B(C₆F₅)₃ Activation of Oxo Tungsten Complexes That Are Relevant to Olefin Metathesis

Dmitry V. Peryshkov, William P. Forrest, Richard R. Schrock,* Stacey J. Smith, and Peter Müller

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Supporting Information

ABSTRACT: We have found that coordination of B(C₆F₅)₃ to an oxo ligand in tungsten oxo alkylidene bis(aryloxide) complexes, where the aryloxide is O-2,6-(mesityl)C₆H₅ (HMTO) or 2,6-diadamantyl-4-methylphenoxy (dAdPO), accelerates the formation of metallacyclobutane complexes from alkylidenes as well as the rearrangement of metallacyclopentane complexes. In contrast, a tungstacyclopentane complex, W(O)(C₄H₈)(OHMT)₂, is relatively stable toward rearrangement in the presence of B(C₆F₅)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)(CH₄-t-Bu)(dAdPO)₂ in the presence of both ethylene and B(C₆F₅)₃.

In the early days of the synthesis of olefin metathesis catalysts from Mo(VI) and W(VI) oxo complexes, Osborn proposed that coordination of AlX₃ and other Lewis acids to oxo ligands in W(VI) oxo neopentyl complexes could promote α-hydrogen abstraction reactions to give oxo alkylidene complexes. The alkylidene complexes that actually were formed were oxo-free W(CH₄-t-Bu)(OR)₂X₂ complexes (X = Cl, Br). These species were then activated by Lewis acids such as GaBr₃, through attack on the halide to produce [W(CH₄-t-Bu)](OR)₂X₃[GaBr₅X₃] complexes, which were shown to be highly active olefin metathesis catalysts. 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)(CH₄-t-Bu)₄Cl₂ (where L = PMe₃, for example) were prepared, isolated, and shown to metatize olefins readily in the presence of AlCl₃.

Although several structural studies of B(C₆F₅)₃ bound to various metal and main-group X=O bonds have been published, the consequences of “activation” of the metal through coordination of a relatively well-behaved Lewis acid such as B(C₆F₅)₃ to the oxo ligand in oxo alkylidene complexes have not been explored to our knowledge. We have found that W(O)(CH₄-t-Bu)(OHMT)(Me₂Pyr)(PMe₂Ph) (OHMT = O-2,6-(mesityl)C₆H₅, Me₂Pyr = 2,5-dimethylpyrrole) reacts with B(C₆F₅)₃ to give PhMe₂PB(C₆F₅)₃ and a complex in which B(B(C₆F₅)₃)₃ is reversibly bound to the oxo ligand and that addition of 2 equivalents of B(C₆F₅)₃ to W(O)(CH₄-t-Bu)(OHMT)(Me₂Pyr)(PMe₂Ph) 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)(CH₄-t-Bu)(OHMT)(Me₂Pyr)(PMe₂Ph) alone, which gives essentially only (Z)-7-tetradecene, the 7-tetradecene formed in the relatively rapid reaction in the presence of B(C₆F₅)₃ is only 20% Z. Therefore, we wanted to explore reactions between a relatively well behaved Lewis acid (B(C₆F₅)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)(CH₄-t-Bu)(OHMT)₂ (1a) to be prepared by treating W(O)(CH₄-t-Bu)Cl₂(PMe₂Ph)₂ with 2 equiv of LiOHMT. W(O)(CH₄-t-Bu)(OHMT)₂ reacts with ethylene to give the square-pyramidal metallacyclobutane complex W(O)(C₆H₅)₂(OHMT)₂, from which ethylene is lost in vacuo to give W(O)(CH₂)₂(OHMT)₂ (1b), which is relatively stable toward bimolecular decomposition and which has been crystallographically characterized. 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(C₆F₅)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(NC₆F₅)(CHCMe₂Ph)(ODFT)₂ (ODFT = O-2,6-(C₆F₅)₂C₆H₃) and W(NC₆F₅)(CH₄-t-Bu)(ODFT)₂. Addition of 0.5 equiv of B(C₆F₅)₃ to 1b in CD₂Cl₂ at room temperature results in collapse of the two methyldiene proton NMR resonances in 1b into the baseline. Cooling the sample resulted in reappearance of the methyldiene resonances for 1b along with a broad resonance for a methyldiene ligand in a B(C₆F₅)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 Hsyn and Hanti, respectively, in a methyldiene complex, most likely one in which B(C₆F₅)₃ is bound to the oxo ligand. Therefore, the four resonances found at ~80 °C can be ascribed to methyldiene...
proton resonances in W(O)(CH2)(OHMT)2 and W[OB-(C6F5)3](CH2)(OHMT)2 (eq 1); the ratio of 1b to 1b[B-(C6F5)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(C6F5)3] is fast on the NMR time scale at −50 °C (Figure 1), even though the rate of interconversion of 1b and 1b[B(C6F5)3] at that temperature is slow.

