

Syntheses of β,β' -Disubstituted Tungstacyclopentanes From Terminal Olefins and Their Conversions to Alkylidenes

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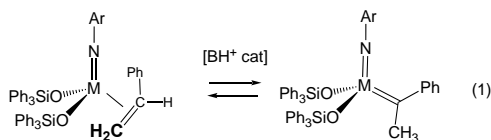
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ABSTRACT: β,β' -Disubstituted tungstacyclopentane complexes have been prepared through addition of propylene, 1-heptene, 1,6-heptadiene, 1,7-octadiene, or diallylaniline to unsubstituted tungstacyclopentane complexes, $W(NR)(OR')_2(C_4H_8)$; tungstacyclopentanes are formed from the dienes. Several tungstacyclopentanes have been prepared from $W(NR)(OR')_2Cl_2$ complexes through alkylation and reduction with diethylzinc in the presence of the olefin. The synthesized complexes include those in which $NR = NPh$, NPh_3 , or $N-2,6-i-Pr_2C_6H_3$ and $OR' = OSiPh_3$ or $OCMe_2(CF_3)$. The tungstacyclopentane complexes are stable in the dark, but upon exposure to violet (405 λ_{max}) or blue (445 nm λ_{max}) LED light they form alkylidenes, largely through α hydrogen abstraction; ring-contraction to give a tungstacyclobutane is a minor reaction pathway only for the β,β' -dimethyltungstacyclopentane. Preliminary DFT calculations suggest that one electron is promoted from the HOMO (comprised of the two W-C σ bonds) into an empty d_{xy} orbital to give what could be viewed as a $W(V)CH_2CHRCHRCH_2'$ complex. Abstraction of an H_α by the radical chain end yields an alkylidene, while abstraction of an H_γ leads to ring-contraction to give a tungstacyclobutane. The rates of the photochemical reactions for the β,β' -disubstituted tungstacyclopentanes vary do not vary dramatically with solvent (toluene, thf, $CDCl_3$) or wavelength. Twelve compounds were characterized through single crystal X-ray diffraction studies.

INTRODUCTION

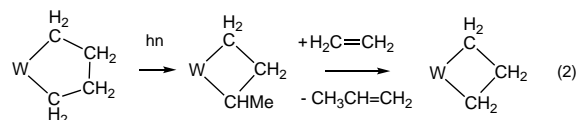
Examples of what has come to be called the olefin metathesis reaction^{1,2} were first published in the literature in 1964 by Banks and Bailey,³ although the phenomenon had been described earlier in the patent literature by Eleuterio.⁴ The first catalysts contained Mo or W oxides, deposited on silica or alumina. Homogeneous versions were first prepared through addition of an aluminum alkyl to a variety of soluble Mo and W compounds.² The discovery of the synthesis of alkylidenes through α hydrogen abstraction⁵ ultimately allowed the synthesis and study of homogeneous Mo and W metathesis catalysts in large variety.^{6,7} Many of the principles learned from homogeneous chemistry have been shown to be relevant to catalysts bound to a support, often silica.⁸ The most active Mo and W-based olefin metathesis initiators are four-coordinate, high oxidation state 14 electron complexes, formally d^0 if the alkylidene is counted as a dianionic ligand; an example is $Mo(NAr)(CH-t-Bu)[OCMe(CF_3)_2]_2$ ($Ar = 2,6$ -diisopropylphenyl). Evidence has been accumulating in the last twenty years that alkylidenes are formed from reduced (d^2) Mo or W sites in solution^{9,10} or on surfaces.¹¹⁻¹³ However, long-standing questions concerning how Mo, W, or Re alkylidenes ($M=CH_2$, $M=CHR$, or $M=CRR'$) are formed in classical catalyst systems in the absence of alkylating an agent remained unanswered until recently.

One of the proposed mechanisms of forming an alkylidene complex from an olefin complex¹⁴ in solution is a "protonation/deprotonation" reaction (eq 1), the first examples of which were published in 2021.¹⁵ Molybdenum(IV) or tungsten(IV)



styrene complexes can be protonated slowly with dimethylanilinium (BH^+ in eq 1) to yield a mixture (~2:1) of styrene and phenethylidene complexes; the intermediate is a cationic $M(VI)$ phenethyl complex. Interconversion is slow and so far appears to be limited to styrene and its derivatives.^{16,17}

In 2022 it was found that tungstacyclopentane complexes, $W(NR)(OSiPh_3)_2(C_4H_8)$ ($R = Ar$ or CPh_3), formed through addition of ethylene to a $W(IV)$ ethylene complex, would rearrange under ethylene in the absence of acid through a light-induced (405 or 445 nm) "ring-contraction"¹⁸⁻²³ to give a square pyramidal (SP) α -methyl-substituted tungstacyclopentane intermediate (eq 2; $W = W(NAr)(OSiPh_3)_2$ or $W(NCPh_3)(OSiPh_3)_2$).²⁴ (Ambient fluorescent light is adequate, but slow.) Conversion of the SP intermediate to a trigonal bipyramid (TBP) followed by loss of propylene gives



a methylene complex, which reacts with ethylene to form the unsubstituted SP tungstacyclobutane complex, $W(NR)(OSiPh_3)_2(C_3H_6)$. $W(NAr)(OSiPh_3)(OSi_{surf})(C_4H_8)$ (OSi_{surf} = a surface siloxide), which is formed through deposition of $W(NAr)(OSiPh_3)_2(C_4H_8)$ on silica, also ring-contracts, photochemically or thermally, to give a catalyst that converts ethylene to propylene.²⁵ These results are among those that continue to provide strong evidence that the principles that govern homogeneous metathesis catalysts and catalysts linked to a silica surface are often quite similar.⁸

Metallacyclopentane complexes are known for many transition metals from Groups 4 through 10^{26,27} and are proposed intermediates in the formation of metallacycloheptanes, which

are the required intermediates in the relatively selective trimerization of ethylene to 1-hexene.²⁸ Before α abstraction was discovered,⁵ mechanisms of forming an alkylidene from metallacyclopentane complexes of Mo and W were proposed.^{29, 30} However, no support for these early proposals materialized. Ultimately, a few unsubstituted metallacyclopentane complexes of Mo and W were isolated in reactions between isolated alkylidene complexes and ethylene, as well as in catalytic systems in which ethylene was either added or formed as a product. Therefore, unsubstituted metallacyclopentanes were thought to be end products and could not be transformed into an alkylidene. That conclusion turns out to be incorrect for unsubstituted tungstacyclopentanes, as described above.

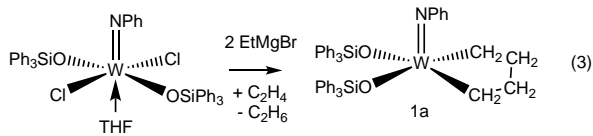
Two important questions arise from the study of unsubstituted tungstacyclopentane complexes.²⁴ First, can substituted analogs of the $W(NR)(OSiPh_3)_2(C_4H_8)$ complexes be formed from two terminal olefins? As far as we are aware, no substituted tungstacyclopentane complex has been reported in the literature. If they can be formed, do substituted tungstacyclopentane complexes also yield alkylidenes upon photolysis? In this paper we show that the answer to both questions is yes for two β, β' -disubstituted tungstacyclopentane analogs of the $W(NR)(OSiPh_3)_2(C_4H_8)$, along with tungstacycloalkanes made from 1,6-heptadiene, 1,7-octadiene, and diallylaniline. Several imido and alkoxide combinations are also shown to behave similarly. These findings suggest that 14e β, β' -disubstituted tungstacyclopentanes can form from tungsten d^2 complexes and two terminal olefins and they rearrange upon photolysis to give alkylidenes, but largely through an α abstraction mechanism, *not* a ring-contraction mechanism.²⁴ To our knowledge the results reported here are the first examples of formation of metathesis-relevant alkylidene complexes from terminal olefins.

RESULTS

Unsubstituted tungstacyclopentanes

The only tungstacyclopentanes whose photolyses have been studied are $W(NCPH_3)(OSiPh_3)_2(C_4H_8)$ and $W(NAr)(OSiPh_3)_2(C_4H_8)$.²⁴ Three others are reported here because they serve as precursors to substituted tungstacyclopentanes that contain a NPh or OR_{F3} ($OR_{F3} = OCM_e_2(CF_3)$) ligand (see later sections). The three new unsubstituted tungstacyclopentanes are $W(NPh)(OSiPh_3)_2(C_4H_8)$ (**1a**), $W(NPh)(OR_{F3})_2(C_4H_8)$ (**2a**), and $W(NAr)(OR_{F3})_2(C_4H_8)$ (**3a**).

Two equivalents of sodium triphenylsiloxide react with $W(NPh)Cl_4(Et_2O)$ in a mixture of diethyl ether and THF gave red crystalline $W(NPh)(OSiPh_3)_2Cl_2(THF)$ in ~45% yield. Single crystals of a diethyl ether adduct were grown from a mixture of dichloromethane and ether. Single crystal X-ray-diffraction (SCXRD) analysis of $W(NPh)(OSiPh_3)_2Cl_2(Et_2O)$ showed it to contain diethyl ether *trans* to the imido ligand and triphenylsiloxide ligands *trans* to one another (Fig S132 in the SI).



Addition of two equivalents of ethyl magnesium bromide to a solution of $W(NPh)(OSiPh_3)_2Cl_2(THF)$ under ethylene led to **1a** (eq 3), which was isolated in ~40% yield. One attractive

mechanistic possibility is that a $W(NPh)(OSiPh_3)_2(CH_2CH_3)_2$ intermediate is formed and decomposes to give $W(NPh)(OSiPh_3)_2(CH_2CH_2)$ and ethane, and **1a** is then formed through addition of ethylene to $W(NPh)(OSiPh_3)_2(CH_2CH_2)$. The proton NMR spectrum of **1a** shows two resonances for the tungstacyclopentane protons at 298 K, but four resonances at 235 K (Fig 1), consistent with interconversion of "up" and "down" α protons and "up" and "down" β protons in a square pyramidal complex through a Berry-type rearrangement³¹ in which a plane of symmetry in an intermediate passes through the carbon atoms in the WC_4 ring. In the analogous $W(NAr)(OSiPh_3)_2(C_4H_8)$ complex²⁴ the α and β proton resonances overlap to a greater extent, but the temperature dependent proton NMR spectra are similar to what is shown for **1a** in Fig 1. The ¹³C NMR chemical shifts for the α carbon atoms in these SP complexes are typically found downfield of those for the β carbon atoms. The ¹³C NMR chemical shifts for α and β carbon atoms in these and all other tungstacyclopentane complexes reported here, along with C_α chemical shifts and J_{CW} coupling constants for six alkylidenes (see later syntheses), are listed in Table 1.

