Reaction of Tungsten η^3-*anti*-Pentadienyl Compounds with Reactive Olefins and Isocyanates: [5 + 2] Cycloaddition versus Acylation

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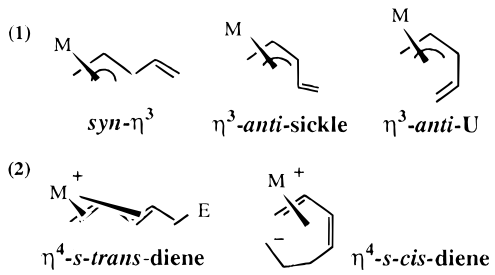
Sequential treatment of $CpW(CO)_3(CH_2C{=}CCMe{=}CH_2)$ (**1**) with CF_3SO_3H and MeOH in cold diethyl ether (−40 °C) gave a 75% yield of $CpW(CO)_3(\eta^3$-*anti*-2-CO_2Me-4-methylpentadienyl) (**2**). Compound **2** reacted with TCNE to afford the novel [5 + 2] cycloaddition adduct **3** in 62% yield; the molecular structure of **3** showed a 1,2-shift of the tungsten fragment, indicating a η^4-*s*-*cis*-diene reaction intermediate. The reaction of **2** with reactive isocyanates $RN{=}C{=}O$ (R = $PhSO_2$, $CH_3C_6H_4SO_2$) in cold CH_2Cl_2 produced **4a** (R = $PhSO_2$) and **4b** (R = $CH_3C_6H_4SO_2$) in 82% and 87% yields, respectively; the two compounds can be regarded as the acylation derivatives of **2**, according to an X-ray diffraction study of **4a**.

Introduction

Transition-metal pentadienyl complexes[1−4] are of great interest in organometallic chemistry due to the variety of geometries for the metal−ligand coordination. The chemistry of these complexes has been studied extensively in recent years. The metal η^3-pentadienyl compounds have two possible structures, i.e., *syn* and *anti* configurations; the latter may have U- and sickle-shaped conformations. Transition-metal-mediated cycloaddition[5] reactions are very useful in organic synthesis; most of the reactions focus on the synthesis of small-ring compounds via [3 + 2], [4 + 2] and [2 + 2 + 2] pathways.[5] In contrast, metal-mediated synthesis of medium-sized rings through higher order annulation is generally more difficult to achieve. Transition-metal propargyl and allyl complexes can undergo [3 + 2] cycloaddition with reactive alkenes and isocyanates.[6,7] Previously, we reported that tungsten η^3-*syn*-pentadienyl compounds underwent addition reactions with a variety of electrophiles *via* η^4-*trans*-diene intermediates.[8,9] In principle, η^3-*anti*-pentadienyl compounds can react with reactive olefins in a [5 + 2] cycloaddition pathway involving an envisaged η^4-*cis*-diene zweitterionic intermediate (Chart 1; bottom two structures).[8,9] Nevertheless, there is no precedent for this in the literature. Here, we report our efforts to achieve such a cycloaddition reaction for a tungsten η^3-*anti*-pentadienyl complex.

Chart 1



Results and Discussion

The starting compound **1** was readily prepared from $NaCpW(CO)_3$ and 1-chloro-4-methyl-4-penten-2-yne; the yield was 84%. As shown in Scheme 1, treatment of **1** with CF_3SO_3H (1.05 equiv) in cold diethyl ether (−40 °C), followed by addition of excess MeOH, afforded **2** in 71% yield after workup. Variable-temperature ^{1}H NMR of **2** showed the presence of the two conformational isomers **2a** and **2b** in a 1:1 molar ratio over the range −60 to 0 °C. Besides two methyl signals, there are ten singlets in the ^{1}H NMR spectra ($CDCl_3$, −40 °C) for the pentadienyl groups of the two species. Assignment of