Addition of 1 equiv of B(C6F5)3 to W(O)(CH-t-Bu)- (OHMT)2 (1a) in C6D6 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(C6F5)3] being formed at room temperature. We presume that little B(C6F5)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(C6F5)3 and 1a in C6D6 led to rapid formation of propylene and a metallacyclopentane complex, W(O)(C4H8)(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(C6F5)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 (CαH) and 2.14 ppm (CβH) in its proton NMR spectrum in C6D8 at 22 °C. Several high oxidation state metallacyclopentane complexes of Mo and W have been reported. Only one type of α and one type of β metallacycle proton resonance suggests that 2 is highly fluxional on the NMR time scale.

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; WC4 ring disorder not shown). The W–Cα 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 (τ = 0.44) with a W=C distance of 1.693(3) Å.

Addition of 13C2H4 to a solution of 2 in C6D6 at room temperature led to the slow incorporation of 13C2H4 into the metallacyclopentane ring over a period of 16 h. At 60 °C under 1 atm of 13C2H4 several hours are required to complete the exchange of 13C2H4 into the WC4H8 ring. The rate of incorporation of 13C2H4 into the WC4H8 ring in the presence of B(C6F5)3, at both 22 and 60 °C is qualitatively the same as the rate in the absence of B(C6F5)3, consistent with the loss of ethylene from the WC4H8 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(C6F5)3.

When 0.2 equiv of B(C6F5)3 is added to a solution of W(O)(13CH2-13CH2-13CH2)(OHMT)2 in the absence of 13C2H4 at 22 °C, the solution’s color changes immediately from yellow to orange and a mixture
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)(13CH$_2$=13CH=13CH)$_2$(OHMT)$_2$ (compare with Mo imido olefin complexes$^{6}$) 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$_2$H$_4$ at room temperature to a solution of W(O)(13CH$_2$=13CH=13CH)$_2$(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 $\beta$-CH bond to give a $\sigma$- or a $\pi$-allyl hydride intermediate and an acceleration of that process in the absence of ethylene and the presence of B(C$_6$F$_5$)$_3$. We attribute the acceleration to coordination of B(C$_6$F$_5$)$_3$ to the oxo ligand.

We made and began to explore the 2,6-diadamantyl-4-methylphenoxy (dAdPO) ligand as a sterically demanding 2,6-disubstituted phenoxy alternative to HMTO. The reaction between W(O)(CH$_{t}$-Bu)Cl$_2$(PPh$_2$Me)$_2$ and 2 equiv of dAdPOLi(THF)$_2$ in benzene at room temperature led to isolation of yellow W(O)(13CH$_{t}$-Bu)(dAdPO)$_2$ (3) in 65% yield (eq 3). The alkylidene is in the syn orientation ($^\gamma$C$_{3h}$H = 118 Hz), and the two phenoxyis are equivalent on the proton NMR time scale at 22 °C. Complex 3 does not react with ethylene (1 atm) in C$_6$D$_6$ at room temperature, presumably due to the high degree of steric hindrance.

Addition of 1 equiv of B(C$_6$F$_5$)$_3$ to 3 in C$_6$D$_6$ did not cause any change in the $^1$H NMR spectrum. However, in the presence of both B(C$_6$F$_5$)$_3$ 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 phenoxy ligands and a doublet with $J_{W,H}$ satellites at 2.98 ppm ($J_{W,H} = 12$ Hz) for one of the olefinic protons. When C$_6$D$_6$ was employed in place of C$_6$H$_{14}$ the doublet at 2.98 ppm was replaced by a singlet (with $J_{W,C}$ 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.

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(phenoxy) complex (Figure 4). No bond lengths or angles are unusual. The C1−C2
olefin in the circumstances found in 4 should be slow on some chemical time scale.  

A significant unknown during the formation of 4 is when B(C₆F₅)₃ is coordinated to the oxo ligand and when it is not. We propose that B(C₆F₅)₃ is required for reaction of the alkylidene with ethylene and for rearrangement of the metallacyclobutane. We might propose that B(C₆F₅)₃ dissociates from the oxo ligand before ethylene can displace trans-4,4-dimethylpent-2-ene via an ethylene/alkylidene with ethylene and for rearrangement of the metallacyclobutane rings also are more resistant to rearrangement to an oxo ligand and when it is not. Outright dissociation of trans-4,4-dimethylpent-2-ene from B(C₆F₅)₃ is coordinated to the oxo ligand and when it is not. We propose that B(C₆F₅)₃ is required for reaction of the alkylidene with ethylene and for rearrangement of the 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.  

The observations described here establish that B(C₆F₅)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. 

We have already shown in a preliminary fashion that B(C₆F₅)₃ accelerates the rate of one olefin metathesis reaction. We ascribe acceleration of all three processes to binding of B(C₆F₅)₃ to an olefin 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(C₆F₅)₃. However, it should be noted that tantalacyclopentane rings also are more resistant to rearrangement to an olefin than tantalacyclobutane rings. It remains to be established if binding of B(C₆F₅)₃ to an olefin 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(C₆F₅)₃ or in terms of the stereoselectivity of a metathesis reaction in the presence versus the absence of B(C₆F₅)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.

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail for R.R.S.: rrs@mit.edu.*

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We are grateful to the National Science Foundation (CHE-111133 to R.R.S.) for financial support. We also thank the National Science Foundation for departmental X-ray diffraction instrumentation (CHE-0946721).

## REFERENCES


