Interconversion of Molybdenum or Tungsten d^2 Styrene Complexes with d^0 1-Phenethylidene Analogs

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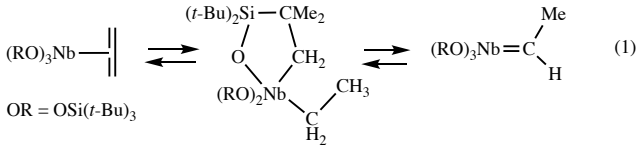
ABSTRACT: Upon addition of 5-15% $PhNMe_2H^+X^-$ (X = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$ or $B(C_6F_5)_4$) to Mo(NAr)(styrene)$(OSiPh_3)_2$ (Ar = N-2,6-*i*-$Pr_2C_6H_3$) in C_6D_6 an equilibrium mixture of Mo(NAr)(styrene)$(OSiPh_3)_2$ and Mo(NAr)(CMePh)$(OSiPh_3)_2$ is formed over 36 h at 45 °C (K_{eq} = 0.36). A plausible intermediate in the interconversion of the styrene and 1-phenethylidene complexes is the 1-phenethyl cation, $[Mo(NAr)(CHMePh)(OSiPh_3)_2]^+$, which can be generated using $[(Et_2O)_2H][B(C_6F_5)_4]$ as the acid. The interconversion can be modeled as two equilibria involving protonation of Mo(NAr)(styrene)$(OSiPh_3)_2$ or Mo(NAr)(CMePh)$(OSiPh_3)_2$ and deprotonation of the α or β phenethyl carbon atom in $[Mo(NAr)(CHMePh)(OSiPh_3)_2]^+$. The ratio of the rate of deprotonation of $[Mo(NAr)(CHMePh)(OSiPh_3)_2]^+$ by $PhNMe_2$ in the α position versus the β position is ~10, or ~30 per H_β. The slow step is protonation of Mo(NAr)(styrene)$(OSiPh_3)_2$ (k_1 = 0.158(4) L/mol·min). Proton sources such as $(CF_3)_3COH$ or Ph_3SiOH do not catalyze the interconversion of Mo(NAr)(styrene)$(OSiPh_3)_2$ and Mo(NAr)(CMePh)$(OSiPh_3)_2$, while the reaction of Mo(NAr)(styrene)$(OSiPh_3)_2$ with pyridinium salts generates only a trace (~2%) of Mo(NAr)(CMePh)$(OSiPh_3)_2$ and forms a monopyridine adduct, $[Mo(NAr)(CHMePh)(OSiPh_3)_2(py)]^+$ (two diastereomers). The structure of $[Mo(NAr)(CHMePh)(OSiPh_3)_2]^+$ has been confirmed in an X-ray study; there is no structural indication that a β proton is activated through a CH_β interaction with the metal. W(NAr)(CMePh)$(OSiPh_3)_2$ is also converted into a mixture of W(NAr)(CMePh)$(OSiPh_3)_2$ and W(NAr)(styrene)$(OSiPh_3)_2$ (K_{eq} = 0.47 at 45 °C in favor of the styrene complex) with 10% $[PhNMe_2H][B(C_6F_5)_4]$ as the catalyst; the time required to reach equilibrium is approximately the same as in the Mo system.

INTRODUCTION

The olefin metathesis reaction was discovered during a search for new heterogeneous olefin polymerization catalysts prepared through deposition of tungsten (or Mo or Re) oxides on silica (or alumina or other oxides).[1] Over a period of 45 years the syntheses of high oxidation state d^0 alkylidene complexes of Ta, Mo, W, and Re have led to an understanding of how (primarily Mo and W) homogeneous complexes metathesize olefins[2,3] via the metallacyclobutane mechanism first proposed by Chauvin in 1971.[4] The experimental studies have been accompanied by many theoretical studies.[5] Significant progress has also been made in understanding heterogeneous metathesis catalysts through surface organometallic chemistry (SOMC).[6]

One of the mysteries that remains unresolved in high oxidation state Mo and W alkylidene chemistry, both classic and modern, is how alkylidenes are formed from metal oxides and simple acyclic olefins.[7] (Formation of alkylidenes from cyclopropenes[8] should be regarded as a special case of Lewis acid initiated cyclopropene ring-opening.) To our knowledge no metathesis-active Mo(VI) or W(VI) alkylidene formed from a simple olefin has been identified and the mechanism of its formation established. There is a growing body of evidence showing that metathesis-active high oxidation state Mo or W alkylidene metathesis initiators are formed from d^2 olefin complexes in homogeneous[9a,b] or SOMC systems.[9c,d] The ability to generate d^0 alkylidenes from d^2 olefin complexes under mild conditions could lead to improved catalyst lifetimes if regeneration could be accomplished continuously, a possibility that is likely to be a reality in some circumstances such as the high temperature synthesis of propylene from ethylene and butenes.[10]

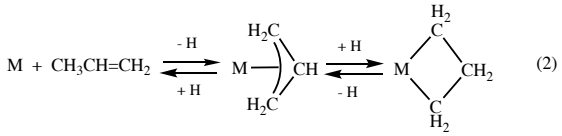
A top contender in terms of a mechanism through which a Mo or W alkylidene complex is formed from an olefin in homogeneous or heterogeneous metathesis catalyst systems[7] is some form of "H-assisted" rearrangement. Two examples outside of Mo and W chemistry are conversion of a tantalum ethylene complex into an ethylidene complex[11] with a $PhPH_2$ catalyst, and conversion of a large variety of $(RO)_3M$(olefin) complexes (OR = OSi(*t*-Bu)$_3$; M = Nb or Ta) into $(RO)_3M$(alkylidene) isomers[12] at high temperatures through formation of an alkyl intermediate, with the H arising via CH activation in the siloxide ligand. (An example is shown in equation 1.) A C-to-C 1,2-proton shift in an olefin is a type of reaction that has been proposed since the early days of metathesis as the origin of an alkylidene.[1d,e] Intramolecular (direct) or intermolecular (indirect) movement of a proton between C- and N-based ligands that are singly, doubly, or triply bound to d^0 early metal centers has considerable precedent in organometallic chemistry that is relevant to olefin metathesis.[3,13-16]



(1)

A second plausible mechanism is formation of an allyl complex from an olefin that contains one or more allylic protons and conversion of that allyl into a M(VI) metallacyclobutane complex through readdition of the H to the central carbon atom

(shown schematically in equation 2 for propene).[6e] Whether that H is best viewed as a proton or a hydride and where it resides in the allyl complex (on the metal or on a ligand) are not known. It is often proposed that H resides on the metal, *i.e.*, the intermediate is a π allyl hydride complex.

