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Proton-Catalyzed Interconversion of Tungsten(VI) Isopropylidene and Propylene Complexes

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ABSTRACT: Additions of two equivalents of (CF₃)₃COH (R_{F9}OH) or (CF₃)₂MeCOH (R_{F6}OH) to W(NAr)₂R₂ complexes (Ar = 2,6-diisopropylphenyl, R = *n*-propyl or *i*-propyl) offer the opportunity to synthesize propylene or isopropylidene olefin metathesis-active complexes in the absence of free propylene. Propylene and isopropylidene complexes (W(NAr)(ArNH₂)(OR_{F9})₂(propylene) and W(NAr)(ArNH₂)(OR_{F9})₂(CMe₂)) are formed at room temperature from both W(NAr)₂(*i*-propyl)₂ and W(NAr)₂(*n*-propyl)₂ complexes upon addition of two equivalents of R_{F9}OH; no W=CHCH₂Me complexes are observed. Similar results are found for W(NAd)₂(propyl)₂ complexes (Ad = 1-adamantyl). Both RNH₂ and RNH₂B(C₆F₅)₃ (R = Ar or Ad) catalyze the interconversion of propylene and isopropylidene complexes. Addition of R_{F6}OH to W(NAr)₂R₂ or W(NAd)₂R₂ complexes leads to mixtures that contain largely propylene complexes. Addition of (CF₃)Me₂COH (R_{F3}OH) to W(NAr)₂(*i*-Pr)₂ yields only propylene complexes. One propylene complex, W(NAd)(OR_{F9})₂(CH₂=CHMe)(dme), was isolated, structurally characterized, and found to react with AdNH₂ to reform W(NAd)(OR_{F9})₂(CMe₂)(AdNH₂). It is proposed that propylene and isopropylidene complexes interconvert through formation of an intermediate isopropyl complex.

INTRODUCTION

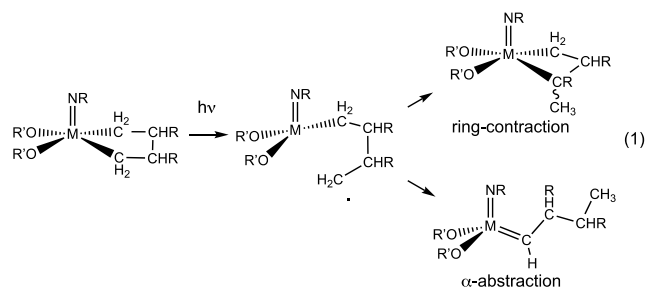
Olefin metathesis¹ was discovered over sixty years ago.²⁻⁴ It has been shown over several decades that neutral complexes of the type M(X)(alkylidene)(Y)(Z) are the most common initiators in homogeneous metathesis systems where M = Mo or W, X is an imido or oxo ligand, and Y and Z are monoanionic ligands such as an alkoxide or a pyrrolide.⁵ (Cationic complexes in which Y or Z is a neutral donor have also been reported.^{6,7}) The initial alkylidene in both homogeneous studies and heterogeneous studies⁸ is usually a neopentylidene or a neophylidene formed through abstraction of an α proton from neopentyl or neophyl ligands by a second alkyl. But how molybdenum or tungsten alkylidene complexes (either terminal, M=CHR, or internal, M=CRR') are formed⁹ from olefins or alkyls that contain β protons has remained unanswered until relatively recently.

Much evidence in the last two decades has suggested that alkylidenes are made from d² olefin complexes, M(X)(olefin)(Y)(Z). Molybdenum imido styrene and *trans*-3-hexene complexes of that type (e.g., Mo(NAr)(OSiPh₃)₂(olefin); Ar = 2,6-diisopropylphenyl) were reported in 2010.¹⁰ It was found that alkenes exchange readily at the Mo(IV) center, unsubstituted Mo(VI) molybdacyclopentane complexes can be formed through addition of ethylene, bound olefins can isomerize via double bond migration, and metathesis-active initiators, presumably Mo(NAr)(OSiPh₃)₂(alkylidene) complexes, are generated in the presence of olefins. Several olefin complexes were found to be active for metathesis of 1-decene or 1-octene at 85–100 °C.

Copéret has shown that tungsten(IV) oxo bisalkoxide bispyridine complexes supported on silica through an Si-O-M linkage yield active metathesis catalysts.¹¹ Key mechanistic

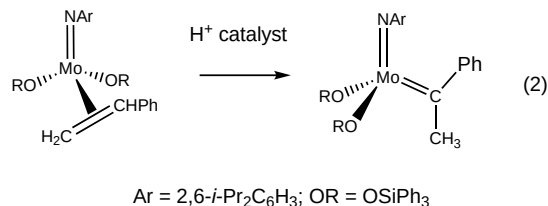
steps that lead to alkylidenes were proposed to involve allylic CH activation, proton transfers catalyzed by pyridine, and activation of metathesis processes by B(C₆F₅)₃. Copéret also reported the structure of 18e W(O)(OR_{F6})₂(pyridine)₂(propylene), which becomes active for the metathesis of propylene in solution upon addition of B(C₆F₅)₃. Other studies continue to strengthen the correlation between homogeneous and heterogeneous olefin metathesis systems that contain Mo or W imido or oxo alkylidene initiators.¹²⁻²⁰

Recent homogeneous studies have uncovered two mechanisms that yield a Mo or W alkylidene from an olefin. One consists of a proposed photochemical M-C bond cleavage (with ~450 nm light) in a metallacyclopentane complex²¹ followed by either ring-contraction^{22,23-25} to give a metallacyclobutane, a key intermediate in metathesis, or α hydrogen abstraction^{5, 26, 27} within the MC₄ ring to give an alkylidene (eq 1).

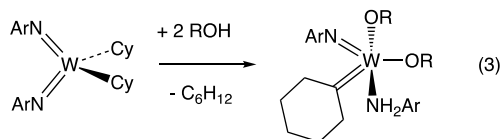


The second mechanism consists of addition of a proton to an alkene to give an alkyl that contains both α and β protons, followed by reversible loss of an α proton to give an internal

alkylidene (an "H_{cat}" reaction^{28, 29}). The first example of an H_{cat} reaction for Mo or W was the equilibrium established between a M(styrene) and a M(CMePh) complex in the presence of a catalytic amount of PhNMe₂H⁺X⁻ (X = B(3,5-(CF₃)₂C₆H₃)₄ or B(C₆F₅)₄) (eq 2).^{30, 31} Intermediate [Mo(NAr)(OSiPh₃)₂(CHMePh)]⁺ (Ar = 2,6-diisopropylphenyl) was structurally characterized. No M=CHCH₂Ph or M(CH₂CH₂Ph)⁺ complexes were observed.



In 2024 it was found that cyclohexylidene complexes, W(NAr)(ArNH₂)(OR)₂(C₆H₁₀) (OR = OR_{F9} or OR_{F6}), are formed through a double protonation of an imido ligand in W(NAr)₂Cy₂ (Cy = cyclohexyl) by two equivalents of R_{F9}OH or R_{F6}OH (eq 3).³² This reaction could consist of an unusually



selective α hydrogen abstraction³³ in a biscyclohexyl intermediate (e.g., W(NAr)(NHAr)(OR_{F9})Cy₂), but it also could consist (partially or wholly) of a β hydrogen abstraction to give a cyclohexene complex followed by isomerization of the cyclohexene to a cyclohexylidene ligand through an H_{cat} reaction. Preliminary deuterium labeling studies with R_{F9}OD support a selective α abstraction. No cyclohexene complex was formed from the cyclohexylidene complex at room temperature in one hour, even after addition of B(C₆F₅)₃. It was suggested that a cyclohexyl/cyclohexallyl intermediate could be formed from two cyclohexenes, and that therefore a cyclohexene complex could be formed from cyclohexene, and *vice versa*, which would be another version of an H_{cat} reaction.³⁴ It should be noted that a bisimido complex such as W(NAr)₂Cy₂ is " π -loaded"³⁵⁻³⁷ (four potential W-N π interactions; see discussion) while only three significant metal-ligand π interactions are present in W(NAr)(ArNH₂)(OR)₂(C₆H₁₀).

