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Fundamental Studies of Molybdenum and Tungsten Methylidene and Metallacyclobutane Complexes[†]

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Addition of ethylene to Mo(NAr)(CHCMe$_2$Ph)(OHIPT)(Pyr) (NAr = N-2,6-i-Pr$_2$C$_6$H$_3$, OHIPT = O-2,6-(2,4,6-i-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$, Pyr = NC$_4$H$_4$) led to the trigonal-bipyramidal metallacyclobutane complex Mo(NAr)(C$_3$H$_6$)(OHIPT)(Pyr), in which the imido and aryloxide ligands occupy axial positions. Mo(NAr)(C$_3$H$_6$)(OHIPT)(Pyr) loses ethylene to give isolable Mo(NAr)(CH$_2$)(OHIPT)(Pyr). W(NAr)(CH$_2$)(OTPP)(Me$_2$Pyr) (OTPP = O-2,3,5,6-Ph$_4$C$_6$H, Me$_2$Pyr = 2,5-Me$_2$NC$_4$H$_2$) was prepared similarly. Single-crystal X-ray studies of Mo(NAr)(CH$_2$)(OHIPT)(Pyr) and W(NAr)(CH$_2$)(OTPP)(Me$_2$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 Mo(NAd)(CH$_2$)(OHIPT)(Pyr) (Ad = 1-adamantyl) yielded only the ethylene complex Mo(NAd)(C$_2$H$_4$)(OHIPT)(Pyr). W(NAr^{tBu})(CH$_2$)(OTPP)(Me$_2$Pyr) (Ar^{tBu} = 2-t-BuC$_6$H$_4$) was isolated upon loss of ethylene from W(NAr^{tBu})(C$_3$H$_6$)(OTPP)(Me$_2$Pyr), but decomposed in solution over a period of several hours at 22 °C. NMR studies of Mo(NAr)(C$_3$H$_6$)(OHIPT)(Pyr) and W(NAr)(C$_3$H$_6$)(OHIPT)(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 Mo(NAr)(C$_3$H$_6$)(OBitet)(Me$_2$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 W(NAr)(C$_3$H$_6$)(OBitet)(Me$_2$Pyr). It could be shown that Mo(NAr)(C$_3$H$_6$)(OBitet)(Me$_2$Pyr) forms an ethylene/methylidene intermediate at 20 °C at a rate that is 4500 times faster than the rate at which W(NAr)(C$_3$H$_6$)(OBitet)(Me$_2$Pyr) forms an ethylene/methylidene intermediate. It is proposed that the stability of methylidene complexes coupled with their high reactivity accounts for the high efficiency of many olefin metathesis processes that employ monoaryloxidepyrrolide catalysts.

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 aryloxide, have been prepared and explored.[2] These MAP (monoaryloxidepyrrolide 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 analogues of MAP species[4] 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 endoselective enyne reactions,[2k] for *Z*-selective metathesis

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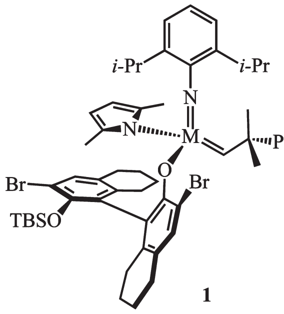
of terminal olefins,[2i] and for efficient and clean ethenolysis reactions.[21] Some of the most interesting catalytic reactions to date have been carried out with derivatives in which the aryloxide is relatively large, e.g., the anion derived from (*R*)-3,3′-dibromo-2′-(*tert*-butyldimethylsilyloxy)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2-ol (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)$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ (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 aryloxide ligand is employed, as in **1**. An important feature of MAP complexes that contain a "large" aryloxide, at least in terms of long-lived activity and low catalyst loadings, is that methylidene 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 methylidene protons (k = 90 s^{-1} at 20 °C) thereby observed.[2g,6] The stability of these 14-electron MAP methylidene species contrasts with the low stability of 14*e* imido methylidene species of the bisalkoxide or biphenolate type.[1] Bisalkoxide imido methylidene species usually are observed only when the total metal electron count is >14, i.e., only when adducts are formed.[7]



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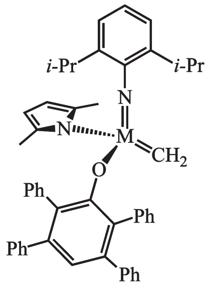

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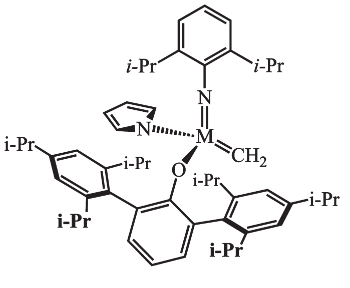

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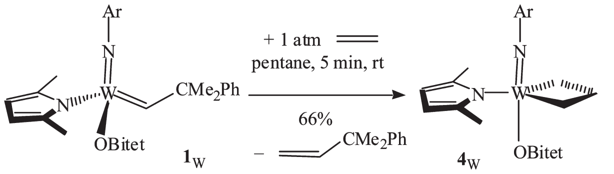
The presence of 14-electron methylidene species that are relatively stable toward bimolecular decomposition, yet highly reactive toward olefins, compelled us to attempt to isolate and crystallographically characterize some examples, since some feature of their structures might be a reason for their increased stability toward bimolecular decomposition. For example, the ground-state structure of a MAP methylidene species could be a dimer that contains two asymmetrically bridging methylidenes, as has been found for some tungsten biphenolate methylidene 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 methylidene complex therefore is an 18-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 W(NAr)(CH$_2$)(OBitet)(Me$_2$Pyr) (Ar = 2,6-diisopropylphenyl, Me$_2$Pyr = 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 eq 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)(Me$_2$Pyr)(OBitet)(CH$_2$)(C$_2$H$_4$) and (*S*)-W(NAr)-(Me$_2$Pyr)(OBitet)(CH$_2$)(C$_2$H$_4$). X-ray studies show that **4**$_W$ and analogous metallacyclobutane species contain axial imido and OBitet ligands, as shown in eq 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.



(1)

Results

X-ray Study of W(NAr)(CH$_2$)(OTPP)(Me$_2$Pyr). In a previous paper[2g] we showed that W(NAr)(CH$_2$)(OTPP)-(Me$_2$Pyr) (**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)(CH$_2$)(Me$_2$Pyr)$_2$ in benzene or by removing ethylene from W(NAr)(C$_3$H$_6$)-(OTPP)(Me$_2$Pyr) *in vacuo*. (W(NAr)(C$_3$H$_6$)(OTPP)(Me$_2$Pyr) can be prepared by treating W(NAr)(CHCMe$_2$Ph)(OTPP)-(Me$_2$Pyr) with ethylene.[2g]) Complex **2**$_W$ (in C$_6$D$_6$) 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

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(6) The exchange of methylidene protons has been shown to be independent of concentration, which rules out any intermolecular scrambling process: King, A. J., unpublished results.