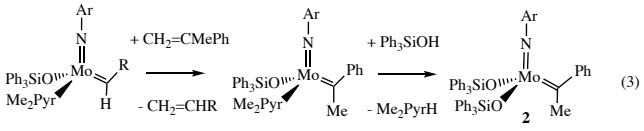


A third plausible mechanism involves formation of a metallacyclopentane complex that can contract to metallacyclobutane complex or rearrange to an olefin that contains an allylic CH bond through a β hydride elimination process.[17]

Rare d^2 olefin complexes of the type Mo(NAr)(olefin)(X)(Y) (X and Y are monoanions) were prepared in 2010.[9b] One is Mo(NAr)(styrene)$(OSiPh_3)_2$ (**1**), a 2:1 mixture of isomers. In the isomer of **1** that was structurally characterized the phenyl group points "up" toward the imido ligand. The *internal* alkylidene analog of the styrene complex would be Mo(NAr)(CMePh)$(OSiPh_3)_2$, a disubstituted alkylidene analogous to several that have been prepared through addition of CH_2=CMePh to Mo=CHCMe$_2$Ph complexes.[18] The *terminal* alkylidene analog of the styrene complex would be Mo(NAr)(CHCH$_2$Ph)$(OSiPh_3)_2$. Because styrene does not contain an allylic proton, we set out to make Mo(NAr)(CMePh)$(OSiPh_3)_2$ (**2**) and explore conditions that might interconvert **1** and **2**.

Results

Molybdenum Studies. Mo(NAr)(CMePh)$(OSiPh_3)_2$ (as a ~28:1 mixture of two alkylidene isomers at 22 °C) was prepared in 49% yield overall as shown in equation 3 (R = CMe$_2$Ph); intermediate Mo(NAr)(CMePh)$(OSiPh_3)$(2,5-dimethylpyrrolide) was not isolated. An X-ray study showed that the structure of **2** (Figure 1) is analogous to that of Mo(NAr)(CMePh)(OMesityl)$_2$[18] with the Mo(1)-N(1) vector lying in the Mo(1)C(1)C(2)(C3) plane of the alkylidene ligand. This structure is consistent with it also being the dominant isomer in solution, according to NOESY studies (Figure S6). The alkylidene is "distorted" with the Mo(1)-C(1)-C(2) angle being 102.67(7)° and the Mo(1)-C(1)-C(3) angle being 138.73(8)°. This distortion is also found in Mo(NAr)(CMePh)(OMesityl)$_2$.[18] The Mo=C distance is 1.9016 (10) Å, which is essentially the same as in Mo(NAr)(CMePh)(OMesityl)$_2$ (1.905(1) Å) and Mo(NAr)(CMePh)(Pyrrolide)(O-2,6-Mesityl$_2$C$_6$H$_3$) (1.903(3) Å).[18]



Interconversion of terminal alkylidene *syn* and *anti* isomers through rotation about the M=C bond has been a topic of interest since the first extensive study in 1993.[19] *Syn* and *anti* isomers have different reactivities and therefore can play an intimate role in selectivities in metathesis reactions. Mo(NAr)(CMePh)$(OSiPh_3)_2$ (**2**) is stable at 45 °C in C_6D_6 for many hours. A van't Hoff plot for the equilibrium between the minor and major isomers (methyl *cis* to NAr and methyl *trans* to NAr) of Mo(NAr)(CMePh)$(OSiPh_3)_2$ (**2**) between 19.4 °C and 90.5 °C shows that ΔH = -2.9(2) kcal mol^{-1} and ΔS = -3.4(7) cal mol^{-1} K^{-1} for conversion of the minor isomer to the major isomer found in the solid state (see Figure 1 and SI). Preliminary studies described in the SI suggest that the isomers interconvert at a rate of ~10^{-2} s^{-1} or less at room temperature. This rate is comparable to rates for interconversion of *syn* and *anti* neopentylidene and neophylidene complexes, although those rates vary significantly with the nature of the alkoxide in bisalkoxide imido alkylidene complexes.

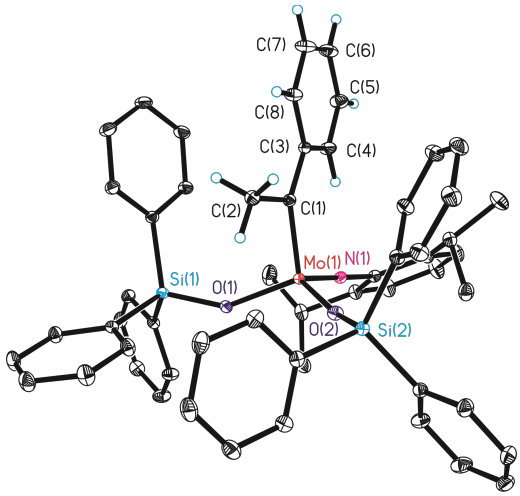


Figure 1. The structure of Mo(NAr)(CMePh)$(OSiPh_3)_2$. Ellipsoids are drawn at the 35% probability level.

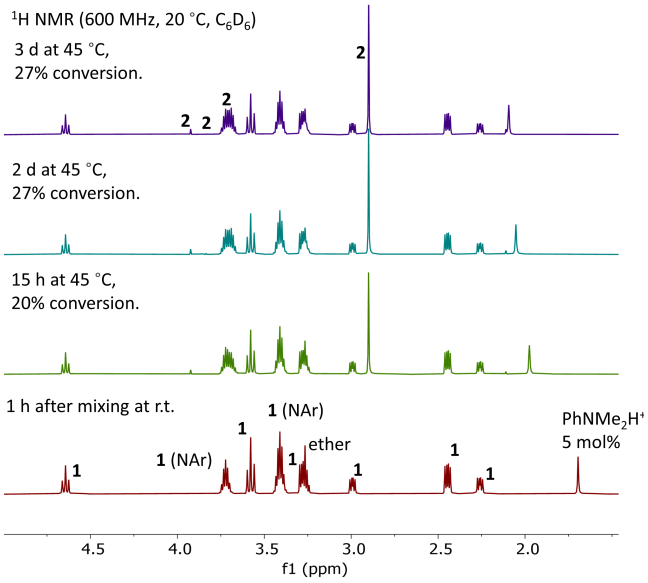


Figure 2. Proton NMR spectra of a typical conversion from **1** to an equilibrium mixture of two isomers of **1** and **2**.

