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# Thiocarbonyl (C S) complexes of tungsten

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SULFUR) COMPLEXES OF TUNGSTEN.

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Thiocarbonyl (C=S) complexes of tungsten

by

William Webster Greaves

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## SYMBOLS AND ABBREVIATIONS

acac	acetylacetonato ligand
All	allyl
Bu	butyl
Bz	benzyl
Cp	$\eta^5$ -cyclopentadienyl
diphos	1,2-bis(diphenylphosphino) ethane
DME	1,2-dimethoxyethane
DNP	2,4-dinitrophenyl
L	a donor ligand
M	a metal atom
Me	methyl
Ph	phenyl
PPN <sup>+</sup>	$\mu$ -azidobis(triphenylphosphorous) cation
Pr	propyl
Py	pyridine
pz	pyrazolyl
R	an organic substituent group unless otherwise defined
S	a coordinating solvent molecule
tdp	tris(dimethylamino)phosphine
THF	tetrahydrofuran
TMS	tetramethylsilane
X	a halogen
$\nu$	infrared stretching frequency or mode

## I. INTRODUCTION

### A. General Comments

The thiocarbonyl ligand, CS, is the simplest variant of the carbonyl ligand, CO, and the study of its complexes allows comparison between the bonding and reactions of the CO and CS ligands. Although metal carbonyl complexes have been known and studied since the end of the nineteenth century,<sup>1</sup> only twelve years have passed since the first preparation of a transition metal thiocarbonyl by Baird and Wilkinson.<sup>2</sup> Now over 100 such compounds have been reported, most of them within the past five years.

The chief reason for the late development of metal thiocarbonyl chemistry is the instability of carbon monosulfide under normal conditions. Above  $-160^{\circ}$  CS polymerizes, and the polymerization often occurs explosively. Therefore, the CS ligand must be incorporated into a complex by indirect methods. At present only two general methods of introducing CS into a complex are known, and only in a few cases can more than one CS ligand be introduced into a complex. The majority of the metal thiocarbonyls are neutral compounds that contain terminal CS ligands; thiocarbonyls with thioketonic and end-to-end CS bridging groups and thiocarbonyl anions are still uncommon.

In addition to the search for alternative ways to introduce the CS ligand into complexes, other aspects of metal thiocarbonyl chemistry are being investigated. Spectroscopic and structural studies have been conducted to show the differences in the bonding of CS and CO to metals, and molecular orbital diagrams have been calculated to explicate these differences. Reactivity studies have shown that the substitution of a CO ligand with CS has a pronounced effect on the reactivity of the complex. The CS ligand itself often has been shown to be unusually reactive. The incorporation of a CS ligand into a complex often results in the formation of a chiral metal center; the separation of some of these optical isomers has led to interest in thiocarbonyl complexes as catalysts for asymmetric organic synthesis. And since many metal carbonyls have been used as homogeneous catalysts in industrial reactions, it is expected that some thiocarbonyls may find similar uses in the future. With all these possibilities to explore, metal thiocarbonyl chemistry should remain a fertile area of research for some time to come.

#### B. The Present Research

Dombek and Angelici have reported the preparation of the complexes  $M(\text{CO})_5\text{CS}$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ),<sup>3</sup> and in later,

fuller accounts they have described the thermal carbonyl substitutions, oxidative additions, and electrophilic and nucleophilic reactions of  $W(CO)_5CS$ .<sup>4,5,6</sup> More recently it was discovered that the reaction of  $Na[C_5H_5]$  with  $Bu_4N[IW(CO)_4CS]$  under anhydrous conditions produced  $Bu_4N[CpW(CO)_2CS]$  in a quantitative yield. Since thiocarbonyl anions are rare, little is known about their reactivity. Also, inasmuch as  $[CpW(CO)_2CS]^-$  and its derivatives would be analogs of the well-known all-carbonyl compounds  $[CpW(CO)_3^-]$  and  $[CpW(CO)_3R]$ , direct comparisons between the chemistry of the thiocarbonyl complexes and the carbonyl complexes could be made. Therefore, it was decided to pursue the investigation of this new thiocarbonyl anion and its derivatives.

The remainder of this introduction is devoted to the chemistry of metal thiocarbonyls and relevant  $\eta^5$ -cyclopentadienyl and pyrazolyborate derivatives of  $W(CO)_6$ . Coverage is intended to be representative only. Three complete reviews of metal thiocarbonyl chemistry are available,<sup>7,8,9</sup> and the literature of the carbonyl complexes is extensive.

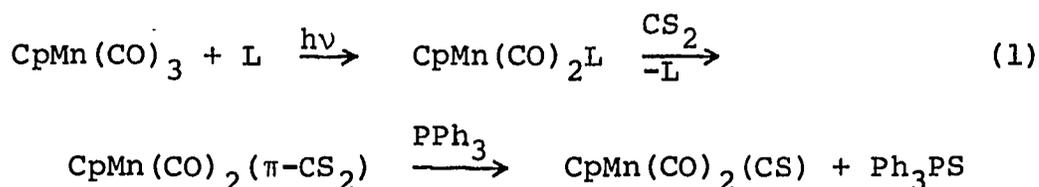
## C. Metal Thiocarbonyl Complexes

### 1. Synthesis of Thiocarbonyl Complexes

Direct synthesis of metal thiocarbonyls from free CS has been attempted, but with little success. As mentioned

above, CS undergoes a violent, exothermic polymerization above  $-160^{\circ}$ . Thus, indirect methods have been used to introduce the CS ligand into the metal complex. These methods may be grouped into two major categories.

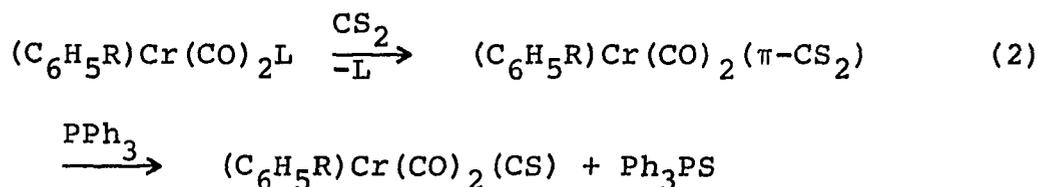
a. Addition of CS<sub>2</sub> to a metal complex followed by cleavage of a C-S bond Most of the reactions which form metal-CS bonds employ CS<sub>2</sub> as the source of CS. The  $\pi$ -CS<sub>2</sub> complexes<sup>7,9</sup> are often the precursors to metal thiocarbonyls, forming the CS ligand by the elimination of a sulfur atom. In most syntheses the elimination reaction must be assisted. For example, the manganese thiocarbonyl complex CpMn(CO)<sub>2</sub>CS<sup>10,11</sup> has been obtained by refluxing CpMn(CO)<sub>2</sub>L (L = cis-cyclooctene) in CS<sub>2</sub> with PPh<sub>3</sub>. The excess PPh<sub>3</sub> abstracts a sulfur atom from the  $\pi$ -CS<sub>2</sub> intermediate (reaction sequence 1). Repetition of the



sequence starting with CpMn(CO)<sub>2</sub>(CS) gave CpMn(CO)(CS)<sub>2</sub>, one of the few bis thiocarbonyls known. Spectroscopic evidence indicates the formation of CpMn(CS)<sub>3</sub> by the use of CpMn(CO)(CS)<sub>2</sub> in this process. It has also been found that CpMn(CO)<sub>2</sub>(THF) reacts with CS<sub>2</sub> and PPh<sub>3</sub> to yield

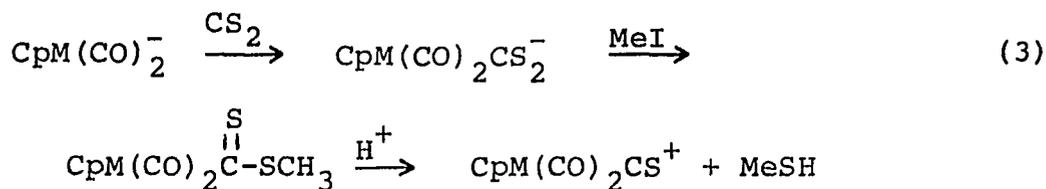
the thiocarbonyl complex. This method was used to prepare  $\text{CpRe}(\text{CO})_2(\text{CS})$ .<sup>11</sup>

A similar reaction sequence was used to prepare  $(\text{C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$  from  $(\text{C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2\text{L}$ <sup>11,12</sup> (where L = cis-cyclooctene or THF, R = H or  $\text{CO}_2\text{Me}$ ), eq. 2. When



L = THF the thiocarbonyl complex was formed in greater yield without addition of  $\text{PPh}_3$ .

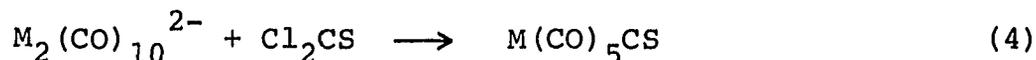
In a few cases the reaction of metal carbonyl anions with  $\text{CS}_2$  can be used to introduce a CS ligand. Successive treatment of  $[\text{CpM}(\text{CO})_2]^-$  (M = Fe<sup>13</sup>, Ru<sup>14</sup>) with  $\text{CS}_2$  and MeI yields the dithioesters,  $\text{CpM}(\text{CO})_2\text{CS}_2\text{Me}$  (eq. 3). Acid cleavage to the thiocarbonyl cation is effected by  $\text{HCl}$ <sup>13</sup> or  $\text{CF}_3\text{SO}_3\text{H}$ <sup>15</sup>, releasing methanethiol. This method seems



to be applicable only to the very nucleophilic<sup>16,17</sup> Fe and Ru carbonyl anions.

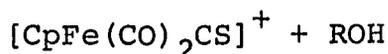
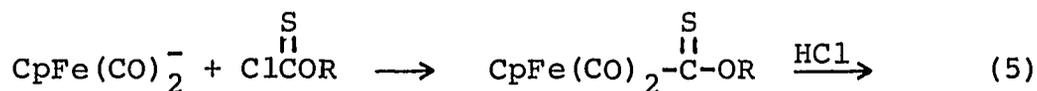
b. Reaction with thiophosgene ( $\text{Cl}_2\text{CS}$ ) and its alkoxy derivatives As mentioned above, Dombek and Angelici<sup>4</sup>

obtained the group VIB thiocarbonyls  $M(\text{CO})_5\text{CS}$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) in low yields by reaction of the dimeric carbonyl anions with thiophosgene (eq. 4). Only  $\text{W}(\text{CO})_5\text{CS}$  could be



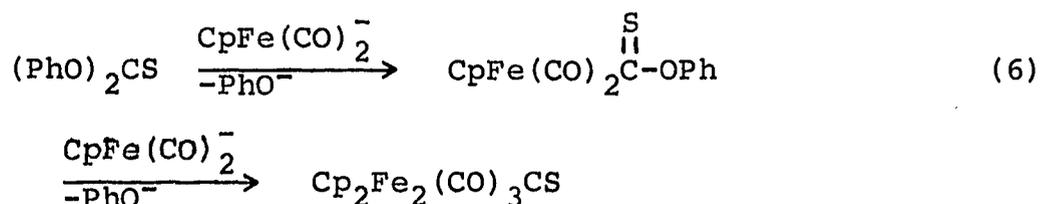
obtained in useful amounts. A higher-yield synthesis of  $\text{Cr}(\text{CO})_5\text{CS}$  has recently been reported (see below).<sup>18</sup>

The iron thiocarbonyl cation  $[\text{CpFe}(\text{CO})_2\text{CS}]^+$  was originally obtained by the oxidative addition of ethyl or methyl chlorothioformate followed by acid cleavage (reaction 5).<sup>19</sup> However, this method has been supplanted



by the carbon disulfide reaction discussed previously.

Reaction of  $\text{CpFe}(\text{CO})_2^-$  with  $(\text{PhO})_2\text{CS}$  (diphenylthionocarbonate) in a 2:1 molar ratio gives thiocarbonyl-bridged  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ .<sup>20,21</sup> This reaction is the first example of the introduction of a CS ligand directly into a bridging position. Experimental evidence has led to the proposal of reaction sequence 6 for the formation of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ :



## 2. The Metal-CS Bond

a. Theoretical studies It is believed that CO and CS bind to metals through a synergistic interaction of metal d orbitals with ligand  $\sigma$  (donor) and  $\pi^*$  (acceptor) orbitals.<sup>22</sup> Early molecular orbital calculations on free CS and free CO by Richards<sup>23</sup> indicate that CS is a better  $\sigma$ -donor than CO because the highest occupied level of CS ( $7\sigma$ ) contains more 2p character and is of higher energy than the corresponding orbital in CO ( $5\sigma$ ). In addition, the empty  $\pi^*$  orbitals of CS are at lower energy than those of CO, so CS is considered the better  $\pi$ -acceptor.

A more recent theoretical study of metal thiocarbonyl complexes confirms Richards's early predictions.<sup>24</sup> Further, the calculations suggest that, to some extent, CS can also act as a  $\pi$ -donor ligand. Overall, the theoretical studies predict that M-CS bonds should be stronger than their CO counterparts; also, the M-CS bonding causes the C-S bond to weaken and destabilizes the remaining M-CO bonds in the complex. The calculations also predict that the thiocarbonyl-carbon has a smaller positive charge than an analogous carbonyl carbon.

The superior  $\pi$ -acceptor ability of CS has been verified by infrared<sup>25</sup> and Mossbauer<sup>26</sup> studies. Other experimental evidence supports the predictions concerning the relative strengths of M-CS and M-CO bonds (see below).

b. IR studies The most common spectroscopic technique used to identify and characterize thiocarbonyl complexes is IR spectroscopy. The metal thiocarbonyls exhibit a strong infrared absorption arising from the C-S stretching mode that is usually as intense as a metal carbonyl  $\nu(\text{CO})$  absorption. The ranges of the  $\nu(\text{CS})$  vibrations observed for the various types of metal thiocarbonyls are displayed in Table 1. In the case of

Table 1. IR ranges for  $\nu(\text{CS})$  modes in metal thiocarbonyls<sup>8</sup>

Type	$\nu(\text{CS}), \text{cm}^{-1}$
Free CS <sup>a</sup>	1274
M-CS	1409 - 1161
M-C(S)-M <sup>b</sup>	1150 - 1100
M-CS-M <sup>c</sup>	1106 - 1048
M-C(SM)-M <sup>d</sup>	1081 - 1017

<sup>a</sup>In CS<sub>2</sub> matrix at -196°C

<sup>b</sup>"Thioketonic" bridge

<sup>c</sup>"End-to-end" bridge

<sup>d</sup>"Triply bridged"

terminal CS groups the  $\nu(\text{CS})$  frequency often appears above the  $1274 \text{ cm}^{-1}$  bond of the free CS molecule, in marked contrast to the  $\nu(\text{CO})$  frequencies in metal carbonyls which, with few exceptions,<sup>27</sup> are always lower than  $\nu(\text{CO})$  for CO itself. This trend has been attributed to the considerable electronic differences between the two ligands. In general, the  $\nu(\text{CS})$  frequency is inversely related to the metal electron density; for terminal CS ligands a linear correlation exists between  $\nu(\text{CS})$  and the C-S distance.<sup>28</sup> Thus the CS stretching frequency reflects the strength or weakness of the C-S bond.

