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Fundamental Studies of Molybdenum and Tungsten Methylidene and
Metallacyclobutane Complexes

by

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Abstract

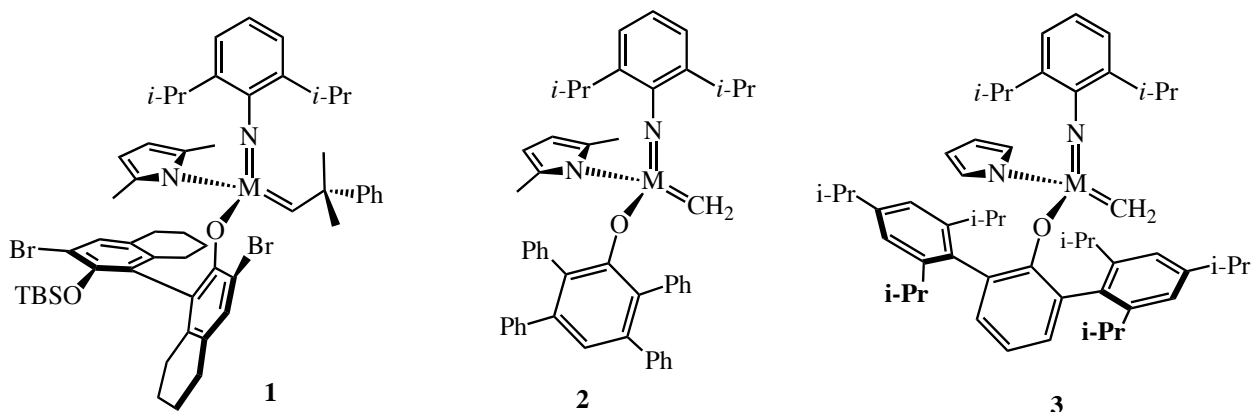
Addition of ethylene to $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OHIPT})(\text{Pyr})$ ($\text{NAr} = \text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3$, $\text{OHIPT} = \text{O-2,6-(2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$, $\text{Pyr} = \text{NC}_4\text{H}_4^-$) led to the trigonal bipyramidal metallacyclobutane complex, $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OHIPT})(\text{Pyr})$, in which the imido and aryloxo ligands occupy axial positions. $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OHIPT})(\text{Pyr})$ loses ethylene to give isolable $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$. $\text{W}(\text{NAr})(\text{CH}_2)(\text{OTPP})(\text{Me}_2\text{Pyr})$ ($\text{OTPP} = \text{O-2,3,5,6-Ph}_4\text{C}_6\text{H}$, $\text{Me}_2\text{Pyr} = 2,5\text{-Me}_2\text{NC}_4\text{H}_2^-$) was prepared similarly. Single crystal X-ray studies of $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$ and $\text{W}(\text{NAr})(\text{CH}_2)(\text{OTPP})(\text{Me}_2\text{Pyr})$ show that they are monomers that contain an η^1 -pyrrolide ligand and a methylidene ligand in which the M-C-H_{anti} angle is smaller than the M-C-H_{syn} angle, consistent with an agostic interaction between CH_{anti} and the metal. Attempts to prepare analogous $\text{Mo}(\text{NAd})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$ ($\text{Ad} = 1\text{-adamantyl}$) yielded only the ethylene complex, $\text{Mo}(\text{NAd})(\text{C}_2\text{H}_4)(\text{OHIPT})(\text{Pyr})$. $\text{W}(\text{NAr}^{t\text{Bu}})(\text{CH}_2)(\text{OTPP})(\text{Me}_2\text{Pyr})$ ($\text{Ar}^{t\text{Bu}} = 2\text{-}t\text{-BuC}_6\text{H}_4$) was isolated upon loss of ethylene from $\text{W}(\text{NAr}^{t\text{Bu}})(\text{C}_3\text{H}_6)(\text{OTPP})(\text{Me}_2\text{Pyr})$,

but decomposed in solution over a period of several hours at 22 °C. NMR studies of $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OHIPT})(\text{Pyr})$ and $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OHIPT})(\text{Pyr})$ species showed them both to be in equilibrium with ethylene/methylidene intermediates before losing ethylene to yield the respective methylidene complexes. Detailed NMR studies of $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ (OBitet is the anion derived from (*R*)-3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol) were carried out and compared with previous studies of $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$. It could be shown that $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ forms an ethylene/methylidene intermediate at 20 °C at a rate that is 4500 times faster than the rate at which $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ forms an ethylene/methylidene intermediate. It is proposed that the stability of methylidene complexes coupled with their high reactivity account for the high efficiency of many olefin metathesis processes that employ MonoAryloxyPyrrolide (MAP) catalysts.

This paper is intended for inclusion in the Seyferth Festschrift issue.

INTRODUCTION

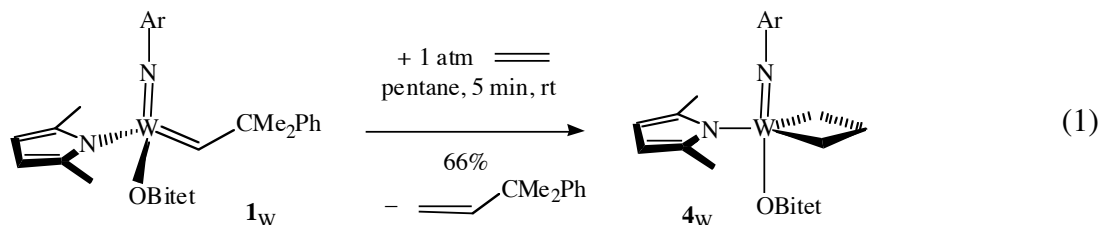
Olefin metathesis reactions catalyzed by high oxidation state molybdenum and tungsten imido alkylidene complexes have been dominated by bisalkoxide or biphenolate and related species.¹ In the last several years new types of imido alkylidene complexes that have the formula $M(NR)(CHR')(OR'')(Pyr)$, where Pyr is a pyrrolide or substituted pyrrolide ligand and OR'' usually is an aryloxy, have been prepared and explored.² These MAP (MonoAryloxyPyrrolide or MonoAlkoxidePyrrolide) species often can be generated *in situ* through addition of $R''OH$ to a $M(NR)(CHR')(Pyr)_2$ species,^{2a,3} an attribute that allows relatively facile examination of many MAP variations, including monosiloxide analogs of MAP species⁴ bound to silica.⁵ Attributes of homogeneous MAP species include their high reactivity in general and their efficiency for enantioselective metathesis reactions,^{2c,h} for formation of new ROMP polymer structures,^{2j} for endo-selective enyne reactions,^{2k} for *Z*-selective metathesis of terminal olefins,²ⁱ and for efficient and clean ethenolysis reactions.^{2l} Some of the most interesting catalytic reactions to date have been carried out with derivatives in which the aryloxy is relatively large, e.g., the anion derived from (*R*)-3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol (HOBitet; see **1**; $M = Mo$ or W), 2,3,5,6-tetraphenylphenol (HOTPP; see **2**; $M = Mo$ or W), or 2,6-(2,4,6-(*i*-Pr)₃C₆H₂)₂C₆H₃ (hexaisopropylterphenol or HOHIPT; see **3**; $M = Mo$ or W). As a consequence of the presence of a stereogenic metal center in MAP species, two diastereomers are formed when an



enantiomerically pure aryloxy ligand is employed, as in **1**. An important feature of MAP complexes that contain a "large" aryloxy, at least in terms of long-lived activity and low catalyst loadings, is that methylenes species, e.g., **2** or **3**, often can be observed in solution, and in some cases appear to be relatively stable. For example, a solution of **2_W** (i.e., M = W) in toluene-*d*₈ can be heated to 80 °C and interconversion on the NMR time scale of the inequivalent methylene protons ($k = 90 \text{ s}^{-1}$ at 20 °C) thereby observed.^{2g,6} The stability of these 14 electron MAP methylene species contrasts with the low stability of 14e imido methylene species of the bisalkoxide or biphenolate type.¹ Bisalkoxide imido methylene species usually are observed only when the total metal electron count is >14, i.e., only when adducts are formed.⁷

The presence of 14 electron methylene species that are relatively stable toward bimolecular decomposition, yet highly reactive toward olefins, compelled us to attempt to isolate and crystallographically characterize some examples, since some feature of their structures might be a reason for their increased stability toward bimolecular decomposition. For example, the ground state structure of a MAP methylene species could be a dimer that contains two asymmetrically bridging methylenes, as has been found for some tungsten biphenolate methylene complexes that contain a 2,6-dichlorophenylimido ligand.⁸ Another possibility is that the pyrrolide is bound in a η^5 manner and that a MAP methylene complex therefore is an 18e electron species, even though a pyrrolide is bound in an η^1 manner in MAP species that contain a neopentylidene or neophylidene ligand.^{2a,c,h,4} Although solid samples of $\text{W}(\text{NAr})(\text{CH}_2)(\text{OBitet})(\text{Me}_2\text{Pyr})$ (Ar = 2,6-diisopropylphenyl, Me_2Pyr = 2,5-dimethylpyrrolide) could be obtained as a 3:1 mixture of diastereomers,^{2g} no crystals of either diastereomer could be obtained that were suitable for an X-ray study.

Highly crystalline unsubstituted tungstacyclobutane complexes can be prepared readily through treatment of a tungsten MAP species with ethylene, as shown in equation 1.^{2g} Compound **4_W** readily exchanges with ethylene and has been studied in detail through NMR methods.^{2g} The NMR studies are consistent with the loss of ethylene from **4_W** to yield



intermediate ethylene/methylidene complexes, (*R*)-W(NAr)(Me₂Pyr)(OBitet)(CH₂)(C₂H₄) and (*S*)-W(NAr)(Me₂Pyr)(OBitet)(CH₂)(C₂H₄). X-ray studies show that **4_W** and analogous metallacyclobutane species contain axial imido and OBitet ligands, as shown in equation 1. All evidence suggests that an olefin approaches the metal in a MAP species (such as **1_W**) *trans* to the pyrrolide, and that the configuration at the metal inverts with each forward metathesis step. The analogous molybdacyclobutane (**4_{Mo}**), the first example of a crystallographically characterized TBP molybdacyclobutane complex, is structurally virtually identical to **4_W**.²¹ Therefore we became especially interested in comparing and contrasting analogous Mo and W chemistry that concerns methylidene and metallacyclobutane species and their interconversion.

RESULTS

X-ray study of W(NAr)(CH₂)(OTPP)(Me₂Pyr).

In a previous paper^{2g} we showed that W(NAr)(CH₂)(OTPP)(Me₂Pyr) (**2_W**) can be prepared in good yield as a yellow powder in a reaction between one equivalent of 2,3,5,6-tetraphenylphenol (HOTPP) and W(NAr)(CH₂)(Me₂Pyr)₂ in benzene or by removing ethylene from W(NAr)(C₃H₆)(OTPP)(Me₂Pyr) *in vacuo*. (W(NAr)(C₃H₆)(OTPP)(Me₂Pyr) can be prepared by treating W(NAr)(CHCMe₂Ph)(OTPP)(Me₂Pyr) with ethylene.^{2g}) Complex **2_W** (in C₆D₆) contains a methylidene H_{syn} resonance at 10.24 ppm (*J*_{CH} = 160 Hz) and a methylidene H_{anti} resonance at 8.75 ppm (*J*_{CH} = 130 Hz). (The H_{syn} proton points toward the imido group, while the H_{anti} proton points away from the imido group.⁹) The *J*_{CH} value for H_{anti} (130 Hz) is typically found to be lower than that for H_{syn}, consistent with a weak CH_{anti} agostic interaction with the metal.¹⁰ Compound **2_W** decomposes in toluene-*d*₈ to a significant degree at 60 °C over

the course of several days, but at room temperature decomposition is minimal over a period of several days at a concentration of ~ 30 mM. Both THF and PMe_3 adducts of $\mathbf{2}_W$ have been prepared and crystallographically characterized.^{2g} Each adduct is best described as a square pyramid with the methylidene in the apical position. The THF is bound *trans* to the imido ligand, while PMe_3 is bound *trans* to the pyrrolide.

