

Ether Complexes of Tungsten with Two Different Binding Modes: An O-Bound Ether and an η^2 -(C=C) Vinyl Ether. Evidence for C—H \cdots O Hydrogen Bonding of Vinylic C—H Groups

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Abstract: The reaction of PhCH(OCH₃)₂ with Cp(CO)₃WH and HOTf gives [Cp(CO)₃W(PhCH₂OCH₃)]⁺OTf⁻. The structure of this benzyl methyl ether complex was determined by single crystal X-ray diffraction and was shown to have the ether bonded to tungsten through the oxygen. This compound was isolated as a kinetic product of the reaction; it decomposes in solution by releasing free PhCH₂OCH₃ and forming Cp(CO)₃WOTf. An analog with the BAr'₄⁻ counterion [Ar' = 3,5-bis(trifluoromethyl)phenyl] is more stable. The reaction of the vinyl acetal CH₂=CHCH(OEt)₂ with Cp(CO)₃WH and HOTf produces [Cp(CO)₃W(η^2 -EtOCH=CHCH₃)]⁺OTf⁻, in which the ether is bonded to tungsten through the C=C bond of the vinyl ether. The crystal structure of this compound shows that the W—C(OEt) distance (2.69(3) Å) is significantly longer than the W—C(CH₃) distance (2.37(3) Å). There are weak C—H \cdots O hydrogen bonds between both vinyl CH's and oxygens of triflate counterions. Evidence is presented that some of these weak hydrogen bonds are maintained in CD₂Cl₂ solution but not in CD₃CN.

Introduction

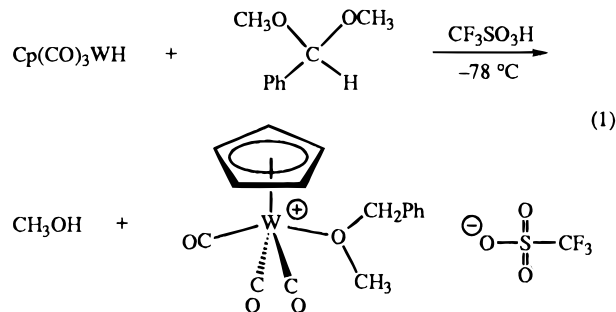
Ethers are “hard” donors and are usually weakly bound to “soft” low-valent metals.¹ The weak binding of ethers is often advantageous in their utilization as solvents for catalytic reactions, since dissociation of the ether ligand creates the vacant coordination site required in many catalytic cycles. Examples of the intermediacy of low-valent ether complexes come from the use of THF as a solvent (and readily displaced ligand) in Rh(I)-catalyzed hydrogenations² and isomerizations.³ Olefin polymerizations catalyzed by Pd(II) complexes utilize Et₂O as a readily displaced ligand on the catalyst precursor.⁴ Some ether complexes are isolable, but many are used *in situ* following their generation from chemical or photochemical methods.

With a few rare exceptions, the ether that becomes a ligand on a metal center was an intact ether molecule that is captured by the metal during the reaction. Et₂O and THF are by far the most commonly encountered ether ligands since the ether ligand usually comes from a solvent molecule. In this paper, we report reactions where ether ligands are created at the metal during the reaction. We have developed procedures for ionic hydrogenations of alkenes,⁵ alkynes,⁶ and ketones,⁷ in which an acid is the source of H⁺ and a transition metal hydride is the H⁻

donor. We now report that the reaction of acetals with acids and Cp(CO)₃WH produces ether complexes in which the acetal is converted to an ether ligand. Crystal structures are reported for one of these complexes containing an oxygen-bonded ether, and for another complex having a vinyl ether, which is bonded through the carbons of the vinyl group. Crystallographic and spectroscopic data indicate the presence of weak C—H \cdots O hydrogen bonds between triflate counterions and both vinyl CH's of the vinyl ether complex.

Results

Oxygen-Bonded Ether Ligands. Addition of triflic acid (CF₃SO₃H, abbreviated as HOTf) to a solution of benzaldehyde dimethyl acetal and Cp(CO)₃WH in CH₂Cl₂ at -78 °C results in a color change from pale yellow to purple. Addition of Et₂O and hexane resulted in the precipitation of the benzyl methyl ether complex [Cp(CO)₃W(PhCH₂OCH₃)]⁺OTf⁻ which has the ether bonded to tungsten through the oxygen (eq 1). While



this ether complex can be isolated as a solid at low temperature, it is a liquid at room temperature (mp 12 °C), so manipulations of the crystalline material and X-ray data collection were carried out at low temperatures. Figure 1 shows an ORTEP diagram of [Cp(CO)₃W(PhCH₂OCH₃)]⁺. Table 1 gives information about the data collection and refinement, and selected bond

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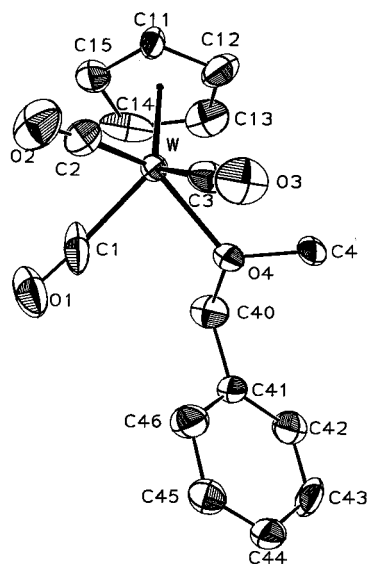
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Table 1. Crystallographic Data from the X-ray Diffraction Studies of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$ and $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$

compound	$[\text{W}(\text{PhCH}_2\text{OCH}_3)]^+$	$[\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+$
formula	$\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_7\text{SW}$	$\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_7\text{SW}$
mol wt	604.21	568.17
space group	$P2_1$	$P2_1$
a , Å	8.530(2)	8.329(2)
b , Å	11.023(2)	7.411(2)
c , Å	12.187(4)	14.505(2)
β , deg	104.25(2)	90.80(2)
V , Å ³	1110.7(5)	895.3(4)
Z	2	2
ρ (calcd), g cm ⁻³	1.807	2.107
temp, K	200	200
radiation	Mo K α	Mo K α
μ , cm ⁻¹	54.5	67.5
absorption correction (max, min) (Difabs)	1.184, 0.709	1.977, 0.847
no. of reflections collected	3574	2976
no. of unique reflections ($F_o > 0$)	2988	2499
no. of reflections used ($F_o > 3\sigma(F_o)$)	2445	2045
2θ limits, deg	4–60	4–60
no. of variables	262	110
R^a	0.049	0.065
R_w	0.058	0.075
max shift/error, final cycle	≤ 0.1	≤ 0.03

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = \{ \sum [w(|F_o| - |F_c|)^2] / \sum [w|F_o|^2] \}^{1/2}$$

**Figure 1.** An ORTEP drawing of the cation of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$. The thermal ellipsoids are at the 50% probability level and the hydrogen atoms are omitted.**Table 2.** Selected Bond Lengths and Angles for $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$

