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Article

Carbonyl Olefination Using Readily Prepared Tungsten Metallacycles

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Treating the bis(imido) $W(NAr)_2Cl_2(DME)$ with 2 equiv of cyclooctyne in pentane results in precipitation of a yellow complex containing a 6-membered metallacycle, $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl_2$ (**1**). This easily accessible compound was tested for its ability to effect carbonyl olefination/ring-closing metathesis (CO/RCM) with two substrates. One ketone was tested, 1-acetyl-1-(3-butenyl)cyclopentane, which generates 1-methylspiro[4.4]non-1-ene on CO/RCM. An ester, 4-benzoyloxybut-1-ene, was also test with **1** for CO/RCM. The dichloride **1** was found to be inactive; consequently, several derivatives were prepared, fully characterized including X-ray diffraction, and tested: $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OEt)_2$ (**2**), $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OC_6H_4\text{-}p\text{-}OMe)_2$ (**3**), $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OC_6F_5)_2$ (**4**), and $W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(Cl)(OTf)$ (**5**). In addition, synthesis of cationic complexes was attempted using **1** with $Na[B(Ar_F)_4]$ or $AlCl_3$. We were unsuccessful in fully characterizing the cations; however, these cations generated in situ show very high activity for CO/RCM with these substrates.

Introduction

Over the last ∼30 years there have been remarkable advances in the chemistry of metal−ligand multiple bonds[1] in general and metal−carbon multiple bonds in particular.[2] Mid- to high-oxidation state metal−carbon double bonds, alkylidenes or Schrock carbenes, have developed into invaluable tools for organic synthesis.

Carbonyl olefination in combination with ring closing metathesis has been extensively used in the synthesis of olefinic rings. Originally, carbonyl olefination[3] with ring closing by Group-6 metals was reported by Grubbs and Fu using derivatives of Schrock's catalyst, $M(=NAr)(=CHR)(OBu^t_{F6})_2$, where M = W or Mo and Ar = 2,6-diisopropy-
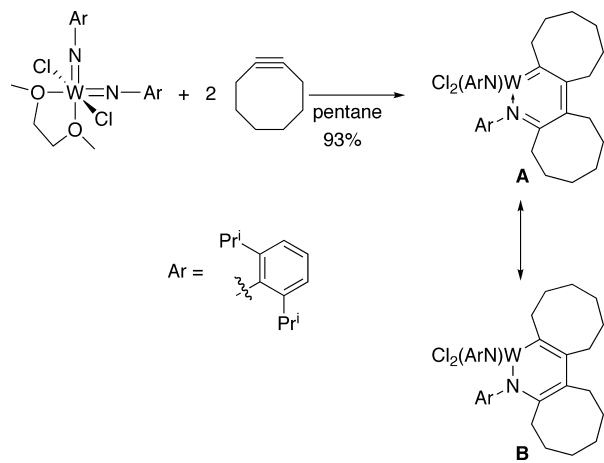
lphenyl.[4] However, the complexes require several steps to access, are quite expensive, and are used stiochiometrically in this application.

There is a long history of using titanium alkylidenes or their surrogates, e.g., Tebbe's reagent, in carbonyl olefination.[5] In addition, several in situ generated and isolable complexes based on titanium have been used and even applied to complex organic syntheses.[6] A very useful system uses a combination of $TiCl_4$, TMEDA, Zn, $PbCl_2$, and CH_2Br_2. The only drawbacks of these systems is the $PbCl_2$ additive, and the very high reactivity with lack of tunability

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(1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

(2) (a) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Chichester, 2003. (b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press, San Diego, 1997. (c) Schrock, R. R. *J. Mol. Catal. A: Chem.* **2004**, *213*, 21–30. (d) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592–4633. (e) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759.

(3) For some seminal papers on tungsten alkylidenes including Wittig-like reactions see (a) Aguero, A.; Kress, J.; Osborn, J. A. *Chem. Commun.* **1986**, 531. (b) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953. (c) Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed.* **1992**, *31*, 1585.

(4) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800.

(5) For seminal references on the Tebbe reagent see (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (c) Krusic, P. J.; Tebbe, F. N. *Inorg. Chem.* **1982**, *21*, 2900.

(6) For some recent titanium-mediated carbonyl methylenation examples see (a) Iyer, K.; Rainier, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 12604. (b) Donohoe, T. J.; Fishlock, L. P.; Lacy, A. R.; Procopiou, P. A. *Org. Lett.* **2007**, *9*, 953. (c) Bennasar, M. L.; Roca, T.; Monerris, M.; Garcia-Diaz, D. *J. Org. Chem.* **2006**, *71*, 7028. (d) Johnson, H. W. B.; Majumder, U.; Rainier, J. D. *J. Am. Chem. Soc.* **2005**, *127*, 848. (e) Kadota, I.; Takamura, H.; Sato, K.; Ohno, A.; Matsuda, K.; Satake, M.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 11893. (f) Nicolaou, K. C.; Postema, M. H. D.; Yue, E. W.; Nadin, A. *J. Am. Chem. Soc.* **1996**, *118*, 10335. (g) Majumder, U.; Rainier, J. D. *Tetrahedron Lett.* **2005**, *46*, 7209.

