Acid-Catalyzed Carbonylation of Lactone to Cyclic Anhydride on Tungsten Metal

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Facile carbonylation of the *cis*-vinyl complex $Cp(CO)_3W[CH{=}CH(COMe)]$ (**2**, Cp = η^5-C_5H_5) followed by cyclization affords the γ-lactone complex $Cp(CO)_2W[\eta^3$-$\overline{CHCHC(Me)OC(O)}]$ (**4**). Further carbonylation of **4** induced by the presence of acid in CH_3CN gives the cyclic anhydride complex $Cp(CO)(CH_3CN)W[\eta^3$-$\overline{CHCHC(Me)C(O)OC(O)}]$ (**9**). The reaction of **4** with Me_2NH causes ring opening to yield the zwitterionic complex $Cp(CO)_2W[\eta^2$-$Me_2N{=}C(Me)$-$CH{=}CHCOOH]$ (**6**). The cyclic anhydride ligand of **9** remains unchanged when **9** is treated with nucleophiles. For example, the reaction of Me_2NH with **9** affords the imine-coordinated complex $Cp(CO)(Me_2NC(Me){=}NH)W[\eta^3$-$\overline{CHCHC(Me)C(O)OC(O)}]$ (**14**), and the reaction of $NaBH_4$ with **9** generates the amine-coordinated complex $Cp(CO)(MeCH_2NH_2)W[\eta^3$-$\overline{CHCHC(Me)C(O)OC(O)}]$ (**15**). The structures of **4**, **6**, **9**, and **14** have also been determined by X-ray diffraction analysis. The allylic ligand in **9** is in an *endo* conformation.

Introduction

Metal-assisted cyclocarbonylation has attracted considerable attention;[1] particularly, dicarbonylation of terminal and/or internal alkynes catalyzed by various transition-metal complexes yielding lactone and other products has been the focus of many reports.[2] Transition-metal-mediated carbonylative ring expansion of various heterocyclic compounds leading to lactones, lactams, and thiolactones has also been reviewed recently.[3] Further carbonylation, however, has received much less attention: indazolone was reacted with CO in the presence of Co catalyst, affording 2,4-dioxo-1,2,3,4-tetrahydroquinazoline,[4] and α-lactams were reacted with CO in the presence of Rh catalyst or with $Co_2(CO)_8$ under a nitrogen atmosphere to yield the azetidine-2,4-dione.[5] The carbonylation of lactone to anhydride has recently been reported in a molybdenum system.[6] We have been interested in carbonylation reactions of unsaturated organic molecules assisted by transition-metal complexes and their regioselectivity.[7] In this paper, we report carbonylation reactions of metal vinyl complexes with a ketone group at C_β, followed by cyclization leading to lactones and further carbonylation of the lactone unit on the metal affording a cyclic anhydride.

Results and Discussion

Synthesis of Lactone Complexes. A mixture of *cis*- and *trans*-vinyl complexes $Cp(CO)_3W(\eta^1$-$CH{=}CHCOMe)$ (**2**) in a 5:1 ratio was isolated by rapid workup in 84% total yield if the reaction of 3-butyn-2-one with $Cp(CO)_3WNa$ (**1**), at 0 °C was quenched with cold hexane as soon as the starting material was depleted, as shown by the IR spectra (about 15 min). However, if carried out at 0 °C for 80 min, the same reaction afforded the allylic γ-lactone complex $Cp(CO)_2W[\eta^3$-$\overline{CHCHC(Me)OC(O)}]$ (**4**) as the only isolable product in 64% yield (see Scheme 1). The molybdenum analogue of the allylic γ-lactone complex $Cp(CO)_2Mo[\eta^3$-$\overline{CHCHC(Me)OC(O)}]$ (**5**) was similarly prepared. However, no vinyl complex could be observed for Mo. All the reactions that yielded **2**−**5** were carried out in the presence of H_2O and MeOH for rendering the proton using THF as a solvent. Facile transformation of **2**-*cis*

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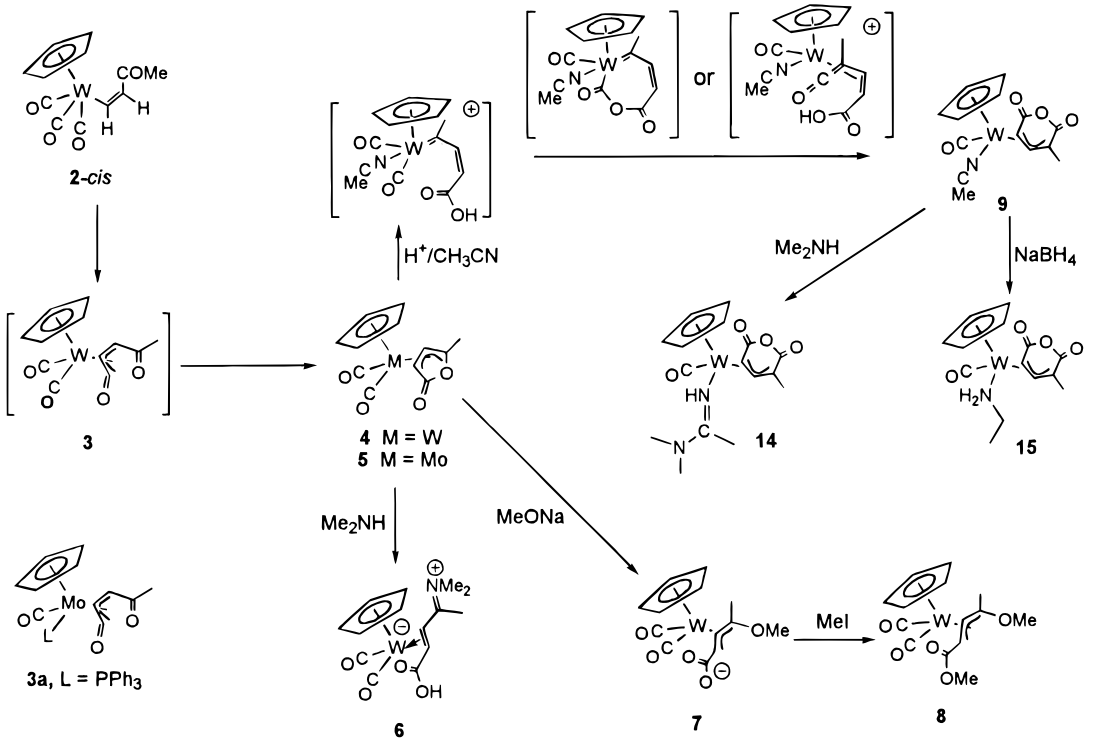
Scheme 1



to **4** was completed within 1 h at room temperature. This transformation in $CDCl_3$ was monitored by NMR spectroscopy. The resonances attributed to **2**-*cis* gradually decreased in intensity, while the resonances attributed to **4** appeared. The **2**-*trans* isomer at the initial stage remained unchanged and finally after 45 min decomposed to give some unidentifiable products.

In the ^{1}H NMR spectrum of the isomeric mixture of **2**, the resonances at δ 8.75, 7.41 and at δ 9.22, 6.79 with the characteristic coupling constants of 11.7 and 17.0 Hz are assigned to the vinyl protons for the *cis* and *trans* isomers, respectively. In $CDCl_3$, **4** displays only one form with the resonances at δ 5.70, 3.36 assignable to the lactone-ring protons, and in CD_3CN at −15 °C, both the *endo* and *exo* isomers are observed in the ^{1}H NMR spectrum. Likewise, the ^{13}C NMR spectrum of **4** in CD_3CN at −15 °C shows resonances at δ 21.7 and 18.7 assignable to the methyl groups of the *endo* and *exo* isomers, respectively. The chemical shifts of the ^{13}C resonances of the three allylic carbon atoms at δ 95.1, 75.8, 29.1 (*endo*) and δ 100.2, 60.1, 26.4 (*exo*) are unusual.[8] The structure of **4** has been firmly established by a single-crystal X-ray diffraction study. An ORTEP drawing is shown in Figure 1. Disorder is found for the lactone ligand; i.e., C(7) and O(2) atoms lie in a symmetry plane. The allylic ligand is in an *exo* conformation with the C(6)−C(7) bond distance (1.33(4) Å) much shorter than the C(7)−C(8) distance (1.53(4) Å), which implies some degree of π conjugation between the η^3-allyl and the lactone carbonyl group.[9] This is compatible with the unusual chemical shift of the ^{13}C

