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Journal

Angewandte Chemie International Edition

ISSN

1433-7851

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Publication Date

2026-06-03

DOI

10.1002/anie.6317497

Angewandte Chemie International Edition

Angewandte International Edition Chemie

How to cite: *Angew. Chem. Int. Ed.* **2026**, 65, e6317497
doi.org/10.1002/anie.6317497

RESEARCH ARTICLE

Conversions of Tungsten(IV) Cycloalkene Complexes to Metathesis-Active Cycloalkylidene Complexes Are Catalyzed by Cycloalkene and Can be Inhibited by Cycloalkene

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Received: 14 April 2026 | **Revised:** 1 May 2026 | **Accepted:** 14 May 2026

Keywords: alkene | alkylidene | imido | ROMP | tungsten

ABSTRACT

Olefin metathesis reactions catalyzed by molybdenum or tungsten alkylidene (M=CRR') complexes are robust methods of forming carbon-carbon double bonds, but how catalytically active alkylidene complexes are formed from olefins alone has not been determined. Here we show that two electron reductions of $W(NR)(OR')_2Cl_2$ complexes in the presence of cyclopentene, cyclohexene, cycloheptene, or cyclooctene yield $W(NR)(OR')_2$(cycloalkene) and/or $W(NR)(OR')_2$(cycloalkylidene) complexes (R = 2,6-diisopropylphenyl (Ar), 2,6-dichlorophenyl (Ar_{Cl}); OR' = $OSiPh_3$, $OCMe_2(CF_3)$ (OR_{F3}), $OCMe(CF_3)_2$ (OR_{F6}), $OC(CF_3)_3$ (OR_{F9})). Mechanistic studies suggest that alkylidenes are formed from unobserved *bis*-alkene complexes through the transfer of an allylic proton from one bound olefin to the second to give an alkyl/allyl intermediate followed by the return of an α proton from the alkyl to form an alkylidene (the AA mechanism). Tungstacyclopentane complexes formed from two equivalents of cyclopentene or cyclohexene can be isolated, but there is no compelling evidence that these complexes can form alkylidenes through a thermal ring-contraction mechanism. In fact, these metallacyclopentanes appear to inhibit alkylidene formation.

1 | Introduction

The first reports of olefin metathesis in the literature, and many subsequent studies, concerned ring-opening metathesis polymerization (ROMP) of strained cycloalkenes (e.g., cyclopentene, cyclooctene, norbornene, etc.; Figure 1A) by catalysts formed from Mo or W complexes (e.g., $W(O)Cl_4$) and an alkylating agent (e.g., $Sn(Butyl)_4$ or $Al(Ethyl)_2Cl$) [1]. Synthetic and mechanistic studies of Mo and W complexes carried out for decades support the well-documented Chauvin mechanism [2] in which a polymerization is initiated by a high-oxidation state alkylidene [3, 4, 5] through successive [2+2] cycloaddition/retrocyclization steps (Figure 1A). But how Mo and W alkylidenes are formed from olefins, and therefore possibly reformed from d^2 "decomposition" products, especially in the absence of alkylating/reducing agents (from metal oxides, metal carbonyls, etc. [6]) has been debated for decades [7].

Most proposals as to how alkylidenes (or metallacyclobutanes) are formed include reduction of the metal to M(IV). Three proposed reactions of olefins with a d^2 Mo or W complex are shown in Figure 1B. In the first, C–H bond activation yields a M(VI) vinyl-hydride intermediate. Subsequent migration of the hydride to the β carbon atom of the vinyl ligand then yields a terminal alkylidene. A second proposal is formation of a metallacyclopentane followed by a ring-contraction [8] to give a metallacyclobutane, a process that has been observed in W(IV) species supported on silica [9, 10] and in photochemical ring-contractions in solution [11, 12, 13]. A third proposal is the formation of an allyl hydride through allylic

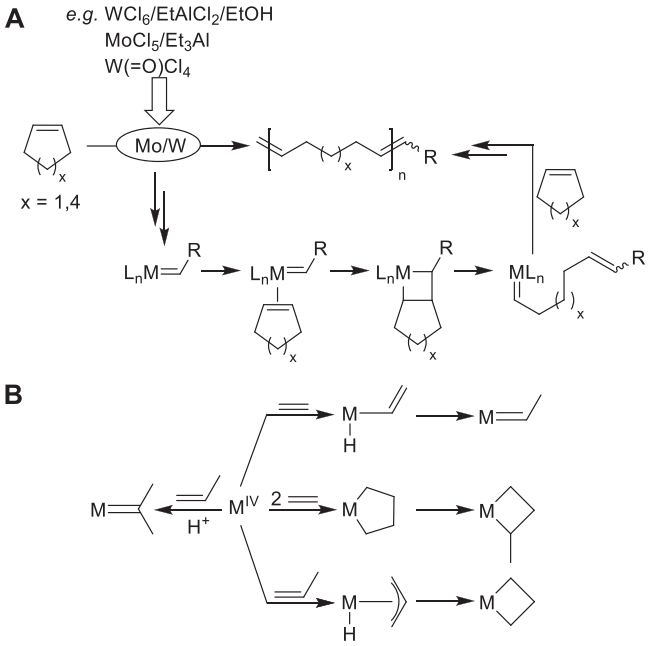


FIGURE 1 | The ring-opening metathesis polymerization of cyclic olefins by representative classic Mo/W initiators (A). Proposed reactions that yield alkylidene or tungstacyclobutane complexes (B).

