Synthesis of Tris(pyrazolyl)borate-Stabilized Vinyl, Allyl, and Homoallyl Tungsten Oxides and Their Selective Oxyfunctionalization by Singlet Oxygen and Dioxirane

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The synthesis of new tris(pyrazolyl)borato-substituted alkenyltungsten complexes and their oxyfunctionalization was investigated. The derivatives **2a**−**e** of the title compounds were prepared in 40−70% yield by Grignard reaction of [Tp*W(O)$_2$Cl] (**1**) [Tp* = hydridotris(3,5-dimethyl-1-pyrazolyl)borato] and subsequent treatment with molecular oxygen. These alkenyltungsten complexes, except the homoallyl complex **2b** with a monosubstituted double bond, displayed a high reactivity toward singlet oxygen ($^1O_2$) to result in the corresponding allylic hydroperoxides by the Schenk ene reaction. While in the photooxygenation of the homoallyl complex **2a** no special influence of the [Tp*W(O)$_2$] fragment was observed, the allyl complexes **2c**,**d** afforded stereoselectively the *Z*-configured products. Stereocontrol derives presumably from hyperconjugative stabilization by the W−C bond (β effect) of the perepoxide-like transition state. The allylic hydroperoxide, derived from the $^1O_2$ ene reaction of the vinyl complex **2e**, led by Hock-type cleavage to methacrolein and the tungstic acid derivative **9e**. Upon photooxygenation in the presence of titanium tetraisopropoxide, only the homoallylic complex **2a** underwent smoothly hydroxy-epoxidation. The other alkenyl complexes were sterically too hindered due to the bulky Tp* ligand. While the homoallyl and methallyl complexes **2a**,**d** were quantitatively epoxidized by dimethyldioxirane (DMD), the vinyl complex **2e** was again too sterically hindered because of the large [Tp*W(O)$_2$] moiety, but its epoxide was obtained with *m*-chloroperbenzoic acid (*m*CPBA) as oxidant. In contrast, when equimolar amounts of methyl(trifluoromethyl)dioxirane (TFD) were used, the vinyl and methyl complexes **20e**,**f** were regioselectively hydroxylated by C−H insertion into a pyrazolyl ring of the Tp* ligand. The present results demonstrate that the selective oxyfunctionalization of the alkenyltungsten complexes **2** by singlet oxygen and dioxiranes is controlled by electronic and steric factors of the [Tp*W(O)$_2$] fragment.

Introduction

The question as to whether or not organometallic intermediates are involved in the metal oxide- and peroxide-mediated oxyfunctionalization of organic substrates continues to be the focus of a longstanding debate.[1] The problem arises from the difficulty in gaining experimental proof for the proposed intermediates such as metalla-2-oxacyclobutanes in the OsO_4-mediated *cis* hydroxylation of olefins or metalla-2,3-dioxacyclopentanes in the epoxidation of olefins by peroxo complexes. Allyl oxo species have been suggested as intermediates in the industrially important allylic oxidation of propene to acrolein with heterogeneous catalysts such as bismuth molybdate.[2]

The oxyfunctionalization of the organic ligands in transition metal complexes has been actively investigated during the last years. However, only a few examples are known for tungsten and molybdenum compounds, most of which concentrate on the introduction of oxo ligands on the coordination center.[3] An exception is the reaction of an η^5-coordinated pentamethylcyclopentadienyl ligand with molecular oxygen.[4] In previous studies we have outlined a synthetic route to stabilize a d^0 methallyl tungsten oxide by use of the closely related, sterically demanding hydridotris(3,5-dimethylpyrazolyl)borate ligand.[5] The so-called Tp* ligand shields one hemisphere of the complex such that the reactive site [W(O)$_2$R]$^+$ is contained in the molecular pocket of the anionic tripod ligand.

These organo tungsten oxides of the type [Tp*W(O)$_2$R] can be prepared by reaction of Grignard reagents with [Tp*W(O)$_2$Cl] (**1**).[5,6] For this study, we decided to prepare pyrazolylborato-stabilized alkenyltungsten oxides and to investigate their functionalization with various oxidants.

Dimethyldioxirane (DMD)[7] has been well established as an oxidant in organometallic chemistry, especially if traditional oxidizing agents like molecular oxygen,

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peracids, permanganate, or hypochlorite fail. Characteristic of this potent oxidant is its mild but selective nature.[7] The reactions are performed under neutral pH conditions, if necessary at subambient temperatures, and acetone is the only side product, which can be easily removed by distillation. In the meantime, for the three major reaction modes of dioxiranes[7] known in organic chemistry, examples have been documented in organometallic chemistry, namely epoxidation,[8] hetereoatom oxidation,[9] and X−H insertion.[10] Additionally, for carbonyl complexes the CO ligand can be oxidized by dioxirane to carbon dioxide, which results either in the formation of oxo complexes[11] or in the decomposition of the complex under liberation of organic ligands.[12] Besides dioxirane, also singlet oxygen ($^1O_2$)[13] was used in our group for the oxyfunctionalization of air-stable, unsaturated organoiron complexes.[14]

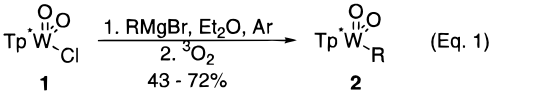
Herein we report on the synthesis of hitherto unknown pyrazolylborato-substituted vinyl, allyl, and homoallyl tungsten oxides and their selective oxyfunctionalization by $^1O_2$ and dioxirane. A priority of this study was to assess the influence of the metal complex fragment on the reaction modes of the various alkenyl ligands toward these oxidants.

Results and Discussion

The reaction of [Tp*W(O)$_2$Cl] (**1**) with Grignard reagents is accompanied by complex redox chemistry. In the reaction of the electron-rich Grignard reagent with the electron-poor tungsten complex **1**, electron transfer seems to be much faster than the substitution of the chloro ligand. The electron-transfer path appears to be favored because the d^0 metal center is efficiently shielded from nucleophilic attack. Furthermore, an equilibrium between κ^3 and κ^2 coordination modes of the Tp* ligand, a process that would generate a reactive site at the metal center for nucleophilic attack, was not observed spectroscopically.

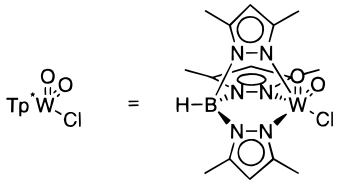
A number of octahedral oxo and imido complexes of group 5−7 metals in their highest oxidation state show this typical kinetic inertness with respect to nucleophilic substitution at the d^0 metal center.[15] Even tetrabutylammonium hydroxide in THF did not react at room temperature with the tungsten complex **1** due to its electronically and coordinatively saturated character. In contrast, an excess of the Grignard reagent prepared from the enyl halides, gave instantly green or blue solutions, which contained a number of paramagnetic and not yet characterized complexes. In part, these may be dinuclear mixed valent compounds without M−C bonds such as the crystallographically characterized complex [Tp*Mo(O)$_2$(μ-O)Mo(O)ClTp*].[16]

The title complexes were prepared by reoxidation of the paramagnetic organometallic intermediates by molecular oxygen. In this way, the colorless or pale yellow homoallyl complexes **2a**,**b**, the allyl complexes **2c**,**d** and the vinyl complex **2e** were isolated in yields of 40−70% (eq 1).



1 **2**

a R = $CH_2CH_2CH{=}CMe_2$
b R = $CH_2CH_2CH{=}CH_2$
c R = $CH_2C(Me){=}CH_2$
d R = $CH_2CH{=}CH_2$
e R = $CH{=}CMe_2$



The spectral data of the complexes **2a**−**e** show no unusual features. It is noteworthy that the derivatives **2a**, **2b**, and **2d** possess β hydrogen atoms in their metal-bound enyl fragments; nevertheless, these organometal oxides are stable at temperatures up to 190 °C. The reluctance with respect to a β-H abstraction has been documented for complexes which are coordinatively and electronically saturated.[17] Thus, recently a number of β-H-containing oxo alkyl complexes of d^0 electronic configuration have been isolated, e.g. [Tp*W(O)$_2$(C$_2$H$_5$)],[6] [W(O)$_2$R$_2$(bpy)] (R = Et, *n*-Pr),[18] [Re(O)$_3$R] (R = Et, *i*-Bu, *n*-Pr, *n*-Bu), and their more stable quinuclidine aducts.[19]

A prerequisite for photooxygenation is that the substrate be inert toward molecular oxygen ($^3O_2$) and photostable. For example, alkyl complexes with highly polar M−C bonds such as d^0 zirconium alkyls are readily autoxidized.[20,21] Fortunately, the less polar metal−

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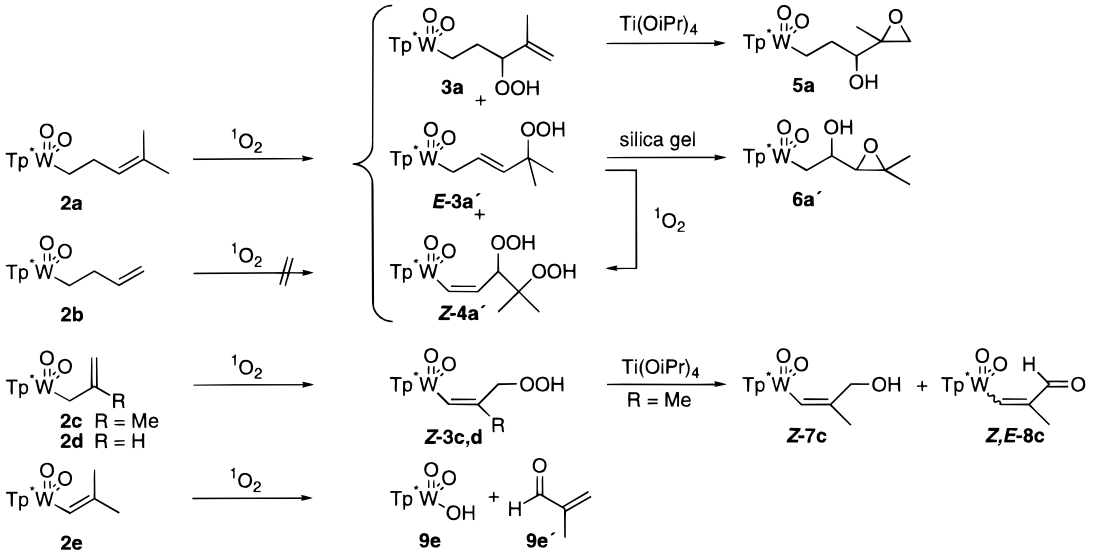
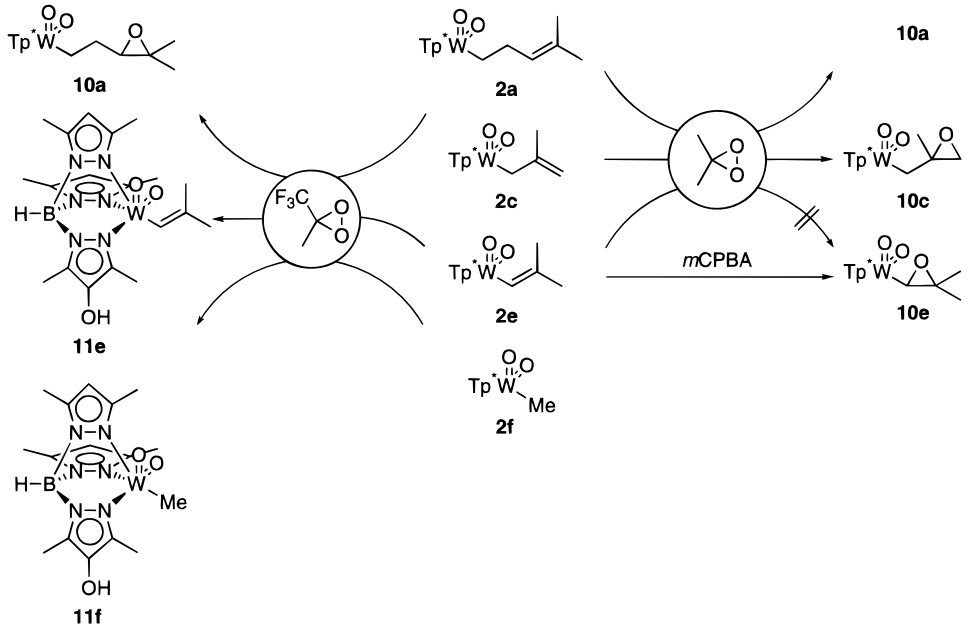
Scheme 1



