

for 1-2 half-lives. After being quenched with cold 1 M HClO<sub>4</sub>, the product mixtures were separately chromatographed on chilled Sephadex columns, with acidified 0.25 M NaClO<sub>4</sub> as the eluent. The O- and S-bonded monothiocarbamate isomers eluted together, followed by the aqua complex. The individual isomer concentrations for mixtures were determined from the absorbances at 295 and 227 nm by using the following data: (NH<sub>3</sub>)<sub>3</sub>CoOC(NHCH<sub>3</sub>)S<sup>2+</sup>,  $\epsilon(295) = 812$ ,  $\epsilon(227) = 16800$ ; (NH<sub>3</sub>)<sub>3</sub>CoSC(NHCH<sub>3</sub>)O<sup>2+</sup>,  $\epsilon(295) = 7895$ ,  $\epsilon(227) = 6406$ . The aqua complex was determined by using  $\epsilon(492) = 47.7$ . Experiments were performed in duplicate. Cobalt recoveries never exceeded about 95% because of the production of black cobaltic sulfide, which remained at the top of the column. The coproduction of Co<sup>II</sup> was detected and determined by using the Kitsen method. In one set of experiments, the S-isomer was reacted for 570 s in 0.1 M NaOH at 25 °C. The only Co<sup>III</sup> species recovered was starting material (37.9%; corresponding to  $k_2(\text{obsd}) = 1.7 \times 10^{-3} \text{ s}^{-1}$  (cf. direct spectrophotometric value,  $1.1 \times 10^{-3} \text{ s}^{-1}$ , Table I, supplementary material). When reaction proceeded for shorter or longer periods, a similar result was obtained, i.e., no aqua product. In a corresponding set of experiments starting with the O-isomer, for reaction at 25 °C for 302 s in 0.1 M NaOH, recovered O-isomer was determined as 26.1%, S-isomer as 38.5%, and aqua complex as 16.6%;

the balance (19.5%) was Co<sup>II</sup> and cobaltic sulfide. The percent consumed O-isomer corresponds to  $k_1(\text{obsd}) = 4.4 \times 10^{-3} \text{ s}^{-1}$  (cf. direct spectrophotometric value,  $4.45 \times 10^{-3} \text{ s}^{-1}$ , Table II, supplementary material), while the amount of S-isomer observed, corrected for its secondary reaction as well as for incomplete reaction of the O-isomer, corresponds to an initial product ratio of 36% aqua complex/64% S-isomer. Another calculation, based on the observed proportion of aqua complex, gave a product distribution of 23% aqua complex/77% S-isomer. A mean distribution of  $70 \pm 7\%$  S-isomer/30  $\pm 7\%$  aqua complex accommodates both sets of results.

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**Registry No.** [(NH<sub>3</sub>)<sub>3</sub>CoSC(NHCH<sub>3</sub>)O](ClO<sub>4</sub>)<sub>2</sub>, 106782-09-6; [(NH<sub>3</sub>)<sub>3</sub>CoOC(NHCH<sub>3</sub>)S]S<sub>2</sub>O<sub>6</sub>, 106782-11-0; [(NH<sub>3</sub>)<sub>3</sub>CoOH](ClO<sub>4</sub>)<sub>2</sub>, 18885-27-3; CH<sub>3</sub>NCS, 556-61-6; OP(OCH<sub>3</sub>)<sub>3</sub>, 512-56-1.

**Supplementary Material Available:** Tables I and II, giving kinetic data (3 pages). Ordering information is given on any current masthead page.

Contribution from the Specialty Chemicals Division, Engelhard Corporation, Menlo Park, New Jersey 08818, and Departments of Chemistry, Wayne State University, Detroit, Michigan 48202, and University of North Dakota, Grand Forks, North Dakota 58202

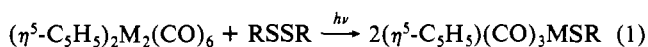
## Preparation and Reactivity of Tricarbonyl( $\eta^5$ -cyclopentadienyl)(organothiolato)tungsten Complexes with Potentially Chelating Thiolate Ligands

Kathryn L. Brandenburg,<sup>†</sup> Mary Jane Heeg,<sup>†</sup> and Harmon B. Abrahamson\*

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The photochemical reaction of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub> with the organic disulfides bis(2-pyridyl) disulfide, bis(2-benzothiazolyl) disulfide, and bis(*o*-aminophenyl) disulfide, using visible irradiation, produces mononuclear tungsten carbonyl complexes containing monodentate thiolate ligands. Disappearance quantum yields for the tungsten dimer in the formation reaction are >0.4 and are higher with 546-nm irradiation than with 366-nm light. Carbonyl loss from ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>3</sub>WSR, R = 2-pyridyl or 2-benzothiazolyl, can be induced thermally, or photochemically with ultraviolet light, to yield dicarbonyl complexes with chelated thiolate ligands. Quantum yields for the chelation reaction are higher with 366-nm than with 436-nm irradiation; values of  $\Phi$  at 366 nm are  $\geq 0.6$  for both benzothiazole- and pyridinethiolates. Similar reactions where R = *o*-aminophenyl do not result in a chelated product, but instead may form oligomers. The monodentate nature of the benzothiazolethiolate ligand in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)W(CO)<sub>3</sub>S-(CNC<sub>6</sub>H<sub>4</sub>S) has been validated by X-ray crystallography. The molecule crystallizes in space group C2/c, with unit cell parameters  $a = 24.03$  (3) Å,  $b = 10.236$  (3) Å,  $c = 12.526$  (4) Å,  $\beta = 95.63$  (4)°, and  $Z = 8$ .

