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$W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$: A Compound Containing η^2(3e)-Acetamido, η^4(4e)-Cyclobutadiene, and η^4(5e)-Butadienyl Ligands

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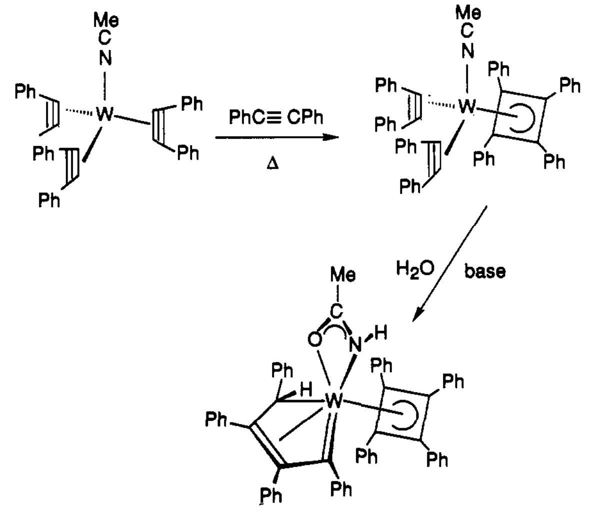
Introduction

Transition metal polyalkyne complexes have played an important role in developing the chemistry of unsaturated organic substrates coordinated onto metal centers.[1] Commonly, the coordinated alkynes react, and in doing so lose their individuality, forming carbocyclic or metallacyclic systems.[2] We have recently described that $W(C_2Ph_2)_3(CH_3CN)$ couples with diphenylacetylene to generate a cyclobutadiene complex $W(\eta^4\text{-}C_4Ph_4)(C_2Ph_2)_2(CH_3CN)$.[3] It is interesting to investigate whether the remaining two alkyne ligands could undergo a further coupling reaction. In this paper we wish to report that hydrolysis of $W(\eta^4\text{-}C_4Ph_4)(C_2Ph_2)_2(CH_3CN)$ in alkaline solution leads to not only hydration of the acetonitrile ligand but also alkyne–alkyne coupling to generate a metallacyclic complex $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$. These results are summarized in Scheme I.

Scheme I



Experimental Section

$W(\eta^4\text{-}C_4Ph_4)(C_2Ph_2)_2(CH_3CN)$ was prepared as described previously.[3a] Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck, GF 254). ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. IR spectrum was taken on a Hitachi-2001 spectrometer. Mass spectra were obtained on a Joel-HX 110 mass spectrometer. Elemental analysis was performed at the NSC Regional Instrumentation Center at National Chen-Kung University.

Synthesis. A 100-mL, three-necked round-bottomed flask was equipped with a magnetic stir bar, a rubber serum stopper, a reflux condenser, and a nitrogen inlet. The stopper was briefly removed, and $W(\eta^4\text{-}C_4Ph_4)(C_2Ph_2)_2(CH_3CN)$ (200 mg, 0.21 mmol), benzene (20 mL), and 0.1 N KOH aqueous solution (20 mL) were introduced against a nitrogen flow. The mixture was refluxed under nitrogen for 15 min, cooled to room temperature, and neutralized with dilute HCl aqueous solution (0.1 N). The organic layer was washed with distilled water and dried over Na_2SO_4. The volatile materials were removed under vacuum, and the residue was separated by TLC, eluting with *n*-hexane/dichloromethane (4:1, v/v). Crystallization of the material forming the orange-yellow band from dichloromethane/methanol yielded air-stable, orange-yellow crystals, formulated as $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$ (82 mg, 0.08 mmol, 39%): mass spectrum (FAB), m/z 955 (M^+, ^{184}W), 897 ($M^+ - CH_3C(O)NH$); IR (KBr) 3440 (br, ν_{N-H}), 1598 (vs, $\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 7.25–6.13 (m, Ph, CHPh, NH), 1.25 (s, CH_3); ^{13}C NMR ($CDCl_3$, 25 °C) δ 250.2 (W=C), 191.2 (C=O), 141.5–124.9 (C_6H_5 and $\eta^4\text{-}C_4Ph_4H$), 88.4 ($\eta^4\text{-}C_4Ph_4$), 67.7 (d, CHPh, $^1J_{C-H}$ = 143 Hz), 25.6 (q, CH_3). Anal. Calcd for $C_{58}H_{45}NOW$: C, 72.59; H, 4.76; N, 1.48. Found: C, 72.90; H, 4.61; N, 1.27.