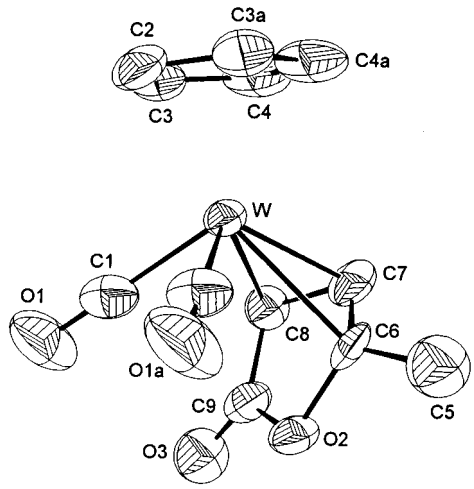


Figure 1. An ORTEP drawing of **4** showing the atom numbering scheme and with 50% probability of the ellipsoid.

resonances described previously. Probably, in addition to the η^3-bonding mode, the η^1:η^2-bonding mode is another form of the allylic ligand, probably through the effect of the neighboring lactone group; however, with the disorder in the crystal, this viewpoint requires further study. The C(6)−O(2) bond length of 1.45(4) Å is longer than that of a regular C−O single bond,[10] consistent with the facile cleavage described below. The structure of **5** displays similar features: namely, a disordered lactone ring and significantly unequal C−C bond lengths in the allylic ligand are observed also in **5**. The distance from the metal to the central carbon of an allylic ligand is typically 0.05−0.19 Å shorter than the distance from the metal to the terminal carbon. This has been attributed to overlap between a filled d orbital

(8) A metal-coordinated η^3-allyl group usually gives ^{13}C resonances at δ 80−90 for a terminal carbon and at δ 110−130 for a central carbon: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 2, pp 176−177.

(9) The corresponding C−C distances of 1.390(7) and 1.415(7) Å in an Mo-coordinated η^3-allyl group are reported in ref 6.

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on the metal and both of the unoccupied orthogonal π^* orbitals of the central carbon.[11] In the allyl system of **4** and **5**, even with the η^1:η^2-bonding anomaly, this same feature is observed.

Formation of **4** could proceed via carbonylation of **2**-*cis*, giving the η^3-acryloyl complex **3** followed by nucleophilic attack of the acetyl oxygen to the acryloyl carbonyl carbon atom to form a five-membered lactone ring with concomitant shift of the allylic coordination onto the three non-carbonyl carbon atoms to give **4**. Such a transformation has been implicated in reactions involving Pd,[12] Rh,[13] Co,[14] and Ni,[15] but no such complex has been isolated by a carbonylation process. The lactonyl complexes of Mo reported by Green and his coworkers[6] were prepared by direct complexation of 1-Me_3SiO-substituted furan followed by a fluoride-anion-induced desilylation. Several previous examples of acryloyl complexes,[16] mostly from carbonylation of vinyl complexes, are known, but none of them form a lactone complex. This mechanism is consistent with our observation that the **2**-*trans* vinyl complex would not yield the lactone product, since after carbonylation, with the acetyl group in a *syn* configuration, formation of a cyclic structure is infeasible.

Interestingly, the complex $Cp(CO)(PPh_3)Mo[\eta^3$-(O)CCHCHCOOMe] (**3a**) is prepared directly from the reaction of the stronger metal nucleophile $Cp(CO)_2(PPh_3)Mo^-$ with $HC{\equiv}CCO_2Me$; i.e., CO insertion takes place but a better donor ligand, PPh_3, in **3a** hinders further attack of the oxygen nucleophile. The similar Mo complex $Cp(CO)(PPh_3)Mo[\eta^3$-(O)CCHCH$_2$] has been prepared[17] via CO insertion of a vinyl precursor. In **3a**, the characteristic ^{13}C resonance at δ 258.1 is assigned to the terminal allylic CO and one of the allylic protons shows J_{H-P} coupling with the PPh_3 ligand. Therefore, we believe that the electronic effect plays an important role in carbonylation of vinyl complex. Facile carbonylation observed in the preparation of **3a** is promoted by the more electron rich metal center with the better σ-donor PPh_3. However, the same factor might hinder cyclization to give the five-membered ring.

Reaction of **4** with Me_2NH first generates the rare zwitterionic olefin-coordinated imine complex $Cp(CO)_2W[\eta^2$-(*Z*)-($Me_2N{=}C$(Me))CH=CHCOOH] (**6-*Z***) in high yield (see Scheme 1). The ν_{CO} stretching bands of **6-*Z*** appear at 1886 and 1790 cm^{-1} in the IR spectrum, indicating localization of the anionic charge at the metal center. In the ^1H NMR spectrum the coupling constant J_{H-H} of 8.0 Hz for the resonances at δ 3.40 and 2.46, attributed

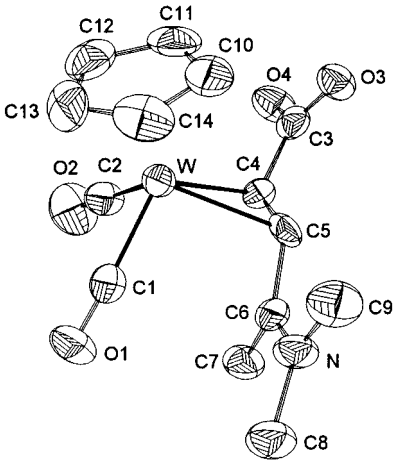

Figure 2. An ORTEP drawing of **6** showing the atom numbering scheme and with 50% probability of the ellipsoid.

to the olefinic protons of **6-*Z***, indicates a *Z* configuration. Complex **6-*Z*** slowly transforms to the corresponding *E* form in about 7 days at −10 °C in CH_2Cl_2 in our attempt to grow single crystals. In the ^1H NMR spectrum, a J_{H-H} value of 14.1 Hz for the resonances at δ 3.15 and 2.70 indicates an *E* configuration. The structure of **6-*E***, as shown in Figure 2, has been determined by a single-crystal X-ray diffraction study. There are two crystallographically independent molecules in the unit cell of **6-*E***, and the two show no significant difference. The olefinic ligand is in an *E* configuration. The C(4)−C(5) bond distance of 1.46(1) Å is characteristic for a η^2-bonded olefin. The C(6)−N bond length of 1.315(9) Å is shorter than that of a regular C−N single bond,[5] consistent with the imine formulation. The following steps rationalize the formation of **6**. Amine attacks the methyl-substituted terminal allylic carbon and causes ring opening at the weaker lactone C−O bond. The resultant allylic complex with a carboxylate group undergoes an *anti*−*syn* transformation followed by a lone pair donation from the amine group to yield **6**. No methylation is observed when **6** is treated with CH_3I.

Treatment of **4** with MeONa follows a similar reaction pathway to afford the yellow allylic product $Cp(CO)_2W[\eta^3$-Me(MeO)CCHCHCOONa] (**7**), which upon treatment with MeI generates $Cp(CO)_2W[\eta^3$-Me(MeO)CCHCHCOOMe] (**8**) in 91% overall yield (see Scheme 1). The ν_{CO} stretchings at 1912 and 1826 cm^{-1} in the IR spectrum of **7** indicate neutral character of the metal center. In the initial stage of the reaction of **4** with MeONa, an intermediate with ν_{CO} stretchings at 1859 and 1753 cm^{-1} in the IR spectrum is observed. The much lower ν_{CO} stretchings could possibly be due to some anionic species resulting from addition of MeO^- at the metal center. Subsequent migration of the methoxy group to the lactone ligand causes opening of the five-membered ring and generates the product. This result is different from that observed in the reaction of amine. This distinct reactivity may be attributed to the reluctance of the oxygen atom to form an oxonium cation.

