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

Lien Lee, Ding-Jen Chen, Ying-Chih Lin,* Yih-Hsing Lo, Chien Hsing Lin, Gene-Hsiang Lee, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

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Facile carbonylation of the cis-vinyl complex Cp(CO)3W[CH=CH(CHCOMe)] (2, Cp = η5-C5H5) followed by cyclization affords the γ-lactone complex Cp(CO)3W[η3-CHCH(Me)OC(O)] (4). Further carbonylation of 4 induced by the presence of acid in CH3CN gives the cyclic anhydride complex Cp(CO)2(CHOH)[η3-CHCH(Me)OC(O)][OC(O)] (9). The reaction of 4 with Me2NH causes ring opening to yield the zwitterionic complex Cp(CO)3W[η2-Me2N=CM(Me)-CH=CHCOOH] (6). The cyclic anhydride ligand of 9 remains unchanged when 9 is treated with nucleophiles. For example, the reaction of Me2NH with 9 affords the imine-coordinated complex Cp(CO)Me2NC(Me)=NHW[η2-CHCH(Me)OC(O)] (14), and the reaction of NaBH4 with 9 generates the amine-coordinated complex Cp(CO)Me2NH2W[η3-CHCHC(Me)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 cyclocondensation has attracted considerable attention; 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. Transition-metal-mediated carbonylative ring expansion of various heterocyclic compounds leading to lactones, lactams, and thiolactones has also been reviewed recently. 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, and α-lactams were reacted with CO in the presence of Rh catalyst or with Co2(CO)8 under a nitrogen atmosphere to yield the azetidine-2,4-dione. The carbonylation of lactone to anhydride has recently been reported in a molybdenum system. We have been interested in carbonylation reactions of unsaturated organic molecules assisted by transition-metal complexes and their regioselectivity. In this paper, we report carbonylation reactions of metal vinyl complexes with a ketone group at Cp, 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[η3-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)3W[η3-CHCH(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)3Mo-[η3-CHCH(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 H2O and MeOH for rendering the proton using THF as a solvent. Facile transformation of 2-cis-

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to 4 was completed within 1 h at room temperature. This transformation in CDCl₃ 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 ¹H 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 CDCl₃, 4 displays only one form with the resonances at δ 5.70, 3.36 assignable to the lactone-ring protons, and in CD₃CN at −15 °C, both the endo and exo isomers are observed in the ¹H NMR spectrum. Likewise, the ¹³C NMR spectrum of 4 in CD₃CN 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 ¹³C 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. 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 η³-allyl and the lactone carbonyl group. This is compatible with the unusual chemical shift of the ¹³C resonances described previously. Probably, in addition to the η³-bonding mode, the η¹:η²-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, 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.

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


(9) The corresponding C–C distances of 1.390(7) and 1.415(7) Å in an Mo-coordinated η³-allyl group are reported in ref 6.
on the metal and both of the unoccupied orthogonal π* orbitals of the central carbon. In the allyl system of 4 and 5, even with the η1:π bonding anomaly, this same feature is observed.

Formation of 4 could proceed via carboxylation of 2-ds, giving the η1-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 Pd12, Rh,13 Co14 and Ni,15 but no such complex has been isolated by a carboxylation process. The lactonyl complexes of Mo reported by Green and his coworkers6 were prepared by direct complexation of 1-Mes-SiO-substituted furan followed by a fluoride-anion-induced desilylation. Several previous examples of acryloyl complexes,16 mostly from carboxylation 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 carboxylation, with the acetyl group in a syn configuration, formation of a cyclic structure is infeasible.

Interestingly, the complex Cp(CO)(PPh3)M(η1:π-C\(CHCHC(O)\)) (3a) is prepared directly from the reaction of the stronger metal nucleophile Cp(CO)2- (PPh3)Mo+ with HC=CHC=O Me; i.e., CO insertion takes place but a better donor ligand, PPh3, in 3a hinders further attack of the oxygen nucleophile. The similar Mo complex Cp(CO)(PPh3)M(η1:π-C\(CHCHC(O)\)) has been prepared17 via CO insertion of a vinyl precursor. In 3a, the characteristic 13C resonance at δ 258.1 is assigned to the terminal allylic CO and one of the allylic protons shows J\(_{H\text{-}H}\) coupling with the PPh3 ligand. Therefore, we believe that the electronic effect plays an important role in carboxylation of vinyl complex. Facile carboxylation observed in the preparation of 3a is promoted by the more electron rich metal center with the better σ-donor PPh3. However, the same factor might hinder cyclization to give the five-membered ring.

