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Emily N. Bolton Date

[5+2] Cycloadditions to Form Oxobicyclo[3.2.1]octanes

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Master of Science

Chemistry

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By
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An abstract of
A thesis submitted to the Faculty of the James T. Laney School of Graduate Studies of Emory University
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Abstract

[5+2] Cycloadditions to Form Oxobicyclo[3.2.1]octanes
By Emily N. Bolton

Organometallic scaffolds have been studied for alternative strategic and structural approaches to enantiomeric bond construction. These scaffolds may be used to synthesize a variety of natural products such as Bao Gong Teng A. Over the past 20 years the Liebeskind lab has focused on one such scaffold, $TpMo(CO)_2(\eta^3$-oxopyranyl) (Tp=hydrido*tris*pyrazolylborato). In this thesis, an analogous tungsten complex, $TpW(CO)_2(\eta^3$-oxopyranyl), has been explored for the purpose of scientific curiosity. The η^3-oxopyranyltungsten scaffold was synthesized in three steps: Achmatowicz oxidative rearrangement of furfuryl alcohol, acetylation of the intermediate , and finally oxidative addition of the substrate to the metal. The reactivity of the resulting η^3-oxopyranyltungsten scaffold was studied through Lewis acid mediated [5+2] cycloadditions. It was observed that the synthesis of the $TpW(CO)_2(\eta^3$-oxopyranyl) scaffold was higher yielding than its molybdenum counter-part, $TpMo(CO)_2(\eta^3$-oxopyranyl) scaffold. Additionally, an unusual Friedel-Crafts product was formed after Grignard reagent addition and in a few of the [5+2] cycloaddition examples.

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Introduction:

Constructing highly functionalized enantiomerically pure organic complexes is a challenging task. Typically, chemists have used chiral auxiliaries,[1,2] traditional enzymatic resolution,[3,4] and metallo-[5-7] or organo-[8-10]catalytic asymmetric transformations to solve this puzzle. An alternative approach that has gained popularity is the use of chiral (non-racemic) organic scaffolds. An organic scaffold is a simple core structure. The core structure is then transformed by the introduction of multiple substituents in order to yield a biologically relevant compound. Scaffolds provide the opportunity to transform a molecule in systematic and predictable ways. This depends on the specific functional groups located on the core.

Chiral, non-racemic organic scaffolds have been employed in the synthesis of complex alkaloids (**Figure 1**).[11-17] Husson and Royer have developed α-cyanomethyl oxazolidine ring scaffolds that have been used for the synthesis of chiral, non-racemic piperidine and pyrrolidine structures.[14] Their studies were focused on the reactivity of α-aminonitriles bearing a chiral substituent. Bosch has been a second predominant figure in this field. Bosch uses chiral non-racemic bicyclic lactams to prepare optically active pyrrolidine and piperidine derivatives.[15,16]

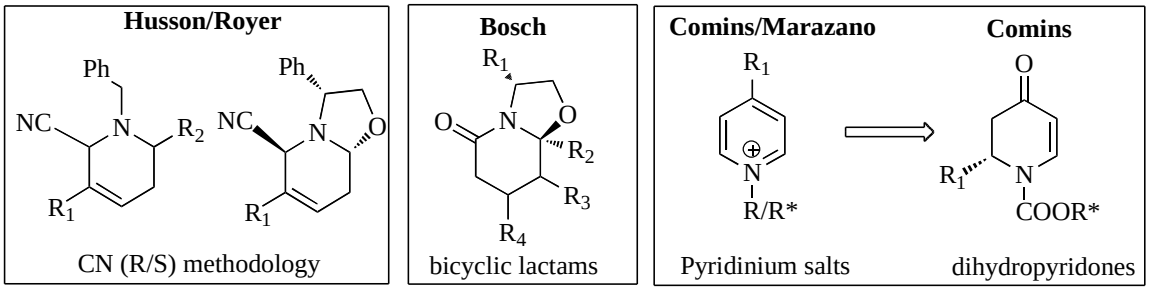


Figure 1. Examples of Organic Scaffolds Used for the Synthesis of Complex Alkaloids

Thirdly, Comins' work is an excellent illustration of the versitality of organic scaffolds. Comins' *N*-acyl-5-vinyl-2,3-dihydro-4-pyridones have been shown to participate in a number of reactions, including enolate acylation, 1,2-/1,4-addition, and electrophilic substitution (**Figure 2**).[11-13,17] Comins utilized these reactions to synthesize complex alkaloids containing the core skeletal properties of dihydropyridones or pyridinium salts.

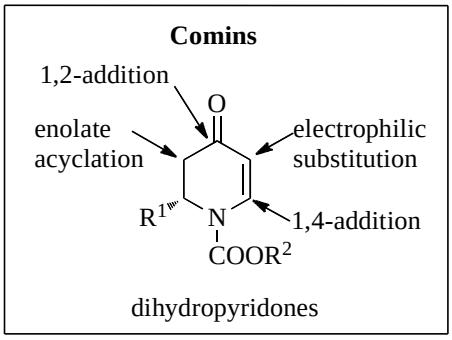


Figure 2. Breakdown of the Comins' Dihydropyridones Scaffold Reactions

The idea of organic scaffolding lead directly to organic enantiomeric scaffolding. A major benefit of the organic enantiomeric scaffolds is that the regio- and stereochemistry of reactions can be controlled due to the configuration of the already present substituents on the scaffold. A variety of different reactions can be performed assymetrically in order to synthesize enantiopure compounds.

This idea has also been applied to organometallic π-complexes.[18-27] A chiral enantiomeric metal compound can be synthesized by complexing a metal to a planar unsymmetrical π-ligand (**Figure 3**). The metal can impart novel reactivity over multiple steps by controlling the introduction of numerous stereocenters. The addition of a substituent typically occurs opposite the metal, primarily due to the steric shielding of one face of the π-ligand by the metal and its auxiliary ligands. Once all the metal

mediated transformations have occurred, the π-allyl is demetallated (**Figure 3**). This will yield an enantiomerically pure substituted organic compound.[28-33]

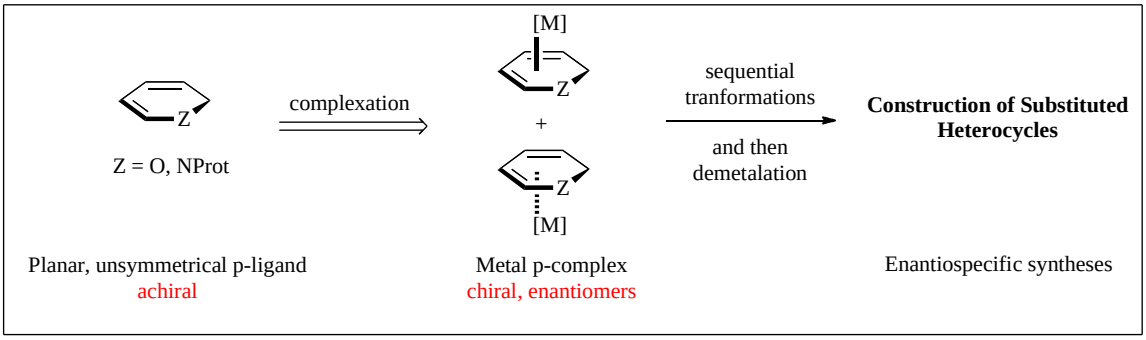


Figure 3. Complexation of the Metal Moiety to a Planar Unsymmetrical π-Ligand

In the past, Pearson, Faller, and Harman have extensively studied metal π-complexes. Pearson's laboratory investigated C-C bond formation in 6- and 7-membered rings with molybdenum-based η^4-cationic cyclic dienes. [19,20,34] The stereocontrolled C-C bonds were formed *via* nucleophilic addition to the cyclodiene molybdenum complexes. Faller explored cationic η^3-molybdenum complexes, such as $[CpMo(NO)(CO)(\eta^3\text{-}C_3H_5)]^+$. [28,29,31,32] These complexes were used in a stoichiometric fashion for the asymmetric synthesis of substituted olefins in high optical purity. Finally, Harman was able to functionalize aromatic compounds with π-basic transition metals. [35-42] For example, $[TpW(NO)(PMe_3)]$ was used to aid in keto-enone tautomerization of a phenyl ketone; ultimately stabilizing the phenol group and making later functionalization of the molecule easier.

The Liebeskind group has developed conceptually new scaffolds, called organometallic scaffolds (**Figure 4**).[21-26,30,33,43-56] Four main Liebeskind scaffolds, **1** – **4**, have been developed. These contain useful functional groups that aid in both regio- and stereocontrol during a reaction. These scaffolds have advanced the field by providing

ways to facilitate a variety of metal mediated transformations that are otherwise difficult to perform in a purely organic system. These organometallic scaffolds have opened up the syntheses of both tetrahydropyran and piperidine heterocycles.

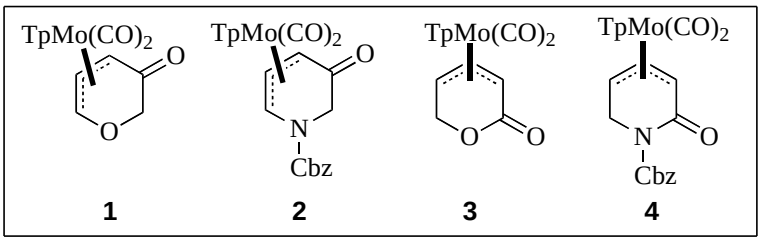


Figure 4. Liebeskind Molybdenum Organometallic Enantiomeric Scaffolds

All four of the Liebeskind scaffolds, **1** – **4**, contain the ligand Tp, hydrido*tris*pyrazolyborate.[57,58] Tp is an anionic scorpionate ligand. It can donate electron density to the metal while also aiding in regio- and stereocontrol (**Figure 5**). Historically, Liebeskind's scaffolds were made with the carbanionic cyclopentadienyl ligand, Cp,.[46,48,51,54] Like Tp, the Cp ligand can donate electron density to the metal in order to stabilize the π-allyl. The disadvantage of Cp is the high basicity and nucleophilicity of the carbanion. These properties can be disruptive to the desired outcome of reactions and contribute to the instability of Cp to air and water. For these reasons Cp was replaced with Tp. Tp is generated as a potassium salt, KTp. It is an air- and moisture-stable white solid that is easily prepared and can be made in large quantities (**Figure 5**).[57] KTp can also be stored for extended periods of time under normal atmospheric conditions.

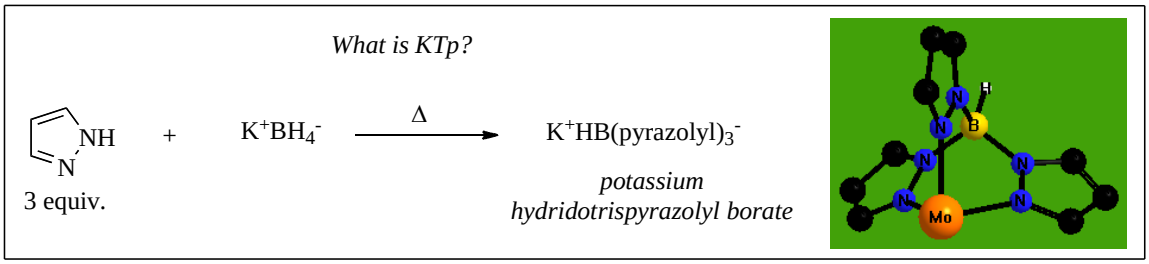
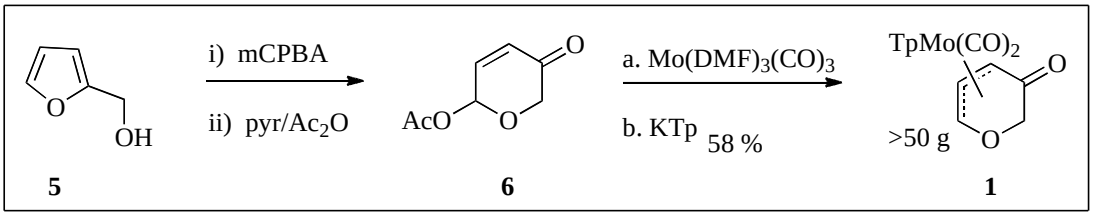


Figure 5. Synthesis of KTp and the Structural Representation of the Tp Ligand

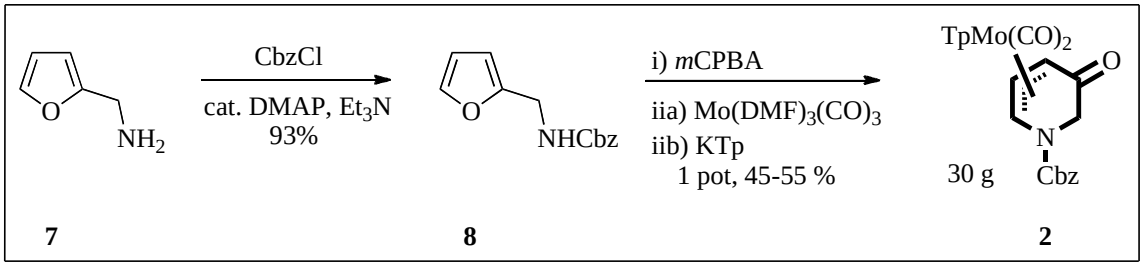
The Liebeskind scaffolds must meet a number of specific criteria.[21-23,30,43-45,49,53,56] All scaffolds are made from inexpensive, readily available material, that yield air-stable high enantiopurity complexes. Asymmetry is introduced to the organic heterocyclic ligand in a stoichiometric fashion. Both the regio- and stereochemistry are controlled by the $TpMo(CO)_2$ moiety on the unsaturated organic ligand.