(7) For a recent review see Hartley, R. C.; Li, J.; Main, C. A.; McKiernan, G. J. *Tetrahedron* **2007**, *63*, 4825.

Scheme 1. Reaction to Generate **1** and Two of the Contributing Resonance Forms

Figure 1. Tungsten and molybdenum complexes tested for carbonyl olefination activity.

Scheme 2. Synthesis of Tungsten Alkoxide Complexes **2**−**4**

2: R = Et, 80%
3: R = C$_6$H$_4$-p-OMe, 83%
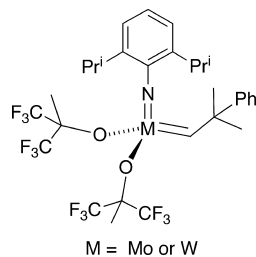**4**: R = C$_6$F$_5$, 78%

of the proposed titanium alkylidene reagent, which will react with most carbonyl substituents present. Even so, these "modified Takai" systems have proven very useful.[7]

As a potential alternative, we have been exploring a readily prepared tungsten metallacycle (Scheme 1).[8] To access the metallacycle, a diimido starting material was treated with 2 equiv of cyclooctyne, which resulted in precipitation of a product in near quantitative yield as a yellow powder. The imido, W(NAr)$_2$Cl$_2$(DME) where Ar = 2,6-diisopropylphenyl, was prepared on a multigram scale using the procedure of Schrock from WO$_2$Cl$_2$, trimethylsilylchloride, H$_2$NAr, and 2,6-lutidine.[9] Cyclooctyne is readily prepared in two steps from cyclooctene using the procedure of Brandsma.[10]

The product has the formula W(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(NAr)Cl$_2$ (**1**) and several potential resonance forms, two of which are labeled **A** and **B** in Scheme 1. Judging from the spectroscopic and crystallographic evidence, the alkylidene resonance form **A** is favored.[8]

Because of ready access to W(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(NAr)Cl$_2$ (**1**), we thought it potentially appropriate for carbonyl olefination where it would be used stoichiometrically in reactions with substrates containing carbonyl groups (e.g., ketones or esters) with pendant olefins (vide infra). The dichloride **1** itself was not active for these reactions. Consequently, we examined the synthesis of various derivatives of **1**, and their activity in carbonyl olefination reactions.

In this manuscript, we report the synthesis, structure, and reactivity of a variety of substituted tungsten metallacycles. In addition, we describe the reactivity of **1** with a variety of different additives. For comparison, we prepared and tested the Schrock complexes W(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$ and Mo(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$ originally used by Grubbs and Fu (Figure 1) for carbonyl olefination with ring closing metathesis.[4]
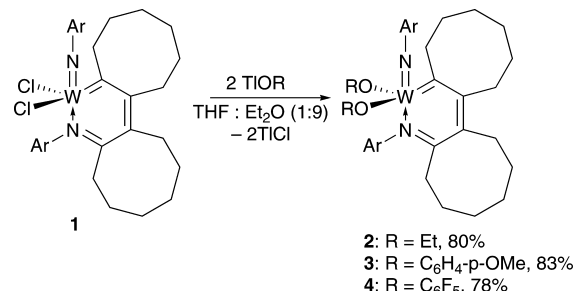
Results and Discussion

Synthesis and Properties of Metallacycle Derivatives. One set of derivatives of **1** that were of interest required replacement of the chlorides with alkoxides similar to the well-known imido alkylidene metathesis catalysts (Figure 1). However, in attempting to explore chloride replacements, many highly nucleophilic alkoxides, that is, alkali metal alkoxides, resulted in formation of a pyrrole[8] byproduct from decomposition of **1**. Fortunately, thallium alkoxides led to clean replacement of chloride in **1**, and a series of complexes was generated. The alkoxide complexes are summarized in Scheme 2. For this study, we prepared complexes bearing alkoxide (OEt, **2**), electron-rich aryloxide (OC$_6$H$_4$-p-OMe, **3**), and electron-deficient aryloxide (OC$_6$F$_5$, **4**) ligands.

Also, we replaced one of the chloride ligands with a triflate by reaction with AgOTf (eq 1). The resulting compound was a mixed triflate chloride metallacycle **5**.
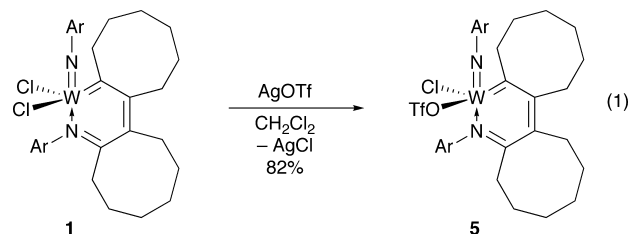
The solid-state structures for compounds **1**−**5** are summarized in Table 1 with emphasis on the metallacyclic fragment. The W−C distances vary from 1.944(4) to 2.039(4) Å in this set of compounds. The 4-carbon backbone in the metallacycle can be examined relative to butadiene as a conjugated 4-carbon system for reference. The C−C and C=C bonds in butadiene have bond lengths of 1.465(5) and 1.336(5) Å, respectively. The C1−C2 distances vary over much of this range for this series, 1.372(5) to 1.438(5) Å. In addition, the C1−C2 and C3−C4 distances vary together

(8) Lokare, K. S.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2004**, *23*, 5386.
(9) Schrock, R. R.; Mudzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(10) Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1978**, 290.

