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Synthesis and Reactions of Tungsten Carbonyl Complexes Containing β-(Chlorocarbonyl)allylic Ligands

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Reactions of tungsten propargyl complex $Cp(CO)_3WCH_2C{\equiv}CH$, **1a**, with amines yielded the (β-amido)allyl complexes $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHR)CH_2)$ (R = Ph, **4a**; R = $(CH_2)_2NH_2$, **4b**). In **4a** and **4b**, the amido groups are bound to the β-carbon of the allylic group. Analogous C–C bond formation occurred when the reaction of complex **1a** with $AlCl_3$ was carried out in the presence of carboxylic acid, affording $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$, **3a**. The Mo analogue $Cp(CO)_2Mo(\eta^3\text{-}CH_2C(COCl)CH_2)$, **3b**, was prepared similarly. Complex **3a** reacted with amines and NaOH, giving **4** and $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, **5**, respectively. In addition, reactions of **3a** with $Cp(CO)_2LW^-$ (L = CO, $P(OMe)_3$) anions yielded the dinuclear complexes $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_2LCp$ (L = CO, **6a**; L = $P(OMe)_3$, **6b**), in which two metal atoms were bridged by a four-carbon $\eta^3{:}\eta^1$ ligand. Complexes **1a**, **1b**, **3a**, **3b**, **4a**, **4b**, **5**, **6a**, **6b**, and **6c** were identified by spectroscopic methods. In addition, the structures of **4a**, **5**, and **6a** were confirmed by single-crystal X-ray diffraction analysis. Crystal data for **4a**: space group $P2_1/c$; $a = 8.696$ (1), $b = 20.691$ (4), $c = 9.114$ (2) Å; $\beta = 108.81$ (2)°; $V = 1552.3$ (5) Å^3; $Z = 4$; $R = 0.030$, $R_w = 0.028$, based on 1920 reflections with $I > 2\sigma(I)$. Crystal data for **5**: space group $P2_1/c$; $a = 10.619$ (4), $b = 7.711$ (1), $c = 13.824$ (2) Å; $\beta = 93.30$ (2)°; $V = 1130.1$ (5) Å^3; $Z = 4$; $R = 0.025$, $R_w = 0.020$, based on 1577 reflections with $I > 2\sigma(I)$. Crystal data for **6a**: space group $Pca2_1$; $a = 16.356$ (3), $b = 7.995$ (2), $c = 14.279$ (2) Å; $V = 1867.1$ (6) Å^3; $Z = 4$; $R = 0.028$, $R_w = 0.023$, based on 1201 reflections with $I > 2\sigma(I)$.

Introduction

The rich chemistry of organometallic complexes containing unsaturated organic ligands has long been a subject of considerable interest.[1] Recently, a review on synthesis and chemical reactivities of metal propargyl complexes has appeared in the literature.[2] In particular, the direct use of the triple bond of propargyl ligands to build heteronuclear complexes with other metal carbonyl complexes was stressed. Similarly, the C≡C triple bonds of metal σ-acetylides[3] have also been employed for the construction of dinuclear complexes. In such dinuclear complexes the acetylide ligand is bound to one metal center in an η^1 fashion and to the other metal center in an η^2 fashion. In both cases, the structural contribution of the allenyl and vinylidene features of the ligand with the triple bond have been stressed.

Roustan and his co-workers have reported alkoxycarbonylation at the β-carbon of the propargyl groups in several W and Mo complexes.[4] In a limited class of transition-metal π-allyl complexes nucleophilic addition was found to occur at the central carbon of the π allylic ligand, leading to the formation of metallacyclobutane complexes.[5] In contrast, in a Pd–allyl system, carbonylation generally takes place regiospecifically at the α-carbon.[6,7] We have reported the transformation of a simple propargyl ligand to an allenyl ligand in a mononuclear tungsten complex.[8] The coexistence of a tungsten propargyl complex and its allenyl analogue enables us to compare the different chemical reactivities of C_3 units bound to metal in different modes. We feel this body of work has revealed a new class of chemical reactions of transition-metal propargyl/allenyl complexes and hope to employ these complexes in order to further study their chemical reactivities. To this end, we investigated the reactions of $AlCl_3$ and several nucleophiles with the tungsten propargyl complexes. In this paper, we report the transformation of an η^1-propargyl ligand to an η^3-allylic ligand with concomitant regiospecific C–C bond formation at the β-carbon center. Even an active chlorocarbonyl group can be introduced to the β-carbon of the C_3 unit by

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using such a synthetic strategy. With such a β-(chlorocarbonyl)allylic ligand, dinuclear complexes bridged by a C_4 unit were prepared. The structural feature on the conjugation of the allylic ligand with the carbonyl group was also studied by X-ray diffraction analysis.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-300WB 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 polystyrene standard. Electron impact mass spectra were determined with a Finnigan TSQ-46C spectrometer. Diethyl ether was distilled from CaH_2 and stored over molecular sieves prior to use. Benzene and CH_2Cl_2 were distilled from LAH and CaH_2, respectively. THF was distilled from sodium–benzophenone. All other solvents and chemicals were reagent grade and used without further purification. $W(CO)_6$ and $Mo(CO)_6$ were purchased from Strem Chemical. Propargyl bromide, aniline, and ethylenediamine were purchased from Merck and were distilled in small quantities before use. Complexes $[CpW(CO)_3]_2$[9] and $[CpW(CO)_2P(OMe)_3]_2Hg$[10] were prepared according to the literature methods. The tungsten anions $CpW(CO)_2L^-$ (L = CO, $P(OMe)_3$) were prepared from the Na/Hg reduction of $[CpW(CO)_3]_2$ and $[CpW(CO)_2(P(OMe)_3)]_2Hg$. $Cp(CO)_3WCH_2C{\equiv}CH$, **1a**, and $Cp(CO)_3MoCH_2C{\equiv}CH$, **1b**, were prepared according to the literature methods.[11] The X-ray diffraction study was carried out at the Instrumentation Center of the National Taiwan University.

Synthesis of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHPh)CH_2)$, 4a. A solution containing the tungsten propargyl complex $Cp(CO)_3WCH_2C{\equiv}CH$ in THF (45 mL) was obtained from the reaction of $Cp(CO)_3WNa$ (260 mg, 0.73 mmol) with propargyl bromide (0.10 mL, 0.84 mmol) at 0 °C. The solution, without purification workup, was treated with aniline (0.10 mL, 1.07 mmol) in THF and stirred at 0 °C for 1 h. The solution changed from a clear, pale yellow to an orange-yellow immediately accompanied by the formation of white precipitate, whereby the solution turned into a yellow colloidal state. The precipitate was NaBr. The solvent was then removed under vacuum at 0 °C and the crude product was extracted by a mixture of benzene/hexane (2:1 v/v). Residue obtained by the removal of the solvent was dissolved by hexane again to give a light greenish yellow solution. The solution was filtered again and dried under vacuum to give $Cp(CO)_2W(\eta^3\text{-}CH_2(CONHPh)CH_2)$, **4a** (272 mg, 80% based on W). Single crystals suitable for X-ray diffraction were grown by sublimation of **4a** under 4×10^{-5} Torr of vacuum at 75 °C. Spectroscopic data for **4a**: IR (THF) 1962, 1942, 1892 and 1864, 1699 cm^{-1}; ^1H NMR (C_6D_6) 8.71 (b, amide-NH), 7.63, 7.27, 7.02 (m, Ph), 5.51 (s, Cp), 3.34 (b, 2H, syn-CH), 1.75 (b, 2H, anti-CH); ^{13}C NMR (C_6D_6) 206.2 (2 terminal CO), 168.5 (amide CON), 89.5 (Cp), 129.1, 121.3, 121.2 (Ph), 24.7 (allyl-terminal C); mass spectrum *m/z* 467 (M^+), 439 ($M^+ - CO$), 411 ($M^+ - 2CO$). Anal. Calcd for $C_{17}H_{15}O_3NW$: C, 43.89; H, 3.25. Found: C, 43.78; H, 3.50.