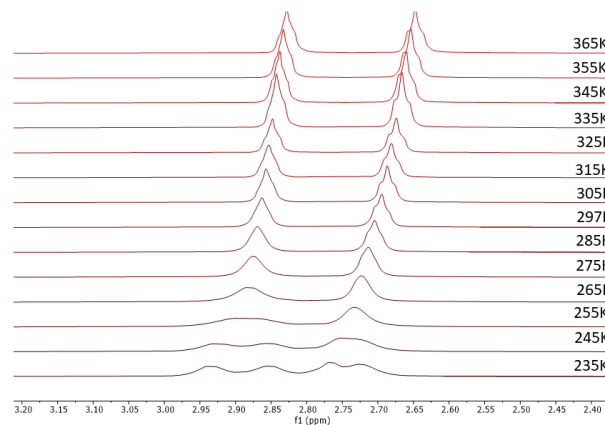


Figure 1. Variable temperature proton NMR spectra of the tungstacyclopentane ring protons in $W(NPh)(OSiPh_3)_2(C_4H_8)$ (**1a**).

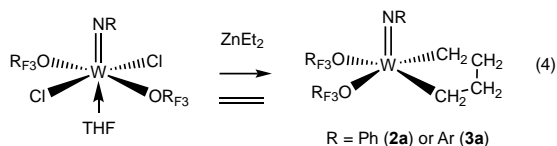
Table 1. Chemical shifts (ppm) for C_α atoms (with J_{CW} values) and C_β atoms in tungstacyclopentanes and alkylidenes formed from them through photolysis.

Compound	δC_α (ppm)	δC_β (ppm)	J_{CW} (Hz)
1a	71.41	36.15	68.8
2a^a	68.64	35.90	69.5
3a^a	69.06	35.35	73.8
4a	81.45, 72.51	51.51, 46.91	67.8, 67.8
5a	78.37, 71.03	56.04, 50.93	64.8, 66.0
6a	76.19	50.89	68.4
7a	77.42	51.54	70.4
8a	81.18, 68.53	54.58, 51.46	70.1, 74.4
9a	79.29, 66.96	54.68, 51.63	72.1, 74.0
10a^b	70.58	46.90	68.1
11	59.53, 52.61	45.34, 36.12	68.6, 66.1
12a	70.66	58.84	69.0
4b	230.13	53.76	189.0
6b	226.7	58.0	-
7b	229.52	58.96	192.5
8b	233.20	59.35	187.2
9b	240.87	60.32	196.4
12b	224.29	56.76	189.9

^aNot isolated in crystalline form. ^b*Cis* isomer; see text.

A SCXRD analysis showed that **1a** has a square pyramidal structure (Fig S133) similar to that found for $W(NAr)(OSiPh_3)_2(C_4H_8)$.²⁴ The WC_4H_8 ring is puckered with $W-C = 2.178(9)$ and $2.185(8)$ Å (see SI for details.)

Compounds **2a** and **3a** (eq 4) can be prepared through addition of one equivalent of diethylzinc to $W(NPh)(OR_{F_3})_2Cl_2(THF)$ or $W(NAr)(OR_{F_3})_2Cl_2(THF)$, respectively, under ethylene. Diethylzinc is potentially more controllable than $EtMgBr$ as an alkylating agent because the risk of overalkylation to give complexes that contain more than two ethyl groups is lower with diethylzinc than with the more reactive Grignard reagent.

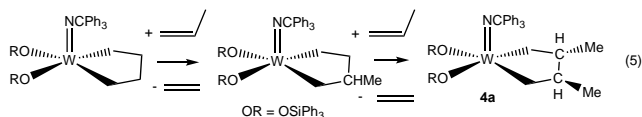


The proton NMR spectrum of **2a** shows only two WC_4 ring proton resonances at room temperature (Fig S17), while the spectrum of **3a** shows four resonances at room temperature (Fig S22), consistent with a slower pseudorotation in $W(NAr)(OR_{F_3})_2(C_4H_8)$ versus $W(NPh)(OR_{F_3})_2(C_4H_8)$, a result that we attribute to the larger size of NAr versus NPh .

Neither **2a** nor **3a** could be isolated in crystalline form (see SI), but they are formed in good yield according to NMR spectra of the crude products and they are prepared and used here as precursors for synthesizing bicyclic tungstacyclopentane derivatives in good yield, as described later.

Monocyclic substituted tungstacycloalkanes

Heating a solution of $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ in toluene- d_8 , under 1 atm of propylene in the dark at 100 °C produces first two isomers of an intermediate β -methyl tungstacyclopentane complex (eq 5). These β -methyl substituted tungstacyclopentane complexes can be observed in 1H NMR spectra in yields as high as $\sim 80\%$, but so far they have not been isolated from the mixture through selective crystallization. According to 1H - 1H NOESY studies the β -methyl group in the major isomer ($\sim 65\%$) of $W(NCPh_3)(OSiPh_3)_2(\beta\text{-Me}C_4H_7)$ points away from the imido ligand; in the minor isomer the methyl group points toward the imido ligand.



The reaction in eq 5 can be taken to $>90\%$ completion if ethylene is removed periodically; **4a** can then be isolated in 88% yield. A single crystal X-ray structural analysis of **4a** (Fig 2) shows its geometrical parameters to be similar to those for $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$,²⁴ except the $W-C$ bond lengths in **4a** ($2.173(0)$ and $2.163(0)$ Å) are slightly shorter than those in $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ ($2.222(0)$ and $2.202(0)$ Å) ($>95\%$ probability on the basis of $\pm 3\sigma$). The two methyl groups in **4a** are *trans* to one another in the β and β' positions on the puckered WC_4 ring.

The reaction between $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ and 1-heptene in the dark under conditions similar to those shown in equation 5 results in formation of the square pyramidal β,β' -dipentyltungstacyclopentane complex,

$W(NCPh_3)(OSiPh_3)_2(\text{Pentyl})_2C_4H_8$ (**5a**). A SCXRD study shows its geometrical parameters (Fig S135) to be similar to those for **4a**.

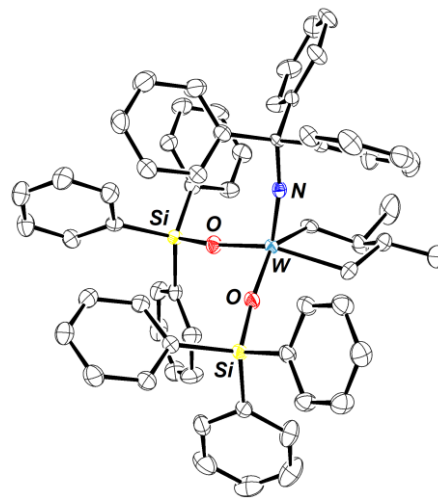


Figure 2. The molecular structure of square pyramidal **4a**. Ellipsoids are plotted at a 30% probability level. Hydrogen atoms, solvent molecules, and low occupancy disordered components are omitted.

Bicyclic tungstacycloalkanes

Given that β,β' -disubstituted tungstacyclopentanes are formed from propylene or 1-heptene, we turned to the synthesis of bicyclic complexes from 1,6-heptadiene and 1,7-octadiene. Tantalabicycloalkane pentamethylcyclopentadienyl dichloride complexes formed from 1,6-heptadiene and 1,7-octadiene were reported some time ago²³ and the 7-tantalabicyclo[3.3.0]octane complex formed from 1,6-heptadiene was crystallographically characterized.^{32,33} It should be noted that 14e monocyclopentadienyl dichloro tantalacyclopentane complexes.^{18-23, 34} are isostructural and isoelectronic with the imido metallacyclopentane complexes reported here and that the only *observable* tantalacyclopentane formed from a terminal olefin was β,β' -disubstituted; an α,β' -disubstituted version was proposed as an unobservable intermediate in catalytic olefin dimerization reactions (see later discussion).

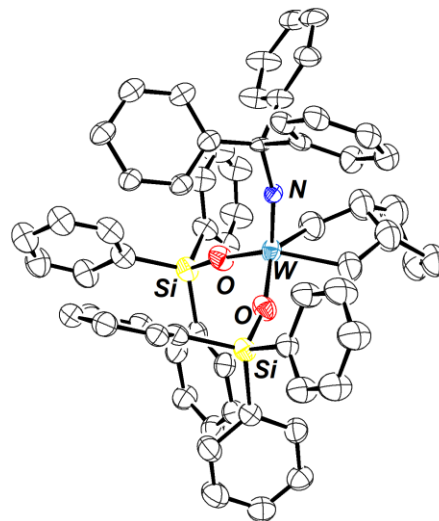
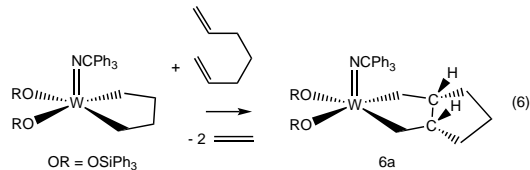
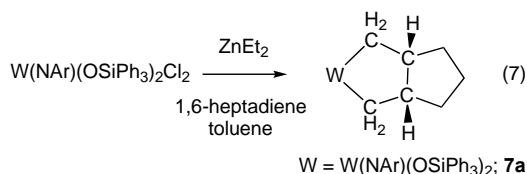


Figure 3. The molecular structure of square pyramidal **6a**. Ellipsoids are plotted at a 30% probability level. Hydrogen atoms, solvent molecules, and low occupancy components are omitted.