Cyclic Anhydride Complex from Carbonylation of the Lactone Complex. In the presence of a catalytic amount of CF_3COOH, **4** in CH_3CN undergoes carbonylation to form another C−C bond, giving Cp(CO)(CH_3CN)W[η^3-CHCHC(Me)C(O)OC(O)] (**9**) in 87%

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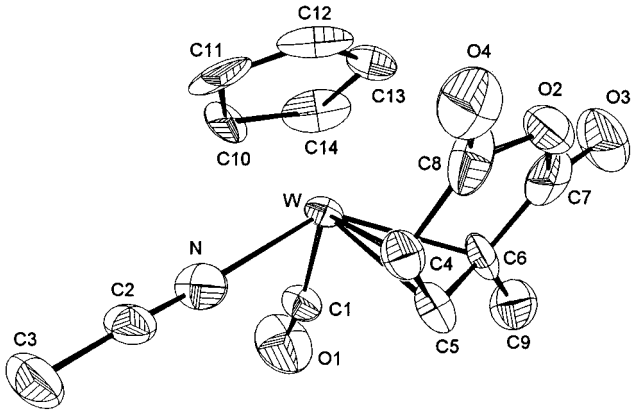

Figure 3. An ORTEP drawing of **9** showing the atom numbering scheme and with 50% probability of the ellipsoid.

isolated yield. No D labeling is observed when a stoichiometric amount of CF_3COOD is used. The IR spectrum of **9** shows only one ν_{CO} band in the terminal carbonyl region. Spectroscopic data are not sufficient to firmly establish the structure of **9**; therefore, an X-ray diffraction analysis was carried out. There are again two crystallographically independent molecules in the unit cell of **9** with no significant differences between them. An ORTEP drawing of one molecule is shown in Figure 3. It is clear that the allylic group embedded in the cyclic anhydride is in an *endo* conformation with the methyl substituent lying *trans* to the coordinated CH_3CN. Also, the two allylic C−C bond distances are about equal (1.36(2) and 1.37(2) Å), indicating a normal allylic ligand. The ^{1}H (δ 5.20, 2.67) and ^{13}C (δ 38.6, 36.1) NMR data for the CH groups of the allylic ligand are also consistent with this observation. The solvent plays an important role in this reaction; i.e., in THF or in chloroform, no reaction is observed. However, if HBF_4 in ether is used, an air-sensitive protonation intermediate is readily formed as a precipitate. The IR spectrum of this intermediate in the terminal carbonyl region gives two sets of absorption bands at 1987, 1915 cm^{-1} and 1963, 1880 cm^{-1}, indicating the presence of two isomers, each possibly with two terminal CO ligands. Thus, protonation presumably occurs at one of the oxygen atoms of the lactone ring with no C−C bond formation in the first step. The ^{1}H NMR data for the allylic group are very similar to those for **4**. In the presence of CH_3CN, this intermediate readily converts to **9** and in CH_3CH_2CN it converts to $Cp(CO)(CH_3CH_2CN)W[\eta^3$-CHCHC(Me)C(O)OC(O)] (**9′**).

A proposed pathway for the formation of **9** is depicted in Scheme 1: protonation at one of the lactone oxygen atoms induced opening of the five-membered ring. This is followed by the shift from a η^3 to η^1 coordination mode of the allylic ligand assisted by the coordination of CH_3CN a solvent molecule, leading to a vinylcarbene intermediate[18] with a pendant carboxylate anion. Our observation that interconversion of the *endo* and *exo* isomers occurs possibly via a η^1-allylic group in CD_3CN but not in $CDCl_3$ is consistent with this proposed pathway. In addition, the much weaker C−O bond of **4**, as determined by the X-ray diffraction analysis, leads to ready rupture of this bond. Nucleophilic attack of the carboxylate onto the terminal CO leads to an acylcarbene, which may undergo further coupling of the carbene with the acylate to yield a η^3 six-membered cyclic anhydride. Carbon−carbon bond formation between the donor atoms of adjacent acyl and alkenyl ligands has been reported.[19] "Carbene migratory insertion",[20] i.e. rearrangement of an alkyl or aryl group at the carbene carbon, has been implicated in many reactions. An alternative pathway would be carbonylation of carbene to yield vinylketene[21] which is followed by ring closure to give **9**. A very similar mechanism for the transformation of a lactonyl to an anhydride ligand has been proposed.[6] A stronger acid such as HBF_4 might protonate the carboxylate group, thus deterring the step of nucleophilic attack or ring closure.

In the reaction of **9** with Me_2NH, the allyl ligand with the cyclic anhydride functionality remains unchanged, but addition of the dimethylamine to the C≡N bond of the coordinated CH_3CN yields $Cp(CO)[Me_2NC(Me)$=NH]$W[\eta^3$-CHCHC(Me)C(O)OC(O)] (**14**).[22] Complex **14** has been characterized by a two-dimensional ^{1}H−^{13}C HMBC NMR experiment as well as by a single-crystal X-ray diffraction analysis. In the ^{1}H NMR spectrum of **14**, the broad resonance at δ 5.53 is assigned to the imine NH, and the two doublet resonances at δ 5.15 and 1.99 are assigned to the ring protons of the cyclic anhydride. In the ^{13}C NMR spectrum, the resonance at δ 171.0 is assigned to the imine C=NH carbon atom. An ORTEP drawing of **14** is shown in Figure 4. The bond distance C(8)−N(1) of 1.296(8) Å, as compared to the C(8)−N(2) distance of 1.345(9) Å, clearly indicates coordination of the imine group. The ^{1}H NMR signal for the imine proton (at δ 5.53) is consistent with this structure.

In the presence of $NaBH_4$, the coordinated CH_3CN ligand of **9** is further reduced to afford the coordinated amine ligand, again while the cyclic anhydride ligand in **9** remains unaltered (see Scheme 1). Specifically, the

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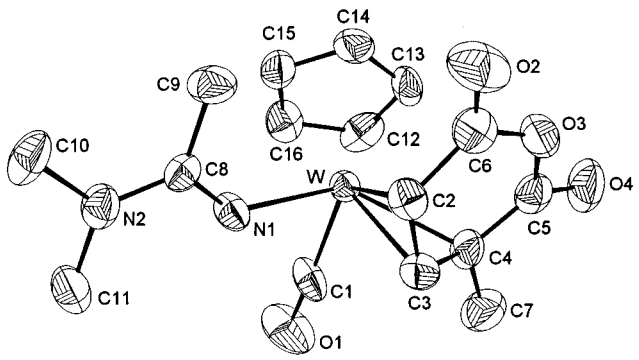

Figure 4. An ORTEP drawing of **14** showing the atom numbering scheme and with 50% probability of the ellipsoid.

reaction gives $Cp(CO)(MeCH_2NH_2)W[\eta^3\text{-}CHCHC(Me)C(O)OC(O)]$ (**15**) in high yield. In the ^1H NMR spectrum of **15**, all the characteristic resonances (δ 5.14 and 2.19) of the cyclic anhydride remain and additional resonances at δ 3.17, 2.76, and 1.02 attributed to the coordinated ethylamine are observed. Unlike the lactonyl ligand in **4**, the cyclic anhydride ligand in **9** is somewhat inert.

Other Vinyl Complexes. To explore the chemical reactivity of other vinyl complexes, we carried out the reaction of **1** with 1.5 equiv of $HC{\equiv}CCO_2Me$ in THF at 0 °C for 1 day, giving a mixture of the *cis* and *trans* isomers (4:1) of $Cp(CO)_3W[CH{=}CH(CO_2Me)]$ (**10**) in about 40% total yield. Interestingly, a similar reaction of **1** with $MeO_2CC{\equiv}CCO_2Me$ in THF at 0 °C for 1 h gives only the *trans*-vinyl complex $Cp(CO)_3W[C(CO_2Me){=}CH(CO_2Me)]$ (**11**) in 65% yield. The presence of the two $-CO_2Me$ substituents may exert steric hindrance; thus, the reaction gave only the *trans* product and its electron-withdrawing ability expedites nucleophilic addition of the metal anion and the rate of the reaction is the fastest among the three alkyne molecules. The preparation of metal vinyl complexes deserves some comment here. A general route to metal vinyl complexes is the insertion of activated acetylenes into metal−hydride bonds.[23] However, the number and variety of factors, such as temperature, solvent, stoichiometry, and polyfunctional nature of both the alkyne and the metal−hydrogen bond, that may affect the process has made the reaction unpredictable. In our study, we found that the reaction of alkynes bearing moderately electron-withdrawing substituents with metal carbonylate anions is actually a better method, giving a relatively higher yield for the preparation of metal vinyl complexes. For comparison, in $CDCl_3$ the reactions of $Cp(CO)_3WH$ with $HC{\equiv}CCO_2Me$ and with $HC{\equiv}CCOMe$ required 4 days and 1 day to afford **10** and directly **4** in only <10% and <40% yields, respectively. The reaction of $Cp(CO)_3WH$ with $MeO_2CC{\equiv}CCO_2Me$ also required 4 days, yielding $[Cp(CO)_2W]_2[MeO_2CC{\equiv}CCO_2Me]$[24] as the major product and less than 30% of **11** as a minor product.

