

Fundamental Studies of Tungsten Alkylidene Imido Monoalkoxidepyrrolide Complexes

Annie J. Jiang, Jeffrey H. Simpson, Peter Müller, and Richard R. Schrock*

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Received February 26, 2009; E-mail: rrs@mit.edu

Abstract: Two diastereomers of the monoalkoxidepyrrolide (MAP) species, $W(NAr)(CH_2)(Me_2Pyr)(OR^*)$ (**1**; Ar = 2,6-diisopropylphenyl, Me_2Pyr = 2,5-dimethylpyrrolide, OR^* = (*R*)-3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-olate), were generated through addition of R^*OH to $W(NAr)(CH_2)(Me_2Pyr)_2$. The unsubstituted tungstacyclobutane species, $W(NAr)(C_3H_6)(Me_2Pyr)(OR^*)$ (**2**), was isolated by treating the mixture of diastereomers of **1** with ethylene. An X-ray study revealed **2** to have a trigonal bipyramidal structure in which the imido and phenoxide ligands are in axial positions. A variety of NMR experiments were carried out on **1** and **2**. The major findings are the following: (i) the methylidene ligands in the two diastereomers of **1** rotate readily about the $W=C$ bond ($k = 2-7\text{ s}^{-1}$ at 22 °C); (ii) NMR studies are consistent with **2** breaking up to give an intermediate alkylidene/ethylene complex, (*R*)- and (*S*)- $W(CH_2)(C_2H_4)$; and (iii) the ethylene in the (*R*)- $W(CH_2)(C_2H_4)$ intermediate can rotate about the W -ethylene bond axis at approximately the same rate as **2** re-forms or ethylene is lost to give **1**. Compound **1** reacts with trimethylphosphine to yield (*R*)-**1(PMe₃)**. Two intermediate PMe_3 adducts were observed and found to convert to (*R*)-**1(PMe₃)** in an intramolecular fashion with an average rate constant at 5 °C of $\sim 1.4 \times 10^{-4}\text{ s}^{-1}$. Both neophylidene (**4**) and methylidene (**5**) MAP species containing 2,3,5,6-tetraphenylphenoxide ligand also were prepared. Compound **5** can be heated to 80 °C, where methylidene rotation about the $W=C$ bond is facile and observable in a variable-temperature 1H NMR spectrum. A $^1H-^1H$ EXSY spectrum of **5** in benzene- d_6 at 20 °C showed that the methylidene protons are exchanging with $k = 90\text{ s}^{-1}$. A structure of **5(THF)** showed it to be a square pyramid with the methylidene ligand in the apical position and THF coordinated *trans* to the imido ligand. Exposure of **5** to ethylene generated the tungstacyclobutane complex, $W(NAr)(C_3H_6)(Me_2Pyr)(OR)$ (**6**), whose structure is analogous to that of **2**. Treatment of **5** with PMe_3 yielded yellow **5(PMe₃)**, an X-ray study of which revealed it to be a square pyramid with the methylidene ligand in the apical position and the phosphine *trans* to the pyrrolide. These studies suggest that metallacyclobutane intermediates in metathesis reactions with MAP species are likely to contain axial imido and phenoxide ligands, that metallacycles are formed when an olefin approaches the metal in a MAP species *trans* to the pyrrolide, and that the configuration at the metal inverts as a consequence of each forward metathesis step.

Introduction

We have been exploring new types of pseudo tetrahedral high oxidation state alkylidene complexes of molybdenum that have the formula $Mo(NR)(CHR')(OR'')(Pyr)$, where Pyr is a pyrrolide ligand such as the parent pyrrolide ($C_4H_4N^-$), 2,5-dimethylpyrrolide (Me_2Pyr), etc.¹ These monoalkoxidepyrrolide (MAP) complexes are prepared through addition of 1 equiv of $R''OH$ to $Mo(NR)(CHR')(Pyr)_2$ complexes.² MAP species are of great interest for several reasons, one being their high efficiency for asymmetric metathesis reactions that may be controlled to a large degree for electronic reasons as the olefin approaches the

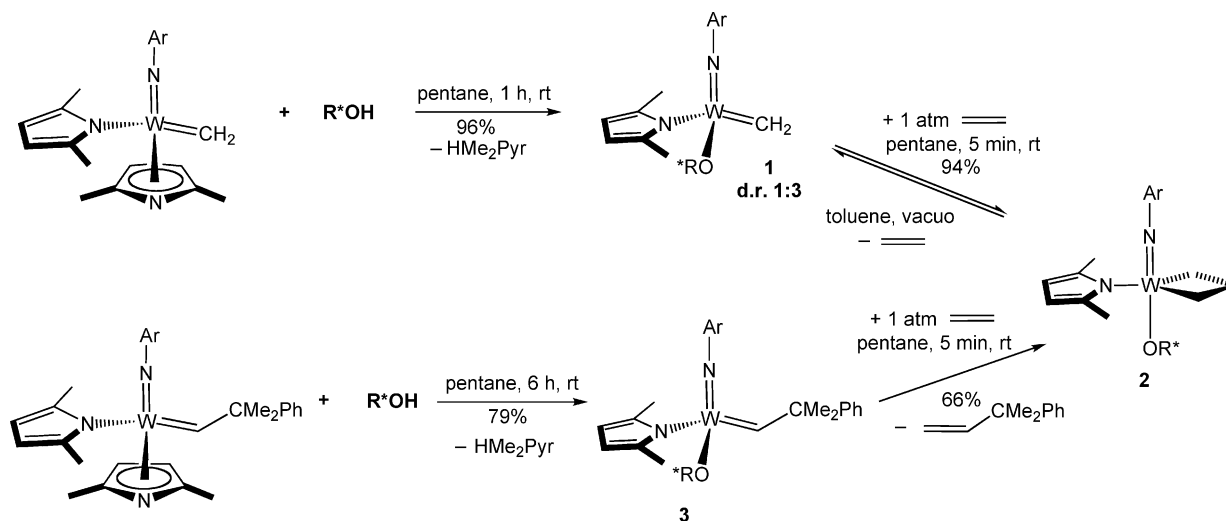
stereogenic metal center. For example, an asymmetric MAP catalyst (as a mixture of diastereomers) in which OR'' is the anion derived from (*R*)-3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol, or the 3,3'-dichloro analogue, can promote a difficult ring-closing reaction of a precursor to the *Aspidosperma* alkaloid, quebrachamine, in 84% yield and 96% ee.^{1c,d} Other reasons include their metathetical activity for enyne metathesis^{1a} and for *Z*-selective and enantioselective ring-opening cross-reactions.^{1f}

Few tungsten analogues of known molybdenum MAP species have been prepared and studied. The known species are $W(NAr)(CHCMe_2Ph)(OAr)(Me_2Pyr)$ (Ar = 2,6-diisopropylphenyl), $W(NAr)(CHCMe_2Ph)[OC(CF_3)_3](Me_2Pyr)$, $W(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2](Me_2Pyr)$, and $W(NAr)(CHCMe_2Ph)(OSi-$

(1) (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*, published online March 13, <http://dx.doi.org/10.1021/cr800502p>. (f) Ibrahim, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844.

(2) (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.

Scheme 1



$\text{Ph}_3(\text{Me}_2\text{Pyr})_2$.³ These species were prepared in order to be tested as co-catalysts for alkane metathesis. (Several are relatively efficient.) In addition to homogeneous tungsten MAP species, there is also evidence that heterogeneous $\text{W}(\text{NR})(\text{CHR}')(\text{Me}_2\text{Pyr})(\text{OSi}_{\text{surf}})$ species can be prepared through addition of $\text{W}(\text{NR})(\text{CHR}')(\text{Me}_2\text{Pyr})_2$ to partially dehydroxylated silica.⁴ Many of the key questions concerning the metathetical reactivity of MAP species are related to methylidene and metallacyclobutane species, stable examples of which are largely restricted to tungsten. Recently we prepared a tungsten methylidene complex, $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})_2$, by treating $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$ with ethylene.⁵ Isolation of $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})_2$ provided us with the opportunity to prepare MAP species derived from it and to explore their fundamental reactions. We report here the first detailed studies of homogeneous tungsten MAP species generated from $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})_2$.

Results

Synthesis and Studies of Methylidene and Tungstacyclobutane Species. Addition of 1 equiv of R^*OH (where R^*OH is (*R*)-3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol) to $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})_2$ in solution at 22 °C after approximately 1 h yielded two diastereomers of $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OR}^*)$ (**1**) (Scheme 1) in a 1:3 ratio. The proton NMR spectrum of **1** showed two methylidene proton resonances at 10.55 and 9.44 ppm ($J_{\text{HH}} = 9$ Hz, $J_{\text{CH}_{\text{syn}}} = 162$ Hz, $J_{\text{CH}_{\text{anti}}} = 133$ Hz) for the major isomer and at 10.63 and 9.97 ppm ($J_{\text{HH}} = 9$ Hz, $J_{\text{CH}_{\text{syn}}} = 163$ Hz, $J_{\text{CH}_{\text{anti}}} = 135$ Hz) for the minor isomer. (The *anti* methylidene proton is the one pointed away from the imido ligand, while the *syn* proton is the one pointed toward the imido group.⁶) The *syn* protons are coupled to tungsten ($J_{\text{HW}} = 16$ Hz), while coupling

of the *anti* proton to tungsten could not be resolved. The assignment of H_{syn} is consistent with NOE experiments described below. Typically a small amount ($\sim 2\%$) of what is believed to be $\text{W}(\text{NAr})(\text{CH}_2)(\text{OR}^*)_2$ forms (with methylidene resonances at 9.70 and 9.21 ppm). In the presence of 2 equiv of R^*OH , $\text{W}(\text{NAr})(\text{CH}_2)(\text{OR}^*)_2$ is generated slowly over a period of 6 days at 60 °C; it has not yet been isolated.

Slow decomposition of $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OR}^*)$ in solution ($\sim 10\%$ over a period of 1 week at -27 °C) is one of the reasons (combined with high solubility) why neither diastereomer could be isolated in crystalline form. Therefore, ethylene was added to the mixture of diastereomers in an attempt to generate the unsubstituted tungstacyclobutane species, $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{Pyr})(\text{OR}^*)$ (**2**). Compound **2** formed readily and could be isolated as yellow shards in good yield. Compound **2** also could be prepared and isolated in 66% yield by exposing a concentrated solution of $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{OR}^*)$ (**3**) (generated in the same manner as **1**) in pentane to 1 atm of ethylene. A reaction between **2** and ~ 1 atm of ^{13}C -labeled ethylene showed that ^{13}C is incorporated into the WC_3 ring in less than 1 min at 0 °C. The C_α resonances in **2** are found at 101.69 and 100.88 ppm ($J_{\text{CW}} = 65$ Hz, $J_{\text{C}\alpha\text{C}\beta} = 13$ Hz, $J_{\text{CH}} = 155$ and 157 Hz respectively), while the C_β resonance is found at -3.58 ppm ($J_{\text{C}\alpha\text{C}\beta} = 13$ Hz, $J_{\text{C}\beta\text{H}} = 154$ Hz). These data are consistent with a trigonal bipyramidal (TBP) structure in which the WC_3 ring is located equatorially.⁷ A TBP structure is one of the two (the other being a square pyramidal structure) that has been observed for bisalkoxide tungstacyclobutane complexes that have been crystallographically characterized in the past or observed in solution.⁷

When **2** was dissolved in toluene and the toluene was removed *in vacuo*, some **1** was present in the resulting solid. After addition and then removal of toluene *in vacuo* 8–10 times, a 1:3 mixture of virtually pure **1** could be prepared as a dry “foam”, but again no crystals of **1** could be obtained.