Eight resonances are found between 2.1 and 4.7 ppm in the proton NMR spectrum of **1** (Figure 2, bottom); six triplet or double doublet resonances are ascribed to the two styrene isomers and two septets to NAr methine resonances in the two isomers.[9b] (The methylene resonance in a trace of diethyl ether overlaps the double doublet resonance near 3.28 ppm in the spectrum in Figure 2.) Upon addition of [PhNMe$_2$H][BAr$^F_4$] (5 mol%; BAr$^F_4$ = B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$) to a solution of **1** in C_6D_6 a methyl resonance for the major isomer of **2** grows in at 2.91

ppm in the proton NMR spectrum along with the NAr methine resonance at 3.72 ppm (Figure 2) and a disubstituted alkylidene carbon resonance at 264 ppm in the ^{13}C NMR spectrum. The methyl resonance in $[PhNMe_2H]^+$ also moves downfield from ~1.69 to ~2.10 ppm (Figure 2), even after a 27% conversion is reached. $[PhNMe_2H][B(C_6F_5)_4]$ is the preferred acid, as the $B(C_6F_5)_4$ anion appears to be more stable than $[BAr^F_4]^-$ to degradation under the reaction conditions. The equilibrium can be approached from either Mo(NAr)(styrene)$(OSiPh_3)_2$ or Mo(NAr)(CMePh)$(OSiPh_3)_2$. A van't Hoff plot between 21.5 and 55 °C (Figure 3) shows ΔH = 1.0(3) kcal mol^{-1} and ΔS = 1.2(9) cal mol^{-1} K^{-1} for conversion of **1** or **2** to the equilibrium mixture of isomers of **1** and **2**; at 298 K ΔG = 0.6 kcal mol^{-1}, with the styrene complex being lower in energy. Movement of the methyl resonance in $[PhNMe_2H]^+$ during the approach to and after equilibrium is reached (Figure 2) suggests that $[PhNMe_2H]^+$ is largely converted into $PhNMe_2$ during the conversion through some irreversible side reaction or reactions at a rate that is somewhat less than the rate of formation of the equilibrium mixture.

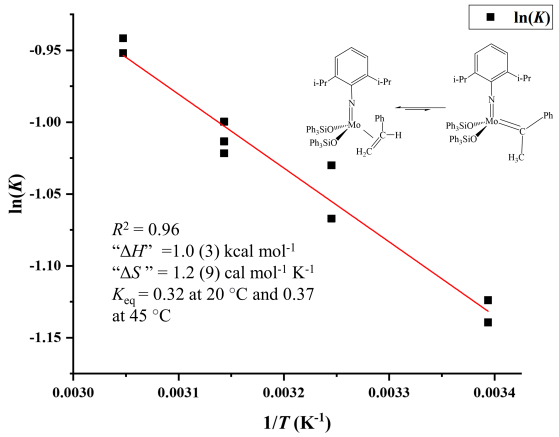
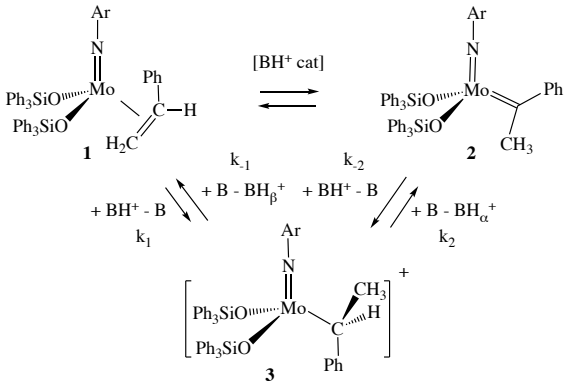


Figure 3. van't Hoff plot for the equilibrium between Mo(NAr)(styrene)$(OSiPh_3)_2$ (**1**) and Mo(NAr)(CMePh)$(OSiPh_3)_2$ (**2**).



Scheme 1. A mechanism of interconverting **1** and **2**.

A proposed mechanism of the dimethylanilinium-catalyzed 1,2-proton shift is shown in Scheme 1. The key intermediate is the cationic 12e 1-phenethyl complex **3**. Complex **3** is formed through protonation of either **1** or **2** and is consumed through deprotonation by the conjugate base ($PhNMe_2$) in the β position to form **1** or in the α position to form **2**. There is no evidence for formation of any $PhNMe_2$ adduct of **3**, as found when pyridinium is the acid (see later). We propose that N in the imido group and O in the Ph_3SiO group are protected against a *significant* amount (>5%) of destructive and *irreversible* protonations by $PhNMe_2H^+$ because of steric crowding and the relatively low basicity of these N and O sites. (The observed slow consumption of $PhNMe_2H^+$ may be the result of destructive protonations.) It is not possible at this stage to know if the protonation sites are the kinetic sites or the thermodynamic sites; we assume for now that they are the kinetic sites. 1-Phenyl complexes are virtually unknown in the literature; a cationic 1-phenethyl complex of Pt(II) was found to have an η^3-benzallylic structure.[20]

Cation **3** can be prepared through addition of $[(Et_2O)_2H][B(C_6F_5)_4]$ to Mo(NAr)(CMePh)$(OSiPh_3)_2$ and isolated as a microcrystalline solid. It is relatively stable under N_2 in the solid state at room temperature but slowly decomposes in solution. The α proton resonance in **3** is found at 4.52 ppm with J_{CH} = 143 Hz and the α carbon resonance at 99.2 ppm in C_6D_6. The β proton (CH*Me*Ph)resonance is found at 2.07 ppm with J_{CH} = 133 Hz and the β carbon resonance at 20.68 ppm in C_6D_6. NMR spectra are consistent with **3** not containing a mirror plane, *i.e.*, two different NAr isopropyl methyl groups and two different $OSiPh_3$ groups are observed. Cation **3** can be observed in small amounts when up to 0.15 equivalents of $PhNMe_2H^+$ are added to **2** (Figures S37-S39). Addition of larger amounts of acid are relatively destructive and it has not been possible to obtain a reliable K_{eq} value for $PhNMe_2H^+$ plus **2** to give **3** plus $PhNMe_2$. Only a small amount of **3** is formed, which suggests that **3** is considerably more acidic than $PhNMe_2H^+$.

Three separate attempts to obtain a crystal of **3** for an X-ray study yielded three crystals of the double salt, $[Mo(NAr)(CHMePh)(OSiPh_3)_2][H_3O][B(C_6F_5)_4]_2 \cdot 1.5$(solvent), where the solvent is a disordered mixture of pentane and dichloromethane. The source of the water for formation of the $[H_3O]^+$ ion is not known (see SI); one possibility is that Ph_3SiOH is formed through some significant decomposition and is converted to $(Ph_3Si)_2O$ and water. Another possibility is that the $[H_3O]^+$ ion is formed from traces of water during the long periods required for obtaining crystals. Only crystals of $[Mo(NAr)(CHMePh)(OSiPh_3)_2][H_3O][B(C_6F_5)_4]_2 \cdot 1.5$(solvent) have been obtained so far, in low yield, and after an extended period.