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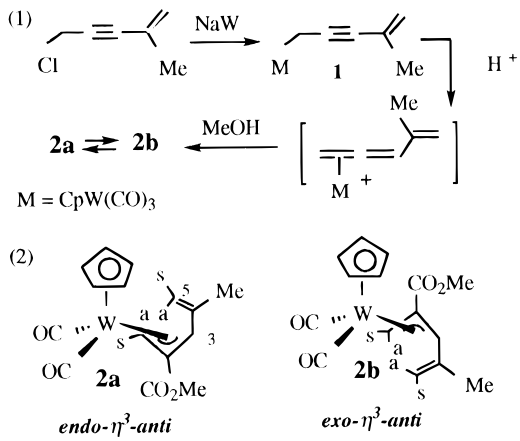
Scheme 1



the NMR signals was made on the basis of $^1H-^{13}C$ NMR correlation spectra as well as proton NOE effects. The two species underwent mutual exchange with an activation energy of 14.6(2) kcal/mol based on the coalescence temperature (T_c = 313 K, $\Delta\delta$ = 136 Hz).[10] The coalescence of NMR signals shows the following site exchanges: C^1H^s(**2a**)/C^1H^s(**2b**), C^1H^a(**2a**)/C^1H^a(**2b**), C^3H(**2a**)/C^3H(**2b**), and C^5H^a(**2a**)/ C^5H^a(**2b**). These two species were characterized to be η^3-*anti*-allyl species on the basis of proton NMR spectral data. Diagnostic for the *anti* structure is the chemical shifts of the H^3 protons of **2a** and **2b**, which have the values δ 5.06 and 4.70 ppm**,** respectively. The C^3H proton of *the syn* isomer is expected to have the chemical shift in the high-field δ 2.50−3.00 ppm region.[11] Therefore, we conclude that the exchange of these two species follows an *endo*−*exo* isomerization process via rotation of the metal−allyl bond as for $CpMo(CO)_2$(allyl) complexes; the observed ΔH (14.6(2) kcal/mol) of **2a** and **2b** is reasonable compared to other reported values (13−14 kcal/mol)[12] for this rotation. According to earlier reports,[12] we assign **2a** (H^{1a} δ 2.83 ppm) and **2b** (H^{1a} δ 2.01 ppm) to *endo* and *exo* conformers, respectively.

The ORTEP drawing of **2** is provided in Figure 1 that shows the vinyl group is *s-cis* to the allyl moiety; the pentadienyl ligand is η^3-coordinated to metal in a U-shaped conformation with the C(5)−C(6) (1.480(13) Å) and C(6)−C(8) (1.364(15) Å) lengths representing single and double bonds, respectively. The conformation of this solid-state structure is the endo form, with the allyl mouth facing the cyclopentadienyl group. The ^1H NMR spectrum (−40 °C) of **2** shows that both sickle-shaped and U-shaped species are present in the solution. For example, irradiation of the H^3 proton (δ 4.70 ppm) of **2b** led to an increase in the intensities of the =CH′ (δ 4.20 ppm) and methyl protons (δ 1.60 ppm) by 2.56% and 2.89%, respectively. A similar NOE effect is also observed for the same protons of **2a**. Generally, the equilibrium between sickle- and U-shaped conformers proceeds too rapidly to observe by ^1H NMR spectroscopy.

Compound **2** reacted smoothly with TCNE (1.0 equiv) in cold THF (−78 °C) to afford **3** as a yellow solid in

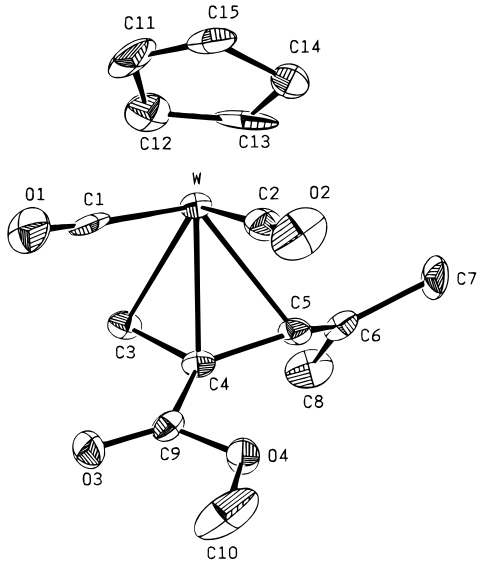
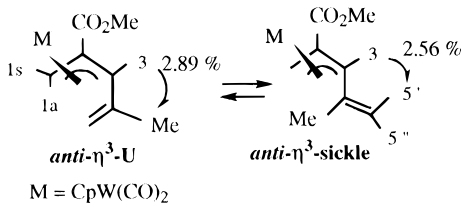


Figure 1. Molecular structure of compound **2**. Selected bond distances (Å) and angles (deg): W−C(3) = 2.294(9), W−C(4) = 2.270(8), W−C(5) = 2.338(7), C(5)−C(6) = 1.480(13), C(6)−C(8) = 1.364(15), C(6)−C(7) = 1.492(14); C(3)−C(4)−C(5) = 120.4(8), C(3)−C(4)-C(9) = 116.1(8), C(4)−C(5)−C(6) = 122.3(21), C(5)−C(6)−C(8) = 124.8(15).