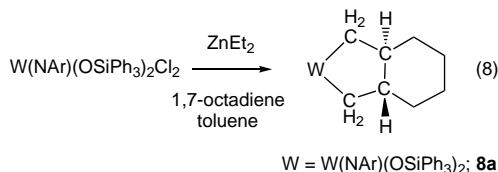
The reaction between $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ and 1,6-heptadiene at 80 °C in the dark leads to formation of the mirror symmetric 7-tungstabicyclo[3.3.0]octane complex, $W(NCPh_3)(OSiPh_3)_2(C_7H_{12})$ (**6a**, eq 6), which was isolated in 77% yield. It was found (Fig 3) to have a geometry analogous to that for the square pyramidal 7-tantalabicyclo[3.3.0]octane complex, $Cp^*TaCl_2(C_7H_{12})$ ($Cp^* = \eta^5-C_5Me_5$), in which the C_5 ring points away from the apical Cp^* ligand.^{32, 33}



Heating a mixture of $W(NAr)(OSiPh_3)_2(C_4H_8)$ and three equivalents of 1,6-heptadiene in the dark at 85 °C for 12 h led to formation of the 7-tungstabicyclo[3.3.0]octane complex, $W(NAr)(OSiPh_3)_2(C_7H_{12})$ (**7a**). A SCXRD analysis showed **7a** to be a square pyramid with the five-membered ring pointing away from the imido ligand (Fig S137), analogous to what is found for **6a** (Fig 3). Compound **7a** also can be prepared from $W(NAr)(OSiPh_3)_2Cl_2$ directly using diethylzinc (eq 7); the yield in one synthesis was 84% on a 300 mg scale.



The reaction between $W(NAr)(OSiPh_3)_2(C_4H_8)$ and 1,7-octadiene also proceeds smoothly in the dark to yield the 8-tungstabicyclo[4.3.0]nonane complex, $W(NAr)(OSiPh_3)_2(C_8H_{14})$ (**8a**), as a single isomer. Use of diethylzinc (eq 8) led to a 71% yield of **8a** on a 300 mg scale. A SCXRD analysis shows **8a** to be a square pyramid with the six-membered ring joined to the WC_4 ring in a *transoid* fashion (Fig 4). The C_6 ring has a chair conformation with the $W-C$ bonds ($W-C = 1.128(16)$ and $1.129(16)$ Å) in equatorial positions in the C_6 ring.



$W(NAr)(OR_{F3})_2(C_8H_{14})$ (**9a**) can be prepared from $W(NAr)(OR_{F3})_2Cl_2$, diethylzinc, and 1,7-octadiene in a manner similar to the syntheses shown in equations 7 and 8 and isolated in 78% yield. A SCXRD study shows the molecular geometry of **9a** (Fig S139) to be similar to that of **8a**, *i.e.*, the configuration in the junction of the two rings is *trans*. $W(NPh)(OR_{F3})_2(C_8H_{14})$ (**10a**) is also prepared readily, but in the crystal chosen for the SCXRD analysis it has a *cis* ring junction with the C_6 ring pointing away from the phenylimido ligand (Fig 5).

A proton NMR spectrum of a sample of **10a** revealed it to be a mixture that contained 70% of the *cis* isomer (*cis*-**10a**) and 30% of the *trans* isomer (*trans*-**10a**). Heating this mixture at

50 °C in toluene converted it to an equilibrium mixture (over a period of 24 h) that contains 88% of the *trans* isomer (Fig 6, eq 9; $\Delta G_{cis,trans} = 1.3$ kcal mol⁻¹ at 50 °C in toluene). A logical intermediate in the interconversion of *cis* and *trans* forms of **10a** is one that contains a diene in which only one $C=C$ bond is bound (eq 9). The $C=C$ face through which the "free" olefin rebinds to W followed by formation of the WC_4 ring determines

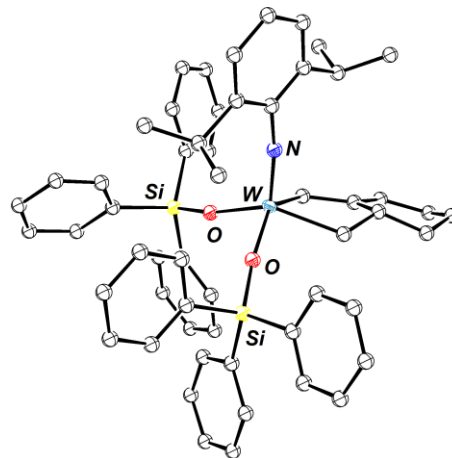


Figure 4. The molecular structure of $W(NAr)(OSiPh_3)_2(trans-C_8H_{14})$ (**8a**) as determined by a SCXRD. Ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity.

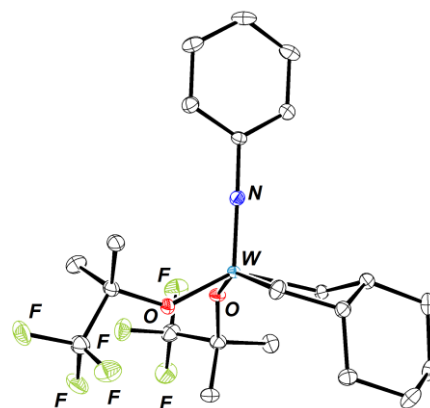


Figure 5. The molecular structure of $W(NPh)(OR_{F3})_2(cis-C_8H_{14})$ (*cis*-**10a**) as determined by SCXRD. Ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity.

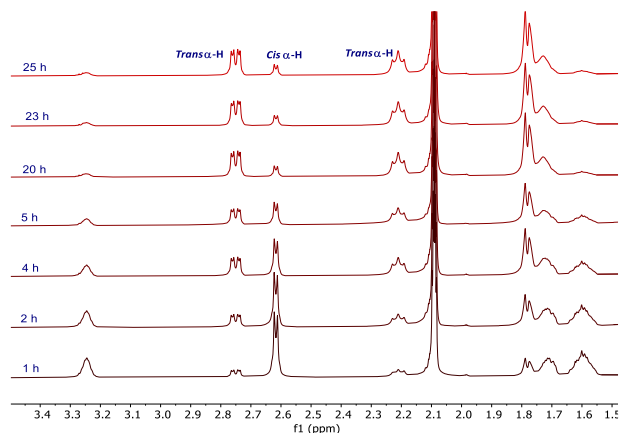
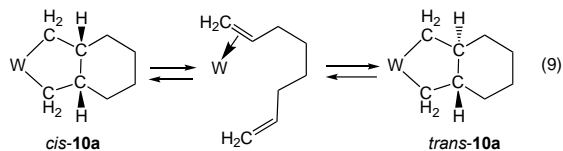


Figure 6. Proton NMR spectra for the conversion of largely *cis*-**10a** to ~80% *trans*-**10a** at equilibrium.

whether *cis*-**10a** or *trans*-**10a** is formed. The conditions for interconversion of *cis*-**10a** and *trans*-**10a** are roughly the same as the conditions required to form bicycloalkanes from unsubstituted tungstacyclopentanes and propylene or 1-heptene, as one might expect.



Trans-**10a**, the lower energy isomer, was selectively crystallized from the *trans*-rich mixture shown in Figure 6 and was confirmed to have a *trans* ring junction configuration, in contrast to *cis*-**10a** (Fig 5). The two W-C bonds are in equatorial positions in the chair form of the six-membered ring in both structures.

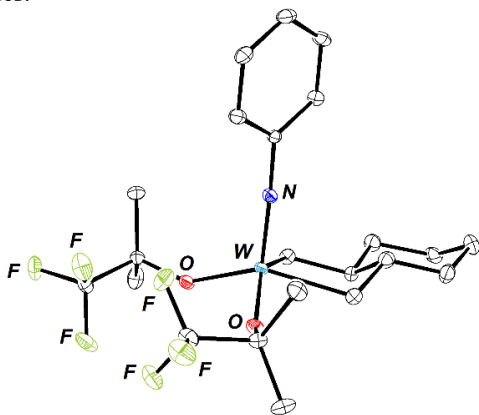


Figure 7. The molecular structure of $W(NPh)(ORF_3)_2(trans-C_8H_{14})$ (*trans*-**10a**) as determined by SCXRD. Ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity.

There is also evidence that "ring-down" and "ring-up" isomers of $W(C_7H_{12})$ complexes can interconvert, but on a (faster) time-scale of the order of a typical pseudorotation process. For example, a small amount (5-10%) of the ring-up isomer of **7a** is found in a solution of the ring-down isomer in toluene- d_8 at 238 K (Fig S47). At 298 K these resonances begin to broaden, consistent with interconversion of the ring-up and ring-down isomers through a pseudorotation process. The energy difference between these ring-up and ring-down isomers appears to be small, *i.e.*, of the order of 1-2 kcal mol⁻¹.

Addition of diallylether to $W(NAr)(OSiPh_3)_2(C_4H_8)$ yields only a β -monosubstituted tungstacyclopentane (**11**) made from one ethylene and one of the two double bonds in diallylether (Fig 8). The ether oxygen coordinates to the metal ($W-O = 2.327(7)$ Å) *trans* to the imido group to form a 16e pseudo-octahedral complex. This result suggests that formation of a six-coordinate complex prevents replacement of the second ethylene to give a bicyclic complex. This proposal is supported by the finding that diallylaniline reacts with $W(NAr)(OSiPh_3)_2(C_4H_8)$ to form the bicyclic compound, $W(NAr)(OSiPh_3)_2(C_6H_{10}NPh)$ (**12a**; eq 10), presumably because the nitrogen atom in $(CH_2=CHCH_2)_2NPh$ does not bind as strongly to the metal as does an oxygen in an ether. The ¹H and ¹³C NMR features of **12a** are similar to those of $W(NAr)(OSiPh_3)_2(C_7H_{12})$ itself.