No carbonylation was observed for **10** and **11** under 1 atm of CO pressure or in the presence of phosphine ligands. Photolytic decarbonylation of **11** resulted in chelation of one of the ester carbonyl oxygens and cleanly gave $Cp(CO)_2W[C(CO_2Me){=}CH(C(O)OMe)]$ (**12**) in 84% yield. The IR spectrum of **12** shows two strong ν_{CO} stretching bands at 1948 and 1873 cm^{-1}, characteristic of a neutral $CpW(CO)_2$ moiety, and a medium-intensity absorption at 1701 cm^{-1} assignable to the ν_{CO} band of the acetate group. In the ^1H NMR spectrum of **12** at room temperature, the characteristic Cp resonance appears at δ 5.51 and the vinyl and acetate protons appear at δ 6.35, 3.89 and 3.82, respectively; all display singlet patterns. On the basis of these spectroscopic data, the structure of **12** most likely contains a five-membered oxametallacycle, even though a four-membered oxametallacycle is an alternative.[25] Various methods are known for preparation of the five-membered oxametallacycles.[26]

In conclusion, a conversion of a lactone complex to a cyclic anhydride via proton-catalyzed carbonylation has been achieved. The acetyl group at the β-carbon of the vinyl ligand on tungsten promotes carbonylation, leading to formation of the γ-lactone complex. Conversion of the lactone complex via carbonylation to cyclic anhydride takes place in the presence of a catalytic amount of CF_3COOH. The cyclic anhydride ligand is inert relative to the coordinated CH_3CN ligand. Thus, nucleophilic attack of amine at the CH_3CN ligand or reduction of CH_3CN to ethylamine by $NaBH_4$ is easily achieved, leaving the cyclic anhydride ligand unaltered.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_2D_6CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. $Cp(CO)_3WNa$,[27] $Cp(CO)_3MoNa$,[28] and $Cp(CO)_2(PPh_3)MoNa$[29] were prepared by following the methods reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrumentation at National Taiwan University.

Preparation of $CpW(CO)_3[CH{=}CHC(O)CH_3]$ (2). A solution of $Cp(CO)_3WNa$ (0.55 g, 1.54 mmol) in 20 mL of THF at −78 °C was transferred to a solution of 3-butyn-2-one (0.16 mL, 2.0 mmol) in 40 mL of MeOH (containing 1 mL of H_2O) at 0 °C, and the reaction mixture was stirred for 15 min. The solvent was rapidly removed under vacuum, and the residue

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was extracted with 30 mL of ca. 5:1 hexane/THF **at 0** °C. The extract was filtered and evaporated to dryness to give ca. 5:1 *cis*/*trans* isomeric yellow solids **2** (0.51 g, 84%). Spectroscopic data for **2** are as follows. IR (cm^{-1}, KBr): 2021 (s), 1920 (vs), 1738 (m), 1512 (s) ν(C═O). ^{1}H NMR (20 °C, ppm; *cis* and *trans* forms were observed in $CDCl_3$): *cis* form, 8.75 (d, J_{H-H} = 11.7 Hz, 1H, ═CH), 7.41 (d, J_{H-H} = 11.7 Hz, 1H, ═CH), 5.59 (s, 5H, Cp), 2.17 (s, 3H, CH_3); *trans* form, 9.22 (d, J_{H-H} = 17.0 Hz, 1H, ═CH), 6.79 (d, J_{H-H} = 17.0 Hz, 1H, ═CH), 5.61 (s, 5H, Cp), 2.17 (s, 3H, CH_3). MS (FAB, *m*/*z*): 404 (M^+, W = 186), 376 (M^+ − CO), 348 (M^+ − 2CO), 334 (M^+ − vinyl), 320 (M^+ − 3CO). Anal. Calcd for $C_{12}H_{10}O_4W$: C, 35.85; H, 2.51. Found: C, 35.74; H, 2.32.

Synthesis of Complex Cp(PPh$_3$)(CO)Mo(η^3-O═CCHCHCOOMe) (3a). To a solution of $Cp(PPh_3)(CO)_2$-MoI (0.25 g, 0.41 mmol) in 20 mL of THF was added BuLi (0.7 mL, 1.6M, 1.12 mmol) at 0 °C. The solution was stirred for 10 min; then HC≡CCOOMe (0.20 mL, 2.24 mmol) and 0.3 mL of MeOH were added. After 40 min, the reaction was quenched with 4 mL of water and the solvent was removed under vacuum. The residue was extracted with ether and the ether solution dried over $MgSO_4$. Removal of ether followed by silica gel packed column chromatography (eluted with 1:1 hexane/ether) yielded the yellow oily product **3a** (0.19 g, 82%). Spectroscopic data for **3a** are as follows. IR (cm^{-1}, $CHCl_3$): 1925 (vs), 1709 (m), 1671 (m) ν(C═O). ^{1}H NMR ($CDCl_3$, ppm): 7.50−7.20 (m, 15H, Ph), 4.81 (s, 5H, Cp), 3.62 (s, 3H, CH_3), 2.91 (dd, J_{P-H} = 11.4 Hz, J_{H-H} = 5.5 Hz, 1H, CH), 1.77 (d, J_{H-H} = 5.5 Hz, 1H, CH). ^{13}C NMR, ($CDCl_3$, ppm): 258.1 (C═O), 238.1 (d, J_{P-C} = 15.8 Hz, M−CO). 177.7 (*C*OOMe), 133.2, 130.4, 128.5 (Ph), 92.7 (Cp), 50.7 (OCH_3), 44.5 (d, J_{P-C} = 3.1 Hz, allylic C), 23.5 (allylic carbon). ^{31}P NMR ($CDCl_3$, ppm): 56.6 (PPh_3). MS (FAB, *m*/*z*): 567 (M^+ + 1), 508 (M^+ + 1 − CO_2Me). Anal. Calcd for $C_{29}H_{25}O_4MoP$: C, 61.71; H, 4.46. Found: C, 61.82; H, 4.74.

Preparation of Cp(CO)$_2$W[η^3-CHCHC(CH$_3$)OC(O)] (4). A solution of $Cp(CO)_3WNa$ (0.55 g, 1.54 mmol) in 20 mL of THF at −78 °C was added to a solution of 3-butyn-2-one (0.16 mL, 2.0 mmol) in 40 mL of MeOH (containing 1 mL of H_2O) at 0 °C, and the reaction mixture was stirred for 80 min. The solvent was then removed under vacuum, and the residue was extracted with 30 mL of ca. 2:1 hexane/CH_2Cl_2. The extract was filtered and evaporated to dryness to give yellow solids **4** (0.40 g, 64%). Spectroscopic data for **4** are as follows. IR (cm^{-1}, KBr): 1943 (vs), 1858 (s), 1739 (m), 1730 (m), 1455 (s) ν(C═O). ^{1}H NMR (−15 °C, ppm; *endo* and *exo* forms were observed in CD_3CN): *exo* form, 5.76 (br, J_{H-H} = 3.1 Hz, 1H, CH), 5.64 (br, 5H, Cp), 3.33 (d, J_{H-H} = 3.1 Hz, 1H, CH), 2.01 (s, 3H, CH_3); *endo* form, 5.88 (br, J_{H-H} = 3.0 Hz, 1H, ═CH), 5.45 (s, 5H, Cp), 3.33 (d, J_{H-H} = 3.0 Hz, 1H, CH), 2.07 (s, 3H, CH_3). ^{13}C NMR (−15 °C, CD_3CN, ppm): *exo* form, 229.8, 223.6 (M−CO), 177.1 (C═O), 100.2, 60.1, 26.4 (allylic carbon), 93.3 (Cp), 18.7 (CH_3); *endo* form, 229.8, 223.6 (M−CO), 177.1 (C═O), 95.1, 75.8, 29.1 (allylic carbon), 93.6 (Cp), 21.7 (CH_3). MS (FAB, *m*/*z*): 404 (M^+, W = 186), 376 (M^+ − CO), 348 (M^+ − 2CO), 334 (M^+ − vinyl), 320 (M^+ − 3CO). Anal. Calcd for $C_{12}H_{10}O_4W$: C, 35.85; H, 2.51. Found: C, 35.82; H, 2.44. The Mo analogue $CpMo(CO)_2[\eta^3$-CHCHC(CH$_3$)OC(O)] (**5**; 0.08 g) is similarly prepared from the reaction of $[CpMo(CO)_3]Na$ (0.10 g, 0.37 mmol) and 3-butyn-2-one (0.04 mL, 0.50 mmol) in 68% yield. Spectroscopic data for **5** are as follows. IR (cm^{-1}, KBr): 1940 (vs), 1845 (s), 1730 (m) ν(C═O). ^{1}H NMR ($CDCl_3$, ppm): 5.56 (d, J_{H-H} = 2.6 Hz, 1H, CH), 5.33 (s, 5H, Cp), 3.54 (d, J_{H-H} = 2.6 Hz, 1H, CH), 2.19 (s, 3H, CH_3). ^{1}H NMR (CD_3CN, ppm): 5.90 (br, J_{H-H} = 2.6 Hz, 1H, ═CH), 5.46 (br, 5H, Cp), 3.49 (d, J_{H-H} = 2.6 Hz, 1H, CH), 2.15 (s, 3H, CH_3). ^{13}C NMR (25 °C, $CDCl_3$, ppm): 221.4 (M−CO), 178.0 (C═O), 94.7, 77.2, 28.9 (allylic carbon), 92.5 (Cp), 21.7 (CH_3). MS (FAB, *m*/*z*): 316 (M^+, Mo = 98), 288 (M^+ − CO), 260 (M^+ − 2CO), 247 (M^+ − vinyl), 232 (M^+ − 3CO). Anal. Calcd for $C_{12}H_{10}O_4Mo$: C, 45.88; H, 3.21. Found: C, 45.80; H, 3.18.