Scheme 2



carbon bonds of all the complexes **2a**−**e** investigated here are inert toward triplet oxygen even under photochemical conditions. Although, photochemically or thermally induced Re−C bond homolysis of labile allyl complex [(η^1-C_3H_5)Re(O)$_3$] has been reported,[22] all our deliberate attempts to induce photochemically or thermally a 1,2 shift of metal-bound vinyl, allyl, or homoallyl ligands onto a terminal oxo ligand were unsuccessful. The latter rearrangement was observed in the irradiation of d^2 rhenium oxo aryl and alkyl complexes of the type [TpRe(O)Cl(R)] in the presence of pyridine.[23]

The organo tungsten complexes **2a**−**e** were oxyfunctionalized by $^1O_2$ (Scheme 1) and the dioxiranes DMD and TFD (Scheme 2) in clean reactions and high yields. Some of the hydroperoxides of the Schenk ene reaction with $^1O_2$ were treated with titanium tetraisopropoxide[24] in order to rearrange them to the corresponding hydroxy epoxides (Scheme 1).

The alkenyl complexes **2a**−**e** showed a greater reactivity toward $^1O_2$ than simple alkenes with the same substitution pattern at their double bond. A control experiment with complex **2a**—photooxygenation without sensitizer—ensured that self-sensitization with molecular oxygen did not take place. In this context it should be mentioned that singlet oxygen generation has been reported in the photolysis of molybdenum peroxo complexes.[25]

Photooxygenation of the dimethyl-substituted homoallyl complex **2a** (Scheme 1) led through the ene reaction to the two allylic hydroperoxides **3a** and (*E*)-**3a′** in a ratio of 65:35. The (*E*)-**3a′** product gave on prolonged photooxygenation the bishydroperoxide (*Z*)-**4a′**. The *Z* configuration of the double bond for product (*Z*)-**4a′** was assessed by comparison of the $^3J_{HH}$ coupling constant with analogous organo silicon or tin derivatives[26] and by NOE effects.

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During silica gel chromatography, besides decomposition, the tertiary hydroperoxide (*E*)-**3a′** rearranged to the hydroxy epoxide **6a′**, of which one diastereomer could be isolated in a yield of 36% (relative to the hydroperoxide (*E*)-**3a′**) after further chromatographic purification. Only traces of (*E*)-**3a′** were obtained after chromatography, contaminated with the **3a** regioisomer. It was not possible to determine the configuration of the hydroxy epoxide **6a′** by comparison of the NMR data with those of analogous compounds, since the spectral differences between the *threo* and *erythro* isomers were too small.[27] Unfortunately, all attempts to obtain adequate crystals of the product **6a′** for an X-ray structure determination failed. When the crude photooxygenation mixture of complex **2a** was treated with *p*-toluenesulfonic acid to simulate the acidic silica gel conditions, complete decomposition of the complexes **3a** und (*E*)-**3a′** was observed. Only free 3,5-dimethylpyrazole was obtained on workup.

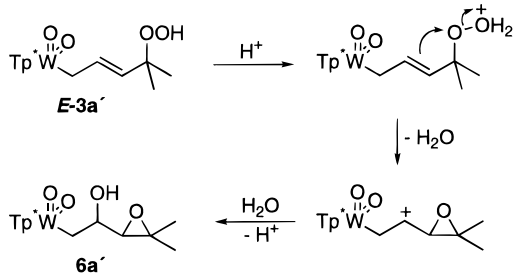
On treatment of the secondary allyl hydroperoxide **3a** with titanium tetraisopropoxide at room temperature (ca. 20 °C), the hydroxy epoxide **5a** was isolated in 59% yield as a 81:19 mixture of *erythro* and *threo* diastereomers (Scheme 1). In contrast, the direct one-pot hydroxy-epoxidation, i.e. photooxygenation in the presence of $Ti(OiPr)_4$, although successful at room temperature, resulted in the hydroxy epoxide **5a** in only 30% yield after chromatography. The hydroxy epoxide derived from the allyl hydroperoxide (*E*)-**3a′** was not detected. At temperatures between −10 and 0 °C, only the hydroperoxide **3a** was obtained after workup.

On intensive irradiation (two 400-W sodium lamps), the monosubstituted double bond in the homoallyl complex **2b** did not react with $^1O_2$ even in deuterochloroform.[28] The methallyl complex **2c** gave on photooxygenation as only product the allylic hydroperoxide (*Z*)-**3c** in 72% after silicagel chromatography, of which the configuration was established by NOE effects. Treatment of the allylic hydroperoxide (*Z*)-**3c** with titanium tetraisopropoxide resulted in the (*Z*)-**7c** alcohol by reduction and a *Z*:*E* mixture (76:24) of the aldehyde **8c** by loss of water. The configuration of the major and minor isomers of **8c** was assigned by NOE experiments. No hydroxy epoxide product could be detected. The alcohol (*Z*)-**7c** was independently prepared by reduction of allyl hydroperoxide (*Z*)-**3c** with triphenylphosphine.

Astonishingly, the unsubstituted allyl complex **2d** was converted relatively rapidly (63% in 2 h) with $^1O_2$ to the allyl hydroperoxide (*Z*)-**3d**. Its configuration was assigned by the $^3J_{HH}$ coupling constant of the double bond in analogy to (*Z*)-**4a′**. On prolonged reaction time, the yield significantly dropped due to decomposition.

The vinyl complex **2e**, with the double bond directly in $p_\pi-d_\pi$ conjugation with the [M═O] moiety, resisted photooxygenation, except under intensive irradiation (two 400-W sodium lamps). After one-day reaction time in deuterochloroform, the tungstic acid derivative **9e** (87% yield on precipitation) and methacrolein (**9e′**) were formed cleanly on full conversion. Even low-temperature NMR spectroscopy revealed no hydroperoxide-containing intermediate, which indicates its spontaneous fragmentation.

Scheme 3



The above photooxygenation results (Scheme 1), the first of their kind for unsaturated organometallic oxides, illustrate that all alkenyl complexes **2a**−**e** with differing chainlength, except derivative **2b**, were reactive toward singlet oxygen despite the immense steric bulk of the Tp* ligand (cone angle[29] of 224°). The greatest reactivity was displayed by the homoallyl complex **2a** with the double bond most distant from the metal center.

Remarkable was the formation of the hydroxy epoxide **6a′** from the tertiary hydroperoxide (*E*)-**3a′** during attempted chromatographic purification (Scheme 1). Rearrangements of allylic hydroperoxides to hydroxy epoxides occur by radical reactions induced with redox-active metal ions[30] or photochemically.[31] Alternatively, dienyl hydroperoxides are known[32] to rearrange under acid catalysis through allyl cations.

As shown in Scheme 3, we propose an ionic mechanism for the silica-gel-catalyzed rearrangement of the tertiary hydroperoxide (*E*)-**3a′** to the epoxy alcohol **6a′**. For stabilization of the intermediary cation in β position to the coordination center, we invoke an hyperconjugative interaction with the tungsten−carbon bond. Hyperconjugative stabilization of cationic species by β-positioned metal groups (β effect) has been well documented for allylic silanes, stannanes, and germanes.[33] Also the $[Tp^*W(O)_2]$ fragment fulfills the requisites for such hyperconjugation[34] in view of the significantly lower electronegativity of tungsten compared to carbon, the electron-donating pyrazolyl ligands, and the good $\sigma-\pi$ overlap for strong C−W bonding.

The lack of ene reactivity of the homoallyl complex **2b** toward $^1O_2$ is expected for substrates with a terminal double bond. This observation signifies that the electron-rich tungsten complex fragment $[Tp^*W(O)_2]$ does not activate such substrates for photooxygenation.

At first glance surprising, however, is the marked reactivity of the allylic hydroperoxide (*E*)-**3a′**, the methallyl complex **2c**, and especially the allyl complex **2d**, all substrates with a mono- or disubstituted double

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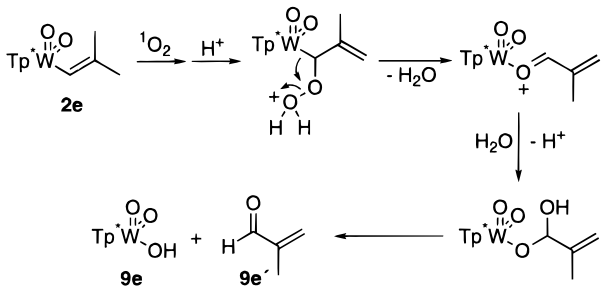
Scheme 4



bond, which notoriously undergo sluggish ene-type photooxygenations.[35] Closer scrutiny suggests a stabilized transition state through π interaction of the developing double bond with the [Tp*W(O)$_2$] fragment. It is a surprising fact that in all ene reactions of this study, the olefinic double bond of the allyl ligand migrates exclusively into $p_\pi-d_\pi$ conjugation with the [W=O] π bond. In this respect, the regioselectivity in the photooxygenation of the methallyl complex **2c**—no abstraction of methyl protons during the ene reaction—provides further support for this explanation. Additionally, like for allylic silanes and stannanes, the low ionization potential[33] favors the ene reaction. In this context, the low affinity of the vinyl complex **2e** toward $^1O_2$ may be accounted for in terms of loss of the double bond π interaction with the tungsten metal at the coordination center during the ene reaction. Under drastic conditions, a reaction can be forced to afford the tungstic acid derivative **9e** and methacrolein (**9e′**), which may be reconciled in terms of Hock-type cleavage[36] of the intermediary hydroperoxide (Scheme 4).

Mechanistically elucidative is the fact that exclusively *Z*-configured double bonds are generated during these ene reactions (Scheme 1). For acyclic alkenes usually the thermodynamically more stable[37] *E*-configured allyl hydroperoxides dominate, whereas in the photooxygenation of allylsilanes and -stannes the *Z*-configured product is preferred.[38] For the allylic substrate **2c**, the steric interaction between the [Tp*W(O)$_2$] fragment and the methyl substituent at the double bond (1,2-allylic strain) applies in the perepoxide type transition state (Scheme 5). The latter is additionally stabilized by secondary orbital interaction with an allylic hydrogen atom through the *cis* effect,[39] which should favor the *Z*-configured product. However, the allylic complexes **2d** and (*E*)-**3a′** have no substituent in the 2-position of the alkenyl chain for 1,2-allylic strain. Shimizu *et al.*[38a] explained the *Z* selectivity of allylsilanes by the hyperconjugative interaction of the C−Si bond with the π system. This is optimal for an orthogonal arrangement of the interacting orbitals, as adopted in the transition state for allyl tungsten complexes and *Z*-configured product results (Scheme 5). Despite the common features of the allyl tungsten complexes with the allylic silanes and stannanes,[26d,38] for the former no metallotropic ene reaction, i. e. migration of the tungsten fragment, has been observed (Scheme 6).