Distances, Å			
W–C(1)	2.01(2)	W–C(3)	1.98(2)
W–C(2)	1.92(2)	W–O(4)	2.206(11)
W–Cp(CEN) ^a	1.97(2)		
Angles, deg			
C(1)–W–C(2)	75.6(8)	C(2)–W–C(3)	75.8(9)
C(1)–W–C(3)	107.1(9)	C(2)–W–O(4)	144.9(6)
C(1)–W–O(4)	83.6(7)	C(3)–W–O(4)	83.9(7)
Cp(CEN) ^a –W–C(1)	123.3(9)	Cp(CEN) ^a –W–C(2)	107.6(9)
Cp(CEN) ^a –W–C(3)	129.0(9)	Cp(CEN) ^a –W–O(4)	107.4(7)

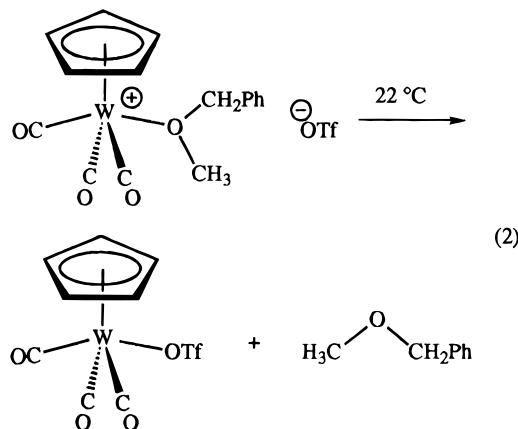
^a Cp(CEN) designates the centroid of the cyclopentadienyl ring.

distances and angles are listed in Table 2. The overall geometry at tungsten is the expected four-legged piano stool arrangement; the W–O bond distance is 2.206(11) Å. The bond from tungsten to the carbonyl “trans” to the ether ligand (C(2)–W–O(4) = 144.9(6)°) is shorter (W–C = 1.92(2) Å) than the W–C distances to the two carbonyls that are trans to each other (W–C

distances of 2.01(2) and 1.98(2) Å). The crystal structure also reveals the presence of a series of weak C–H···O hydrogen bonds, where the C–H's on the Cp ligand are hydrogen bond donors, and the oxygens of the triflate anion are hydrogen bond acceptors. We recently reported⁸ similar C–H···O hydrogen bonds in the structure of the dihydride complex $[\text{Cp}(\text{CO})_2\text{-}(\text{PMe}_3)\text{W}(\text{H})_2]^+\text{OTf}^-$. Details of the hydrogen bonding interactions are tabulated in the Supporting Information, along with an ORTEP diagram showing these interactions. The C···O distances (3.176–3.320 Å) involving C–H's on the Cp ligand are accompanied by C–H···O angles ranging from 115° to 152°, values that are consistent with those found in other C–H···O hydrogen bonds.^{9,10} Additional discussion of hydrogen bonding interactions will be given in a later section.

In the ¹H NMR spectrum of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$ in CD₂Cl₂, the CH₂ protons of the benzyl group appear at δ 4.97 (0.53 ppm downfield compared to free PhCH₂OCH₃), while the CH₃ protons appear at δ 3.75 (0.39 ppm downfield compared to free PhCH₂OCH₃). A similar situation is found in the ¹³C NMR, where the CH₂ and CH₃ carbons of the ether complex appear 18–19 ppm downfield of the free ether.

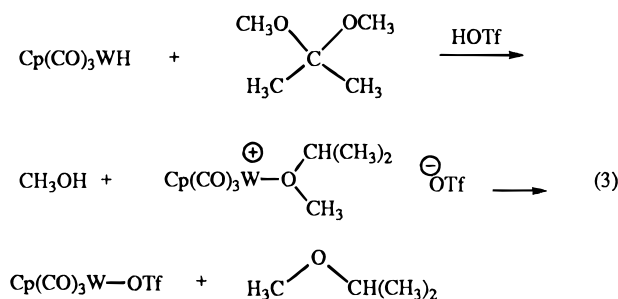
The weakly bound benzyl methyl ether ligand is kinetically stabilized, but the complex is thermodynamically unstable toward displacement of the ether ligand by the triflate counterion, to produce free benzyl methyl ether and Cp(CO)₃WOTf (eq 2). This reaction is about 90% complete in 30 min at



22 °C in CH_2Cl_2 . A more stable ether complex was prepared by using a counterion that is much more weakly coordinating than triflate. The reaction of benzaldehyde dimethyl acetal with $\text{Cp}(\text{CO})_3\text{WH}$ and $[\text{H}(\text{Et}_2\text{O})_2]^+\text{BAR}'_4^-$ [$\text{Ar}' = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$] gave a 93% isolated yield of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{-OCH}_3)]^+\text{BAR}'_4^-$, which is a solid at room temperature. The instability of the compound with the triflate counterion is thus due to displacement of the ether by the triflate, rather than being due to an inherently weak bond of the ether to tungsten.

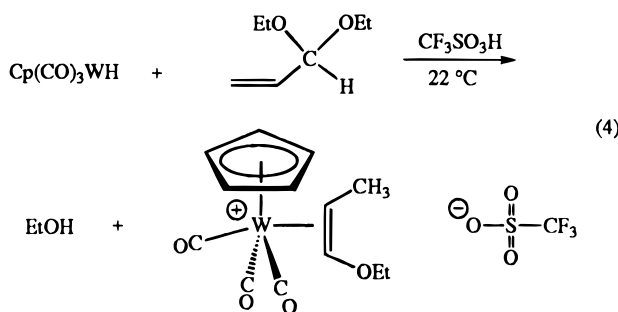
The stronger binding of triflate compared to the ether ligand, implied by eq 2, raises a point about the mechanism of formation of the ether complex. Following protonation of the acetal and loss of methanol, hydride transfer occurs from tungsten to carbon. The formation of the ether complex as a kinetic product suggests that there must be some degree of bond formation between the tungsten and the oxygen, prior to complete cleavage of the W-H bond. Otherwise, if cleavage of the W-H bond had been complete, capture of the 16-electron intermediate $[\text{Cp}(\text{CO})_3\text{W}]^{+}$ (or, more likely, the 18-electron solvated complex, $[\text{Cp}(\text{CO})_3\text{W}(\text{ClCH}_2\text{Cl})]^+$) by OTf^- would have produced $\text{Cp}(\text{CO})_3\text{WOTf}$ as the kinetic product.

Reaction of the ketal 2,2-dimethoxypropane with $\text{Cp}(\text{CO})_3\text{WH}$ and HOTf gave a mixture of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$ and free methyl isopropyl ether (eq 3). When the reaction was



carried out at room temperature, a 56:44 ratio of complexed to free ether was observed after 10 min. Attempts to isolate pure samples of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$ were not successful, but spectroscopic characterization of this compound clearly establishes its identity.