CH activation and subsequently a metallacyclobutane upon migration of the hydride to the central carbon of the allyl ligand [14].

Early studies in tantalum chemistry showed that $PhPH_2$ [15] or a methyl group in an OSi(*t*-Bu)$_3$ ligand [16] can provide the proton required to rearrange an alkene to an alkylidene. More recent studies of Mo and W systems suggest that protons from anilinium salts [17, 18], alcohols [19], silanols on silica [14, 20, 21, 22], or anilines [23] can catalyze the formation of catalytically active secondary (disubstituted) alkylidenes. It has been shown that silica-supported W(O)(OR_{F6})$_2$(olefin)(py)$_2$ complexes (olefin = ethylene or propylene) can be activated with B(C_6F_5)$_3$ and pyridine (py) to form metathesis-active catalysts, if an olefin contains an allylic proton [14, 22]. Pyridine was proposed to move the proton.

In this study, we show that W(IV) cycloalkene complexes are converted (reversibly) to W(VI) cycloalkylidene complexes using a proton provided by a second cycloalkene through allylic CH activation. Furthermore, square pyramidal metallacyclopentane complexes can be formed from two cycloalkenes, and these metallacyclopentanes do not directly lead to alkylidenes and so inhibit alkylidene formation. To our knowledge neither of these phenomena has been observed to date in olefin metathesis systems.

2 | RESULTS

Figure 2 shows that reduction of W(NAryl)(OR)$_2$$Cl_2$ complexes (Aryl = 2,6-diisopropylphenyl (Ar) or 2,6-dichlorophenyl (Ar_{Cl}); OR = $OSiPh_3$, $OCMe_2(CF_3)$ (OR_{F3}), $OCMe(CF_3)_2$ (OR_{F6}), or $OC(CF_3)_3$ (OR_{F9})) with 2% Na amalgam in the presence of a cyclic olefin in THF can yield either a cycloalkene complex or a cycloalkylidene complex, or a mixture of both, depending upon the cycloalkene and conditions. It has been found recently that a propylene and an isopropylidene complex [23] have nearly the same free energy when all other ligands are the same [17, 18], so whether an alkene or an internal alkylidene complex is observed will be determined by what other ligands are present, the coordination geometry, the rate of conversion of alkene to alkylidene, and so forth. Consequently, at this stage, we believe that generalizations are premature. The key cyclic olefin in these studies is cyclohexene, which has no C=C isomers, can form only one alkylidene, cannot possibly form an alkylidyne, and cannot be polymerized through ring-opening metathesis (ROMP) at 22°C. (Cyclopentene, cyclooctene, and cycloheptene are polymerized at 22°C.)

Eight cycloalkene and cycloalkylidene complexes were crystallized and characterized through x-ray diffraction and other standard methods (Figure 3). All syntheses, characterization details, and NMR data for the cycloalkene and cycloalkylidene complexes are provided in the Supporting Information. All olefin complexes have pseudotetrahedral structures in which the olefin's C=C bond axis is essentially perpendicular to the imido W=N bond axis, the W-C distances are ~2.12 Å, and the C-C distances are ~1.47 Å. The olefinic Cα resonances appear at the expected chemical shifts with small $^1J_{CW}$ values (see summaries of NMR and structural parameters in Tables S1 and S13–S15). W(NAr)($OSiPh_3$)$_2$(C8) was isolated as a co-crystallized mixture of W(NAr)($OSiPh_3$)$_2$(*cis*-C8) and W(NAr)($OSiPh_3$)$_2$(*trans*-C8); the percentage of *cis* varied from crystal to crystal, although NMR spectra of the crude product show the ratio of *cis* to *trans* to be consistently ~4:1. Mixtures of alkene and alkylidene complexes are sometimes observed. For example, the crude reaction mixture from which W(NAr_{Cl})(OR_{F6})$_2$(C5) was isolated contained a minor W(NAr_{Cl})(OR_{F6})$_2$(C5) isomer (we propose one with the C_5 ring pointing away from the imido ligand) along with W(NAr_{Cl})(OR_{F6})$_2$(=C5) (see Figure S79). Cycloalkylidene complexes were isolated either as pseudotetrahedral complexes or as distorted square pyramidal THF adducts in which THF is relatively labile. The W=C bond distances are ~ 1.9 Å, and one W-C-C bond angle is smaller than the other, which is common in electron-deficient disubstituted alkylidenes of this type [24]. All cyclopentylidene and cyclohexylidene complexes reported here have Cα chemical shifts in the 240–300 ppm range and J_{CW} values of ~90 Hz (see Table S1).