The method of generating a metathesis-active alkylidene through addition of an alcohol to a bisimido dialkyl complex just described offers the opportunity to explore formation of olefin and/or alkylidene complexes from acyclic alkyls that contain β protons in the absence of olefins in solution. If no olefins are in solution, metallacyclopentane complexes cannot form, nor is olefin metathesis possible if and when an alkylidene is formed. We report here an exploration of the reaction between tungsten bisimido dipropyl complexes and selected alcohols which is aimed at gaining some understanding of the relationships between propyl, propylene, and propylidene complexes. The principles uncovered here should extend to alkyl/alkene/alkylidene chemistry that involves larger metathesizable olefins and to oxo analogs of these imido complexes.

RESULTS

The WNAr system

Both W(NAr)₂(*n*-Pr)₂ and W(NAr)₂(*i*-Pr)₂ can be prepared in high yield from W(NAr)₂Cl₂(dme) (dme = 1,2-dimethoxyethane) and two equivalents of *n*-PrMgCl or *i*-PrMgCl. The structure of W(NAr)₂(*i*-Pr)₂ (Fig 1) shows no evidence of any CH _{α} or CH _{β} agostic interaction^{38, 39} with the metal. W(NAr)₂(*n*-Pr)₂ is formed in high yield and high purity (according to NMR spectra), but we have been able to isolate it only as an oil.

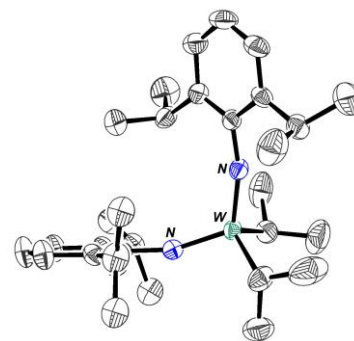
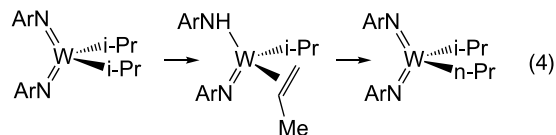


Figure 1. The molecular structure of W(NAr)₂(*i*-Pr)₂ as determined by SCXRD. Ellipsoids plotted at 40% probability level. Hydrogen atoms are omitted for clarity.

W(NAr)₂(*i*-Pr)₂ begins to isomerize within minutes in C₆D₆ at room temperature. After 24 h a single product, W(NAr)₂(*n*-Pr)(*i*-Pr), is formed, according to NMR data (Figure S34). Subsequent formation of W(NAr)₂(*n*-Pr)₂ was not observed. A single measurement at 22 °C showed the conversion in C₆D₆ to be first order with $k = 6.0 \times 10^{-5} \text{ sec}^{-1}$ ($t_{1/2} = 3.2 \text{ h}$). The reaction also takes place in the solid state, but much more slowly. We propose that the reaction mechanism consists of migration of a β H from an isopropyl group to an imido nitrogen to give an intermediate W(NAr)(HNAr)(propylene)(*i*-Pr) complex (eq 4); return of the amido H to the olefinic CH carbon in the propylene ligand yields the *n*-propyl ligand. The migrating H is best described as a proton (see later discussions). All of the complexes in eq 4 have four potential W-ligand interactions with π character. It is not clear why a second isomerization to yield W(NAr)₂(*n*-Pr)₂ does not take place on the same time scale as the first isomerization.



Addition of two equivalents of R_{F9}OH to freshly prepared W(NAr)₂(*i*-Pr)₂ yields a mixture of W(NAr)(ArNH₂)(OR_{F9})₂(CMe₂) and primarily two isomers of unsymmetric W(NAr)(ArNH₂)(OR_{F9})₂(CH₂=CHMe) after 3.5 h at room temperature (eq 5, Figure S41). The number of significant π interactions decreases from four to three in this reaction, or even two if the W(olefin) unit is considered to be a metallacyclopentane. We were initially surprised to find that addition of two equivalents of R_{F9}OH to W(NAr)₂(*n*-Pr)₂ also leads to a mixture of W(NAr)(ArNH₂)(OR_{F9})₂(CMe₂) and

$W(NAr)(ArNH_2)(OR_{F9})_2(CH_2=CHMe)$, largely the former initially. $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ can be crystallized selectively from these mixtures.

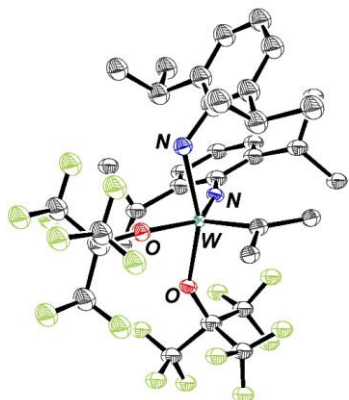
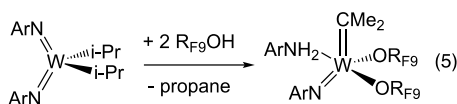
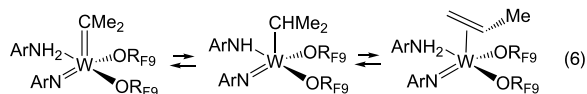


Figure 2. The molecular structure of $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ as determined by SCXRD.

The structure of $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ (Fig 2) is biased toward a square pyramid ($\tau = 0.32$,⁴⁰ $W-NH_2 = 2.299 \text{ \AA}$, $W=N = 1.748 \text{ \AA}$) with the isopropylidene ligand tipped away from the imido ligand ($W-C_{\alpha}-C_{\beta} = 109.1^\circ$ and 135.7°), which is a common phenomenon in high oxidation state disubstituted alkylidene complexes of Mo and W.^{41, 42} A plausible explanation is that the bound aniline NH proton in 16 electron $W(NAr)(ArNH_2)(OR_{F9})_2(CH_2=CHMe)$ is activated toward migration to the propylene ligand to give $W(NAr)(ArNH)(OR_{F9})_2(CHMe_2)$ (three π bonds) and the isopropyl α proton returns to the $ArNH$ ligand to give the isopropylidene complex (cf. the equilibration of $M(CH_2=CHPh)$ and $M(CMePh)$ complexes with anilinium^{30,31}). No $W(NAr)(ArNH_2)(OR_{F9})_2(CHCH_2Me)$ is observed in either reaction. Low temperature NMR studies confirm that the $ArNH_2$ ligand is partially dissociated in $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ at room temperature, but bound on the NMR time scale at low temperature (Figure S13) in an asymmetric complex (Fig 2). Therefore, some $ArNH_2$ in solution could remove the activated proton in $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ and deposit it on the isopropylidene ligand because $ArNH_3^+$ is approximately as acidic as dimethylanilinium.