Crystals of $\mathbf{2}_W$ suitable for an X-ray study were obtained from a concentrated toluene solution at -27 °C or a concentrated benzene solution at room temperature. As shown in Figure 1, $\mathbf{2}_W$ is a 14e monomeric species that contains an η^1 -dimethylpyrrolide. The $\text{W}=\text{C}$ distance is $1.908(4)$ Å, which is similar to $\text{M}=\text{C}$ bond lengths in other Mo and W neophylidene and neopentylidene MAP species.^{2a,c,h} The methylidene protons in $\mathbf{2}_W$ (and other methylidene complexes described later) were located in the Fourier synthesis and subsequently refined semi-freely (see Supporting Information). The CH_2 plane is turned approximately 8° out of the $\text{N1}-\text{W}-\text{C1}$ plane. The $\text{W}-\text{C1}-\text{H1a}$ angle ($\text{H1a} = \text{H}_{anti}$) is $107(4)^\circ$ and the $\text{W}-\text{C1}-\text{H1b}$ angle ($\text{H1b} = \text{H}_{syn}$) is $136(3)^\circ$. The smaller $\text{W}-\text{C1}-\text{H1a}$ angle (by 29°) is consistent with a CH_{anti} agostic interaction with the metal.¹⁰ In the structure of the THF adduct (THF *trans* to the imido ligand), $\text{W}-\text{C}-\text{H}_{anti}$ is $118.1(16)^\circ$ and $\text{W}-\text{C}-\text{H}_{syn}$ is $122.5(17)^\circ$, while in the structure of the PMe_3 adduct (PMe_3 *trans* to the pyrrolide), $\text{W}-\text{C}-\text{H}_{anti}$ is $119.5(17)^\circ$ and $\text{W}-\text{C}-\text{H}_{syn}$ is $133.5(16)^\circ$.^{2g} To our knowledge $\mathbf{2}_W$ is the first 14 electron tungsten imido methylidene species to be crystallographically characterized. These structural data provide the first direct evidence that in a methylidene species the alkylidene is distorted from a symmetrical structure for electronic reasons, not because of steric interaction between a *syn* substituent and the imido group. Isolation of $\mathbf{2}_W$ confirms the proposal that it is relatively stable toward bimolecular decomposition to give a metal-metal dimer or a M(IV) ethylene complex.¹¹ Addition of ethylene to $\mathbf{2}_W$ immediately yields the known, crystallographically characterized TBP tungstacyclobutane complex, $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OTPP})(\text{Me}_2\text{Pyr})$.^{2g}

Synthesis of Mo(NAr)(C₃H₆)(OHIPT)(Pyr) and Mo(NAr)(CH₂)(OHIPT)(Pyr).

Exposure of a pentane solution of Mo(NAr)(CHCMe₂Ph)(OHIPT)(Pyr) to 1 atm of ethylene led to formation of the molybdacyclobutane complex, Mo(NAr)(C₃H₆)(OHIPT)(Pyr) (**5**_{M0}), OHIPT = hexaisopropylterphenoxide, Pyr = NC₄H₄⁻) and its isolation as a yellow powder in 51% yield. Compound **5**_{M0} can be recrystallized from a concentrated solution in a mixture of pentane and ether as fine feathery crystals. Removal of ethylene *in vacuo* from a solution of **5**_{M0} in toluene yielded Mo(NAr)(CH₂)(OHIPT)(Pyr) (**3**_{M0}), which could be isolated from pentane as yellow blocks in 88% yield. The ¹H NMR spectrum of **3**_{M0} in benzene-*d*₆ showed two H_α doublet resonances at δ 12.18 ppm (H_{anti}, J_{CH} = 138 Hz, J_{HH} = 5 Hz) and 12.06 ppm (H_{syn}, J_{CH} = 163 Hz, J_{HH} = 5 Hz). Note that the H_{anti} proton resonance is found downfield of the H_{syn} resonance, in contrast to what is found in **2**_W. A sample of **5**_{M0} in benzene-*d*₆ was exposed to ¹³C-ethylene and then vacuum was applied to remove ethylene and reform **3**_{M0} in which the methyldene carbon atom was partially ¹³C labeled (~66%). The J_{CH} values were confirmed easily in the labeled compound.

The solid-state structure of **3**_{M0} (Figure 2) is analogous to that of **2**_W (Figure 1). The Mo=C distance (1.892(5) Å) is the same as the W=C distance (1.908(4) Å) in **2**_W. The Mo-C1-H1a (Mo-C-H_{anti}) angle is 105(3)° and Mo-C1-H1b (Mo-C-H_{syn}) angle is 131(3)°, a difference of 26°, again consistent with a CH_{anti} agostic interaction.¹⁰ As found in **2**_W, the CH₂ plane in **3**_{M0} is turned from the N1-Mo-C1 plane by about 8°. The structural study of **3**_{M0} is the first (to our knowledge) of a 14e molybdenum imido methyldene species.

Interestingly, **3**_{M0} appears to be more stable in benzene solution than the molybdacyclobutane (**5**_{M0}) at the same concentration. For example, a 20 mM solution of **3**_{M0} showed little decomposition over a period of 3 days at room temperature, although over the same time period a 20 mM solution of **5**_{M0} decomposed to a significant degree. Since only trace amounts of propene are observed in ¹H NMR spectra, β hydride rearrangement of the molybdacyclobutane complex cannot be the major mode of decomposition. Therefore we

propose that bimolecular decomposition of $\mathbf{3}_{M_0}$ is the major decomposition pathway and that bimolecular decomposition is accelerated by ethylene. (See Discussion Section.) Both $\mathbf{5}_{M_0}$ and $\mathbf{3}_{M_0}$ are stable for weeks in the solid state at $-27\text{ }^\circ\text{C}$.

Compound $\mathbf{5}_{M_0}$ appears to be much more stable toward loss of ethylene than structurally characterized $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{Pyr})(\text{OBitet})$, which had to be isolated from the reaction between $\text{Mo}(\text{NAr})(\text{CHCMe}_3)(\text{Me}_2\text{Pyr})(\text{OBitet})$ and ethylene (1 atm) at $-30\text{ }^\circ\text{C}$ in a 1:1 mixture of pentane and tetramethylsilane.^{2e} When ethylene was removed from a solution of $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{Pyr})(\text{OBitet})$, mixtures of the two diastereomers of $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OBitet})$ (H_α at 12.35 and 12.13 ppm for one diastereomer, 12.94 and 12.24 ppm for the other diastereomer) were observed. The two diastereomers of $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OBitet})$ decompose to a significant degree in C_6D_6 at $22\text{ }^\circ\text{C}$ in the absence of ethylene over a period of 1-2 days.^{2e} (NMR studies involving $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{Pyr})(\text{OBitet})$ and $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OBitet})$ are described later in this paper.)

Complexes that contain a N(o-t-BuC₆H₄) or NAdamantyl ligand

We also became interested in whether metallacyclobutane and methylenide species could be isolated in which the imido ligand is smaller than 2,6-diisopropylphenylimido. Adamantylimido is a good choice since it is an alkylimido derivative, adamantylimido species have revealed special reactivities in certain circumstances, and an adamantylimido ligand is small relative to a 2,6-diisopropylphenylimido ligand.^{2j} $\text{Mo}(\text{NAd})(\text{CHCMe}_3)(\text{OHIPT})(\text{Pyr})$ (**6**), prepared as described in the literature,^{2j} was shown in an X-ray study to be a 14e pseudotetrahedral species that contains an η^1 -pyrrolide and a *syn* alkylidene⁹ (Figure 3). Bond lengths and angles are similar to other MAP species of this general type. The Mo-C1-H1 angle ($101.6(17)^\circ$) should be compared with the M-C-H_{anti} angles in **2_W** ($107(4)^\circ$) and **3_{M₀}** ($105(3)^\circ$) described above (Figures 1 and 2).

Addition of ethylene (1 atm) to **6** afforded initially what we propose to be one or more metallacyclobutane or metallacyclopentane species (~80%) and starting material (~20%). Multiplet resonances attributed to the metallacycle(s) are found at 3.81 ($J_{\text{CH}} = 139$ Hz), 2.36 ($J_{\text{CH}} = 145$ Hz), 2.24 ($J_{\text{CH}} = 146$ Hz), and 0.71 ($J_{\text{CH}} = 154$) ppm in a 1:1:1:1 ratio. The remaining **6** was consumed over a period of 24 hours and an ethylene complex was formed in a yield of >95%. The four proton resonances attributed to the ethylene in Mo(NAd)(C₂H₄)(OHIPT)(Pyr) are found at 2.73, 2.32, 2.01, and 0.35 ppm, and the carbon resonances appear at 55.23 ppm ($J_{\text{CC}} = 38$ Hz, $J_{\text{CH}} = 154$ Hz and 155 Hz) and 46.41 ppm ($J_{\text{CC}} = 38$ Hz, $J_{\text{CH}} = 158$ Hz and 158 Hz). So far we have not been able to isolate Mo(NAd)(C₂H₄)(OHIPT)(Pyr) as a crystalline solid. At no time during the formation of the ethylene complex could a methylidene species be observed. Therefore the main conclusion is that in the presence of ethylene Mo(NAd)(CH₂)(OHIPT)(Pyr) decomposes to Mo(NAd)(C₂H₄)(OHIPT)(Pyr) readily. Two crystallographically characterized neutral ethylene complexes of this general type are known, Mo(N-2,6-Cl₂C₆H₃)(CH₂CH₂)(Biphen)(Et₂O)¹² and W(N-2,6-Cl₂C₆H₃)(CH₂CH₂)(Biphen)(THF),⁸ along with one cationic species, {Mo(NAr)(CH₂CH₂)[OCMe(CF₃)₂](THF)₃}⁺.¹³

The synthesis of W(NAr^{tBu})(CHCMe₂Ph)(OTPP)(Me₂Pyr) (Ar^{tBu} = 2-t-BuC₆H₄) was carried out through addition of 2,3,5,6-tetraphenylphenol to W(NAr^{tBu})(CHCMe₂Ph)(Me₂Pyr)₂. Upon exposure of a solution of W(NAr^{tBu})(CHCMe₂Ph)(OTPP)(Me₂Pyr) to ethylene, W(NAr^{tBu})(C₃H₆)(OTPP)(Me₂Pyr) (**7**) formed in high yield and could be isolated as yellow needles from a mixture of diethyl ether and benzene. Compound **7** is relatively stable in the solid state, but in benzene it decomposes over the course of 4 h. Dissolution of **7** in toluene or benzene and removal of the volatiles *in vacuo* yielded W(NAr^{tBu})(CH₂)(OTPP)(Me₂Pyr) (**8**) after six such cycles. Compound **8** could not be isolated and analyzed because it is not stable in solution for more than an hour or two at a concentration of ~10 mM. NMR studies suggest that the rate of rotation of the methylidene ligand in W(NAr^{tBu})(CH₂)(OTPP)(Me₂Pyr) is 230 s⁻¹ at 20 °C, which is ~2.5 times faster than the rate found in the analogous 2,6-diisopropylphenyl imido complex (90 s⁻¹ at 20 °C).^{2g}

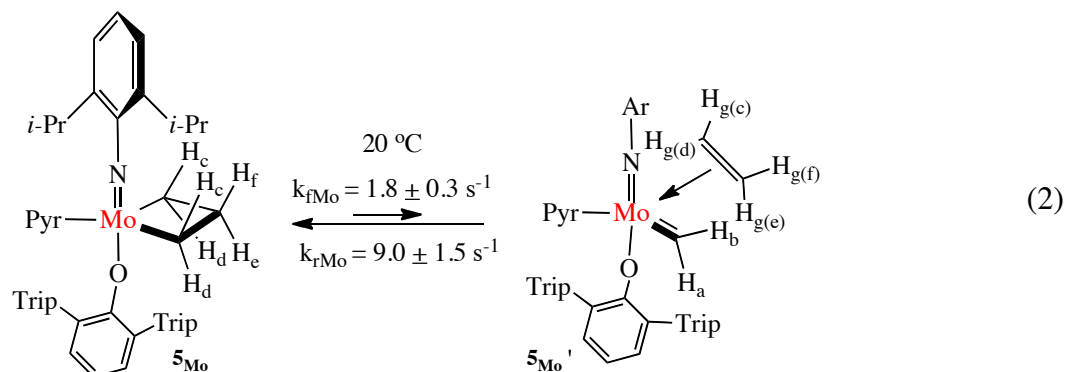
Attempts to prepare $W(NAr^{tBu})(CHCMe_2Ph)(Me_2Pyr)(OBitet)$ by treating $W(NAr^{tBu})(CHCMe_2Ph)(Me_2Pyr)_2$ with one equivalent of $HOBitet$ on ~ 0.5 g scale led only to an oily residue, the 1H NMR spectrum of which suggested the presence of two *syn* diastereomers with alkylidene H_α resonances at 9.90 ppm ($J_{CH} = 116$ Hz, $J_{WH} = 15$ Hz) and 9.45 ppm ($J_{CH} = 113$ Hz, $J_{WH} = 15$ Hz) in a 2:1 ratio. Addition of ethylene (1 atm) to crude $W(NAr^{tBu})(CHCMe_2Ph)(Me_2Pyr)(OBitet)$ yielded only to intractable material.