The *erythro*:*threo* diastereomeric ratio (dr = 81:19) in the hydroxy-epoxidation of the allyl hydroperoxide **3a** with titanium tetraisopropoxide (Scheme 1) indicates that the bulky tungsten complex fragment [Tp*W(O)$_2$] does not exercise any pronounced steric influence on the oxygen transfer at the titanium template. For comparison, a *tert*-butyl group at the hydroperoxy carbon atom exerts more effective diastereomeric differentiation (dr = 95:5).[40]

In contrast, the Ti(OiPr)$_4$-catalyzed hydroxy-epoxidation failed for the (*Z*)-**3c** derivative, and apparently steric restrictions are responsible for the observed reduction to the allylic alcohol (*Z*)-**7c**. Reductions of the hydroperoxide by the titanium catalyst are known to occur for sterically encumbered or electronically deactivated substrates with simultaneous Oppenauer-type oxidation of an isopropylate ligand in the titanium template to acetone.[24a] The diastereomeric pair of (*Z*,*E*)-**8c** aldehydes derives presumably from elimination of water from the allylic hydroperoxide (*Z*)-**3c** with subsequent *cis*−*trans* isomerization induced by titanium tetraisopropoxide.

The epoxidation of the alkenyltungsten complexes **2a** and **2c** with DMD afforded quantitatively the epoxides **10a** and **10c** (Scheme 2). In contrast, the vinyl complex **2e** resisted epoxidation by this oxidant. The use of a high excess of DMD led to decomposition of the tungsten complex. Unexpectedly, successful was the epoxidation of the vinyl complex **2e** with *m*CPBA (3 equiv), which gave the epoxide **10e** in 56% yield at 65% conversion, one of the few cases in which *m*CPBA performs better than DMD.[41] The peracid epoxidation of substrate **2c** was, however, disadvantageous due to the labile nature of the resulting epoxide **10c** toward acid-catalyzed rearrangement and hydrolysis.

On attempted Weitz−Scheffer oxidation[42] of the vinyl complex **2e** with H_2O_2/NaOH in methanol/dichloromethane or acetone and alternatively with *t*-BuOOH/Bu_4NOH in toluene, the tungsten complex **2e** was reisolated. This nucleophilic epoxidation method, which works well for the electron-poor enones, confirms that the Tp*W(O)$_2$ group provides for an electron-rich double bond and is subject to electrophilic attack.

The use of the much more reactive TFD[43] for the oxyfunctionalization of vinyl complex **2e**, which resisted DMD, furnished a surprising result in that oxidation did not occur at the alkenyl chain but on the tris(pyrazolyl)borato ligand. Selectively one pyrazolyl ring was hydroxylated *trans* to an oxo ligand to afford the complex **11e** (70% yield at 55% conversion). The reaction was performed at 0 °C under an oxygen gas atmosphere to prevent undesirable radical chain processes.

The unsymmetrical nature of this oxidized octahedral tungsten complex was evident since all signals of the three pyrazolyl ligands in the hydroxylated product

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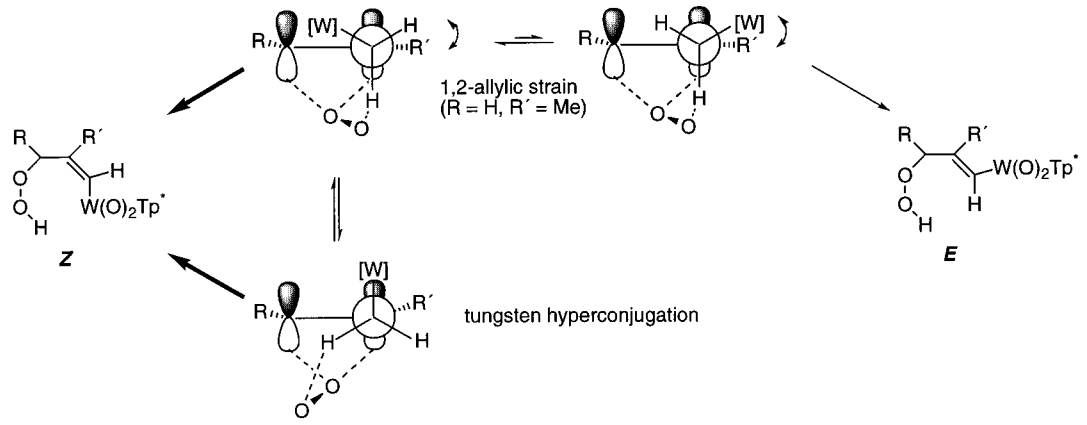
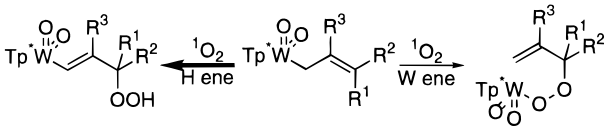
Scheme 5



Scheme 6



appeared at different chemical shift values in the NMR spectra. Alternatively, the regioselective hydroxylation in the pyrazolyl ring *trans* to the vinyl chain would result in two sets of signals (2:1 ratio) in the NMR spectra due to its C_s symmetry. Analogously, the methyl complex **2f** led with TFD to the corresponding hydroxy product **11f** in 68% yield at 32% conversion. The use of excess TFD resulted in higher conversions for both substrates **2e** and **2f**, but unselectively a mixture of various hydroxylated products was obtained. In contrast, treatment of homoallyl complex **2b** with TFD gave the epoxide **10a** but no C−H insertion into a pyrazolyl ring.

Since the photooxygenation of alkenyltungsten complexes showed similarities to that of analogous silanes and stannanes, it is of interest to compare the epoxidation results with those of the main-group metal complexes. As the DMD oxidation offers an excellent entry to the epoxides of vinylsilanes,[44] this method is also convenient for the epoxidation of the homoallyl and methallyl tungsten complexes **2a** and **2c** (Scheme 2). Especially the labile epoxide **10c** was obtained in excellent yields under such neutral and mild reaction conditions, whereas *m*CPBA led predominantly to rearrangement and hydrolysis. Also the epoxides of allylic silanes[45] and stannanes[46] are usually quite labile and tend to rearrange or react further under the peracid epoxidation conditions. An exception in the epoxidation of alkenyltungsten complexes is demonstrated in the vinyl derivative **2e**, for which *m*CPBA, which is also often used for epoxidation of homoallylic[46a] and vinylic[47,48] silanes and stannanes, and not DMD was the oxidant of choice. Presumably the steric hindrance between the bulky Tp* ligand and the methyl groups of the dioxirane is so severe that the attack of DMD through the preferred planar spiro-type transition state[49] for the oxygen transfer is prevented. The greater steric demand of DMD *versus m*CPBA[50] has been established and is well-documented in the reduced reactivity of sterically crowded vinylsilanes toward DMD.[41]

The above steric effects are so prominent that the much more reactive TFD oxidant avoids the epoxidation of the shielded double bond in the vinylic complex **2e** in favor of hydroxylation of the pyrazolyl ring (Scheme 2). Expectedly, the methyl−tungsten complex **2f** without an alkenyl ligand is exclusively hydroxylated by TFD at the pyrazolyl ligand. These results demonstrate the much higher oxidation power of this fluorinated dioxirane *versus* DMD to perform C−H insertion. In this context, the halogenation in the hydridotris(3,5-dimethylpyrazolyl)borato ligand of a molybdenum complex with an excess of chlorine or bromine is known,[51] which proceeds simultanously in all three pyrazolyl rings.

The regioselectivity in the hydroxylation of the tungsten complexes with deficient amounts of TFD reveals that due to the strong *trans* effect of the oxo ligands, the two pyrazolyl rings in the *trans* position are weaker bound and, thus, more electron-rich and more reactive toward electrophilic attack.[52] In contrast, statistical attack of the dioxirane should have resulted in the two possible regioisomeric hydroxylated pyrazole products in a ratio of 2:1. The selective hydroxylation of a pyrazole ring system has not been observed so far. Hydroxylated tris(pyrazolyl)borates may be useful ligands for the immobilization of metal ions on polymeric materials.

In summary, the alkenyltungsten complexes **2a**−**e** with d^0 electronic configuration are similar to the related unsaturated silanes and stannanes in their behavior toward oxyfunctionalization. An exception constitutes the vinyl compound **2e**, for which the preferred oxidation mode is strongly controlled by the steric hindrance of the bulky Tp* ligand. A set of oxyfunctionalized tungsten-containing olefins has now

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become available through the novel oxidation chemistry with $^1O_2$ and dioxiranes, which might serve as useful building blocks in preparative organometallic chemistry.

Experimental Section

IR spectra were obtained on a Bruker IFS 25 or a Perkin Elmer Model 1420 instrument, UV spectra on a Hewlett-Packard 8452 A spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz), a Bruker AMX 400 (400 MHz), or a Bruker DMX 600 (600 MHz) spectrometer by using $CDCl_3$ as internal standard. Mostly the signals of the three pyrazolyl ligands appeared magnetically inequivalent. The signal of the B−H proton in the ^{1}H NMR spectra apppeared very broad due to the quadrupole moment of boron and was only detected by 600 MHz spectroscopy. For the assignment of the NMR signals in some cases COSY spectra had to be employed. The mass balance of crude product mixtures in the ^{1}H NMR spectra was determined by using the signals of the pyrazolyl protons at δ 6 as internal standard. Mass spectra were obtained on a Finnigan MAT 90. The *m/z* values correspond to the most abundant isotopomers. The peak pattern reflects the natural isotopomer distribution. As all new substances did not show a defined melting point, the decomposition temperature was determined for the starting materials by differential thermoanalysis on a DuPont 9000 apparatus. All solvents were purified by standard literature methods. Petroleum ether (bp 30−50 °C) was used throughout. TLC was performed on Polygram Sil G W (40 × 80 mm), Machery & Nagel. Silica gel (63−200 mesh; Woelm) was employed for column chromatography, silica gel (32−64 mesh; Woelm) for flash chromatography. Chloroform was employed as solvent for placing the crude reaction mixtures on the column since it possesses the best solubility for the oxyfunctionalized complexes. The known complexes **1**,[5,6] **2c**,[5] and **2f**[5] and the Grignard reagents[52] were synthesized according to the literature procedure. DMD[53] and TFD[43] were prepared as acetone or trifluoroacetone solutions by the published procedures and dried over molecular sieves (4 Å) at −20 °C before use.