We found that the conversion of the tungsten bis OR_{F3} cyclohexene complexes in which the imido ligand is NAr or NAr_{Cl} to cyclohexylidenes can be observed in the absence of any obvious proton source except cyclohexene. For example, the ^{1}H NMR spectrum of an analytically pure sample of W(NAr_{Cl})(OR_{F3})$_2$(C6) (**1**; C6 = cyclohexene) in C_6D_6 is shown in Figure 4. This spectrum contains signals for the coordinated cyclohexene in **1** and initially a barely observable signal for a trace of free cyclohexene at 5.68 ppm (< 1% cyclohexene/W). Over 72 h, the signals for **1** decrease and signals for the β-hydrogens in the cyclohexylidene complex, W(NAr_{Cl})(OR_{F3})$_2$(=C6) (**2**), appear at 3.87 and 4.45 ppm. After 72 h at room temperature, the reaction mixture consists of an approximate 1:1 mixture of **1** and **2**. As the reaction progresses, cyclohexene continues to be formed, reaching 0.1 equiv cyclohexene/W at the end of the

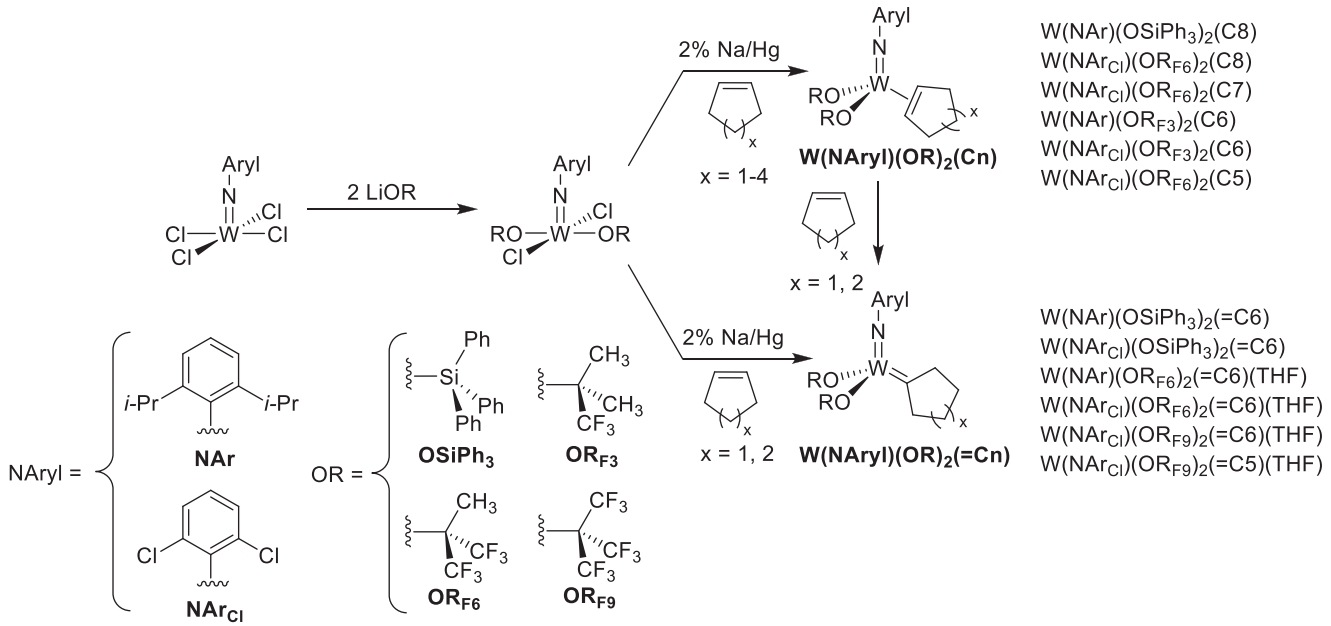


FIGURE 2 | Cycloalkene (CX) or cycloalkylidene (=CX) complexes (X = ring size) isolated through reduction.