NMR Studies of the $M(NAr)(C_3H_6)(OHIPT)(Pyr)$ systems

2D 1H - 1H NOESY/EXSY experiments were performed on the Mo and W versions of the $M(NAr)(C_3H_6)(OHIPT)(Pyr)$ complexes. These experiments were analogous to those reported for $W(NAr)(C_3H_6)(Me_2Pyr)(OBitet)$ in the first paper in this series.^{2g} Unfortunately, it was not possible to study the $Mo(OHIPT)$ and $W(OHIPT)$ complexes in as much detail as the $W(OBitet)$ species. (A full discussion and details can be found in the Supporting Information.)

For $W(NAr)(C_3H_6)(Me_2Pyr)(OBitet)$ the kinetic data could be fit only when $W(NAr)(CH_2)(C_2H_4)(Me_2Pyr)(OBitet)$ was proposed as an intermediate.^{2g} The same was found to be the case in the $OHIPT$ systems examined here. The precise structure of the $M(CH_2)(C_2H_4)$ species is not known. (See Discussion section.) In the analysis that follows it is arbitrarily drawn as a TBP species with the ethylene and methyldiene ligands in equatorial positions (equation 2).

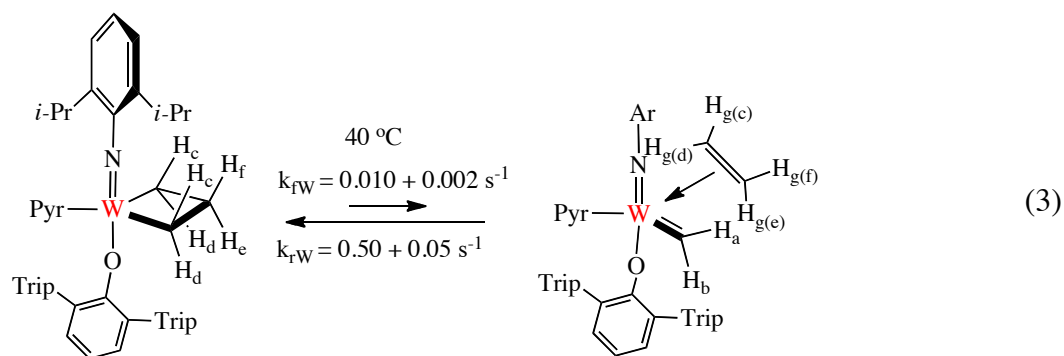
In a 20 mM solution of $Mo(NAr)(C_3H_6)(OHIPT)(Pyr)$ ($\mathbf{5}_{Mo}$) in benzene- d_6 at 20 °C $\sim 14\%$ of $Mo(NAr)(CH_2)(OHIPT)(Pyr)$ ($\mathbf{3}_{Mo}$) and 86% of $\mathbf{5}_{Mo}$ are observed (Figure S3 in the Supporting Information). Proton resonances in each species were assigned on the basis of NOE studies (Figure S4). In the interconversion of $Mo(NAr)(C_3H_6)(OHIPT)(Pyr)$ ($\mathbf{5}_{Mo}$) and $Mo(NAr)(CH_2)(C_2H_4)(OHIPT)(Pyr)$ ($\mathbf{5}_{Mo}'$) protons *d* exchange exclusively with *a*, and *c* mainly with *b* (equation 2). The assignment of *a* and *b* are consistent with the J_{CH} values determined through partial ^{13}C labeling of $\mathbf{5}_{Mo}$ ($J_{CH} = 138$ Hz for $H_a = H_{anti}$ and $J_{CH} = 163$ Hz for $H_b = H_{syn}$,



vide supra). Pyrrolide resonances in 5_{Mo} and $5_{\text{Mo}'}$ were employed in order to determine the rate of interconversion of 5_{Mo} and $5_{\text{Mo}'}$ (Figure S5). An examination of the system at mixing times of 60, 100, 130, 150, 200, 250, and 300 ms allowed the rate constants for the forward process ($1.8 \pm 0.3 \text{ s}^{-1}$) and the reverse ($9.0 \pm 1.5 \text{ s}^{-1}$) at $20 \text{ }^\circ\text{C}$ to be determined. The ratio of k_{rMo} to k_{fMo} (5.0) is consistent with the ratio of 5_{Mo} to 3_{Mo} found in the 1D NMR experiment above. Protons *a* and *b* in a sample of $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$ (free of ethylene) *do not exchange* with a mixing time of 200 ms at $20 \text{ }^\circ\text{C}$; therefore any rotation of the methyldiene ligand about the Mo-C axis would have to take place at a rate of $<0.2 \text{ s}^{-1}$. A rate of $<0.2 \text{ s}^{-1}$ contrasts dramatically with a rate of rotation of the methyldiene in $\text{W}(\text{NAr}^{\text{tBu}})(\text{CH}_2)(\text{OTPP})(\text{Me}_2\text{Pyr})$ (230 s^{-1} at $20 \text{ }^\circ\text{C}$; *vide supra*) or $\text{W}(\text{NAr})(\text{CH}_2)(\text{OTPP})(\text{Me}_2\text{Pyr})$ (90 s^{-1} at $20 \text{ }^\circ\text{C}$).^{2g}

In a 20 mM solution of $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OHIPT})(\text{Pyr})$ (C_3H_6 resonances at δ 4.24, 3.52, -0.78, and -1.11 ppm) in benzene- d_6 at $20 \text{ }^\circ\text{C}$ the metallacycle protons did not exchange with each other at any significant rate. At $40 \text{ }^\circ\text{C}$ approximately 2% $\text{W}(\text{NAr})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$ (δ 10.30 and 9.38 ppm) could be observed in the ^1H NMR spectrum. The model that was employed for the Mo system was employed for the W system, as described in the Supporting Information (see Figures S6 and S7). The forward rate constant at $40 \text{ }^\circ\text{C}$ (k_{fW}) was found to be $0.010 \pm 0.002 \text{ s}^{-1}$ and the reverse (k_{rW}) was found to be $0.50 \pm 0.05 \text{ s}^{-1}$, for a $k_{\text{rW}}/k_{\text{fW}} = 50$ (equation 3). The ratio of k_{rW} to k_{fW} is larger by a factor of 10 in the W system (at $40 \text{ }^\circ\text{C}$), and the molybdacyclobutane (at $20 \text{ }^\circ\text{C}$) breaks up 180 times faster than the tungstacycle (at $40 \text{ }^\circ\text{C}$). It

was impractical to measure the rate of methyldiene rotation in $W(NAr)(CH_2)(OHIPT)(Pyr)$ because the concentration of $W(NAr)(CH_2)(OHIPT)(Pyr)$ was too low. To our knowledge these are the first data that quantitate the "greater stability" of tungstacyclobutane complexes versus molybdacyclobutane complexes, both in terms of the rate of loss of ethylene and the position of the equilibrium between the metallacycle and methyldiene species.



In the $W(NAr^{tBu})(C_3H_6)(OTPP)(Me_2Pyr)$ system the protons of the metallacyclobutane (four on the C_α carbons and two on the C_β carbon) were assigned using 2D 1H - 1H NOESY/EXSY NMR spectroscopy. The pattern of behaviors and rates of exchange is similar to the 2,6-diisopropylphenyl imido system. (See Supporting Information.)

When vacuum was applied to a solution of $W(NAr^{tBu})(C_3H_6)(OTPP)(Me_2Pyr)$, the methyldiene species that was generated exhibited broad methyldiene proton resonances at 10.09 and 9.09 ppm in the proton NMR spectrum in C_6D_6 at 22 °C. Proton *a* (δ 10.09 ppm, $J_{CH} = 156$ Hz, which was obtained by labeling the C_α with ^{13}C) is assigned the methyldiene proton *syn* to the imido ligand and *b* (δ 9.09 ppm, $J_{CH} = 128$ Hz) to the methyldiene proton *anti* to the imido ligand, which confirmed the assignments made through 2D NMR studies. 2D 1H - 1H NOESY/EXSY spectra of a 40 mM sample with 2 ms mixing time at 20 °C (Figure S3 and S10) illustrated that the *syn* and *anti* protons exchange at a rate of $230 s^{-1}$, which is about two times faster than that in $W(NAr)(CH_2)(OTPP)(Me_2Pyr)$ ($90 s^{-1}$) and approximately 100 times faster than $W(NAr)(CH_2)(OBitet)(Me_2Pyr)$ ($4\text{-}5 s^{-1}$). The rapid rate of exchange of methyldiene

protons in $W(\text{NAr}^{\text{tBu}})(\text{C}_3\text{H}_6)(\text{OTPP})(\text{Me}_2\text{Pyr})$ accounts for the breadth of the methylene proton resonance in room temperature spectra.

NMR studies of $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{Pyr})(\text{OBitet})$

In a previous paper we reported that $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$ reacts cleanly with 1 equiv of enantiomerically pure HOBitet to generate $\mathbf{1}_{\text{Mo}}$ as a mixture of two diastereomers.^{2c,2h} When ethylene (1 atm) is added to a solution of $\mathbf{1}_{\text{Mo}}$ in toluene- d_8 (30 mM) very broad ethylene (δ 5.25 ppm) and methylene proton resonances are observed at 20 °C. When the reaction is cooled under an ethylene atmosphere, $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{pyr})(\text{OBitet})$ ($\mathbf{4}_{\text{Mo}}$), was isolated and recrystallized from a 1:1 mixture of pentane and tetramethylsilane at -30 °C in the presence of ethylene (1 atm). An X-ray structural study of $\mathbf{4}_{\text{Mo}}$ revealed it to have a TBP structure in which the imido and the aryloxy ligands are in the axial positions.²¹ The proton NMR spectrum of $\mathbf{4}_{\text{Mo}}$ is typical for a TBP metallacycle with H_α resonances at 6.16, 5.69, 5.24, and 5.03 ppm and H_β resonances at 0.74 and -0.16 ppm at -70 °C. The isolation of $\mathbf{4}_{\text{Mo}}$ allowed us to carry out NMR studies analogous to those on the tungsten analog and to compare tungsten and molybdenum data.