Photolysis of metal-metal-bonded carbonyl dimers is known to produce reactive metal carbonyl radicals.<sup>1,2</sup> These photo-generated radicals react with organic disulfides to produce metal carbonyl thiolate complexes, e.g.<sup>3-5</sup>



M = Mo, W

Reactions of metal carbonyl dimers with organic disulfides can also form metal thiolate complexes via thermal routes.<sup>6,7</sup> In cases where subsequent chelation reactions are possible, thermal routes form only bidentate compounds.<sup>8</sup>

The loss of CO from metal carbonyl compounds has been observed to occur by both photochemical and thermal pathways. Photochemical reactions of metal carbonyls result in the dissociative loss of a carbonyl ligand,<sup>2,9</sup> and thermal substitutions proceed by a dissociative mechanism with the loss of CO as the rate-determining step.<sup>10</sup> The resulting coordinatively unsaturated compound may recombine with CO or react with another two-electron-donor ligand. Intramolecular substitution is easily brought

about with  $\pi$ - or  $\sigma$ -donor systems linked to  $\sigma$ -bonded ligands.<sup>4,5,11,12</sup>  $\sigma$ -to- $\pi$  rearrangements as a consequence of CO lability have been observed for several organometallic compounds.<sup>11</sup>

Previous work has shown the photoreaction of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub> with a thiuram disulfide to be an efficient method to prepare a mononuclear tungsten complex containing a monodentate dithiocarbamate ligand,<sup>4,5</sup> whereas previous thermal routes only resulted in chelated complexes.<sup>8</sup> The results presented below confirm the usefulness of this method for the production of mononuclear tungsten complexes with monodentate thiolate ligands regardless of the type of potentially chelating ligand used. We also report a detailed investigation of the subsequent photochemical and thermal reactivity of these products containing monodentate thiolate ligands.

\* To whom correspondence should be addressed at the University of North Dakota.

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<sup>†</sup> Wayne State University.

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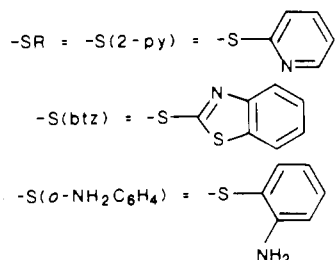
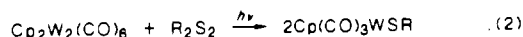
**Table I.** Electronic and Carbonyl-Region Infrared Spectral Data for  $\text{CpW}(\text{CO})_3\text{SR}$ 

RS	wavelength, nm ( $\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$ ) <sup>a</sup>	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$ <sup>b</sup>
<i>o</i> -NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> S	475 (1250)	2026, 1937 (br)
(2-py)S	472 (2040)	2033, 1951, 1930
(2-btz)S	473 (2020), 314 (14900)	2039, 1959, 1938
Me <sub>2</sub> dtc	460 (1230) <sup>c</sup>	2036, 1958, 1932 <sup>c</sup>

<sup>a</sup>In toluene solution. <sup>b</sup>In methylene chloride solution. <sup>c</sup>Data from ref 5.

## Results and Discussion

**Synthesis and Characterization.** The photochemical reaction of  $\text{Cp}_2\text{W}_2(\text{CO})_6$  with organic disulfides using visible irradiation produces mononuclear tungsten carbonyl complexes with monodentate thiolate ligands.<sup>13</sup>



The tungsten thiolate complexes were prepared by a photochemical method (see Experimental Section), isolated, purified, and characterized spectroscopically. A representative complex ( $\text{R} = 2\text{-benzothiazolyl}$ ) gives a satisfactory elemental analysis, and a single-crystal X-ray diffraction structure determination (see below) provides conclusive evidence of the monodentate nature of the ligand.

Carbonyl-region infrared spectra (Table I) show that all three products are tricarbonyl species, indicating that the potential additional ligating sites on the side chains of the thiolate ligands are not bound. Thus, this synthetic method can be used to produce monodentate/mononuclear metal thiolate complexes, where the thermal routes yield only chelated complexes.

**Photochemistry of the Cross-Coupling Reaction.** Visible irradiation of a mixture of  $\text{Cp}_2\text{W}_2(\text{CO})_6$  and  $\text{RSSR}$  in toluene produces changes in the color of the solution from red to orange or golden yellow as the visible absorption maximum changes from that for  $\text{Cp}_2\text{W}_2(\text{CO})_6$  to that for the product  $\text{Cp}(\text{CO})_3\text{WSR}$ . Electronic spectral data for these compounds are given in Table I. Infrared spectra of solutions irradiated in sealed solution cells show a decrease in the intensity of carbonyl stretching bands of the dimer and growth of bands associated with  $\text{Cp}(\text{CO})_3\text{WSR}$ . Following the concentrations of the reactant and the products by UV-vis spectroscopy shows that the 2:1 product-to-reactant ratio expected from reaction 2 is found. Retention of isosbestic points throughout the experiment reinforces the clean nature of the transformation. The reaction can be pushed to completion, with rates of product formation and dimer consumption decreasing at longer irradiation times as the fraction of light absorbed by the reactant decreases.

Both visible and ultraviolet and irradiations are effective for the cross-coupling reaction (reaction 1) of  $\text{Cp}_2\text{W}_2(\text{CO})_6$  with an organic disulfide.<sup>14</sup> In reactions where the disulfide bears a potential chelating group (studied here), the primary photoproduct is sensitive to ultraviolet irradiation, but not to visible light, and secondary photolysis produces a chelated product (see below). In these cases where chelation reactions of the primary photoproduct are possible, use of visible irradiation minimizes secondary pho-

**Table II.** Quantum Yields for the Reaction of  $\text{Cp}_2\text{W}_2(\text{CO})_6$  with  $\text{S}_2\text{R}_2$ <sup>a</sup>

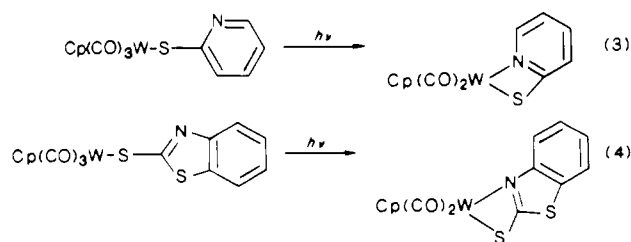
(RS) <sub>2</sub> <sup>b</sup>	irradn wavelength, nm <sup>c</sup>	quantum yields <sup>d</sup>	
		disappearance	appearance
[(2-py)S] <sub>2</sub>	366	0.58 (3)	1.07 (8)
	546	0.72 (4)	1.36 (8)
[(2-btz)S] <sub>2</sub>	366	0.39 (2)	0.78 (3)
	546	0.62 (3)	1.16 (6)
Me <sub>2</sub> dtc) <sub>2</sub>	546	0.44 (6) <sup>e</sup>	0.86 (12) <sup>e</sup>
	546	0.97 (8) <sup>e,f</sup>	1.92 (20) <sup>e,f</sup>