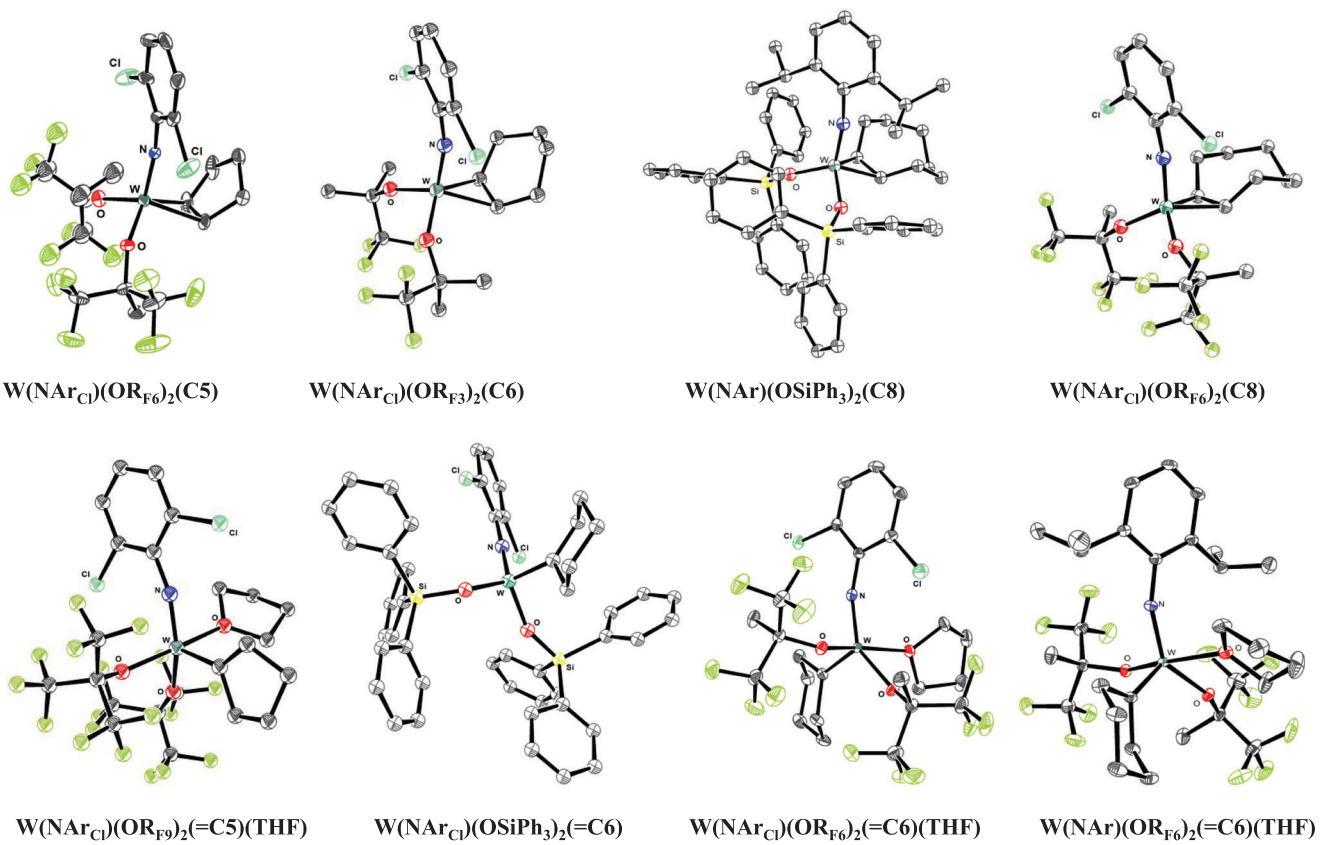


FIGURE 3 | Structurally-characterized cycloalkene (above) and cycloalkylidene complexes (below).

reaction; the maximum yield of **2** is ~35%. Formation of a trace of cyclohexene initially, and more throughout the reaction, as well as the relatively low yield of **2**, are currently ascribed to some decomposition reaction (or reactions) during conversion of **1** to **2**.

Addition of 1–2 equivalents of cyclohexene accelerates the rate of formation of **2** from **1** dramatically and leads to higher yields of **2**. In ~12 h **1** is converted to give **2** in 76% yield (by NMR vs. an internal standard). However, the conversion is inhibited in the presence of 10 equiv of cyclohexene and a tungstacyclopentane