Vinyl Ether Complexes of Tungsten. The reaction of $\text{Cp}(\text{CO})_3\text{WH}$ and HOTf with a vinyl acetal also results in reduction of the acetal to an ether, but in this case the resultant tungsten complex is bound to the ether through the vinyl carbons, rather than through a lone pair on the oxygen (eq 4). In contrast to



the oxygen-bonded compounds described above with OTf^- counterions, the tungsten complex containing the *cis*-1-ethoxypropene ligand is a stable solid at room temperature. The analogous compound with a BAR'_4^- counterion was synthesized

Scheme 1

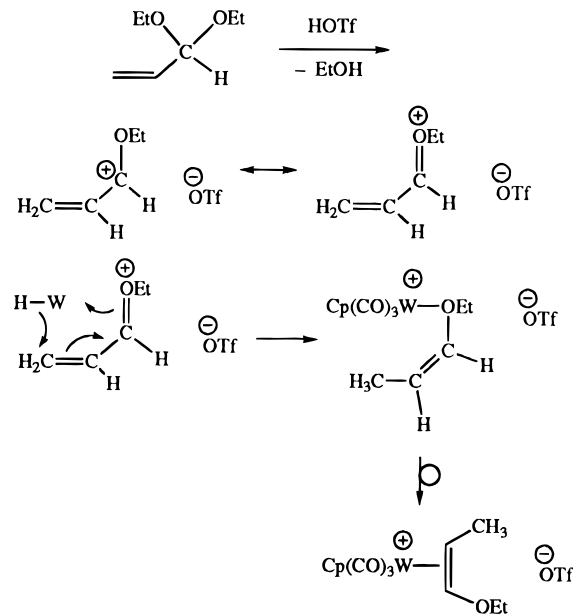


Table 3. Selected Bond Lengths and Angles for $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$

Distances (Å)			
W-C(1)	2.05(4)	W-C(3)	2.02(3)
W-C(2)	1.96(2)	W-C(42)	2.37(3)
W-Cp(CEN) ^a	1.97(3)	W-C(43)	2.69(3)
C(42)-C(43)	1.38(4)		
Angles (deg)			
C(1)-W-C(2)	82(1)	C(2)-W-C(3)	75(1)
C(1)-W-C(3)	135(1)	C(2)-W-C(42)	122.9(9)
C(1)-W-C(42)	84(1)	C(2)-W-C(43)	92.3(8)
C(1)-W-C(43)	72(1)	C(3)-W-C(42)	77(1)
C(43)-W-C(42)	30.9(9)	C(3)-W-C(43)	71(1)
Cp(CEN) ^a -W-C(1)	115(1)	Cp(CEN) ^a -W-C(2)	121(1)
Cp(CEN) ^a -W-C(3)	110(1)	Cp(CEN) ^a -W-C(42)	115(1)
Cp(CEN) ^a -W-C(43)	146(1)		

^a Cp(CEN) designates the centroid of the cyclopentadienyl ring.

from the reaction of the same acetal with $\text{Cp}(\text{CO})_3\text{WH}$ and $[\text{H}(\text{Et}_2\text{O})_2]^+\text{BAR}'_4^-$.

The proposed mechanism for the formation of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ is given in Scheme 1. Protonation of one of the acetal oxygens by HOTf , followed by loss of EtOH , gives a carbenium ion that is stabilized by the ethoxy group. Hydride transfer from $\text{Cp}(\text{CO})_3\text{WH}$ to the terminal CH_2 carbon (Michael-type 1,4-addition) of this intermediate would initially produce an oxygen-bonded ether complex. Isomerization of the oxygen-bonded ether to the $\eta^2\text{-C}=\text{C}$ bonded vinyl ether would give the observed *cis*-1-ethoxypropene complex.

The structure of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ was determined by single crystal X-ray diffraction. Table 1 gives information about the data collection and refinement, and selected bond distances and angles are listed in Table 3. The vinyl ether is bonded to the tungsten as an $\eta^2\text{-olefin}$, as shown by the ORTEP diagram in Figure 2. The bonding of the $\text{C}=\text{C}$ bond to the tungsten is distinctly asymmetric: $\text{W-C}(\text{OEt})$ distance of 2.69(3) Å is significantly longer than the $\text{W-C}(\text{CH}_3)$ distance of 2.37(3) Å.

An unusual feature of the crystal structure is evidence for weak hydrogen bonding of both of the vinyl protons to oxygens of triflate anions. Figure 3 shows how one triflate anion hydrogen bonds to vinyl protons on separate vinyl ethers: one oxygen of the triflate bonds to the CH_3CH vinyl proton, while another oxygen on the same triflate bonds to the EtOCH vinyl

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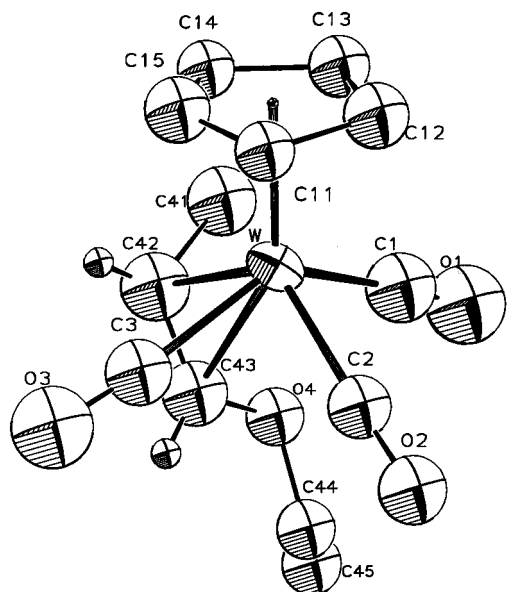


Figure 2. An ORTEP drawing of the cation of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$, showing the atom labeling scheme. The thermal ellipsoids are at the 50% probability level, and hydrogen atoms are omitted except for the two vinylic hydrogen atoms.

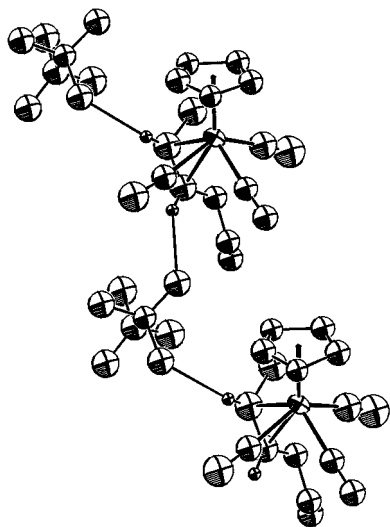


Figure 3. An ORTEP drawing of two formula units of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ showing the vinylic $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds to the oxygens of the triflate anions which hold them together along the a axis in the crystal lattice ($\angle\text{C42}-\text{H42}\cdots\text{O13}$ ($x, -1 + y, z$) = 151° , $\text{C}\cdots\text{O}$ = 3.253 \AA ; $\angle\text{C43}-\text{H43}\cdots\text{O11}$ ($-1 + x, -1 + y, z$) = 156° ; $\text{C}\cdots\text{O}$ = 3.491 \AA).

proton of a different molecule of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+$. This network of $\text{C}=\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds helps to connect the structure together in the crystal lattice. A $\text{C}\cdots\text{O}$ distance of 3.253 \AA (and a corresponding $\text{C}-\text{H}\cdots\text{O}$ angle of 151°) was found for the interaction of the CH_3CH with one oxygen of a triflate anion. The $\text{O}-\text{CH}$ vinyl proton of the same vinyl ether is hydrogen bonded to a different triflate counterion, with a $\text{C}\cdots\text{O}$ distance of 3.491 \AA ($\text{C}-\text{H}\cdots\text{O}$ angle of 156°).

