more strongly bent than the analogous *trans*-O–Mo–C<sub>β</sub> angle (175°) in 7.

(35) There is no competing exchange with 3-hexyne or any other species that might obscure the data otherwise; the activation parameters ( $\Delta H^\ddagger = 57.7 \pm 0.3$  kJ·mol<sup>-1</sup>,  $\Delta S^\ddagger = 8.6 \pm 1.3$  J·mol<sup>-1</sup>·K<sup>-1</sup>) are derived from line-shape analyses and Eyring plots, see ref 24.

(36) The different product distribution in the reactions of 2 with 2-butyne or 3-hexyne is attributed to increased stabilization of the metallatetrahydrene 4 by dispersion interactions between the ethyl substituents and the neighboring phenyl groups of the ligand framework; this interaction is less pronounced in 8 carrying smaller methyl groups; this aspect is subject to further investigation.

(37) Thiele, C. M.; Petzold, K.; Schleucher, J. EASY ROESY: Reliable Cross-Peak Integration in Adiabatic Symmetrized ROESY. *Chem. - Eur. J.* **2009**, *15*, 585–588.

(38) The observed exchange peak of C<sub>α</sub> with butyne is small compared to the one to C<sub>α'</sub> and not visible at shorter spin-lock times (50 ms); therefore, we cannot decide whether it arises from a direct pathway or from a two-step exchange process via C<sub>α'</sub> (see the SI for further details).

(39) The assignment and interpretation are based on the computed NMR spectra of 9 at the B3LYP-D3(BJ)/def2-TZVPP level of theory; for details, see the SI.

(40) Since the system is catalytically competent and shows several exchange processes, accurate activation parameters for the interconversion of the methyl substituents at the C<sub>α</sub>/C<sub>α'</sub> positions could not be deduced; moreover, the sample is not stable over longer measurement times as needed for such investigations.

(41) The diastereomeric tautomer 10, in which the overall geometry of 9 is retained but the π-bonds are shuffled, could neither be located by DFT nor detected by NMR; its formation and evolution by “productive” [2 + 2] cycloreversion are impeded by the unfavorable alignment of the Mo=C<sub>α'</sub> (Mo≡C<sub>α'</sub>) bond with one of the π-donating R<sub>3</sub>SiO– groups in the *trans*-position that compete for the same orbitals at metal.

(42) For details, see the SI; all calculations were conducted with the development version of the ORCA program package: Neese, F. The ORCA Program System. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73–78.

(43) Neese, F. Software Update: The ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, *8*, No. e1327.

(44) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. Preparation of Rhenium(VII) Monoimido Alkylidyne Complexes and Metathesis of Acetylenes via Rhenacyclobutadiene Intermediates. *J. Am. Chem. Soc.* **1988**, *110*, 2686–2687.

(45) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. Rhenium(VII) Monoimido Alkylidyne Complexes. The Importance of Face Selectivity in the Metathesis of Acetylenes via Rhenacyclobutadiene Intermediates. *J. Am. Chem. Soc.* **1991**, *113*, 135–144.

(46) Berry, R. S. Correlation of Rates of Intramolecular Tunneling Processes, with Application to Some Group V Compounds. *J. Chem. Phys.* **1960**, *32*, 933–938.

(47) Since the metallacyclobutadiene ring is adjacent to two M–O bonds, a pseudorotation around both bonds is possible; for symmetry reasons, both processes are equally likely and yield the same product, i.e., 9'. Because the geometry changes from square-monopyramidal to trigonal-bipyramidal back to square-monopyramidal, the total 9 to 9' isomerization resembles an inverse-Berry pseudorotation.

(48) The computed barrier of pseudorotation for the molybdenacyclobutadiene 9 ( $\Delta G^\ddagger = 58.7$  kJ mol<sup>-1</sup>) is actually very close to the experimental barrier height of the pseudorotation of the tungstenacyclobutadiene 5 ( $\Delta G^\ddagger(25^\circ\text{C}) = 55.1 \pm 0.7$  kJ mol<sup>-1</sup>).

(49) For the bent but catalytically inactive rhenacyclobutadiene complex described in ref 44, a similar pseudorotation had been proposed to explain the features of its NMR spectra; strikingly, however, the chemical shift differences between C<sub>α</sub>/C<sub>α'</sub> (277.9/199.7 ppm) are much higher than in catalytically competent 9 (234.2/235.7 ppm).

(50) TS1 shows rather long Mo–C<sub>α</sub> (3.401 Å) and C<sub>α</sub>–C<sub>β</sub> (3.369 Å) bond distances. References 11, 18, and 33 report a large variety of computed bond lengths for such TSs with C–C distances ranging from 2.18 Å to 3.65 Å and M–C distances ranging from 2.11 Å to 3.55 Å. “Early” TSs are most likely due to higher steric demand of the ligands, which modulate the energy landscape, and higher electrophilicity of the metal.

(51) A comparison of TS1 when using complexes 1 and 2c is provided in ref 11. These authors found only slightly shorter bond lengths in the case of 1, probably due to the similar sterical demand and electrophilicity of the metal. The fact that they report significantly shorter bond lengths than were found herein, but a much higher barrier, is likely due to the different computational methods used and, perhaps, the complexity of the system.