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$B(C_6F_5)_3$ Activation of Oxo Tungsten Complexes That Are Relevant to Olefin Metathesis

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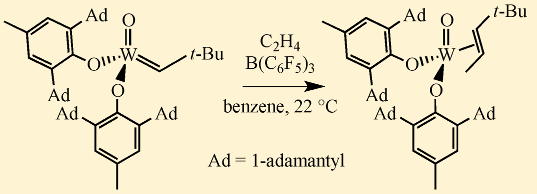
Supporting Information

ABSTRACT: We have found that coordination of $B(C_6F_5)_3$ to an oxo ligand in tungsten oxo alkylidene bis(aryloxide) complexes, where the aryloxide is O-2,6-(mesityl)$_2$C$_6$H$_3$ (HMTO) or 2,6-diadamantyl-4-methylphenoxide (dAdPO), accelerates the formation of metallacyclobutane complexes from alkylidenes as well as the rearrangement of metallacyclobutane complexes. In contrast, a tungstacyclopentane complex, $W(O)(C_4H_8)(OHMT)_2$, is relatively stable toward rearrangement in the presence of $B(C_6F_5)_3$. A careful balance of steric factors allows a single isomer of W(O)(*trans*-4,4-dimethylpent-2-ene)(dAdPO)$_2$ to be formed from W(O)(CH-*t*-Bu)(dAdPO)$_2$ in the presence of both ethylene and $B(C_6F_5)_3$.



In the early days of the synthesis of olefin metathesis catalysts from Mo(VI) and W(VI) oxo complexes,[1] Osborn proposed[1g−i] that coordination of AlX_3 and other Lewis acids to oxo ligands in W(VI) oxo neopentyl complexes could promote α-hydrogen abstraction reactions[2] to give oxo alkylidene complexes. The alkylidene complexes that actually were formed were oxo-free W(CH-*t*-Bu)(OR)$_2$X$_2$ complexes (X = Cl, Br). These species were then activated by Lewis acids such as $GaBr_3$ through attack on the halide to produce [W(CH-*t*-Bu)(OR)$_2$X][GaBr$_3$X] complexes, which were shown to be highly active olefin metathesis catalysts.[1j] Therefore, Lewis acid coordination to an oxo ligand is likely to be a central feature of olefin metathesis by classical catalysts formed from Mo or W oxo complexes and alkylating agents. In 1980 well-defined oxo alkylidene complexes of the type W(O)(CH-*t*-Bu)L$_2$Cl$_2$ (where L = PMe$_3$, for example) were prepared, isolated, and shown to metathesize olefins readily in the presence of $AlCl_3$.[3]

Although several structural studies of $B(C_6F_5)_3$ bound to various metal and main-group X═O bonds have been published,[4] the consequences of "activation" of the metal through coordination of a relatively well-behaved Lewis acid such as $B(C_6F_5)_3$ to the oxo ligand in oxo alkylidene complexes have not been explored to our knowledge. We have found that W(O)(CH-*t*-Bu)(OHMT)(Me$_2$Pyr)(PMe$_2$Ph) (OHMT = O-2,6-(mesityl)$_2$C$_6$H$_3$, Me$_2$Pyr = 2,5-dimethylpyrrolide) reacts with $B(C_6F_5)_3$ to give $PhMe_2PB(C_6F_5)_3$ and a complex in which $B(C_6F_5)_3$ is reversibly bound to the oxo ligand and that addition of 2 equivalents of $B(C_6F_5)_3$ to W(O)(CH-*t*-Bu)(OHMT)(Me$_2$Pyr)(PMe$_2$Ph) yields a catalyst that converts 90% of 1-octene to 7-tetradecene in 1 h at 22 °C (0.2 mol % loading). In contrast to the metathesis homocoupling of 1-octene by W(O)(CH-*t*-Bu)(OHMT)(Me$_2$Pyr)(PMe$_2$Ph) alone, which gives essentially only (*Z*)-7-tetradecene, the 7-tetradecene formed in the relatively rapid reaction in the presence of $B(C_6F_5)_3$ is only 20% *Z*.[5] Therefore, we wanted to explore reactions between a relatively well behaved Lewis acid ($B(C_6F_5)_3$) and a variety of tungsten oxo complexes that are relevant to olefin metathesis, in particular, alkylidene and metallacyclobutane complexes.