Reaction of 4 with MeONa first generates the rare wittetricarboxylic anion coordinated imine complex Cp(CO)2W[\(\eta^1\)-MeMeN=CM(Me)CH-COOH] (6-Z) in high yield (see Scheme 1). The ν\(_{\text{CO}}\) 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\(_{H\text{-}H}\) of 8.0 Hz for the resonances at δ 3.40 and 2.46, attributed to the definic 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 CH2Cl2 in our attempt to grow single crystals. In the 1H NMR spectrum, a J\(_{H\text{-}H}\) 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 definic ligand is in an E configuration. The C(4)-(C(5) bond distance of 1.46(1) Å is characteristic for a η1-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 CH3I.

Treatment of 4 with MeONa follows a similar reaction pathway to afford the yellow allylic product Cp(CO)2W[\(\eta^1\)-MeMeO]CH-COOH] (7), which upon treatment with Mel generates Cp(CO)2W[\(\eta^1\)-MeMeO]CH-COOH (7), which upon treatment with Mel generates Cp(CO)2W[\(\eta^1\)-MeMeO]CH-COOH (8) in 91% overall yield (see Scheme 1). The ν\(_{\text{CO}}\) stretching 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\(_{\text{CO}}\) stretchings at 1859 and 1753 cm\(^{-1}\) in the IR spectrum is observed. The much lower ν\(_{\text{CO}}\) 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 ofamine. This distinct reactivity may be attributed to the reluctance of the oxygen atom to form an oxonium cation.

**Cyclic Anhydride Complex from Carboxylation of the Lactone Complex.** In the presence of a catalytic amount of CF3COOH, 4 in CH3CN undergoes carboxylation to form another C–C bond, giving Cp(CO)(CH3CN)W[\(\eta^1\)-CHC\(H\)C(Me)\(\text{O}\)OC(O)] (9) in 87% yield. The characteristic ν\(_{\text{CO}}\) stretchings of 9 appear at 1750 and 1715 cm\(^{-1}\) in the IR spectrum.
isolated yield. No D labeling is observed when a stoichiometric amount of CF₃COOD is used. The IR spectrum of 9 shows only one νCO 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 CH₂CN. 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 1H (δ 5.20, 2.67) and 13C (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 HBF₄ 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 1H NMR data for the allylic group are very similar to those for 4. In the presence of CH₃CN, this intermediate readily converts to 9 and in CH₂CH₂CN it converts to Cp(CO)(CH₂CH₂CN)₄W[η⁵-CHCH(Me)OC(O)(O)Me]⁻ (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 of a η⁵ to η⁶ coordination mode of the allylic ligand assisted by the coordination of CH₃CN to a solvent molecule, leading to a vinylcarbene intermediate with a pendant carbonylate anion. Our observation that interconversion of the endo and exo isomers occurs possibly via a η⁵-allylic group in CD₃CN but not in CDC₃ 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 η³ six-membered cyclic anhydride. Carbon–carbon bond formation between the donor atoms of adjacent acyl and alkenyl ligands has been reported.²⁵ “Carbene migratory insertion”,²⁵ 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 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.²⁵ A stronger acid such as HBF₄ might protonate the carbonylate group, thus deterring the step of nucleophilic attack or ring closure.

In the reaction of 9 with Me₂NH, the allylic ligand with the cyclic anhydride functionality remains unchanged, but addition of the dimethylamine to the C≡N bond of the coordinated CH₂CN yields Cp(CO)[Me₂NC(Me)=NH][W[η⁵-CHCH(Me)OC(O)(O)Me]]⁻ (14).²² Complex 14 has been characterized by a two-dimensional ¹H–¹³C HMBC NMR experiment as well as by a single-crystal X-ray diffraction analysis. In the ¹H 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 ¹³C 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 ¹H NMR signal for the imine proton (at δ 5.53) is consistent with this structure.

In the presence of NaBH₄, the coordinated CH₂CN 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