Synthesis of $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$, 3a. A solution of $AlCl_3$ (0.58 g, 4.34 mmol)/fumaric acid (0.50 g, 4.34 mmol) in THF (35 mL) was added slowly at 0 °C to a solution of **1a** (1.62 g, 4.34 mmol) in 45 mL of THF. The solution was allowed to warm to room temperature and then was stirred for 1.5 h. The solvent was removed under vacuum and the residue extracted by 5 × 150 mL of hexane, and the solution was subsequently filtered. Removal of the solvent at 0 °C gave **3a** (1.56 g, 3.81 mmol) as a yellow powder in 88% yield. Spectroscopic data for **3a**: IR (C_6H_{14}) 1997 s, 1939 s, 1981 s, 1903 s (ν_{CO}, exo/endo = 10:1 forms), 1741 m, 1727 sh (ν_{COCL}) cm^{-1}; ^1H NMR (C_2D_6CO) 5.61 (s, Cp), 2.94 (s, br, allyl-syn CH), 1.82 (s, br, allyl-anti CH); ^{13}C NMR (C_6D_6) 219.4 (2 t-CO), 168.7 (COCl), 87.8 (Cp), 27.2 (2 allyl-t C); mass spectrum *m/z* 410 (M^+), 354 ($M^+ - 2CO$), 347 (M^+ - CO, Cl), 342 (M^+ - CO, C_3H_4). Anal. Calcd for $C_{11}H_9O_3ClW$: C, 32.44; H, 2.22. Found: C, 32.66; H, 2.11.

Synthesis of $Cp(CO)_2Mo(\eta^3\text{-}CH_2C(COCl)CH_2)$, 3b. A solution of $AlCl_3$ (0.27 g, 2.04 mmol)/fumaric acid (0.24 g, 2.04 mmol) in THF (15 mL) was added slowly at 0 °C to a solution of **1b** (0.58 g, 2.04 mmol) in 30 mL of THF. The solution was allowed to warm to room temperature and was then stirred for 1.5 h. The solvent was removed under vacuum, the product in the residue was extracted by 5 × 80 mL of hexane, and the solution was filtered. Removal of the solvent gives **3b** (0.55 g, 1.72 mmol) as a yellow powder in 84% yield. Spectroscopic data for **3b**: IR (C_6H_{14}) 2002 s, 1947 s, 1977 s, 1911 s (ν_{CO}, exo/endo = 5:4 forms), 1743 m, 1733 sh (ν_{COCl}) cm^{-1}; ^1H NMR (C_2D_6CO) 5.52 (s, Cp), 3.09 (s, allyl-syn CH), 2.00 (s, br, allyl-anti CH); ^{13}C NMR (C_2D_6CO) 233.1 (2 t-CO), 158.8 (COCl), 91.4 (Cp), 37.4 (2 allyl-t C); mass spectrum *m/z* 324 (m^+), 289 ($M^+ - Cl$); 268 ($M^+ - 2CO$). Anal. Calcd for $C_{11}H_9O_3ClMo$: C, 41.21; H, 2.83. Found: C, 41.35; H, 3.01.

Reaction of 3a with $NH_2CH_2CH_2NH_2$. A solution of **3a** (0.16 g, 0.38 mmol) in THF (5 mL) was added slowly at 0 °C to a solution of ethylenediamine (0.70 mL) in 5 mL of THF. The solution was allowed to warm to room temperature and was then stirred for 0.5 h. The solvent was removed under vacuum and the residue dissolved in a mixture of benzene (25 mL) and H_2O (15 mL), and the solution was filtered. The organic layer was separated and dried by $MgSO_4$. Removal of benzene followed by washing with 3 × 10 mL portions of cooled *n*-pentane gave $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHCH_2CH_2NH_2)CH_2)$, **4b** (0.15 g), as an orange microcrystalline solid in 90% yield. Spectroscopic data for **4b**: IR (CH_3Cl) 1966 s, 1890 s (ν_{CO}), 1637 (ν_{CONHR}) cm^{-1}; ^1H NMR (D_2O 5.29 (s, Cp), 3.25 (t, 2H, CH_2, J_{H-H} 6.7 Hz), 2.86 (s, br, allyl-syn CH), 2.77 (t, 2H, CH_2, J_{H-H} 6.7 Hz), 1.47 (s, br, allyl-anti CH); ^{13}C NMR (DMSO-d_6) 226.3 (2 t-CO), 166.8 (CONH), 89.0 (Cp), 42.41, 41.66 (2 CH_2), 24.5 (2 allylic CH_2); mass spectrum *m/z* 434 (M^+), 418 ($M^+ - NH_2$), 406 ($M^+ - CO$), 378 ($M^+ - 2CO$), 319 ($M^+ - CONHC_2H_4NH_2$). Anal. Calcd for $C_{13}H_{16}O_3N_2W$: C, 36.26; H, 4.30. Found: C, 36.66; H, 4.11.

Reaction of 3a with NaOH. A solution of **3a** (0.28 g, 0.68 mmol) in benzene (55 mL) was added slowly at room temperature to an aqueous solution of NaOH (0.05 M, 15 mL). The solution was stirred for 2.5 h and then was neutralized by 1 mL of HCl solution (0.1 M). The organic layer was separated from the aqueous layer and dried by $MgSO_4$ (2.2 g). Then the solvent was removed under vacuum to give the crude product $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, **5** (0.25 g), in 95% yield. Pure complex **5** as a yellow microcrystalline solid was isolated by slow evaporation of a 5:1 $CHCl_3$/hexane solution of **5** and obtained in 45% yield. Complex **5** can also be obtained from the reaction of **1a** with H_2O, but the yield is lower and difficult to purify. Spectroscopic data for **5**: IR (CH_3Cl) 1979 s, 1956 sh, 1909 s, 1874 sh (ν_{CO}), 1601 s (ν_{COOH}) cm^{-1}; ^1H NMR (CD_3CN) 5.40 (s, Cp), 3.00 (s, br, allyl-syn CH), 1.65 (s, br, allyl-anti CH); ^{13}C NMR (C_2H_6CO) 224.2 (2 t-CO), 171.5 (COOH), 89.2 (Cp), 26.1 (2 allylic CH_2); mass spectrum *m/z* 392 (m^+), 375 ($M^+ - OH$), 347 (M^+ - CO, OH), 319 (M^+ - 2CO, OH), 305 (M^+ - COOH, C_3H_4). Anal. Calcd for $C_{11}H_6O_4W$: C, 34.23; H, 1.57. Found: C, 34.57; H, 1.90.

