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Thermal Formation of Metathesis-Active Tungsten Alkylidene Complexes from Cyclohexene

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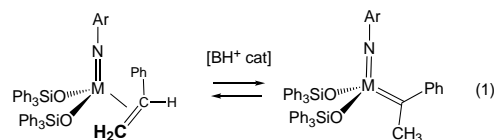
ABSTRACT: A 7-tungstabicyclo[4.3.0]nonane complex forms slowly upon addition of cyclohexene to the ethylene complex, $W(NAr)(OSiPh_3)_2(C_2H_4)$, at 22 °C. A single crystal X-ray study showed its structure to be closest to a square pyramid ($\tau = 0.23$). At 22 °C loss of cyclohexene or ring-contraction of the 7-tungstabicyclo[4.3.0]nonane complex is slow. Above ~80 °C cyclohexene is ejected to give $W(NAr)(OSiPh_3)_2(C_2H_4)$, but a sufficient amount of the 7-tungstabicyclo[4.3.0]nonane complex remains in the presence of cyclohexene and ring-contracts to yield methylenecyclohexane and a methylenecyclohexene complex, *or* ethylene and a cyclohexylidene complex. Other complexes that have been observed include a 8-tungstabicyclo[4.3.0]nonane complex formed from 1,7-octadiene, a 7-tungstabicyclo[4.2.0]octane complex (formed from a methylenecyclohexene complex and cyclohexene), and a methylenecyclohexane complex. ¹³C-Labeling studies show that the exo methylene group in methylenecyclohexane and in the α positions in the 8-tungstabicyclo[4.3.0]nonane come from ethylene. An alternative ring-contraction of a tungstacyclopentane made from two molecules of cyclohexene cannot be excluded when concentrations of ethylene are low. A cyclohexylidene complex could also form from two cyclohexenes via a new proposed "alkyl/allyl" mechanism. The results reported here are the first experimental confirmations that a tungstacyclopentane can ring-contrast thermally at a substituted WC_α position to form a tungstacyclobutane and therefore metathesis-active alkylidenes.

INTRODUCTION

The first olefin metathesis catalysts^{1,2} reported in the scientific literature in 1964³ were prepared through deposition of molybdenum or tungsten carbonyl complexes or oxides on alumina and exposure of that alumina to olefins at elevated temperatures. It was later shown that homogeneous olefin metathesis initiators could be prepared through addition of alkylating agents to high oxidation state Mo and W complexes (oxides, chlorides) in hydrocarbon solvents.^{2,4} When alkyls do not contain any β hydrogen atom (*e.g.*, neopentyl), four-coordinate, 14e, terminal alkylidene complexes ($M=CHR$) could be prepared through α hydrogen abstraction in a dialkyl complex.⁵ This approach allowed homogeneous Mo and W metathesis initiators that contain a terminal alkylidene to be synthesized and studied in large variety;⁶⁻⁸ internal alkylidenes ($M=CRR'$) have been prepared and studied relatively recently.^{9,10} Active sites in heterogeneous catalysts have been found to resemble those documented for homogeneous catalysts.¹¹⁻¹⁴

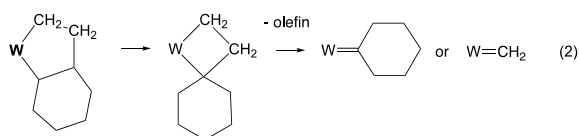
A long-standing question in olefin metathesis by Mo or W catalysts has been how metathesis-active catalysts are formed in the *absence* of alkylating agents, *i.e.*, from olefins themselves.¹⁵ The rate of forming alkylidenes from olefins, and reforming alkylidenes, would seem to be an important contributor to the turnover efficiency of many olefin metathesis reactions. Sporadic evidence that has accumulated for twenty years suggests that alkylidenes are formed from reduced (d^2) Mo or W sites in solution¹⁶⁻¹⁸ or on supports.^{13,19,20,21} Among the proposed mechanisms are formation from a single olefin through (*e.g.*) its "rearrangement" to an alkylidene, or formation through

ring-contraction of a metallacyclopentane (made from two olefins) to an α -substituted metallacyclobutane.^{22,23} It was found in 2021 that a high oxidation state alkylidene of Mo or W can be formed from a single olefin through a "protonation/deprotonation" reaction (eq 1; B = dimethylaniline) in which an alkylidene or an olefin isomer is protonated to give a cationic alkyl.²⁴⁻²⁶ More recently it has been shown that an alkylidene can be formed from a metallacyclopentane through a light-induced M-C bond cleavage followed by ring-contraction²⁷⁻³² or by α hydrogen abstraction within the metallacyclopentane ring.



Because an electronically excited state can relax to a vibrationally excited state in which M-C bond cleavage subsequently takes place, an important question is whether an alkylidene can form via M-C cleavage in a metallacyclopentane in the absence of light. If so, what type of metallacyclopentane would be required? There is strong evidence for selective cleavage of a secondary Ta-C bond in an unobservable α,β' -disubstituted tantalacyclopentane made from $TaCp^*Cl_2(RCH=CH_2)$ ($Cp^* = \eta^5-C_5Me_5$) and $RCH=CH_2$ at 50 °C in the process of dimerizing $RCH=CH_2$ specifically to two dimers (see discussion section).²⁷⁻³² A way to enforce formation of a metallacyclopentane that contains a secondary M-C bond and prevent conversion to a more stable metallacyclopentane is

to make an α,β -disubstituted metallacyclopentane from ethylene and a cyclic olefin that has no double bond isomers. Only one Mo or W metallacyclopentane of this type, $\text{Mo}(\text{NC}_6\text{F}_5)(^{13}\text{CH}_2^{13}\text{CH}_2/\text{NBE})(\text{DFTO})_2$ ($\text{DFTO} = \text{O}-2,6-(\text{C}_6\text{F}_5)_2\text{C}_6\text{H}_3$; NBE = norbornene), has been observed to our knowledge.³³ It was prepared through addition of NBE to $\text{Mo}(\text{NC}_6\text{F}_5)(^{13}\text{CH}_2^{13}\text{CH}_2)(\text{DFTO})_2$ at -70°C . Upon raising the temperature to -50°C , norbornene was polymerized rapidly but no ^{13}C above natural abundance was observed in the polynorbornene.¹ If the cyclic olefin *cannot* be polymerized or isomerized, then it might be possible to observe an unambiguous ring-contraction. Cyclohexene is such an olefin. It has long been known that it is essentially inert to metathesis polymerization or cross-metathesis with a second olefin.^{1, 34, 35} Any double bond isomerization would be degenerate. Therefore we explored the possibility of observing the alkylidenes shown in eq 2 where $\mathbf{W} = \text{W}(\text{NAr})(\text{OSiPh}_3)_2$ ($\text{Ar} = 2,6$ -diisopropylphenyl) along with any organic products.