The third X-ray solution of the double salt is of publishable quality; a drawing of the Mo cation is shown in Figure 4. The phenyl, methyl, and H on the phenethyl α carbon atom interdigitate between the two sterically demanding $OSiPh_3$ groups and NAr group, with the phenyl group in the phenethyl ligand pointing away from the NAr group. The Mo-C(1) bond (2.098(4) Å) is ~0.2 Å longer than the Mo=C bond in **2** (1.9016(10) Å), while the Mo-C-C angles are 97.9(3)° (Mo-C(1)-C(3)) and 112.8(3)° (Mo-C(1)-C(3)). The methine proton on C(1) was located and refined, but the error in its position is naturally relatively large (Mo-C(1)-H = 103(3)°). The only other crystallographically characterized Mo(VI) alkyl cation of this type of which we are aware is $[Mo(NAr)(CH_2CMe_2Ph)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]^+$,[21] in which Mo-C = 2.113(4) Å and Mo-C-C = 110.1(3)°. No other secondary alkyl (cationic or not) of Mo(VI) has been reported as far as we know. The relatively large Mo-C(1)-C(3) angle (112.8(3)°) suggests that there is no classic β agostic CH interaction in the methyl group, while the relatively small Mo-C(1)-H angle (103(3)°) may provide a hint as to why the α proton is removed more readily than a β proton by $PhNMe_2$ or Et_3N (see

Discussion section below). At this stage we have no reason to propose that rotation about the M-C bond in **3** is slower than the chemical time scale, although it should be noted that rotamers of an isopropyl group in niobium(V) complexes that have agostic CH interactions, according to structural studies, have been detected in low temperature NMR studies and the barriers between rotamers have been found to be of the order of ~10-20 kcal mol^{-1}.[22]

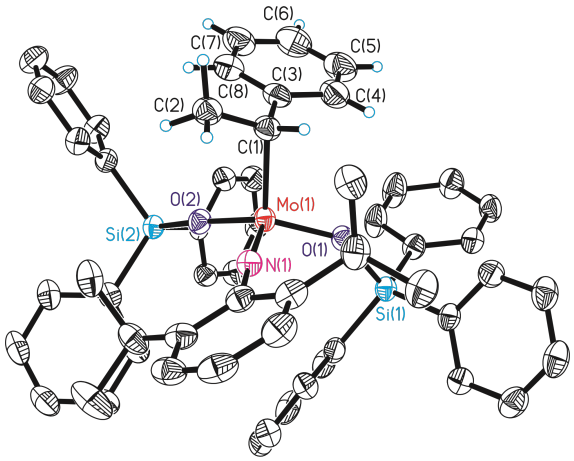


Figure 4. A drawing of [Mo(NAr)(CHMePh)(OSiPh$_3$)$_2$]$^+$. Ellipsoids are drawn at the 35% probability level.

Cation **3** is deprotonated by 10 equivalents of dimethylaniline at 22 °C to give a mixture of **2** and **1** in a ratio of ~10:1, which is the ratio of k_2 (α deprotonation; Scheme 1) to k_{-1} (β deprotonation) (Figures S51-52). Therefore, the α proton in **3** is removed ~30 times faster than any given β proton is removed. Dramatically faster α *elimination* in Mo(IV) and W(IV) complexes to give alkylidene hydrides have been noted in systems that are not metathesis active,[23] but formation of an alkylidene hydride from an alkyl through α elimination is not equivalent to deprotonation of a cationic alkyl by an external base. In contrast, deprotonation of **3** with 2 equiv of NEt$_3$ yields a k_2/k_{-1} of ~4 and no further change in the resulting mixture of **1** and **2** (Figures S53), consistent with the finding that Et$_3$NH$^+$ is not a catalyst for interconversion of **1** and **2**. The significantly faster rate of removing the α proton from **3** also suggests that the rate-limiting step for the isomerization of **1** to **2** is protonation of **1** to form **3**, as found in modeling studies (see below).

We explored triphenylphosphine as a base knowing that the pK$_a$ of Ph$_3$PH$^+$ in water is 2.7[24] and that PPh$_3$ is unlikely to bind to **3** for steric reasons. Addition of ~2 equivalents of PPh$_3$ to [Mo(NAr)(CHMePh)(OSiPh$_3$)$_2$]$^+$ in C$_6$D$_6$ generates an isomerization-inactive mixture that contains **2** and [Mo(NAr)(CHMePh)(OSiPh$_3$)$_2$]$^+$ in a ratio of 16:1 (see Figure S54). These results suggest that the phenethyl α proton in [Mo(NAr)(CHMePh)(OSiPh$_3$)$_2$]$^+$ is removed more readily than the proton from PPh$_3$H$^+$.

The conversion of **1** to **3** and **3** to **2**, and the reverse, as shown in Scheme 1, can be modeled using the COPASI simulation program.[25] (The amounts of PhNMe$_2$ and PhNMe$_2$H$^+$ are determined through the average chemical shift of the aniline/anilinium methyl group during the conversion; see Figure 2. A description of the simulation can be found in the SI.) A reliable value for k_1 can be determined; at 20 °C k_1 = 0.158(4) L/mol·min. Other values obtained are k_{-1} = 117(11) L/(mol·min), k_2 = 1460(240) L/(mol·min) and k_{-2} = 7.7(1.6) L/(mol·min). The resulting K_{eq} = 0.26(7) and k_2/k_{-1} = 12(2) match the experimental values within experimental error. Another simulation of a less accurate run (a consequence of it being a more dilute sample) yielded k_1 = 0.156(4) L/mol·min, k_{-1} = 87(23) L/(mol·min), k_2 = 2840(940) L/(mol·min), k_{-2} = 16.6(7.0) L/(mol·min), K_{eq} = 0.31(18) and k_2/k_{-1} = 33(14). More accurate determinations of rate constants other than k_1 are not possible with the experimental data available at this time. Including both Mo(styrene) isomers and both Mo=CMePh isomers in the model also is not viable at this stage. (See SI, section 7.) Finally, attempts to model the reaction between **2** and acid to give the equilibrium mixture is not possible because protonation of the alkylidene is too fast to follow using routine NMR methods (see SI).

The analogous reaction between Pyridinium$^+$ and **1** gives an amount of **2** that is only barely detectable by proton NMR (1-2%) in 2 days at 45 °C even though the pK$_a$ of PhNMe$_2$H$^+$ (5.1)[26] and that of PyH$^+$ (5.2)[27] in water are comparable. Addition of one equivalent of PyH$^+$ to **2** leads to formation of what we propose to be two diastereomers of 14e [Mo(NAr)(CHMePh)(OSiPh$_3$)$_2$(py)]$^+$ (**3**(py)), according to a proton NMR spectrum that contains two doublets (at 2.02 and 2.12 ppm) for the methyl proton in the 1-phenethyl group in the two diastereomers of a complex that contains *cis* OSiPh$_3$ ligands (Figure S40). Therefore essentially no PyH$^+$ or pyridine is in solution to catalyze the conversion of **1** to **2** via **3** at a significant rate. A sterically demanding acid and relatively poorly coordinating conjugate base therefore seem to be required for an efficient conversion of **1** to **2**. As noted above, triethylammonium is simply too weak an acid to protonate either **1** or **2** and therefore is not a catalyst for their interconversion. Triethylamine, (CF$_3$)$_3$COH, and Ph$_3$SiOH all were inactive for conversion of **1** to a mixture of **1** and **2**.