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(9) 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$_{anti}$ a proton.

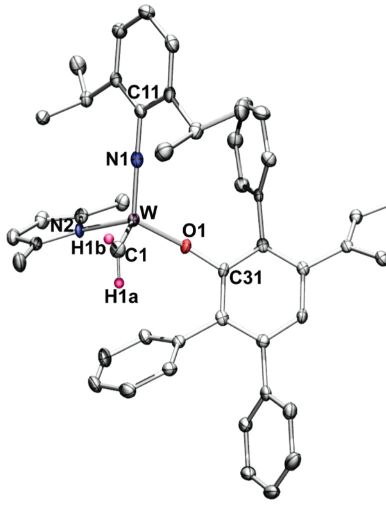

Figure 1. Thermal ellipsoid drawing of W(NAr)(CH_2)(OTPP)(Me_2Pyr) (2_W) (50% probability). Hydrogen atoms except for those on the methylidene are removed for clarity. Selected bonds (Å) and angles (deg): W−N1 = 1.758(4), W−N2 = 2.020(4), W−O1 = 1.913(3), W−C1 = 1.908(4), W−N1−C11 = 176.8(3), W−O1−C31 = 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°.

the metal.[10] Compound $\mathbf{2_W}$ 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 14*e* monomeric species that contains an η^1-dimethylpyrrolide. The W═C distance is 1.908(4) Å, which is similar to M═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 semifreely (see Supporting Information). The CH_2 plane is turned approximately 8° out of the N1−W−C1 plane. The W−C1−H1a angle (H1a = H_{anti}) is 107(4)°, and the W−C1−H1b angle (H1b = H_{syn}) is 136(3)°. The smaller W−C1−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), W−C−H_{anti} is 118.1(16)° and W−C−H_{syn} is 122.5(17)°, while in the structure of the PMe_3 adduct (PMe_3 *trans* to the pyrrolide), W−C−H_{anti} is 119.5(17)° and W−C−H_{syn} is 133.5(16)°.[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 W(NAr)(C_3H_6)(OTPP)(Me_2Pyr).[2g]

Synthesis of Mo(NAr)(C_3H_6)(OHIPT)(Pyr) and Mo(NAr)(CH_2)(OHIPT)(Pyr). Exposure of a pentane solution of Mo(NAr)($CHCMe_2Ph$)(OHIPT)(Pyr) to 1 atm of ethylene led to formation of the molybdacyclobutane complex Mo(NAr)(C_3H_6)(OHIPT)(Pyr) ($\mathbf{5_{Mo}}$) (OHIPT = hexaisopropylterphenoxide, Pyr = NC_4H_4) and its isolation as a yellow powder in 51% yield. Compound $\mathbf{5_{Mo}}$ 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 $\mathbf{5_{Mo}}$ in toluene yielded Mo(NAr)(CH_2)(OHIPT)(Pyr) ($\mathbf{3_{Mo}}$), which could be isolated from pentane as yellow blocks in 88% yield. The ^1H NMR spectrum of $\mathbf{3_{Mo}}$ 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 $\mathbf{2_W}$. A sample of $\mathbf{5_{Mo}}$ in benzene-d_6 was exposed to ^{13}C-ethylene, and then vacuum was applied to remove ethylene and re-form $\mathbf{3_{Mo}}$ in which the methylidene carbon atom was partially ^{13}C labeled (~66%). The J_{CH} values were confirmed easily in the labeled compound.

The solid-state structure of $\mathbf{3_{Mo}}$ (Figure 2) is analogous to that of $\mathbf{2_W}$ (Figure 1). The Mo═C distance (1.892(5) Å) is the same as the W═C distance (1.908(4) Å) in $\mathbf{2_W}$. The Mo−C1−H1a (Mo−C−H_{anti}) angle is 105(3)°, and the 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 $\mathbf{2_W}$, the CH_2 plane in $\mathbf{3_{Mo}}$ is turned from the N1−Mo−C1 plane by about 8°. The structural study of $\mathbf{3_{Mo}}$ is the first (to our knowledge) of a 14*e* molybdenum imido methylidene species.

Interestingly, $\mathbf{3_{Mo}}$ appears to be more stable in benzene solution than the molybdacyclobutane ($\mathbf{5_{Mo}}$) at the same concentration. For example, a 20 mM solution of $\mathbf{3_{Mo}}$ showed little decomposition over a period of 3 days at room temperature, although over the same time period a 20 mM solution of $\mathbf{5_{Mo}}$ decomposed to a significant degree. Since only trace amounts of propene are observed in the ^1H NMR spectra, β-hydride rearrangement of the molybdacyclobutane complex cannot be the major mode of decomposition. Therefore we propose that bimolecular decomposition of $\mathbf{3_{Mo}}$ is the major decomposition pathway and that bimolecular decomposition is accelerated by ethylene. (See Discussion section.) Both $\mathbf{5_{Mo}}$ and $\mathbf{3_{Mo}}$ are stable for weeks in the solid state at −27 °C.

Compound $\mathbf{5_{Mo}}$ appears to be much more stable toward loss of ethylene than structurally characterized Mo(NAr)(C_3H_6)(Me_2Pyr)(OBitet), which had to be isolated from the reaction between Mo(NAr)($CHCMe_3$)(Me_2Pyr)(OBitet) and ethylene (1 atm) at −30 °C in a 1:1 mixture of pentane and tetramethylsilane.[21] When ethylene was removed from a solution of Mo(NAr)(C_3H_6)(Me_2Pyr)(OBitet), mixtures of

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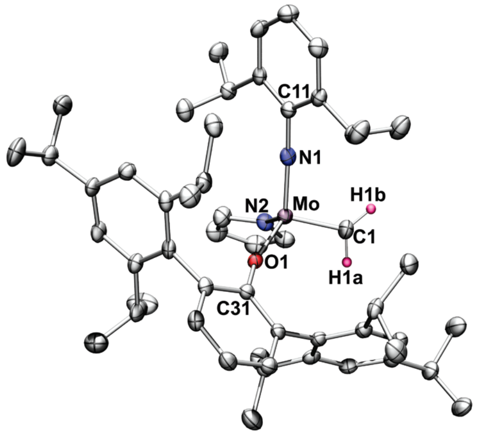

Figure 2. Thermal ellipsoid drawing of Mo(NAr)(CH_2)(OHIPT)(Pyr) ($\mathbf{3_{Mo}}$) (50% probability). Hydrogen atoms except for those on the methylidene are removed for clarity. Selected bonds (Å) and angles (deg): Mo−N1 = 1.737(4), Mo−N2 = 2.035(4), Mo−O1 = 1.911(3), Mo−C1 = 1.892(5), Mo−N1−C11 = 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°.

the two diastereomers of Mo(NAr)(CH_2)(Me_2Pyr)(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 Mo(NAr)(CH_2)(Me_2Pyr)(OBitet) decompose to a significant degree in C_6D_6 at 22 °C in the absence of ethylene over a period of 1−2 days.[2e] (NMR studies involving Mo(NAr)(C_3H_6)(Me_2Pyr)(OBitet) and Mo(NAr)(CH_2)(Me_2Pyr)(OBitet) are described later in this paper.)