It has been noted that if a major change takes place within a complex, such as replacing CO with  $\text{PPh}_3$ , the shift of the  $\nu(\text{CS})$  frequency will be as expected from the analogous carbonyl system. However, smaller changes, such as replacing  $\text{PPh}_3$  with  $\text{PMe}_2\text{Ph}$ , can lead to anomalous shifts.<sup>9</sup>

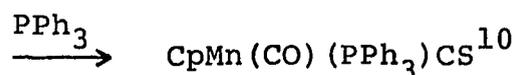
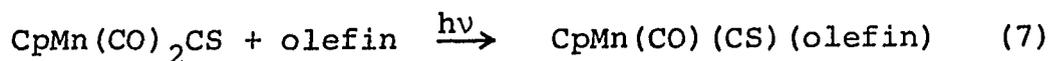
c. NMR studies Numerous data have been reported for the  $^{13}\text{C}$  NMR chemical shifts of the CS ligands. Thiocarbonyl carbon resonances are at extremely low fields, comparable to those found for metal carbene complexes,<sup>29,30</sup> although the M-CS linkage is different from M-CR<sub>2</sub>.<sup>31</sup> The currently reported range of the CS resonances is 286-396 ppm downfield from TMS.<sup>8</sup> These results have been interpreted as supporting the importance

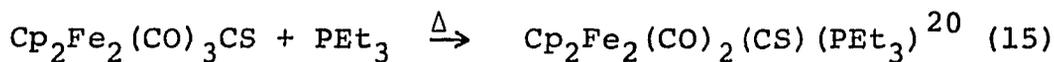
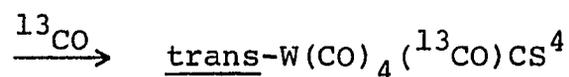
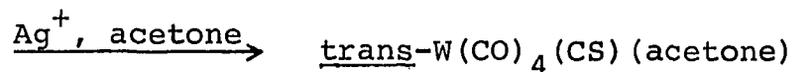
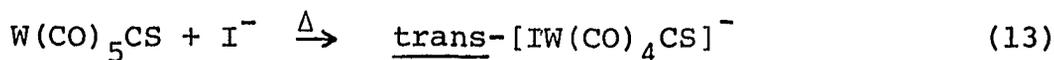
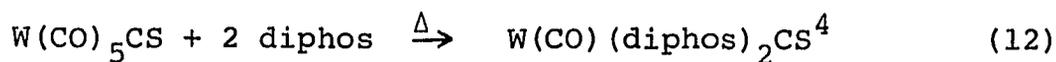
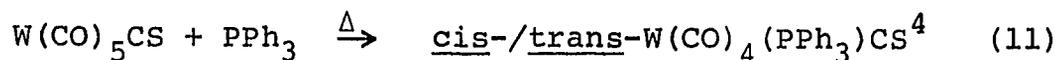
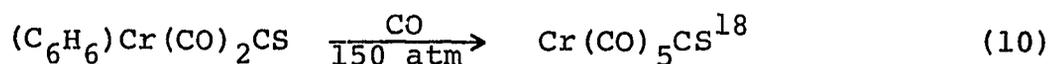
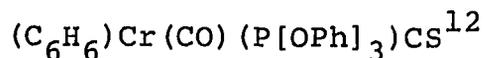
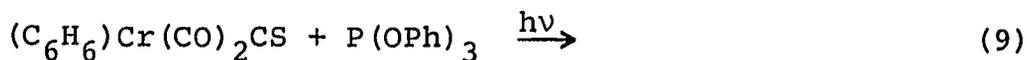
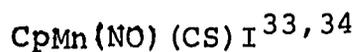
of the polar resonance structure  $M-\overset{+}{C}=\bar{S}$ .<sup>32</sup> Another interesting feature in the  $^{13}\text{C}$  spectra is that replacement of a CO group by CS in a carbonyl complex produces an upfield shift of the remaining CO resonances, whereas substitution of CO with other monodentate ligands usually affords a downfield shift.<sup>8</sup> This effect has been attributed to the greater  $\pi$ -acceptor character of CS relative to other ligands.

d. Mass spectra data The stronger bonding of M-CS linkages compared to M-CO linkages is evident in the mass spectral data. One of the prominent ions in the mass spectra of most metal thiocarbonyls is the  $M\text{-CS}^+$  ion which results from the loss of all ligands other than CS.<sup>8</sup>

### 3. Reactions of metal thiocarbonyl complexes

a. Reactions at the metal Numerous thermal and photochemical substitution reactions of metal thiocarbonyls, using both mono- and polydentate ligands, have been reported. Most of these reactions involve the replacement of CO by another ligand (see eqs. 7 to 15 for examples).





Kinetic studies<sup>4, 32</sup> have verified the general observation that complexes with terminal thiocarbonyl ligands

undergo ligand substitution more readily than their carbonyl counterparts.

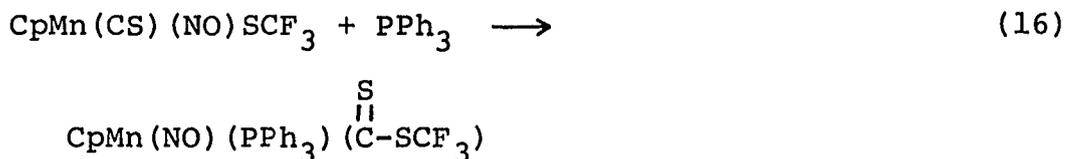
The substitution reactions of the cyclopentadienyl and arene thiocarbonyl complexes form a chiral metal center, and enantiomers of  $(o\text{-Me}_2\text{C}_6\text{H}_4)\text{Cr}(\text{CO})(\text{P}[\text{OPh}]_3)\text{CS}$  have been resolved.<sup>36</sup> These complexes might become catalysts for asymmetric organic synthesis. The reaction of  $(\text{C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2(\text{CS})$  ( $\text{R} = \text{H}, \text{CO}_2\text{Me}$ ) with CO is the best method for preparing  $\text{Cr}(\text{CO})_5\text{CS}$ .<sup>18</sup> The preparation of trans- $[\text{W}(\text{CO})_4\text{CS}]^-$  is interesting because of its stereoselectivity and its relevance to research discussed in this dissertation. Finally, the substitution reactions of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$  are the first reported for a bridging-thiocarbonyl complex; they are also the first examples of a thiocarbonyl complex which undergoes CO replacement less readily than its carbonyl analog.<sup>20</sup>

Successive treatment of  $\text{W}(\text{CO})_5\text{CS}$  with  $\text{Br}_2$  and  $\text{PPh}_3$  gives the seven-coordinate  $\text{W}(\text{II})$  complex  $\text{W}(\text{CO})_2(\text{CS})(\text{PPh}_3)_2\text{Br}_2$ .<sup>5</sup> This oxidative addition product does not lose a CO ligand to form a six-coordinate species, as does the carbonyl analog, and the authors have suggested that the more strongly bonding CS occupies the face-capping position in the molecule from which dissociation would seem most favorable. Bromine oxidatively cleaves the bridged-thiocarbonyl complex

$[\text{CpFe}(\text{CO})(\text{CS})]_2$  producing two equivalents of  $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ .<sup>37</sup> Similar reactions with halogens have been observed for  $[\text{CpRu}(\text{CO})(\text{CS})]_2$ ,<sup>14</sup> but in these cases  $\text{CpRu}(\text{CO})_2\text{X}$  and other unidentified products are formed as well.

The thiocarbonyl complex  $\text{Cp}_2\text{Fe}_3(\text{CO})_3\text{CS}$  reacts rapidly with  $\text{Na}(\text{Hg})$  to give a mixture of  $\text{Na}[\text{CpFe}(\text{CO})_2]$  and  $\text{Na}[\text{CpFe}(\text{CO})(\text{CS})]$ .<sup>21</sup> This is the first thiocarbonyl anion to be produced by reduction of a thiocarbonyl complex. All attempts to reduce the analogous  $[\text{CpFe}(\text{CO})(\text{CS})]_2$  have failed.<sup>37</sup> Like the dicarbonyl anion,  $[\text{CpFe}(\text{CO})(\text{CS})]^-$  is highly reactive and extremely air-sensitive; it also displaces the chloride in  $\text{Ph}_3\text{MCl}$  ( $\text{M} = \text{Sn}$  and  $\text{Ge}$ ) to give the metal-metal bonded derivative  $\text{CpFe}(\text{CO})(\text{CS})\text{MPh}_3$ .<sup>21</sup>

Efraty and coworkers<sup>34</sup> have reported products from the reaction of  $(\text{C}_5\text{H}_4\text{R})\text{Mn}(\text{NO})(\text{CS})\text{R}'$  ( $\text{R} = \text{H}, \text{Me}; \text{R}' = \text{C}_4\text{H}_7, \text{SCF}_3$ ) with  $\text{PPh}_3$  which they claim are examples of intramolecular insertion of the CS ligand (eq. 16). However,



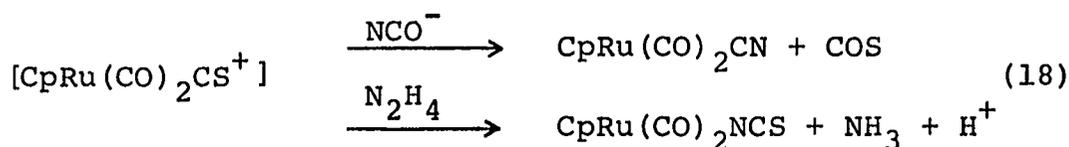
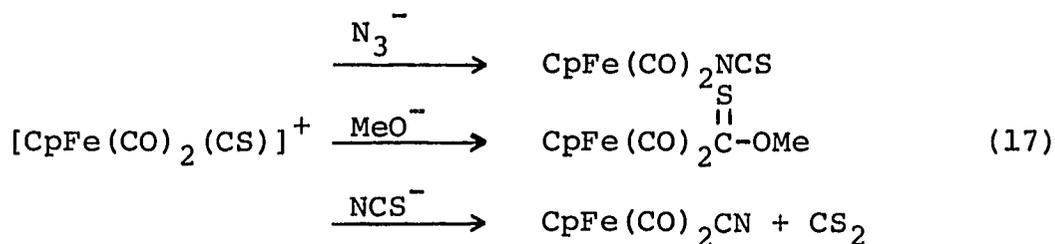
the data supporting those claims is slight and appears inconclusive.

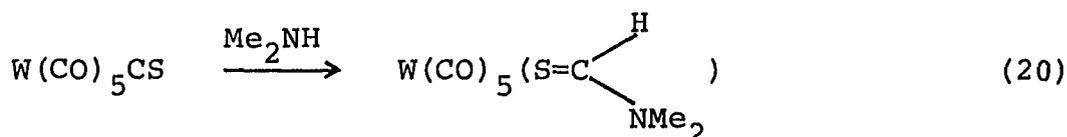
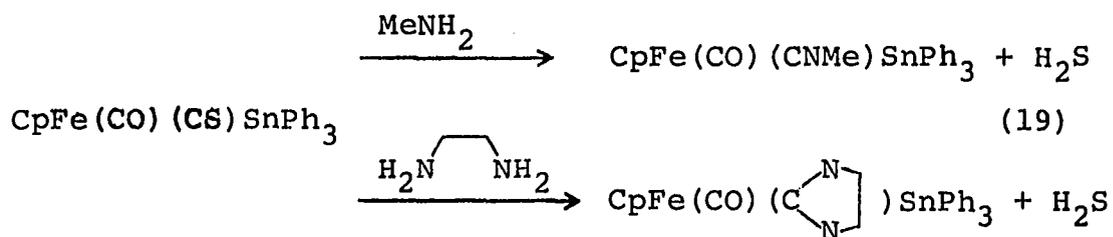
b. Nucleophilic attack at the thiocarbonyl ligand

The thiocarbonyl carbon generally exhibits a greater

reactivity towards nucleophilic attack than the carbonyl carbon. This reactivity appears contrary to the high electron density assigned to the CS carbon by theoretical studies, but it provides additional support for the polar resonance structure  $M-\overset{+}{C}=\bar{S}$  postulated by Bodner from his  $^{13}\text{C}$  NMR studies. Recently, Lichtenberger and Fenske<sup>24</sup> suggested that such reactions are controlled by the energy of the complex frontier orbitals rather than the charge density at the CS carbon.

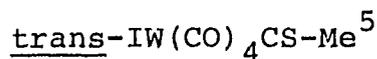
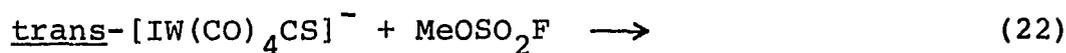
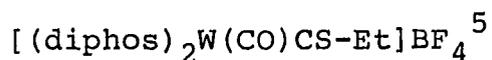
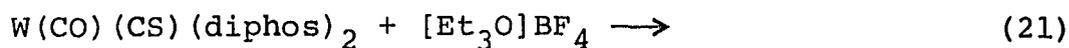
The reactions of  $[\text{CpFe}(\text{CO})_2\text{CS}]^+$ ,<sup>38</sup>  $[\text{CpRu}(\text{CO})_2\text{CS}]^+$ ,<sup>14</sup>  $\text{CpFe}(\text{CO})(\text{CS})\text{SnPh}_3$ ,<sup>21</sup> and  $\text{W}(\text{CO})_5\text{CS}^6$  with nucleophiles have been studied, and representative examples appear below, reaction schemes 17 to 20. Whether or not reaction





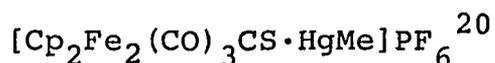
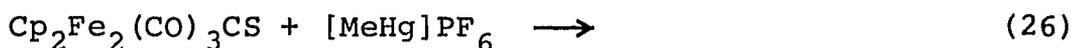
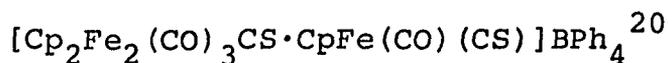
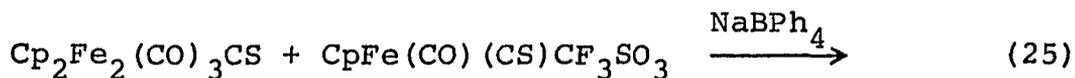
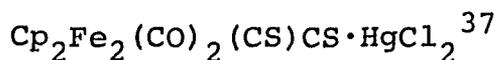
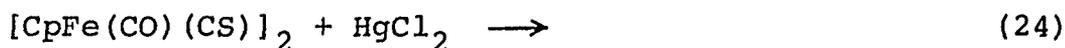
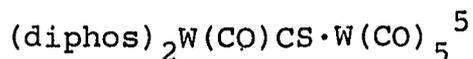
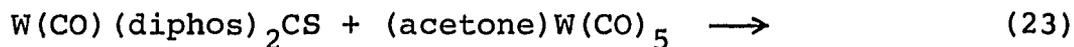
with nucleophiles is a general property of thiocarbonyl ligands remains to be established.

c. Electrophilic reactions at the thiocarbonyl ligand Two complexes with terminal thiocarbonyl ligands have been observed to undergo reaction with organic electrophiles (eqs. 21 and 22). The products of these

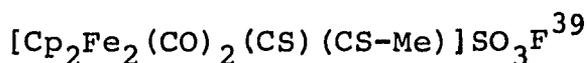
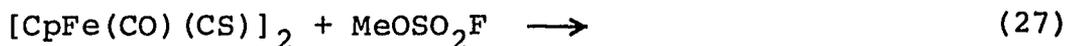


reactions contain the first examples of the mercaptocarbyne ligand,  $\text{CS-R}^+$ . The formation of "end-to-end" bridged

species of thiocarbonyls can also be regarded as reactions of thiocarbonyl complexes with electrophiles (eqs. 23 - 26).

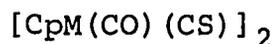
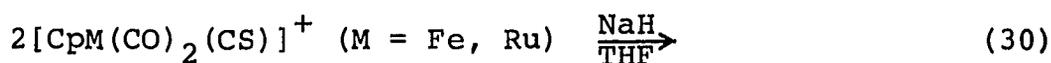


"Ketonic" bridging-thiocarbonyl complexes of iron react with organic electrophiles to give cationic species which contain an alkylated bridging-thiocarbonyl, not a mercaptocarbyne ligand (eqs. 27 to 28).





d. Reactions forming bridging thiocarbonyls The "thioketonic" bridged complexes  $[\text{CpMn}(\text{NO})(\text{CS})]_2$ <sup>34</sup> and  $[\text{CpM}(\text{CO})(\text{CS})]_2$  (M = Fe, Ru)<sup>39,14</sup> have been prepared by reductive methods (eqs. 29 and 30). In all of these



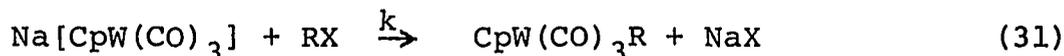
compounds, the CS ligands occupy bridge positions only. With the exception of  $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ , which was discussed earlier, these are the only examples of this type of thiocarbonyl complex presently known.

