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.1−6 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).7−9 A new generation of “canopy catalysts” of type 2 distinguished by a tripodal silanolate ligand framework shows an even better application profile.10−13

Scheme 1. Overview

In consideration thereof, it was perplexing to find that addition of excess 3-hexyne to a solution of 2a (R = 4-MeOC₆H₄-) in [D₈]-toluene afforded the metallatetrahedrane 4 as the only detectable and isolable intermediate (Scheme 2).10−12 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);14−19 metallatetrahedranes, in contrast, are considered to be unreactive sinks and/or gateways to catalyst decomposition.20−23 The exclusive formation of 4 from one of the best available catalysts is therefore non-intuitive.10,11 A veritable conundrum accrues when the behavior

Received: February 4, 2021
Published: April 7, 2021
of the tungsten analogue 3 (R = 2,6-Me2C6H3−) 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.24 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-MeOC6H4−) endowed with monodentate silanolate, 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 [D8]-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 C2-symmetric in solution since only one signal is observed for the two Cα-atoms (δC = 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 Cα− and Cβ-atoms with free 3-hexyne, thus implying that the product-forming (“productive”) and the substrate-regenerating (“unproductive”) [2 + 2] cycloreversions are equally likely.26

Highly sensitive steel-blue crystals suitable for X-ray diffraction could be grown from a solution of 7 in Et2O at −85 °C. This result is deemed rewarding since pertinent information about the structure of molybdenacyclobutadienes in the solid state is very limited.19,26–28

The Mo(+6) center of 7 adopts a coordination geometry in between trigonal-bipyramidal and square-pyramidal (τs = 0.37, Figure 1).29 The bond lengths are uneven: whereas the Mo1−C2 bond is only slightly shorter than the Mo1−C3 bond, the difference is more pronounced for C1−C2 versus C1−C3 (Figure 2).30,31 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);18 this peculiar situation may explain why their interconversion in solution is fast even at −90 °C as manifested in the spectra of Cα− symmetry.32,33

The comparison of 7 with the structure of tungstenacyclobutadiene 5 derived from the catalytically incompetent tungsten alkyldyne 3 is also informative, as it allows the effect of the tripodal “canopy” ligand architecture to be assessed (Figure 2). In contrast to 7, complex 5 is closer to square-pyramidal than trigonal-bipyramidal (τs ≈ 0.14).29 The metallacyclic core is much more distorted in all bond distances,24,34 this distortion persists in solution in that the Cα/Cβ-atoms of 5 are inequivalent as manifested in discrete shifts and notably different J1,C,W coupling constants indicative of substantial “double” bond character for the short W−Cβ bond but “single” bond character for the longer W−Cα.24 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 Cα and Cβ 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 all-ethyl-substituted tungstenacyclobutadiene 6.24 The core of 6 must be similarly distorted since the Cα/Cβ-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.35

As mentioned above, the reaction of the molybdenum alkyldyne 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).36 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 then to commence exchanging with 2-butyne (see the SI).

The shifts of the methyl groups at the Cα− and Cβ− 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.39,40 Equally informative are the EXSY data, which show two different dynamic processes: First, the methyl groups at Cα−/Cβ− exchange with 2-butyne (11) much more readily than at Cα (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.25 Second, interconversion of the methyl substituents at the Cα−/Cβ− 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 x-bonds with formation of a hypothetical tautomer 10 is equally excluded,41 even if 10 were...
reached, release of the product would be strongly disfavored by the clash of the incipient alkylidyne 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. 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 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 alkylidyne 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 π-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 geometry with two oxygen atoms and the former Cα-atom occupying equatorial positions, whereas the third oxygen and the former Cα′ are axially disposed. Related metallacyclobutadienes are known in the literature; the arguably most relevant one is a rhenacycle, in which Cβ is tilted out of the M−Cα−Cα′ plane by no less than 34°, importantly, however, this complex does not undergo [2 + 2] cycloreversion and is hence catalytically incompetent.
Intermediate 12 is not static but succumbs to Berry pseudorotation\textsuperscript{39} about the adjacent M–O bond,\textsuperscript{47} which exchanges the axial and equatorial C\textsubscript{α} positions via TS\textsubscript{BR}; 12/12\textprime, in turn, connect to two distinct metallacyclobutadienes 9/9\textprime, in which the C\textsubscript{α}/C\textsubscript{β} atoms and their substituents R\textsubscript{1}/R\textsubscript{3} are mutually exchanged, whereas C\textsubscript{β} remains in place (Scheme 4).\textsuperscript{48,49}