The racemic molybdenum scaffolds $TpMo(\eta^3$-oxopyranyl), **1**, and $TpMo(CO)_2(\eta^3$-pyridinyl), **2**, are formed in a similar fashion to one another. First, furfuryl alcohol, **5**, is subjected to an Achmatowicz rearrangement[59] followed by acylation of the alcohol to form the acetate, **6**. Second, oxidative addition to a zero-valent molybdenum source, $Mo(DMF)_3(CO)_3$, is performed. This is followed by a ligand exchange to yield the desired $TpMo(CO)_2(\eta^3$-oxopyranyl), **1**, in a 58% yield (**Scheme 1**).[24] The racemic scaffold $TpMo(CO)_2(\eta^3$-pyridinyl), **2**, is synthesized through the same process, except furfuryl amine, **7**, is protected with Cbz-Cl to yield compound **8**, prior to the Achmatowitz rearrangement (**Scheme 2**).[24,59] The synthesis of racemic $TpMo(CO)_2(\eta^3$-pyridinyl), **2**, is a one pot synthesis with a yield of 45 – 55% yield.

Scheme 1. Synthesis of TpMo(η^3-allyl) Pyranyl Scaffold

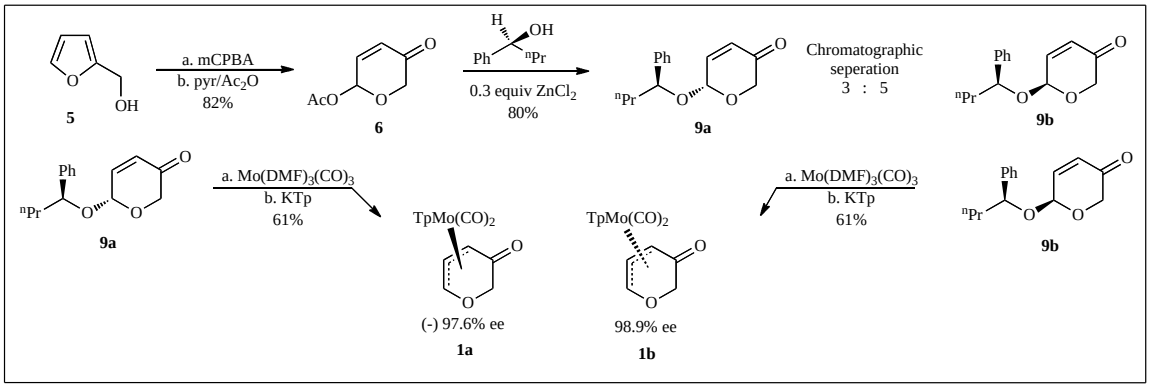


Scheme 2. Synthesis of TpMo(η^3-allyl) Pyridinyl Scaffold



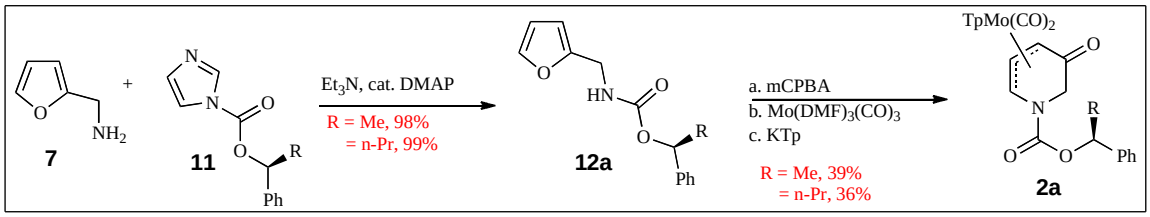
Liebeskind has also synthesized TpMo$(CO)_2$(η^3-oxopyranyl), **1a** and **1b**, and TpMo$(CO)_2$(η^3-pyridinyl), **2a**, scaffolds in high enantiopurity. These enantiomeric scaffolds are applied to the generation of heterocyclic structures in high enantiomeric excess. The syntheses of these scaffolds are similar to the racemic scaffolds, shown above (**Scheme 1** and **2**). The η^3-oxopyranyl enantiomeric scaffolds, **1a** and **1b**, are prepared with the use of a chiral auxillary to form diastereomers, **9a** and **9b**. These diastereomers are separated by column chromatography. Each diastereomer will then be metallated the same way as the racemic scaffolds**, 1** and **2**, forming the η^3-oxopyranyl scaffolds, **1a** and **1b**, in high optical purity(**Scheme 3**).[24]

Scheme 3. Synthesis of a η^3-Pyranyl Organometallic Enantiomeric Scaffold



The enantiomeric η^3-pyridinyl scaffold, **2a**, is prepared by using a chiral nitrogen-protecting group, **11**. This protecting group, **11**, will protect the furfuryl amine, **7**, and will eventually generate the $TpMo(CO)_2(\eta^3$-pyridinyl) scaffold, **2a**, as diastereomers (**Scheme 4)**.[24] The diastereomers are separated in high diastereomeric purity by column chromatography. The yields for the metallation steps are low in comparison to the enantiomeric synthesis of the η^3-pyranyl scaffold, **1a** and **1b**.

Scheme 4. The Synthesis of the Organometallic Enantiometric $TpMo(CO)_2(\eta^3$-pyridinyl) Scaffold



The Liebeskind organometallic enantiomeric scaffolds have been used to construct a variety of small natural products (**Figure 6**).[45] For example, 2,3,6-trisubstituted piperidine rings[21,49] are prepared *via* sequencial functionalization of the nitrogen heterocyclic molybdenum scaffold. Also, [4+2][22,44], [5+2],[22,26,45,47,55] and [5+3][43] cycloadditions have been employed for the construction of natural products, such

as tropanes. More recently, 1,5-Michael like reactions have been employed as a powerful way to access oxo- and aza[3.2.1]bicyclics in high enantiomeric excess.[24,56]

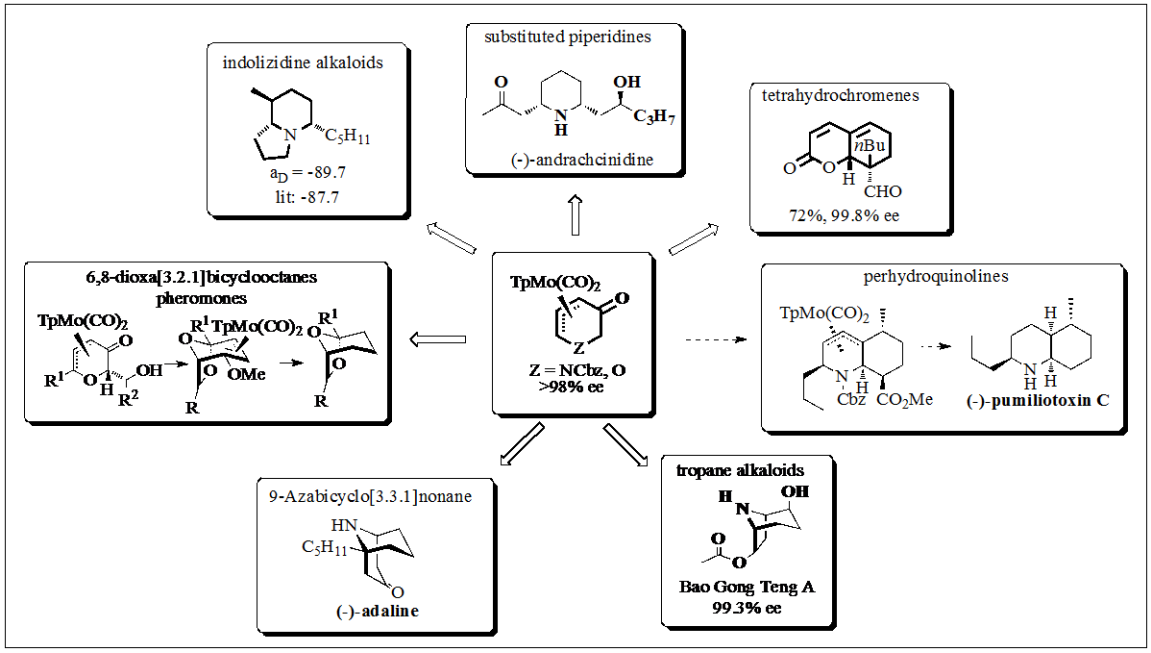


Figure 6. Versatility of the Organometallic Enantiomeric Scaffolds

From an exploratory perspective, this thesis describes a concise investigation of a new metal scaffold, $TpW(CO)_2(\eta^3$-oxopyranyl). The new scaffold is investigated through a [5+2] cycloaddition reaction. The relative reactivities (stability, handling, and preparation) plus the spectroscopic properties (IR, ^{1}H NMR, and ^{13}C NMR) of each compound synthesized is discussed below.

Results and Discussion:

1) Zero-Valent Tungsten Sources:

The first challenge to develop the $TpW(CO)_2(\eta^3$-oxopyranyl) scaffold was to determine the best zero-valent tungsten source to form a stable π-allyl during the metallation of the organic oxopyranyl ligand, **6**. Several different zero-valent tungsten

complexes were synthesized to test the formation of a stable π-allyl. Each of the tungsten sources was tested under a variety of solvents and conditions attempting to metallate the oxopyranyl ligand.

Initially, $W(CO)_3(MeCN)_3$ and $W(CO)_3(EtCN)_3$ were chosen because of their precedent in the literature for the ability to generate π-allyl complexes.[60-62] $W(CO)_3(MeCN)_3$ and $W(CO)_3(EtCN)_3$ were prepared following literature procedures using photochemical activation (1 day) or thermal conditions (6 days).[63-65] The highest yields occurred by the photochemical procedure. Using this procedure, $W(CO)_3(MeCN)_3$ was produced in 46% yield and $W(CO)_3(EtCN)_3$ in 66% yield. The photochemical procedure was also favored because of the substantially shorter synthesis time. There was a major drawback with the two *tris*-nitrile complexes, however. Over time, they would decompose when exposed to air and become unsuitable for synthesis.

The next zero-valent tungsten source chosen was $W(CO)_3(DMF)_3$. It was investigated because it is the analogous to $Mo(CO)_3(DMF)_3$, which is used for the preparation of the molybdenum oxopyranyl scaffold, **1**.[53] The procedure described in the literature was not reproducible. An attempt was made to generate $W(CO)_3(DMF)_3$ "in situ" just prior to metallation of 5-acetoxydihydropyran-3-one, **6**, but the synthesis was unsuccessful. With these negative results, $W(CO)_3(DMF)_3$ was abandoned as a possible zero-valent tungsten source.