Reaction of 3a with $Cp(CO)_3W^-$. Freshly prepared complex **3a** (0.42 g, 1.02 mmol) in THF was treated with $Cp(CO)_3W^-$ (0.40 g, 1.12 mmol) in THF at 0 °C for 2 h, yielding an orange-yellow solution. The solvent was then removed under vacuum and the crude residue was extracted by 2 × 60 mL of benzene. Removal of the benzene gave $Cp(CO)_2W(\mu\text{-}\eta^3{:}\eta^1\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, **6a** (0.51 g, 71% yield). Recrystallization by diffusing hexane vapor into the CH_2Cl_2 solution of the crude product gave a

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Table I. Crystal and Intensity Collection Data for $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHC_6H_5)CH_2)$, 4a, $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, 5, and $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, 6a

mol formula	$C_{17}H_{15}NO_3W$, **4a**	$C_{11}H_{10}O_4W$, **5**	$C_{19}H_{14}O_6W_2$, **6a**
mol wt	465.16	391.05	706.01
space group	$P2_1/c$	$P2_1/c$	$Pca2_1$
a, Å	8.696 (1)	10.619 (4)	16.356 (3)
b, Å	20.691 (4)	7.711 (1)	7.995 (2)
c, Å	9.114 (2)	13.824 (2)	14.279 (2)
β, deg	108.81 (2)	93.30 (2)	90.00
V, Å^3	1552.3 (5)	1130.1 (5)	1867.1 (6)
Z	4	4	4
cryst dimens, mm	0.2 × 0.2 × 0.4	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.2
radiation		Mo Kα, λ = 0.710 69 Å	
2θ range, deg	2–50	2–50	2–45
scan type		$2\theta/\omega$	
total no. of rflns	2728	1983	1281
no. of unique rflns, $I > 2\sigma(I)$	1920	1577	1201
R	0.030	0.025	0.028
R_w	0.028	0.020	0.023

Table II. Fractional Coordinates and Isotropic Temperature Factors of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHC_6H_5)CH_2)$, 4a

	x	y	z	B_{eq},[a] Å^2
W	0.47714 (6)	0.129100 (18)	0.16313 (5)	2.800 (19)
C1	0.3731 (16)	0.0785 (5)	0.3410 (12)	5.0 (6)
C2	0.2507 (15)	0.1154 (5)	0.2419 (13)	5.0 (7)
C3	0.2212 (16)	0.0870 (6)	0.0962 (13)	5.9 (7)
C4	0.3181 (18)	0.0379 (5)	0.1034 (13)	5.5 (7)
C5	0.4164 (16)	0.0293 (5)	0.2570 (13)	5.3 (8)
C6	0.7456 (14)	0.0990 (4)	0.2519 (12)	4.0 (6)
C7	0.7312 (13)	0.1656 (4)	0.2737 (10)	3.0 (5)
C8	0.6406 (15)	0.1867 (5)	0.3660 (11)	4.1 (6)
C9	0.8131 (13)	0.2115 (4)	0.1960 (10)	3.0 (5)
O9	0.8523 (9)	0.1957 (3)	0.0831 (7)	3.4 (4)
N10	0.8473 (11)	0.2706 (4)	0.2650 (8)	3.1 (4)
C11	0.9269 (12)	0.3237 (4)	0.2217 (10)	2.8 (5)
C12	0.8762 (13)	0.3852 (5)	0.2429 (11)	3.4 (5)
C13	0.9499 (15)	0.4387 (4)	0.2055 (11)	4.1 (6)
C14	1.0710 (15)	0.4296 (5)	0.1413 (12)	4.5 (6)
C15	1.1213 (13)	0.3696 (5)	0.1181 (11)	4.1 (6)
C16	1.0511 (13)	0.3138 (5)	0.1586 (11)	3.6 (5)
C17	0.5149 (13)	0.1296 (5)	−0.0401 (11)	3.9 (6)
O17	0.5247 (11)	0.1280 (4)	−0.1626 (8)	5.3 (4)
C18	0.4149 (14)	0.2156 (5)	0.0876 (12)	4.1 (6)
O18	0.3694 (12)	0.2667 (3)	0.0341 (10)	6.6 (6)

[a] $B_{eq} = (8\pi^2/3)\sum(U_{ij})(a_i)(a_j)(a_i^*)(a_j^*)$.

crystalline complex. Spectroscopic data for **6a**: IR (CH_3Cl_2) 2018 s, 1960 s, 1930, 1919 s, 1882 sh, 1861 m (ν_{CO}) cm^{-1}; ^1H NMR (C_2D_6CO, 240 K) isomer A 5.80 (s, Cp), 5.43 (s, Cp), 2.55 (s, br, 2H, syn-CH_2), 1.70 (s, br, 2H, anti-Ch_2); isomer B 5.84 (s, Cp), 5.42 (s, Cp), 2.77 (s, br, 2H, syn-CH_2), 1.05 (s, br, 2H, anti-CH_2); A:B = 5:2; ^{13}C NMR (C_6D_6) 220.4, 215.4, 204.6 (5 t-CO), 163.0 (COW) 95.6 (Cp), 90.0 (br, Cp), 126.2 (allyl-center C), 33.9 (2 allylic CH_2); mass spectrum $m/4z$ 710 (M^+), 682 ($M^+ - CO$), 654 ($M^+ - 2CO$), 626 ($m^+ - 3CO$), 598 ($M^+ - 4CO$), 570 ($M^+ - 5CO$). Anal. Calcd for $C_{19}H_{14}O_6W_2$: C, 32.32; H, 2.00. Found: C, 32.45; H, 2.27.

Reaction of 3b with $Cp(CO)_3W^-$. Freshly prepared complex **3b** (0.51 g, 1.60 mmol) in THF was treated with $Cp(CO)_3W^-$ (0.63 g, 1.76 mmol) in THF at 0 °C for 2 h, yielding a golden yellow solution. Then the solvent was removed under vacuum and the crude residue was extracted by 2 × 60 mL benzene. Removal of the solvent gave $Cp(CO)_2Mo(\mu\text{-}\eta^3\text{:}\eta^1\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, **6c** (0.70 g, 70% yield). Recrystallization using diffusion of hexane vapor into the CH_2Cl_2 solution of the crude products gave a crystalline complex contaminated with unidentified product. Spectroscopic data for **6c**: IR (CH_3Cl_2) 2014 s, 1967 sh, 1950 s, 1924 s, 1918 sh, 1877 m, 1601 m (ν_{CO}) cm^{-1}; ^1H NMR ($CDCl_3$, 233 K) isomer A 5.67 (s, Cp), 5.16 (s, Cp), 2.89 (s, br, 2H, syn-CH_2), 1.02 (s, br, 2H, anti-CH_2); isomer B 5.58 (s, Cp), 5.16 (s, Cp), 2.66 (s, br 2H, syn-CH_2), 1.76 (s, br, 2H anti-CH_2); A:B = 4:3; mass spectrum m/z 596 ($M^+ - CO$), 568 ($m^+ - 2CO$), 540 ($m^+ - 3CO$), 512 ($M^+ - 4CO$), 484 ($M^+ - 5CO$), 556 ($M^+ - 6CO$). Anal. Calcd for $C_{19}H_{14}O_6WMo$: C, 36.92; H, 2.28. Found: C, 36.80; H, 2.27.

Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHC_6H_5)CH_2)$, 4a

W–C(1)	2.343 (10)	C(6)–C(7)	1.403 (13)
W–C(2)	2.321 (12)	C(7)–C(8)	1.395 (15)
W–C(3)	2.283 (13)	C(7)–C(9)	1.495 (13)
W–C(4)	2.299 (11)	C(9)–O(9)	1.228 (11)
W–C(5)	2.359 (10)	C(9)–N(10)	1.364 (12)
W–C(6)	2.296 (12)	N(10)–C(11)	1.421 (12)
W–C(7)	2.243 (10)	C(11)–C(12)	1.380 (13)
W–C(8)	2.272 (10)	C(11)–C(16)	1.392 (14)
W–C(17)	1.982 (9)	C(12)–C(13)	1.375 (14)
W–C(18)	1.932 (10)	C(13)–C(14)	1.373 (17)
C(1)–C(2)	1.382 (17)	C(14)–C(15)	1.355 (15)
C(1)–C(5)	1.397 (17)	C(15)–C(16)	1.409 (14)
C(2)–C(3)	1.398 (16)	C(17)–O(17)	1.147 (11)
C(3)–C(4)	1.309 (19)	C(18)–O(18)	1.178 (12)
C(4)–C(5)	1.397 (17)		
C(6)–W–C(7)	36.0 (3)	W–C(7)–C(8)	73.1 (6)
C(6)–W–C(8)	63.7 (4)	W–C(7)–C(9)	123.5 (6)
C(6)–W–C(17)	82.8 (4)	C(6)–C(7)–C(8)	119.1 (9)
C(6)–W–C(18)	120.9 (4)	C(6)–C(7)–C(9)	118.6 (9)
C(7)–W–C(8)	36.0 (4)	C(8)–C(7)–C(9)	122.3 (8)
C(7)–W–C(17)	89.0 (4)	W–C(8)–C(7)	70.9 (6)
C(7)–W–C(18)	88.3 (4)	C(7)–C(9)–O(9)	122.2 (8)
C(8)–W–C(17)	120.6 (4)	C(7)–C(9)–N(10)	114.7 (8)
C(8)–W–C(18)	80.4 (4)	O(9)–C(9)–N(10)	123.1 (9)
C(17)–W–C(18)	76.9 (4)	C(9)–N(10)–C(11)	128.2 (7)
C(2)–C(1)–C(5)	109.3 (10)	N(10)–C(11)–C(12)	117.9 (9)
W–C(2)–C(1)	73.6 (7)	N(10)–C(11)–C(16)	120.9 (8)
W–C(2)–C(3)	70.8 (7)	C(12)–C(11)–C(16)	121.2 (9)
C(1)–C(2)–C(3)	104.9 (10)	C(11)–C(12)–C(13)	120.8 (9)
C(2)–C(3)–C(4)	111.1 (11)	C(12)–C(13)–C(14)	118.5 (9)
C(3)–C(4)–C(5)	109.0 (10)	C(13)–C(14)–C(15)	121.5 (9)
C(1)–C(5)–C(4)	105.7 (10)	C(14)–C(15)–C(16)	121.3 (9)
W–C(6)–C(7)	69.9 (6)	C(11)–C(16)–C(15)	116.6 (9)
W–C(7)–C(6)	74.1 (6)	W–C(17)–O(17)	174.6 (10)
		W–C(18)–O(18)	175.9 (10)

Table IV. Fractional Coordinates and Isotropic Temperature Factors of $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, 5

	x	y	z	B_{eq},[a] Å^2
W	0.22600 (3)	0.05196 (4)	0.145294 (22)	2.281 (11)
C1	0.0495 (9)	−0.0324 (12)	0.2247 (7)	6.7 (6)
C2	0.1484 (11)	−0.0611 (14)	0.2892 (6)	7.9 (6)
C3	0.2224 (9)	−0.1870 (14)	0.2493 (8)	7.2 (6)
C4	0.1644 (9)	−0.2348 (10)	0.1604 (7)	6.1 (5)
C5	0.0575 (8)	−0.1355 (12)	0.1463 (7)	5.4 (5)
C6	0.1419 (8)	0.2613 (10)	0.0879 (6)	3.9 (4)
O6	0.0917 (6)	0.3772 (7)	0.0530 (5)	6.5 (4)
C7	0.2536 (7)	0.0207 (10)	0.0083 (5)	3.2 (4)
O7	0.2614 (6)	−0.0016 (8)	−0.0740 (4)	5.4 (4)
C8	0.4425 (7)	0.0334 (11)	0.1613 (6)	4.1 (4)
C9	0.4053 (7)	0.2111 (9)	0.1639 (5)	2.8 (3)
C10	0.3274 (8)	0.2558 (10)	0.2405 (5)	3.7 (4)
C11	0.4372 (7)	0.3339 (9)	0.0884 (5)	3.1 (3)
O12	0.4039 (5)	0.4892 (6)	0.0933 (4)	4.5 (3)
O13	0.5008 (6)	0.2813 (7)	0.0204 (4)	4.7 (3)

[a] $B_{eq} = (8\pi^2/3)\sum(U_{ij})(a_i)(a_j)(a_i^*)(a_j^*)$.

Reaction of 3a with $Cp(CO)_2[P(OMe)_3]W^-$. Freshly prepared complex **3a** (0.16 g, 0.38 mmol) in CH_3CN was treated with $Cp(CO)_2[P(OMe)_3]W^-$ (0.18 g, 0.40 mmol) at 0 °C for 2 h, yielding an orange-yellow solution. The solvent was removed under vacuum, and the crude product was extracted by benzene. Recrystallization using diffusion of hexane vapor into the CH_2Cl_2 solution of the crude products gave crystalline complex $Cp(CO)_2W(\mu\text{-}\eta^3\text{:}\eta^1\text{-}CH_2C(CO)CH_2)W(CO)_2[P(OMe)_3]Cp$, **6b** (0.19 g, 63% yield). Spectroscopic data for **6b**: IR (CH_3CN) 1978 s, 1943 vs, 1909 s, 1861 s (ν_{CO}), 1629 (ν_{COW}) cm^{-1}; ^1H NMR (CD_3CN, 256 K) 5.43 (s, Cp), 5.40 (s, Cp), 3.46 (d, 9H, $P(OMe)_3$, $J_{H\text{-}p}$ 12.1 Hz), 2.99 (s, br, 2H, allyl-syn CH_2), 1.68 (s, br, 2H, allyl-anti CH_2); ^{13}C NMR (CD_3CN, 256 K) 223.1 (2 t-CO), 167.1 (COW), 89.3 (Cp), 88.8 (Cp), 77.9 (allyl-center C), 52.8 (d, $P(OMe)_3$, $J_{C\text{-}P}$ 3.8 Hz), 25.6 (2 allylic CH_2); ^{31}P NMR (CD_3CN, 256 K) 161.1

Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) of $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, 5

W–C(1)	2.319 (8)	C(1)–C(5)	1.351 (13)
W–C(2)	2.364 (9)	C(2)–C(3)	1.384 (17)
W–C(3)	2.339 (9)	C(3)–C(4)	1.392 (15)
W–C(4)	2.319 (8)	C(4)–C(5)	1.374 (13)
W–C(5)	2.301 (8)	C(6)–O(6)	1.134 (9)
W–C(6)	1.987 (8)	C(7)–O(7)	1.158 (9)
W–C(7)	1.948 (8)	C(8)–C(9)	1.427 (11)
W–C(8)	2.302 (7)	C(9)–C(10)	1.423 (11)
W–C(9)	2.268 (7)	C(9)–C(11)	1.463 (10)
W–C(10)	2.281 (7)	C(11)–O(12)	1.252 (9)
C(1)–C(2)	1.355 (15)	C(11)–O(13)	1.257 (9)
C(6)–W–C(7)	78.6 (3)	W–C(6)–O(6)	177.7 (7)
C(6)–W–C(8)	120.8 (3)	W–C(7)–O(7)	175.2 (6)
C(6)–W–C(9)	87.7 (3)	W–C(9)–C(8)	73.1 (4)
C(6)–W–C(10)	81.8 (3)	W–C(9)–C(10)	72.3 (4)
C(7)–W–C(8)	83.1 (3)	W–C(9)–C(11)	119.8 (5)
C(7)–W–C(9)	90.3 (3)	C(8)–C(9)–C(10)	115.2 (7)
C(7)–W–C(10)	123.6 (3)	C(8)–C(9)–C(11)	121.8 (7)
C(2)–C(1)–C(5)	110.5 (9)	C(10)–C(9)–C(11)	122.8 (7)
C(1)–C(2)–C(3)	106.8 (8)	W–C(10)–C(9)	71.3 (4)
C(2)–C(3)–C(4)	107.8 (8)	C(9)–C(11)–O(12)	120.2 (7)
C(3)–C(4)–C(5)	107.3 (8)	C(9)–C(11)–O(13)	118.8 (7)
C(1)–C(5)–C(4)	107.6 (8)	O(12)–C(11)–O(13)	121.0 (7)

