

# Synthesis and Reactivity of 7-Chloro-7-[tricarbonyl( $\eta^5$ -cyclopentadienyl)tungstenio]-dibenzonorcaradiene

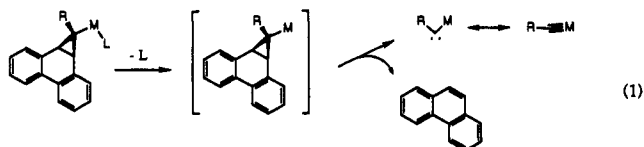
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The synthesis and reactivity of 7-chloro-7-(tricarbonylcyclopentadienyltungstenio)dibenzonorcaradiene (**2**) are described. Upon photolysis, **2** undergoes net CO dissociation and  $\alpha$ -elimination of Cl to produce a metastable cyclopropylidene complex (**3**) that subsequently rearranges to an  $\eta^2$ -dibenzocycloheptatetraene complex (**4**), which has been characterized by a single-crystal X-ray diffraction study. The transformations of **2** to **3** and **3** to **4** are both relatively insensitive to the presence of exogenous CO, suggesting that CO dissociation may not be a rate-limiting step in either reaction.

Substituted norcaradienes are useful precursors for the generation of carbenes, and a variety of carbenes have been prepared by eliminating benzene from norcaradienes.<sup>1</sup> This methodology is particularly well-suited for preparing carbenes from dibenzonorcaradienes, where there are fewer competing side reactions and the carbene-stabilizing effect of heteroatoms can accelerate the rate of carbene extrusion.<sup>2</sup> We have been exploring the possibility of using the carbene-stabilizing potential of transition metals to prepare metal-alkylidene complexes via carbene extrusion reactions of 7-metallo-dibenzonorcaradiene complexes (eq 1).

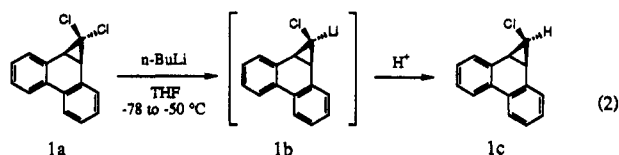


In this paper we report the synthesis and reaction chemistry of 7-chloro-7-(tricarbonylcyclopentadienyltungstenio)dibenzonorcaradiene (**2**). Upon thermolysis or photolysis this complex does not afford the desired metal-alkylidene complex. Instead,  $\alpha$ -elimination of chloride affords a metastable cyclopropylidene complex (**3**), which subsequently rearranges to an interesting  $\eta^2$ -dibenzocycloheptatetraene complex (**4**).

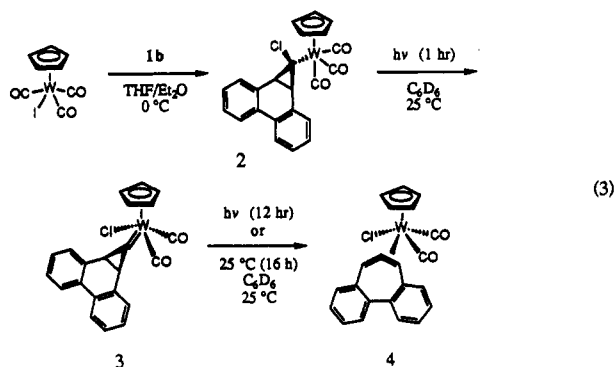
## Results and Discussion

The lithiation of readily available 7,7-dichlorodibenzonorcaradiene<sup>3</sup> (**1a**) affords **1b**, which upon reaction with CpW(CO)<sub>3</sub>I affords moderate yields ( $\geq 50\%$ ) of the corresponding metal-alkyl complex **2**. The stereochemistry of **2** was inferred from the protonation reactions of **1b** and