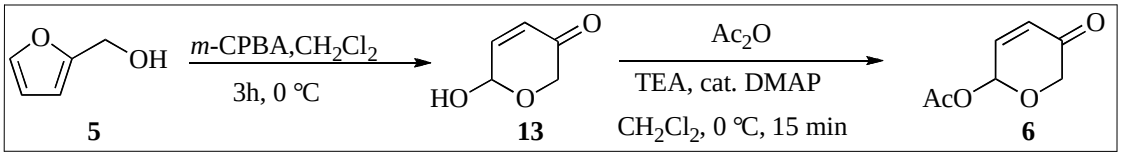
Two additional tungsten complexes, $W(CO)_3(pyr)_3$ and $W(CO)_3(tol)$, were explored. The $W(CO)_6$ was refluxed in pyridine to form $W(CO)_3(pyr)_3$ (98% yield). This synthesis is extremely easy and $W(CO)_3(pyr)_3$ can be stored for extended periods of time exposed to air. The synthesis of $W(CO)_3(tol)$ goes through $W(CO)_3(pyr)_3$ as an

intermediate.[66] $W(CO)_3(pyr)_3$ is refluxed in toluene producing a moderate synthetic yield of 50%. A drawback to using $W(CO)_3(tol)$ as the zero-valent tungsten source is that it takes two steps to synthesize. For this reason, the formation of $W(CO)_3(tol)$ was attempted by refluxing $W(CO)_6$ in toluene, but the desired product was not observed. There was only starting material detected after one day of refluxing.

2) Preparation of the η^3-5-Oxo-pyranyl Tungsten Scaffold:

5-Acetoxydihydropyran-3-one, **6**, was synthesized by treating furfuryl alcohol, **5**, with *m*-chloroperbenzoic acid, *m*-CPBA, and going through the Achmatowicz rearrangement (**Scheme 5**).[59] The second step is acylation of the 2º alcohol, **13**, to give a better leaving group for the metallation step. These steps were performed without any purification. Both reactions are typically a spot to spot conversion, seen by TLC in 1:1 hexanes: EtOAc, with no unwanted side products.

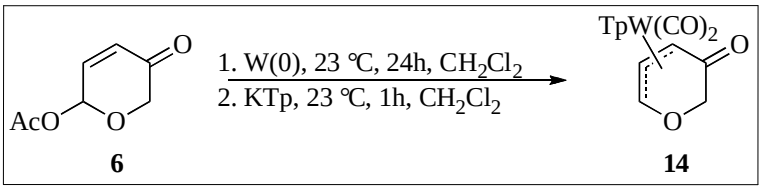
Scheme 5. Synthesis of 5-Acetoxydihydropyran-3-one from Furfuryl Alcohol



The identical metallation of 5-acetoxydihydropyran-3-one, **6**, with $Mo(CO)_3(DMF)_3$ to form the $TpMo(CO)_2(\eta^3$-oxopyranyl) scaffold, **1**, was applied to access the analogous oxopyranyl tungsten scaffold, **14** (**Table 1**).[53] It was necessary to run the reactions for a longer period of time due to the slower rate of formation of the corresponding tungsten scaffold, **14**. The yields for the η^3-5-oxo-pyranyl tungsten scaffold, **14**, were ≤ 20% with the two nitrile complexes (**Table 1**, Entries **1** and **2**). The $W(CO)_3(tol)$ produced a 25% yield result (**Table 1**, Entry **3**), while the $W(CO)_3(pyr)_3$ complex (**Table 1**, Entry **4**) gave the highest overall yield of 30%. The two nitrile

complexes, $W(CO)_3(MeCN)_3$ and $W(CO)_3(EtCN)_3$ were abandoned due to low yield and lack of stability to air at this point.

Table 1. The General Synthesis of η^3-Oxopyranyl Tungsten Scaffold, **14**, using the Procedure for Molybdenum Oxopyranyl Scaffold, **1**



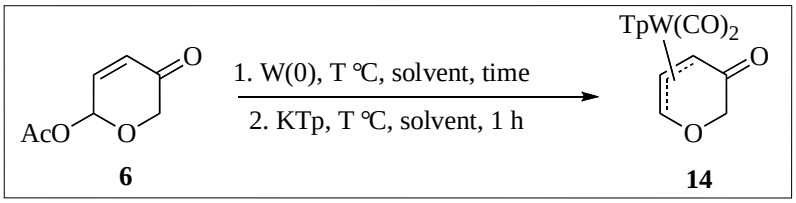
6 **14**

Entry	W(0) source	Yield (%)
1	$W(CO)_3(MeCN)_3$	18
2	$W(CO)_3(EtCN)_3$	20
3	$W(CO)_3$(tol)	25
4	$W(CO)_3(pyr)_3$	30

In order to increase the reaction rate, the metallation was run under reflux conditions in CH_2Cl_2. Both $W(CO)_3(pyr)_3$ and $W(CO)_3$(tol) showed an overall increase in the formation of the desired product, **14** (**Table 2**, Entries **1** and **2**). The remainder of the reaction mixture was starting material. Because the yields were only moderate after refluxing for ~24 hours, an alternative solvent was explored. THF was selected because it has been used in the formation of metal π-allyl complexes.[62] THF was also used because the refluxing temperature is higher than CH_2Cl_2, pushing the reaction to completion. Unexpectedly, when the reaction was run in THF the yield of the desired product, **14**, decreased (**Table 2**, Entries **3** and **4**). Instead there was a substantial amount of an undesired side product detected after the disappearance of the starting material. The unknown side product was shown to contain the Tp ligand. It is common at elevated temperatures for KTp to bind to a tungsten zero-valent source, forming $TpW(CO)_3$.[67]

The side product IR data did not match the IR data of $TpW(CO)_3$. The data showed that the side product is a different TpW complex than $TpW(CO)_3$. The isolated side product was never identified.

Table 2. Optimization of the Synthesis of η^3-5-Oxo-Pyranyl Tungsten Scaffold



6 **14**

Entry	W(0)	T ºC	Solvent	Time (h)	Yield (%)
1	$W(CO)_3$(tol)	Reflux	CH_2Cl_2	24	32
2	$W(CO)_3(pyr)_3$	Reflux	CH_2Cl_2	20	40
3	$W(CO)_3(pyr)_3$	Reflux	THF	20	9
4	$W(CO)_3$(tol)	Reflux	THF	24	17
5	$W(CO)_3(pyr)_3$	1. Reflux 2. 23 ºC	1. CH_2Cl_2 2. THF	18 2	70

In order to decrease the formation of the unknown TpW complex the synthesis of the η^3-5-oxo-pyranyl tungsten scaffold, **14**, was done in two steps. The zero-valent tungsten source was refluxed in CH_2Cl_2 with 5-acetoxydihydropyran-3-one, **6**, overnight. After the oxidative addition of the metal, the solvent was switched to THF. Following the solvent switch, KTp was added at 23 ºC (**Table 2**, Entry **5**). This method increased the yield for the metallation reaction significantly. The $W(CO)_3(pyr)_3$ complex had an overall yield of 70%. This is the desired route for the synthesis of the racemic η^3-5-oxo-pyranyl tungsten scaffold, **14**.

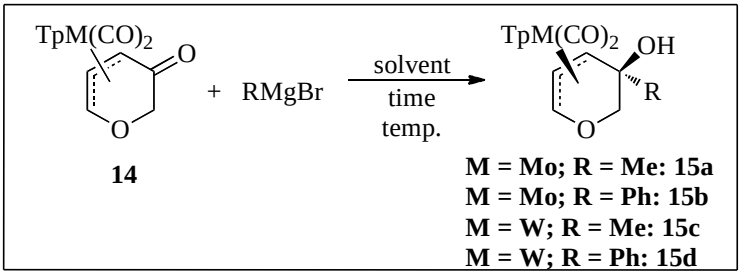
This new tungsten scaffold, **14**, was applied initially to study the same [5+2] cycloaddition reactions done with molybdenum. The [5+2] cycloaddition precursor was accessed *via* a Grignard reagent addition on η^3-5-oxo-pyranyl tungsten, **14**, followed by

elimination. Two systems were investigated one containing a methyl substituent and the other a phenyl substituent.

3) Synthesis of η^3-5-Hydroxy-5-methyl (or phenyl)pyranyl Tungsten Compound:

The synthesis of η^3-5-hydroxy-5-methyl (or phenyl) pyranyl tungsten complexes, **15a** or **15b**, were performed using a reliable procedure with different Grignard reagents, MeMgBr and PhMgBr. Previously, the molybdenum scaffold, **14**, was dissolved in CH_2Cl_2 in the presence of methyl Grignard (1 equiv) for 2h at lowered temperatures (**Table 3**, Entry **1**). The complex, **15a**, was immediately carried to the following step of the synthesis because of the loss of enantiomeric purity seen after the methyl addition product was purified.[23] The η^3-5-hydroxy-5-phenyl pyranyl molybdenum complex, **15b**, was isolated in 83% yield (**Table 3**, Entry **2**) after flash column chromatography purification.[23]

Table 3. Optimization of the Synthesis of η^3-5-Hydroxy-5-Methyl (or Phenyl) Pyranyl Metal Complexes



Entry	Metal	R, equiv	Solvent	Time (h)	Temp (ºC)	Yield (%)
1	Mo	Me, 1	CH_2Cl_2	2	-78 – 23	Not isolated
2	Mo	Ph, 1	CH_2Cl_2	2	-40 – 23	83
3	W	Ph, 1	CH_2Cl_2	2	-78 – 23	23
4	W	Me, 5	CH_2Cl_2	24	-78 – 23	20
5	W	Ph, 5	THF	24	-78 – 23	39
6	W	Me, 5	THF	24	-78 – 23	54
7	W	Me, 10	THF	2	0 - 23	92
8	W	Ph, 10	THF	2	0 - 23	80

The η^3-5-hydroxy-5-methyl (and phenyl) pyranyl tungsten compounds, **15c** or **15d**, were isolated as 3º alcohols through column chromatography. The tungsten alcohol complex synthesis of **15c** and **15d** was carried out in THF rather than CH_2Cl_2 (**Table 3**, Entries **3-6**). The yields were moderate for η^3-5-hydroxy-5-phenyl pyranyl tungsten, **15c**, compared to the molybdenum reaction yield (**Table 3**, Entry **2**). This could be due to the basic Grignard reagent deprotonating the starting material to form the enolate.

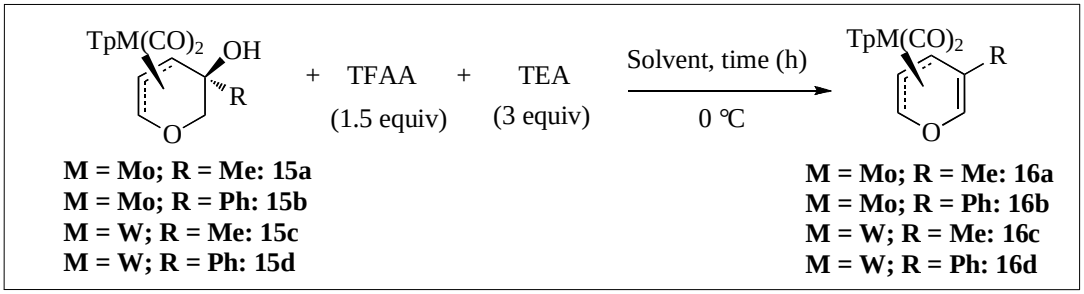
The side product formation from the Grignard additions was rectified with the use of $CeCl_3$. $CeCl_3$ is a Lewis acid that will inhibit the formation of an enolate from the addition of the Grignard reagent. $CeCl_3$ is specifically used for the 1,3-addition of an alkyl to a ketone.[68-71] The yields for the synthesis of η^3-5-hydroxy-5-methyl and phenyl pyranyl tungsten compounds, **15c** and **15d**, went up to 92% and 80%, respectively when using $CeCl_3$ (**Table 3**, Entries **7** and **8**). The drawback to using $CeCl_3$ is that it is extremely hydrophilic. In order for the optimum result of the Gringard addition, the $CeCl_3$ must be completely water-free and made directly prior to the substitution step.

4) Synthesis of the Fully Unsaturated Tungsten Scaffold:

Following the Grignard addition, dehydrogenation of the 3º alcohol, **15a** – **d**, was achieved with TFAA and TEA to generate the fully unsaturated metal scaffold, **16a - d** (**Table 4**). The molybdenum alcohol elimination step was run for 2.5 h in CH_2Cl_2 giving the expected compound in 90% yield when R = Me (**Table 4**, Entry **1**) and 82% yield for R = Ph (**Table 4**, Entry **2**). For the tungsten 3º alcohol elimination step the reaction conditions were slightly modified from those employed with the molybdenum 3º alcohol. This was done due to the low yield when the elimination was run in CH_2Cl_2 (~ 40%), therefore, the solvent was changed to THF. THF resulted in good to excellent yields

(**Table 4**, Entries **3** and **4**). The reaction was run for only 30 min due to the presence of a side reaction occurring at longer reaction times.