Table 1. Bond Distances (Å) for the Metallacycles in Compounds **1**−**5** from X-ray Diffraction

[W]	W−C1	C1−C2	C2−C3	C3−C4	C4−N	N−W	^{13}C NMR[a]
W(NAr)Cl$_2$ (**1**)	1.944(4)	1.438(5)	1.404(5)	1.458(5)	1.315(4)	2.120(3)	278
W(NAr)(OEt)$_2$ (**2**)	2.030(5)	1.371(7)	1.449(8)	1.384(7)	1.390(6)	2.004(4)	235
W(NAr)[OC$_6$H$_4$(OMe)]$_2$ (**3**)	2.039(4)	1.372(5)	1.463(5)	1.381(5)	1.408(5)	1.991(3)	247
W(NAr)(OC$_6$F$_5$)$_2$ (**4**)	1.983(4)	1.404(5)	1.452(5)	1.409(5)	1.370(5)	2.003(3)	268
W(NAr)Cl(OTf) (**5**)	1.960(5)	1.420(7)	1.433(7)	1.414(6)	1.361(6)	1.999(4)	278

[a] ^{13}C NMR chemical shift in ppm for the resonance assigned to the alkylidene carbon.
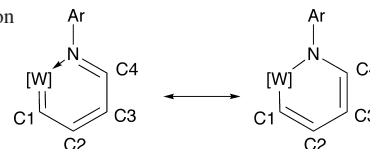
and are the same within error in all the complexes. The C4−N distance ranges from 1.315(4) to 1.408(5) Å, which can be compared to typical C−N and C=N distances of 1.472 and 1.276 Å.[11] The W−N distances are not particularly sensitive to changes in ligands on W and, excluding dichloride **1** (vide infra), only vary from 1.991(3) to 2.006(3) Å.

The most noticeable deviation in the data when explaining the structures using only these two resonance forms is the C2−C3 distances. These distances are the same within error for all the compounds prepared except the dichloride **1**, which seems to exhibit more double bond character. While some possible trends can be picked out among the alkoxides like the favoring of resonance form **A** for more electron-withdrawing ligands, compare compounds **3** and **4**, there is no discernible pattern for all the ligands used in the study.

It is currently unknown exactly what is leading to the structural deviations from these two expected resonance forms. However, two observations can be made that are affecting the structure and likely leading to the deviations from this simple bonding model. Both of these observations are effects (steric and electronic) resulting from the fact that the structures are not flat, as might be expected for a metallapyridinium. First, the structure has an "envelope" conformation with W forming the "flap". The C3 carbon is curled slightly toward a monoanionic ligand on the metal, C1 for example, in most cases, and sterics in that position may be greatly affecting the structure of the metallacycle. In the case of bis(perfluorophenyl) **4**, the metallacycle curls away from these large ligands. Second, the imido may be competing with π-type orbitals within the metallacycle; filling of these orbitals has been postulated to lead to similar ring distortions in metallabenzene complexes.[12] What is known is that the electronic structure of these complexes appears quite complex and a variety of factors seem to influence their structure.

In Figure 2 are two representations of the solid state structure for W(NAr)(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(OEt)$_2$ (**2**) to illustrate the conformation of the metallacycle. Details for all the complexes characterized by X-ray diffraction can be found in the Supporting Information. In this structure, in fact
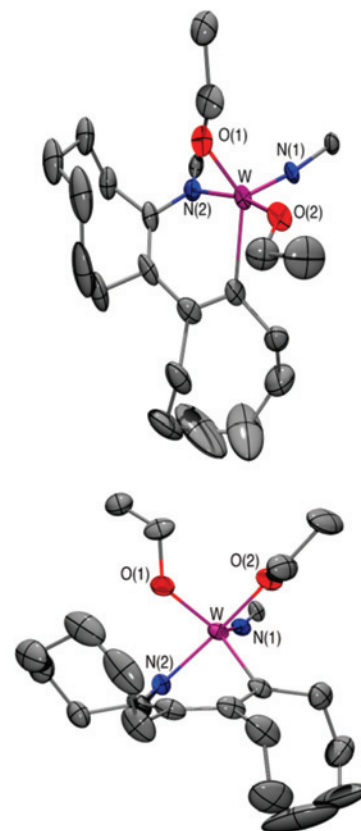