(3) Bailey, B. C.; Schrock, R. R.; Kundu, S.; Goldman, A. S.; Huang, Z.; Brookhart, M. *Organometallics* **2009**, *27*, 355.

(4) Blanc, F.; Berthoud, R.; Copéret, C.; Lesage, A.; Emsley, L.; Singh, R.; Kreckmann, T.; Schrock, R. R. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12123.

(5) Kreckmann, T.; Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 5702.

(6) *Syn* and *anti* isomers of monosubstituted (CHR) alkylidenes are named according to which direction the *substituent* points. Therefore, a *syn* monosubstituted alkylidene contains a proton that is *anti* with respect to the imido ligand. A methylidene species, of course, has no *syn* and *anti* isomers, just *syn* and *anti* protons.

(7) (a) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evtitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (c) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (d) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

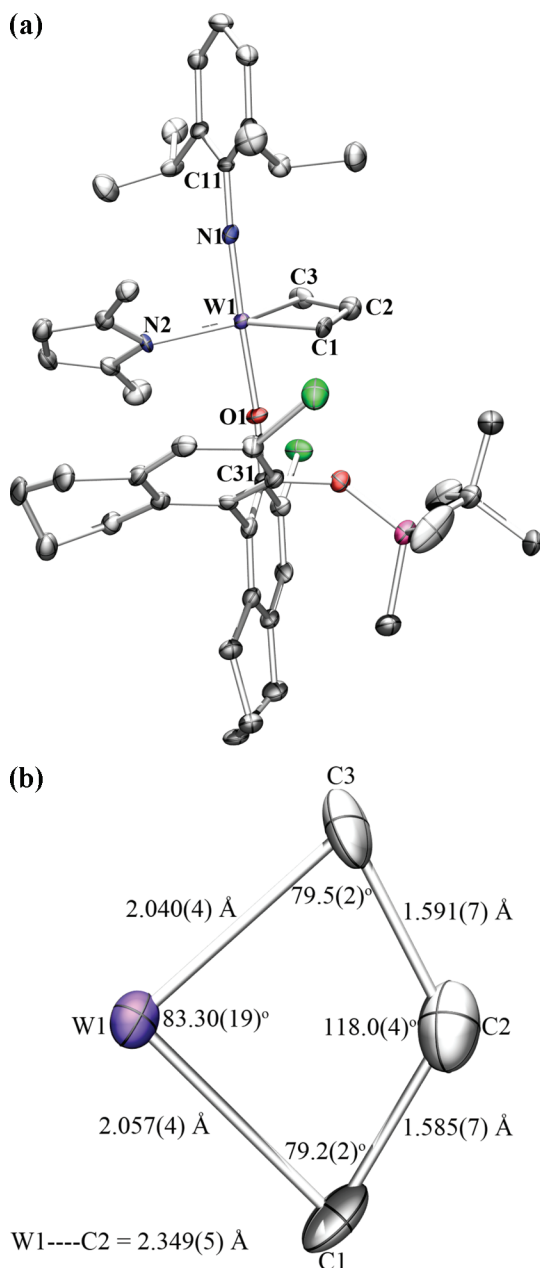


Figure 1. (a) POV-Ray rendering of $W(NAr)(C_3H_6)(Me_2Pyr)(OR^*)$ (**2**). Thermal ellipsoids are at 50% probability level. Hydrogen atoms are omitted for clarity. Distances (Å) and angles (°): W1–N1 = 1.765(3), W1–N2 = 2.063(3), N1–W1–O1 = 177.25(13), N1–W1–C3 = 89.99(16), O1–W1–C3 = 87.39(14), N1–W1–C1 = 93.63(15), O1–W1–C1 = 85.25(14), N1–W1–N2 = 93.77(13), O1–W1–N2 = 88.70(12), C3–W1–N2 = 136.51(16), C1–W1–N2 = 139.42(16), C11–N1–W1 = 173.3(3), C31–O1–W1 = 171.4(3). (b) The tungstacyclobutane core of **2**. Thermal ellipsoids are at 50% probability level.

An X-ray study of **2** revealed it to have a TBP structure in which the imido and phenoxide ligands are in axial positions (Figure 1a; also see Table S2a in the Supporting Information). An example of a crystallographically characterized unsubstituted TBP tungstacyclobutane is $W(NAr)(C_3H_6)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$.^{7a} The WC_3 ring in **2** is essentially planar, and the observed distances and angles (Figure 1b) are virtually identical to those observed in $W(NAr)(C_3H_6)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$, including a relatively short $W\cdots C2$ distance of 2.349(5) Å. The $W–O1–C31$ angle in **2** is 171.4(3)°, which should be compared with the $W–O_{ax}–C$ angle (172.4(13)°) and the $W–O_{eq}–C$ angle

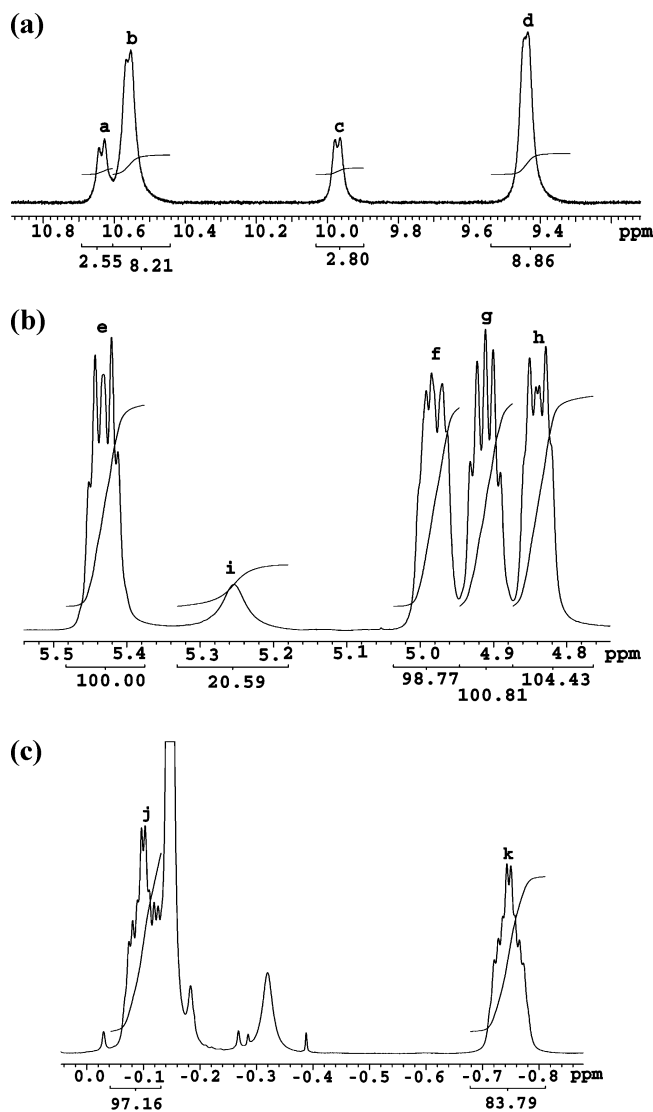
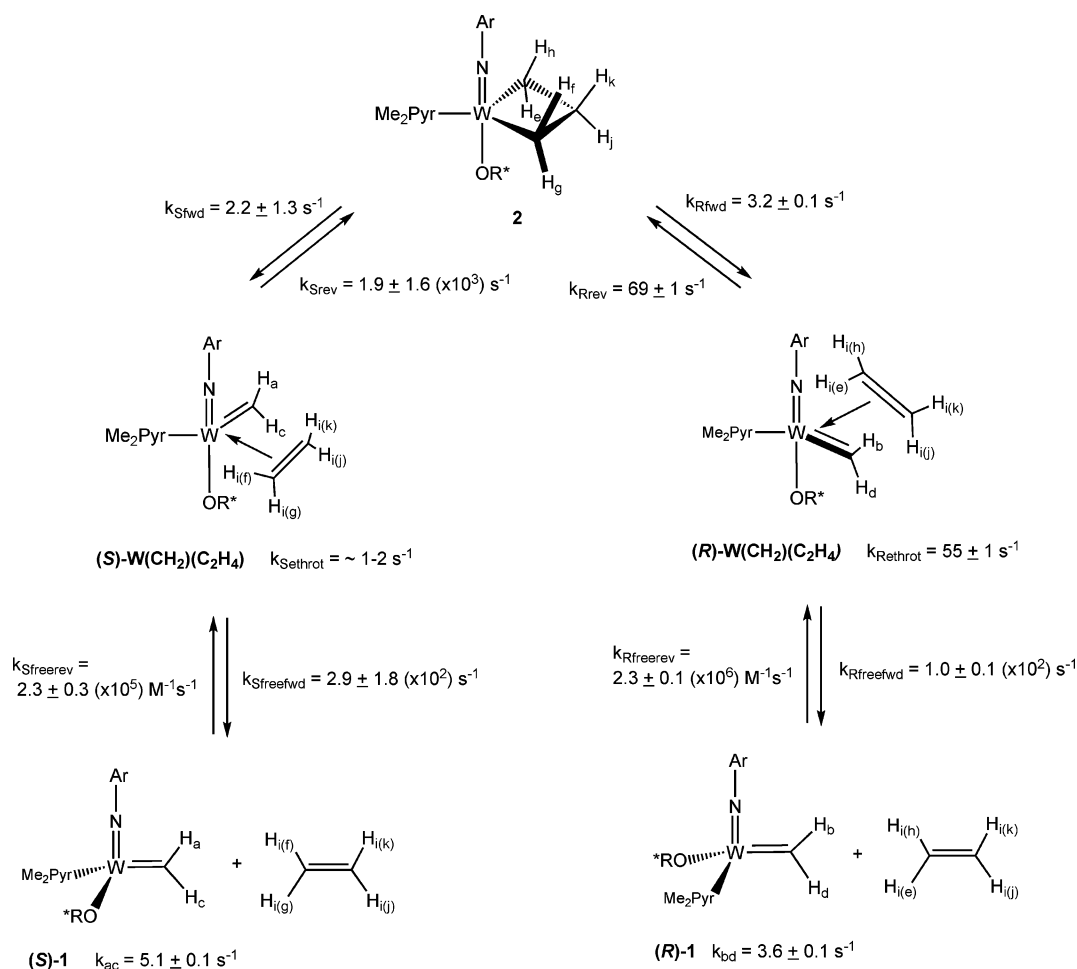


Figure 2. (a) Expansion of the 1H NMR spectrum in the alkylidene region for **2** in C_6D_6 . (b) Expansion of the 1H NMR spectrum in the H_a region for **2** in C_6D_6 . (c) Expansion of the 1H NMR spectrum in the H_β region for **2** in C_6D_6 .

(146.6(11)°) in $W(NAr)(C_3H_6)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$. (Since the $W–O_{ax}–C$ angle in TBP $W(NAr)[CH(SiMe_3)CH(SiMe_3)CH_2][OCMe(CF_3)_2]_2$ is only 149.3(8)°,^{7a} large $W–O_{ax}–C$ angles most likely arise primarily as a consequence of steric interactions.) The torsion angle between the rings in the OR^* ligand in **2** is 73.1°. The Me_2Pyr ligand is twisted so that its plane lies approximately parallel to the plane of one of the rings of the OR^* ligand. The diisopropylphenyl group in the imido ligand is then oriented in a way that minimizes steric interactions between the isopropyl groups and the pyrrolide ligand.