Table 4. The Conditions Required for the Synthesis of the Fully Unsaturated Compound



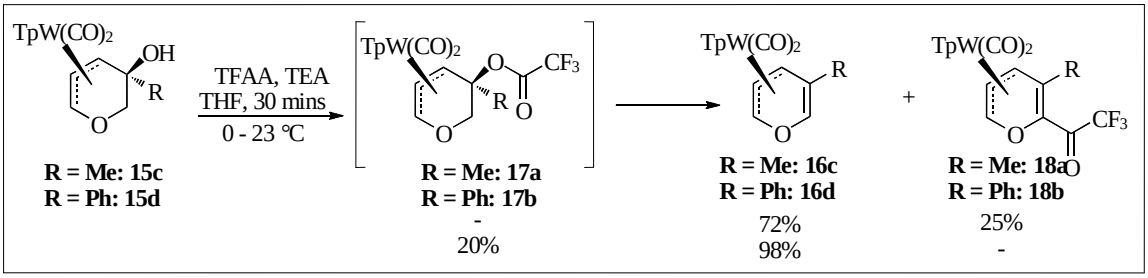
M = Mo; R = Me: 15a
M = Mo; R = Ph: 15b
M = W; R = Me: 15c
M = W; R = Ph: 15d

M = Mo; R = Me: 16a
M = Mo; R = Ph: 16b
M = W; R = Me: 16c
M = W; R = Ph: 16d

Entry	Metal (M)	R	Solvent	Time (h)	Yield (%)
1	Mo	Me	CH_2Cl_2	2.5	90
2	Mo	Ph	CH_2Cl_2	2.5	82
3	W	Me	THF	0.5	95
4	W	Ph	THF	0.5	98

The methyl substituted alcohol, **15c**, formed the expected product, **16c**, in 72% yield (**Scheme 6**). However, it reacted with excess TFAA remaining in the reaction mixture to form the Friedel-Craft product **18a**. By keeping the temperature at 0 ºC, the formation of the Friedel-Craft product, **18a**, was eliminated. The trifluoromethyl group was identified to be part of compound **18a** by running a ^{19}F NMR. The spectrum contained a single peak at -78 ppm in agreement with a trifluoromethyl group adjacent to a ketone. The elimination of the tungsten substituted phenyl alcohol, **15d**, did not show any of the phenyl Friedel-Craft product, **18b**. It was observed, via ^{1}H NMR, that the substituted phenyl complex, **15d**, went through a trifluoroacetate intermediate, **17b**, during the elimination step to form complex **16d**. The tungsten methyl substituted trifluoroacetate intermediate, **17c**, and the molybdenum trifluoroacetate intermediate were never observed during the reaction.

Scheme 6. Formation of a Friedel-Craft Side Product in the Elimination Step



R = Me: 15c
R = Ph: 15d

R = Me: 17a
R = Ph: 17b
-
20%

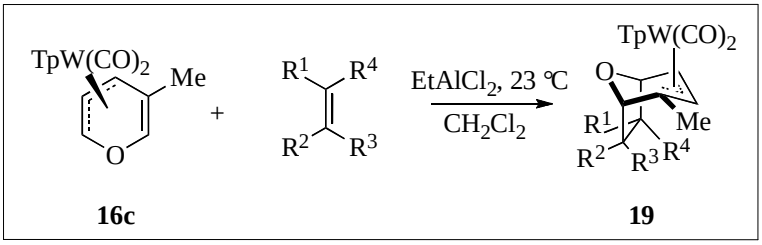
R = Me: 16c
R = Ph: 16d
72%
98%

R = Me: 18a
R = Ph: 18b
25%
-

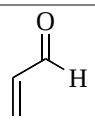
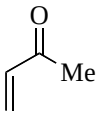
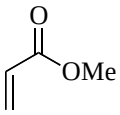
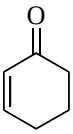
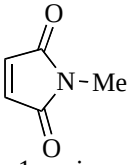
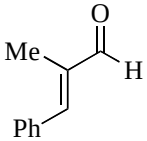
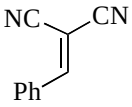
5) Synthesis of a Variety of [5+2] Cycloadducts:

A variety of dienophiles were selected to generate [5+2] cycloadducts (**Table 5**, Entries **1** – **7**). Optimization of the [5+2] cycloaddition reactions was accomplished with methyl vinyl ketone as the dienophile. Four different Lewis acids ($TiCl_4$, Et_2AlCl, $ZnCl_2$, and $EtAlCl_2$) were screened to determine the appropriate conditions for the tungsten [5+2] cycloaddition. The most effective Lewis acid for both tungsten and molybdenum was $EtAlCl_2$.[53] The $EtAlCl_2$ was used in both a catalytic amount (**Table 5**, Entries **1**, **4**, **6**) and in a stoichiometric amount (**Table 5**, Entries **2 - 3**, **5**, and **7**), depending on the reactivity of the dienophile.

Table 5. The [5+2] Cycloaddition of the Eliminated η^3-Methylpyranyl Tungsten Complexes



16c **19**

Entry	Alkene	#	$EtAlCl_2$, time	Yield (%); exo:endo
1	 1 equiv	**19a**	20%, 2.5h	95, 2:1
2	 3 equiv	**19b**	100%, 1.5h	75, 3:1
3	 1.5 equiv	**19c**	150%, 1.5h	95, 2:1
4	 2 equiv	**19d**	20%, 4h	80, ?
5	 1 equiv	**19e**	110%, 10 mins	70, exo only
6	 1 equiv	**19f**	20%, 3h	90, exo only
7	 3 equiv	**19g**	100%, 1.5h	90, exo only

The yields for the [5+2] cycloaddition reactions using the η^3-pyranyl tungsten scaffold, **16c**, gave similar yields as its molybdenum counterpart, **16a**. The *exo* and *endo* assignments for the tungsten [5+2] cycloadditions were assigned with the aid of previous molybdenum [5+2] cycloaddition work.[53] The *exo* and *endo* products were never isolated separately from one another making it difficult to distinguish between the two configurations. The data reported in the experimental sections of this report is for the *exo* configuration only. Further work will need to be done to determine with certainty that the *exo* and *endo* assignments were made properly.

There were two main differences that emerged between the tungsten and molybdenum [5+2] cycloaddition reactions. In the tungsten reactions, there was a decrease in the *exo*: *endo* ratio. Secondly, several Friedel Craft products, **20d**, **20e**, and **20g**, were observed during purification of three of the tungsten [5+2] cycloaddition reactions (**Figure 7**). These Friedel-Craft products were also difficult to purify.

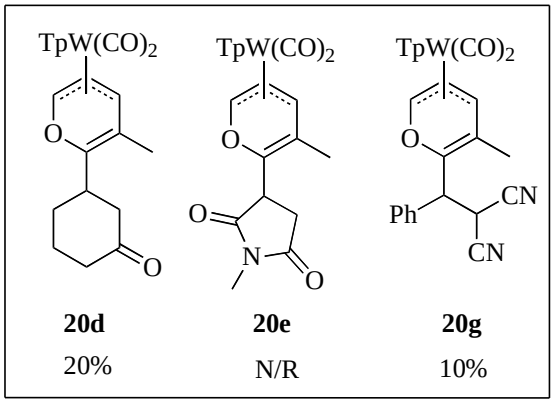


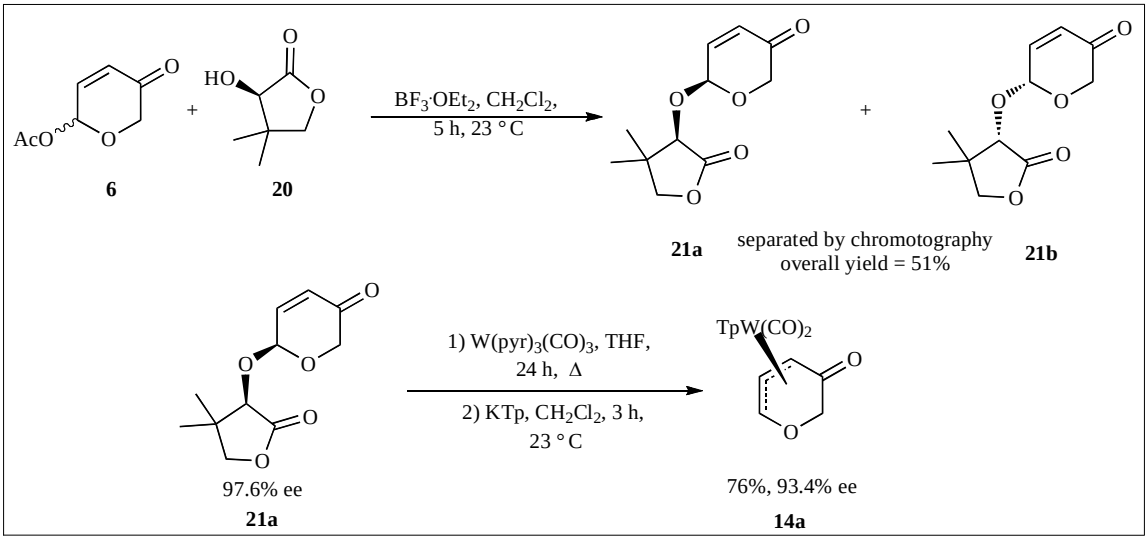
Figure 7. Friedel Craft Side Products of the [5+2] Cycloaddition Reactions

6) Synthesis of the Enantiomeric TpW(CO)$_2$(η^3-oxopyranyl) Scaffold:

The first organometallic enantiomeric TpW(CO)$_2$(η^3-oxopyranyl) scaffold, **14a**, has also been synthesized. The synthesis of the tungsten enantiomeric scaffold, **14a**,

starts with 5-acetoxydihydropyran-3-one, **6**, reacting with the chiral auxillary, (R)-(-)-pantolactone, **20**, to form two diastereomers, **21a** and **21b** in a 51% overall yield (**Scheme 7**). The two diastereomers were separated *via* column chromatography in a 3:1 ratio of **21a**:**21b**. Diastereomer, **21a**, participated in oxidative addition to $W(CO)_3(pyr)_3$ followed by ligand exchange to form the enantiomeric $TpW(CO)_2(\eta^3$-oxopyranyl) scaffold, **14a**, with a yield of 76% and an overall ee of 94.3%. The enantiomeric scaffold synthesis was done identically to the racemic tungsten scaffold once the (R)-pantolactone-substituted-2*H*-pyran-3(6*H*)-one, **21a**, was formed. The yield for the tungsten enantiomeric oxopyranyl scaffold, **14a**, was similar to that of the racemic tungsten oxopyranyl scaffold, **14**.

Scheme 7. The Synthesis of the Enantiomeric $TpW(CO)_2(\eta^3$-oxopyrany) Scaffold



7) Spectral Property Differences Between Molybdenum and Tungsten Scaffolds:

The spectral properties of the $TpMo(CO)_2(\eta^3$-oxopyranyl) scaffold, **1**, and the $TpW(CO)_2(\eta^3$-oxopyranyl) scaffold, **3**, were compared. Based on their electronegativity, molybdenum and tungsten scaffolds are expected to show differences in the metal

carbonyls in IR. This was observed for the two oxopyranyl scaffolds, **1** and **14**. The tungsten scaffold, **14**, shows lower stretches for its metal carbonyls (**Figure 8**). This is because tungsten induces a stronger π-backbonding effect to the carbonyls directly attached to it. This is derived from tungsten having a lower electronegativity than molybdenum.

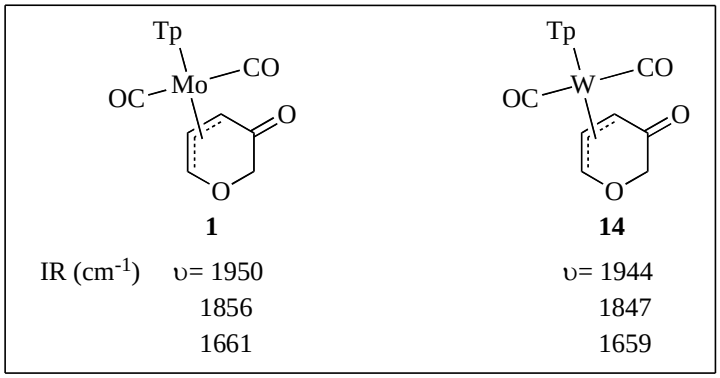


Figure 8. Relevant IR Data to Show the Differences Between Molybdenum and Tungsten Scaffolds

Another spectral property that was investigated for the two oxopyranyl scaffolds, **1** and **14** was ^{1}H NMR. There were only slight differences in the ^{1}H NMR shifts for tungsten and molybdenum η^3-oxopyranyl scaffolds, **1** and **14**, in the protons belonging to the π-allyl system (**Figure 9**). The tungsten π-allyl protons are more shielded than the molybdenum allyl protons. This trend is also in agreement with the differences in electronegativity of the two metals.

