Cycloaddition of Tungsten−η^1-3-Furyl Compounds with Alkenes and Alkynes: Syntheses and Ring Cleavage of Tungsten−η^1-Oxabicycloheptene and −η^1-Oxabicycloheptadiene Compounds

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Cycloaddition of tungsten−η^1-3-furyl compounds with a variety of organic alkenes and alkynes proceeds smmothly at ambient conditions, yielding tungsten−η^1-oxabicyclo[2.2.1]-heptene and −η^1-oxabicyclo[2.2.1]heptadiene compounds in high regioselectivities and stereoselectivities. The cycloaddition is proposed to proceed via a mechanism involving a zwitterion intermediate. Cleavage of oxygen bridges of η^1-oxabicyclo[2.2.1]heptenes and η^1-oxabicyclo[2.2.1]heptadienes occurs on treatment of CF_3SO_3H and Lewis acid, leading to atypical carbon−carbon bond scission and deoxygenation reactions to give highly substituted benzene and furan derivatives, respectively. The role of the tunsten fragment in these demetalation reactions is discussed in detail.

Introduction

Transition metal η^1-five-membered heterocyclics such as η^1-pyrrolyl, η^1-furyl, and η^1-thienyl complexes[1−3] have attracted considerable attention because of their interesting reaction chemistry.[1−3] Most of them are prepared with the heterocyclic ring linked to the metal center at the C(2) carbon; the number of η^1-3-metalated heterocyclics are quite limited.[1a,2b,3] We previously reported the preparation of tungsten−η^1-furyl compounds in 2-metalated (**A**) and 3-metalated forms (**B**).[3] The reaction chemistry of these two species reveals that $CpW(CO)_3$ functions as an electron-donating group that enhances oxidation and electrophilic alkylation of the furyl ring via stabilization of tungsten−η^1-furylium intermediates.[3] One notable reaction of organic furans is [4 + 2]-cycloaddition with dienophiles for which the reactivity is enhanced by the presence of an alkoxy group.[4−6] The resulting 7-oxabicyclo[2.2.1]heptene and 7-oxabicyclo[2.2.1]heptadiene are valuable for syntheses of important organic substances. A particular transformation in such syntheses involves treatment of these compounds with strong acid to cleave the oxygen bridge, respectively yielding functionalized benzenes and phenols as depicted in Scheme 1.[7,8] In this paper, we report[9] [4 + 2]-cycloaddition of these tungsten−η^1-furyl compounds and acid-promoted ring cleavage of the resulting oxabicyclic products. [4 + 2]-cycloadditions of metal-coordinated aromatic heterocycles were previously reported for $Os(NH_3)_5(\eta^2$-pyrrole)[10] but still remained unknown for η^1-metalated aromatic heterocycles.

Results and Discussion

[4 + 2]-Cycloaddition with Alkynes. Syntheses of tungsten−η^1-furyl compounds **1**−**3** were based on methods that were previously reported;[3a] the η^1-2-metalated species **4** was obtained from proton-catalyzed isomerization of the corresponding η^1-3-metalated isomer **1** (Scheme 2).[3a] Cycloaddition of η^1-3-furyl complexes **1**−**3** with reactive alkynes such as dimethyl acetylenedicarboxylate, dicyanoacetylene, hex-3-yn-2,5-dione, and ethyl propiolate proceeded smoothly under ambient condi-

(1) For transition-metal−η^1-furyl compounds, see: (a) Jones, W. D.; Dong, L.; Myers, A. W. *Organometallics* **1995**, *14*, 855. (b) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583. (c) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 3800. (d) Pannell, K. H.; Cea-Olivares, R.; Toscano, R. A.; Kapoor, R. N. *Organometallics* **1987**, *6*, 1821.

(2) For transition metal−η^1-pyrrolyl and −η^1-thienyl compounds, see: (a) Johnson, T. D.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728. (b) Robertson, M. J.; White, C. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1994,** *116*, 5190. (c) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (d) Ng, M. M. P.; Roper, W. R.; Wright, L. J. *Organometallics* **1994**, *13*, 2563. (e) Erker, G.; Petrenz, R.; Kruger, C.; Lutz, F.; Weiss, A.; Werner, S. *Organometallics* **1992**, *11*, 1646.

(3) (a) Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530. (b) Wang, S.-H.; Shiu, L.-H.; Shu, H.-G.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1994**, *116*, 5967. (c) Fan, J.-S.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1997**, *16*, 4232.

(4) Review articles: (a) Oppolzer, W.; Weinreb, S. M.; Boger, D. L.; Roush, W. R. In *Comprehensive Organic Synthesis: Combining C-C π-Bonds;* Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, chapter 4.1−4.4., p 81.

(5) (a) Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087. (b) Kametani, T.; Hibino, S. *Adv. Heterocycl. Chem*. **1987**, *42*, 245. (c) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis;* Academic Press: Orlando, FL, 1987.

(6) Hammer, J. *1,4-Cycloaddition Reactions, the Diels−Alder Reaction in Heterocyclic Synthesis;* Academic Press: New York, 1967.

(7) Wong, H. N. C.; Ng, T.-Y.; Wong, T.-Y.; Xing, Y.-D. *Heterocycles* **1984**, *22*, 875.

(8) Hart, H.; Nwokogu, G. *J. Org. Chem*. **1981**, *46*, 1509.

(9) Part of this paper has appeared in an earlier communication: Shiu, L.-H.; Shu, H.-K.; Cheng, D.-H.; Wang, S.-L.; Liu, R.-S. *J. Chem. Soc., Chem. Commun*. **1996**, 1041.

(10) Gonzalez, J.; Koonts, J. I.; Myers, W. H.; Hodges, L. M.; Sabat, M.; Nilsson, K. R.; Neely, L. K.; Harman, W. D. *J. Am. Chem. Soc.* **1995**, *117*, 3405.

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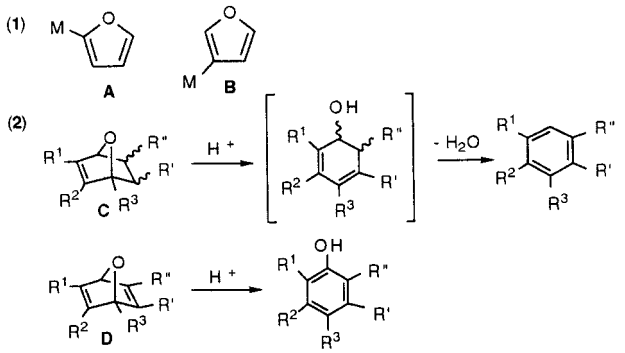
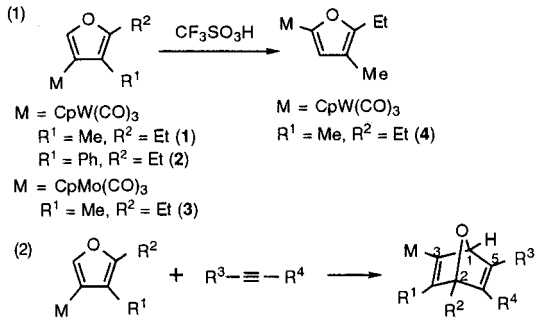
Scheme 1