Synthesis of Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](4-methyl-3-pentenyl)tungsten(VI) (2a). To a suspension of 1.92 g (3.50 mmol) of the chloro complex **1** in THF (30 mL) was added at room temperature (ca. 20 °C) dropwise 18.1 mL of a 0.58 M solution of (4-methyl-3-pentenyl)-magnesium bromide (10.5 mmol) in diethyl ether under an argon gas atmosphere. The reaction mixture was stirred for 30 min at 30 °C, whereby a dark blue solution was formed. After cooling to −5 °C, the gas volume of the reaction flask was surged with oxygen gas until the solution became orange. The solvent was evaporated (20 °C/10^{-2} Torr), the residue was dissolved in dichloromethane (15 mL) and washed with a saturated aqueous solution of ammonium chloride (15 mL). After passing the organic phase through a column filled with 5 g of Celite and 3 g of anhydrous $MgSO_4$, the remaining clear solution was evaporated (20 °C/10^{-2} Torr) and the crude product was recrystallized from hexane/dichloromethane (10:1) to afford 1.50 g (72%) of the colorless complex **2a** as powder, mp 196 °C dec; IR (Nujol): 3123 (ν_{C-H}), 2552 (ν_{B-H}), 1542 ($\nu_{C=N}$), 1448, 1419, 1375, 1364, 1209, 1191, 1071, 1042, 948 ($\nu_{W=O}$), 912 ($\nu_{W=O}$), 858, 818, 803, 782, 644, 475 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 6H, 5′, 6′-H), 1.88−1.92 (m, 2H, 2′-H), 2.23 (s, 3H, 5-CH_3), 2.26 (s, 6H, 5-CH_3), 2.49 (s, 3H, 3-CH_3), 2.62 (s, 6H, 3-CH_3), 2.86−2.92 (m, 2H, 1′-H), 5.00−5.04 (m, 1H, 3′-H), 5.75 (s, 1H, 4-H), 5.77 (s, 2H, 4-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6 (2q, 5-CH_3), 12.8 (q, 5-CH_3), 14.6 (2q, 3-CH_3), 15.5 (q, 3-CH_3), 17.6 (q, C-5′), 25.6 (q, C-6′), 36.6 (t, C-2′), 57.3 (t, C-1′, $^1J_{WC}$ = 115.4 Hz), 107.3 (d, C-4), 107.7 (2d, C-4), 129.0 (s, C-4′), 130.5 (d, C-3′), 144.0 (2s, C-3), 147.1 (s, C-3), 153.2 (2s, C-5), 153.4 (s, C-5); MS (70 eV), *m/z* (%): 596 (2) [M^+], 513 (100) [$M^+ - C_6H_{11}$]. Anal. Calcd for $C_{21}H_{33}BN_6O_2W$ (596.2): C, 42.31; H, 5.58; N, 14.10. Found: C, 41.96; H, 5.33; N, 13.80.

Synthesis of (3-Butenyl)dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato]tungsten(VI) (2b). To a suspension of 2.00 g (3.65 mmol) of the chloro complex **1** in THF (40 mL) was added at room temperature (ca. 20 °C) dropwise 11.5 mL of a 0.95 M solution of 3-butenylmagnesium bromide (11.0 mmol) in diethyl ether under an argon gas atmosphere. The reaction mixture was stirred for 30 min at 30 °C, whereby a violet-blue solution was formed. After cooling to −5 °C, the gas volume of the reaction flask was purged with oxygen gas until the solution became orange. The solvent was evaporated (20 °C/10^{-2} Torr), and the residue was dissolved in dichloromethane (15 mL) and washed with a saturated aqueous solution of ammonium chloride (15 mL). After passing the organic phase through a column filled with 5 g of Celite and 3 g of anhydrous $MgSO_4$, the remaining clear solution was evaporated (20 °C/10^{-2} Torr) and the crude product was recrystallized from hexane/dichloromethane (10:1) to afford 1.16 g (56%) of the colorless complex **2b** as powder, mp 193 °C dec; IR (Nujol): 3134 (ν_{C-H}), 2551 (ν_{B-H}), 1633 ($\nu_{C=C}$), 1541 ($\nu_{C=N}$), 1448, 1418, 1367, 1212, 1186, 1074, 1044, 949 ($\nu_{W=O}$), 911 ($\nu_{W=O}$), 858, 816, 790, 691, 648, 640, 472 cm^{-1}; UV (CH_2Cl_2), λ_{max} (log ϵ): 284 (3.75), 464 (1.96) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00−2.04 (m, 2H, 2′-H), 2.33 (s, 3H, 5-CH_3), 2.37 (s, 6H, 5-CH_3), 2.58 (s, 3H, 3-CH_3), 2.69 (s, 6H, 3-CH_3), 3.03−3.09 (m, 2H, C-1′), 4.84 (d, J = 10.0 Hz, 1H, 4′-H), 4.92 (d, J = 17.0 Hz, 1H, 4′-H), 5.85 (s, 1H, 4-H), 5.88 (2s, 2H, 4-H), 5.89−5.94 (m, 1H, 3′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4 (2q, 5-CH_3), 12.6 (q, 5-CH_3), 14.6 (2q, 3-CH_3), 15.5 (q, 3-CH_3), 41.7 (t, C-2′), 55.3 (t, C-1′, $^1J_{WC}$ = 115.7 Hz), 107.4 (d, C-4), 107.8 (2d, C-4), 112.3 (t, C-4′), 144.1 (2s, C-3), 147.1 (s, C-3), 144.3 (d, C-3′), 153.2 (2s, C-5), 153.4 (s, C-5); MS (70 eV), *m/z* (%): 568 (1) [M^+], 513 (100) [$M^+ - C_4H_7$]. Anal. Calcd for $C_{19}H_{29}BN_6O_2W$ (568.1): C, 40.17; H, 5.14; N,14.79. Found: C, 40.36; H, 5.07; N, 14.57.

Synthesis of Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](2-propenyl)tungsten(VI) (2d). To a suspension of 2.10 g (3.87 mmol) of the chloro complex **1** in THF (40 mL) was added at room temperature (ca. 20 °C) dropwise 22.1 mL of a 0.70 M solution of 2-propenylmagnesium bromide (15.5 mmol) in diethyl ether under an argon gas atmosphere. The reaction mixture was stirred for 5 min at room temperature, whereby a dark blue solution was formed. After cooling to −5 °C, the gas volume of the reaction flask was purged with oxygen gas until the solution became orange. The solvent was evaporated (20 °C/10^{-2} Torr), and the residue was dissolved in dichloromethane (15 mL) and washed with a saturated aqueous solution of ammonium chloride (15 mL). After passing the organic phase through a column filled with 5 g of Celite and 3 g of anhydrous $MgSO_4$, the remaining clear solution was evaporated (20 °C/10^{-2} Torr). The pale yellow crude product, which contained large amounts of the colorless Tp^*_2Mg byproduct, was extracted with warm acetonitrile (2 × 30 mL). Evaporation of the extract, recrystallization from hexane/dichloromethane (10:1), and drying at 50 °C/3−10 Torr yielded 0.920 g (43%) of the pale yellow complex **2d** as powder, mp 220 °C dec; IR (Nujol): 3126 (ν_{C-H}), 3073 (ν_{C-H}), 2547 (ν_{B-H}), 1612 ($\nu_{C=C}$), 1546 ($\nu_{C=N}$), 1447, 1421, 1384, 1219, 1182, 1072, 1042, 958 ($\nu_{W=O}$), 918 ($\nu_{W=O}$), 866, 800, 789, 782, 697, 638, 479 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H, 5-CH_3), 2.38 (s, 6H, 5-CH_3), 2.56 (s, 3H, 3-CH_3), 2.78 (s, 6H, 3-CH_3), 2.66 (d, J = 7.9 Hz, 2H, 1′-H), 4.61 (d, J = 10.4 Hz, 1H, 3′-H), 4.78 (d, J = 16.9 Hz, 1H, 3′-H), 5.84 (s, 1H, 4-H), 5.90 (s, 2H, 4-H) 6.57−6.68 (m, 1H, 2′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4 (2q, 5-CH_3), 12.6 (q, 5-CH_3), 14.8 (2q, 3-CH_3), 15.5 (q, 3-CH_3), 59.1 (t, C-1′, $^1J_{WC}$ = 105 Hz), 107.4 (d, C-4), 107.9 (2d, C-4), 110.7 (t, C-3′), 144.2 (2s, C-3), 147.2 (s, C-3), 145.4 (d, C-2′), 153.2 (2s, C-5), 153.6 (s, C-5); MS (70 eV), *m/z* (%): 553 (1) [$M^+ - H$], 513 (100) [$M^+ - C_3H_5$]. Anal. Calcd

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for $C_{18}H_{27}BN_6O_2W$ (554.1): C, 39.02; H, 4.91; N, 15.12. Found: C, 39.44; H, 4.83; N, 14.87.

Synthesis of Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](2-methyl-1-propenyl)tungsten(VI) (2e). To a suspension of 1.79 g (3.26 mmol) of the chloro complex **1** in THF (40 mL) was added at room temperature (ca. 20 °C) dropwise 7.61 mL of a 0.60 M solution of (2-methyl-1-propenyl)magnesium bromide (4.56 mmol) in diethyl ether under an argon gas atmosphere and stirred for 20 min. The blue-green reaction mixture was cooled to 5 °C, and 10 mL of oxygen gas was injected by means of a gas syringe through a septum into the reaction mixture, which subsequently turned orange in color. After 10 min, the solvent was removed in vacuo (20 °C/10^{-2} Torr) and the residue was dissolved in dichloromethane (15 mL) and washed with a saturated aqueous solution of ammonium chloride (2 × 10 mL). The organic phase was passed through a column filled with 5 g of Celite and 3 g of anhydrous $MgSO_4$. An orange-brown crude material precipitated on adding hexane (50 mL) to the concentrated dichloromethane solution. Its suspension in cold diethyl ether (5 mL) was transferred onto a column of 3 g of Celite. The brown impurities were washed out with a 1:1 mixture of diethyl ether/hexane (100 mL), and the product was extracted with boiling diethyl ether (6 × 20 mL). On evaporation of the ether (20 °C/10^{-2} Torr), the resulting solid was washed with pentane (2 × 20 mL) and dried at 50 °C/3−10 Torr to afford 1.04 g (56%) of the complex **2e** as colorless powder, mp 217 °C dec; IR (Nujol): 3121 (ν_{C-H}), 2540 (ν_{B-H}), 1593 ($\nu_{C=C}$), 1543 ($\nu_{C=N}$), 1448, 1419, 1390, 1365, 1208, 1187, 1071, 1046, 951 ($\nu_{W=O}$), 909 ($\nu_{W=O}$), 860, 814, 793, 785, 777, 694, 653, 470 cm^{-1}; UV (CH_2Cl_2), λ_{max} (log ϵ): 288 (3.90) nm; ^1H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 3H, 3′-H), 2.11 (s, 3H, 4′-H), 2.36 (s, 3H, 5-CH_3), 2.37 (s, 6H, 5-CH_3), 2.46 (s, 6H, 3-CH_3), 2.69 (s, 3H, 3-CH_3), 5.82 (s, 2H, 4-H), 5.89 (s, 1H, 4-H) 6.39 (s br, 1H, 1′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.4 (2q, 3-CH_3), 15.6 (q, 3-CH_3), 27.5 (q, C-3′), 30.0 (q, C-4′), 107.2 (2d, C-4), 107.5 (d, C-4), 143.8 (2s, C-3), 146.9 (s, C-3), 152.1 (s, C-2′), 153.3 (2s, C-5), 153.8 (s, C-5), 167.9 (d, C-1′, $^1J_{WC}$ = 146.6 Hz); MS (70 eV), *m/z* (%): 568 (84) [M^+], 513 (77) [$M^+ - C_4H_7$]. Anal. Calcd for $C_{19}H_{29}BN_6O_2W$ (568.1): C, 40.17; H, 5.14; N, 14.79. Found: C, 40.53; H, 5.06; N, 14.31.

