

Z-Selective Olefin Metathesis Reactions Promoted by Tungsten Oxo Alkylidene Complexes

Dmitry V. Peryshkov,[†] Richard R. Schrock,^{*,†} Michael K. Takase,[†] Peter Müller,[†] and Amir H. Hoveyda[‡]

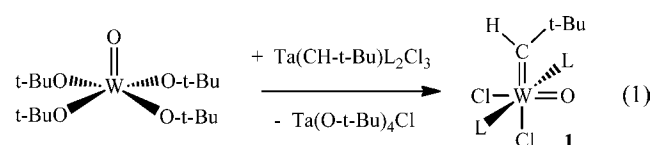
[†]Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

[‡]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

S Supporting Information

ABSTRACT: Addition of LiOHMT (OHMT = *O*-2,6-dimesitylphenoxide) to $W(O)(CH-t-Bu)(PMe_2Ph)_2Cl_2$ led to $WO(CH-t-Bu)Cl(OHMT)(PMe_2Ph)$ (**4**). Subsequent addition of $Li(2,5-Me_2C_4H_2N)$ to **4** yielded yellow $W(O)(CH-t-Bu)(OHMT)(Me_2Pyr)(PMe_2Ph)$ (**5**). Compound **5** is a highly effective catalyst for the *Z*-selective coupling of selected terminal olefins (at 0.2% loading) to give product in >75% yield with >99% *Z* configuration. Addition of 2 equiv of $B(C_6F_5)_3$ to **5** afforded a catalyst activated at the oxo ligand by $B(C_6F_5)_3$. $5 \cdot B(C_6F_5)_3$ is a highly active catalyst that produces thermodynamic products (~20% *Z*).

Early in the development of olefin metathesis catalysts that contain tungsten, it was shown that metathetically more active and reproducible systems were produced when tungsten oxo complexes were deliberately employed or were present as impurities in WCl_6 .¹ The possibility that oxo alkylidene complexes, e.g., $W(O)(CHR)X_2$ ($X = \text{chloride, alkoxide, etc.}$), are the true catalysts in at least some of the “classical” olefin metathesis systems became more likely when **1** ($L = PMe_3$ and other phosphines) was prepared and isolated in good yield (eq 1).² Compound **1** was the first high-oxidation-state tungsten alkylidene complex that would both (i) metathesize terminal and internal olefins (in the presence of a trace of $AlCl_3$) and (ii) produce a new alkylidene that could be observed as a consequence of olefin metathesis.

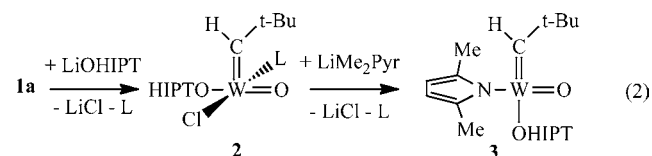


By the time **1** was discovered, tantalum alkylidene complexes had been turned into functional olefin metathesis catalysts through use of alkoxides as ligands.³ Therefore, although some attempts were made to prepare a $W(O)(CH-t-Bu)(OR)_2$ species from **1**, no bisalkoxide species could be isolated. In view of the synthetic problems encountered upon attempted alkylation of oxo complexes, including removal of the oxo ligand entirely,¹¹ and to protect alkylidenes against bimolecular decomposition, attention turned to the synthesis of imido alkylidene complexes of W and Mo, especially those containing a phenylimido ligand such as $N(2,6-i-Pr_2C_6H_3)$.⁴ Consequently,

interest in oxo alkylidene complexes in the last 25 years has been sparse.⁵

The most recent development in Mo and W imido alkylidene chemistry has been monoaryloxo monopyrrolide (MAP) complexes.⁶ One of the most interesting discoveries is the ability of some MAP catalysts to promote *Z*-selective metathesis reactions as a consequence of the presence of a relatively “large” aryloxo and “small” imido group.⁷ The preferred metal for *Z*-selective couplings of terminal olefins at this time appears to be tungsten, and the most successful aryloxo ligand has been *O*-2,6-(2,4,6-triisopropylphenyl) $_2C_6H_3$ or OHIPT. (The more active molybdenum complexes⁸ appear to isomerize the *Z* product to *E*.) It has been proposed that the high steric demands of the OHIPT ligand force all of the metallacyclobutane substituents to one side of the metallacycle ring and therefore allow only *Z* products to form. Since an oxo ligand is smaller than any NR ligand, the question arose as to whether MAP versions of tungsten oxo alkylidene complexes would be useful *Z*-selective catalysts.

