Tungstacyclopentane Ring-Contraction Yields Olefin Metathesis Catalysts

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ABSTRACT: Exposure of a solution of the square pyramidal tungstacyclopentane complex, $W(NAr)(OSiPh_3)_2(C_4H_8)$ (Ar = 2,6-*i*-$Pr_2C_6H_3$), to ethylene at 22 °C in ambient (fluorescent) light slowly leads to formation of propylene and the square pyramidal tungstacyclobutane complex, $W(NAr)(OSiPh_3)_2(C_3H_6)$. No reaction takes place in the dark, but the reaction is >90% complete in ~15 minutes in blue LED light (~450 nm λ_{max}). The intermediates are proposed to be (first) an α methyl tungstacyclobutane complex ($W(NAr)(OSiPh_3)_2(\alpha MeC_3H_5)$) and then from it, a β methyl version. The TBP versions of each can lose propylene and form a methylene complex, and in the presence of ethylene, the unsubstituted tungstacyclobutane complex, $W(NAr)(OSiPh_3)_2(C_3H_6)$. The W-$C_\alpha$ bond in an unobservable TBP $W(NAr)(OSiPh_3)_2(C_4H_8)$ isomer in which the C_4H_8 ring is equatorial is proposed to be cleaved homolytically by light A hydrogen atom moves or is moved from C3 to the terminal C4 carbon in the butyl chain as the bond between W and C3 forms to give the TBP α methyl tungstacyclobutane complex. Essentially the same behavior is observed for $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ as for $W(NAr)(OSiPh_3)_2(C_4H_8)$, except the rate of consumption of $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ is about half that of $W(NAr)(OSiPh_3)_2(C_4H_8)$. In this case an α methyl substituted tungstacyclobutane intermediate is observed and the overall rate of formation of $W(NCPh_3)(OSiPh_3)_2(C_3H_6)$ and propylene from $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ is ~20 times slower than in the NAr system. These results constitute the first documented examples of forming a metallacyclobutane ring from a metallacyclopentane ring (ring-contraction) and establish how metathesis-active methylene and metallacyclobutane complexes can be formed, and re-formed, in the presence of ethylene. They also raise the possibility that ambient light could play a role in some metathesis reactions that involve ethylene and tungsten-based imido alkylidene olefin metathesis catalysts, if not others.

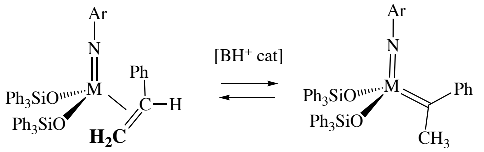
INTRODUCTION

The olefin metathesis reaction, variations of which were discovered over 60 years ago, often involves ethylene, *e.g.*, as a product of coupling of two terminal olefins to give an internal olefin (equation 1) or as a reactant in the reverse of that reaction ("ethenolysis").[1-4] In the largest commercial olefin metathesis process today, ethylene is dimerized to 2-butenes, which are then metathesized at ~400 °C with ethylene to give propylene over a catalyst that consists of WO_3 and MgO on silica.[5] The mechanism of forming the initial alkylidene in that heterogeneous process has been the subject of various proposals for some time,[6-10] but to our knowledge no report has appeared that shows definitively how an alkylidene is formed and what type it is. There seems to be some agreement that the supported catalyst is a d^0 alkylidene (if the alkylidene is counted as a dianion) of the type $W(O)(alkylidene)(OSi_{surf})_2$, where OSi_{surf} ligands are surface siloxides.[10-15] There is also evidence that reduction of W(VI) sites to W(IV) sites in model heterogeneous metathesis catalysts results in olefin binding and alkylidene formation,[16] probably in a continuous fashion in which the metal cycles between monometallic W(IV) olefin complexes and W(VI) alkylidenes. (In a supported catalyst at low loadings no bimetallic process should be possible.)

$$RCH{=}CH_2 \rightleftharpoons CH_2{=}CH_2 + RCH{=}CHR \qquad (1)$$

Ethylene also figures strongly in olefin metathesis by d^0 Mo-based or W-based catalysts for the synthesis of organic compounds in terms of efficiency and stereocontrol of the olefin metathesis reaction; knowing "when to add it, when to remove it, and when to avoid it" can be crucial.[17] The mechanism of forming the initial alkylidene in a homogeneous metathesis reaction has also been the subject of much discussion, but again to our knowledge no report has appeared that shows definitively what alkylidene is formed and how.[18]

Several decades of solution studies that employ well-characterized d^0 Mo or W alkylidene initiators of homogeneous olefin metathesis reactions that are formed through α hydrogen abstraction in a dialkyl (usually dineopentyl or dineophyl) complex have produced abundant evidence that 14 electron TBP (trigonal bipyramidal) metallacyclobutane complexes with the MC_3 ring in equatorial positions and an axial oxo or imido ligand are required intermediates.[19-26] Solution studies have also documented how alkylidenes decompose, with bimolecular coupling of alkylidenes (to give monometallic or bimetallic d^2 metal complexes) in sterically less demanding circumstances or rearrangement of a metallacyclobutane intermediate to an olefin being the most common (in the absence of water and oxygen or other destructive impurities). The first examples of how a d^2 olefin complex can be transformed into an alkylidene complex in a high oxidation state Mo or W olefin metathesis system[18] were published only recently;[18] a protonation/deprotonation mechanism (with dimethylanilinium as the acid) allows an equilibrium to be established between Mo or W styrene complexes and phenethylidene complexes (~2:1) with a cationic phenethyl complex being the intermediate.[27] The reaction is slow relative to most metathesis reactions, but the equilibrium can be established readily (equation 2; Ar = 2,6-diisopropylphenyl, M = Mo or W, BH^+ is dimethylanilinium).



(2)

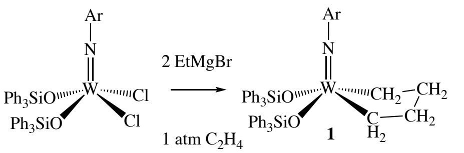
In the last few years 14e d^2 Mo and W complexes (*e.g.*, olefin complexes) have been shown to initiate some slow olefin metathesis reactions in the absence of any added acid under what might be considered forcing conditions (in terms of temperature, time, and substrate reactivity);[28-29] the initial alkylidene in those reactions was proposed to be formed in only low yield and could not be identified. Also, Mo and W d^0 metallacyclobutane complexes are formed and can be isolated when ethylene is present and metallacyclo*pentane* complexes can ultimately be formed.[30-39] Metallacyclopentane complexes are often proposed or observed as intermediates in catalytic dimerization of ethylene.[40] An unsubstituted metallacyclopentane complex has been viewed as a "dead end" product of metathesis, but surprisingly few metallacyclopentane complexes have been isolated as the final metal-based product in metathesis systems, in contrast to the many metallacyclobutane complexes that can be observed or isolated.[29, 36-37, 39, 41]

In this investigation we turn to the question concerning how an alkylidene might be formed from a metallacyclopentane complex in the absence of a Brønsted acid in solution.