<sup>a</sup>Quantum yields were measured in toluene solutions containing  $(3\text{--}5) \times 10^{-4}$  M tungsten dimer and  $(1\text{--}1.5) \times 10^{-3}$  M disulfide. See the Experimental Section for details of procedures. <sup>b</sup>See footnote 13 for abbreviations. <sup>c</sup>Irradiation intensities were  $1 \times 10^{-6}$  einstein/min at 366 nm and  $(3\text{--}5) \times 10^{-7}$  einstein/min at 546 nm. <sup>d</sup>Standard deviation (from the data reduction) of the last digit is in parentheses. Total error of the determination is 2 or 3 times this amount. <sup>e</sup>Data from ref 5. <sup>f</sup>Equal concentrations ( $4 \times 10^{-4}$  M) of tungsten dimer and thiuram disulfide were used.

tolysis. Thermal chelation reactions are minimized by photolysis at 0 °C.

The quantum yields for disappearance of the tungsten dimer and formation of the monodentate tungsten thiolate product are listed in Table II. The ratio  $N$  of quantum yield for appearance of product to quantum yield for disappearance of metal dimer ranges from 1.84 to 2.00, giving additional evidence that both halves of the tungsten dimer are involved in the formation of products, again following the stoichiometry of reaction 2. The disappearance quantum yields for the tungsten dimer in reaction 2 are quite substantial with 546-nm irradiation, as is the case for analogous photoreaction using tetramethylthiuram disulfide<sup>5</sup> (see Table II). In addition, note that the visible-wavelength (546-nm) quantum yields are substantially higher than those for ultraviolet (366-nm) irradiation. A similar pattern is seen for a number of other disulfides.<sup>14</sup> This may indicate that the excited state of  $\text{Cp}_2\text{W}_2(\text{CO})_6$  populated by 366-nm excitation ( $\sigma \rightarrow \sigma^*$ )<sup>1,2,15</sup> decays both by CO loss and by homolytic cleavage, while the lowest reactive excited state populated by visible irradiation ( $\pi d \rightarrow \sigma^*$ )<sup>1,2,15</sup> produces only radical cleavage. This is consistent with the observation of carbonyl-loss intermediates produced by ultraviolet irradiation,<sup>1,16</sup> while we see no products involving CO loss with 546-nm excitation. An alternative explanation of the wavelength dependence involves the consideration of intensity and optical density effects,<sup>17</sup> for which lower values of each favor higher quantum yields. A detailed analysis of both of these potential explanations will be presented separately.<sup>14</sup>

**Photochemical Chelation.** Irradiation of either  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-py})$  or  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  with broad-band ultraviolet irradiation leads to loss of one carbon monoxide ligand, forming a dicarbonyl chelated complex:



Ultraviolet irradiation of either of the two tricarbonyltungsten compounds produces changes in the color of the solution from golden yellow or orange to bright yellow as the absorption maxima shift from those associated with the tungsten thiolate monodentate complexes to those of the chelated complexes. Isosbestic points are maintained throughout the photolysis [ $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$ ,

(13) Abbreviations used in this paper: Cp =  $\eta^5$ -cyclopentadienyl; 2-py = 2-pyridyl; 2-btz = 2-benzothiazolyl; *o*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub> = *o*-aminophenyl; Me<sub>2</sub>dtc = dimethyldithiocarbamate.  
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**Table III.** Electronic and Carbonyl-Region Infrared Spectral Data for  $\text{Cp}(\text{CO})_2\text{WSR}^a$ 

SR	wavelength, nm ( $\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$ ) <sup>b</sup>	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$ <sup>c</sup>
S(2-btz)	400 (1960)	1948, 1853
S(2-py)	421 (3770)	1945, 1849
$\text{Me}_2\text{dtc}$	417 (3780) <sup>d</sup>	1936, 1839 <sup>d</sup>

<sup>a</sup> Chelated complex. <sup>b</sup> In toluene; measured after photolysis of the corresponding tricarbonyl compound did not show any further changes. Extinction coefficients were calculated by taking the final concentration of dicarbonyl compound as equal to the initial concentration of tricarbonyl. Retention of isosbestic points throughout the photolyses supports the absence of decomposition. <sup>c</sup> In methylene chloride. <sup>d</sup> References 4 and 5.

**Table IV.** Quantum Yields for Carbonyl Loss from  $\text{CpW}(\text{CO})_3\text{X}$ 

X	quantum yield <sup>a</sup>	
	at 366 nm	at 436 nm
S(2-btz) <sup>b</sup>	0.67 (2)	0.41 (2)
S(2-py) <sup>b</sup>	0.60 (3)	0.201 (7)
$\text{Me}_2\text{dtc}^{b,c}$	0.30 (10)	0.10 (4)
$\text{Cl}^d$	0.44 (4)	0.11 (1)
$\text{Br}^d$	0.41 (4)	0.08 (1)
$\text{I}^d$	0.23 (2)	0.029 (1)

<sup>a</sup> Standard deviation (from the data reduction) of the last digit is in parentheses. Total error of the determination is 2 or 3 times this amount. <sup>b</sup> In toluene. Reaction is chelation of N or S atom of thiolate side chain. <sup>c</sup> References 4 and 5. <sup>d</sup> In benzene; ref 18. Reaction is substitution by  $\text{PPh}_3$ .

430 nm;  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-py})$ , 460 nm], showing the consistent formation of product. Infrared spectra of the solutions irradiated by broad-band ultraviolet light in sealed solution cells show a decrease in the carbonyl bands of  $\text{CpW}(\text{CO})_3\text{SR}$  and an increase in the carbonyl bands of the chelated dicarbonyl complex. Electronic and infrared spectral data for the chelated complexes are shown in Table III.