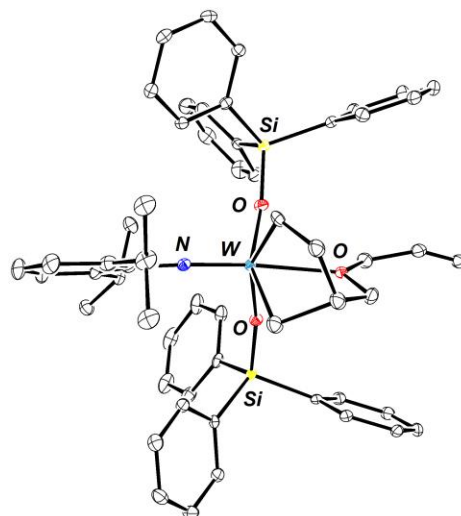
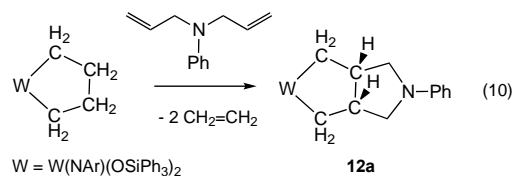


Figure 8. The molecular structure of $W(NAr)(OSiPh_3)_2[\beta-(CH_2OCH_2CH=CH_2)C_4H_7]$ (**11**) as determined by SCXRD. Ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted for clarity.



Photolyses

Tungstacyclopentane complexes were photolyzed under nitrogen or (for **1a**) ethylene either in a glass vessel wrapped with blue LED strips ($\lambda_{max} = 445$ nm, ~93 mW power) or, for greater temperature control, accuracy, and reproducibility, in an NMR probe in a modified J-Young NMR tube using a 405 nm LED optical fiber light source (~100mW power; see SI) that is inserted through an inner 2mm tube within the NMR tube. All rates of consumption of the tungstacyclopentane were followed by proton NMR and found to be first order in W with high R values for ln(k) vs. T plots. The results can be found in Table 2. The first two entries (for $W(NAr)(OSiPh_3)_2(C_4H_8)$ and $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$ under ethylene) are taken from the initial paper.²⁴

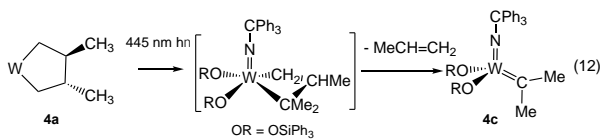
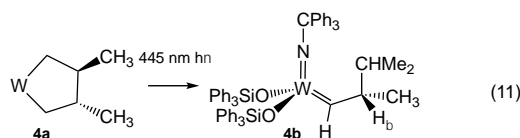
Irradiation of $W(NPh)(OSiPh_3)_2(C_4H_8)$ (**1a**) in toluene- d_8 at 445 nm under ethylene, was followed by ¹H NMR for 30 min and gave a >90% conversion of (**1a**) to propylene and the unsubstituted tungstacyclobutane complex, $W(NPh)(OSiPh_3)_2(C_3H_6)$ (**1b**). This result is essentially the same as that obtained for the photolysis of $W(NAr)(OSiPh_3)_2(C_4H_8)$ under ethylene to give propylene and (largely SP) $W(NAr)(OSiPh_3)_2(C_3H_6)$.²⁴ However, **1b** is a mixture of TBP and SP forms, according to ¹H and ¹³C NMR studies, with the TBP form predominating (~90%). The characteristic resonances for the TBP form are found at 98.70 ppm (C_α) and -4.40 ppm (C_β), while the resonances for the SP form are found at 45.31 ppm (C_α) and 22.92 ppm (C_β). Only a trace of the TBP form was found in the ¹³C NMR spectrum of $W(NAr)(OSiPh_3)_2(C_3H_6)$ at low temperatures.²⁴ Proton NMR spectra at room temperature suggest that SP and TBP forms of $W(NAr)(OSiPh_3)_2(C_3H_6)$ interconvert on the NMR time scale.²⁴ No crystal of **1b** suitable for a SCXRD study could be

obtained. The rate of consumption of **1a** in thf-d₈ is significantly less than in tol-d₈ ($k = 10 \times 10^{-4} \text{ s}^{-1}$ vs. $35 \times 10^{-4} \text{ s}^{-1}$), but coordination of THF to the metal in 14e **1a** is likely, which would also likely alter the HOMO/LUMO energy gap (see the later discussion of the mechanism).

Table 2. Rate constants for consumption of tungstacyclopentane complexes at 298 K upon irradiation at 445 nm or 405 nm (OR = OSiPh₃; OR_{F3} = OCF₃)

	$\lambda(\text{nm})$	solvent	$k(10^{-4} \text{ s}^{-1})$
W(NAr)(OR) ₂ (C ₄ H ₈)	445	tol-d ₈	35
W(NCPh ₃)(OR) ₂ (C ₄ H ₈)	445	tol-d ₈	18
W(NPh)(OR) ₂ (C ₄ H ₈)	1a	tol-d ₈	35
W(NPh)(OR) ₂ (C ₄ H ₈)	1a	thf-d ₈	10
W(NCPh ₃)(OR) ₂ (Me ₂ C ₄ H ₆)	4a	tol-d ₈	9.1
W(NCPh ₃)(OR) ₂ (Pent ₂ C ₄ H ₆)	5a	tol-d ₈	1.7
W(NCPh ₃)(OR) ₂ (C ₇ H ₁₂)	6a	tol-d ₈	5.5
W(NAr)(OR) ₂ (C ₇ H ₁₂)	7a	tol-d ₈	10
W(NAr)(OR) ₂ (C ₇ H ₁₂)	7a	405	9.5
W(NAr)(OR) ₂ (C ₇ H ₁₂)	7a	CDCl ₃	14
W(NAr)(OR) ₂ (C ₈ H ₁₄)	8a	tol-d ₈	11
W(NAr)(OR) ₂ (C ₈ H ₁₄)	8a	405	6.6
W(NAr)(OR) ₂ (C ₈ H ₁₄)	8a	CDCl ₃	12
W(NAr)(OR) ₂ (C ₈ H ₁₄)	8a	thf-d ₈	7.0
W(NAr)(OR _{F3}) ₂ (C ₈ H ₁₄)	9a	tol-d ₈	3.0
W(NAr)(OR _{F3}) ₂ (C ₈ H ₁₄)	9a	405	4.1
W(NAr)(OR _{F3}) ₂ (C ₈ H ₁₄)	9a	CDCl ₃	3.8
W(NPh)(OR _{F3}) ₂ (C ₈ H ₁₄)	10a	tol-d ₈	3.0
W(NAr)(OR) ₂ (C ₆ H ₁₀ NPh)	12a	tol-d ₈	8.0

Irradiation of a solution of **4a** under molecular nitrogen at 405 nm in a modified J-Young NMR tube at 243 K led to its conversion (~89%) to (~95%) **4b**, which has primarily the *syn*



form (eq 11), along with ~5% **4c** (eq 12). Compound **4b** is proposed to be formed when a hydrogen atom is removed from an α carbon atom in **4b** by an α' carbon atom (α hydrogen abstraction⁵). Ring-contraction¹⁸⁻²³ is proposed to give the α, α, β -trimethyl tungstacyclobutane intermediate shown in eq 12, which then yields **4c** after loss of propylene from the intermediate's TBP form. (See later discussion.) At 243 K the rate of consumption of **4a** is first order in W with $k_{243} = 2.9 \times 10^{-4} \text{ s}^{-1}$. At room temperature ~20% of **4c** is formed along with ~80% of **4b** and $k_{298} = 1.9 \times 10^{-4} \text{ s}^{-1}$ for consumption of **4a**. Addition of isobutene to the mixture of **4b** and **4c** converts all **4b** to **4c** through metathesis (Fig S82). The only ring-contraction observed for the complexes reported here is that shown in eq 12. The dominant α abstraction pathway (eq 11) contrasts with the ring-contraction observed for unsubstituted tungstacyclopentane analogs.²⁴

Variable temperature kinetic studies for consumption of **4a** between 243 and 298 K (Fig 9) reveal that $\Delta H^\ddagger = 2.3 \text{ kcal/mol}$ and $\Delta S^\ddagger = 0.0 \text{ kcal/mol}$, consistent with only a small thermal contribution to the activation energy of a photochemical rate limiting step, as one would expect.

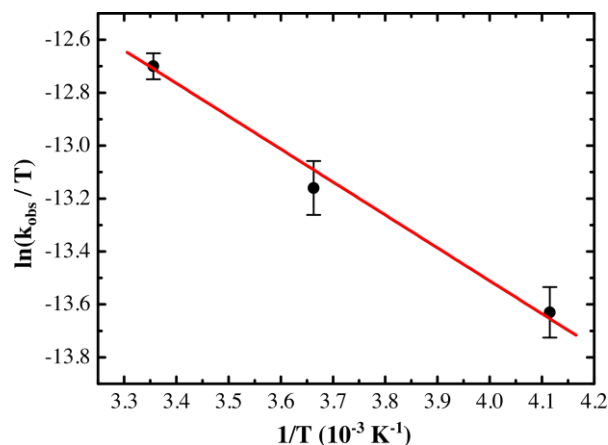
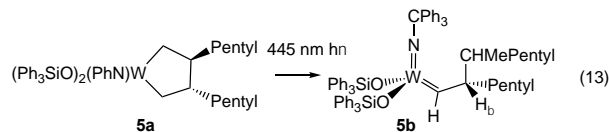
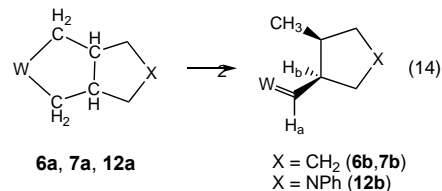


Figure 9. Eyring plot of nine rate constants (three runs at three temperatures) for photolysis of **4a** (see SI for details).

Irradiation of **5a** at 298 K yields only the alkylidene **5b** (eq 13) formed through α hydrogen abstraction. There is no evidence for any ring-contraction analogous to that shown in equation 12, which suggests that the rate of α abstraction is much faster than the rate of ring-contraction as the size of the substituents in the β and β' positions increases. As discussed later, the α hydrogen abstraction and ring-contraction products are proposed to arise from the same photochemical intermediate.