When $\mathbf{4}_{\text{Mo}}$ is dissolved in toluene- d_8 , an equilibrium is established between $\mathbf{4}_{\text{Mo}}$, methylene diastereomers (*S*)-**9** and (*R*)-**9**, and ethylene. At -20 °C and 30 mM initial concentration of $\mathbf{4}_{\text{Mo}}$, ~60% $\mathbf{4}_{\text{Mo}}$, ~40% (*S*)-**9** and (*R*)-**9**, and ethylene (0.6% in solution relative to the total concentration of metal complexes) are observed. (See Scheme 1 and supporting information.) Four methylene proton resonances are observed for the diastereomers of **9** (Figure 4a), six metallacyclobutane resonances are observed for metallacycle $\mathbf{4}_{\text{Mo}}$ (Figures 4b and 4c), and a broad resonance is observed for ethylene (Figure 4b). The ethylene resonance is found at approximately the chemical shift where it would be expected in the free form. The ratio of the two diastereomers at -20 °C is (*S*)-**9**:(*R*)-**9** = 1:4. Metallacyclobutane and methylene resonances have been identified by 2D HSQC and NOESY/EXSY NMR methods described in the Supporting Information.

A reaction between $\mathbf{4}_{\text{Mo}}$ and ~ 1 atm of ^{13}C -labeled ethylene showed that ^{13}C is incorporated into the MoC_3 ring in less than 1 min at 20°C . The C_α resonances in $\mathbf{4}_{\text{Mo}}$ are found at 102.2 and 101.2 ppm, while the C_β resonance is located at -1.1 ppm, all consistent with the TBP geometry observed in the solid state. The reaction mixture was placed under vacuum to remove the excess ethylene and (*S*)- $\mathbf{9}$ and (*R*)- $\mathbf{9}$ were observed. The J_{CH} values were established for *anti* protons *a* and *c* ($J_{\text{CH}} = 140$ and 138 Hz) and for *syn* protons *b* and *d* ($J_{\text{CH}} = 163$ and 165 Hz; see Supporting Information).

An EXSY experiment of the mixture of (*R*)- $\mathbf{9}$ and (*S*)- $\mathbf{9}$ at 20°C with no ethylene present revealed that *a* and *b*, and *c* and *d*, respectively, do not exchange even at 200 ms EXSY mixing time (see Figure S27). The fact that the methyldene protons do not exchange suggests that rotation about the $\text{M}=\text{C}$ bond must take place at a rate of $<0.2\text{ s}^{-1}$, as was also found in $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$ (*vide supra*). This result contrasts with several examples of faster rotation about the $\text{W}=\text{C}$ bond noted earlier.

Details concerning the breakup and reformation of $\mathbf{4}_{\text{Mo}}$ at -20°C (Scheme 1) can be obtained employing the same methods as those employed in the analogous tungsten system. (These methods are described in detail in the Supporting Information). As in the tungsten system, formation of an intermediate ethylene/methyldene complex is most consistent with the data. The ethylene concentration is higher than what would be expected on the basis of published solubility data in benzene,¹⁴ although different conditions (solvent, etc.) in this experiment probably limit the reliability of the solubility data. Data shown in Scheme 1 for (*S*) forms are much less accurate than data for (*R*) forms as a consequence of the (*S*) forms being present in much lower concentrations ($\sim 10\%$ of (*R*) forms). Since we do not accurately know the amount of free ethylene in solution, we do not know accurately the second order rate for reforming the ethylene/methyldene intermediate and the position of the equilibria between the ethylene/methyldene intermediates and the methyldene species and free ethylene.

It is not possible to obtain data for $\mathbf{4}_{\text{Mo}}$ above -20°C as a consequence of rapid exchange processes, but data could be obtained at -30°C , -40°C , and -50°C (Table S2; see Supporting

Information). Since data for the (*R*) forms are the most accurate we only compare values for k_{Rfwd} and k_{Rrev} at different temperatures here. The values of k_{Rfwd} (in s^{-1} ; see Table S2) at four temperatures were found to be 34.0 (-20 °C), 5.88 (-30 °C), 0.850 (-40 °C), and 0.0913 (-50 °C). From an Eyring plot (Figure 5) it was found that $\Delta H^\ddagger = 21.6 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 34.4 \pm 1.6 \text{ e.u.}$ A value for k_{Rfwd} for $\mathbf{4}_{\text{Mo}}$ at 20 °C was calculated employing these parameters; $k_{\text{Rfwd}}(\text{Mo})_{20^\circ}$ was found to be $1.45 \times 10^4 \text{ s}^{-1}$ (Scheme 2). Since the value for $k_{\text{Rfwd}}(\text{W})_{20^\circ} = 3.2 \pm 0.1 \text{ s}^{-1}$,^{2g} the ratio of $k_{\text{Rfwd}}(\text{Mo})_{20^\circ}$ to $k_{\text{Rfwd}}(\text{W})_{20^\circ}$ is ~ 4500 . In a similar manner the values for $\Delta H^\ddagger = 13.2 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 3.4 \pm 1.4 \text{ e.u.}$ for $k_{\text{Rrev}}(\text{Mo})_{20^\circ}$ were determined; $k_{\text{Rrev}}(\text{Mo})_{20^\circ}$ was found to be 4900 s^{-1} , which is a factor of 71 larger than $k_{\text{Rrev}}(\text{W})_{20^\circ}$ (69 s^{-1}). Therefore at 20 °C the value of $k_{\text{Rrev}}(\text{Mo})_{20^\circ}/k_{\text{Rfwd}}(\text{Mo})_{20^\circ} = 0.34$, which should be compared with a value of $k_{\text{Rrev}}(\text{W})_{20^\circ}/k_{\text{Rfwd}}(\text{W})_{20^\circ} = 21.56$.^{2g} The values for k_{Rfreefwd} as a function of temperature are not well-behaved, which suggests that the rate constants for k_{Rfreefwd} and k_{Rfreerev} for both (*R*) and (*S*) forms are not reliable. To our knowledge these are the first quantitative data that demonstrate the relative stabilities of a high oxidation state molybdacyclobutane complex versus the analogous tungstacyclobutane complex.

DISCUSSION

The work reported here confirms that reactive 14 electron methyldiene species under the right circumstances can be relatively stable toward bimolecular decomposition. We have proposed that bimolecular decomposition involves (first) formation of an unsymmetrically bridging bis- μ -methyldiene species; one example, heterochiral $[\text{W}(\text{NAr}_{\text{Cl}})(\text{Biphen})(\mu\text{-CH}_2)]_2$ (where Ar_{Cl} is 2,6-dichlorophenylimido), has been crystallographically characterized.⁸ Homochiral $[\text{W}(\mu\text{-NAr}_{\text{Cl}})(\text{Biphen})]_2(\mu\text{-CH}_2\text{CH}_2)$ has also been crystallographically characterized.⁸ Both are logical intermediates in decomposition of a methyldiene species to an olefin-free $\text{W}=\text{W}$ species¹¹ or to a monomeric ethylene complex.¹² One potentially important unknown detail (since another equivalent of ethylene is required) is the role of ethylene in the conversion of an intermediate bimetallic species into monomeric ethylene complexes. There is

evidence in the literature that ethylene accelerates decompositions in W imido alkylidene¹⁵ and Re alkylidyne alkylidene¹⁶ systems. Therefore, the right combination of sterically bulky ligands can ensure methylidene stability, either through slowing formation of bis- μ -CH₂ species, or slowing the reaction of bis- μ -CH₂ intermediates with ethylene to give two ethylene complexes. Stability of methylidene species combined with high reactivity are bound to lead to relatively efficient and long-lived metathesis catalysts.

It has long been observed qualitatively that TBP tungstacyclobutane complexes are more stable toward loss of olefin than molybdacyclobutane complexes. We now have the first direct comparison of the rate of cleavage of an unsubstituted molybdacycle with the rate of cleavage of an unsubstituted tungstacycle to an ethylene/methylidene intermediate, and comparison of the subsequent rates of loss of ethylene from the Mo and W ethylene/methylidene intermediates. The stability of especially an unsubstituted tungstacyclobutane toward loss of ethylene early in the development of imido alkylidene catalysts was one of the reasons why molybdenum catalysts were sought, i.e., ethylene formed in a metathesis process could sequester tungsten in the form of an unsubstituted metallacyclobutane.¹⁷ Relatively more facile loss of an olefin from a metallacyclobutane also should apply to substituted metallacycles. The more rapid loss of olefin from molybdacyclobutanes could contribute to a relatively high metathesis activity for molybdenum complexes in a variety of circumstances compared to tungsten analogs, as in the recently reported *Z*-selective coupling of terminal olefins, which are more successful employing the "less reactive" tungsten catalysts for the substrates examined so far.²¹

We are surprised not only by the stability of certain methylidene complexes, but by the relatively rapid rate of rotation of W=CH₂ species about the W=C bond, i.e., interconversion of *syn* and *anti* methylidene protons. Confirmed rates at 22 °C in complexes discussed here vary from 4-5 s⁻¹ up to 230 s⁻¹. These rates are summarized in Table 1. Since we so far have not observed *anti* isomers of 14 electron substituted alkylidenes in MAP species, we do not know whether *syn* and *anti* monosubstituted alkylidenes also interconvert readily. We suspect that methylidene rotation cannot be compared directly with rates of interconversion of *syn* and *anti*

isomers. The reason is that if the $M=CH_{anti}$ agostic interaction is an important stabilizing feature that allows *syn* and *anti* isomers of substituted alkylidenes to be observed, one could argue that the agostic interaction never fully disappears in the process of rotating the methylidene ligand, and could even act as a means of lowering the energy of the transition state in which the methylidene has rotated by 90° and the $M=C$ bond has been formally broken.

A relatively slow rotation of methylidene ligands in molybdenum species was unexpected. So far we can only say that rotation rates are $<0.2 \text{ s}^{-1}$ for the two Mo species that we have explored. Rotation of tungsten methylidenes may be significantly faster than molybdenum methylidenes if the agostic interaction is stronger for tungsten than for molybdenum and the transition state in which the methylidene has rotated 90° therefore stabilized to a greater degree than for molybdenum.

The presence in the kinetic scheme of an intermediate ethylene/methylidene complex has led to well-behaved temperature dependencies for the rate constants for its formation and for reformation of the metallacycle in the $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ system. These data, in combination with those generated in the $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ investigation,^{2g} give us confidence that the ethylene/methylidene intermediate exists. The values for ΔS^\ddagger for k_{Rfwd} ($34.4 \pm 1.6 \text{ e.u.}$) and for ΔS^\ddagger for $k_{\text{Rrev}}(\text{Mo})_{20}$ ($3.4 \pm 1.4 \text{ e.u.}$) are consistent with significant disorder in the transition state leading to the ethylene/methylidene intermediate and with more order in the transition state leading back to the metallacyclobutane complex, respectively. The value of $k_{\text{Rrev}}(\text{Mo})_{20}/k_{\text{Rfwd}}(\text{Mo})_{20} = 0.34$ at 20°C suggests that more ethylene/methylidene complex is present at 20°C than metallacyclobutane. It is important to note that the structure of the ethylene/methylidene intermediate is not known at this stage, so interconversion of the metallacyclobutane complex and the ethylene/methylidene complex may include a component that consists of a change in geometry at the metal center and/or even a high degree of fluxionality for the five-coordinate ethylene/methylidene species. The apparent relatively high stability of metallacyclobutane species toward loss of ethylene when the aryloxide is OHIPT suggests that details concerning exactly how the olefin leaves the metallacycle (twisting, sliding,

etc.) are likely to be important. To our knowledge the only evidence (prior to that reported here and in a previous paper^{2g}) for an alkylidene/olefin complex in high oxidation state species is formation of a cycloheptene/cyclopentylidene species at low temperatures upon addition of cycloheptene to $[\text{W}(\text{C}_5\text{H}_8)(\text{OCH}_2\text{CMe}_3)_2\text{Br}_2]\text{GaBr}_3$.¹⁸

CONCLUSIONS

Reactive methylidene MAP species under the right circumstances are relatively stable toward bimolecular decomposition or as yet poorly defined ethylene-catalyzed decomposition processes. In the solid state the methylidene complex is a monomer containing an η^1 -pyrrolide ligand and the methylidene ligand is distorted in a manner consistent with an agostic CH_{anti} interaction. Methylidenes rotate about the $\text{W}=\text{C}$ bond at rates that vary from 3.6 s^{-1} to 230 s^{-1} , but rotation about $\text{Mo}=\text{C}$ bonds is comparatively slow ($<0.2 \text{ s}^{-1}$). MAP metallacyclobutane species break up at widely differing rates to give intermediate ethylene/methylidene intermediates. In $\text{M}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ systems, the rate of metallacycle breakup has been found to be 4500 times faster when $\text{M} = \text{Mo}$ than when $\text{M} = \text{W}$ at $20 \text{ }^\circ\text{C}$.