Quantum yields for the photoinduced chelation of the monodentate complexes  $\text{CpW}(\text{CO})_3\text{S}(2\text{-btz})$  and  $\text{CpW}(\text{CO})_3(2\text{-py})$  are listed in Table IV. The ratio of the quantum yield of the appearance of the chelated complex to quantum yield of disappearance of the monodentate complex is 1.0, which indicates there are no other decomposition routes at these wavelengths. The primary process for the chelation reactions of  $\text{CpW}(\text{CO})_3\text{S}(2\text{-btz})$  and  $\text{CpW}(\text{CO})_3\text{S}(2\text{-py})$  is the labilization of one carbonyl ligand, leaving a vacant coordination site, which is filled efficiently by the donor atom (N or S) on the pyridyl and benzothiazolyl groups. Similar values are seen in quantum yields for carbonyl substitution in other  $\text{CpW}(\text{CO})_3\text{X}$  complexes (see Table IV). The primary process proposed<sup>5,18</sup> for these substitution reactions is the expulsion of a carbonyl ligand, followed by coordination of the substituting ligand.

In the cases where the thiolate ligand SR is S(2-py) or  $\text{Me}_2\text{dtc}$ ,<sup>5</sup> there is only one atom (N or S, respectively) on the ligand side chain with a lone pair capable of filling the vacant coordination site left after CO loss, and so assignment of the likely structure of the chelated ligands is straightforward. With SR = S(2-btz), however, there are two atoms (N and S) with the potential to coordinate and form a four-membered chelate ring. Because all of the  $\text{Cp}(\text{CO})_2\text{W}(\text{chelate})$  compounds studied to date do not readily crystallize, but tend to form powders, the ideal data to answer this question (from an X-ray crystal structure determination) are not available.

Three pieces of more circumstantial evidence point to nitrogen as the likely chelating atom on the benzothiazolyl group. The most telling of these are changes in the infrared spectrum of a KBr pellet of  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  after heating to 120 °C for 30 min. The tricarbonyl complex has a strong band assignable to  $\nu(\text{C}\equiv\text{N})$  at 1420  $\text{cm}^{-1}$  that shifts to 1390  $\text{cm}^{-1}$  on conversion to

**Table V.** Rate Constants and Activation Parameters for Thermal Carbonyl Loss from  $\text{Cp}(\text{CO})_3\text{WSR}^a$ 

R	$[\text{Cp}(\text{CO})_3\text{WSR}]$ , mM	$T$ , °C <sup>b</sup>	$10^5 k_{\text{obsd}}$ , $\text{s}^{-1}$	$\Delta H^\ddagger$ , kJ/mol	$\Delta S^\ddagger$ , J/(K mol)
2-py	0.36	39	0.40 (2)	113 (3)	13 (8)
		49	1.785 (5)		
		60	6.79 (9)		
		68	18.0 (5)		
2-btz	0.55	40	0.215 (7)	113 (7)	5 (20)
		49	0.71 (5)		
		59.5	2.24 (8)		
		70	11.00 (6)		
$\text{Me}_2\text{dtc}^c$	0.5	41	0.29 (2)	110 (2)	-3 (5)
		52.5	1.36 (17)		
		60	3.32 (23)		
		63.75	5.6 (7)		
		72.0	13.5 (18)		

<sup>a</sup> Calculated from absorbance changes; see Experimental Section for details. Standard deviation of last digit is in parentheses. <sup>b</sup> Measured in reference cell;  $\pm 0.5$  °C. <sup>c</sup> Raw data from ref 5 transformed to  $\text{s}^{-1}$  basis; activation parameters recalculated. ( $\Delta S^\ddagger$  was incorrectly listed as 51 J/(K mol) in ref 5.)

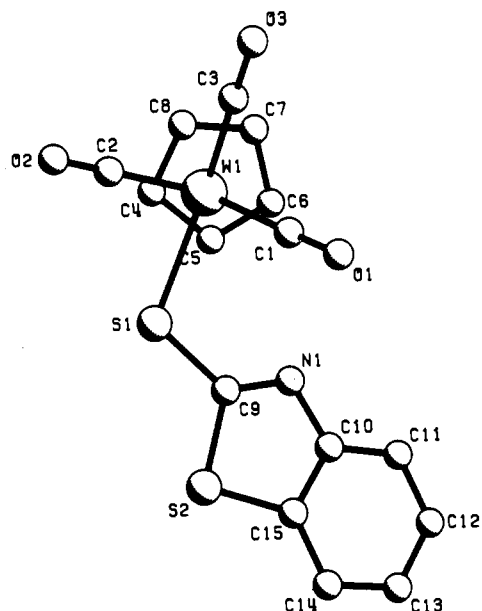
the dicarbonyl. (Aromatic  $\nu(\text{C}\equiv\text{C})$  frequencies shift very slightly from 1449, 1453  $\text{cm}^{-1}$  to 1450, 1458  $\text{cm}^{-1}$ .) In addition, the carbonyl-region infrared spectrum of the dicarbonyl complex with a chelated benzothiazolethiolate ligand is closer to that of the chelated pyridinethiolate (N,S coordination) than to that of  $\text{Me}_2\text{dtc}$  (S,S coordination). Also supporting the assignment of N,S chelation in the btz compound is the fact that thermal reactions in the solid state, where the nitrogen of the btz ligand is poised to intercept any vacant coordination site generated on tungsten (see below), give a  $\text{Cp}(\text{CO})_2\text{WS}(2\text{-btz})$  chelate identical with that generated by photolysis in solution.

Unlike reactions of S(2-py) and S(2-btz) complexes (above), ultraviolet irradiation of  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SW}(\text{CO})_3\text{Cp}$  results in spectral changes that are not clean. There is a substantial growth in the visible spectrum from 800 to 500 nm not observed for the chelation reactions discussed above. Isosbestic points are not maintained, indicating the inconsistent formation of several different products or possible decomposition. Infrared spectral changes for the reaction of  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SW}(\text{CO})_3\text{Cp}$  in methylene chloride solution induced by ultraviolet light show only a decrease in the carbonyl bands; no appearance of new carbonyl bands associated with a possible product are observed. All of the stable chelated products (S(2-py), S(2-btz), and  $\text{Me}_2\text{dtc}$ ) form four-membered rings. In the case of  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SW}(\text{CO})_3\text{Cp}$ , a chelated complex would form a five-membered ring. Possibly the angle formed by the five-membered ring would be too large and is not as favorable as that of the four-membered ring. If the bidentate complex is not stable, then dimers, trimers, or oligomers may be formed after the loss of CO.