A freshly crystallized sample of $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ after one day in toluene or benzene at 22°C becomes a mixture that consists of $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ and primarily two isomers of $W(NAr)(ArNH_2)(OR_{F9})_2(\text{propylene})$ (one arbitrary possible structure is shown in eq 6; Figures 3 and S44), according to proton NMR spectra at 22°C . The ratio of isopropylidene to propylene complexes is estimated to be 3:2 through integration of the propylene and isopropylidene methyl resonances. In the propylene isomers the $C=C$ axis and the $W=N$ axis are likely



to be roughly perpendicular to one another, with the propylene methyl group pointing toward or away from the imido group and with alkoxides that are *cis* or *trans* to one another. As in the structure shown in Figure 2, the τ values can be far from zero, characteristic of an ideal square pyramidal complex. Isopropylidene and propylene complexes have essentially the same energy in these mixtures. We propose that this equilibration involves formation of intermediate $W(NAr)(ArNH)(OR_{F9})_2(CHMe_2)$ (eq 6). The fact that no *n*-propylidene complex is observed suggests that the system is under thermodynamic control and that the energy of any *n*-propylidene complex is $>2\text{--}3 \text{ kcal}$ higher than the energy of any isopropylidene or propylene complexes. Addition of ethylene to the 3:2 mixture shown in Figure 3b immediately yields the unsubstituted tungstacyclobutane in 60% yield (via formation of a methylene followed by its reaction with ethylene) and 40% of the tungstacyclopentane complexes (via replacement of propylene by two ethylenes), along with the expected amounts of propylene and isobutene H (eq 7 and Figure S45). Therefore, ethylene can be used as a quench to assay the ratio of alkylidene to alkene complexes. The 3:2 ratio is a measure of the relative amounts of all isopropylidene to all propylidene complexes, four or five-coordinate (adducts). Because we do not know details about the concentrations of four-coordinate versus five-coordinate adducts, a precise determination of the energy differences of isopropylidene versus propylene complexes is not possible.

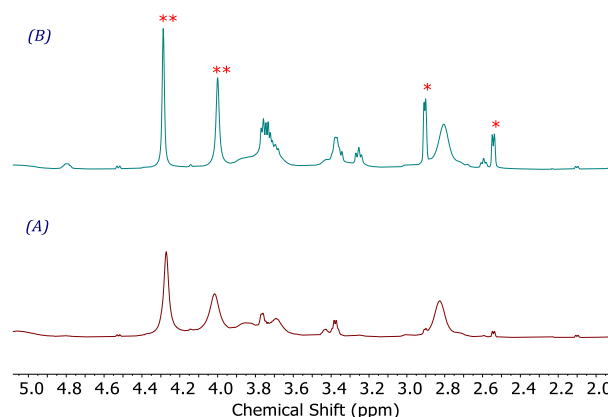
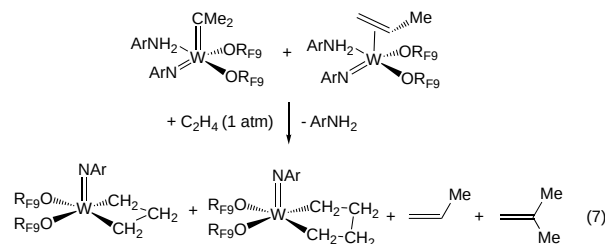


Figure 3. Partial 1H NMR spectrum (22°C) of a mixture of $W(NAr)(ArNH_2)(OR_{F9})_2(\text{propylene})$ and $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$ from $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$; (a) after 10 min; (b) after 6 h (*propylene methyl resonances; **isopropylidene methyl resonances).



The labile $ArNH_2$ can be scavenged from solution through addition of one equivalent of $B(C_6F_5)_3$ to $W(NAr)(ArNH_2)(OR_{F9})_2(CMe_2)$. $ArNH_2B(C_6F_5)_3$ ⁴³ and $W(NAr)(OR_{F9})_2(CMe_2)$ are formed immediately, but

$W(NAr)(OR_{F9})_2(CMe_2)$ then isomerizes in 24 h to yield a mixture of $W(NAr)(OR_{F9})_2(CMe_2)$ and primarily two isomers of $W(NAr)(OR_{F9})_2(propylene)$ in a 1:9 ratio (Figure S46). Equilibration in the presence of $ArNH_2B(C_6F_5)_3$ is faster than equilibration in the absence of $B(C_6F_5)_3$ (eq 6). Therefore, we propose that $ArNH_2B(C_6F_5)_3$ itself can provide the proton that catalyzes that interconversion (see discussion section). (The solid state structure of $ArNH_2B(C_6F_5)_3$ ⁴³ was determined and is shown in Figure S80.) $ArNH_2B(C_6F_5)_3$ is an example of a Lewis acid-activated Brønsted acid,⁴⁴ one that could deliver a proton directly (intermolecularly) to the propylene or isopropylidene ligands, much as anilinium would.

The NAd system

$W(NAd)_2(n-Pr)_2$ and $W(NAd)_2(i-Pr)_2$ (Ad = 1-adamantyl) can be prepared in high purity from $[W(NAd)_2(AdNH_2)Cl_2]_2$ ⁴⁵ and the respective Grignard reagents, although the yields currently are poor (25-30%) under the conditions employed so far. $W(NAd)_2(i-Pr)_2$ crystallizes readily; $W(NAd)_2(n-Pr)_2$ is microcrystalline. The structure of $W(NAd)_2(i-Pr)_2$ (Figure 4) is analogous to that of $W(NAr)_2(i-Pr)_2$ with no evidence for any α or β CH interactions with the metal. Unlike $W(NAr)_2(i-Pr)_2$, $W(NAd)_2(i-Pr)_2$ is unchanged in solution after 24 h; no $W(NAd)_2(i-Pr)(n-Pr)$ is formed.

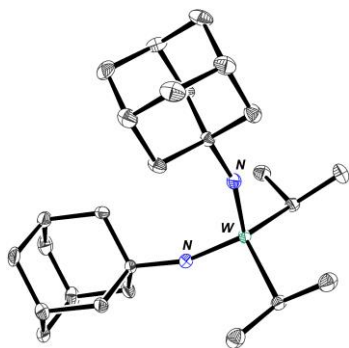


Figure 4. The molecular structure of $W(NAd)_2(i-Pr)_2$ as determined by SCXRD.

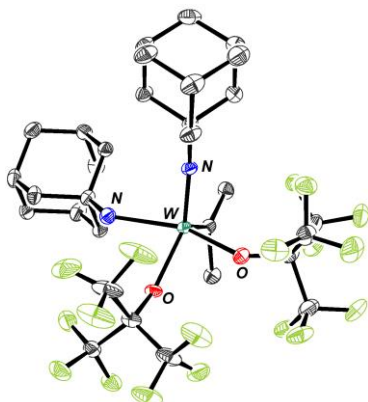


Figure 5. The molecular structure of $W(NAd)(AdNH_2)(OR_{F9})_2(CMe_2)$ as determined by SCXRD.

Both $W(NAd)_2(n-Pr)_2$ and $W(NAd)_2(i-Pr)_2$ react readily with two equivalents of $R_{F9}OH$ to give $W(NAd)(AdNH_2)(OR_{F9})_2(CMe_2)$. Its structure (Figure 5) is closer to a square pyramid ($\tau = 0.24$) with $W-C_{\alpha}-C_{\beta} = 110.8^\circ$ and 134.9° and $W=C = 1.905 \text{ \AA}$. NMR spectra of

$W(NAd)(AdNH_2)(OR_{F9})_2(CMe_2)$ suggest that $AdNH_2$ is not dissociating from the metal on the NMR time scale. $W(NAd)(AdNH_2)(OR_{F9})_2(CMe_2)$ is unchanged in C_6D_6 after one week at 22°C and after heating the solution to 80°C for one hour. Either the isopropylidene complex is simply more thermodynamically stable than the propylene analog or conversion is blocked when the amine is $AdNH_2$. If it is $AdNH_2$ in solution that deprotonates a coordinated $AdNH_2$ (see discussion), $AdNH_3^+$ is probably not acidic enough to protonate the isopropylidene ligand.^{30, 31, 46}

When one equivalent of $B(C_6F_5)_3$ is added to a sample of $W(NAd)(AdNH_2)(OR_{F9})_2(CMe_2)$, $AdNH_2B(C_6F_5)_3$ is formed which then catalyzes conversion of the alkylidene to a mixture of $W(NAd)(OR_{F9})_2(CMe_2)$ ($\sim 15\%$) and primarily two isomers of $W(NAd)(OR_{F9})_2(propylene)$ ($\sim 85\%$) (Figures S68 and S69). These results are comparable to those found for formation of $W(NAr)(OR_{F9})_2(CMe_2)$ and $W(NAr)(OR_{F9})_2(propylene)$ isomers discussed above.