Complexes That Contain a N(o-t-BuC_6H_4) or NAdamantyl Ligand. We also became interested in whether metallacyclobutane and methylidene 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] Mo(NAd)($CHCMe_3$)(OHIPT)(Pyr) (**6**), prepared as described in the literature,[2j] was shown in an X-ray study to be a 14*e* pseudotetrahedral species that contains an η^1-pyrrolide and a *syn* alkylidene[9] (Figure 3). Bond lengths and angles are similar to other MAP species of this general type. The Mo−C1−H1 angle (101.6(17)°) should be compared with the M−C−H_{anti} angles in $\mathbf{2_W}$ (107(4)°) and $\mathbf{3_{Mo}}$ (105(3)°) 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_{CH} = 139 Hz), 2.36 (J_{CH} = 145 Hz), 2.24 (J_{CH} = 146 Hz), and 0.71 (J_{CH} = 154) ppm in a 1:1:1:1 ratio. The remaining **6** was consumed over a period of 24 h, and an ethylene complex was formed in a yield of >95%. The four proton resonances attributed to the ethylene in Mo(NAd)(C_2H_4)(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_{CC} = 38 Hz, J_{CH} = 154 and 155 Hz) and 46.41 ppm (J_{CC} = 38 Hz, J_{CH} = 158 and 158 Hz). So far we have not been able to isolate Mo(NAd)(C_2H_4)(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)(CH_2)(OHIPT)(Pyr) decomposes to Mo(NAd)(C_2H_4)(OHIPT)(Pyr) readily. Two crystallographically characterized neutral ethylene complexes of this general type are known, Mo(N-2,6-$Cl_2C_6H_3$)(CH_2CH_2)(Biphen)(Et_2O)[12] and W(N-2,6-Cl_2-C_6H_3)(CH_2CH_2)(Biphen)(THF),[8] along with one cationic species, $\{$Mo(NAr)(CH_2CH_2)[OCMe(CF_3)$_2$](THF)$_3\}^+$.[13]

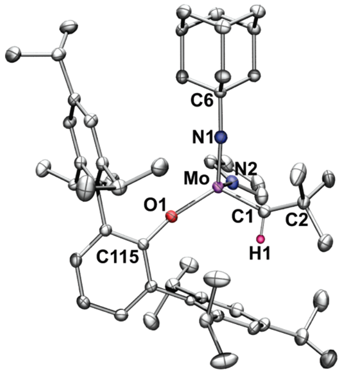

Figure 3. Thermal ellipsoid drawing of Mo(NAd)($CHCMe_3$)(OHIPT)(Pyr) (**6**) (50% probability). Hydrogen atoms (except for H1) are removed for clarity. Selected bonds (Å) and angles (deg): Mo−N1 = 1.707(2), Mo−N2 = 2.040(2), Mo−O1 = 1.9124(15), Mo−C1 = 1.886(2), Mo−N1−C6 = 167.54(16), Mo−O1−C115 = 167.55(15), Mo−C1−C2 = 143.25(18).

The synthesis of W(NAr^{tBu})($CHCMe_2Ph$)(OTPP)(Me_2Pyr) (Ar^{tBu} = 2-t-BuC_6H_4) was carried out through addition of 2,3,5,6-tetraphenylphenol to W(NAr^{tBu})($CHCMe_2Ph$)(Me_2Pyr)$_2$. Upon exposure of a solution of W(NAr^{tBu})($CHCMe_2Ph$)(OTPP)(Me_2Pyr) to ethylene, W(NAr^{tBu})(C_3H_6)(OTPP)(Me_2Pyr) (**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})(CH_2)(OTPP)(Me_2Pyr) (**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})(CH_2)(OTPP)(Me_2Pyr) 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 a ∼0.5 g scale led only to an oily residue, the ^{1}H 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 an intractable material.

NMR Studies of the M(NAr)(C_3H_6)(OHIPT)(Pyr) Systems. 2D ^{1}H−^{1}H 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

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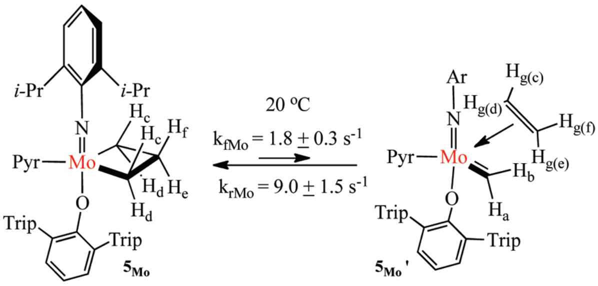
(12) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. A.; Hultzsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.

(13) Jiang, A. J.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 4428.

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 methylidene ligands in equatorial positions (eq 2).

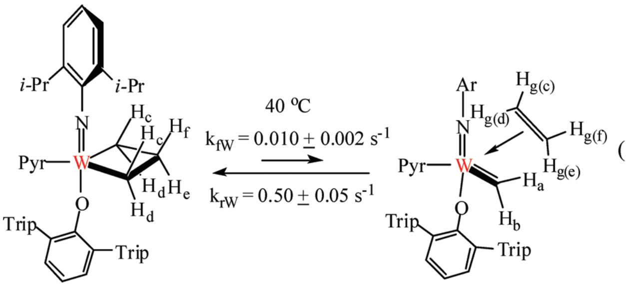
In a 20 mM solution of Mo(NAr)(C_3H_6)(OHIPT)(Pyr) ($\mathbf{5_{Mo}}$) in benzene-d_6 at 20 °C ~14% of Mo(NAr)(CH_2)(OHIPT)(Pyr) ($\mathbf{3_{Mo}}$) and 86% of $\mathbf{5_{Mo}}$ are observed (Figure S3 in the Supporting Information). Proton resonances in each species were assigned on the basis of NOE 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* (eq 2). The assignments 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},