Scheme 2



entry	η¹-furyl	acetylene	Product (yields)
1	**1**	$R^3 = R^4 = CO_2Me$	**5** (91%)
2	**2**	$R^3 = R^4 = CO_2Me$	**6** (90%)
3	**3**	$R^3 = R^4 = CO_2Me$	**7** (90%)
4	**1**	$R^3 = R^4 = CN$	**8** (85%)
5	**1**	$R^3 = R^4 = COMe$	**9** (89%)
6	**1**	$R^3 = H$, $R^4 = CO_2Et$	**10** (93%)

tions, and yields exceeded 85% as shown in Scheme 2. Characterization of the adducts **5**−**10** was straightforward and easily elucidated from their NMR, IR, and mass spectral data. Only one regioisomer was obtained for the adduct **10**; its structure was confirmed by both its proton-NOE effect and the observed coupling constant $J_{15} = 3.2$ Hz. Irradiation of the C(1)−H proton signal (δ 5.13 ppm) of **10** showed an increased intensity of the signal due to the C(5)−H proton (δ 7.76 ppm) by 3.0%. We obtained single crystals of compound **6** for X-ray diffraction studies;[11] its ORTEP drawing appears in Figure 1. Although 2-metalated isomer **4** was expected to be more electronically favorable for cycloaddition reaction than its 3-metalated isomer because the metal fragment of the former is conjugated to the furyl group, compound **4** failed to react with dimethyl acetylenedicarboxylate even under reflux in CH_3CN, perhaps attributable to a congested enviroment around the quaternary C(1) carbon of the expected adduct, which links to a bulky $CpW(CO)_3$ fragment and to a bridging oxygen.

Cycloadditions with Alkenes. The η^1-3-metalated furyl complexes **1**−**3** are reactive toward alkenes such

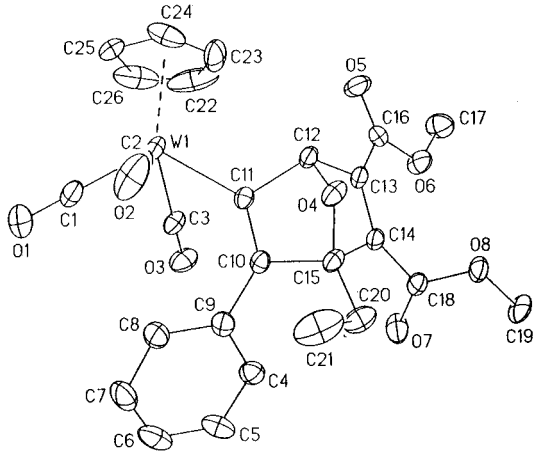
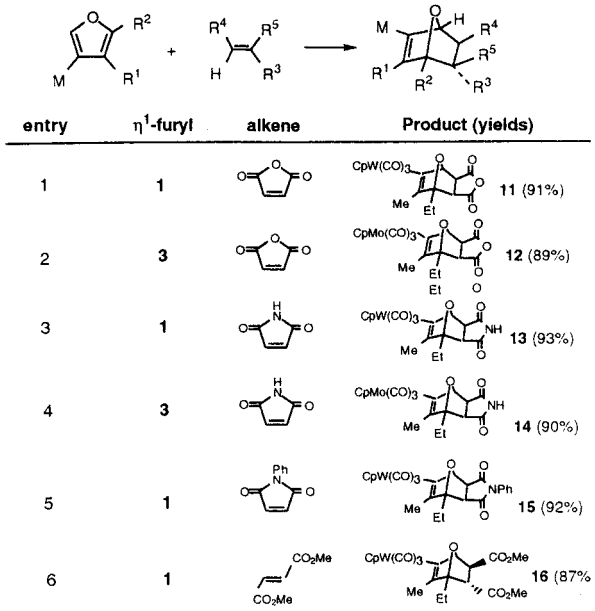


Figure 1. ORTEP drawing of one independent molecule of **6**. Pertinent distances (Å): W(1)−C(11) = 2.231(7), C(10)−C(11) = 1.343(10), C(12)−O(4) = 1.425(9), C(15)−O(4) = 1.446(9), C(13)−C(14) = 1.319(11).

Scheme 3

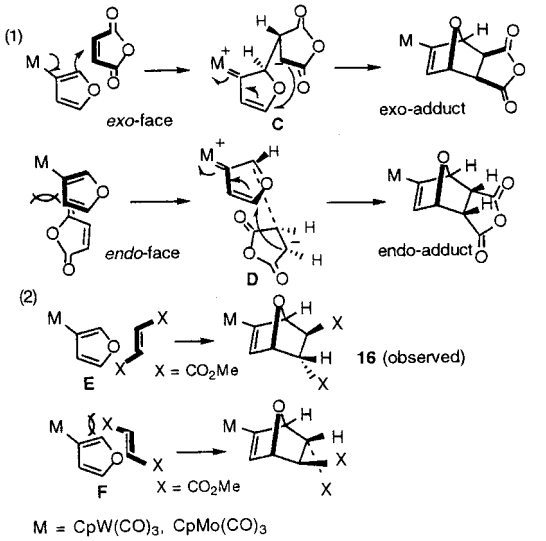


as maleic anhydride, maleimide, *N*-phenylmaleimide, and dimethyl fumarate; the reaction proceeded smoothly under ambient conditions (23 °C, CH_2Cl_2). The yields are summarized in Scheme 3. In entries 1−6, only one stereoisomer was obtained for the cycloaddition adducts **11**−**16**. The structure is assigned as the *exo* isomer on the basis of the lack of the vicinal coupling ($J_{16} = 0$ Hz) between the two methine protons at the C(1) and C(6) carbons.[12] Similarly to the alkyne cases, the 2-metalated furyl compound **4** failed to react with maleic anhydride in CH_3CN even at elevated temperatures. Completion of reaction between 3-methylfuran and maleic anhydride requires gentle heating, yielding a mixture of *exo* and *endo* products with the *exo* isomer as the major species.[13] The presence of the $CpW(CO)_3$ fragment of **1**−**3** clearly enhances the reactivity and *exo*-selectivity. Attempts to use NMR to elucidate the reaction intermediate for cycloaddition of **1** with maleic

(11) Compound **6** crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.452(4)$ Å, $b = 12.263(4)$ Å, $c = 19.916(5)$ Å, $\beta = 90.28(3)°$, $V = 2552.9(13)$ Å^3, $Z = 4$. Each asymmetric unit contains two independent molecules. Data were collected on a Siemens R3m/V diffractometer, using Mo Kα radiation. The final $R = 0.0366$ and $R_w = 0.0389$ for 3204 reflections > $3.0\sigma(I)$ out of 4537 unique reflections.