RESULTS

Synthesis of a cyclohexylidene complex

$\text{W}(\text{NAr})(\text{OSiPh}_3)_2(\text{cyclohexylidene})$ (**1**) can be prepared from $\text{W}(\text{CH}-t\text{-Bu})$ and methylenecyclohexane (MCH; eq 3), a method that has been used to make other disubstituted alkylidenes in this category.^{9, 26, 36, 37} The molecular structure of **1** (Fig 1) is similar to the structures of other disubstituted alkylidenes, and to that of *syn*- $\text{W}(\text{CH}-t\text{-Bu})$ (Fig S49). A tungsten cyclohexylidene complex, $\text{W}(\text{C}_6\text{H}_{10})(\text{OCH}_2-t\text{-Bu})_2\text{I}_2$, was said to have been prepared through a reaction between $\text{W}(\text{CH}-t\text{-Bu})(\text{OCH}_2-t\text{-Bu})_2\text{I}_2$ and methylenecyclohexane, but no details were provided.³⁸ $\text{Nb}[\text{OSi}(t\text{-Bu})_3]_3(\text{cyclohexylidene})$ was synthesized from $\text{Nb}[\text{OSi}(t\text{-Bu})_3]_3(\text{cyclohexene})$ through an internal C-H activation in a Silox ligand and was structurally characterized.³⁹

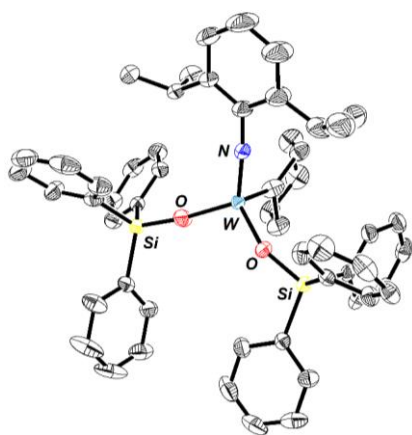
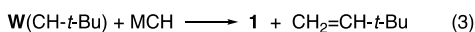


Figure 1. The molecular structure of **1** (thermal ellipsoids are plotted at 40% and hydrogen atoms are omitted).

The $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angles in **1** are significantly different ($135.8(9)^\circ$ and $109.9(7)^\circ$), with the larger $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angle being

that in which C_β points toward the imido group. Five sets of methylene resonances are observed for the cyclohexylidene ring at 22°C in proton NMR spectra. Resonances for protons in β positions of the alkylidene (pointing toward or away from the imido group) are found at 3.63 and 4.52 ppm; the isopropyl methine CH resonance in the NAr ligand is found in the same region (at 3.74 ppm; Fig S3). The α carbon resonance in **1** is found at 244 ppm in its ^{13}C NMR spectrum (Fig S4).

A solution of **1** is unchanged when heated to 100°C for two days in toluene- d_8 under nitrogen at a concentration of 0.01–0.02 M. There is no evidence for bimolecular coupling of cyclohexylidene ligands or for formation of a $\mathbf{W}(\text{cyclohexene})$ complex, which would be analogous to reported $\mathbf{Mo}(\text{olefin})$ complexes (olefin = ethylene, styrene, or *trans*-3-hexene; $\mathbf{Mo} = \text{Mo}(\text{NAr})(\text{OSiPh}_3)_2$) (Fig S45).¹⁷ A mixture of **1** and cyclohexene (10 equiv) is also unchanged upon being heated to 100°C for 24h (Fig S46). However, we were surprised to find that **1** *does* react with deuterated cyclohexene in a degenerate fashion.

Heating a mixture of **1** and 10 equiv of cyclohexene- d_{10} for 14 h at 100°C led to formation of ~ 0.8 equiv of $\text{C}_6\text{H}_9\text{D}$ and (we propose) a C_6HD_9 cyclohexylidene complex when cyclohexene- d_{10} is in excess. The resonances for the methylene protons in the β position on the C_6 ring in **1** decrease while resonances for a CHD proton in the two β positions of the cyclohexylidene ring are relatively sharp and shifted upfield of the β CH_2 resonances (Fig 2; see expanded views and Fig S47). The free $\text{C}_6\text{H}_9\text{D}$ that is formed contains D in each olefinic, allylic, and homoallylic position, consistent with isomerization of the $\text{C}=\text{C}$ bond around the ring in C_6HD_9 . There is no evidence for any H/D exchange into the imido ligand's methine or methyl position.

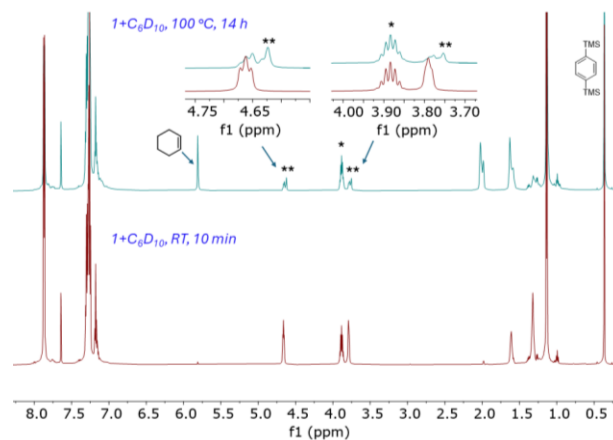
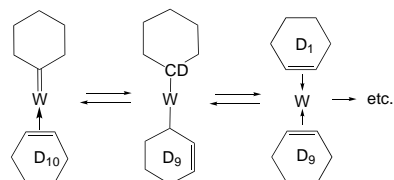


Figure 2. Reaction of **1** with cyclohexene- d_{10} ; * CHMe_2 resonances in **1** and ** CHD resonances in the two β positions of the C_6 ring in **1**.

A proposed mechanism for the H/D exchange is shown in Scheme 1. If a tetrasubstituted tungstacyclobutane ring cannot form from a cyclohexene adduct of **1**, a 14e cyclohexyl/cyclohexenyl (σ allyl) intermediate forms instead through allylic CH



Scheme 1. A mechanism that leads to H/D exchange.

activation. Formation of a 16e analog that contains an η^3 -allyl is not required. Transfer of a β H from the cyclohexyl ring back to the cyclohexenyl ligand would then yield a biscyclohexene complex. Of course, the proposed complexes could have either TBP (trigonal bipyramidal) or SP (square pyramidal) forms, and isomers of each. Interconversions of all could be key features of their chemistry.

The reverse of what is shown in Scheme 1 could be a way to turn a cyclohexene complex into a cyclohexylidene complex, but one that does *not* involve formation of, and ring-contraction of, a metallacyclopentane complex, which is the main topic of this paper. The possibility of forming an alkyl/allyl intermediate (Scheme 1) will clearly require further study in due course.