The presence of a relatively small oxo ligand instead of an imido ligand allows W(O)(CH-*t*-Bu)(OHMT)$_2$ (**1a**) to be prepared by treating W(O)(CH-*t*-Bu)Cl$_2$(PMe$_2$Ph)$_2$ with 2 equiv of LiOHMT.[6] W(O)(CH-*t*-Bu)(OHMT)$_2$ reacts with ethylene to give the square-pyramidal metallacyclobutane complex W(O)(C$_3$H$_6$)(OHMT)$_2$, from which ethylene is lost *in vacuo* to give W(O)(CH$_2$)(OHMT)$_2$ (**1b**), which is relatively stable toward bimolecular decomposition and which has been crystallographically characterized.[6] Since the presence of two sterically demanding OHMT ligands appears to prevent facile bimolecular reactions of bis(OHMT) species, bis(OHMT) species would appear to offer the best opportunity to carry out mechanistic studies that concern activation of the metal through addition of $B(C_6F_5)_3$ to the oxo ligand. The only other bis(aryloxide) complexes in which the aryloxide is a sterically demanding 2,6-terphenoxide are complexes of the type Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(ODFT)$_2$ (ODFT = O-2,6-(C$_6$F$_5$)$_2$C$_6$H$_3$) and W(NC$_6$F$_5$)(CH-*t*-Bu)(ODFT)$_2$.[7]

Addition of 0.5 equiv of $B(C_6F_5)_3$ to **1b** in CD_2Cl_2 at room temperature results in collapse of the two methylidene proton NMR resonances in **1b** into the baseline. Cooling the sample resulted in reappearance of the methylidene resonances for **1b** along with a broad resonance for a methylidene ligand in a $B(C_6F_5)_3$ adduct of **1b** at ~8.0 ppm (Figure 1). At −80 °C the resonance at ~8.0 ppm is resolved into two broadened resonances at 8.91 and 7.27 ppm that we ascribe to H_{syn} and H_{anti}, respectively, in a methylidene complex, most likely one in which $B(C_6F_5)_3$ is bound to the oxo ligand. Therefore, the four resonances found at −80 °C can be ascribed to methylidene

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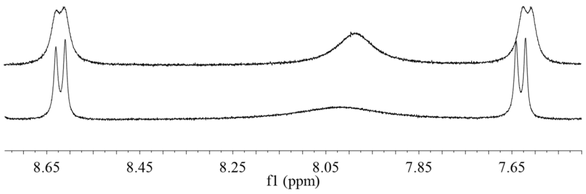
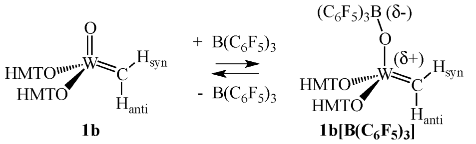


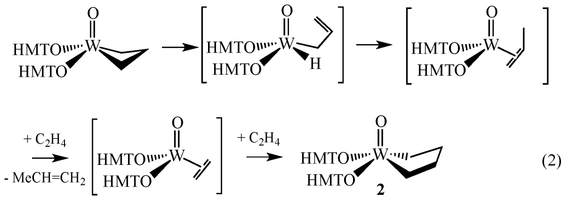
Figure 1. Alkylidene region of the proton NMR spectrum of a mixture of $W[OB(C_6F_5)_3](CH_2)(OHMT)_2$ and $W(O)(CH_2)(OHMT)_2$ in CD_2Cl_2 at −40 °C (top) and −50 °C (bottom).