Addition of 1,2-dimethoxyethane (dme) to the mixture of $W(NAd)(OR_{F9})_2(CMe_2)$ and $W(NAd)(OR_{F9})_2(propylene)$ described above allows $W(NAd)(OR_{F9})_2(propylene)(dme)$ to be isolated in low yield. The methyl resonance for the methyl group of the minor propylene isomer (at 253 K) in this sample (at 2.44 ppm; Fig S29) amounts to 11% of the total. Variable temperature NMR spectra (Figure S28) show that coordinated dme exchanges with dme in solution and leads to relatively broad resonances at room temperature.

The crystal of $W(NAd)(OR_{F9})_2(propylene)(dme)$ chosen for SCXRD contains only the isomer in which the methyl group of the propylene ligand is pointed toward the imido ligand and the C-C axis is perpendicular to the W-N axis (Figure 6). The W-C distances are 2.173 $\text{\AA}$ (CHMe) and 2.150 $\text{\AA}$ (CH₂) with a

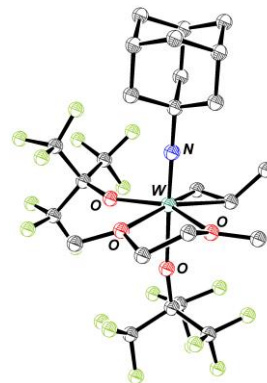
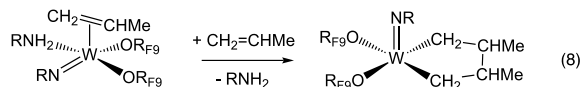


Figure 6. The molecular structure of $W(NAd)(OR_{F9})_2(CH_2=CHMe)(dme)$ as determined by SCXRD.

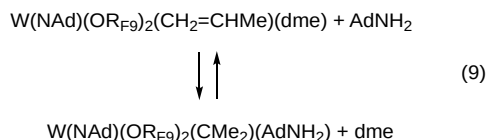
C-C distance of 1.423 $\text{\AA}$. The W-C distances in $W(NAd)(OR_{F9})_2(propylene)(dme)$ are $\sim 0.25 \text{ \AA}$ longer than the W-C distances in $W(NAd)(AdNH_2)(OR_{F9})_2(CMe_2)$ (Fig 5). The structure in Figure 6 should be compared to that for $W(O)(OR_{F6})_2(CH_2=CHMe)py_2$ in which the pyridine ligands are *trans* to one another and the propylene is disordered over two positions with the methyl group pointing up toward (the major isomer) or away from the oxo ligand.¹¹ For one of the propylene ligands in $W(O)(OR_{F6})_2(CH_2=CHMe)py_2$ the W-C distances are 2.206(9) $\text{\AA}$ (CHMe) and 2.19(3) $\text{\AA}$ (CH₂) with a C-C distance of 1.406(11) $\text{\AA}$. To our knowledge the only other reported W(IV) propylene complex in this category is $W(O)(O-2,6-bis-1-adamantylphenoxide)_2(CH_2=CHMe)$ (as a mixture of

two isomers) which was only observed by ^{13}C NMR in solution.¹⁸ In the analogous crystallographically-characterized four-coordinate $\text{W}(\text{O})(\text{O}-2,6\text{-bis-1-adamantylphenoxide})_2(\text{trans-}t\text{-BuCH=CHMe})$ complex, $\text{W-C} = 2.113(4) \text{ \AA}$ ($\text{CH-}t\text{-Bu}$) and $2.148(4) \text{ \AA}$ with $\text{C1-C2} = 1.468(7) \text{ \AA}$.

Addition of propylene (1 atm) to a solution of $\text{W}(\text{NAd})(\text{OR}_{\text{F9}})_2(\text{CH}_2=\text{CHMe})(\text{dme})$ in C_6D_6 leads immediately to formation of the square pyramidal β,β' -disubstituted tungstacyclopentane complex shown in eq 8 ($\text{R} = \text{Ad}$), an analog of crystallographically-characterized $\text{W}(\text{NCPH}_3)(\text{OSiPh}_3)_2(\text{trans-}\beta,\beta'\text{-Me}_2\text{C}_4\text{H}_6)$.²⁵ Square pyramidal β,β' -Disubstituted tungstacyclopentanes made from terminal olefins are the only ones that have been observed.

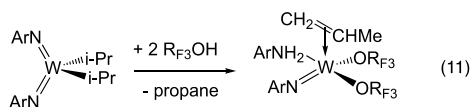
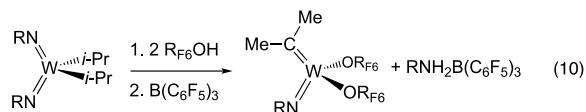


Heating a solution of $\text{W}(\text{NAd})(\text{OR}_{\text{F9}})_2(\text{CH}_2=\text{CHMe})(\text{dme})$ in toluene- d_8 to 40°C for 40 h led to ~10% formation (versus an internal standard) of methyl resonances characteristic of isopropylidene complexes. The same experiment in the presence of one equivalent of AdNH_2 led to formation of approximately 50% $\text{W}(\text{NAd})(\text{AdNH}_2)(\text{OR}_{\text{F9}})_2(\text{CMe}_2)$ relative to dme present in the sample after heating the sample to 40°C (Figures S73 and S74). Interestingly, no $\text{W}(\text{NAd})(\text{AdNH}_2)(\text{OR}_{\text{F9}})_2(\text{CMe}_2)$ is formed when five equivalents of AdNH_2 are added to $\text{W}(\text{NAd})(\text{OR}_{\text{F9}})_2(\text{CH}_2=\text{CHMe})(\text{dme})$ and the solution heated to 40°C .



Other alcohols

Addition of two equivalents of $\text{R}_{\text{F6}}\text{OH}$ to $\text{W}(\text{NAr})_2(i\text{-Pr})_2$ leads to a mixture of $\text{W}(\text{NAr})(\text{ArNH}_2)(\text{OR}_{\text{F6}})_2(\text{CMe}_2)$ and isomers of $\text{W}(\text{NAr})(\text{ArNH}_2)(\text{OR}_{\text{F6}})_2(\text{propylene})$ in a ratio of ~1:10 (vs. ~3:2 in the OR_{F9} system) in C_6D_6 after 24 h at 22°C (Fig S48). The same ratio is observed if $\text{R}_{\text{F6}}\text{OH}$ is added to $\text{W}(\text{NAr})_2(i\text{-Pr})_2$ followed by $\text{B}(\text{C}_6\text{F}_5)_3$ (eq 10, Fig S52).

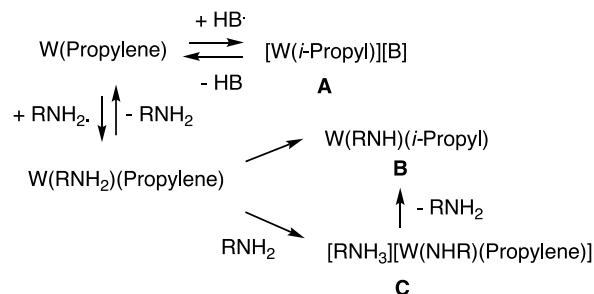


Addition of two equivalents of $\text{R}_{\text{F6}}\text{OH}$ to $\text{W}(\text{NAd})_2(i\text{-Pr})_2$ followed by one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ also forms a mixture of $\text{W}(\text{NAd})(\text{OR}_{\text{F6}})_2(\text{CMe}_2)$ and two isomers of $\text{W}(\text{NAd})(\text{OR}_{\text{F6}})_2(\text{propylene})$ in a ratio of ~1:10 in C_6D_6 after 24 h at 22°C (Fig S64). (Equilibration in the absence of $\text{B}(\text{C}_6\text{F}_5)_3$ is slow and inconclusive in the $\text{NAd}/\text{R}_{\text{F6}}\text{OH}$ system.) Finally, addition of two equivalents of $(\text{CF}_3)\text{Me}_2\text{COH}$ ($\text{R}_{\text{F3}}\text{OH}$) to $\text{W}(\text{NAr})_2(i\text{-Pr})_2$ in C_6D_6 after 24 h led to formation of only a

mixture of propylene complexes (eq 11, Figures S53 and S54). No isopropylidene or n -propylidene complex was observed.