Scheme 2



64% isolated yield. Spectral data indicated that **3** had a seven-membered-ring structure with TCNE linking to the two carbon termini of the U-shaped pentadienyl group. In the ^1H NMR spectra, the C(4) and C(7) methylene protons showed two AB quartets in the δ 2.75−4.05 ppm region. This proposed structure was further confirmed by an X-ray diffraction study; the ORTEP drawing shown in Figure 2 reveals that $CpW(CO)_2$ has undergone a 1,2-shift and become coordinated to the C(3)Me, C(4), and C(5) carbons in an η^3-allylic bonding fashion. Scheme 3 shows a plausible formation mechanism of **3**. The reaction was initiated by nucleophilic attack of the vinylic $=CH_2$ carbon[9] of **2** at TCNE, yielding the zwitterionic intermediate **A**, which underwent subsequent ring closure to give the observed product. In principle, both U- and sickle-shaped conformers are reactive toward TCNE; only the former can yield a cycloaddition product. The high yield of **3** (64%) implies that the reactivity of the U-shaped conformer toward TCNE is considerably higher than that for the sickle-shaped conformer.

We also examined the reaction of **2** with reactive isocyanates. Treatment of **2** with RN=C=O (R = $PhSO_2$, $CH_3C_5H_4SO_2$) in cold CH_2Cl_2 afforded **4a** and **4b** in 87% and 82% yields, respectively. Spectral data for **4a** and **4b** were not consistent with those expected for cycloaddition products. For example, ^1H NMR spectra of **4a** showed the presence of NH (δ 8.03 ppm) and =CH (δ 5.34 ppm) protons. ^1H NMR spectra (CD_2Cl_2, −40 °C) for **4a** and **4b** showed that only *endo* isomer was present in the solution. An X-ray diffraction study

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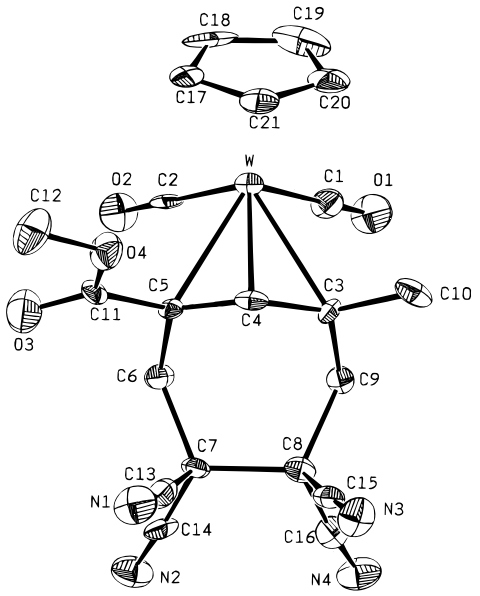
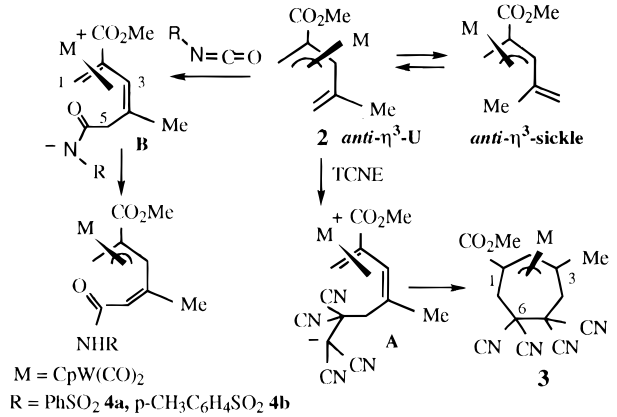


Figure 2. Molecular structure of compound **3**. Selected bond distances (Å) and angles (deg): W−C(3) = 2.406(10), W−C(4) = 2.195(11), W−C(5) = 2.362(10), C(3)−C(10) = 1.557(16), C(3)−C(4) = 1.398(10), C(4)−C(5) = 1.444(16), C(5)−C(11) = 1.437(15), C(11)−O(3) = 1.200(14); C(3)−C(4)−C(5) = 122.1(19), C(4)−C(5)−C(11) = 118.3(9), C(4)−C(3)−C(10) = 118.3(9).