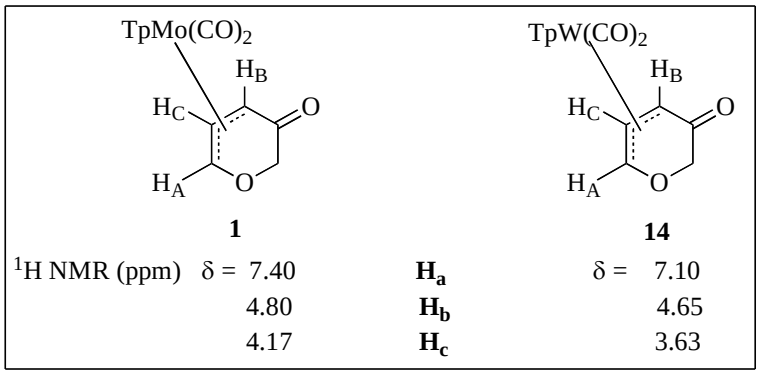


Figure 9. ^{1}H NMR Data of the η^{3}-Allyl Protons for the Tungsten and Molybdenum η^{3}-5-Oxopyranyl Scaffold

Conclusion

In this study, the first example of a tungsten oxopyranyl scaffold, **14,** was synthesized. The tungsten scaffold, **14**, was investigated through a variety of [5+2] cycloaddition reactions. In order to access the [5+2] cycloadduct, nucleophilic addition followed by elimination of the oxopyranyl tungsten scaffold, **14**, was necessary. The [5+2] cycloaddition reactions gave moderate to excellent yields. It was observed that there were significant differences between molybdenum and tungsten in both reactivity and spectral properties. Switching molybdenum for tungsten had an effect on the reaction rates. Almost all the tungsten reactions were slower. Also, the tungsten compounds showed a slight difference in reactivity from the molybdenum compounds. In both the elimination reaction and three of the [5+2] cycloadditon reactions Friedel Craft acylation products were detected. This "*unusual"* reactivity could lead to the formation of a stereocontrolled stereocenter at the C6 position, allowing for different natural product synthesis targets to be made. Spectroscopically, the differences in chemical shifts and IR frequencies were attributed to differences in electronegativity of

the metals. Tungsten shielded the π-allyl protons more than molybdenum because tungsten has a lower electronegativity than molybdenum. The tungsten compounds also had lower carbonyl stretching frequencies due to larger π-backbonding in the metal carbonyl bonds.

In the future, the *exo* and *endo* [5+2] cycloaddition products need to be isolated from one another. An NOE NMR experiment will need to be run to determine that the correct ^{1}H NMR assignments were made. The Friedel-Craft products from the [5+2] cycloaddition reactions should be further tested. Also, it will be beneficial to determine a way to favor the formation of only the Friedel-Craft acylation products. Finally, the enantiomeric TpW(CO)$_2$(η^3-oxopyranyl) scaffold, **14a**, needs to be applied to the [5+2] cycloaddition reactions.

Experimental

Methods and Materials

Unless specified all reactions were performed under positive pressure of dry argon or nitrogen. All solvents were dried and degassed before use. Optima grade solvents were bought from Fisher Scientific Company (www.fishersci.com) and degassed with argon. All chemicals were purchased from Aldrich Chemical Co. (www.aldrich.com) and used as received. KTp was prepared following a literature procedure.[57,58] Reactions were run in solvents dispensed and used directly from a Seca Solvent System purchased from Glass Contour. Cold baths were generated as follows: 0 ºC, ice/water; -40 ºC dry ice/acetone; -78 ºC, dry ice/acetone

Analytical thin-layer chromatography (TLC) was performed with commercial Merck KGaA aluminium-backed silica gel plates (thickness: 200 μm) with fluorescent indicator (F-254). Visualization was accomplished with UV light, 5% phosphomolybdic acid in ethanol, and $KMnO_4$ stain (oxidation reaction only). Purification of compounds was performed with a mixture of hexanes and ethyl acetate on 32-63 silica gel.

Unless otherwise indicated, all ^1H NMR and ^{13}C NMR spectra were recorded on a VNMR 400 (400MHz for ^1H, 100 MHz for ^{13}C) or a Unity 600 MHz (600 MHz for ^1H, 150 MHz for ^{13}C) spectrometer in $CDCl_3$ at room temperature with internal $CHCl_3$ as the reference (7.26 ppm for ^1H and 77.2 ppm for ^{13}C). Infrared spectra were recorded on an ASI React IR 1000 FT-IR spectrometer, equipped with a silicon probe, or a Nicolet™ 380 FT-IR spectrometer, equipped with a diamond plate. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67–100%), m (medium 40-67%), w (weak 20-40%) and br (broad). High performance liquid chromatography (HPLC) was done at 23 ºC on an Agilent 1100 system with a quaternary pump. The separations were performed on DAICEL chiral CHIRALPAK AD/OD/AS[72] reversed phase columns using a Waters™ 486 UV detector. HPLC grade solvents were used. The melting points on all the compounds still need to be taken.

1. Tungsten Metallation Sources

I. Synthesis of tricarbonyltrisacetonitriletungsten, $W(CO)_3(Me_3CN)_3$[65]

$W(CO)_6$ (476.4 mg, 1.354 mmol) was placed in a 100-mL Schlenk flask, under argon, with a large excess of acetonitrile (35 mL). The clear solution was irradiated with a UV lamp at 250 nm for 24 h generating a green solution. Acetonitrile was removed by

evaporation under reduced pressure and the resulting yellow solid was washed with ether until the filtrate became clear. This left 216.4 mg (46%) of $W(CO)_3(Me_3CN)_3$.

IR (cm^{-1}): 2930 (w), 2853 (w), 2019 (s), 1876 (s), 1830 (s).

The synthesis above can also be performed under argon with refluxing conditions. The yields are similar, but the reaction took two days. Due to the substantial amount of time required for this synthesis the irradiation method was favored.[63]

II. Synthesis of tricarbonyltrispropionitriletungsten, $W(CO)_3(EtCN)_3$[65]

Under argon, $W(CO)_6$ (431.7 mg, 1.23 mmol) was placed in a 100-mL Schlenk flask and dissolved in propionitrile (33 mL). The solution was irradiated with a UV lamp (250 nm) for 18 h. The green-yellow slurry was filtered and washed with ether, yielding a yellow solid (350 mg, 66%).

IR (cm^{-1}): 2934 (s), 2876 (m), 2019 (m), 1938 (s), 1891 (s). 1841(s).

The synthesis above can also be performed under argon with refluxing conditions. The yields are similar but the reaction took six days . Due to the substantial amount of time required for this synthesis the irradiation method was favored.[64]

III. Synthesis of tricarbonyltrispyridinetungsten, $W(CO)_3(pyr)_3$[73]

Under argon, pyridine (220 mL) and $W(CO)_6$ (11.54 g, 0.0328 mol) were refluxed for 24 h in a 500-mL Schlenk flask. During the reflux the solution went from clear to bright orange. After 24 h the solution was cooled to 23 ºC. Ether was added to the solution and an orange precipitate crashed out. The Schlenk flask was placed in an ice bath for 10 minutes before the solid was filtered through a course 250-mL glass frit that was open to air. The orange crystalline solid (16.3 g, 98%) was washed with ether until the filtrate became clear.

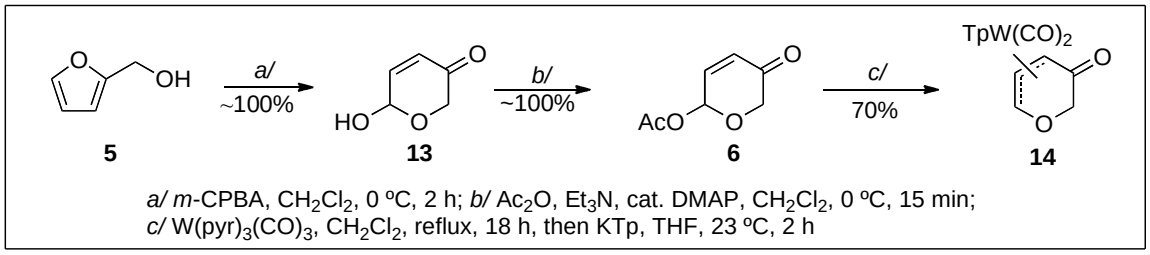
TLC: R_f = 0.38 (hexanes:EtOAc, 1:1); **IR** (cm^{-1}): 2007 (w), 1861 (s), 1818 (s), 1764 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.74 (dt, *J* = 2.0, 8.0 Hz, 2H), 7.76 (tt, *J* = 2.4, 10.4 Hz, 1H), 7.23 (dt, *J* = 1.2, 6.8 Hz, 2H).

IV. Synthesis of tricarbonyltoluenetungsten, W(CO$_3$)(tol).[66,73]

Under argon, a 250-mL Schlenk flask containing $W(pyr)_3(CO)_3$ (519.6 mg, 6.57 mmol) was refluxed in toluene (160 mL) for 20 h. The reaction mixture was cooled to 23 ºC and the excess toluene was removed under vacuum to yield a yellow solid. The solid was washed with pentane until the filtrate became clear. $W(CO)_3$(tol) (185 mg, 50%) was dried under vacuum for 2 h before storing.

IR (cm^{-1}): 2961 (w), 2930 (w), 2007 (w), 1926 (s), 1876 (s), 1826 (s).

2. Synthesis of the Racemic Tungsten Pyranyl Scaffold



*I. Synthesis of 6-hydroxy-6H-pyran-3-one, **13***

Furfuryl alcohol, **5**, (2.0 mL, 2.314 mmol, 1 equiv) was added to CH_2Cl_2 (50 mL) and the solution was cooled to 0 ºC. *m*CPBA (77%, 4.00 g, 3.01 mmol, 1 equiv) was added to the clear solution in two equal portions with a 15 min interval between the two additions. The white suspension was stirred open to air for 2 h while being slowly warmed to 23 ºC. The reaction was filtered through a coarse glass frit to remove *m*-chlorobenzoic acid. The filtrate was concentrated to dryness and assumed to have a 100% yield.

II. Synthesis of 6-acetoxy-6H-pyran-3-one, ***6***

The crude 6-hydoxy-6*H*-pyran-3-one, **13**, (2.864 g, 25 mmol, 1 equiv) was dissolved in CH_2Cl_2 and cooled to 0 ºC. Acetic anhydride (3.6 mL, 3.77 mmol, 1.5 equiv) was added drop-wise yielding a golden brown solution. Triethylamine (7.0 mL, 5.02 mmol, 2 equiv) was added drop-wise to the stirring solution followed by addition of 4-*N,N*-(dimethylamino)-pyridine (0.61 g, 0.5 mmol, 0.2 equiv). The reaction was run under argon. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (25 mL) after 15 min. The organic layer was washed with 1:1 H_2O:$NaHCO_3$ (2 x 50 mL). The combined organic layers were dried over $MgSO_4$. The slurry was filtered and concentrated to dryness. The crude product (assumed a 100% yield) was used for the next step without further purification.