General Procedure A for the Photooxygenations. The photooxygenations were performed in a Schlenk tube by passing a slow stream of dried ($CaCl_2$, P_2O_5) oxygen gas through the reaction solution while externally irradiating with two 150-, 250-, or 400-W sodium lamps in the presence of catalytic amounts (ca. 1 mg) of the sensitizer tetraphenylporphine (TPP) in dichoromethane or deuterochloroform at −30 °C. The reaction progress was monitored by TLC or NMR spectroscopy. The solvent was evaporated (20 °C/20 Torr) and the residue flash-chromatographed on silica gel with mixtures of diethyl ether, petroleum ether, and acetone as eluent. The products were obtained as colorless solids.

Photooxygenation of Homoallyl Complex 2a: Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](3-hydroperoxy-4-methyl-4-pentenyl)tungsten(VI) (3a), (*E*)-Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](4-hydroperoxy-4-methyl-2-pentenyl)tungsten(VI) ((*E*)-3a′), (*Z*)-Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](3,4-dihydroperoxy-4-methyl-1-pentenyl)tungsten(VI) ((*Z*)-4a′), and Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](2-hydroxy-4-methyl-3,4-oxiranylpentyl)tungsten(VI) (6a′). (a) Short Reaction Time (15 min). According to the general procedure A, 167 mg (0.280 mmol) of the homoallyl complex **2a** was photooxygenated in dichloromethane (20 mL) for 15 min by irradiation with two 150-W sodium lamps. The NMR spectra of the crude reaction mixture showed complete conversion to the two allylic hydroperoxides **3a** and (*E*)-**3a′** in a ratio of 65:35 with a mass balance of 73%. As eluent for the flash chromatography of the crude product was used diethyl ether/petroleum ether (2:1), which was replaced by pure diethyl ether toward the end of the column chromatography. In succession, 97.0 mg (55%) of the secondary allyl hydroperoxide **3a**, 5.00 mg (3%) of the tertiary allyl hydroperoxide (*E*)-**3a′** (as mixture with isomer **3a**), and 22.0 mg (13%) of the hydroxy epoxide **6a′** (only one diastereomer of unknown configuration) were isolated. The **3a**:(*E*)-**3a′**:**6a′** product ratio was 78:4:18 and the mass balance 70% after chromatography.

(b) Long Reaction Time (2.5 h). According to the general procedure A, 160 mg (0.268 mmol) of the homoallyl complex **2a** was photooxygenated in dichloromethane (20 mL) for 2.5 h by irradiation with two 150-W sodium lamps. The NMR spectra of the crude reaction mixture showed complete conversion to the allylic hydroperoxide **3a** and the bishydroperoxide (*Z*)-**4a′** in a ratio of 78:22 with a mass balance of 68%. After flash chromatography with diethyl ether/petroleum ether (2:1) as eluent, 93.0 mg (55%) of the secondary allyl hydroperoxide **3a**, and 17.0 mg (10%) of the bishydroperoxide (*Z*)-**4a′** were isolated. The **3a**:(*Z*)-**4a′** product ratio was 85:15 and the mass balance 65% after chromatography.

3a: R_f [diethyl ether/petroleum ether (2:1)] = 0.29; IR (KBr): 3280 (ν_{OO-H}), 2900 (ν_{C-H}), 2540 (ν_{B-H}), 1525 ($\nu_{C=N}$), 1430, 1400, 1370, 1350, 1200, 1065, 1035, 945 ($\nu_{W=O}$), 900 ($\nu_{W=O}$), 850, 805, 780, 640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.76 (s, 3H, 6′-H), 1.95 (m, 2H, 1′-H), 2.34 (s, 3H, 5-CH_3), 2.37 (s, 6H, 5-CH_3), 2.57 (s, 3H, 3-CH_3), 2.70 (s, 6H, 3-CH_3), 2.42−2.80 (m, 2H, 2′-H), 4.28 (t, *J* = 6.6 Hz, 1H, 3′-H), 4.97 (s, 2H, 5′-H), 5.87 (s, 1H, 4-H), 5.89 (s, 1H, 4-H), 5.90 (s, 1H, 4-H), 8.08 (br s, 1H, OOH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.5 (q, 5-CH_3), 12.5 (q, 5-CH_3), 12.6 (q, 5-CH_3), 14.6 (2q, 3-CH_3), 15.5 (q, 3-CH_3), 17.5 (q, C-6′), 38.2 (t, C-2′), 51.5 (t, C-1′, $^1J_{WC}$ = 115.5 Hz), 94.6 (d, C-3′), 107.4 (d, C-4), 107.9 (2d, C-4), 113.8 (t, C-5′), 144.0 (s, C-4′), 144.1 (s, C-3), 144.2 (s, C-3), 147.2 (s, C-3), 153.3 (s, C-5), 153.4 (2s, C-5); MS (70 eV), *m/z* (%): 513 (13) [$M^+ - C_6H_{11}O_2$], 418 (11) [$M^+ - C_6H_{11}O_2$ − pz*], 96 (100) [pz*H^+], 95 (87) [pz*$^+$], 41 (53) [$C_2H_3N^+$], the molecular ion *m/z* at 628 was not observed. Anal. Calcd for $C_{21}H_{33}BN_6O_4W$ (628.2): C, 40.15; H, 5.29; N, 13.38. Found: C, 40.42; H, 5.16; N, 13.21.

(*E*)-3a′: R_f [diethyl ether/petroleum ether (2:1)] = 0.21; ^1H NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 6H, 5′-H, 6′-H), 2.36 (s, 3H, 5-CH_3), 2.39 (s, 6H, 5-CH_3), 2.54 (s, 3H, 3-CH_3), 2.45−2.80 (m, 2H, 1′-H), 2.80 (s, 6H, 3-CH_3), 5.18 (d, *J* = 15.7 Hz, 1H, 3′-H), 5.89 (s, 1H, 4-H), 5.90 (s, 1H, 4-H), 5.93 (s, 1H, 4-H), 6.48 (dt, *J* = 15.7, 8.2 Hz, 1H, 2′-H), the signal for the hydroperoxy proton was not observed; ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (q, 5-CH_3), 12.6 (2q, 5-CH_3), 14.5 (q, 3-CH_3), 14.6 (q, 3-CH_3), 14.9 (q, 3-CH_3), 24.3 (2q, C-5′, C-6′), 55.5 (t, C-1′, $^1J_{WC}$ = 104.3 Hz), 81.7 (s, C-4′), 107.4 (d, C-4), 108.0 (2d, C-4), 129.2 (d, C-2′), 140.0 (d, C-3′), 144.2 (s, C-3), 144.4 (s, C-3), 147.5 (s, C-3), 153.2 (s, C-5), 153.3 (s, C-5), 153.6 (s, C-5).

(*Z*)-4a′: R_f [diethyl ether/petroleum ether (2:1)] = 0.21; IR (KBr): 3470 (ν_{OO-H}), 3280 (ν_{OO-H}), 2940 (ν_{C-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1525 ($\nu_{C=N}$), 1430, 1400, 1370, 1350, 1200, 1065, 1035, 940 ($\nu_{W=O}$), 900 ($\nu_{W=O}$), 850, 800, 630 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.24 (s, 3H, 5′-H or 6′-H), 1.47 (s, 3H, 5′-H or 6′-H), 2.39 (s, 6H, 5-CH_3), 2.40 (s, 3H, 5-CH_3), 2.53 (s, 3H, 3-CH_3), 2.57 (s, 3H, 3-CH_3), 2.63 (s, 3H, 3-CH_3), 4.64 (br s, 1H, BH), 5.44 (d, *J* = 9.2 Hz, 1H, 3′-H), 5.86 (s, 2H, 4-H), 5.95 (s, 1H, 4-H), 6.88 (ddd, *J* = 13.4, 0.6 Hz, 1H, 1′-H, $^2J_{WH}$ = 6.5 Hz), 7.40 (dd, *J* = 13.4, 9.1 Hz, 1H, 2′-H), 9.00 (br s, 1H, OOH), 9.71 (br s, 1H, OOH); ^{13}C NMR (150 MHz, $CDCl_3$): δ 12.4 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 15.9 (2q, 3-CH_3), 15.6 (q, 3-CH_3), 21.2 (q, C-5′ or C-6′), 22.3 (q, C-5′or C-6′), 83.7 (s, C-4′), 91.4 (d, C-3′), 107.6 (d, C-4), 107.7 (d, C-4), 107.8 (d, C-4), 143.0 (d, C-2′), 144.3 (s, C-3), 144.5 (s, C-3), 147.8 (s, C-3), 153.8 (s, C-5), 154.0 (s, C-5), 154.1 (s, C-5), 174.9 (d, C-1′, $^1J_{WC}$ = 147.0 Hz); MS (70 eV), *m/z* (%): 606 (1) [$M^+ - C_3H_4N$], 513 (15) [$M^+ - C_6H_{11}O_4$], 418 (8) [$M^+ - C_6H_{11}O_4$ − pz*], 96 (100) [pz*H^+], 95 (80) [pz*$^+$], 43 (21) [$C_3H_7^+$], 41 (27) [$C_2H_3N^+$], the molecular ion at *m/z* 660 was not observed. Anal. Calcd for $C_{21}H_{33}$-

BN_6O_6W (660.2): C, 38.21; H, 5.04; N, 12.73. Found: C, 38.46; H, 5.07; N, 12.62.

6a′: R_f (diethyl ether) = 0.23; IR (KBr): 3440 (ν_{O-H}), 2960 (ν_{C-H}), 2940 (ν_{C-H}), 2520 (ν_{B-H}), 1540 ($\nu_{C=N}$), 1445, 1415, 1380, 1360, 1210, 1070, 1040, 960 ($\nu_{W=O}$), 920 ($\nu_{W=O}$), 860, 815, 645 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.34 (s, 3H, 5′-H or 6′-H), 1.51 (s, 3H, 5′-H or 6′-H), 2.02 (dd, J = 14.4, 7.4 Hz, 1H, 1′-H), 2.17 (dd, J = 14.4, 5.9 Hz, 1H, 1′-H), 2.36 (s, 3H, 5-CH_3), 2.38 (s, 3H, 5-CH_3), 2.39 (s, 3H, 5-CH_3), 2.58 (s, 3H, 3-CH_3), 2.70 (s, 6H, 3-CH_3), 2.85 (d, J = 8.3 Hz, 1H, 3′-H), 4.24 (m, 1H, 2′-H), 5.91 (s, 3H, 4-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (q, 5-CH_3), 12.5 (q, 5-CH_3), 12.7 (q, 5-CH_3), 14.9 (q, 3-CH_3), 15.0 (q, 3-CH_3), 15.4 (q, 3-CH_3), 19.9 (q, C-5′or C-6′), 25.1 (q, C-5′or C-6′), 59.0 (t, C-1′, $^1J_{WC}$ = 118.6 Hz), 59.9 (s, C-4′), 70.6 (d, C-2′), 74.6 (d, C-3′), 107.5 (d, C-4), 108.0 (2d, C-4), 144.4 (s, C-3), 144.6 (s, C-3), 147.4 (s, C-3), 153.2 (s, C-5), 153.5 (2s, C-5); MS (70 eV), m/z (%): 556 (9) [$M^+ - C_4H_8O$], 513 (83) [$M^+ - C_6H_{11}O_2$], 418 (27) [$M^+ - C_6H_{11}O_2$ − pz*], 96 (100) [pz*H^+], 95 (84) [pz*$^+$], 41 (38) [$C_2H_3N^+$], the molecular ion at m/z 628 was not observed. Anal. Calcd for $C_{21}H_{33}BN_6O_4W$ (628.2): C, 40.15; H, 5.29; N, 13.38. Found: C, 39.99; H, 5.23; N, 13.24.