Scheme 4. Crucial Berry Pseudorotation

Because of the lost C\textsubscript{β} symmetry, only the “unproductive” cycloreversion is facile for metallacyclobutadiene 9 via the low-lying TS\textsubscript{1}.\textsuperscript{50,51} “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\textsubscript{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\textprime via 12/12\textprime entails exchange of the R\textsuperscript{1} and R\textsuperscript{3} substituents on one and the same tautomeric form of the α-system (Scheme 5). The small barrier TS\textsubscript{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 by an unprecedented mechanism that involves a single tautomeric form of the metallacyclobutadiene which appears in two differently substituted formats (9/9\textprime). 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\textsubscript{3}Si– groups allow this handicap to be counterbalanced.\textsuperscript{10}

Finally, one needs to consider that the interconversion of 9 and 9\textprime 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 °C, whereas 8 was static; productive and unproductive [2 + 2] cycloreversions are obviously ongoing, but the metallatetrahedrane is not engaged. The new mechanism allows this observation to be readily explained, since the barrier TS\textsubscript{BR} for pseudorotation is lower than TS3 connecting 9 and 8.

Moreover, if a metallatetrahedrane were to connect 9/9\textprime, all three C atoms would eventually get scrambled. However, the EXSY-NMR experiments showed only exchange of C\textsubscript{α}/C\textsubscript{β}, but no exchange of C\textsubscript{α}/C\textsubscript{β}. 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\textsubscript{α}/R\textsubscript{1} and C\textsubscript{β}/R\textsubscript{3} are broadened, whereas the resonances of C\textsubscript{β}/R\textsubscript{2} remain sharp.

Taken together, these data suggest that the metallatetrahedrane 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\textprime and connects them with the metallatetrahedrane 8; since TS2 and TS3 are of similar magnitude, a metallatetrahedrane can—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 tripodal 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, or by emailing data_
Author Contributions

A.H. and J.H. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Generous financial support by the MPG is gratefully acknowledged. We thank Mr. N. Nöthling and Dr. R. Goddard, Mülheim, for solving the X-ray structure, and the analytical departments of our institute for excellent support.