**2**, which both afford high yields of the known *endo*-7-chlorodibenzonorcaradiene (**1c**)<sup>4</sup> (reaction 2).



The photolysis (C<sub>6</sub>D<sub>6</sub>, 15 °C, 1 h) of **2** dissociates one carbonyl ligand and affords a 37% isolated yield of a new dibenzonorcaradiene complex, which was identified as **3** on the basis of combustion analysis and <sup>13</sup>C, <sup>1</sup>H, and IR spectral data. Of particular spectroscopic relevance was the presence of two carbonyl bands in the IR spectrum (CCl<sub>4</sub>, 2038 (s), 1969 (m) cm<sup>-1</sup>), two carbonyl resonances in the <sup>13</sup>C NMR spectrum ( $\delta$  210.73, 206.45;  $J_{CW} \sim 82$  Hz), and a <sup>13</sup>C resonance at  $\delta$  255.51 ( $J_{CW} = 56.1$  Hz) for the tungsten-alkylidene moiety.



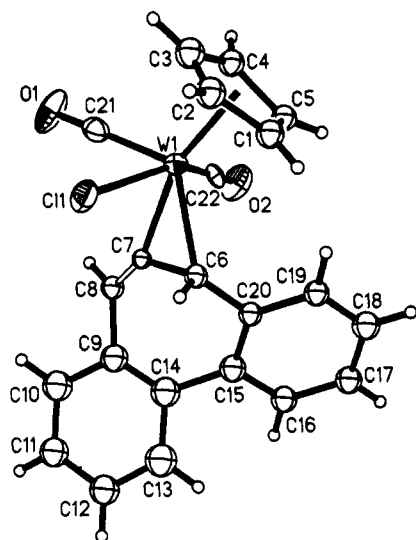
Cyclopropylidene complex **3** appears to be indefinitely stable at  $-40$  °C, but it slowly decomposes (C<sub>6</sub>D<sub>6</sub>, 16 h) upon warming to 25 °C. A typical product mixture contains numerous decomposition products, including trace amounts of phenanthrene, but the major decomposition product (67% by <sup>1</sup>H NMR yield) is an interesting new  $\eta^2$ -dibenzocycloheptatetraene complex (**4**) that preserves the stoichiometry of **3**. This same product is also obtained by the thermolysis of **2** (C<sub>6</sub>D<sub>6</sub>, 80 °C, 24 h or solid

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**Figure 1.** ORTEP plot of 4. Tungsten, chlorine, and carbonyl ligands were refined anisotropically. All other non-hydrogen atoms were refined isotropically. For clarity, thermal ellipsoids are plotted at 50% probability, the ether of solvation is omitted, and only one of the two crystallographically independent molecules from the asymmetric unit is shown. Selected distances (Å) and angles (deg) are as follows: W1–Cl1, 2.495 (6); W1–C6, 2.265 (20); W1–C7, 2.184 (17); C6–C7, 1.458 (29); C7–C8, 1.279 (26); W1–C21, 2.005 (27); W1–C22, 1.992 (28); W1–Cp centroid, 1.996; C6–W1–C7, 38.2 (7); Cl1–W1–C21, 81.9 (6); Cl1–W1–C22, 150.6 (6); C21–W1–C22, 86.8 (10); W1–C7–C6, 73.9 (10); W1–C7–C8, 147.2 (17); C6–C7–C8, 135.6 (19).

state, 120 °C, 0.01 Torr), but decomposition is much more extensive and the yield is correspondingly lower.

Our assignment of 4 as an  $\eta^2$ -dibenzocycloheptatetraene complex on the basis of spectroscopic data and a combustion analysis was confirmed by a single-crystal X-ray diffraction study. An ORTEP plot of 4 is shown in Figure 1.

The ether solvate of 4 crystallizes in the space group  $P2_1/c$  with two crystallographically independent molecules in the asymmetric unit ( $Z = 8$ ). The coordinated double bond, C7–C8, is significantly longer than the uncoordinated carbon–carbon double bond, C6–C7, and the bond angle for the coordinated allene unit, C6–C7–C8, is approximately 135°. The relatively high  $R$  factor for the structure ( $R_F = R_{wF} = 7.6\%$ ) does not warrant a more detailed discussion of bond distances and angles, but the bonding appears to be quite similar to that of a 1,2-cycloheptatetraene–iron complex that was crystallographically characterized by Jones and co-workers.<sup>5a</sup>