RESULTS

The Tungsten Diisopropylphenylimido (NAr) System

As a starting point we chose to prepare a tungstacyclopentane complex with the formula $W(NAr)(OSiPh_3)_2(C_4H_8)$, an analog of known $Mo(NAr)(OSiPh_3)_2(C_4H_8)$ (Ar = 2,6-*i*-$Pr_2C_6H_3$).[29] $W(NAr)(OSiPh_3)_2Cl_2$ can be prepared readily from $W(NAr)Cl_4$ and two equivalents of $LiOSiPh_3$. Treatment of $W(NAr)(OSiPh_3)_2Cl_2$ with two equivalents of EtMgBr under ethylene produces yellow isolable $W(NAr)(OSiPh_3)_2(C_4H_8)$ (**1**, equation 3) in modest yield (50-60%). An ethylene complex formed through β H abstraction in a diethyl complex is a plausible intermediate with the metallacyclopentane being formed through addition of ethylene to the ethylene complex. This synthesis of **1** avoids an alkylidene, so any reactions that could be ascribed to a residual amount of alkylidene are unlikely. Related tungsten imido bisamido metallacyclopentane complexes reported by Boncella were prepared using $BrMg(CH_2)_4MgBr$ or through reaction of an alkylidene with ethylene.[41]



(3)

$W(NAr)(OSiPh_3)_2(C_4H_8)$ was purified through multiple recrystallizations in the absence of ethylene. It is stable in hydrocarbon solution under ethylene in the dark in the absence of air and water and light for days at 22 °C; no change is observed after three days at 90 °C (Fig S10). A single crystal X-ray diffraction analysis (SCXRD; Figure 1; see SI for details) confirms that **1** is essentially a square pyramid (SP) with the imido group in the apical position, as are all other structurally characterized five-coordinate metallacyclopentane complexes of Mo(VI) and W(VI). The β carbon atoms of the WC4 ring typically are disordered in a "wig-wag" fashion over two β carbon positions. Some structural details for one conformer of **1** are compared with other tungstacycles reported here and in the literature in Table 1.

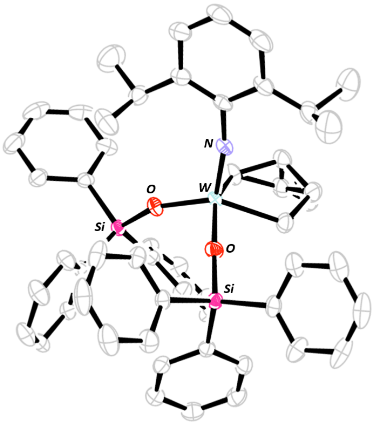


Figure 1. A thermal ellipsoid drawing of **1**. Ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted.

Table 1. A comparison of some ring structural details for SP Tungstacyclopentanes reported here and others in the literature.

Compound	W-C_α (Å)	C_α-W-C_α(°)	τ
1[a]	2.187, 2.158	74.41	0.016
4	2.203, 2.208	74.90	0.018
$W(Ar_{Cl})(Biphen)(C_4H_8)$[b,36]	2.129, 2.112	75.14	
$W(O)(HMTO)_2(C_4H_8)$[39]	2.172, 2.157	74.63	
$W(NAryl)(Pyr)(OR)(C_4H_8)$[c,37]	2.048,2.076	83.26	
3	2.170, 2.172	63.07	0.040
6	2.185, 2.201	62.80	0.034
$W(NAr)(OR)_2C_4H_8)$[d,42-43]	2.14, 2.17	63.4	

[a] One of two conformers (see SI). [b] Ar_{Cl} = 2,6-C_6H_3; Biphen = *rac*-3,3'-*t*-Bu-5,5',6,6'-tetramethylbiphenoxide. [c] W(N-3,5-$Me_2C_6H_3$)(2,5-dimethypyrrolide)(O-2,6-MesitylC_6H_3)(C_4H_8). [d] OR = $OCMe_2CF_3$

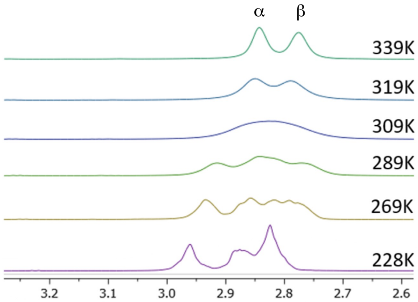
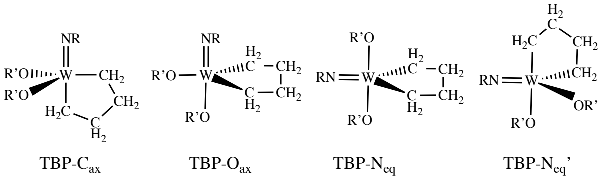


Figure 2. Partial VT 600 MHz Proton NMR spectra of **1**.

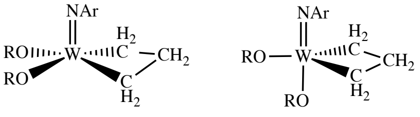


TBP-C_{ax} TBP-O_{ax} TBP-N_{eq} TBP-N_{eq}'

Figure 3. The four possible TBP intermediates in a five-coordinate rearrangement process.

$W(NAr)(OSiPh_3)_2(C_4H_8)$ is fluxional on the proton NMR time scale and all metallacycle proton resonances at 309 K and 600 MHz are found within a single broad resonance at ~2.8 ppm (Figure 2). At 339 K the pattern for the metallacycle proton resonances consists of two resonances, one for α and one for β protons as a consequence of "up" and "down" ring protons interconverting through a Berry-type five-coordinate rearrangement in which the metallacycle "flips over," but α and β protons do not interconvert and ethylene does not exchange into the WC_4 ring on the time scale of this fluxional process. The four TBP intermediates that can be part of a five-coordinate Berry-type rearrangement process are shown in Figure 3; none has been observed. Because the imido group in isolated or observable TBP metallacyclobutane complexes in this category is always in an axial position we propose that TBP-N_{eq} and TBP-N_{eq}' are higher in energy than TBP-O_{ax} and TBP-C_{ax}. TBP-C_{ax} and TBP-O_{ax} can be formed from **1** through one 90° turnstile process. Of the two only TBP-C_{ax} contains a plane of symmetry and therefore is required for equilibration of up and down protons. TBP-N_{eq} also has a plane of symmetry, but on the basis of data presented later we believe that the lowest energy "thermal" fluxional process takes place via TBP-C_{ax} alone. The metallacyclopentane ring resonances in **1** begin to resolve below 289K in the 600 MHz NMR spectrum, but at 228 K the pattern is relatively broad and unstructured. We propose that the WC_4 ring is not planar at the lowest temperatures in solution, as observed in the solid state (Figure 1). A nonplanar SP WC4 ring would be unsymmetric with eight inequivalent protons with all resonances within a relatively narrow chemical shift range. Similar fluxional and temperature dependent behavior has been found for $Mo(NAr)(OSiPh_3)_2(C_4H_8)$.[29]

Under an atmosphere of $^{13}CH_2{=}^{13}CH_2$ in toluene-d_8 **1** slowly exchanges ethylene to yield $W(NAr)(^{13}CH_2{}^{13}CH_2CH_2CH_2)(OSiPh_3)_2$ and $W(NAr)(^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(OSiPh_3)_2$, and resolved ring ^{13}C resonances at 22 °C that consist of two multiplets for C_α and C_β at 70.8 and 35.4 ppm. We propose that exchange of ethylene into the ring takes place through reversible loss of ethylene to form an ethylene intermediate. If the reaction is performed in room light and monitored as shown in Figure 4, within ~1 hour at 22 °C singlet resonances for C_α and C_β grow into the multiplets, consistent with formation of metallacyclopentanes in which an α or β ^{13}C is not next to another ^{13}C; one such variation is $W(NAr)(^{13}CH_2CH_2{}^{13}CH_2CH_2)(OSiPh_3)_2$. This finding is consistent with ethylene undergoing degenerative metathesis ($C_2H_4 + {}^{13}C_2H_4 \leftrightarrow 2\ {}^{13}CH_2{=}CH_2$). On roughly the same time scale propylene is formed along with a metal complex (**3**; see SP-**3** and Figure 6**)** that has broad proton resonances at 44.5 and 22.9 ppm in a 2:1 ratio (Figure 4). At -40 °C (Figure 5) these broad resonances sharpen to give resonances characteristic of ~98% square pyramidal $W(NAr)(CH_2CH_2CH_2)(OSiPh_3)_2$ (SP-**3**) at 44.9 and 23.0 ppm mixed with ~2% of a trigonal bipyramidal form (TBP-**3**) in which the metallacylobutane ring occupies equatorial positions, according to characteristic α to β carbon resonances found at 100.9 and -4.3 ppm for a TBP metallacyclobutane complex (not shown in Figure 5; see Figure S16). The broadening of the ring carbon resonances for SP-**3** at 22 °C (Figure 4) can be ascribed to interconversion of SP-**3** and the small amount of TBP-**3** present on the NMR time scale at 22 °C. Structures of a variety of d^0 Mo and W SP and TBP metallacyclobutane complexes, the diagnostic features of their proton and carbon NMR spectra, and the fact that SP and TBP forms can interconvert readily have all been well-documented for more than two decades.[42-442-44] The most stable form of each and the rate of their interconversion (if known) is highly dependent on the nature of the monoanionic ligands present (often alkoxides or aryloxides).