proton resonances in $W(O)(CH_2)(OHMT)_2$ and $W[OB(C_6F_5)_3](CH_2)(OHMT)_2$ (eq 1); the ratio of **1b** to **1b**[$B(C_6F_5)_3$] is approximately 1:1 at −80 °C. (An accurate ratio is limited by integration errors.) Note that interconversion of the syn and anti protons in the methylidene ligand in **1b**[$B(C_6F_5)_3$] is fast on the NMR time scale at −50 °C (Figure 1), even though the rate of interconversion of **1b** and **1b**[$B(C_6F_5)_3$] at that temperature is slow.



1b **1b[B(C$_6$F$_5$)$_3$]** (1)

Addition of 1 equiv of $B(C_6F_5)_3$ to $W(O)(CH\text{-}t\text{-}Bu)(OHMT)_2$ (**1a**) in C_6D_6 at room temperature resulted in a slight broadening of the alkylidene α proton resonance, but essentially no shift in the position of the alkylidene resonance, consistent with only a small amount of **1a**[$B(C_6F_5)_3$] being formed at room temperature. We presume that little $B(C_6F_5)_3$ is bound to the oxo ligand in **1a** because of the greater steric demand of the neopentylidene ligand relative to a methylidene ligand. Addition of ethylene (1 atm) to a mixture of $B(C_6F_5)_3$ and **1a** in C_6D_6 led to rapid formation of propylene and a metallacyclopentane complex, $W(O)(C_4H_8)(OHMT)_2$ (**2**), over a period of a few minutes (eq 2). No metallacyclobutane intermediate could be observed. The formation of propylene suggests that the intermediate metallacyclobutane complex rearranges to a propylene complex in the presence of $B(C_6F_5)_3$. Ethylene then displaces propylene to form an ethylene complex and ultimately **2** (eq 2). The ring proton resonances in **2** are found at 1.42 ppm ($C_\alpha H$) and 2.14 ppm ($C_\beta H$) in its proton NMR spectrum in C_6D_6 at 22 °C. Several high oxidation state metallacyclopentane complexes of Mo and W have been reported.[8] Only one type of α and one type of β metallacycle proton resonance suggests that **2** is highly fluxional[8c] on the NMR time scale.



(2)

Compound **2** can be isolated as a yellow solid from acetonitrile. An X-ray study reveals that the metallacyclopentane ring is disordered between two orientations (Figure 2; WC_4 ring disorder not shown). The W−C_α distances are 2.158(7) Å and 2.171(5) Å. (See the Supporting Information for complete details.) The metal center adopts a geometry that is approximately halfway between TBP and SP ($\tau = 0.44$)[9] with a W=O distance of 1.693(3) Å.

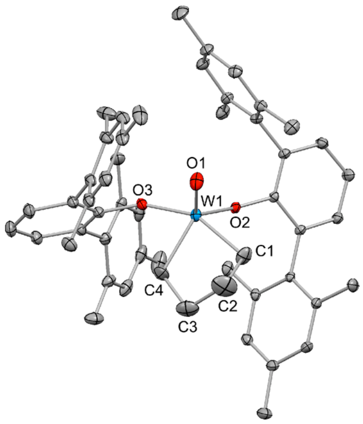


Figure 2. Thermal ellipsoid plot (50% probability) of $WO(C_4H_8)(OHMT)_2$ (**2**). Hydrogen atoms have been omitted for clarity. Solvent molecules are not shown.

Addition of $^{13}C_2H_4$ to a solution of **2** in C_6D_6 at room temperature led to the slow incorporation of $^{13}C_2H_4$ into the metallacyclopentane ring over a period of 16 h. At 60 °C under 1 atm of $^{13}C_2H_4$ several hours are required to complete the exchange of $^{13}C_2H_4$ into the WC_4H_8 ring. The rate of incorporation of $^{13}C_2H_4$ into the WC_4H_8 ring in the presence of $B(C_6F_5)_3$ at both 22 and 60 °C is qualitatively the same as the rate in the absence of $B(C_6F_5)_3$, consistent with the loss of ethylene from the WC_4H_8 ring being the slow step in the exchange process. The rate of loss of ethylene from **2** does not appear to increase in the presence of $B(C_6F_5)_3$.