The most attractive mechanism for the formation of 3 from 2 involves CO dissociation and  $\alpha$ -elimination of chloride, but the rate at which 3 is formed from 2 is relatively unaffected by the presence of exogenous CO. If  $\alpha$ -migration is indeed the mechanism by which 3 is formed, migration of chlorine must be substantially faster than exchange of CO from the solvent cage with exogenous CO.  $\alpha$ -Migration of chlorine has been observed in a number of

systems,<sup>7</sup> but it is interesting to note that most known  $\alpha$ -substituted cyclopropyl complexes of transition metals do not appear to react via  $\alpha$ -migratory elimination pathways.<sup>8</sup> In fact, the formation of cyclopropylidene complexes from  $\alpha$ -substituted cyclopropyl complexes is quite rare and has only been observed under conditions where the  $\alpha$ -substituent can be intermolecularly abstracted without generating a coordinatively unsaturated metal center.<sup>6bc,9</sup>

We have not extensively explored the mechanism of the rearrangement of 3 to 4 except to note that exogenous CO (670 Torr) does not decrease the rate of the rearrangement reaction. In fact, the presence of exogenous CO during the transformation of 3 to 4 might actually produce a slight rate enhancement: the reaction of 3 under CO (670 Torr) is 80% complete after 13 h at 25 °C in the dark, whereas an identical reaction performed under N<sub>2</sub> (670 Torr) is only 46% complete. The mechanistic significance of this observation is questionable, however, because 4 reacts slowly with CO to produce CpW(CO)<sub>3</sub>Cl, as well as a number of other products derived from decomposition reactions of the free allene. Whatever the case, the relative insensitivity of the reaction to the presence of added CO certainly militates against the intermediacy of free carbenes and allenes, which should poorly compete with large excesses of CO for any coordinatively unsaturated metal complex in this system. It is possible, of course, that dissociation of CO is rate-limiting and that rearrangement to 4 is simply faster than exchange between CO in the solvent cage and free CO, but we currently favor a CO-independent, "one-step" intramolecular rearrangement of 3 to 4. This reaction would be similar to the reaction proposed by Lisko and Jones,<sup>9a</sup> and it would avoid the formation of highly energetic, coordinatively unsaturated intermediates.

There are surprisingly few examples of transition-metal-mediated cyclopropylidene-to-allene rearrangements, and all previous examples have occurred so rapidly that the intermediacy of the cyclopropylidene complex could only be inferred from their methods of preparation.<sup>6b,c,9</sup> To the best of our knowledge, the rearrangement of 3 to 4 represents the first case where both the starting cyclopropylidene complex and the resulting allene complex have been isolated and spectroscopically characterized.

## Experimental Section

**General Procedures.** Unless otherwise noted, all manipulations were performed under an atmosphere of dry nitrogen using either standard Schlenk techniques or a Vacuum Atmospheres Corp. Dri-Lab. Tetrahydrofuran (THF) and Et<sub>2</sub>O were distilled from sodium benzophenone ketyl. Benzene and hexanes were freshly distilled from dark purple solutions of potassium benzophenone ketyl containing tetraglyme. CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and CCl<sub>4</sub> were distilled from CaH<sub>2</sub> at atmospheric pressure. Column

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and filtration chromatographies were performed with basic alumina (Brockman Activity I, 80–200 mesh) which had been dried at 140 °C for 24 h.

