Reactivity of a Tungsten Carbonyl σ-Allenyl Complex: Regiospecific C–C Bond Formation and Structure of Azatungstacyclobutane and Oxatungstacyclopentene Complexes

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Mild thermolysis of $Cp(CO)_3WCH_2C{\equiv}CH$ (**1a**; Cp = η^5-C_5H_5) in benzene gives $Cp(CO)_3WCH{=}C{=}CH_2$ (**2**). Reaction of **2** with RNH_2 provides the azatungstacyclobutane $Cp(CO)_2W[\eta^2$-$CH(CONHR)CHCH_3(NHR)]$ (**3a**, R = CH_3; **3b**, R = C_6H_5; **3c**, R = $CH_2C_6H_5$; **3d**, R = $CHMe_2$) as the major product. Complex **3** is formed by the additions of one amine to the terminal CO and another amine to the β-carbon of the allenyl group, along with the coupling of the resulting amido group and the α-carbon of the C_3 unit. The allylic complex $Cp(CO)_2W[\eta^3$-$CH_2CHCH(CONHR)]$ (**4**) is also isolated as a minor product. Treatment of **2** with alcohol in benzene affords a mixture of $Cp(CO)_2W[\eta^3$-$CH_2CHCH(COOR')]$ (**5a**, R' = CH_3; **5b**, R' = C_2H_5; **5c**, R' = C_3H_3) and $Cp(CO)_2W[\eta^2$-$C(CH_3){=}CHC(O)OR']$ (**6a**, R' = CH_3; **6b**, R' = C_2H_5; **6c**, R' = C_3H_3). If this reaction is carried out in THF, only **5** is obtained, and in acetonitrile **6** is the only product. *In the reactions of* **2** *leading to* **3**–**6**, *the regiospecific C–C bond formation occurs at the α-carbon. In contrast, the similar coupling reaction of the propargyl complex takes place at the β-carbon.* The structures of **3a** and **6c** have been confirmed by X-ray diffraction analyses. Crystal data for **3a**: space group $C2/c$, a = 20.551(8) Å, b = 11.100(4) Å, c = 12.784(3) Å, β = 94.60(3)°, V = 2907(2) Å^3, Z = 8, R = 0.031, R_w = 0.024, based on 1889 reflections with $I > 2\sigma(I)$. Crystal data for **6c**: space group $P2_1/c$, a = 10.7202(9) Å, b = 16.0349(14) Å, c = 8.4403(12) Å, β = 102.234(9)°, V = 1417.9(3) Å^3, Z = 4, R = 0.019, R_w = 0.015, based on 2027 reflections with $I > 2\sigma(I)$.

Introduction

In organic chemistry, the propargyl and the allenyl groups are considered to be more or less similar, and the rearrangement of the propargyl to the allenyl fragments or the reverse process is well-known.[1] However, in organometallic systems it is generally believed that the reactivities of these two moieties could be significantly different by bonding to a metal. Transition-metal propargyl and allenyl complexes have thus attracted a great deal of attention in recent years as new type of organometallic intermediates that may display distinctive reactivities.[2] In the reaction of a metal carbonylate anion with nonsubstituted propargyl halide, the allenyl complex is usually obtained; i.e., treatment of $(dmgH)_2(py)Co^-$ (dmgH = dimethylglyoximate, py = pyridine) with propargyl halide first yields $(dmgH)_2(py)CoCH_2C{\equiv}CH$, and then $(dmgH)_2(py)CoCH{=}C{=}CH_2$ is obtained through an S_N2' displacement reaction.[3] It is also known that electrophilic attack at a propargyl ligand usually results in formation of a π-allene complex.[4] In comparison with the well-documented[5] studies of the allylic C_3H_5 ligand in either a η^1- or a η^3-bonding mode, the chemistry of unsaturated C_3H_3 and C_3H_4 ligands such as propargyl, allenyl, and allene have been much less studied. Such C_3 ligands could bond to the metal in various modes and display rich reactivities. We are interested in the carbon–carbon bond formation induced by nucleophilic addition onto a metal carbonyl complex containing a propargyl or allenyl ligand. The carbon–carbon bond formation of the allenyl complex occurs at the α-carbon of the C_3 unit, while that of the propargyl complex takes place at the β-carbon.[6] This paper provides a full account of the chemistry of the allenyl complex communicated earlier in preliminary form.

Results and Discussion

Transformation of a σ-Propargyl to a σ-Allenyl Ligand. The light yellow σ-propargyl complex Cp-

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$(CO)_3WCH_2C{\equiv}CH$ (**1a**), at 60 °C, is converted to the reddish brown σ-allenyl complex $Cp(CO)_3WCH{=}C{=}CH_2$ (**2**) in 80% yield. When a concentrated benzene solution of **1a** containing a small amount of suspended NaBr is used, the thermolytic reaction gives the highest yield. Removal of the solvent from **2** usually causes decomposition. Complex **2** is therefore identified by spectroscopic methods. In the ^1H NMR spectrum, the resonances of the CH_2 and CH protons of **2** appear at δ 3.94 and 5.36, respectively, with $^4J_{H-H} = 6.7$ Hz. In the ^{13}C NMR spectrum, the α-carbon of **2** appears at δ 48.5. For comparison, the corresponding CH_2 and CH resonances of **1a** are at δ 1.90 and 2.28 with $^4J_{H-H} = 2.8$ Hz and the ^{13}C resonance of the α-carbon is at δ −33.3.

The Co allenyl complex $(dmgH)_2(py)CoCH{=}C{=}CH_2$ was derived from a S_N2' displacement reaction of $(dmgH)_2(py)CoCH_2C{\equiv}CH$.[3] The transformation of **1a** to **2** may thus proceed via the same S_N2' mechanism or alternatively via a metal migration mechanism. When the propargyl complex **1a** is treated with the metal nucleophile $(C_5H_4Me)(CO)_3W^-$, the expected allenyl product $(C_5H_4Me)(CO)_3WCH{=}C{=}CH_2$ is not observed. This indicates that the transformation should be an intramolecular process. Also, the rate of transformation of **1a** to **2** is not changed by the presence of $Cp(CO)_3W^-$. In three propargyl complexes with different cyclopentadienyl groups, the rate decreases in the following order: $C_5H_4Me > C_5H_5 > C_5H_4COMe$. The methyl group on the cyclopentadienyl ligand enhances the rate of transformation.

The following observations are worthwhile for distinguishing between the 1,3-hydrogen shift and the metal migration mechanisms. For the phosphite-substituted propargyl complex $Cp(CO)_2[P(OMe)_3]WCH_2C{\equiv}CH$ (**1b**), the transformation to the corresponding allenyl compound takes longer than 2 weeks and the yield is low.[7] The pure *trans*-**1b** gives a mixture of *cis*- and *trans*-allenyl products $Cp(CO)_2[P(OMe)_3]WCH{=}C{=}CH_2$. The fact that the configuration of the metal center has been modified during the isomerization may very well imply that partial cleavage of the M−C bond should have occurred, thus suggesting the metal migration mechanism. Conversion of $Cp(CO)_3WCH_2C{\equiv}CD$, prepared from $BrCH_2C{\equiv}CD$,[8] to $Cp(CO)_3WCD{=}C{=}CH_2$ exclusively provides firm evidence for the metal migration mechanism. Similarly, the manganese complex $(CO)_5MnCH_2C{\equiv}CD$ gives $(CO)_5MnCD{=}C{=}CH_2$ exclusively. A η^3-propargyl ligand[2b,9] recently reported in several complexes might play a role in this transformation. For **1**, however, this kind of bonding mode would require either loss of CO or a η^5 to η^3 slippage of the Cp ligand. The role of NaBr in this transformation is not clear. Nevertheless, we believe this may have something to do with the acidity of the terminal proton. No such transformation is observed in the γ-substituted propargyl complexes. In the H−D exchange reaction of the methyl protons (possibly acidic) in $[Cp(CO)_2W(\eta^4\text{-}1,1\text{-}$dimethyltrimethylenemethane$)]^+$ cation with d_6-acetone, NaBr or NaI is also needed.[10]

Reactions of the σ-Allenyl Complex 2 with Amines. Reaction of **2** with methylamine gives the red crystalline azatungstacyclobutane $Cp(CO)_2W[\eta^2\text{-}CH(CONHCH_3)CH(CH_3)NHCH_3]$ (**3a**) as the major product in 60−75% yield. The minor product, with about 5% yield, is the yellow η^3-allylic complex $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(CONHCH_3)]$, (**4a**) resulting from addition of only one amine molecule to **2** and a similar coupling step. Even though **4a** can be purified by chromatography, this causes significant decomposition of the major product. Therefore, careful separation of two colors of solid after crystallization permits isolation of the minor product. Dissolution of **4a** in CD_3CN allows spectroscopic characterization of the product.