DISCUSSION

Proton transfers in high oxidation state transition metal chemistry that involve imido or amido ligands include the facile interconversion of imido and amido ligands in molybdenum(VI) and tungsten(VI) imido/amido complexes (N_α to N_α H-transfer)³⁵⁻³⁷ and CH activation in alkanes by Ti and Zr imido complexes.⁴⁷ The imido/amido studies³⁵⁻³⁷ focus on the role of ArNH_2 in catalyzing proton movement among imido and amido ligands and the formation of kinetic versus thermodynamic imido/amido complexes as products. A central feature of the proton movement by ArNH_2 in these imido/amido systems was proposed to be the accessibility of a relatively low energy largely ligand-centered nonbonding molecular orbital (LCNBO) that is susceptible to electrophilic attack as a consequence of " π -loading"³⁵⁻³⁷ (>3 significant M-N π interactions). What is accomplished through the proton-catalyzed interconversion of isopropylidene and propylene complexes is the equivalent of a "1,2-H shift" in a bound olefin, which so far has not been directly observed within to our knowledge.⁹ Although we cannot exclude that possibility, the H_{cat} reactions reported here, in our opinion, seem far more likely to be the mechanism (or mechanisms) of interconversion of the propylene and isopropylidene complexes reported here.



Scheme 1. Three plausible mechanisms of forming an isopropyl complex from a propylene complex (HB = an acid/base).

While proton-catalyzed interconversion of propylene and isopropylidene complexes via formation of an isopropyl intermediate seems to be a solid conclusion, the precise mechanisms are uncertain. We can think of three variations which are shown only in terms of forming the isopropyl intermediate in Scheme 1. (The isopropylidene complex is formed in similar reverse reactions of those shown in Scheme 1.) One is transfer of a proton from N to C intramolecularly in the five-coordinate ArNH_2 or AdNH_2 adducts to give an amido/isopropyl complex (**B**) via an unsymmetrical N-H-C transition state that contains a bridging proton.⁴⁸ Formation of $\text{W}(\text{NAr})_2(n\text{-Pr})(i\text{-Pr})$ from $\text{W}(\text{NAr})_2(i\text{-Pr})_2$ discussed in this work is an example of this type of intramolecular mechanism. A second variation seems likely in the case of reactions catalyzed by $\text{RNH}_2[\text{B}(\text{C}_6\text{F}_5)_3]$ that have been observed here, namely a proton bound to N in $\text{RNH}_2[\text{B}(\text{C}_6\text{F}_5)_3]$ is acidic enough to directly protonate a propylene ligand to give **A**, which is analogous to equilibration when the source of H is anilinium and the anion is weakly coordinating.⁴⁴ The resulting anion, $\{\text{RNH}[\text{B}(\text{C}_6\text{F}_5)_3]\}^-$ when $\text{RNH}_2[\text{B}(\text{C}_6\text{F}_5)_3]$ is the source of H may or may not bind to the metal, depending upon the circumstances. In a third variation

some amine in solution deprotonates the coordinated amine in a 16e adduct of a propylene complex to give **C**. Delivery of that proton to the propylene complex to yield the isopropyl complex (**B**) would be possible if the ammonium cation in the intermediate salt is acidic enough.

n-Propylidene complexes should be able to form in a manner similar to the way isopropylidenes are formed, but we have not observed any *n*-propylidene complexes in this work. If *n*-propylidenes were to form, it now seems like they almost certainly would isomerize to isopropylidenes via H_{cat} reactions. Therefore, *n*-propylidenes are likely to be $>2\text{--}3\text{ kcal mol}^{-1}$ higher in energy than isopropylidenes. Formation of what appear to be lower energy, but still metathesis-active, internal or secondary alkylidenes^{41,42} in situations when metathesis-active alkylidenes are formed in classical metathesis systems may have been overlooked for decades. Internal alkylidenes are more difficult to observe in routine NMR spectra, their concentrations may be low, complex mixtures of alkylidene, olefin, and metallacyclopentane complexes could be formed, internal alkylidenes are consumed through metathesis reactions, and olefin isomerization could complicate matters further.

A fundamental problem prevents us from drawing many conclusions concerning the relative energies of various propylene versus isopropylidene complexes that have been observed here. Firstly, equilibria have to be confirmed and measured, which requires that total energy differences between compounds on each side of the equation must be $< 2\text{ kcal mol}^{-1}$. Secondly, binding RNH_2 to one or both propylene and isopropylidene complexes to some unknown degree *itself* involves binding energies of $>2\text{ kcal mol}^{-1}$. Finally, even if labile RNH_2 could be removed completely and instantly from mixtures of adducts, mixtures of four-coordinate propylene and isopropylidene complexes would be formed which we expect can no longer interconvert, and therefore are not at equilibrium. Therefore, we are left with a collection of relatively qualitative results concerning relative energies of various propylene and isopropylidene complexes discussed here.

The only trend that we can propose is that the more electrophilic the metal (which changes with the nature of the alkoxides and imido ligands, coordination number, the nature of donor ligands, etc.), the more isopropylidenes are favored over propylenes as ligands. This trend perhaps largely is a consequence of $W=C$ bonds being $\sim 0.25\text{ \AA}$ shorter than $W-C$ bonds in an olefin complex and π overlap likely being more efficient in a $W=C$ bond than in a $W(\text{olefin})$ bond; thus the lower the electron count and coordination number the more an isopropylidene is preferred. Interestingly, electron-withdrawing alkoxides (*e.g.*, hexafluoro-*t*-butoxides) have long been known to lead to some of the highest metathesis activities, and although there are likely to be several reasons for high metathesis activity, high electrophilicity of the metal is one of them.

It is interesting to note that it has been proposed that cyclohexylidenes can be formed from two cyclohexenes^{28,29} on the basis of H/D exchange reactions at $100\text{ }^\circ\text{C}$ in which *cyclohexene* donates a proton to a second cyclohexene to form a cyclohexyl/cyclohexallyl complex from a bis olefin complex instead of a metallacyclopentane complex.³⁴ So it may turn out that an intramolecular proton source could be an olefin itself if it has an allylic H. The studies that led to the chemistry described here suggests that bound $R_{F6}OH$ or $R_{F9}OH$ can also protonate imido ligands in bisimido complexes and lead to formation of

alkene and alkylidene ligands. Whether an alkoxide could remove or move a proton as efficiently as a nitrogen-based ligand is not known.

CONCLUSIONS

The results reported here are consistent with a proton in RNH_2 or $RNH_2[B(C_6F_5)_3]$ catalyzing interconversion of a propylene and isopropylidene ligand. The three plausible mechanisms (Scheme 1) are intramolecular proton transfers in 16e complexes, protonation by a neutral external acid, or deprotonation by a neutral external base (Scheme 1). The fact that no *n*-propylidenes have been observed suggests that they are higher in energy than isopropylidenes. The principles uncovered here should extend to tungsten alkyl/alkene/alkylidene chemistry that involves larger alkyls, analogous molybdenum chemistry, and analogous oxo alkyl/alkene/alkylidene chemistry. Proton-catalyzed alkene to alkylidene isomerizations may be the way to form alkylidenes from olefins in many classical homogeneous or heterogeneous olefin metathesis systems, but details of mechanisms in the presence of olefins have been obscured by olefin isomerization and especially by facile subsequent metathesis reactions (the desired and relatively rapid reaction) in the majority of circumstances.¹⁰ It remains to be seen to what extent continuous *reformation* of alkylidenes from olefin complexes contributes to catalyst longevity, but how reformation could be demonstrated in the presence of olefins and rapid metathesis is not obvious.