(2)

vide supra). Pyrrolide resonances in $\mathbf{5_{Mo}}$ and $\mathbf{5_{Mo}}'$ were employed in order to determine the rate of interconversion of $\mathbf{5_{Mo}}$ and $\mathbf{5_{Mo}}'$ (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 ± 0.3 s^{-1}) and the reverse (9.0 ± 1.5 s^{-1}) at 20 °C to be determined. The ratio of k_{rMo} to k_{fMo} (5.0) is consistent with the ratio of $\mathbf{5_{Mo}}$ to $\mathbf{3_{Mo}}$ found in the 1D NMR experiment above. Protons *a* and *b* in a sample of Mo(NAr)(CH_2)(OHIPT)(Pyr) (free of ethylene) *do not exchange* with a mixing time of 200 ms at 20 °C; therefore any rotation of the methylidene ligand about the Mo−C axis would have to take place at a rate of < 0.2 s^{-1}. A rate of < 0.2 s^{-1} contrasts dramatically with a rate of rotation of the methylidene in W(NAr^{tBu})(CH_2)(OTPP)(Me_2Pyr) (230 s^{-1} at 20 °C; *vide supra*) or W(NAr)(CH_2)(OTPP)(Me_2Pyr) (90 s^{-1} at 20 °C).[2g]

In a 20 mM solution of W(NAr)(C_3H_6)(OHIPT)(Pyr) (C_3H_6 resonances at δ 4.24, 3.52, −0.78, and −1.11 ppm) in benzene-d_6 at 20 °C the metallacycle protons did not exchange with each other at any significant rate. At 40 °C approximately 2% W(NAr)(CH_2)(OHIPT)(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 °C (k_{fW}) was found to be 0.010 ± 0.002 s^{-1} and the reverse (k_{rW}) was found to be 0.50 ± 0.05 s^{-1}, for a k_{rW}/k_{fW} = 50 (eq 3). The ratio of k_{rW} to k_{fW} is larger by a factor of 10 in the W system (at 40 °C), and the molybdacyclobutane (at 20 °C) breaks up 180 times faster than the tungstacycle (at 40 °C). It was impractical to measure the rate of methylidene 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, in terms of both the rate of loss of ethylene and the position of the equilibrium between the metallacycle and methylidene species.



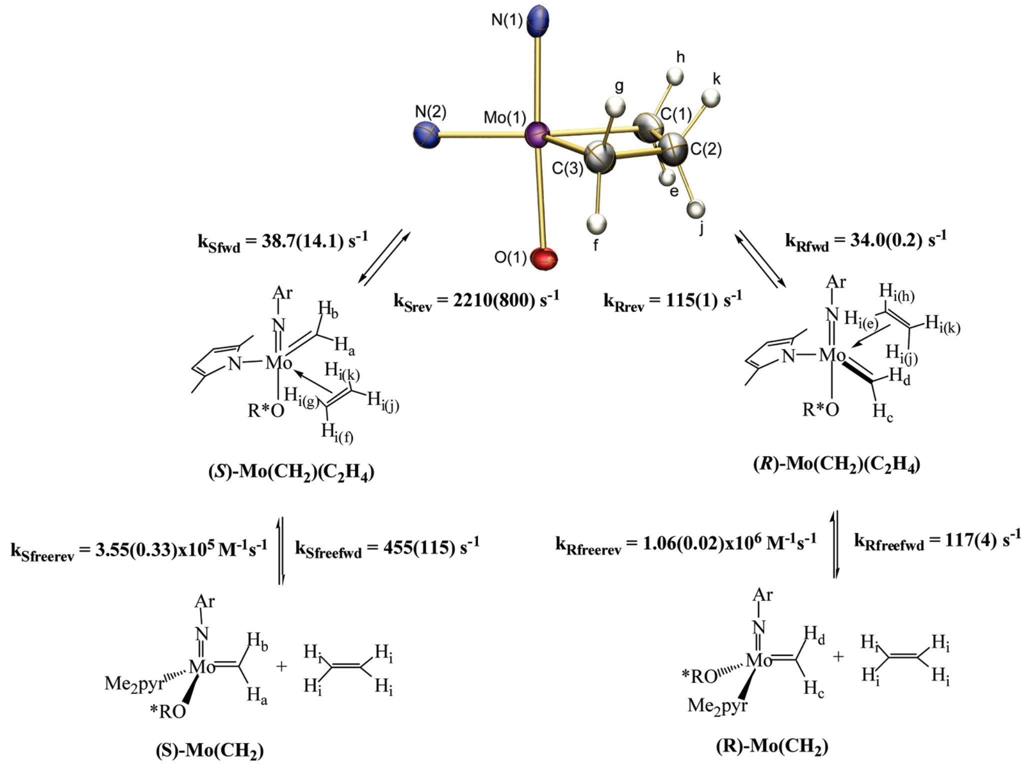
(3)

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 methylidene species that was generated exhibited broad methylidene 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 methylidene proton *syn* to the imido ligand and *b* (δ 9.09 ppm, J_{CH} = 128 Hz) to the methylidene proton *anti* to the imido ligand, which confirmed the assignments made through 2D NMR studies. 2D $^1H-^1H$ NOESY/EXSY spectra of a 44 mM sample with 2 ms mixing time at 20 °C (Figures S8 and S10) illustrated that the *syn* and *anti* protons exchange at a rate of 230 s^{-1}, which is about 2 times faster than that in W(NAr)(CH_2)(OTPP)(Me_2Pyr) (90 s^{-1}) and approximately 100 times faster than that in W(NAr)(CH_2)(OBitet)(Me_2Pyr) (4−5 s^{-1}). The rapid rate of exchange of methylidene protons in W(NAr^{tBu})(C_3H_6)(OTPP)(Me_2Pyr) accounts for the breadth of the methylidene proton resonance in room-temperature spectra.

NMR Studies of Mo(NAr)($\mathbf{C_3H_6}$)($\mathbf{Me_2Pyr}$)(OBitet). In a previous paper we reported that Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)$_2$ reacts cleanly with 1 equiv of enantiomerically pure HOBitet to generate $\mathbf{1_{Mo}}$ as a mixture of two diastereomers.[2c,h] When ethylene (1 atm) is added to a solution of $\mathbf{1_{Mo}}$ in toluene-d_8 (30 mM), very broad ethylene (δ 5.25 ppm) and methylidene proton resonances are observed at 20 °C. When the reaction is cooled under an ethylene atmosphere, Mo(NAr)(C_3H_6)(Me_2pyr)(OBitet) ($\mathbf{4_{Mo}}$) 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 $\mathbf{4_{Mo}}$ revealed it to have a TBP structure in which the imido and the aryloxide ligands are in the axial positions.[21] The proton NMR spectrum of $\mathbf{4_{Mo}}$ 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 $\mathbf{4_{Mo}}$ allowed us to carry out NMR studies analogous to those on the tungsten analogue and to compare tungsten and molybdenum data.