For **3a** in solution, two interconvertible isomers are detected by ^1H NMR. The ratio of the two isomers is 4:1 and 13:1 in acetonitrile and in benzene, respectively. The major isomer of **3a** displays two methyne resonances at δ 3.41 and 2.30 and three methyl resonances at δ 2.50, 1.98, and 0.89 as well as a Cp resonance at δ 5.45. The coupling constant between the two protons at the α- and β-carbon atoms in the azatungstacyclobutane ring is 5.7 Hz, indicating a cis configuration, and that between the proton on the β-carbon and NH is 10.9 Hz, indicating a trans configuration. This is confirmed by the X-ray structure determination described below. In the ^{13}C spectrum of **3a**, the resonance at δ 7.9 with a pair of tungsten satellites with $J_{W-C} = 34.9$ Hz is assigned to the α-carbon. The ^1H NMR data of the minor isomer of **3a** shows a similar pattern with several resonances overlapped with that of the major isomer. The coupling constants between the α-CH, β-CH, and MNH protons of the minor product are comparable, indicating similar configurations. A single-crystal X-ray diffraction study reveals only one isomer. However, when the solid is redissolved in acetonitrile, the same 4:1 ratio is again obtained. This indicates that the two isomers are most likely due to the puckering of the four-membered ring (see Scheme 1). Similar puckering of four-membered metallacycles has been observed in iron[11] and tungsten[12] metallacyclobutane complexes and was called butterfly flipping.

The four allylic protons of **4a** are nonequivalent and in the ^1H NMR spectrum display four multiplets at δ 4.49, 2.75, 1.81, and 1.22 assignable to the central, syn, and two anti protons, respectively. The coupling constant of 8.7 Hz between the central proton and the proton on the substituted allylic carbon reveals the syn configuration in the allylic ligand. It is known that, for the monosubstituted allylic complex, the α-substituted one preferably adopts an exo conformation (with respect to the Cp ligand).[13] Thus, the exo form should be the favorable conformation for **4a**.

Formations of **3** and **4** are rationalized on the basis of additions of amine nucleophiles to the allenyl and to the terminal carbonyl ligands. Formation of **3** proceeds

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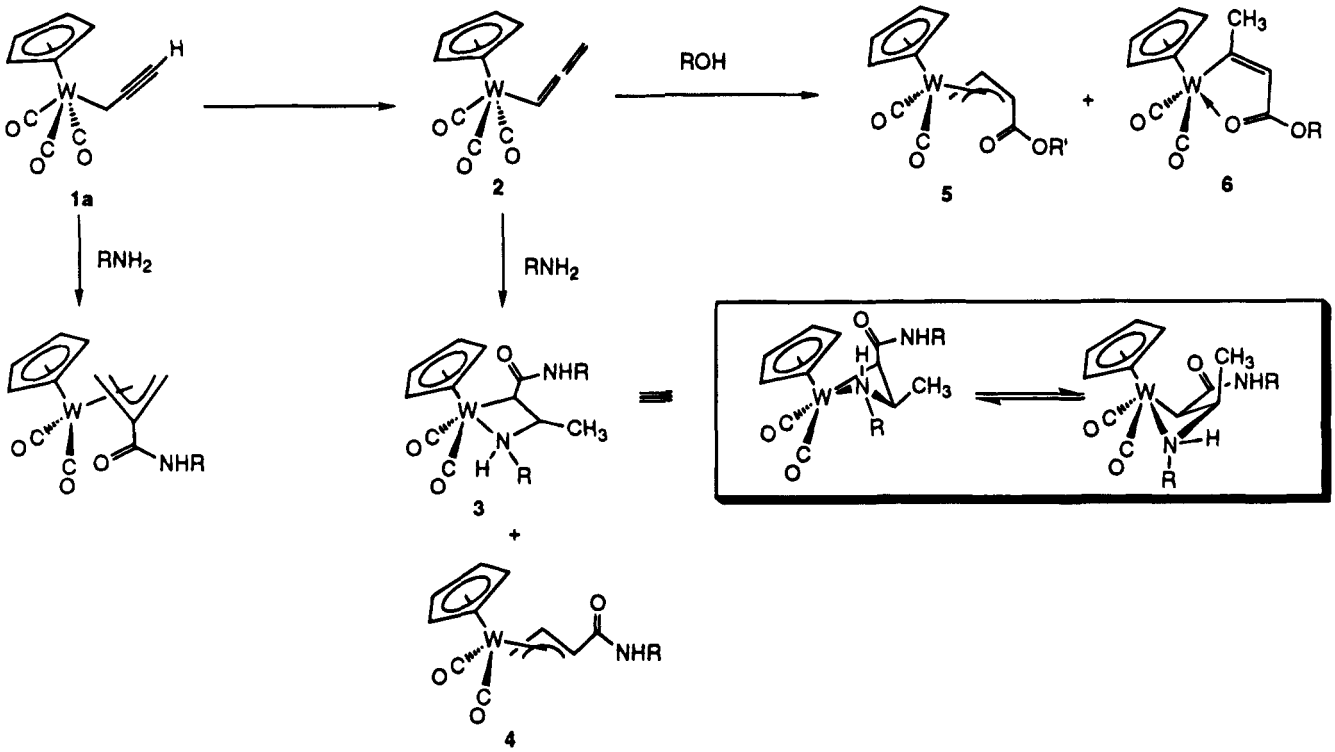
Scheme 1



via two amine additions, one at the terminal CO giving an amido group and the other at the β-carbon of the allenyl group (across the terminal double bond), accompanied by a regiospecific coupling of the amido group with the α-carbon of the allenyl ligand and the coordination of the amine to the tungsten metal center. Since the same coupling reaction is not observed in a metal vinyl complex,[14] we believe that the coupling step should precede the step of nucleophilic addition to the β-carbon. Complex **4** is formed through nucleophilic addition to the terminal CO followed by the same regiospecific coupling, but without the second nucleophilic addition at the center carbon of the allenyl group. Use of 1 equiv of amine did not change the reaction course. It is worth noting that the regiospecificity of the carbon–carbon bond formation is different from that observed in **1a**, where the C–C bond formation takes place at the β-carbon of the propargyl group.[15] The regiospecificity at the β-carbon is also observed in a series of π-allene complexes.[4d]

Crystal Structure of the Azatungstacyclobutane Complex. The molecular structure of **3a** is confirmed by an X-ray diffraction study. Figure 1 gives a view of a single molecule along with the atomic numbering scheme. The selected bond distances and angles are given in Table 1. The stereo structure of the four-membered ring, which is puckered, is shown in Figure 2. The W–C_α(10) and W–N(7) bond distances of 2.276(8) and 2.224(6) Å are typical of a single bond, as are the C(10)–C(8) and C(8)–N(7) bonds. Three of the internal angles are close to 95 ± 5°, while the fourth bond angle C(10)–W–N(7) is 61.0(3)°. The W–C_α bond length is longer than a typical W–C single bond in high-oxidation-state tungsten complexes (generally 2.15 Å).[16] The W–C(8) distance is 2.775(8) Å, too long to be called a bonding interaction. The dihedral angle between the N(7)–W–C(10) plane and the N(7)–C(8)–C(10) plane is 37.4(6)°, almost enough to place the cisoid α-amide and β-methyl groups in pseudo-axial and pseudo-equatorial positions. The torsion angle of C(11)–C(10)–C(8)–C(9) is 41.2(5)°, and the torsion angle of H(7)–N(7)–C(8)–H(8) is 179.2(9)°, the latter being consistent with the relatively large H–H coupling constant observed in the ^{1}H NMR spectrum.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3a

W–C(1)	2.31(1)	C(3)–C(4)	1.41(2)
W–C(2)	2.30(1)	C(4)–C(5)	1.35(1)
W–C(3)	2.312(8)	C(6)–N(7)	1.47(1)
W–C(4)	2.347(8)	N(7)–C(8)	1.469(9)
W–C(5)	2.35(1)	C(8)–C(9)	1.53(1)
W–N(7)	2.224(6)	C(8)–C(10)	1.52(1)
W–C(10)	2.276(8)	C(10)–C(11)	1.48(1)
W–C(14)	1.872(9)	C(11)–O(11)	1.238(9)
W–C(15)	1.968(8)	C(11)–N(12)	1.34(1)
C(1)–C(2)	1.34(2)	N(12)–C(13)	1.43(1)
C(1)–C(5)	1.34(2)	C(14)–O(14)	1.21(1)
C(2)–C(3)	1.40(2)	C(15)–O(15)	1.143(9)
N(7)–W–C(10)	61.0(3)	C(9)–C(8)–C(10)	119.1(7)
N(7)–W–C(14)	89.9(3)	W–C(10)–C(8)	91.6(5)
N(7)–W–C(15)	125.9(3)	W–C(10)–C(11)	110.9(5)
C(10)–W–C(14)	113.2(3)	C(8)–C(10)–C(11)	116.3(7)
C(10)–W–C(15)	78.1(3)	C(10)–C(11)–O(11)	123.3(7)
C(14)–W–C(15)	74.5(3)	C(10)–C(11)–N(12)	117.3(7)
W–N(7)–C(6)	122.4(5)	O(11)–C(11)–N(12)	119.4(7)
W–N(7)–C(8)	95.2(4)	C(11)–N(12)–C(13)	123.4(7)
C(6)–N(7)–C(8)	115.1(6)	W–C(14)–O(14)	175.5(7)
N(7)–C(8)–C(9)	114.4(6)	W–C(15)–O(15)	179.0(8)
N(7)–C(8)–C(10)	99.5(6)		