Experimental

General

Unless otherwise stated, all manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Pentane, diethyl ether, dichloromethane, benzene, and toluene were dried and deoxygenated by an argon purge followed by passage through activated alumina in a solvent purification system and storage over $4\text{ \AA}$ molecular sieves. Solvents not containing halogens or nitriles were tested with a standard purple solution of sodium benzophenone ketyl in THF before use. $W(NAr)_2Cl_2(DME)$,⁴⁹ $[W(NAd)_2Cl(\mu-Cl)(H_2NAd)]_2$,⁴⁵ and $ArNH_2B(C_6F_5)_3$ ⁴³ were prepared according to reported procedures. Perfluoro-*t*-butanol and hexafluoro-*t*-butanol were purchased from Oakwood chemical and Alfa chemical respectively and stored over activated $4\text{ \AA}$ molecular sieves. 1,4-TMS benzene, isopropyl magnesium chloride and *n*-propyl magnesium chloride were purchased from Sigma-Aldrich; $B(C_6F_5)_3$ was purchased from Alfa chemical and sublimed before use. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed, and dried over activated $4\text{ \AA}$ molecular sieves for at least 24 h prior to use. NMR spectra were recorded on Bruker Avance 600 MHz and Bruker Avance 500 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. 1,4-TMS benzene (resonances at 7.52 ppm and 0.24 ppm) was the added internal standard in some instances.

Synthesis of $W(NAr)_2(n\text{-Pr})_2$. $W(NAr)_2Cl_2(dme)$ (1.5 g, 2.16 mmol, 1 eq), a magnetic stir bar, and diethyl ether (30 mL) were added to a 125 mL flask. The flask was cooled to $-30\text{ }^\circ\text{C}$ in

glovebox. A -30 °C solution of *n*-propyl magnesium chloride in Et₂O (2 M, 2.2 mL, 4.5 mmol, 2 eq, diluted with 7 mL of Et₂O) was then added dropwise to it and the mixture was allowed to warm to RT and stirred for 3 h. The orange solution immediately turned yellow, and a white precipitate began to form. The solvent was removed *in vacuo* and the crude product was extracted into pentane and the solution was filtered through a plug of Celite. All the volatiles were removed *in vacuo* to give the W(NAr)₂(*n*-Pr)₂ as orange oil; yield 1.1 g (81%). Anal. Calcd for C₂₈H₄₄N₂W: C, 58.06; H, 7.80; N, 4.51. Found C, 57.41; H, 7.87; N, 4.52.

Synthesis of W(NAr)₂(*i*-Pr)₂. The procedure was the same as described for the synthesis of W(NAr)₂(*n*-Pr)₂. Analytically pure product can be obtained as yellow orange crystals via recrystallization from pentane at -30 °C overnight; yield 0.68 g (51%) starting with 1.5 g of W(NAr)₂Cl₂dme. *Note: W(NAr)₂(*i*-Pr)₂ isomerizes to a mixture of W(NAr)₂(*i*-Pr)₂ and W(NAr)₂(*i*-Pr)(*n*-Pr) within 24 h at RT in solution; *t*_{1/2} = 3.5 h.* Anal. Calcd for C₂₈H₄₄N₂W: C, 58.06; H, 7.80; N, 4.51. Found C, 57.71; H, 7.74; N, 4.50.

Synthesis of W(NAr)(ArNH₂)(OR_{F9})₂(CMe₂). W(NAr)₂(*i*-Pr)₂ (0.9 g, 1.45 mmol, 1 equiv), a magnetic stir bar, and pentane (15 mL) were added to a 125 mL flask. The flask was cooled to -30 °C and a cold solution (-30 °C) of R_{F9}OH (0.719 g, 3.05 mmol, 2.1 equiv) in 5 mL of pentane was added dropwise over a period of 3 min. The mixture was warmed to room temperature. After 3.5 h the color of the solution had changed from orange to red. All volatiles were then removed *in vacuo*. The sticky residue were dissolved in diethyl ether (~2 mL). Two batches of orange crystals were obtained by keeping the ether solution in the freezer at -30 °C for two weeks; yield 471 mg, 31 %. Anal. Calcd for WC₃₅H₄₃N₂ (0.2 Et₂O): C, 40.52; H, 4.20; N, 2.63. Found C, 40.98; H, 4.31; N, 2.86. (The amount of ether in this sample was quantitated through proton NMR.)

Synthesis of W(NAd)₂(*n*-Pr)₂. [W(NAd)₂Cl(μ-Cl)(H₂NAd)]₂ (2.50 g, 1.77 mmol) was dissolved in 75 mL of diethyl ether and the solution was cooled to -30 °C. A cooled (-30 °C) solution of 2 M *n*-PrMgCl in 5 mL diethyl ether (3.65 mL, 7.30 mmol, 4.1 eq) was added dropwise. The mixture was stirred at room temperature for 3 h and the solution was evaporated to dryness under reduced pressure. The solid was extracted with pentane and the mixture was filtered through a pad of Celite and the volume of the filtrate reduced to ~5 mL. The solution was cooled to -30 °C overnight and the resulting precipitate was isolated on a glass frit to give the product in 30% yield (0.61 g, 1.1 mmol) as a reddish-tan solid.

Synthesis of W(NAd)₂(*i*-Pr)₂. The procedure was the same as for the synthesis of W(NAd)₂(*n*-Pr)₂ starting with [W(NAd)₂Cl(μ-Cl)(AdNH₂)]₂ (3.24 g, 2.30 mmol) in 100 mL of diethyl ether and 2 M *i*-PrMgCl in 10 mL diethyl ether (4.72 mL, 9.43 mmol, 4.1 eq). The product was obtained in 23% yield (0.60 g, 1.1 mmol) as a tan solid. Crystals suitable for single-crystal X-ray diffraction were grown from a pentane solution at -30 °C.

Synthesis of W(NAd)(OR_{F9})₂(CMe₂)(AdNH₂). W(NAd)₂(*i*-Pr)₂ (564 mg, 0.99 mmol) was dissolved in ~4 mL of pentane and nonafluoro-*tert*-butanol (0.28 mL, 2.0 mmol, 2 eq) was

added dropwise. The resulting dark red solution was stirred for 1.5 h at room temperature, at which point an orange precipitate was observed. The reaction mixture was cooled to -30 °C overnight and the precipitate was collected by filtration on a glass frit to give the title compound in 76% yield (0.75 g, 0.76 mmol) as a light orange powder. Crystals suitable for single-crystal X-ray diffraction were grown from a pentane solution at -30 °C. Anal. Calcd for C₃₁H₃₈F₁₈N₂O₂W: C, 37.37; H, 3.84; N, 2.81. Found: C, 37.81; H, 3.92; N, 2.77.

Synthesis of W(NAd)(OR_{F9})₂(CH₂=CHMe)(dme).

W(NAd)(OR_{F9})₂(CMe₂)(H₂NAd) (500 mg, 0.50 mmol) was dissolved in 30 mL of toluene and B(C₆F₅)₃ (257 mg, 1 equiv) was added as a solution in 10 mL of toluene. The solution was stirred for 1 h at room temperature, the volatiles evaporated under reduced pressure, and the residue then triturated with pentane (3x10 mL). The red residue was dissolved in 12 mL of pentane and the solution was placed in a liquid nitrogen cooled cold well for 20 minutes along with a frit containing Celite. The cloudy solution was filtered through Celite to remove AdNH₂B(C₆F₅)₃ and the filtrate volume was reduced to ~3 mL then again cooled for 10 minutes. The solution was decanted and the supernatant evaporated under reduced pressure. The red residue was dissolved in ~5 mL of DME. The mixture was stirred for 30 min and the volatiles evaporated under reduced pressure. This residue was dissolved in ~2 mL of diethyl ether, and the solution was cooled to -30 °C overnight to give the crystalline product in a 21% yield (98 mg, 0.10 mmol). Anal. Calcd for C₃₅H₃₁F₁₈NO₄W: C, 32.10; H, 3.34; N, 1.50. Found C, 31.95; H, 3.37; N, 1.57.