Figure 2. Two views of the structure from X-ray diffraction for W(NAr)(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(OEt)$_2$ (**2**). Hydrogens and all but the *ipso*-carbon of the 2,6-diisopropylphenyl groups excluded for clarity. Ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): W−N(1) 1.740(4); W−O(1) 1.934(3); W−O(2) 1.971(3); W−N(2) 2.004(4); N(2)−W−C(1) 86.6(2).

for derivatives **2**-**5**, the two cyclooctyne rings are *anti* across the 6-membered metallacycle (Figure 2). In dichloride **1**, however, the two rings are *syn* across this metallacycle (Figure 3), and the cyclooctyne-derived rings are both *anti* to the tungsten "flap" of the 6-membered ring envelope. Considering the largest deviations in the bond distances for the metallacycles also occur in **1**, one can surmise that the cyclooctyne conformations are strongly affecting the structure of the metallacycle. In addition, the NMR spectra of all these metallacycles are quite complex and temperature dependent; it seems several conformers are accessible in solution.

In Table 1 are also collected the chemical shifts for the alkylidene carbons of the complexes from the ^{13}C NMR spectra. The trends are fairly consistent with what might be expected. For example, within the class of alkoxides, the

(11) Typical C−N bond distance from (a) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972. C=N distance taken from. (b) Masuda, J. D.; Wie, P.; Stephan, D. W. *Dalton Trans.* **2003**, 3500. for compound ArN=C(Me)CH$_2$PPh$_2$ because of similar steric effects to our case and electronically isolated imine bond.
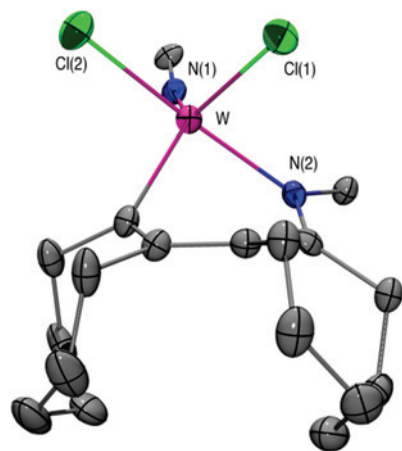(12) Zhu, J.; Jia, G.; Lin, Z. *Organometallics* **2007**, *26*, 1986.

Figure 3. Structure from X-ray diffraction for W(NAr)(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)Cl$_2$ (**1**). Hydrogens and all but the *ipso*-carbon of the 2,6-diisopropylphenyl groups excluded for clarity. Ellipsoids at the 50% probability level. Details for the structure can be found in ref 8.

Scheme 3. Substrates Tested in This Exploratory Study and the Products of Carbonyl Olefination

chemical shift increases from OEt to OC$_6$H$_4$-*p*-OMe to OC$_6$F$_5$, that is, the chemical shift increases from electron-rich to electron-deficient alkoxides.

In addition to the complexes described in detail above, we attempted to isolate and characterize the cation [W(NAr)(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)Cl]$^+$ by reaction of **1** with 1 equiv of sodium tetrakis[(3,5-bis(trifluoromethyl)phenyl]borate (Na[B(Ar$_F$)$_4$]). However, the product was an oil that was not induced to provide a solid on repeated attempts at crystallization. The amount of NaCl produced suggested that all the Na[B(Ar$_F$)$_4$] added had reacted. Two new resonances appeared in the ^{13}C NMR spectrum at 254 and 234 ppm. The generated complex(es) was active for carbonyl olefination (vide infra).

Reactivity in Carbonyl Olefination. For this study we examined two different test substrates, one a ketone (**6a**) and the other an ester (**7a**). Their structures along with the expected ring-closed products are shown in Scheme 3. Carbonyl olefination of ketone **6a** should generate the spiroolefin product **6b**. Similarly, carbonyl olefination of **7a** derived from esterification of benzoic acid with 3-butenol should result in the 4,5-dihydrofuran **7b**.[13] The cyclic vinyl ether **7b** was readily observed by gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS) of crude reaction mixtures. However, the compound hydrolyzed during attempted purification by column chromatography. As a result, the hydrolysis product, 4-hydroxyl-1-phenyl-1-butanone (**7c**), was isolated.[14]

The isolated and fully characterized derivatives **1**−**5** were found to be extremely slow or inactive for carbonyl olefination with both of the substrates **6a** and **7a**. Consequently, we turned to reagents that could potentially generate cationic metallacycles to examine their reactivity.
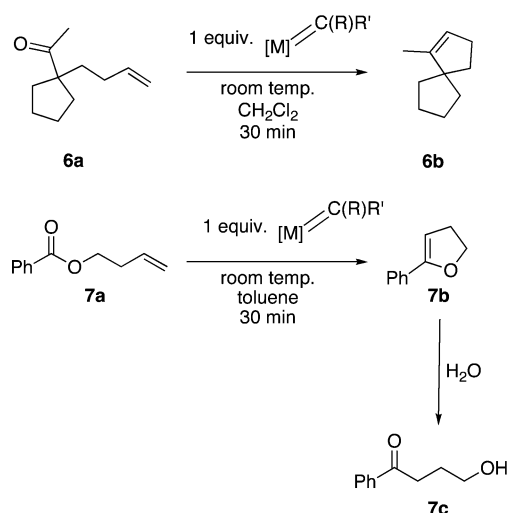
Table 2. Results of Carbonyl Olefination and Ring Closing Metathesis Reactions

mediator	additive	6a → 6b % yield^a	7a → 7b % yield^b
1	AlCl$_3$	81	52
1	ZnCl$_2$		NR^c
1	Ag[SbF$_6$]		NR^c
1	Na[B(Ar$_F$)$_4$]	84	37^d
W(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$		75	50^d
Mo(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$		86	NR^c