Reactions of Aaztungstacyclobutane Complexes. Similar azatungstacyclobutane complexes Cp(CO)$_2$W-

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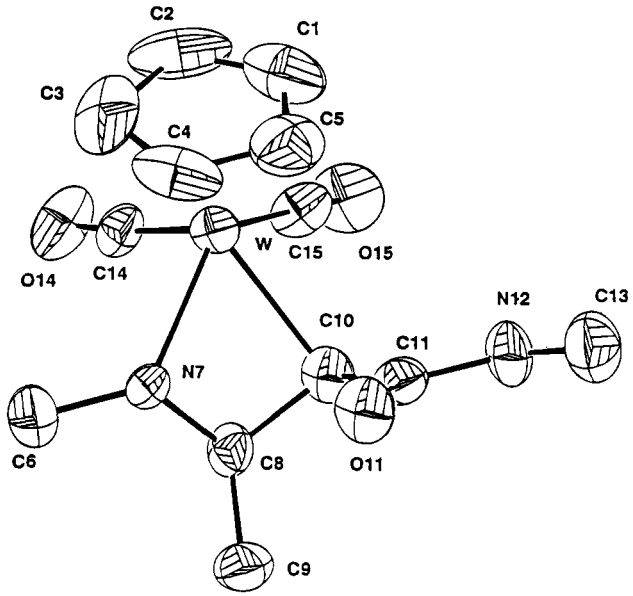

Figure 1. Structure of compound **3a** showing the atom-numbering scheme.

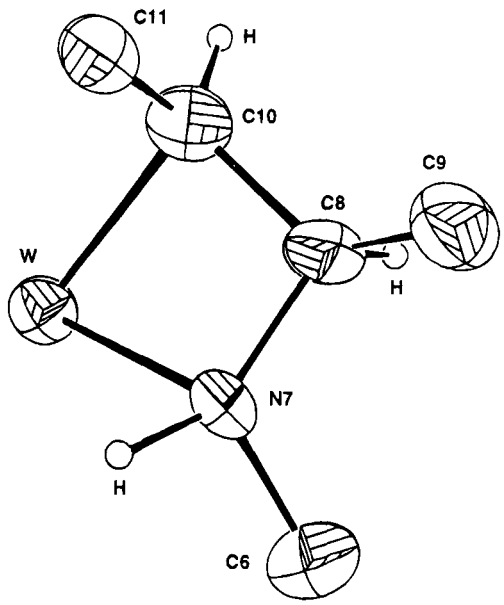

Figure 2. Stereostructure of the four-membered ring of the azatungstacyclobutane **3a**.

$[\eta^2$-CH(CONHR)CH(CH_3)NHR] (**3b**, R = C_6H_5; **3c**, R = $CH_2C_6H_5$; **3d**, R = $CHMe_2$) have been prepared. Above 60 °C all the azatugnstacyclobutane complexes **3** are not stable, undergoing ligand extrusion to give an organic α,β-unsaturated amide (see Scheme 2). The trans configuration of the olefin is determined from the large coupling constant (15.9 Hz) of the two olefinic protons. At room temperature, however, the complexes of aliphatic amines are stable and those of aromatic amines are unstable. Complex **3b**, prepared from aniline, in solution decomposes upon exposure to air or under UV irradiation. The half-life for the decomposition of **3b** in CH_3CN at room temperature is 8 h, and at 60 °C the half-life is about 5 min. The reaction of **2** with an aromatic amine containing an electron-withdrawing group, i.e. *p*-nitroaniline, does not give the azatungstacyclobutane but only gives the α,β-unsaturated amide MeHC=CH($CONHC_6H_4NO_2$) and the minor product $Cp(CO)_2W[\eta^3$-$CH_2CHCH(CONHC_6H_4NO_2)]$ (**4e**). The unsaturated organic amide should be derived from the unstable azatungstacyclobutane. In contrast, at room temperature the benzylamine complex **3c** in solution is stable; no decomposition was found for 7 days. Complex **3d** is also a stable compound. It seems that the electronic effect may be more important in determining the stability of the four-membered ring and the steric bulk may only play a minor role. Interestingly, only one isomer is seen in the ^{1}H NMR spectrum of **3c,d**.

Along with the formation of the α,β-unsaturated amide *trans*-MeHC=CH(CONHPh), the decomposition of **3b** presumably also gives the metal amido complex $Cp(CO)_2WNHPh$.[17] When this process is monitored by NMR, an intermediate showing also the trans configuration (J_{H-H} = 15.7 Hz) of the olefinic protons is observed and is converted to the final product (see Scheme 2). The intermediate is presumably $Cp(CO)_2W$-(NHPh)[MeHC=CH(CONHPh)].[18] The resonances of the two olefinic protons at higher field relative to that of the free olefin may indicate that the olefin is still coordinated to the metal. This step is analogous to the metathesis process of a metallacycle, except that it is an irreversible one. Note that in the transformation of an azatungstacyclobutane to the olefin the cis configuration of the protons in **3** has been changed. The identification of the amido complex is indirectly achieved by trapping the unstable amido product with triethylphosphine to give $Cp(CO)_2(PEt_3)WNHPh$ (**9**), which is identified by spectroscopic methods. The ^{31}P NMR spectrum of **9** displays a resonance at δ 6.46 with a pair of tungsten satellites (J_{W-P} = 258.3 Hz).

Reactions of the σ-Allenyl Complex with Alcohol. Reaction of **2** with the alcohol R′OH in benzene also gives two products, i.e. the η^3-allylic complex $Cp(CO)_2W[\eta^3$-$CH_2CHCH(COOR')]$ (**5a**, R′ = CH_3; **5b**, R′ = CH_2CH_3; **5c**, R′ = $CH_2C{\equiv}CH$) and the five-membered oxatungstacyclopentene $Cp(CO)_2W[\eta^2$-$C(CH_3){=}CHCO$-OR′] (**6a**, R′ = CH_3; **6b**, R′ = CH_2CH_3; **6c**, R′ = $CH_2C{\equiv}CH$) (see Scheme 1). Complexes **5** and **6** are not interconvertible. Perhaps the most striking observation from this type of reaction is the pronounced effect of the solvent on the reaction. When the reaction is carried out in THF, only **5** is obtained, and in acetonitrile only **6** is obtained. The two elementary steps involved in the formation of **5** and **6** are similar to those in the amine reactions. The structural differences between **5** and **6** are a result of protonation at the β- and γ-positions of the σ-allenyl ligand. In THF, the protonation occurs at the β-carbon to give **5**; in CH_3CN, however, protonation occurs at the γ-carbon to give **6**. Although addition of an alkoxyl group to the terminal CO occurs in either THF or CH_3CN solvent, the suscepbility of protonation at the β-position by alcohol in THF causes a complete change during further reaction as compared with the analogous reaction in CH_3CN.

In the ^{1}H NMR spectrum of **5a**, four resonances at δ 4.18, 3.36, 3.26, and 2.76, all displaying ddd patterns, are assigned to the four inequivalent allylic protons.

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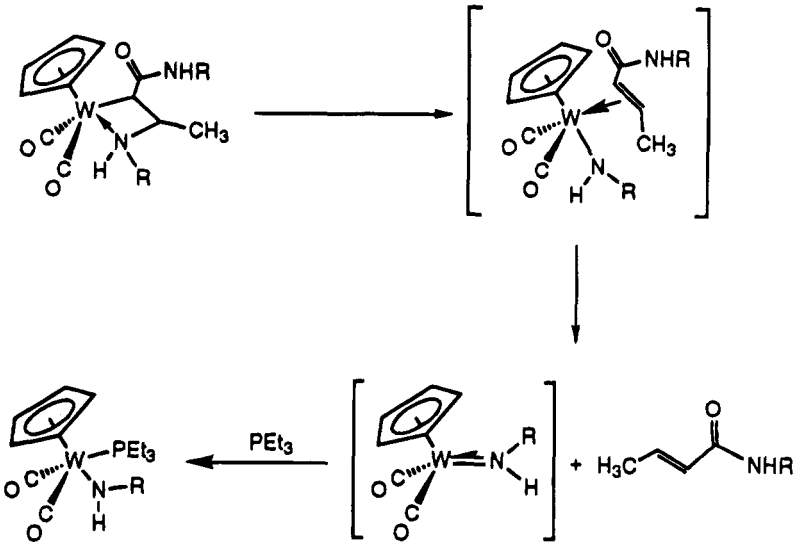
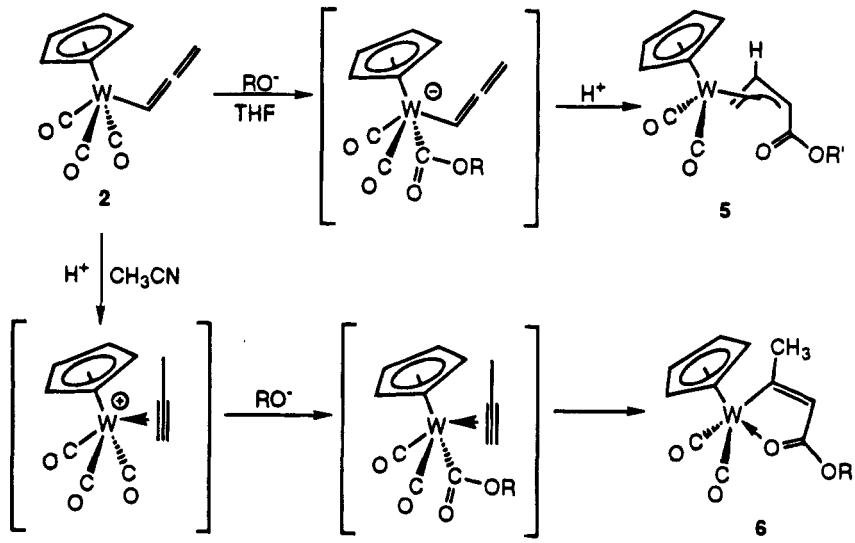
Scheme 2