Conversion of W(NAd)(OR_{F9})₂(dme)(CH₂=CHMe) to W(NAd)(OR_{F9})₂(CMe₂)(AdNH₂). A solution of W(NAd)(OR_{F9})₂(dme)(CH₂=CHMe) (25.0 mg, 26 μmol) in toluene-*d*₈ (0.5 mL) was mixed with 4.0 mg of 1-adamantylamine (26 μmol, 1 eq) and 2.0 mg of 1,4-TMSbenzene as an internal standard and the solution was sealed in a J. Young NMR tube. The solution immediately turned from orange to yellow and was observed at room temperature for 4 days at which point a mixture of isopropylidene and propylene complexes was observed. The solution was heated to 40 °C for a total of 41 h resulting in ~49% conversion to W(NAd)(OR_{F9})₂(CMe₂)(AdNH₂) with respect to DME resonances. (See Figures S73 and S74 in the SI.)

ASSOCIATED CONTENT

Complete NMR data, X-ray data, and details of mechanistic studies.

Accession Codes

CCDC 2419292, 2419294, 2423749, 2423750, 2424113, and 2429145. 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. All synthetic work was carried out by MM and LT. SCXRD studies were carried out by VC.

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References

- (1) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press, 1997.
- (2) Eleuterio, H. S. U.S. Patent 3,074,918. 1963.
- (3) Eleuterio, H. S. Olefin metathesis; chance favors those minds that are best prepared. *J. Molec. Catal.* **1991**, 65, 55–61.
- (4) Banks, R. L.; Bailey, G. C. Olefin Disproportionation; a New Catalytic Process. *Indust. Eng. Prod. Res. Develop.* **1964**, 3, 170–173.
- (5) Schrock, R. R. High Oxidation State Multiple Metal-Carbon Bonds. *Chem. Rev.* **2002**, 102, 145–180.
- (6) Stohr, L.; Fajman, C.; Schowner, R.; Elser, I.; Fuchs, A.; Hauser, P. M.; Bhattacharya, S.; Wang, D. R.; Buchmeiser, M. R. Interconversion Rates and Reactivity of Syn- and Anti-rotamers of Neutral and Cationic Molybdenum and Tungsten Imido Alkylidene N-Heterocyclic Carbene Complexes. *Organometallics* **2023**, 42, 2910–2920.
- (7) Bhattacharya, S.; Ziegler, F.; Wang, D. R.; Frey, W.; Buchmeiser, M. R. Olefin Metathesis and Stereoselective Ring-Opening Metathesis Polymerization with Neutral and Cationic Molybdenum(VI) Imido and Tungsten(VI) Oxo Alkylidene Complexes Containing N-Chelating N-Heterocyclic Carbenes. *Organometallics* **2024**, 43, 677–688.
- (8) Copéret, C.; Comas-Vives, A.; Conley, M. P.; Estes, D. P.; Fedorov, A.; Mougél, V.; Nagae, H.; Nunez-Zarur, F.; Zhizhko, P. A. Surface Organometallic and Coordination Chemistry toward Single-Site Heterogeneous Catalysts: Strategies, Methods, Structures, and Activities. *Chem. Rev.* **2016**, 116, 323–421.
- (9) Schrock, R. R.; Copéret, C. Formation of High-Oxidation-State Metal-Carbon Double Bonds. *Organometallics* **2017**, 36, 1884–1892.
- (10) Marinescu, S. C.; King, A. J.; Schrock, R. R.; Singh, R.; Müller, P.; Takase, M. K. Simple Molybdenum(IV) Olefin Complexes of the Type Mo(NR)(X)(Y)(olefin). *Organometallics* **2010**, 29, 6816–6828.
- (11) Chan, K. W.; Lam, E.; D'Anna, V.; Allouche, F.; Michel, C.; Safonova, O. V.; Sautet, P.; Coperet, C. C-H Activation and Proton Transfer Initiate Alkene Metathesis Activity of the Tungsten(IV)-Oxo Complex. *J. Am. Chem. Soc.* **2018**, 140, 11395–11401.
- (12) Copéret, C.; Berkson, J. Z.; Chan, K. W.; de Jesus Silva, J.; Zhizhko, P. A. Olefin metathesis: what have we learned about homogeneous and heterogeneous catalysts from surface organometallic chemistry? *Chem. Sci.* **2021**, 12, 3092–3115.
- (13) Chan, K. W.; Mance, D.; Safonova, O. V.; Copéret, C. Well-Defined Silica-Supported Tungsten(IV)-Oxo Complex: Olefin Metathesis Activity, Initiation, and Role of Brønsted Acid Sites. *J. Am. Chem. Soc.* **2019**, 141, 18286–18292.
- (14) Yamamoto, K.; Chan, K. W.; Mougél, V.; Nagae, H.; Tsurugi, H.; Safonova, O. V.; Mashima, K.; Copéret, C. Silica-supported isolated molybdenum di-oxo species: formation and activation with organosilicon agent for olefin metathesis. *Chem. Comm.* **2018**, 54, 3989–3992.
- (15) Mougél, V.; Chan, K.-W.; Siddiqi, G.; Kawakita, K.; Nagae, H.; Tsurugi, H.; Mashima, K.; Safonova, O.; Copéret, C. Low Temperature Activation of Supported Metathesis Catalysts by Organosilicon Reducing Agents. *ACS Cent. Sci.* **2016**, 2, 569–576.
- (16) Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. Z-Selective Olefin Metathesis Reactions Promoted by Tungsten Oxo Alkylidene Complexes. *J. Am. Chem. Soc.* **2011**, 133, 20754–20757.
- (17) Peryshkov, D. V.; Schrock, R. R. Synthesis of Tungsten Oxo Alkylidene Complexes. *Organometallics* **2012**, 31 (20), 7278–7286.
- (18) Peryshkov, D. V.; Forrest, W. P.; Schrock, R. R.; Smith, S. J.; Muller, P. B(C₆F₅)₃ Activation of Oxo Tungsten Complexes That Are Relevant to Olefin Metathesis. *Organometallics* **2013**, 32, 5256–5259.
- (19) Conley, M. P.; Mougél, V.; Peryshkov, D. V.; Forrest, W. P.; Gajan, D.; Lesage, A.; Emsley, L.; Coperet, C.; Schrock, R. R. A Well-Defined Silica-Supported Tungsten Oxo Alkylidene Is a Highly Active Alkene Metathesis Catalyst. *J. Am. Chem. Soc.* **2013**, 135, 19068–19070.
- (20) Gani, T. Z.; Berkson, Z. J.; Zhu, R.; Kang, J. H.; Di Iorio, J. R.; Chan, K. W.; Consoli, D. F.; Shaikh, S. K.; Copéret, C.; Román-Leshkov, Y. Promoting active site renewal in heterogeneous olefin metathesis catalysts. *Nature* **2023**, 617, 524–528.
- (21) Blom, B.; Clayton, H.; Kilkenny, M.; Moss, J. R. Metallocycloalkanes - Synthesis, Structure and Reactivity of Medium to Large Ring Compounds *Adv. Organomet. Chem.* **2006**, 54, 149–205.
- (22) McLain, S. J.; Sancho, J.; Schrock, R. R. Metallocyclopentane to Metallocyclobutane Ring Contraction. *J. Am. Chem. Soc.* **1979**, 101, 5451–5453.
- (23) Boudjelel, M.; Riedel, R.; Schrock, R. R.; Conley, M. P.; Berges, A.; Carta, V. Tungstacyclopentane Ring-Contraction Yields Olefin Metathesis Catalysts. *J. Am. Chem. Soc.* **2022**, 144, 10929–10942.
- (24) Rodriguez, J.; Boudjelel, M.; Mueller, L. J.; Schrock, R. R.; Conley, M. P. Ring Contraction of a Tungstacyclopentane Supported on Silica: Direct Conversion of Ethylene to Propylene. *J. Am. Chem. Soc.* **2022**, 144, 18761–18765.