REFERENCES

(1) Fürstner, A. Alkyne Metathesis on the Rise. Angew. Chem., Int. Ed. 2013, 52, 2794–2819.
(2) Ehrhorn, H.; Tamm, M. Well-Defined Alkyne Metathesis Catalysts: Developments and Recent Applications. Chem.—Eur. J. 2019, 25, 3190–3208.
(3) Schrock, R. R.; Czekelius, C. Recent Advances in the Synthesis and Applications of Molybdenum and Tungsten Alkylidyne and Alkylidyne Catalysts for the Metathesis of Alkenes and Alkynes. Adv. Synth. Catal. 2007, 349, 55–77.
(4) Zhang, W.; Moore, J. S. Alkyne Metathesis: Catalysts and Synthetic Applications. Adv. Synth. Catal. 2007, 349, 93–120.
(5) Fürstner, A.; Davies, P. W. Alkyne Metathesis. Chem. Commun. 2005, 2307–2320.
(6) Yang, H.; Jin, Y.; Du, Y.; Zhang, W. Application of Alkyne Metathesis in Polymer Synthesis. J. Mater. Chem. A 2014, 2, 5986–5993.
(7) Heppkehausen, J.; Stade, R.; Goddard, R.; Fürstner, A. Practical New Siloxy-based Alkyne Metathesis Catalysts with Optimized Activity and Selectivity Profiles. J. Am. Chem. Soc. 2010, 132, 11045–11057.
(8) Heppkehausen, J.; Stade, R.; Kondoh, A.; Seidel, G.; Goddard, R.; Fürstner, A. Optimized Synthesis, Structural Investigations, Ligand Tuning and Synthetic Evaluation of Siloxy-based Alkyne Metathesis Catalysts. Chem. - Eur. J. 2012, 18, 10281–10299.
(9) Schaubach, S.; Gebauer, K.; Ungeheuer, F.; Hoffmeister, L.; Ilg, M. K.; Wirtz, C.; Fürstner, A. A Two-Component Alkyne Metathesis Catalyst System with an Improved Substrate Scope and Functional Group Tolerance: Development and Applications to New Product Synthesis. Chem. - Eur. J. 2016, 22, 8494–8507.
(10) Hillenbrand, J.; Leuttsch, M.; Yannakakis, E.; Gordon, C.; Wille, C.; Nöthling, N.; Copéret, C.; Fürstner, A. Canopy Catalysts for Alkyne Metathesis: Molybdenum Alkylidyne Complexes with a Triiodinated Ligand Framework. J. Am. Chem. Soc. 2020, 142, 11279–11294.
(11) Hillenbrand, J.; Leuttsch, M.; Fürstner, A. Molybdenum Alkylidyne Complexes with Triiodinated Silanolate Ligands: The Next Generation of Alkyne Metathesis Catalysts. Angew. Chem., Int. Ed. 2019, 58, 15690–15696.
(12) Thompson, R. R.; Rotella, M. E.; Du, P.; Zhou, X.; Fromczek, F. R.; Kumar, R.; Gutierrez, O.; Lee, S. Siloxide Podand Ligand Scaffold for Molybdenum-Catalyzed Alkyne Metathesis and Isolation of a Dynamic Metallatetrahedrane Intermediate. Organometallics 2019, 38, 4054–4059.
(13) For important recent progress reached by an alternative catalyst design, see: Cui, M.; Bui, W.; Sun, H. H. Y.; Williams, I. D.; Jia, G. Robust Alkyne Metathesis Catalyzed by Air Stable d2 Re(V) Alkylidyne Complexes. J. Am. Chem. Soc. 2020, 142, 13339–13344.
(14) Katz, T. J.; McGinnis, J. Mechanism of the Olefin Metathesis Reaction. J. Am. Chem. Soc. 1975, 97, 1592–1594.
(15) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. Metathesis of Acetylenes by Tungsten(VI)-Alkylidyne Complexes. J. Am. Chem. Soc. 1981, 103, 3932–3934.
(16) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. Reaction of Tungsten(VI) Alkylidyne Complexes with Acetylenes to Give Tungstenacyclobutadiene and Cyclopentadienyl Complexes. J. Am. Chem. Soc. 1982, 104, 6808–6809.
(17) Schrock, R. R. High-Oxidation-State Molybdenum and Tungsten Alkylidyne Complexes. Acc. Chem. Res. 1986, 19, 342–348.
(18) Zhu, J.; Jia, G.; Lin, Z. Theoretical Investigation of Alkyne Metathesis Catalyzed by W/Mo Alkylidyne Complexes. Organometallics 2006, 25, 1812–1819.
(19) Cui, M.; Lin, R.; Jia, G. Chemistry of Metallacyclobutadienyls. Chem. - Asian J. 2018, 13, 895–912.
(20) Churchill, M. R.; Fettinger, J. C.; McCullough, L. G.; Schrock, R. R. Transformation of a Tungstenacyclobutadiene Complex into a Nonfusional 𝜃3-Cyclopropenyl Complex by Addition of a Donor Ligand. The X-ray Structure of W(𝜃2-C2H2)(C3H5CM)(CMe3)3(PMe3)2Cl. J. Am. Chem. Soc. 1984, 106, 3556–3567.
(21) Schrock, R. R.; Murdzek, J. S.; Freudenberg, J. H.; Churchill, M. R.; Ziller, J. W. Preparation of Molybdenum and Tungsten Neopentylidyne Complexes of the Type (η5-C5Me5)(O2CR)2. Their Reactions with Acetylenes, and the X-ray Structure of the 𝜃3-Cyclopropenyl Complex W(η4-C2H2)(C3H5CM)(O2CR)3. Organometallics 1986, 5, 25–33.
(22) Woo, T.; Folga, E.; Ziegler, T. Density Functional Study of Acetylene Metathesis Catalyzed by High Oxidation State Molybdenum and Tungsten Carbyne Complexes. Organometallics 1993, 12, 1289–1298.
(23) Lin, Z.; Hall, M. B. Stabilities of Metallacyclobutadiene and Metallatetrahedrane Complexes. Organometallics 1994, 13, 2878–2884.
(24) Hillenbrand, J.; Leuttsch, M.; Gordon, C. P.; Copéret, C.; Fürstner, A. 1H-2H NMR Spectroscopy Guides the Search for Tungsten Alkylidyne Catalyts for Alkyne Metathesis. Angew. Chem., Int. Ed. 2020, 59, 21758–21768.
(25) For symmetrical alkynes such as 2-butyne or 3-hexyne used to form (that is, substrate-regenerating) and the (that is, substrate-regenerating) cycloreversion are degenerate; these denominations are used to illustrate the fate of a putative unsymmetrical substrate.
Alkyne Metathesis: DFT Investigations on Model Complexes of Group Compounds Containing Nitrogen-Sulfur Donor Ligands: The Crystal Synthesis, Structure, and Spectroscopic Properties of Copper(II) low (1.5 kcal
6 Metallacyclobutadienes.