#### D. Metal Carbonyl Complexes

As said before, the thiocarbonyl complex  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  and its derivatives would be analogs of well-known all-carbonyl complexes, and this study was intended to draw comparisons between the chemistry of those two classes of compounds. A discussion of selected carbonyl complexes and their relevant chemistry follows.

1. The  $\eta^5$ -cyclopentadienyltricarbonyltungsten (1-) ion

Of the several synthetic routes leading to the anionic complex  $[\text{CpW}(\text{CO})_3]^-$ <sup>40-42</sup> the most convenient is the reaction of  $\text{Na}[\text{C}_5\text{H}_5]$ <sup>43</sup> with  $\text{Et}_4\text{N}[\text{W}(\text{CO})_5\text{I}]$ ,<sup>44</sup> since the starting materials are easily prepared and stored and the reaction conditions are relatively mild.<sup>45</sup> The most important reaction of  $[\text{CpW}(\text{CO})_3]^-$  is nucleophilic displacement, and the reaction occurs at the metal center, eq. 31. Dessy and his coworkers<sup>46</sup> found that

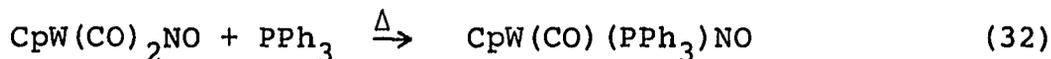


for the above reaction  $k = 500$  on a scale of  $k = 1$  (for  $[\text{CpCr}(\text{CO})_3]^-$ ) to  $k = 7 \times 10^7$  (for  $[\text{CpFe}(\text{CO})_2]^-$ ).

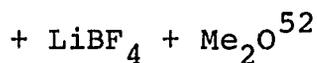
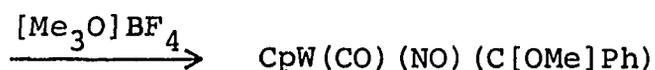
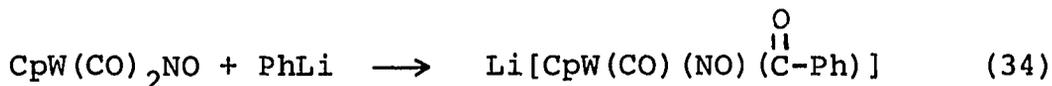
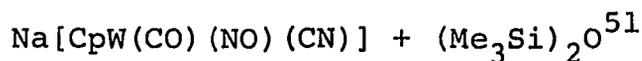
2.  $\eta^5$ -Cyclopentadienyldicarbonylnitrosyltungsten,  $\text{CpW}(\text{CO})_2\text{NO}$

Fischer and his fellow workers<sup>47</sup> first prepared  $\text{CpW}(\text{CO})_2\text{NO}$  by allowing a solution of  $\text{Na}[\text{CpW}(\text{CO})_3]$  to react with  $\text{NO}$ , but now the preferred method is treatment of a solution of  $\text{Na}[\text{CpW}(\text{CO})_3]$  with glacial acetic acid followed by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald).<sup>48</sup> Recently the reaction of  $\text{CpW}(\text{CO})_3\text{H}$  with Diazald was also reported to yield  $\text{CpW}(\text{CO})_2\text{NO}$ .<sup>49</sup>

The nitrosyl complex can be easily converted into a monosubstituted derivative by refluxing with a ligand in a suitable solvent, eq. 32.<sup>50</sup> The monosubstituted



product has a chiral metal center. Disubstituted derivatives of the molybdenum analog are known, but no such tungsten complexes have been reported. Reaction of  $\text{CpW(CO)}_2\text{NO}$  with  $\text{NOPF}_6$  at low temperature also produces the dinitrosyl complex,  $[\text{CpW(CO)(NO)}_2]\text{PF}_6$ .<sup>49</sup> The remaining CO ligand is easily replaced with neutral (L) or anionic ( $\text{X}^-$ ) Lewis bases. Strong nucleophiles attack  $\text{CpW(CO)}_2\text{NO}$  at a carbonyl carbon, eqs. 33 and 34.

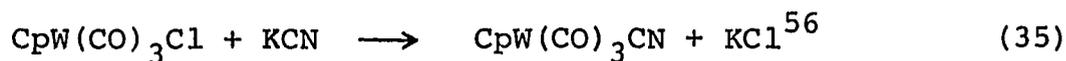


### 3. $\eta^5$ -Cyclopentadienyltricarbonyltungsten halides, $\text{CpW(CO)}_3\text{X}$

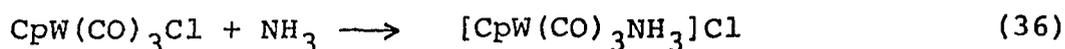
The common precursor to the halide complexes is  $\text{CpW(CO)}_3\text{H}$ . Reaction of the hydride with  $\text{CCl}_4$ <sup>40</sup> or  $\text{CBr}_4$ <sup>53</sup> produces  $\text{CpW(CO)}_3\text{Cl}$  or  $\text{CpW(CO)}_3\text{Br}$  respectively, and  $\text{CpW(CO)}_3\text{I}$  is prepared by allowing the hydride to react with  $\text{MeI}$ <sup>40</sup> or  $\text{I}_2$ .<sup>53</sup> The bromide and iodide complexes

can also be obtained from the reaction of  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  (see below) with an excess of the respective halogen.<sup>54-55</sup>

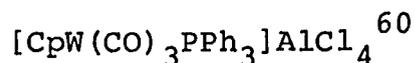
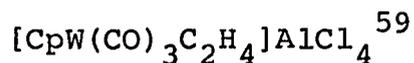
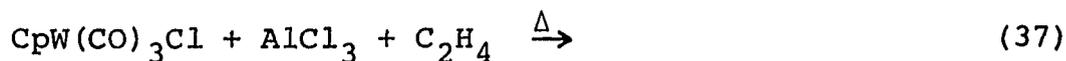
The halide ligand can be displaced by strong nucleophiles. When the nucleophile is negatively charged the product is neutral, eq. 35. The substitution of a



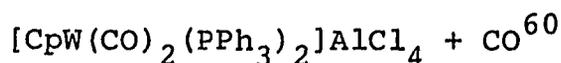
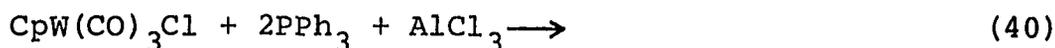
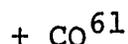
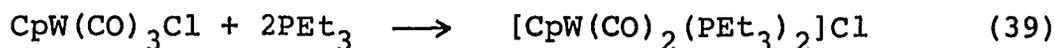
halide anion by a neutral ligand, however, leads to a cationic complex,  $[\text{CpW}(\text{CO})_3\text{L}]^+$ . This reaction may occur in two ways. Direct displacement occurs with ammonia and hydrazine,<sup>57</sup> eq. 36, but the use of a Lewis acid to



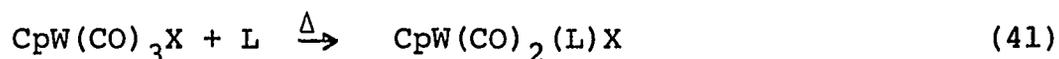
promote the abstraction of the halide anion has been employed to produce  $[\text{CpW}(\text{CO})_4]^{+58}$  and its monosubstituted derivatives, two of which are cited below:



Dicarbonyl cationic derivatives containing Lewis bases,  $[\text{CpW}(\text{CO})_2\text{L}_2]^+$ , have also been obtained by direct displacement and Lewis-acid promoted halide expulsion. Representative examples are shown in reactions 39 and 40.



Substitution of carbon monoxide in the derivatives  $\text{CpM}(\text{CO})_3\text{X}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) has been accomplished with a variety of donor ligands; but the molybdenum complexes have been more extensively studied than the tungsten complexes.<sup>60-64</sup> Equation 41 illustrates the



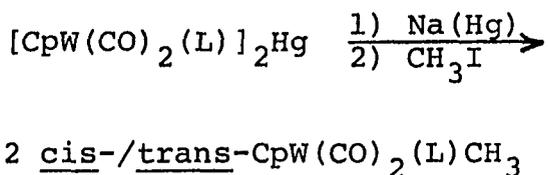
general substitution behavior of  $\text{CpW}(\text{CO})_3\text{X}$ . Unlike  $\text{CpMo}(\text{CO})_3\text{X}$ , the tungsten compounds do not form disubstituted complexes  $\text{CpW}(\text{CO})(\text{L})_2\text{X}$ , probably because of the stronger W-CO bond.<sup>64</sup> Complexes of the formula  $\text{CpM}(\text{CO})_2(\text{L})\text{X}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) can exist in two isomeric forms called cis and trans isomers.<sup>64</sup> The relative proportions of these



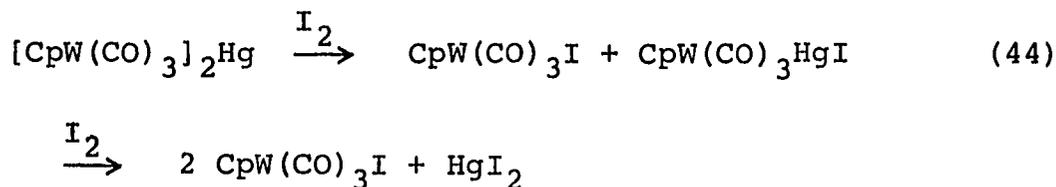
$\text{Na}[\text{CpW}(\text{CO})_3]$ <sup>71</sup> or by the action of mercury metal on  $[\text{CpW}(\text{CO})_3]_2$ .<sup>72</sup> The mercuric halide derivatives  $\text{CpW}(\text{CO})_3\text{HgX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or SCN}$ ) are generally synthesized in turn by exchange between  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  and  $\text{HgX}_2$  in acetone solution, eq. 42.<sup>73</sup>



The reaction of phosphines and phosphites with  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  produces complexes of the type  $[\text{CpW}(\text{CO})_2(\text{L})]_2\text{Hg}$ .<sup>74</sup> The complexes are reduced by sodium amalgam, and treatment of the reduced solutions with acetic acid or methyl iodide gives mono-substituted hydride and methyl complexes which exist as cis and trans isomers in solution, eq. 43.<sup>74</sup> Trans-metallation of  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$



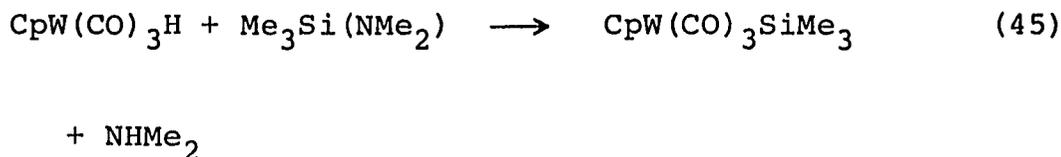
with Cd or Zn has been performed.<sup>75</sup> Cleavage of  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  with acid or halogen has also been studied. Reaction with HCl proceeds with cleavage of only one W-Hg bond and formation of  $\text{CpW}(\text{CO})_3\text{Cl}$  and  $\text{CpW}(\text{CO})_3\text{HgCl}$ ,<sup>76</sup> while reaction with excess iodine gives two equivalents of  $\text{CpW}(\text{CO})_3\text{I}$ .<sup>54</sup> The latter reaction appears to be a stepwise process, eq. 44.



The exchange reaction between  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  and  $\text{HgX}_2$  has been mentioned already. Addition of  $\text{NaSn}(\text{OH})_3$  to a solution of  $\text{CpW}(\text{CO})_3\text{HgI}$  reverses the exchange reaction, causing formation of  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$ .<sup>74</sup> Chromatography of  $\text{CpW}(\text{CO})_3\text{HgCl}$  on alumina also gives  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$ , leaving  $\text{HgCl}_2$  on the column;<sup>72</sup> in this case the alumina is probably the cause of the reversal.

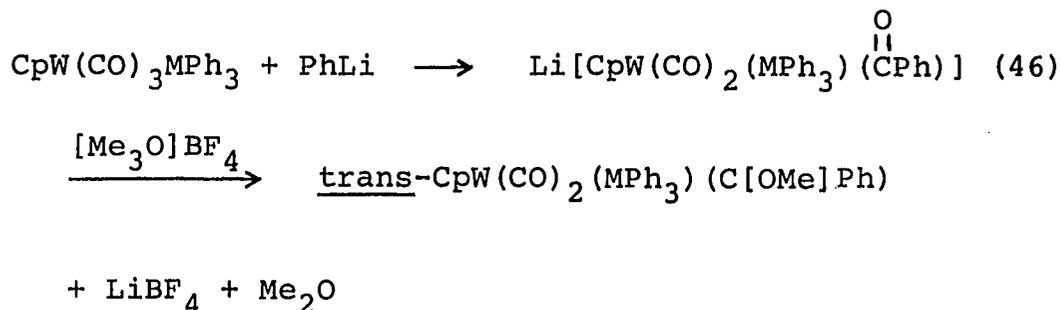
5.  $\text{CpW}(\text{CO})_3\text{MR}_3$  (M = Si, Ge, Sn, or Pb; R = Me or Ph)

Metal-metal bonded complexes of the general formula  $\text{CpW}(\text{CO})_3\text{MR}_3$  (M = Ge, Sn, or Pb; R = Me or Ph) are normally prepared by the reaction of  $\text{Na}[\text{CpW}(\text{CO})_3]$  with the appropriate halide  $\text{R}_3\text{MX}$ ;<sup>48-80</sup> however, the silyl derivatives must be produced from  $\text{CpW}(\text{CO})_3\text{H}$ , eq. 45.<sup>81</sup>



Hydrogen chloride cleaves the tin-carbon bond in the trimethyltin and triphenyltin derivatives, forming a mixture of  $\text{CpW}(\text{CO})_3\text{SnR}_2\text{Cl}$  and  $\text{CpW}(\text{CO})_3\text{SnRCl}_2$ .<sup>78,82</sup> On the other hand,  $\text{I}_2$ ,  $\text{HgX}_2$ , and  $\text{RHgX}$  cleave the tin-tungsten bond

in the same complexes, producing  $\text{CpW}(\text{CO})_3\text{I}$ ,  $\text{CpW}(\text{CO})_3\text{HgX}$ , and  $\text{CpW}(\text{CO})_3\text{HgR}$  respectively.<sup>83</sup> A series of carbene derivatives have been prepared by the reaction of organolithium reagents with  $\text{CpW}(\text{CO})_3\text{MPh}_3$  ( $\text{M} = \text{Ge}$  or  $\text{Sn}$ ) followed by alkylation, eq. 46.<sup>84</sup>



The monosubstituted complexes  $\text{CpW}(\text{CO})_2(\text{L})\text{MR}_3$  ( $\text{L} = \text{PR}_3$  or  $\text{P}(\text{OR})_3$ ;  $\text{M} = \text{Ge}$ ,  $\text{Sn}$ , or  $\text{Pb}$ ; and  $\text{R} = \text{Me}$  or  $\text{Ph}$ )<sup>70,85,86</sup> are prepared by reduction of  $\text{CpW}(\text{CO})_2(\text{L})\text{I}$  with sodium amalgam followed by addition of  $\text{R}_3\text{MX}$ . These complexes exist only as the trans isomer.

#### 6. Organosulfur derivatives of $\eta^5$ -cyclopentadienyltricarbonyltungsten (1-)

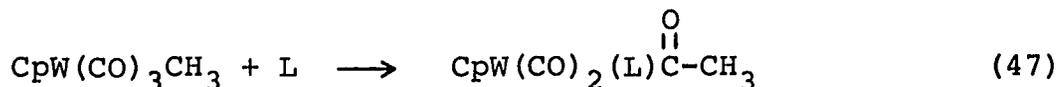
$\eta^5$ -Cyclopentadienyltricarbonyltungsten chloride reacts smoothly with  $\text{Na}[\text{SMe}]$  or  $\text{Na}[\text{SPh}]$  to yield compounds of the formula  $\text{CpW}(\text{CO})_3\text{SR}$ .<sup>87</sup> The binuclear species  $[\text{CpW}(\text{CO})_2\text{SR}]_2$ , which contain bridging  $\text{SR}$  ligands, are obtained by thermal or photochemical decomposition of the mononuclear complex.