Scheme 1. Details of Processes Involving Loss of Ethylene from Mo(NAr)(C_3H_6)(OBitet)(Me_2Pyr) in Solution at −20 °C



When $\mathbf{4_{Mo}}$ is dissolved in toluene-d_8, an equilibrium is established between $\mathbf{4_{Mo}}$, methylidene diastereomers (*S*)-**9** and (*R*)-**9**, and ethylene. At −20 °C and 30 mM initial concentration of $\mathbf{4_{Mo}}$, ~60% $\mathbf{4_{Mo}}$, ~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 methylidene proton resonances are observed for the diastereomers of **9** (Figure 4a), six metallacyclobutane resonances are observed for metallacycle $\mathbf{4_{Mo}}$ (Figure 4b and c), 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 methylidene resonances have been identified by 2D HSQC and NOESY/EXSY NMR methods described in the Supporting Information.

A reaction between $\mathbf{4_{Mo}}$ 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 $\mathbf{4_{Mo}}$ 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*)-**9** and (*R*)-**9** were observed. The J_{CH} values were established for *anti* protons *a* and *c* (J_{CH} = 140 and 138 Hz) and for *syn* protons *b* and *d* (J_{CH} = 163 and 165 Hz; see Supporting Information).

An EXSY experiment of the mixture of (*R*)-**9** and (*S*)-**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 methylidene protons do not exchange suggests that rotation about the M=C bond must take place at a rate of < 0.2 s^{-1}, as was also found in Mo(NAr)(CH_2)(OHIPT)(Pyr) (*vide supra*). This result contrasts with several examples of faster rotation about the W=C bond noted earlier.

Details concerning the breakup and re-formation of $\mathbf{4_{Mo}}$ 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/methylidene 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 (~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 re-forming the ethylene/methylidene intermediate and the position of the equilibria between the ethylene/methylidene intermediates and the methylidene species and free ethylene.

It is not possible to obtain data for $\mathbf{4_{Mo}}$ above −20 °C as a consequence of rapid exchange processes, but data could be obtained at −30, −40, and −50 °C (Table S2; see Supporting Information). Since data for the *R* forms are the most accurate, we compare values only 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 $\Delta H^\ddagger = 21.6 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = 34.4 \pm 1.6$ eu. A value for k_{Rfwd} for $\mathbf{4_{Mo}}$ at 20 °C was calculated employing these parameters; $k_{Rfwd}(Mo)_{20°}$ was found to be 1.45×10^4 s^{-1} (Scheme 2). Since the value for $k_{Rfwd}(W)_{20°} = 3.2 \pm 0.1$ s^{-1},[2g] the ratio of $k_{Rfwd}(Mo)_{20°}$ to $k_{Rfwd}(W)_{20°}$ is ~4500. In a similar manner the values for $\Delta H^\ddagger = 13.2 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = 3.4 \pm 1.4$ eu

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(14) Jolley, J. E.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1958**, *80*, 1050.

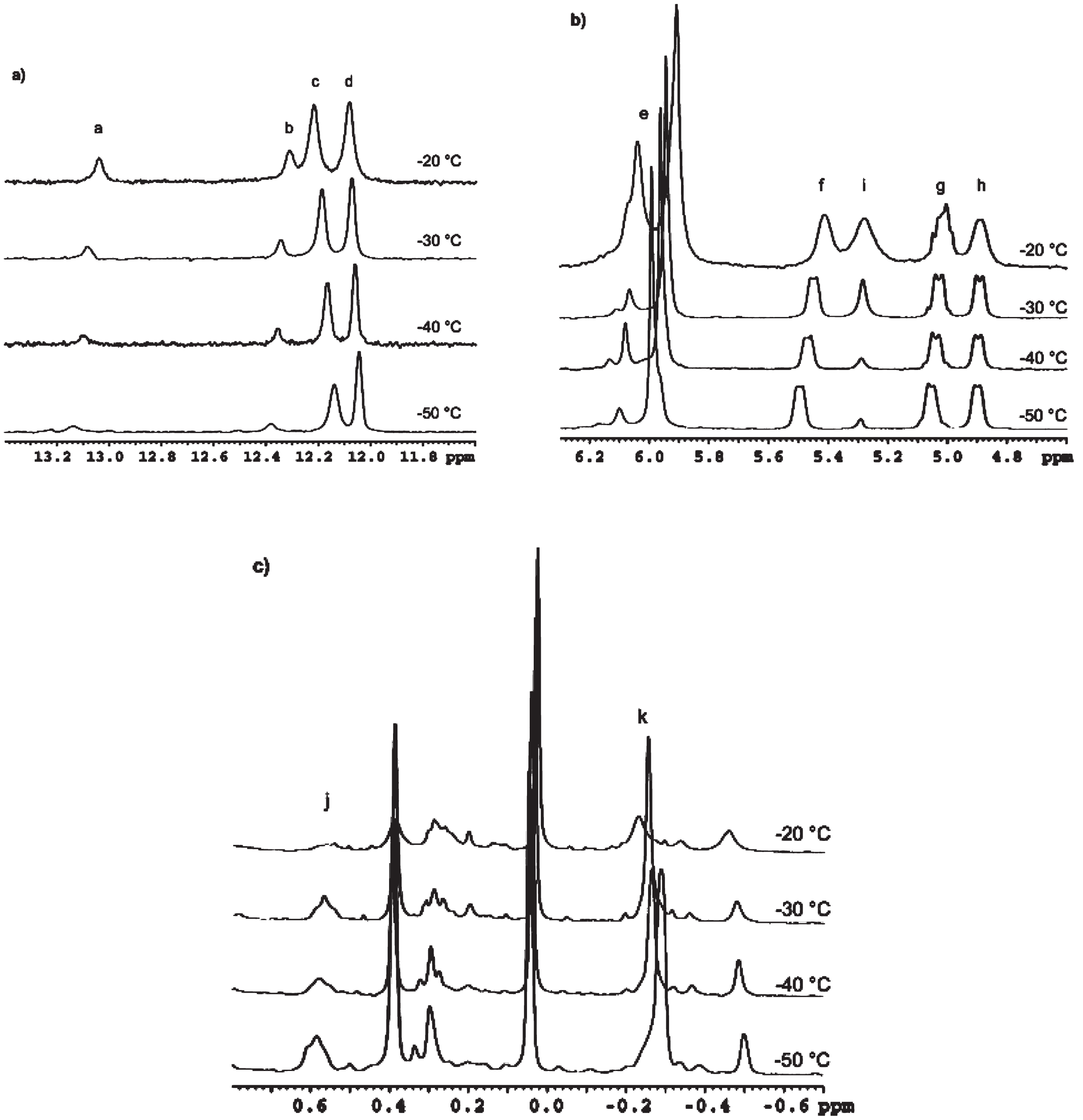

Figure 4. Proton NMR spectra of $Mo(NAr)(C_3H_6)(OBitet)(Me_2Pyr)$ ($\mathbf{4_{Mo}}$) in toluene-d_8 at −20, −30, −40, and −50 °C. (a) Expansion of the ^{1}H NMR spectrum in the alkylidene region for (*S*)- and (*R*)-$Mo(NAr)(CH_2)(Me_2Pyr)(OBitet)$ (1:4 ratio of (*S*)-**9** and (*R*)-**9**)). (b) Expansion of the ^{1}H NMR spectrum in the H_α region for $Mo(NAr)(C_3H_6)(OBitet)(Me_2Pyr)$ ($\mathbf{4_{Mo}}$). (c) Expansion of the ^{1}H NMR spectrum in the H_β region for $\mathbf{4_{Mo}}$. (See Scheme 1 for labels.)