ligands. Photolytic decarboxylation of \( \text{11} \) resulted in cleavage of one of the ester carbonyl oxygens and cleanly gave \( \text{Cp(CO)W[IC(CO)OMe]CH(\text{C(O)OMe})} \) (\( \text{12} \)) in 84% yield. The IR spectrum of \( \text{12} \) shows two strong \( \nu_{\text{C=O}} \) stretching bands at 1948 and 1873 cm\(^{-1}\), characteristic of a neutral \( \text{Cp(W(CO)}_{2}\) moiety, and a medium-intensity absorption at 1701 cm\(^{-1}\) assignable to the \( \nu_{\text{C=O}} \) band of the acetate group. In the \( ^{1}H \) NMR spectrum of \( \text{12} \) at room temperature, the characteristic Cp resonance appears at \( \delta \) 5.51 and the vinyl and acetate protons appear at \( \delta \) 6.35, 3.89 and 3.82, respectively; all display singlet patterns. On the basis of these spectroscopic data, the structure of \( \text{12} \) 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 \( \beta \)-carbon of the vinyl ligand on tungsten promotes carbonylation, leading to formation of the \( \gamma \)-lactone complex. Conversion of the lactone complex via carbonylation to cyclic anhydride takes place in the presence of a catalytic amount of \( \text{CF}_3\text{COOH} \). The cyclic anhydride ligand is inert relative to the coordinated \( \text{CH}_2\text{CN} \) ligand. Thus, nucleophilic attack of amine at the \( \text{CH}_2\text{CN} \) ligand or reduction of \( \text{CH}_3\text{CN} \) to ethylamine by \( \text{NaBH}_4 \) 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. \( \text{CH}_3\text{CN} \) and \( \text{CH}_3\text{Cl}_2 \) were distilled from \( \text{CaH}_2 \) and diethyl ether and \( \text{THF} \) from \( \text{Na/ketyl} \). 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 \( \delta \) with residual protons in the solvent as an internal standard (\( \text{CDCl}_3 \), \( \delta \) 7.24; \( \text{CD}_2\text{CN} \), \( \delta \) 1.93; \( \text{CD}_3\text{CO} \), \( \delta \) 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. \( \text{Cp(CO)WNa}^{27} \), \( \text{Cp(CO)MnNa}^{28} \) and \( \text{Cp(CO)P(PhH)_3MnNa}^{29} \) 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 \( \text{CpW(CO)}_{3}\text{[CH}^\text{\text{-}}\text{CH(CO)OMe)CH}] \) \( \text{(2)} \).** A solution of \( \text{Cp(CO)WNa} (0.35 g, 1.54 mmol) \) in 20 mL of \( \text{THF} \) at \(-78^\circ \text{C} \) was transferred to a solution of 3-butyln-2-one (0.16 mL, 2.0 mmol) in 40 mL of \( \text{MeOH} \) (containing 1 mL of \( \text{H}_2\text{O} \)) at \(-78^\circ \text{C} \), and the reaction mixture was stirred for 15 min. The solvent was rapidly removed under vacuum, and the residue

\[(\text{2}) (a) \text{Alt, H. G.; Herrmann, G. S.; Engelhardt, H. E.; Rogers, R. D.; Organomet. Chem. 1987, 331, 329. (b) van der Zijden, A. A. H.; Bosch, H. W.; Berke, H. Organometallics 1992, 11, 563.} \]

\[(\text{25}) (a) \text{Alt, H. G.; Hermmann, G. S.; Engelhardt, H. E.; Rogers, R. D.; Organomet. Chem. 1987, 331, 329. (b) van der Zijden, A. A. H.; Bosch, H. W.; Berke, H. Organometallics 1992, 11, 563.} \]


\[(\text{27}) \text{Lee, L.; Wu, I. Y.; Lin, Y. C.; Lee, G. H.; Wang, Y. Organometallics 1994, 13, 2521.} \]


\[(\text{29}) \text{Kegley, S. E.; Brookhart, M.; Husk, G. R. Organometallics 1982, 1, 760.} \]
was extracted with 30 mL of ca. 51 hexane/THF at 0 °C. The extract was filtered and evaporated to dryness to give ca. 51 cis-trans isomeric yellow solids 2 (0.51 g, 84%). Spectroscopic data for 2 are as follows. IR (cm⁻¹, KBr): 2921 (s), 2852 (s), 1665 (m), 1608 (m), 1455 (s), 1415 (s), 1337 (m), 1248 (m), 1160 (m), 1047 (w), 882 (m), 760 (m), 716 (w), 694 (w), 610 (m). MS (FAB, m/z): 508 (M⁺ + 2CO, 300), 334 (M⁺ - vinyl), 248 (M⁺ - vinyl), 247 (M⁺ - CO). Anal. Calcld for C₂₂H₁₆₂O₃: C, 72.38; H, 3.83. Found: C, 72.17; H, 3.83.