Scheme 3



From the 2D heteronuclear proton–carbon correlational NMR spectrum, the two protons at δ 3.26 and 2.76 are found to attach to the same carbon atom (δ 39.3). The other two resonances at δ 4.18 and 3.36 are thus assigned to the central proton and the proton on the ester-substituted allylic terminal carbon. The relatively smaller coupling constant of 7.1 Hz (compared to 8.7 Hz in **4a**) between these two protons suggests an anti configuration of the ester group.

The ^{1}H NMR resonances attributed to the C_3 moiety of **6** display an intensity ratio of 3:1, significantly different from the 1:1:1:1 pattern of **5**. In addition to the Cp (δ 5.52) and the methoxy (δ 3.81) resonances, the peak at 2.89 is assigned to the methyl group and that at δ 6.19 is assigned to the vinyl proton. The mass spectrum of **6a** shows parent peaks as well as fragmentations by loss of two CO ligands. These spectroscopic data are insufficient to distinguish between the vinyl ether complex $Cp(CO)_3W[\eta^1$-$CH{=}C(OR)CH_3]$ and **6**. Therefore, the propargyl analogue **6c** was prepared, and its structure has been determined by an X-ray diffraction analysis.

Formation of **5** proceeds via addition of an alkoxy group to the terminal CO followed by a regiospecific coupling of the resulting COOR group with the α-carbon of the allenyl ligand and protonation at the β-carbon, giving the η^3-allylic group. The electrophilic nature of the central carbon of the allenyl ligand has been demonstrated in the reaction of **2** with amine. We therefore believe that the alkoxy addition should occur prior to the protonation at the β-carbon atom. On the other hand, complex **6** may be formed through the formation of a π-bound propyne intermediate by protonation at the γ-carbon possibly prior to the nucleophilic addition (see Scheme 3). In **6**, the tungsten metal has migrated from C_α to C_β, indicative of possible π-coordination of the C_α–C_β moiety. Unlike the reaction of **2** with amine, the reaction of alcohol with **2** gives no four-membered-ring oxatungstacyclobutane complex.

The carbon–carbon bond formation between the donor atoms of adjacent acyl and alkenyl ligands has been reported.[19] Various methods are known for the preparation of five-membered oxametallacycles, notably, coupling of alkynes with metal acyl[20] and insertion of HC≡CCOOMe into the Re–Re bond followed by coor-

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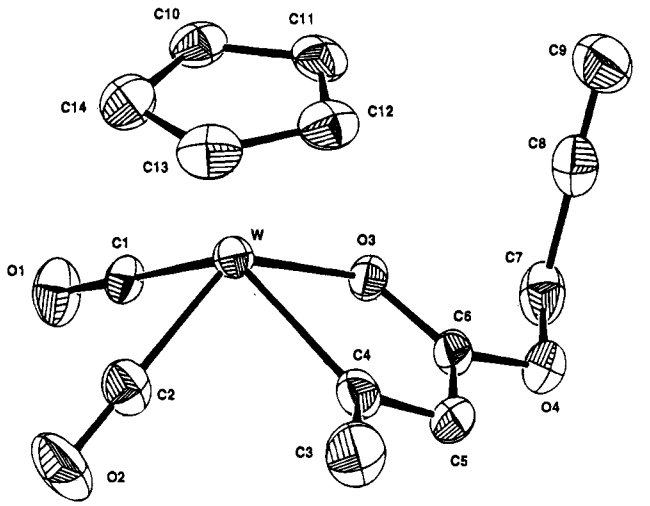

Figure 3. Structure of compound **6c** showing the atom-numbering scheme.

dination of ketonic oxygen.[21] Grubbs and his co-workers used ketal cyclopropene to prepare 2-metallafuran.[22] A recent paper reported the reaction of alkyne with an Re dimer having a bridging CO, affording a 3-metallafuran.[23]

The carbon–carbon bond formation in the reactions of nucleophiles with the propargyl complex **1a** takes place regiospecifically at the β-carbon of the C_3 unit. This bond formation is accompanied by the transformation of the σ,η^1-propargyl ligand into a π,η^3-allylic ligand. The β-(chlorocarbonyl)allyl complex $Cp(CO)_2W[\eta^3\text{-}CH_2C(COCl)CH_2]$ was obtained from the reaction of $AlCl_3$ with **1a** in the presence of protic acid.[10] These reactions are believed to proceed via a η^2,π-allene intermediate supposedly obtained from protonation at the terminal carbon of the propargyl ligand. The (η^2-allene)iron complexes have been reported in the literature.[4a-c] The simple π,η^2-allene complex was not obtained from the protonation of **1a**. However, in the reaction of **1a** with Ph_3CPF_6, the π-allene complex $Cp(CO)_3W[\pi\text{-}CH_2{=}C{=}CHCPh_3]PF_6$ (**8**) was isolated in essentially quantitative yield.[24] Reaction of **8** with MeO^- did give the π-(α,β-disubstituted)allylic product $Cp(CO)_2W[\eta^3\text{-}CH_2C(COOCH_3)CHCPh_3]$. The carbon–carbon bond formation of the allene unit is similar to that of the propargyl complex. A rare example of the carbon–carbon bond formation at the α-carbon of the propargyl ligand in a Co complex is through a direct CO insertion reaction.[25]

Crystal Structure of the Oxatungstacyclopentene Complex 6c. The molecular structure of **6c** has been determined by an X-ray diffraction study. The ORTEP diagram is shown in Figure 3, and Table 2 contains selected bond distances and angles. Complex **6c** is considered as having a 2-metallafuran ring[26] and may be viewed as having a vinyl ester like rather than carbenoid structure.[27] The ketonic oxygen atom O(3) of the carboxylate group is coordinated to the metal atom to form a five-membered oxatungstacyclic ring (W–O(3) = 2.162(3) Å). Adams[21] recently reported the structure of a Re-substituted metallacycle with carboxylate in which the s-cis conformation was observed. In metallacycles with (silyloxy)- or alkoxyvinyl units,[28] both s-trans and s-cis have been observed. The M–C(4)–C(5) angle of 115.5(3)° in **6c** is constrained by the five-membered-ring structure. The W–C(4) bond length of 2.154(4) Å is longer than that of a normal tungsten alkylidene complex, and a substantial amount of π-delocalization of the chelating five-membered ring is indicated by its structure (C(4)–C(5) = 1.353(7) Å and C(5)–C(6) = 1.392(7) Å), which lies intermediate between that of a tungsten enolate and a chelating enone, although the bond lengths are slightly closer to those of the latter resonance form.[29]

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6c

W–C(1)	1.979(4)	C(4)–C(5)	1.353(7)
W–C(2)	1.925(5)	C(5)–C(6)	1.392(7)
W–O(3)	2.162(3)	C(6)–O(3)	1.268(5)
W–C(4)	2.154(4)	C(6)–O(4)	1.333(5)
W–C(10)	2.339(4)	C(7)–O(4)	1.435(6)
W–C(11)	2.374(5)	C(7)–C(8)	1.452(7)
W–C(12)	2.248(4)	C(8)–C(9)	1.155(8)
W–C(13)	2.383(4)	C(10)–C(11)	1.383(7)
W–C(14)	2.272(4)	C(10)–C(14)	1.409(7)
C(1)–O(1)	1.153(5)	C(11)–C(12)	1.417(7)
C(2)–O(2)	1.169(6)	C(12)–C(13)	1.404(8)
C(3)–C(4)	1.507(7)	C(13)–C(14)	1.427(7)
C(1)–W–C(2)	76.7(2)	C(3)–C(4)–(5)	118.6(4)
C(1)–W–C(4)	124.7(2)	C(4)–C(5)–C(6)	114.6(4)
C(1)–W–O(3)	81.0(1)	C(5)–C(6)–O(3)	120.4(4)
C(2)–W–C(4)	77.9(2)	C(5)–C(6)–O(4)	119.6(4)
C(2)–W–O(3)	123.9(2)	O(3)–C(6)–O(4)	120.0(4)
C(4)–W–O(3)	74.1(2)	C(8)–C(7)–O(4)	113.5(4)
W–C(1)–O(1)	176.9(3)	C(7)–C(8)–C(9)	179.3(5)
W–C(2)–O(2)	179.0(2)	W–O(3)–C(6)	115.4(3)
W–C(4)–C(3)	125.7(3)	C(7)–O(4)–C(7)	117.5(3)
W–C(4)–C(5)	115.5(3)		