^{a} GC-FID %yield versus dodecane internal standard with 1 equiv of mediator and 1 equiv of additive in CH$_2$Cl$_2$ for 30 min. ^{b} GC-FID %yield versus dodecane internal standard with 1 equiv of mediator and 1 equiv of additive in toluene for 30 min. ^{c} No cyclization observed. ^{d} Reaction run in CH$_2$Cl$_2$.

Four different additives were tested (AlCl$_3$, ZnCl$_2$, Ag[SbF$_6$], and Na[B(Ar$_F$)$_4$]), and the results are summarized in Table 2.

With the additives examined, AlCl$_3$ and Na[B(Ar$_F$)$_4$] were both found to be effective and both had comparable activity to W(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$ with these substrates. Several attempts were made to isolate and identify the cyclooctyne-derived byproduct resulting from carbonyl olefination with the metallacycle, but we were unable to identify the fate of this fragment. However, the byproduct did not offer difficulties with isolation of the desired organic products in these cases.

Concluding Remarks. From readily prepared W(NAr)(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)Cl$_2$ (**1**) we were able to generate a series with alternative monoanionic ligands. All five members of this series were structurally characterized, and the differences in the metallacyclic fragment are shown in Table 1. It is apparent from the structures that there are large steric and electronic components to the structure within the metallacycle. It is also surmised from the structures that the conformation of the cyclooctyl rings is both flexible and affects the metallacycle.

The members of this series were tested for their activity in carbonyl olefination with two different substrates, and it was found that these isolable and fully characterized complexes were of only moderate to low activity. Generating cationic derivatives with AlCl$_3$

(13) For a recent alternative synthesis of 2-phenyl-4,5-dihydrofuran **7b** by decarbonylative ring expansion of a cyclopropanyl carboxylic acid see (a) Jahngen, E.; Mallett, J.; O'Connor, R.; Fischer, S. *Arkivoc* **2007**, 135.

(14) For a recently reported alternative synthesis of compound **7c** by hydrolysis of phenyl cyclopropanyl ketone see (a) Yang, Y.-H.; Shi, M. *J. Org. Chem.* **2005**, *70*, 10082; Several other methodologies have been applied to its synthesis.

Table 3. Parameters from X-ray Diffraction Experiments

	2	**3**	**4**	**5·CH_2Cl_2**
formula	$C_{44}H_{68}N_2O_2W$	$C_{54}H_{72}N_2O_4W$	$C_{52}H_{57}F_{10}N_2O_2W$	$C_{42}H_{56}Cl_3F_3N_2O_3SW$
formula wt.	840.85	996.99	1115.85	1020.18
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$	$P2(1)/c$
a (Å)	10.997(2)	12.642(4)	11.527(3)	12.5476(15)
b (Å)	12.995(2)	18.226(5)	13.555(3)	18.636(2)
c (Å)	14.851(2)	21.063(6)	16.502(4)	18.746(2)
α (deg)	95.753(3)		93.980(4)	
β (deg)	101.330(2)	101.976(5)	90.787(4)	91.330(2)
γ (deg)	91.158(2)		110.872(4)	
volume (Å^3)	2068.7(5)	4748(2)	2401.5(10)	4382.2(9)
Z	2	4	2	4
μ (mm^{-1})	2.828	2.480	2.486	2.919
$D_{calc.}$ (g cm^{-3})	1.350	1.395	1.543	1.546
total reflections	17986	40046	20769	37281
unique refl. (R_{int})	5959 (0.0417)	6824 (0.0591)	6893 (0.0574)	6313 (0.0853)
$R(F_0)$ ($I > 2\sigma$)	0.0284	0.0244	0.0262	0.0296
$R_w(F_0^2)$ ($I > 2\sigma$)	0.0618	0.05	0.0583	0.0632

and Na[B(Ar$_F$)$_4$] was found to give compounds with excellent reactivity for carbonyl olefination comparable to W(NAr)(CHCMe$_2$Ph)(OBu$^t_{F6}$)$_2$.

These tungsten metallacycles offer very good thermal stability and are only mildly water sensitive, generating a μ-oxo metallacyclic complex on hydrolysis.[8] Even though the behavior of the metallacycle is complex and seems to depend heavily on the steric and electronic nature of the other ligands, these systems can have reactivity similar to alkylidenes, especially when cationic.