Preparation of CpW(CO)$_2$[η^2-Me$_2$N═CMeCH═CHCOOH] (6). To a yellow solution of **4** (0.10 g, 0.25 mmol) in 30 mL of CH_3CN was added 0.08 mL (0.71 mmol, 40% in H_2O) of Me_2-NH by a syringe, resulting in a color change to orange-red. The mixture was stirred for 15 min, and then the solvent was removed in vacuo. The residue was washed with hexane and recrystallized from CH_2Cl_2/hexane to give the orange-red solid **6-*Z*** (0.10 g, 88%). The *Z* configuration is determined by the J_{H-H} value (8.0 Hz) between the two olefinic protons. Spectroscopic data for **6-*Z*** are as follows. IR (cm^{-1}, CH_3CN): 1886 (vs), 1790 (s), 1683 (m), 1623 (m) ν(C═O). ^{1}H NMR ($CDCl_3$, ppm): 5.28 (s, 5H, Cp), 3.40 (d, J_{H-H} = 8.0 Hz, 1H, ═CH), 2.94 (s, 6H, 2 NCH_3), 2.46 (d, J_{H-H} = 8.0 Hz, 1H, ═CH), 1.80 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 242.9, 234.3 (M−CO), 183.1 (C═N), 161.6 (CO_2H), 90.7 (Cp), 35.5 (NCH_3), 37.6, 27.4 (2 ═CH), 17.6 (CH_3). MS (FAB, *m*/*z*): 449 (M^+, W = 186), 421 (M^+ − CO), 393 (M^+ − 2CO). Anal. Calcd for $C_{14}H_{17}NO_4W$: C, 37.60; H, 3.83. Found: C, 36.95; H, 3.64. Upon recrystallization between the interface of the ether/CH_2Cl_2 solution at −10 °C for 7 days, complex **6-*Z*** converted to **6-*E***. ^{1}H NMR data for **6-*Z*** ($CDCl_3$, ppm): 5.42 (s, 5H, Cp), 3.15 (d, J_{H-H} = 14.1 Hz, 1H, ═CH), 2.70 (d, J_{H-H} = 14.1 Hz, 1H, ═CH), 2.17 (s, 6H, 2 NCH_3), 2.12 (s, 3H, CH_3). The structure of complex **6-*E*** was confirmed by single-crystal X-ray diffraction analysis. The reaction of **4** (0.10 g, 0.25 mmol) with $EtNH_2$ (0.05 mL, 70% in H_2O, 0.77 mmol) gave the product $CpW(CO)_2[\eta^2$-EtN-(H)═CMeCH═CHCOOH] (**6a**) (0.10 g, 0.021 mmol) in 84% yield. Spectroscopic data for **6a-*Z*** are as follow. IR (cm^{-1}, CH_3CN): 1882 (vs), 1790 (s), 1681 (m), 1620 (m) ν(C═O). ^{1}H NMR ($CDCl_3$, ppm): 11.4 (br, 1H, ═NH), 5.31 (s, 5H, Cp), 3.32 (d, J_{H-H} = 7.2 Hz, 1H, ═CH), 3.17 (m, 2H, CH_2N), 2.96 (q, J_{H-H} = 7.2 Hz, 2H, 2 NCH_2), 2.46 (d, J_{H-H} = 7.2 Hz, 1H, ═CH), 2.20 (s, 3H, CH_3), 1.26 (t, J_{H-H} = 7.2 Hz, 3H, CH_3), 1.09 (t, J_{H-H} = 7.2 Hz, 3H, CH_3). MS (FAB, *m*/*z*): 446 (M^+, W = 186), 418 (M^+ − CO), 391 (M^+ − 2CO).

Reaction of 4 with MeONa. To a solution of **4** (0.10 g, 0.25 mmol) in CH_3CN was added a MeOH solution containing MeONa (0.02 g, 0.37 mmol), and the solution was stirred at room temperature for 2.5 h. (If monitored by the IR spectra, the reaction first gave an intermediate with the IR absorption bands at 1859 and 1753 cm^{-1} in about 10 min. This intermediate disappeared in about 40 min.) The solvent was removed from the resulting light yellow solution, and the product was extracted with 2 × 10 mL of CH_2Cl_2. After filtration, the volume of the filtrate was reduced to about 5 mL and 20 mL of hexane was added to bring about a light yellow precipitate, which was filtered and washed with 2 × 5 mL of hexane. The product was dried under vacuum and was identified as Cp-$(CO)_2W[\eta^3$-Me(MeO)CCHCHCOONa] (**7**) by spectroscopic techniques. Spectroscopic data for **7** are as follows. IR (cm^{-1},v CH_3CN): 1912 (s), 1826 (s), 1704 (m) ν(C═O). ^{1}H NMR (CD_3-CN, ppm): 5.47 (s, 5H, Cp), 4.48 (d, J_{H-H} = 8.7 Hz, 1H, CH), 3.29 (s, 3H, CH_3), 1.77 (d, J_{H-H} = 8.7 Hz, 1H, CH), 1.53 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 235.5, 229.5 (M−CO), 181.2 (C═O), 117.5 (allyl central C), 93.7 (Cp), 56.1 (OCH_3), 54.0, 34.2 (2 CH), 20.6 (CH_3). All isolated complex **7** was further treated with MeI (0.05 mL, 0.80 mmol) in 20 mL of CH_3CN. The solution was heated to 55 °C for 1 h, and after cooling the solvent was removed under vacuum. The product was extracted with 2:1 hexane/CH_2Cl_2, and after removal of the solvent, $Cp(CO)_2W[\eta^3$-Me(MeO)CCHCHCOOMe] (**8**; 0.10 g) was obtained in 91% yield. Spectroscopic data for **8** are as follows. IR (cm^{-1}, CH_3CN): 1925 (s), 1837 (s), 1691 (w) ν(C═O). ^{1}H NMR ($CDCl_3$, ppm): 5.39 (s, 5H, Cp), 4.52 (d, J_{H-H} = 8.3 Hz, 1H, CH), 3.65, 3.34 (s, 6H, 2 OCH_3), 1.77 (d, J_{H-H} = 8.3 Hz, 1H, CH), 1.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 232.8, 224.9 (M−CO), 176.4 (C═O), 117.8 (allyl central C), 92.4 (Cp), 55.5, 51.6 (2 OCH_3), 52.4, 25.9 (2 CH), 19.8 (CH_3). MS (FAB, *m*/*z*): 448 (M^+), 420 (M^+ − CO), 392 (M^+ − 2CO).