Scheme 3



of **4a** has been performed with the ORTEP drawing given in Figure 3 that confirms the endo conformation. Compound **4a** adopts a sickle-shaped conformation with the five C(3)−C(7) carbons (ORTEP labeling) representing a η^3-pentadienyl group. Compound **4a** is envisaged to derive from the starting compound **2**, in which the vinyl proton is replaced with a $CONHSO_2Ph$ group. In this case the reaction can be considered to be an acylation reaction; compound **2** functions as a pentadienyl anion equivalent. Notably, the two bulky amide and metal−allyl groups are *cis* to each other. We propose the formation mechanism of **4a** and **4b** in Scheme 4 that involves the intermediate **B**, structurally related to **A**. In this intermediate, the newly generated amide anion is highly basic, so as to abstract the C^5 methylene protons, leading to formation of a *cis-anti*-pentadienyl group. A rapid intramolecular hydrogen transfer of this *σ-cis* (referring to C(4)−C(5) bond) intermediate **B** will give the observed *cis* product.

In this study, we have examined the reaction of a tungsten η^3-*anti*-pentadienyl complex with TCNE and isocyanates, leading to [5 + 2] and acylation reactions,

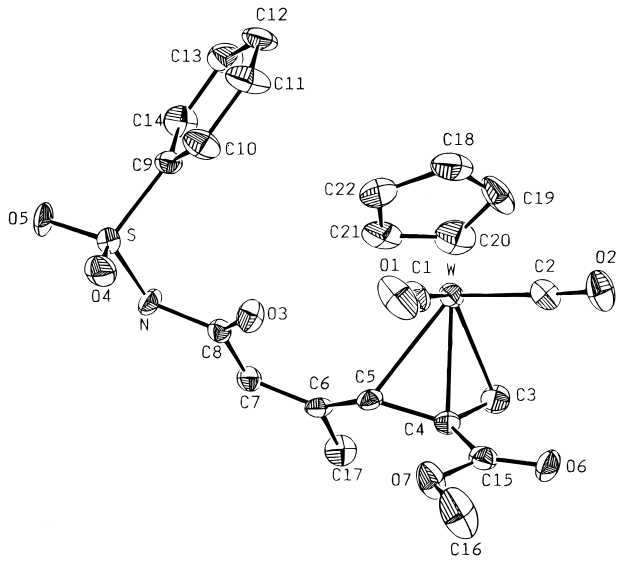


Figure 3. Molecular structure of compound **4a**. Selected bond distances (Å) and angles (deg): W−C(3) = 2.260(8), W−C(4) = 2.257(8), W−C(5) = 2.347(80), C(3)−C(10) = 1.557(16), C(3)−C(4) = 1.430(12), C(4)−C(5) = 1.446(14), C(5)−C(6) = 1.464(13), C(6)−C(7) = 1.343(13), C(7)−C(8) = 1.455(13), C(8)−O(3) = 1.214(11), C(3)−C(4)−C(5) = 119.2(8), C(4)−C(5)−C(6) = 126.1(7), C(5)−C(6)−C(7) = 121.0(8).

respectively; the former is more valuable in organic reactions. Although this π-allyl complex exists in two conformations, only the U-shaped conformer is the reactive species in the two reactions. To achieve the cycloaddition, the carbon anion generated in zwitterionic intermediate **A** and **B** must be nonbasic, such as $C(CN)_2^-$; otherwise the reaction leads to deprotonation.

Experimental Section

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, $BF_3{\cdot}Et_2O$, TCNE, propargyl alcohol, and sodium were obtained commercially and used without purification. 1-Chloro-4-methyl-4-penten-2-yne was prepared according to a literature report.[13]