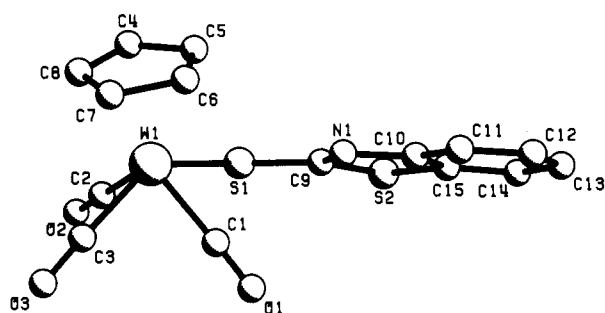
**Thermal Chelation.** The chelation of the monodentate complexes (reactions 3 and 4) can be induced thermally as well as photochemically. The thermal loss of CO from  $\text{Cp}(\text{CO})_3\text{WSR}$  (R = 2-btz or 2-py) at different temperatures was followed in solution by UV-vis absorption spectroscopy. Plots of log of the concentration of the tricarbonyl complex vs. time are linear. First-order rate constants are listed in Table V. The values for the activation enthalpy and entropy (Table V) were calculated from plots of  $\ln(k_{\text{obsd}}/T)$  vs.  $1/T$ . The values of  $\Delta H^\ddagger$  are the same for the different ligands, consistent with loss of CO as the primary process. The small values for the entropy of activation are also consistent with CO loss as the primary thermal process.<sup>19</sup>

Infrared spectroscopic changes were observed after heating a KBr pellet containing  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SW}(\text{CO})_3\text{Cp}$  for 40 min at 105 °C, conditions sufficient to induce chelation for the analogous 2-py and 2-btz compounds. The infrared data show carbonyl bands at slightly different positions and intensities. The peaks associated

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**Figure 1.** Molecular structure of  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  showing the labeling scheme. Hydrogen atoms are not shown, and atoms are drawn as spheres of arbitrary radius. The proximity of N1 to the tungsten atom can be clearly seen.



**Figure 2.** Molecular structure of  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  along a line bisecting the angle  $\text{W-S1-C9}$ , a viewpoint chosen to emphasize the planarity of the  $\text{S}(2\text{-btz})$  ligand. Atoms are drawn as spheres of arbitrary radius.

with the  $\text{NH}_2$  substituent decrease. The carbonyl-region infrared data indicate that  $o\text{-NH}_2\text{C}_6\text{H}_4\text{SW}(\text{CO})_3\text{Cp}$  is not forming a chelated dicarbonyl complex but may be forming dimers or oligomers with tungsten–nitrogen bonds.

**Molecular Structure.** Figures 1 and 2 show perspective views of  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  and define the atom-numbering scheme. Final positional parameters are given in Table VI. Bond lengths and angles are shown in Tables VII and VIII. Listings of thermal parameters (Table A), hydrogen atomic parameters (Table B), least-squares planes and displacements (Table C), and observed and calculated structure factors (Table D) have been deposited as supplementary material.

The crystal structure consists of discrete neutral molecules. The tungsten atom is surrounded by a square-pyramidal coordination sphere with a cyclopentadienyl ligand occupying the apical position. Three carbonyls and a  $\text{S}(2\text{-btz})$  ligand occupy the basal sites. This “piano stool” geometry has been well documented in tungsten–carbonyl–cyclopentadienyl complexes.<sup>5,20–24</sup> The tungsten–carbonyl distances are within the predicted range and show nearly

**Table VI.** Atomic Positional Parameters with Esd's in Parentheses

atom	x	y	z
W1	0.37776 (2)	0.53743 (4)	0.34728 (3)
S1	0.3253 (2)	0.4573 (4)	0.4972 (3)
S2	0.2110 (2)	0.4006 (4)	0.5502 (3)
C1	0.3212 (5)	0.420 (1)	0.267 (1)
O1	0.2903 (4)	0.3542 (9)	0.2213 (8)
C2	0.4328 (5)	0.428 (1)	0.438 (1)
O2	0.4633 (4)	0.3658 (9)	0.4877 (8)
C3	0.4205 (6)	0.451 (1)	0.240 (1)
O3	0.4440 (5)	0.399 (1)	0.1772 (9)
C4	0.3984 (8)	0.737 (1)	0.428 (1)
C5	0.3417 (6)	0.741 (1)	0.390 (1)
C6	0.3369 (7)	0.732 (1)	0.284 (2)
C7	0.3899 (8)	0.724 (1)	0.248 (1)
C8	0.4255 (7)	0.727 (1)	0.337 (1)
C9	0.2544 (6)	0.474 (1)	0.461 (1)
N1	0.2286 (5)	0.5327 (9)	0.3803 (9)
C10	0.1717 (6)	0.524 (1)	0.380 (1)
C11	0.1323 (6)	0.575 (1)	0.303 (1)
C12	0.0774 (6)	0.558 (1)	0.313 (1)
C13	0.0589 (7)	0.490 (2)	0.396 (2)
C14	0.0967 (9)	0.435 (2)	0.476 (1)
C15	0.1530 (6)	0.455 (1)	0.467 (1)

**Table VII.** Bond Lengths (Å) (with Esd's)

W–C1	2.006 (12)	C5–C6	1.333 (22)
W–C2	1.998 (11)	C6–C7	1.393 (22)
W–C3	1.979 (14)	C7–C8	1.331 (20)
W–S1	2.500 (3)	S1–C9	1.728 (14)
W–Cp <sup>a</sup>	1.998 (15)	C9–N1	1.287 (16)
W–C4	2.315 (12)	C10–N1	1.369 (18)
W–C5	2.339 (13)	S2–C9	1.764 (12)
W–C6	2.325 (13)	S2–C15	1.749 (15)
W–C7	2.310 (11)	C10–C11	1.386 (21)
W–C8	2.268 (13)	C10–C15	1.403 (19)
C1–O1	1.121 (14)	C11–C12	1.345 (20)
C2–O2	1.116 (13)	C12–C13	1.371 (25)
C3–O3	1.146 (15)	C13–C14	1.397 (27)
C4–C5	1.401 (24)	C14–C15	1.381 (23)
C4–C8	1.381 (22)		

<sup>a</sup>Cp indicates the centroid of the cyclopentadienyl group.