Melting points were determined in sealed capillaries under dry nitrogen using a Mel-temp melting-point apparatus and are uncorrected. Infrared spectra were recorded with a Analect RFX-40 FTIR spectrometer. NMR spectra were recorded with a General Electric QE-300 spectrometer ( $^1\text{H}$ , 300.1 MHz;  $^{13}\text{C}$ , 75.48 MHz) or General Electric GN-500 spectrometer ( $^1\text{H}$ , 500.1 MHz;  $^{13}\text{C}$ , 125.03 MHz).  $^1\text{H}$  NMR chemical shifts are reported as  $\delta$  values in ppm relative to residual  $^1\text{H}$  resonances in the deuterated solvents:  $\text{CHCl}_3$  ( $\delta$  7.260),  $\text{C}_6\text{D}_6$  ( $\delta$  7.150),  $\text{THF-}d_8$  ( $\delta$  1.730).  $^{13}\text{C}$  NMR chemical shifts were measured relative to a solvent resonance ( $\text{CDCl}_3$ ,  $\delta$  77.00;  $\text{C}_6\text{D}_6$ ,  $\delta$  128.00).  $^1\text{H}$  NMR coupling constants are reported in Hz and refer to apparent multiplicities. High-resolution mass spectra were recorded on a VG Analytical 7070E spectrometer. Low-resolution mass spectra were obtained on a Finnigan 4000 GC/MS/DS spectrometer. Chemical ionization mass spectra were obtained by using isobutane and a voltage of 100 eV. Electron-impact mass spectra were obtained by using an ionizing potential of 70 eV. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Thermolysis experiments were conducted in a constant-temperature oil bath ( $\pm 2$  °C) in the dark to avoid possible competitive photochemical reactions.

**Synthesis of *endo*-7-Chloro-*exo*-7-[tricarbonyl( $\eta^5$ -cyclopentadienyl)tungsten]dibenzonorcaradiene (2).** *n*-Butyllithium (1.6 mL of 2.5 M hexane solution, 4.0 mmol) was added dropwise to a stirred solution of **1a**<sup>3</sup> (1.00 g, 3.83 mmol) in THF (25 mL) at  $-78$  °C. The reaction mixture was slowly warmed to  $-50$  °C while the progress of the transmetalation reaction was monitored by TLC (silica gel, hexane;  $R_f$  0.35 for **1a** and 0.15 for **1c**). After 30 min at  $-50$  °C, the intense blue solution contained negligible amounts of **1a** according to TLC. The solution was again cooled to  $-78$  °C, and then it was rapidly transferred via cannula to a 0 °C solution of  $\text{CpW}(\text{CO})_3\text{I}$ , which had been previously prepared by the reaction  $\text{CpW}(\text{CO})_3\text{Na}^{10}$  (1.43 g, 4.02 mmol in 50 mL of THF) with  $\text{I}_2$  (1.12 g, 4.41 mmol) in  $\text{Et}_2\text{O}$  (50 mL). The reaction mixture was allowed to warm to room temperature. After 1 h, the burgundy-colored solution was concentrated *in vacuo* to approximately 10 mL, ether ( $\sim 10$  mL) was added, the alkali halide salts were removed by vacuum filtration, and then the filtrate was evaporated (25 °C, 1 Torr) to afford a viscous slurry of crude **2**. The addition of benzene (5–10 mL) produced a bright yellow solid, which was collected by filtration, washed with benzene ( $2 \times 10$  mL) and ether (5 mL), and then dried under vacuum (25 °C,  $10^{-2}$  Torr). The yellow microcrystalline sample of **2** obtained in this manner was pure according to  $^1\text{H}$  NMR spectroscopy (1.14 g, 53%) and could be used without further purification. Analytically pure material was obtained by carefully layering ether on a concentrated THF solution of **2** and allowing the layers to diffuse overnight at  $-40$  °C.

For **2**: mp 165 °C dec; FT IR ( $\text{CCL}_4$ ) 2031 (s), 1954 (s), 1919 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500.1 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$  7.984 (app d,  $J = 7.7$  Hz, 2H, aromatic), 7.397 (app d,  $J = 7.3$  Hz, 2H, aromatic), 7.33–7.26 (m, 4H, aromatic), 5.683 (s, 5H, Cp), 3.094 (s, 2H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.03 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$  228.28 ( $J_{\text{CW}} = 57.5$  Hz, one M–CO), 217.37 ( $J_{\text{CW}} = 80.5$  Hz, two M–CO's), 133.06, 131.79, 130.04, 127.44, 126.74, 122.28 (aromatic C's), 93.52 (Cp), 41.16 (CH's), 9.68 (C<sub>7</sub>); CIMS (100 eV, isobutane) *m/e* (relative intensity) 559 (MH<sup>+</sup>, 1), 179 (base); EIMS (70 eV, direct inlet) *m/e* (relative intensity) 502 (M<sup>+</sup>–2CO, 1), 474 (M<sup>+</sup>–3CO, 4), 438 (23, M<sup>+</sup>–3CO–Cl), 352 (CpW(CO)<sub>2</sub>≡CCl<sup>+</sup>, 5), 324 (CpW(CO)≡CCl<sup>+</sup>, 6), 296 (CpW≡CCl<sup>+</sup>, 3), 178 (C<sub>14</sub>H<sub>10</sub><sup>+</sup>, 100). Anal. Calcd for C<sub>23</sub>H<sub>15</sub>ClO<sub>3</sub>W: C, 49.45; H, 2.71. Found: C, 49.73; H, 2.59.