(12) Tada, M.; Mutoh, N.; Shimizu, T. *J. Org. Chem.* **1995**, *60*, 550.
(13) (a) Herndon, W. C.; Lee, M. F. *J. Org. Chem.* **1978**, *43*, 518. (b) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537.

Scheme 4



anhydride was unsuccessful; only signals of **1** and **11** were detected in the course of reaction. On the basis of our previous observation[3a] for the alkylation of **1** with $RCHO{\cdot}BF_3{\cdot}Et_2O$, we spectulate that the reaction likely proceeds via a mechanism defferent from a concerted Diels−Alder addition. A reaction mechanism proposed in Scheme 4 accounts for the stereochemistry of the maleic anhydride adduct (eq 1). Maleic anhydride preferably approaches metal−η^1-2-furan from the *exo* face to initiate the reaction. Addition of the metal−vinyl bond to maleic anhydride generated a zwitterion **C**, proceeding to the *exo*-adduct via rapid ring closure. It is unfavorable for maleic anhydride to approach the metal−η^1-furan from the *endo* face because of steric hindrance between the metal fragment and the maleic plane. The stereochemistry of the dimethyl fumarate adduct **16** can also be rationalized, on the basis of this mechanism. We envisage that dimethyl fumarate preferably approaches the furyl plane with its ester group away from the metal fragment as shown in structure **E**, finally yielding the observed product represented by **16**. Structure **F** is clearly more sterically hindered because of the steric interaction between metal and ester group. In principle, this mechanism is similar to those for [3 + 2]-cycloaddition of allylsilanes, -stannanes, or -iron complexes.[14−16]

Ring Cleavage of η^1-Oxabicyclic Compounds. We studied cleavage of the oxygen bridge of the above oxabicyclic compounds to investigate the role of the metal fragment. The reactions were undertaken in the presence of CF_3SO_3H or $BF_3{\cdot}Et_2O$. Table 1 shows results for representative compounds. In a typical operation, η^1-oxabicyclic compounds were treated with acid (1 equimolar) in cold CH_2Cl_2 (−78 °C), and the temperature was brought to 23 °C before quenching with water. Entries 1 and 2 show results for CF_3SO_3H cleavage of tungsten−η^1-oxabicycloheptadienes **5** and **10**. Deoxygenated products **17** and **19** were formed preferably with 65% and 80% yields, respectively, whereas the expected phenol derivative **18** was produced only in entry 1 as a biproduct **18** (28%). Treatment of molybdenum analogue **5** with CF_3SO_3H led to cleavage of the Mo−C bond to yield free 7-oxabicyclo-[2.2.1]heptadiene **20** in 80% yield in addition to a little of the phenol derivative **18** (5%). $BF_3{\cdot}Et_2O$ was ineffective to cleave the oxygen ring of compound **5** but gave the starting η^1-furyl compound **1** in 85% yield (entry 4). Other Lewis acids $SnCl_4$ and $TiCl_4$ produced analogous results. Reactions between η^1-oxabicycloheptene and CF_3SO_3H showed distinct reaction chemistry. As shown in entry 5, treatment of compound **13** with CF_3SO_3H liberated 2-alkylated furan compound **21** in 78% yield. η^1-Oxabicycloheptenes **14**−**16** (entries 6−8) followed the same reaction pathway, and similar 2-alkylated furan products **21**, **23**, and **24** were obtained in high yields (>63%). Byproduct **22** was obtained in 26% yield for molybdenum compound **14** (entry 6). Opening of the oxygen bridges of **15** and **16** can also be achieved with $BF_3{\cdot}Et_2O$ and Bu_4NI (entries 9 and 10), and the furan compounds **23** and **24** were obtained in 74% and 69% yields, respectively, in addition to $CpW(CO)_3I$. This phenomenon differs from that observed for η^1-oxabicycloheptadiene **5** (entry 4).

Table 1. Reaction Results

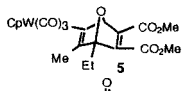
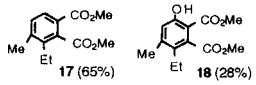
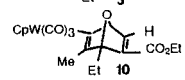
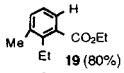
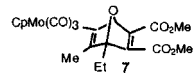
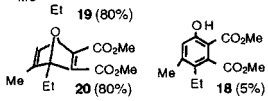
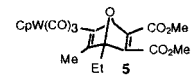
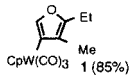
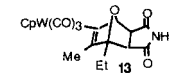
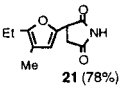
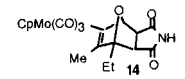
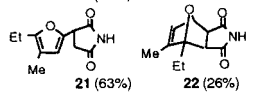
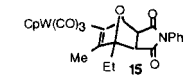
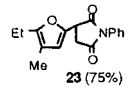
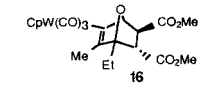
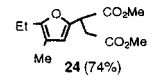
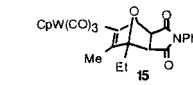
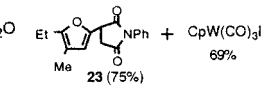
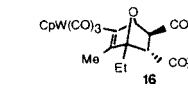
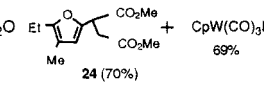
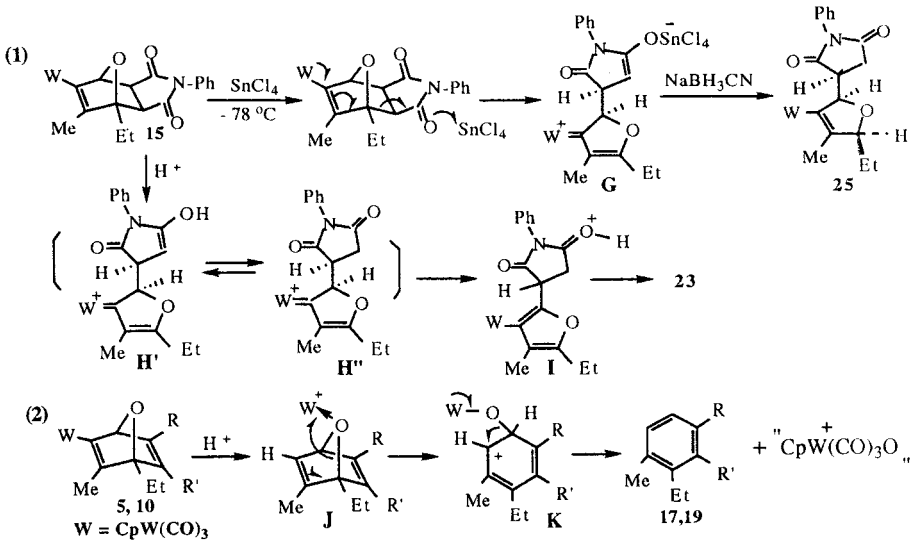
entry	η^1-oxabicyclic	acid	product (yields)
1		CF_3SO_3H	 **17** (65%) **18** (28%)
2		CF_3SO_3H	 **19** (80%)
3		CF_3SO_3H	 **20** (80%) **18** (5%)
4		$BF_3{\cdot}Et_2O$	 **1** (85%)
5		CF_3SO_3H	 **21** (78%)
6		CF_3SO_3H	 **21** (63%) **22** (26%)
7		CF_3SO_3H	 **23** (75%)
8		CF_3SO_3H	 **24** (74%)
9		(1) $BF_3{\cdot}Et_2O$ (2) Bu_4NI	 **23** (75%) + $CpW(CO)_3I$ 69%
10		(1) $BF_3{\cdot}Et_2O$ (2) Bu_4NI	 **24** (70%) + $CpW(CO)_3I$ 69%