The proton NMR spectrum (in benzene- d_6) of a 47 mM solution of **2** showed the sample to contain **2** (~90%), the two diastereomers of **1** (~10% total), and ethylene (5% in solution relative to the total concentration of metal complexes). Methylidene proton resonances (four) are observed for the diastereomers of **1**, metallacyclobutane resonances (six) are observed for **2**, and a (broad) resonance is observed for ethylene (see Figure 2; also see Figure S1 in the Supporting Information). Metallacyclobutane and methylidene resonances have been identified as shown in Scheme 2 by 2D HSQC, NOESY, and EXSY NMR methods described in the Supporting Information.

Scheme 2



Resonances *a* and *c* (δ 10.63 and 9.97 ppm) are ascribed to the minor, (*S*)-methylidene species ((*S*)-**1**; *a* is *syn*, *c* is *anti*), while resonances *b* and *d* (δ 10.55 and 9.44 ppm) are ascribed to the major, (*R*)-methylidene species ((*R*)-**1**; *b* is *syn*, *d* is *anti*). The *R* and *S* configurations of **1** were assigned on the basis of the species generated when **2** loses ethylene. The broadened ethylene peak (*i* in Figure 2b) at 5.26 ppm and the presence of broadened resonances for (*R*)-**1** and (*S*)-**1** in samples of **2** in benzene-*d*₆ at 22 °C suggest that ethylene is lost from **2** to give (*R*)-**1** and (*S*)-**1** at a rate sufficient to give detectable resonance broadening in the 1D ¹H NMR spectrum. The equilibrium mixture of diastereomers found for W(NAr)(CH₂)(Me₂Pyr)(OR*) (*S*:*R* = 1:3) should be compared with the equilibrium mixture found for Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)(OR*) diastereomers (*S*:*R* = 2:1).^{1b}

An EXSY experiment of the mixture of (*R*)-**1** and (*S*)-**1** at 20 °C with no ethylene present reveals that *a* and *c* exchange; 27.6% of the (*S*)-**1** undergoes a 180° rotation during the 50 ms EXSY mixing time (Figure S4 in the Supporting Information). A *b*-*d* exchange cross peak is also evident, but it is weaker and superimposed on a COSY cross peak; only 5.1% of (*R*)-**1** undergoes a 180° rotation during the same 50 ms EXSY mixing time. Rate constants can be extracted for exchange of *a* and *c* (k_{ac}) and exchange of *b* and *d* at 20 °C. For (*S*)-**1**, k_{ac} was found to be 7 s⁻¹, while for (*R*)-**1**, k_{bd} was found to be 2 s⁻¹ by fitting the data to a simplified model as described in the NMR Studies and Calculations section in the Supporting Information. Exchange of methylidene protons is ascribed to rotation about the

W=C bond, a process that has been documented for molybdenum imido alkylidene bisalkoxide complexes that contain a substituted alkylidene in the form of interconversion of *syn* and *anti* isomers of those alkylidenes.⁸ However, $k_{s/a}$ (for conversion of *syn* to *anti* isomers of monosubstituted alkylidenes⁶) and $k_{a/s}$ (for conversion of *anti* to *syn* monosubstituted alkylidenes⁶) often differ dramatically, with $k_{a/s}$ being often much larger than $k_{s/a}$. The rate-limiting step also can differ by as much as 6 orders of magnitude from one compound to another, depending upon the nature of (primarily) the alkoxide. Methylidene rotation is a simpler (i.e., degenerate) version of interconversion of *syn* to *anti* isomers of monosubstituted alkylidenes. To our knowledge, these are the first observations and measurements of methylidene rotation in high oxidation state alkylidene complexes of Mo and W.

Experiments (2D ¹H-¹H EXSY) employing **2** at 20 °C reveal that proton *a* exchanges with protons *h* and *e*, but the *a*-*h* cross peak is stronger than the corresponding *a*-*e* cross peak, consistent with loss of *f,g,k,j*-ethylene to give (*S*)-**1** (Scheme 2; also see Figure S5 in the Supporting Information). The strong *a*-*h* cross peak suggests that *syn* proton *h* becomes *syn* proton *a*. Exchange of *a* and *c* protons through W=C rotation then gives rise to *a*-*e* and *c*-*h* cross peaks. Similarly, *b* and *d* exchange with both *f* and *g*. Since *b* and *d* exchange through methylidene rotation more slowly than do *a* and *c*, the *f*-*d* and *g*-*b* cross peaks are relatively small compared to the *f*-*b* and *g*-*d* cross

(8) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

peaks, respectively. The breakup of **2** to give an (*R*)-W(CH₂)(C₂H₄) intermediate (*vide infra* and Scheme 2) and re-formation of **2** have rate constants k_{Rfwd} (forward) = 3.2 ± 0.1 s⁻¹, while k_{Rrev} (reverse) = 69 ± 1 s⁻¹; formation of (*S*)-W(CH₂)(C₂H₄) has k_{Sfwd} = 2.2 ± 1.3 s⁻¹ and k_{Srev} = $(1.9 \pm 1.6) \times 10^3$ s⁻¹. The values associated with the *S* diastereomer have large uncertainties which can be attributed to the low concentrations of the *S* species (see NMR Studies and Calculations in the Supporting Information).

At 5 °C with a 200 ms EXSY mixing time, resonance *h* shows a strong cross peak with resonance *j*, while resonance *e* shows a strong cross peak with resonance *k* (Figure S6 in the Supporting Information). This result suggests that the ethylene in (*R*)-W(CH₂)(CH₂) can rotate about the W–ethylene bond axis and re-form **2** before it is lost from the metal to give (*R*)-**1**. At 20 °C with a 200 ms EXSY mixing time, resonances *e* and *h* show equal intensity exchange cross peaks with resonances *j* and *k*, thus indicating that the ethylene is rapidly coming on and off the metal, a process that is rapid enough to scramble *h* and *e* (Figure S7 in the Supporting Information). However, under these conditions, resonance *f* shows only an exchange cross peak with resonance *j*, while resonance *g* shows only an exchange cross peak with resonance *k*, indicating that ethylene can rotate in intermediate (*S*)-W(CH₂)(CH₂) before it is lost to yield (*S*)-**1**. In comparison, the (*S*)-W(CH₂)(CH₂) exchange cross peaks (corresponding to ethylene rotation) are observable at 20 °C, and those of (*R*)-W(CH₂)(CH₂) are already evident at 5 °C, which is an indication that ethylene rotation in (*S*)-W(CH₂)(CH₂) is relatively slow compare to that of the *R* species. Two other observations suggest the presence of an W(CH₂)(CH₂) species: (1) An ¹H–¹H EXSY spectrum of **2** at 20 °C (200 ms) (Supporting Information, Figure S8) shows that protons *a* and *c* exchange with *j* and *k* equally because ethylene exchanges readily in (*R*)-W(CH₂)(CH₂). On the other hand, proton *b* exchanges with *j*, but not with *k*, and *d* exchanges with *k*, but not with *j*; i.e., in (*S*)-W(CH₂)(CH₂), competing rate constants favor return of the methylidene/olefin species to the metallacycle, thereby enabling detection of ethylene rotation (Scheme 2). (2) While examination of the 1D ¹H NMR spectrum showed that the ethylene resonance is broad, the 2D ¹H–¹H EXSY NMR spectra showed that the chemical shift of the free ethylene was downfield from that of ethylene in (*R*)-W(CH₂)(C₂H₄) and (*S*)-W(CH₂)(C₂H₄), thus providing direct spectroscopic evidence that ethylene exists in a free and a bound state as W(CH₂)(C₂H₄), and also that only bound ethylene exchanges with the tungstacycle (see Figure S9 in the Supporting Information).

To our knowledge, these are the first observations for imido alkylidene complexes that support formation of an intermediate alkylidene/olefin complex and rotation of the olefin about the metal–olefin bond axis in that species. The rate constant ($k_{Rethrot}$) corresponding to the rotation of the ethylene coordinated in (*R*)-W(CH₂)(CH₂) is 55 ± 1 s⁻¹, while $k_{Sethrot}$ can only be estimated as 1–2 s⁻¹ (the large k_{Srev} limits the lifetime of (*S*)-W(CH₂)(CH₂)). In (*R*)-W(CH₂)(CH₂), k_{Rfwd} = 100 ± 10 s⁻¹ and k_{Rfrev} = $(2.3 \pm 0.1) \times 10^6$ M⁻¹ s⁻¹. The values for the *S* species are k_{Sfwd} = 290 ± 180 s⁻¹ and k_{Sfrev} = $(2.3 \pm 0.3) \times 10^5$ M⁻¹ s⁻¹. The rate constants for ethylene rotation in the (*R*)-alkylidene/olefin complex are similar in magnitude to k_{Rrev} and k_{Rfrev} , which suggests that ethylene may rotate at most once before the complex re-forms **2** or breaks up to yield **1** and free ethylene. Ethylene rotation in the alkylidene/olefin is slower in the (*S*)-alkylidene/olefin species, and its concentration is low

in solution relative to the *R* species, which may explain why ethylene rotation in (*S*)-W(CH₂)(CH₂) is not apparent even at 90 ms mixing time. (However, recall that at longer mixing time (200 ms), there is spectroscopic evidence that ethylene rotates in (*S*)-W(CH₂)(C₂H₄), *vide supra*.) The k_{Rfrev} is an order of magnitude larger than k_{Sfrev} , suggesting that the (*R*)-methylidene reacts faster than the (*S*)-methylidene with free ethylene. Again, we believe that the uncertainties in the rate constants associated with the *S* diastereomers are large because the concentrations of the *S* species in solution are relatively low compared to those of the metallacycle and the *R* species.

Synthesis and Studies of Trimethylphosphine Derivatives. Trimethylphosphine has often been employed as an indicator of where an olefin binds in a four-coordinate high oxidation state alkylidene species. When PMe₃ (5 equiv) was added to the mixture of (*S*)-**1** and (*R*)-**1**, or to **2**, in benzene-*d*₆, essentially a single diastereomer of a PMe₃ adduct formed in less than 15 min at room temperature. In the case of **2**, ethylene gas evolved immediately upon addition of PMe₃. The proton NMR spectrum of this adduct contains two multiplets at δ 11.74 (H_{syn}) and 11.55 ppm (H_{anti}). Exposing a sample of the adduct in benzene-*d*₆ to a vacuum in order to remove all solvent and then redissolving the sample in benzene-*d*₆ did not produce any PMe₃-free species. This behavior contrasts with that observed in the analogous W(NAr)(CHCMe₂Ph)(OR*)(Me₂Pyr)(PMe₃) complexes (*vide infra*) or Mo(NAr)(CHCMe₂Ph)(OR*)(Me₂Pyr)(PMe₃) complexes; in the latter, PMe₃ is dissociated to a significant degree at 22 °C at a concentration of ~ 0.1 M.^{1b} ¹H–¹H EXSY spectra at 20 °C with 200 ms mixing time did not indicate any exchange of the methylidene protons in the trimethylphosphine methylidene adduct.

The phosphine adduct of W(NAr)(CH₂)(OR*)(Me₂Pyr)(PMe₃) can be isolated readily. A preliminary single-crystal X-ray structure of W(NAr)(CH₂)(Me₂Pyr)(OR*)(PMe₃) established that it is the (*R*)-diastereomer with a structure analogous to that for (*R*)-Mo(NAr)(CHCMe₂Ph)(OR*)(Me₂Pyr)(PMe₃); the PMe₃ is *trans* to the pyrrolide, and the methylidene ligand is approximately in an axial position in a square pyramid. Although the data are not sufficiently accurate to have full confidence in bond lengths and angles, a high-quality structure of a related PMe₃ adduct of this general type is presented later in this paper.