In addition to these hydrogen bonds involving the vinyl $\text{C}-\text{H}$ bonds, there is additional hydrogen bonding of the $\text{C}-\text{H}$ bonds of the Cp rings to triflate anions, similar to those described above for $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$. These hydrogen bonds involving the Cp ring have $\text{C}\cdots\text{O}$ distances ranging from 3.294 to 3.667 \AA , and $\text{C}-\text{H}\cdots\text{O}$ angles ranging from 117° to 169° . The Supporting Information contains further details of the

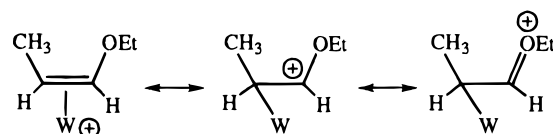


Figure 4. Resonance forms of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+$.

hydrogen bonding interactions, along with an ORTEP diagram showing the Cp $\text{C}-\text{H}$ hydrogen bonds.

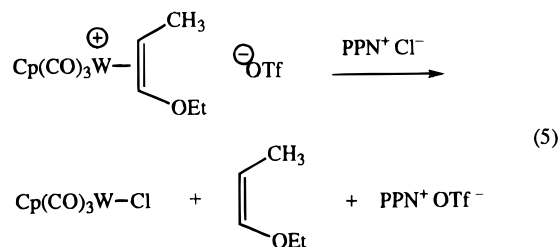
The complete network of hydrogen bonding found in the crystal structure is unlikely to be maintained in solution, but our observations do support some degree of hydrogen bonding for the $\text{C}-\text{H}$ groups of the vinyl ether and Cp ligands. In $\text{CD}_2\text{-Cl}_2$, the ^1H NMR chemical shifts of the CH_2 and CH_3 resonances of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+$ differ by no more than 0.03 ppm for the OTf^- compared to the BAR'_4^- counterion. In contrast, the Cp and vinyl protons appear farther downfield in the OTf^- compound compared to the BAR'_4^- complex. The difference is 0.13 ppm for the Cp protons, but is much larger for the vinyl protons (0.30 ppm for CH_3CH and 0.50 ppm for EtOCH). Addition of PPN^+OTf^- [PPN^+ = bis(triphenylphosphine)iminium] to a CD_2Cl_2 solution of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{BAR}'_4^-$ causes a change of the ^1H NMR chemical shifts of the Cp and both vinyl protons to those observed for the triflate complex $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$. The downfield chemical shifts observed in the OTf^- complex indicates that these protons are hydrogen bonded to oxygen atoms of the triflate counterion in solution. This solvent is relatively nonpolar, and substantial ion pairing¹¹ occurs. No significant change ($<0.02 \text{ ppm}$) in the chemical shift of any of the ^1H NMR resonances of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ were found as a function of concentration ($5\text{--}50 \text{ mM}$) in CD_2Cl_2 . We suggest that this unusual observation of weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding being maintained in solution is a result of ion pairing to bring the cationic metal complex together with the triflate anion. Once ion pairing occurs, the molecule can position itself in a suitable orientation for the weak hydrogen bonds to form. Further support for this interpretation is the observation that in CD_3CN solvent, none of the ^1H NMR chemical shifts of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+$ differ by more than 0.03 ppm for the OTf^- compared to the BAR'_4^- counterion. In this much higher polarity solvent, ion pairing is disfavored, and the strength of the hydrogen bonding is insufficient (in the absence of ion pairing) to result in any observable $\text{C}-\text{H}\cdots\text{O}$ interactions.

In the ^{13}C NMR spectrum of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$, the chemical shift of CH_3CH at $\delta 34.9$ ($J_{\text{CH}} = 164 \text{ Hz}$) is over 60 ppm upfield compared to the free olefin ($\delta 100.9$).¹² Upfield shifts of this magnitude or larger are commonly observed upon coordination of olefins to transition metals. In contrast, the EtOCH carbon appears at $\delta 157.2$ ($J_{\text{CH}} = 183 \text{ Hz}$), which is *downfield* of the corresponding resonance for the free olefin ($\delta 145.6$).¹² In a similar way as uncomplexed vinyl ethers are stabilized by resonance, the vinyl ether complex is stabilized by resonance forms having the formal positive charge on carbon or oxygen (Figure 4). The modest change in ^{13}C NMR chemical shift of the EtOCH carbon upon complexation may reflect the significant contribution of these latter two resonance forms, insofar as they have no formal bond between carbon and tungsten. The larger $^1J_{\text{CH}}$ coupling constant for the EtOCH carbon (compared to CH_3CH) is also consistent with a greater relative amount of sp^2 than sp^3 character.

(11) For a review of ion pairing effects on metal carbonyl anions, see: Darendbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221–274.

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In contrast to the displacement of the oxygen-bound ether ligand of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+$ by triflate, $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ is stable at room temperature. Displacement of the vinyl ether ligand does occur readily upon addition of PPN^+Cl^- , however, producing $\text{Cp}(\text{CO})_3\text{WCl}$ and free *cis*-1-ethoxypropene (eq 5).



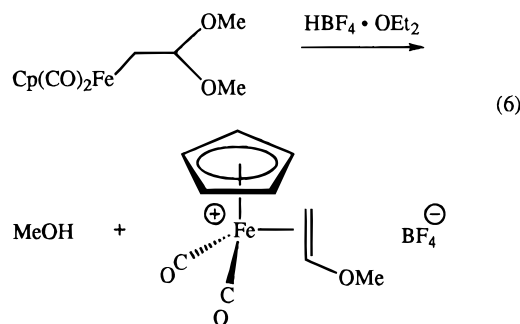
Discussion

Transition Metal Complexes with Oxygen-Bonded Ether Ligands. The vast majority of previously reported oxygen-bonded ether complexes involve THF or Et_2O ligands. The manganese complex $\text{Cp}(\text{CO})_2\text{Mn}(\text{THF})$ is readily prepared by photolysis of $\text{CpMn}(\text{CO})_3$ in THF solution. The chemistry of this compound and its Re analog is particularly well-developed.¹³ In many cases these highly reactive THF complexes are not isolated but are generated *in situ*, and the labile THF ligand is displaced by stronger donors. The related $\text{Cp}^*(\text{CO})_2\text{Re}(\text{THF})$ complex was isolated by Casey and co-workers,¹⁴ and was found to convert thermally to the unusual dimeric compound $\text{Cp}^*(\text{CO})_2\text{Re}=\text{Re}(\text{CO})_2\text{Cp}^*$.