Photolysis of **6a** ($\text{W} = \text{W}(\text{NCPh}_3)(\text{OSiPh}_3)_2$), **7a** ($\text{W} = \text{W}(\text{NAr})(\text{OSiPh}_3)_2$), and **12a** ($\text{W} = \text{W}(\text{NAr})(\text{OSiPh}_3)_2$), all at 445 nm, gave the alkylidenes **6b**, **7b**, and **12b**, respectively (eq 14) in high yields through α hydrogen abstraction. The doublet alkylidene H_α resonances for **6b**, **7b**, and **12b** appear at 8.09, 8.09, and 7.92 ppm, respectively, for the major (*syn*) isomer, while the C_α resonances are found at 226.7, 229.5, and 224.3 ppm, respectively. The five rate constants listed for **6a**, **7a**, and **12a** ($5.5, 10, 9.5, 14, 8.0 \times 10^{-4} \text{ s}^{-1}$) differ by a factor of approximately two at most (Table 2).



Irradiation of **8a** and **9a** yields the alkylidenes **8b** and **9b** shown in equation 15. The H_α and C_α resonances for the major *syn* isomer of **8b** are found at 7.98 and 233.2 ppm; for **9b** they are found at 8.64 and 240.9 ppm. The structure of **9b** was confirmed through SCXRD (Fig 10). At this point **9b** is the only

structurally characterized alkylidene formed from a tungstacyclopentane through α abstraction. The rate constants for **8a** (OSiPh₃) and **9a** (OR_{F3}) reveal that the reaction is slower by a factor of 2-3 for the OR_{F3} complexes.

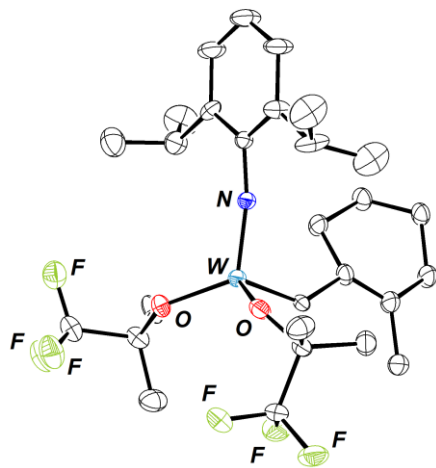
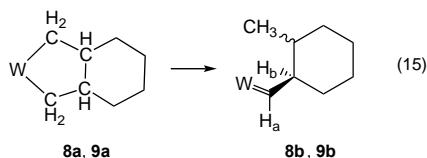
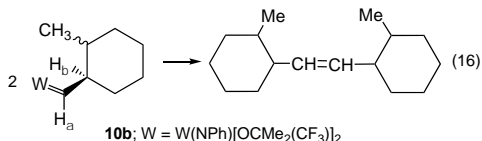


Figure 10. The molecular structure of **9b** as determined through a SCXRD study. Ellipsoids are plotted at 30% probability level. Hydrogen atoms are omitted.

The rate of consumption of W(NPh)(OR_{F3})₂(C₈H₁₄) (**10a**) upon photolysis is the same as that for W(NAr)(OR_{F3})₂(C₈H₁₄) (**9a**), but the product of α abstraction, W(NPh)(OR_{F3})₂(CHC₇H₁₃) (**10b**), decomposes bimolecularly to give more than one of the four possible olefin isomers (eq 16; the isomers were not identified) at a rate that is competitive with formation of **10b**. The alkylidene α hydrogen resonance for the major isomer of **10b** (at 8.47 ppm) can be observed only at the beginning of the photochemical reaction. The instability of **10b** contrasts with the stability of **9b** at comparable concentrations (~0.01 mM). We ascribe the instability of **10b** to the larger size of the NAr ligand in **9b** relative to the NPh ligand in **10b**.



Tungsten alkylidenes that are smaller than a neopentylidene (formed through reaction of a neopentylidene or neophylidene complex with an internal linear olefin) decompose to give W=W complexes.^{35, 36} The phenylimido ligand is simply too small to prevent bimolecular coupling at the concentrations found in these experiments. The metal-containing product or products formed through bimolecular decomposition of **10b** was/were not identified. When **10a** is photolyzed under ethylene, **10b** is effectively trapped by ethylene to give W(NPh)(OR_{F3})₂(C₃H₆) (see Fig S110); none of the olefins formed through coupling of alkylidenes (eq 16) is observed.

Mechanism

We propose that the photochemical step in all photochemical reactions that yield alkylidenes from tungstacyclopentanes reported here is rate-limiting and irreversible. Preliminary DFT calculations suggest that the LUMO in W(NCPh₃)(OSiPh₃)₂(C₄H₈), **4a**, or **6a** is an empty d_{xy} orbital that lies parallel to the plane of the two basal O atoms and two basal C atoms, while the HOMO is comprised of two W-C σ bonds (see SI). A photoexcitation that promotes an electron from the HOMO into the empty d_{xy} orbital (a $\sigma_{WC} \rightarrow d_{xy}$ transition) is calculated to have the absorption envelope shown in Figure 11 (top) for **4a** (which includes six excited states). The calculated absorption envelopes for the same transition in W(NCPh₃)(OSiPh₃)₂(C₄H₈) and **6a** are essentially identical to that for **4a** (see SI).

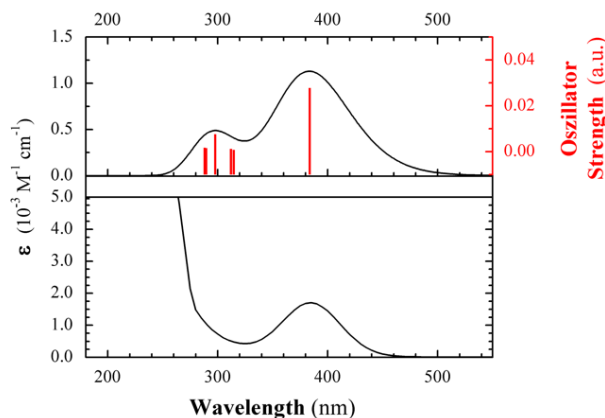


Figure 11. Observed UV/vis spectrum for **4a** (bottom) and calculated absorption envelope for six upper vibrational states by TD-DFT (see Fig S130).

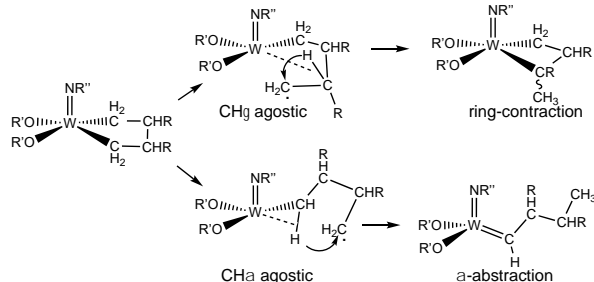
The partial UV/vis spectrum of **4a** (Fig 11 bottom) contains a weak absorption at ~380 nm that we assign to the $\sigma_{WC} \rightarrow d_{xy}$ transition into the zero vibrational level of the excited state. Absorption spectra for several other tungstacyclopentanes reported here are virtually identical to that for **4a**, except for slight differences in λ_{max} and ϵ (Table 3). The absorption at ~380 nm overlaps with the LED light emission envelope with λ_{max} at 405 nm (Fig S75). A LED emission envelope at half height is typically ~35 nm wide.

Table 3. Summary of UV/vis spectra of four bicyclic complexes.

	λ_{max} (nm)	ϵ (M ⁻¹ cm ⁻¹)
W(NAr)(OSiPh ₃) ₂ (C ₇ H ₁₂)	376	1833
W(NAr)(OSiPh ₃) ₂ (C ₈ H ₁₄)	386	1877
W(NAr)(OR _{F3}) ₂ (C ₈ H ₁₄)	371	1444
W(NPh)(OR _{F3}) ₂ (C ₈ H ₁₄)	374	748

Subsequent to or concurrent with the $\sigma_{WC} \rightarrow d_{xy}$ excitation, we propose that a W-C bond is cleaved to give a W(V)CH₂CHRCHRCH₂ intermediate (Scheme 1). The hydrocarbon chain in W(V)CH₂CHRCHRCH₂ is also conformationally relatively flexible, which could allow for CH_α, CH_β, or CH_γ agostic interactions³⁷ in the C₄ chain with the electron-deficient metal. Any such interaction should activate a hydrogen atom toward abstraction by the radical end group. Abstraction of H_α would lead to formation of a terminal alkylidene. Abstraction of H_γ would lead to ring-contraction to give an α methyltungstacyclobutane. Abstraction of H_β by C_α' would lead

to formation of an olefin complex, *e.g.*, 2,3-dimethyl-1-butene if R = Me, but only traces of 2,3-dimethyl-1-butene are observed, and at low T. The proposal shown in Scheme 1 could well be an oversimplification. An option is a concerted reaction for either ring-contraction or α abstraction, or both, without breaking a M-C bond. Further studies will be necessary to establish the details, which will have to include when an excited state relaxes to a ground state.



Scheme 1. A proposed mechanism for ring-contraction and α abstraction

1,2-Hydrogen atom shifts in free hydrocarbon radicals have prohibitively high barriers,³⁸ which suggests that a ring-contraction must be assisted through a CH_γ agostic interactions, as proposed above. What was called an "agostic-assisted hydride shift" in a d⁰ tantalacycloheptane complex (from C_β to C_{α'} to give 1-hexene), where apparently a Ta-C bond cleavage was not invoked, was calculated to be a relatively low energy process in theoretical studies concerning ethylene trimerization.³⁹ When R = H (Scheme 1), ring-contraction is the fastest process. When R = Me, ring-contraction and α abstraction compete, but α abstraction dominates (~80% at 298 K). When R is larger than Me or is part of a five- or six-membered ring, ring-contraction slows and only α abstraction is observed.

We first proposed²⁴ that unobservable TBP analogs of the SP tungstacyclopentane complexes are the crucial intermediates that lead to ring-contraction of unsubstituted tungstacyclopentanes, but now prefer the $\sigma_{WC} \rightarrow d_{xy}$ transition and M-C bond cleavage in the SP form of the tungstacyclopentane as an explanation. Further details of the H abstraction steps at this stage are not yet available.