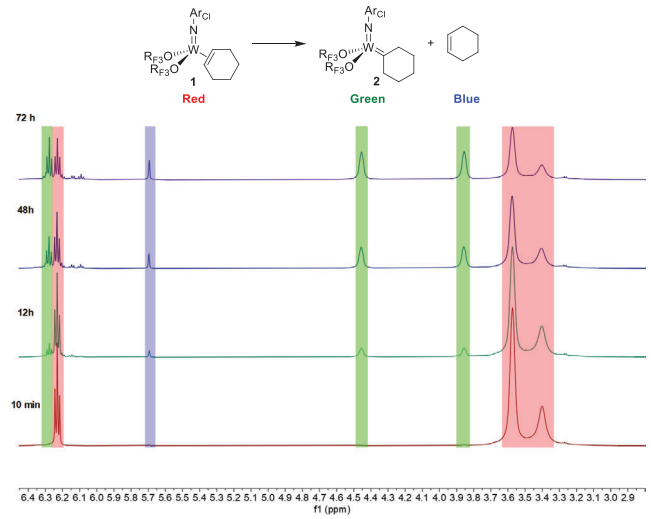
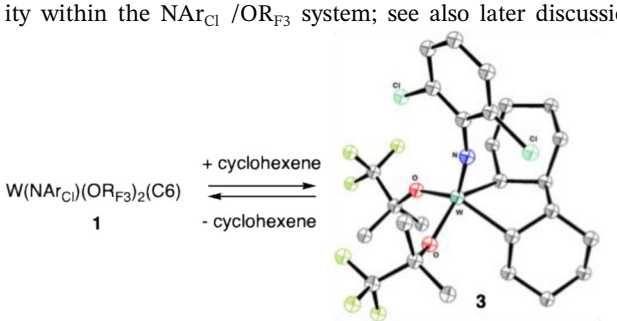


FIGURE 4 | Portion of the ^{1}H NMR spectrum in which W(NAr$_{Cl}$)(OR$_{F3}$)$_2$(C6) (**1**) is converted into a mixture containing it, W(NAr$_{Cl}$)(OR$_{F3}$)$_2$(=C6) (**2**), and free cyclohexene over the course of 72 h in C_6D_6. Typical concentrations of W are 60 mM (see Supporting Information).

complex made from two cyclohexenes, W(NAr$_{Cl}$)(OR$_{F3}$)$_2$(6,6) (**3**) (Equation 1), is formed. The τ value (0.10) for the structure of **3** suggests that it is essentially a square pyramid. Isolated samples of **3** lose cyclohexene in solution to form mixtures of **1** and **3**. If samples are kept at or below 298 K, little **2** forms in these mixtures and an equilibrium is established between **1**, **3**, and free cyclohexene (see Figures S87 and S88); K_{eq} for the reaction in Equation (1) at 298 K was found to be 55 ± 4 M^{-1} using ^{1}H NMR or ^{19}F NMR methods. (We are not confident of a temperature-dependent study of this equilibrium in view of the noted thermal instability within the NAr$_{Cl}$ /OR$_{F3}$ system; see also later discussion.)



(1)

A comparison of the initial rates of formation of **2** versus five quantities of cyclohexene added is shown in Figure 5. (Each point is an average of three and the initial concentration of **1** is the same in all runs; see Table S2 in the Supporting Information for a complete list of values.) In the absence of added cyclohexene the "background" initial rate of forming **2** is 1.2(2) × 10^{-7} M s^{-1}. But as discussed above, cyclohexene is formed (10% vs. W in final mix) and this background reaction therefore is also likely catalyzed by cyclohexene. In the presence of 10 equivalents of cyclohexene per tungsten **3** is virtually the only compound in solution and the initial rate of forming **2** is even lower (4.6(2) × 10^{-8} M s^{-1}) than the background rate. The rates of forming **2** and the yields of **2** maximize when ~1.5 equivalents of cyclohexene are added (Figure 5). These results suggest that cyclohexene not

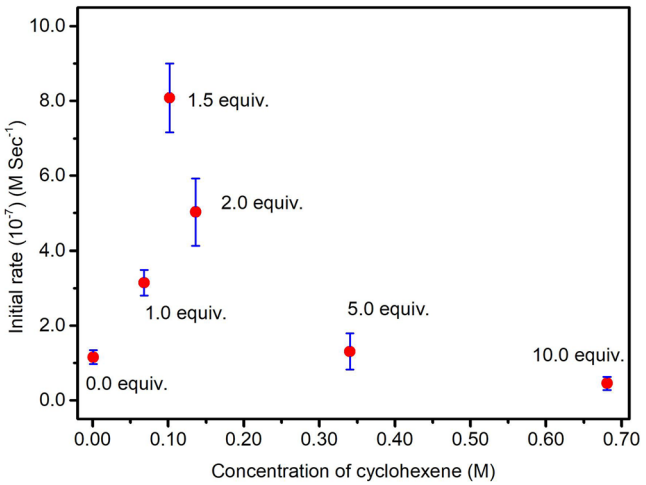
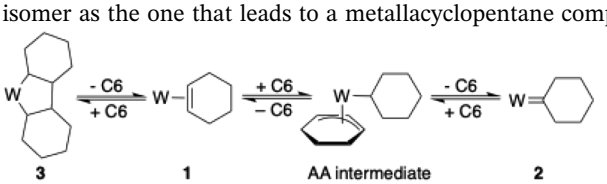


FIGURE 5 | Initial rates of forming **2** from **1** versus added cyclohexene (x axis). The rates were recorded for the first ~10% of **2** formed (see Table S2 for details).

only catalyzes formation of **2** from **1**, but also inhibits formation of **2** through formation of **3** because, we propose, **2** is not formed readily and directly from **3** under these conditions. In the presence of light, other tungstacyclopentanes of the type described here form alkylidenes through a photochemical W-C bond cleavage followed by either ring-contraction or α-H abstraction [9, 11, 13]. Modeling the proposed reactions through detailed kinetic analyses were only partially successful, in part, we propose, due to unidentified decompositions.