Synthesis of $CpW(CO)_3(\eta^1$-4-methyl-4-penten-2-yn-1-yl) (1). To a THF solution (100 mL) of $CpW(CO)_3Na$ (ca. 56.8 mmol) was slowly added 1-chloro-4-methyl-4-penten-2-yne (7.20 g, 62.8 mmol) in THF (150 mL); the mixture was stirred for 5 h at 23 °C. The solution was evaporated to dryness, and the residues were chromatographed over a silica column to give a yellow band (R_f 0.75, 1/1 diethyl ether/hexane) that yielded **1** as a yellow solid (18.7 g, 45.4 mmol, 84%). IR (Nujol, cm^{-1}): ν(CO) 2013 (s), 1904 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 5.49 (5H, s, Cp), 5.09 (1H, s, =CH), 5.04 (1H, s, =CH), 2.01 (2H, s, C^1H_2), 1.86 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 228.9, 216.4 (W−CO), 128.2 (C^4), 118.4 (C^5), 99.1, 82.7 (C^2, C^3), 92.5 (Cp), 24.1 (Me), −31.7(C^1). Mass (75 eV): *m/z* 412 (M^+), 356 ($M^+ - 2CO$). Anal. Calcd for $C_{14}H_{12}WO_3$: C, 40.77; H, 2.94. Found: C, 40.66; H, 2.89.

Synthesis of $CpW(CO)_2$((1,2,3-η)-*anti*-2-(methoxycarbonyl)-4-methyl-2,4-pentadien-1-yl) (2). To a diethyl ether (30 mL) of **1** (0.30 g, 0.73 mmol) was added CF_3SO_3H (0.80 mmol, 1.1 equiv) at −40 °C; the solution was stirred for 1 h,

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Table 1. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement[a]

	2	3	4
formula	$WC_{15}H_{16}O_4$	$WC_{21}H_{16}N_4O_4$	$WC_{22}H_{21}NO_7S$
fw	444.13	572.23	627.31
diffractometer used	Nonius	Nonius	Nonius
space group	monoclinic, $P2_1$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a (Å)	8.1764(11)	11.1141(17)	8.1499(9)
b (Å)	10.5415(18)	10.818(3)	19.583(3)
c (Å)	8.7661(11)	17.140(4)	14.5664(18)
β (deg)	103.852(10)	103.865(14)	101.201(9)
V (Å^3)	733.59(18)	2000.8(8)	2280.6(5)
Z	2	4	4
D_{calcd} (g cm^{-3})	2.011	1.900	1.827
λ (Å)	0.7107	0.7107	0.7107
$F(000)$	422.	1100.	1220.
unit cell detn: no.; 2θ range (deg)	25; 21.00−31.10	24; 15.00−23.12	25; 12.48−22.10
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan width (deg)	$2(0.70 + 0.35 \tan\theta)$	$2(0.75 + 0.35 \tan\theta)$	$2(0.65 + 0.35 \tan\theta)$
scan speed (deg min^{-1})	2.06−5.50	5.50−8.24	2.06−8.24
2θ(max) (deg)	50.0	45.0	45.0
hkl ranges	−9 to +9, 0−12, 0−10	−11 to +11, 0−11, 0−18	−8 to +8, 0−21, 0−15
μ (cm^{-1})	80.500	59.260	52.030
cryst size (mm)	0.05 × 0.10 × 0.15	0.03 × 0.08 × 0.10	0.10 × 0.10 × 0.15
transmission	0.658; 1.000	0.940; 1.000	0.944; 1.000
temp (K)	298.00	298.00	298.00
no. of measd rflns	1370	2618	2979
no. of obsd rflns ($I > 2.0\sigma(I)$)	1224	1819	2074
no. of unique rflns	1370	2618	2979
R_F;R_w	0.021; 0.016	0.035; 0.033	0.030; 0.029
GOF	1.49	1.44	1.08
refinement program	NRCVAX	NRCVAX	NRCVAX
no. of atoms	36	46	53
no. of refined params	181 (1224 out of 1370 rflns)	272 (1819 out of 2618 rflns)	290 (2074 out of 2979 rflns)
minimize function	$\sum(w\|F_o - F_c\|^2)$	$\sum(w\|F_o - F_c\|^2)$	$\sum(w\|F_o - F_c\|^2)$
weighting scheme	$(1/\sigma^2)F_o$	$(1/\sigma^2)F_o$	$(1/\sigma^2)F_o$
g (2nd ext coeff) × 10^4	0.271(12)	0.41(4)	0.1(3)
$(\Delta/\sigma)_{max}$	0.0860	0.0540	0.0002
(D-map) max, min (e Å^{-3})	−0.540; 0.470	−0.720; 1.350	−0.430; 0.500