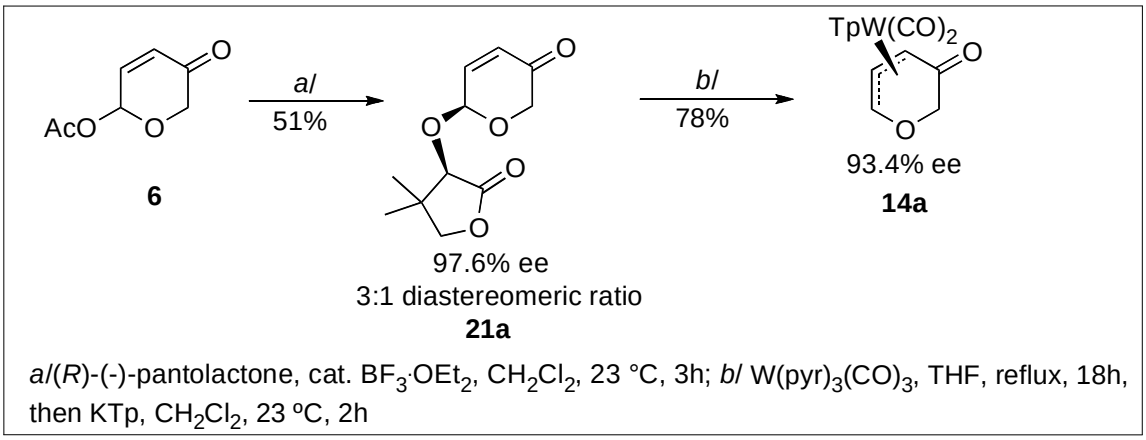
III. Synthesis of Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-5-oxo-5,6-dihydro-2H-pyran-2-yl]tungsten, ***14***

In a Schlenk flask, CH_2Cl_2 (40 mL) was added to $W(CO)_3(pyr)_3$ (19.32 g, 0.038 mol, 1 equiv) and crude 6-acetoxy-5-oxo-5,6-dihydro-2*H*-pyran, **6**, (5.96 g, 0.038 mol, 1 equiv). The reaction was refluxed under argon for 24 h. The orange solution was cooled to 23 ºC and a solvent switch from CH_2Cl_2 to THF (40 mL) was done. Solid KTp (12.80 g, 0.052 mol, 1.1 equiv) was added to the stirring solution in one large portion. After 2 h, the solution was filtered through a short plug of silica using 1:1 hexanes: EtOAc. The orange solution was dried under reduced pressure then triturated with ether to yield a yellow-orange crystalline solid (14.60 g, 70%).

TLC: R_f = 0.42 (hexanes:EtOAc, 2:1); **IR** (cm^{-1}): 1953 (s), 1864 (s), 1737 (s), 1652 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.57 (d, *J* = 2.0 Hz, 1H), 8.01 (d, *J* = 1.6 Hz, 1H), 7.77

(d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 2.0, 4.8 Hz, 1H), 6.30 (t, *J* = 2.4 Hz, 1H), 6.29 (t, *J* = 2.0 Hz, 1H), 6.24 (t, *J* = 2.4 Hz, 1H), 4.65 (dd, *J* = 2.4, 6.4 Hz, 1H), 3.63 (dd, *J* = 5.2, 6.0 Hz, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 3.30 (d, *J* = 17.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 216.5, 193.9, 154.9, 148.9, 144.9, 142.2, 136.8, 135.2, 107.3, 106.8, 106.7, 98.9, 97.7, 66.6, 63.4, 58.2; **HRMS**: (ESI) found for $C_{16}H_{15}BWN_6O_4$ $[M-H]^+$: 550.0757.

3. Synthesis of Enantiomerically Pure Tungsten Pyranyl Scaffold



a/(*R*)-(-)-pantolactone, cat. $BF_3{\cdot}OEt_2$, CH_2Cl_2, 23 °C, 3h; *b*/ $W(pyr)_3(CO)_3$, THF, reflux, 18h, then KTp, CH_2Cl_2, 23 ºC, 2h

I. Synthesis of (R)-pantolactone-substituted-2H-pyran-3(6H)-ones, ***21a and 21b***[74]

(*R*)-(-)-Pantolactone (99% ee, 4.948 g, 0.038 mol, 1 equiv) was dissolved in CH_2Cl_2 (50 mL) under argon and stirred for 10 min in a 250-mL round bottom flask. 6-Acetoxy-6*H*-pyran-3-one, **6**, (5.932 g, 0.038 mol, 1 equiv) was added to the solution drop-wise using CH_2Cl_2 (~15 mL) to transfer the material. A catalytic amount of $BF_3{\cdot}OEt_2$ (0.95 mL, 0.008 mmol, 0.2 equiv) was added drop-wise to the stirring mixture at 0 ºC. The reaction was stirred for 3 h at 23 ºC. The two diastereomers were separated by purification on a column of silica gel using 5:1 hexanes:EtOAc (4.258 g, 50%, 97.6% ee).

TLC: R_f = 0.46 (hexanes:EtOAc, 1:1); **IR** (cm^{-1}): 2964 (m), 2937 (m), 1780 (s), 1710 (s); **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.01 (dd, *J* = 3.6, 10.2 Hz, 1H), 6.19 (d, *J* = 10.5 Hz,

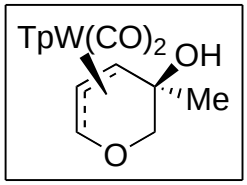
1H), 5.81 (dd, *J* = 0.6, 3.3 Hz, 1H), 4.45 (d, *J* = 16.8 Hz, 1H), 4.25 (s, 1H), 4.14 (d, *J* = 17.1 Hz, 1H), 4.03 (d, *J* = 9.0 Hz, 1H), 3.97 (d, *J* = 9.3 Hz, 1H), 1.24 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) 193.7, 174.6, 143.5, 127.8, 91.6, 78.3, 76.1, 66.0, 40.0, 22.9, 19.3.

II. Dicarbonyl[hydridotris(1-pyrazoly)borato][η-(2,3,4)-5-oxo-5,6-dihydro-2H-pyran-2-yl]tungsten, ***14a*** *and* ***14b***

This procedure follows the synthesis of enatiopure dicarbonyl[hydridotris(1-pyrazoly)borato][η-(2,3,4)-5-oxo-5,6-dihydro-2H-pyran-2-yl]molybdenum.[53] Under argon, (*R*)-Pantolactone-substituted-2*H*-pyran-3(6*H*)-one, **21a** and **21b** (329.9 mg, 1.47 mmol, 97.6% ee, 1 equiv) was dissolved in THF (~2 mL). The solution was added drop-wise to a Schlenk flask containing a solution of $W(CO)_3(pyr)_3$ (1.498 g, 2.94 mmol, 2 equiv) and THF (10 mL). The orange solution was stirred continuously for 18 h under refluxing conditions. The reaction was cooled to 23 ºC and THF was removed under vacuum. CH_2Cl_2 (10 mL) was used to dissolve the intermediate, followed by the addition of KTp (409.5 mg, 1.62 mmol, 1.1 equiv) in one large portion, at 23 ºC. The reaction was stirred for 2 h after the addition of KTp. The yellow-green solution was run through a short plug of silica gel and concentrated to dryness. The solid was purified by flash column chromatography with 1:1 hexanes:EtOAc as the eluting solvent. A bright yellow product (612.4 mg, 76%, 93.4% ee) was recovered. The ee was determined by comparing the racemate to this high ee compound using the HPLC system mentioned below. The spectral data for the racemic version of this compound can be found above.

HPLC: Daicel Chiralpak AS-RH: gradient solvent system used (% MeCN in H_2O with 0.1% TFA) = 0-5 mins, 60 to 40%; 5-15 mins, 50 to 50%; 15-20 mins, 60 to 40%, 1.0 mL/min, 254 nm.

4. Synthesis of (±)-Dicarbonyl[hydrio*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-methyl-5-hydroxy-2*H*-pyran-2-yl]tungsten, 15c



I. Synthesis with MeMgBr

Methyl magnesium bromide (3.0 M in diethyl ether, 1.6 mL, 4.66 mmol, 5 equiv) was added drop-wise to a solution of tungsten pyranyl scaffold (513 mg, 0.932 mmol, 1 equiv) in THF (10 mL) under argon at -78 ºC. The solution was slowly warmed to 23 ºC over a period of 2 h, and the reaction was stirred for additional 20 h at 23 ºC. The reaction was quenched with one piece of ice. The filtrate was concentrated to dryness and purified by flash column chromatography using 3:1 hexanes:EtOAc to yield a yellow solid (283 mg, 54%).

II. Synthesis using $CeCl_3$·MeMgBr[70]

$CeCl_3.7H_2O$ (366.7 mg, 0.98 mmol, 10 equiv) was ground into a very fine powder using a mortar and pistol. The cerium was weighed quickly, to limit exposure to the air, due to cerium being highly hydrophilic. The white powder was added to an oven dried 3-necked flask heated to 130 - 140 ºC over a period of 3 h, under vacuum. Once the appropriate temperature is reached the cerium is left under vacuum for 5 h. Following

the allotted time, an oven dried stir bar is added to the flask. The fine white powder is stirred continuously for 18h.

The reaction vessel was placed under argon and cooled to 23 ºC. The vessel was cooled to 0 ^{o}C for 10 minutes before dry THF (5 mL) was added to the 3-necked round bottom flask. The white slurry was stirred for 18 h.

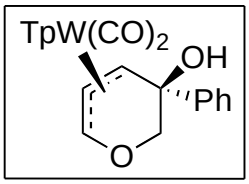
The reaction was cooled to 0 ºC and chilled (~0 ºC) MeMgBr (3.0M in diethyl ether, 0.33 mL, 0.98 mmol, 10 equiv) was added drop-wise to the white suspension and left for 2 h. Dicarbonyl[hydrido*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]tungsten, **14**, (54.0 mg, 0.098 mmol, 1 equiv) was added in one portion to the white slurry and stirred for 3 h.

The reaction was quenched with 10% acetic acid in water, which was added drop-wise till all cerium solid disappeared. CH_2Cl_2 (10 mL) was added to the reaction mixture. The organic layer was washed with brine, followed by a saturated aqueous solution of $NaHCO_3$ One final wash was performed with brine. The organic layer was dried over $MgSO_4$, followed by filtration. The filtrate was concentrated under vacuum and purified by flash chromatography on a silica column using 2:1 hexanes:EtOAc to yield a pale yellow solid (50.9 mg, 92% yield).

TLC: R_f = 0.59 (hexanes:EtOAc, 1:1); **IR** (cm^{-1}): 3579 (w), 3126 (w), 2949 (m), 2501 (m), 1924 (s), 1809 (s), 1504 (s); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.54 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 2.4 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 2H), 7.51 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 2.4, 4.8 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 1H), 6.24 – 6.22 (m, 2H), 4.28 (br d, *J* = 7.2 Hz, 1H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.02 (s, 1H), 2.89 (dd, *J* = 4.4, 7.2 Hz, 1H), 2.55 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 226.1, 216.2,

148.2, 143.0, 142.5, 136.5, 136.4, 134.9, 106.9, 106.4, 106.1, 101.5, 74.7, 71.6, 67.8, 52.0, 32.3; **HRMS**: (ESI) found for $C_{17}H_{18}BWN_6O_4$ $[M-H]^+$: 567.11431.

5. Synthesis of (±)-Dicarbonyl[hydrio*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-phenyl-5-hydroxy-2*H*-pyran-2-yl]tungsten, 15d



I. Synthesis with PhMgBr

Phenyl magnesium bromide (3.0M in diethyl ether, 0.4 mL, 0.129 mmol, 1.5 equiv) was added drop-wise to the tungsten pyranyl scaffold, **14**, (47.0 mg, 0.086 mmol) in THF (10 mL) under argon at -40 ºC. The reaction was kept at -40 ºC for 2 h, warmed to 23 ºC and stirred for an additional 4 h at that temperature. The reaction was quenched with a small piece of ice and purified identically to the (±)dicarbonyl[hydrio*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-methyl-5-hydroxy-2*H*-pyran-2-yl]tungsten synthesis. The solution was concentrated to dryness and yielded a bright yellow solid (24.8 mg, 51%).

II. Synthesis with PhLi and $CeCl_3.7\ H_2O$.[70]

$CeCl_3.7H_2O$ (396.4 mg, 1.06 mmol, 10 equiv) was ground into a very fine powder using a mortar and pistol. The cerium was weighed quickly, to limit exposure to the air, due to cerium being highly hydrophilic. The white powder was added to an oven dried 3-necked flask heated to 130 - 140 ºC over a period of 3 h, under vacuum. Once the appropriate temperature is reached the cerium is left under vacuum for 5 h. Following the allotted time, an oven dried stir bar is added to the flask. The fine white powder is stirred continuously for 18h.

The reaction vessel was placed under argon and cooled to 23 ºC. The vessel was cooled to 0 ºC for 10 minutes before dry THF (5 mL) was added to the 3-necked round bottom flask. The white slurry was stirred for 18 h.

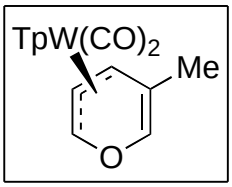
The reaction was cooled to 0 ºC and chilled PhLi (~0 ºC, 1.9M in dibutyl ether, 0.56 mL, 1.07 mmol, 10 equiv) was added drop-wise to the white slurry and left for 2 h. Dicarbonyl[hydrido*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl]tungsten, **14**, (60.2 mg, 0.107 mmol, 1 equiv) was added in one portion to the white slurry and stirred for 3 h.