Each of the mononuclear and the binuclear complexes undergoes facile  $\text{CS}_2$  insertion, producing the characteristic alkyl- or aryl-trithiocarbonato complexes  $\text{CpW}(\text{CO})_2(\text{S}_2\text{C-SR})$ .

7. The  $\sigma$ -methyl and  $\sigma$ -phenyl derivatives of  $\eta^5$ -cyclopentadienyltricarbonyltungsten (1-)

Fischer *et al.*<sup>88</sup> first reported that  $\text{CpW}(\text{CO})_3\text{Me}$  was produced by the reaction of  $\text{CpW}(\text{CO})_3\text{H}$  and diazomethane. Piper and Wilkinson<sup>40</sup> used Fischer's method to prepare  $\sigma$ -methyl complexes and they also found that Grignard reagents can react with the halide complexes  $\text{CpM}(\text{CO})_3\text{X}$  (M = Mo or W) to give the corresponding  $\sigma$ -alkyl complexes. However, in the same publication Piper and Wilkson reported that the preferred method of preparing  $\text{CpW}(\text{CO})_3\text{Me}$  was the reaction of  $\text{Na}[\text{CpW}(\text{CO})_3]$  with  $\text{MeI}$ . To date, the only synthesis of  $\text{CpW}(\text{CO})_3\text{Ph}$  that has been reported is interaction of  $[\text{Ph}_2\text{I}]\text{BF}_4$  and  $\text{Na}[\text{CpW}(\text{CO})_3]$ .<sup>89</sup>

Refluxing acetonitrile solutions of  $\text{CpW}(\text{CO})_3\text{CH}_3$  with various phosphines yields the acyl complexes trans- $\text{CpW}(\text{CO})_2(\text{L})\text{COCH}_3$ ; eq. 47;<sup>90</sup> this is an example of a "CO



insertion" reaction. Barnett and Treichel<sup>91</sup> produced minute quantities of a substituted  $\sigma$ -methyl complex  $\text{CpW}(\text{CO})_2(\text{L})\text{Me}$  by irradiating a solution of  $\text{CpW}(\text{CO})_3\text{Me}$  and  $\text{PPh}_3$ , but

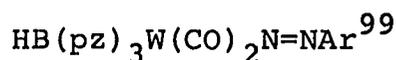
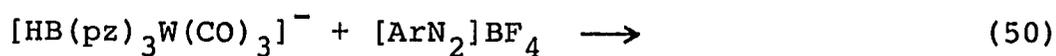
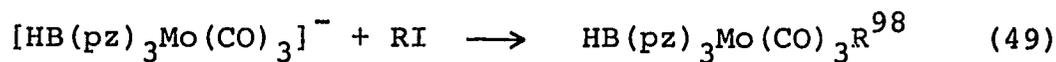
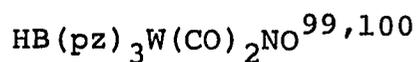
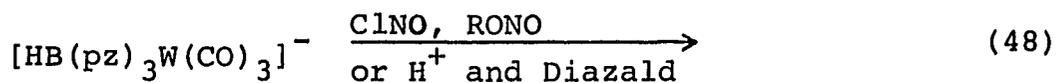
these compounds have been more readily prepared by treating a solution of  $\text{Na}[\text{CpW}(\text{CO})_2\text{L}]$  ( $\text{L} = \text{phosphine or phosphite}$ ) with  $\text{MeI}$ .<sup>86</sup> In contrast, irradiation of a solution of  $\text{CpW}(\text{CO})_3\text{Ph}$  and  $\text{PPh}_3$  or  $\text{P}(\text{OPh})_3$  gives the substituted  $\sigma$ -phenyl complex  $\text{CpW}(\text{CO})_2(\text{L})\text{Ph}$  in 75-80% yield.<sup>92</sup> Thermal reactions of  $\text{CpW}(\text{CO})_3\text{Ph}$  with  $\text{PPh}_3$  or  $\text{P}(\text{OPh})_3$  produce the same product in lower yield, and no CO insertion product is observed.<sup>92</sup> The  $\text{CpW}(\text{CO})_2(\text{L})\text{R}$  complexes exist as a mixture of cis and trans isomers, the relative amount of each isomer depending on the nature of  $\text{L}$ .<sup>54,65</sup>

#### 8. Carbyne complexes

In 1973 Fischer and his coworkers<sup>93</sup> reported the first carbyne complexes, trans- $\text{X}(\text{CO})_4\text{W}\equiv\text{CR}$ . These complexes contain a terminal, sp-hybridized-carbon to tungsten bond. Recently they found that  $[\text{C}_5\text{H}_5]^-$  reacts with some trans- $\text{Br}(\text{CO})_4\text{W}\equiv\text{CR}$  derivatives to form carbyne complexes of the general formula  $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{WCR}$ .<sup>94-96</sup>

#### 9. Hydrotris(1-pyrazolyl)boratetricarbonyltungsten (1-) and its derivatives

Potassium hydrotris(1-pyrazolyl)borate,  $\text{K}[\text{HB}(\text{pz})_3]$ ,<sup>97</sup> reacts with  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo or W}$ ) to yield anions of structure  $[\text{HB}(\text{pz})_3\text{M}(\text{CO})_3]^-$  which can be isolated as the tetraethylammonium salts.<sup>98</sup> Representative reactions of  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_3]^-$  complexes are shown below, eqs. 48-50.



Despite the polypyrazalyborate being a  $\sigma$ -donor ligand instead of a  $\pi$ -donor ligand like cyclopentadienide, the chemistry of  $[\text{HB}(\text{pz})_3\text{M}(\text{CO})_3]^-$  is much like that of  $[\text{CpM}(\text{CO})_3]^-$ .<sup>101</sup> Polypyrazalyborate derivatives are considerably more stable than the analogous cyclopentadienide complexes.<sup>101</sup>

## II. EXPERIMENTAL

### A. General Procedures

All reactions were performed at room temperature and under an atmosphere of prepurified nitrogen unless otherwise specified. Schlenk ware (or similar apparatus) and the standard inert atmosphere techniques were used.<sup>102</sup> Amalgam reductions were carried out in the common amalgam reduction apparatus.<sup>103</sup> The exchange of  $\text{PF}_6^-$  for other anions was accomplished with a 1 x 25 cm column of Amberlite IRA-400 resin charged with  $\text{PF}_6^-$  in acetone or methanol. Most of the compounds mentioned below were crystallized by "slow evaporation": the compound was dissolved in a suitable solvent, and a higher-boiling solvent in which the compound was less soluble was added; the solvent was then evaporated under reduced pressure (50-60 torr) at room temperature with a rotary evaporator. Elemental analyses were performed by Chemalytics, Inc. or Galbraith Laboratories.

### B. Spectra

Infrared spectra were recorded on a Perkin Elmer 337 or 237B grating spectrophotometer. The sodium chloride cells used for most spectra had a path length of 1 mm. The spectra were expanded on an auxiliary recorder, and

the band positions were determined using gaseous CO (in the carbonyl region) and polystyrene (in the thiocarbonyl region) as references. Band positions are believed to be accurate to within  $2 \text{ cm}^{-1}$ .

Proton NMR spectra were recorded with Varian A-60 and Varian HA-100 spectrometers; variable-temperature proton NMR spectra were obtained on the Varian HA-100 instrument. All  $^{13}\text{C}$  NMR spectra were measured with a Bruker HX-90 spectrometer operating in the Fourier transform mode at 22.64 MHz; to reduce the data collection time,  $\text{Cr}(\text{acac})_3$  was added to the sample in a concentration of  $\sim 35 \text{ mg per ml}$ .<sup>104</sup> TMS was the standard of reference for all NMR spectra.

### C. Solvents

1,2-Dimethoxyethane was refluxed over fresh  $\text{LiAlH}_4$  for 5 hours and then distilled under nitrogen into dry-containers; it was stored in dark bottles over Baker type 4A molecular sieves and a coil of copper wire.

Tetrahydrofuran was distilled from  $\text{LiAlH}_4$  or  $\text{NaK}_{2.8}$  immediately before use. All other solvents used were commercial reagent grade products. Acetone was stored over  $\text{CaSO}_4$ ; other solvents were maintained over Baker Type 4A molecular sieves. Solvents were deaerated by flushing with nitrogen before use.

## D. Reagents

1. Organic compounds

Amines requiring purification were distilled from KOH. Phosphines and phosphites were fractionally distilled under nitrogen or, when appropriate, recrystallized. Methyl isocyanide,<sup>105</sup> thiocarbonyldiimidazole, and diphenylthionocarbonate<sup>20</sup> were prepared and donated by M. Quick. Chloro-2,4-dinitrobenzene was recrystallized from ethyl alcohol, as was p-nitrobenzylbromide. Commercial [PPN]Cl was crystallized from acetone with diethyl ether. [PPN]N<sub>3</sub> was prepared from [PPN]Cl and NaN<sub>3</sub> by the usual metathesis procedure;<sup>106</sup> [PPN]I, from [PPN]Cl and NaI. The oxidizing agents [Ph<sub>3</sub>C]BF<sub>4</sub> and [C<sub>7</sub>H<sub>7</sub>]BF<sub>4</sub> were obtained by published procedures.<sup>107</sup> Phenylsulfenylchloride<sup>108</sup> and phenylselenenylbromide<sup>109</sup> were prepared according to methods found in the fifth volume of Fieser and Fieser's Reagents for Organic Synthesis, while p-toluyldiazonium tetrafluoroborate<sup>110</sup> was obtained by a method found in Organic Reactions, vol. 5. Triphenylphosphonium cyclopentadienylide<sup>111</sup> was prepared by reacting cyclopentadiene with bromine and triphenylphosphine. The lithium reagents p-lithio-N,N-dimethylaniline<sup>112</sup> and pentafluorophenyllithium<sup>113,114</sup> were prepared by allowing η-butylolithium to react with ethereal solutions of the corresponding aryl halides at -78°C;

all lithium reagents were transferred to reaction vessels by syringe.

## 2. Inorganic and organometallic compounds

Commercial NaI and  $\text{AgBF}_4$  were dried over  $\text{P}_4\text{O}_{10}$ , and THF solutions of  $\text{AgBF}_4$  were maintained at  $0^\circ\text{C}$  under a nitrogen atmosphere.  $\text{C}_8\text{K}$  was prepared by heating a mixture of dry graphite and potassium under nitrogen, stirring the mixture all the while; it was reacted in situ.<sup>42</sup>

The complex  $[\text{CpFe}(\text{CO})_2]_2$  was recrystallized from a 3:1 solution of hexane and methylene chloride at  $-20^\circ\text{C}$ . The metal carbonyl  $\text{Mn}_2(\text{CO})_{10}$  was sublimed ( $70^\circ$ , 0.01 torr) and used in the preparation of  $\text{Mn}(\text{CO})_5\text{Br}$ .<sup>115</sup> Samples of  $[\text{CpFe}(\text{CO})_2\text{CS}]\text{PF}_6$  and  $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$  were kindly provided by J. W. Dunker. Other metal carbonyl halides used in this work, e.g.  $\text{CpFe}(\text{CO})_2\text{Cl}$  and  $\text{CpMo}(\text{CO})_3\text{Cl}$ , were samples made several years ago by W. Jetz.

## 3. Other compounds

All other reagents used in this research (except those mentioned below) were commercial products of the highest purity available and were used as received.

### E. Preparation of Thiocarbonyl Reagents

Two thiocarbonyl reagents,  $W(CO)_5CS^4$  and  $Bu_4N[IW(CO)_4CS]$ ,<sup>4</sup> were used throughout this research project. The published procedures for making these complexes resulted in a low yield of  $Bu_4N[IW(CO)_4CS]$ . In an attempt to increase the yield the procedures were modified. An account of these modifications is given below, along with the methods of preparation finally settled upon.

#### 1. Preparation of $W(CO)_5CS$

The reported synthesis of  $W(CO)_5CS$  is reduction of  $W(CO)_6$  with sodium amalgam in THF followed by reaction with thiophosgene, and the yield is around 12% based on  $W(CO)_6$ .<sup>4</sup> In the course of this project different methods of reduction were tested in this preparation. The use of potassium amalgam instead of sodium amalgam decreased the yield to around 6%;  $C_8K$  led to no product at all. It is known that the reduction of  $W(CO)_6$  with sodium amalgam in THF gives a mixture of anions, of which  $Na_2[W_2(CO)_{10}]$  is the predominant species, while  $C_8K$  reduction is reported to give only  $K_2[W_2(CO)_{10}]$ .<sup>42</sup> Since  $K_2[W_2(CO)_{10}]$  had not given  $W(CO)_5CS$ , it was thought that another anion produced from the amalgam reduction, possibly  $Na[W(CO)_5]$ , might be the reactive species. Sodium amalgam reduction of  $W(CO)_6$  in DME at room temperature

gives  $\text{Na}_2[\text{W}(\text{CO})_5]$  almost exclusively,<sup>116</sup> but when this method of reduction was employed the yield of  $\text{W}(\text{CO})_5\text{CS}$  fell to 0.5%. The search for a new reduction method was abandoned.

Thiocarbonyldiimidazole and diphenylthionocarbonate were substituted for thiophosgene to see if a new thiocarbonyl reagent would increase the yield of  $\text{W}(\text{CO})_5\text{CS}$ . Neither worked. Thiocarbonyldiimidazole did not react at all, and the only products isolated from the reaction between  $\text{K}_2[\text{W}_2(\text{CO})_{10}]$  and  $(\text{PhO})_2\text{C}=\text{S}$  were tungsten hexacarbonyl and phenol.

The published method of preparing  $\text{W}(\text{CO})_5\text{CS}$  was found to be the most convenient route to that complex. What follows is a more complete procedure than has appeared before.<sup>117</sup>

A 1000 ml, three necked, round bottom flask fitted with a mechanical stirrer and a reflux condenser connected to a mercury bubbler was flushed with nitrogen for several minutes. A positive pressure of  $\text{N}_2$  was maintained thereafter. Mercury ( $\sim 120$  ml) was added to the flask, and a sodium amalgam was prepared by stirring the mercury vigorously while adding pieces of clean Na metal (7.0 g, 304 mmol, cut into about ten pieces) one at a time, against a counter current of nitrogen.

After the amalgam had cooled, 400 ml of dry THF was added to the flask, followed by 50.0 g (142 mmol) of  $W(CO)_6$ . An electric heating mantle was then fitted under the flask, and the mixture was vigorously stirred and heated to reflux under  $N_2$  for 12-18 hr.

The mixture was then cooled to room temperature. A positive  $N_2$  pressure was maintained while the mechanical stirrer was replaced with a glass stopper and the condenser was replaced with a 90° bent tube. The solution was decanted under a  $N_2$  flush through the 90° bent tube into a 500 ml pressure-equalizing addition funnel fitted with a small side-arm flask.

A nitrogen source was then connected to the side-arm to maintain positive  $N_2$  pressure over the solution until the bent tube at the top of the funnel was replaced with a nitrogen inlet. Any amalgam which had been transferred was drained through the funnel stopcock into the small flask. The flask was removed; the funnel was fitted with a distilling tube with section adapter; and the entire apparatus was placed on a 2000 ml, single-necked, round bottom flask containing 150 ml of dry THF, 14 ml (183 mmol) of thiophosgene, and a magnetic stir bar. After the apparatus had been flushed with  $N_2$  for a few minutes, the THF-thiophosgene solution was stirred vigorously with the magnetic stirrer and the contents of

the funnel were added rapidly (<5 min) to the flask. Large amounts of gas were liberated during this reaction. Frothing occurred. The black solution was stirred under N<sub>2</sub> until it cooled to room temperature.

The solution was transferred to a 1000 ml round bottom flask, rinsing the reaction vessel with THF, and it was concentrated under water-aspirator vacuum on a rotary evaporator to about 400 ml. Then the solution was transferred to a 500 ml flask, using THF to rinse the 1000 ml flask, and evaporation was continued until almost all solvent had been removed.