Table VI. Fractional Coordinates and Isotropic Temperature Factors of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, 6a

	x	y	z	B_{eq},[a] $Å^2$
W1	–0.29386 (4)	–0.43728 (8)	–0.64550	2.48 (3)
W2	–0.48130 (4)	–0.09177 (8)	–0.42832 (7)	2.93 (3)
C1	–0.1715 (10)	–0.4770 (23)	–0.5685 (12)	4.6 (10)
C2	–0.1522 (8)	–0.4355 (18)	–0.6579 (14)	3.7 (9)
C3	–0.1796 (10)	–0.5612 (21)	–0.7185 (12)	3.8 (9)
C4	–0.2172 (9)	–0.6867 (18)	–0.6613 (18)	6.1 (13)
C5	–0.2114 (11)	–0.6313 (2)	–0.5646 (13)	4.5 (10)
C6	–0.3339 (11)	–0.371 (3)	–0.7739 (13)	5.0 (11)
O6	–0.3537 (8)	–0.3345 (17)	–0.8445 (8)	6.4 (8)
C7	–0.4011 (9)	–0.546 (3)	–0.6511 (13)	5.1 (11)
O7	–0.4600 (6)	–0.6278 (16)	–0.6590 (10)	6.0 (7)
C8	–0.3045 (10)	–0.1903 (16)	–0.6387 (16)	3.8 (9)
O8	–0.3050 (8)	–0.0476 (13)	–0.6456 (12)	6.8 (8)
C9	–0.3566 (10)	–0.3811 (20)	–0.5082 (11)	3.1 (8)
O9	–0.3214 (6)	–0.4190 (14)	–0.4371 (8)	4.1 (6)
C11	–0.3427 (13)	–0.0150 (24)	–0.4206 (13)	6.5 (11)
C12	–0.3892 (13)	0.129 (3)	–0.4388 (17)	8.5 (14)
C13	–0.4420 (12)	0.1555 (22)	–0.3585 (20)	9.4 (16)
C14	–0.4210 (13)	0.036 (3)	–0.2951 (16)	9.9 (16)
C15	–0.3666 (13)	–0.062 (3)	–0.3291 (14)	7.3 (14)
C16	–0.5790 (14)	–0.1428 (22)	–0.3678 (16)	6.9 (13)
O16	–0.6439 (8)	–0.1737 (20)	–0.3239 (10)	8.7 (10)
C17	–0.5584 (11)	0.0047 (23)	–0.5090 (12)	4.5 (10)
O17	–0.6092 (10)	0.0699 (19)	–0.5612 (10)	8.5 (9)
C18	–0.4936 (10)	–0.3802 (18)	–0.4242 (15)	4.3 (10)
C19	–0.4443 (9)	–0.3284 (20)	–0.4985 (10)	2.5 (7)
C20	–0.4897 (10)	–0.2389 (22)	–0.5690 (11)	3.7 (9)

[a] $B_{eq} = (8\pi^2/3)\sum(U_{ij})(a_i)(a_j)(a_i^*)(a_j^*)$.

Table VII. Selected Interatomic Distances (Å) and Bond Angles (deg) of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, 6a

W(1)–C(1)	2.305 (16)	C(4)–C(5)	1.45 (3)
W(1)–C(2)	2.324 (14)	C(6)–O(6)	1.098 (22)
W(1)–C(6)	2.018 (18)	C(7)–O(7)	1.171 (20)
W(1)–C(7)	1.959 (16)	C(8)–O(8)	1.145 (16)
W(1)–C(8)	1.985 (13)	C(9)–O(9)	1.205 (19)
W(1)–C(9)	2.258 916)	C(9)–C(19)	1.502 (21)
W(2)–C(12)	2.323 (17)	C(11)–C(12)	1.40 (3)
W(2)–C(13)	2.306 (19)	C(11)–C(15)	1.41 (3)
W(2)–C(16)	1.862 (23)	C(12)–C(13)	1.45 (4)
W(2)–C(17)	1.875 (18)	C(13)–C(14)	1.36 (4)
W(2)–C(18)	2.315 (14)	C(14)–C(15)	1.28 (3)
W(2)–C(19)	2.225 (15)	C(16)–O(16)	1.26 (3)
C(1)–C(2)	1.36 (3)	C(17)–O(17)	1.232 (22)
C(1)–C(5)	1.40 (3)	C(18)–C(19)	1.40 (3)
C(2)–C(3)	1.400 (24)	C(19)–C(20)	1.441 (22)
C(3)–C(4)	1.43 (3)		
C(6)–W(1)–C(7)	77.8 (8)	W(1)–C(8)–O(8)	171.0 (19)
C(6)–W(1)–C(8)	75.8 (9)	W(1)–C(9)–O(9)	117.7 (11)
C(6)–W(1)–C(9)	126.1 (6)	W(1)–C(9)–C(19)	124.7 (11)
C(7)–W(1)–C(8)	111.4 (7)	O(9)–C(9)–C(19)	116.7 (14)
C(7)–W(1)–C(9)	73.5 (7)	W(2)–C(16)–O(16)	177.5 (17)
C(8)–W(1)–C(9)	73.7 (7)	W(2)–C(17)–O(17)	179.1 (15)
C(16)–W(2)–C(17)	78.3 (9)	W(2)–C(18)–C(19)	68.6 (9)
C(16)–W(2)–C(18)	72.3 (7)	W(2)–C(19)–C(9)	122.7 (11)
C(16)–W(2)–C(19)	104.9 (7)	W(2)–C(19)–C(18)	75.7 (9)
C(17)–C(2)–C(18)	111.5 (7)	W(2)–C(19)–C(20)	75.6 (9)
C(17)–W(2)–C(19)	104.8 (7)	C(9)–C(19)–C(18)	122.6 (14)
C(18)–W(2)–C(19)	35.7 (7)	C(9)–C(19)–C(20)	124.6 (14)
W(1)–C(6)–O(6)	178.2 (17)	C(18)–C(19)–C(20)	112.4 (13)
W(1)–C(7)–O(7)	171.5 (16)		

($J_{W\text{-}P}$ 490.9 Hz, $P(OMe)_3$); mass spectrum m/z 806 (M^+), 778 ($M^+ - CO$), 750 ($M^+ - 2CO$), 682 ($M^+ - L$), 654 ($M^+ - CO, L$). Anal. Calcd for $C_{21}H_{23}O_8PW_2$: C, 31.45; H, 2.89. Found: C, 31.58; H, 3.11.