Table 1 shows atypical reaction pathways in acid cleavage of metal−η^1-oxabicycloheptadienes and −η^1-oxabicycloheptenes; the outcomes are distinct from those expected from common oxabicyclic compounds as illustrated in Scheme 1. The reaction mechanism deserves further investigation. For entries 9 and 10 (Table 1), reaction between $BF_3{\cdot}Et_2O$ and **15** and **16** led to formation of unknown cationic species that then reacted

(14) Welker, M. E. *Chem. Rev.* **1992**, *92*, 4280.
(15) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.
(16) Herdon, J. W.; Wu, C.; Harp, J. J. *Organometallics*, **1990**, *9*, 3157.

Scheme 5



with Bu_4NI to yield observed products **23**, **24**, and CpW(CO)$_3$I. As shown in Scheme 5, treatment of **15** with $SnCl_4$, followed by reduction with $NaBH_3CN$, delivered an alkylated *cis*-2,5-dihydrofur-3-yl complex **25**, of which the X-ray structure[17] is shown in Figure 2. This information indicates that $SnCl_4$ reacted with **15** to form a metal carbenium salt **G** (Scheme 5). In this reaction mechanism, $SnCl_4$ preferentially attacks at the carbonyl group of **15** to build a positive charge at the N−C=O carbon, together with the electron-donating effect of CpW(CO),[3a] leading to cleavage of the carbon−carbon bond to generate the tungsten carbenium. Addition of hydride at the oxonium carbon of species **G** tends to proceed opposite to the alkylated substituent to yield **25** in a *cis* configuration. The results for CF_3SO_3H acidification of **13**−**16** (Table 1, entries 5−8) can also be rationalized on the basis of this mechanism. We envision that CF_3SO_3H also produces tungsten−carbenium species **H′** and **H″** via protonation at the imide carbonyl group. This cation is kinetically unstable in solution; its instability is attributed to the imide oxygen basicity of **H″** that causes deprotonation to give furyl complex **I**. Further proton cleavage of the W−C σ bond of **I** gave 2-alkylated furans.

To account for CF_3SO_3H-promoted deoxygenation of tungsten−η^1-oxabicycloheptadienes **5** and **10**, we propose a mechanism in Scheme 5. The results in Table 1 (entries 1−3) indicates that cleavage of the metal−carbon bond[18,19] of metal−η^1-oxabicyclodienes is the preferred pathway to yield species **J**. Tungsten(II) is more oxophilic than molybdenum(II) to form higher oxidation species,[20] and rearrangement of species **J** generates the O-bound oxabicyclicdiene species **K**. Further cleavage of the W−O bond of **K** via oxidation of tungsten center led to deoxygenation products **17** and **19**. An alternative pathway of **K** involves the loss of one proton to give a phenol derivative like **18** as a minor reaction product.

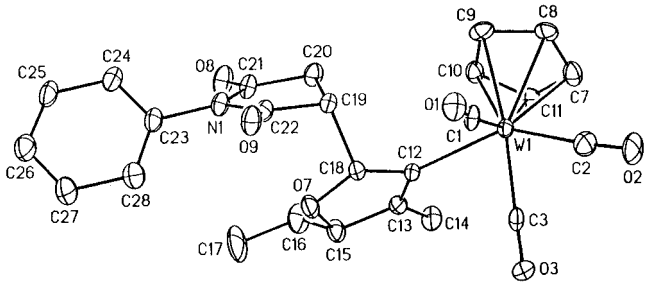


Figure 2. ORTEP drawing of one independent molecule of **25**. Pertinent distances (Å): W(1)−C(12) = 2.272(6), C(12)−C(13) = 1.322(10), C(22)−O(9) = 1.118(9), C(21)−O(8) = 1.205(9).

Conclusion

In this work, we report [4 + 2]-cycloadditions of metal−η^1-2-furan compounds with various alkenes and alkynes to yield η^1-oxabicycloheptenes and oxabicycloheptadienes in high regioselectivities and stereoselectivities. This cycloaddition is proposed to proceed via a zwitterion intermediate. Cleavage of oxygen bridges of these resulting products occurs on treatment of CF_3SO_3H and Lewis acid, leading to atypical carbon−carbon bond scission and deoxygenation reactions. These reaction pathways are distinct from those for common oxabicycloheptenes and oxabicycloheptadienes; the metal fragment plays an important role in these uncommon bond scissions.

Experimental Section

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, dicyclopentadiene, propargyl alcohol, and sodium were obtained commercially and used without purification. Syntheses of metal−η^1-furan compounds **1**−**4** have been described previously.[3a]

(17) Compound **25** crystallizes in the monoclinic space group $P2_1/c$, with a = 13.295(2) Å, b = 16.502(2) Å, c = 21.717(2) Å, β = 97.82(2)°, V = 4710.9(10) Å^3, Z = 8. Each asymmetric unit contains two independent molecules. Data were collected on a Siemens R3m/V diffractometer, using Mo Kα radiation. Final R = 0.0408 and R_w = 0.0513 for 6673 reflections > 3.0$\sigma(I)$ out of 8094 unique reflections.

(18) Robertson, M. J.; White, C. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 5190.

(19) Dong, L.; Duckett, K. F.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992,** *114*, 151.

(20) Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402.

(I) General Procedure for Synthesis of Tungsten−η^1-7-Oxabicyclo[2.2.1]heptadienes and −7-Oxabicyclo[2.2.1]-heptenes. (1) Synthesis of Compound 5. To a CH_2Cl_2 solution of compound **1** was added dimethyl acetylenedicarboxylate (64 mg, 0.45 mmol) at 23 °C; the mixtures were stirred for 2 h. The solution was concentrated, and flash chromatography yielded **5** as a yellow solid (239 mg, 0.41 mmol, 91%): IR (neat, cm^{-1}) ν(CO) 2015 (s), 1910 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (5H, s, Cp), 5.36 (1H, s, OC*H*), 3.76 (3H, s, CO_2Me), 3.69 (3H, s, CO_2Me), 2.12 (1H, ABq, J = 7.5, 1.5 Hz, CH*H*′CH_3), 1.93 (1H, ABq, J = 7.5, 1.5 Hz, C*H*H′Me), 1.71 (3H, s, Me), 0.92 (3H, t, J = 7.5 Hz, Me); ^{13}C NMR (100 MHz; $CDCl_3$) δ 226.3, 214.2, 210.1, 166.2, 163.5, 157.9, 150.4, 128.1, 99.7, 94.0, 91.6, 51.9, 51.9, 21.1, 15.6, 8.77; MS (75 eV *m*/*e*) 584 (M^+). Anal. Calcd for $C_{21}H_{20}WO_8$: C, 43.17; H, 3.45. Found: C, 43.15; H, 3.44.