Our current proposal is that several five-coordinate, probably interconverting, biscyclohexene isomers are formed in reactions between **1** and cyclohexene. One of these is an intermediate for forming a tungstacyclopentane reversibly. Another is a precursor to the cyclohexyl-cyclohexallyl complex (the AA intermediate in Equation (2); C6 = cyclohexene) in which an allylic CH bond is cleaved and a proton transferred to the second cyclohexene. Return of an α-H from the cyclohexyl to the cyclohexallyl ligand completes the conversion of **1** to **2**. The (reversible) AA reaction was first proposed to explain the H/D exchange between W(NAr)(OSiPh$_3$)$_2$(=C6) and C_6D_{10} to give C_6H_9D and W(NAr)(OSiPh$_3$)$_2$(=C6-d$_9$) initially [25] followed by C=C bond isomerization, an inherent consequence of the AA reaction. (Formation of both *cis* and *trans* cyclooctene ligands in W(NAr)(OSiPh$_3$)$_2$(C8), as noted earlier, can also be ascribed to the AA reaction.) Although two cyclohexenes are required to make an AA intermediate, it is attractive to propose that the bisolefin precursor to the AA intermediate is not the same isomer as the one that leads to a metallacyclopentane complex.



(2)

The results of several experiments are consistent with the AA mechanism in Equation (2) being the one that leads to **2**. For example, the reaction between W(NAr$_{Cl}$)(OR$_{F3}$)$_2$(C6-d$_{10}$) (**1-d$_{10}$**) and cyclohexene-d$_{10}$ gave only W(NAr$_{Cl}$)(OR$_{F3}$)$_2$(=C6-d$_{10}$)

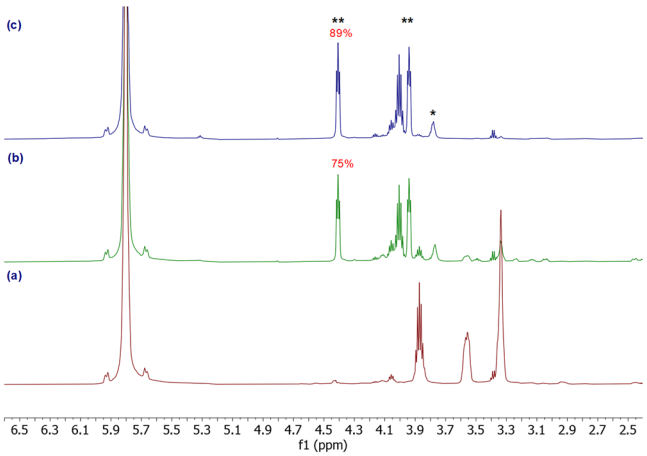


FIGURE 6 | Formation of W(NAr)(OR_{F3})$_2$(=C6) (89%; **) from W(NAr)(OR_{F3})$_2$(C6) in the presence of 10 equiv of cyclohexene; (a) RT, 10 min; (b) 80°C, 1.5 h; (c) 80°C, 2.5 h (*THF).