Isolation of a monoethylene complex (2) and a 7-tungstabicyclo[4.3.0]nonane complex (3)

A $W(NAr)(OSiPh_3)_2$ (ethylene) complex, an analog of $Mo(NAr)(OSiPh_3)_2(CH_2=CH_2)$,¹⁷ is required to test the proposal shown in equation 2. It has been proposed that the tungstacyclopentane complex, $W(NAr)(OSiPh_3)_2(C_4H_8)$, reacts with terminal olefins, 1,7-octadiene, or 1,6-heptadiene⁴⁰ via 14e tungsten monoolefin complexes. Examples of 16e or 18e $W(VI)$ imido or oxo ethylene complexes are $W(N-2,6-Cl_2C_6H_3)(Biphen)(THF)(CH_2=CH_2)$ ([Biphen]²⁻ = 3,3'-di-*t*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate),⁴¹ $W(NPh)[1,2-(NTMS)_2C_6H_3](PMe_3)_2(CH_2=CH_2)$,⁴² and $W(O)[OCMe(CF_3)_2]_2(pyridine)_2(CH_2=CH_2)$.¹³

Refluxing a benzene solution of $W(NAr)(OSiPh_3)_2(C_4H_8)$ and periodically removing ethylene *in vacuo* yields a red-orange solution that contains largely the monoethylene complex, $W(CH_2=CH_2)$ (2, Fig 3). Mixtures that contain 90-95% $W(CH_2=CH_2)$ (Fig 3) can be prepared in this manner and pure orange 2 can be crystallized selectively from those mixtures (Figs S7-S10). $W(NAr)(OSiPh_3)_2(CH_2=CH_2)$ is relatively stable in refluxing benzene in the absence of air and moisture. Details as to exactly how an olefin exchanges into or out of a metallacyclopentane complex are still not known.

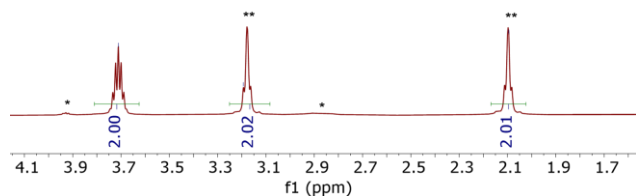
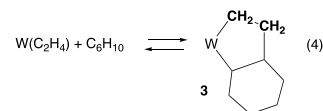


Figure 3. A portion of the NMR spectrum of $W(CH_2=CH_2)$ (2); ** ethylene proton resonances in $W(CH_2=CH_2)$; * residual methine and methylene resonances in $W(C_4H_8)$.

Compound 2 *slowly* reacts with neat cyclohexene at RT to give (after ~1h) a product whose proton NMR spectrum shows a pattern of 14 resonances between 1.0 and 3.7 ppm (Fig S11) that are in the same region as the seven found in the proton NMR spectrum of the major isomer of the mirror symmetric 8-tungstabicyclo[4.3.0]nonane complex made from $W(C_4H_8)$ and 1,7-octadiene (see below).⁴⁰ The presence of two isopropyl NAr methyl resonances is consistent with the product having no symmetry. NMR correlations show the product to be largely one isomer of the 7-tungstabicyclo[4.3.0]nonane complex, 3 (eq 4; Figs S13 and S14). The α carbon resonances are found at 93.43 ppm (substituted C_α) and 65.25 ppm ($C_\alpha H_2$). For comparison the $^{13}C_\alpha H_2$ resonance in

$Mo(NC_6F_5)(^{13}CH_2^{13}CH_2/NBE)(DFTO)_2$ (DFTO = decafluoroterphenoxide; NBE = norbornene)³³ is found at 84.7 ppm at -78 °C. The chemical shift (93.43 ppm) for the substituted α carbon atom in the WC_4 ring in 3 is not outside the range of chemical



shifts (~70-95 ppm) typically observed for Mo or W metallacyclopentane complexes of this general type (see Table S1 in the SI). The largest C_α shift has been observed in the unsubstituted molybdacyclopentane complex, $Mo(N-2,6-Cl_2C_6H_3)(C_4H_8)(Benz_2Bitet)$ (94.5 and 76.0 ppm; $Benz_2Bitet$ is a biphenoxide).⁴¹

A single crystal X-ray diffraction study showed the structure of 3 to be closest to a square pyramid (Fig 4; $\tau = 0.23$). The W-C distances (2.174(3) Å and 2.177(3) Å) are stistically the same, W-O distances (1.9080(16) Å and 1.8898(16) Å) are the same, and W-N = 1.734(2) Å. In short, there is no evidence that the substituted W- C_α bond in 3 is longer than the other W-C bond in the ground state structure of 3. Studies of any five-coordinate rearrangement of 3, and therefore the accessibility of other structures, including TBP isomers of 3, is prevented by loss of cyclohexene (or possibly also ethylene; see below).

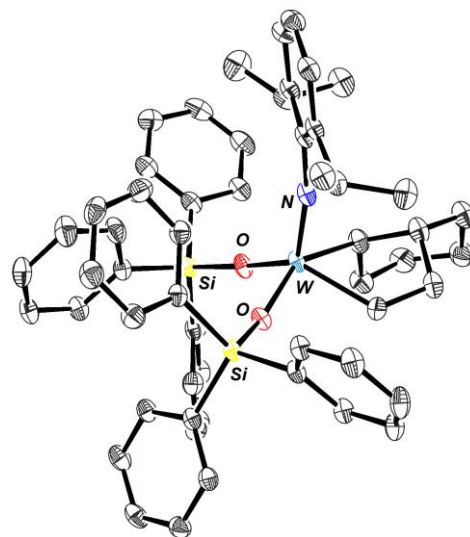
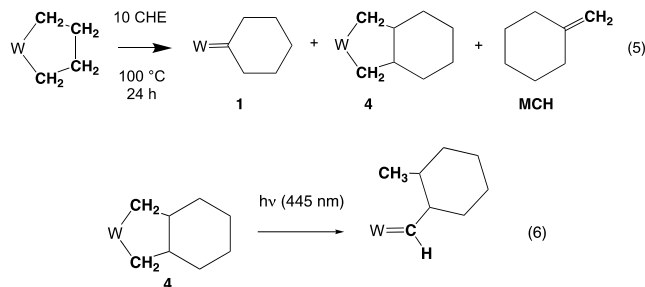


Figure 4. The structure of the 7-tungstabicyclo[4.3.0]nonane complex (3).

When a solution containing 3 (~0.01 M) is heated at temperatures up to ~80 °C, 3 loses cyclohexene to give 2 (Fig S19). At 80 °C only ~10% of the original 3 remains. However, the calculated values for ΔG_f for W (ethylene) and W (cyclohexene) (see later section) reveal that (unknown) W (cyclohexene) could also be thermally accessible from 3 through loss of ethylene. Loss of ethylene from 3 may have complicated equilibrium studies that we attempted. Upon heating 3 in solution to 100 °C in the presence of cyclohexene, 1 and methylenecyclohexane are formed in 61% and 56% yields, respectively (Figs S16-S18). These and other products and mechanisms of their formation are described in detail in the next section.