More closely related to the W compounds reported in this paper are cationic ether complexes reported by Beck and co-workers. The weakly bound tetrafluoroborate ligand of $\text{Cp}(\text{CO})_3\text{MoFBF}_3$ is displaced by THF, giving $[\text{Cp}(\text{CO})_3\text{Mo}(\text{THF})]^+\text{BF}_4^-$.¹⁵ An Et_2O complex of tungsten, $[\text{Cp}(\text{CO})_3\text{W}(\text{OEt}_2)]^+\text{PF}_6^-$ was also prepared by Beck.¹⁶ Yi and co-workers recently reported¹⁷ the crystal structure of the closely related Cp^* complex, $[\text{Cp}^*(\text{CO})_3\text{W}(\text{OEt}_2)]^+\text{BAR}'_4^-$. The W—O distance of 2.197(7) Å reported for this compound is essentially identical to the W—O distance of 2.206(11) Å found for $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$ and to the W—O distance of 2.186(9) Å we determined for the alcohol complex $[\text{Cp}(\text{CO})_3\text{W}(\text{PrOH})]^+\text{OTf}^-$.

An unusual feature of our synthetic route to $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+$ is that the ether ligand is formed during the reaction, rather than being added as an intact ether molecule to a vacant coordination site on the metal. A previous example involving the formation of an ether ligand at a metal center comes from the synthesis of $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{OEt}_2)]^+\text{PF}_6^-$ by transfer of an ethyl group from the oxonium salt $\text{Et}_3\text{O}^+\text{PF}_6^-$ to the alkoxide oxygen of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{OEt})$.¹⁸

Transition Metals Complexes with Vinyl Ether Ligands. Rosenblum and co-workers have prepared^{19,20} vinyl ether complexes of iron that provide useful comparisons with our tungsten vinyl ether complex. A similarity of one of their preparative procedures (eq 6) to ours is in the acid-induced



alcohol elimination from an acetal functionality. Other aspects of the synthetic procedures differ, however, since their Fe starting material has a bond to carbon in the starting material, whereas a metal hydride bond is cleaved in eq 4 to create a site for eventual binding of the vinyl ether. A crystal structure determination of the iron vinyl ether complex²¹ showed that the η^2 -olefin ligand was not bound symmetrically to Fe. The precision of the Fe—C distances was compromised due to crystallographic disorder, but a lower limit of 0.12 Å was set for the amount that the Fe—CHOMe distance exceeded the Fe—CH₂ distance. A distorted structure was also found for the vinyl alcohol complex $\text{Pt}(\text{Cl})(\text{acac})(\eta^2\text{-H}_2\text{C}=\text{CHOH})$, where the Pt—C distance to the α -carbon was 2.222(8) Å and that to the β -carbon was 2.098(8) Å.²² The difference in bond lengths between metal and carbon is larger for $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ than for either of these two compounds, but is less than the difference of about 0.7 Å found for Fe—C distances in the vinylamine complex $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CHNMe}_2)]^+$.²¹

In addition to the synthetic and structural work, Rosenblum and co-workers investigated reactions of their iron vinyl ether complexes, exploiting their utility as vinyl cation equivalents for a variety of organic synthetic reactions.²⁰ Such reactions involve high regioselectivity in the addition of nucleophiles to the Fe—CHO carbon, and reflect the significant localization of positive charge at this carbon (cf resonance forms drawn in Figure 4). The asymmetrical structures of the vinyl ether complexes are a reflection of resonance forms having formal positive charges at carbon or oxygen. Eisenstein and Hoffmann carried out a detailed molecular orbital analysis²³ showing how the amount of activation of an olefin complex toward nucleophilic addition is enhanced dramatically by slipping of the olefin from symmetrical η^2 -coordination towards η^1 -coordination.

A totally different route to η^2 -vinyl ether complexes was recently reported by Arndtsen and Bergman,²⁴ who synthesized $[\text{Cp}^*(\text{PMe}_3)(\text{H})\text{Ir}(\eta^2\text{-H}_2\text{C}=\text{CHOEt})]^+\text{BAR}'_4^-$ from a route involving C—H activation of Et_2O by the dichloromethane complex $[\text{Cp}^*(\text{PMe}_3)(\text{CH}_3)\text{Ir}(\text{ClCH}_2\text{Cl})]^+\text{BAR}'_4^-$.

C—H···O Hydrogen Bonds. The most unusual aspect of the crystal structure of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ is the network of hydrogen bonds between the triflate anions and C—H bonds of the coordinated vinyl ether ligand. We are not aware of any previous examples of C—H bonds of

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coordinated alkenes acting as hydrogen bond donors. Free alkenes (and alkynes), however, are known to form C—H···O hydrogen bonds to oxygen. An analysis²⁵ of 622 C—H···O geometries from 131 alkene structures in the Cambridge Structural Database found a mean C···O distance of 3.64 Å. The C···O distances of 3.253 and 3.491 Å found for the vinylic C—H bonds of the alkene (vinyl ether) complex [Cp(CO)₃W(η²-EtOCH=CHCH₃)]⁺OTf⁻ are both shorter than this average distance. This comparison, however, is between free alkenes and our metal-complexed alkene. The tungsten fragment of [Cp(CO)₃W(η²-EtOCH=CHCH₃)]⁺OTf⁻, with its positive charge and electron-accepting CO ligands, withdraws electron density from the alkene. One effect of this overall donation of electron density from the alkene to the metal is to increase the acidity of the vinylic C—H bonds. It has been shown that C—H···O hydrogen bonds involving more acidic C—H groups generally result in shorter C···O distances.¹⁰ Thus the comparison of these two C···O distances in our organometallic complex with those from organic alkene structures may be influenced significantly by the electronic effect of the metal on the acidity of the C—H groups. The enhanced acidity of the vinylic C—H groups by the metal is probably greater for CH₃CH compared to the EtOCH. An electronic effect that would contribute to the enhanced relative acidity of the CH₃CH is the formal positive charge on the the EtOC carbon, as shown in the resonance form in the middle of Figure 4. This acidity effect is consistent with the observation of a shorter C···O distance for the C—H···O hydrogen bond involving CH₃CH compared to the one involving EtOCH.

While information about C···O distances is reliably determined from the X-ray structure, hydrogen atoms are not precisely located by X-ray diffraction data since x-rays locate electron density rather than the nuclear positions. An estimate of the H···O distances may be made by setting the C—H distances to 1.08 Å, the average C—H distance found for alkene C—H bonds from structures determined by neutron diffraction.²⁶ This calculation results in an H···O distance of 2.28 Å for CH₃CH···O interaction and an H···O distance of 2.48 Å for the EtOCH···O interaction. Both of these H···O distances are less than 2.7 Å, the sum of van der Waals radii for H (1.2 Å) and oxygen (1.5 Å).²⁷ Even though the C—H···O interactions here are within the van der Waals radii, this is not an absolute requirement for the interaction to have an influence on the structure. Desiraju has pointed out that “the C—H···O bond is not really a van der Waals contact but is primarily electrostatic; as its strength therefore falls off much more slowly with distance, it is viable at distances equal to or greater than the van der Waals limit.”²⁸