(3) Synthesis of Compound 6. Compound **2** (0.20 g, 0.41 mmol) and dimethyl acetylenedicarboxylate (57 mg, 0.41 mmol) afforded compound **6** as a yellow solid (0.24 g, 0.37 mmol, 90%): IR (neat, cm^{-1}) ν(CO) 2015 (vs), 1910 (vs); ^{1}H NMR (300 MHz, toluene-d_8) δ 7.74−7.27 (6H, m, Ph), 6.02 (1H, s, OC*H*), 4.90 (5H, s, Cp), 3.69 (3H, s, CO_2Me), 3.71 (3H, s, CO_2Me), 2.21 (1H, ABq, J = 7.3, 1.5 Hz, CH*H*′Me), 2.32 (1H, ABq, J = 7.3, 1.5 Hz, C*H*H′Me), 1.23 (3H, t, J = 7.5 Hz, CHH′*Me*); ^{13}C NMR (75 MHz, toluene-d_8) δ 230.2, 219.7, 217.5 (3W−CO), 168.6, 168.7, 157.6, 155.6, 154.7, 142.2, 132.1, 131.0, 127.7, 137.2, 103.2, 98.7, 94.4, 54.3, 25.0, 11.6; MS (75 eV, *m*/*e*) 646 (M^+), 618 (M − CO), 590 (M − 2CO), 562 (M − 3CO). Anal. Calcd for $C_{26}H_{22}WO_8$: C, 48.32; H, 3.43. Found: C, 48.25; H, 3.40.

(4) Synthesis of 7. Compound **3** (0.20 g, 0.56 mmol) and dimethyl acetylenedicarboxylate (80 mg, 0.56 mmol) afforded **7** as a yellow solid (0.25 g, 0.50 mmol, 90%): IR (neat, cm^{-1}) ν(CO) 2010 (s), 1920 (s); ^{1}H NMR (400 MHz; $CDCl_3$) δ 5.54 (5H, s, Cp), 5.34 (1H, s, OC*H*), 3.77 (3H, s, CO_2Me), 3.71 (3H, s, CO_2Me), 2.15 (1H, ABq, J = 7.2, 1.5 Hz, C*H*H′Me), 1.95 (1H, ABq, J = 7.2, 1.5 Hz, CH*H*′Me), 1.74 (3H, s, Me), 0.93 (3H, t, J = 7.2 Hz, CHH′*Me*); ^{13}C NMR (100 MHz; $CDCl_3$) δ 238.2, 225.8, 223.9, 166.1, 163.2, 156.5, 155.6, 149.7, 99.5, 93.3, 93.2, 52.0, 51.9, 21.0, 15.0, 8.7; MS (75 eV *m*/*e*) 496 (M^+). Anal. Calcd for $C_{21}H_{20}WO_8$: C, 50.82; H, 4.06. Found: C, 50.76; H, 4.04.

(5) Synthesis of 8. Compound **1** (1.50 g, 3.37 mmol) and dicyanoacetylene (256 mg, 3.37 mmol) afforded **8** as a yellow solid (1.48 g, 2.86 mmol, 85%): IR (neat, cm^{-1}) ν(CO) 2019(s), 1931(s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 5.59 (1H, s, OC*H*), 5.55 (5H, s, Cp), 2.25 (1H, ABq, J = 7.3, 1.5 Hz, C*H*H′Me), 2.10 (1H, ABq, J = 7.3, 1.5 Hz, CH*H*′Me), 1.79 (3H, s, Me), 1.01 (3H, t, J = 7.3 Hz, CHH′*Me*); ^{13}C NMR (75 MHz; $CDCl_3$) δ 224.4, 214.7, 213.7, 157.7, 142.7, 141.2, 129.8, 112.5, 111.9, 100.3, 96.9, 91.4, 20.9, 17.0, 8.50; MS (75 eV *m*/*e*) 518 (M^+). Anal. Calcd for $C_{19}H_{14}WN_2O_4$: C, 44.04; H, 2.72. Found: C, 44.02; H, 2.68.

(6) Synthesis of 9. Compound **1** (0.20 g, 0.45 mmol) and hex-3-yn-2,5-dione (49.5 mg, 0.45 mmol) afforded **9** as a yellow solid (0.22 g, 0.40 mmol, 89%): IR (neat, cm^{-1}) ν(CO) 2019 (s), 1940(s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 5.52 (5H, s, Cp), 5.42 (1H, s, OC*H*), 2.21 (3H, s, CO_2Me), 2.14 (3H, s, CO_2Me), 1.90 (1H, ABq, J = 7.4, 1.5 Hz, CH*H*′Me, 1.85 (1H, ABq, J = 7.4, 1.5 Hz, C*H*H′Me), 1.75 (3H, s, Me), 0.84 (3H, t, J = 7.4 Hz, CHH′*Me*); ^{13}C NMR (75 MHz; $CDCl_3$) δ 226.5, 215.9, 214.5, 202.2, 194.0, 164.3, 156.3, 154.9, 130.5, 130.5, 100.2, 93.7, 92.1, 30.6, 29.0, 21.3, 15.7, 8.8; MS (75 eV *m*/*e*) 552 (M^+). Anal. Calcd for $C_{21}H_{20}WO_6$: C, 45.67; H, 3.65. Found: C, 45.56; H, 3.63.

(7) Synthesis of 10. Compound **1** (0.20 g, 0.45 mmol) and ethyl propiolate (44.1 mg, 0.45 mmol) afforded **10** as a yellow solid (0.22 g, 0.41 mmol, 91%): IR (neat, cm^{-1}) ν(CO) 2010 (s), 1930 (s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.76 (1H, d, J = 3.2 Hz, =CH), 5.48 (5H, s, Cp), 5.13 (1H, d, J = 3.2 Hz, OC*H*), 4.13 (2H, q, J = 7.5 Hz, CH_2CH$_3$), 2.42 (1H, ABq, J = 7.5, 1.8 Hz, C*H*H′CH_3), 2.15 (1H, ABq, J = 7.5, 1.8 Hz, CH*H*′CH_3), 1.82 (3H, s, Me), 1.32 (3H, t, J = 7.5 Hz, CHH′C*H*$_3$), 0.95 (3H, t, J = 7.5 Hz, CH_2*Me*); ^{13}C NMR (100 MHz; $CDCl_3$) δ 226.5, 215.8, 214.5 (3 W−CO), 164.6, 162.2, 156.6, 148.8, 123.0, 97.8, 93.3, 91.0, 60.8, 22.6, 15.8, 14.2, 9.2; MS (75 eV *m*/*e*) 540 (M^+). Anal. Calcd for $C_{20}H_{20}WO_6$: C, 44.47; H, 3.73. Found: C, 44.45; H, 3.71.