Table I. Experimental Data for the X-ray Diffraction Study

chem formula $C_{58}H_{45}NOW$	fw 954.85
a = 11.583(1) Å	space group $P2_1/n$
b = 17.662(2) Å	
c = 23.456(2) Å	λ = 0.709 30 Å
β = 97.004(8)°	ρ_{calcd} = 1.452 g/cm^3
V = 4762.6(9) Å^3	μ = 2.63 mm^{-1}
Z = 4	$R_F{}^a$ = 0.038
T = 25 °C	$R_w{}^a$ = 0.035

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum|F_o|^2]\}^{1/2}$.

Structure Determination. A crystal of $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$ with approximate dimensions 0.25 × 0.11 × 0.16 mm was mounted in a thin-walled glass capillary and aligned on the Nonius CAD-4 diffractometer. Diffraction data were collected with Mo Kα radiation (λ = 0.709 30 Å) using $\theta/2\theta$ scan mode. Lattice parameters were determined from 20 randomly selected reflections with 2θ angle in the range 19.34–30.34°. The structure was solved by the heavy-atom method and refined by least-square cycles. HN and H(5) were located from a Fourier map and positionally refined. Other hydrogen atoms were calculated according to their idealized positions. Non-hydrogen atoms were refined anisotropically. The data collection and refinement parameters are given in Table I. Atomic positional parameters and selected interatomic distances and angles are collected in Tables II and III, respectively.

Results and Discussion

Hydrolysis of $W(\eta^4\text{-}C_4Ph_4)(C_2Ph_2)_2(CH_3CN)$ in refluxing benzene–KOH aqueous solution produces $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$ in 39% yield. In neutral conditions (water–benzene mixture), the product mixture is complex and only a low yield of $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$ (<5%) is obtained.

The molecular structure of $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$ is illustrated in Figure 1. The structure consists of discrete molecules with each tungsten unit bonded to one acetamido, one tetraphenylcyclobutadiene, and one tetraphenylbutadienyl group. The acetamido ligand (N–O–C9–C10, plane 1), cyclobutadiene ring (C1–C4, plane 2), and butadienyl ligand

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Table II. Selected Atomic Coordinates and B_{iso}[a] Values for $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$

	x	y	z	B_{iso}, Å^2
W	0.34559(3)	0.184426(20)	0.239293(15)	2.550(15)
N	0.2976(5)	0.2983(3)	0.21961(24)	1.7(3)
O	0.3184(5)	0.2248(3)	0.14860(23)	3.7(3)
C1	0.5004(7)	0.2181(5)	0.2993(3)	2.8(4)
C2	0.5058(7)	0.1356(4)	0.2928(3)	2.3(4)
C3	0.5286(7)	0.2255(5)	0.2403(3)	2.9(4)
C4	0.5299(7)	0.1431(5)	0.2334(3)	2.9(4)
C5	0.2645(7)	0.0752(5)	0.2026(3)	2.4(4)
C6	0.1625(7)	0.1206(4)	0.2068(3)	2.5(4)
C7	0.1566(8)	0.1577(4)	0.2592(3)	2.4(3)
C8	0.2570(7)	0.1573(4)	0.3022(3)	2.6(4)
C9	0.2989(8)	0.2914(5)	0.1665(4)	4.1(5)
C10	0.2805(11)	0.3542(6)	0.1236(5)	6.6(7)
C11	0.5181(7)	0.2705(5)	0.3484(3)	2.8(4)
C21	0.5099(7)	0.0708(5)	0.3314(3)	2.9(4)
C31	0.5651(7)	0.2907(5)	0.2077(3)	3.5(4)
C41	0.5753(8)	0.0905(5)	0.1925(3)	2.9(4)
C51	0.2843(7)	0.0338(5)	0.1482(4)	3.1(4)
C61	0.0713(7)	0.1338(5)	0.1572(3)	2.9(4)
C71	0.0490(7)	0.1997(5)	0.2707(3)	2.9(4)
C81	0.2477(8)	0.1355(5)	0.3614(3)	3.2(4)
HN	0.302(6)	0.340(4)	0.245(3)	2.8(16)
H5	0.297(5)	0.042(3)	0.2395(24)	1.3(14)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Selected Bond Distances (Å) and Angles (deg) for $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$