Reactions of cyclohexene with $W(C_4H_8)$

Cyclohexene (10 equiv) reacts with 80%-labeled $W(^{13}C_4H_8)$ in toluene- d_8 at 100 °C for 24 h in the dark under nitrogen to give a mixture of **1**, the 8-tungstabicyclo[4.3.0]nonane complex (**4**),⁴⁰ and methylenecyclohexane (MCH) in approximately a 2:1:2 ratio (eq 5). The ^{13}C label ends up in the

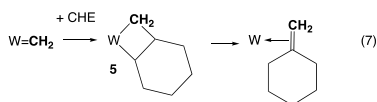


positions shown (bold type in eq 5) in **4** and MCH (Figs S23-S29). According to proton NMR spectra containing 1,4-TMS₂C₆H₄ as an internal standard the yield of **1** is ~40-45% and of **4** is ~20-25% for a 60-70% combined yield of **1** and **4** versus $W(^{13}C_4H_8)$ at 100 °C after 24 h in the dark in multiple experiments. The yields of **1** and MCH are lower than those found when **3** is heated in the presence of cyclohexene (61% and 56%, respectively) due to a second equivalent of ethylene being available from $W(C_4H_8)$. Photolysis of the mixture of **1**, **4**, and MCH (eq 5) at 445 nm⁴⁰ leads to rapid conversion of **4** to the alkylidene formed through α hydrogen abstraction (eq 6) with the labeled carbons in the α and δ positions (Fig S30). Ambient (fluorescent) light produces the same product slowly over a period of several days.⁴³

A methylenecyclohexane complex ($W(MCH)$) is also likely to be in the mixture of compounds shown in eq 5 on the basis of a CH₂ resonance observed at 48 ppm in the ^{13}C labeling studies (Fig S27). Although formation of $W(MCH)$ has not been verified through synthesis, it should be noted that $Mo(CH_2=CMePh)$ ($^{13}CH_2$ resonances at 55.84 and 53.66 ppm in two isomers) and $Mo(CH_2=CH-t-Bu)$ ($^{13}CH_2$ resonances at 50.19 and 51.50 ppm in two isomers) have been isolated and characterized.²⁶

Under an atmosphere of ethylene a solution of $W(C_4H_8)$ in toluene in the presence of cyclohexene is unchanged after 24 h at 90 °C. (Only a trace of MCH is formed.) The reaction shown in eq 5 is slow under these conditions because very little **2** is formed in the presence of a large amount of ethylene.

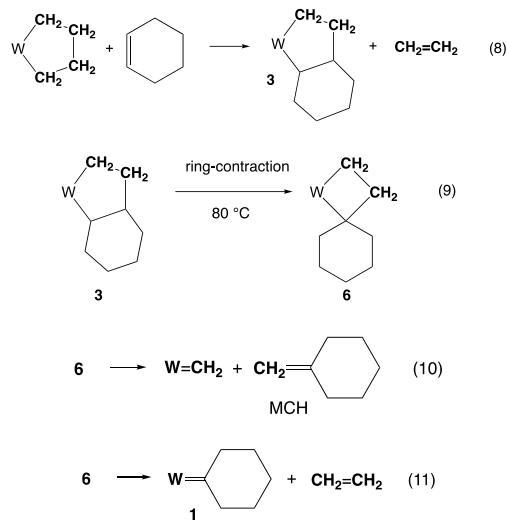
When only 3.5 equivalents of cyclohexene are added to $W(^{13}C_4H_8)$ in toluene- d_8 and the solution is heated to 100 °C for 24 h in the dark, ~30% of what we propose to be the 7-tungstabicyclo[4.2.0]octane complex (**5**, eq 7) and MCH are formed on the basis of proton and carbon NMR correlation studies; no **1**



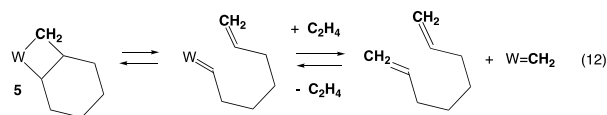
nor **4** is present (Fig S40). The $C_\alpha H_2$ resonance in the ^{13}C NMR spectrum of **5** is found at 55.92 ppm ($J_{CW} = 41.3$ Hz) and that for the $C_\alpha H$ (naturally abundant) is found at 47.87 ppm (Fig S40). These chemical shifts should be compared with those in (square pyramidal) $W(C_3H_6)$ ($C_\alpha H_2$ at 45.0 ppm, $J_{CW} = 46.4$

Hz), $W(NCPh_3)(OSiPh_3)_2(C_3H_6)$ ($C_\alpha H_2$ at 44.1 ppm, $J_{CW} = 42.6$ Hz), and $W(NCPh_3)(OSiPh_3)_2(CHMeCH_2CH_2)$ ($C_\alpha H_2$ at 43.5 ppm and $C_\alpha H$ at 59.5 ppm).⁴³ We propose that the MCH complex is formed from **5** through migration of H_β to the substituted C_α (eq 7); MCH can then be displaced by ethylene or cyclohexene.

The results presented so far can be explained as shown in equations 8-11. The 7-tungstabicyclo[4.3.0]nonane complex (**3**, eq 8) contracts above 80 °C in the dark to give the tungstacyclobutane intermediate, **6** (eq 9). The tertiary W-C bond in **6** should be even weaker than the secondary W-C bond in **3**. A methylenecyclohexane complex and MCH could form from **6** (eq 10) or **1** could form through loss of ethylene (eq 11); both could take place under different conditions and at different times, in part because $W(CH_2)$ and **1** have essentially the same free energy of formation at 100 °C (see later section). The methylenecyclohexane complex would then react with cyclohexene to give **5** (eq 7).

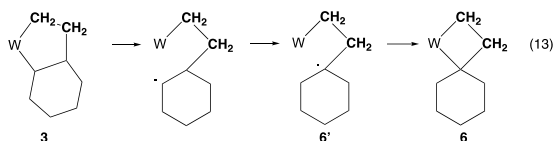


We propose that **5** also ring-opens and reacts with ethylene to give 1,7-octadiene, as shown in eq 12. No free 1,7-octadiene has been observed in any reaction mixture (e.g., Fig S44), which is consistent with the facts that cyclohexene cannot be polymerized or cross-metathesized with ethylene. Small oligomers of oligocyclohexene reportedly can form at -78 °C with an efficient classical catalyst, but these oligomers evolve cyclohexene when an unquenched reaction is warmed to RT.³⁴ We know that $W(C_4H_8)$ reacts with 1,7-octadiene to give **4**,⁴⁰ and that **4** reacts with ethylene in toluene- d_8 at 100 °C to give only $W(C_4H_8)$ and cyclohexene (Fig S33). We conclude that some 1,7-octadiene is formed, but it is observable only as a consequence of being trapped as thermally stable **4** as all ethylene eventually is consumed or evolved.



The ring-contraction process is shown in more detail in eq 13. We propose that the more substituted W-C α bond cleaves selectively and the biradical **6'** is formed when what was H_β in the C_6 ring of **3** moves to C_α . At that point either a W-C bond could form to give **6**, or the methylenecyclohexane complex and MCH could form directly from **6'** without forming **6**. We propose that

these two processes compete to give either an unobservable methylidene complex and methylenecyclohexane (eq 10) or **1** and ethylene (eq 11). The methylidene complex is then trapped by cyclohexene to give **5** (eq 7).