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. Diethyl ether was distlled from CaH_2 and

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stored over molecular sieves prior to use. CH_2Cl_2 was distilled from CaH_2. THF and benzene were distilled from sodium–benzophenone. All other solvents and reagents were reagent grade and used without further purification. $W(CO)_6$ was purchased from Strem Chemical, and amine and alcohol reagents were purchased from Janssen Chimica, except for methylamine, which was purchased from Union Carbide. Propargyl bromide was obtained from Merck and was distilled in small quantities before use. The complexes $[CpW(CO)_3]_2$[30] and $CpW(CO)_3CH_2C{\equiv}CH$ (**1a**) and $CpW(CO)_3CH_2C{\equiv}CD$[31] were prepared according to the literature methods. The tungsten anion $CpW(CO)_3^-$ was prepared from the Na/Hg reduction of $[CpW(CO)_3]_2$ and can be stored as a Et_4N salt. NMR spectra were recorded on a Bruker AM-300WB or a Bruker ACF-200 spectrometer and are reported in units of parts per million with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24). IR spectra were measured on a Perkin-Elmer 983 instrument, and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Fast atom bombardment and electron impact mass spectra were determined with a JEOL SX-102A spectrometer.

Transformation of the Propargyl Complex to the Allenyl Complex. The tungsten propargyl complex **1a** (1.08 g, 2.7 mmol) was dissolved in 10 mL of benzene, and NaBr (0.028 g, 0.27 mmol) powder was added. The solution was heated to 65 °C for 45 min. The solution turned from yellow to dark red. The reaction was monitored by the disappearance of a ν(CO) absorption of **1a** at 2081 cm^{-1} in the IR spectrum. In this reaction it is better to use a concentrated solution with some NaBr added to obtain a higher yield of **2**. The solvent was then removed under reduced pressure. The product is extracted with 6 × 15 mL hexane to give the red-brown solid $Cp(CO)_3W(\eta^1\text{-}CH{=}C{=}CH_2)$ (**2**), yield ca. 80% (0.81 g with some contamination). Spectroscopic data for **2** are as follows. IR (cm^{-1}, C_6H_6): 2023 (s), 1926 (vs). ^1H NMR (25 °C, CD_3CN): 5.57 (s, 5H, Cp), 5.36 (t, 1H, J_{H-H} = 6.7 Hz, CH), 3.94 (d, 2H, J_{H-H} = 6.7 Hz, CH_2). ^{13}C NMR (25 °C, $C_6D_5CD_3$): 229.1, 215.9 (CO), 209.6 (=C=), 95.2 (Cp), 62.0 (=CH_2), 48.5 (M–CH=). MS (*m/z*, 20 eV): 374 (M^+), 346 (M^+ − CO), 318 (M^+ − 2CO), 290 (M^+ − 3CO). The reactions of **2** described below used the benzene solution directly prepared from **1** without purification.

Reaction of 2 with Amines. An aliquot of $MeNH_2$ (3 mL) was obtained from gaseous methylamine by condensation using a cold finger filled with liquid N_2/acetone slurry and was dissolved in 10 mL of benzene. Addition of the $MeNH_2$ solution to **2** (0.95 g, 2.56 mmol in 40 mL of benzene) led to a color change from reddish brown to dark red. The solvent and excess amine were removed under reduced pressure after the mixture was stirred for 1 h. Extraction of the residue with 3 × 75 mL of hexane followed by removal of the solvent in vacuo gave a mixture of $Cp(CO)_2W[\eta^2\text{-}CH(CONHCH_3)CH(CH_3)NHCH_3]$ (**3a**) and $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(CONHCH_3)]$ (**4a**). The total yield of the mixture was 0.91 g. Pure complex **3a** (0.69 g), which displayed two isomers in the ^1H NMR spectrum, was obtained from repeated recrystallization by diffusion of hexane into the CH_2Cl_2 solution of the mixture; isolated yield 68%. Spectroscopic data for **3a** are as follows. IR (cm^{-1}, CH_3CN): 1943 (m), 1916 (s), 1856 (m), 1806 (s), 1629 (s). ^1H NMR (25 °C, CD_3CN, isomer A): 5.87 (br, NH, J_{H-H} = 4.7 Hz), 5.45 (s, 5H, Cp), 4.20 (br, 1H, M–NH), 3.41 (m, 1H, J_{H-H} = 10.9, 6.3, 5.7 Hz, β-CH), 2.50 (d, 3H, J_{H-NH} = 5.9 Hz, N–CH_3), 2.30 (d, 1H, J_{H-H} = 5.7 Hz, α-CH), 1.98 (d, 3H, J_{H-H} = 4.7 Hz, N–CH_3), 0.89 (d, 3H, J_{H-H} = 6.3 Hz, β-CCH_3). ^{13}C NMR (25 °C, C_6D_6, isomer A): 257.5, 254.5 (CO), 183.3 (CONH), 94.7 (Cp), 67.4 (β-CCH_3), 43.9 (M–NCH_3), 25.1 (CONHCH_3), 22.7 (γ-CH_3), 7.9 (α-CH, J_{W-C} = 34.9 Hz). ^1H NMR (25 °C, CD_3CN, isomer B): 5.87 (br, NH, J_{NH-H} = 4.7 Hz), 5.64 (s, 5H, Cp), 4.20 (br, 1H, NH), 3.91 (m, 1H, J_{H-H} = 10.9, 6.4, 5.7 Hz, β-CH), 2.50 (d, 3H, J_{H-H} = 5.9 Hz, CH_3), 2.37 (d, 1H, J_{H-H} = 5.7 Hz, α-CH), 1.96 (d, 3H, J_{H-H} = 4.7 Hz, CH_3), 0.93 (d, 3H, J_{H-H} = 6.4 Hz, CH_3). MS (*m/z*, 20 eV): 436 (M^+), 408 (M^+ − CO), 380 (M^+ − 2CO), 365 (M^+ − CH(CONHMe)), 351 (M^+ − 2CO − NHMe). Anal. Calcd for $C_{13}H_{18}O_3N_2W$: C, 35.96; H, 4.18; N, 6.45. Found: C, 35.79; H, 4.05; N, 6.40. The minor product **4a** was obtained from the recrystallization of the crude mixture. Among the red crystals of **3a**, a small quantity of yellow crystals of **4a** was observed under a microscope. These yellow crystals were manually separated from the batch under the microscope and characterized by ^1H NMR and mass spectroscopy. The yield was estimated to be about 5%. Spectroscopic data for **4a** are as follows. ^1H NMR (CD_3CN): 5.48 (s, 5H, Cp), 4.49 (ddd, 1H, J_{H-H} = 10.3, 8.7, 7.3 Hz, central CH), 2.75 (dd, 1H, J_{H-H} = 7.3, 1.8 Hz, syn CH), 2.66 (d, 3H, J_{H-H} = 7.4 Hz, CH_3), 1.81 (dd, 1H, J_{H-H} = 8.7, 2.6 Hz, anti CH), 1.22 (ddd, 1H, J_{H-H} = 10.3, 2.6, 1.8 Hz, anti CH). MS (*m/z*, 20 eV): 405 (M^+), 377 (M^+ − CO), 349 (M^+ − 2CO). Anal. Calcd for $C_{12}H_{13}O_3NW$: C, 35.75; H, 3.25; N, 3.48. Found: C, 35.79; H, 3.40; N, 3.34.