We chose to attempt to prepare $W(O)(CH-t-Bu)(OHIPT)(Me_2Pyr)$ ($Me_2Pyr = 2,5\text{-dimethylpyrrolide}$) from $W(O)(CH-t-Bu)(PMe_2Ph)_2Cl_2$ (**1a**), hoping that both PMe_2Ph ligands would dissociate from the metal in the crowded coordination sphere. The reaction between $WO(CH-t-Bu)Cl_2(PMe_2Ph)_2$ and LiOHIPT in benzene at 22 °C for 14 h led to isolation of off-white $WO(CH-t-Bu)Cl(OHIPT)(PMe_2Ph)$ (**2**) in 60% yield (eq 2). Two isomers of **2** were present in a 3:2 ratio according to ¹H, ¹³C, and ³¹P NMR spectra. Both were determined to be *syn*-alkylidenes on the basis of $J_{C\alpha H}$ values for the alkylidene of 123 Hz (major isomer) and 117 Hz (minor isomer). The phosphine remains bound to tungsten on the NMR time scale ($J_{PW} = 420$ and 379 Hz, respectively) at 22 °C. An X-ray crystal structure [see the Supporting Information (SI)] revealed a distorted square-pyramidal geometry with the neopentylidene ligand in the apical position and the phosphine ligand trans to chloride. The alkylidene was found to be disordered over the *syn* and *anti* orientations in a 91:9 ratio.



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The other isomer of **2** could be (for example) one in which the OHIPT and Cl ligands (eq 2) have switched positions.

Treatment of **2** with Li(Me₂Pyr) in benzene at 60 °C for 16 h led to formation of yellow W(O)(CH-t-Bu)(OHIPT)(Me₂Pyr) (**3**) in 80% isolated yield. An X-ray structure of **3** showed it to have a pseudotetrahedral geometry, a *syn*-alkylidene, and an η¹-Me₂Pyr ligand (Figure 1). We had considered

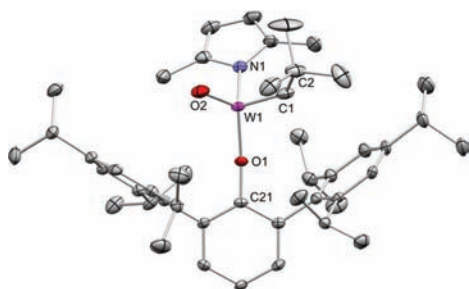
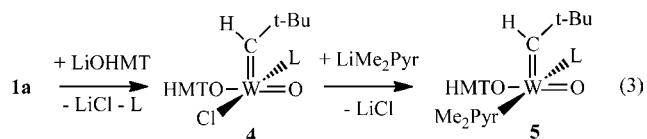


Figure 1. Thermal ellipsoid plot (50% probability) of *syn*-W(O)(CH-t-Bu)(OHIPT)(Me₂Pyr) (**3**). H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W1–C1 = 1.886(3), W1–O2 = 1.695(3), W1–O1 = 1.868(2), W1–N1 = 2.001(2), W1–O1–C21 = 166.9(2), W1–C1–C2 = 136.7(3).

the possibility that PMe₂Ph would be lost from the coordination sphere because of binding of the pyrrolide ligand in an η⁵ fashion, thereby producing an electron count of 18 at the metal. However, other steric factors alone appeared to be sufficient to cause 14-electron **3** to be formed.

The analogous reaction between **1** and LiOHMT (OHMT = *O*-2,6-dimesitylphenoxide) in benzene at 22 °C for 3 h led to the isolation of yellow WO(CH-t-Bu)Cl(OHMT)(PMe₂Ph) (**4**) in 70% yield (eq 3). As with **2**, the ¹H NMR spectrum of the product contained two alkylidene doublet resonances corresponding to two isomers of **4** in a 87:13 ratio. The values of ¹J_{CH} (122 and 116 Hz) suggested that both isomers are *syn*-alkylidenes. Addition of Li(Me₂Pyr) to **4** in toluene at –30 °C followed by stirring the mixture at 22 °C for 10 h afforded yellow W(O)(CH-t-Bu)(OHMT)(Me₂Pyr)(PMe₂Ph) (**5**) in 70% isolated yield. An X-ray structure of **5** (Figure 2) showed it to be a square pyramid with the *syn*-neopentylidene in the apical position and the phosphine bound trans to the pyrrolide.