for $k_{\mathrm{Rrev}}(\mathrm{Mo})_{20°}$ were determined; $k_{\mathrm{Rrev}}(\mathrm{Mo})_{20°}$ was found to be 4900 s^{-1}, which is a factor of 71 larger than $k_{\mathrm{Rrev}}(\mathrm{W})_{20°}$ (69 s^{-1}). Therefore at 20 °C the value of $k_{\mathrm{Rrev}}(\mathrm{Mo})_{20°}/k_{\mathrm{Rfwd}}(\mathrm{Mo})_{20°} = 0.34$, which should be compared with a value of $k_{\mathrm{Rrev}}(\mathrm{W})_{20°}/k_{\mathrm{Rfwd}}(\mathrm{W})_{20°} = 21.56$.[2g] The values for k_{Rfreefwd} as a function of temperature are not well behaved, which suggests that the rate constants for k_{freefwd} and k_{freerev} for both the *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 methylidene 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-methylidene species; one example, heterochiral $[W(NAr_{Cl})(Biphen)(\mu\text{-}CH_2)]_2$ (where Ar_{Cl} is 2,6-dichlorophenylimido), has been crystallographically characterized.[8] Homochiral $[W(\mu\text{-}NAr_{Cl})(Biphen)]_2(\mu\text{-}CH_2CH_2)$ has also been crystallographically characterized.[8] Both are logical intermediates in decomposition of a methylidene species to an olefin-free W=W species[11] 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 alkylidene[15]

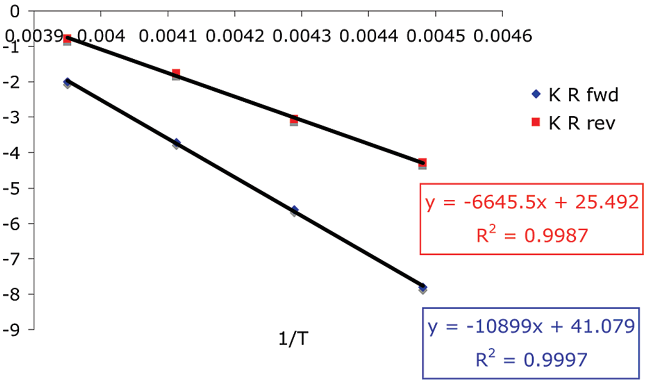

Figure 5. Eyring plots for k_{Rfwd} and k_{Rrev} at −20, −30, −40, and −50 °C for cleavage and re-formation of Mo(NAr)(C_3H_6)(OBitet)(Me_2Pyr) (see Scheme 1).

and Re alkylidyne alkylidene[16] systems. Therefore, the right combination of sterically bulky ligands can ensure methylidene stability, through either slowing formation of bis-μ-CH_2 species or slowing the reaction of bis-μ-CH_2 intermediates with ethylene to give two ethylene complexes. The 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; that is, 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 analogues, 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.[2i]

We are surprised not only by the stability of certain methylidene complexes but by the relatively rapid rate of rotation of W=CH_2 species about the W=C bond, i.e., interconversion of *syn* and *anti* methylidene protons. Confirmed rates at 20 °C in complexes discussed here vary from 4 to 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 $< 0.2\ s^{-1}$ 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 is 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 re-formation of the metallacycle in the Mo(NAr)(C_3H_6)(OBitet)(Me_2Pyr) system. These data, in combination with those generated in the W(NAr)(C_3H_6)(OBitet)(Me_2Pyr) investigation,[2g] give us confidence that the ethylene/methylidene intermediate exists. The values for $\Delta S^{\ddagger}$ for k_{Rfwd} (34.4 ± 1.6 eu) and for $\Delta S^{\ddagger}$ for k_{Rrev}(Mo) (3.4 ± 1.4 eu) 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 $k_{\mathrm{Rrev}}(\mathrm{Mo})_{20°}/k_{\mathrm{Rfwd}}(\mathrm{Mo})_{20°} = 0.34$ 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 [W(C_5H_8)(OCH_2CMe_3)$_2$$Br_2$]$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 W=C bond at rates that vary from 3.6 s^{-1} to 230 s^{-1}, but rotation about Mo=C bonds is comparatively slow

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[15] Tsang, W. C. P.; Hultzsch, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652.

[16] 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.

[17] Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

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Scheme 2. Comparison of the Rate Constants for Interconversion of Mo(NAr)(C_3H_6)(OBitet)(Me_2Pyr) and (*R*)-Mo(NAr)(CH_2)(C_2H_4)(OBitet)(Me_2Pyr) with Interconversion of W(NAr)(C_3H_6)(OBitet)(Me_2Pyr) and (*R*)-W(NAr)(CH_2)(C_2H_4)(OBitet)(Me_2Pyr) at 20 °C

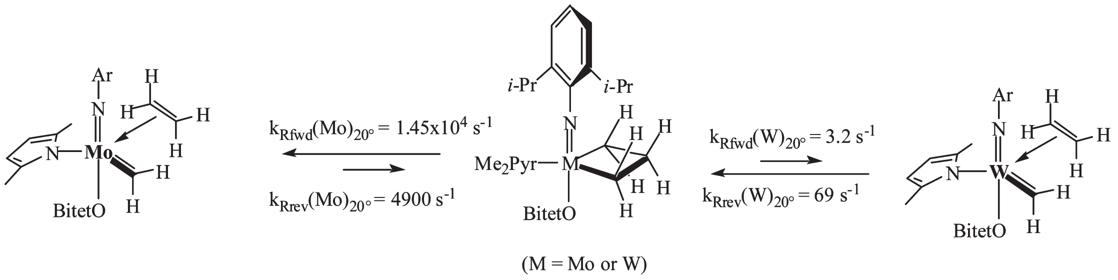

Table 1. Rates of Exchange of Methylidene Protons at 20 °C

methylidene species	rate (s^{-1})
Mo(NAr)(CH_2)(OHIPT)(Pyr)	< 0.2
Mo(NAr)(CH_2)(OBitet)(Me_2Pyr)	< 0.2
W(NAr$^{t\text{-}Bu}$)(CH_2)(OTPP)(Me_2Pyr)	230
W(NAr)(CH_2)(OTPP)(Me_2Pyr)[2g]	90
(*R*)-W(NAr)(CH_2)(OBitet)(Me_2Pyr)[2g]	3.6
(*S*)-W(NAr)(CH_2)(OBitet)(Me_2Pyr)[2g]	5.1

(< 0.2 s^{-1}). MAP metallacyclobutane species break up at widely differing rates to give intermediate ethylene/methylidene intermediates. In M(NAr)(C_3H_6)(OBitet)(Me_2Pyr) systems, the rate of metallacycle breakup has been found to be 4500 times faster when M = Mo than when M = W at 20 °C.