Reaction of **2** with aniline was carried out using the same procedure as that in methylamine, except that no condensation step is necessary. The reaction gave $Cp(CO)_2W[\eta^2\text{-}CH(CONHC_6H_5)CH(CH_3)NHC_6H_5]$ (**3b**) and $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(CONHC_6H_5)]$ (**4b**) in 73% and <5% yields, respectively. Spectroscopic data for **3b** are as follows. IR (cm^{-1}, CH_3CN): 1936 (m), 1916 (s), 1853 (m), 1812, (s), 1664 (m), 1624 (w). ^1H NMR (25 °C, CD_3CN, isomer A): 8.16 (br, CONH), 7.68–7.08 (m, 10H, Ph), 6.50 (br, 1H, M–NH), 5.53 (s, 5H, Cp), 4.51 (m, 1H, J_{H-H} = 10.8, 6.3, 5.8 Hz, β-CH), 2.86 (d, 1H, J_{H-H} = 5.8 Hz, α-CH), 0.89 (d, 3H, J_{H-H} = 6.3 Hz, CH_3). ^{13}C NMR 25 °C, CD_3CN, isomer A): 185.0 (CONH), 141.8, 129.9, 128.5, (Ph), 93.9 (Cp), 64.3 (β-CCH_3), 24.1 (γ-CH_3), 11.6 (α-CH). ^1H NMR (25 °C, CD_3CN, isomer B): 7.89 (br, NH), 7.68–7.08 (m, 10H, Ph), 6.50 (br, 1H, M–NH), 5.53 (s, 5H, Cp), 4.99 (m, 1H, J_{H-H} = 11.4, 6.4, 6.2 Hz, β-CH), 2.65 (d, 1H, J_{H-H} = 6.4 Hz, α-CH), 1.04 (d, 3H, J_{H-H} = 6.2 Hz, CH_3). MS (*m/z*, 20 eV): 560 (M^+), 467 (M^+ − $C_6H_5NH_2$), 439 (M^+ − $C_6H_5NH_2$ − CO), 411 (M^+ − $C_6H_5NH_2$ − 2CO). Anal. Calcd for $C_{23}H_{22}O_3N_2W$: C, 49.48; H, 3.97; N, 5.02. Found: C, 49.79; H, 4.01; N, 5.10. Spectroscopic data for **4b** are as follows. ^1H NMR (CD_3CN): 7.68–7.08 (m, 5H, Ph), 5.54 (s, 5H, Cp), 4.59 (ddd, 1H, J_{H-H} = 10.3, 8.7, 7.3 Hz, central CH), 2.58 (dd, 1H, J_{H-H} = 7.3, 1.8 Hz, syn CH), 1.99 (d, 1H, J_{H-H} = 8.7 Hz, anti CH), 1.34 (dd, 1H, J_{H-H} = 10.3, 1.8 Hz, anti CH). MS (*m/z*, 20 eV): 467 (M^+), 439 (M^+ − CO), 411 (M^+ − 2CO).

Reaction of **2** with benzylamine was carried out using the same procedure as that in aniline. The reaction gave $Cp(CO)_2W[\eta^2\text{-}CH(CONHCH_2C_6H_5)CH(CH_3)NHCH_2C_6H_5]$ (**3c**) in 62% yield. In the NMR spectrum, only one isomer was seen and no allylic complex was observed. Spectroscopic data for **3c** are as follows. IR (cm^{-1}, THF): 1916 (s), 1911 (s), 1641 (m). ^1H NMR (25 °C, C_2D_6CO): 7.50–7.18 (m, 10H, Ph), 7.39 (br, 1H, NH), 4.87 (s, 5H, Cp), 4.71 (br, 1H, M–NH), 4.45 (dd, 1H, J_{H-H} = 14.6, 8.0 Hz, one of NCH_2), 4.42 (dd, 1H, J_{H-H} = 11.6, 10.5 Hz, one of M–NCH_2), 4.39 (d, 1H, J_{H-H} = 14.6, 14.5 Hz, one of NCH_2), 3.73 (m, 1H, J_{H-H} = 10.8, 6.3, 5.7 Hz, β-CH), 3.23 (dd, 1H, J_{H-H} = 11.6, 11.5 Hz, one of M–NCH_2), 2.48 (d, 1H, J_{H-H} = 5.7 Hz, α-CH), 1.14 (d, 3H, J_{H-H} = 6.3 Hz, CH_3). ^{13}C NMR (25 °C, C_2D_6CO): 256.9, 238.5 (CO), 184.7 (CONH), 141.5, 137.7, 130.5, 129.9, 128.5 (Ph), 95.2 (Cp), 67.9 (β-CCH_3), 58.9 (CH_2Ph), 43.0 (CH_2Ph), 23.6 (γ-CH_3), 10.7 (α-CH). MS (*m/z* 20 eV): 588 (M^+), 560 (M^+ − CO), 532 (M^+ − 2CO). Anal. Calcd for $C_{25}H_{26}O_3N_2W$: C, 51.21; H, 4.47; N, 4.78. Found: C, 51.49; H, 4.55; N, 4.60.

The reaction of **2** with isopropylamine was carried out using the same procedure mentioned above. The reaction gave $Cp(CO_2W[\eta^2CH(CONHC_3H_7)CH(CH_3)NHC_3H_7]$ (**3d**) and Cp-

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$(CO)_2W[\eta^3\text{-}CH_2CHCH(CONHC_3H_7)]$ (**4d**) in 72% and 3% yields, respectively. Spectroscopic data for **3d** are as follows: IR (cm^{-1}, CH_3CN): 2007 (m), 1907 (s), 1851 (m), 1799 (s), 1705 (s), 1629 (m). ^1H NMR (25 °C, CD_3CN): 6.00 (br, 1H, NH), 5.43 (s, 5H, Cp), 4.74 (br, 1H, M—NH), 3.98 (m, 1H, $CHMe_2$), 3.59 (m, 1H, J_{H-H} = 11.2, 6.2, 6.0 Hz, β-CH), 2.90 (m, 1H, $CHMe_2$), 2.20 (d, 1H, J_{H-H} = 6.0 Hz, CH), 1.13, 1.07, 0.95, 0.93 (12H, 4 Me groups), 0.85 (d, 1H, J_{H-H} = 6.2 Hz, CH_3). ^{13}C NMR (25 °C, CD_3CN): 257.2, 236.1 (CO), 185.0 (CONH), 96.6 (Cp), 64.7 (β-CCH_3), 51.8 (CH_2Ph), 43.0 (CH_2Ph), 23.6 (γ-CH_3), 10.7 (α-CH). MS (*m/z*, 20 eV): 492 (M^+), 464 (M^+ − CO), 436 (M^+ − 2CO). Anal. Calcd for $C_{17}H_{26}O_3N_2W$: C, 41.65; H, 5.35; N, 5.71. Found: C, 41.56; H, 5.24; N, 5.60. Spectroscopic data for **4d** are as follows. ^1H NMR (CD_3CN): 7.21 (br, 1H, NH), 5.46 (s, 5H, Cp), 4.50 (ddd, 1H, J_{H-H} = 10.1, 8.9, 7.3 Hz, central CH), 3.86 (m, 1H, $CHMe_2$), 2.76 (dd, 1H, J_{H-H} = 7.3, 1.8 Hz, syn CH), 1.81 (d, 1H, J_{H-H} = 8.9 Hz, anti CH), 1.21 (dd, 1H, J_{H-H} = 10.1, 1.8 Hz, anti CH), 1.11 (d, 6H, J_{H-H} = 6.5 Hz, CH_3).

Decomposition of Azametallacyclobutane. Complex **3b** (0.25 g, 0.448 mmol) was dissolved in 7 mL of THF, and the solution was heated at 60 °C for 35 min. After the mixture was cooled to room temperature, excess triethylphosphine (0.3 mL) was added and the solution stirred for 3.5 h. Solvent and excess phosphine were removed under vacuum, and the residue was extracted with hexane. The crude products were passed through a silica gel packed column. Hexane eluted the organic product CH_3CH=$CHC(O)NHC_6H_5$ (**7b**), and CH_2Cl_2 eluted $Cp(CO)_2(PEt_3)W(\eta^1\text{-}NHC_6H_5)$ (**9**). Spectroscopic data for **9** are as follows. IR (cm^{-1}, THF): 1942, 1920, 1850 (s). ^1H NMR (25 °C, CD_3CN): 7.78, 7.31, 7.03 (m, 5H, Ph), 5.68 (s, 5H, Cp), 5.41 (br, 1H, NH), 1.79 (m, 6H, CH_2), 1.07 (m, 9H, CH_3). ^{31}P NMR (CD_3CN): 6.46 (PEt_3, J_{W-P} = 258.3 Hz). MS (*m/z*, 20 eV): 505 (M^+), 478 (M^+ − CO), 450 (M^+ − 2CO), 427 (M^+ − Ph), 413 (M^+ − PhNH). Anal. Calcd for $C_{19}H_{26}O_2NPW$: C, 44.29; H, 5.09; N, 2.72. Found: C, 44.49; H, 5.05; N, 2.40. Spectroscopic data for **7b** are as follows. IR (cm^{-1}, CH_3CN): 3631, 3541, (m, ν(NH)), 1629 (m, ν(C=O)). ^1H NMR (25 °C, CD_3CN): 8.32 (br, NH), 7.61, 7.59, 7.09 (m, 5H, Ph), 6.90 (dd, 1H, J_{H-H} = 15.9, 6.9 Hz, =CH), 6.05 (dd, 1H, J_{H-H} = 15.9, 1.7 Hz, =CH), 1.87 (dd, 3H, J_{H-H} = 6.9, 1.7 Hz, CH_3). ^{13}C NMR (25 °C, CD_3CN): 165.9 (C=O), 142.2, 130.4, 127.1, 125.2 (Ph), 121.6 (=CH), 119.0 (=CH), 18.5 (CH_3). MS (*m/z* 20 eV): 161 (M^+), 93 (M^+ − CO), 69 (M^+ − PhNH).