**Photochemical Synthesis of 3.** A solution of **2** (225 mg, 403 μmol) in benzene (15 mL) was placed in a 150 mm × 18 mm

Pyrex test tube with a stir bar and photolyzed for 1 h at a distance of 13 cm with a 450-W Hanovia medium-pressure lamp. The temperature of the sample was maintained at approximately 15 °C by placing the test tube inside an ice-water-cooled condenser, which was blanketed with dry air to prevent condensation. Evaporation of the solvent (25 °C, 10 Torr) afforded an orange residue, which was washed with cold THF ( $-40$  °C,  $3 \times 1$  mL) to remove unreacted **2**, CpW(CO)<sub>3</sub>Cl, and miscellaneous organic side products. The crude orange solid was dissolved in approximately 1 mL of THF at 25 °C, and then precipitated by slowly adding hexane. Pure microcrystalline **3** was obtained by quickly decanting the solvent, washing with ether (1 mL), and drying *in vacuo* (25 °C,  $10^{-2}$  Torr). Yield: 80 mg (37%). The compound decomposed upon standing at room temperature, but can be stored indefinitely at  $-40$  °C in the dark.

For **3**: FT IR ( $\text{CCL}_4$ ) 2038 (s), 1969 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500.1 MHz, THF-*d*<sub>8</sub>,  $-60$  °C)  $\delta$  8.106 (d,  $J = 8.6$  Hz, 1H, aromatic), 8.064 (app d,  $J = 8.0$  Hz, 1H, aromatic), 7.657 (d,  $J = 8.6$  Hz, 1H, aromatic), 7.594 (d,  $J = 7.4$  Hz, 1H, aromatic), 7.48–7.31 (m, 2H, aromatic), 7.321 (app t, 1H, aromatic), 7.293 (app t, 1H, aromatic), 5.935 (s, 5H, Cp), 3.406 (d,  $J = 11$  Hz, 1H, CH), 3.296 (d,  $J = 11$  Hz, 1H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.03 MHz, THF-*d*<sub>8</sub>,  $-60$  °C)  $\delta$  255.51 ( $J_{\text{CW}} = 56.1$  Hz, carbene C), 210.73 ( $J_{\text{CW}} = 81.9$  Hz, one M–CO), 206.45 ( $J_{\text{CW}} = 82.5$  Hz, one M–CO), 131.72 (q), 130.85 (q), 130.35 (two C's, q), 130.29, 129.79 (q), 129.08, 129.00, 127.95, 127.72, 124.61, 123.81 (aromatic C's), 99.67 (Cp), 43.36 (CH), 40.39 (CH); CIMS (100 eV, isobutane) *m/e* (relative intensity) 496 (MH<sup>+</sup>–Cl), 179 (base); EIMS (70 eV, direct inlet) *m/e* (relative intensity) 440 (1), 192 (23), 191 (18), 178 (C<sub>14</sub>H<sub>10</sub><sup>+</sup>, 100).

**Photochemical Synthesis of 4.** A solution of **3** (524 mg, 0.938 mmol) in benzene (30 mL) was placed in a 160 mm × 5 mm glass tube under nitrogen and photolyzed for 12 h at a distance of 7.5 cm with a 150-W sunlamp. Evaporation of the solvent (25 °C, 0.1 Torr) afforded a brown residue, which was dissolved in THF (0.5 mL); the solution was placed on a 2-cm pad of basic Al<sub>2</sub>O<sub>3</sub> in a 15-mL medium sintered glass frit. Elution with ether afforded a yellow band of CpW(CO)<sub>3</sub>Cl and phenanthrene. Further elution with THF afforded an orange fraction, which was concentrated *in vacuo* (25 °C, 10 Torr) to a volume of  $\sim 5$  mL. Analytically pure **4** was obtained by carefully layering ether (10 mL) over the solution and cooling to  $-40$  °C overnight. Yield: 293 mg (59%) as an orange microcrystalline solid.