The PMe₂Ph ligand in **5** is partially dissociated at room temperature and rapidly exchanging on and off the metal. The alkylidene resonance is broad, and its chemical shift is concentration-dependent (8.57–9.14 ppm for 4–48 mM solutions in C₆D₆). Variable-temperature ¹H and ³¹P NMR studies of a 20 mM solution of **5** in CD₂Cl₂ showed that the phosphine is “bound” below –30 °C, as indicated by a sharp ³¹P signal corresponding to the coordinated ligand (1.80 ppm, ¹J_{PW} = 289 Hz). On the basis of the chemical shift for free and coordinated phosphine, the value of the equilibrium constant for phosphine dissociation was estimated as 0.015 M at room

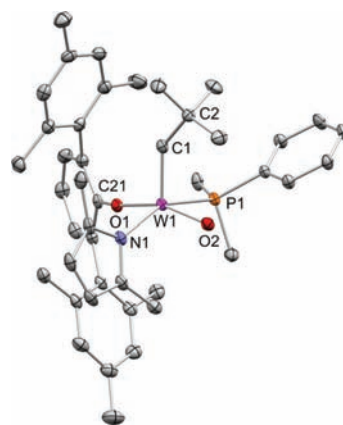


Figure 2. Thermal ellipsoid plot (50% probability) of *syn*-W(O)(CH-t-Bu)(OHMT)(Me₂Pyr)(PMe₂Ph) (**5**). H atoms have been omitted for clarity. Solvent molecules are not shown. Selected bond distances (Å) and angles (deg): W1–C1 = 1.900(3), W1–O2 = 1.717(2), W1–O1 = 1.964(2), W1–N1 = 2.074(2), W1–P1 = 2.580(1), W1–O1–C21 = 159.8(2), W1–C1–C2 = 141.0(2).

temperature. This value corresponds to 57% dissociation of phosphine in a 20 mM solution of **5** in C₆D₆.

Both **3** and **5** react with ethylene to give an unsubstituted metallacyclobutane complex (and *t*-butylethylene) that has a square pyramidal structure (presumably with the oxo ligand in the apical position) on the basis of chemical shifts of metallacyclopentane protons in the range 0.7–4.5 ppm.⁹ The reaction of **3** with ethylene is relatively slow and what we propose is an intermediate square pyramidal β-*t*-butylmetallacyclobutane complex can be observed before free *t*-butylethylene is formed. In the case of compound **5**, a methylidene complex is formed in addition to the unsubstituted square pyramidal metallacyclopentane. In both systems the unsubstituted metallacyclopentane slowly decompose over a period of 24 h to unidentified products. A square pyramidal metallacyclobutane made from imido alkylidenes has been proposed to be further from the transition state for olefin loss than is the alternative TBP metallacyclopentane.^{10a} Extensive calculations have been performed on several high oxidation state metathesis systems that include metallacyclobutane complexes.^{10b,c}

Both **3** and **5** serve as initiators for the polymerization of 5,6-dicarbomethoxynorbornadiene (DCMNBD). The polymerization of 50 equiv of DCMNBD was relatively slow (hours) with **3**, and propagation was faster than initiation. The resulting polymer was >99% *cis*, 90% syndiotactic. The polymerization of 50 equiv of DCMNBD with **5** was relatively fast (minutes), and all of the initiator was consumed. The resulting polymer was >99% *cis*, 98% syndiotactic.^{7b} These results suggest that the steric crowding is significantly greater in **3** than in **5** after phosphine is lost and is in fact too great to allow the formation of highly regular *cis*,*syndiotactic*-poly(DCMNBD) from **3**.

Homocoupling of neat terminal olefins with **3** took place slowly (hours) at room temperature. In contrast, **5** was found to be highly active and highly *Z*-selective (Table 1). A catalyst loading as low as 0.2 mol % yielded up to 86% conversion in 6 h for several of the six chosen substrates. No *trans* product could be observed in the ¹H NMR spectra of the *Z* products (see the SI).

Only a small increase in conversion was found for reaction times >6 h, which suggests that the majority of the catalyst has decomposed at this stage. Decomposition of a catalyst prior to isomerization of the *Z* product to *E* can be a desirable feature of

Table 1. Conversions (%) of Neat Terminal Olefins to Homocoupled >99% Z Metathesis Products Promoted by 5

time	substrate ^a /catalyst loading					
	S1/0.2 %	S2/0.2 %	S3/0.2 %	S4/0.2 %	S5/0.2 %	S6/1 %
10 min	28	44	65	—	28	—
30 min	39	67	75	—	39	—
1 h	47	79	75	2	47	10
6 h	66	86	—	—	73 ^b	—
24 h	72	88	—	11	—	59

^aS1 = 1-octene, S2 = allylbenzene, S3 = allylboronic acid pinacol ester, S4 = allylSiMe₃, S5 = 1-decene, S6 = methyl-10-undecenoate.