**Table VIII.** Bond Angles (deg) (with Esd's)

C1–W–C2	109.1 (6)	W–C2–O2	179.2 (1.2)
C1–W–C3	76.4 (5)	W–C3–O3	178.1 (1.3)
C2–W–C3	77.0 (6)	S1–C9–S2	115.1 (7)
S1–W–C1	79.2 (4)	S1–C9–N1	129.6 (1.0)
S1–W–C2	75.2 (4)	S2–C9–N1	115.3 (1.0)
S1–W–C3	134.2 (4)	C9–N1–C10	111.8 (1.1)
Cp <sup>a</sup> –W–S1	112.5 (4)	C9–S2–C15	88.5 (7)
Cp–W–C1	125.1 (6)	N1–C10–C11	126.1 (1.3)
Cp–W–C2	125.8 (6)	N1–C10–C15	115.5 (1.3)
Cp–W–C3	113.3 (6)	C11–C10–C15	118.4 (1.3)
C4–C5–C6	109.0 (1.5)	C10–C11–C12	120.3 (1.5)
C5–C6–C7	109.5 (1.4)	C11–C12–C13	121.5 (1.6)
C6–C7–C8	105.4 (1.4)	C12–C13–C14	120.7 (1.5)
C7–C8–C4	112.3 (1.5)	C13–C14–C15	117.4 (1.5)
C8–C4–C5	103.9 (1.5)	C14–C15–C10	121.7 (1.5)
W–S1–C9	109.3 (4)	C14–C15–S2	129.5 (1.3)
W–C1–O1	178.7 (1.1)	C10–C15–S2	108.8 (1.1)

<sup>a</sup>Cp indicates the centroid of the cyclopentadienyl group.

linear  $\text{W-C-O}$  angles ( $178\text{--}179^\circ$ ). Bond angles about tungsten in the basal plane average  $77(2)^\circ$  (cis); opposite angles are  $109.1(6)^\circ$  for  $\text{C1-W-C2}$  and  $134.2(4)^\circ$  for  $\text{S1-W-C3}$ . These values are close to those observed in the similar complex  $\text{CpW}(\text{CO})_3(\text{Me}_2\text{dte})$ ,<sup>5</sup> where the basal plane consists of three carbonyl groups and a dithiocarbamate sulfur:  $76(2)^\circ$  (cis) and opposite angles of  $104.3(1)$  and  $134.3(1)^\circ$  for  $\text{OC-W-CO}$  and  $\text{S-W-CO}$ , respectively.

The cyclopentadienyl group in  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  is slightly canted with respect to the tungsten atom. It is tilted away from the tungsten in the direction of the  $\text{S}(\text{btz})$  ligand. The  $\text{W-C}(\text{Cp})$

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lengths range from 2.34 (1) Å for W–C5 to 2.27 (1) Å, for W–C8. The distance from tungsten to the centroid of the cyclopentadienyl ligand is 2.00 (2) Å. The canting of the Cp group is slightly less than that seen in the Me<sub>2</sub>dtc analogue,<sup>5</sup> where W–C distances range from 2.297 (3) to 2.383 (4) Å; the direction of canting and the W–centroid distance are the same in the two structures. Other CpW(CO)<sub>3</sub>X compounds show more distortion (X = Cl,<sup>24</sup> W(CO)<sub>3</sub>Cp<sup>25</sup>) in the W–Cp linkage.

The W–S linkage of 2.500 (3) Å was expected.<sup>5</sup> The fused rings are planar (Table C), and this plane includes S1; the displacement of S1 from the plane of the rings is 0.03 (1) Å. Tungsten lies 0.41 (1) Å out of this best plane. Unlike in the dithiocarbamate ligand of ref 5, the nitrogen atom of the heterocycle is positioned closer to the metal than the sulfur atom of the heterocycle. Both these nitrogen and sulfur atoms have lone pairs associated with them, but neither are close enough to W for a bonding interaction (W...N1 = 3.650 Å, W...S2 = 5.146 Å), although W...N is approximately equal to the sum of van der Waals radii.<sup>5,26,27</sup> Chelation by this S(2-btz) ligand through N1 is likely involved in the photochemical reaction of the complex (see above).

The existence of nearly van der Waals contacts between the tungsten atom and nitrogen in this structure and between tungsten and sulfur in the structure of Cp(CO)<sub>3</sub>W(Me<sub>2</sub>dtc)<sup>5</sup> may induce some asymmetry into the W(CO)<sub>3</sub> unit in these molecules. It is highly suggestive that these are two of the three compounds (Cp(CO)<sub>3</sub>WSR, R = 2-py, 2-btz, or C(S)NMe<sub>2</sub>) that can successfully be induced to chelate and that all three show a full splitting into three bands in the carbonyl stretching region of the infrared spectrum. All other Cp(CO)<sub>3</sub>WSR compounds studied<sup>4,14</sup> display a broad band, sometimes with a shoulder, in place of the two lowest energy (E symmetry) bands in the three compounds with chelate potential. Note also that Cp(CO)<sub>3</sub>WS(*o*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) could not be successfully chelated and displays the latter two-band infrared pattern.

An extended conjugated  $\pi$  system exists in the fused rings: the C9–N1 distance of 1.287 (16) Å indicates a double bond between them, and the N1–C10 distance of 1.369 (18) Å shows appreciable double-bond character (cf. 1.27 and 1.48 Å for simple double and single C–N bond lengths<sup>27</sup>). Some delocalization may extend through the ligating sulfur atom, S1, since the distance S1–C9 of 1.728 (14) Å is significantly shorter than comparable distances in either CpW(CO)<sub>3</sub>(Me<sub>2</sub>dtc) [1.769 (3) Å]<sup>5</sup> or bis(benzothiazolyl) disulfide [1.765 (4) Å].<sup>28</sup>

## Conclusions

Photoinduced reactions of tungsten dimer with organic disulfides form mononuclear tungsten tricarbonyl complexes with monodentate thiolate ligands. Tungsten carbonyl thiolate complexes with potential ligating sites on the side chains of the sulfur compounds (either sulfur or nitrogen) form chelated complexes both thermally and photochemically by the loss of a carbonyl ligand. Quantum yields for the two complexes studied, Cp(CO)<sub>3</sub>WS(2-btz) and Cp(CO)<sub>3</sub>WS(2-py), are higher than quantum yields for carbonyl loss from similar compounds. This indicates either more efficient chelation by the incoming group or more efficient CO loss. The thermal activation energies and enthalpies are the same for all of the compounds. The molecular structure of Cp(CO)<sub>3</sub>WS(2-btz) is not surprising, but it provides evidence implicating nitrogen as the additional ligating atom in chelated Cp(CO)<sub>2</sub>WS(2-btz).