The intermediate **3i**, supposedly an olefin amide complex, was detected when the decomposition was monitored by ^1H NMR. Spectroscopic data for **3i** are as follows. ^1H NMR (25 °C, CD_3CN): 8.51 (br, 1H, CONH), 7.61, 7.59, 7.09 (m, Ph), 5.96 (s, 5H, Cp), 6.57 (dd, 1H, J_{H-H} = 15.7, 6.9 Hz, =CH), 5.45 (dd, 1H, J_{H-H} = 15.7, 1.7 Hz, =CH), 1.78 (dd, 3H, J_{H-H} = 6.9, 1.7 Hz, CH_3). Complex **3i** transformed into a new complex, presumably $Cp(CO)_2WNHPh$, and the free olefin **7b**. ^1H NMR of $Cp(CO)_2WNHPh$ (25 °C, CD_3CN): 7.68−7.04 (m, Ph), 5.59 (s, 5H, Cp).

Reaction of 2 with *p*-Nitroaniline. Addition of *p*-$H_2NC_6H_4NO_2$ (1.0 mL in 5 mL of benzene) to a solution of **2** (0.32 g, 0.85 mmol in 15 mL of benzene) led to a color change from dark brown to dark red. The solvent was removed under reduced pressure after the mixture was stirred for 1 h. Extraction with 2 × 30 mL of CH_2Cl_2 followed by removal of the solvent gave a yellow oily product which contained a mixture of CH_3CH=$CHCONHC_6H_4NO_2$ (**7e**; 20% yield) and $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(CONHC_6H_4NO_2)]$ (**4e**; about 3%). ^1H NMR data for **7e**: 9.80 (br, NH), 8.17, 7.95 (m, 4H, Ph), 6.97 (dd, 1H, J_{H-H} = 15.16, 6.88 Hz, CH), 6.19 (dd, 1H, J_{H-H} = 15.16, 1.62 Hz, CH), 1.84 (dd, 3H, J_{H-H} = 6.88, 1.62 Hz, CH_3). ^1H NMR data for **4e** (CD_3CN): 8.09, 7.82, 7.65 (m, 4H, Ph), 7.21 (br, NH), 5.52 (s, 5H, Cp), 4.51 (ddd, 1H, J_{H-H} = 10.1, 8.8, 8.0 Hz, central CH), 2.76 (dd, 1H, J_{H-H} = 8.0, 1.8 Hz, CH), 2.04 (d, 1H, J_{H-H} = 8.8 Hz, CH), 1.39 (dd, 1H, J_{H-H} = 10.1, 1.8 Hz, CH).

Reaction of Allenyl Complex 2 with Alcohol. Addition of MeOH (1.5 mL in 10 mL of benzene) to a solution of **2** (0.95 g, 2.56 mmol in 40 mL of benzene) led to a color change from dark brown to light orange. The solvent was removed under reduced pressure after the mixture was stirred for 2 h. The yellow oily products were obtained by extraction of the residue with 3 × 75 mL of hexane followed by removal of the sovlent, yielding a mixture of $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(COOMe)]$ (**5a**) and $Cp(CO)_2W[\eta^2\text{-}C(CH_3)$=$CHCOOMe]$ (**6a**). The total yield of the mixture was 88% (0.91 g). Pure complex **5a** can be obtained from recrystallization by diffusion of hexane vapor into a CH_2Cl_2 solution of the mixture. The yield of **5a** thus obtained was 65% (0.67 g), and the minor product **6a** was obtained from running the reaction in CH_3CN, described below. Spectroscopic data for **5a** are as follows. IR (cm^{-1}, hexane): 1974 (s), 1906 (s), 1893 (sh), 1718 (sh), 1707 (m). ^1H NMR (25 °C, CD_3CN): 5.54 (s, 5H, Cp), 4.18 (ddd, 1H, J_{H-H} = 11.1, 8.0, 7.1 Hz, CH), 3.61 (s, 3H, Me), 3.36 (m, 1H, J_{H-H} = 7.1, 1.5, 0.8 Hz, CH), 3.26 (ddd, 1H, J_{H-H} = 8.0, 1.5, 1.1 Hz, CH), 2.76 (ddd, 1H, J_{H-H} = 11.1, 1.1, 0.8 Hz, CH). ^{13}C NMR (25 °C, CD_3CN): 228.2, 226.6, 177.1, 92.6 (s, Cp), 64.6 (CH), 50.8 (s, Me), 39.3 (CH_2), 27.2 (CH). MS (*m/z*, 20 eV): 406 (M^+), 350 (M^+ − 2CO). Anal. Calcd for $C_{12}H_{12}O_4W$: C, 35.67; H, 2.99. Found: C, 35.78; H, 3.15. Spectroscopic data for **6a** are as follows. ^1H NMR (25 °C, CD_3CN): 6.19 (q, 1H, J_{H-H} = 1.1 Hz, CH), 5.52 (s, 5H, Cp), 3.81 (s, 3H, OCH_3), 2.85 (d, 1H, J_{H-H} = 1.1 Hz, CH_3). ^{13}C NMR (25 °C, CD_3CN): 240.0 (M—C=), 115.9 (=CH), 93.7 (s, Cp), 54.0 (OCH_3), 32.1 (CH_3). MS (*m/z*, 20 eV): 406 (M^+), 378 (M^+ − CO), 375 (M^+ − OCH_3), 350 (M^+ − 2CO), 335 (M^+ − CH=CMeOMe), 322 (M^+ − 3CO). Anal. Calcd for $C_{12}H_{12}O_4W$: C, 35.67; H, 2.99. Found: C, 35.69; H, 2.87. The analogous products $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(COOEt)]$ (**5b**) and $Cp(CO)_2W[\eta^2\text{-}C(CH_3)$=$CHCOOEt]$ (**6b**), obtained from the reaction of C_2H_5OH with **2** (0.50 g, 1.35 mmol), were isolated in ca. 80% (0.45 g, mixture of **5b** and **6b**) total yield. Recrystallization gave **5b** (0.39 g). Spectroscopic data for **5b** are as follows. ^1H NMR (25 °C, CD_3CN): 5.54 (s, 5H, Cp), 4.20 (ddd, 1H, J_{H-H} = 11.1, 8.0, 7.0 Hz, CH), 3.89 (AB, 2H, J_{H-H} = 6.9 Hz, OCH_2), 3.74 (d, 1H, J_{H-H} = 7.0 Hz, CH), 3.22 (d, 1H, J_{H-H} = 8.0 Hz, CH), 2.75 (d, 1H, J_{H-H} = 11.1 Hz, CH), 1.11 (t, 3H, J_{H-H} = 6.9 Hz, CH_3). ^{13}C NMR (25 °C, CD_3CN): 176.6 (C=O), 92.6 (Cp), 64.5 (CH), 59.8 (CH_2), 38.9 (OCH_2), 37.3 (CH), 14.3 (CH_3). MS (*m/z*, 20 eV): 420 (M^+), 392 (M^+ − CO), 364 (M^+ − 2CO). Anal. Calcd for $C_{13}H_{14}O_4W$: C, 37.34; H, 3.38. Found: C, 37.49; H, 3.13. Spectroscopic data for **6b** are as follows. ^1H NMR (25 °C, CD_3CN): 6.13 (q, 1H, J_{H-H} = 1.2 Hz, CH), 5.58 (s, 5H, Cp), 4.26 (q, 2H, J_{H-H} = 7.2 Hz, OCH_2), 2.85 (d, 3H, J_{H-H} = 1.2 Hz, CH_3), 1.24 (t, 3H, J_{H-H} = 7.2 Hz, CH_3). ^{13}C NMR (25 °C, CD_3CN): 116.2 (=CH), 93.6 (s, Cp), 60.8 (OCH_2), 35.8 (CH_3), 14.7 (CH_2CH_3). MS (*m/z*, 20 eV): 420 (M^+), 382 (M^+ − CO), 375 (M^+ − OCH_2CH_3), 364 (M^+ − 2CO), 336 (M^+ − 2CO), 335 (M^+ − CH=CMeOEt). The reaction of **2** with propargyl alcohol in benzene similarly gave a mixture of $Cp(CO)_2W[\eta^3\text{-}CH_2CHCH(COOCH_2C{\equiv}CH)]$ (**5c**) and $Cp(CO)_2W[\eta^2\text{-}C(CH_3)$=$CHCOOCH_2C{\equiv}CH]$ (**6c**). Spectroscopic data for **5c** are as follows. IR (cm^{-1}, KBr): 2121 (w), 1934 (s), 1841 (s), 1703 (m), 1139 (m). ^1H NMR (25 °C, CD_3CN): 5.55 (s, 5H, Cp), 4.53 (ABX, 1H, J_{H-H} = 15.9, 2.5 Hz, OCH), 4.40 (ABX, 1H, J_{H-H} = 15.9, 2.5 Hz, OCH), 4.23 (ddd, 1H, J_{H-H} = 11.1, 7.9, 6.8 Hz, CH), 3.75 (d, 1H, J_{H-H} = 6.8 Hz, CH), 3.26 (d, 1H, J_{H-H} = 7.90 Hz, =CH), 2.75 (d, 1H, J_{H-H} = 11.0 Hz, =CH), 2.68 (t, 1H, J_{H-H} = 2.5 Hz, ≡CH). ^{13}C NMR (25 °C, CD_3CN): 228.1, 226.3 (2CO), 176.1 (C=O), 92.7 (Cp), 79.5 (≡CH), 75.7 (—C≡), 64.7 (CH), 51.5 (OCH_2), 39.5 (CH_2), 36.3 (=CH). MS (*m/z*, 70 eV): 430 (M^+), 402 (M^+ − CO), 374 (M^+ − 2CO). Anal. Calcd for $C_{14}H_{12}O_4W$: C, 39.28; H, 2.83. Found: C, 39.45; H, 2.69. Spectroscopic data for **6c** are as follows. IR (cm^{-1}, KBr): 2123 (w), 1934 (s), 1857 (s), 1530 (m), 1193 (m). ^1H NMR (25 °C, CD_3CN): 6.23 (q, 1H, J_{H-H} = 1.1 Hz, CH), 5.52 (s, 5H, Cp), 4.81 (d, 2H, J_{H-H} = 2.4 Hz, CH_2),