SP-**3** TBP-**3**

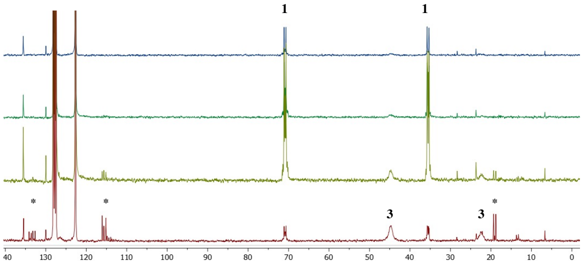


Figure 4. Conversion of ^{13}C labeled **1** to propylene (*) and **3** (top to bottom = 10 min, 2 h, 6 h, 5 days.

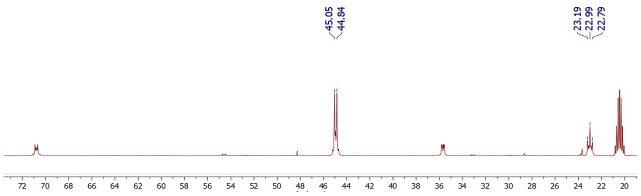


Figure 5. Expanded spectra at -40°C showing ring carbon resonances in **3** and residual **1**

The rate of consumption of **1** under ethylene to give **3** and propylene is essentially complete in 15 minutes in a blue light strip LED photoreactor (~450 nm light with a power of ~100 mW) in C_6D_6 or pentane. The rate of the irradiated reaction is significantly faster than shown in Figure 4. Complex **3** can be isolated in 80% yield from the mixture and crystals obtained through recrystallization under an atmosphere of ethylene. Its molecular structure determined by SCXRD (Figure 6) shows its geometrical parameters to be similar to those published for other SP metallacyclobutane complexes. W-C_α bond lengths are about the same as in metallacyclopentanes of this general type, but the C_α-W-C_α angles are uniformly smaller (~10°). SP Mo(VI) and W(VI) metallacyclobutanes of this general type have W-C_α bond lengths that are ~0.1 Å longer (here 2.170 and 2.172 Å) than their metathesis-active TBP forms. All evidence so far suggests that in general only TBP metallacycles in which the C_3 ring occupies two equatorial positions and an imido (or

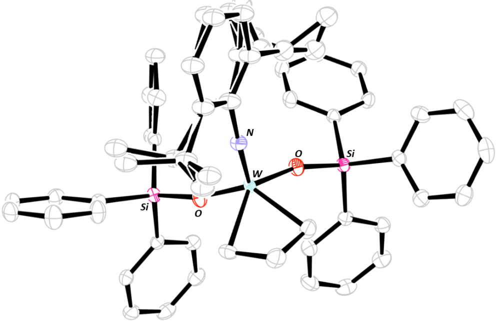


Figure 6. A thermal ellipsoid drawing of **3**. Ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted.

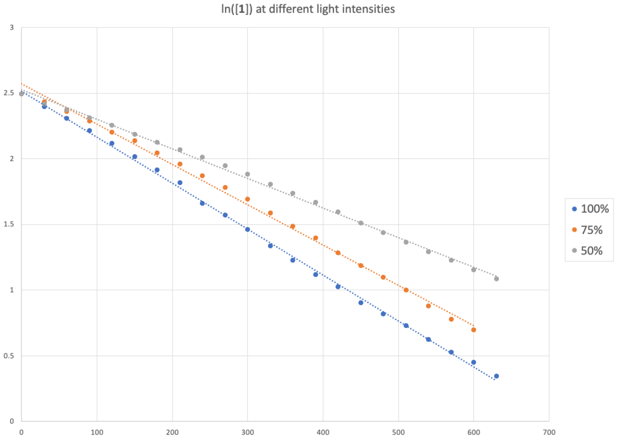


Figure 7. Log plots for the consumption of **1** versus time at three light power levels.

oxo) group is in an axial position can lose an olefin and therefore are potentially active metathesis catalysts. A key requirement is that an empty d orbital be present in the trigonal plane to facilitate formation of the double bond in an alkylidene on one side of the metallacycle or the other as an olefin leaves.[45]

A log plot of the consumption of **1** in 450 nm light under an atmosphere of ethylene is linear with an R value of 0.999 (Figure 7). Conversions were measured by proton NMR at 22 °C with 30 second exposures, taking care to minimize any exposure to light other than the LEDs and to maintain a constant temperature. The reaction is first order in **1** with $k = 3.5\text{x}10^{-3}$ s^{-1}. When the power to the LED reactor is reduced to 75% and then 50%, the rate decreases accordingly, to $3.1\text{x}10^{-3}$ s^{-1} and $2.2\text{x}10^{-3}$ s^{-1}, respectively (Figure 7). A plot of these limited rate data versus power fits a quadratic relationship (R = 0.999; Figure S24). The relationship of the light *output* versus power input for a single LED was found to be linear between 8 and 12 v when the power was increased from 6 v to 12 v, so these results suggest that the photolysis is a type of two photon event, some of which are known to be accessible with LEDs or sunlight.[46-47] One of many possibilities is that one photon is absorbed at one energy that leads to a vibrationally excited TBP form in equilibrium with the ground state SP form, and the TBP form absorbs a photon of a different energy and results in fast and irreversible W-C bond cleavage. (See later section for more discussion.)

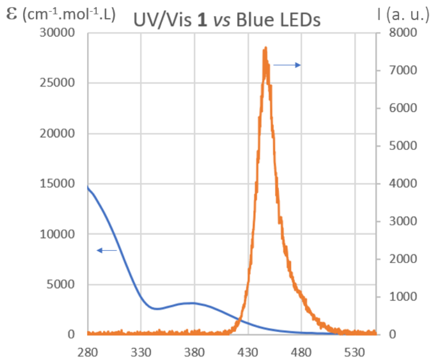


Figure 8. UV visible spectrum of **1** in pentane (ε ~3000 $M^{-1}cm^{-1}$ at 380 nm) and LED emission (orange).

The partial UV/Vis spectrum of a sample of **1** is shown in Figure 8 along with a superimposed emission spectrum of the LEDs used in the reactor. (See Figure S21 for the emission spectrum of laboratory light.) The LED emission spectrum overlaps with the absorption spectrum of **1** between 420 and 470 nm. The overlap suggests that **1** can absorb light from the LEDs, but the proposal above would suggest that the absorption spectrum in Figure 8 contains little, if any, absorption from the photolizeable intermediate. We hope to obtain more details in future studies.

When a sample of ^{13}C labeled **1** (**1**-^{13}C) was exposed to room light in the *absence* of ethylene at room temperature, a ^{13}C NMR spectrum of the resulting mixture showed dozens of bona fide carbon resonances arising from a complex mixture of products, in addition to resonances for **1** and **3** (see Figure S31). No free ethylene or propylene is observed. *After this complex mixture is exposed to ethylene, primarily only **1**, **3**, and propylene are present* (see Figures S36 and S37). These results prove that ethylene does not induce ring-contraction but simply reacts readily with several intermediates to give **1** or **3** and propylene.