The fact that PMe₃ is firmly bound to W creates the opportunity to determine the rate of rearrangement of five-coordinate PMe₃ adducts. In a series of experiments, 10, 30, and 60 equiv amounts of PMe₃ were vacuum transferred onto a frozen sample of W(NAr)(CH₂)(OR*)(Me₂Pyr) in methylene chloride-*d*₂ at 77 K (see Supporting Information for details). The samples were then thawed at –78 °C and examined by proton NMR at 5 °C. Compounds (*S*)-**1** and (*R*)-**1** were consumed, and three PMe₃ adducts were formed, the major one being (*R*)-**1**(PMe₃) (75%; ¹H multiplets at 11.66 and 11.31 ppm; Figure 3; ³¹P δ at 3.71 ppm with J_{PW} = 283 Hz). The other two adducts have methylidene proton resonances at δ 12.68 and 11.92 ppm (7%, “adduct A”; ³¹P δ 4.83 ppm) and δ 11.53 and 11.46 ppm (18%, “adduct B”; ³¹P δ at –4.83 ppm (J_{PW} = 258 Hz)). Over the course of several hours at 5 °C, adducts A and B are converted to (*R*)-**1**(PMe₃). The conversions of A and B to (*R*)-**1**(PMe₃) do not depend on PMe₃ concentration and are first order in W. In the case where 10 equiv of PMe₃ is added, the rate constants for conversion of A and B to (*R*)-**1**(PMe₃) are 8.1×10^{-3} and 7.4×10^{-3} min⁻¹, respectively (see Figure S10 in the Supporting Information). When 30 equiv of PMe₃ is added, the rate constants are 8.6×10^{-3} and 7.7×10^{-3} min⁻¹,

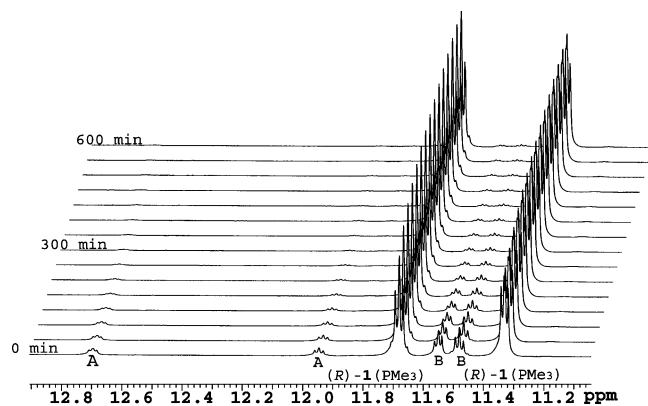


Figure 3. Proton NMR spectra of PMe_3 adducts A and B (at 5 °C) formed upon addition of 30 equiv of trimethylphosphine to diastereomers of $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OR}^*)$ and their conversion to $(R)\text{-W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OR}^*)(\text{PMe}_3)$.

respectively (see Figure S11 in the Supporting Information). When 60 equiv of PMe_3 is added, the observed rate constants are 8.5×10^{-3} and $1.1 \times 10^{-2} \text{ min}^{-1}$, respectively (see Figure S12 and Table S1 in the Supporting Information). Therefore, the average rate constant for conversion of A and B to $(R)\text{-1}(\text{PMe}_3)$ is $\sim 1.4(1) \times 10^{-4} \text{ s}^{-1}$ ($t_{1/2} \approx 80 \text{ min}$) at 5 °C. Conversions of A and B to $(R)\text{-1}(\text{PMe}_3)$ correspond to the rate of intramolecular rearrangement of A and B to $(R)\text{-1}(\text{PMe}_3)$, presumably as a consequence of a series of Berry or turnstile processes.^{1b,9} These results would suggest that any similar five-coordinate rearrangement of (R) - or $(S)\text{-W}(\text{CH}_2)(\text{C}_2\text{H}_4)$ (Scheme 2) is likely to be approximately 2 orders of magnitude smaller than other processes that involve (R) - or $(S)\text{-W}(\text{CH}_2)(\text{C}_2\text{H}_4)$, namely formation of **1** or **2**.

Yellow solids were isolated when $(S)\text{-W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (**3**) was treated with 2 equiv of PMe_3 in pentane. When the isolated solid was examined by proton NMR in C_6D_6 , after 20 min in solution, the mixture consisted of free PMe_3 and five other species: $(R)\text{-3}$ (3%, 9.98 ppm), $(S)\text{-3}$ (43%, 9.45 ppm), $(R)\text{-3}(\text{PMe}_3)$ (25%, 11.53 ppm, $J_{\text{PH}} = 6 \text{ Hz}$), $(S)\text{-3}(\text{PMe}_3)$ (21%, 13.21 ppm, $J_{\text{PH}} = 4 \text{ Hz}$), and $(S')\text{-3}(\text{PMe}_3)$ (a second type of S species, 8%, 11.61 ppm). These assignments are similar to those obtained for the analogous Mo system^{1b} and were confirmed through 2D $^1\text{H}\text{-}^1\text{H}$ EXSY NMR studies (see Figure S13 in the Supporting Information). After 24 h at room temperature, the mixture in solution consisted of $(R)\text{-3}$ (10%), $(S)\text{-3}$ (25%), $(R)\text{-3}(\text{PMe}_3)$ (53%), $(S')\text{-3}(\text{PMe}_3)$ (3%), and $(S)\text{-3}(\text{PMe}_3)$ (9%). These observations suggest that PMe_3 does not bind to the neophylidene MAP complex as strongly as it does to the methyldiene analogue, presumably for steric reasons. The relative amounts of PMe_3 adducts and PMe_3 -free diastereomers present after 1 day suggest that PMe_3 catalyzes inversion of the metal center, as in the Mo system, through formation of five-coordinate PMe_3 adducts.^{1b}

Synthesis and Studies of Species That Contain the 2,3,5,6-Tetraphenylphenoxide Ligand. When 1 equiv of 2,3,5,6-tetraphenylphenol (ROH) was added to $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$

or $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})_2$ in benzene, $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{OR})$ (**4**, Scheme 3) and $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OR})$ (**5**, Scheme 3) were isolated in good yields as yellow powders. Complex **4** (in benzene- d_6) exhibits an H_α resonance at δ 8.43 ppm and a C_α resonance at δ 263.50 ppm ($J_{\text{CH}} = 116 \text{ Hz}$, $J_{\text{WH}} = 16 \text{ Hz}$, and $J_{\text{CW}} = 190 \text{ Hz}$), consistent with **4** being a *syn* isomer in which the neophylidene group faces toward the imido ligand.⁶ Complex **5** (in benzene- d_6) contains an H_{syn} resonance at 10.24 ppm ($J_{\text{CH}} = 160 \text{ Hz}$) and an H_{anti} resonance at 8.75 ppm ($J_{\text{CH}} = 130 \text{ Hz}$). The two methyldiene resonances are broad as a consequence of rotation about the $\text{W}=\text{C}$ bond on the NMR time scale, as shown through variable-temperature studies. The variable-temperature ^1H NMR spectrum of **5** (Figure 4) showed that each proton resonance is a doublet at 0 °C and the resonances coalesce at ~ 60 °C; **5** withstands being heated to 80 °C in this process with little decomposition. The $^1\text{H}\text{-}^1\text{H}$ EXSY spectrum of **5** in benzene- d_6 at 20 °C with 5 ms of mixing time showed that the methyldiene protons are exchanging with $k = 90 \text{ s}^{-1}$ (calculated using a simplified model described in the Supporting Information; also see Figure S14 in the Supporting Information). Compound **5** decomposes in toluene- d_8 to a significant degree at 60 °C over the course of several days; identification of the decomposition products was not pursued.

Recrystallization of **5** from a 1:1 mixture of tetrahydrofuran and diethyl ether afforded **5(THF)** as yellow crystals. A single-crystal X-ray study showed **5(THF)** to be a square pyramid with the methyldiene ligand in the apical position and THF coordinated *trans* to the imido ligand (Figure 5; see Table S2a in the Supporting Information for additional details). Relevant distances and angles can be found in the Figure 5 caption. A molecule of disordered diethyl ether is present in the lattice of the crystal. When a sample of **5(THF)** is dissolved in benzene and the volatiles are removed *in vacuo*, both tetrahydrofuran and diethyl ether were removed after three cycles, and solvent-free **5** was obtained.

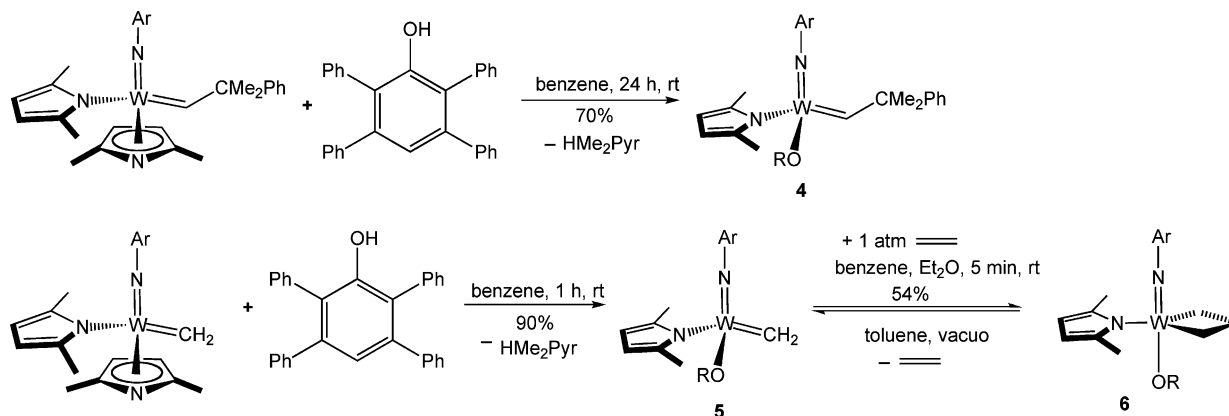
Exposure of a degassed sample of **5** (in benzene/ether) to 1 atm of ethylene generated the tungstacyclobutane complex, $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OR})(\text{Me}_2\text{Pyr})$ (**6**), which could be isolated in moderate yields (Scheme 3). Recrystallization of **6** from a 1:1 mixture of benzene and ether afforded yellow-orange crystals. A single-crystal X-ray study (Figure 6; see Table S2b in the Supporting Information for details) showed **6** to be a TBP species similar to **2**. The W1-O1-C31 angle in **6** ($159.73(13)^\circ$) is smaller than the same angle in **2** ($171.4(3)^\circ$), presumably as a consequence of less demanding steric interactions in **6**.

Proton NMR spectra of a sample of **6** in C_6D_6 ($\sim 0.076 \text{ M}$) showed H_α resonances at 4.27 ppm (H_α) and 3.34 ppm (H_β ; Scheme 4). The H_β resonances are found at -0.94 ppm (H_α) and -1.40 ppm (H_β). Protons *c* and *f* are *syn* (they lie above the plane of the metallacycle and point toward the imido group), while protons *d* and *e* are *anti* (they lie below the plane of the metallacycle and point toward the phenoxide) (Scheme 4). These assignments are based on NOE contacts between proton *f* and the methyl group of the imido isopropyl group, between proton *e* and the Ar-H from phenyl ring of the phenoxide ligand, and between proton *d* and the Ar-H from the phenyl ring of the phenoxide ligand (see Figure S15 in the Supporting Information).