Preparation of Complex Cp₂W(CO)(CH₃CN)(O)(OC)₂ (O)(2). A solution of Cp₂W(CO)(CH₃CN)O(OC)₂ (0.55 g, 1.54 mmol) in 20 mL of THF at −78 °C was added to a solution of 3-butyne-2-one (0.16 mL, 2.0 mmol) in 40 mL of MeOH (containing 1 mL of H₂O) 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/CH₂Cl₂. 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). ¹H NMR (−15 °C, ppm): endo and exo forms were observed in CD₂CN: exo form, 5.76 (br, J = 3.8 Hz, 1H, CH), 5.64 (br, 5H, CH₃), 5.33 (d, J = 3.8 Hz, 1H, CH₂), 2.01 (s, 3H, CH₃); endo form, 5.88 (br, J = 3.8 Hz, 1H, CH), 5.45 (s, 5H, Cp), 3.33 (d, J = 3.8 Hz, 1H, CH), 2.07 (s, 3H, CH₃). ¹³C NMR (−15 °C, CD₂CN): ppm, 223.6 (M − CO), 177.1 (C=O), 177.1 (C=O), 100.2, 60.1, 26.4 (allylic carbon), 93.3 (C₆H₅), 22.9, 223.6 (M − CO), 177.1 (C=O), 177.1 (C=O), 100.2, 60.1, 26.4 (allylic carbon), 93.3 (C₆H₅). MS (FAB, m/z): 404 (M⁺, W = 186), 375 (M⁺ - CO), 348 (M⁺ - vinyl), 320 (M⁺ - 3CO). Anal. Calcld for C₂₉H₁₈₂O₄W: C, 73.69; H, 4.46. Found: C, 73.61; H, 4.46.

Preparation of Cp₂W(CO)(CH₃CN)(O)(OC)(O)(O)(O) (4). To a solution of Cp₂W(CO)(CH₃CN)O(OC)(O)(O)(O) (5) (0.08 g) is similarly prepared from the reaction of [Cp₂W(CO)(CH₃CN)O] (0.10 g, 0.37 mmol) and 3-butyne-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). ¹H NMR (CD₂CN): ppm, 2.56 (d, J = 2.8 Hz, 1H, CH), 5.33 (d, J = 2.8 Hz, 1H, CH), 2.19 (s, 3H, CH₃). ¹³C NMR (CD₂CN): ppm, 5.90 (br, J = 2.6 Hz, 1H, CH), 5.46 (br, 5H, CH₃), 3.49 (d, J = 2.6 Hz, 1H, CH₂), 2.15 (s, 3H, CH₃). ¹³C NMR (CD₂CN): ppm, 221.4 (M − CO), 178.0 (C=O), 94.7, 77.2, 28.9 (allylic carbon), 92.5 (Cp), 21.7. (CH₃). MS (FAB, m/z): 316 (M⁺, M = 98), 288 (M⁺ - CO), 260 (M⁺ - 2CO), 247 (M⁺ - vinyl), 232 (M⁺ - 3CO). Anal. Calcld for C₂₉H₁₈₂O₄W: C, 74.07; H, 3.21. Found: C, 74.08; H, 3.21.
CH), 5.05 (s, 5H, Cp), 2.67 (d, w, 1H, CH), 5.70 (br, 5H, Cp), 3.35, 2.76 (br, 2H, NCH2), 2.19 (d, j = 4.7 Hz, 1H, CH), 2.09 (s, 3H, Me). Anal. Found: C, 37.95; H, 2.96; N, 3.16. Conf: 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 HBF4 (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 (cm−1, THF): 1987 (vs), 1963 (s), 1880 (m) ν(C=O). 1H NMR (CD3CN, ppm): 4.33 (d, j = 4.7 Hz, 1H, CH), 5.05 (s, 3H, Cp), 3.27, 2.76 (br, 2H, NCH2), 1.99 (d, j = 4.7 Hz, 1H, CH), 2.09 (s, 3H, Me). 13C NMR (CD3CN, ppm): 175.8, 175.5 (C=O), 172.1 (C=O), 167.1 (C=O), 151.2 (C=O), 135.0 (CN), 123.5 (CN), 116.8 (CN), 103.2 (CN). MS (FAB, m/z): 447 (M+), 419 (M+ − CO), 405 (M+ − CH3), 387 (M+ − CH2NH2CO). Anal. Found: C, 37.69; H, 3.83; N, 3.31. Conf: C, 37.95; H, 4.09; N, 3.36.