Among the possible complexes in the photolyzed mixture described above that should give **3** in the presence of ethylene, and could be present in some detectible concentration, are those shown in Figure 9. (TBP versions are not shown, as they are proposed to be higher in energy than SP forms.) All (except **2e)** have two isomers (methyl "up" or "down" with respect to the imido group). Both monomeric methylene complexes[48-49] similar to **2e** and (rare) dimeric versions in which two methylene ligands bridge two tungsten atoms unsymmetrically are known.[36] One methylene dimer has been structurally characterized in a study concerning W(NAr$_{Cl}$) complexes (Ar$_{Cl}$ = 2,6-dichlorophenyl).[36] It should be noted that α *t*-butyl substituted SP metallacyclobutane complexes analogous to SP-**2a** have been prepared through addition of ethylene to neopentylidene complexes at low temperatures, but they lose *t*-butylethylene readily at RT to give an intermediate methylene complex.[43] β-*t*-Butyl-substituted SP metallacyclobutane complexes analogous to SP-**2b** then form through readdition of *t*-butylethylene to the methylene complex. Only a β-*t*-butyl-substituted SP metallacyclobutane complex could be structurally characterized (Table 1).[42-43] In that structure the β *t*-butyl group points "down" (an "equatorial" position in the bent WC$_3$ ring).

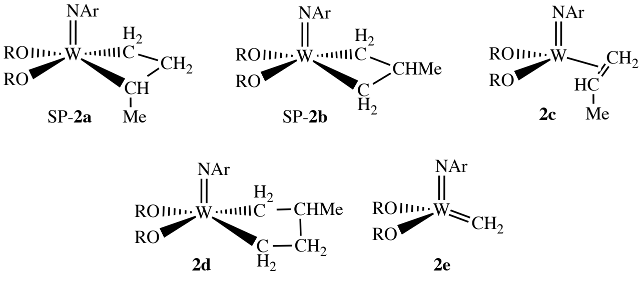
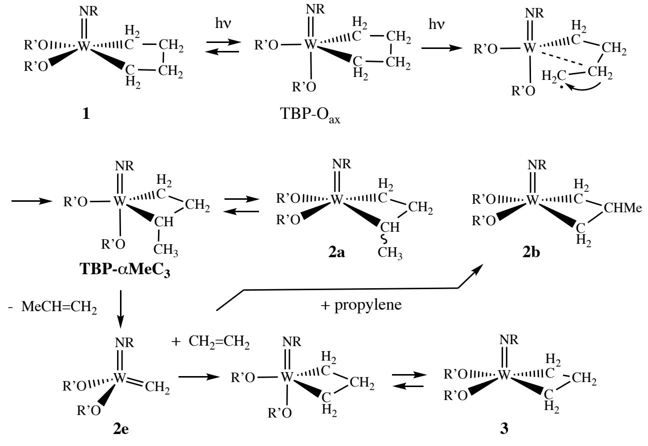


Figure 9. Plausible intermediates formed upon photolysis of **1** in the absence of ethylene.

Resonances for two minor components of the mixture that can be identified by 2D multinuclear NMR are methylene complexes (see Figures S29 and S30). One resonance is a singlet at 171 ppm (J_{CW} = 63 Hz) and the other a singlet at 208 ppm. (The 208 ppm resonance is too weak to determine J_{CW} in spectra obtained so far.) A chemical shift of 208 ppm is characteristic of a monomeric methylene complex, while that at 171 ppm with one J_{CW} = 63 Hz is characteristic of a dimeric methylene complex that contains two bridging methylene ligands (**(2e)₂**).[36] The methylene protons in these two forms could be observed in the proton NMR spectrum at 8.1, 9.2, 10.6, and 11.4 ppm (Figure S28). The monomer and dimer are likely to be in chemical equilibrium on some time scale, but interconversion is slow on the ^{13}C NMR time scale at 22 °C. Multiple overlap of many resonances, especially in the 40-50 ppm (ring CH) region, hinder identification of any specific set of resonances with 100% certainty in ^{13}C NMR labeled compounds. However, we found that addition of propylene to **1** (see Figure S39) generates a single major compound that we propose is a β-methyl metallacyclo*pentane* complex (**2d**) formed through exchange of propylene into the WC_4 ring in **1**. Addition of propylene to **3** (see Figure S41) generates a single major compound that we propose is a methyl-substituted metallacyclobutane complex (**2a** and/or **2b**) formed through exchange of propylene into the WC_3 ring. A comparison of ^{13}C NMR spectra for **2d** and **2a** and/or **2b** with a ^{13}C NMR spectrum of the complex mixture of complexes shown in Figure 9 reveals that **2d** and **2a** and/or **2b** comprise ~50% of the complex mixture obtained upon photolysis of **1** in the absence of ethylene (Figure S43). Further studies, preferably X-ray studies of isolated compounds, will be required to positively identify the proposed methyl-substituted metallacycles.

If we assume, for the sake of argument, that TBP-O_{ax} is the photolyzeable form, the first-formed tungstacyclobutane would be (TBP-αMeC_3; Scheme 1). Metathesis-active TBP-αMeC_3 then either converts to SP-αMeC_3 (**2a**) or loses propylene to give a methylene complex (**2e**, Scheme 1). SP-αMeC_3 (**2a**) must return to a TBP-αMeC_3 before it can make SP-βMeC_3 (**2b**) via reaction of the methylene complex with propylene. The final product (**3**) is formed through addition of ethylene to a methylene complex.



Scheme 1. A plausible mechanism for ring-contraction.

Conversion of TBP-O_{ax} to TBP-αMeC_3 must involve a shift of an H from C3 in the W(V) intermediate to C4 at the end of the butyl radical chain as the W-C3 bond forms (see Scheme 1). This process can be viewed as a form of abstraction of a hydrogen atom from a former β CH_2 group in the WC_4 ring by a radical center next to it at the end of the C_4 chain. The CH_2 H atom could also move to the metal to form a butenyl hydride before being transferred to the terminal C4 carbon to form the methyl group as the new W-C bond is formed to give TBP-αMeC_3. The sensitivity of high oxidation state early transition metal peralkyl complexes to light, along with light-stimulated α and β H abstraction or elimination reactions have been known for decades, but only qualitative observations have been published to our knowledge. It is interesting to note that luminescence of some five-coordinate complexes of Os(VI) nitrides have been proposed to take place specifically from a form with a structure that lies *between* an ideal TBP or SP,[50] so it is not possible at this point to assign the precise nature of the higher energy photolyzeable form. (See discussion section for further details and arguments.)

The Tritylimido ($NCPh_3$) Variation

Of the many possible variations of **1** that could be explored, we chose to prepare one that contains a tritylimido ligand. We chose tritylimido because it has been rarely used in inorganic or organometallic chemistry,[51-52] because $NCPh_3$ may be even more sterically demanding than NAr (and occupies a different, more spherical space), and simply because trityl is not an aryl.