Experimental Section

General Procedures. 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] W(NAr)($CHMe_2Ph$)(Me_2Pyr)$_2$,[21] W(NAr)($CHCMe_2Ph$)(Pyr)$_2$(DME),[21] W(NAr^{Cl})($CHCMe_3$)(Pyr)$_2$(DME),[21] Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)$_2$,[2a] Mo(NAr)($CHCMe_2Ph$)(Pyr)$_2$,[3a] **1$_{Mo}$**,[2c,h] **4$_{Mo}$**,[21] and **9**[21] were all prepared according to literature procedures.

Mo(NAr)(C_3H_6)(OHIPT)(Pyr). A 50 mL Schlenk flask was charged with a stir bar and a solution of Mo(NAr)($CHCMe_2Ph$)(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 °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. A yellow, fluffy solid precipitated immediately and was filtered off and dried *in vacuo* for 1 h; yield 0.480 g (51%). The product can be recrystallized from a concentrated solution of a 1:1 mixture of pentane and diethyl ether at −27 °C as a fine, feathery solid. ^{1}H NMR shows that in solution ~15% of the sample is the methylidene species and ~8% of the expected ethylene is observed: ^{1}H NMR (500 MHz, C_6D_6) δ 7.32 (m, 2, Pyr-*H*), 7.26 (d, 2, Ar-*H*, J_{HH} = 8 Hz), 7.21 (s, 4, Ar-*H*), 6.89 (t, 1, Ar-*H*, J_{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, C*H*Me$_2$), 3.59−2.24 (br, 4, C*H*Me$_2$), 2.89 (sept, 2, C*H*Me$_2$), 1.32 (d, 12, C*H*Me$_2$, J_{HH} = 7 Hz), 1.30−1.02 (m, 24, C*H*Me$_2$), 1.00 (d, 12, C*H*Me$_2$, J_{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 $C_{55}H_{76}MoN_2O$: 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 °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%): ^{1}H NMR (500 MHz, C_6D_6) δ 12.21 (d, 1, *anti*-MoCH_α, J_{HH} = 5 Hz), 12.10 (d, 1, *syn*-MoCH_α, J_{HH} = 5 Hz), 7.35 (s, 2, Ar-*H*), 7.21 (s, 2, Ar-*H*), 7.12 (d, 2, Ar-*H*, J_{HH} = 7 Hz), 6.97 (m, 3, Ar-*H*), 6.91 (t, 1, Ar-*H*, J_{HH} = 7 Hz), 6.37 (m, 4, Pyr-H), 3.50 (sept, 2, C*H*Me$_2$), 2.98 (sept, 2 C*H*Me$_2$), 2.90 (m, 4, C*H*Me$_2$), 1.31 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.28 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.22 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.19 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.15 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.14 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.10 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.05 (d, 6, CH*Me$_2$*, J_{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 $C_{53}H_{72}MoN_2O$: 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: ^{1}H NMR (500 MHz, C_6D_6) δ 12.18 (J_{CH} = 138 Hz, *anti*-MoCH_α), 12.06 (J_{CH} = 163 Hz, *syn*-MoCH_α).

***In Situ* Synthesis of Mo(NAd)(C_2H_4)(OHIPT)(Pyr).** Mo(NAd)($CHCMe_3$)(OHIPT)(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: ^{1}H 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_{HH} = 8 Hz), 6.89 (t, 1, Ar-*H*, J_{HH} = 8 Hz), 6.67 (m, 2, Pyr-*H*), 6.53 (m, 2, Pyr-*H*), 2.95 (m, 6, C*H*Me$_2$), 2.73 (m, 1, MoC$_2$*H$_4$*), 2.32 (m, 1, MoC$_2$*H$_4$*), 2.01 (m, 1, MoC$_2$*H$_4$*), 1.63 (s, 3, Ad-*H*), 1.47 (s, 6, Ad-*H*), 1.41 (d, 12, CH*Me$_2$*, J_{HH} = 7 Hz), 1.28 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 1.20 (s, 6, Ad-*H*), 1.19 (d, 12, CH*Me$_2$*, J_{HH} = 7 Hz), 1.17 (d, 6, CH*Me$_2$*, J_{HH} = 7 Hz), 0.35 (m, 1, MoC$_2$*H$_4$*); ^{13}C NMR (125 MHz, C_6D_6) δ 55.23 (Mo*C$_2$*H$_4$, J_{CC} = 38 Hz, J_{CH} = 154 and 155 Hz), 46.41 (Mo*C$_2$*H$_4$, J_{CC} = 38 Hz, J_{CH} = 158 and 158 Hz).

W(NAr^{tBu})$_2$(NC_5H_5)$_2$Cl$_2$. In the glovebox, a 500 mL Schlenk flask was charged with a stir bar and WO_2Cl_2 (22.18 g, 77.35 mmol)

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in 50 mL of dimethoxyethane. 2-*tert*-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 glovebox 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%): ^{1}H NMR (500 MHz, C_6D_6) δ 8.92 (d, 4, Ar-*H*, $J_{HH} = 5$ Hz), 7.74 (dd, 2, Ar-*H*, $J_{HH} = 8$ and 1 Hz), 7.30 (dd, 2, Ar-*H*, $J_{HH} = 8$ and 1 Hz), 7.06, (t, 2, Ar-*H*, $J_{HH} = 7$ Hz), 6.71 (t, 2, Ar-*H*, $J_{HH} = 7$ Hz), 6.66 (t, 2, Ar-*H*, $J_{HH} = 7$ Hz), 6.27 (t, 4, Ar-*H*, $J_{HH} = 7$ Hz), 1.52 (s, 18, *tert*-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 $C_{30}H_{36}Cl_2N_4W$: C, 50.94; H, 5.13; N, 7.92. Found: C, 50.99; H, 5.17; N, 7.76.