A 10 ml, straight-sided beaker was placed in the flask and imbedded in the black product, directly under the joint. Next, a water-cooled sublimation probe with a vacuum inlet was inserted into the flask, and then the flask was immersed in an oil bath at 50-60°C. The contents were sublimed under static vacuum (i.e., the apparatus is closed after being evacuated). Some residual solvent always condensed on the probe and dripped into the small beaker. This liquid was removed by pipette at intervals of fifteen minutes until no more collected in the beaker. Then the probe was dried and the solid product was collected. The solid was removed from the probe about every ten hours.

Approximately 10-15 g of yellow crystals, a mixture of  $W(CO)_6$  and 3-6 g  $W(CO)_5CS$ , were obtained. Much of the  $W(CO)_6$  was removed by dissolving the yellow solid in 400 ml of warm hexane and allowing the solution to slowly cool to  $0^\circ$  in a refrigerator. The solution was decanted from the pale yellow crystals (mainly  $W(CO)_6$ ) and evaporated to dryness to yield 4-7 g of a mixture which was 60-90%  $W(CO)_5CS$ .

The amount of  $W(CO)_5CS$  in this mixture was determined by preparing a solution of about 20 mg of the mixture in 50.0 ml of hexane and measuring the absorbance of  $W(CO)_5CS$  at 420 nm. Since  $W(CO)_6$  absorption is negligible at this wavelength, the concentration of  $W(CO)_5CS$  was calculated from its molar extinction coefficient,  $7.52 \times 10^2 \text{ l cm}^{-1} \text{ mole}^{-1}$ . From the concentration of  $W(CO)_5CS$  in the solution, the composition of the mixture can be calculated.

## 2. Preparation of $Bu_4N[trans-IW(CO)_4CS]$ <sup>117</sup>

The preparation was performed on mixtures of  $W(CO)_6$  and  $W(CO)_5CS$ . The  $W(CO)_5CS$  content of each mixture was determined by visible spectroscopy as noted above.

For example, a mixture of  $W(CO)_6$  and  $W(CO)_5CS$  containing 3.68 g  $W(CO)_5CS$  (10.0 mmol) was placed in a 250 ml, two neck flask with 3.68 g  $[Bu_4N]I$  (10.0 mmol). The flask was flushed with  $N_2$ ; 125 ml of dry THF was

added; and the flask was connected to an  $N_2$  source and a mercury bubbler. The solution was stirred at  $50^\circ C$  in an oil bath for 1.5 hr. and then concentrated to about 25 ml on a rotary evaporator. Precipitation of the golden product was completed by addition of 50-75 ml of diethyl ether. The solid (6.6 g, 90%) was washed with ether, hexane, and pentane. It was dried in vacuo overnight. The  $[Bu_4N]I$  was never used in excess, and the crude product was employed without further purification.

#### F. Preparation of Pyrazolylborate and Cyclopentadienide Salts

##### 1. Preparation of potassium hydrotris(1-pyrazolyl)borate, $K[HB(pz)_3]$ <sup>98</sup>

A sample of  $K[HB(pz)_3]$  was donated by L. Bowyer. During preparation of the reagent, the amount of hydrogen released by the reaction of  $K[BH_4]$  with molten pyrazole was monitored by water displacement. What follows is a scaled-down version of Trofimenko's original procedure.<sup>118</sup>

A mixture of 5.40 g (0.1 mole) of finely divided  $K[BH_4]$  and 27.2 g (0.4 mole) of pyrazole, together with a stir bar, was placed in a 250 ml, single necked flask equipped with a condenser. The condenser was vented into a calibrated 10 l flask that had been filled with water and inverted in a large tank of water.

The oil bath was heated to 90°, and the mixture was allowed to melt while being stirred. Hydrogen evolution began.

The temperature was raised to 125°, and the reaction was allowed to proceed until about 3.5 l of H<sub>2</sub> had evolved. Then the temperature was gradually raised to 190°. Approximately 7.5 l of gas were evolved after the solution had been stirred at 190° for 2.5 hr.

The mixture was cooled to 150° and then poured into 69 ml of stirring toluene. After seven minutes the toluene mixture was filtered hot. The white precipitate was first washed with 200 ml of hot toluene, and then, with 100 ml of hot hexane. After a final washing with 200 ml of cool hexane, the product was dried in vacuo for 8-10 hr. The yield was usually about 65%.

M.P. 185-190°. IR(nujol): 2440 cm<sup>-1</sup>.

## 2. Preparation of sodium cyclopentadienide

The published procedures for Na[C<sub>5</sub>H<sub>5</sub>]<sup>71,119</sup> gave an impure product and were inconvenient for small-scale reactions. A preparation was developed from the reaction of cyclopentadiene with NaH.

Cyclopentadiene was distilled from a commercial sample of dicyclopentadiene under a N<sub>2</sub> atmosphere. To purify the cyclopentadiene, it was redistilled at 40° under N<sub>2</sub> just before use. The distillate was collected

at 0°; afterward it was transferred by syringe to a flame-dried flask sealed with an air-tight septum and stored at -20° under N<sub>2</sub>. The cyclopentadiene was never stored longer than 24 hr. If stored for a longer period the Na[C<sub>5</sub>H<sub>5</sub>] solution was dark red and decomposed quickly.

A 120 ml Schlenk tube<sup>102</sup> with stir bar was attached to a vacuum/N<sub>2</sub> line and capped with an air-tight septum. The tube was flame-dried twice in vacuo and then filled with N<sub>2</sub>. The septum was removed, and dry, crystalline NaH (0.85 g, 35 mm) was added to the tube against a counter current of N<sub>2</sub>. (Powdered NaH suspended in mineral oil could be used if it was washed first with benzene and then with hexane, thoroughly dried in vacuo, and stored over P<sub>2</sub>O<sub>5</sub> in a N<sub>2</sub> atmosphere. However, the resulting solution was deep red and a significant amount of black impurity precipitated.) The tube was capped again, evacuated, refilled with N<sub>2</sub>, and immersed in a 0° ice bath. A positive pressure of N<sub>2</sub> was maintained during the reaction. Dry THF (67 ml) was added from a syringe, and the solution was stirred vigorously. Cyclopentadiene (3.0 ml, 2.4 g, 36.0 mmol) was added slowly from a syringe. The evolution of hydrogen from the reaction caused a froth; so the cyclopentadiene was added in one ml portions. A portion was injected, the bubbling was allowed to subdue, and then the next portion

was injected. The  $H_2$  was allowed to escape through the vacuum/ $N_2$  line into a hood. After two hours at  $0^\circ$  the reaction was less vigorous; the mixture was allowed to warm slowly to room temperature. When no more bubbles were observed rising to the surface of the mixture (usually after 12 hours), the tube was purged with  $N_2$ . At this point the solution was pink with a gray impurity suspended in it. Stirring was discontinued, the tube was removed from the vacuum line, and the mixture was stored at  $0^\circ$  under  $N_2$ . The impurity settled to the bottom, leaving a pale pink solution of  $Na[C_5H_5]$ .

This solution was approximately 0.5 M  $Na[C_5H_5]$ . The actual concentration was determined by adding the solution to an accurately weighed sample of  $Bu_4N[IW(CO)_4CS]$  in THF at  $60^\circ$  until the IR spectrum showed that all of the thiocarbonyl reagent had reacted (see below, Preparation of  $Bu_4N[CpW(CO)_2CS]$ , Sect. 4).

Whenever  $Na[C_5H_5]$  was needed for a reaction, the desired amount of solution was transferred to the reaction vessel by syringe. The solution could be stored at  $0^\circ$  for about six weeks if the tube was purged with  $N_2$  periodically.

The procedure has been scaled-up successfully, and it has been modified to produce more concentrated solutions. A solution of sodium methylcyclopentadienide,  $Na[CH_3C_5H_4]$ ,

has been prepared in a similar manner. The above procedure appears less stringent than the one recently reported by Miller, et al.<sup>120</sup>

#### G. Synthesis and Reactions of Thiocarbonyl Complexes

##### 1. Preparation of [SC-W(CO)<sub>4</sub>-P(Ph)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>

A solution of Bu<sub>4</sub>[IW(CO)<sub>4</sub>CS] (1.4 g, 2.0 mmol) in 40 ml of acetone was stirred at 0°C while AgBF<sub>4</sub> (0.39 g, 2.0 mmol) in 20 ml of acetone was added from an equi-pressure dropping funnel. Silver iodide precipitated immediately; the reaction vessel was covered with aluminum foil to prevent the reduction of silver cation. The resulting suspension was filtered after 45 minutes. Diphos (0.39 g, 1.0 mmol) was added to the cold filtrate, and a yellow precipitate formed. Next, the reaction mixture was filtered, and the yellow powder was washed with hexane and dried in vacuo. The product was dissolved in a minimum of CHCl<sub>3</sub> and placed at the top of a 2 x 40 cm column of silica gel. Elution with CHCl<sub>3</sub> gave a yellow band that was collected and evaporated to a powdery residue. Recrystallization from chloroform with hexane gave yellow crystals. (0.87 g, 82% based on tungsten).

IR(CS<sub>2</sub>): 2057vw, 1988w, 1949s, 1241m. <sup>31</sup>P NMR(CDCl<sub>3</sub>): singlet at 9.62 ppm downfield from 85% H<sub>3</sub>PO<sub>4</sub> external

standard. Anal. Calc. for  $C_{36}H_{24}O_8P_2S_2W_2$ : C, 40.09; H, 2.22. Found: C, 39.93; H, 2.33.

## 2. Reaction of $[SC-W(CO)_4-P(Ph)_2CH_2]_2$ with amines

When  $[SC-W(CO)_4-P(Ph)_2CH_2]_2$  (0.10 mmol) was stirred in THF with butylamine (5.0 mmol), along with pyridine (0.3 ml) and  $CaH_2$  (0.10 g), about 75% conversion to the isocyanide complex  $[BuNC-W(CO)_4-P(Ph)_2CH_2]_2$  was observed after five days. The new complex showed an infrared absorption at  $2130\text{ cm}^{-1}$ . All attempts to separate the complex from the excess amine resulted in decomposition of the product.

Hexanediamine (10.0 mmol) was allowed to react with  $[SC-W(CO)_4-P(Ph)_2CH_2]_2$  (0.10 mmol) in 50 ml of THF in the presence of pyridine and  $CaH_2$ . Four days later the IR spectrum showed that all the thiocarbonyl ligand had reacted. Attempts to isolate the product,  $[H_2NRNC-W(CO)_4-P(Ph)_2CH_2]_2$ , by column chromatography or protonation of the amine groups were unsuccessful.

## 4. Preparation of $Bu_4N[CpW(CO)_2CS]$

The thiocarbonyl complex  $Bu_4N[CpW(CO)_2CS]$  was synthesized by allowing  $Bu_4N[IW(CO)_4CS]$  to react with  $Na[C_5H_5]$ . All efforts to isolate the thiocarbonyl anion as the  $Bu_4N^+$ ,  $Et_4N^+$  or  $PPN^+$  salts produced oils which could not be crystallized. Therefore  $Bu_4N[CpW(CO)_2CS]$  was

always prepared and reacted in situ; it was identified by its infrared spectrum.

Two methods for preparing  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  were devised. Each method required anhydrous conditions to achieve a good yield of the cyclopentadienyl derivative. The reactions were performed in Schlenk ware on a vacuum/ $\text{N}_2$  line, and all glassware was flame-dried in vacuo just before use. After the  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$  was placed in the reaction vessel it was heated gently under vacuum to drive off any residual moisture. The reactions were conducted under a positive pressure of  $\text{N}_2$ .

In method A, a solution of  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$  (0.71 g, 1.0 mmol) in 50 ml of THF was stirred at  $0^\circ$  while an equivalent of  $\text{Na}[\text{C}_5\text{H}_5]$  (2.0 ml of a 0.5 M solution, 1.0 meq) was added by syringe. The solution was allowed to stir at  $0^\circ$  for 15 min, and then the reaction vessel was transferred to a water bath at  $60^\circ$ . Vigorous bubbling was observed as the solution warmed. After 1.5 hours at  $60^\circ$  the gas evolution had ceased; the mixture was yellow-brown and cloudy, owing to the formation of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  and the precipitation of  $\text{NaI}$ . The mixture was cooled to  $0^\circ$ , and a small amount of *i*-PrOH (0.5 to 1.0 ml) was added to destroy any remaining  $\text{Na}[\text{C}_5\text{H}_5]$ . The infrared spectrum showed complete conversion to the  $\eta^5$ -cyclopentadienyl complex.

IR(CH<sub>2</sub>Cl<sub>2</sub>): 1890s, 1804vs.

Method B involved the removal of iodide from the reaction mixture and was used whenever iodide would interfere with a subsequent reaction of the thiocarbonyl anion. Silver tetrafluoroborate (0.19 g, 1.0 mmol) in 20 ml of THF was added to a stirred solution of Bu<sub>4</sub>N[IW(CO)<sub>4</sub>CS] (0.71 g, 1.0 mmol) in 40 ml of THF at 0°. Silver iodide precipitated, and the reaction vessel was covered to prevent its decomposition to silver metal. After 40 min at 0° the suspension was filtered. Addition of Na[C<sub>5</sub>H<sub>5</sub>] (2.0 ml of a 0.5 M solution, 1.0 mmol) to the yellow filtrate caused an immediate color change to deep red. The red solution was allowed to stir at 0° for 15 min and then was heated to 60° in a water bath. Vigorous CO evolution was observed and the color faded to yellow-brown. The bubbling stopped after about 1.5 hours at 60°. The solution was cooled to 0°, and a few drops of i-PrOH (0.5 to 1.0 ml) were added to destroy any excess Na[C<sub>5</sub>H<sub>5</sub>]. Again, only the desired product was observed in the infrared spectrum of a sample (see above).

##### 5. Preparation of Bu<sub>4</sub>N[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS]

The hydrotris(1-pyrazolyl)borate derivative of W(CO)<sub>5</sub>CS, [HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS]<sup>-</sup>, was always prepared and reacted in situ. A solution of Bu<sub>4</sub>N[IW(CO)<sub>4</sub>CS] (0.71 g, 1.0 mmol) in 40 ml of acetone was stirred at 0° while

2.0 ml of a 0.5 M solution of  $\text{AgBF}_4$  in acetone was added by drops. After stirring for one hour the resulting suspension was filtered. The filtrate was treated with  $\text{K}[\text{HB}(\text{pz})_3]$  (0.25 g, 1.0 mmol) and stirred at reflux until the IR spectrum showed only two strong CO bonds, at 1884 and  $1787\text{ cm}^{-1}$ , corresponding to  $\text{Bu}_4\text{N}[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]$ . The solution was then cooled to  $0^\circ$  and filtered through Celite before further reaction.

#### 6. Preparation of $\text{CpW}(\text{CO})(\text{CS})\text{NO}$

The complex  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 4, method B) was generated by the reaction of  $\text{AgBF}_4$  with  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$ , followed by filtration and treatment of the filtrate with  $\text{Na}[\text{C}_5\text{H}_5]$ . The solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  was cooled to  $0^\circ$ ; glacial acetic acid (0.02 ml) was added, followed by N-methyl-N-nitroso-p-toluenesulfonamide (0.22 g, 1.0 mmol) and then more glacial acetic acid (0.10 ml). The solution was stirred at  $0^\circ$  for five minutes and then was heated to  $40^\circ$  for two hours. A vigorous evolution of gas was observed. The solution then was cooled to  $0^\circ$ , filtered through Celite, and evaporated under reduced pressure. The residue was dissolved in 5 ml  $\text{CH}_2\text{Cl}_2$ . Chromatography on a Florisil column (2 x 40 cm) with  $\text{CH}_2\text{Cl}_2$  gave a green-brown solution which contained a mixture of compounds. This solution was evaporated under reduced pressure. The

residue was extracted with 10 ml of CS<sub>2</sub> and placed on the top of a silica gel column (2.5 x 65 cm) in CS<sub>2</sub>. Elution with the same solvent developed three bands; in order of elution these were: green, yellow and pink. The green band was identified as CpW(CO)(CS)NO; the yellow, as CpW(CO)<sub>2</sub>NO.<sup>48</sup> The pink product was not isolated. The thiocarbonyl solution was evaporated slowly to give a solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> with hexane at -20° gave olive needles of CpW(CO)(CS)NO. A typical yield was 0.20 g (0.57 mmol, 57%).