(8) Synthesis of 11. Compound **1** (0.20 g, 0.45 mmol) and maleic anhydride (44.1 mg, 0.45 mmol) afforded **11** as a yellow solid (0.22 g, 0.41 mmol, 91%): IR (neat, cm^{-1}) ν(CO) 2030 (s), 1930 (s); ^{1}H NMR (400 MHz; $CDCl_3$) δ 5.59 (5H, s, Cp), 4.92 (1H, s, OCH), 3.04 (1H, d, J = 6.4 Hz, CH), 2.68 (1H, d, J = 6.4 Hz, CH), 1.96−2.10 (2H, m, CH_2CH$_3$), 1.62 (3H, s, Me), 0.96 (3H, t, J = 7.3 Hz, CH_2*CH*$_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 225.4, 215.6, 213.1 (3W−CO), 171.1, 169.4, 152.7, 125.7, 94.7, 93.5, 91.7, 52.1, 51.0, 21.2, 14.3, 9.8; MS (75 eV *m*/*e*) 540 (M^+). Anal. Calcd for $C_{19}H_{16}WO_7$: C, 42.25; H, 2.99. Found: C, 42.19; H, 2.95.

(9) Synthesis of 12. Compound **3** (0.20 g, 0.56 mmol) and maleic anhydride (55. mg, 0.56 mmol) afforded **12** as a yellow solid (0.23 g, 0.50 mmol, 89%): IR (neat, cm $^{-1}$) ν(CO) 2030 (s), 1930 (s); ^{1}H NMR (400 MHz; $CDCl_3$) δ 5.57 (5H, s, Cp), 4.84 (1H, s, OCH), 3.16 (1H, d, J = 6.6 Hz, CH), 2.77 (1H, d, J = 6.6 Hz, CH), 2.03 (2H, q, J = 7.4 Hz, CH_2CH$_3$), 1.61 (3H, s, Me), 0.96 (3H, t, J = 7.4 Hz, CH_2*CH*$_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 236.8, 226.1, 224.0 (3W−CO), 171.3, 169.5, 152.5, 139.4, 94.4, 92.8, 52.0, 50.8, 21.1, 13.7, 8.7; MS (75 eV *m*/*e*) 452 (M^+). Anal. Calcd for $C_{19}H_{16}MoO_7$: C, 50.46; H, 3.57. Found: C, 50.43; H, 3.53.

(10) Synthesis of 13. Compound **1** (0.20 g, 0.45 mmol), and maleimide (44 mg, 0.45 mmol) afforded **13** as a yellow solid (0.23 g, 0.42 mmol, 93%): IR (neat, cm^{-1}) ν(CO) 2020 (s), 1930 (s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.85 (1H, br, NH), 5.59 (5H, s, Cp), 4.67 (1H, s), 2.90 (1H, d, J = 6.3 Hz, OCH), 2.53 (1H, d, J = 6.3 Hz, OCH), 2.05 (2H, m, CH_2CH$_3$), 1.61 (3H, s, Me), 0.96 (3H, t, J = 7.4 Hz, CH_2*CH*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 236.8, 226.1, 224.0 (3W−CO), 175.4, 175.3, 152.5, 139.4, 93.4, 91.8, 51.0, 50.8, 21.0, 12.5, 8.8, MS (75 eV *m*/*e*) 539 (M^+). Anal. Calcd for $C_{19}H_{17}O_6WN$: C, 42.32; H 3.18. Found: C, 42.28; H, 3.16.

(11) Synthesis of 14. Compound **3** (0.20 g, 0.56 mmol) and maleimide (54 mg, 0.56 mmol) afforded **14** as a yellow solid (0.23 g, 0.50 mmol, 90%): IR (neat, cm^{-1}) ν(CO) 2030 (s), 1930 (s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.66 (1H, br, NH), 5.53 (5H, s, Cp), 4.70 (1H, s, OC*H*), 2.85 (1H, d, J = 6.2 Hz, CH), 2.53 (1H, d, J = 6.2 Hz, CH), 2.04 (2H, m, CH_2CH$_3$), 1.59 (3H, s, Me), 0.95 (3H, t, J = 7.3 Hz, CH_2*CH*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 236.7, 225.1, 223.2 (3W−CO), 175.3, 174.2, 152.5, 138.4, 93.4, 91.8, 51.0, 50.6, 22.0, 11.5, 8.6; MS (75 eV *m*/*e*) 451 (M^+). Anal. Calcd for $C_{19}H_{17}MoNO_6$: C, 50.57; H 3.80. Found: C, 50.46; H, 3.79.

(12) Synthesis of 15. Compound **1** (0.20 g, 0.45 mmol) and *N*-phenylmaleimide (78 mg, 0.45 mmol) afforded **15** as a yellow solid (0.25 g, 0.41 mmol, 92%): IR (neat, cm^{-1}) ν(CO) 2030 (s), 1930 (s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.25−7.56 (5H, m, Ph), 5.78 (5H, s, Cp), 4.91 (1H, s, OCH), 2.99 (1H, d, J = 6.4 Hz, CH), 2.66 (1H, d, J = 6.4 Hz, CH), 2.13 (2H, m, *CH*$_2$CH$_3$), 1.73 (3H, s, Me), 1.01 (3H, t, J = 7.2 Hz, CH_2*CH*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 226.1, 212.1, 211.7 (3W−CO), 174.8, 173.7, 151.7, 131.6, 128.3, 127.7, 123.9, 123.5, 93.6, 92.3, 91.3, 51.4, 50.2, 22.2, 15.0, 9.6; MS (75 eV *m*/*e*) 615 (M^+). Anal. Calcd for $C_{25}H_{21}WNO_6$: C, 48.80; H 3.44. Found: C, 48.77; H, 3.39.

(13) Synthesis of 16. Compound **1** (0.20 g, 0.45 mmol) and dimethyl fumarate (65 mg, 0.45 mmol) afforded **16** as a yellow solid (0.24 g, 0.41 mmol, 92%): IR (neat, cm^{-1}) ν(CO) 2010 (s), 1930 (s); ^{1}H NMR (300 MHz; $CDCl_3$) δ 5.44 (5H, s, Cp), 4.69 (1H, s), 3.50 (3H, s, CO_2Me), 3.45 (3H, s, CO_2Me), 3.08 (1H, d, J = 4.2 Hz, CH), 2.64 (1H, d, J = 4.2 Hz, CH), 1.95 (2H, m, CH_2CH$_3$), 1.45 (3H, s, *Me*), 0.84 (3H, t, J = 7.3 Hz, CH_2*CH*$_3$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 226.9, 215.0, 213.7-(3W−CO), 173.0, 170.8, 152.3, 122.9, 92.7, 92.5, 90.7, 51.8,

51.2, 50.1, 49.3, 23.1, 15.1, 8.2; MS (75 eV *m*/*e*) 586 (M^+). Anal. Calcd for $C_{21}H_{22}WO_8$: C, 43.02; H 3.78. Found: C, 42.98; H, 3.75.