Photooxygenation of Methallyl Complex 2c: (*Z*)-Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](3-hydroperoxy-2-methyl-1-propenyl)tungsten(VI) ((*Z*)-3c). According to the general procedure A, 97.0 mg (0.171 mmol) of the methallyl complex **2c** was photooxygenated in dichloromethane (10 mL) for 1 h by irradiation with two 150-W sodium lamps. After flash chromatography with diethyl ether/petroleum ether (2:1) as eluent, 74.0 mg (72%) of the allyl hydroperoxide (*Z*)-**3c** was isolated. R_f [diethyl ether/petroleum ether (2:1)] = 0.20; IR (KBr): 3280 (ν_{OO-H}), 2960 (ν_{C-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1525 ($\nu_{C=N}$), 1430, 1400, 1370, 1350, 1200, 1060, 940 ($\nu_{W=O}$), 900 ($\nu_{W=O}$), 855, 800, 640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.88 (s, 3H, 4′-H), 2.38 (s, 9H, 5-CH_3), 2.48 (s, 6H, 3-CH_3), 2.68 (s, 3H, 3-CH_3), 4.94 (br s, 2H, 3′-H), 5.85 (s, 2H, 4-H), 5.93 (s, 1H, 4-H), 6.45 (br s, 1H, 1′-H), 8.81 (br s, 1H, OOH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.6 (2q, 3-CH_3), 15.7 (q, 3-CH_3), 24.9 (q, C-4′), 83.0 (t, C-3′), 107.4 (2d, C-4), 107.7 (d, C-4), 144.1 (2s, C-3), 147.3 (s, C-3), 150.4 (s, C-2′), 153.5 (2s, C-5), 153.9 (s, C-5), 168.5 (d, C-1′, $^1J_{WC}$ = 146.7 Hz); MS (70 eV), m/z (%): 600 (1) [M^+], 513 (25) [$M^+ - C_4H_7O_2$], 418 (48) [$M^+ - C_4H_7O_2$ − pz*], 96 (100) [pz*H^+], 95 (85) [pz*$^+$], 41 (27) [$C_2H_3N^+$]. Anal. Calcd for $C_{19}H_{29}BN_6O_4W$ (600.2): C, 38.03; H, 4.87; N, 14.00. Found: C, 37.90; H, 4.74; N, 13.77.

Photooxygenation of Allyl Complex 2d: (*Z*)-Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](3-hydroperoxy-1-propenyl)tungsten(VI) ((*Z*)-3d). According to the general procedure A, 145 mg (0.262 mmol) of the allyl complex **2d** was photooxygenated in deuterochloroform (5 mL) for 2 h by irradiation with two 250-W sodium lamps. After flash chromatography with diethyl ether/petroleum ether (2:1) as eluent, besides 40.0 mg (37%) of the starting material, 67.0 mg (60%) of the allyl hydroperoxide (*Z*)-**3d** was isolated, which was only moderately soluble in chloroform. The conversion was 63%, the mass balance 71%. R_f [diethyl ether/petroleum ether (2:1)] = 0.28; R_f (diethyl ether) = 0.52; IR (KBr): 3300 (ν_{OO-H}), 2920 (ν_{C-H}), 2540 (ν_{B-H}), 1535 ($\nu_{C=N}$), 1445, 1415, 1380, 1360, 1210, 1070, 1040, 950 ($\nu_{W=O}$), 905 ($\nu_{W=O}$), 860, 810, 645 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.38 (s, 9H, 5-CH_3), 2.50 (s, 6H, 3-CH_3), 2.65 (s, 3H, 3-CH_3), 4.96 (br s, 2H, 3′-H), 5.85 (s, 2H, 4-H), 5.93 (s, 1H, 4-H), 6.79 (d, J = 13.5 Hz, 1H, 1′-H), 7.48 (dt, J = 13.7, 5.6 Hz, 1H, 2′-H), 8.36 (br s, 1H, OOH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.8 (2q, 3-CH_3), 15.6 (q, 3-CH_3), 81.2 (t, C-3′), 107.5 (2d, C-4), 107.6 (d, C-4), 142.3 (d, C-2′), 144.2 (2s, C-3), 147.5 (s, C-3), 153.5 (2s, C-5), 153.8 (s, C-5), 171.0 (d, C-1′, $^1J_{WC}$ = 147.6 Hz); MS (70 eV), m/z (%): 568 (18) [$M^+ - H_2O$], 513 (37) [$M^+ - C_3H_5O_2$], 418 (49) [$M^+ - C_3H_5O_2$ − pz*], 96 (100) [pz*H^+], 95 (88) [pz*$^+$], 84 (100) [$C_5H_{10}N^+$], 57 (11) [$C_3H_5O^+$], 41 (22) [$C_2H_3N^+$], the molecular ion at m/z 586 was not observed. Anal. Calcd for $C_{18}H_{27}BN_6O_4W$ (586.1): C, 36.89; H, 4.64; N, 14.34. Found: C, 36.74; H, 4.64; N, 14.26.

Photooxygenation of Vinyl Complex 2e: Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato]hydroxytungsten(VI) (9e) and Methacrolein (9e′). According to the general procedure A, 91.0 mg (0.160 mmol) of the vinyl complex **2e** was photooxygenated in deuterochloroform (5 mL) for 1 d by irradiation with two 400-W sodium lamps. The NMR spectra of the crude reaction mixture showed complete conversion to the tungsten acid derivative **9e** and methacrolein (**9e′**) as only products. The methacrolein and the solvent were evaporated (20 °C/20 Torr), and the residue was dissolved in a minimum volume of chloroform (ca. 1−2 mL). Upon addition of petroleum ether, 74.0 mg (87%) of the acid **9e** precipitated, which decomposed on filtration over florisil.

9e: IR (KBr): 3350 (ν_{O-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1530 ($\nu_{C=N}$), 1435, 1400, 1370, 1355, 1200, 1065, 1040, 940 ($\nu_{W=O}$), 895 ($\nu_{W=O}$), 860, 805, 690, 650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 2.35 (s, 10H, 5-CH_3, OH), 2.70 (s, 9H, 3-CH_3), 5.87 (s, 3H, 4-H), the signal at δ 2.35 diminishes to 9H by shaking the sample with D_2O; ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (3q, 5-CH_3), 14.4 (3q, 3-CH_3), 107.5 (3d, C-4), 144.9 (3s, C-3), 153.2 (3s, C-5); MS (70 eV), m/z (%): 530 (7) [M^+], 513 (7) [M^+ − HO], 435 (34) [M^+ − pz*], 96 (100) [pz*H^+], 95 (86) [pz*$^+$], 41 (25) [$C_2H_3N^+$]. Anal. Calcd for $C_{15}H_{23}BN_6O_3W$ (530.1): C, 33.99; H, 4.37; N, 15.85. Found: C, 33.94; H, 4.10; N, 15.83.

Reaction of Hydroperoxy Complex 3a with Titanium Tetraisopropoxide: Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](3-hydroxy-4-methyl-4,5-oxiranylpentyl)tungsten(VI) (5a). To a solution of 72.0 mg (0.115 mmol) of the allyl hydroperoxide **3a** in dry dichloromethane (20 mL) was added 16.0 mg (0.058 mmol) of titanium tetraisopropoxide and stirred for 2 h at room temperature in the presence of ca. 1.0 g molecular sieves (4 Å). The molecular sieves were removed by filtration, and the reaction mixture was stirred for 0.5 h after addition of water (one drop) and diethyl ether (20 mL). After drying over $MgSO_4$, the solution was filtered over Celite and the solvent was evaporated (20 °C/20 Torr). Column chromatography with diethyl ether/acetone (2:1) as eluent gave 43.0 mg (59%) of the epoxy alcohol **5a** (81:19 mixture of *erythro* and *threo* diastereomers) as colorless powder. The conversion was greater than 98%. R_f [diethyl ether/acetone (2:1)] = 0.59; IR (KBr): 3420 (ν_{O-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1530 ($\nu_{C=N}$), 1430, 1400, 1370, 1355, 1200, 1065, 1035, 945 ($\nu_{W=O}$), 905 ($\nu_{W=O}$), 855, 805, 780, 640 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) for the *erythro* diastereomer: δ 1.30 (s, 3H, 6′-H), 1.95 (m, 1H, 1′-H), 2.11 (m, 1H, 1′-H), 2.27 (s, 3H, 5-CH_3), 2.30 (s, 6H, 5-CH_3), 2.42−2.52 (m, 1H, 2′-H), 2.48 (d, J = 4.8 Hz, 1H, 5′-H), 2.50 (s, 3H, 3-CH_3), 2.59−2.69 (m, 1H, 2′-H), 2.64 (s, 3H, 3-CH_3), 2.66 (s, 3H, 3-CH_3), 2.81 (d, J = 4.8 Hz, 1H, 5′-H), 3.53 (dd, J = 8.5, 2.9 Hz, 1H, 3′-H), 4.55 (br s, 1H, BH), 5.79 (s, 1H, 4-H), 5.81 (s, 2H, 4-H); ^1H NMR (600 MHz, $CDCl_3$) for the *threo* diastereomer: δ 1.29 (s, 3H, 6′-H), 1.86 (m, 1H, 1′-H), 2.01 (m, 1H, 1′-H), 2.27 (s, 3H, 5-CH_3), 2.30 (s, 6H, 5-CH_3), 2.42−2.69 (m, 2H, 2′-H), 2.50 (s, 3H, 3-CH_3), 2.53 (d, J = 4.8 Hz, 1H, 5′-H), 2.63 (s, 3H, 3-CH_3), 2.65 (s, 3H, 3-CH_3), 2.69 (d, J = 4.8 Hz, 1H, 5′-H), 3.23 (dd, J = 8.6, 4.3 Hz, 1H, 3′-H), 4.55 (br s, 1H, BH), 5.80 (s, 2H, 4-H), 5.82 (s, 1H, 4-H); ^{13}C NMR (150 MHz, $CDCl_3$) for the *erythro* diastereomer: δ 12.6 (2q, 5-CH_3), 12.8 (q, 5-CH_3), 15.6 (2q, 3-CH_3), 16.1 (q, 3-CH_3), 18.5 (q, C-6′), 41.0 (t, C-2′), 50.6 (t, C-5′), 52.3 (t, C-1′, $^1J_{WC}$ = 116.1 Hz), 59.4 (s, C-4′), 76.5 (d, C-3′), 107.6 (d, C-4), 108.1 (2d, C-4), 144.2 (s, C-3), 144.3 (s, C-3), 143.4 (s, C-3), 153.5 (s, C-5), 153.6 (2s, C-5); ^{13}C NMR (150 MHz, $CDCl_3$) for the *threo* diastereomer: δ 12.6 (2q, 5-CH_3), 12.8 (q, 5-CH_3), 15.6 (2q, 3-CH_3), 16.1 (q, 3-CH_3), 16.1 (q, C-6′), 41.2 (t, C-2′), 51.8 (t, C-1′), 52.8 (t, C-5′), 59.9 (s, C-4′), 80.1 (d, C-3′), 107.6 (d, C-4), 108.1 (2d, C-4), 144.2 (s, C-3), 144.3 (s, C-3), 143.4 (s, C-3), 153.5 (s, C-5), 153.6 (2s, C-5), the concentration of the *threo* diastereomer was to low too determine $^1J_{WC}$; MS (70 eV), m/z (%): 628 (1) [M^+], 513 (62) [$M^+ - C_6H_{11}O_2$], 418 (25) [$M^+ - C_6H_{11}O_2$ − pz*], 96 (100) [pz*H^+], 95 (95) [pz*$^+$], 41 (28)

[$C_2H_3N^+$]. Anal. Calcd for $C_{21}H_{33}BN_6O_4W$ (628.2): C, 40.15; H, 5.29; N, 13.38. Found: C, 39.89; H, 5.29; N, 13.04.