	Bond Distances		
W–N	2.122(6)	W–O	2.229(5)
W–C1	2.221(8)	W–C2	2.278(8)
W–C3	2.238(8)	W–C4	2.276(8)
W–C5	2.269(8)	W–C6	2.440(8)
W–C7	2.342(9)	W–C8	1.957(8)
N–C9	1.254(11)	N–HN	0.94(6)
O–C9	1.278(11)	C1–C2	1.466(11)
C1–C3	1.466(11)	C1–C11	1.473(12)
C2–C4	1.459(11)	C2–C21	1.459(11)
C3–C4	1.465(12)	C3–C31	1.472(12)
C4–C41	1.477(12)	C5–C6	1.442(11)
C5–C51	1.512(11)	C5–H5	1.07(6)
C6–C7	1.401(11)	C6–C61	1.491(11)
C7–C8	1.444(11)	C7–C71	1.504(12)
C8–C81	1.457(11)	C9–C10	1.496(13)
	Bond Angles		
N–W–O	59.11(21)	N–C9–O	116.1(8)
W–N–C9	95.1(5)	W–N–HN	127(4)
C9–N–HN	134(4)	N–C9–C10	125.3(9)
O–C9–C10	118.6(9)	C2–C1–C3	88.4(6)
C2–C4–C3	88.8(6)	C1–C2–C4	91.5(6)
C1–C3–C4	91.2(7)	W–C1–C11	133.5(6)
W–C2–C21	127.0(5)	W–C3–C31	125.4(6)
W–C4–C41	130.7(6)	W–C5–C51	129.2(5)
W–C5–H5	93(3)	W–C6–C61	132.7(5)
W–C7–C71	138.7(5)	W–C8–C81	152.8(6)
C51–C5–H5	110(3)	C6–C5–C51	122.5(7)
C6–C5–H5	116(3)	C5–C6–C7	116.6(7)
C5–C6–C61	122.8(7)	C7–C6–C61	120.4(7)
C6–C7–C8	119.4(7)	C6–C7–C71	121.2(7)
C8–C7–C71	119.4(7)	C7–C8–C81	121.4(7)

(C5–C8, plane 3) are essentially planar with the maximum atomic displacement from plane being 0.01(1), 0.02(1), and 0.00(1) Å, respectively. The dihedral angles between plane 1 and plane 2, plane 1 and plane 3, and plane 2 and plane 3 are 15.5(5), 56.7(5), and 72.5(5)°, respectively.

The cyclobutadiene group is bonded to the tungsten atom with W–C1 = 2.221(8) Å and W–C3 = 2.238(8) Å being slightly shorter than W–C2 = 2.278(8) Å and W–C4 = 2.276(8) Å. The phenyl groups connected to the cyclobutadiene ring are *exo* to W. Thus they are bent away from the cylcobutadiene plane by angles averaging 11.8°. The cyclobutadiene C–C bond distances are about equal, 1.46 ± 0.01 Å, closely resembling those found for $W(\eta^4\text{-}C_4Ph_4)(C_2Ph_2)_2(CO)$[3] (1.47 ± 0.02 Å).

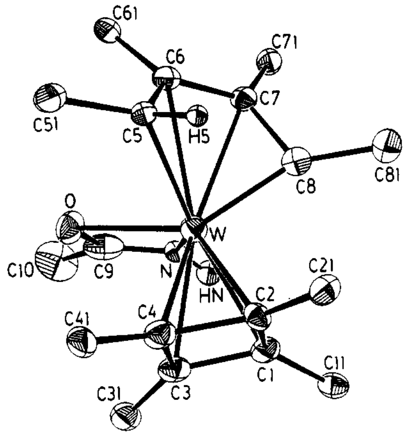
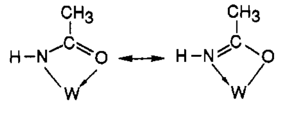


Figure 1. Molecular structure of $W(\eta^4\text{-}C_4Ph_4)(\eta^4\text{-}C_4Ph_4H)(\eta^2\text{-}CH_3C(O)NH)$ showing the atomic labeling scheme used in the text. The phenyl groups and methyl hydrogen atoms have been omitted for clarity.

The acetamido group is η^2-coordinated to W with W–N = 2.122(6) Å being significantly shorter than W–O = 2.229(5) Å. The W–N distance is compatible with that in other imido complexes.[4] The N, O, C9, and C10 atoms lie in a plane, and the tungsten atom lies only 0.17(1) Å out of this plane. Furthermore, since the distances of C9–N (1.25(1) Å) and C9–O (1.28(1) Å) are comparable and close to a C=N or C=O double-bond length,[5] two resonance structures can be drawn to represent the $W(\eta^2\text{-}CH_3C(O)NH)$ fragment.



Since neutral η^2-$CH_3C(O)NH$ group and η^4-C_4Ph_4 ring are normally considered as three- and four electron donors, respectively, the remaining η^4-C_4Ph_4H ligand must provide five electrons to the tungsten atom to satisfy the 18-electron rule. Consistently, the η^4-C_4Ph_4H group appears to have a tungsten–carbon double bond to C8 (1.957(8) Å), a single bond to C5 (2.269(8) Å), and a π-donation from C6 and C7 to W (2.440(8) and 2.342(9) Å, respectively). Distances from C5 to C8 around the butadienyl carbon skeleton are 1.44(1), 1.40(1), and 1.44(1) Å, respectively. The phenyl groups connected to C5 and C6 are slightly bent away from the butadienyl plane by angles 3.5, 10.6 (*endo* to W), and −5.5° (*exo* to W) for C5, C6, and C7, respectively, whereas the phenyl group connected to C8 is bent away −41.8°. Moreover, the atoms W, C7, C8, and C81 are about on the same plane and ∠C7–C8–C81 = 121.4(7)°, implying a carbene carbon for the C8 atom. The hydrogen atom is located on a terminal carbon C5 in a pseudo-*anti* position with C5–H5 = 1.07(6) Å. The bond angles ∠C51–C5–H5 = 110(3), ∠C6–C5–C51 = 122.5(7), and ∠C6–C5–H5 = 116(3)° suggest that C5 is in a distorted tetrahedral environment.