As a consequence of computational studies (see next section) we have to entertain the possibility that when the ethylene concentration is low relative to cyclohexene a tetrasubstituted tungstacyclopentane can form from two equivalents of cyclohexene and can contract to yield **1** and cyclohexene. In fact, all of the products just described can be accounted for if **1** is formed from a tungstacyclopentane made from two cyclohexenes; ethylene then reacts with **1**, etc. However, the rate of contraction of **3** would seem to be approximately the same as that for the tetrasubstituted tungstacyclopentane and **3** seems likely to be formed more readily until the ethylene concentration is low. A cyclohexylidene complex could also be formed from two cyclohexenes through a variation of the reaction shown in Scheme 1.

Computational studies

The DFT (B3LYP-D3) computed free energies at 100 °C relative to $\mathbf{W}(\text{C}_4\text{H}_8)$ for a selection of the various observed or proposed intermediates and isomers thereof discussed here (in kcal/mol) are shown in Fig. 5. The SP structures have the imido ligand in an axial position (N_{ax}); the TBP isomers contain an axial imido and siloxide and the metallacycle α carbons and one siloxide are in equatorial positions ($N_{\text{ax}}\text{C}_{\text{eq}}\text{C}_{\text{eq}}$).

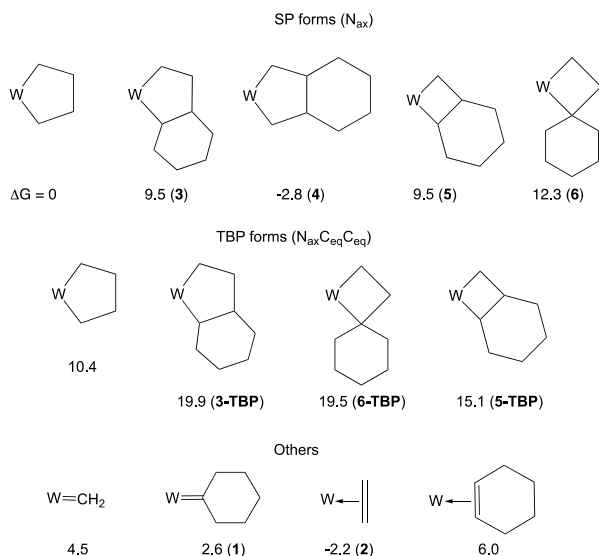


Figure 5. B3LYP-D3 relative free energies at 100 °C for several observed, proposed, or alternative intermediates in reactions of cyclohexene with **2** or $\mathbf{W}(\text{C}_4\text{H}_8)$.

All free energies of the compounds shown in Figure 5 differ by < 20 kcal/mol relative to $\mathbf{W}(\text{C}_4\text{H}_8)$, which suggests that all structures shown are relatively accessible thermally at 100 °C. A number of comparisons are illustrative. For example, the

relative free energies of the observed complexes (**1** - **5**) are 2.6, -2.2, 9.5, -2.8, and 9.5 kcal/mol, respectively. The energy of **3** (9.5 kcal/mol) is also comparable to that of the ring-contracted intermediate (**6**; 12.3 kcal/mol). The calculated relative free energies of the methylidene complex (4.5 kcal/mol), the cyclohexylidene complex, **1** (2.6 kcal/mol), the ethylene complex (**2**; -2.2 kcal/mol), and the unknown cyclohexene complex (6.0 kcal/mol) are also within 10 kcal/mol of one another. The reactions shown in equations 10 and 11 therefore seem equally plausible. The energies of the cyclohexylidene and cyclohexene complexes, as well as methylidene and ethylene complexes, are similar to what has been observed experimentally in studies of the interconversion of various styrene and phenethylidene complexes through an acid-catalyzed mechanism.²⁶ No terminal olefin complexes were observed in the acid-catalyzed interconversions.

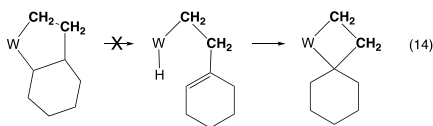
TBP forms are higher in energy than analogous SP forms by as much as ~10 kcal/mol, which is consistent with the fact that no TBP isomers were observed in this study. Some TBP and SP forms of metallacyclobutanes in the literature^{44,45} have been found to have essentially the same energy. Only SP metallacyclopentanes of this type have been observed, but they are known to be fluxional on either proton or carbon NMR time-scales with barriers of the order of 10-15 kcal/mol. Two intermediates or transition states are possible in a Berry-type pseudorotation in which α protons above the ring interchange with those below, and β protons above the ring with those below. One, a TBP with equatorial imido and metallacyclopentane carbon atoms has $\Delta G^\circ = 16.0$ kcal mol⁻¹. The other is a TBP structure with an axial imido group and an axial metallacyclopentane carbon atom ($N_{\text{ax}}\text{C}_{\text{ax}}\text{C}_{\text{eq}}$).⁴³ However, all attempts to locate a minimum for a $N_{\text{ax}}\text{C}_{\text{ax}}\text{C}_{\text{eq}}$ structure led to either the TBP with equatorial imido and metallacycle carbon atoms ($N_{\text{eq}}\text{C}_{\text{eq}}\text{C}_{\text{eq}}$) or to the observed SP structure with an axial imido ligand. These calculations are consistent with the fact that, to our knowledge, there is no example in the literature of d^0 five-coordinate TBP monoimido complex of the type being discussed here with either a $N_{\text{ax}}\text{C}_{\text{ax}}\text{C}_{\text{eq}}$ or $N_{\text{eq}}\text{C}_{\text{eq}}\text{C}_{\text{eq}}$ structure. Our working hypothesis is that the thermally accessible $N_{\text{ax}}\text{C}_{\text{ax}}\text{C}_{\text{eq}}$ form (with or without an energy minimum) is the form in which $\text{W}-\text{C}_{\text{ax}}$ bond *trans* to the axial imido ligand is cleaved.

Finally, the calculated free energy of an SP metallacyclopentane formed from two cyclohexenes was found to be 16.1 kcal/mol greater than that for $\mathbf{W}(\text{C}_4\text{H}_8)$, vs. 9.5 kcal/mol for **3**. Therefore, under some conditions ethylene conceivably could be completely displaced from the metal completely and a tetrasubstituted metallacyclopentane could be formed and contract to give cyclohexene and **1**.