IR(CS<sub>2</sub>): 1990s, 1680s, 1260s. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ5.87s (Cp). <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ-94.4 (Cp), -215.1 (CO), -329.7 (CS). Mass spectrum: parent ion at m/e 350.

Anal. Calc. for C<sub>7</sub>H<sub>5</sub>NO<sub>2</sub>SW: C, 23.94; H, 1.43. Found: C, 23.81; H, 1.50.

#### 7. Preparation of HB(pz)<sub>3</sub>W(CO)(CS)NO

A freshly prepared acetone solution of Bu<sub>4</sub>N[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS] (1.0 mmol; Sect. 5) was evaporated under reduced pressure, and the residue was dissolved in 20 ml of CH<sub>2</sub>Cl<sub>2</sub>. Nitrosonium hexafluorophosphate (0.174 g, 1.0 mmol) was added, and the solution was stirred about 6 hr, until gas evolution ceased. The reaction mixture was then evaporated to dryness. The residue was dissolved in a minimum amount of CS<sub>2</sub> and eluted on a silica gel column (2.5 x 60 cm) with the

same solvent. Careful elution gave two bands, green and then yellow, that were never fully resolved. The green band was identified as  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$ ; the yellow, as  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{NO}$ .<sup>99</sup> The green solution was collected and evaporated to dryness. Crystallization from methylene chloride with hexane at  $-20^\circ$  gave emerald crystals (0.244 g, 49%). The thiocarbonyl complex  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$  was always contaminated with some  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{NO}$ ; neither chromatography nor recrystallization separated these compounds completely.

IR( $\text{CS}_2$ ): 1982s, 1670s, 1252s.  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -106.0 (pz), -135.8 (pz), -143.9 (pz), -217.9 ( $\text{C}=\text{O}$ ), -319.2 ( $\text{C}\equiv\text{S}$ ). Mass spectrum: parent ion at  $m/e = 499$ .

Anal. Calc. for  $\text{C}_{11}\text{H}_{10}\text{BN}_7\text{O}_2\text{SW}$ : C, 26.47; H, 2.02; N, 19.64. Found: C, 29.73; H, 3.00; N, 17.97.

#### 8. Reaction of $\text{CpW}(\text{CO})(\text{CS})(\text{NO})$ with $\text{MeNH}_2$

A slow stream of  $\text{MeNH}_2$  was bubbled through a solution of  $\text{CpW}(\text{CO})(\text{CS})\text{NO}$  (0.19 g, 0.53 mmol) in 10 ml of THF for 20 min; an orange color developed immediately. On stirring the mixture for six hours at room temperature an orange solution and a small amount of greenish precipitate were obtained. The mixture was evaporated under reduced pressure, and the residue was extracted with 5 ml of  $\text{CH}_2\text{Cl}_2$ . The resulting solution was eluted on a Grade III Woelm alumina column (2 x 40 cm) with the

same solvent, and the orange eluate was evaporated to a powder. Crystallization from methylene chloride with hexane at  $-20^{\circ}$  gave orange needles of the isocyanide complex,  $\text{CpW}(\text{CO})(\text{CNMe})\text{NO}$ , in 60% yield.

IR( $\text{CH}_2\text{Cl}_2$ ): 2141m, 1911s, 1601s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 3.77s ( $\text{CH}_3$ ), 5.60s (Cp). Mass spectrum: parent ion at m/e 348. Anal. Calc. for  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{W}$ : C, 27.61; H, 2.32. Found: C, 27.52; H, 2.32.

9. Reaction of  $\text{CpW}(\text{CO})(\text{CS})\text{NO}$  with ethylenediamine

The thiocarbonyl complex (0.33 mmol) was stirred with ethylenediamine (0.33 mmol) and pyridine (0.10 ml) in 10 ml of THF. A color change from green to orange was observed. The IR spectrum of a sample of the solution showed one CO band at  $\sim 1890\text{ cm}^{-1}$  and no CN band, indicating the probable formation of a cyclic carbene complex. The reaction mixture then evaporated to dryness on a roto-evaporator. The orange residue was insoluble in organic solvents and water; it was not identified. The reaction was repeated without the pyridine catalyst, but the results were the same.

10. Preparation of  $\text{CpW}(\text{CO})_2(\text{CS-DNP})$ , DNP = 2,4-dinitrophenyl

Addition of chloro-2,4-dinitrobenzene (0.20 g, 1.0 mmol) to a solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 4, method A) in 50 ml of THF at  $0^{\circ}$  produced a red solution which continued to darken until it was black. After 15 min

the solution was filtered through Celite. Evaporation of the filtrate under reduced pressure gave a black residue which was extracted with 50 ml portions of Et<sub>2</sub>O until the extract was colorless. The ether extracts were combined and evaporated to a dark red solid. The solid was dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub> and eluted on a Florisil column (2 x 40 cm) with the same solvent. A purple band eluted first, followed by a deep red band. The purple band contained CpW(CO)<sub>2</sub>(CS)Cl, identified by its IR spectrum (see below). The red band was collected, and the red material remaining on the column was eluted with Et<sub>2</sub>O. The red eluates were combined and evaporated to a solid. Copper-colored crystals of CpW(CO)<sub>2</sub>(CS-DNP) were obtained by recrystallizing the solid from CH<sub>2</sub>Cl<sub>2</sub> with hexane at -20° (0.20 g, 40%).

IR(CS<sub>2</sub>): 2001s, 1930s, 1350m. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ5.8s (Cp), 8.50 doublet of doublets (Ph, J = 9 Hz, J' = 2 Hz), 9.05d (Ph, J = 2 Hz), 9.05d (Ph, J = 9 Hz). <sup>13</sup>C NMR(CDCl<sub>3</sub>): δ-92.5 (Cp), -121.2 (Ph), -127.1 (Ph), -128.2 (Ph), -138.5 (Ph), -219.3 (C≡O), -261.7 (W-C-S).  
Anal. Calc. for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>SW: C, 32.57; H, 1.56. Found: C, 32.40; H, 1.49.

#### 11. Preparation of HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS-Me)

One millimole of iodomethane (0.14 g, 0.062 ml) was added to a solution of Bu<sub>4</sub>N[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS] (1.0 mmol;

Sect. 5). The IR spectrum of the reaction mixture showed bands at 1979 and 1893  $\text{cm}^{-1}$ . After the solution had stirred for 30 min, it was evaporated to dryness and the residue was dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$ . This solution was placed on the top of a 2 x 40 cm column of Florisil and eluted with  $\text{CH}_2\text{Cl}_2$ . The single orange band was collected, concentrated, diluted with hexane and cooled to  $-20^\circ$ , yielding orange crystals of the desired S-methyl derivative (0.41 g, 80%).

IR( $\text{CS}_2$ ): 1979s, 1893s.  $^1\text{H}$  NMR( $\text{CS}_2$ ):  $\delta$ 2.60s ( $\text{CH}_3$ ), 6.17t (pz), 7.55m,br (pz), 7.75m,br (pz).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -17.4 (S- $\text{CH}_3$ ), -105.7 (pz), -144.9 (pz), -135.2 (pz), -224.7 ( $\text{C}\equiv\text{O}$ ), -264.4 (W-C-S). Mass spectrum: parent ion at  $m/e = 509$ . Anal. Calc. for  $\text{C}_{13}\text{H}_{13}\text{BN}_6\text{O}_2\text{SW}$ : C 30.42, H 2.73, N 16.5. Found: C 30.14, H 2.61, N 16.66.

## 12. Preparation of $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2(\text{CS-Et})$

Iodoethane (0.16 g, 1.0 mmol) was injected into a solution of  $\text{Bu}_4\text{N}[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 5) by syringe. The solution was heated to  $40^\circ$  for thirty minutes, and then was cooled to RT and evaporated to a dark residue. The residue was dissolved in  $\text{CS}_2$  and eluted on a 2 x 40 cm column of silica gel in  $\text{CS}_2$ . An orange band was collected and evaporated to dryness. Recrystallization from hexane at  $-20^\circ$  gave thin gold plates of  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2(\text{CS-Et})$ . The average yield was 54%.

IR(CS<sub>2</sub>): 1979s, 1892s. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ1.45t (CH<sub>3</sub>)  
 2.97q (CH<sub>2</sub>), 6.12t (pz), 7.50d (pz), 7.54m (pz). Anal.  
 Calc. for C<sub>14</sub>H<sub>15</sub>BN<sub>6</sub>O<sub>2</sub>SW: C, 31.96; H, 2.87; N, 15.97.  
 Found: C, 31.89; H, 1.20; N, 15.69.

13. Preparation of HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS-DNP), DNP = 2,4-dinitrophenyl

A solution of Bu<sub>4</sub>N[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS] (1.0 mmol; Sect. 5) in acetone was cooled to 0° and then an equivalent of chloro-2,4-dinitrobenzene (0.21 g, 1.0 mmol) was added against a counter current of nitrogen. Upon warming to RT the yellow solution turned red. After one hour the solution was filtered through Celite and evaporated to dryness. A solution of the residue in a minimum of CH<sub>2</sub>Cl<sub>2</sub> was eluted on a Florisil column (2 x 4 cm) with the same solvent. A single red band was eluted with CH<sub>2</sub>Cl<sub>2</sub>, and red material that remained on the column was eluted with ether. The red solutions were combined and evaporated to a black powder. Deep red crystals of HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS-DNP) were obtained from a 3:1 mixture of chloroform and hexane at -20°.

IR(CS<sub>2</sub>): 1999s, 1914s. <sup>1</sup>H NMR(CDCl<sub>3</sub>): at -60°;  
 6.22s (pz), 6.38s (pz), 7.71d' (pz), 7.78d (pz),  
 8.02d (pz), 8.35 doublet of doublets (Ph, J = 9 Hz,  
 J' = 3 Hz), 9.02d (Ph, J = 3 Hz), 9.06d (Ph, J = 9 Hz).

Anal. Calc. for  $C_{18}H_{13}BN_8O_6SW$ : C, 32.55; H, 1.97; N, 16.87. Found: C, 32.89; H, 2.00; N, 16.41.

14. Further reactions of the thiocarbonyl anions with organic halides

Spectroscopic evidence for the formation of mercaptocarbyne complexes was obtained in low-temperature reactions of  $Bu_4N[CpW(CO)_2CS]$  with MeI,  $MeOSO_2F$ , EtI, and BzBr; but the isolated products were oils. The thiocarbonyl anion reacted with *i*-PrI,  $(Ph)_2PCl$ , acetyl chloride, and benzoyl chloride, presumably to give similar S-adducts, but the stabilities were too low to permit isolation of the desired complexes. Under the same conditions,  $Ph_2CHCl$  did not react and *p*-nitrobenzylbromide gave only trans- $CpW(CO)_2(CS)Br$  (see below).

The pyrazolyborate complex  $[HB(pz)_3W(CO)_2(CS)]^-$  formed a solid S-adduct upon reaction with *i*-PrI, but the orange powder decomposed upon contact with air. The reactions of BzBr and  $AllBr$  with  $Bu_4N[HB(pz)_3W(CO)_2CS]$  also appeared to give S-adducts; these products, however, were oils. *N,N*-dimethylcarbonyl chloride did not react with the pyrazolyborate thiocarbonyl anion.

15. Preparation of  $CpW(CO)_2(CS)SePh$

Phenylselenenyl bromide was prepared by literature methods<sup>108</sup> and recrystallized from pentane. Addition of

PhSeBr (0.24 g, 1.0 mmol) to a solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 4, method A) at  $0^\circ$  gave a purple solution. The solution was warmed to RT and then filtered through Celite and evaporated to dryness under reduced pressure. The dark residue was dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  and placed on a 2 x 40 cm Florisil column in  $\text{CH}_2\text{Cl}_2$ ; elution with the same solvent gave a purple band. The purple solution was concentrated to 30 ml under reduced pressure; then it was diluted with 30 ml of hexane and slowly evaporated to give purple crystals. The product was re-dissolved in  $\text{CS}_2$  and carefully eluted through a silica gel column (2.5 x 60 cm) with  $\text{CS}_2$ . The product separated into three components: a yellow band (identified as  $(\text{Ph}_2\text{Se})_2$ ), a purple band (trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{Br}$ ), and a magenta band ( $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$ ). The solution of  $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$  was evaporated and large, magenta crystals were obtained by recrystallization from methylene chloride with hexane at  $-20^\circ$  (0.18 g, 35%).

IR( $\text{CS}_2$ ): 2008sh, 2000m, 1958s, 1262s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.67s (Cp, cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$ ), 5.73s (Cp, trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$ ), 7.18m (Ph), 7.48m (Ph). Anal. Calc. for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{SSeW}$ : C, 33.29; H, 1.99. Found: C, 33.50; H, 2.10.

A similar reaction with PhSCl also gave a purple solution. The IR spectrum of a sample of the solution

suggested that trans-CpW(CO)<sub>2</sub>(CS)SPh had formed; but the product decomposed before it could be isolated.

IR(CS<sub>2</sub>): 2025m, 1975s, 1260s.

When an equivalent of 2,4-dinitrophenylsulfenylchloride was added to a solution of Bu<sub>4</sub>N[CpW(CO)<sub>2</sub>CS] in THF, the solution turned red. Elution of the product through a Florisil column (2 x 40 cm) with CH<sub>2</sub>Cl<sub>2</sub> gave a purple compound which was identified as trans-CpW(CO)<sub>2</sub>(CS)Cl. An orange band was then eluted with Et<sub>2</sub>O. The orange material exhibited an IR spectrum indicative of a trans-substituted complex but decomposed before it could be purified or crystallized.

IR(CS<sub>2</sub>): 2020m, 2013m, 1967s, 1275s.

The pyrazolylborate derivative, Bu<sub>4</sub>N[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS], reacted immediately with PhSCl to give a light orange solution. The IR spectrum of this solution showed two strong CO bands at 2000 and 1900 cm<sup>-1</sup> and no CS band, suggesting the formation of a HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS-R) complex. However, the CO bands disappeared as the reaction mixture stirred at 0° under N<sub>2</sub>, and the product was never isolated.

#### 16. Preparation of cis-CpW(CO)<sub>2</sub>(CS)MPh<sub>3</sub> (M = Sn, Pb)

A solution of Bu<sub>4</sub>N[CpW(CO)<sub>2</sub>CS] (1.0 mmol; Sect. 4, method A) was cooled to 0°, and Ph<sub>3</sub>SnCl (0.39 g, 1.0 mmol) was added. After 10 min the solution was filtered through

Celite and evaporated under reduced pressure. The residue was slurried with  $\text{CH}_2\text{Cl}_2$  and placed on a 2 x 40 cm column of Florisil. Elution with  $\text{CH}_2\text{Cl}_2$  gave one gold band. The gold solution was concentrated to 30 ml, diluted with 30 ml of hexane, and evaporated slowly to 10 ml. Yellow crystals of cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$  were filtered from the solution. An analytical sample was recrystallized from  $\text{CH}_2\text{Cl}_2$  with hexane at  $-20^\circ$  (0.41 g, 60%).

IR( $\text{CS}_2$ ): 1988s, 1924s, 1238s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.31s (Cp), 7.25m (Ph).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -89.0 (Cp), -122.5 (Ph), -122.7 (Ph), -130.3 (Ph), -134.4 (Ph), -199.9 (CO), -201.3 (CO), -283.3 (CS). Anal. Calc. for  $\text{C}_{26}\text{H}_{20}\text{O}_2\text{SSnW}$ : C, 44.66; H, 2.88. Found: C, 44.13; H, 2.56.

The analogous reaction with  $\text{Ph}_3\text{PbCl}$  gave golden cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{PbPh}_3$  in 51% yield.

IR( $\text{CS}_2$ ): 1985s, 1926m, 1237s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.47s (Cp), 7.44m (Ph).  $^{13}\text{C}$  NMR( $\text{CD}_2\text{Cl}_2$ ):  $\delta$ -90.5 (Cp), -128.1 (Ph), -129.1 (Ph), -137.5 (Ph), -151.9 (Ph), -215.3 (CO), -218.0 (CO), -311.7 (CS). Anal. Calc. for  $\text{C}_{26}\text{H}_{20}\text{O}_2\text{PbSW}$ : C, 39.64; H, 2.56. Found: C, 39.59; H, 2.52.