Experimental

General. General procedures can be found in a previous paper.^{2g} 2,3,5,6-Tetraphenylphenol (HOTPP),¹⁹ 3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol (HOBitet),^{2c,d} hexaisopropylterphenol (HIPTOH),²⁰ $\text{W}(\text{NAr})(\text{CHMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$,²¹ $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Pyr})_2(\text{DME})$,²¹ $\text{W}(\text{NAr}^{\text{Cl}})(\text{CHCMe}_3)(\text{Pyr})_2(\text{DME})$,²¹ $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$,^{2a} $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Pyr})_2$,^{3a} $\mathbf{1}_{\text{Mo}}$,^{2c,2h} $\mathbf{4}_{\text{Mo}}$,²¹ and $\mathbf{9}^{21}$ were all prepared according to literature procedures.

$\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OHIPT})(\text{Pyr})$. A 50 mL Schlenk flask was charged with a stir bar and a solution of $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Pyr})_2$ (0.580 g, 1.083 mmol) and HOHIPT (0.540 g, 1.083 mmol) in diethyl ether (2 mL) and pentane (4 mL). The yellow solution was stirred and heated at $60 \text{ }^\circ\text{C}$ in a closed system for 24 h. The mixture was cooled to room temperature and filtered

through glass wool. The filtrate was degassed via three freeze-pump-thaw cycles and exposed to 1 atm of ethylene. Yellow fluffy solid precipitated immediately and was filtered off and dried *in vacuo* for 1 h; yield 0.480g (51%). The product can be recrystallized from a concentrated solution of 1:1 mixture of pentane and diethyl ether at $-27\text{ }^{\circ}\text{C}$ as a fine, feathery solid. ^1H NMR shows that in solution, $\sim 15\%$ of the sample is the methyldiene species and $\sim 8\%$ of the expected ethylene is observed: ^1H NMR (500 MHz, C_6D_6) δ 7.32 (m, 2, Pyr-*H*), 7.26 (d, 2, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 7.21 (s, 4, Ar-*H*), 6.89 (t, 1, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.80 (m, 3, Ar-*H*), 6.21 (m, 2, Pyr-*H*), 4.30 (m, 2, CH_α), 3.94 (m, 2, CH_α), 3.65 (sept, 2, CHMe_2), 3.59-2.24 (br, 4, CHMe_2), 2.89 (sept, 2, CHMe_2), 1.32 (d, 12, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.30-1.02 (m, 24, CHMe_2), 1.00 (d, 12, CHMe_2 , $J_{\text{HH}} = 7$ Hz), -0.15 (br m, 1, CH_β), -0.65 (br m, 1, CH_β); ^{13}C NMR (125 MHz, C_6D_6) δ 160.32, 151.22, 158.57, 156.07, 148.32, 147.24, 136.58, 132.30, 131.87, 130.76, 124.24, 123.82, 122.33, 119.38, 114.87, 109.26, 100.19 (WC_α), 35.15, 31.52 (br s), 29.00 (br s), 26.86, 24.65, 23.43, -0.80 (WC_β). Anal. Calcd for $\text{C}_{55}\text{H}_{76}\text{MoN}_2\text{O}$: C, 75.31; H, 8.73; N, 3.19. Found: C, 75.21; H, 8.76; N, 3.21.

Mo(NAr)(CH_2)(OHIPT)(Pyr). A 20 mL vial was charged with a stir bar and a solution of Mo(NAr)(C_3H_6)(Pyr)(OHIPT) (0.443 g, 0.505 mmol) in diethyl ether (2 mL) and toluene (2 mL). The volatiles were removed *in vacuo*. Toluene was added to the residue, and vacuum was applied to the dark yellow solution. This process was repeated once more. Pentane was added to the residue and the volatiles were removed *in vacuo*; this process was repeated until the sample became a yellow foam. A small amount of pentane was added and the solution was allowed to sit at $-27\text{ }^{\circ}\text{C}$. After 24 h, the mother liquor was decanted, and the crystals were washed with cold pentane and dried *in vacuo* for 2 h; yield 0.375 g (87%): ^1H NMR (500 MHz, C_6D_6) δ 12.21 (d, 1, *anti*- MoCH_α , $J_{\text{HH}} = 5$ Hz), 12.10 (d, 1, *syn*- MoCH_α , $J_{\text{HH}} = 5$ Hz), 7.35 (s, 2, Ar-*H*), 7.21 (s, 2, Ar-*H*), 7.12 (d, 2, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 6.97 (m, 3, Ar-*H*), 6.91 (t, 1, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 6.37 (m, 4, Pyr-*H*), 3.50 (sept, 2, CHMe_2), 2.98 (sept, 2, CHMe_2), 2.90 (m, 4, CHMe_2), 1.31 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.28 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.22 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.19 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.15 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.14 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.10 (d, 6, CHMe_2 ,

$J_{\text{HH}} = 7$ Hz), 1.05 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 278.15 (MoC_α), 159.44, 154.83, 149.24, 147.80, 147.70, 145.16, 134.49, 133.42, 132.22, 131.37, 127.52, 123.09, 122.61, 121.80, 121.59, 111.08, 35.24, 31.77, 31.55, 29.35, 26.13, 25.70, 25.07, 25.05, 24.60, 24.55, 23.56, 22.94. Anal. Calcd for $\text{C}_{53}\text{H}_{72}\text{MoN}_2\text{O}$: C, 74.97; H, 8.55; N, 3.30. Found: C, 74.65; H, 8.47; N, 3.33.

A sample was degassed via three freeze-pump-thaw cycles and exposed to ^{13}C -ethylene. A vacuum was applied to remove ethylene and regenerate the methylidene complex as a mixture of ^{13}C labeled (~60%) and unlabeled species: ^1H NMR (500 MHz, C_6D_6) δ 12.18 ($J_{\text{CH}} = 138$ Hz, *anti*- MoCH_α), 12.06 ($J_{\text{CH}} = 163$ Hz, *syn*- MoCH_α).

***In situ* synthesis of $\text{Mo}(\text{NAd})(\text{C}_2\text{H}_4)(\text{OHIPT})(\text{Pyr})$.** $\text{Mo}(\text{NAd})(\text{CHCMe}_3)(\text{OHIPT})(\text{Pyr})$ (0.015 g, 0.017 mmol) and 0.6 mL of benzene- d_6 was added to a Teflon-seal J-Young tube. The yellow solution was degassed by three freeze-pump-thaw cycles. The solution was exposed to 1 atm of ethylene or ^{13}C -ethylene: ^1H NMR (500 MHz, C_6D_6) δ 7.28 (s, 2, Ar-*H*), 7.25 (s, 2, Ar-*H*), 7.08 (d, 2, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.89 (t, 1, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.67 (m, 2, Pyr-*H*), 6.53 (m, 2, Pyr-*H*), 2.95 (m, 6, CHMe_2), 2.73 (m, 1, MoC_2H_4), 2.32 (m, 1, MoC_2H_4), 2.01 (m, 1, MoC_2H_4), 1.63 (s, 3, Ad-*H*), 1.47 (s, 6, Ad-*H*), 1.41 (d, 12, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.28 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.20 (s, 6, Ad-*H*), 1.19 (d, 12, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 1.17 (d, 6, CHMe_2 , $J_{\text{HH}} = 7$ Hz), 0.35 (m, 1, MoC_2H_4); ^{13}C NMR (125 MHz, C_6D_6) δ 55.23 (MoC_2H_4 , $J_{\text{CC}} = 38$ Hz, $J_{\text{CH}} = 154$ and 155 Hz), 46.41 (MoC_2H_4 , $J_{\text{CC}} = 38$ Hz, $J_{\text{CH}} = 158$ and 158 Hz).

$\text{W}(\text{NAr}^{\text{tBu}})_2(\text{NC}_5\text{H}_5)_2\text{Cl}_2$. In the glove box, a 500 mL Schlenk flask was charged with a stir bar and WO_2Cl_2 (22.18 g, 77.35 mmol) in 50 mL of dimethoxyethane. 2-*t*-Butylaniline (24.31 g, 162.92 mmol) was added. The flask was taken out of the box and purged with N_2 on the Schlenk line. Under N_2 , 2,6-lutidine (37 mL, 318 mmol) and trimethylchlorosilane (98 mL, 776 mmol) were added to the solution with vigorous stirring. The mixture was stirred at 65 °C for 2 days and then cooled to room temperature. In the glove box the mixture was filtered through a frit and the orange salt was extracted with a pyridine (50 mL) and benzene (300 mL) mixture. The two portions of the filtrates were combined and solvents were removed *in vacuo*.

Pentane was added to the orange-red residue. The precipitated red powder was filtered off and rinsed with pentane; yield 47 g (86%): ^1H NMR (500 MHz, C_6D_6) δ 8.92 (d, 4, Ar-*H*, $J_{\text{HH}} = 5$ Hz), 7.74 (dd, 2, Ar-*H*, $J_{\text{HH}} = 8$ and 1 Hz), 7.30 (dd, 2, Ar-*H*, $J_{\text{HH}} = 8$ and 1 Hz), 7.06, (t, 2, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 6.71 (t, 2, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 6.66 (t, 2, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 6.27 (t, 4, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 1.52 (s, 18, t-butyl); ^{13}C NMR (125 MHz, C_6D_6) δ 152.52, 138.15, 127.61, 127.12, 127.03, 125.76, 124.33, 119.16, 118.41, 31.26, 29.97. Anal. Calcd for $\text{C}_{30}\text{H}_{36}\text{Cl}_2\text{N}_4\text{W}$: C, 50.94; H, 5.13; N, 7.92. Found: C, 50.99; H, 5.17; N, 7.76.

$\text{W}(\text{NAr}^{\text{tBu}})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$. A 500 mL flask was charged with a stir bar, $\text{W}(\text{NAr}^{\text{tBu}})_2(\text{NC}_5\text{H}_5)_2\text{Cl}_2$ (11.77 g, 16.64 mmol) and 200 mL of ethyl ether. The solution was chilled at -30 °C for 2 h and $\text{MgCl}(\text{CH}_2\text{CMe}_2\text{Ph})$ (0.5 M, 67 mL, 33.28 mmol) was added dropwise to the solution. Over the course of half an hour, the solution changed from red to bright yellow. The mixture was allowed to stir overnight at room temperature, and then filtered through a bed of Celite. The solvents were removed from the yellow filtrate *in vacuo*. Pentane (50 mL) was added to the resulting yellow powder, and the slurry was filtered to afford a fine yellow powder; yield 9.273 g (72%): ^1H NMR (500 MHz, C_6D_6) δ 7.38 (d, 4, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 7.26 (m, 2, Ar-*H*), 7.16 (t, 4, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 7.04, (m, 4, Ar-*H*, $J_{\text{HH}} = 7$ Hz), 6.80 (m, 4, Ar-*H*), 1.75 (s, 4, $\text{CH}_2\text{CMe}_2\text{Ph}$), 1.60 (s, 18, t-butyl), 1.50 (s, 12, $\text{CH}_2\text{CMe}_2\text{Ph}$); ^{13}C NMR (125 MHz, C_6D_6) δ 154.56 ($J_{\text{CW}} = 36$ Hz), 151.90, 140.63, 131.84, 129.13, 127.14, 126.63, 126.61, 126.31, 125.46, 92.63 ($J_{\text{CW}} = 100$ Hz), 41.65, 35.80, 33.78, 30.78. Anal. Calcd for $\text{C}_{40}\text{H}_{52}\text{N}_2\text{W}$: C, 64.51; H, 7.04; N, 3.76. Found: C, 64.24; H, 6.89; N, 3.72.