(II) General Procedure for CF_3SO_3H Cleavage of Tungsten−η^1-7-Oxabicyclo[2.2.1]heptadienes and −7-Oxabicyclo[2.2.1]heptenes. (14) CF_3SO_3H Acidification of Compound 5. To a CH_2Cl_2 solution (5.0 mL) of compound **5** (200 mg, 0.34 mmol) was added CF_3SO_3H (3.0 μL, 0.03 mmol) at −78 °C, and the solution was stirred for 2 h before being brought to 23 °C in a period of 8 h. To the solution was added a saturated $NaHCO_3$ solution, and the organic layer was extracted with diethyl ether (2 × 20 mL), concentrated, and eluted through a preparative silica TLC (diethyl ether/hexane = 1/1) to yield compound **17** (R_f = 0.34, 52 mg, 0.23 mmol, 65%) and **18** (R_f = 0.25, 24 mg, 0.10 mmol, 28%), respectively.

Spectral Data for 17. IR (neat, cm^{-1}): ν(CO) 1746 (s), 1740 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 7.74 (1H, d, *J* = 8.0 Hz, =CH), 7.21 (1H, d, *J* = 8.0 Hz, =CH), 3.91 (3H, s, CO_2-Me), 3.82 (3H, s, CO_2Me), 2.59 (2H, q, *J* = 7.3 Hz, C*H*$_2$CH$_3$), 2.36 (3H, s, Me), 1.13 (3H, t, *J* = 7.3 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 170.2, 166.1, 142.0, 139.6, 135.5, 131.0, 127.6, 125.3, 52.3, 52.2, 23.9, 19.5, 14.3. MS (75 eV *m*/*e*): 236 (M^+). HRMS: calcd for $C_{13}H_{16}O_4$, 236.1048; found, 236.1045.

Spectral Data for 18. IR (neat, cm^{-1}): ν(CO) 1735 (s), 1730 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 10.77 (1H, d, OH), 6.86 (1H, s), 3.89 (3H, s, CO_2Me), 3.88 (3H, s, CO_2Me), 2.48 (2H, q, *J* = 7.4 Hz, CH$_2$C*H*$_3$), 2.32 (3H, s, Me), 1.01 (3H, t, *J* = 7.4 Hz, C*H*$_2$C*H*$_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 169.8, 169.3, 159.7, 145.6, 134.6, 130.8, 120.4, 106.5, 52.6, 52.1, 23.4, 19.8, 14.6. MS (75 eV *m*/*e*): 252 (M^+). HRMS: calcd for $C_{13}H_{16}O_5$, 252.0997; found, 252.0992.

(15) CF_3SO_3H Acidification of Compound 10. Compound **10** (200 mg, 0.37 mmol) and CF_3CO_2H (0.04 mmol) in cold CH_2Cl_2 (−78 °C) afforded compound **19** (56 mg, 0.30 mmol, 80%): IR (neat, cm^{-1}) ν(CO) 1720 (s); ^1H NMR (300 MHz; $CDCl_3$) δ 7.60 (1H, d, *J* = 5.4 Hz, =CH), 7.24 (1H, d, *J* = 6.0 Hz, =CH), 7.24 (1H, dd, *J* = 6.0, 5.4 Hz, CH), 4.35 (2H, q, *J* = 7.4 Hz, CH$_2$C*H*$_3$), 2.88 (2H, q, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 2.35 (3H, s, Me), 1.39 (3H, t, *J* = 7.4 Hz, CH$_2$C*H*$_3$), 1.19 (3H, t, *J* = 7.3 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 168.7, 143.0, 137.0, 133.4, 127.7, 125.3, 60.7, 23.4, 19.4, 14.4, 14.2. MS (75 eV *m*/*e*) 192 (M^+); HRMS calcd for $C_{12}H_{16}O_2$ 192.1150, found: 192.1145.

(16) CF_3SO_3H Acidification of Compound 7. Compound **7** (200 mg, 0.40 mmol) and CF_3CO_2H (0.04 mmol) in cold CH_2Cl_2 (−78 °C) afforded compounds **20** (80 mg, 0.32 mmol, 80%) and **21** (4.14 mg, 0.02 mmol, 5%), respectively: IR (neat, cm^{-1}) ν(CO) 1745 (s), 1730 (s); ^1H NMR (300 MHz, $CDCl_3$) δ 6.62 (1H, d, *J* = 6.1 Hz, =CH), 5.54 (1H, d, *J* = 6.1 Hz, OCH), 3.86 (3H, s, CO_2Me), 3.76 (3H, s, CO_2Me), 2.19 (1H, ABq, *J* = 7.4, 1.5 Hz, C*H*H′CH$_3$), 2.05 (1H, ABq, *J* = 7.4, 1.5 Hz, CH*H*′CH$_3$), 1.89 (3H, s, Me), 0.99 (3H, t, *J* = 7.3 Hz, CHH′C*H*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 164.5, 162.5, 156.1, 155.9, 152.3, 136.0, 99.1, 82.1, 52.1, 52.1, 20.0, 16.5, 14.5; MS (75 eV *m*/*e*) 252 (M^+); HRMS calcd for $C_{13}H_{16}O_5$ 252.0997, found 252.0992.

(17) CF_3SO_3H Acidification of Compound 13. Compound **13** (200 mg, 0.37 mmol) and CF_3CO_2H (0.04 mmol) in cold CH_2Cl_2 (−78 °C) afforded compound **21** (60 mg, 0.29 mmol, 78%): IR (neat, cm^{-1}) ν(CO) 1753 (s), 1723 (s); ^1H NMR (300 MHz; $CDCl_3$) δ 8.40 (1H, br, NH), 6.05 (1H, s, =CH), 4.05 (1H, t, *J* = 6.5 Hz, CH), 3.19 (1H, dd, *J* = 10.5, 6.5 Hz, CH*H*′), 3.03 (1H, dd, *J* = 10.5, 6.5 Hz, C*H*H′), 2.56 (2H, q, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.80 (3H, s, Me), 1.25 (3H, t, *J* = 7.4 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 175.4, 175.3, 152.5, 144.6, 114.0, 111.4, 41.3, 35.3, 19.2, 12.7, 9.5; MS (75 eV *m*/*e*) 207 (M^+); HRMS calcd for $C_{11}H_{13}NO_3$ 207.0895, found: 207.0893.