[a] $R_F = \sum(F_o - F_c)/\sum(F_o)$. $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$. GOF = $[\sum(w)F_o - F_c)^2)/((\text{no. of rflns}) - (\text{no. of params})]^{1/2}$. Three standard reflections were monitored every 3600 s; intensity variation was <2%.

gradually depositing yellow precipitates. To this solution was added MeOH (10 mL), and the mixture was stirred for 20 min before further addition of saturated $NaHCO_3$ solution (20 mL). The organic layer was extracted with diethyl ether (2 × 20 mL), concentrated, and eluted through a silica column to develop a yellow band that yielded **2** (R_f 0.66, 1/1 diethyl ether/hexane) as a yellow solid (0.23 g, 0.52 mmol, 71%). IR (Nujol, cm^{-1}): ν(CO) 1958(s), 1884(s); ^{1}H NMR (400 MHz, CD_2Cl_2): *endo* isomer, δ 5.16 (5H, s, Cp), 4.70 (1H, s, C^{3}H), 4.44 (1H, s, =CH), 4.20 (1H, s, =CH), 3.71 (3H, s, OMe), 3.49 (1H, d, C^{1}H^s, J = 1.5 Hz), 2.83 (1H, d, C^{1}H^a, J = 1.5 Hz), 1.60 (3H, s, Me); *exo* isomer, δ 5.30 (5H, s, Cp), 5.04 (1H, s, C^{3}H), 4.91 (1H, s, =CH), 4.75 (1H, s, =CH), 3.57 (3H, s, OMe), 3.38 (1H, d, C^{1}H^s, J = 1.8 Hz), 2.01 (1H, d, C^{1}H^a, J = 1.8 Hz), 1.03 (3H, s, Me). ^{13}C NMR (100 MHz, CD_2Cl_2): *endo* isomer, δ 223.3, 221.2 (W−CO), 171.3 (*C*O$_2$Me), 144.9 (C^4), 105.4 (C^5), 93.4 (Cp), 62.7 (C^2), 52.6 (C^3), 51.6 (OMe), 28.8 (C^1), 24.9 (Me); *exo* isomer, δ 223.6, 222.4 (W−CO), 174.3 (*C*O$_2$Me), 146.7 (C^4), 115.6 (C^5), 90.7 (Cp), 76.5 (C^2), 59.1 (C^3), 52.4 (OMe), 33.2 (C^1), 19.1 (Me). Mass (75 eV): m/z 444 (M$^+$), 416 (M$^+$ − CO), 388 (M$^+$ − 2CO). Anal. Calcd for $C_{15}H_{16}WO_4$: C, 40.57; H, 3.63. Found: C, 40.33; H, 3.69.

Synthesis of CpW(CO)$_2$((1*S,3*R**)-(1,2,3-η)-1-(methoxycarbonyl)-3-methyl-5,5,6,6-tetracyano-2-cyclohepten-1-yl) (3).** To a stirred THF (12 mL) solution of **2** (0.20 g, 0.45 mmol) was slowly added TCNE (0.060 g, 0.48 mmol) at −78 °C. The solution was warmed to 23 °C and stirred for an additional 2 h. To the solution was added water (5 mL); the mixture was concentrated and extracted with diethyl ether (2 × 20 mL). The extract was concentrated and eluted through a silica column to yield a yellow band (R_f 0.35, 4/1 diethyl ether/hexane) of **3** (0.16 g, 0.29 mmol, 64%). IR (Nujol, cm^{-1}): ν(CO) 1954 (s), 1879 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.65 (5H, s, Cp), 5.03 (1H, s, C^{2}H), 4.03 (1H, d, C^{7}H*H*′, J = 17.1 Hz), 3.73 (3H, s, OMe), 3.43 (1H, d, C^{4}H*H*′, J = 17.0 Hz), 3.09 (1H, dd, C^{4}H*H*′, J = 17.0 Hz), 2.75 (1H, dd, C^{7}H*H*′, J = 17.1 Hz), 2.06 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 226.1, 224.7 (W-CO), 174.4 (*C*O$_2$Me), 112.9, 112.2, 111.6, 111.3 (CN), 96.3 (Cp), 63.4 (C^2), 61.5 (C^1), 45.9 (OMe), 45.5, 44.3, 44.0 (C^3, C^5, C^6), 40.9, 34.6 (C^4, C^7), 30.6 (Me). MS (75 eV): m/z 572 (M$^+$), 416 (M$^+$ − 2CO). Anal. Calcd for $C_{21}H_{16}WO_4N_4$: C, 44.08; H, 2.82. Found: C, 44.60; H, 3.06.