Table 3. Crystal and Intensity Collection Data for $Cp(CO)_2W[\eta^2\text{-}CH(CONHMe)CHMeNHMe]$ (3a) and $Cp(CO)_2W[\eta^2\text{-}C(CH_3)=CHC(O)OC_3H_3]$ (6c)

mol formula	$C_{13}H_{18}N_2O_3W$ (**3a**)	$C_{14}H_{12}O_4W$ (**6c**)
mol wt	435.15	428.09
space group	*C2/c*	$P2_1/c$
a, Å	20.551(8)	10.7202(9)
b, Å	11.100(4)	16.0349(14)
c, Å	12.784(3)	8.4403(12)
β, deg	94.60(3)	102.234(9)
V, Å^3	2907(2)	1417.9(3)
Z	8	4
cryst dimens, mm^3	0.23 × 0.21 × 0.12	0.05 × 0.22 × 0.45
radiation	Mo Kα, λ = 0.710 69 Å	
2θ range, deg	2−50	
scan type	$\theta/2\theta$	
total no. of rflns	2557	2486
no. of unique rflns, $I > 2\sigma(I)$	1889	2027
R	0.031	0.019
R_w	0.024	0.015

2.88 (d, 3H, J_{H-H} = 1.1 Hz, CH_3), 2.82 (t, 1H, J_{H-H} = 2.4 Hz, ≡CH). ^{13}C NMR (25 °C, CD_3CN): 243.3 (M−C=), 115.6, (=CH), 93.6 (s, Cp), 78.7 (≡CH), 76.8 (−C≡), 55.0 (OCH_2), 36.2 (CH_3). MS (*m/z* 20 eV): 430 (M^+), 402 (M^+ − CO), 374 (M^+ − 2CO), 347 ($M^+ - CO_2C_3H_3$).

Solvent Effects. If the reaction of **2** with MeOH was carried out in THF, using the same procedures, only complex **5a** was obtained in 92% yield. Complex **6a** can be obtained in pure form if the reaction is carried out in CH_3CN (yield 85%).

X-ray Analysis of 3a and 6c. Single crystals suitable for an X-ray diffraction study of **3a** were grown. The X-ray diffraction study was carried out at the Instrumentation Center of National Taiwan University. A suitable single crystal of dimensions 0.23 × 0.21 × 0.12 mm^3 was glued to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections (10.0° < 2θ < 25°). Cell constants and other pertinent data are collected in Table 3. Data were collected using the $\theta-2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The scan angle was determined for each reflection according to the equation 0.8 + 0.35 tan θ. Three check reflections were measured every 30 min throughout the data collection period and showed no apparent decay.

The raw intensity data were converted to structural factor amplitudes and their esd's by correction for scan speed, background, and Lorentz−polarization effects. An empirical absorption based on the azimuthal scan data was applied to the intensities. Crystallographic computations were carried out on a Microvax III computer using the NRCC structure determination package.[32] Merging of equivalent and duplicate reflections gave a total of 2557 unique measured data, for which 1889 were considered observed ($I > 2.0\sigma(I)$). The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the position of the metal, and then refined via standard least-squares and difference Fourier techniques. The quantity mimimized by the least-squares program was $w(|F_o| - |F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the netural atoms were used.[33] All other non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. Final refinement using full-matrix least squares converged smoothly to values of $R = 0.031$ and $R_w = 0.024$. Final values of all refined atomic positional parameters (with esd's) are listed in Table 4. Tables of selected least-squares planes and thermal parameters are given in the supplementary material.

The procedures for the structure determination of **6c** were similar. The final residuals of the refinement were $R = 0.019$ and $R_w = 0.015$. Final values of all refined atomic positional parameters (with esd's) are listed in Table 5. Tables of thermal parameters are given in the supplementary material.

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Table 4. Positional Parameters for the Non-Hydrogen Atoms of $Cp(CO)_2W[\eta^2\text{-}CH(CONHCH_3)CHCH_3(NHCH_3)]$ (3a)

atom	*x*	*y*	*z*	*B*,[a] Å^2
W	0.327086(17)	0.19721(3)	0.23627(3)	2.805(15)
C(1)	0.3483(5)	−0.0029(9)	0.2736(8)	6.2(7)
C(2)	0.3193(5)	0.0018(10)	0.1762(9)	7.0(7)
C(3)	0.3615(6)	0.0632(9)	0.1136(8)	6.7(6)
C(4)	0.4171(4)	0.0904(8)	0.1820(8)	5.4(6)
C(5)	0.4069(5)	0.0499(9)	0.2790(8)	5.7(6)
C(6)	0.3709(5)	0.4159(9)	0.0871(7)	4.8(5)
N(7)	0.3830(3)	0.3576(6)	0.1902(5)	3.0(3)
C(8)	0.3676(4)	0.4315(7)	0.2802(6)	3.3(4)
C(9)	0.4145(5)	0.5368(8)	0.3047(7)	4.3(5)
C(10)	0.3625(4)	0.3327(8)	0.3618(6)	3.4(4)
C(11)	0.4245(4)	0.2927(8)	0.4176(6)	3.2(4)
O(11)	0.4776(3)	0.2956(6)	0.3781(4)	3.9(3)
N(12)	0.4218(4)	0.2486(7)	0.5149(6)	3.8(3)
C(13)	0.4768(5)	0.1984(10)	0.5749(7)	5.2(5)
C(14)	0.2544(4)	0.2507(8)	0.1514(6)	3.6(4)
O(14)	0.2058(3)	0.2772(6)	0.0961(5)	5.9(4)
C(15)	0.2544(4)	0.1981(9)	0.3275(6)	4.1(5)
O(15)	0.2115(3)	0.1988(7)	0.3793(5)	6.3(4)

[a] *B* is the mean of the principal axes of the thermal ellipsoid.

Table 5. Positional Parameters for the Non-Hydrogen Atoms of $Cp(CO)_2W[\eta^2\text{-}C(CH_3)-CHC(O)OC_3H_3]$ (6c)

atom	*x*	*y*	*z*	*B*,[a] Å^2
W	0.237697(18)	0.063446(11)	0.214077(21)	2.788(8)
C(1)	0.2380(4)	0.04621(24)	−0.0181(5)	3.26(21)
C(2)	0.4162(4)	0.0666(3)	0.2086(5)	4.5(3)
C(3)	0.4107(5)	0.1824(4)	0.4908(7)	6.8(3)
C(4)	0.3001(4)	0.1757(3)	0.3477(5)	4.10(23)
C(5)	0.2264(5)	0.2438(3)	0.3031(6)	4.3(3)
C(6)	0.1210(5)	0.23008(25)	0.1778(5)	3.65(23)
C(7)	−0.0700(5)	0.2742(3)	0.0022(6)	4.9(3)
C(8)	−0.1677(5)	0.2258(3)	0.0562(6)	4.7(3)
C(9)	−0.2461(5)	0.1881(4)	0.0994(7)	6.4(3)
C(10)	0.1070(5)	−0.0532(3)	0.2160(5)	4.35(25)
C(11)	0.0662(5)	0.0051(3)	0.3147(6)	4.6(3)
C(12)	0.1676(5)	0.0228(3)	0.4479(5)	4.8(3)
C(13)	0.2722(5)	−0.0261(3)	0.4293(6)	5.0(3)
C(14)	0.2352(5)	−0.0733(3)	0.2835(6)	5.0(3)
O(1)	0.2420(3)	0.03333(19)	−0.1513(3)	5.13(18)
O(2)	0.5246(3)	0.0686(3)	0.2052(4)	7.30(24)
O(3)	0.1023(3)	0.15902(15)	0.1112(3)	3.14(13)
O(4)	0.0389(3)	0.29201(17)	0.1290(4)	4.49(17)

[a] *B* is the mean of the principal axes of the thermal ellipsoid.

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Supplementary Material Available: Details of the structural determination for complexes **3a** and **6c**, including tables of fractional coordinates, anisotropic thermal parameters, and all bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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