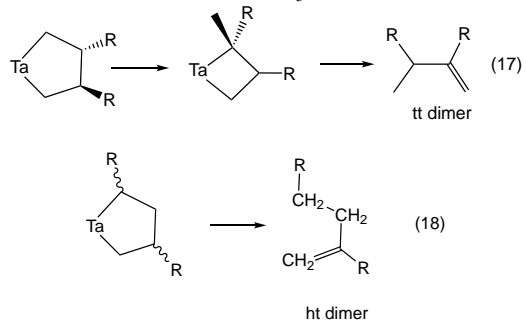
DISCUSSION

The reactions reported here are (fortunately) photochemical, which allows tungstacycles to be prepared and isolated in the dark and mechanistic studies to be carried out, usually in the absence of any olefins and metathesis reactions. Sensitivity of d⁰ transition metal alkyls to light has been noted for several decades.⁴⁰⁻⁶¹ Light was found to accelerate the background (dark) α hydrogen abstraction in the first studies of α abstraction reactions in 14e SP CpTa(CH₂-*t*-Bu)₂Cl₂ and Cp*Ta(CH₂-*t*-Bu)₂Cl₂ complexes.⁴² α Hydrogen abstraction reactions that give d⁰ alkylidene complexes from complexes that contain two or more alkyls usually do not require light, but some do require light (*e.g.*, formation of Re(NAr)₂(CH₂SiMe₃)(CHSiMe₃) from Re(NAr)₂(CH₂SiMe₃)₃).⁵³ Light has been known for some time to promote other types of CH cleavage reactions (*e.g.*, β hydrogen abstraction) in early metal alkyls. The evidence so far suggests that the photochemical transition that we are observing in the tungstacyclopentanes that are photolyzed here is a HOMO to LUMO promotion of one electron that results in what could be viewed in the simplest terms as a reduction of W(VI) to

W(V) and cleavage of one W-C bond.

Early studies of tantalum chemistry are relevant to what we report here. In the first article that described a well-behaved α abstraction in CpTa(CH₂-*t*-Bu)₂Cl₂ in the dark to give a neopentylidene complex⁴² it was noted that α abstraction was dramatically accelerated in sunlight and that a Ta-C bond cleavage to give a Ta(IV)/neopentyl radical pair followed by rapid abstraction of an agostic CH_α in a neighboring TaCH₂-*t*-Bu group by the neopentyl radical before it can escape to solution was a viable explanation. The presence of both *cis* and *trans* isomers of the CpTa(CH₂-*t*-Bu)₂Cl₂ complexes, and ready interconversion of them, complicated any more detailed explanation of a role of light. The 14e imido tungstacyclopentane complexes discussed here are isostructural and isoelectronic with the cyclopentadienyl tantalacyclopentane complexes.

Studies of CpTaCl₂(olefin) complexes and equilibria between them and tantalacyclopentane complexes in the presence of olefin are also relevant to the chemistry reported here. The only observable tantalacyclopentane, *trans*-Cp*Ta(CH₂CHMeCHMeCH₂)Cl₂, is in equilibrium with propylene and Cp*Ta(MeCH=CH₂)Cl₂. The Cp*Ta(CH₂CHMeCHMeCH₂)Cl₂ ring contracts at 50°C to give an unobservable α,α,β trimethyl tantalacyclobutane complex that does not lose an olefin, but rearranges to give 2,3-dimethyl-1-butene, the tail-to-tail or tt dimer of propylene (eq 17). When R = CH₂-*t*-Bu only the ht (head-to-tail) dimer is formed from an unobservable α,β' -disubstituted tantalacyclopentane (eq 18). It was proposed that formation of an α,α -disubstituted tantalacyclobutane intermediate analogous to that shown in eq 17 is sterically "blocked" when R = CH₂-*t*-Bu, and that while the α,β' -disubstituted tantalacyclopentane is disfavored relative to the β,β' version, it appears to be much more susceptible to rearrangement, thereby allowing an ht dimer to be formed at a rate that is not much less than the rate of formation of a tt dimer when R = CH₃.



It seems unlikely that the photochemical mechanism can be thermally accessible in β,β' -disubstituted (or unsubstituted) tungstacyclopentanes. In view of the results for tantalacyclopentanes described above, different substitution patterns on the WC₄ ring, especially tungstacyclopentanes that are substituted in the α -position, may be more prone to formation of an alkylidene. However, it is certainly still possible that an alkylidene is formed thermally in a monoolefin complex instead of a metallacyclopentane complex.

CONCLUSIONS

We have shown that primarily, if not exclusively, α abstraction takes place upon photolysis (at 405 or 445 nm) of β,β' -disubstituted tungstacyclopentanes (dimethyl or dipentyl) and tungstacyclopentane complexes prepared from unsubstituted tungstacyclopentane complexes and 1,6-heptadiene or 1,7-

octadiene. The tungstacyclic complexes can be prepared more conveniently from dialkoxide dichloride complexes using diethyl zinc as the reducing agent in the presence of the diene. The key step of the photochemical reaction is promotion of one electron from a σ_{WC} HOMO to an empty d_{xy} orbital in a SP isomer. It should be noted that this same empty d_{xy} orbital in a d^0 TBP metallacyclobutane is required for metathesis activity.⁶² Metallacyclopentanes appear to have potential to be the source of alkylidenes that are made from olefins. Because metallacyclopentanes can be formed under catalytic metathesis conditions, alkylidenes could be regenerated in metathesis systems from reduced (d^2) tungsten complexes, thermally as well as photochemically. Unsubstituted molybdacyclopentane complexes are known,^{10,63-66} so it seems likely that some of the principles uncovered here for tungsten will be observed in analogous molybdenum chemistry.

Experimental

General. Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a N_2 atmosphere. Commercially available reagents were dried and degassed prior to use. 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. $W(NCPh_3)(OSiPh_3)_2Cl_2$,²⁴ $W(NCPh_3)(OSiPh_3)_2(C_4H_8)$,²⁴ $W(NAr)(OSiPh_3)_2Cl_2$,²⁴ $W(NAr)(OSiPh_3)_2(C_4H_8)$,²⁴ and $W(NAr)Cl_4(Et_2O)$ ⁶⁷ were prepared according to reported procedures. $NaOSiPh_3$ was prepared from Ph_3SiOH and NaH in Et_2O at room temperature. $EtMgBr$ (3.0 M in Et_2O) was used as received from Sigma-Aldrich. Ethylene (UHP) and propylene (UHP) were 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 700 MHz, 600 MHz, 500 MHz, and 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 chemical shifts are reported in ppm relative to trichlorofluoromethane as an external standard. Photolyses with blue (445) LEDs were carried out with 30 Blue 5050 surface mounted device (SMD) LEDs (nominal power 3.1mW for each), powered by a 12V DC power supply with an inline DC dimmer. Photolyses with violet light (405 nm) were carried out in a modified J Young NMR tube using a Prizmatix fiber coupled LED light source (nominal power output 27 mW). UV/Vis spectra were recorded on a Cary 60 Agilent spectrophotometer.

Synthesis of $W(NPh)(OSiPh_3)_2Cl_2(THF)$

$W(NPh)Cl_4(Et_2O)$ (0.5 g, 1.02 mmol, 1 equiv) was dissolved in a mixture of Et_2O (20 mL) and THF (4 mL) in a vial and a stir bar was added. The vial was placed at $-30^\circ C$ in the fridge of the glovebox and left overnight. $NaOSiPh_3$ (0.62 g, 2.08 mmol, 2 eq) was added as a solid in portions over twenty minutes. The color of the solution changed slowly from dark green to brick red after stirring the mixture at room temperature for 2 h. The volatiles were removed *in vacuo* and the solid

residue was washed with 5 mL of Et_2O and 10 mL of pentane. Dichloromethane was added to the sample and the mixture was filtered. The filtrate was concentrated to 15 mL. A few drops of THF were added and the mixture was stored at $-30^\circ C$ overnight. Three crops of the red crystalline product were collected, washed twice with cold CH_2Cl_2 (4 mL), and then once with pentane (6 mL); yield ~45% yield (0.44 g). The red crystals appear as a pink powder when crushed. A benzene solution of this compound is orange. Single crystals suitable for diffraction were grown from a concentrated solution of dichloromethane. Anal. Calcd for $C_{46}H_{43}Cl_2NO_3Si_2W$: C, 57.03; H, 4.47; N, 1.45. Found: C, 56.75; H, 4.41; N, 1.47.

Synthesis of $W(NPh)(OR_{F3})_2Cl_2(THF)$.

$W(NPh)Cl_4(Et_2O)$ (0.5 g, 1.02 mmol, 1 equiv) was dissolved in a mixture of Et_2O (20 mL) and THF (5 mL) and a stir bar was added. In another vial $LiOCMe_2CF_3$ (273 mg, 2.04 mmol, 2 equiv) was dissolved in Et_2O (5 mL). Both the vials were left at $-30^\circ C$ overnight. The ether solution of $LiOCMe_2CF_3$ was added dropwise to $W(NPh)Cl_4(Et_2O)$ solution over a period of ten minutes. The color of the solution changed slowly from dark green to red, and finally to yellow after 2 h. This solution was filtered through a plug of Celite. The volatiles were removed from the filtrate *in vacuo*, and the solid residue was recrystallized from pentane at $-30^\circ C$ to afford golden yellow crystals; yield 85% (0.58 g). Anal. Calcd for $C_{18}H_{25}Cl_2F_6NO_3W$: C, 32.17; H, 3.75; N, 2.08. Found: C, 32.18; H, 3.70; N, 2.10.

Synthesis of $W(NAr)(OR_{F3})_2Cl_2(THF)$.

A solution of $W(NAr)Cl_4(Et_2O)$ (0.5 g, 0.87 mmol, 1 equiv) in a mixture of Et_2O (20 mL) and THF (5 mL) at $-30^\circ C$ was added to a solution of $LiOCMe_2CF_3$ (233 mg, 1.74 mmol, 2 equiv) in Et_2O (5 mL) at $-30^\circ C$ dropwise over a period of ten minutes. The color of the solution changed slowly from dark green to red, and finally light yellow after stirring the solution at room temperature for 20 h. This solution was filtered through a plug of Celite, the volatiles were removed and the solid was recrystallized from pentane at $-30^\circ C$ to afford golden yellow crystals; yield 90% (0.59 g). Anal. Calcd for $C_{24}H_{37}Cl_2F_6NO_3W$: C, 38.12; H, 4.93; N, 1.85. Found: C, 38.33; H, 4.93; N, 1.85.