- (25) Schrock, R. R.; Riedel, R.; Maji, M.; Conley, M.; Carta, V. Syntheses of β,β' -Disubstituted Tungstacyclopentanes From Terminal Olefins and Their Conversions to Alkylidenes. *Organometallics* **2023**, *42*, 2038–2051.
- (26) Wood, C. D.; McLain, S. J.; Schrock, R. R. Multiple Metal Carbon Bonds. 13. Preparation and Characterization of Monocyclopentadienyl Mononeopentylidene Complexes of Niobium and Tantalum Including the First Details of an α -Abstraction Process. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.
- (27) Schrock, R. R. Recent Advances in Olefin Metathesis Chemistry. *Chem. Rev.* **2009**, *109*, 3211–3226.
- (28) Freundlich, J.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. Organometallic Complexes of Tantalum That Contain the Triamidoamine Ligand, $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$, Including an Ethylidene Complex Formed via a Phosphine-Catalyzed Rearrangement of an Ethylene Complex. *J. Am. Chem. Soc.* **1994**, *116*, 6476.
- (29) Hirsekorn, K. F.; Veige, A. S.; Marchak, M. P.; Koldobskaya, Y.; Wolczanski, P. T.; Cundari, T. R.; Lobkovsky, E. B. Thermodynamics, Kinetics, and Mechanism of $(\text{silox})_3\text{M}(\text{olefin})$ to $(\text{silox})_3\text{M}(\text{alkylidene})$ Rearrangements (M = Nb, Ta) *J. Am. Chem. Soc.* **2005**, *127*, 4809–4830.
- (30) Liu, S.; Boudjelel, M.; Schrock, R. R.; Conley, M. P.; Tsay, C. Interconversion of Molybdenum or Tungsten d^2 Styrene Complexes with d^0 1-Phenethylidene Analogs. *J. Am. Chem. Soc.* **2021**, *143*, 17209–17218.
- (31) Liu, S.; Schrock, R. R.; Conley, M. P.; Tsay, C.; Carta, V. An Exploration of the Acid-Catalyzed Interconversion of $\text{Mo}(\text{NAr})(\text{CR}1\text{R}2)(\text{OR})_2$ Complexes and Their $\text{Mo}(\text{NAr})(\text{Olefin})(\text{OR})_2$ Isomers (Ar = 2,6-*i*-Pr₂C₆H₃, OR = OSiPh₃ or OAr). *Organometallics* **2023**, *42*, 2251–2261.
- (32) Maji, M.; Riedel, R.; Schrock, R. R.; Conley, M. P.; Carta, V. Syntheses of Tungsten Imido Cyclohexylidene Complexes Using Perfluoro-*t*-butanol or Hexafluoro-*t*-butanol as Acids. *Angew. Chem. Int. Ed.* **2024**, e202410923.
- (33) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.-Y.; O'Donoghue, M. B.; Davis, W. M.; Reiff, W. M. The Synthesis and Decomposition of Alkyl Complexes of Molybdenum(IV) that Contain a $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ Ligand. Direct Detection of α Elimination Processes that are more than Six Orders of Magnitude Faster than β Elimination Processes. *J. Am. Chem. Soc.* **1997**, *119*, 11876–11893.
- (34) Maji, M.; Sousa-Silva, A.; Solans-Monfort, X.; Schrock, R. R.; Conley, M. P.; Farias, P.; Carta, V. Thermal Formation of Metathesis-Active Tungsten Alkylidene Complexes from Cyclohexene. *J. Am. Chem. Soc.* **2024**, *146*, 18661–18671.
- (35) Morrison, D. L.; Rodgers, P. M.; Chao, Y. W.; Bruck, M. A.; Grittini, C.; Tajima, T. L.; Alexander, S. J.; Rheingold, A. L.; Wigley, D. E. Intramolecular vs. Intermolecular α -Hydrogen Abstraction in the Generation of Multiple Imido Complexes: Synthesis, Reactivity, and Structural Studies of the d^0 Tris(imido) Functional Group of Tungsten. *Organometallics* **1995**, *14*, 2435–2446.
- (36) Morrison, D. L.; Wigley, D. E. Multiple-Imido Complexes of Molybdenum: Synthesis and Reactivity of the d^0 $\text{Mo}(=\text{NR})_3$ Functional Group. *Inorg. Chem.* **1995**, *34*, 2610–2616.
- (37) Chao, Y. W.; Rodgers, P. M.; Wigley, D. E.; Alexander, S. J.; Rheingold, A. L. Tris(phenylimido) Complexes of Tungsten: Preparation and Properties of the d^0 $\text{W}(=\text{NR})_3$ Functional Group. *J. Am. Chem. Soc.* **1991**, *113*, 6326–6328.
- (38) Brookhart, M.; Green, M. L. H.; Wong, L. Carbon-Hydrogen-Transition Metal Bonds. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.
- (39) Brookhart, M.; Green, M. L. H.; Parkin, G. L. Agostic Interactions in transition metal compounds. *Proc. Natl. Acad. Sci.* **2007**, *104*, 6908–6914.
- (40) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen-Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate. *Dalton Trans.* **1984**, 1349–1356.
- (41) Taylor, J. W.; Schrock, R. R.; Tsay, C. Molybdenum Disubstituted Alkylidene Complexes. *Organometallics* **2020**, *39*, 658–661.
- (42) Taylor, J. W.; Schrock, R. R.; Tsay, C. Synthesis of Molybdenum Imido 2-Adamantylidene Complexes Through Alpha Hydrogen Abstraction. *Organometallics* **2020**, *39*, 2304–2308.
- (43) Antiñolo, A.; Carrillo-Hermosilla, F.; Fernández-Galán, R.; Martínez-Ferrer, J.; Alonso-Moreno, C.; Bravo, I.; Moreno-Blázquez, S.; Salgado, M.; Villaseñor, E.; Albaladejo, J. Tris(pentafluorophenyl) borane as an efficient catalyst in the guanylation reaction of amines. *Dalton Trans.* **2016**, *45*, 10717–10729.
- (44) Yamamoto, H.; Kentaro, F. “Designer Acids”: Combined Acid Catalysis for Asymmetric Synthesis. *Angew. Chem. Int. Ed.* **2005**, *44*, 1924–1942.
- (45) Jeong, H.; Axtell, J.; Török, B.; Schrock, R. R.; Müller, P. Syntheses of Tungsten *t*-Butylimido and Adamantylimido Alkylidene Complexes Employing Pyridinium Chloride as the Acid. *Organometallics* **2012**, *31*, 6522–6525.
- (46) Liu, S.; Schrock, R. R.; Conley, M. P.; Carta, V. Formation of a Molybdenum Alkylidene from 1,7-Octadiene via Rearrangement of an 8-Molybdabicyclo[4.3.0]nonane. *Organometallics* **2023**, *42*, 2321–2325.
- (47) Wolczanski, P. T. Activation of carbon–hydrogen bonds via 1, 2-RH-addition/-elimination to early transition metal imides. *Organometallics* **2018**, *37*, 505–516.
- (48) Wolczanski, P. T. Activation of Carbon–Hydrogen Bonds via 1,2-RH-Addition/Elimination to Early Transition Metal Imides. *Organometallics* **2018**, *35*, 505–516.
- (49) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; *et al.* Further Studies of Imido Alkylidene Complexes of Tungsten, Well-Characterized Olefin Metathesis Catalysts with Controllable Activity. *Organometallics* **1990**, *9*, 2262–2275.

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