$W(NCPh_3)Cl_4(THF)$ can be prepared in a reaction between Ph_3CN_3 and WCl_4 that is analogous to the synthesis of $Mo(NCPh_3)Cl_4(THF)$.[53] An X-ray study of $W(NCPh_3)Cl_4(THF)$ showed that THF is bound *trans* to the imido group (see the SI). $W(NCPh_3)Cl_4(THF)$ reacts with $NaOSiPh_3$ in diethyl ether to give $W(NCPh_3)(OSiPh_3)_2Cl_2$, a single crystal X-ray diffraction analysis of which (see SI) showed it to contain *trans* chlorides and *trans* siloxides. Addition of two equivalents of EtMgBr to $W(NCPh_3)(OSiPh_3)_2Cl_2$ under ethylene gave $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ (**4**) in good yield (56%). SCXRD (Figure 10 and SI) showed **4** to have a square pyramidal structure (τ = 0.018) analogous to that for **1**. Its proton NMR spectrum of at 22 °C shows a pattern for the C_4H_8 protons similar to what is observed for **1** at 249 K (Figure 2). Even at 80 °C a 2:2:4 pattern for the ring protons is observed, not a 4:4 pattern, as for **1** at 359 K (Figure 2). Therefore, the rate of equilibration of up and down protons via a TBP-C$_{ax}$ form of **4** appears to be significant slower in **4** than it is in **1**.

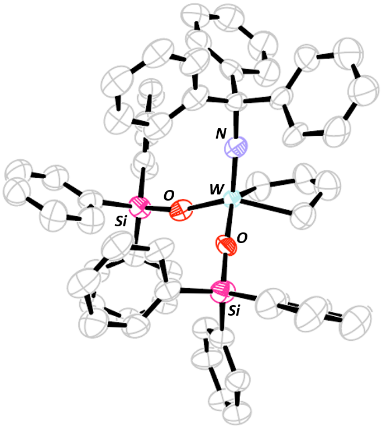


Figure 10. A thermal ellipsoid drawing of W(NCPh$_3$)(OSiPh$_3$)$_2$(C$_4$H$_8$) (**4**). Ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted.

Purified **4** is thermally stable in the dark in the presence or absence of ethylene. In some samples of **4** that have not been purified through recrystallization 1-butene is formed in the presence of ethylene, even in the dark, but 1-butene is *not* formed in rigorously purified samples. We conclude that **4** is not a catalyst for formation of 1-butene. The nature of the catalyst impurity that forms 1-butene has not been identified.

Compound **4** is consumed upon exposure to blue LED light **4** and W(NCPh$_3$)(OSiPh$_3$)$_2$(C$_3$H$_6$) (**6**) and propylene are formed. The rate of consumption of **4** is first order in **4** (k = 1.8 x 10^{-3} s^{-1} and 1.5 x 10^{-3} s^{-1} in two experiments), which is about half the rate of consumption of **1** (k = 3.5 x 10^{-3} s^{-1}) under similar conditions. An intermediate (**5**) in the reaction forms and decays slowly as **6**, the final product, is formed (Figure 11). The process can be modeled with experimental data to extract a value of k = 0.10 x 10^{-3} s^{-1} for the decay of **5**. The overall rate of formation of **6** therefore is ~1/20th the rate of formation of **3**. Proton NMR analyses of mixtures that contain varying amounts and up to >50% **5** (see Figure 11) are consistent with the intermediate being an SP-αMeC$_3$ complex (**5α**; see SI). Protons on the ring correlate with carbon resonances for **5α** being at 43.5 ppm (CH$_2$ C$_\alpha$), 59.5 ppm (CH C$_\alpha$), and 30.5 ppm (C$_\beta$). The ~60 ppm resonance is consistent with a downfield shift of a typical CH$_2$ C$_\alpha$ resonance at ~45 ppm to a methine-like CHR resonance at ~60 ppm. We believe this to be the first chemical shift of a substituted α carbon atom resonance in a metallacyclobutane compound of this type to be observed. Unexpectedly, labeling of **4** by exposing it to ^{13}C ethylene in the absence of light is extremely slow and has not produced labeled **4** in our hands so far. Other approaches to labeled **4** apparently will be required in order to support the proposals obtained through proton NMR studies.

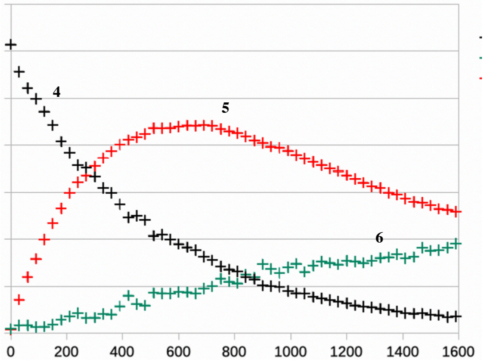


Figure 11. Growth and decay of intermediate **5**.

Formation of **6** and propylene are essentially complete in ~6 h and **6** can be isolated in 67% yield and structurally characterized. Compound **6** is a square pyramid (τ = 0.034) analogous to that for W(NAr)(OSiPh$_3$)$_2$(C$_3$H$_6$) (Table 1).

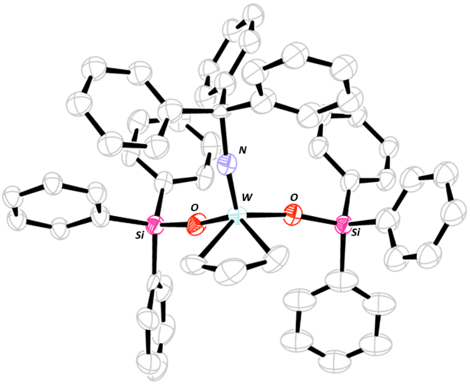
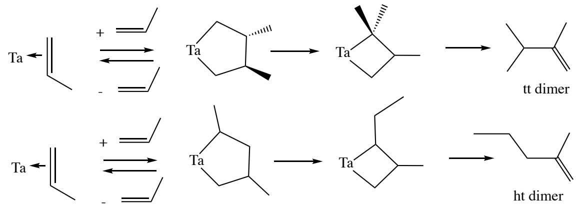


Figure 12. Thermal ellipsoid drawing of **6**. Ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted.

Preliminary NMR studies of **6** under an atmosphere of propylene suggest that a β substituted tungstacyclobutane version of **5** (**5β**) is formed, but no **5α**. Therefore **5β** seems to be lower in energy than **5α** by at least ~2 kcal mol^{-1}.

DISCUSSION

Metallacyclopentane ring-contraction was proposed in 1979 during a study of Cp*TaCl$_2$(olefin) (Cp* = η^5-C$_5$Me$_5$) and fluxional tantallacyclopentane complexes made from them through addition of an olefin, and catalytic dimerization of olefins.[54-58] Those studies showed that Cp*Cl$_2$Ta(olefin) complexes, including a Cp*Cl$_2$Ta(propylene) complex, could be prepared (and isolated) through dialkylation of Cp*TaCl$_4$, and that propylene could be dimerized to 2,3-dimethyl-1-butene (the tt, or tail-to-tail, dimer of propylene, 98%) and 2-methyl-1-pentene (the ht, or head-to-tail, dimer, 2%) in the presence of Cp*Cl$_2$Ta(propylene) at 50 °C (Scheme 2). It was proposed that the tt dimer of propylene is formed from the observable *trans*-β,β' dimethyl tantallacyclopentane complex and that the ht dimer is formed from an unobservable α,β' dimethyl tantallacyclopentane complex. Detailed deuterium labeling studies were consistent only with a mechanism in which a TaC$_4$ ring contracts to a TaC$_3$ ring to make each type of dimer. It was found that "the overall rate of dimerization [of CH$_2$=CHCH$_2$R] decreases as the size of R increases (the exception being ethylene, which is dimerized



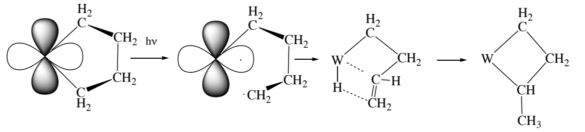
Scheme 2. Mechanisms of forming the tt and ht propylene dimers.

slowest of all), and the product composition switches over from virtually all tt dimer in the case of propylene to exclusively the ht dimer in the case of 4,4-dimethyl-l-pentene" [where R = *t*-Bu]. Effectively, ring-contraction to give the tt dimer isretarded for large CH_2R while ring-contraction to give the ht dimer is accelerated for large CH_2R. These results also led to the proposal[54] 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. Whether light plays any role in the rate of dimerization was not mentioned in these studies. Catalytic formation of 1-butene from $Cp^*Cl_2Ta(C_4H_8)$ is relatively slow and that process was not studied in any detail. Analogous tantalum Cp complexes were short-lived (a few turnovers) as catalysts for dimerizing terminal olefins and were not explored as catalysts.