## Experimental Section

**Materials and Equipment.** Potassium bromide was dried in an oven at 100 °C for 24 h and stored in a desiccator over Drierite. Toluene was dried by storing over anhydrous magnesium sulfate. All of the organic disulfides used were commercially available. Bis(*o*-aminophenyl) di-

sulfide was purified by dissolving in toluene, filtering to remove the solid impurities, and removing the solvent from the filtrate by slow evaporation in air. All other organic disulfides were used as received. The compound CpW(CO)<sub>3</sub>CH<sub>2</sub>Ph was available from previous studies.<sup>5,29</sup>

Infrared spectra were obtained with Beckman 4250, Perkin-Elmer 283B, and Nicolet 5-MX spectrophotometers. Electronic spectral data were collected on a Hitachi 100-80 ultraviolet–visible absorption spectrophotometer, and proton NMR spectra were recorded on an IBM NR-80B instrument. Mass spectra were obtained with a Hewlett Packard 5985 GC/MS/DS operating in the direct-insertion mode. Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected.

**Syntheses of Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub>.** The tungsten dimer was prepared by thermolysis of CpW(CO)<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>30</sup> under various conditions. Thermolysis under 1 atm air or nitrogen at 140 °C gave yields of 74% and 65%, respectively, while thermolysis under vacuum gave the highest yields (90%). The benzyl compound, CpW(CO)<sub>3</sub>CH<sub>2</sub>Ph (0.845 g, 1.99 mmol), was placed in a sealed tube under vacuum. The sealed tube was placed in the oven at 140 °C for 0.75 h. When the tube had cooled, it was opened, toluene was added, and the mixture was stirred until the Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub> had dissolved. The solution was placed on a grade I neutral alumina column. Elution with a 1:1 mixture of hexane and toluene removed the unreacted benzyl compound, and a toluene/methylene chloride mixture removed the tungsten dimer. The solvent was slowly evaporated from open beakers in the dark, yielding the purple tungsten dimer compound (0.594 g, 0.89 mmol, a 90% yield based on Cp(CO)<sub>3</sub>WCH<sub>2</sub>Ph).

**Synthesis of Cp(CO)<sub>3</sub>WS(2-btz).** The compound Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub> (0.101 g, 0.15 mmol) and an excess of bis(2-benzothiazolyl) disulfide, (C<sub>6</sub>H<sub>4</sub>N-SCS-)<sub>2</sub> (0.0995 g, 0.30 mmol), were combined in a 250-mL round-bottom flask with 30 mL of toluene. The solution was stirred and deaerated with a stream of nitrogen for about 15 min; it was then cooled to 0 °C and irradiated with a 60-W incandescent lamp for 1.25 h. The resultant solution was warmed to room temperature and applied to a grade III neutral alumina column. The unreacted tungsten dimer (oily when solvent was removed) was eluted as a purple band with toluene, and an orange band was then eluted with methylene chloride. The solvent was slowly evaporated in the dark in open beakers, leaving a bright orange solid, CpW(CO)<sub>3</sub>S(2-btz) (0.0526 g, 0.11 mmol, 35% yield based on Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub>), mp 128–129 °C dec. Mass spectra show a very small parent ion peak and subsequent loss of three carbonyl groups. The recrystallized sample had a satisfactory elemental analysis (MicAnal). [Anal. Calcd for C<sub>15</sub>H<sub>9</sub>NO<sub>3</sub>S<sub>2</sub>W: C, 36.09; H, 1.82; N, 2.81; S, 12.55. Found: C, 36.28; H, 1.72; N, 2.77; S, 12.55.] The 80-MHz <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) consists of a singlet at  $\delta$  5.85 (5 H, cyclopentadienyl) and a multiplet centered at  $\delta$  7.5 (4 H, benzo). Infrared carbonyl stretching frequencies and electronic absorption band positions are given in Table I.

**Synthesis of Cp(CO)<sub>3</sub>WS(2-py).** The solid compounds Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub> (0.050 g, 0.075 mmol) and bis(2-pyridyl) disulfide, (2-NC<sub>5</sub>H<sub>4</sub>S)<sub>2</sub> (0.050 g, 0.11 mmol), were dissolved in 50 mL of toluene. The solution was deaerated with a stream of nitrogen, cooled to 0 °C, and photolyzed for 2 h with visible light (tungsten lamp). The resultant solution, wrapped in aluminum foil, was then stored in the refrigerator for 1 day, after which it was warmed to room temperature, placed on an alumina column, and eluted with toluene, methylene chloride, and finally methanol. The band came off as a dark orange band and upon slow evaporation of the solvent in the dark yielded an oil. The oil was placed in the dark for 4 days, after which microcrystals formed (0.0396 g, 0.089 mmol, a 60% yield based on Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub>). The 80-MHz <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) consists of a singlet at  $\delta$  5.77 (5 H, cyclopentadienyl) and two quartets, one centered at  $\delta$  8.36 and the other at  $\delta$  7.26 (total 4 H, pyridyl). Infrared carbonyl stretching frequencies and electronic spectral data are given in Table I.