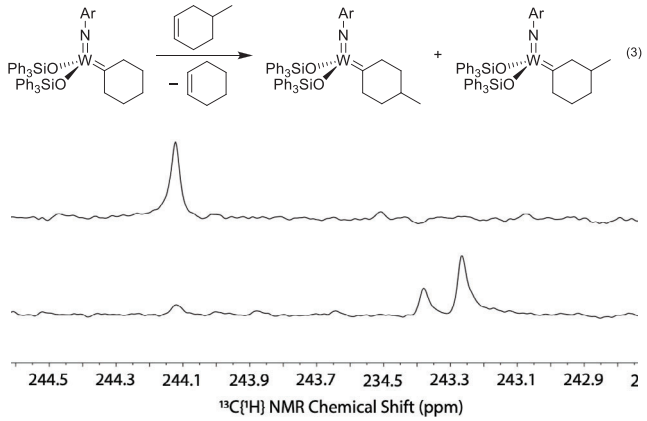


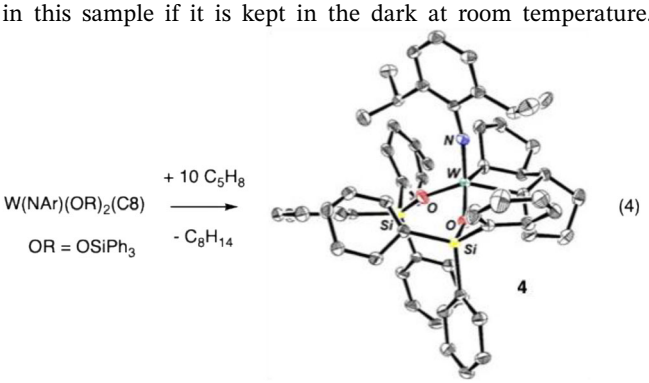
FIGURE 7 | ^{13}C NMR spectrum of the alkylidene Cα region of W(NAr)($OSiPh_3$)$_2$(=C6) (top) and after heating to 100°C in the presence of 20 equivalents of 4-methylcyclohexene in tol-d_8 (bottom).

(**2-d$_{10}$**). No H was found in the cyclohexylidene ligand in **2** above background levels (< 1%). We also found that the reaction between W(NAr_{Cl})(OR_{F3}-d_6)$_2$(C6) and cyclohexene yields only W(NAr_{Cl})(OR_{F3}-d_6)$_2$(=C6) and no D is present in the cyclohexylidene. Therefore the OR_{F3} ligand is not a proton source in this reaction. The isotope effect (k_H/k_D) for the conversion of **1-d$_{10}$** to **2-d$_{10}$** was found to be 3.4 (one experiment), while there is essentially no isotope effect (k_H/k_D = 1.2(2); two experiments) for conversion of W(NAr_{Cl})(OR_{F3}-d_6)$_2$(C6) to W(NAr_{Cl})(OR_{F3}-d_6)$_2$(=C6).

Conversion of a cyclohexene to a cyclohexylidene complex can also be observed in the NAr system, as shown in Figure 6. In the absence of any added cyclohexene W(NAr)(OR_{F3})$_2$(C6) is stable at 80°C and no free cyclohexene or W(NAr)(OR_{F3})$_2$(=C6) is formed. However, in the presence of 10 equiv of cyclohexene W(NAr)(OR_{F3})$_2$(C6) is converted into W(NAr)(OR_{F3})$_2$(=C6) in 89% yield versus an internal standard at 80°C in 1–2 h. We ascribe the higher yields of the cyclohexylidene product in the NAr system compared versus the NAr_{Cl} system to the greater stability of W(NAr)(OR_{F3})$_2$(=C6). Weak resonances characteristic of W(NAr)(OR_{F3})$_2$(6,6) between 3.0 and 3.5 ppm are barely visible in Figure 6 after 75% conversion. The reaction is relatively slow at 50°C, but resonances characteristic of approximately equal amounts of W(NAr)(OR_{F3})$_2$(6,6), W(NAr)(OR_{F3})$_2$(C6), and W(NAr)(OR_{F3})$_2$(=C6) can clearly be observed (see Figures S82–S84). In an analogous reaction between W(NAr)(OR_{F3})$_2$(cyclohexene-d_{10}) and cyclohexene-d_{10} no protons appear in the W(NAr)(OR_{F3})$_2$(cyclohexylidene-d_{10}) product and k_H/k_D was found to be 2.1 (one experiment). Therefore, although protons in the isopropyl groups of the NAr ligand recently have been found to be dehydrogenated in chemistry related to the chemistry described here [26], the isopropyl groups are not the source of a proton in the results described here.

Finally, the proposal shown in Equation (2), and the H/D exchange studies mentioned earlier, together suggest that a methyl-substituted cyclohexene could react with W(NAr)($OSiPh_3$)$_2$(=C6) to give free cyclohexene and one or more new substituted cyclohexylidene complexes. In fact, W(NAr)($OSiPh_3$)$_2$(=C6) reacts with 20 equivalents of 4-methylcyclohexene at 100°C to give (after 40 h) cyclohexene and a mixture of what we propose are primarily two methylated cycloalkylidene complexes with Cα resonances near 243.3 ppm, close to that for W(NAr)($OSiPh_3$)$_2$(=C6) at 244.3 ppm (Equation 3 and Figure 7). These results confirm that the cyclohexylidene complex reacts with 4-methylcyclohexene, cyclohexene is lost, a methyl-substituted cyclohexylidene is formed, and isomerization is observed in the process. All observations are consistent with the proposed AA mechanism.

Preliminary studies show that the reactions established here for cyclohexene are also observed for cyclopentene. Addition of 10 equivalents of cyclopentene to a C_6D_6 solution of W(NAr)($OSiPh_3$)$_2$(C8) led to displacement of cyclooctene and formation of the tungstacyclopentane complex formed from two cyclopentenes, W(NAr)($OSiPh_3$)$_2$(5,5) (**4**), shown in Equation (4) (see Figures S85 and S86). Its square pyramidal structure is analogous to that found for W(NAr_{Cl})(OR_{F3})$_2$(6,6) (**3**; Equation 1). Dissolution of **4** in toluene-d_8 yielded a mixture of the cyclopentene complex, W(NAr)($OSiPh_3$)$_2$(C5), **4**, and cyclopentene; no cyclopentylidene or polycyclopentene was observed in this sample if it is kept in the dark at room temperature.