^bThe aliquot was taken after 7 h.

the coupling reaction. The reactions were run on a 200 mg scale in a closed vessel with a volume of ~20 mL. Homocoupling of 1-decene at 0.5 Torr did not show a significant increase in turnover in comparison with the reaction carried out under 1 atm nitrogen. We ascribe the relatively low turnover in the case of allyl-TMS (S4) to steric issues and that in the case of methyl-10-undecenoate (S6, at 1% catalyst loading) to ester binding to W. These results should be compared with those obtained employing a W(N-3,5-Me₂C₆H₃) catalyst system.^{7f}

A long-standing question in classical olefin metathesis catalyst systems based on tungsten has been the role of a Lewis acid. One might expect that a Lewis acid in **5** could bind to the oxo ligand and thereby create a more electrophilic metal center and more reactive catalysts. Indeed, we found that addition of Lewis acids to **5** significantly speeds up metathesis reactions. For example, addition of 2 equiv of B(C₆F₅)₃ to **5** resulted in a catalyst that converted 90% of 1-octene to 7-tetradecene in 1 h at 22 °C (0.2 mol % loading). However, the 7-tetradecene was only 20% Z. Since pure (Z)-7-tetradecene (in C₆D₆) is isomerized to a 78:22 mixture of (E)- and (Z)-tetradecene by 1 mol % **5** in the presence of 2 equiv of B(C₆F₅)₃ in 15 min, any (Z)-7-tetradecene that is formed initially in the homocoupling reaction should be isomerized rapidly to a 4:1 E:Z mixture.

Addition of 2 equiv of B(C₆F₅)₃ to **5** led to the formation of (Me₂PhP)[B(C₆F₅)₃] and 5·B(C₆F₅)₃. The B(C₆F₅)₃ in 5·B(C₆F₅)₃ is labile at room temperature, as demonstrated by a broadened alkylidene signal in the ¹H NMR spectrum at 7.30 ppm. The ¹H NMR spectrum of a 45 mM solution of 5·B(C₆F₅)₃ at -60 °C shows a sharp alkylidene resonance at 7.06 ppm. An X-ray structure of 5·B(C₆F₅)₃ showed that B(C₆F₅)₃ is coordinated to the oxo ligand (Figure 3). The W1–O2–B1 unit is bent [the W1–O2–B1 angle is 159.9(1)°]. The W1–O2 distance [1.759(2) Å] is elongated relative to those in **5** [1.717(2) Å] and **3** [1.695(3) Å] and slightly shorter than those in reported B(C₆F₅)₃ adducts of tungsten oxo complexes.¹¹ Relatively weak coordination of B(C₆F₅)₃ to the oxo ligand is also indicated by the B1–O2 bond length of 1.571(3) Å, which is longer than that in any of the B(C₆F₅)₃ adducts of transition-metal oxo complexes in the literature [1.484(3)–1.558(2) Å]. The average values of the C–B–C and O–B–C angles (112.6 and 106.1°, respectively) also suggest that B(C₆F₅)₃ is relatively weakly coordinated.

We conclude that tungsten oxo alkylidene complexes are effective Z-selective catalysts for the metathesis coupling of terminal olefins. We ascribe the selectivity to the small size of the oxo ligand relative to OHMT, the low rate of isomerization of the initial Z product relative to that for coupling of terminal

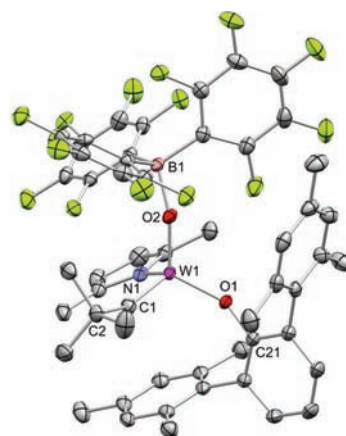


Figure 3. Thermal ellipsoid plot (50% probability) of W(O)(B(C₆F₅)₃)(CH-t-Bu)(OHMT)(Me₂Pyr) [5·B(C₆F₅)₃]. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W1–C1 = 1.868(2), W1–O2 = 1.759(2), W1–O1 = 1.860(2), W1–N1 = 1.968(2), B1–O2 = 1.571(3), W1–O1–C21 = 150.9(1), W1–C1–C2 = 155.4(2).

olefins, and decomposition of the active catalyst under the conditions employed.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details for all compounds and crystal parameters, data acquisition parameters, and CIF files for complexes **2**, **3**, **5**, and 5·B(C₆F₅)₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

rrs@mit.edu

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