When 0.2 equiv of $B(C_6F_5)_3$ is added to a solution of $W(O)(^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(OHMT)_2$ (Figure 3a; ArO = HMTO) in the *absence* of $^{13}C_2H_4$ at 22 °C, the solution's color changes immediately from yellow to orange and a mixture

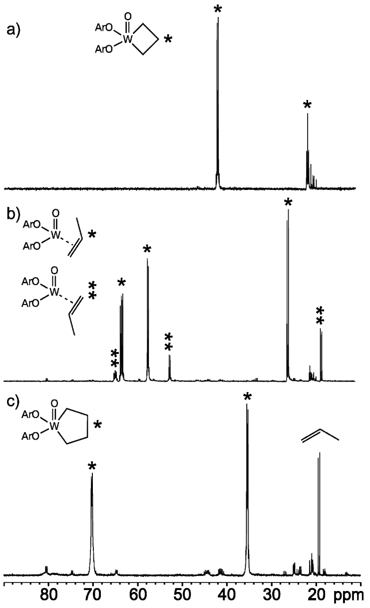
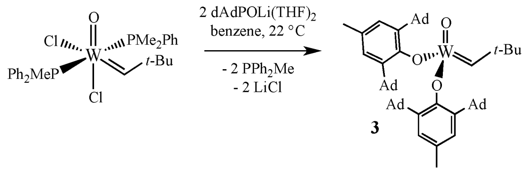


Figure 3. ^{13}C NMR spectra: (a) selected region of the spectrum of $W(O)(^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(OHMT)_2$ in C_6D_6 in the absence of $^{13}C_2H_4$; (b) the sample in (a) after addition of 0.2 equiv of $B(C_6F_5)_3$; (c) the sample in (b) after exposure to 1 atm of $^{13}C_2H_4$ for 3 h.

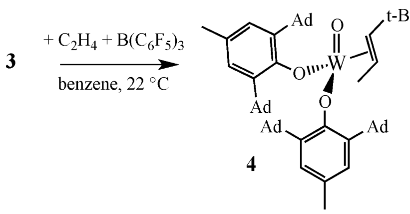
of two ^{13}C-labeled propylene complexes are formed in a ratio of approximately 5:1 (Figure 3b). Since the propylene's C=C axis lies approximately perpendicular to the W=O axis in $W(O)(^{13}CH_2{=}^{13}CH^{13}CH_3)(OHMT)_2$ (compare with Mo imido olefin complexes[8c]) the two possible isomers must contain the methyl group "up" or "down" with respect to the oxo ligand (Figure 3b). Addition of 1 atm of $^{13}C_2H_4$ at room temperature to a solution of $W(O)(^{13}CH_2{=}^{13}CH^{13}CH_3)(OHMT)_2$ resulted in a color change back to yellow and formation of **2** and free propylene (Figure 3c). These results are consistent with rearrangement of a metallacyclobutane complex to a propylene complex through cleavage of a β-CH bond to give a σ- or a π-allyl hydride intermediate and an acceleration of that process in the absence of ethylene and the presence of $B(C_6F_5)_3$. We attribute the acceleration to coordination of $B(C_6F_5)_3$ to the oxo ligand.

We made and began to explore the 2,6-diadamantyl-4-methylphenoxide (dAdPO) ligand as a sterically demanding 2,6-disubstituted phenoxide alternative to HMTO. The reaction between W(O)(CH-*t*-Bu)$Cl_2(PPh_2Me)_2$ and 2 equiv of dAdPOLi$(THF)_2$ in benzene at room temperature led to isolation of yellow W(O)(CH-*t*-Bu)$(dAdPO)_2$ (**3**) in 65% yield (eq 3). The alkylidene is in the syn orientation ($^1J_{C\alpha H}$ = 118 Hz), and the two phenoxides are equivalent on the proton NMR time scale at 22 °C. Complex **3** does not react with ethylene (1 atm) in C_6D_6 at room temperature, presumably due to the high degree of steric hindrance.