$\text{W}(\text{NAr}^{\text{tBu}})(\text{CHCMe}_2\text{Ph})(\text{OTf})_2(\text{DME})$. A sample of $\text{W}(\text{NAr}^{\text{tBu}})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$ (12.80 g, 17.19 mmol) was dissolved in DME (30 mL) and pentane (200 mL). The solution was chilled to -30 °C for 2 h, and then triflic acid (7.74 g, 51.57 mmol) was added in one portion. The solution changed from bright yellow to orange immediately upon addition of triflic acid. The solution was allowed to stir at room temperature for 24 h. All volatiles were removed *in vacuo* and the resulting residue was extracted with toluene (300 mL) and the mixture was filtered through a bed of Celite. Solvents were removed from the filtrate *in vacuo* to give a yellow

powder. Pentane was added to the powder, and the mixture was filtered off to afford a yellow powder; yield 8.88 g (61%). A ^1H NMR spectrum shows four isomers in a 0.12, 0.03, 1.00, and 0.45 ratio. Only chemical shifts of the major isomer and those that are discernable are reported: ^1H NMR (500 MHz, C_6D_6) δ 12.01 (s, 0.12, CHCMe_2Ph), 11.50 (s, 0.03, CHCMe_2Ph), 11.12 (s, 1, CHCMe_2Ph), 10.70 (s, 0.45, CHCMe_2Ph), aryl region is messy, 3.61 (s, 3, DME), 3.12 (br s, 2, DME), 2.79 (s, 3, DME), 2.75, (br s, 2, DME), many peaks in alkyl region to pick out CHCMe_2Ph , 1.49 (s, 18, t-butyl). Anal. Calcd for $\text{C}_{26}\text{H}_{35}\text{F}_6\text{NO}_8\text{S}_2\text{W}$: C, 36.67; H, 4.14; N, 1.64. Found: C, 36.45; H, 3.99; N, 1.85.

W(NAr^{tBu})(CHCMe₂Ph)(Me₂Pyr)₂. Lithium 2,5-dimethyl pyrrolide (1.435 g, 14.200 mmol, 2.5 equiv) and W(NAr^{tBu})(CHCMe₂Ph)(OTf)₂(DME) (4.837 g, 5.680 mmol) were mixed in a 50 mL flask. A stir bar and toluene (20 mL) were added. The resulting cloudy yellow solution was allowed to stir overnight at room temperature. The solution was filtered through a bed of Celite and solvents were removed from the filtrate *in vacuo*. Pentane was added to the residue. The precipitated yellow powder was collected to afford 1.772 g of product (48% yield). The compound could be recrystallized from a concentrated toluene solution to give yellow blocks, but the powder is pure as judged by elemental analysis and ^1H NMR: ^1H NMR (500 MHz, C_6D_6) δ 10.90 (s, 1, *syn*- CHCMe_2Ph , $J_{\text{CH}} = 123$ Hz), 7.35 (d, 2, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 7.29 (d, 1, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 7.15, (m, 3, Ar-*H*), 7.02 (t, 1, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.83 (m, 2, Ar-*H*), 5.95 (br s, 4, Pyr-*H*), 2.16 (s, 12, Pyr-*Me*), 1.65 (s, 6, CHCMe_2Ph), 1.33 (s, 9, t-butyl); ^{13}C NMR (125 MHz, C_6D_6) δ 281.17 (CHCMe_2Ph), 155.06 ($J_{\text{CW}} = 42$ Hz), 151.65, 142.49, 135.03, 128.80, 127.14, 126.85, 126.69, 126.32, 126.21, 106.85 (br s, Pyr), 57.39, 35.84, 33.28, 30.16, 17.80 (br s, *Me*-Pyr). Anal. Calcd for $\text{C}_{32}\text{H}_{41}\text{N}_3\text{W}$: C, 58.99; H, 6.34; N, 6.45. Found: C, 59.12; H, 6.33; N, 6.42.

W(NAr^{tBu})(CHCMe₂Ph)(OTPP)(Me₂Pyr). A 20 mL scintillation vial was charged with a stir bar, W(NAr^{tBu})(CHCMe₂Ph)(Me₂Pyr)₂ (0.604 g, 0.927 mmol), and HOTPP (0.369 g, 0.927 mmol). Benzene (10 mL) was added to the mixture. The mixture was allowed to stir at room temperature overnight and filtered through glass wool. The solvents were removed from the

filtrate *in vacuo*. Pentane was added to the residue, and the yellow precipitate was filtered off; yield 0.759 g (86%): ^1H NMR (500 MHz, C_6D_6) δ 8.11 (s, 1, *syn*- CHCMe_2Ph , $J_{\text{CH}} = 113$ Hz, $J_{\text{WH}} = 16$ Hz), 7.05 (m, 29), 6.11 (br s, 2, Pyr-*H*), 5.89 (d, 1, Ar-H, $J_{\text{HH}} = 8$ Hz), 2.61 (br s, 3, Pyr-*Me*), 1.92 (br s, 3, Pyr-*Me*), 1.53 (s, 3, CHCMe_2Ph), 1.23 (s, 3, CHCMe_2Ph), 1.20 (s, 9, t-butyl); ^{13}C NMR (125 MHz, C_6D_6) δ 258.77 (CHMe_2Ph), 159.64, 155.76, 152.13, 154.30, 142.60, 142.43, 137.00, 134.40, 132.99 (v. br), 131.88 (v. br), 130.99, 130.53, 128.50, 127.89, 127.85, 127.10, 126.90, 126.72, 126.30, 126.25, 126.07, 110.66, 54.22, 35.64, 34.24, 30.75, 30.66. Anal. Calcd for $\text{C}_{56}\text{H}_{54}\text{N}_2\text{OW}$: C, 70.44; H, 5.70; N, 2.93. Found: C, 70.60; H, 5.92; N, 2.95.

W(NAr^{tBu})(C₃H₆)(OTPP)(Me₂Pyr). A 50 mL Schlenk flask was charged with a stir bar and a solution of W(NAr^{tBu})(CHCMe_2Ph)(OTPP)(Me₂Pyr) (0.759 g, 0.795 mmol) in diethyl ether (3 mL) and benzene (1 mL). The solution was degassed by three freeze-pump-thaw cycles and exposed to 1 atm of ethylene at room temperature. The yellow cloudy solution became clear immediately upon the addition of ethylene. All volatiles were removed from the solution after stirring it at room temperature overnight. The residue was recrystallized from ~2 mL of ether and a few drops of benzene to afford fine yellow needles; yield 0.356 g (52% yield). A ^1H NMR spectrum shows that in solution, 11% of the sample is the methyldiene species (*vide infra*) and ~2% of ethylene (broad signal) are observed: ^1H NMR (500 MHz, C_6D_6) δ 7.05 (m, 25, Ar-*H*), 6.14 (s, 2, Pyr-*H*), 4.28 (br s, 2, CH_α), 3.35 (br s, 2, CH_α), 2.39 (s, 6, Pyr-*Me*), 1.19 (s, 9, t-butyl), -0.99 (br s, 1, CH_β), -1.60 (br s, 1, CH_β); ^{13}C NMR (125 MHz, C_6D_6) δ 159.23, 156.07, 144.56, 143.00, 142.61, 141.97, 139.01, 137.30, 133.95, 132.53, 132.14, 131.39, 131.16, 130.48, 129.26, 137.90, 127.22, 126.74, 126.47, 126.14, 110.55, 109.31, 102.00 (WC_α), 31.78, 30.85, 17.10, -4.12 (WC_β). Anal. Calcd for $\text{C}_{49}\text{H}_{48}\text{N}_2\text{OW}$: C, 68.06; H, 5.59; N, 3.24. Found: C, 68.18; H, 5.84; N, 3.21.

A sample was degassed via three freeze-pump-thaw cycles and exposed to ^{13}C -ethylene. ^{13}C NMR (125 MHz, C_6D_6) δ 102.00 (WC_α , $J_{\text{CH}} = 159$ Hz, $J_{\text{CW}} = 80$ Hz), -4.12 (WC_β , $J_{\text{CH}} = 154$ Hz). This compound decomposes over the course of ~4 h in solution at room temperature.

***In situ* synthesis of W(NAr^{tBu})(CH₂)(OTPP)(Me₂Pyr).**

W(NAr^{tBu})(C₃H₆)(OTPP)(Me₂Pyr) (0.023 g, 0.027 mmol) and benzene-*d*₆ (0.6 mL) were added to a 2.9 mL J-Young tube and the solvent was removed. Benzene-*d*₆ was added and the volatiles were removed *in vacuo* four more times: ¹H NMR (500 MHz, C₆D₆) δ 10.10 (v br s, 1, *syn*-CH_a), 9.09 (v. br s, 1, *anti*-CH_a), 7.32 (s, 1, Ar-*H*), 7.18 (m, 9, Ar-*H*), 6.94, (m, 14, Ar-*H*), 6.16 (m, 1, Ar-*H*), 6.06 (s, 2, Pyr-*H*), 2.09 (s, 6, Pyr-*Me*), 1.30 (s, 9, t-butyl).

A sample of W(NAr^{tBu})(C₃H₆)(OTPP)(Me₂Pyr) in benzene-*d*₆ was degassed via three freeze-pump-thaw cycles, exposed to ¹³C-ethylene, and then vacuum was applied to remove ethylene to generate the methylidene species: ¹H NMR (500 MHz, C₆D₆) δ 10.10 (*syn*-CH_a, *J*_{CH} = 156 Hz), 9.09 (*anti*-CH_a, *J*_{CH} = 128 Hz); ¹³C NMR (125 MHz, C₆D₆) δ 242.09 (WC_a, *J*_{CW} = 183 Hz). W(NAr^{tBu})(CH₂)(OTPP)(Me₂Pyr) decomposes over a period of ~2 h in solution at room temperature.

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Supporting Information Available. Experimental details for all NMR experiments and X-ray structural studies. Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

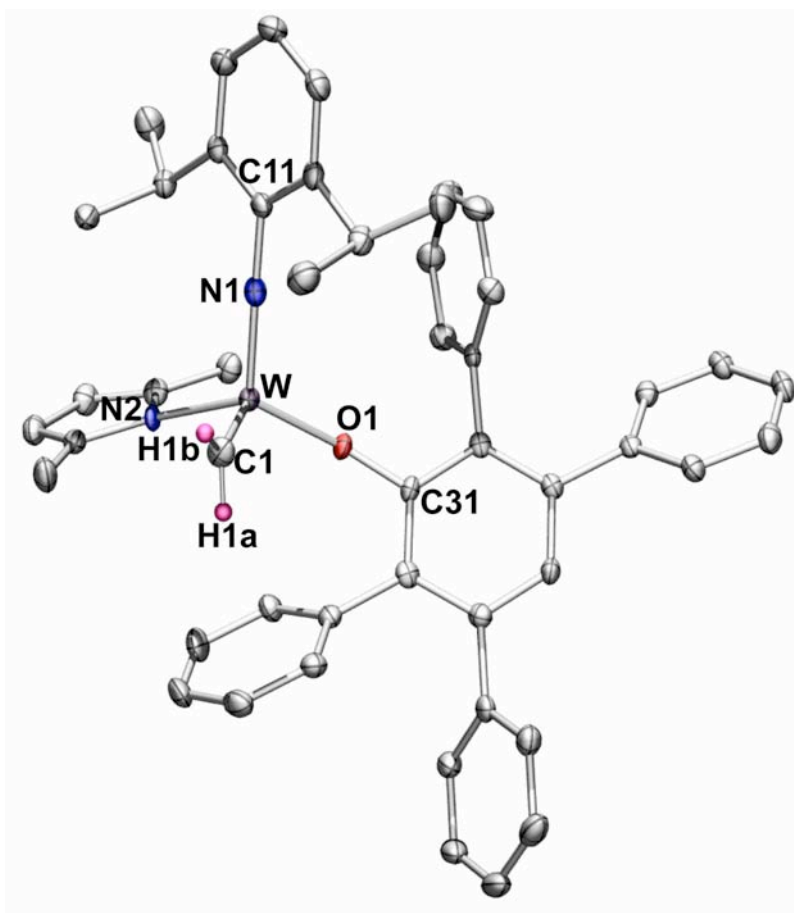


Figure 1. A thermal ellipsoid drawing of $W(NAr)(CH_2)(OTTP)(Me_2Pyr)$ (**2_w**) (50% probability). Hydrogen atoms except for those on the methylene are removed for clarity. Selected bonds (Å) and angles (°): $W-N1 = 1.758(4)$, $W-N2 = 2.020(4)$, $W-O1 = 1.913(3)$, $W-C1 = 1.908(4)$, $W-N1-C11 = 176.8(3)$, $W-O1-C31 = 148.4(3)$, $W-C1-H1a = 107(4)$, $W-C1-H1b = 136(3)$, $H1a-C1-H1b = 117(5)$. The angle between planes through $H1a-C1-H1b$ and $N1-W-C1$ is 7.7° .