(18) CF_3SO_3H Acidification of Compound 14. Compound **14** (200 mg, 0.44 mmol) and CF_3CO_2H (0.05 mmol) in cold CH_2Cl_2 (−78 °C) afforded compounds **21** (57 mg, 0.27 mmol, 63%) and **22** (24 mg, 0.11 mmol, 26%).

Spectral Data for 22. IR (neat, cm^{-1}): ν(CO) 1753 (s), 1720 (s). ^1H NMR (300 MHz; $CDCl_3$): δ 8.10 (1H, br, NH), 6.08 (1H, d, *J* = 6.1 Hz, =CH), 5.15 (1H, d, *J* = 6.1 Hz, OCH), 3.00 (1H, d, *J* = 6.4 Hz, CH), 2.68 (1H, d, *J* = 6.4 Hz, CH), 2.15 (2H, m, C*H*$_2$CH$_3$), 1.83 (3H, s, Me), 1.04 (3H, t, *J* = 7.3 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ 175.6, 175.5, 148.1, 132.0, 92.3, 80.0, 54.1, 50.5, 21.1, 12.1, 8.8. MS (75 eV *m*/*e*): 207 (M^+). HRMS: calcd for $C_{11}H_{13}NO_3$, 207.0895; found, 207.0893.

(19) CF_3SO_3H Acidification of Compound 15. Compound **15** (200 mg, 0.33 mmol) and CF_3CO_2H (0.04 mmol) in cold CH_2Cl_2 (−78 °C) afforded compound **23** (70 mg, 0.25 mmol, 75%): IR (neat, cm^{-1}) ν(CO) 1725 (s), 1710 (s); ^1H NMR (300 MHz; $CDCl_3$) δ 7.24−7.50 (5H, m, Ph), 6.13 (1H, s, =CH), 4.18 (1H, t, *J* = 6.4 Hz, CH), 3.23 (1H, dd, *J* = 10.5, 6.4 Hz, C*H*H′), 3.13 (1H, dd, *J* = 10.5, 6.4 Hz, C*H*H′), 2.56(2H, q, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.85 (3H, s, Me), 1.25 (3H, t, *J* = 7.4 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 174.9, 174.6, 153.2, 145.6, 132.6, 129.1, 128.5, 114.1, 111.4, 40.1, 34.3, 19.2, 12.8, 7.2; MS (75 eV *m*/*e*) 283 (M^+); HRMS calcd for $C_{17}H_{17}NO_3$ 283, found 283.1208.

(21) Demetalation of Compound 15 with BF_3·Et_2O. To a CH_2Cl_2 solution (15 mL) of compound **15** (200 mg, 0.33 mmol) was added BF_3·Et_2O (0.03 mL, 0.33 mmol) at −78 °C, and the solution was stirred for 2 h and Bu_4NI added (121 mg, 0.33 mmol) before it was brought to 23 °C in a period of 8 h. To the solution was added a saturated $NaHCO_3$ (5 mL) solution; the organic layer was extracted with diethyl ether (2 × 15 mL), concentrated, and eluted through a preparative silica TLC (diethyl ether/hexane = 1/1) to yield compound **23** (70 mg, 0.25 mmol, 75%) and $CpW(CO)_3I$ (104 mg, 0.23 mmol, 69%).

(22) Demetalation of Compound 16 with BF_3·Et_2O. Compound **16** (200 mg, 0.34 mmol), BF_3·Et_2O (0.34 mmol), and Bu_4NI (0.34 mmol) in cold CH_2Cl_2 (−78 °C) afforded compound **24** (65 mg, 0.26 mmol, 75%) and $CpW(CO)_3I$ (108 mg, 0.23 mmol, 69%): IR (neat, cm^{-1}) ν(CO) 1760 (s), 1742 (s); ^1H NMR (300 MHz; $CDCl_3$) δ 5.91 (1H, s, =CH), 4.21 (1H, t, *J* = 6.4 Hz, CH), 3.71 (3H, s, CO_2Me), 3.67 (3H, s, CO_2Me), 3.20 (1H, dd, *J* = 10.4, 6.4 Hz, C*H*H′), 2.75 (1H, dd, *J* = 10.4, 6.4 Hz, CH*H*′), 2.51 (2H, q, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 1.87 (3H, s, Me), 1.21 (3H, t, *J* = 7.4 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 172.5, 171.5, 152.3, 147.8, 114.5, 110.1, 52.4, 51.8, 41.1, 35.1, 19.3, 12.8, 9.6; MS (75 eV *m*/*e*) 254 (M^+); HRMS calcd for $C_{13}H_{18}O_5$ 254.1154, found 254.1149.

(23) Synthesis of Compound 25. To a CH_2Cl_2 solution (15 mL) of compound **15** (200 mg, 0.33 mmol) was added $SnCl_4$ (0.04 mL, mmol) at −78 °C, and the solution was stirred for 2 h before addition of $NaBH_3CN$ (20.7 mg, 0.33 mmol). The solution was warmed to 23 °C in a period of 8 h and added to a saturated $NaHCO_3$ (5 mL) solution; the organic layer was extracted with diethyl ether (2 × 15 mL), concentrated, and eluted through a silica column (diethyl ether/hexane = 1/1) to yield compound **25** (R_f = 0.34, 181 mg, 0.29 mmol, 89%): IR (neat, cm^{-1}) ν(CO) 2030 (s), 1930 (s); ^1H NMR (300 MHz; $CDCl_3$) δ 7.25−7.47 (5H, m, ph), 5.58 (5H, s, Cp), 5.27 (1H, s, OC*H*), 4.38 (1H, br d, *J* = 7.3 Hz, OCH), 3.29 (1H, m, COCH), 2.56 (2H, d, *J* = 7.3 Hz, CH_2), 1.77 (3H, s, Me), 1.25 (2H, m, *J* = 7.4 Hz, C*H*$_2$CH$_3$), 0.95 (3H, t, *J* = 7.4 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz; $CDCl_3$) δ 226.0, 216.1, 214.7, (3W−CO), 178.6, 177.5, 152.1, 132.5, 128.3, 128.1, 126.1, 98.1, 92.1, 90.5, 42.5, 30.0, 28.6, 18.0, 10.1; MS (75 eV *m*/*e*) 617 (M^+), Anal. Calcd for $C_{25}H_{23}WO_6N$: C, 48.64; H 3.76. Found: C, 48.59; H, 3.74.

X-ray Diffraction Studies of 6 and 25. Single crystals of **6** and **25** were sealed in glass capillaries under an inert atmosphere. Data for **6** and **25** were collected on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation. The structures of **6** and **25** were solved by direct methods; all data reduction and structural refinements were performed with the Siemens SHELXTL-PLUS package. Crystal data and details of data collection and structural analyses of these three compounds are provided in the Supporting Information. For all structures, all non-hydrogen atoms were refined with anisotropic parameters and all

hydrogen atoms included in the structure factors were placed in idealized positions.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for compounds **6** and **25** (15 pages). Ordering information is given on any current masthead page.

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