W(NAr^{tBu})$_2$(CH$_2$CMe$_2$Ph)$_2$. A 500 mL flask was charged with a stir bar, W(NAr^{tBu})$_2$(NC$_5$H$_5$)$_2$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 MgCl(CH$_2$CMe$_2$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%): ^{1}H NMR (500 MHz, C_6D_6) δ 7.38 (d, 4, Ar-*H*, $J_{HH} = 7$ Hz), 7.26 (m, 2, Ar-*H*), 7.16 (t, 4, Ar-*H*, $J_{HH} = 8$ Hz), 7.04, (m, 4, Ar-*H*, $J_{HH} = 7$ Hz), 6.80 (m, 4, Ar-*H*), 1.75 (s, 4, C*H$_2$*CMe$_2$Ph), 1.60 (s, 18, *tert*-butyl), 1.50 (s, 12, CH$_2$C*Me$_2$*Ph); ^{13}C NMR (125 MHz, C_6D_6) δ 154.56 ($J_{CW} = 36$ Hz), 151.90, 140.63, 131.84, 129.13, 127.14, 126.63, 126.61, 126.31, 125.46, 92.63 ($J_{CW} = 100$ Hz), 41.65, 35.80, 33.78, 30.78. Anal. Calcd for $C_{40}H_{52}N_2W$: C, 64.51; H, 7.04; N, 3.76. Found: C, 64.24; H, 6.89; N, 3.72.

W(NAr^{tBu})(CHCMe$_2$Ph)(OTf)$_2$(DME). A sample of W(NAr^{tBu})$_2$(CH$_2$CMe$_2$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*, 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 ^{1}H 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 discernible are reported: ^{1}H NMR (500 MHz, C_6D_6) δ 12.01 (s, 0.12, C*H*CMe$_2$Ph), 11.50 (s, 0.03, C*H*CMe$_2$Ph), 11.12 (s, 1, C*H*CMe$_2$Ph), 10.70 (s, 0.45, C*H*CMe$_2$Ph), 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), too many peaks in alkyl region to pick out CHC*Me$_2$*Ph, 1.49 (s, 18, *tert*-butyl). Anal. Calcd for $C_{26}H_{35}F_6NO_8S_2W$: C, 36.67; H, 4.14; N, 1.64. Found: C, 36.45; H, 3.99; N, 1.85.

W(NAr^{tBu})(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$. Lithium 2,5-dimethylpyrrolide (1.435 g, 14.200 mmol, 2.5 equiv) and W(NAr^{tBu})(CHCMe$_2$Ph)(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 ^{1}H NMR: ^{1}H NMR (500 MHz, C_6D_6) δ 10.90 (s, 1, *syn*-C*H*CMe$_2$Ph, $J_{CH} = 123$ Hz), 7.35 (d, 2, Ar-*H*, $J_{HH} = 8$ Hz), 7.29 (d, 1, Ar-*H*, $J_{HH} = 8$ Hz), 7.15, (m, 3, Ar-*H*), 7.02 (t, 1, Ar-*H*, $J_{HH} = 8$ Hz), 6.83 (m, 2, Ar-*H*), 5.95 (br s, 4, Pyr-*H*), 2.16 (s, 12, Pyr-*Me*), 1.65 (s, 6, CHC*Me$_2$*Ph), 1.33 (s, 9, *tert*-butyl); ^{13}C NMR (125 MHz, C_6D_6) δ 281.17 (*C*HCMe$_2$Ph), 155.06 ($J_{CW} = 42$ 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 $C_{32}H_{41}N_3W$: C, 58.99; H, 6.34; N, 6.45. Found: C, 59.12; H, 6.33; N, 6.42.

W(NAr^{tBu})(CHCMe$_2$Ph)(OTPP)(Me$_2$Pyr). A 20 mL scintillation vial was charged with a stir bar, W(NAr^{tBu})(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (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%): ^{1}H NMR (500 MHz, C_6D_6) δ 8.11 (s, 1, *syn*-C*H*CMe$_2$Ph, $J_{CH} = 113$ Hz, $J_{WH} = 16$ Hz), 7.05 (m, 29), 6.11 (br s, 2, Pyr-*H*), 5.89 (d, 1, Ar-H, $J_{HH} = 8$ Hz), 2.61 (br s, 3, Pyr-*Me*), 1.92 (br s, 3, Pyr-*Me*), 1.53 (s, 3, CHC*Me$_2$*Ph), 1.23 (s, 3, CHC*Me$_2$*Ph), 1.20 (s, 9, *tert*-butyl); ^{13}C NMR (125 MHz, C_6D_6) δ 258.77 (*C*HMe$_2$Ph), 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 $C_{56}H_{54}N_2OW$: C, 70.44; H, 5.70; N, 2.93. Found: C, 70.60; H, 5.92; N, 2.95.

W(NAr^{tBu})(C$_3$H$_6$)(OTPP)(Me$_2$Pyr). A 50 mL Schlenk flask was charged with a stir bar and a solution of W(NAr^{tBu})(CHCMe$_2$Ph)(OTPP)(Me$_2$Pyr) (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 ^{1}H NMR spectrum shows that in solution 11% of the sample is the methylidene species (*vide infra*) and ∼2% of ethylene (broad signal) is observed: ^{1}H 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, *tert*-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 $C_{49}H_{48}N_2OW$: 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, $J_{CH} = 159$ Hz, $J_{CW} = 80$ Hz), −4.12 (WC_β, $J_{CH} = 154$ Hz). This compound decomposes over the course of ∼4 h in solution at room temperature.

***In Situ* Synthesis of W(NAr^{tBu})(CH$_2$)(OTPP)(Me$_2$Pyr).** W(NAr^{tBu})(C$_3$H$_6$)(OTPP)(Me$_2$Pyr) (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: ^{1}H NMR (500 MHz, C_6D_6) δ 10.10 (v br s, 1, *syn*-CH_α), 9.09 (v br s, 1, *anti*-CH_α), 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, *tert*-butyl).

A sample of W(NAr^{tBu})(C$_3$H$_6$)(OTPP)(Me$_2$Pyr) in benzene-*d*$_6$ was degassed via three freeze−pump−thaw cycles and exposed to ^{13}C-ethylene, and then vacuum was applied to remove ethylene to generate the methylidene species: ^{1}H NMR (500 MHz, C_6D_6) δ 10.10 (*syn*-CH$_a$, J_{CH} = 156 Hz), 9.09 (*anti*-CH$_a$, J_{CH} = 128 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 242.09 (WC_a, J_{CW} = 183 Hz). W(NAr^{tBu})(CH$_2$)(OTPP)(Me$_2$-Pyr) 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. This material is available free of charge via the Internet at http://pubs.acs.org.

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