Synthesis of $W(NPh)(OSiPh_3)_2Cl_2(C_4H_8)$ (**1a**).

$W(NPh)(OSiPh_3)_2Cl_2(THF)$ (600 mg, 0.62 mmol, 1 equiv) was dissolved in toluene (120 mL) in a 1L J. Young Flask. The solution was freeze-pump-thawed three times, and then 15 psi of ethylene was added. The solution was cooled to $-78^\circ C$ and $EtMgBr$ (3M in Et_2O , 0.41 mL, 1.24 mmol, 2 equiv) was added dropwise. The solution was brought back to room temperature in the dark, and stirred for 12 hours (under ethylene). The solvents were removed from the reaction mixture and the dark yellow residue was extracted in pentane (60 mL) and the mixture was filtered. The filtrate was concentrated to 10 mL and stood at $-30^\circ C$. Yellow **1a** was isolated through filtration; yield ~40% yield (220 mg, 0.25 mmol). Single crystals of adequate quality for X-Ray diffraction analysis were grown from a concentrated solution of diethyl ether. Compound **1a** should be stored in the dark as it is sensitive to ambient light in solution. Anal. Calcd for $C_{46}H_{43}NO_2Si_2W$: C, 62.65; H, 4.92; N, 1.59. Found: C, 62.63; H, 4.86; N, 1.65.

Synthesis of W(NPh)(OR_{F3})₂(C₄H₈) (2a).

W(NPh)(OR_{F3})₂Cl₂(THF) (600 mg, 0.89 mmol, 1 equiv) was dissolved in toluene (120 mL) in a 1L J. Young Flask. The solution was freeze-pump-thawed three times, and then 15 psi of ethylene was added. The solution was then cooled to -78°C and Et₂Zn (1M in hexane, 0.89 mL, 0.89 mmol, 1 equiv) was added dropwise. The solution was brought back to room temperature in the dark and stirred overnight (under ethylene). The solvents were removed from the reaction mixture and the dark yellow residue was extracted with pentane (40 mL) and the mixture was filtered. The filtrate was concentrated to 5 mL and stood at -30°C. After removal of all volatile components *in vacuo* 2a was used in other syntheses described below; it could not be obtained in crystalline form.

Synthesis of W(NAr)(OR_{F3})₂(C₄H₈) (3a).

W(NAr)(OR_{F3})₂Cl₂(THF) (600 mg, 0.79 mmol, 1 equiv) was dissolved in toluene (120 mL) in a 1L J. Young Flask. The solution was subject to three freeze-pump-thaw cycles, and then 15 psi of ethylene was added. The solution was then cooled to -78°C and Et₂Zn (1M in hexane, 0.79 mL, 0.79 mmol, 1 equiv) was added dropwise. The solution was brought back to room temperature in the dark and stirred overnight (under ethylene). The solvents were removed from the reaction mixture *in vacuo* and the dark yellow residue was extracted in pentane (40 mL). The mixture was filtered and the filtrate was concentrated to 5 mL and stood at -30°C. After removal of all volatile components *in vacuo* 3a was used in other syntheses described below; it could not be obtained in crystalline form.

Synthesis of W(NCPh₃)(OSiPh₃)₂(Me₂C₄H₆) (4a).

A degassed solution of W(NCPh₃)(OSiPh₃)₂(C₄H₈) (500 mg, 0.477 mmol) in toluene (30 mL) was stirred in a sealed 500 mL J. Young flask under an atmosphere of propylene (15 psi) at 80°C for 2 h in the dark. NMR spectroscopic analysis of an aliquot showed that W(NCPh₃)(OSiPh₃)₂(β-MeC₄H₇) isomers were formed as intermediates (see SI). All volatiles were removed *in vacuo*, the residue was redissolved in toluene (30 mL), the solution was degassed (2 freeze-pump-thaw cycles), and the solution was stirred under an atmosphere of propylene (15 psi) at 80°C for 2 h in the dark. The exchange of solvent and atmosphere as well as exposure to propylene was repeated as described. After another 2 h of stirring the solution at 80°C in the dark, the volatiles were removed *in vacuo* and the crude product was recrystallized from toluene at -30°C in the dark to obtain 4a (260 mg, 0.247 mmol, 88% from two crops) as yellow crystals of adequate quality for single crystal X-ray structural analysis. Anal. Calcd for C₆₁H₅₇NO₂Si₂W: C, 68.08; H, 5.34; N, 1.30. Found: C, 67.97; H, 5.29; N, 1.41.

Synthesis of W(NCPh₃)(OSiPh₃)₂(Pent₂C₄H₆) (5a).

A degassed mixture of W(NCPh₃)(OSiPh₃)₂(C₄H₈) (250 mg, 0.239 mmol, 1.0 equiv) and 1-heptene (250 mg, 2.55 mmol, 11 equiv) in toluene (10 mL) was stirred in a sealed 100 mL J. Young tube and heated at 80°C for 3 h in the dark. All volatiles were removed *in vacuo*, the residue was dissolved in toluene (10 mL) and 1-heptene (250 mg, 2.55 mmol, 11 equiv) was added. The mixture was degassed (two freeze-pump-thaw cycles) and resubjected heating at 80 °C. The reaction progress was monitored by ¹H NMR spectroscopy and repeated until the starting material and intermediates were

consumed and product formed. The volatiles were removed *in vacuo* and the crude product was recrystallized from toluene at room temperature to obtain 5a (190 mg, 0.162 mmol, 67% from two crops) as brown crystals. Single crystal X-ray structural analysis revealed excessive twinning in the sample and a significant degree of disorder that mostly involved the pentyl groups. Calcd for C₆₉H₇₃NO₂Si₂W: C, 69.74; H, 6.19; N, 1.18. Found: C, 68.70; H, 6.40; N, 1.20. Two other attempted analyses failed; the reasons are not known.

Synthesis of W(NCPh₃)(OSiPh₃)₂(C₇H₁₂) (6a).

A degassed mixture of W(NCPh₃)(OSiPh₃)₂(C₄H₈) (250 mg, 0.239 mmol, 1.0 equiv) and 1,6-heptadiene (23 mg, 0.239 mmol, 1.0 equiv) in toluene (10 mL) was stirred in a sealed 100 mL J. Young tube at 80°C for 3 h in the dark. All volatiles were removed *in vacuo*, the residue was redissolved in toluene (10 mL), the solution was degassed (2 freeze-pump-thaw cycles) and resubmitted to the reaction conditions. Removal of atmosphere and resubjection to the reaction conditions was repeated until formation of the product was complete. The volatiles were removed *in vacuo* and the crude product was recrystallized from toluene at -30°C to obtain 6a (200 mg, 0.184 mmol, 77% from two crops) as a red solid. Anal. Calcd for C₆₂H₅₇NO₂Si₂W: C, 68.43; H, 5.28; N, 1.29. Found: C, 68.46; H, 5.44; N, 1.17.

Synthesis of W(NAr)(OSiPh₃)₂(C₇H₁₂) (7a)

In a 100 mL J-Y flask, W(NAr)(OSiPh₃)₂(C₄H₈) (100 mg, 0.104 mmol), 1,6-heptadiene (30 mg, 0.32 mmol, 3 equiv) and toluene (10 mL) were added. The tube was heated and stirred in an oil bath at 85 °C for 12 h. The 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 crystalline solid was washed once with cold pentane (0.2 mL) to afford 7a in ~86% yield (92 mg). Single crystals suitable for diffraction can be grown from a concentrated solution of pentane. Anal. Calcd for C₅₅H₅₉NO₂Si₂W: C, 65.66; H, 5.91; N, 1.39. Found: C, 65.81; H, 6.04; N, 1.52.

Synthesis of W(NAr)(CHC₆H₁₁)(OSiPh₃)₂ (7b)

Compound 7a (10 mg, 0.01 mmol) was dissolved in C₆D₆ (0.5 mL) in a J. Young NMR tube. The mixture was irradiated with LEDs (λ_{max} = 445 nm, 93 mW). The reaction was followed by ¹H NMR for 35 minutes, at which time >90% of 7a had been converted to 7b.

A larger scale synthesis was carried out by dissolving W(NAr)(OSiPh₃)₂(C₇H₁₂) (100 mg, 0.10 mmol) in toluene (10 mL) in a 100 mL J. Young flask. A stir bar was added and the solution was then irradiated with blue LEDs (λ_{max} = 445 nm, 93 mW) at room temperature. Irradiation was continued until all starting material was converted to product (monitored by ¹H NMR spectroscopy). The volatiles were removed under vacuum and the solid residue was extracted into 10 mL of pentane. This mixture was filtered through a plug of Celite, and the filtrate was evaporated to give a yellow residue. This residue was dissolved in ~0.3 mL Et₂O followed by the addition of ~0.5 mL of pentane and the solution was stored at -30 °C for few days. Yellow crystals were formed, which were filtered off, rinsed with cold pentane twice, and dried *in vacuo* to afford 7b in 61%

yield (61 mg). Anal. Calcd for $C_{55}H_{59}NO_2Si_2W$: C, 65.66; H, 5.91; N, 1.39. Found: C, 65.69; H, 5.92; N, 1.33.

Synthesis of $W(NAr)(OSiPh_3)_2(C_8H_{14})$ (**8a**).

$W(NAr)(OSiPh_3)_2(C_4H_8)$ (100 mg, 0.104 mmol), 1,7-octadiene (34 mg, 0.32 mmol, 3 equiv), toluene (10 mL), and a stir bar were added to a 100 mL J. Young flask. The flask was heated in an oil bath at 85 °C and the mixture was stirred for 12 h. The volatiles were removed *in vacuo* and the solid residue was extracted in 10 mL of pentane. This solution was filtered through a plug of celite, and the filtrate was concentrated to 0.5 mL. A few drops of diethyl ether were added to this pentane solution and it was stored at -30°C and a yellow crystalline solid obtained. The product was washed twice with cold pentane (0.2 mL x 2) to afford **8a** in ~73% yield (78 mg). Single crystals suitable for diffraction can be grown from a concentrated solution of diethyl ether. Anal. Calcd for $C_{56}H_{61}NO_2Si_2W$: C, 65.94; H, 6.03; N, 1.37. Found: C, 65.72; H, 6.22; N, 1.53.