Formation of a W=C double bond is further evidenced by ^{13}C NMR spectrum which shows a low field signal at δ 250.2 characteristic of a alkylidene type carbon.[6] A doublet at δ 67.7

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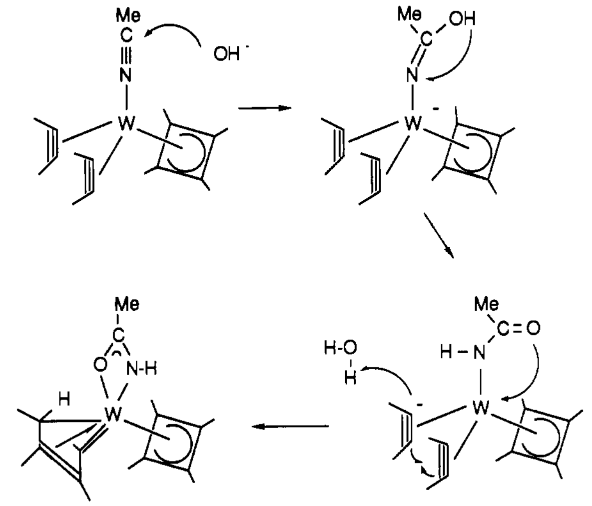
is attributed to the $\underline{C}$HPh carbon with ${}^1J_{C-H}$ = 143 Hz. The cyclobutadiene carbons give a sharp singlet at δ 88.4, revealing that the cyclobutadiene ligand is fluxional with facile ring rotation. The amido carbonyl carbon resonance at δ 191.2 is 19 ppm downfield of the shift observed for free acetamide (δ 172.7).[7] The ^{1}H NMR spectrum shows the phenyl protons in the range δ 7.25–6.13 and methyl protons at δ 1.25. However, no unique signal is evident for the CHPh or N–H proton; presumably these resonances appear among the phenyl protons. The chemical shifts for imido protons have been observed ranging from δ 9.2 to 4.1.[8] The infrared spectrum in a KBr disk includes a broad band at 3440 cm^{-1}, assigned to ν(N–H), and a strong peak at 1598 cm^{-1}, assigned to ν(C=O).

Apparently, alkyne–alkyne coupling is preceded by hydration of the acetonitrile ligand, since hydrolysis of the analogous compound W(η^4-C_4Ph_4)(C_2Ph_2)$_2$(CO)[3] gives no reaction. It has been observed that transformation of coordinated nitriles to N-bonded carboxamido complexes is a key step in the hydrolysis of nitriles to the corresponding carboxamide catalyzed by metal ions.[9] A similar conversion might occur in this reaction to generate [W(η^4-C_4Ph_4)(C_2Ph_2)$_2$(η^1-NHC(O)CH_3)]$^-$, and subsequent chelating of the carbonyl oxygen to the tungsten atom would cause alkyne–alkyne coupling followed by abstraction of a proton from water to give the title compound (Scheme II). It is likely that hydrolysis of the acetonitrile ligand takes place during the OH$^-$ stage, and not during the H$^+$ addition or TLC, because the reactant W(η^4-C_4Ph_4)(C_2Ph_2)$_2$(CH_3CN) is stable during TLC and analysis of the organic layer before adding H$^+$ shows formation of the ultimate product. The η^4-C_4R_4H ligands have been prepared previously by protonation of tungsten(II) and molybdenum(II) bisalkyne complexes,[10] hydride attack on a cationic π-cyclobutadiene ruthenium(II) derivative,[11] and elimination of a hydride from a π-butadiene group[12] or coupling of η^2-vinyl and alkyne ligands on a molybdenum(II) center.[12,13] Therefore, our observation, combining nitrile hydrolysis and alkyne–alkyne coupling to generate a η^4-C_4Ph_4H moiety on a low oxidation state tungsten center, is noteworthy.

Scheme II



Acknowledgment. This research was supported by the National Science Council of the Republic of China.

Supplementary Material Available: Listings of crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (8 pages). Ordering information is given on any current masthead page.

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