A proton NMR spectrum of a sample of **6** in C_6D_6 ($\sim 0.076 \text{ M}$) shows only a trace (3%) of **5**. 2D $^1\text{H}\text{-}^1\text{H}$ EXSY spectra of **6** with mixing time of 100 ms at 20 °C indicate that the methyldiene protons are exchanging with the protons in the

(9) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Gillespie, P.; Hoffman, P.; Klusacek, H.; Marquarding, D.; Pfohl, S.; Ramirez, R.; Tsois, E. A.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 687. (c) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70. (d) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168. (e) Mislaw, K. *Acc. Chem. Res.* **1970**, *3*, 321. (f) Muettterties, E. L. *Acc. Chem. Res.* **1970**, *3*, 266. (g) Muettterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636. (h) Muettterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 4115.

Scheme 3



metallacycle and ethylene is exchanging with the metallacycle (see Figure S16 in the Supporting Information). Within the tungstacycle, protons *e* exchange only with *c*, and *d* only with

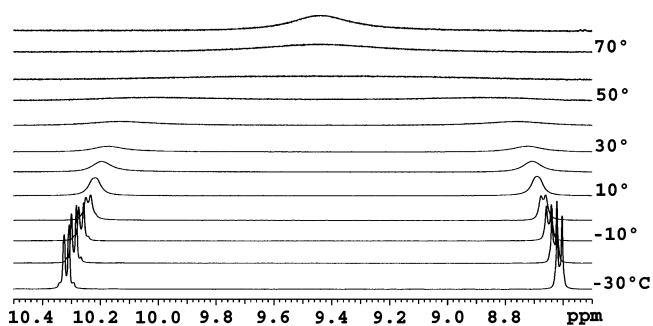


Figure 4. Variable-temperature ^1H NMR spectrum of $\text{W}(\text{NAr})(\text{CH}_2)(\text{OR})(\text{Me}_2\text{Pyr})$ (**5**) in $\text{toluene-}d_8$.

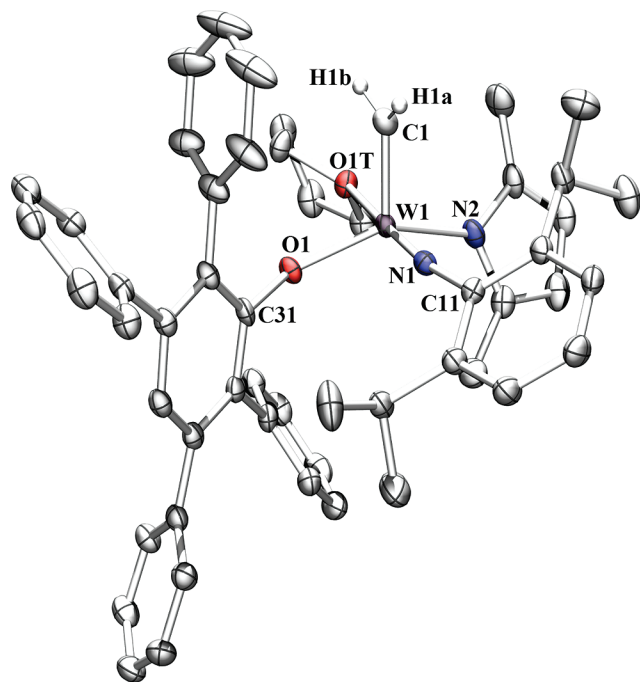


Figure 5. POV-Ray rendering of $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OR})(\text{THF})$ (**5(THF)**); shown is the major component of the whole molecule disorder. Thermal ellipsoids are at 50% probability level. All hydrogen atoms except for the methylenic hydrogens are omitted for clarity. Distances (\AA) and angles ($^\circ$): $\text{W1-N1} = 1.738(2)$, $\text{W1-C1} = 1.900(3)$, $\text{W1-N2} = 2.070(2)$, $\text{W1-O1} = 1.971(3)$, $\text{W1-O1T} = 2.2966(19)$, $\text{W1-N1-C11} = 167.3(3)$, $\text{W1-O1-C31} = 135.0(3)$, $\text{O1T-W1-N1} = 173.88(11)$, $\text{O1-W1-N2} = 132.24(17)$.

f, which suggests that ethylene rotates 180° in an intermediate $\text{W}(\text{CH}_2)(\text{C}_2\text{H}_4)$ complex (Scheme 4), as found in **2**. At 20°C , approximately 10% of methylenic is found in solution for complex **2** ($\sim 0.06\text{ M}$), but only 3% of the methylenic is found in solution for **6** ($\sim 0.08\text{ M}$). With a 100 ms mixing time, approximately 50% of the methylenic species from **2** exchanges with the metallacycle, while 80% of the methylenic species formed from complex **6** exchanges with the metallacycle.

When **5** is treated with 5 equiv of PMe_3 , essentially one PMe_3 adduct is formed. PMe_3 bound to tungsten is not removed readily

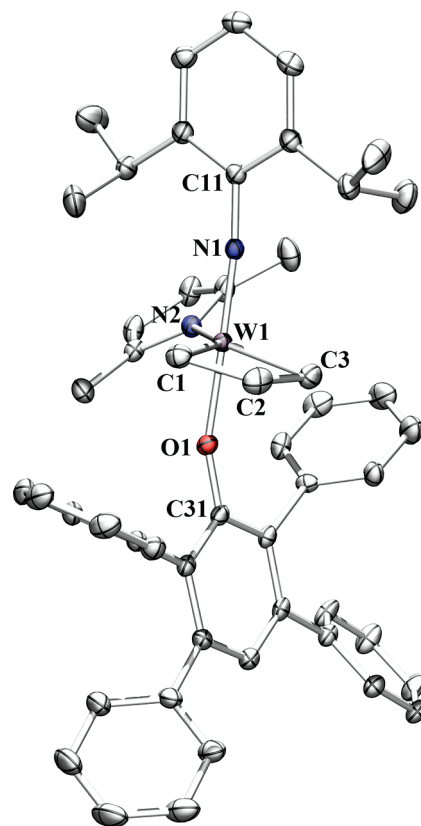
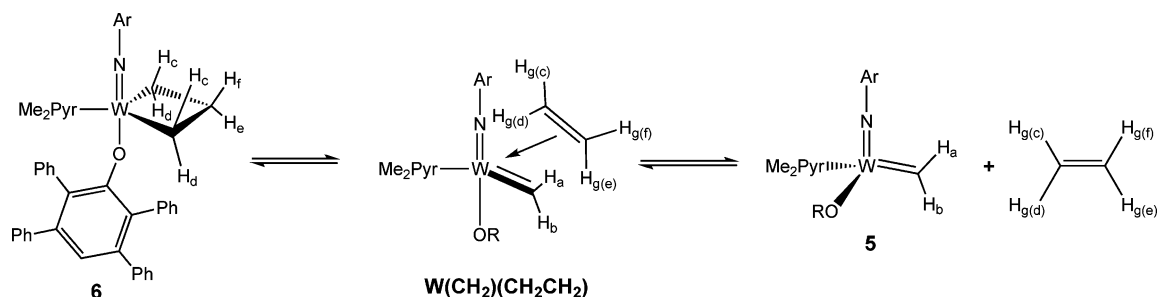


Figure 6. POV-Ray rendering of $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{Me}_2\text{Pyr})(\text{OR})$ (**6**). Thermal ellipsoids are at 50% probability level. Hydrogen atoms, minor components of disorders, and disordered solvent are omitted for clarity. Distances (\AA) and angles ($^\circ$): $\text{W1-N1} = 1.7676(17)$, $\text{W1-C1} = 2.057(2)$, $\text{W1-C2} = 2.368(2)$, $\text{W1-C3} = 2.058(2)$, $\text{C1-C2} = 1.603(3)$, $\text{C2-C3} = 1.597(3)$, $\text{W1-N2} = 2.0581(18)$, $\text{W1-O1} = 1.9703(15)$, $\text{W1-N1-C11} = 173.43(14)$, $\text{W1-O1-C31} = 159.73(13)$, $\text{W1-C1-C2} = 79.58(12)$, $\text{W1-C3-C2} = 79.67(13)$, $\text{C1-C2-C3} = 117.44(18)$, $\text{O1-W1-N1} = 178.55(6)$, $\text{N2-W1-C3} = 137.52(8)$, $\text{N2-W1-C1} = 137.84(8)$.

Scheme 4



in vacuo. Proton NMR spectra showed the H_{syn} resonance at δ 11.33 ppm (triplet, $J_{CH} = 159$ Hz, $J_{HH} = 7$ Hz, $J_{WH} = 13$ Hz, $J_{PH} = 6$ Hz) and the H_{anti} resonance at δ 10.33 ppm (quartet $J_{PH} = 5$ Hz). 1H - 1H EXSY spectra at 20 °C with 200 ms mixing time showed little exchange of the methylidene protons ($k \leq 0.1$ s $^{-1}$). Yellow crystals of compound **5**(PMe $_3$) were isolated by diffusion of diethyl ether into a concentrated benzene solution of **5**(PMe $_3$). X-ray diffraction revealed the solid-state structure to be a square pyramid with the methylidene ligand in the apical position, the phosphine *trans* to the pyrrolide, and the aryloxy *trans* to the imido group (Figure 7; see Table S2b in the Supporting Information for details). The W1–C1 distance is 1.900(2) Å, which is the same as the tungsten–carbon distance in the structure of **5**(THF). The W1–P1 distance is 2.5228(6) Å, which is slightly shorter than the Mo–P distance (2.5703(11) Å) in (*R*)-Mo(NAr)(CHCMe $_2$ Ph)(OR*)(Me $_2$ Pyr).^{1b} It should be noted that tetrahydrofuran binds *trans* to the imido ligand in **5**(THF), while PMe $_3$ binds *trans* to the pyrrolide in **5**(PMe $_3$). An olefin is believed to approach the metal *trans* to the pyrrolide

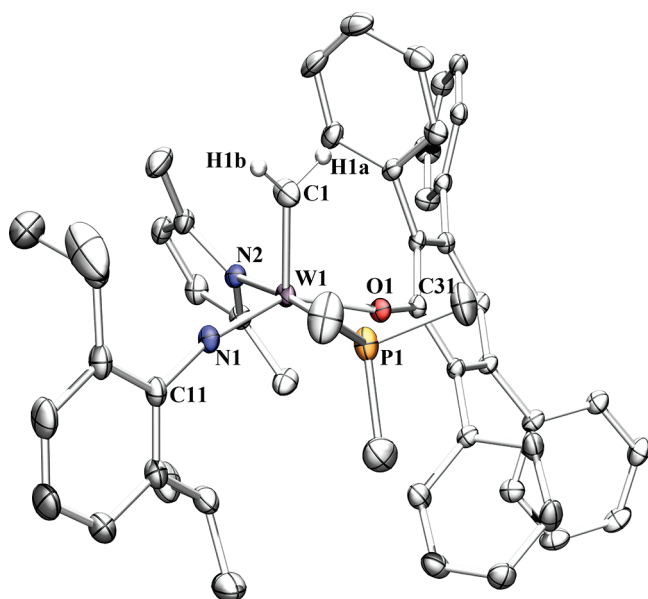


Figure 7. POV-Ray rendering of W(NAr)(CH $_2$)(Me $_2$ Pyr)(OR)(PMe $_3$) (**5**(PMe $_3$)). Thermal ellipsoids are at 50% probability level. Hydrogens except for those of the methylidene ligand are excluded for clarity. Distances (Å) and angles (°): W1–C1 = 1.900(2), W1–P1 = 2.5228(6), W1–O1 = 1.9937(13), W1–N1 = 1.7617(16), W1–N2 = 2.1303(17), W1–N1–C11 = 166.72(16), W1–O1–C31 = 149.28(13), N2–W1–P1 = 167.31(5), N1–W1–O1 = 147.28(7).

on the basis of calculations in simplified models that contain “donor” (methyl) and “acceptor” (methoxide) ligands.¹⁰

Discussion and Conclusions

Tungsten imido alkylidene bisalkoxide complexes have been studied in the past in order to establish the role of metallacyclobutane species in various olefin metathesis reactions and to establish structure.^{7d} The primary motives behind this study were the same, but for MAP species. MAP diastereomers provide an opportunity to follow the metathesis process involving an unsubstituted metallacyclobutane intermediate in minute detail.