Experimental Section

General Considerations. All manipulations of air sensitive materials were carried out in an MBraun glovebox under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N$_2$ to remove oxygen. NMR solvents (C$_6$D$_6$ and CDCl$_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH$_2$ under dry N$_2$. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. The cyclooctyne metallacycles are typically present in various different conformers (vide supra); the spectra are reported here as they appear at room temperature. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Celite was dried at >200 °C under dynamic vacuum for at least 16 h, then stored under inert atmosphere. W(CHCMe$_2$Ph)(NAr)[OCMe(CF$_3$)$_2$]$_2$[15] and Mo(CHCMe$_2$Ph)(NAr)[OCMe(CF$_3$)$_2$]$_2$[16] were prepared as reported in literature. W(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(=NAr)Cl$_2$ (1) was prepared as previously reported.[8] Thallium ethoxide was purchased from Strem Chemical Co. and was used without purification. Thallium alkoxide salts were prepared as reported in the literature.[17] Silver triflate

(15) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(16) Fox, H. H.; Lee, J.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(17) (a) Zechmann, C. A.; Boyle, T. J.; Pedrotty, D. M. *Inorg. Chem.* **2001**, *40*, 2177–2184. (b) Childress, M. V.; Millar, D.; Alam, T. M.; Kreisel, K. A.; Yap, G. P. A.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L.; Doerrer, L. H. *Inorg. Chem.* **2006**, *45*, 3864–3877.

was purchased from Aldrich Chemical Co. and was used without further purification. Na[B(Ar$_F$)$_4$] was prepared using the literature procedure.[18] Parameters from X-ray diffraction experiments are given in Table 3.

General Procedure for the Preparation of W(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(NAr)(OR)$_2$. In a glovebox, to a near frozen solution of W(C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(NAr)Cl$_2$ (1) (1 mmol, 1 equiv) in 2 mL of ether/THF (9:1) was added TlOR (2 mmol, 2 equiv). The solution was allowed to reach room temperature and stirred for 2 h. To check for reaction completion, an aliquot of the reaction mixture was filtered through Celite to remove TlCl and removed from the box. The aliquot was added to dilute nitric acid (0.25 M) and treated with 50 mg of AgNO$_3$ in 1 mL of distilled water. The absence of a white precipitate corresponding to AgCl indicated reaction completion. Volatiles then were removed from the reaction in vacuo. The product was redissolved in a small amount of pentane, and the solution was filtered through Celite to remove TlCl. The product was crystallized from a minimum amount of pentane at −35 °C.

W(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(NAr)(OEt)$_2$ (2). The compound was recrystallized as bright orange crystals from pentane in 80% isolated yield. ^{1}H NMR (500 MHz, C$_6$D$_6$): 6.83−7.07 (m, 6 H), 4.56−4.64 (m, 3 H), 4.38−4.48 (m, 4 H), 4.22−4.27 (m, 3 H), 3.73−3.84 (m, 5 H), 3.58−3.64 (m, 6 H), 2.73−2.86 (m, 6 H), 2.55−2.67 (m, 6 H), 2.19−2.26 (m, 6 H), 1.52−1.94 (m, 6 H), 1.24−1.34 (m, 6 H), 1.16−1.19 (m, 4 H), 1.05 (d, 4 H, J_{CH} = 7.0 Hz), 0.95 (d, 3 H, J_{CH} = 7.0 Hz). ^{13}C NMR (125 MHz, C$_6$D$_6$): 234.94 (C$_\alpha$), 150.99, 150.67, 148.6, 146.60, 143.71, 141.60, 128.29, 127.08, 126.03, 125.48, 124.75, 124.26, 122.75, 67.32, 65.09, 41.72, 34.35, 31.81, 30.17, 30.80, 29.43, 28.32, 28.09, 27.98, 27.92, 27.78, 27.12, 25.66, 25.62, 25.23, 24.45, 24.01, 23.58, 20.62, 20.17. Anal. Calcd for C$_{44}$H$_{68}$N$_2$O$_2$W: C, 62.85; H, 8.15; N, 3.33. Found: C, 63.08; H, 8.28; N, 3.30. Mp = 196−198 °C (dec).

W(=C$_8$H$_{12}$=C$_8$H$_{12}$=NAr)(NAr)(OC$_6$H$_4$-p-OMe)$_2$ (3). The compound was recrystallized as dark orange crystals from pentane in 83% isolated yield. ^{1}H NMR (300 MHz, C$_6$D$_6$): 7.00−7.10 (m, 7 H), 6.68−6.86 (m, 7 H), 4.37−4.53 (m, 2 H), 3.41−3.65 (m, 3 H), 3.74 (s, 3 H), 3.26 (s, 3 H), 2.93−2.81 (m, 1 H), 2.62−2.77 (m, 2 H), 2.00−2.35 (m, 4 H), 1.34−1.83 (m, 16 H), 1.14 (d, 12 H, J_{CH} = 6.6 Hz), 1.08 (d, 12 H, J_{CH} = 6.9 Hz). ^{13}C NMR (75 MHz, C$_6$D$_6$): 246.67 (C$_\alpha$), 158.67, 158.59, 153.81, 153.46, 152.89, 150.72, 148.58, 146.02, 145.80, 143.79, 143.14, 127.14, 125.14, 124.87, 124.47, 123.05, 121.67, 120.47, 114.16, 113.99, 55.21, 55.10, 42.06, 34.97, 32.20, 30.63, 30.57, 29.99, 29.23, 28.61, 28.57, 28.23, 28.12,

(18) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.