Attempted Synthesis of $Cp(CO)_2M_1(\mu\text{-}\eta^3{:}\eta^1\text{-}CH_2C(CO)CH_2)Mo(CO)_3Cp$ (M_1 = W, Mo). Attempts to prepare the title compounds have been unsuccessful. The reaction has been carried out in several common organic solvents such as THF and CH_3CN in various temperature ranges from 0 to –40 °C. Slow addition of either the $Cp(CO)_3Mo^-$ anion in THF solution or **3a** to the other part all resulted in a mixture of products not separable by column chromatography or recrystallization.

X-ray Analysis of 4a, 5, and 6a. Yellow single crystals suitable for an X-ray diffraction study of **4a** were grown by sublimation under 4×10^{-5} Torr vacuum at 75 °C for 10 days. Single crystals of **5** and **6a** suitable for X-ray diffraction were grown by recrystallization from hexane solutions. The diffraction data were collected at room temperature on a Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ_α = 0.710 37 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.[12]

A suitable single crystal of **4a** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 25 accurately centered reflections with 2θ values in the range from 19.0 to 26.3°. Cell constants and other pertinent data were collected in Table I. Data were collected using the ω–2θ 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 $A + B \tan\theta$, for which A and B were set at the values of 0.75 and 0.35, respectively. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The structure was first solved by the using heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized 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 neutral atoms were used.[13] The non-hydrogen atoms were refined anisotropically. 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. All hydrogen atoms were assigned isotropic thermal parameters 1–2 $Å^2$ larger then the equivalent B_{iso} of the atom to which they were bonded. The final residuals of this refinement were R = 0.030 and R_w = 0.028.

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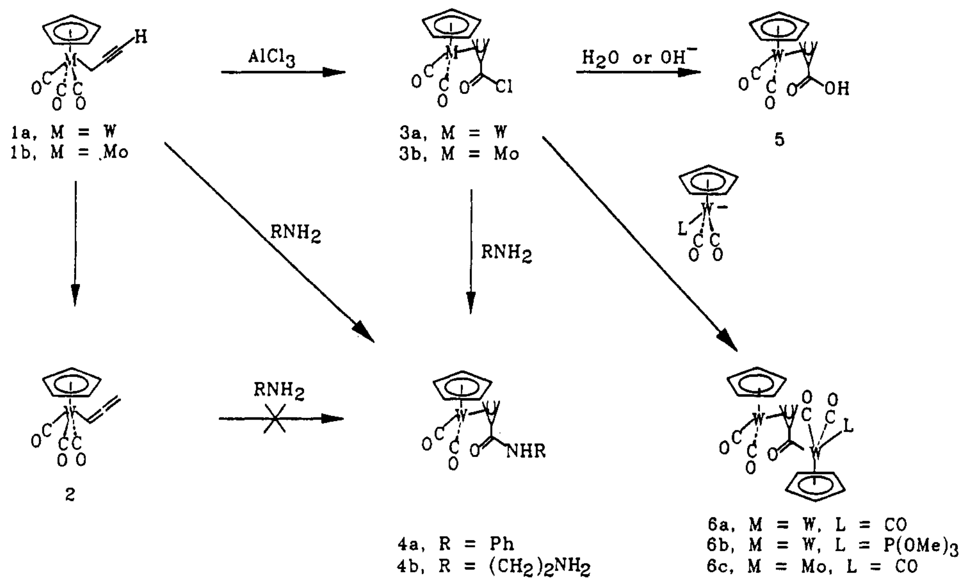
Scheme I



The procedures for **5** and **6a** were similar to those for **4a**. The unit cell constants were also determined from 24 accurately centered reflections. Cell constants and other pertinent data were collected in Table I. The final scan speed ranged from 2 to 7° min^{-1}. The ω-scan angle was determined for each reflection according to the equation $A + B \tan \theta$, for which A and B were set at the values of 0.7 and 0.35, respectively. The structures were first solved by using the heavy-atom method (Patterson synthesis), which led to the location of the positions of the metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The final residuals of this refinement were $R = 0.025$ and $R_w = 0.020$ for **5** and $R = 0.027$ and $R_w = 0.022$ for **6a**. Because of the noncentrosymmetric space group in **6a**, an additional η parameter was included in the least-squares refinement in order to determine the correctness of the enantiomorph.[13] Final values of all refined atomic positional parameters (with esd's) and selected bond distances and bond angles are listed in Tables II–VII. Tables of thermal parameters are given in the supplementary material.

Results and Discussion

Reactions of Tungsten Propargyl Complex Cp(CO)$_3$WCH$_2$C≡CH, 1a, with Amines. Treatment of the propargyl complex **1a** with excess aniline resulted in an immediate reaction from which an orange, benzene-soluble complex, Cp(CO)$_2$W(η^3-CH$_2$C(CONHC$_6$H$_5$)CH$_2$), **4a**, was obtained in 80% yield. The carbamoyl group from the nucleophilic attack of amine to one of the terminal CO was introduced to the β-carbon of the allylic ligand. Reactions of several primary amines such as methylamine, ethylamine, and ethylenediamine with **1a** also gave products of the same type. The ^{1}H and ^{13}C NMR spectra of **4a** were consistent with that of an η^3-allylic complex. In acetone solution the methylene protons of **4a** appeared as two broad resonances at δ 3.34 and 1.75 ppm in the ^{1}H NMR spectrum assignable to the syn and anti protons of the allylic ligand, respectively.[14] On the basis of the chemical shift of anti protons, complex **4a** was assigned an endo conformation in acetone. From the X-ray diffraction study described below, the endo conformation was the more stable form in the solid state. In acetone, the exo isomer was not observed even at −60 °C. However, in benzene at 10 °C, the endo and exo isomers of complex **4a** were obtained in a ratio of 1:1.5 as indicated by ^{1}H NMR. The IR spectrum of **4a** in benzene also showed two sets of absorption peaks, with the same intensity. The diethylcarbamoyl compelx NiI(Et$_2$NH)$_2$(CONEt$_2$) has been shown to undergo insertion of allene to give a stable allylic complex, NiI(Et$_2$NH)(η^3-CH$_2$C(CONEt$_2$)CH$_2$). Acidification of the product gave *N,N*-diethylmethylacrylamide.[15] Roustan and his co-workers have reported the alkoxycarbonylation of the Mo propargyl complexes and found that C–C bond formation occurred at the β-position of the C$_3$ unit.[4]

Complex **1a** underwent metal migration to give the metal allenyl complex Cp(CO)$_3$WCH=C=CH$_2$, **2**, under mild condition.[8b] In the reaction of **1a** with amine the C–C bond formation took place at the β-carbon of the propargyl ligand to give **4**. In the same reaction of complex **2** with amine the C–C bond formation took place at the α-carbon of the allenyl ligand, producing an azametallacycle complex, Cp(CO)$_2$WCH(CONHR)CH(CH$_3$)NHR.[16] Formation of **4** could be accounted for by a three-step process. Protonation of the propargyl group first formed a cationic π-allenyl intermediate.[17] This was followed by nucleophilic attack of amine at the terminal CO to give a carbamoyl group. Finally, migration of the carbamoyl group to the center carbon resulted in formation of **4**. Protonation of the σ-allenyl complex **2** did not yield a π-allenyl intermediate.