For **4**: mp 134–137 °C dec; FT IR ( $\text{CCL}_4$ ) 2036 (s), 1979 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500.1 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$  7.633 (d,  $J = 7.5$  Hz, 1H), 7.516 (d,  $J = 7.6$  Hz, 1H), 7.37–7.24 (m, 6H), 6.952 (d,  $J = 7.4$  Hz, 1H), 5.769 (s, 5H, Cp), 4.098 (d,  $J = 2.4$  Hz, 1H, =CH–);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.03 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$  211.25 ( $J_{\text{CW}} = 65.8$  Hz, M–CO), 206.69 ( $J_{\text{CW}} = 74.3$  Hz, M–CO), 169.44 ( $J_{\text{CW}} = 11.0$  Hz, allenic C), 149.76 (q), 142.59 (q), 141.12 (q), 140.62 (q), 132.01, 121.91, 131.55, 128.98, 127.22, 127.05, 126.68, 126.53 (aromatic C's), 121.82 (allenic CH), 99.67 (Cp), 28.40 ( $J_{\text{CW}} = 10.3$  Hz, allenic CH); CIMS (100 eV, isobutane) *m/e* (relative intensity) 496 (MH<sup>+</sup>–Cl, 2), 179 (base); EIMS (70 eV, direct inlet) *m/e* (relative intensity) 440 (2), 192 (53), 191 (48), 178 (C<sub>14</sub>H<sub>14</sub><sup>+</sup>, 100). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>ClO<sub>2</sub>W: C, 49.79; H, 2.85. Found: C, 49.39; H, 2.89.

**Thermolysis of 2 under Vacuum and CO (670 Torr).** Identical samples of **2** (5 mg, 0.053 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL) were prepared in 5-mm Pyrex NMR tubes; one tube was sealed under vacuum, while the other was sealed under 670 Torr of CO. Thermal reactions were conducted side-by-side and analyzed periodically by  $^1\text{H}$  NMR spectroscopy. After 42 h at 60 °C, 55% of the sample sealed under vacuum had reacted to give **4**, CpW(CO)<sub>3</sub>Cl, and phenanthrene in yields of 21%, 3%, and 4%, respectively. For the sample sealed under CO, 49% of the starting material had reacted and the yields of **4**, CpW(CO)<sub>3</sub>Cl, and phenanthrene were 26%, 13%, and  $\sim 1\%$ , respectively. The reaction temperature was then raised to 80 °C for 24 h. For the sample sealed under vacuum, 76% of the starting material had reacted and the yields of **4**, CpW(CO)<sub>3</sub>Cl, and phenanthrene were 18%, 12%, and 6%, respectively. For the reaction performed under CO, 87% of the starting material had reacted and the

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yields of 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene were 31%, 47%, and 13%, respectively. In all spectra recorded at intermediate times, the relative yields of all products in both reactions were comparable and only traces of 3 could be detected.

The thermolysis of solid 2 (110 °C,  $10^{-2}$  Torr, overnight) produced small amounts of sublimate containing 2, 3, and 4 in an approximate ratio of 1:1:0.5. Trace amounts of  $\text{CpW}(\text{CO})_3\text{Cl}$  and phenanthrene were also observed by  $^1\text{H}$  NMR spectroscopy.

These results strongly suggest that the thermal transformation of 2 to 4 occurs via 3 and without CO dissociation prior to the rate-determining step.