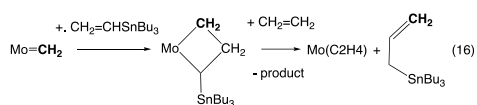
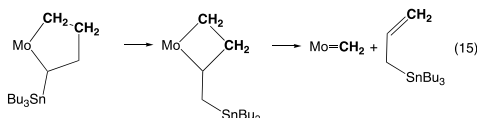
DISCUSSION

The work described here strongly supports the proposal that α -substituted five-coordinate d^0 imido disiloxy tungstacyclopentanes can form and ring-contract thermally and selectively. We propose that this contraction involves cleavage of the most substituted $\text{W}-\text{C}$ bond to yield an intermediate $\mathbf{W}(\text{V})$ complex that contains a carbon-based radical (eq 13). A selective β -H elimination (eq 14) does not seem to be a viable alternative explanation, considering that the H_β that moves seems to be relatively inaccessible compared to a H_β in a CH_2 group and that a $\text{W}-\text{CHR}$ - bond is weaker than a $\text{W}-\text{CH}_2$ - bond. We cannot ex-

clude an essentially concerted or "metal-assisted,"⁴⁶ but still selective, process, but a W-C α cleavage is the most attractive proposal at this stage.



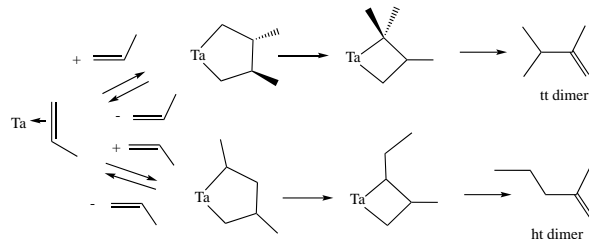
A catalytic reaction at 22 °C between $^{13}\text{C}_2\text{H}_4$ and two equivalents of $\text{CH}_2=\text{CHSnBu}_3$ has been reported to yield two equivalents of $^{13}\text{CH}_2=\text{CHCH}_2\text{SnBu}_3$.¹⁶ The initiator is $\text{Mo}(\text{NAr})(\text{C}_2\text{H}_4)(\text{Biphenoxide})$. The observed rate constant at 22 °C is $4.70 \times 10^{-6} \text{ s}^{-1}$. The mechanism was proposed to consist of formation and ring-contraction of an unobservable metallacyclopentane made from $^{13}\text{C}_2\text{H}_4$ and $\text{CH}_2=\text{CHSnBu}_3$ that contains the tributyl tin group in the α position, as shown in eqs 15 and 16. This result relies on a ring-contraction in which the substituted W-C α bond cleaves selectively (eq 15). The proposed α -substituted metallacyclopentane (eq 16) was not observed. The reaction between ethylene and two equivalents of cyclohexene to yield two equivalents of methylenecyclohexane, a version of the reactions shown in eqs 15 and 16, is extremely slow, as mentioned above, because too little $\text{W}(\text{CH}_2=\text{CH}_2)$ is available through dissociation of ethylene from $\text{W}(\text{C}_4\text{H}_8)$.



It was noted in the introduction that $\text{Mo}(\text{NC}_6\text{F}_5)(^{13}\text{CH}_2^{13}\text{CH}_2/\text{NBE})(\text{DFTO})_2$ (69%) was formed through addition of NBE to $\text{Mo}(\text{NC}_6\text{F}_5)(^{13}\text{CH}_2^{13}\text{CH}_2)(\text{DFTO})_2$ at -70 °C.³³ Upon raising the temperature to -50 °C, norbornene is polymerized rapidly but no ^{13}C measurably above natural abundance is observed in the polynorbornene.¹ It now seems possible that in the presence NBE the amount of $\text{Mo}(\text{NC}_6\text{F}_5)(^{13}\text{CH}_2^{13}\text{CH}_2/\text{NBE})(\text{DFTO})_2$ at -50 °C or above and the rate of Mo-C bond cleavage of the substituted C α are both large enough to generate a trace of Mo(norbornylidene) (and $^{13}\text{CH}_2=^{13}\text{CH}_2$) through ring-contraction. The Mo(norbornylidene) then initiates polymerization of the remaining NBE. Depending upon conditions, any free $^{13}\text{CH}_2=^{13}\text{CH}_2$ could react with the trace of alkylidene chain-end after polymerization is complete to give a ROMP polymer capped with a $^{13}\text{CH}_2$ group. In fact, this was proposed for polymerization of 5,6-dicarboxymethoxynorbornene by $\text{Mo}(\text{NC}_6\text{F}_5)(^{13}\text{CH}_2^{13}\text{CH}_2)(\text{DFTO})_2$ where some ^{13}C above natural abundance was detected in the polymer. Formation and contraction of a metallacyclopentane from two equivalents of norbornene to give a norbornylidene cannot be excluded.

The formation of two dimers of $\text{RCH}=\text{CH}_2$ at 50 °C from tantalacyclopentanes formed from $\text{TaCp}^*\text{Cl}_2(\text{RCH}=\text{CH}_2)$ and $\text{RCH}=\text{CH}_2$ ²⁷⁻³² is shown in Scheme 2; this early Ta chemistry is relevant to the chemistry described here. For $\text{RCH}_2\text{CH}=\text{CH}_2$ the tt (tail-to-tail) dimer is formed from the (often observable) β,β' -disubstituted metallacycle and the ht (head-to-tail) dimer is

formed from the selective rearrangement of unobservable α,β' -disubstituted tantalacyclopentanes. The ratio of the two depends upon the steric demands of the R group in $\text{RCH}_2\text{CH}=\text{CH}_2$, with a tt dimer being formed (98%) when R = Me and ht dimer when R = $\text{CH}_2-t\text{-Bu}$. It was stated that "the MC $_4$ to MC $_3$ ring-contraction is a straightforward and reasonable way of forming an alkylidene ligand from olefins...assuming that some MC $_3$ complexes which form in this manner will cleave to give metathesis-type products instead of rearranging" to an olefin.²⁸ It was proposed that the rate of formation of the ht dimer is *accelerated* significantly over the rate of formation



Scheme 2. Dimerization of propylene to give tt and ht dimers via tantalacyclopentane ring-contraction.

of any tt dimer when the R group is large. Although the ring-contraction of the tantalacyclopentanes of each type were proposed to involve a β elimination and readdition process, Ta-C bond cleavage to give a Ta(IV) intermediate with a radical attached followed by H migration now seems to be equally if not more likely for tantalum complexes that are isoelectronic and isostructural with the tungsten imido complexes discussed here. No mention was made as to a possible role of light in the tantalum studies. It is interesting to note that rearrangement of the metallacyclobutane formed through ring-contraction to the olefin dimer product also consists of movement of H β to the most substituted C α .

Metallacyclopentanes are dialkyl complexes and therefore related to dineopentyl or dineophyl complexes that undergo α abstraction to give neopentylidene or neophylidene complexes from d⁰ Ta, Mo, W, and Re alkyl complexes. The influence of light in α abstraction reactions was noted in the first study of formation of neopentylidene complexes of the type TaCpCl $_2(\text{CH}-t\text{-Bu})$ from dineopentyl derivatives,⁴⁷ as was a mechanism in which Ta-C bond cleavage was involved in both thermal and photochemical α abstraction reactions. Some α abstractions clearly require light; formation of $\text{Re}(\text{NAr})_2(\text{CH}_2\text{SiMe}_3)(\text{CHSiMe}_3)$ from $\text{Re}(\text{NAr})_2(\text{CH}_2\text{SiMe}_3)_3$ is one example.⁴⁸ Photochemical or thermal metal-carbon bond cleavage is plausibly a common step in both α hydrogen abstraction and ring-contraction reactions. Therefore a photochemical ring-contraction could also be essentially a thermal ring-contraction.