(3)

Addition of 1 equiv of $B(C_6F_5)_3$ to **3** in C_6D_6 did not cause any change in the ^{1}H NMR spectrum. However, in the presence of *both* $B(C_6F_5)_3$ and ethylene (1 atm), a solution of **3** changed from yellow to orange-red over a period of 2 h and a single product, W(O)(*trans*-4,4-dimethylpent-2-ene)$(dAdPO)_2$ (**4**), was formed (eq 4), according to NMR data and an X-ray structure (vide infra). Characteristic features of the proton NMR spectrum of **4** include inequivalent phenoxide ligands and a doublet with J_{WH} satellites at 2.98 ppm (J_{HH} = 12 Hz) for one of the olefinic protons. When C_2D_4 was employed in place of C_2H_4, the doublet at 2.98 ppm was replaced by a singlet (with J_{WC} satellites), consistent with one of the two olefinic protons in the olefin in **4** now being D, presumably that on C(2) of the *trans*-4,4-dimethylpent-2-ene. Complex **4** could be isolated as an orange-red powder in 53% yield.



(4)

Single crystals of **4** were grown by layering a solution in pentane with acetonitrile and storing the sample at −30 °C. An X-ray diffraction study confirmed that **4** is the *trans*-4,4-dimethylpent-2-ene tungsten(IV) oxo bis(phenoxide) complex (Figure 4). No bond lengths or angles are unusual. The C1−C2 bond of the olefin is oriented ~90° with respect to the W1−O1 bond, as expected on the basis of structurally characterized examples of Mo imido olefin complexes.[8c] The O1−W1−C1 angle is 96.7°, and the O1−W1−C2 angle is 105.7°, which suggests that the olefin is twisted 4.5° from an orthogonal (90°) relationship between the W1−O1 and C1−C2 vectors, presumably in response to the steric hindrance within the primary coordination sphere.

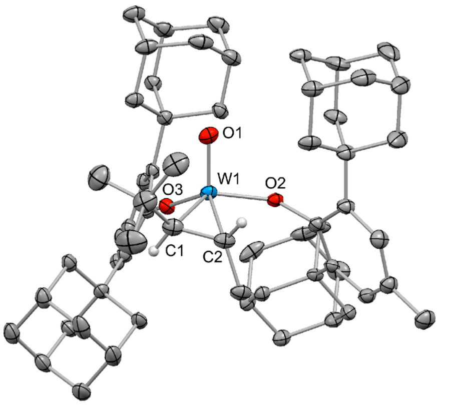
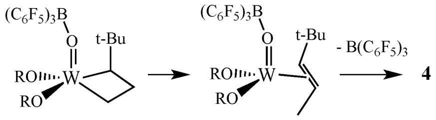


Figure 4. Thermal ellipsoid plot (50% probability) of W(O)(*trans*-4,4-dimethylpent-2-ene)$(dAdPO)_2$ (**4**). Hydrogen atoms have been omitted for clarity except for the olefinic hydrogens. Solvent molecules are not shown. Selected bond distances (Å) and angles (deg): W1−C1 = 2.113(4), W1−C2 = 2.148(4), C1−C2 = 1.468(7); C1−W1−C2 = 40.1(2), O1−W1−O2 = 102.4(2), O1−W1−O3 = 118.5(2), O3−W1−O2 = 108.9(2).