C. E.; Maron, C.; Tamm, M. Studies on Molybdena- and Tungsten 2,4,6-Trimethylbenzylidene Complexes with Fluoroalkoxide Ligands OC(CF3)nMe3 (n = 0–3). Organometallics 2017, 36, 3398–3406.

(28) A compilation of the few molybdenacyclobutadienes that have been crystallographically caracterized 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: Ehhorn, 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. The geometry of the [Mo7] fragment in 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: Ehhorn, 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.

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

(31) Suresh, C. H.; Freking, 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 one intermediate that averages the square-prismatic and trigonal-bipyrimal forms, see ref 18.

(33) For a catalytically active canonical tungsten catalyst, the barrier for the interconversion of the square-monopyramidal tautomers A/B via a trigonal-bipyrimal transition state C was also computed to be very low (1.5 kcal mol⁻¹), see: Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, 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–C1 angle (166°) is more strongly bent than the analogous trans-O–Mo–C0 angle (175°) in 7.

(35) There is no competing experiment with 3-hexyne or any other species that might obscure the data otherwise; the activation parameters (ΔH° = 57.7 ± 0.3 kJ mol⁻¹, ΔS° = 8.6 ± 1.3 J mol⁻¹ K⁻¹) 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 and 3-hexyne is attributed to increased stabilization of the metalatetrahedrane 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 9 with butyne is small compared to the one to C4, 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 C4 (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 substrates at the C4/C9 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 p-bond is shuffled, could neither be located by DFT nor detected by NMR; its formation and evolution by “productive” [2 + 2] cyclopropanation is impeded by the unfavorable alignment of the Mo≡Cα (Mo≡Cβ) bond with one of the β-donating R3SiO– 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 Rheinum(VII) Monooimido Alkyldiene Complexes and Metathesis of Acetylenes via Rheincyclobutadiene Intermediates. J. Am. Chem. Soc. 1988, 110, 2686–2687.

(45) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. Rheinum(VII) Monooimido Alkyldiene Complexes. The Importance of Face Selectivity in the Metathesis of Acetylenes via Rheincyclobutadiene 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 Mo–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-bipyrimal 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 (ΔG° = 58.7 kJ mol⁻¹) is actually very close to the experimental barrier height of the pseudorotation of the tungstenacyclobutadiene 5 (ΔG°(25 °C) = 55.1 ± 0.7 kJ mol⁻¹).

(49) For the bent but catalytically inactive rheincyclobutadiene 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 C6/C7 (277.9/199.7 ppm) are much higher than in catalytically competent 9 (234.2/235.7 ppm).

(50) TS1 shows roughly long Mo–Cα (3.401 Å) and C9–C8 (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 electronegativity 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, possibly due to the similar steric demand and electronegativity 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.