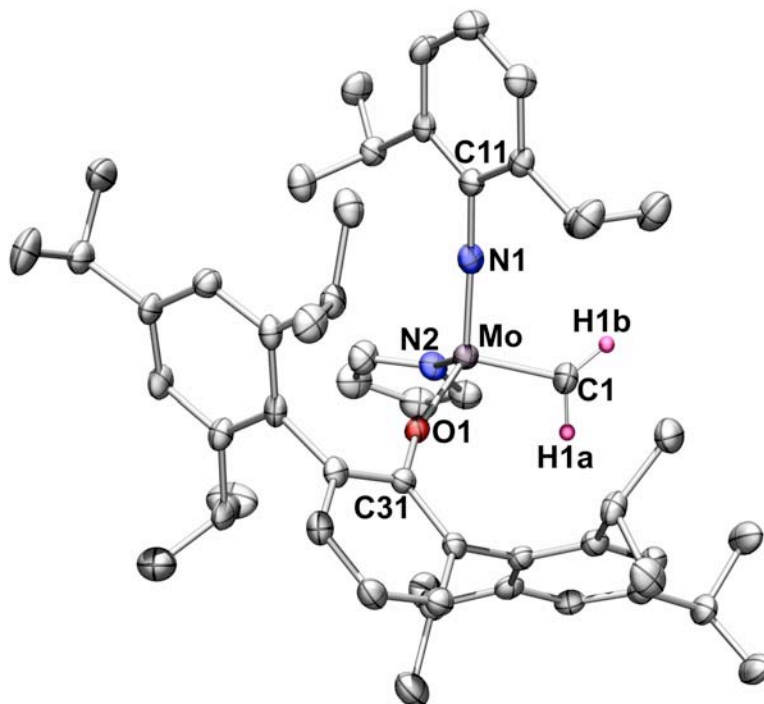


Figure 2. A thermal ellipsoid drawing of Mo(NAr)(CH₂)(OHIPT)(Pyr) (**3_{Mo}**) (50% probability). Hydrogen atoms except for those on the methylene are removed for clarity. Selected bonds (Å) and angles (°): Mo-N1 = 1.737(4), Mo-N2 = 2.035(4), Mo-O1 = 1.911(3), Mo-C1 = 1.892(5), Mo-N1-C11 = 171.1(3), Mo-O1-C31 = 160.3(3), Mo-C1-H1a = 105(3), Mo-C1-H1b = 131(3), H1a-C1-H1b = 124(5). The angle between planes through H1a-C1-H1b and N1-Mo-C1 is 7.7°.

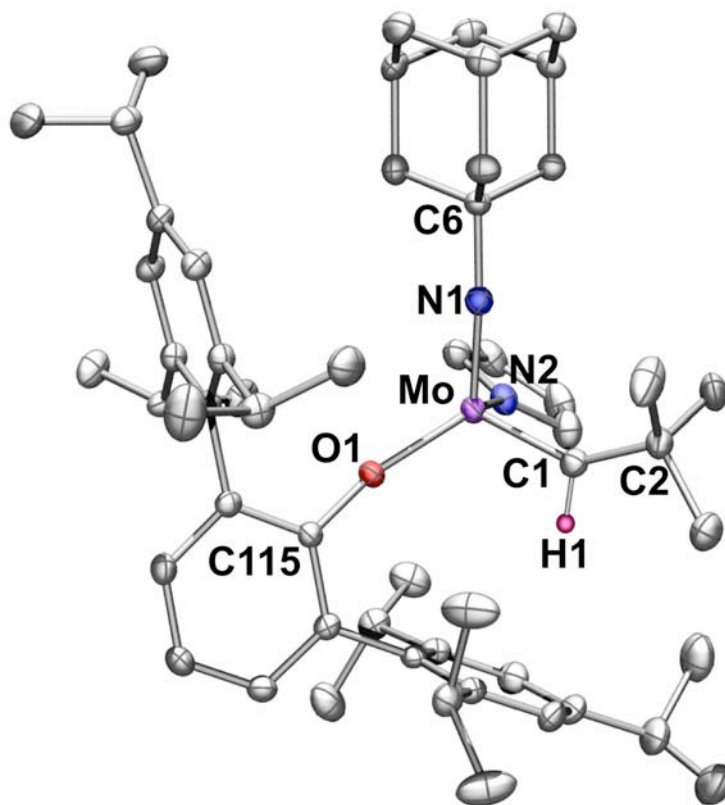


Figure 3. A thermal ellipsoid drawing of Mo(NAd)(CHCMe₃)(OHIPT)(Pyr) (**6**) (50% probability). Hydrogen atoms (except for H1) are removed for clarity. Selected bonds (Å) and angles (°): Mo-N1 = 1.707(2), Mo-N2 = 2.040(2), Mo-O1 = 1.9124(15), Mo-C1 = 1.886(2), Mo-N1-C6 = 167.54(16), Mo-O1-C115 = 167.55(15), Mo-C1-C2 = 143.25(18).

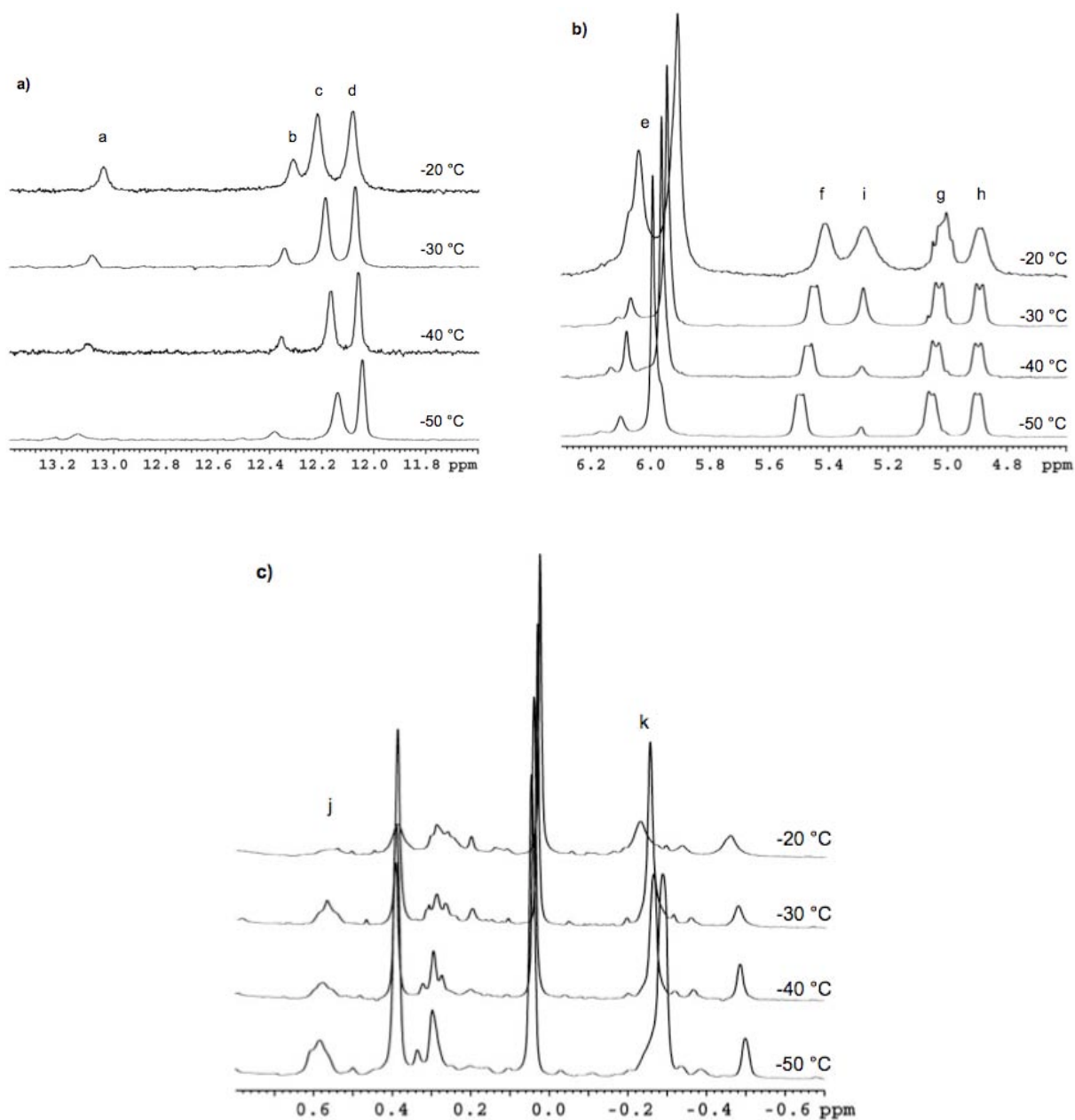


Figure 4. Proton NMR spectra of Mo(NAr)(C₃H₆)(OBitet)(Me₂Pyr) (**4**_{Mo}) in toluene-d₈ at -20 °C. (a) Expansion of the ¹H NMR spectrum in the alkylidene region for (*S*)- and (*R*)-Mo(NAr)(CH₂)(Me₂Pyr)(OBitet) (1 : 4 ratio of (*S*)-**9** and (*R*)-**9**); (b) Expansion of the ¹H NMR spectrum in the H_α region for Mo(NAr)(C₃H₆)(OBitet)(Me₂Pyr) (**4**_{Mo}). (c) Expansion of the ¹H NMR spectrum in the H_β region for **4**_{Mo}. (See Scheme 1 for labels.)