Tungsten Studies. An important question is whether tungsten complexes analogous to **1** and **2** can be equilibrated in a similar manner. Neither W(NAr)(CMePh)(OSiPh$_3$)$_2$ nor W(NAr)(styrene)(OSiPh$_3$)$_2$ is known. W(NAr)(CMePh)(OSiPh$_3$)$_2$ (**4**) can be prepared in a manner analogous to that shown for Mo in equation 3 and isolated as orange crystals. It also consists of a ~30:1 mixture of two isomers with J_{CW} = 183 Hz for the alkylidene α carbon atom (δ C$_\alpha$ = 231.6 ppm). As far as we are aware, **4** is the only tungsten(VI) imido alkylidene complex in which the alkylidene is disubstituted although tungsten oxo 2-adamantylidene complexes have been isolated recently.[28] We have not yet found a route to W(NAr)(styrene)(OSiPh$_3$)$_2$. Tungsten imido olefin complexes are rare; examples are W(NAr$_{Cl2}$)(C$_2$H$_4$)(Biphenoxide)(THF) (Ar$_{Cl2}$ = 2,6-Cl$_2$C$_6$H$_3$),[29] W(NPh)(olefin)[1,2-(TMSN)$_2$C$_6$H$_4$](PMe$_3$)$_2$ (olefin = ethylene, propylene, styrene),[30a] and W(N-*t*-Bu)(OSi-*t*-Bu$_3$)$_2$(C$_2$H$_4$).[30b]

Upon addition of 10 mol% of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] to W(NAr)(CMePh)(OSiPh$_3$)$_2$ the acid is partially consumed immediately to give a mixture of W(NAr)(CMePh)(OSiPh$_3$)$_2$ and [W(NAr)(CHMePh)(OSiPh$_3$)$_2$][B(C$_6$F$_5$)$_4$] (**5**). If this mixture is heated to 45 °C for two days an equilibrium mixture of W(NAr)(styrene)(OSiPh$_3$)$_2$ (which has an eight multiplet pattern for two isomers similar that found in the Mo analog) and W(NAr)(CMePh)(OSiPh$_3$) (**4**) is generated with K_{eq} = 0.47 = [W(NAr)(CMePh)(OSiPh$_3$)$_2$/[W(NAr)(styrene)(OSiPh$_3$)$_2$] (see SI). Neither isomer of W(NAr)(styrene)(OSiPh$_3$)$_2$ has yet been

isolated from the equilibrium mixture, but extensive NMR correlation experiments (see SI), and the similarities in NMR spectra of the equilibrium mixture (Figure S47) with those shown in Figure 2 leave no doubt that two W(NAr)(styrene)$(OSiPh_3)_2$ isomers are formed in the equilibrium mixture.

Addition of 1.0 equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ to W(NAr)(CMePh)$(OSiPh_3)_2$ in C_6D_6 generates a mixture that contains 65% W(NAr)(CMePh)$(OSiPh_3)_2$ and $PhNMe_2$ (K_{eq} = [**4**][$PhNMe_2H^+$]/[**5**][$PhNMe_2$] = 3.5). This experiment reveals that the pK_a of **5** is only slightly less than that of $PhNMe_2H^+$ (which is ~5.1 in water), in contrast to the much lower pK_a for **3** (<2.7; see above).

The addition of 0.85 equivalents of $[(Et_2O)_2H][B(C_6F_5)_4]$ to W(NAr)(CMePh)$(OSiPh_3)_2$ yields [W(NAr)(CHMePh)$(OSiPh_3)_2$][$B(C_6F_5)_4$] (**5**), the analog of **3**, which was isolated as a yellow solid. The α proton resonance in the phenethyl ligand is found at 4.93 ppm and the α carbon resonance at 89.8 ppm at 243 K with $^1J_{CH}$ = 137 Hz and $^1J_{CW}$ = 104 Hz (*cf.* 4.52 ppm, 99.2 ppm, and 143 Hz, respectively, for **3**). Addition of two equivalents of NEt_3 to **5** generates only **4**, consistent with $k_2 >> k_{-1}$; also no isomerization to give W(NAr)(styrene)$(OSiPh_3)_2$ isomers was observed over the course of 24 h.

It has not been possible to model the conversion of **4** to the equilibrium mixture of tungsten complexes. (The Mo system also could not be modeled starting with **2**, as noted above.) We hope to be able to abstract information analogous to that obtained in the Mo system once we have W(NAr)(styrene)$(OSiPh_3)_2$ in hand. However, the time frame for formation of the equilibrium mixture of tungsten complexes, the similarity of the equilibrium constant so obtained with that found for Mo complexes, and the isolation and deprotonation of the 1-phenethyl cation together strongly suggest that the mechanism of forming the equilibrium mixture of tungsten complexes is analogous to that proposed for the Mo system (Scheme 1). Therefore, we expect that the rate-limiting step in the tungsten system is also protonation of W(NAr)(styrene)$(OSiPh_3)_2$ to give **5**. The similarities between the Mo and W systems are striking.

Discussion

It is instructive to view the proposed mechanism of interconverting the styrene and phenethylidene complexes in terms of a free energy diagram (shown for Mo in Figure 5). We will assume that a diagram for the W-catalyzed reaction is similar with exception of the energy level for the phenethyl cation (see below). Several issues that are ignored for now are isomers of both the styrene complex and the phenethylidene complex. The major and minor isomers of the styrene complexes are close in energy, but the isomers of the phenethylidene complexes differ in energy by ~2 kcal. We also cannot address the possible role of cationic phenethyl rotamers and how deprotonation of the cation might depend upon what rotamers are present and the time scale for interconversion of rotamers[22] versus deprotonation. These are all topics for future investigations.

We know that a styrene complex is slightly more stable than a phenethylidene complex. We also know for Mo that the highest barrier is the protonation of the styrene complex (k_1 = 0.158(4) L/mol·min) to give the phenethyl cation and that the energy of TS2 is lower than TS1 ($k_2 > k_{-1}$). The energy of the Mo phenethyl cation appears to be higher than that of the Mo phenethylidene complex, as shown in Figure 5, but the energy of the W phenethyl cation is about the same as that of the W phenethylidene complex (and the W styrene complex) when anilinium is the acid. It makes sense that a phenethylidene complex is easier to protonate than a styrene complex, especially if protonation of the styrene complex is viewed as protonation of a M-C bond in a metallacyclopropane complex versus protonation of a M=C bond. It appears that the W=C bond is easier to protonate than the Mo=C bond. Therefore we would expect that k_1 for the W(styrene) complex also will be greater than k_1 for the Mo(styrene) complex once such studies become possible.

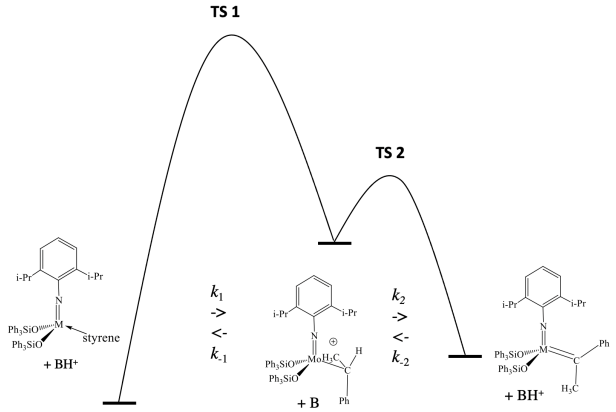


Figure 5. Schematic free energy diagram for interconversion of Mo(NAr)(styrene)$(OSiPh_3)_2$ and Mo(NAr)(CMePh)$(OSiPh_3)_2$.