However, after this sample is heated to 90°C for 12 h in the dark, cyclopentene (25%), W(NAr)($OSiPh_3$)$_2$(5,5) (31%), W(NAr)($OSiPh_3$)$_2$(C5) (26%), and W(NAr)($OSiPh_3$)$_2$(=C5) (18%) are all present in the room temperature proton NMR spectrum (see Figures S80 and S81). Upon addition of 10 or more

equivalents of cyclopentene to W(NAr)($OSiPh_3$)$_2$(cyclopentene) at a concentration of ~20 mM for W, only W(NAr)($OSiPh_3$)$_2$(5,5) and cyclopentene were present after 1 day in the dark; no W(NAr)($OSiPh_3$)$_2$(=C5) nor polycyclopentene was observed. Therefore, the cyclopentylidene complex must be formed at a temperature of ~80°C or above, we propose through the AA reaction.

Addition of 10 equiv of cyclooctene to W(NAr)($OSiPh_3$)$_2$(C8) led to formation of polycyclooctene at room temperature in 48 h with little W(NAr)($OSiPh_3$)$_2$(C8) being consumed; no other complex that contains cyclooctene could be identified in spite of the fact that an alkylidene, presumably a cyclooctylidene, must have formed and initiated oligomerization. Oligomerization of cyclooctene under these conditions can be ascribed to an estimated ΔG_o of −3.1 kcal/mol for ROMP [1].

3 | Conclusions

The results reported here confirm that in the absence of another proton source (as described in the introduction), cyclohexylidenes and cyclopentylidenes are formed thermally in the dark from two equivalents of the cycloalkene, we propose through an AA reaction. There is little information at this stage as to whether H transfers directly from one olefin to another or indirectly through "proton shuttling" via N-based ligands, O-based ligands, or external equivalents thereof, and so forth. Proton shuttles have been invoked in a wide variety of chemistry, including transition metal-catalyzed reactions [14, 27–40]. Other proton-transfers between C-, N-, and O-based ligands have been proposed in high oxidation state Group 4 [41, 42, 43] and tungsten [44–48] chemistry.

The reactions discussed here are also consistent with the behavior of well-defined catalysts supported on silica, even at the high temperatures characteristic of classical metal oxide on silica-catalyzed reactions. For example, Copéret found that thermal formation of an alkylidene from an alkene on silica requires d^2 metal sites, olefins that have allylic protons, and possibly surface SiOH entities [14, 20, 21, 22]. Román-Leshkov and Copéret [21, 49] have shown that olefins that are not readily involved in metathesis reactions can be "promoters" that lead to "active-site renewal" (in heterogeneous catalyst parlance); the most efficient reported promoter is tetramethylethylene, which can be converted to 2,3-dimethyl-1-butene through isomerization. Efficient promoters obviously should not be removed readily from the reaction through metathesis or other side reactions. So far, cyclohexene (in the homogeneous studies reported here and elsewhere [25, 50]) and tetramethylethylene (in heterogeneous studies [21, 49]) are in this category.

In our opinion, there is no reason why variations of the principles outlined here cannot operate in analogous chemistry of W oxo complexes, Mo complexes, or for acyclic olefins, although details could differ significantly. However, it should be noted that gathering mechanistic information of the kind reported here will likely be complicated by isomerization of linear olefins and (often relatively rapid and usually desirable) metathesis reactions. The results described here should help us begin to understand in more detail how catalytically active alkylidenes can be formed, and possibly reformed, from olefins. Such information is destined to be helpful in the design of longer-lived Mo and W-based olefin metathesis systems.

Author Contributions

Milan Maji: conceptualization, investigation, methodology, validation, writing – review and editing. **Kanu Das**: conceptualization, investigation, methodology, validation, writing – review and editing. **Logan Trowbridge**: investigation. **Richard R. Schrock**: conceptualization, writing – review and editing, investigation. **Matthew P. Conley**: conceptualization, investigation, writing – review and editing. **Veronica Carta**: methodology, formal analysis.

Acknowledgments

RRS is grateful to the University of California at Riverside for financial support. MPC thanks the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, Catalysis Science Program, for support through award DE-SC0023344.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: Complete NMR data, x-ray data, and details of experimental procedures, techniques, and methods. Accession Codes CCDC 2473419, 2473420, 2473421, 2473424, 2473426, 2473429, 2473430, 2473431, 2480195, 2480450. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Additional references have been cited within the Supporting Information [11, 13, 25, 51–57].