Synthesis of $W(NAr)(CHC_7H_{13})(OSiPh_3)_2$ (**8b**)

Compound **8a** (10 mg, 0.01 mmol) was dissolved in toluene- d_8 (0.5 mL) in a J. Young NMR tube. The mixture was irradiated with blue LEDs ($\lambda_{max} = 445$ nm, 93 mW) and the reaction was followed by 1H NMR for 40 minutes; >92% of **8a** was converted to **8b**.

A larger scale synthesis of this compound was performed by dissolving compound **8a** $W(NAr)(OSiPh_3)_2(C_7H_{12})$ (170 mg, 0.167 mmol), in toluene (15 mL) in a 100 mL J. Young flask, which was then irradiated with blue LEDs ($\lambda_{max} = 445$ nm, 93 mW). Irradiation was continued at room temperature until and monitored by 1H NMR spectroscopy until all starting material was converted to product. The volatiles were removed *in vacuo* and the solid residue was extracted into ~10 mL of pentane. This solution was filtered through a plug of Celite, and the filtrate was evaporated to dryness to give an orange residue. This residue was dissolved in ~1.5 mL of pentane and the solution was stored at -30 °C for few days to give an orange crystalline solid which was then washed with cold pentane twice and exposed to vacuum to afford **8b** in 68% yield (116 mg). Anal. Calcd for $C_{56}H_{61}NSi_2O_2W$: C, 65.94; H, 6.03; N, 1.37. Found: C, 65.93; H, 6.04; N, 1.32.

Synthesis of $W(NAr)(OR_{F3})_2(C_8H_{14})$ (**9a**).

$W(NAr)Cl_2(OR_{F3})_2(THF)$ (300 mg, 0.396 mmol, 1 equiv), 1,7-octadiene (65 mg, 0.594 mmol, 1.5 equiv) and toluene (60 mL) were added to a 500 mL J. Young flask. The reaction mixture was cooled to -78 °C and Et_2Zn (1 equiv) was added dropwise. The mixture was stirred overnight at room temperature and then heated in an oil bath at 80 °C and for 4 h. All volatiles were removed under vacuum and the solid residue was extracted with 10 mL of pentane. This solution was filtered through a plug of Celite, and the solvent was removed from the filtrate *in vacuo*. The residue was dissolved in ~ 1 mL diethyl ether and the solution was stored at -30°C to give a yellow crystalline solid. The product was washed twice with cold ether (0.2 mL x 2). A second batch of crystals was obtained from the supernatant ether solution. The total overall yield of **9a** was 78% (87 mg). Single crystals suitable for diffraction were grown from a concentrated solution of diethyl ether. Anal.

Calcd for $C_{28}H_{43}F_6NO_2W$: C, 46.48; H, 5.99; N, 1.94. Found: C, 46.28; H, 5.94; N, 1.89.

Synthesis of $W(NAr)(CHC_7H_{13})(OR_{F3})_2$ (**9b**)

Compound **9a** (8 mg, 0.01 mmol) was dissolved in C_6D_6 (0.5 mL) in a J. Young NMR tube. The mixture was irradiated with blue LEDs ($\lambda_{max} = 445$ nm, 93 mW). The reaction was followed by 1H NMR for 90 minutes; ~ 92% of **9a** was converted to **9b**.

A larger scale synthesis was performed by adding compound **9a** (90 mg, 0.124 mmol) to toluene (10 mL) in a 100 mL J Y flask. The solution was stirred and irradiated with blue LEDs ($\lambda_{max} = 445$ nm, 93 mW). Irradiation was continued at room temperature until all starting material was converted to product (monitored by 1H NMR spectroscopy). The volatiles were removed *in vacuo* and the solid residue was extracted with ~10 mL of pentane. This mixture was filtered through a plug of Celite, and the filtrate was evaporated to dryness to give an orange solid. This solid was dissolved in ~0.2 mL of pentane and the solution was stood at -30 °C for few days. Yellow crystals formed, which were washed with cold pentane once, and exposed to vacuum to afford **9b** in 72% yield (65 mg). Single crystals suitable for X-ray diffraction were grown from a concentrated solution in pentane. Anal. Calcd for $C_{28}H_{43}F_6NO_2W$: C, 46.48; H, 5.99; N, 1.94. Found: C, 45.36; H, 6.20; N, 1.91.

Synthesis of $W(NPh)(OR_{F3})_2(C_8H_{14})$ (**10a**)

$W(NPh)Cl_2(OR_{F3})_2(THF)$ (600 mg, 0.89 mmol, 1 equiv), 1,7-octadiene (294 mg, 2.67 mmol, 3 equiv) and toluene (120 mL) were added to a 500 mL J. Young flask. The reaction mixture was cooled to -78 °C and Et_2Zn (0.89 mL, 1 equiv) was added dropwise. The mixture was stirred overnight at room temperature. The volatiles were removed *in vacuo* and the solid residue was extracted with 60 mL of pentane. This solution was filtered through a plug of Celite, and the volatiles were removed *in vacuo*. The residue was dissolved in pentane (3 mL) and the solution was kept at -30°C to obtain yellow crystalline solid. This solid compound was washed once with cold pentane (0.2 mL) to afford **10a** in 68% yield (386 mg). Anal. Calcd for $C_{22}H_{31}F_6NO_2W$: C, 41.33; H, 4.89; N, 2.19. Found: C, 40.84; H, 4.73; N, 2.32.

Synthesis of $W(NAr)(OSiPh_3)_2[\beta-(CH_2OCH_2CH=CH_2)C_4H_7]$ (**11**)

$W(NAr)(OSiPh_3)_2(C_4H_8)$ (100 mg, 0.104 mmol), diallyl ether (30.6 mg, 0.31 mmol, 3 equiv), and toluene (6 mL) were added to a 100 mL J. Young flask, and the flask was heated at 80 °C for 20 h. The volatiles were removed *in vacuo* and the solid residue was extracted into 10 mL of pentane. This solution was filtered through a plug of Celite, and the solvent was removed *in vacuo* to give a yellow residue. This residue was dissolved in 2 mL of diethyl ether and the solution was kept at -30°C. The yellow crystalline solid filtered off and washed once with cold diethyl ether (0.2 mL) to afford **11** in 46% yield (49 mg). Single crystals suitable for diffraction were grown from a concentrated solution of diethyl ether. Anal. Calcd for $C_{56}H_{61}NO_3Si_2W$: C, 64.92; H, 5.93; N, 1.35. Found: C, 64.91; H, 5.90; N, 1.39.

Synthesis of $W(NAr)(OSiPh_3)_2(C_6H_{10}NPh)$ (**12a**).

$W(NAr)(OSiPh_3)_2(C_4H_8)$ (100 mg, 0.1 mmol), *N,N*-diallylaniline (18 mg, 0.1 mmol, 1 equiv) and toluene (10 mL)

were added to a 100 mL J. Young flask, and the flask was heated at 80 °C for 6 h. The volatiles were removed *in vacuo* and the solid residue was extracted with 15 mL of pentane. This solution was filtered through a plug of Celite. The solvent was removed *in vacuo* to afford a yellow foam which was then dissolved in 2 mL of pentane and the solution was kept at -30°C. The desired compound oiled out from the pentane solution. The supernatant was decanted and the oily residue was exposed to vacuum to give bright yellow solid **12a** in 61% yield (66 mg). Anal. Calcd for C₆₀H₆₂N₂O₂Si₂W: C, 66.53; H, 5.77; N, 2.59. Found: C, 66.74; H, 5.78; N, 2.58.

Synthesis of W(NAr)(CHC₅H₉NPh)(OSiPh₃)₂ (**12b**)

W(NAr)(OSiPh₃)₂(C₄H₈) (100 mg, 0.1 mmol), *N,N*-dialylaniline (18 mg, 0.1 mmol, 1 equiv) and toluene (10 mL) were added to a 100 mL J. Young flask, and the flask was heated at 80 °C for 6 h. The volatiles were removed *in vacuo* and the solid residue was extracted into 15 mL of pentane and the pentane solution was filtered through a plug of Celite. The solvent was removed *in vacuo* to afford a yellow solid which was then dissolved in 2 mL of pentane. The solution was stored at -30°C. The product was deposited in the pentane solution as an oil. The supernatant was decanted and the oily residue was exposed to vacuum to give bright yellow **12b** in 61% yield (66 mg). Anal. Calcd for C₆₀H₆₂N₂O₂Si₂W: C, 66.53; H, 5.77; N, 2.59. Found: C, 66.01; H, 5.74; N, 2.61

Observation of W(NPh)(OSiPh₃)₂(C₃H₆) (**1b**)

Compound **1a** (15 mg, 0.017 mmol) was dissolved in toluene-d₈ (0.5 mL) in a J. Young NMR tube. The contents were subjected to a freeze-pump-thaw (FPT) procedure and 15 psi of C₂H₄ was added. The mixture was irradiated with Blue LEDs ($\lambda_{\text{max}} = 445 \text{ nm}$, 93 mW). The reaction was followed by ¹H NMR for 30 minutes to yield propylene and **1b** (>90% conversion; Fig S122).

Observation of W(NPh)(OR_{F3})₂(C₃H₆) (**2b**)

Compound **2a** was photolyzed under ethylene as described for **1a** above to give **2b** (Fig S124).

A detailed description of all photolyses, including those to give **4b**, **5b**, and **6b** can be found in the SI.

ASSOCIATED CONTENT

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

Accession Codes

CCDC 2238915, 2254024, 2254025, 2254026, 2254027, 2254028, 2254029, 2258632, 2258633, 2259541, 2259542, and 2261464 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, 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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Contributions

RR discovered α abstraction in NCPH₃ tungstacyclopentane complexes, synthesized NCPH₃ complexes, carried out DFT calculations, and designed the *in situ* NMR tube photoreactor. MM prepared and explored all variations that do not contain a NCPH₃ group, and perfected the use of ZnEt₂ for metallacyclopentane syntheses. All single crystal X-ray diffraction studies were carried out by VC.

Notes

The authors declare no competing financial interest.

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