Preparation of CpW(CO)(CH$_3$CN)[η^3-CHCHC(CH$_3$)C-(O)OC(O)] (9). A solution of **4** (0.50 g, 1.24 mmol) in 45 mL

Table 1. Crystal and Intensity Collection Data for $Cp(CO)_2W[\eta^3$-CHCHC(Me)OC(O)] (4), $Cp(CO)_2W[\eta^2$-Me_2N=C(Me)CHCHCOOH] (6), $Cp(CO)(CH_3CN)W[\eta^3$-CHCHC(Me)C(O)OC(O)] (9), and $Cp(CO)(Me_2NC(Me)=NH)W[\eta^3$-CHCHC(Me)C(O)OC(O)] (14)

mol formula	$C_{12}H_{10}O_4W$ (**4**)	$C_{15}H_{20}NO_4WCl_2$ (**6**)	$C_{14}H_{13}O_4NW$ (**9**)	$C_{16}H_{20}N_2O_4W$ (**14**)
mol wt	401.05	533.08	443.11	488.19
space group	*Pnma*	$P\bar{1}$	$P2_1/c$	$C2/c$
a, Å	10.996(2)	8.042(2)	14.222(5)	26.991(7)
b, Å	12.564(4)	10.449(3)	13.894(4)	8.387(3)
c, Å	8.393(3)	22.006(6)	13.989(3)	14.940(3)
α, deg		82.32(3)		
β, deg		84.21(3)	102.62(2)	102.85(2)
γ, deg		84.83(2)		
V, Å^3	1159.5(6)	1815.1(8)	2697.3(15)	3297.3(16)
Z	4	4	8	8
cryst dimens, mm^3	0.10 × 0.20 × 0.45	0.35 × 0.45 × 0.5	0.20 × 0.30 × 0.40	0.30 × 0.30 × 0.30
Mo Kα radiation: *γ*, Å		0.7093		
2*θ* range, deg	2−50	2−45	2−50	2−50
scan type		*θ*/2*θ*		
total no. of rflns	1061	4743	4735	2895
no. of unique rflns, $I > 2\sigma(I)$	716	3914	3265	1725
abs cor, *μ*, cm^{-1}	101.59	65.16	87.47	71.76
transmission factors	0.507−1.000	0.659−1.000	0.591−1.000	0.826−1.000
R	0.028	0.026	0.046	0.021
R_w	0.029	0.025	0.047	0.021
GOF	2.51	2.34	2.64	1.82
Δ*ρ* (in final map), e/Å^3	−0.86, +0.99	−0.81, +0.99	−2.65, +2.29	−0.72, +0.67

Table 2. Selected Bond Distances (Å) and Angles (deg) of $Cp(CO)_2W[\eta^3$-CHCHC(Me)OC(O)] (4)

W−C	1.940(12)	C(4)−C(4)a	1.35(3)
W−C(2)	2.290(15)	C(4)−C(3)	1.367(19)
W−C(4)	2.359(10)	C(7)−C(6)	1.33(4)
W−C(3)	2.313(11)	C(7)−C(8)	1.53(4)
W−C(7)	2.206(13)	O(3)−C(9)	1.19(4)
W−C(6)	2.36(3)	C(6)−O(2)	1.45(4)
W−C(8)	2.40(3)	C(6)−C(5)	1.47(4)
C(1)−O(1)	1.155(14)	C(9)−O(2)	1.39(3)
C(2)−C(3)	1.429(20)	C(9)−C(8)	1.41(4)
C(1)−W−C(1)a	79.8(4)	C(7)−C(6)−C(5)	121(3)
W−C(1)−O(1)	178.1(9)	O(2)−C(6)−C(5)	117(3)
C(3)−C(2)−C(3)a	105.5(15)	O(3)−C(9)−O(2)	115.5(24)
C(4)a−C(4)−C(3)	109.4(12)	O(3)−C(9)−C(8)	134(3)
C(2)−C(3)−C(4)	107.9(14)	O(2)−C(9)−C(8)	110(3)
C(6)−C(7)−C(8)	102.1(22)	C(6)−O(2)−C(9)	103.9(20)
C(7)−C(6)−O(2)	113.1(2)	C(7)−C(8)−C(9)	105(3)

of CH_3CN at 0 °C was treated with CF_3COOH (0.1 mL, 1.29 mmol), and the reaction mixture was stirred for 15 min. Then the solvent was removed under vacuum, and the residue was extracted with 30 mL of ca. 2:1 hexane/CH_2Cl_2. The extract was filtered and evaporated to dryness to give the orange-yellow solid **9** (0.48 g, 87%). Spectroscopic data for **9** are as follows. IR (cm^{-1}, CH_2Cl_2): 1917 (s), 1722 (s), 1682 (m) *ν*(C═O). ^{1}H NMR ($CDCl_3$, ppm): 5.20 (d, J_{H-H} = 4.7 Hz, 1H, CH), 5.05 (s, 5H, Cp), 2.67 (d, J_{H-H} = 4.7 Hz, 1H, CH), 2.51 (MeCN), 2.00 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): 231.6 (J_{W-C} = 179.5 Hz, W−CO), 176.0, 175.2 (C═O), 135.0 (CN), 93.0 (Cp), 75.3 (CH), 38.6 (J_{W-C} = 21.5 Hz, *C*Me), 36.1 (J_{W-C} = 19.7 Hz, CH), 23.6 (CH_3), 4.6 (*C*H_3CN). MS (FAB, *m*/*z*): 443 (M$^+$), 402 (M$^+$ − CH_3CN), 374 (M$^+$ − CH_3CN,CO), 318 (M$^+$ − $C_6H_5O_3$). Anal. Calcd for $C_{14}H_{13}O_4NW$: C, 37.95; H, 2.96; N, 3.16. Found: C, 37.69; H, 2.75; N, 3.07. The reaction can also be carried out in the presence of a catalytic amount of acid. The reaction of **4** (0.50 g, 1.24 mmol) with HBF_4 (2.00 mL) in 20 mL of ether at −78 °C for 30 min afforded a protonation intermediate (0.41 g, 65%) as a red precipitate, which was washed with 20 mL of hexane. Spectroscopic data for the protonation intermediate are as follows. IR (cm^{-1}, THF): 1987 (vs), 1963 (s), 1915 (m), 1880 (m) *ν*(C═O). ^{1}H NMR (C_2D_6CO, ppm): 5.93 (d, J_{H-H} = 2.5 Hz, 1H, CH), 5.70 (br, 5H, Cp), 3.35 (d, J_{H-H} = 3.1 Hz, 1H, CH), 2.08 (s, 3H, CH_3). MS (FAB, *m*/*z*): 403 (M$^+$ − BF_4), 375 (M$^+$ − BF_4, CO), 347 (M$^+$ − BF_4, 2CO).

Reaction of 9 with Amine. A solution of **9** (0.10 g, 0.23 mmol) in 15 mL of CH_3CN was treated with Me_2NH (0.05 mL, 40% in H_2O), and the reaction mixture was stirred for 15 min. Then the solvent was removed under vacuum, and the residue was extracted with 30 mL of ca. 2:1 hexane/CH_2Cl_2. The extract was filtered and evaporated to dryness to give the orange-yellow solid $Cp(CO)[Me_2NC(Me)=NH]W[\eta^3$-CHCHC(Me)C(O)OC(O)] (**14**; 0.10 g, 91%). Spectroscopic data for **14** are as follows. IR (cm^{-1}, CH_3CN): 1875 (s), 1709 (s), 1665 (s) *ν*(C═O); 1570 (m) *ν*(C═N). ^{1}H NMR ($CDCl_3$, ppm): 5.53 (br s, 1H, NH), 5.15 (d, J_{H-H} = 4.9 Hz, 1H, CH), 4.96 (s, 5H, Cp), 2.92 (br, 6H, NMe_2), 2.04 (s, 3H, MeC═), 1.99 (d, J_{H-H} = 4.9 Hz, 1H, CH), 1.98 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, ppm): 240.1 (CO), 175.8, 175.5 (C═O), 171.0 (C═N), 93.7 (Cp), 76.6 (CH), 42.1 (CH), 39.0 (NCH_3), 38.3 (*C*CH_3), 23.1 (CH_3), 20.3 (*C*H_3C═N). MS (FAB, *m*/*z*): 488 (M$^+$), 460 (M$^+$ − CO). Anal. Calcd for $C_{16}H_{20}O_4N_2W$: C, 39.36; H, 4.13; N, 5.73. Found: C, 38.95; H, 4.29; N, 5.96.

Reaction of 9 with $NaBH_4$. A solution of **9** (0.10 g, 0.23 mmol) in 20 mL of CH_3OH was treated with $NaBH_4$ (0.095 g, 2.51 mmol), and the reaction mixture was stirred for 10 min, giving a red-brown solution. Then the solvent was removed under vacuum, and the residue was extracted with 2 × 10 mL of CH_2Cl_2. The extract was filtered and evaporated to about 3 mL; then 20 mL of hexane was added to cause precipitation of the orange-yellow product, which was filtered and dried under vacuum to give $Cp(CO)(MeCH_2NH_2)W[\eta^3$-CHCHC(Me)C(O)OC(O)] (**15**; 0.087 g, 85%). Spectroscopic data for **15** are as follows. IR (cm^{-1}, CH_3CN): 1890 (s), 1709 (s), 1662 (m) *ν*(C═O). ^{1}H NMR (CD_3CN, ppm): 5.14 (d, J_{H-H} = 4.7 Hz, 1H, CH), 5.05 (s, 5H, Cp), 3.17, 2.76 (br, 2H, NCH_2), 2.19 (d, J_{H-H} = 4.7 Hz, 1H, CH), 1.94 (Me), 1.02 (t, J_{H-H} = 7.1 Hz, 3H, CH_3). ^{13}C NMR (CD_3CN, ppm): 241.7 (CO), 176.7, 176.0 (C═O), 94.1 (Cp), 75.9 (CH), 48.7 (NCH_2), 37.9 (*C*Me), 38.0 (CH), 24.1 (CH_3), 18.6 (*C*H_3). MS (FAB, *m*/*z*): 447 (M$^+$), 419 (M$^+$ − CO), 402 (M$^+$ − $CH_3CH_2NH_2$), 374 (M$^+$ − CH_3CH_2-NH_2,CO). Anal. Calcd for $C_{14}H_{17}O_4NW$: C, 37.60; H, 3.83; N, 3.13. Found: C, 37.95; H, 4.09; N, 3.36.