**Photochemical Reactions of 2 under CO and under  $\text{N}_2$ .** Identical samples of 2 (5 mg, 0.053 mmol) in  $\text{C}_6\text{H}_6$  (0.3 mL) were prepared in 5-mm Pyrex NMR tubes; one tube was sealed under 670 Torr of CO, while the other was purged with a steady stream of dry nitrogen. Photolysis reactions were conducted side-by-side using a 450-W Hanovia lamp as described above and analyzed periodically by  $^1\text{H}$  NMR spectroscopy. After 5 min, 93% of the sample under nitrogen had reacted to give 3, 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene in yields of 55%, 5%, 13%, and 8%, respectively. For the sample sealed under CO, 88% of the starting material was consumed after 5 min and the yields of 3, 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene were 39%, 3%, 12%, and 8%, respectively. After an additional 5 min of photolysis, only traces of starting material remained in the sample under nitrogen and the yields of 2, 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene were 48%, 4%, 15%, and 12%, respectively. For the reaction performed under CO, 5% of the starting material was unreacted and the yields of 2, 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene were 38%, 6%, 21%, and 15%, respectively. After 50 min of total photolysis time, the sample under nitrogen had 2, 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene in yields of 23%, 12%, 19%, and 22%. The corresponding yields for the reaction performed under CO were 20%, 11%, 35%, and 25%. Except for the somewhat higher yields of  $\text{CpW}(\text{CO})_3\text{Cl}$  obtained under CO, which presumably resulted from CO-trapping reactions of other decomposition products, the relative yields of all products in both reactions were very similar. These results strongly suggest that the photochemical transformations of 2 to 3 and 3 to 4 do not involve CO dissociation reactions prior to the rate-determining step.

**Thermal Reactions of 3 under Vacuum and CO (670 Torr).** Identical samples of 3 (10. mg, 0.019 mmol) in  $\text{C}_6\text{H}_6$  (0.8 mL) were prepared in NMR tubes; one tube was sealed under vacuum,

while the other was sealed under 670 Torr of CO. Both tubes were wrapped in Al foil to exclude light and allowed to stand at 25 °C. The progress of the reactions was periodically monitored by  $^1\text{H}$  NMR spectroscopy. After 13 h at 25 °C, 44% of the starting material from the sample sealed under  $\text{N}_2$  had reacted to afford 4. For the sample sealed under an atmosphere of CO, 80% of the starting material had reacted to give 4,  $\text{CpW}(\text{CO})_3\text{Cl}$ , and phenanthrene in yields of 30%, 30%, and 18%, respectively.

**Collection of X-ray Diffraction Data for  $\text{C}_{22}\text{H}_{15}\text{O}_2\text{ClW}$  (4).** Crystals of 4 suitable for X-ray diffraction were grown from slow diffusion of ether carefully layered onto a concentrated THF solution of 4 at -40 °C. Crystal data for 4 [ $\text{C}_{22}\text{H}_{15}\text{O}_2\text{ClW} \cdot \frac{1}{2}\text{C}_4\text{H}_{10}\text{O}$ , fw 567.7] are as follows: monoclinic  $P2_1/c$ ,  $a = 13.462(5)$  Å,  $b = 23.100(4)$  Å,  $c = 13.413(3)$  Å,  $\beta = 100.84(3)^\circ$ ,  $V = 4097(2)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.841$  g/cm<sup>3</sup> ( $Z = 8$ ). A total of 5832 unique reflections with  $4.0 \leq 2\theta \leq 45.0^\circ$  were collected on a Syntex P2<sub>1</sub> diffractometer at 183 K with use of graphite-monochromated Mo  $K\alpha$  radiation. The structure was solved by direct methods (SHELXTL-PLUS). Full-matrix least-squares refinement of positional and thermal parameters for all non-hydrogen atoms led to convergence with  $R_F = 7.6\%$ ,  $R_{wF} = 7.6\%$ , and  $\text{GOF} = 1.64$  for 314 variables refined against those 3992 data with  $|F_o| > 3.0\sigma|F_o|$ . (Anisotropic thermal ellipsoids were used for W, Cl, and CO ligands; isotropic ellipsoids were used for all others.) All other details regarding the crystal structure appear in the supplementary material.

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**Supplementary Material Available:** X-ray crystal data for 4, including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles, and ORTEP figures (14 pages). Ordering information is given on any current masthead page.

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