Direct Hydroxy-Epoxidation of Homoallyl Complex 2a with Titanium Tetraisopropoxide: Dioxo[hydridotris-(3,5-dimethyl-1-pyrazolyl)borato](3-hydroxy-4-methyl-4,5-oxiranylpentyl)tungsten(VI) (5a). Analogous to the general procedure A, 102 mg (0.121 mmol) of the homoallyl complex **1a** was photooxygenated at 20 °C in dry dichloromethane (25 mL) in the presence of 16.0 mg (0.058 mmol) of titanium tetraisopropoxide and ca. 1.0 g molecular sieves (4 Å) by irradiation with two 150-W sodium lamps for 2 h. The molecular sieves were removed by filtration, and the reaction mixture was stirred for 0.5 h after addition of water (one drop) and diethyl ether (20 mL). After drying over $MgSO_4$, the solution was filtered over Celite and the solvent was evaporated (20 °C/20 Torr). Column chromatography with diethyl ether/acetone (2:1) as eluent gave 33.0 mg (30%) of the epoxy alcohol **5a** (81:19 mixture of *erythro* and *threo* diastereomers) as colorless powder. The conversion was greater than 98%.

Reaction of Hydroperoxy Complex (*Z*)-3c with Titanium Tetraisopropoxide: (*Z*)-Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](3-hydroxy-2-methyl-1-propenyl)tungsten(VI) ((*Z*)-7c), (*Z*)-Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](2-methyl-3-oxo-1-propenyl)tungsten(VI) ((*Z*)-8c), and (*E*)-Dioxo[hydridotris-(3,5-dimethyl-1-pyrazolyl)borato](2-methyl-3-oxo-1-propenyl)tungsten(VI) ((*E*)-8c). To a solution of 110 mg (0.183 mmol) of the allyl hydroperoxide (*Z*)-**3c** in dry dichloromethane (20 mL) was added 52.0 mg (0.183 mmol) of titanium isopropoxide and stirred for 4 h at room temperature (ca. 20 °C) in the presence of ca. 1.0 g molecular sieves (4 Å). The molecular sieves were removed by filtration and the reaction mixture stirred for 0.5 h after addition of water (0.18 mL) and diethyl ether (20 mL). After drying over $MgSO_4$, the solution was filtered over Celite and the solvent was evaporated (20 °C/20 Torr). The NMR spectrum of the crude reaction mixture showed that, besides traces of the starting material, the allylic alcohol (*Z*)-**7c** and the aldehydes (*Z*)-**8c** and (*E*)-**8c** (80:20 mixture) had been formed in a ratio of 76:24. Flash chromatography with diethyl ether as eluent gave besides 2.00 mg (2%) of the starting material, 24.0 mg (23%) of the aldehyde **8c** and 57.0 mg (54%) of the alcohol (*Z*)-**7c** as colorless powders. The conversion was 98%, the mass balance 78%, and the (*Z*)-**7c**:**8c** product ratio 71:29 after chromatography.

(*Z*)-7c: R_f (diethyl ether) = 0.27; IR (KBr): 3470 (ν_{O-H}), 2960 (ν_{C-H}), 2930 (ν_{C-H}), 2520 (ν_{B-H}), 1540 ($\nu_{C=N}$), 1450, 1420, 1390, 1370, 1210, 1075, 955 ($\nu_{W=O}$), 910 ($\nu_{W=O}$), 870, 820, 650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.92 (s, 3H, 4′-H), 2.38 (s, 9H, 5-CH_3), 2.49 (s, 6H, 3-CH_3), 2.66 (s, 3H, 3-CH_3), 4.46 (br s, 2H, 3′-H), 5.84 (s, 2H, 4-H), 5.93 (s, 1H, 4-H), 6.37 (br s, 1H, 1′-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.2 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.7 (2q, 3-CH_3), 15.6 (q, 3-CH_3), 26.3 (q, C-4′), 69.0 (t, C-3′), 107.4 (2d, C-4), 107.7 (d, C-4), 144.1 (2s, C-3), 147.4 (s, C-3), 153.3 (2s, C-5), 153.5 (s, C-2′), 153.8 (s, C-5), 166.6 (d, C-1′, $^1J_{WC}$ = 146.2 Hz); MS (70 eV), *m*/*z* (%): 418 (1) [$M^+ - C_4H_7O$ − pz*], 96 (100) [pz*H^+], 95 (80) [pz*$^{+}$], 41 (29) [$C_2H_3N^+$], the molecular ion at *m*/*z* 584 was not observed. Anal. Calcd for $C_{19}H_{29}BN_6O_2W$ (584.1): C, 39.07; H, 5.00; N, 14.39. Found: C, 38.79; H, 4.91; N, 14.19.

8c: R_f (diethyl ether) = 0.56; IR (KBr): 2960 (ν_{C-H}), 2920 (ν_{C-H}), 2540 (ν_{B-H}), 1670 ($\nu_{C=O}$), 1540 ($\nu_{C=N}$), 1445, 1415, 1385, 1365, 1210, 1070, 955 ($\nu_{W=O}$), 910 ($\nu_{W=O}$), 860, 815, 650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) for the *Z*-isomer: δ 1.83 (d, *J* = 1.2 Hz, 3H, 4′-H), 2.40 (s, 15H, 3-CH_3, 5-CH_3), 2.65 (s, 3H, 3-CH_3), 5.87 (s, 2H, 4-H), 5.96 (s, 1H, 4-H), 7.52 (br s, 1H, 1′-H), 10.56 (br s, 1H, 3′-H); ^1H NMR (200 MHz, $CDCl_3$) for the *E*-isomer: δ 2.21 (s, 3H, 4′-H), 2.35 (s, 6H, 5-CH_3), 2.40 (s, 9H, 3-CH_3, 5-CH_3), 2.66 (s, 3H, 3-CH_3), 5.87 (s, 2H, 4-H), 5.97 (s, 1H, 4-H), 7.83 (br s, 1H, 1′-H), 9.32 (s, 1H, 3′-H); ^{13}C NMR (50 MHz, $CDCl_3$) for the *Z*-isomer: δ 12.4 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.7 (2q, 3-CH_3), 15.6 (q, 3-CH_3), 19.8 (q, C-4′), 107.7 (2d, C-4), 107.8 (d, C-4), 144.6 (2s, C-3), 147.8 (s, C-3), 150.3 (s, C-2′), 153.5 (2s, C-5), 154.1 (s, C-5), 186.5 (d, C-1′, $^1J_{WC}$ = 151.4 Hz), 199.8 (d, C-3′); ^{13}C NMR (50 MHz, $CDCl_3$) for the *E*-isomer: δ 12.4 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.7 (q, C-4′), 15.3 (2q, 3-CH_3), 15.6 (q, 3-CH_3), 107.7 (2d, C-4), 107.8 (d, C-4), 144.6 (2s, C-3), 147.9 (s, C-3), 153.4 (s, C-2′), 153.6 (2s, C-5), 154.1 (s, C-5), 195.4 (d, C-1′), 196.2 (d, C-3′), the concentration was too low to determine $^1J_{WC}$; MS (70 eV), *m*/*z* (%): 582 (17) [M^+], 513 (8) [$M^+ - C_4H_5O$], 418 (22) [$M^+ - C_4H_5O$ − pz*], 96 (33) [pz*H^+], 95 (39) [pz*$^{+}$], 69 (100) [$C_4H_5O^+$], 41 (50) [$C_2H_3N^+$]. HRMS calcd for $^{12}C_{19}{}^1H_{27}{}^{10}B^{14}N_6{}^{16}O_3{}^{182}W$ (M^+): 579.1756; found: 579.1756.

General Procedure B for the Epoxidation with DMD. To the tungsten complex, dissolved in dichloromethane (10 mL), was added at once 1.1−1.2 equiv of DMD as a solution in acetone at room temperature (ca. 20 °C). The reaction mixture was stirred until all dioxirane was consumed (negative peroxide test with KI in HOAc). After evaporation of the solvent (20 °C/20 Torr), the pure epoxide was obtained in quantitative yield as colorless powders.

Epoxidation of Homoallyl Complex 2a with DMD: Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](4-methyl-3,4-oxiranylpentyl)tungsten(VI) (10a). According to the general procedure B, from 48.0 mg (0.081 mmol) of the homoallyl complex **2a** and 1.00 mL of a 0.099 M solution of DMD (0.099 mmol) was isolated after a reaction time of 30 min 50.0 mg (100%) of the epoxide **10a**, which was stable on filtration over florisil with diethyl ether as solvent, but decomposed on silica gel. IR (KBr): 2940 (ν_{C-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1525 ($\nu_{C=N}$), 1430, 1400, 1370, 1350, 1200, 1060, 1035, 940 ($\nu_{W=O}$), 905 ($\nu_{W=O}$), 800, 640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.28 (s, 3H, 5′-H or 6′-H), 1.31 (s, 3H, 5′-H or 6′-H), 2.02 (m, 2H, 1′-H), 2.34 (s, 3H, 5-CH_3), 2.38 (s, 6H, 5-CH_3), 2.56 (m, 2H, 2′-H), 2.56 (s, 3H, 3-CH_3), 2.70 (m, 1H, 3′-H), 2.72 (s, 3H, 3-CH_3), 2.73 (s, 3H, 3-CH_3), 5.87 (s, 1H, 4-H), 5.89 (s, 2H, 4-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (q, 5-CH_3), 12.5 (q, 5-CH_3), 12.6 (q, 5-CH_3), 14.6 (q, 3-CH_3), 14.7 (q, 3-CH_3), 15.5 (q, 3-CH_3), 18.8 (q, C-5′or C-6′), 25.0 (q, C-5′or C-6′), 36.4 (t, C-2′), 51.2 (t, C-1′, $^1J_{WC}$ = 118.0 Hz), 58.8 (s, C-4′), 69.4 (d, C-3′), 107.4 (d, C-4), 107.8 (2d, C-4), 144.1 (s, C-3), 144.2 (s, C-3), 147.2 (s, C-3), 153.1 (s, C-5), 153.3 (s, C-5), 153.4 (s, C-5); MS (70 eV), *m*/*z* (%): 612 (3) [M^+], 513 (100) [$M^+ - C_6H_{11}O$], 418 (14) [$M^+ - C_6H_{11}O$ − pz*], 96 (25) [pz*H^+], 95 (23) [pz*$^{+}$], 41 (15) [$C_2H_3N^+$]. Anal. Calcd for $C_{21}H_{33}BN_6O_3W$ (612.2): C, 41.20; H, 5.43; N, 13.73. Found: C, 40.89; H, 5.47; N, 13.45.