Our spectroscopic and structural data⁷ on the alcohol complex [Cp(CO)₃W(PrOH)]⁺OTf⁻ also provided evidence for hydrogen bonding of a triflate anion to a ligand bound to tungsten. The crystal structure of this compound revealed a hydrogen bond between the alcohol OH proton and an oxygen on the triflate

anion (O···O distance of 2.63(1) Å). This O—H···O hydrogen bond is significantly stronger than the C—H···O hydrogen bonds found here for [Cp(CO)₃W(η²-EtOCH=CHCH₃)]⁺OTf⁻. The role of hydrogen bonding has long been recognized in biological structures²⁹ and is receiving attention in organic structures for “crystal engineering.”^{28,30} Additionally, the influence of weak C—H···O hydrogen bonding interactions on the crystal structures of organometallic complexes has been increasingly recognized and analyzed recently.³¹

Reductive Cleavage of Acetals To Give Ethers. Formation of ethers by reductive cleavage of acetals has been previously reported to occur using a variety of hydride reagents, often in conjunction with Lewis acids. Among the reagents reported for this transformation are LiAlH₄/AlCl₃,³² LiAlH₄/TiCl₄,³³ Zn(BH₄)₂/Me₃SiCl,³⁴ borane,³⁵ catecholborane,³⁶ CIBH₂·OEt₂,³⁷ and aluminum reagents such as ⁱBu₂AlH.³⁸ The use of Et₃SiH/CF₃CO₂H developed by Kursanov and co-workers is effective for ionic hydrogenations of a wide variety of organic substrates,³⁹ and can be used at 50 °C for reductive cleavage of acetals to ethers. Trialkylsilanes can also be used in conjunction with Lewis acids⁴⁰ or superacids⁴¹ to effect this transformation.

In view of these well-developed and convenient synthetic procedures, the most novel synthetic aspect of this work is in the unusual route to ether complexes of a low-valent transition metal, rather than in providing an especially attractive alternative route for this organic transformation.

Conclusion

The reaction of acetals with strong acids and the transition metal hydride Cp(CO)₃WH produces cationic tungsten complexes containing ether ligands. This is an unusual reaction since the ether ligand is generated during the reaction, whereas most oxygen-bonded ether complexes are produced by adding

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an intact ether molecule to a metal complex containing either a vacant coordination site or a readily displaced ligand. The oxygen-bonded ether complex $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$ was structurally characterized by X-ray diffraction. The reaction of a vinyl acetal with $\text{Cp}(\text{CO})_3\text{WH}$ and HOTf also produces a cationic tungsten complex having an ether ligand, but in this case the vinyl ether is bonded to the metal through the C=C bond. A noteworthy feature of the structural study of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$ is asymmetric binding of the two carbons to the tungsten. In addition, the crystal structure reveals a network of weak C—H...O hydrogen bonds between both vinyl CH's and oxygens of triflate counterions. Evidence is presented from ^1H NMR data that some of these hydrogen bonds persist in CD_2Cl_2 solution.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. ^1H NMR chemical shifts were referenced to the residual proton peak of CD_2Cl_2 at δ 5.32. Elemental Analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). $\text{Cp}(\text{CO})_3\text{WH}^{42}$ and $[\text{H}(\text{Et}_2\text{O})_2]^+\text{BAR}'_4^-$ [$\text{Ar}' = 3,5$ -bis(trifluoromethyl)phenyl] were prepared by literature methods. Organic reagents were obtained commercially and were used without purification. NMR spectra were recorded on a Bruker AM-300 spectrometer. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer.

Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$. HOTf (50 μL , 0.57 mmol) was added slowly to a solution of $\text{Cp}(\text{CO})_3\text{WH}$ (160 mg, 0.48 mmol) and benzaldehyde dimethyl acetal (90 μL , 0.60 mmol) in CH_2Cl_2 (10 mL) at -78°C . The reaction mixture was stirred for 1 h at -78°C , during which time the solution turned from yellow to purple. Et_2O (30 mL) and hexane (10 mL) were added by vacuum transfer, and the mixture was stirred an additional 10 min. The resulting purple precipitate was isolated by filtration, washed with Et_2O (60 mL), and dried under vacuum to give $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{OTf}^-$ (142 mg, 50%). Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product at -78°C . This complex decomposes to produce $\text{Cp}(\text{CO})_3\text{WOTf}$ and free $\text{PhCH}_2\text{OCH}_3$ (90% complete in 30 min at 22°C in CD_2Cl_2). ^1H NMR (CD_2Cl_2 , 250 K): δ 7.44–7.23 (m, 5H, Ph), 6.29 (s, 5H, Cp), 4.97 (s, 2H, PhCH_2O), 3.75 (s, 3H, 1H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 230 K): δ 223.4 (2 CO), 220.5 (CO), 131.3 (*ipso*-C), 129.8 (*ortho*-C), 128.8 (*meta*-C), 128.0 (*para*-C), 95.5 (Cp), 93.6 (PhCH_2O), 75.7 (OCH_3). IR (Fluorolube): $\nu(\text{CO})$ 2067 (s), 1982 (vs), 1947 (vs) cm^{-1} , mp: 12°C . The NMR of free $\text{PhCH}_2\text{OCH}_3$ is given for comparison. ^1H NMR (CD_2Cl_2): δ 7.35–7.30 (m, 5H, Ph), 4.44 (s, 2H, PhCH_2O), 3.36 (s, 3H, 1H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 305 K): δ 138.7 (*ipso*-C), 128.4 (*ortho*-C), 127.8 (*meta*-C), 127.6 (*para*-C), 74.7 (PhCH_2O), 58.1 (OCH_3).

Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{BAR}'_4^-$. Benzaldehyde dimethyl acetal (60 μL , 0.40 mmol) was added to a solution of $\text{Cp}(\text{CO})_3\text{WH}$ (80 mg, 0.24 mmol) and $[\text{H}(\text{Et}_2\text{O})_2]^+\text{BAR}'_4^-$ (200 mg, 0.198 mmol) in toluene (15 mL) at -15°C . The reaction mixture was stirred for 30 min at -15°C while the volatile products (Et_2O and MeOH) were removed under vacuum. Then the solvent was evaporated, and the purple residue was dissolved in CH_2Cl_2 (5 mL). Hexane (30 mL) was slowly added, and the purple solid was collected by filtration, washed with hexane (30 mL), and dried under vacuum. Recrystallization from CH_2Cl_2 /hexane at -78°C gave $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCH}_2\text{OCH}_3)]^+\text{BAR}'_4^-$ as a microcrystalline solid (244 mg, 0.185 mmol, 93%). ^1H NMR (CD_2Cl_2): δ 7.72 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 7.56–7.22 (m, 5H, Ph), 6.01 (s, 5H, Cp), 4.82 (s, 2H, $\text{PhCH}_2\text{OCH}_3$), 3.73 (s, 3H, $\text{PhCH}_2\text{OCH}_3$). ^{13}C NMR (CD_2Cl_2 , 255 K): δ 222.6 (2 CO), 218.7 (CO), 161.7 (1:1:1:1 quartet, *ipso*-C, $J_{\text{CB}} = 49$ Hz), 134.7 (s, *ortho*-C of BAR'_4), 131.4 (s, *ipso*-C of Ph), 130.4 (s, *para*-C of Ph), 129.8, 128.8 (2 s, *ortho* and *meta*-C's of Ph), 128.6 (q,

$^2J_{\text{CF}} = 28$ Hz, *meta*-C of BAR'_4), 124.5 (q, $J_{\text{CF}} = 272$ Hz, CF_3), 117.5 (*para*-C of BAR'_4), 95.2 (Cp), 94.1 ($\text{PhCH}_2\text{OCH}_3$), 76.1 ($\text{PhCH}_2\text{OCH}_3$). IR (CH_2Cl_2): $\nu(\text{CO})$ 2065 (s), 1995 (m), 1964 (vs) cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{27}\text{BF}_3\text{O}_4\text{W}$: C, 43.73; H, 2.06. Found: C, 43.39; H, 2.34.

Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$. HOTf (5 μL , 0.057 mmol) was added at 22°C to a solution of $\text{Cp}(\text{CO})_3\text{WH}$ (16 mg, 0.048 mmol) and 2,2-dimethoxypropane (4 μL , 0.033 mmol) in CD_2Cl_2 (0.6 mL). The color turned from pale yellow to wine-red when the solution was shaken, and an ^1H NMR spectrum recorded after 10 min indicated a 56:44 ratio of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$ to free $\text{CH}_3\text{O}^i\text{Pr}$; $\text{Cp}(\text{CO})_3\text{WOTf}$ was also observed (1:1 ratio compared to free $\text{CH}_3\text{O}^i\text{Pr}$). The conversion of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$ to free $\text{CH}_3\text{O}^i\text{Pr}$ and $\text{Cp}(\text{CO})_3\text{WOTf}$ proceeded cleanly at room temperature. In view of the thermal sensitivity of $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$, an attempt was made to prepare this complex at low temperature. HOTf (70 μL , 0.77 mmol) was slowly added to a solution of 2,2-dimethoxypropane (100 μL , 0.81 mmol) and $\text{Cp}(\text{CO})_3\text{WH}$ (200 mg, 0.60 mmol) in CH_2Cl_2 (10 mL) at -78°C . No color change was observed, but the solution turned to wine-red after being warmed to -40°C . Et_2O (20 mL) was added, and a red-purple precipitate formed, but the precipitate became an oil at room temperature. Attempts to isolate a pure solid from this reaction were not successful. Data for $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{O}^i\text{Pr})]^+\text{OTf}^-$ are as follows. ^1H NMR (CD_2Cl_2): δ 6.23 (s, 5H, Cp), 4.18 (septet, $J = 6.5$ Hz, 1H, $\text{OCH}(\text{CH}_3)_2$), 3.69 (s, 3H, OCH_3), 1.17 (d, $J = 6.5$ Hz, 6H, $\text{OCH}(\text{CH}_3)_2$). IR (Fluorolube): $\nu(\text{CO})$ 2057 (vs), 1983 (s), 1942 (vs) cm^{-1} . The NMR of free $\text{CH}_3\text{O}^i\text{Pr}$ is given for comparison. ^1H NMR (CD_2Cl_2): δ 3.45 (septet, $J = 6.3$ Hz, 1H, $\text{OCH}(\text{CH}_3)_2$), 3.23 (s, 3H, OCH_3), 1.08 (d, $J = 6.3$ Hz, 6H, $\text{OCH}(\text{CH}_3)_2$).

Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{OTf}^-$. HOTf (100 μL , 1.13 mmol) was added to a solution of $\text{Cp}(\text{CO})_3\text{WH}$ (200 mg, 0.60 mmol) and acrolein diethyl acetal (140 μL , 0.92 mmol) in CH_2Cl_2 (10 mL) under Ar. The solution was stirred for 20 min at 22°C , during which time the solution turned from yellow to orange. Et_2O (30 mL) and hexane (10 mL) were added by vacuum transfer, and the resulting precipitate was isolated, washed with Et_2O (60 mL), and dried under vacuum to give a yellow microcrystalline solid (217 mg, 0.382 mmol, 64%). Crystals suitable for diffraction studies were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product at -75°C . ^1H NMR (CD_2Cl_2): δ 8.00 (d, $J = 3.6$ Hz, 1H, EtOCH), 5.99 (s, 5H, Cp), 4.46 (dq, $J = 10.2$ Hz, 7.1 Hz, 1H, OCHHCH_3), 4.24 (dq, $J = 10.2$ Hz, 7.1 Hz, 1H, OCHHCH_3), 4.14 (dq, $J = 5.8$ Hz, 3.6 Hz, 1H, $=\text{CHCH}_3$), 1.89 (d, $^3J = 5.8$ Hz, 3H, $=\text{CHCH}_3$), 1.43 (t, $J = 7.1$ Hz, 3H, OCH_2CH_3). ^1H NMR (CD_3CN): δ 7.82 (d, $J = 3.8$ Hz, 1H, EtOCH), 5.96 (s, 5H, Cp), 4.40 (dq, $J = 10.3$ Hz, 7.1 Hz, 1H, OCHHCH_3), 4.24 (dq, $J = 10.3$ Hz, 7.1 Hz, 1H, OCHHCH_3), 3.84 (dq, $J = 5.8$ Hz, 3.8 Hz, 1H, $=\text{CHCH}_3$), 1.82 (d, $^3J = 5.8$ Hz, 3H, $=\text{CHCH}_3$), 1.35 (t, $J = 7.1$ Hz, 3H, OCH_2CH_3). ^{13}C NMR (CD_2Cl_2 , 220 K, gated decoupled): 217.9 (CO), 216.1 (CO), 214.4 (CO), 157.2 (d, $J_{\text{CH}} = 183$ Hz, EtOCH), 120.0 (q, $J_{\text{CF}} = 320$ Hz, CF_3SO_3), 93.2 (Cp), 74.3 (t, $J_{\text{CH}} = 149$ Hz, OCH_2CH_3), 34.9 (d, $J_{\text{CH}} = 164$ Hz, $\text{CH}_3\text{CH}=\text{C}$), 16.4 (q, $J = 129$ Hz, $\text{CH}_3\text{CH}=\text{C}$), 13.7 (q, $J = 128$ Hz, OCH_2CH_3). IR (CH_2Cl_2): $\nu(\text{CO})$ 2052 (s), 1978 (vs), 1962 (vs) cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_7\text{SW}$: C, 29.59; H, 2.66. Found: C, 29.83, H, 2.42.