Among the significant findings reported here is that 14e methylidene species can be long-lived. Methylidene stability is likely to be a key feature of any efficient metathesis reaction in which ethylene is employed or generated. It is not clear at this stage why some MAP species yield relatively stable methylidene complexes in the presence of ethylene, while others do not. An explanation that is based solely upon prevention of bimolecular (bimetallic) decomposition of methylidenes through steric hindrance is one possibility. However, one also must acknowledge the possibility that ethylene encourages irreversible rearrangement of one or more metallacyclobutane intermediates to an olefin complex,^{11,12} a process that would remove alkylidenes from a given system. Since ethylene-catalyzed rearrangement of a metallacyclobutane requires formation of a six-coordinate species, the bulky OR* and OR phenoxides in the MAP methylidene complexes described here may slow that process by preventing attack on a metallacyclobutane to yield a six-coordinate species.

Facile rotation of a methylidene ligand about the W=C bond was somewhat surprising to us. Since no *anti* alkylidene isomer of any MAP species has been observed, the rate of methylidene rotation is the only evidence that *syn* and *anti* alkylidene isomers of MAP species might also interconvert readily. An important caveat is that methylidene rotation may be inherently much faster than interconversion of *syn* and *anti* isomers of a substituted methylidene; this issue remains to be resolved. The symmetric nature of a methylidene and a lack of steric hindrance may allow the transition state for methylidene rotation (90° to the N_{imido}–W–C plane) to be accessed more readily than that for a monosubstituted alkylidene.

We also were surprised that formation of W(C $_2$ H $_4$)(CH $_2$) intermediates was found to be most consistent with the various

(10) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129*, 8207.

(11) Tsang, W. C. P.; Hultzsck, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652.

(12) Leduc, A.-M.; Salameh, A.; Soulvong, D.; Chabanas, M.; Basset, J.-M.; Copéret, C.; Solans-Monfort, X.; Clot, E.; Eisenstein, O.; Boehm, V. P. W.; Roeser, M. *J. Am. Chem. Soc.* **2008**, *130*, 6288.

NMR studies. To our knowledge, only one other example of olefin coordination and rotation in a high oxidation state alkylidene species has been reported, that being cycloheptene coordination and rotation in the cyclopentylidene complex $[\text{W}(\text{C}_5\text{H}_8)(\text{OCH}_2\text{CMe}_3)_2\text{Br}_2]\text{GaBr}_3$.¹³ It should be noted, however, that in the case of $[\text{W}(\text{C}_5\text{H}_8)(\text{OCH}_2\text{CMe}_3)_2\text{Br}_2]\text{GaBr}_3$, formation of the tungstacyclobutane intermediate is likely to be slower than in the analogous reactions described here, because of both the disubstituted nature of the alkylidene and the fact that the olefin is an internal olefin. Olefin coordination has usually, but not always, been considered in theoretical studies as a distinct step in the metathesis process.^{10,14} (See also reviews of alkylidene chemistry.¹⁵) There is no indication of simultaneous ethylene and methylidene rotation in the $\text{W}(\text{C}_2\text{H}_4)(\text{CH}_2)$ intermediates studied here. All evidence so far suggests that alkylidenes can rotate only in pseudo tetrahedral 14e species, not 16e adducts. If the rate of rearrangement of a $\text{W}(\text{CH}_2)(\text{C}_2\text{H}_4)$ intermediate is roughly the same as that of rearrangement of a PMe_3 adduct that we have observed here, then rearrangement of $\text{W}(\text{CH}_2)(\text{C}_2\text{H}_4)$ is approximately 2 orders of magnitude too slow relative to loss of ethylene to form **1** or re-formation of **2**.

An important feature of MAP species is the difference between a pyrrolide and an alkoxide. Eisenstein has proposed that a “donor” (D) and an “acceptor” (A) combination is highly beneficial in metathesis reactions catalyzed by $\text{M}(\text{NR})(\text{CHR}')(\text{D})(\text{A})$ species.^{10,12,14} It is not yet known whether high efficiency of the pyrrolide/alkoxide (or pyrrolide/aryloxide) combination adheres to the theory concerning D/A combinations or not. Pyrrolide may not be required, since species of the type $\text{Mo}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OR})$ (e.g., $\text{OR} = \text{OAr}$) are highly active for difficult ring-closing reactions.¹⁶ MAP species are being studied at this point because of the relative ease of preparing them from bispyrrolide precursors and the possibility of varying the nature of the pyrrolide to a significant degree.^{2b}

On the basis of the results presented here and preliminary studies involving analogous molybdenum species,^{1b,f} it now seems highly likely that ethylene approaches a pseudo tetrahedral $\text{M}(\text{NR})(\text{CH}_2)(\text{Pyr})(\text{OR}'')$ species *trans* to the pyrrolide (Pyr) and that the resulting metallacyclobutane species is a TBP in which the NR and OR'' ligands occupy axial positions. This mechanism is likely to be valid for substituted olefins approaching a *syn*- $\text{M}(\text{NR})(\text{CHR}')(\text{Pyr})(\text{OR}'')$ species. The product olefin is then lost readily *trans* to the pyrrolide, a process that results overall in formation of an alkylidene product in which the configuration at the metal center has inverted. This conclusion is based on the assumption that the five-coordinate metallacyclobutane complex itself does not undergo any competitive intramolecular rearrangement before the olefin product is lost, an assumption that is supported by the NMR studies reported here. Specifically, the $^1\text{H}-^1\text{H}$ NOESY/EXSY data show that

two hydrogens on separate α carbon atoms in the unsubstituted metallacyclobutane *do not* exchange in a manner consistent with a Berry or turnstile process. Therefore, any metathesis reaction (including otherwise degenerate reactions) leads to inversion at the metal center. In order to take advantage of asymmetry at the metal center in a MAP species in an asymmetric metathesis reaction, it would seem necessary that only one diastereomer takes part in a reaction that leads to product. This is the essence of the proposed utility of MAP species as a mixture of diastereomers in asymmetric metathesis reactions.^{1c,d}

There is an unexpected bonus if the mechanism for MAP species involves TBP metallacyclobutane intermediates with axial NR and OR'' groups. If only *syn* alkylidenes are accessible in MAP species (so far no *anti* species have been observed), then it would seem possible to restrict metallacyclobutane intermediates derived from a *syn* alkylidene to those in which up to three substituents on the metallacycle can point only toward a “small” imido group, and none can point toward a “large” OR' group. In this situation, only *cis* olefins can be formed in a metathesis process. This argument was employed in order to explain why *Z*-selective and enantioselective ring-opening/cross-metathesis reactions are catalyzed by stereogenic-at-Mo adamantylimido complexes.^{1f} Since the nature of at least three of the ligands in a MAP species (imido, pyrrolide, alkoxide) can be varied to a significant degree, the possibility of controlling not only asymmetric reactions but also symmetric reactions such as *Z*-selective coupling of internal or terminal linear or cyclic olefins holds some promise. One should add ring-opening metathesis polymerization to the list of reactions that remain to be explored with new MAP species.

Finally, it should be pointed out that what we learn through fundamental studies involving tungsten alkylidenes improves our understanding of metathesis in general by either Mo or W species. The reason is based on more than a close structural and functional similarity of Mo and W imido alkylidene complexes; preliminary results have shown that tungsten MAP species can produce metathesis results that are equivalent, or even superior, to those obtained with molybdenum MAP complexes in certain ring-closing or enyne metathesis reactions.¹⁷ It also should be noted that a survey of approximately 40 high oxidation state alkylidene catalysts for alkane metathesis revealed that tungsten catalysts outperformed the molybdenum analogues in many cases.³ Therefore, it should not be assumed that molybdenum will outperform tungsten in olefin metathesis chemistry in general.

Experimental Section

General Comments. Glassware was oven-dried at 175 °C and purged with nitrogen on a dual-manifold Schlenk line or cooled in the evacuated antechamber of a nitrogen-filled glovebox. Experiments were conducted in either a nitrogen-filled glovebox or an air-free dual manifold Schlenk line. Pentane was washed first with H_2SO_4 , then water, and then saturated aqueous NaHCO_3 and dried over CaCl_2 pellets for at least 2 weeks prior to use in the solvent purification system. HPLC-grade diethyl ether, toluene, tetrahydrofuran, pentane, and methylidene chloride were sparged with nitrogen and passed through activated alumina. Benzene was passed through a copper catalyst. Organic solvents were then stored over activated 4 Å Linde-type molecular sieves. Methylene chloride- d_2 , benzene- d_6 , and toluene- d_8 were sparged with nitrogen and stored under activated 4 Å Linde-type molecular sieves prior to use. NMR spectra were obtained on Varian 300 or 500 MHz spectrometers,

(13) Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1585.

(14) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *Dalton Trans.* **2006**, 3077.

(15) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Schrock, R. R. In *Carbene Chemistry*; Bertrand, G., Ed.; FontisMedia/Marcel Dekker: Lausanne and New York, 2002; p 205. (c) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; p 8. (d) Schrock, R. R. *J. Mol. Catal. A* **2004**, *213*, 21. (e) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748. (f) Schrock, R. R. *Le Prix Nobel*, 2005; Almqvist & Wiksell International: Stockholm, Sweden, 2006; p 206. (g) Schrock, R. R.; Czekelius, C. C. *Adv. Synth. Catal.* **2007**, *349*, 55.

(16) Sinha, A. Ph.D. Thesis, Massachusetts Institute of Technology, 2006; p 88.

(17) Zhao, Y., unpublished results.

reported in δ (parts per million) relative to tetramethylsilane, and referenced to the residual ^{13}C signals of the deuterated solvent (^1H (δ) benzene 7.16, methyldiene chloride 5.32, toluene 2.09; ^{13}C (δ) benzene 128.39, methyldiene chloride 54.00, toluene 20.40). ^{31}P NMR spectra are reported in δ (parts per million) relative to 85% H_3PO_4 and referenced to PMe_3 resonance at -62.00 ppm. Midwest Microlab, LLC provided the elemental analyses. LiMe_2Pyr was synthesized by adding $\text{Li-}n\text{-Bu}$ to 2,5-dimethylpyrrole in diethyl ether that had been chilled to -27°C ; the salt was filtered off and dried *in vacuo*. 2,3,5,6-Tetraphenylphenol (ROH),¹⁸ (*R*)-3,3'-dibromo-2'-(*tert*-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol (R^*OH),^{1d} $\text{W}(\text{NAr})(\text{CHMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$,⁵ and $\text{W}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})_2$ ⁵ were prepared according to reported procedures. All other reagents were used without further purification unless noted otherwise.