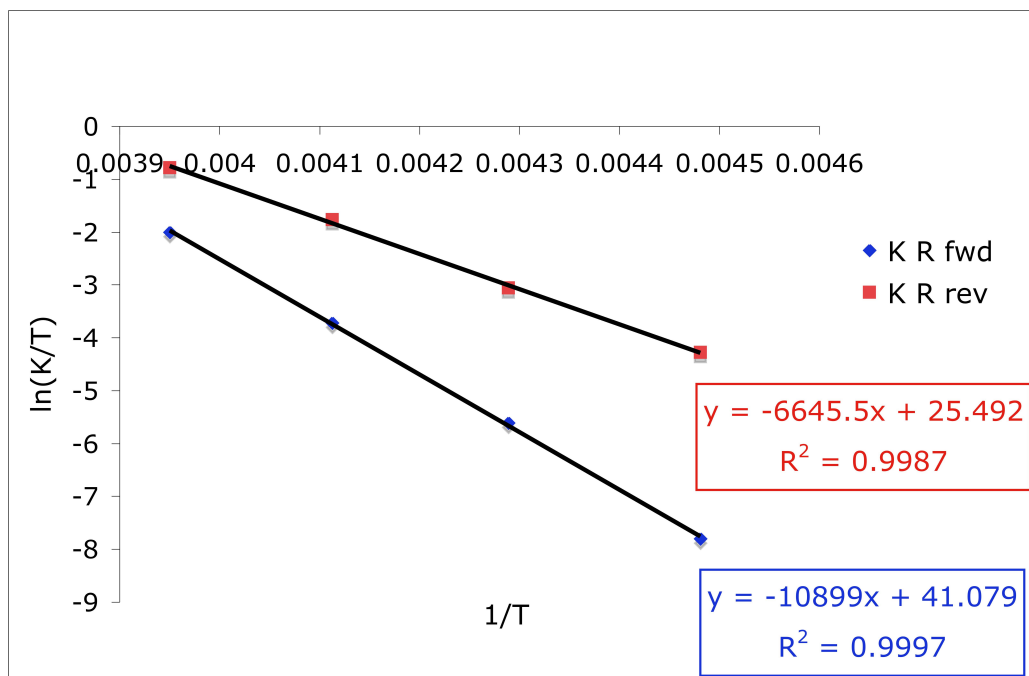
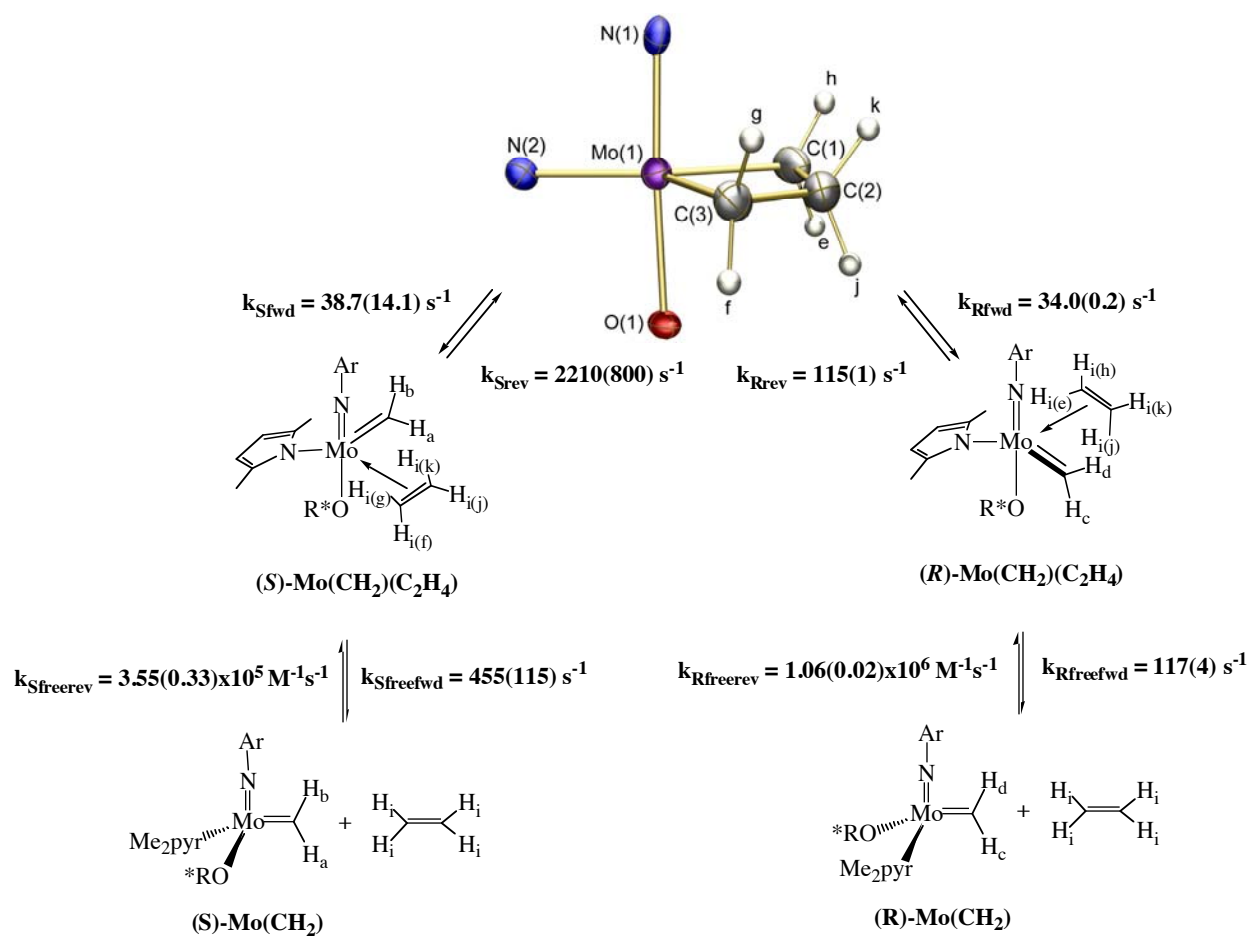
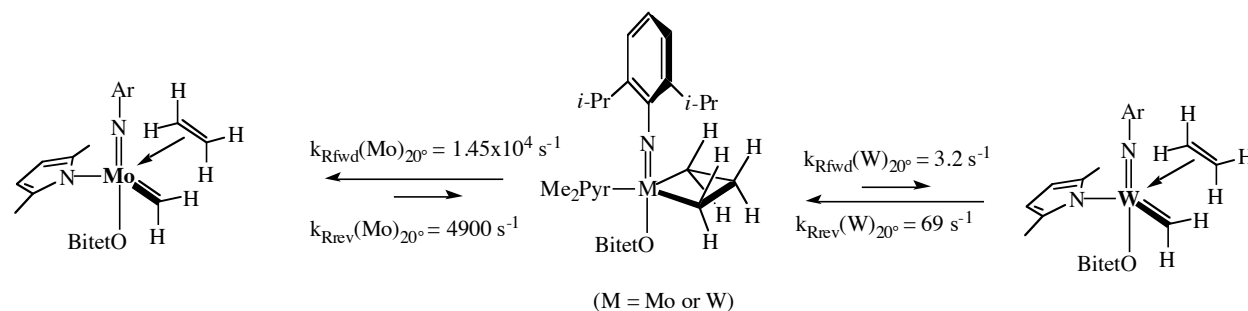


Figure 5. Eyring plots for k_{Rfwd} and k_{Rrev} at -20, -30, -40, and -50 °C for cleavage and reformation of $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ (see Scheme 1).



Scheme 1. Details of processes involving loss of ethylene from Mo(NAr)(C₃H₆)(OBitet)(Me₂Pyr) in solution at -20 °C.



Scheme 2. A comparison of the rate constants for interconversion of $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ and $(R)\text{-Mo}(\text{NAr})(\text{CH}_2)(\text{C}_2\text{H}_4)(\text{OBitet})(\text{Me}_2\text{Pyr})$ with interconversion of $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OBitet})(\text{Me}_2\text{Pyr})$ and $(R)\text{-W}(\text{NAr})(\text{CH}_2)(\text{C}_2\text{H}_4)(\text{OBitet})(\text{Me}_2\text{Pyr})$ at 20 °C.

Table 1. Rates of exchange of methyldene protons at 20 °C.

<u>Methyldene species</u>	<u>Rate (s⁻¹)</u>
Mo(NAr)(CH ₂)(OHIPT)(Pyr)	< 0.2
Mo(NAr)(CH ₂)(OBitet)(Me ₂ Pyr)	< 0.2
W(NAr ^{t-Bu})(CH ₂)(OTPP)(Me ₂ Pyr)	230
W(NAr)(CH ₂)(OTPP)(Me ₂ Pyr) ^{2g}	90
(<i>R</i>)-W(NAr)(CH ₂)(OBitet)(Me ₂ Pyr) ^{2g}	3.6
(<i>S</i>)-W(NAr)(CH ₂)(OBitet)(Me ₂ Pyr) ^{2g}	5.1

References

1. (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4592. (c) Schrock, R. R. in *Handbook of Metathesis*, Grubbs, R. H., Ed., Wiley-VCH, Weinheim, 2003, p. 8. (d) Schrock, R. R. *Angew. Chem. Int. Ed.* **2006**, *45*, 3748. (e) Schrock, R. R.; Czekelius, C. C. *Adv. Syn. Catal.* **2007**, *349*, 55.
2. (a) Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654. (b) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 58. (c) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933. (d) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943. (e) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211.
(f) Ibrahim, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.*, **2009**, *131*, 3844.
(g) Jiang, A. J.; Simpson, J. H.; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 7770. (h) Meek, S. J.; Malcolmson, S. J.; Li, B.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16407. (i) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630. (j) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. (k) Lee, Y.-J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10652. (l) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10840.
3. (a) Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373. (b) Marinescu, S. C.; Singh, R.; Hock, A. S.; Wampler, K. M.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 6570.
4. Wampler, K. M.; Hock, A. S.; Schrock, R. R. *Organometallics* **2007**, *26*, 6674.
5. (a) Blanc, R.; Berthoud, R.; Salameh, A.; Basset, J.-M.; Copéret, C.; Singh, R.; Schrock, R. R. *J. Am. Chem. Soc.* **2007**, *129*, 8434. (b) Blanc, F.; Berthoud, R.; Copéret, C.; Lesage, A.;

-
- Emsley, L.; Singh, R.; Kreickmann, T.; Schrock, R. R. *Proc. Nat. Acad. Sci.* **2008**, *105*, 12123.
- The exchange of methyldene protons has been shown to be independent of concentration, which rules out any intermolecular scrambling process; King, A. J., unpublished results.
 - Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.
 - Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 1279.
 - It should be noted that *syn* and *anti* nomenclature in an imido M=CHR complex refers to the direction in which the *R* substituent points, e.g., a *syn* M=CHR complex contains an H_{anti} α proton.
 - (a) Solans-Monfort, X.; Eisenstein, O. *Polyhedron* **2006**, *25*, 339. (b) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *Dalton Trans.* **2006**, 3077. (c) Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *Organometallics* **2005**, *24*, 1586.
 - (a) Lopez, L. P. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 9526. (b) Lopez, L. P. H.; Schrock, R. R.; Müller, P. *Organometallics* **2006**, *25*, 1978. (c) Lopez, L. P. H.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 3857.
 - Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. A.; Hultsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.
 - Jiang, A. J.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 4428.
 - Jolley, J. E., Hildebrand, J. H. *J. Am. Chem. Soc.* **1958**, *80*, 1050.
 - Tsang, W. C. P.; Hultsch, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652.
 - Leduc, A.-M.; Salameh, A.; Soulivong, D.; Chabanas, M.; Basset, J.-M.; Copéret, C.; Solans-Monfort, X.; Clot, E.; Eisenstein, O.; Boehm, V. P. W.; Roeper, M. *J. Am. Chem. Soc.* **2008**, *130*, 6288.
 - Feldman J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
 - Kress, J.; Osborn, J. A. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1585.

-
19. Yates, P.; Hyre, J. E. *J. Org. Chem.* **1962**, *27*, 4101.
 20. Stanciu, C; Olmstead, M. M.; Phillips, A. D.; Stender, M.; Power, P. P. *Eur. J. Inorg. Chem.* **2003**, 3495.
 21. Kreickmann, T.; Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 5702.

TOC graphic and synopsis for

Fundamental Studies of Molybdenum and Tungsten Methylidene and Metallacyclobutane Complexes

by

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Methylidene species such as $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{OHIPT})(\text{Pyr})$ ($\text{NAr} = \text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3$, $\text{OHIPT} = \text{O-2,6-(2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$, $\text{Pyr} = \text{NC}_4\text{H}_4^-$) and related species are relatively stable but highly reactive as a consequence of hindered bimolecular coupling of methylidenes. It is proposed that the stability of methylidene complexes coupled with their high reactivity account for the high efficiency of many olefin metathesis processes that employ MonoAryloxyPyrrolide (MAP) catalysts.