**Synthesis of *o*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SW(CO)<sub>3</sub>Cp.** The compounds Cp<sub>2</sub>W<sub>2</sub>(CO)<sub>6</sub> (0.050 g, 0.075 mmol) and bis(*o*-aminophenyl) disulfide, (*o*-NH<sub>2</sub>PhS)<sub>2</sub> (0.050 g, 0.20 mmol), were placed in a 250-mL round-bottom flask. Toluene (50 mL) was added, and the solution was stirred and deaerated with nitrogen for 1/2 h. The round-bottom flask was placed in ice, stirring was continued, and the solution was irradiated with a 60-W desk lamp for 1 h. After that time, the solution was warmed to room temperature and applied to the top of a silica gel column. The unreacted tungsten dimer was eluted first with toluene, and then methylene chloride was used to remove the remaining orange band. An orange oil was left after slow evaporation of solvent in the dark. The flask was then placed in the refrigerator and opened to the air. The oil formed an orange solid

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Table IX. Experimental Crystallographic Data

formula	$\text{WS}_2\text{NC}_{15}\text{O}_3\text{H}_9$
mol wt	499.22
cryst dimens, mm	$0.50 \times 0.47 \times 0.17$
cryst system	monoclinic
space group	$C2/c$
cell dimens <sup>a</sup>	
<i>a</i> , Å	24.03 (3)
<i>b</i> , Å	10.236 (3)
<i>c</i> , Å	12.526 (4)
β, deg	95.63 (4)
<i>V</i> (Å <sup>3</sup> )	3066 (4)
<i>Z</i>	8
calcd density, g cm <sup>-3</sup>	2.163
scan method	$\theta/2\theta$
radiation	Mo Kα ( $\lambda = 0.71069$ Å)
monochromator	graphite crystal
scan angle, deg	$0.80 + 0.20 \tan \theta$
max scan time, s	45
2θ range, deg	3–50
octants collected	$\pm h, +k, +l$
no. of total data	2923
no. of obsd data, $I_o \geq 3\sigma(I)$	2214
$\mu$ , cm <sup>-1</sup>	82.0
transmission coeff	0.268–0.034
<i>F</i> (000)	1888
<i>R</i> <sub>1</sub> , <i>R</i> <sub>2</sub>	0.057, 0.075
<i>w</i>	$(\sigma_F)^{-2}$

<sup>a</sup>Lattice constants calculated from 48 high-angle reflections measured at  $\pm 2\theta$ .

(0.0313 g, 0.069 mmol, a 46% yield based on  $\text{Cp}_2\text{W}_2(\text{CO})_6$ ), mp 72–80 °C dec. The 80-MHz <sup>1</sup>H NMR spectrum (in  $\text{CDCl}_3$ ) consists of a singlet at  $\delta$  5.73 (5 H, cyclopentadienyl) and a multiplet centered at  $\delta$  6.84 (4 H, aromatic). Infrared carbonyl stretching frequencies and electronic spectral data are given in Table I.

**Photochemical Procedures.** The irradiation source used for preparative visible-light photochemistry was a 60-W incandescent lamp. The reactions were monitored by UV–vis or infrared spectroscopy. Quantum yields were measured on 4 mL of solution containing the reactants in a 1 cm path length cuvette with attached tube that was degassed by at least three freeze–pump–thaw cycles. The sample was irradiated with a Hanovia medium-pressure mercury arc lamp source in a water-cooled quartz jacket, with the desired spectral lines isolated with Corning filters. The intensity was determined by ferrioxalate actinometry.<sup>31</sup>

**Quantum Yield Calculations.** The concentrations of the reactant and the product as a function of time were calculated from changes in absorbance at the wavelength maximum of the reactant and the product, respectively, by using a standard two-component analysis with extinction coefficients determined from standard solutions of purified compounds.

Quantum yields were determined for each irradiation time, by using changes in reactant concentration to calculate disappearance yields and changes in product concentration for corresponding appearance yields. Corrections were made for incomplete absorption of the starting material and the inner-filter effect where appropriate.<sup>32</sup> Calculations were per-

formed in a differential manner, and the corrected values calculated for each time interval were averaged over the course of the photolysis.<sup>33</sup> Reported quantum yields are the average of at least two independent determinations under the same conditions.

**Thermal Procedures.** Solutions of the  $\text{CpW}(\text{CO})_3\text{SR}$  compounds in toluene were freeze–thaw–degassed and then sealed in an optical cell. A circulating bath was used to regulate temperature. A stoppered cell of pure solvent was used as a reference. An open cell with a thermometer in it was placed in the sample side for approximately 30 min, and when the temperature remained constant, it was recorded. The sample cell was placed in the instrument and allowed to equilibrate for about 5 min. (Without equilibration, convection currents made the spectra too noisy, especially at higher temperatures.) Quantitative data were measured by recording the absorbances at the wavelength maxima for both the reactant and product and using a two-wavelength calculation to determine the concentrations. The rate constants for the reactions were calculated from the plots of  $\ln(\text{concentration})$  vs. time.<sup>34</sup> Data were collected at several temperatures in order to calculate the activation enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) from a plot of  $\ln(k/T)$  vs.  $1/T$ , by using standard linear regression analysis.

**X-ray Structure Solution and Refinement.** Red crystals of  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$  were in the form of plates and were light-sensitive. A sample that had been dipped in India ink was mounted on a Nonius CAD-4 automated diffractometer, and axial photos indicated the monoclinic crystal system. Three reflections were used to check for orientation and intensity during data collection and showed a drop of 43% of original intensity throughout data collection. Decay corrections were applied. Gaussian integration absorption corrections were applied by the method of indexing crystal faces. The structure was solved by heavy-atom techniques and refined as a full matrix in least-squares calculations.<sup>35</sup> Hydrogen atoms were placed in calculated positions and held invariant while their isotropic thermal parameters were all tied to a single variable; all non-hydrogen atoms were refined anisotropically. In a final cycle of least-squares refinement, the maximum shift was  $<0.01\sigma$ . No systematic correction for secondary extinction was made. On a final difference map there were four peaks representing 1–3 e Å<sup>-3</sup> near the tungsten atom. The number of observations was 2214, and the number of variable parameters was 200. The final *R* values for observed reflections are *R* = 0.057 and *R*<sub>w</sub> = 0.075. For all, including weak, reflections *R* = 0.066 and *R*<sub>w</sub> = 0.077. Neutral-atom scattering factors and corrections for anomalous dispersion were from ref 36. Other details of the crystallographic experiment are given in Table IX.

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**Supplementary Material Available:** For  $\text{Cp}(\text{CO})_3\text{WS}(2\text{-btz})$ , tables of thermal parameters (Table A), hydrogen atomic parameters (Table B), and calculated least-squares planes (Table C) (3 pages); a listing of observed and calculated structure factors (Table D) (15 pages). Ordering information is given on any current masthead page.

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