$\text{W}(\text{NAr})(\text{CH}_2)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (1). $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (0.791 g, 0.746 mmol; see below) was dissolved in toluene (10 mL) in a 20 mL scintillation vial containing a stir bar. A vacuum was applied to remove all of the volatile components from the yellow solution. This procedure was repeated eight times. Pentane (10 mL) was added to the residue, and the volatiles were removed two more times. The yellow foam was crushed with a spatula to give a fluffy yellow powder; yield = 0.740 g (96%): ^1H NMR (500 MHz, C_6D_6) δ 10.63 (d, 0.33, *syn* (*S*)- WCH_α , $J_{\text{CH}} = 163$ Hz, $J_{\text{WH}} = 16$ Hz, $J_{\text{HH}} = 9$ Hz), 10.55 (d, 1, *syn* (*R*)- WCH_α , $J_{\text{CH}} = 162$ Hz, $J_{\text{WH}} = 16$ Hz, $J_{\text{HH}} = 9$ Hz), 9.97 (d, 0.33, *anti* (*S*)- WCH_α , $J_{\text{CH}} = 135$ Hz, $J_{\text{HH}} = 9$ Hz), 9.44 (d, 1, *anti* (*R*)- WCH_α , $J_{\text{CH}} = 133$ Hz, $J_{\text{HH}} = 9$ Hz), 7.39 (s, 1, Ar-*H*), 7.30 (s, 0.33, Ar-*H*), 7.10 (m, 5.33, Ar-*H*), 6.07 (s, 0.66, Pyr-*H*), 6.06 (s, 2, Pyr-*H*), 3.72 (sept, 0.66, CHMe_2), 3.67 (sept, 2, CHMe_2), 2.46 (m, 8), 2.31 (s, 1.98, *Me*), 2.29 (s, 6, *Me*), 1.98 (m, 3), 1.49 (m, 10.28), 1.23 (d, 6, CHMe_2), 1.22 (d, 1.98, CHMe_2), 1.18 (d, 6, CHMe_2), 1.14 (d, 1.98, CHMe_2), 1.00 (s, 9, *OSi-*t*-BuMe}_2*), 0.95 (s, 3, *OSi-*t*-BuMe}_2*), 0.35 (s, 3, *OSi-*t*-BuMe}_2*), 0.20 (s, 1, *OSi-*t*-BuMe}_2*), -0.18 (s, 1, *OSi-*t*-BuMe}_2*), -0.32 (s, 3, *OSi-*t*-BuMe}_2*); ^{13}C NMR (125 MHz, C_6D_6) δ 247.78 (WC_α , $J_{\text{CW}} = 187$ Hz), 243.32 (WC_α , $J_{\text{CW}} = 186$ Hz), 156.65 ($J_{\text{CW}} = 9$ Hz), 156.27 ($J_{\text{CW}} = 11$ Hz), 152.97 ($J_{\text{CW}} = 37$ Hz), 152.92 ($J_{\text{CW}} = 37$ Hz), 148.88, 148.35, 146.71, 146.49, 137.52, 137.33, 137.19, 136.65, 134.82, 134.69, 134.49, 134.45, 134.32, 134.21, 133.81, 133.19, 132.45, 132.01, 130.41, 130.16, 130.07, 127.98, 127.70, 123.18, 113.45, 113.39, 112.35, 111.98, 110.74, 110.67, 29.98, 29.89, 29.82, 29.61, 28.86, 28.78, 28.46, 28.34, 27.76, 27.58, 26.72, 26.70, 24.61, 24.35, 24.22, 24.06, 23.54, 23.47, 23.35, 23.31, 23.22, 22.99, 22.96, 19.19, 19.17, 17.65, 17.57, -1.79 , -2.26 , -3.02 , -3.27 . Anal. Calcd for $\text{C}_{45}\text{H}_{60}\text{Br}_2\text{N}_2\text{O}_2\text{SiW}$: C, 52.34; H, 5.86; N, 2.71. Found: C, 52.40; H, 6.05; N, 2.89.

$\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (2). A 50 mL Schlenk flask was charged with a stir bar and a yellow solution of $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (3.550 g, 3.085 mmol; see below) in pentane (30 mL). The sample was degassed by three successive freeze, pump, and thaw cycles. One atmosphere of ethylene was added to the degassed sample at room temperature. A yellow powder precipitated immediately. The yellow powder was filtered off and exposed to a vacuum for 30 min. The filtrate was transferred back to the 50 mL Schlenk flask, and the procedure was repeated two more times to afford second and third crops of product; total yield = 2.153 g (66%). Using a solution of *in situ* generated $\text{W}(\text{NAr})(\text{CH}_2)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ as the starting material also gives the desired product. The yellow powder can be recrystallized from pentane to give yellow blocks, but the powder is pure as judged by ^1H NMR and elemental analysis. A 0.171 M solution in C_6D_6 contained 2% and 5% of the (*S*)-**1** and (*R*)-**1** diastereomers in the proton NMR spectrum: ^1H NMR (500 MHz, C_6D_6) δ 7.25 (s, 1, Ar-*H*), 7.23 (s, 1, Ar-*H*), 6.95 (d, 2, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.77 (t, 1, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 5.90 (s, 2, Pyr-*H*), 5.40 (m, 1, WCH_α), 4.96 (m, 1, WCH_α), 4.88 (m, 1, WCH_α), 4.81 (m, 1, WCH_α), 3.58, (sept, 2, CHMe_2), 2.41 (s, 6, Pyr-*Me}_2*), 1.93 (m, 16), 1.16 (d, 6, CHMe_2),

1.00 (d, 6, CHMe_2), 0.88 (s, 9, *OSi-*t*-BuMe}_2*), 0.40 (s, 3, *OSi-*t*-BuMe}_2*), -0.11 (br m, 1, WCH_β), -0.15 (s, 3, *OSi-*t*-BuMe}_2*), -0.75 (br m, 1, WCH_β); ^{13}C NMR (125 MHz, C_6D_6) δ 157.25, 149.40, 148.36 ($J_{\text{CW}} = 38$ Hz), 147.62, 139.40, 136.00, 133.99, 133.75, 133.71, 133.42, 131.80, 131.08, 129.88, 127.56, 123.03, 112.89, 111.48, 109.41, 101.69 (WC_α , $J_{\text{CW}} = 64$ Hz), 100.88 (WC_α , $J_{\text{CW}} = 66$ Hz), 29.76, 29.69, 28.90, 28.81, 27.00, 26.94, 24.96, 24.44, 23.62, 23.58, 23.33, 22.83, 19.67, 16.84, -1.55 , -3.03 , -3.58 (WC_β). When a degassed sample of $\text{W}(\text{NAr})(\text{CH}_2)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ or $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (~ 0.03 M in C_6D_6) was exposed to ^{13}C -ethylene, ^{13}C was incorporated into the tungstacyclobutane in seconds at room temperature: ^{13}C NMR (125 MHz, C_6D_6) δ 101.69 (WC_α , $J_{\text{CH}} = 155$ Hz), 100.88 (WC_α , $J_{\text{CH}} = 157$ Hz), -3.58 (WC_β , $J_{\text{CH}} = 154$ Hz, $J_{\text{Ca}\beta} = 13$ Hz). Anal. Calcd for $\text{C}_{47}\text{H}_{64}\text{Br}_2\text{N}_2\text{O}_2\text{SiW}$: C, 53.22; H, 6.08; N, 2.64. Found: C, 52.94; H, 6.30; N, 2.66.

$\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (3). $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$ (0.160 g, 0.236 mmol) and R^*OH (0.134 g, 0.236 mmol) were mixed as solids in a 20 mL scintillation vial containing a stir bar. Pentane (10 mL) was added to the mixture, and the yellow solution was allowed to stir for 6 h at room temperature. A vacuum was applied in order to reduce the solvent volume to ~ 2 mL, and the concentrated mixture was left in a refrigerator at -27°C for 24 h. Yellow blocks were filtered off and dried *in vacuo* for 2 h; yield = 0.227 g (79%): ^1H NMR (500 MHz, C_6D_6) δ 9.42 (s, 1, *anti* WCH_α , $J_{\text{CH}} = 112$ Hz, $J_{\text{WH}} = 14$ Hz), 7.30 (m, 3, Ar-*H*), 7.06 (m, 7, Ar-*H*), 5.79 (br s, 2, Pyr-*H*), 3.87 (br s, 2, CHMe_2), 2.24 (m, 10), 1.76 (s, 3, *Me*), 1.71 (s, 3, *Me*), 1.45 (s, 24), 0.96 (s, 9, *OSi-*t*-BuMe}_2*), 0.06 (s, 3, *OSi-*t*-BuMe}_2*), 0.04 (s, 3, *OSi-*t*-BuMe}_2*); ^{13}C NMR (125 MHz, C_6D_6) δ 263.42 (WC_α , $J_{\text{CW}} = 198$ Hz), 157.56 ($J_{\text{CW}} = 7$ Hz), 152.14 ($J_{\text{CW}} = 37$ Hz), 150.72, 147.87, 147.22 (br s), 136.94, 135.19, 135.06, 133.37, 133.15, 132.92, 129.46, 129.32, 128.80, 127.74, 126.57, 126.52, 123.46, 113.29, 111.43, 110.68 (br s), 106.86, 53.50 ($J_{\text{CW}} = 16$ Hz), 34.79, 33.81, 31.59, 29.73, 29.23, 29.12, 28.82, 28.28, 26.74, 24.38, 23.55, 23.47, 23.40, 23.13, 23.08, 19.33, 14.66, -2.24 , -2.45 . Anal. Calcd for $\text{C}_{54}\text{H}_{70}\text{Br}_2\text{N}_2\text{O}_2\text{SiW} \cdot \text{C}_5\text{H}_{10}$ (pentane): C, 57.94; H, 6.76; N, 2.29. Found: C, 57.59; H, 6.32; N, 2.45.

$\text{W}(\text{NAr})(\text{CH}_2)(\text{OR}^*)(\text{Me}_2\text{Pyr})(\text{PMe}_3)$ ((*R*)-1**(PMe_3)).** A 20 mL scintillation vial was charged with a stir bar and $\text{W}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OR}^*)(\text{Me}_2\text{Pyr})$ (0.215 g, 0.203 mmol) in pentane (5 mL). PMe_3 (104 μL , 1.02 mmol) was added to the yellow mixture via syringe; ethylene evolved immediately from the solution. The solution was allowed to stir for 2 min at room temperature. Vacuum was applied in order to remove all the volatiles. Diethyl ether (a few drops) and pentane (~ 2 mL) were added to the yellow foam, and the solution was left in a refrigerator at -27°C for 2 d. A yellow crystalline solid was filtered off and dried *in vacuo* for 2 h; yield = 0.197 g (82%): ^1H NMR (500 MHz, C_6D_6) δ 11.74 (t, 1, *syn* WCH_α , $J_{\text{HH}} = 6$ Hz, $J_{\text{WH}} = 13$ Hz, $J_{\text{PH}} = 6$ Hz), 11.55 (q, 1, *anti* WCH_α , $J_{\text{HH}} = 6$ Hz, $J_{\text{PH}} = 4$ Hz), 7.34 (s, 1, Ar-*H*), 7.31 (s, 1, Ar-*H*), 7.00 (d, 2, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.88 (t, 1, Ar-*H*, $J_{\text{HH}} = 8$ Hz), 6.02 (br s, 2, Pyr-*H*), 4.05 (br s, 2, CHMe_2), 2.06 (m, 16), 1.21 (d, 3, CHMe_2), 1.18 (d, 3, CHMe_2), 1.15 (d, 6, CHMe_2), 0.91 (s, 9, *OSi-*t*-BuMe}_2*), 0.38 (s, 3, *OSi-*t*-BuMe}_2*), -0.01 (s, 3, *OSi-*t*-BuMe}_2*); ^{13}C NMR (125 MHz, C_6D_6) δ 268.48 (WC_α), 157.72, 151.18 ($J_{\text{CP}} = 2$ Hz, $J_{\text{CW}} = 39$ Hz), 149.03, 146.55, 140.53, 136.68, 134.33, 133.56, 132.68, 131.87, 130.64, 129.48, 126.37, 123.34, 111.99, 111.76, 108.13 (br s), 29.92, 29.76, 29.16, 28.89, 28.02, 26.71, 25.08, 24.59, 23.72, 23.49, 23.33, 22.67, 21.14 (br s), 20.23, 18.47 (br s), 17.62, 17.41, -1.68 , -2.57 ; ^{31}P NMR (121 MHz, C_6D_6) δ 5.50 ($J_{\text{PW}} = 269$ Hz). A sample of the complex was degassed and exposed to 1 atm of ^{13}C ethylene: ^1H NMR (500 MHz, C_6D_6) δ 11.74 (WCH_α , $J_{\text{CH}} = 158$ Hz), 11.55 (WCH_α , $J_{\text{CH}} = 140$ Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 268.48 (WC_α , $J_{\text{CW}} = 168$ Hz, $J_{\text{CP}} = 13$ Hz). Anal. Calcd for $\text{C}_{48}\text{H}_{69}\text{Br}_2\text{N}_2\text{O}_2\text{SiPW} \cdot \text{C}_4\text{H}_{10}\text{O}$ (Et_2O): C, 52.80; H, 6.73; N, 2.37. Found: C, 52.68; H, 6.46; N, 2.37.