Preparation of $CpW(CO)_3[CH=CHCO_2CH_3]$ (10). A solution of $Cp(CO)_3WNa$ prepared from Na/Hg reduction of $[CpW(CO)_3]_2$ (0.14 g, 0.21 mmol) in 20 mL of THF was added to a solution of methyl propynoate (0.05 mL, 0.71 mmol) in 20 mL of THF (containing 1.0 mL of H_2O and 1.0 mL of MeOH)

Table 3. Selected Bond Distances (Å) and Angles (deg) of $Cp(CO)_2W[\eta^2$-$Me_2N{=}C(Me)CHCHCOOH]$ (6)

W−C(1)	1.944(7)	W′−C(1′)	1.923(8)
W−C(2)	1.920(8)	W′−C2′	1.923(8)
W−C(4)	2.253(7)	W′−C(4′)	2.242(6)
W−C(5)	2.285(7)	W′−C(5′)	2.255(7)
C(1)−O(1)	1.164(9)	C(1′)−O(1′)	1.179(9)
C(2)−O(2)	1.179(9)	C(2′)−O(2′)	1.173(9)
C(3)−C(4)	1.456(9)	C(3′)−C(4′)	1.466(9)
C(3)−O(3)	1.241(8)	C(3′)−O(3′)	1.219(8)
C(3)−O(4)	1.320(9)	C(3′)−O(4′)	1.329(8)
C(4)−C(5)	1.455(10)	C(4′)−C(5′)	1.423(9)
C(5)−C(6)	1.460(9)	C(5′)−C(6′)	1.476(9)
C(6)−C(7)	1.500(10)	C(6′)−C(7′)	1.473(11)
C(6)−N	1.315(9)	C(6′)−N′	1.323(10)
C(8)−N	1.458(9)	C(8′)−N′	1.441(11)
C(9)−N	1.444(10)	C(9′)−N′	1.446(11)
C(1)−W−C(2)	77.8(3)	C(1′)−W′−C(2′)	77.0(3)
W−C(1)−O(1)	176.5(6)	W′−C(1′)−O(1′)	177.9(7)
W−C(2)−O(2)	179.6(6)	W′−C(2′)−O(2′)	178.5(8)
C(4)−C(3)−O(3)	125.2(6)	C(4′)−C(3′)−O(3′)	124.8(6)
C(4)−C(3)−O(4)	112.8(6)	C(4′)−C(3′)−O(4′)	113.2(6)
O(3)−C(3)−O(4)	121.9(6)	O(3′)−C(3′)−O(4′)	122.0(6)
C(3)−C(4)−C(5)	116.7(6)	C(3′)−C(4′)−C(5′)	116.2(6)
C(4)−C(5)−C(6)	122.4(6)	C(4′)−C(5′)−C(6′)	122.1(6)
C(5)−C(6)−C(7)	120.4(6)	C(5′)−C(6′)−C(7′)	119.9(7)
C(5)−C(6)−N	119.7(6)	C(5′)−C(6′)−N′	120.0(7)
C(7)−C(6)−N	119.5(6)	C(7′)−C(6′)−N′	120.0(6)
C(6)−N−C(8)	122.5(6)	C(6′)−N′−C(8′)	121.6(7)
C(6)−N−C(9)	121.5(6)	C(6′)−N′−C(9′)	121.8(6)
C(8)−N−C(9)	114.8(6)	C(8′)−N′−C(9′)	116.5(7)

Table 4. Selected Bond Distances (Å) and Angles (deg) of $Cp(CO)(CH_3CN)W[\eta^3$-$CHCHC(Me)C(O)OC(O)]$ (9)

W−N	2.142(14)	W′−N1′	2.121(13)
W−C(1)	1.950(17)	W′−C(1′)	1.947(19)
W−C(4)	2.266(16)	W′−C(4′)	2.278(15)
W−C(5)	2.113(16)	W′−C(5′)	2.174(14)
W−C(6)	2.241(15)	W′−C(6′)	2.293(14)
N−C(2)	1.103(23)	N′−C(2′)	1.134(23)
C(1)−O(1)	1.166(22)	C(1′)−O(1′)	1.174(23)
C(2)−C(3)	1.433(25)	C(2′)−C(3′)	1.48(3)
C(4)−C(5)	1.364(23)	C(4′)−C(5′)	1.441(25)
C(4)−C(8)	1.47(3)	C(4′)−C(8′)	1.44(3)
C(5)−C(6)	1.375(22)	C(5′)−C(6′)	1.437(22)
C(6)−C(7)	1.42(3)	C(6′)−C(7′)	1.466(25)
C(6)−C(9)	1.52(3)	C(6′)−C(9′)	1.508(23)
C(7)−O(2)	1.365(25)	C(7′)−O(2′)	1.398(23)
C(7)−O(3)	1.219(23)	C(7′)−O(3′)	1.194(21)
C(8)−O(2)	1.400(23)	C(8′)−O(2′)	1.393(23)
C(8)−O(4)	1.192(25)	C(8′)−O(4′)	1.178(23)
N−W−C(1)	85.6(6)	N′−W′−C(1′)	86.1(6)
W−N−C(2)	176.5(13)	W′−N′−C(2′)	173.9(14)
W−C(1)−O(1)	171.2(14)	W′−C(1′)−O(1′)	175.2(12)
N−C(2)−C(3)	176.2(20)	N′−C(2′)−C(3′)	179.4(20)
C(5)−C(4)−C(8)	117.8(14)	C(5′)−C(4′)−C(8′)	123.6(14)
C(4)−C(5)−C(6)	119.6(15)	C(4′)−C(5′)−C(6′)	110.8(13)
C(5)−C(6)−C(7)	116.0(16)	C(5′)−C(6′)−C(7′)	120.4(14)
C(5)−C(6)−C(9)	122.7(15)	C(5′)−C(6′)−C(9′)	118.9(14)
C(7)−C(6)−C(9)	112.4(14)	C(7′)−C(6′)−C(9′)	113.5(14)
C(6)−C(7)−O(2)	120.6(16)	C(6′)−C(7′)−O(2′)	118.1(14)
C(6)−C(7)−O(3)	125.6(19)	C(6′)−C(7′)−O(3′)	127.1(18)
O(2)−C(7)−O(3)	113.6(18)	O(2′)−C(7′)−O(3′)	114.7(16)
C(4)−C(8)−O(2)	116.6(15)	C(4′)−C(8′)−O(2′)	115.6(15)
C(4)−C(8)−O(4)	126.2(18)	C(4′)−C(8′)−O(4′)	127.0(18)
O(2)−C(8)−O(4)	117.1(18)	O(2′)−C(8′)−O(4′)	117.4(17)
C(7)−O(2)−C(8)	121.0(14)	C(7′)−O(2′)−C(8′)	122.9(13)