The behavior of a strong acid or base (versus $PhNMe_2H^+$ and $PhNMe_2$) can be understood readily. A strong acid such as $[(Et_2O)_2H][B(C_6F_5)_4]$ simply protonates either the styrene or alkylidene complex to give the phenethyl cation and the conjugate base (diethyl ether) is not strong enough to deprotonate the cation even in the α position. Conversely, a weak acid such as $[Et_3NH][B(C_6F_5)_4]$ is not able to protonate either the styrene or alkylidene complex and therefore is also not a catalyst for their interconversion. There is enough dimethylanilinium and dimethylaniline in solution to both protonate **1** and **2** and deprotonate **3**, respectively, without destroying either the styrene or alkylidene complex rapidly. The TS1 and TS2 barriers depend upon the nature of the base (B), which is one reason why deprotonations of the phenethyl cation by $PhNMe_2$ or NEt_3 lead to different ratios of **1** to **2**.

An important feature of the highly electron deficient 12e phenethyl cation is that it will readily coordinate a donor such as pyridine after **1** is protonated to give that cation. In short, pyridinium and pyridine are both removed from solution and equilibration therefore slows drastically. A 12e phenethyl cation also may be especially susceptible to deprotonation in the α position. The structure of the 12e Mo cation may provide some hints as to why that is plausible, although it can be risky to attempt to explain kinetics from a ground state structure. Nevertheless, according to the structure there is no evidence for a β agostic interaction and a Mo-C(1)-H angle of 103(3)° implies that Mo-C(1)-H = 94-112° with 95% certainty (+/- 3σ). The ^{13}C NMR chemical shift for the relatively deshielded C_α (at 99.20 ppm) indicates some degree of π character in the Mo–C_α bond, while the shielded resonance for C_β (at 20.68 ppm) indicates that there is little, if any, interaction of a β CH bond with Mo.[5a] It seems plausible that the α proton in **3** ends up in a

position where it can be abstracted more readily because of steric interactions between the methyl and phenyl groups in the phenethyl ligand and the large NAr and $OSiPh_3$ ligands. An enhancement of the rate of α proton abstraction as a consequence of steric crowding in the secondary coordination sphere is an important reason why formation of neopentylidene complexes from d^0 dineopentyl complexes is the most facile compared to proton abstraction from CH_2SiMe_3 and benzyl ligands, in that order, and why α proton abstraction from a methyl in a dimethyl complex to give a methylene is so rare.[2] It also should be noted that α proton abstraction in d^0 dineopentyl complexes is *accelerated* through coordination of donor ligands because the base that removes the α proton is "internal," *i.e.*, another alkyl ligand. Finally, α proton abstraction (intramolecular) has been shown to be preferred in sterically crowded tantalum triamidoamine complexes for CH_2CH_2R dialkyls as the size of the R group increases (R = H, Me, Et, *i*-Pr, *t*-Bu).[32] These arguments would suggest that the α proton may be more "activated" in the five-coordinate 14e adduct of **3**, but that proton is also relatively inaccessible for steric reasons and therefore not as readily removed by an *external* base as in the 12 e complex.

A variety of investigations concerning α agostic versus β agostic CH interactions in d^0 alkyl complexes have been carried out,[31] but with rare exceptions[33] and until recently[5c] those investigations have not taken (or could not take) into account the possibility of forming an alkylidene instead of an olefin. The work reported here suggests that Mo(VI) and W(VI) cationic secondary alkyls may be accessible in a variety of circumstances and that it will now be possible to test the proposals in the previous paragraph and to address the issues concerning olefin and alkylidene interconversion that are relevant to olefin metathesis more broadly.

It remains to be determined whether mechanisms that require reversible protonation of the imido or alkoxide ligands and proton migration within the primary coordination sphere are plausible alternatives to the one proposed here. We also have to determine whether the allyl/metallacyclobutane pathway (eq 2) is a competitive or possibly even dominant pathway for forming d^0 alkylidenes from olefins when allylic protons are present. We hope that future studies of the many possible homogeneous variations of what has been reported here will further delineate the mechanism(s) of interconverting molybdenum and tungsten alkylidene and olefin complexes within the context of forming active olefin metathesis catalysts and begin to unify the fundamentals of proton movement within the primary coordination sphere of high oxidation state Mo and W complexes relevant to olefin metathesis.

It should be pointed out that in a silica-supported W(O)(olefin)[$OCMe(CF_3)_2]_2py_2$ system[6e] it was found that styrene is metathesized and that the metathesis activity is proportional "to the presence of [acidic] surface OH groups that open other initiation pathways." Pyridinium/pyridine-catalyzed rearrangement of styrene to some alkylidene via a mechanism that is a variation of that proposed here, is an intriguing possibility.

Conclusions

We conclude that (i) the Mo and W imido styrene and 1-phenethylidene complexes reported here interconvert via protonation of each to give intermediate M(VI) 1-phenethyl cations; (ii) the equilibrium constants between the styrene and phenethylidene complexes are approximately the same in the Mo and W systems; (iii) the free energy difference between the (more stable) olefin and alkylidene complexes at equilibrium is of the order of ~0.6 kcal/mol or less; (iv) deprotonations of the 1-phenethyl cations in the α positions are dramatically faster than in the β positions, possibly because steric interactions in the secondary coordination sphere hinder β abstraction and promote α abstraction; and (v) secondary alkyls may play a far more important role in forming an alkylidene from an olefin than previously suspected. The long-standing proposal that only a small amount of alkylidene is likely to be formed from an olefin complex because the alkylidene is relatively high in energy compared to an olefin complex is incorrect for the Mo and W styrene and 1-phenethylidene analogs reported here, and could prove to be incorrect more generally in due course.