Preparation of $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{BAR}'_4^-$. $\text{Cp}(\text{CO})_3\text{WH}$ (80 mg, 0.24 mmol), $[\text{H}(\text{Et}_2\text{O})_2]^+\text{BAR}'_4^-$ (200 mg, 0.20 mmol), and toluene (10 mL) were added to a flask. The solution was cooled to -15°C , and acrolein diethyl acetal (50 μL , 0.32 mmol) was added. The reaction mixture was stirred for 30 min at -15°C , during which time the color changed from pale yellow to red-brown. The solvent was removed under vacuum, and the yellow-brown residue was dissolved in CH_2Cl_2 (5 mL). Hexane (30 mL) was slowly added, and the resulting precipitate was collected by filtration, and washed with hexane (50 mL). Recrystallization from CH_2Cl_2 /hexane at -78°C gave $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-EtOCH}=\text{CHCH}_3)]^+\text{BAR}'_4^-$ as a microcrystalline solid (236 mg, 0.184 mmol, 92%). ^1H NMR (CD_2Cl_2): δ 7.72 (br, 8H, *o*-H), 7.70 (d, $J \approx 4$ Hz, partly obscured by overlap with the resonance at δ 7.72, EtOCH), 7.56 (br, 4H, *p*-H), 5.86 (s, 5H, Cp), 4.41 (dq, $J = 10.1$ Hz, 7.1 Hz, 1H, OCHHCH_3), 4.23 (dq, $J = 10.1$ Hz, 7.1 Hz, 1H, OCHHCH_3), 3.64 (dq, $J = 5.8$ Hz, 3.8 Hz, 1H, $=\text{CHCH}_3$), 1.88 (d, $J = 5.8$ Hz, 3H, $=\text{CHCH}_3$), 1.45 (t, $J = 7.1$ Hz, 3H, OCH_2CH_3). ^1H NMR (CD_3CN): δ 7.80 (d, $J = 3.8$ Hz, 1H, EtOCH), 7.67 (m, Ar'_4),

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5.95 (s, 5H, Cp), 4.40 (dq, $J = 10.3$ Hz, 7.1 Hz, 1H, OCHHCH₃), 4.24 (dq, $J = 10.3$ Hz, 7.1 Hz, 1H, OCHHCH₃), 3.81 (dq, $J = 5.8$ Hz, 3.8 Hz, 1H, =CHCH₃), 1.82 (d, $J = 5.8$ Hz, 3H, =CHCH₃), 1.35 (t, $J = 7.1$ Hz, 3H, OCH₂CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 255 K): δ 216.8 (CO), 214.8 (CO), 212.3 (CO), 161.5 (1:1:1:1 quartet, *ipso*-C, $J_{CB} = 49$ Hz), 158.0 (s, EtOCH), 134.5 (s, *ortho*-C), 128.5 (q, *meta*-C, $^2J_{CF} = 28$ Hz), 124.3 (q, $J_{CF} = 272$ Hz, CF₃), 117.3 (s, *para*-C), 92.9 (s, Cp), 75.6 (s, CH₃CH=CHOCH₂CH₃), 33.4 (s, CH₃CH=), 17.0 (s, CH₃-CH=), 13.6 (s, OCH₂CH₃). IR (CH₂Cl₂): ν (CO) 2059 (s), 1990 (vs), 1968 (vs) cm⁻¹. Anal. Calcd for C₄₅H₂₇BF₂₄O₄W: C, 42.15; H, 2.12. Found: C, 42.36; H, 2.01.

Reaction of [Cp(CO)₃W(η^2 -EtOCH=CHCH₃)]⁺OTf⁻ with [PPN]⁺Cl⁻. [PPN]⁺Cl⁻ (12 mg, 0.021 mmol) [PPN⁺ = bis(triphenylphosphine)iminium] was added to a solution of Cp(CO)₃W(η^2 -EtOCH=CHCH₃)]⁺OTf⁻ (11 mg, 0.019 mmol) in CD₂Cl₂ (0.55 mL). The solution was shaken, and an ¹H NMR spectrum of the resulting red-brown solution showed the formation of *cis*-1-ethoxypropene and Cp(CO)₃WCl. ¹H NMR (CD₂Cl₂) of *cis*-1-ethoxypropene: δ 5.95 (dq, $J = 6.2$ Hz, $J = 1.6$ Hz, 1H, EtOCH), 4.35 (quintet, $J = 6.6$ Hz, 1H, =CHCH₃), 3.76 (q, $J = 7.0$ Hz, 2H, OCH₂CH₃), 1.53 (dd, $J = 6.8$ Hz, $J = 1.6$ Hz, 3H, =CHCH₃), 1.22 (t, $J = 7.0$ Hz, 3H, OCH₂CH₃). ¹H NMR (CD₂Cl₂) of Cp(CO)₃WCl: δ 5.78 (s, 5H, Cp).

Collection and Reduction of X-ray Data. Crystals of [Cp(CO)₃W(PhCH₂OCH₃)]⁺OTf⁻ were purple prisms. Since the melting point of the crystals was about 12 °C, they were coated with petroleum jelly on a glass slide placed on a Petri dish filled with dry ice. A crystal of dimensions 0.14 × 0.24 × 0.32 mm was selected and sealed inside a glass capillary which was quickly transferred to an Enraf Nonius CAD-4 diffractometer equipped with a low-temperature device and cooled to 200K. Diffraction data indicated monoclinic symmetry with systematic absences $k = 2n + 1$, consistent with the space groups $P2_1$ and $P2_1/m$.

Crystals of [Cp(CO)₃W(η^2 -EtOCH=CHCH₃)]⁺OTf⁻ were yellow prisms. A crystal of dimensions 0.14 × 0.28 × 0.37 mm was coated with petroleum jelly and sealed inside a glass capillary. ω scans of the crystals were broad and a crystal with an ω scan width of 0.6° was selected for data collection. Diffraction data indicated monoclinic symmetry with systematic absences $k = 2n + 1$, consistent with the space groups $P2_1$ and $P2_1/m$.

Crystal data and information about the data collection are provided in Tables 1 and S1 (Supporting Information).

Determination and Refinement of the Structures. The structures⁴⁴ were solved by standard heavy atom Patterson methods. In the least-squares refinement,⁴⁴ anisotropic temperature parameters were used for all the non-hydrogen atoms of [Cp(CO)₃W(PhCH₂OCH₃)]⁺OTf⁻, while for [Cp(CO)₃W(η^2 -EtOCH=CHCH₃)]⁺OTf⁻ all the non-hydrogen

atoms were refined isotropically except for the tungsten atom for which anisotropic temperature parameters were used. The quantity $\sum_w(|F_o| - |F_c|)^2$ was minimized. Hydrogen atoms were placed at calculated (C-H = 0.95 Å) positions and allowed to "ride" on the atom to which they were attached. A common isotropic thermal parameter was refined for the hydrogen atoms. Gaussian and empirical (ψ scans) absorption corrections were tried for both structures but resulted in very large peaks near the tungsten atom in both structures. After an isotropic refinement of both structures the original data were corrected using a Fourier absorption correction (DIFABS). In the final difference Fourier map for [Cp(CO)₃W(PhCH₂OCH₃)]⁺OTf⁻ the peaks were less than ± 1.9 e⁻/Å³ (near the tungsten atom) and for [Cp(CO)₃W(η^2 -EtOCH=CHCH₃)]⁺OTf⁻ the peaks were less than ± 3.1 e⁻/Å³ (near the tungsten atom). In both cases the acentric space group, $P2_1$, was used for the solution and refinement of the structures. The handedness of the structure was checked and the model which resulted in the lower R_w value is reported here. E-statistics, as well as failed attempts to refine both structures in the centrosymmetric space group, indicated that the acentric space group was the correct choice.

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Supporting Information Available: Additional experimental details of the data collection and reduction for the X-ray diffraction structures, complete listing of bond lengths and angles, final positional parameters, final thermal parameters for the non-hydrogen atoms, calculated hydrogen atom positions, details of the proposed hydrogens bonds, and ORTEP diagrams (19 pages). See any current masthead page for ordering and Internet access instructions.

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