Preparation of C6H5OHN4W (10). A solution of C6H5OHN4W prepared from NaH reduction of C6H5OHN4W (0.14 g, 0.21 mmol) in 20 mL of THF was added to a solution of methyl propionate (0.05 mL, 0.71 mmol) in 20 mL of THF (containing 1.0 mL of H2O and 1.0 mL of MeOH). Spectroscopic data for 10 are as follows (cm−1, CH3CN): 3180 (s), 3110 (s), 3020 (s), 1709 (s), 1669 (s), 1597 (s). MS (FAB, m/z): 447 (M+), 419 (M+ − CO), 405 (M+ − CH3), 387 (M+ − CH2NH2CO). Anal. Found: C, 37.95; H, 4.09; N, 3.36.
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). ¹H
NMR (ppm, cis and trans forms were observed in CDCl₃): cis
form, 8.76 (d, J = 12.0 Hz, 1H, H₁, =CH), 6.93 (d, J = 12.0
Hz, 1H, =CH₂), 5.60 (s, 5H, Cp), 3.67 (s, 3H, CH₃); trans form,
9.19 (d, J = 19.5 Hz, 1H, H₁, =CH), 6.37 (d, J = 19.5 Hz,
1H, CH₂), 5.58 (s, 5H, Cp), 3.65 (s, 3H, CH₃). MS (FAB, m/z):
420 (M⁺), 392 (M⁺ - CO), 364 (M⁺ - 2CO), 336 (M⁺ - 3CO).
The reaction of Cp(CO)₃WH with methyl propionate (0.02 mL, 0.28 mmol)
gave no product at room temperature and upon heating gave 10 in
only about 10% yield. Cp(CO)₃WH (0.45 g, 1.26 mmol) and DMAD (0.20 mL) in 68% yield. Spectroscopic data for 11 are
as follows. IR (cm⁻¹, THF): 2035 (s), 1940 (vs), 1740 (m), 1701 (m)
was prepared similarly from the reaction of [Cp(CO)₃]Na (0.45
mmol, 1.26 mmol) and DMAD (0.20 mL) in 68% yield. Spectro-
scopic data for 11 are as follows. IR (cm⁻¹, THF): 2035 (s), 1940
(vs), 1740 (m), 1701 (m) ν(C=O). ¹H NMR (CDCl₃, ppm):
6.54 (s, 1H, =CH), 5.56 (s, 5H, Cp), 3.73, 3.69 (s, 6H, 2
CH₂). ¹³C NMR (CDCl₃, ppm): 226.3, 210.0 (M - CO), 151.2
(=CH₂), 178.2, 167.3 (CO), 132.6 (J= =CH), 93.1 (Cp), 51.6, 51.3
(2 CH₂). MS (FAB, m/z): 478 (M⁺), 450 (M⁺ - CO), 422 (M⁺
H, 2.54. Found: C, 35.44; H, 2.70.

**Attemded 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 CD₃CN was added methyl propionate (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 ¹H 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 CDCl₃, 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 propionate
was similarly carried out first at room temperature. In CDCl₃
for 3 days, the reaction yielded the Z product Cp(CO)₃WCl
trans (4/1) isomers, 40% after recrystallization from hexane.
Spectroscopic data for 10 are as follows. IR (cm⁻¹, THF
(mixture)): 2027 (s), 1942 (vs), 1685 (m), 1550 (s) ν(C=O).
¹H NMR (ppm, cis and trans forms were observed in CDCl₃):
cis form, 8.69 (d, J = 12.0 Hz, 1H, =CH), 6.93 (d, J = 12.0
Hz, 1H, =CH₂), 5.60 (s, 5H, Cp), 4.10 (q, J = 7.1 Hz,
CH₂), 1.18 (t, J = 7.1 Hz, 3H, CH₃); trans form, 8.97 (d, 
J = 16.0 Hz, 1H, =CH), 6.80 (d, J = 16.0 Hz, 1H, CH),
5.61 (s, 5H, Cp), 4.10 (q, J = 7.1 Hz, OCH₂), 1.18 (t, J = 7.1 Hz,
J = 7.1 Hz, 3H, CH₃).
Photolysis of 11. Complex 11 (0.08 g, 0.17 mmol) was dissolved in C₆D₆, 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)₂[W(CO₂Me)=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 (CDCl₃, ppm): 6.35 (s, 1H, =CH), 5.51 (s, 5H, Cp), 3.89, 3.82 (s, 6H, 2 CH₃). ¹³C NMR (CDCl₃): 218.6 (M-CO); 185.3 (ω-C=), 181.3, 176.8 (CO), 114.1 (β-CH), 92.6 (Cp), 54.2, 51.7 (2 CH₃). MS (FAB, m/z): 450 (M⁺), 422 (M⁺ - CO), 394 (M⁺ - 3CO). Anal. Calcd for C₁₃H₁₂O₆W: 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.