17. Reaction of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  with other organometallic halides

The thiocarbonyl anion appeared to react with  $\text{Ph}_3\text{GeCl}$ ,  $(\text{CH}_3)_3\text{SnCl}$ ,  $\text{PhHgCl}$ , and  $\text{CH}_3\text{HgCl}$  to give the desired bimetallic derivatives. However, these products were unstable and could not be isolated. When  $(\text{Ph}_3\text{P})\text{AuCl}$  was added to a solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$ , the IR spectrum of the resultant mixture showed two strong CO bands but no CS band. Apparently an S-adduct was formed; however, this product was also unstable. Reaction of  $\text{CpM}(\text{CO})_3\text{Cl}$  ( $\text{M} = \text{Mo}, \text{W}$ ) with  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  gave only  $[\text{CpM}(\text{CO})_3]_2$ ; reaction of  $\text{Mn}(\text{CO})_5\text{Br}$ , only  $\text{Mn}_2(\text{CO})_{10}$ . Addition of  $\text{CpFe}(\text{CO})_2\text{Cl}$ ,  $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ , or  $[\text{CpFe}(\text{CO})_2\text{CS}]\text{PF}_6$  to a solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  caused changes in the IR spectrum of the solution, but no products were isolated. The thiocarbonyl anion did not react with trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{Br}$ .

18. Reaction of  $\text{CpW}(\text{CO})_2(\text{CS})\text{MPh}_3$  ( $\text{M} = \text{Sn}, \text{Pb}$ ) with  $\text{MeNH}_2$

A sample of cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$  (0.24 g, 0.33 mmol) was placed in a 20 ml heavy-walled Pyrex tube with a magnetic stirring bar. The tube was tightly capped with a self-sealing rubber-lined cap, evacuated, and filled with  $\text{N}_2$ . Ten milliliters of THF were injected from a syringe. After a mercury bubbler was connected to the tube by syringe,  $\text{MeNH}_2$  was introduced into the tube and

allowed to bubble through the solution for 15 minutes. Then the bubbler was disconnected and the reaction vessel was pressurized to ~2 atm with MeNH<sub>2</sub>. The solution was stirred for 20 hours at 50°; afterward, it was cooled to RT and evaporated under reduced pressure. The residue was extracted with 5 ml of benzene and eluted on a column of Grade III Woelm alumina (2 x 40 cm) with benzene. The colorless product was recovered by collecting 50 ml portions of eluate, measuring the infrared spectrum of each portion, and then combining all portions showing a CN stretch. Evaporation to a white powder and crystallization from CH<sub>2</sub>Cl<sub>2</sub> with hexane at -20° gave colorless crystals of the isocyanide complex, CpW(CO)<sub>2</sub>(CNMe)SnPh<sub>3</sub> in 63% yield.

A mixture of cis(\*) and trans isomers. IR(C<sub>6</sub>H<sub>12</sub>): 2105m(br), 1947vs\*, 1932w, 1888vs\*, 1875s. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ2.94s (CNCH<sub>3</sub>\*, J<sub>Sn-CNCH<sub>3</sub>\*</sub> = 14 Hz), 3.68s (CNCH<sub>3</sub>), 5.21s (Cp), 5.35s (Cp\*), 7.58m (Ph). Anal. Calc. for C<sub>27</sub>H<sub>23</sub>NO<sub>2</sub>SnW: C, 46.59; H, 3.34. Found: C, 46.74; H, 3.50.

Repeating the procedure with CpW(CO)<sub>2</sub>(CS)PbPh<sub>3</sub> (0.27 g, 0.34 mmol) gave yellow needles of the complex CpW(CO)<sub>2</sub>(CNMe)PbPh<sub>3</sub>.<sup>121</sup> (0.08 g, 30%).

A mixture of cis (\*) and trans isomers. IR(C<sub>6</sub>H<sub>12</sub>): 2112m, 1950s\*, 1936sh, 1892s\*, 1882m(sh). <sup>1</sup>H NMR(CDCl<sub>3</sub>):

$\delta 2.96s$  ( $CNCH_3^*$ ,  $J_{Pb-CNCH_3^*} = 29$  Hz),  $3.61s$  ( $CNCH_3$ ,  $J_{Pb-CNCH_3} = 8$  Hz),  $5.16s$  (Cp,  $J_{Pb-Cp} = 6$  Hz),  $5.34s$  (Cp\*,  $J_{Pb-Cp^*} = 2$  Hz),  $7.41m$  (Ph). Anal. Calc. for  $C_{27}H_{23}NO_2PbW$ : C, 41.33; H, 2.96. Found: C, 41.50; H, 3.04.

19. Reaction of  $cis-CpW(CO)_2(CS)MPh_3$  ( $M = Sn, Pb$ ) with ethylenediamine

Ethylenediamine (0.08 ml, 1.2 mmol) was refluxed with  $cis-CpW(CO)_2(CS)SnPh_3$  (0.24 g, 0.34 mmol) in 25 ml of THF. After 12 hr the IR spectrum of a sample of the solution showed two CO bands at 1903 and 1827  $cm^{-1}$ , no CS band, and no CN band, indicating the probable formation of the cyclic amino carbene complex,  $CpW(CO)_2(CN_2C_2H_6)SnPh_3$ . However, the instability of the complex prevented its isolation by extraction or column chromatography.

The analogous reaction with  $cis-CpW(CO)_2(CS)PbPh_3$  gave only unreacted starting material and an insoluble, unstable green material that could not be identified.

20. Reaction of  $cis-CpW(CO)_2(CS)SnPh_3$  with  $[PPN]N_3$

A slurry of  $[PPN]N_3$  (0.15 g, 0.25 mmol) and  $cis-CpW(CO)_2(CS)SnPh_3$  (0.18 g, 0.25 mmol) in 25 ml of THF was stirred for 24 hr. The solution darkened to orange, and the IR spectrum of a sample of the mixture showed three absorbances (at 2055m, 1920m, and 1805s) which might be expected for the desired product,  $PPN[CpW(CO)_2(NCS)SnPh_3]$ .

The mixture was cooled to 0°, an excess of CH<sub>3</sub>I was added, and then the mixture was slowly warmed to RT. The IR spectrum now showed two bands at 1952s and 1867m, suggesting that cis-CpW(CO)<sub>2</sub>(NCS-CH<sub>3</sub>)SnPh<sub>3</sub> had formed. However, the product decomposed before it could be isolated.

21. Reaction of cis-CpW(CO)<sub>2</sub>(CS)MPh<sub>3</sub> (M = Sn, Pb) with C<sub>6</sub>H<sub>5</sub>Li

A solution of cis-CpW(CO)<sub>2</sub>(CS)SnPh<sub>3</sub> (0.18 g, 0.25 mmol) in 40 ml of THF was cooled to -78°. Upon injection of PhLi (0.26 ml of a 1.0 M solution, 0.26 mmol), the solution darkened to a gold color. The temperature was raised slowly to 0°, and then MeOSO<sub>2</sub>F (0.021 ml, 0.25 mmol) was introduced by syringe. Evaporation, extraction of the oily residue with benzene, and elution on a column of Grade III Woelm alumina with benzene gave two compounds. One compound was a white powder, identified by spectra as Ph<sub>4</sub>Sn; the other, an orange oil, was CpW(CO)<sub>2</sub>(CS-Me).

IR: 1990s, 1920s. <sup>1</sup>H NMR: δ2.35 (CH<sub>3</sub>), 5.40 Cp).

A similar reaction occurred when a THF solution of cis-CpW(CO)<sub>2</sub>PbPh<sub>3</sub> (0.27 g, 0.33 mmol) was treated with an equivalent of PhLi, followed by MeOSO<sub>2</sub>F. The solution was evaporated under reduced pressure, and the residue was extracted with pentane, yielding a white solid and

a yellow solution. The white solid was  $\text{Ph}_4\text{Pb}$ ; the yellow solution contained  $\text{CpW}(\text{CO})_2(\text{CS-Me})$ .

22. Reaction of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  with  $\text{HgI}_2$  and preparation of  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$

The reaction of less than half an equivalent of  $\text{HgI}_2$  (0.20 g, 0.44 mmol) with  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 4, method A) in 50 ml of THF produced a bright yellow solution. The solvent was evaporated under reduced pressure; the residue was dissolved in a minimum of  $\text{CH}_2\text{Cl}_2$  and eluted on a Florisil column (2 x 40 cm) with  $\text{CH}_2\text{Cl}_2$ . The yellow eluate was evaporated to an orange powder, tentatively identified as  $\text{Hg}[\text{CpW}(\text{CO})\text{CS}]_2$ . Yield of the powder was 57%. Attempts to crystallize the product were unsuccessful.

IR( $\text{CS}_2$ ): 1980sh, 1975s, 1920m, 1900sh, 1198m(br).

$^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.83s (Cp).

An excess of  $\text{HgI}_2$  (0.60 g, 1.3 mmol) was added against a counter-current of nitrogen to a THF solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 4, method A) at  $0^\circ$ , and the mixture was stirred for 30 min. At this point, an IR spectrum of a sample of the solution showed carbonyl bands at 1980, 1975, 1920, and 1900  $\text{cm}^{-1}$  and a thiocarbonyl band at 1198  $\text{cm}^{-1}$ , suggesting that the species in solution was  $\text{Hg}[\text{CpW}(\text{CO})_2\text{CS}]_2$ . The solution was warmed to room temperature, and the solvent was

evaporated under reduced pressure. The residue was slurried in  $\text{CH}_2\text{Cl}_2$  and placed on a 2 x 40 cm column of Florisil. Elution with  $\text{CH}_2\text{Cl}_2$  gave an ochre solution which was diluted with 30 ml of hexane and slowly evaporated to give orange crystals of  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$  (73%). An analytical sample was recrystallized from methylene chloride with hexane at  $-20^\circ$ .

IR( $\text{CS}_2$ ): 1990s, 1945s, 1268m, 1234s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.76s (Cp). Mass spectrum: parent ion at 672 (using  $^{198}\text{Hg}$  and  $^{182}\text{W}$ ). Anal. Calc. for  $\text{C}_8\text{H}_5\text{HgIO}_2\text{SW}$ : C, 14.20; H, 0.74. Found: C, 14.29; H, 0.89.

23. Preparation of trans-CpW(CO)<sub>2</sub>(CS)X (X = I, Br, Cl)

Iodine (0.25 g, 1.0 mmol) was allowed to react with a solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  (1.0 mmol; Sect. 4, method A) in 50 ml of THF at  $0^\circ$ , causing an immediate color change to magenta. The solution was stirred an additional 10 min, filtered through Celite, and then evaporated under reduced pressure. Extracting the residue with  $\text{CH}_2\text{Cl}_2$  and rapidly eluting on a 2 x 40 cm Florisil column with  $\text{CH}_2\text{Cl}_2$  separated a purple solution. Thirty milliliters of hexane were added, and the solution was evaporated slowly to yield deep-purple crystals of trans-CpW(CO)<sub>2</sub>(CS)I (77%). The product was usually dried in vacuo and used without further purification. An

analytical sample was recrystallized from methylene chloride with hexane at  $-20^{\circ}$ .

IR( $\text{CS}_2$ ): 2025m, 2015w, 1972s, 1940vw, 1267s.  
 $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.84s (Cp).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -93.55 (Cp),  
 -195.01 (CO), -310.52 (CS). Mass spectrum: parent ion  
 at  $m/e = 475$ . Anal. Calc. for  $\text{C}_8\text{H}_5\text{IO}_2\text{SW}$ : C, 20.18;  
 H, 1.06. Found: C, 20.21; H, 1.11.

When a solution of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  was treated with bromine (0.15 g, 1.0 mmol), followed by the isolation procedure described above, purple crystals of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{Br}$  were obtained in 65% yield.

IR( $\text{CS}_2$ ): 2030m, 1975s.

The thiocarbonyl anion reacted with  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , or  $[\text{Cp}_2\text{Fe}]\text{FeCl}_4$  to form trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{Cl}$ .

IR( $\text{CS}_2$ ): 2036m, 1979s, 1270s.

#### 24. Preparation of trans-HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS)I

The complex-salt  $\text{Bu}_4\text{N}[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]$  (1.0 mmol) was prepared as in Sect. 5 and cooled to  $0^{\circ}$ . Iodine (0.26 g, 1.0 mmol) in 10 ml of acetone was added over 5 min from an equi-pressure dropping funnel. After 10 minutes more the solution was filtered through Celite, and the solvent was evaporated under reduced pressure. The residue was extracted with 3 ml of  $\text{CH}_2\text{Cl}_2$ , and the extract was eluted on a Florisil column (2 x 40 cm) with  $\text{CH}_2\text{Cl}_2$ , yielding a single red band. The eluate was

collected, diluted with 30 ml of hexane, and slowly evaporated to give carmine needles of trans- $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2(\text{CS})\text{I}$  (0.22 g, 33%). Again, the product was dried in vacuo and used without further purification. An analytical sample was recrystallized from a methylene chloride solution with hexane at  $-20^\circ$ .

IR( $\text{CS}_2$ ): 2017m, 1961s, 1243s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 6.23t (pz), 7.61d (pz), 8.45t (pz).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -106.68 (pz), -136.43 (pz), -146.56 (pz), -233.97 (CO), -299.86 (CS). Anal. Calc. for  $\text{C}_{12}\text{H}_{10}\text{BIN}_6\text{O}_2\text{SW}$ : C, 23.09; H, 1.61. Found: C, 23.17; H, 1.57.

25. Reaction of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  with  $\text{PPh}_3$

A mixture of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  (0.53 g, 1.1 mmol) and triphenylphosphine (0.29 g, 1.1 mmol) in 50 ml of toluene was refluxed for 2.5 hr. The resulting dark red solution was cooled to room temperature, filtered through Celite, and evaporated to dryness under reduced pressure at  $50^\circ$ . The residue was slurried in 10 ml of  $\text{CS}_2$  and placed on a 2 x 40 cm silica gel column. Careful development with  $\text{CS}_2$  resolved the product into 3 bands; in order of elution they were purple, yellow, and dark red. The purple band was eluted with  $\text{CS}_2$  and contained trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$ , identified by its IR spectrum. The yellow band was also eluted with  $\text{CS}_2$ , and on evaporation yielded a minute amount of trans- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{I}$ , identified

by its spectra. Elution of the last band with  $\text{CH}_2\text{Cl}_2$  gave a dark solution which was diluted with hexane until crystallization began. Slow evaporation produced wine-colored crystals of  $\text{CpW}(\text{CO})(\text{CS})(\text{PPh}_3)\text{I}$  (0.56 g, 78%). The analytical sample was obtained from  $\text{CH}_2\text{Cl}_2$  with hexane at  $-20^\circ$ .

IR( $\text{CS}_2$ ): 1964s, 1225s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.62s (Cp), 7.52m (Ph).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -94.57s (Cp), -127 to -134m (Ph), -224.52d (CO,  $J_{\text{P-CO}} = 10.0$  Hz), -353.10d (CS,  $J_{\text{P-CS}} = 23.8$  Hz). Anal. Calc. for  $\text{C}_{25}\text{H}_{20}\text{IOPSW}$ : C, 42.28; H, 2.84. Found: C, 42.53; H, 2.87.

The only product isolated from the reaction between trans-CpW(CO)<sub>2</sub>(CS)I and two-equivalents of  $\text{PPh}_3$  in toluene at  $100^\circ$  was  $\text{CpW}(\text{CO})(\text{CS})(\text{PPh}_3)\text{I}$ , even when a halide acceptor such as  $\text{AlCl}_3$  or  $\text{AgPF}_6$  was added to the reaction mixture.