Documented ring-contractions of metallacyclopentanes to metallacyclobutanes are unknown except for the studies mentioned above.[59] To our knowledge the only other possible ring-contraction that has appeared in the literature is decomposition of $Cp(CO)_2Re(C_4H_8)$ ($Cp = \eta^5\text{-}C_5H_5$) in the presence of PMe_3 at 100 °C to yield methylcyclopropane and $ReCp(CO)_2(PMe_3)$.[60] Although some tantalum complexes have been shown to have some metathesis activity upon replacing chloride ligands with alkoxides,[61] metathesis activity was not long-lived and the details of the metathesis reaction were not explored in favor of pursuing tungsten- and molybdenum-based metathesis catalysts. Proposed substituted tantallacyclobutane intermediates in the Cp* system described above apparently only rearrange.

We have been able to obtain the results reported here in part because relatively low energy SP metallacyclobutanes are much more stable than the TBP forms required for metathesis. **(**It has often been proposed in the literature that certain $W(C_3H_6)$ complexes, even TBP forms in some cases, are too stable toward loss of ethylene to be efficient metathesis catalysts, at least at 22 °C.) The dominance of SP complexes is clearly advantageous for mechanistic studies, but of course, not for catalytic olefin metathesis.

We focussed on TBP-O_{ax} as the photolizeable form because available data show that five-coordinate W(VI) imido complexes in which the imido group is in the axial position are lowest in energy. More importantly, the equatorial W-C_α bonds are likely to be shorter by ~0.1Å in that form compared to the SP form (2.17 Å), just as W-C bonds in TBP metallacyclobutanes are ~0.1 Å shorter (typically 2.05 Å) than in SP metallacyclobutanes (2.15 Å). The presence and orientation of the empty d orbital in the trigonal plane of the TBP-O_{ax} form, as in the TBP metallacyclobutane, would give the alpha carbon atoms in TBP-O_{ax} π character.[62] This d orbital may even be involved in the photochemical W-C cleavage or in facilitating or enabling movement of the H atom to give a butenyl hydride intermediate (equation 4). Addition of W-H across the C=C bond in a butenyl hydride then could give a TBP α methyl tungstacyclobutane. Similar arguments could justify the choice of TBP-N_{eq} (Figure 3) as the photolizeable form, even though it may be higher in energy than TBP-O_{ax}. Detailed studies and calculations clearly will be necessary.



(4)

Photolysis has been known for some time to promote α hydrogen abstraction and other types of CH cleavage reactions in main group and early transition metal d^0 alkyl chemistry, especially in crowded five-coordinate complexes, and, in alkylidene chemistry, to establish equilibrium mixtures of *syn* and *anti* alkylidene isomers.[63-82] In some of the earliest studies of α hydrogen abstraction in Cp tantalum neopentyl complexes to give neopentylidene complexes the sensitivity of neopentyl complexes such as $CpTa(CH_2\text{-}t\text{-}Bu)_2Br_2$ toward light, especially sunlight, was noted.[65] It was suggested that deprotonation of a neighboring nucleophilic alkyl in the α position and M-C bond cleavage followed by an α H atom abstraction from a neighboring alkyl in many cases were likely to be indistinguishable. The differing rates of conversion of $CpTa(CH_2\text{-}t\text{-}Bu)_2X_2$ (X = Cl or Br) complexes (which have both *cis* and *trans* square pyramidal forms) to $CpTa(CH\text{-}t\text{-}Bu)_2X_2$ complexes and the effect of light are all dramatic, but this system has not been studied further to our knowledge.

In our opinion the possible role of even room light in α abstraction and related reactions in general has not been fully appreciated or explored. In 1987 Rothwell noted that $Ta(CH_2SiMe_3)_3Cl_2$ has an absorption band (presumably a formally spin forbidden LMCT) that maximizes around 350 nm and whose tail extends beyond 400 nm.[74] He also noted similar bands in other niobium and tantalum alkyls and that the position of those absorptions depends to a significant degree upon the nature of the accompanying ligands, alkoxides in particular, as one might expect. There is a not-so-distant analogy between an α abstraction reaction to give a W=C bond and abstraction of a hydrogen atom from a neighboring methylene group (Figure 4) to give an α methyl tungstacyclobutane ring.

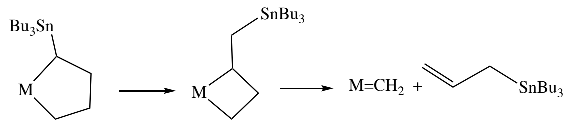
It is interesting to note that we have prepared metallacyclopentane complexes reported here through diethylation of a dichloride precursor. Therefore, selective α hydrogen abstraction in an ethyl ligand is not required to form an alkylidene when β hydrogen abstraction is possible. As long as ethylene and a metallacyclopentane can be made, formation of metathesis-active alkylidenes through ring-contraction is viable.

A reduced accessibility of the intermediate required for W-C cleavage and subsequent ring-contraction may be part of the reason for slower ring-contraction in **4**, compared to **1**. Clearly many more experimental studies of alkoxide and imido (or oxo) variations, and theoretical studies, will be required to elucidate the many details and outcomes of these and other ring-contractions. There are also significant opportunities for detailed photochemical studies aimed at determining exactly how a W-C bond is cleaved. We have found no reference to any transition metal-carbon bond cleavage that has characteristics of a two photon reaction.

Rearrangement of Mo or W metallacyclo*butanes* to olefins is thought to be a common mode of decomposition of alkylidenes, but in fact it has rarely been documented in detail. In one case an isolable metallacyclobutane formed when a W(CH-*t*-Bu) complex reacts with ethylene to give an α-*t*-Bu metallacyclobutane was found to rearrange to *trans*-5,5-dimethyl-2-pentene, which remained bound to the metal because it could not be replaced by ethylene in this particular sterically crowded complex.[39] In the same paper an isolated unsubstituted metallacyclobutane complex was shown to rearrange to give two isomers of a propylene complex in the presence of $B(C_6F_5)_3$. These are two rarely observed rearrangements of substituted and unsubstituted metallacyclobutanes to an olefin in a metathesis-relevant system. Whether unsubstituted metallacyclobutanes (SP or TBP) of the type explored here rearrange to propylene, thermally or photochemically, is not yet known. Interestingly, it has been proposed that certain SP complexes may be especially prone to rearrangement of a metallacyclobutane to an olefin, a rearrangement that can involve ethylene.[83] Because unsubstituted metallacyclopentanes of Mo(VI) and W(VI) that have been observed or isolated from metathesis reactions are prepared in reactions between ethylene and alkylidenes, this work begins to establish (*inter alia*) how unsubstituted MC_4 and MC_3 rings (*e.g.*, **1** and **3**) can be prepared from one another under ethylene at relatively low temperatures.

One important question is whether ring-contraction can take place in the absence of light. Because α abstraction in certain dialkyl complexes that lack a β proton can take place thermally, yet in some cases requires light,[76] we suspect that the answer may be yes. The high temperatures required in the commercial ethylene to propylene chemistry with silica-supported WO_3 catalysts could be necessary for a variety of reasons, one being thermal ring-contraction and W-C bond homolysis.