Synthesis of CpW(CO)$_3$((1,2,3-η)-2-(methoxycarbonyl)-4-methyl-5-(((phenylsulfonyl)amino)carbonyl)-2,4-pentadien-1-yl) (4a). Compound **4a** was prepared similarly from **2** (0.020g, 0.45 mmol) and phenylsulfonyl isocyanate (0.080 g, 0.48 mmol); the yield was 82% (0.23 g, 0.37 mmol). IR (Nujol, cm^{-1}): ν(CO) 1976 (vs), 1905 (vs), 1690 (s). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.03 (1H, s, NH), 7.54−7.67 (5H, m, Ph), 5.34 (1H, s, C^{5}H), 5.25 (5H, s, Cp), 4.86 (1H, s, C^{3}H), 3.86 (1H, dd, C^{1}H^s, J = 1.2 Hz), 3.76 (3H, s, OMe), 2.83 (1H, dd, C^{1}H^a J = 1.2 Hz), 1.27 (3H, s, Me). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 220.3, 219.5 (W−CO), 166.0 (*C*O$_2$Me), 162.1, 133.0, 128.3, 127.9 (Ph), 163.9 (C^6), 139.3 (C^4), 122.5 (C^5), 93.1 (Cp), 66.8 (C^2), 51.7 (C^3), 49.0 (OMe), 40.2 (C^1), 20.9 (C^4*Me*). MS (75 eV): m/z 627 (M$^+$), 599 (M$^+$ − CO), 571 (M$^+$ − 2CO). Anal. Calcd for $C_{22}H_{21}WO_7NS$: C, 42.13; H, 3.37. Found: C, 42.50; H, 3.43.

Synthesis of CpW(CO)$_3$((1,2,3-η)-2-(methoxycarbonyl)-4-methyl-5-(((*p*-tolylsulfonyl)amino)carbonyl)-2,4-pentadien-1-yl) (4b). Compound **4b** was prepared similarly from **2** (0.020 g, 0.45 mmol) and phenylsulfonyl isocyanate (0.090 g, 0.48 mmol) in cold CH_2Cl_2 (−40 °C); the yield was 87% (0.25 g, 0.39 mmol). IR (Nujol, cm^{-1}): ν(CO) 1974 (s), 1909 (s), 1689 (s). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.56 (1H, s, NH), 7.65, 7.31 (4H, 2d, Ph), 5.37 (1H, s, C^{5}H), 5.21 (5H, s, Cp), 4.81 (1H, s, C^{3}H), 3.76 (3H, s, OMe), 3.67 (1H, dd, C^{1}H^s, J = 1.2 Hz), 2.85 (1H, dd, C^{1}H^a J = 1.2 Hz), 2.41 (3H, s, PhMe), 2.01 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.1, 220.9 (W−CO),

172.2 (CO_2Me), 165.6, 145.6, 130.3, 128.9 (Ph), 164.3 (C^6), 137.4 (C^4), 107.6 (C^5), 94.1 (Cp), 76.4 (C^2), 52.4 (C^3), 52.4 (OMe), 30.3 (C^1), 23.1 (C^4*Me*), 22.2 (PhMe). MS (75 eV): *m*/*z* 641 (M^+), 613 ($M^+ - CO$), 585 ($M^+ - 2CO$). Anal. Calcd for $C_{23}H_{23}WO_7NS$: C, 43.07; H, 3.61. Found: C, 43.60; H, 3.84.

X-ray Diffraction Studies of 2, 3, and 4a. Single crystals of **2**, **3**, and **4a** were sealed in glass capillaries under an inert atmosphere. Data for **2**, **3**, and **4a** were collected on a Nonius CAD 4 using graphite-monochromated Mo Kα radiation. The structures of **2**, **3**, and **4a** were solved by direct and heavy-atom methods, respectively; all data reduction and structural refinements were performed with the NRCCSDP package. Crystal data, details of data the collection, and structural analysis of these three compounds are given in Table 1. For all structures, all non-hydrogen atoms were refined with anisotropic parameters, and all hydrogen atoms included in the structure factors were placed in idealized positions.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for compounds **2**, **3**, and **4a** (16 pages). Ordering information is given on any current masthead page.

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