Experimental Section

General Information. All experiments were carried out in a vacuum or under nitrogen using standard Schlenk or glovebox techniques unless otherwise specified. All glassware was dried in an oven before use. Diethyl ether, *n*-pentane and CH_2Cl_2 were degassed, passed through activated alumina columns under Ar using solvent purification system, and stored over 4Å Linde-type molecular sieves in the glovebox before use. Pentane was washed with H_2SO_4, followed by water and saturated solution of aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets for at least 2 weeks prior to addition to the solvent purification system. Triphenylsilanol (Sigma-Aldrich) was dried under vacuum before use. α-Methylstyrene (TCI), triethylamine (TCI), and N,N-dimethylaniline (Alfa Aesar) were dried over CaH_2, followed by vacuum transfer or distillation under vacuum, and were stored over 4Å molecular sieves. $Mo(NAr)(CHMe_2Ph)(2,5\text{-}Me_2NC_4H_2)(OSiPh_3)$,[9b] $Mo(NAr)(styrene)(OSiPh_3)_2$,[9b] and $W(NAr)(CHMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$[34] (NAr = N-2,6-*i*-$Pr_2C_6H_3$) were synthesized according to literature procedures. The synthesis of $Mo(NAr)(CH_2{=}CH_2)(2,5\text{-}Me_2NC_4H_2)(OSiPh_3)$[9b] was modified to improve the yield and consistency; details are reported below. $PhNMe_2HBAr^F$ and $pyHBAr^F$ (BAr^F = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$ or $B(C_6F_5)_4$) were synthesized by treating N,N-dimethylanilinium chloride or pyridinium chloride with $NaB(3,5\text{-}(CF_3)_2C_6H_3)_4$ or $[Li(Et_2O)_{2.5}][B(C_6F_5)_4]$[35] in dichloromethane. $[H(OEt_2)_2][B(C_6F_5)_4]$ was synthesized from $[Li(Et_2O)_{2.5}][B(C_6F_5)_4]$ according to a literature procedure[36] using 1.0 M HCl in ether instead of HCl gas. Benzene-d_6 (Sigma-Aldrich), CD_2Cl_2 (Cambridge Isotope Laboratories) and toluene-d_8 (Cambridge Isotope Laboratories) were degassed and stored over 4Å Linde-type molecular sieves before use.

The 1D ^1H , ^{13}C, ^{19}F, and 2D ^1H-^1H COSY, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC and ^1H-^1H NOESY NMR data were recorded on a Bruker Avance 300 spectrometer at 7.05 T or a Bruker Avance 600 spectrometer at 14.09 T. Chemical shifts are reported in δ units (positive shifts to higher frequency) relative to TMS (^1H, ^{13}C), set by assigning appropriate shifts to residual solvent signals or to an external standard of neat $CFCl_3$ (^{19}F) by sample replacement. X-ray crystallographic data were collected on a Bruker D8 Venture Duo diffractometer with a Bruker Photon III CPAD detector at the X-ray Laboratory at the University of California, Riverside. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Only selected NMR chemical shifts and other data are provided here. A full listing can be found in the SI.

Synthesis of $Mo(NAr)(CMePh)(OSiPh_3)_2$ (2). $Mo(NAr)(CHMe_2Ph)(2,5\text{-}Me_2NC_4H_2)(OSiPh_3)$ (125 mg, 0.162

mmol), toluene (6 mL), α-methylstyrene (630 mg, 5.33 mmol) and a stir bar were added to a 100 mL Schlenk flask equipped with a Teflon valve. The flask was heated for 5 days at 110 °C on an oil bath with the valve tightly closed. All volatiles where then removed under vacuum, and the dark residue was extracted with pentane (10 mL), and the extract was filtered through Celite. The filtrate was evaporated to dryness to give a red-orange oil that contains mostly isomers of Mo(NAr)(CMePh)(2,5-$Me_2NC_4H_2$)($OSiPh_3$), accordiong to NMR spectra. This oil was redissolved in diethyl ether (5 mL), to which $HOSiPh_3$ (36 mg, 0.13 mmol) was added in one batch. The resulting solution was stirred at room temperature for 1 h. All volatiles were removed under vacuum, and the residue was washed with pentane (3 × 1) mL to leave behind a pink solid. This pink solid was recrystallized in a mixture of diethyl ether (~2 mL) and a couple of drops of pentane at -30 °C to give three crops of products, which were then dried under vacuum (40 μBar) at 45 °C for 18 hours to remove the solvent molecules trapped in the crystal lattice; yield 73 mg (49%). Anal. Calcd for $C_{56}H_{55}MoNO_2Si_2$: C, 72.62; H, 5.99; N, 1.51. Found: C, 72.63; H, 5.93; N, 1.56. A single crystal suitable for X-ray studies was obtained by vapor diffusion of pentane into a concentrated solution of **2** in diethyl ether at room temperature.

Major isomer (alkylidene methyl group *trans* to NAr group): ^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 3.70 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*Me_2), 2.91 (s, 3 H alkylidene CH_3, $^1J_{HH}$ = 131.2 Hz), 0.85 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$); ^{13}C NMR (151 MHz, C_6D_6, 20 °C): δ 264.09 (s, Mo=C), 19.07 (s, alkylidene CH_3).

Minor isomer (alkylidene methyl group *cis* to NAr group, selected resonances): ^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 3.93 (s, 3 H, alkylidene CH_3, $^1J_{CH}$ = 131.2 Hz), 3.84 (m, 2H, C*H*Me_2), 0.98 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$); ^{13}C NMR (151 MHz, C_6D_6, 20 °C): δ 37.88 (s, alkylidene CH_3), 29.08 (s, *C*HMe_2), 23.65 (s, CH*Me*$_2$). The alkylidene carbon resonance was identified on an HMBC spectrum at 277 ppm.

Synthesis of [Mo(NAr)(CHMePh)($OSiPh_3$)$_2$][B(C_6F_5)$_4$] (3). To a -30 °C solution of Mo(NAr)(CMePh)($OSiPh_3$)$_2$ (**2**) (70 mg, 0.067 mmol) in CH_2Cl_2 (5 mL) was added dropwise a -30 °C solution of [H(OEt_2)$_2$][B(C_6F_5)$_4$] (57 mg, 0.069 mmol) in CH_2Cl_2 (10 mL) over 10 min. The mixture was stirred for 5 min at room temperature then all volatiles were immediately removed under vacuum to remove all ether. The residue was washed with pentane (3×2 mL), redissolved in dichloromethane (~1 mL), and the solution was chilled at -30 °C overnight. Some white solid formed, and was removed by filtration, and all DCM was removed under vacuum. The resulting oil was washed with pentane (1 mL) and all volatiles were removed under vacuum to give a brown foam; yield (75 mg) 61%. Anal. Calcd for $C_{80}H_{56}MoNO_2Si_2BF_{20}$: C, 59.82; H, 3.51; N, 0.87. Found: C, 58.96; H, 3.57; N, 0.98. We propose that the low carbon result is the result of protonolysis of **3** to yield Ph_3SiOH and then water and $(Ph_3Si)_2O$ (Figure S7). The double salt [Mo(NAr)(CHMePh)($OSiPh_3$)$_2$][H_3O][B(C_6F_5)$_4$]$_2$(solvent)$_{1.5}$ was the only crystalline compound that could be obtained (three times) in attempts to obtain a crystal suitable for an X-ray study.