The reaction was quenched with 10% acetic acid in water, which was added drop-wise untill all the cerium solid disappeared. CH_2Cl_2 (10 mL) was added to the reaction mixture. The organic layer was washed with brine, followed by a saturated aqueous solution of $NaHCO_3$. One final wash was performed with brine. The organic layer was dried over $MgSO_4$, followed by filtration. The filtrate was concentrated under vacuum and purified by flash chromatography on a silica column using 2:1 hexanes:EtOAc to yield a pale yellow solid (48.3 mg, 80%).

TLC: R_f = 0.53 (hexanes:EtOAc, 2:1); **IR** (cm^{-1}): 2494 (br w), 1934 (s), 1837 (s), 1598 (w), 1505 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.58 (d, *J* =2.0 Hz, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.83 (t, *J* = 2.0 Hz, 2H), 7.81 (d, *J* = 1.2 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.29-7.27 (m, 1H), 6.89 (dd, *J* = 2.0, 4.4 Hz, 1H), 6.30 (t, *J* = 2.0 Hz, 1H), 6.24 (t, *J* = 2.0, 1H), 6.18 (t, *J* = 2.0 Hz, 1H), 4.38 (br d, *J* = 7.6 Hz, 1H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.25 (br s, 1H), 2.97 (dd, *J* = 4.8, 7.2 Hz, 1H), 2.87 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 226.7, 216.5, 149.3, 148.3, 143.4, 142.4, 136.6, 135.0, 129.9, 128.6, 128.4, 127.4, 126.1, 125.0,

120.9, 115.5, 107.0, 106.4, 106.1, 101.0, 74.4, 73.9, 68.8, 53.1, 14.4. HRMS data still needs to be taken.

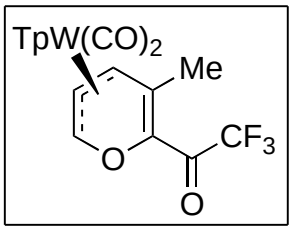
6. Synthesis of Dicarbonyl[hydrido*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-methyl-2*H*-pyran-2-yl]tungsten, 16c



Under argon, compound **15c** (151.6 mg, 0.32 mmol, 1 equiv) was dissolved in CH_2Cl_2 (5 mL) at 0 ºC for 5 min. TFAA (0.07 mL, 0.48 mmol, 1.5 equiv) and triethylamine (0.13 mL, 0.96 mmol, 3.0 equiv) were added drop-wise to the golden solution at 0 ºC. The reaction was stirred for 15 min and flushed through a short plug of silica gel. The solution was purified by flash chromatography in 2:1 hexanes:EtOAc, neutralized with 1% triethylamine. The yellow solid (143.9 mg, 95%) was isolated and characterized.

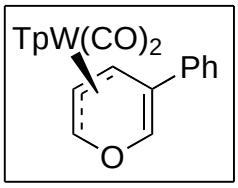
TLC: R_f = 0.74 (hexanes:EtOAc, 3:1); **IR** (cm^{-1}): 2490 (w), 1930 (s), 1841 (s), 1505 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.31 (d, *J* = 1.6 Hz, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 2.4, 4.4 Hz, 1H), 6.26 (t, *J* = 2.4 Hz, 1H), 6.24 (t, *J* = 2.4 Hz, 1H), 6.20 (t, *J* = 2.4 Hz, 1H), 5.63 (s, 1H), 4.23 (dd, *J* = 2.4, 6.0 Hz, 1H), 1.97 (dd, *J* = 4.4, 6.0 Hz, 1H), 1.89 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 221.9, 215.9, 147.0, 142.8, 141.5, 136.4, 136.2, 134.8, 130.2, 118.3, 106.4, 106.3, 106.0, 100.9, 55.6, 40.0, 19.1; **HRMS**: (ESI) found for $C_{17}H_{16}BWN_6O_3$ $[M-H]^+$: 547.10078.

If the reaction is run for a longer period of time, a second product begins to form. This will become the major product at longer reaction times. This product was characterized and determined to be the trifluoroacylation product, 18a:



TLC: R_f = 0.68 (hexanes:EtOAc, 3:1); **IR** (cm^{-1}): 2923 (w), 2851 (w), 1949 (s), 1867 (s), 1691 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 2.0 Hz, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.67 (br s, 2H), 7.54 (dd, *J* = 0.8, 1.6 Hz, 1H), 7.38 (dd, *J* = 1.6, 2.8 Hz, 1H), 6.31 (t, *J* = 2.4 Hz, 1H); 6.28 (t, *J* = 2.4 Hz, 1H), 6.23 (t, *J* = 2.4 Hz, 1H), 4.37 (dd, *J* = 2.8, 0.8 Hz, 1H), 2.54 (s, 3H), 2.11 (t, *J* = 5.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 219.8, 213.4, 146.7, 145.9, 142.8, 142.5, 136.7, 135.2, 132.2, 106.7, 106.4, 98.8, 59.0, 41.0, 21.7; **^{19}F NMR** ($CDCl_3$, 400 MHz): δ -78; **HRMS**: (ESI) found for $C_{19}H_{16}BWN_6O_4F_3$ $[M-H]^+$: 643.08289.

7. Synthesis of Dicarbonyl[hydrido*tris*(1-pyrazolyl)borato][η-(2,3,4)-5-phenyl-2*H*-pyran-2-yl]tungsten, 16d

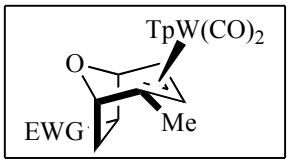


Under argon, compound **15d** (25.1 mg, 0.039 mmol, 1 equiv) was dissolved in CH_2Cl_2 (2 mL) at 0 ºC for 5 min. TFAA (8.2 mL, 0.059 mmol, 1.5 equiv) and triethylamine (17 mL, 0.12 mmol, 3.0 equiv) were added drop-wise to the golden solution at 0 ºC. The

reaction was stirred for 15 min and flushed through a short plug of silica gel. The solution was purified by flash chromatography in 2:1 hexanes:EtOAc, neutralized with 1% triethylamine. The yellow solid (24.4 mg, 98%) was isolated and characterized.

TLC: R_f = 0.58 (hexanes:EtOAc, 1:1); **IR** (cm^{-1}): 1922 (s), 1833 (s), 1710 (s), 1640 (w), 1505 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.31 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 2.4 Hz, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.65 (br s, 2H), 7.52 – 7.39 (m, 3H), 7.38 – 7.35 (m, 2H), 7.29 (dd, *J* = 2.4, 4.4 Hz, 1H), 7.28 – 7.26 (m, 1H), 6.29 (t, *J* = 2.4 Hz, 1H), 6.27 (t, *J* = 2.4 Hz, 1H), 6.19 (t, *J* = 2.4 Hz, 1H), 4.89 (dd, *J* = 2.4, 6.4 Hz, 1H), 2.11 (dd, *J* = 4.4, 6.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): 216.5, 180.9, 149.7, 149.3, 148.3, 143.4, 142.3, 136.5, 136.4, 134.9, 128.5, 127.4, 127.3, 127.1, 124.9, 107.0, 106.4, 106.1, 101.1, 74.4, 73.9, 86.8, 53.2. HRMS still needs to be taken.

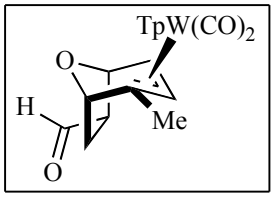
8. Synthesis of [5+2] Cycloaddition Products



General procedure for the [5+2] cycloadditions

Under argon, the 3-methyl-□^{3}-pyranyltungsten complex, **16c**, (1.0 equiv) and the indicated conjugate alkene (equiv varies) were dissolved in CH_2Cl_2 (molarity varies). $EtAlCl_2$ (1.0 M in methylene chloride, equiv varies) was added *via* syringe, and the mixture was stirred at 23 ºC for the appropriate time. The reaction was quenched slowly with H_2O (2 mL) and a minimal amount of HCl (1.2 M) in order to dissolve the aluminum salts. The organic layer was passed through a pad of silica gel with 1:1 hexanes: ethyl acetate, concentrated, and purified by flash chromatography to afford products as yellow solids.

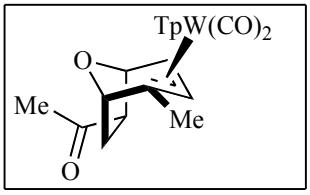
I. Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-6-hydrocarbonyl-2-methyl-8-oxo-bicyclo[3.2.1]oct-3-en-2-yl]tungsten, ***19a***



Following the general procedure, acrolein (10 μL, 0.14 mmol, 2.0 equiv) and the 3-methyl-□^{3}-pyranyltungsten complex, **16c** (38.3 mg, 0.07 mmol, 1.0 equiv) were stirred at 23 ºC for 4 h, in presence of $EtAlCl_2$ (0.07 mL, 0.07 mmol, 1.0 equiv). The ^{1}H NMR showed a 2:1 *exo: endo* ratio of products. The yellow solid (39.4 mg**,** 95%) was isolated and characterized.

TLC: R_f = 0.55 (hexanes:EtOAc, 1:1); **IR** (cm^{-1}): 1922 (s), 1833 (s), 1717 (s), 1409 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.54 (d, *J* = 4.0 Hz, 1H), 8.58 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.65-7.63 (m, 3H), 7.48 (d, *J* = 1.6 Hz, 1H), 6.23-6.25 (m, 2H), 6.17 (t, *J* = 2.4 Hz, 1H), 4.47 (d, *J* = 3.2 Hz, 1H), 4.10 (d, *J* = 6.4 Hz, 1H), 3.71 (dd, *J* = 3.2, 6.4 Hz, 1H), 3.37 (ap quin, *J* = 3.6 Hz, 1H), 2.89 (d, *J* = 6.4 Hz, 1H), 2.42-2.28(m, 2H), 1.81 (s, 3H). **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 222.8, 217.9, 201.9, 147.6, 147.1, 140.1, 137.3, 136.2, 134.6, 106.5, 106.1, 105.9, 83.5, 78.6, 75.7, 60.8, 57.7, 56.9, 33.1, 29.9, 22.5. HRMS still needs to be taken.

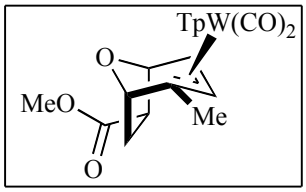
II. Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-6-methylcarbonyl-2-methyl-8-oxa-bicyclo[3.2.1]oct-3-en-2-yl]tungsten, ***19b***



Following the general procedure, methyl vinyl ketone (20 μL, 0.21 mmol, 3.0 equiv), $EtAlCl_2$ (70 μL, 0.07 mmol, 1.0 equiv) and the3-methyl-□^{3}-pyranyltungsten complex, **16c**, (38.3 mg, 0.07 mmol, 1 equiv) were stirred at 23 ºC for 2 h. The crude ^{1}H NMR showed a 3: 1 *exo: endo*. The yellow solid (32.3 mg**,** 75%) was isolated and characterized.

TLC: R_f = 0.47 (hexanes:EtOAc, 3:1); **IR** (cm^{-1}): 2958 (w), 2930 (w), 2869 (w), 2580 (br, w), 1939 (s), 1877 (s), 1710 (m), 1505 (w), 1409 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.58 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.65 – 7.63 (m, 3H), 7.48 (d, *J* = 2.4 Hz, 1H), 6.25 (t, *J* = 2.4 Hz, 1H), 6.32 (t, *J* = 2.4 Hz, 1H), 6.17 (t, *J* = 2.4 Hz, 1H), 4.36 (d, *J* = 3.2 Hz, 1H), 4.10 (d, *J* = 6.0 Hz, 2H), 3.70 (dd, *J* = 2.8, 6.4 Hz, 1H), 3.53 (dd, *J* = 5.2, 8.4 Hz, 1H), 2.90 (d, *J* = 6.8 Hz, 1H), 2.31-2.28 (m, 1H), 2.21 (s, 3H), 2.05 (s, 1H), 1.80 (s, 3H). HRMS still needs to be taken.

III. Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-6-methoxycarbonyl-2-methyl-8-oxa-bicyclo[3.2.1]oct-3-en-2-yl]tungsten, ***19c***

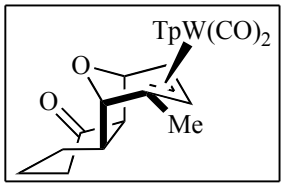


Following the general procedure methyl acrylate (10 μL, 0.105 mmol, 1.5 equiv), $EtAlCl_2$ (70 μL, 0.07 mmol, 1.0 equiv) and the 3-methyl-□^{3}-pyranyltungsten complex, **16c**, were stirred at 23 ºC for 7 h. The crude ^{1}H NMR showed a 2:1 *exo:endo* ratio. The yellow solid (42.3 mg**,** 95%) was isolated.

IR (cm^{-1}): 2949 (w), 2482 (w), 1937 (s), 1850 (s), 1733 (m), 1409 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.62 (d, *J* = 2.4 Hz, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H),

7.67 – 7.64 (m, 2H), 7.47 (d, *J* = 1.8, 1H), 6.23 (t, *J* = 2.4 Hz, 1H), 6.21 (t, *J* = 2.4 Hz, 1H), 6.17 (t, *J* = 2.4 Hz, 1H), 4.67 (d, *J* = 3.6 Hz, 1H), 3.93 (d, *J* = 2.4 Hz, 1H), 3.73 (dd, *J* = 3.6, 8.8 Hz, 1H), 3.71 (s, 3H), 3.67 (d, *J* = 4.4, 1H), 3.05 (dd, *J* = 2.8, 9.2, 1H), 2.36 – 2.34 (m, 1H), 2.33 (dd, *J* = 2.8, 8.0, 1H), 2.19 (s, 3H); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 223.0, 218.5, 173.8, 146.1, 145.3, 139.0, 136.6, 135.4, 105.4, 105.3, 105.0, 95.2, 77.1, 76.8, 66.3, 63.4, 52.0, 50.0, 34.9, 22.5. HRMS still needs to be taken.

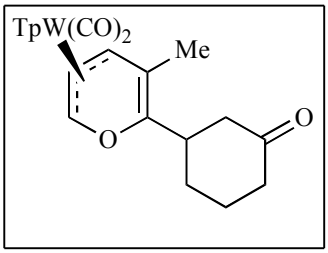
IV. Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-9,10,11)-9-methyl-12-oxa-tricyclo[6.3.1.0]dodec-10-en-3-on-9-yl]tungsten, ***19d***



Following the general procedure cyclohexenone (10 μL, 0.06 mmol, 1.0 equiv), $EtAlCl_2$ (10 μL, 0.01 mmol, 0.2 equiv) and the 3-methyl-□^{3}-pyranyltungsten complex, **16c**, (38.8 mg, 0.06 mmol, 1 equiv) was stirred at 23 ºC for 4 h. The reaction yielded at yellow solid (24.3 mg, 73%).

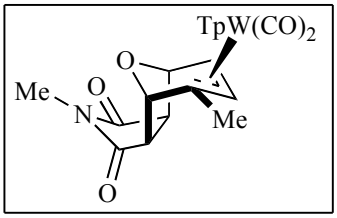
IR (cm^{-1}): 2935 (w), 2489 (w), 1915 (s), 1826 (s), 1705 (m), 1504 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.57 (d, *J* = 1.6 Hz, 1H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.64-7.63 (m, 2H), 7.47 (d, *J* = 2.0 Hz, 1H), 6.25 (t, *J* = 3.6 Hz, 1H), 6.23 (t, *J* = 2.8 Hz, 1H), 6.16 (t, *J* = 2.0 Hz, 1H), 4.53 (d, *J* = 3.2 Hz, 1H), 3.78 (dd, *J* = 3.2, 6.8 Hz, 1H), 3.72 (s, 1H), 3.31 (dd, *J* = 8.8 Hz, 1H), 3.05-2.98 (m, 1H), 2.90 (d, *J* = 6.8 Hz, 1H), 2.41-2.43 (m, 1H), 2.31-2.27 (m, 1H), 1.85 (s, 3H), 1.75-1.67 (m, 1H), 1.52-1.45 (m, 1H); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 223.6, 217.9, 210.1, 146.1, 145.4, 139.5, 136.3, 135.1, 133.9, 105.4, 105.3, 105.0, 94.0, 84.3, 78.0, 66.1, 64.0, 57.3, 46.5, 38.4.

There is a side product to this reaction, **20d**.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (d, *J* = 2.0, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.63 – 7.62 (m, 2H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 2.0, 4.0, 1H), 6.26 (t, *J* = 1.6 Hz, 1H), 6.24 (t, *J* = 1.6 Hz, 1H), 6.20 (t, *J* = 1.6 Hz, 1H), 5.63 (s, 1H), 4.24 (dd, *J* = 1.6, 6.0 Hz, 1H), 3.99 (s, 1H), 2.26 – 2.22 (m, 2H), 1.95 – 1.92 (m, 2H), 1.89 (s, 3H). IR, ^{13}C NMR, and HRMS still need to be taken.

V. Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(8,9,10)-4,8-dimethyl-11-oxa-4-aza-tricyclo[5.4.1.0]undec-9-ene-3,5-dion-8-yl]tungsten, ***19e***

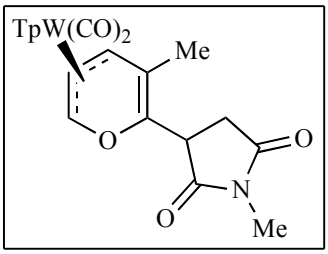


Following the general procedure *N*-methylmaleimide (7.70 mg, 0.07 mmol, 1.0 equiv), $EtAlCl_2$ (77 μL, 0.07 mmol, 1.1 equiv) and the 3-methyl-□^{3}-pyranyltungsten complex, **16c**, (38.2 mg, 0.07 mmol, 1 equiv) was stirred at 23 ºC for 20 min. The crude ^{1}H NMR showed a 6:5 *exo: endo* ratio. The yellow solid (33.2 mg, 70%) was isolated and characterized.

IR (cm^{-1}): 2983 (w), 2478 (br w), 1930 (s), 1845 (s), 1770 (w), 1695 (w), 1501 (w); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.57 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 6.27 (t, *J* =2.0 Hz, 1H),

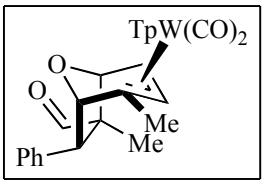
6.23 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.4 Hz, 1H), 4.56 (d, *J* = 2.8 Hz, 1H), 3.79 (dd, *J* = 3.2, 6.8 Hz, 1H), 3.69 (d, *J* = 7.2Hz, 1H), 3.57 (d, *J* = 6.8 Hz, 1H), 2.94 (s, 3H), 2.93 (d, *J* = 9.6 Hz, 1H), 1.88 (s, 3H); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 223.4, 218.7, 176.8, 176.6, 146.1, 145.3, 139.1, 136.5, 136.4, 134.4, 105.5, 105.4, 105.1, 90.1, 80.7, 77.1, 67.1, 62.1, 52.3, 25.6, 22.0. HRMS still needs to be taken.

There is a side product to this reaction, **20e**.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.62 (br s, 2H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.12 (dd, *J* = 2.0, 4.0, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 6.23 (t, *J* = 2.0 Hz, 1H), 6.22 (t, *J* = 2.4 Hz, 1H), 4.26 (dd, *J* = 2.0, 6.0 Hz, 1H), 3.78 – 3.70 (m, 2H), 3.03 (s, 3H), 2.92 – 2.87 (m, 1H), 2.79 – 2.72 (m, 1H), 2.05 (s, 3H). IR, ^{13}C NMR, and HRMS still need to be taken.

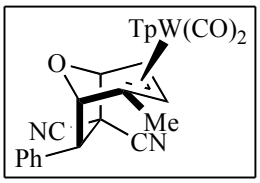
VI. Dicarbonyl[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-6-hydrocaarbonyl-2,6-dimethyl-7-phenyl-8-oxa-bicyclo[3.2.1]oct-3-en-2-yl]tungsten, ***19f***



Following the general procedure (*E*)-2-PhCHCH(Me)CHO (10 μL, 0.07 mmol, 1.0 equiv), $EtAlCl_2$ (10 μL, 0.01 mmol, 0.2 equiv) and the 3-methyl-□^{3}-pyranyltungsten

complex, **16c**, (38.2 mg, 0.07 mmol) was stirred at 23 ºC for 4 h. The reaction yielded a yellow solid (29.0 mg, 65%) that was separated and characterized

IR (cm^{-1}): 2961 (w), 2922 (w), 2853 (w), 1930 (s), 1841 (s), 1718 (w), 1505 (w), 1455 (w), 1409 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 10.2 (s, 1H), 9.18 (s, 1H), 8.58 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.65-7.63 (m, 2H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.31 – 7.18 (m, 5H), 6.28 (t, *J* = 2.4 Hz, 1H), 6.18 (t, *J* = 2.0 Hz, 1H), 6.16 (t, *J* = 2.0 Hz, 1H), 4.40 (d, *J* = 3.2Hz, 1H), 4.30 (s, 1H), 4.17 (d, *J* = 2.8 Hz, 1H), 3.64 (dd, *J* = 3.2, 6.4 Hz, 1H), 3.52 (s, 1H), 3.15 (d, *J* = 6.4 Hz, 1H), 1.83 (s, 3H), 1.71 (s, 3H); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 222.7, 218.1, 203.9, 147.6, 147.2, 142.5, 140.2, 139.2, 137.4, 136.3, 134.9, 134.6, 131.8, 129.1, 128.4, 128.1, 127.4, 106.5, 106.2, 106.1, 106.0, 84.3, 83.2, 78.9, 63.9, 61.5, 53.1, 29.9, 22.8, 18.0. HRMS still needs to be taken.



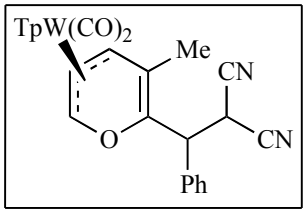
VII. Dicarbony[hydridotris(1-pyrazolyl)borato][η-(2,3,4)-6,6-dicyano-2-methyl-7-phenyl-8-oxa-bicyclo[3.2.1]oct-3-en-2-yl]tungsten, ***19g***

Following the general procedure benzylidene malononitrile (10.3 mg, 0.07 mmol, 1.0 equiv), $EtAlCl_2$ (10 μL, 0.01 mmol, 0.2 equiv) and the 3-methyl-□^{3}-pyranyltungsten complex, **16c**, (38.2 mg, 0.07 mmol, 1 equiv) was stirred at 50 ºC for 3 h. The reaction yielded a yellow solid (42.3 mg, 90%) that was isolated and characterized.

IR (cm^{-1}): 2961(w), 2926 (m), 2856 (w), 1938 (s), 1849 (s), 1722 (br w), 1594 (w), 1505 (w) 1409 (m); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.57 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.52

(d, *J* = 2.4 Hz, 1H), 7.41-7.36 (m, 5H), 6.31 (t, *J* = 2.4 Hz, 1H), 6.28 (t, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.4 Hz, 1H), 4.96 (d, *J* = 3.2 Hz, 1H), 4.31 (s, 1H), 4.20 (s, 1H), 3.90 (dd, *J* = 3.2, 6.4 Hz, 1H), 3.19 (d, *J* = 6.8 Hz, 1H), 1.85 (s, 3H); **^{13}C NMR** ($CDCl_3$, 150 MHz): δ 221.6, 216.5, 147.5, 147.2, 140.6, 137.7, 136.6, 134.9, 130.9, 129.3, 129.2, 129.1, 129.0, 128.6, 106.7, 106.6, 106.2, 85.7, 85.3, 79.9, 64.5, 60.4, 52.5, 47.3, 29.9, 22.5. HRMS still needs to be taken.

There is a side product to this reaction, **20g**.



^{1}H NMR ($CDCl_3$, 400MHz): δ 8.30 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.90 – 7.92 (m, 2H), 7.78 (s, 1H), 7.62 – 7.66 (m, 3H), 7.52 – 7.56 (m, 2H), 7.50 (d, *J* = 2.0, 1H), 7.18 (dd, *J* = 2.0, 4.0 Hz, 1H), 6.26 (t, *J* = 2.4 Hz, 1H), 6.24 (t, *J* = 2.4 Hz, 1H), 6.20 (t, *J* = 2.4 Hz, 1H), 5.63 (s, 1H), 4.24 (dd, *J* = 2.0, 6.0 Hz, 1H), 1.95 (dd, *J* = 4.8, 6.0 Hz, 1H), 1.89 (s, 3H). HRMS and IR still need to be taken.

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