We propose that the *α-tert*-butyl-substituted metallacyclobutane forms from **3** in the presence of ethylene only when $B(C_6F_5)_3$ is coordinated to the oxo ligand (eq 5). The *α-tert*-butyl-substituted metallacyclobutane ring then rearranges via a stereoselective 2,1-shift of the β proton to α carbon C(1) to give **4**. The intermediate in the rearrangement is proposed to be a σ-allyl hydride complex, of which two basic types are possible, as shown in Figure 5 (**A** and **B**). By analogy with rearrangements of metallacyclopentane and metallacyclobutane complexes of tantalum,[11] the final step can be viewed either as a "reductive elimination" of olefin from **A** or as a "reinsertion" of the C=C bond into the metal−hydride bond in **B** to give bound *trans*-4,4-dimethylpent-2-ene. An alternative is the π-allyl hydride **C**. We cannot know whether the observed orientation of the olefin, relative to the alternative with the methyl group "up" and the *tert*-butyl group "down", is a kinetic or a thermodynamic phenomenon, even though rotation of an



(5)

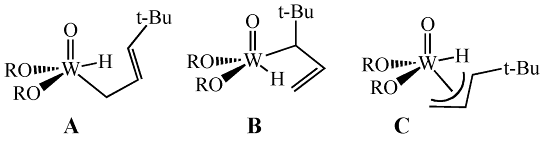


Figure 5. Plausible σ-allyl hydride or π-allyl hydride intermediates in the metallacyclobutane rearrangement that produces **4**.

olefin in the circumstances found in **4** should be slow on some chemical time scale.[8c]

A significant unknown during the formation of **4** is when $B(C_6F_5)_3$ is coordinated to the oxo ligand and when it is not. We propose that $B(C_6F_5)_3$ is required for reaction of the alkylidene with ethylene and for rearrangement of the metallacyclobutane. We might propose that $B(C_6F_5)_3$ dissociates from the oxo ligand before ethylene can displace *trans*-4,4-dimethylpent-2-ene via an ethylene/*trans*-4,4-dimethylpent-2-ene intermediate, although such a bis(olefin) intermediate apparently is not viable for steric reasons whether $B(C_6F_5)_3$ is coordinated to the oxo ligand or not. Outright dissociation of *trans*-4,4-dimethylpent-2-ene from **4** to give "W(O)(dAdPO)$_2$" clearly also is not viable under the reaction conditions, in spite of the steric demands of the *trans*-4,4-dimethylpent-2-ene ligand. Finally, we cannot exclude the possibility that the β hydrogen has migrated to an oxo or an alkoxide oxygen in the intermediate allyl complex, although the oxidation state of the metal in that circumstance would be W(IV) instead of W(VI), which is not likely to be favorable.

The observations described here establish that $B(C_6F_5)_3$ accelerates formation of a metallacyclobutane from an alkylidene and rearrangement of a metallacyclobutane to an olefin. This rearrangement takes place in the absence of ethylene and so cannot involve insertion of ethylene into the hydride, an option that has been discussed recently in detailed theoretical studies.[10] We have already shown in a preliminary fashion that $B(C_6F_5)_3$ accelerates the rate of one olefin metathesis reaction.[5] We ascribe acceleration of all three processes to binding of $B(C_6F_5)_3$ to an oxo ligand. In light of these observations, it is not obvious why **2** is so stable to β-hydride rearrangement of the metallacyclopentane ring in the presence of $B(C_6F_5)_3$. However, it should be noted that tantalacyclopentane rings also are more resistant to rearrangement to an olefin than tantalacyclobutane rings.[11] It remains to be established if binding of $B(C_6F_5)_3$ to an oxo ligand eventually results in abstraction of the oxo ligand and formation of metathesis-inactive products or other types of metathesis-active complexes. At this stage we also do not know whether there is any trend in terms of acceleration of the rate of metathesis reactions versus metallacyclobutane rearrangement by $B(C_6F_5)_3$ or in terms of the stereoselectivity of a metathesis reaction in the presence versus the absence of $B(C_6F_5)_3$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental details for all compounds and crystal parameters and data acquisition parameters for complexes **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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