Epoxidation of Methallyl Complex 2c with DMD: Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](2-methyl-2,3-oxiranylpropyl)tungsten(VI) (10c). According to the general procedure B, from 101 mg (0.178 mmol) of the methallyl complex **2c** and 2.80 mL of a 0.0706 M solution of DMD (0.198 mmol) was isolated after a reaction time of 45 min 104 mg (100%) of the epoxide **10c**, which decomposed on filtration over florisil with diethyl ether as solvent. IR (KBr): 2940 (ν_{C-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1530 ($\nu_{C=N}$), 1420, 1400, 1370, 1350, 1200, 1065, 1035, 950 ($\nu_{W=O}$), 905 ($\nu_{W=O}$), 855, 810, 640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.47 (s, 3H, 4′-H), 2.03−2.40 (m, 2H, 1′-H), 2.35 (s, 6H, 5-CH_3), 2.35 (s, 3H, 5-CH_3), 2.53 (s, 3H, 3-CH_3), 2.68 (s, 6H, 3-CH_3), 3.55 (d, *J* = 10.9 Hz, 1H, 3′-H), 3.64 (d, *J* = 10.9 Hz, 1H, 3′-H), 5.90 (s, 3H, 4-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4 (2q, 5-CH_3), 12.6 (q, 5-CH_3), 14.9 (q, 3-CH_3), 15.0 (q, 3-CH_3), 15.4 (q, 3-CH_3), 27.4 (q, C-4′), 67.5 (t, C-1′, $^1J_{WC}$ = 117.8 Hz), 73.4 (t, C-3′), 74.0 (s, C-2′), 107.4 (d, C-4), 108.0 (d, C-4), 108.1 (d, C-4), 144.4 (s, C-3), 144.5 (s, C-3), 147.4 (s, C-3), 153.1 (s, C-5), 153.3 (s, C-5), 153.4 (s, C-5); MS (70 eV), *m*/*z* (%): 584 (7) [M^+], 513 (100) [$M^+ - C_4H_7O$], 418 (42) [$M^+ - C_4H_7O$ − pz*], 96 (62) [pz*H^+], 95 (56) [pz*$^{+}$], 41 (27) [$C_2H_3N^+$]. Anal. Calcd for $C_{19}H_{29}BN_6O_3W$ (584.1): C, 39.07; H, 5.00; N, 14.39. Found: C, 38.91; H, 5.15; N, 14.05.

Epoxidation of Vinyl Complex 2e with *m*CPBA: Dioxo[hydridotris(3,5-dimethyl-1-pyrazolyl)borato](2-methyl-1,2-oxiranylpropyl)tungsten(VI) (10e). To a suspension

of 54.0 mg (0.095 mmol) of the vinyl complex **2e** and 33.0 mg of sodium hydrogen carbonate (as buffer) in dichloromethane (15 mL) was added at room temperature (ca. 20 °C) within 1.5 h 49.0 mg (0.285 mmol) of *m*CPBA as solution in dichloromethane (10 mL). After stirring for additional 18.5 h (negative peroxide test with KI in HOAc), the reaction mixture was washed in sequence with a saturated solution of sodium hydrogen carbonate, water and a saturated solution of sodium hydrogen carbonate (each 15 mL). After drying over $MgSO_4$ and evaporation of the solvent (20 °C/20 Torr), the crude product was worked up by column chromatography on silica gel with diethyl ether/petroleum ether (2:1) as eluent. Besides 19.0 mg (35%) of the starting material, 20.0 mg (56%) of the epoxide **10e** was isolated as colorless powder. The conversion was 65%, the mass balance 71%. The use of flash chromatography on silica gel was not favorable since the product showed a tendency to hydrolyze on the column. R_f [diethyl ether/petroleum ether (2:1)] = 0.33; IR (KBr): 2940 (ν_{C-H}), 2900 (ν_{C-H}), 2530 (ν_{B-H}), 1530 ($\nu_{C=N}$), 1440, 1405, 1375, 1355, 1200, 1065, 1040, 950 ($\nu_{W=O}$), 910 ($\nu_{W=O}$), 855, 805, 640 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.40 (s, 3H, 3′-H or 4′-H), 1.78 (s, 3H, 3′-H or 4′-H), 2.37 (s, 3H, 5-CH_3), 2.39 (s, 6H, 5-CH_3), 2.51 (s, 6H, 3-CH_3), 2.89 (s, 3H, 3-CH_3), 3.81 (s,1H, 1′-H, $^2J_{WH}$ = 11.0 Hz), 5.89 (s, 1H, 4-H), 5.90 (s, 2H, 4-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.5 (2q, 5-CH_3), 12.7 (q, 5-CH_3), 14.0 (q, 3-CH_3), 14.6 (q, 3-CH_3), 15.6 (q, 3-CH_3), 25.2 (q, C-3′or C-4′), 26.3 (q, C-3′or C-4′), 61.0 (s, C-2′), 100.1 (d, C-1′, $^1J_{WC}$ = 119.4 Hz), 107.6 (d, C-4), 107.7 (d, C-4), 107.9 (d, C-4), 144.4 (s, C-3), 144.6 (s, C-3), 147.6 (s, C-3), 152.9 (s, C-5), 153.8 (s, C-5), 155.8 (s, C-5); MS (70 eV), *m*/*z* (%): 584 (20) [M^+], 513 (100) [$M^+ - C_4H_7O$], 418 (1) [$M^+ - C_4H_7O$ − pz*], 95 (13) [pz*$^+$], 69 (27) [$C_4H_5O^+$], 41 (27) [$C_2H_3N^+$]. Anal. Calcd for $C_{19}H_{29}BN_6O_3W$ (584.1): C, 39.07; H, 5.00; N, 14.39. Found: C, 39.11; H, 5.11; N, 14.22.

General Procedure C for the Oxyfunctionalization with TFD. To the tungsten complex dissolved in dichloromethane (50 mL) was added at once at 0 °C under an oxygen gas atmosphere under vigorous stirring a solution of TFD in trifluoroacetone. The reaction mixture became instantly light yellow and the peroxide test (KI in HOAc) was negative within a few seconds. After evaporation of the solvent (20 °C/20 Torr), the crude product was purified by flash chromatography on silica gel with diethyl ether/petroleum ether (2:1) as eluent.

Reaction of Homoallyl Complex 2a with TFD: Epoxide 10a. According to the general procedure C, from 15.0 mg (0.025 mmol) of the homoallyl complex **2a** and 0.11 mL of a 0.24 M solution of TFD (0.026 mmol) the epoxide **10a** was obtained in a yield of 83%. The conversion was 85% and the mass balance 86%.

Reaction of Vinyl Complex 2e with TFD: Bis(3,5-dimethyl-1-pyrazolyl)borato]dioxo[hydrido(3,5-dimethyl-4-hydroxy-1-pyrazolyl)(2-methyl-1-propenyl)tungsten-(VI) (11e). According to the general procedure C, from 31.0 mg (0.055 mmol) of the vinyl complex **2e** and 0.13 mL of a 0.35 M solution of TFD (0.046 mmol) were isolated on flash chromatography 14.0 mg (45%) of the starting material and 12.0 mg (70%) of the hydroxy compound **11e**. The conversion was 55%, the mass balance 84%. R_f [diethyl ether/petroleum ether (2:1)] = 0.21; IR (KBr): 3240 (ν_{O-H}), 2940 (ν_{C-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1570, 1525 ($\nu_{C=N}$), 1430, 1400, 1360, 1250, 1200, 1060, 940 ($\nu_{W=O}$), 890 ($\nu_{W=O}$), 780, 725, 680, 630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.80 (d, J = 1.1 Hz, 3H, 4′-H), 2.10 (s, 3H, 3′-H), 2.32 (s, 3H, 5-CH_3), 2.36 (s, 9H, 3-CH_3, 5-CH_3), 2.48 (s, 3H, 3-CH_3), 2.66 (s, 3H, 3-CH_3), 5.82 (s, 1H, 4-H), 5.90 (s, 1H, 4-H), 6.36 (br s, 1H, 1′-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 9.3 (q, 5-CH_3), 10.9 (q, 5-CH_3), 12.4 (q, 5-CH_3), 12.6 (q, 3-CH_3), 14.5 (q, 3-CH_3), 15.6 (q, 3-CH_3), 27.5 (q, C-3′), 30.0 (q, C-4′), 107.3 (d, C-4), 107.5 (d, C-4), 131.7 (s, C-4), 136.2 (s, C-3), 141.9 (s, C-3), 143.8 (s, C-3), 146.9 (s, C-5), 152.3 (s, C-2′), 153.3 (s, C-5), 153.8 (s, C-5), 167.9 (d, C-1′, $^1J_{WC}$ = 146.5 Hz); MS (70 eV), *m*/*z* (%): 584 (1) [M^+], 418 (1) [$M^+ - C_4H_7$ − pz*O], 111 (31) [pz*O$^+$], 96 (19) [pz*H$^+$], 95 (45) [pz*$^+$], 69 (45) [$C_4H_5O^+$], 57 (100) [$C_3H_8N^+$, $C_3H_6O^+$], 41 (28) [$C_2H_3N^+$]. Anal. Calcd for $C_{19}H_{29}BN_6O_3W$ (584.1): C, 39.07; H, 5.00; N, 14.39. Found: C, 38.81; H, 5.21; N, 13.95.

Reaction of Methyl Complex 2f with TFD: Bis(3,5-dimethyl-1-pyrazolyl)borato]dioxo[hydrido(3,5-dimethyl-4-hydroxy-1-pyrazolyl)methyltungsten(VI) (11f). According to the general procedure C, from 50.0 mg (0.095 mmol) of the methyl complex **2f** and 0.29 mL of a 0.32 M solution of TFD (0.093 mmol) were isolated on flash chromatography 34.0 mg (68%) of the starting material and 11.0 mg (65%) of the hydroxylated product **11f**. The conversion was 32%, the mass balance 88%. R_f [diethyl ether/petroleum ether (2:1)] = 0.21; IR (KBr): 3480 (ν_{O-H}), 2940 (ν_{C-H}), 2900 (ν_{C-H}), 2520 (ν_{B-H}), 1530 ($\nu_{C=N}$), 1430, 1350, 1250, 1200, 1065, 945 ($\nu_{W=O}$), 900 ($\nu_{W=O}$), 800 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.19 (s, 3H, 1′-H, $^2J_{WH}$ = 9.8 Hz), 2.32 (s, 3H, 5-CH_3), 2.34 (s, 3H, 5-CH_3), 2.36 (s, 3H, 5-CH_3), 2.61 (s, 3H, 3-CH_3), 2.62 (s, 3H, 3-CH_3), 2.68 (s, 3H, 3-CH_3), 4.60 (br s, 1H, BH), 5.86 (s, 1H, 4-H), 5.88 (s, 1H, 4-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 9.3 (q, 5-CH_3), 11.2 (q, 5-CH_3), 12.4 (q, 5-CH_3), 12.6 (q, 3-CH_3), 14.1 (q, 3-CH_3), 14.6 (q, 3-CH_3), 29.7 (q, C-1′, $^1J_{WC}$ = 101.8 Hz), 107.5 (d, C-4), 107.7 (d, C-4), 131.6 (s, C-4), 136.5 (s, C-3), 141.6 (s, C-3), 143.9 (s, C-3), 147.1 (s, C-5), 153.2 (s, C-5), 153.7 (s, C-5); MS (70 eV), *m*/*z* (%): 544 (6) [M^+], 529 (100) [$M^+ - CH_3$], 433 (9) [$M^+ - CH_2$ − pz*O], 419 (84) [$M^+ - CH_2$ − pz*O], 95 (6) [pz*$^+$]. Anal. Calcd for $C_{16}H_{25}BN_6O_3W$ (544.1): C, 35.32; H, 4.63; N, 15.45. Found: C, 35.00; H, 4.16; N, 15.50.

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