It should be pointed out that ring-contraction is a mechanism of forming an alkylidene complex from two olefins. A monoolefin version has been referred to in the organometallic literature as the 1,2-H shift mechanism, especially for cyclic olefins that are initiators for their polymerization through ROMP.¹ To our knowledge an intramolecular 1,2-H shift in an olefin complex to yield an alkylidene (or the reverse) has never been demonstrated unambiguously, and *olefins are always present in solution*. Both ring-contraction of a metallacyclopentane

tane and the alkyl/allyl mechanism shown in Scheme 1 are viable alternatives to a 1,2-H shift that involves only one olefin.

Thermal (often reversible) M-C bond cleavage in transition metal complexes has been explored and discussed since the mid 1950s,⁴⁹⁻⁵³ especially with respect to catalytic reactions in which a metal-carbon bond is lost or formed (alkyl migration to a ligand, β hydride elimination, oxidative addition, etc.). Discussions of that nature continue today^{52, 54} and include the role of visible light⁵⁵ and radical formation induced through coordination of a ligand.^{54, 56} In short, thermal M-C bond cleavage can hide, unrecognized, in plain sight. The case for M-C bond cleavage in a metallacyclopentane can be built in part as a consequence of the fact that the carbon-based radical that is formed upon M-C bond cleavage in a metallacyclopentane cannot escape to solution. When M-C bond cleavage is part of an α or β , or other H_x abstraction in a dialkyl complex, the radical may or may not escape before an H is abstracted.

The reaction mechanism shown in Scheme 1 is a plausible alternative way to form a cyclohexylidene from cyclohexene that involves two cyclohexenes. At this stage we have no other evidence for it, and we have much evidence that a cyclohexylidene is formed through ring-contraction of **3**. Other proposed ring-contractions discussed above add support for the metallacyclopentane ring-contraction hypothesis.

CONCLUSIONS

The main conclusions to be drawn from this work are that a tungsten cyclohexylidene and a methylenidene complex are both likely to be formed through formation and thermal contraction of a metallacyclopentane made from ethylene and cyclohexene, and the W-C bond that cleaves (selectively) is secondary (W-CHR-). Therefore, we can propose that metallacyclopentanes that have one secondary W-C bond can form and can ring-contrast thermally. Those that contain two W-CH₂ bonds are thermally *relatively* stable, but can ring-contrast in light. A tungstacyclopentane made from two cyclohexenes is possible, but it would seem to offer no advantage in terms of forming a cyclohexylidene over a tungstacycle made from ethylene and cyclohexene. A reverse of the reaction shown in Scheme 1 may be yet another way to make a cyclohexylidene from cyclohexene, but further studies are required.

Fluxional processes in five-coordinate or pseudo-five-coordinate complexes in all of the reactions discussed here are likely to be required in order to access other isomers. The calculated energies of the metallacyclopentanes with TBP forms and two equatorial W-C bonds are only slightly higher in energy than the SP forms (Fig 5) and therefore likely to be accessible through Berry-type pseudorotations. Because ethylene is not lost readily from **W**(C₄H₈), a five-coordinate rearrangement can be observed on the NMR time scale, in some cases even at room temperature.⁴³

To our knowledge, this is the first report of formation of metathesis-relevant alkylidenes from an olefin in the absence of a (so far, rare) protonation/deprotonation mechanism (eq 1), or some variation of it such as that shown in Scheme 1. It is important to note that *two* olefins are required to make an alkylidene, not one. It would not be surprising to us if similar results were to be documented for other internal olefins, or for complexes attached to silica,⁵⁷ or in analogous Mo chemistry, or for variations that contain similar ligands (fluorinated alkoxides, oxos, etc.). Further investigations will be required to clarify the many issues and to explore other mechanisms through which

metathesis-active alkylidene complexes might be formed from olefins.

Experimental

General procedures

All the reactions were performed using standard Schlenk or glovebox techniques under an N₂ atmosphere. Commercially available reagents were dried and degassed prior to use. Diethyl ether, benzene, and toluene were dried and deoxygenated by argon purge, passed through activated alumina in a solvent purification system, and stored over 4 Å molecular sieves. Pentane was washed with H₂SO₄, followed by water and saturated solution of aqueous NaHCO₃, and dried over CaCl₂ pellets for at least 2 weeks prior to addition to the solvent purification system. Non-halogenated and non-nitrile containing solvents were tested with a standard purple solution of sodium benzophenone ketyl in THF to confirm effective oxygen and moisture removal prior to use. Cyclohexene was purchased from Alfa Aesar and dried over calcium hydride. W(NAr)Cl₄(THF),⁵⁸ W(NAr)₂(CH₂-*t*-Bu)₂,⁵⁸ W(CH-*t*-Bu)(NAr)(OSO₂CF₃)₂(dme),⁵⁸ W(NAr)(OSiPh₃)₂(C₄H₈),⁴³ and W(NAr)(OSiPh₃)₂(C₈H₁₄)⁴⁰ were prepared according to reported procedures. Ethylene Ultra High Purity were used as received from Airgas. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., and degassed, and dried over Na/benzophenone and stored under activated 4 Å molecular sieves for at least 24 h prior to use. ¹³C-Labeled W(NAr)(OSiPh₃)₂(C₄H₈) was prepared as reported literature^[41] in a J. Young Pressure NMR tube (Norell® S-5-300-MW-IPV-8). The 1D ¹H, ¹³C, and 2D ¹H-¹H COSY and ¹H-¹³C HSQC NMR spectra were recorded on Bruker Avance 600 MHz and 500 MHz spectrometers. ¹H and ¹³C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent as an internal standard. Elemental analyses were carried out at Atlantic Microlab, Inc., Norcross, GA.

Synthesis of W(NAr)(CH-*t*-Bu)(OSiPh₃)₂

W(NAr)(CH-*t*-Bu)(OSO₂CF₃)₂(DME) (0.5 g, 0.61 mmol, 1 equiv) was dissolved in Et₂O (20 mL) and a stir bar was added to the solution. Another vial was charged with NaOSiPh₃ (0.365 g, 1.22 mmol, 2 eq) in Et₂O. Both vials were placed at -30°C in the freezer of the glovebox and left overnight. The contents of the first vial were added dropwise to the second and the mixture was stirred at room temperature for 2 h. The volatiles were removed *in vacuo*. The solid residue was extracted in pentane (~20 mL) and the mixture was filtered through a plug of Celite. The filtrate was concentrated to 3 mL and stored at -30°C overnight. Three crops of the yellow solid were collected; yield 62% (0.37 g). Anal. Calcd for C₅₃H₅₇NO₂Si₂W: C, 64.95; H, 5.86; N, 1.43. Found: C, 65.14; H, 5.88; N, 1.49. Single crystals of the product suitable for x-ray diffraction were grown from a concentrated solution of pentane at -30 °C.