Synthesis of Cp(CO)$_2$M(η^3-CH$_2$C(COCl)CH$_2$) (3a, M = W; 3b, M = Mo). Treatment of complex **1a** with excess AlCl$_3$, in the presence of fumaric acid, resulted in formation of complex **3a**. This yellow, water-sensitive powder (Scheme I) was isolated in 95% yield. Under N$_2$ and at low temperature, complex **3a** is stable in C$_6$H$_6$ and in hexane. We found that purification by extraction with hexane gave **3a** with the highest degree of purity. Since

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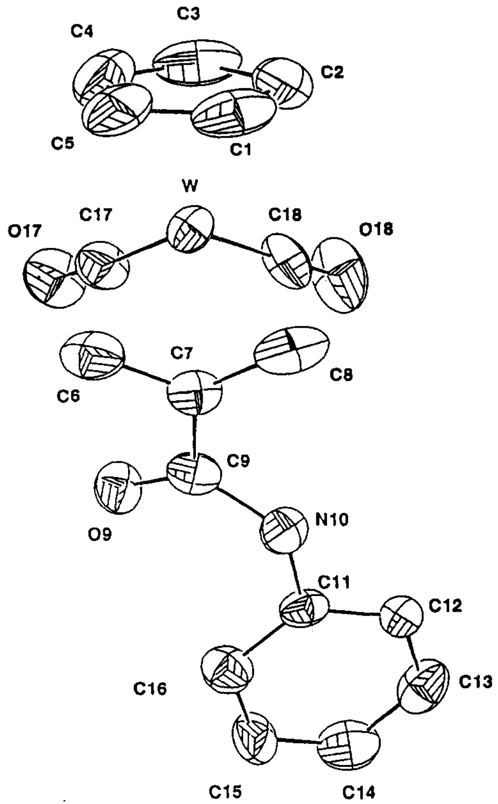

Figure 1. ORTEP drawing of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHC_6H_5)CH_2)$, **4a**.

solubility of **3a** in hexane was low, a large quantity of hexane was used during extraction of **3a**. It was surprising that the same type of reaction, i.e., the regiospecific C–C bond formation at the β-position of the propargyl ligand, was revealed in the reaction of a Lewis acid with metal propargyl complex. The structure of **3a** was assigned on the basis of the spectroscopic data and on the chemical reactivities in the reactions with organic nucleophiles. In addition to the Cp resonance, the characteristic allylic resonances of **3a** at δ 2.94 and 1.82 were also observed in the ^1H NMR spectra. Unlike complex **4a**, no endo/exo isomer could be observed in the NMR spectra of **3a** even at low temperature. However, the endo/exo isomers in a 10:1 ratio were seen in the IR spectra of **3a** when dissolved in hexane. In the IR spectra, the CO stretching of the chlorocarbonyl group of **3a** appeared as a medium absorption peak in the region of 1700–1740 cm^{-1}. The Mo analogue **3b** could be prepared similarly from the reaction of $Cp(CO)_3MoCH_2C{\equiv}CH$ with $AlCl_3$. For **3b** in hexane the endo/exo isomers in a 1.2:1 ratio were seen in the IR spectra. Complex **3a** as well as **1a** reacted with excess water to give $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, **5**. Substituting NaOH for H_2O resulted in higher yield of **5**. Treatment of **5** with a trace amount of water and slight heat resulted in the release of methacrylic acid from **3a**. Also the reaction of complex **3a** with aniline produced complex **4a** in quantitative yield.

Structure Determination of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHC_6H_5)CH_2)$, 4a, and $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, 5. Both complexes **4a** and **5** were also identified on the basis of their single-crystal X-ray analysis, which provided unambiguous structural assignment as illustrated in Figures 1 and 2, respectively. Interatomic distances and angles of **4a** and **5** have been collected and recorded in Table III and Table V, respectively. It is clear that the allylic ligands of **4a** and **5** are each bonded to the metal in an η^3-fashion and in an endo conformation in both complexes. The allylic ligands of **4a** and **5** were coordinated symmetrically to the tungsten metals with two approximately equal C–C bonds as shown in Figures 1 and 2. Distances within the allyl fragment were C(6)–C(7) = 1.40 (1) and C(8)–C(7) = 1.40 (1) Å in **4a** and C(8)–C(9) = 1.43 (1) and C(9)–C(10) = 1.42 (1) Å in **5**. The angles between two carbonyls were 76.9 (4) and 78.6 (3)° for **4a** and **5**, respectively, which were smaller than the 82.5 (2)° found in a Mo allyl complex.[18] The W–C–O angles were from 174.6 (10) to 175.9 (10)° for **4a** and from 175.2 (6) to 177.7 (7)° for **5**. The W–C distances of W–CO groups were between 1.93 (1) and 1.98 (1) Å for **4a** and between 1.95 (1) and 1.99 (1) Å for **5**, and C–O distances were 1.15 (1)–1.18 (1) for **4a** and 1.13 (1)–1.16 (1) Å for **5**. As expected, in both complexes, the M–C distance to the central carbon atom of the allylic fragment was shorter than the M–C distances to the terminal positions.[19]

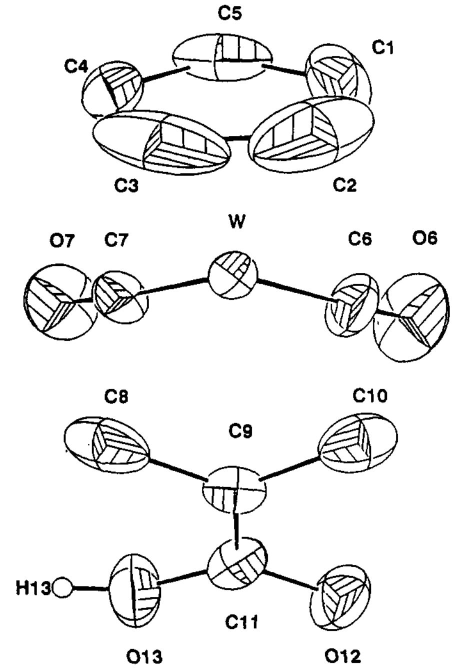

Figure 2. ORTEP drawing of $Cp(CO)_2W(\eta^3\text{-}CH_2C(COOH)CH_2)$, **5**.

Reactions of 3a and 3b with Metal Anions. Anionic metal nucleophiles such as $Cp(CO)_2LW^-$ (L = CO, $P(OMe)_3$) substituted the Cl atom of **3a**, affording dinuclear complexes, $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_2LCp$ (**6a**, L = CO; **6b**, L = $P(OMe)_3$). Similarly, a molybdenum–tungsten heterodinuclear analogue, $Cp(CO)_2Mo(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, **6c**, was prepared from the reaction of **3b** with $Cp(CO)_3W^-$. Complex **6a** was identified by spectroscopic methods as well as X-ray diffraction analysis. The CO stretching of the bridging ligand gave an absorption band at 1657 cm^{-1}. In the mass spectrum, **6a** gave a parent peak as well as fragmentation by the loss of CO ligands. For **6a** in CD_3Cl at room temperature, three sharp single resonances, which appeared at δ 5.61, 5.25, and 2.76, respectively, were assigned to the two cyclopentadienyl groups and syn protons of the

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[18] (a) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. (b) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227.

[19] (a) Alt, H. G.; Engelhardt, H. E.; Wrackmeyer, B. *J. Organomet. Chem.* **1989**, *379*, 289. (b) Vong, W. J.; Peng, S. M.; Lin, S. H.; Lin, W. J.; Liu, R. S. *J. Am. Chem. Soc.* **1991**, *113*, 573.