$\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR})(\text{Me}_2\text{Pyr})$ (4). $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2$ (0.486 g, 0.715 mmol) and ROH (0.299 g, 0.751 mmol,

(18) Yates, P.; Hyre, J. E. *J. Org. Chem.* **1962**, *27*, 4101.

1.05 equiv; R = 2,3,4,5-tetraphenyl) were mixed as solids in a 20 mL scintillation vial containing a stir bar. Benzene (10 mL) was added to the mixture, and the yellow solution was allowed to stir for 24 h at room temperature. The mixture was filtered through glass wool, and the volume of the filtrate was reduced *in vacuo* to give an oil. Pentane (~10 mL) was added to the oil. After 20 min of stirring, the mixture was exposed to vacuum to reduce the solvent to ~5 mL. Yellow solids precipitated out. The solids were filtered off and redissolved in THF and pentane (10 mL, 1:1 mixture), and the solution was left in a refrigerator at $-27\text{ }^{\circ}\text{C}$ for 24 h. Yellow crystals were filtered off and dried *in vacuo* for 2 h; yield = 0.510 g (70%): $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 8.43 (s, 1, *anti* WCH_α , $J_{\text{CH}} = 116\text{ Hz}$, $J_{\text{WH}} = 16\text{ Hz}$), 7.09 (m, 29, Ar-*H*), 6.04 (s, 2, Pyr-*H*), 3.57 (m, 2, $\frac{1}{2}$ THF), 3.25 (sept, 2, CHMe_2), 2.01 (s, 6, *Me*), 1.64 (s, 3, *Me*), 1.42 (m, 2, $\frac{1}{2}$ THF), 1.28 (s, 3, *Me*), 1.10 (d, 6, CHMe_2), 0.91 (d, 6, CHMe_2), about half a molecule of THF is observed; $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 263.50 (WC_α , $J_{\text{CW}} = 190\text{ Hz}$), 159.08, 152.28 ($J_{\text{CW}} = 38\text{ Hz}$), 151.79, 146.47, 142.81, 142.15, 137.45, 136.02 (br s), 132.40, 131.45, 130.50, 128.92, 128.56, 128.46, 128.06, 127.91, 127.17, 127.10, 127.00, 126.34, 123.43, 110.71, 68.15, 53.39, 33.87, 33.37, 28.41, 26.16, 24.41, 24.32, 17.96 (br s). Anal. Calcd for $\text{C}_{58}\text{H}_{58}\text{N}_2\text{OW}$: C, 70.87; H, 5.95; N, 2.85. Found: C, 70.45; H, 6.37; N, 2.62.

W(NAr)(CH₂)(OR)(Me₂Pyr) (5). W(NAr)(CH₂)(Me₂Pyr)₂ (0.831 g, 1.480 mmol) and ROH (0.590 g, 1.480 mmol) were mixed as solids in a 50 mL flask containing a stir bar. Benzene (20 mL) was added to the mixture, and the orange solution was allowed to stir for 1.5 h at room temperature. Vacuum was applied in order to remove the volatiles. Pentane was added to the red oil, and the mixture was allowed to stir for 30 min. Yellow solids precipitated out. The solids were filtered off and dried *in vacuo* for 2 h; yield = 1.153 g (90%). W(NAr)(CH₂)(OR)(Me₂Pyr) is pure as judged by $^1\text{H NMR}$ and elemental analysis. Compound **5** recrystallizes from a mixture of 1:1 THF and Et₂O to give yellow-orange blocks: $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 10.24 (s, 1, *syn* WCH_α), 8.75 (s, 1, *anti* WCH_α), 7.09 (m, 24, Ar-*H*), 6.16 (s, 2, Pyr-*H*), 3.43 (sept, 2, CHMe_2), 2.07 (s, 6, Pyr-*Me*), 1.15 (d, 6, CHMe_2), 1.05 (d, 6, CHMe_2); $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 240.70 (WC_α , $J_{\text{CW}} = 186\text{ Hz}$), 158.75, 153.08 ($J_{\text{CW}} = 36\text{ Hz}$), 144.97, 142.45, 141.75, 137.45, 134.66, 131.77 (br s), 131.28, 130.51, 128.96, 128.58, 127.90, 127.66, 127.26, 126.81, 122.86, 110.70, 28.90, 25.20, 23.37, 17.58; $^1\text{H NMR}$ (500 MHz, toluene-*d*₈, $-20\text{ }^{\circ}\text{C}$) δ 10.29 (d, $J_{\text{CH}} = 160\text{ Hz}$, $J_{\text{WH}} = 13\text{ Hz}$, $J_{\text{HH}} = 9\text{ Hz}$), 8.63 (d, $J_{\text{CH}} = 130\text{ Hz}$, $J_{\text{HH}} = 9\text{ Hz}$). 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, 67.81; H, 5.60; N, 3.27. Anal. Calcd for $\text{C}_{49}\text{H}_{48}\text{N}_2\text{OW}\cdot\text{C}_4\text{H}_8\text{O}$ (THF) $\cdot\text{C}_4\text{H}_{10}\text{O}$ (Et₂O): C, 67.72; H, 6.58; N, 2.77. Found: C, 67.91; H, 6.57; N, 2.90.

W(NAr)(C₃H₆)(OR)(Me₂Pyr) (6). A 50 mL Schlenk flask was charged with a stir bar and W(NAr)(CH₂)(OR)(Me₂Pyr) (1.130 g, 1.306 mmol) in 15 mL of benzene and 15 mL of ether. Not all of the yellow solids dissolved, and the solution was cloudy. The mixture was degassed by three successive freeze, pump, and thaw

cycles. The sample was exposed to 1 atm of ethylene at room temperature. The solution became orange immediately. A vacuum was applied in order to remove all volatiles. Ether and pentane (20 mL, 1:1 mixture) were added to the red oil. Yellow solids precipitated and were filtered off. The filtrate was degassed again, exposed to 1 atm of ethylene, and left in a refrigerator at $-27\text{ }^{\circ}\text{C}$ for 24 h. A yellow powder was filtered off. The process was repeated to give a third crop. The total crude yield is 1.010 g (87%). The powder was redissolved in a 1:1 mixture of benzene and ether. The solution was left in a refrigerator at $-27\text{ }^{\circ}\text{C}$ for 1 day to give 0.691 g (54%) of the product. The solid-state structure shows that the crystals contain one molecule of benzene: $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 7.01 (m, 24, Ar-*H*), 6.07 (s, 2, Pyr-*H*), 4.27 (m, 2, WCH_α), 3.42, (sept, 2, CHMe_2), 3.34 (m, 2, WCH_α), 2.37 (s, 6, Pyr-*Me*), 0.94 (d, 12, CHMe_2), -0.94 (br m, 1, WCH_β), -1.40 (br m, 1, WCH_β); $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 159.13, 149.16, 147.98, 142.95, 142.93, 139.34, 134.71, 132.34, 132.14, 130.48, 128.92, 128.22, 127.36, 127.03, 126.74, 124.97, 122.93, 109.28, 101.11 (WC_α , $J_{\text{CW}} = 66\text{ Hz}$), 28.73, 24.47, 18.12, -3.52 (WC_β). Anal. Calcd for $\text{C}_{57}\text{H}_{58}\text{N}_2\text{OW}\cdot\text{C}_6\text{H}_6$ (benzene): C, 70.51; H, 6.02; N, 2.89. Found: C, 70.29; H, 5.98; N, 2.91.

W(NAr)(CH₂)(OR)(Me₂Pyr)PMe₃ (5(PMe₃)). A 20 mL vial was charged with a stir bar and **5** (0.242 g, 0.279 mmol) in ~3 mL of benzene. PMe₃ (144 μL , 1.397 mmol) was added via syringe to the yellow solution. The mixture was stirred at room temperature for 20 min, and vacuum was applied to remove the volatiles. Ether was diffused into the yellow oil. The sample was left in a refrigerator at $-27\text{ }^{\circ}\text{C}$ for 2 days. The microcrystalline yellow solid was filtered off; yield 0.173 g (66%): $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 11.33 (t, 1, *syn* WCH_α , $J_{\text{CH}} = 159\text{ Hz}$, $J_{\text{HH}} = 7\text{ Hz}$, $J_{\text{WH}} = 13\text{ Hz}$, $J_{\text{PH}} = 6\text{ Hz}$), 10.33 (q, 1, *anti* WCH_α , $J_{\text{CH}} = 139\text{ Hz}$, $J_{\text{HH}} = 7\text{ Hz}$, $J_{\text{PH}} = 5\text{ Hz}$), 7.05 (m, 24, Ar-*H*), 6.42 (s, 2, Pyr-*H*), 3.78 (sept, 2, CHMe_2), 2.49 (s, 6, Pyr-*Me*), 1.18 (d, 6, CHMe_2), 1.13 (d, 6, CHMe_2), 1.15 (d, 6, CHMe_2), 0.48 (d, 9, PMe_3); $^{13}\text{C NMR}$ (125 MHz, C_6D_6) δ 268.54 (WC_α), 160.32, 151.30, 146.35, 143.52, 143.47, 143.03, 140.53, 139.57, 134.25, 133.40 (br s), 132.55, 130.59, 130.50, 130.11, 128.15, 128.09, 126.99, 126.95, 126.62, 126.58, 126.44, 124.65, 123.43, 108.73, 29.03, 25.36, 24.57, 21.47, 15.93, 15.72; $^{31}\text{P NMR}$ (121 MHz, C_6D_6) δ 9.04 ($J_{\text{PW}} = 272\text{ Hz}$). Anal. Calcd for $\text{C}_{52}\text{H}_{57}\text{N}_2\text{OPW}$: C, 66.38; H, 6.11; N, 2.98. Found: C, 66.55; H, 6.24; N, 2.93.

Acknowledgment. We thank the National Science Foundation for research support (CHE-0554734 to R.R.S.).

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

JA9012694