Synthesis of W(NAr)(OSiPh₃)₂(cyclohexylidene) (**1**)

In a 50 mL J.-Y. flask, N(Ar)(CH-*t*-Bu)(OSiPh₃)₂ (50 mg, 0.05 mmol, 1 equiv), methylenecyclohexane (49 mg, 0.5 mmol, 10 equiv), a magnetic stir bar, and benzene (5 mL) were added. The flask was heated and the mixture stirred in an oil bath at 60 °C for 6 h. All volatiles were removed under vacuum and the solid residue was extracted with 10 mL of pentane. This mixture was filtered through a plug of Celite, and the filtrate was concentrated to ~0.5 mL. This solution was stored at -30°C. The yellow solid was washed with cold pentane (~0.2 mL) to afford

the desired compound in 36% yield (19 mg). Anal. Calcd for $C_{54}H_{57}NO_2Si_2W$: C, 65.38; H, 5.79; N, 1.41. Found: C, 65.14; H, 5.86; N, 1.36. Single crystals of **1** suitable for diffraction were grown from a concentrated solution in pentane and diethyl ether (2:1).

Synthesis of $W(NAr)(OSiPh_3)_2(C_2H_4)$ (**2**)

$W(NAr)(OSiPh_3)_2(C_2H_4)$ (200 mg, 0.21 mmol) was dissolved in benzene (40 mL); the solution and a stir bar were added to a 500 mL J. Young flask. This flask was subjected to three freeze/pump/thaw cycles and then heated in an oil bath at 100 °C under a static vacuum for 12 h. The reaction mixture was exposed to vacuum ($\sim 100 \mu\text{bar}$) for 2-3 sec every 30 min for 4 h. All solvents were removed *in vacuo* and another 40 mL of benzene was added to the residue and the process repeated two more times. Pentane (~ 15 mL) was added to the final solid residue and the mixture was filtered through a plug of Celite. The filtrate was concentrated to 8 mL and stored at -30°C overnight. The first three crops of orange solids were discarded. The orange-yellow solid from the fourth fraction consisted of $>95\%$ pure **2** in $\sim 35\%$ yield (68 mg; see NMR spectrum in Fig 3). Anal. Calcd for $C_{50}H_{51}NO_2Si_2W$: C, 64.03; H, 5.48; N, 1.49. Found: C, 63.68; H, 5.64; N, 1.49.

Synthesis of 7-tungstabicyclo[4.3.0]nonane (**3**)

$W(NAr)(OSiPh_3)_2(C_2H_4)$ (90 mg, 0.10 mmol, 1 equiv), cyclohexene (160 mg, 2.0 mmol, 20 equiv), and a magnetic stir bar were added to a 20 mL glass vial. This reaction mixture was stirred at ambient temperature in dark for 1h. All volatiles were removed *in vacuo*. Pentane (3 mL) was added to dissolve the yellow solid. All solvent was again removed *in vacuo* and the yellow residue was extracted with 10 mL of pentane. This solution was filtered through a plug of Celite, and the filtrate was concentrated to ~ 5 mL. After 12 h at RT the orange-yellow crystals that had formed were discarded and the solvent was then removed *in vacuo* to provide yellow **3** in $\sim 62\%$ yield (60 mg). X-ray quality crystals were obtained through slow evaporation of a concentrated pentane solution at room temperature. Anal. Calcd for $C_{56}H_{61}NO_2Si_2W$: C, 65.94; H, 6.03; N, 1.37. Found: C, 65.89; H, 5.97; N, 1.34.

Reactions of cyclohexene with $W(NAr)(OSiPh_3)_2(C_2H_4)$

Compound **2** (10 mg, 0.01 mmol), cyclohexene (8.2 mg, 0.1 mmol, 10 equiv), 1,4-*bis*-trimethyl silyl benzene (0.15 mL of a stock solution in C_6D_6), and C_6D_6 (0.35 mL) were added to a J. Young NMR tube. (The 1,4-*bis*-trimethylsilyl benzene served as an internal standard.) After 1 h the solution of **3** was heated in a oil bath at 100 °C for 14 h and the mixture was analyzed at 22 °C by NMR methods.

Reactions of cyclohexene with $W(NAr)(OSiPh_3)_2(C_4H_8)$

$W(NAr)(OSiPh_3)_2(C_4H_8)$ (10 mg, 0.01 mmol), cyclohexene (8.2 mg, 0.1 mmol, 10 equiv), 1,4-*bis*-trimethyl silyl benzene (0.15 mL from a stock solution in toluene- d_8), and toluene- d_8 (0.35 mL) were added to a J. Young NMR tube. (The 1,4-*bis*-trimethylsilyl benzene served as an internal standard.) This tube was heated in an oil bath at 100 °C for 24 h and analyzed at 22 °C by NMR methods as described in the text and SI.

Computational Studies

DFT Calculations are performed with the B3LYP density functional^{59, 60} as implemented in Gaussian16.C.02 package.⁶¹

Dispersion forces are taken into account by adding Grimme's D3 empirical correction.⁶² Geometry optimizations are performed representing main group elements with the 6-31G(d,p)^{63, 64} basis sets and W with the Stuttgart pseudopotential and the associated basis sets increased with a f polarization function (BS1).^{65, 66} The final energies are obtained through single point calculations at the BS1 optimized geometry in which the basis sets for main group elements is increased to 6-311++G(d,p) and solvation effects⁶⁷ are included with the SMD continuum model and toluene as solvent.⁶⁸ The nature of the stationary points is verified by vibrational analysis. Thermal corrections are computed at 373.15 K and 1 atm in gas phase with the smaller basis sets. The reported Gibbs energies are, thus, computed as $G_{373}^\circ = G_{gp}^\circ + \Delta G_{solv}^\circ$ where G_{gp}° is the gas phase Gibbs energy and ΔG_{solv}° the solvation Gibbs energy. This methodology is essentially equal to that used in recent contributions on the olefin metathesis reaction with d^0 metal alkylidenes in which the performance of B3LYP-D3 has been compared to other functionals and found that all functionals lead essentially to equivalent results.^{69, 70}

Accession Codes

CCDC files 2293446, 2293449, and 2342699 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif 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.

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Notes

The authors declare no competing financial interest.

SUPPORTING INFORMATION

Table of metathesis-relevant Mo and W metallacyclopentanes, NMR data and spectra, additional experimental procedures,

techniques, methods, and results, and details of the single crystal X-ray and theoretical studies.

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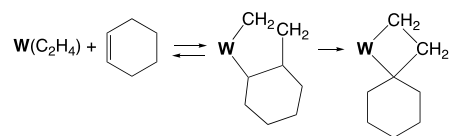
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Table of Contents Artwork



W = W(NAr)(OSiPh₃)₂; Ar = 2,6-*i*-Pr₂C₆H₃