^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 4.52 (q, 1 H, $^3J_{HH}$ = 7.8 Hz, $^1J_{CH}$ = 143.2 Hz, MoC*H*MePh), 3.19 (m, 2 H, C*H*Me_2), 2.07 (d, 3 H, $^3J_{HH}$ = 7.4 Hz, $^1J_{CH}$ = 133 Hz, MoCH*Me*Ph), 0.76 (d, 6 H, $^2J_{HH}$ = 6.5 Hz, CH*Me*$_2$), 0.75 (d, 6 H, $^2J_{HH}$ = 6.5 Hz, CHC*Me*$_2$); ^{13}C NMR (151 MHz, C_6D_6, 20 °C): δ 99.22 (s, Mo-*C*HMePh), 29.66 (s, *C*HMe_2), 23.82 (s, CH*Me*$_2$), 23.16 (s, CH*Me*$_2$), 20.68 (MoCH*Me*Ph).

Synthesis of Mo(NAr)(CH_2=CH_2)(2,5-$Me_2NC_4H_2$)($OSiPh_3$). This compound was prepared via a variation of the synthesis reported in the literature. Mo(NAr)($CHMe_2Ph$)(2,5-$Me_2NC_4H_2$)($OSiPh_3$) (250 mg, 0.32 mmol), a stir bar, and diethyl ether (10 mL) were added to a 100 mL Schlenk flask equipped with a Teflon valve. The solution was degassed by a freeze-pump-thaw sequence (3 times), and 1 atm of ethylene was introduced. The Teflon valve was then closed and the mixture was stirred for 1 h at room temperature, during which the orange solution turned red. The solvent was quickly removed *in vacuo* and the flask was immediately brought into the glovebox. Pentane (4 mL) was added to dissolve the red residue, which we speculate is a metallacyclopentane complex. The resulting solution was immediately transferred to a vial. The vial was capped and sealed with tape (within 5 min from addition of pentane) and left to stand at room temperature for 30 min, during which dark red crystals of the ethylene complex gradually formed. The mixture was further stored at -30 °C overnight to give the product as dark red crystals; yield 170 mg (79%). The proton NMR chemical shifts are consistent with literature values.[9b] Anal. Calcd for $C_{38}H_{44}MoN_2OSi$: C, 68.24; H, 6.63; N, 4.19. Found: C, 67.94; H, 6.48; N, 4.16.

A second crop of crystals (20 mg, containing traces of CH_2=CHMe_2Ph) can be obtained by further concentrating the mother liquor to ~2 mL, and can be used in the following steps of synthesis without purification.

Synthesis of W(NAr)(CMePh)($OSiPh_3$)$_2$ (4). W(NAr)($CHMe_2Ph$)(2,5-$Me_2NC_4H_2$)$_2$ (338 mg, 0.50 mmol, 1 eq) and Ph_3SiOH (137 mg, 0.50 mmol, 1 eq) were each dissolved in 5 mL of diethyl ether and the solutions were cooled at -30°C. The solution of Ph_3SiOH was then added to the tungsten complex dropwise and the mixture was stirred 30 minutes at room temperature. Volatiles were removed *in vacuo* the residue was redissolved in pentane and all solvent removed in vacuo; the redissolution and evacuation was repeated five times. The light-yellow W(NAr)($CHMe_2Ph$)($OSiPh_3$)(2,5-dimethylpyrrolide) intermediate was dissolved in C_6H_6 (10 mL), and H_2CCPhMe (1.18 g, 10 mmol, 20 eq) was added. The yellow solution was transferred to a J. Young flask which was closed and heated at 100°C for 5 days. Volatiles were removed *in vacuo* at 50°C at 10^{-3} mbar for 12 h. The brown residue was dissolved in Et_2O (5 mL) and Ph_3SiOH (137 mg, 0.50 mmol, 1 eq) was added as a solution in Et_2O (5 mL). The mixture was stirred for 1 hour at room temperature and volatiles were removed *in vacuo*. The brown residue was dissoved in a mixture Et_2O and pentane and the mixture was filtered through Celite. The filtrate was left at -30°C overnight and **4** was obtained as orange crystals; yield 250 mg (50% over 3 steps). Anal. Calcd for $C_{56}H_{55}WNO_2Si_2$: C, 66.33%; H, 5.47%, N, 1.38%, Found: C, 66.41%; H, 5.59%, N, 1.46%.

Major isomer (97%) : ^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 3.66 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, C*H*Me_2), 3.44 (s, 3 H, $^1J_{CH}$ = 128 Hz, $^3J_{HW}$ = 31 Hz, CPh*Me*), 0.88 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$,); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 20 °C): δ 231.6 (s, $^1J_{WC}$ = 183 Hz, W=*C*), 14.3 (s, alkylidene CH_3). Minor isomer (3%, selected resonances): ^{1}H NMR (600 MHz, C_6D_6, 20 °C): δ 4.85 (s, 3H, alkylidene CH_3), 3.68 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, C*H*Me_2), 0.99 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH*Me*$_2$); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 20 °C): δ 35.4 (s, alkylidene CH_3), 28.8 (s, *C*HMe_2), 23.6 (s, CH*Me*$_2$). The alkylidene carbon resonance (W=C) was identified on an HMBC spectrum at 241 ppm.

Synthesis of [W(NAr)(CHMePh)(OSiPh$_3$)$_2$][B(C$_6$F$_5$)$_4$] (5). W(NAr)(CMePh)(OSiPh$_3$)$_2$ (**4**; 45 mg, 0.044 mmol, 1 eq) and H(OEt$_2$)[B(C$_6$F$_5$)$_4$] (31 mg, 0.037 mmol, 0.85 eq) were separately dissolved in 3 mL of CH_2Cl_2 and the solutions were cooled to -30°C. The solution of H(OEt$_2$)$_2$[B(C$_6$F$_5$)$_4$] was then added to the solution of **4** dropwise and the mixture was stirred 30 minutes at room temperature. The volatiles were removed *in vacuo* and the residue was dissolved in dichloromethane (1 mL). Pentane was added to yield an orange oil which was subjected to high vacuum to give **5** as a yellow foam; yield 78% (49 mg): ^{1}H NMR (600 MHz, CD_2Cl_2, 20 °C): 4.93 (q, 1 H, $^3J_{HH}$ = 7 Hz, $^1J_{CH}$ = 137 Hz, WC*H*MePh), 3.22 (sept, 2 H, $^3J_{HH}$ = 7 Hz, C*H*Me$_2$), 2.82 (d, 3 H, $^3J_{HH}$ = 7 Hz, WCH*Me*Ph), 0.85 (d, 6 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 0.82 (d, 6 H, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$); ^{13}C NMR (151 MHz, CD_2Cl_2, 20 °C): δ 89.8 (s, $^1J_{CW}$ = 104 Hz, W*C*HMePh), 29.4 (s, *C*HMe$_2$), 24.2 (s, CHMe*Me*), 23.3 (s, CHMe*Me*), 21.8 (s, WCH*Me*Ph). Three elemental attempts have failed so far with %C being low by ~0.85%.

ASSOCIATED CONTENT

NMR spectra of compounds, complete listing of NMR data, X-ray data, modeling methods, and details of other experimental procedures summarized in the text.

Accession Codes

CCDC 2095604, 2100589. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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