Another question that is raised by the results reported here is whether α-substituted metallacyclopentanes, and perhaps other types of substituted metallacyclopentanes, can form and ring-contract. We noted earlier that a β-substituted metallacyclopentane is observed upon photolysis of **1** in the absence of ethylene, but a small substituent in the β-position should have relatively minor consequences in terms of ring-contraction. Interestingly, an α-substituted metallacyclopentane has been proposed to be formed from ethylene and $Bu_3SnCH{=}CH_2$ in the Mo-catalyzed olefin homologation reaction between ethylene and $Bu_3SnCH{=}CH_2$ to give $Me_3SnCH_2CH{=}CH_2$.[84] Decomposition of the "cross metallacyclopentane" to give $Me_3SnCH_2CH{=}CH_2$ (equation 5) is still a valid proposal, because propylene was not reported to be a product in the homologation process. The tin-substituted M-C_α bond also may be more susceptible to homolytic cleavage compared to an unsubstituted M-C_α bond, for both steric and electronic reasons. The possibility that light is required for the reaction shown in equation 5 was not mentioned.



(5)

The results presented here constitute the first proven ring-contractions in high oxidation state W complexes relevant to olefin metathesis and therefore a way of forming an initial methylene and metallacyclobutane and *reforming* that methylene or metallacyclobutane from ethylene. Reformation of metathesis-active methylene or metallacyclobutane complexes may be especially important in ethenolysis reactions. We expect to be able to determine how the rate of ring-contraction varies with the steric and electronic character of the other ligands present (here $OSiPh_3$, NAr, $NCPh_3$, O) and with the metal (Mo or W). We suspect that more electron-withdrawing alkoxides, which prefer TBP metallacylobutane complexes over SP, in general, and are more efficient olefin metathesis catalysts, are likely to be more efficient at ring-contraction also. Showing whether ring-contraction is thermally accessible will be challenging if metathesis is faster than ring-contraction. It is important also to determine whether ring-contraction is observable in complexes grafted to silica.[12]

Whether ring-contraction is viable for olefins that contain allylic protons is an unanswered question.[18] At this point allylic CH activation to form an "allyl hydride" is still a plausible way to make an alkylidene from olefins that contain allylic protons, although in the presence of a significant amount of ethylene processes of the type described here seem likely to dominate. The flexibility of Mo and W olefin metathesis systems in terms of ligand variations offers many opportunities to explore the many important issues touched on here in detail.

Finally, the results presented here suggest that ambient light could play a role (in terms of catalyst longevity or selectivity) in metathesis reactions when ethylene is present, at least when tungsten-based imido alkylidene metathesis catalysts are employed, if not others. Therefore, published results concerning efficiency, etc., may have to be revised as the effect of light is explored.

Conclusion

We conclude that ring-contraction (RC) of an unsubstituted tungstacyclopentane complex in the presence of visible light is now a viable way to make propylene and W(VI) methylene complexes or unsubstituted tungstacyclobutanes from ethylene. Some form of ring-contraction could prove to be a relatively general way to make metathesis catalysts of Mo and W from olefins in the absence of protons.

Experimental

General. Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a N_2 atmosphere. Tetrahydrofuran, diethyl ether, dichloromethane, and toluene were dried and deoxygenated by argon purge followed by passage through activated alumina in a solvent purification system followed by storage over 4 Å molecular sieves. 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. WCl[85], tritylazide,[86] and $W(NAr)Cl_4(Et_2O)$[87] were prepared according to published procedures. $NaOSiPh_3$ was made from Ph_3SiOH and NaH in Et_2O at room temperature. EtMgBr was used as received from Sigma-Aldrich. Ethylene Ultra High Purity was used as received from Airgas. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed, and dried over activated 4 Å molecular sieves for at least 24 h prior to use. NMR spectra were recorded on Bruker Avance 600 MHz, Bruker Avance 500 MHz and Bruker Avance 300 MHz spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent as an internal standard.^{19}F and ^{31}P chemical shifts are reported in ppm relative to respectively fluorobenzene and H_3PO_4 as external standards. Irradiations with Blue LEDs were realized with 30 Blue 5050 SMD (nominal power 3.1 mW, on a strip), powered by a 12V DC power supply and with an inline DC dimmer. The fluorescent tube installed in the laboratory is Sylvania FO32/835/ECO. Emission spectra were measured with the spectrometer OceanOptics USB4000. UV/Vis spectra were recorded using a Cary 60 Agilent spectrophotometer.

Synthesis of $\mathrm{W(NAr)(OSiPh_3)_2Cl_2(Et_2O)}$. $\mathrm{W(NAr)Cl_4(Et_2O)}$ (3.5 g, 6 mmol, 1 eq) was dissolved in 50 mL of $\mathrm{Et_2O}$ in a flask and a stir bar was added. The flask was cooled to -30°C (12 h) and $\mathrm{NaOSiPh_3}$ (3.63 g, 12 mmol, 2 eq) was added as a solid in portions over one hour. The green solution turned to a light pink and a precipitate formed. The slurry was stirred for 2 h at room temperature and then filtered. The desired product is poorly soluble in diethyl ether. The filter cake was washed with 20 mL of $\mathrm{Et_2O}$ and 20 mL of pentane and then extracted with dichloromethane (DCM) until the extract was colorless (around 200 mL). The extract was concentrated to 30 mL and stood at -30°C in order to obtain red crystals of $\mathrm{W(NAr)(OSiPh_3)_2Cl_2(Et_2O)}$; yield 4.68 g (70%). The red crystals appear as a pink powder when crushed. A benzene solution of this compound is orange. Anal. Calcd for $\mathrm{C_{52}H_{57}Cl_2NO_3Si_2W}$: C, 59.20; H, 5.45; N, 1.33. Found: C, 59.58; H, 5.10; N, 1.38.

Synthesis of $\mathrm{W(NAr)(OSiPh_3)_2(C_4H_8)}$ (1). $\mathrm{W(NAr)(OSiPh_3)_2Cl_2(Et_2O)}$ (500 mg, 0.474 mmol, 1.0 eq.) was dissolved in toluene (100 mL) in a 1L J. Young Flask. The solution was freeze pump thaw three times, and then re-pressurized with 15 psi of ethylene. The solution was then cooled to -78°C and EtMgBr (3M in $\mathrm{Et_2O}$, 0.32 mL, 0.96 mmol, 2 eq.) was added dropwise. The solution was brought back to room temperature in the dark, and stirred 2 hours (under ethylene). The solvents were removed from the reaction mixture over a period of one hour and the dark yellow residue was stirred in pentane (50 mL) and the mixture was filtered. This operation was repeated until the pentane extract was colorless. The filtrate was concentrated to 20 mL and stood at -30°C. Compound **1** was filtered off as yellow crystals; yield 253 mg (0.262 mmol, 55%). The crystals were of adequate quality for single crystal X-Ray diffraction. Compound **1** is sensitive to ambient light in solution as described in the text. Anal. Calcd for $\mathrm{C_{52}H_{55}NO_2Si_2W}$: C, 64.65; H, 5.74; N, 1.45. Found: C, 64.42; H, 5.79; N, 1.56.

Synthesis of $\mathrm{W(NAr)(OSiPh_3)_2(C_3H_6)}$ (3). Compound **1** (15 mg, 0.016 mmol) was dissolved in $\mathrm{C_6D_6}$ (0.5 mL) in a J. Young NMR tube. The contents were subjected to a freeze-pump-thaw (FPT) procedure and 15 psi of $\mathrm{C_2H_4}$ was then added. The mixture was irradiated with Blue LEDs ($\lambda_{\mathrm{Max}} = 446$ nm, 93 mW). The reaction was followed by ^{1}H NMR for 30 minutes. Propylene and **2** were formed (>90% yield) in 15 minutes. After 30 minutes the tube was evacuated (just to remove $\mathrm{C_6D_6}$ and propylene, prolonged vacuum led to degradation). The residue was redissolved in *tol-d_8* in order to analyze the mixture at a lower temperature. The conversion of **1** was >95% and the yield of **2** >95% (*vs* 1,4-bis-trimethylsilylbenzene as an internal standard). Compound **2** is unstable upon manipulation in solution in the absence of ethylene.