28.02, 27.39, 27.15, 26.25, 25.82, 25.61, 25.46, 25.08, 24.45, 24.15, 23.77, 22.66, 22.55. Examples of the variable temperature ^{1}H NMR spectra for this compound are included in the Supporting Information. Anal. Calcd for $C_{54}H_{72}N_2O_4W$: C, 65.05; H, 7.28; N, 2.81. Found: C, 65.30; H, 7.92; N, 2.53. Mp 118−120 °C.

W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(OC_6F_5)$_2$ (4). The compound was recrystallized as light orange crystals from pentane in 78% isolated yield. ^{1}H NMR (300 MHz, C_6D_6): 6.77−7.04 (m, 6 H), 4.41−4.46 (m, 1 H), 4.16−4.46 (m, 1 H), 3.89−4.00 (m, 1 H), 3.54−3.69 (m, 3 H), 2.64−3.01 (m, 2 H), 2.43−2.49 (m, 1 H), 2.27 (sept, 2 H, J_{CH} = 6.9 Hz), 1.91−1.98 (m, 1 H), 1.60−1.98 (m, 6 H), 1.41−1.53 (m, 6 H), 1.34−1.39 (m, 10 H), 1.23 (d, 3 H, J_{CH} = 6.9 Hz), 0.95−1.22 (m, 3 H), 0.88 (d, 6 H, J_{CH} = 6.9 Hz), 0.76 (d, 6 H, J_{CH} = 6.6 Hz). ^{13}C NMR (75 MHz, C_6D_6): 268.17 ($C_α$), 164.19, 148.99, 147.59, 146.51, 145.21, 140.89, 130.72, 128.59, 128.55, 125.46, 124.51, 123.12, 38.87, 35.51, 34.39, 32.00, 31.51, 30.25, 30.13, 30.07, 29.80, 28.77, 28.33, 27.38, 27.06, 26.07, 25.92, 25.58, 25.50, 25.46, 25.21, 25.07, 24.99, 24.59, 22.67, 14.21. ^{19}F NMR (282 MHz, CDCl$_3$): −160.0 (quar, J_{FF} = 9.87 Hz), −167.47 (t, J_{FF} = 21.71 Hz), −181.58 to −181.81 (m, J_{FF} = 9.87 Hz). Anal. Calcd for $C_{52}H_{58}N_2O_2F_{10}W$: C, 55.92; H, 5.23; N, 2.51. Found: C, 55.82; H, 5.38; N, 2.43. Mp = 210−212 °C (dec).

W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)(Cl)(OTf) (5). In a glovebox, to a near frozen solution of W(C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl$_2$ (1) (100 mg, 0.1217 mmol, 1 equiv) in 2 mL of CH$_2$Cl$_2$ was added AgOTf (30.3 mg, 0.1217 mmol, 1 equiv). The solution was allowed to reach room temperature and stir for 2 h. The volatiles were removed in vacuo, and the product was redissolved in ether. The AgCl precipitate was removed by filtration through Celite. The volatiles of the filtrate were removed in vacuo to give a viscous oil. The resulting oil was crystallized from ether at −35 °C to give 5 (93.3 mg, 0.0994 mmol, 82%). ^{1}H NMR (300 MHz, C_6D_6): 7.07 (1 H), 7.03 (1 H), 6.89−7.00 (m, 1 H), 6.69−6.88 (m, 3 H), 4.80 (s, 1 H), 4.31 (sept, 2 H, J_{CH} = 6.9 Hz), 3.98 (sept, 2 H, J_{CH} = 6.9 Hz), 2.84−2.96 (m, 1 H), 2.29−2.50 (m, 6 H), 1.61−1.96 (m, 6 H), 1.40−1.59 (m, 10 H), 1.32 (d, 3 H, J_{CH} = 6.9 Hz), 1.26 (d, 3 H, J_{CH} = 6.9 Hz), 1.24 (d, 6 H, J_{CH} = 6.9 Hz), 1.20 (d, 6 H, J_{CH} = 6.9 Hz), 0.97 (d, 3 H, J_{CH} = 6.6 Hz), 0.73 (d, 3 H, J_{CH} = 6.6 Hz). ^{13}C NMR (74.5 MHz, CDCl$_3$): 277.93 ($C_α$), 147.04, 142.32, 140.53, 129.68, 129.04, 128.19, 125.33, 124.49, 124.32, 124.01, 122.66, 65.82, 41.93, 30.46, 30.33, 29.70, 29.55, 29.12, 28.53, 27.89, 27.56, 26.47, 25.99, 25.68, 25.22, 24.96, 24.84, 24.70, 24.40, 24.03, 23.38, 15.23. ^{19}F NMR (282 MHz, CDCl$_3$): −77.83 (s). Mp = 155−157 °C (dec).