at 0 °C, and the reaction mixture was stirred for 24 h while it was warmed to room temperature. Then the solvent was removed under vacuum, and the residue was extracted with 2 × 10 mL of ether. The extract was filtered and evaporated to dryness to give the yellow product **10** (0.07 g mixture of *cis*/*trans* (4/1) isomers, 40%) after recrystallization from hexane. Spectroscopic data for **10** are as follows. IR (cm^{-1}, THF (mixture)): 2029 (s), 1933 (vs), 1695 (m), 1554 (s) ν(C=O). ^{1}H NMR (ppm, *cis* and *trans* forms were observed in $CDCl_3$): *cis* form, 8.76 (d, J_{H-H} = 12.0 Hz, 1H, =CH), 6.93 (d, J_{H-H} = 12.0 Hz, 1H, =CH), 5.60 (s, 5H, Cp), 3.67 (s, 3H, CH_3); *trans* form, 9.19 (d, J_{H-H} = 19.5 Hz, 1H, =CH), 6.37 (d, J_{H-H} = 19.5 Hz, 1H, CH), 5.58 (s, 5H, Cp), 3.65 (s, 3H, CH_3). MS (FAB, *m*/*z*): 420 (M^+), 392 (M^+ − CO), 364 (M^+ − 2CO), 336 (M^+ − 3CO). The reaction of $Cp(CO)_3WH$ (0.05 g, 0.15 mmol) with methyl propynoate (0.02 mL, 0.28 mmol) gave no product at room temperature and upon heating gave **10** in only about 10% yield. $CpW(CO)_3[\eta^1$-$C(CO_2Me){=}CH(CO_2Me)]$ (**11**; 0.08 g) was prepared similarly from the reaction of $[CpW(CO)_3]Na$ (0.45 g, 1.26 mmol) and DMAD (0.20 mL) in 65% yield. Spectroscopic data for **11** are as follows. IR (cm^{-1}, THF): 2035 (s), 1940 (vs), 1740 (m), 1701 (m) ν(C=O). ^{1}H NMR ($CDCl_3$, ppm): 6.54 (s, 1H, =CH), 5.56 (s, 5H, Cp), 3.73, 3.69 (s, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, ppm): 226.3, 210.0 (M−CO), 151.2 (α-C=), 178.2, 167.3 (CO), 132.6 (β-=CH), 93.1 (Cp), 51.6, 51.3 (2 CH_3). MS (FAB, *m*/*z*): 478 (M^+), 450 (M^+ − CO), 422 (M^+ − 2CO), 394 (M^+ − 3CO). Anal. Calcd for $C_{14}H_{12}O_7W$: C, 35.32; H, 2.54. Found: C, 35.44; H, 2.70.

Table 5. Selected Bond Distances (Å) and Angles (deg) of $Cp(CO)(Me_2NC(Me){=}NH)W[\eta^3$-$CHCHC(Me)C(O)OC(O)]$ (14)

W−N(1)	2.186(5)	C(2)−C(3)	1.436(10)
W−C(1)	1.954(7)	C(2)−C(6)	1.440(10)
W−C(2)	2.266(7)	C(3)−C(4)	1.441(10)
W−C(3)	2.164(7)	C(4)−C(5)	1.424(10)
W−C(4)	2.269(7)	C(4)−C(7)	1.508(11)
N(1)−C(8)	1.296(8)	C(5)−O(3′)	1.391(9)
N(2)−C(8)	1.345(9)	C(5)−O(4)	1.213(9)
N(2)−C(10)	1.468(9)	C(6)−O(2)	1.193(9)
N(2)−C(11)	1.455(9)	C(6)−O(3′)	1.394(9)
C(1)−O(1)	1.144(8)	C(8)−C(9)	1.503(10)
N(1)−W−C(1)	81.69(24)	C(4)−C(5)−O(3)	120.5(6)
W−N(1)−C(8)	136.8(4)	C(4)−C(5)−O(4)	126.1(7)
C(8)−N(2)−C(10)	123.2(6)	O(3)−C(5)−O(4)	113.2(6)
C(8)−N(2)−C(11)	120.2(6)	C(2)−C(6)−O(3)	126.8(7)
C(10)−N(2)−C(11)	116.5(6)	C(2)−C(6)−O(3)	116.9(6)
W−C(1)−O(1)	177.1(7)	O(2)−C(6)−O(3)	116.3(7)
C(3)−C(2)−C(6)	121.8(6)	N(1)−C(8)−N(2)	122.0(6)
C(2)−C(3)−C(4)	112.2(6)	N(1)−C(8)−C(9)	120.9(6)
C(3)−C(4)−C(5)	117.5(6)	N(2)−C(8)−C(9)	117.1(6)
C(3)−C(4)−C(7)	119.5(6)	C(5)−O(3)−C(6)	120.9(5)
C(5)−C(4)−C(7)	112.5(6)		

Attempted Preparation of 10 from $Cp(CO)_3WH$. The attempted reactions were carried out in NMR tubes and monitored by NMR spectra. To a solution of $Cp(CO)_3WH$ (0.05 g) in 0.5 mL of CD_3CN was added methyl propynoate (0.02 mL, 0.18 mmol) at room temperature, and the solution was mixed thoroughly. After 2 h, no new material other than the starting material was observed in the ^{1}H NMR spectrum. Then the solution was heated to reflux for 4 days to give a complex mixture in which only ca. 10% of **10** was observed. If the reaction was carried out in $CDCl_3$, the major product was $Cp(CO)_3WCl$ (about 75%) with only about 10% of the desired product **10**. The reaction of $Cp(CO)_3WH$ with ethyl propynoate was similarly carried out first at room temperature. In $CDCl_3$ for 3 days, the reaction yielded the *Z* product $CpW(CO)_3[CH{=}CHCO_2Et]$ (**16**; 10%) and $Cp(CO)_3WCl$ (about 75%) along with the starting material. Further heating led to decomposition of the starting material, and the reaction yielded a complex mixture. In CD_3CN, both *E* and *Z* products are observed. Spectroscopic data for **16** are as follows. IR (cm^{-1}, THF (mixture)): 2027 (s), 1942 (vs), 1685 (m), 1550 (s) ν(C=O). ^{1}H NMR (ppm, *cis* and *trans* forms were observed in $CDCl_3$): *cis* form, 8.69 (d, J_{H-H} = 12.0 Hz, 1H, =CH), 6.93 (d, J_{H-H} = 12.0 Hz, 1H, =CH), 5.60 (s, 5H, Cp), 4.10 (q, J_{H-H} = 7.1 Hz, OCH_2), 1.18 (t, J_{H-H} = 7.1 Hz, 3H, CH_3); *trans* form, 8.97 (d, J_{H-H} = 16.0 Hz, 1H, =CH), 6.80 (d, J_{H-H} = 16.0 Hz, 1H, CH), 5.61 (s, 5H, Cp), 4.10 (q, J_{H-H} = 7.1 Hz, OCH_2), 1.18 (t, J_{H-H}

= 7.1 Hz, 3H, CH_3). MS (FAB, *m*/*z*): 434 (M^+), 406 ($M^+ - CO$), 378 ($M^+ - 2CO$), 360 ($M^+ - 3CO$).

Photolysis of 11. Complex **11** (0.08 g, 0.17 mmol) was dissolved in C_6D_6, and the solution was irradiated with a 450 W Hg lamp at room temperature for 30 min. The ^1H NMR spectra indicated formation of $Cp(CO)_2W[C(CO_2Me)=CH(C(O)OMe)]$ (**12**) as the single observable product. The solvent was removed under vacuum, and the product was extracted with 2 × 20 mL of ether. After filtration, ether was removed and complex **12** (0.055 g, 0.12 mmol) was isolated after recrystallization from hexane in 72% yield. Spectroscopic data for **12** are as follows. IR (cm^{-1}, KBr): 1948 (vs), 1873 (s), 1701 (m), 1534 (m) ν(C=O). ^1H NMR ($CDCl_3$, ppm): 6.35 (s, 1H, =CH), 5.51 (s, 5H, Cp), 3.89, 3.82 (s, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$): 218.6 (M−CO); 185.3 (α-C=), 181.3, 176.8 (CO), 114.1 (β-=CH), 92.6 (Cp), 54.2, 51.7 (2 CH_3). MS (FAB, *m*/*z*): 450 (M^+), 422 ($M^+ - CO$), 394 ($M^+ - 3CO$). Anal. Calcd for $C_{13}H_{12}O_6W$: C, 34.85; H, 2.70. Found: C, 34.92; H, 2.76.

X-ray Structure Determination. Many of the details of the crystal structure analyses carried out on **4**, **6**, **9**, and **14** are in Table 1. Data were collected on a CAD4 automatic four-circle diffractometer at 297 K. Corrections for Lorentz−polarization and X-ray absorption effects were applied, the latter by an empirical method using an ω scan. The structures were solved by Patterson methods and refined using the NRCVAX programs. All non-hydrogen atoms were refined anisotropically during the final least-squares cycles, and all hydrogen atoms were included at geometrically calculated positions at a fixed distance of 0.96 Å from their parent atom. Selected bond distances and angles are listed in Tables 2−5 for **4**, **6**, **9**, and **14**, respectively.

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Supporting Information Available: Details of the structural determination for complexes **4**, **6**, **9**, and **14**, including tables of fractional coordinates, anisotropic thermal parameters, and all bond distances and angles and text giving synthetic details and characterization data for **5** and **11** (13 pages). Ordering information is given on any current masthead page.

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