X-ray quality crystals were obtained by dissolving **1** (15 mg, 0.016 mmol) in a mixture of toluene and pentane in a 1:10 ratio in a J. Young NMR tube. The tube was subjected to FPT and 15 psi of $\mathrm{C_2H_4}$ then admitted. The mixture was irradiated for 1 h; the tube was shaken regularly. The tube was stood at -30°C for 3 days, and the x-ray quality crystals were harvested.

Light induced isomerization of 1 without ethylene. Compound **1** (25 mg, 0.026 mmol) was dissolved in $\mathrm{C_6D_6}$ (0.6 mL) in a J. Young NMR tube. The a FPT procedure 15 psi of $^{13}\mathrm{C_2H_4}$ were added and the tube was heated to 50°C for 30 min in the dark. Volatiles were removed *in vacuo* and the residue was redissolved in tol-d_8 (0.5 mL). The tube was left under laboratory light for 48 h. (For rthe emission of the laboratory light; see Figure S21.) A complex mixture containing methylidene complexes (see below), SP methyl-substituted metallacyclobutanes, SP methyl-substituted metallacyclopentanes, and unknown complexes was formed. ^{13}C-INADEQUATE 2D and DEPT experiments were recorded. The "$\mathrm{H_2C\text{-}C(H)\text{-}CH_3}$" pattern was detected at least four times, consistent with formation of methyl-substituted SP metallacyclobutane complexes. Monomeric and dimeric methylidene resonances were identified by ^{13}C NMR and HMBC. Some of the likely compounds in the mixture are shown in Figure 9.

Synthesis of $\mathrm{W(NCPh_3)Cl_4(THF)}$. Triphenylmethyl azide (6.1 g, 21.5 mmol, 1.0 eq) was added to a suspension of $\mathrm{WCl_4}$ (7.0 g, 21.5 mmol, 1.0 eq) in 70 mL of toluene and 30 mL of THF. The mixture was vigorously stirred at 50°C for 24 h (Caution: Gas evolution!) and the dark red solution was concentrated to 5 mL. The red precipitate was collected by filtration, washed with THF (5 mL) and dried *in vacuo* to obtain the title compound in 92% yield (13 g, 19.8 mmol). The bright red solid was recrystallized from THF at -30°C to obtain red block shaped crystals of adequate quality for single crystal X-ray diffraction. Anal. Calcd for $\mathrm{C_{23}H_{23}Cl_4NOW}$: C, 42.17; H, 3.54; N, 2.14. Found: C, 42.43; H, 3.54; N, 2.30.

Synthesis of $\mathrm{W(NCPh_3)(OSiPh_3)_2Cl_2(THF)}$. $\mathrm{NaOSiPh_3}$ (2.7 g, 9.16 mmol, 2.0 eq) was added in small portions over one hour to a stirred solution of $\mathrm{W(NCPh_3)Cl_4(THF)}$ (3.0 g, 4.58 mmol, 1.0 eq) in 50 mL of $\mathrm{Et_2O}$ at -30°C. The light green slurry was stirred for another two hours at room temperature and filtered through a pad of celite. The solid was extracted with toluene (100 mL), the filtrate was concentrated to 20 mL, layered with pentane, and stored overnight at room temperature to obtain the title compound in 79% yield (4.1 g, 3.62 mmol) as yellow needles. The crystals were of adequate quality for single crystal X-Ray diffraction. Anal. Calcd for $\mathrm{C_{59}H_{53}Cl_2NO_3Si_2W}$: C, 62.44; H, 4.71; N, 1.23. Found: C, 62.73; H, 4.74; N, 1.22.

Synthesis of $\mathrm{W(NCPh_3)(OSiPh_3)_2(C_4H_8)}$ (4). EtMgBr (3.0 M in $\mathrm{Et_2O}$, 0.29 mL, 0.881 mmol, 2.0 eq.) was added dropwise to a degassed solution of $\mathrm{W(NCPh_3)(OSiPh_3)_2Cl_2(THF)}$ (500 mg, 0.441 mmol, 1.0 eq.) in toluene (30 mL) under an atmosphere of ethylene (15 psi) at -78°C. The solution was left to warm to room temperature in the dark and stirred for another 2 hours (Caution: Do not seal the flask before the solution reached room temperature due to potential evaporation of condensed ethylene.) The mixture was concentrated to 10 mL and filtered through a pad of celite. The filtrate was evaporated, the yellow residue was triturated with pentane (2 x 10 mL) and $\mathrm{Et_2O}$ (2 x 10 mL) and recrystallized from toluene at -30°C to obtain **4** in 56% yield (260 mg, 0.247 mmol) as yellow crystals. The crystals were of adequate quality for single crystal X-Ray diffraction. **4** is sensitive to ambient light in solution as described in the text. Anal. Calcd for $\mathrm{C_{59}H_{53}NO_2Si_2W}$: C, 67.61; H, 5.10; N, 1.34. Found: C, 67.47; H, 5.23; N, 1.20.

Synthesis of $\mathrm{W(NCPh_3)(OSiPh_3)_2(C_3H_6)}$ (6). A solution of **4** (25 mg, 23.9 µmol) in toluene-d_8 (0.50 mL) in a J. Young NMR tube was subjected to a freeze-pump-thaw (FPT) procedure and subsequently exposed to an atmosphere of $\mathrm{C_2H_4}$ (15 psi). Irradiation with blue LEDs ($\lambda_{\mathrm{Max}} = 446$ nm, 93 mW) for 1 h resulted in >90% conversion of **4** to a mixture of **6**, propylene, and $\mathrm{W(NCPh_3)(OSiPh_3)_2(CH(CH_3)CH_2CH_2)}$. The latter was converted to **6** and propylene over the course of 12 h in the dark at room temperature. The solution was concentrated to less than 50 μL, C_2H_4 was admitted (15 psi), and the sealed sample was stored at -30°C for 3 days to obtain **6** in 69% yield (17 mg, 16.4 μmol) as yellow crystals. The crystals were of adequate quality for single crystal X-Ray diffraction.

Photoinduced isomerization of 4 under a nitrogen atmosphere. A solution of 4 (25 mg, 23.9 μmol) in toluene-d_8 (0.50 mL) in a J. Young NMR tube was irradiated with blue LEDs (λ_{Max} = 446 nm, 93 mW) for 1 h at -78°C, during which time the solution turned from light yellow to deep orange. The sample was immediately transferred to an NMR instrument with the probe pre-cooled to -30°C. 1D and 2D 1H NMR data were in agreement with $W(NCPh_3)(OSiPh_3)_2(CH(CH_3)_{ax}CH_2CH_2)$ **5α** being formed as the major product as well as traces of $W(NCPh_3)(OSiPh_3)_2(CH(CH_3)_{eq}CH_2CH_2)$ (see SI).

ASSOCIATED CONTENT

Complete NMR data, X-ray data, and details of experimental procedures, techniques, and methods.

Accession Codes

CCDC 2149778, 2149779, 2167035, 2164644, 2164645, 2164646. 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.

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Notes

The authors declare no competing financial interest.

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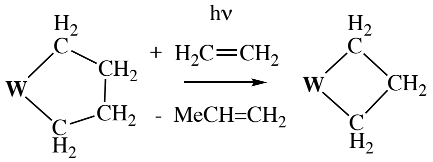
Table of Contents Artwork



W = W(NR)(OSiPh$_3$)$_2$
(R = 2,6-*i*-Pr$_2$C$_6$H$_3$ or CPh$_3$)