Representative Carbonyl Olefination Procedure to Produce 1-Methylspiro[4.4]non-1-ene (6b). In a glovebox, W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)(Cl)$_2$ (1) (200 mg, 0.246 mmol, 1 equiv) in CH$_2$Cl$_2$ (2 mL) was added to a solution of AlCl$_3$ (33 mg, 0.246 mmol, 1 equiv) and 1-acetyl-1-(3-butenyl)cyclopentane (6a, 40 mg, 0.240 mmol, 1 equiv) in CH$_2$Cl$_2$ (3 mL). The resulting mixture was stirred vigorously. After 30 min, the reaction mixture was taken outside the glovebox, quenched with distilled water (0.2 mL), and concentrated in vacuo. The product 6b can be purified by column chromatography (silica gel, 250−400 mesh, pentane) as a light yellow oil (21 mg, 0.154 mmol, 64%). R$_f$ = 0.80 (SiO$_2$, hexanes). ^{1}H NMR (CDCl$_3$, 500 MHz): 5.28−5.29 (m, CH, 1H), 2.15−2.28 (m, CH_2, 2H), 1.69−1.72 (m, 2 H), 1.59−1.64 (m, 6 H), 1.54−1.58

(m, CH_2, 2 H), 1.31−1.36 (m, CH_2, 2 H), 1.25 (s, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz): 145.60, 123.78, 57.20, 39.89, 36.07, 29.45, 25.06, 12.42. MS (EI) m/z = 136 (M$^+$). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.30; H, 11.62.

Representative Carbonyl Olefination Procedure to Produce 4-Hydroxy-1-phenylbutanone (7c). In a glovebox, W(NAr)(=C_8H_{12}=C_8H_{12}=NAr)(Cl)$_2$ (1) (200 mg, 0.246 mmol, 1 equiv) in toluene (2 mL) was added to a solution of AlCl$_3$ (33 mg, 0.246 mmol, 1 equiv) and 4-benzoyloxybut-1-ene (7a, 42 mg, 0.241 mmol, 1 equiv) in toluene (3 mL). The resulting mixture was stirred vigorously. After 3.5 h, the reaction mixture was taken outside the glovebox, quenched with distilled water (0.2 mL), and concentrated in vacuo. The product 7c can be purified by column chromatography (silica gel, 250−400 mesh, hexanes then acetone:hexane 1:9 to 2:8) as a colorless oil (18 mg, 0.11 mmol, 45.5%).[19] R$_f$ = 0.70 (SiO$_2$, acetone:hexane, 2:8). ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 7.94−7.97 (m, o-Ph, 2 H), 7.51−7.56 (m, p-Ph, 1H), 7.41−7.46 (m, m-Ph, 2 H), 3.72 (t, C(O)CH_2, 2 H, J_{CH} = 6 Hz), 3.11 (t, HOCH_2, 2 H, J_{CH} = 6.9 Hz), 2.00 (pent, CH$_2$CH_2CH$_2$, 2 H, J_{CH} = 6.6 Hz), 1.91 (br s, OH, 1 H). ^{13}C NMR (CDCl$_3$, 75 MHz) δ: 200.52, 136.85, 133.11, 128.58, 128.07, 62.29, 35.26, 26.90. MS (EI) m/z = 164 (M$^+$).

Reaction of W(=C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl$_2$ (1) with Na[B(Ar$_F$)$_4$]. In a glovebox, to a near frozen solution of W(C_8H_{12}=C_8H_{12}=NAr)(NAr)Cl$_2$ (1) (100 mg, 0.122 mmol, 1 equiv) in CH$_2$Cl$_2$ (2 mL) was added sodium tetrakis[(3,5-bis(trifluoromethyl)phenyl]borate (Na[B(Ar$_F$)$_4$]) (119 mg, 0.134 mmol, 1.1 equiv). The solution was allowed to reach room temperature and stir for 2 h. The NaCl precipitate was filtered through a weighed pipet with glass filter paper and Celite. The Celite was washed with CH$_2$Cl$_2$ (4 mL). The pipet with its contents was dried to a constant weight, and the amount of NaCl formed during the reaction was recorded (6.5 mg, 91% yield). The volatiles of the filtrate were removed in vacuo to give a viscous oil. The resulting oil was dissolved in CDCl$_3$, and NMR spectra were recorded. Conversion was complete after 2 h according to ^{13}C NMR spectroscopy. There were two new $C_α$ resonances in the ^{13}C NMR. ^{13}C{^{1}H} NMR (75.6 MHz, CDCl$_3$): 254 ($C_α$) and 234 ($C_α$). ^{19}F NMR (282 MHz, CDCl$_3$): −63.10. The ^{1}H and ^{13}C NMR spectra are included in the Supporting Information.

Supporting Information Available: Tables for the X-ray diffraction studies, NMR spectra for the crude mixture from Na[B(Ar$_F$)$_4$] reaction with 1, VT NMR spectra for 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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