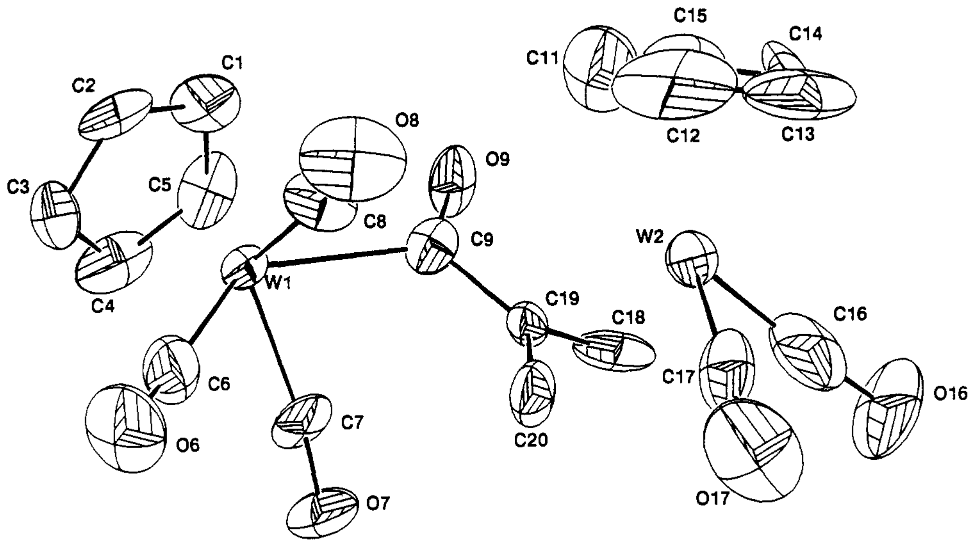

Figure 3. ORTEP drawing of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, **6a**.

allylic ligand. The anti protons of the allylic ligand gave a broad resonance at δ 1.38. In C_2D_6CO, at room temperature, one of the Cp resonances (5.82) appeared as a broad peak, while the other (5.40) remained as a sharp singlet. Low-temperature ^1H NMR spectra revealed two isomers of complex **6a**. At 280 K, there was only one sharp singlet resonance assignable to the Cp of the $Cp(CO)_3W$ moiety all others were broad resonances. Lowering the temperature to 240 K, complex **6a** exhibited two sets of resonances. This is due to the endo/exo conformational exchange of the allylic ligand bound to the $Cp(CO)_2W$ moiety. Resonance of the anti protons of the endo isomer falls in the upper field region relative to that of the anti protons of the syn protons of the endo isomer.[20] At 240 K, the endo/exo ratio is 5:3. For **6c**, the ratio is 3:5. At 263 K, the endo and exo isomers of complex **6c** can be well resolved in a endo/exo ratio of 5:3, even in $CDCl_3$. Interestingly, unlike **6a**, complex **6b** gives only one isomer in NMR spectra. This could be attributed to the steric effect of the phosphite ligand.

Attempts to prepare the title compounds using the anionic $CpM(CO)_3^-$ moiety have been unsuccessful. The attempted reactions have been carried out in several common organic solvents such as THF and CH_3CN and at various temperatures ranges from 0 to −40 °C. Slow addition of either $Cp(CO)_3Mo^-$ or **3a** to the other part all resulted in a mixture of products not separable by recrystallization. Due to higher nucleophilicity of the Mo anion we were unable to obtain pure $Cp(CO)_2W(CH_2C(CO)CH_2)Mo(CO)_3Cp$. Similarly attempts to prepare the Mo analogue of **6a** yielded an inseparable mixture.

Structure of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CO)CH_2)W(CO)_3Cp$, 6a. Complex **6a** was also identified by single crystal X-ray diffraction analysis which provided unambiguous structural assignment as illustrated in Figure 3. Interatomic distances and angles **6a** have been collected and recorded in Table VII. The molecule consists of a $Cp(CO)_2W$ (W(2)) unit connected to a $Cp(CO)_3W$ (W(1)) unit by a $\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_4H_4O$ ligand, with the allyl group bound to the $Cp(CO)_2W$ unit and the acyl carbon attached to the $Cp(CO)_3W$ unit. Unlike **4a** and **5** with the endo conformation, complex **6a** adopts an exo conformation of the allylic ligand. Distances within the allyl fragment are C(18)–C(19) = 1.40 (3) and C(19)–C(20) = 1.44 (2) Å. The W–C–O angles of the terminal CO's range from 170 (2) to 179 (2)°, with the W–CO distances ranging from 1.86 (2) to 2.02 (2), and the C–O distances from 1.10 (2) to 1.26 (3) Å. The average shorter W–CO and longer C–O on the W(2) indicate the stronger π-donor ability of the allylic ligand. The C(9)–C(19) distance of 1.52 (2) Å is typical of a single bond and the C(9)–O(9) distance of 1.21 (2) Å is typical of a double bond. These distances are to be contrasted with the comparable ones in **4a** and **5**, where the corresponding C—C and C=O distances are 1.50 (1) Å and 1.23 (1) Å in **4a** and 1.46 (1) Å and 1.252 (9) Å in **5**. These distances are related to the dihedral angle between the allylic plane and the plane made of carbonyl group and the atom next to the carbonyl carbon atom, see Table VIII. While the C–C bond of **5** is the shortest among the three, the dihedral angle of 3.2 (8)° is the smallest, indicating good coplanarity and thus better π delocalization. The more electropositive tungsten atom of **6a** reduces the delocalization of π electrons, causing the increase of the C–C bond, whereby increasing the dihedral angle to 30 (1)°. The allylic ligands of **4a**, **5**, and **6a** are all coordinated symmetrically to the tungsten with two approximately equal C–C bonds having somewhat shorter bond length in **4a**, as shown in the figures. As expected, the M–C distance to the central carbon atom of the allylic fragment was shorter than the distances to the terminal positions.[19]

Table VIII. Structural Parameters of the β-Substituted Allylic Ligand of Complexes 4a, 5, and 6a

	4a	5	6a
dihedral angle (deg)[a]	22.8 (6)	3.2 (8)	29.5 (11)
C—C (Å)[b]	1.50 (1)	1.46 (1)	1.52 (2)
C=O (Å)[c]	1.23 (1)	1.252 (9)	1.21 (2)

[a] The dihedral angle between the allylic plane and the plane made of the carbonyl group and the heteroatom. [b] Bond distance between the β-carbon of the allylic ligand and the carbonyl carbon. [c] Bond distance between C and O atoms of the carbonyl group attached to the β-carbon of the allylic group.

Conclusion. In the reactions of the propargyl complexes mentioned above, the C–C bond formation took place at the β-position of the original propargyl ligand. Alkoxycarbonylation of the propargyl ligand at the carbon by alcohol has been observed in other metal complexes,

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(20) Powell, P. *Organometallic Chemistry*; Chapman and Hall: New York, 1988; 2nd Ed.; Chapter 8, p 253–258.

and our results on the reactivities of complexes **1a** and **1b** are consistent with those reported by Roustan. It is, therefore, not unexpected that the allylic ligand and the Cp are in an endo configuration. Formation of a β-(chlorocarbonyl)allylic ligand from the reaction of AlX_3 (X = Br, Cl) with **1a** and **1b** enables us to attach another metal to the allylic moiety of the molecule. Heterobimetallic compounds can also be prepared using such a ligand. Chemical reactivities, including the photodecarbonylation of such dinuclear complexes, will be the subject of a future report.

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Supplementary Material Available: Details of the structural determination for complexes **4a**, **5**, and **6a**, including listings of anisotropic thermal parameters and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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