26. Reaction of trans-CpW(CO)<sub>2</sub>(CS)I with P(OPh)<sub>3</sub>

Triphenylphosphite (0.15 ml, 0.17 g, 0.55 mmol) and trans-CpW(CO)<sub>2</sub>(CS)I (0.24 g, 0.50 mmol) were refluxed in 40 ml of toluene for 2 hr. After the solution was cooled and filtered through Celite the solvent was removed under reduced pressure. The residue was slurried in 3 ml of  $\text{CS}_2$ , and the mixture was chromatographed on a silica gel column (2 x 40 cm). Carbon disulfide eluted the trans-CpW(CO)<sub>2</sub>(CS)I that remained and the small

amount of  $\text{CpW}(\text{CO})_2(\text{P}[\text{OPh}]_3)\text{I}$  formed during the reaction. Methylene chloride washed the final red band from the column. Addition of 40 ml of hexane to the  $\text{CH}_2\text{Cl}_2$  eluate followed by slow evaporation gave burgandy crystals of  $\text{CpW}(\text{CO})(\text{CS})(\text{P}[\text{OPh}]_3)\text{I}$ , (65%). The product was recrystallized from  $\text{CH}_2\text{Cl}_2$  with hexane at  $-20^\circ$ .

IR( $\text{CS}_2$ ): 1974s, 1240s.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 5.30s (Cp), 7.42m (Ph).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ ):  $\delta$ -94.11s (Cp), -121.60d (Ph), -125.22s (Ph), -130.23d (Ph), -218.94d (CO,  $J_{\text{P-CO}} = 10.4$  Hz), -348.39d (CS,  $J_{\text{P-CS}} = 37.2$  Hz). Anal. Cal. for  $\text{C}_{25}\text{H}_{20}\text{IO}_4\text{PSW}$ : C, 39.59; H, 2.66. Found: C, 39.82; H, 2.75.

27. Reaction of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  with tdp.

A solution of the thiocarbonyl (0.25 g, 0.5 mmol) in 40 ml of toluene was heated to  $105^\circ$ , and then tris-(dimethylamino)phosphine (0.12 ml, 0.11 g, 0.6 mmol) was added from a syringe. After 3 hr the solution was cooled to RT, filtered through Celite, and evaporated to dryness under reduced pressure. The residue was washed with three 10 ml portions of pentane. The remaining solid was dissolved in a mixture of  $\text{CH}_2\text{Cl}_2$  and hexane at  $-20^\circ$ , giving black crystals of  $\text{CpW}(\text{CO})(\text{CS})(\text{tpd})\text{I}$  (0.12 g, 19%). Repeated crystallizations from methylene chloride with hexane at  $-20^\circ$  afforded large, rhomboid crystals of the product.

IR(CS<sub>2</sub>): 1958s, 1221s. <sup>1</sup>H NMR(CDCl<sub>3</sub>):  
 δ2.68d (CH<sub>3</sub>, J<sub>P-CH<sub>3</sub></sub> = 8 Hz), 5.60s (Cp). <sup>13</sup>C NMR(CDCl<sub>3</sub>):  
 δ-39.46s (CH<sub>3</sub>), -94.7s (Cp), -227.35d (CO, J<sub>P-CO</sub> = 10.4 Hz),  
 -355.86 (CS, J<sub>P-CS</sub> = 29.8 Hz).

28. Reaction of trans-CpW(CO)<sub>2</sub>(CS)I with CNMe

Methylisocyanide (0.03 ml, 0.021 g, 0.50 mmol) was added to a refluxing solution of trans-CpW(CO)<sub>2</sub>(CS)I (0.24 g, 0.50 mmol) in 25.0 ml of toluene (Note: It was important to heat the solution above 100° before the addition of CNMe, otherwise a side reaction decreased the yield of the product. (See below.) The solution was allowed to stir 40 min at 110°, then it was cooled to room temperature and filtered through Celite. The solvent was evaporated under reduced pressure. The residue was extracted with a minimum of benzene, and the extract was eluted on a column of Grade III Woelm alumina (2 x 40 cm) with benzene. Two bands were resolved, purple (trans-CpW(CO)<sub>2</sub>(CS)I) and red (CpW(CO)(CS)(CNMe)I). The red eluate was collected, diluted with 30 ml of hexane, and slowly evaporated to give an 83% yield of dark red CpW(CO)(CS)(CNMe)I. The analytical sample was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> with hexane at -20°.

IR(CS<sub>2</sub>): 1969s, 1241s. IR(CCl<sub>4</sub>): 2178m, 1977s.  
<sup>1</sup>H NMR(CDCl<sub>3</sub>): δ3.95s (CH<sub>3</sub>), 5.74s (Cp). <sup>13</sup>C NMR(CDCl<sub>3</sub>):  
 δ-31.44 (CH<sub>3</sub>), -93.91 (Cp), -141.20 (W-C-N), -222.95 (CO),

-353.62 (CS). Anal. Calc. for  $C_9H_8INOSW$ : C, 22.10; H, 1.65. Found: C, 22.04; H, 1.71.

When CNMe was allowed to react with trans- $CpW(CO)_2(CS)I$  below  $100^\circ$ , the yield of  $CpW(CO)(CS)(CNMe)I$  was low, some trans- $CpW(CO)_2(CS)I$  remained unreacted, and a yellow oil was observed. The oil was identified by its IR and NMR spectra as  $[CpW(CO)(CS)(CNMe)_2]I$ , replacement of the iodide anion with  $PF_6^-$  failed to induce crystallization.

IR( $CH_2Cl_2$ ): 2200s, 1970s, 845s.

29. Reaction of trans- $CpW(CO)_2(CS)I$  with  $PMe_2Ph$

The thiocarbonyl (0.16g, 0.33 mmol) was dissolved in 45 ml of toluene and heated to  $105^\circ$ , then  $PMe_2Ph$  (0.05 ml, 0.048 g, 0.34 mmol) was introduced by syringe. (NOTE: The solution was heated above  $100^\circ$  before addition of  $PMe_2Ph$  to avoid a competing side reaction. See below.) Two hours later the mixture was cooled and filtered through Celite, and the filtrate was evaporated under reduced pressure at  $50^\circ$ . The residue was dissolved in  $CH_2Cl_2$ . Chromatography on a 2 x 40 cm Florisil column with  $CH_2Cl_2$  separated two bands: the remaining trans- $CpW(CO)_2(CS)I$  eluted first, followed by the product. The second, red band was collected and evaporated to a powder. Dark red crystals of  $CpW(CO)(CS)(PMe_2Ph)I$  were obtained from methylene chloride with hexane at  $-80^\circ$  (63%).

IR(CS<sub>2</sub>): 1967s, 1220s. <sup>1</sup>H NMR(CDCl<sub>3</sub>):  
 δ2.21d (CH<sub>3</sub>, J<sub>P-CH<sub>3</sub></sub> = 9.5 Hz), 5.52s (Cp), 7.55m (Ph).  
<sup>13</sup>C NMR(CDCl<sub>3</sub>): δ-16.9d (CH<sub>3</sub>, J<sub>P-CH<sub>3</sub></sub> = 36 Hz),  
 -93.78 (Cp), -127.32 (Ph), -127.72 (Ph), -129.76 (Ph),  
 -130.74 (Ph), -131.07 (Ph), -132.91 (Ph), -135.15 (Ph),  
 -224.09d (CO, J<sub>P-CO</sub> = 10.0 Hz),  
 -352.77d (CS, J<sub>P-CS</sub> = 24.0 Hz). Anal. Calc. for  
 C<sub>15</sub>H<sub>16</sub>IOPSW = C, 30.74; H, 2.76. Found: C, 30.90;  
 H, 2.95.

When a solution of trans-CpW(CO)<sub>2</sub>(CS)I and PMe<sub>2</sub>Ph in toluene was stirred below 100° the yield of CpW(CO)(CS)(PMe<sub>2</sub>Ph)I was low, some trans-CpW(CO)<sub>2</sub>(CS)I remained, and a golden-yellow precipitate was observed. The precipitate was soluble only in polar organic solvents. An IR spectrum of the precipitate in CH<sub>2</sub>Cl<sub>2</sub> exhibited one CO band at 1930 cm<sup>-1</sup>, and its <sup>1</sup>H NMR spectrum indicated that there were two PMe<sub>2</sub>Ph ligands per molecule. The precipitate was formulated as [CpW(CO)(CS)(PMe<sub>2</sub>Ph)<sub>2</sub>]I. It was observed that as the temperature of the reaction mixture was increased the amount of precipitate decreased until, above 105°, there was no precipitate at all.

### 30. Preparation of trans-[CpW(CO)(CS)(PMe<sub>2</sub>Ph)<sub>2</sub>]PF<sub>6</sub>

A mixture of trans-CpW(CO)<sub>2</sub>(CS)I (0.12 g, 0.25 mmol) and PMe<sub>2</sub>Ph (0.07 ml, 0.068 g, 0.50 mmol) in 30 ml of

toluene was heated to 80° for 2 hr, giving a red solution and a golden yellow precipitate. Filtering the solution through a fritted-glass funnel and washing with CS<sub>2</sub> gave trans-[CpW(CO)(CS)(PMe<sub>2</sub>Ph)<sub>2</sub>]I as an orange powder (83%). The powder was dissolved in acetone, and the solution was passed through a column of Amberlite IRA-400 anion exchange resin in the PF<sub>6</sub><sup>-</sup> form. The eluate was evaporated to about 5 ml under reduced pressure, a layer of ether (10 ml) was carefully placed on top of the eluate, and the mixture was cooled to -20° for 48 hr. Small translucent crystals of trans-[CpW(CO)(CS)(PMe<sub>2</sub>Ph)<sub>2</sub>]PF<sub>6</sub> were obtained (70%).

IR(CH<sub>2</sub>Cl<sub>2</sub>): 1930s, 845s. IR(CH<sub>3</sub>CN): 1932s, 1234s.

<sup>1</sup>H NMR(CD<sub>3</sub>CN): δ2.18 doublet of doublets

(CH<sub>3</sub>, J<sub>P-CH<sub>3</sub></sub> = 10 Hz, J'<sub>P-CH<sub>3</sub></sub> = 3 Hz),

5.40t (Cp, J<sub>P-Cp</sub> = 3 Hz), 7.52m (Ph). <sup>13</sup>C NMR(CD<sub>3</sub>CN):

δ-16.34 (CH<sub>3</sub>), -17.20 (CH<sub>3</sub>), -18.25 (CH<sub>3</sub>), -19.18 (CH<sub>3</sub>),

-95.49d (Cp, J<sub>P-Cp</sub> = 28 Hz), -130.58 (Ph), -132.36 (Ph),

-133.02 (Ph), -134.40 (Ph), -229.76t (CO, J<sub>P-CO</sub> = 21 Hz),

-338.07t (CS, J<sub>P-CS</sub> = 21 Hz). <sup>31</sup>P NMR(CD<sub>3</sub>CN): singlet at

8.89 ppm downfield from 85% H<sub>3</sub>PO<sub>4</sub> external standard.

Anal. Calc. for C<sub>23</sub>H<sub>27</sub>F<sub>6</sub>OP<sub>3</sub>SW: C, 37.21; H, 3.67.

Found: C, 37.16; H, 3.78.

32. Reaction of trans-[CpW(CO)(CS)(PMe<sub>2</sub>Ph)<sub>2</sub>]PF<sub>6</sub> with nucleophiles

A solution of trans-[CpW(CO)(CS)(PMe<sub>2</sub>Ph)<sub>2</sub>]PF<sub>6</sub> in 10 ml of THF saturated with MeNH<sub>2</sub> was stirred in a sealed tube at 50° under an MeNH<sub>2</sub> atmosphere. After 5 days, the CO band in the IR spectrum had shifted from 1930 to 1840 cm<sup>-1</sup> and a new band had appeared at 2100 cm<sup>-1</sup>, indicating the probable formation of trans-[CpW(CO)(CNMe)(PMe<sub>2</sub>Ph)<sub>2</sub>]PF<sub>6</sub>. The product was not isolated.

An equivalent of PhLi was added to a THF solution of the thiocarbonyl complex at -78° and then the solution was warmed to 0°. The IR spectrum of a sample of the solution showed one carbonyl band at 1875 cm<sup>-1</sup>. All efforts to isolate any product of this reaction failed, probably because of the instability of the products.

33. Reaction of trans-CpW(CO)<sub>2</sub>(CS)I with carbanions

The thiocarbonyl complex (0.24 g, 0.5 mmol) was dissolved in 40 ml of THF and cooled to -78°. Methyl lithium (0.25 ml of a 2 M solution) was introduced by syringe, and the solution faded to orange. Warming the solution to RT and evaporating the solvent under reduced pressure gave an orange residue that was dissolved in CS<sub>2</sub> and eluted on a silica gel column (2 x 40 cm) with CS<sub>2</sub>. The yellow eluate was collected and dried to an intractable

oil. The IR and NMR spectra of this product was identical to those of  $\text{CpW}(\text{CO})_2\text{CS-Me}$  produced from the reaction of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  with  $\text{MeI}$ ; that complex was also a yellow oil.

IR( $\text{CS}_2$ ): 1985s, 1911s, 1130w.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$ 2.58s ( $\text{CH}_3$ ), 5.65s (Cp).

Spectroscopic evidence for the formation of similar mercaptocarbyne complexes was obtained in low temperature reactions of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  with  $\text{PhLi}$ ,  $p\text{-Me}_2\text{N-C}_6\text{H}_4\text{Li}$ ,  $\text{C}_6\text{F}_5\text{Li}$ , and  $\text{Na}[\text{C}_5\text{H}_5]$ , but the isolated products were oils. The thiocarbonyl complex did not react with  $\text{Na}[\text{CH}(\text{CO}_2\text{CH}_3)_2]$ .

34. Reaction of trans-HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS)I with RLi  
(R = Me, Ph)

Methyl lithium (0.5 ml of a 1.0 M solution, 0.5 mmol) was added by syringe to a solution of trans- $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2(\text{CS})\text{I}$  (0.31 g, 0.5 mmol) in 30 ml of THF at  $-78^\circ$ . The solution immediately turned golden yellow. After warming to room temperature. 0.10 ml of *i*-PrOH was added to destroy any remaining  $\text{MeLi}$ . The solvent was evaporated under reduced pressure, and the residue was dissolved in 3 ml of  $\text{CH}_2\text{Cl}_2$ . Elution on a Florisil column (2 x 40 cm) with  $\text{CH}_2\text{Cl}_2$  gave a single orange band. Dilution with 30 ml of hexane and then slow evaporation of the solvent produced orange crystals of

HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS-CH<sub>3</sub>) (0.21 g, 81%). An analytical sample was obtained from CH<sub>2</sub>Cl<sub>2</sub> with hexane at -20° (See Sect. 11).

IR(CS<sub>2</sub>): 1979s, 1892s. <sup>1</sup>H NMR(CDCl<sub>3</sub>): δ2.59 (CH<sub>3</sub>), 6.17t (pz), 7.55m (pz), 7.75m (pz). Anal. Calc. for C<sub>13</sub>H<sub>13</sub>BN<sub>6</sub>O<sub>2</sub>SW: C, 30.42; H, 2.73; N, 16.58. Found: C, 30.54; H, 2.66; N, 16.26.

The same procedure with PhLi at 0° also produced a yellow solution. The IR spectrum of a sample of this solution showed carbonyl bands at 1885 and 1785 cm<sup>-1</sup>, suggesting the probable formation of Li[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS].

35. Reaction of CpW(CO)(CS)(PPh<sub>3</sub>)I with RLi (R = Ph, Me)

Adding PhLi (0.25 ml of a 2 M solution of CpW(CO)(CS)(PPh<sub>3</sub>)I (0.35 g, 0.50 mmol) in 40 ml of THF at 0° caused the solution to fade to an ochre color. Isopropyl alcohol (0.10 ml) was added to destroy any remaining PhLi. After warming to RT, the solvent was evaporated under reduced pressure. The residue was extracted with 15 ml of benzene and filtered through a fritted-glass funnel. Then the volume was reduced to 5 ml. The resulting solution was eluted on a 2 x 40 cm column of Grade II Woelm alumina with benzene. Three bands always developed; in order of elution these were: Yellow (CpW(CO)(PPh<sub>3</sub>)CS-Ph), red (unreacted CpW(CO)(CS)(PPh<sub>3</sub>)I, and another yellow (remained on column, see below). The first band was collected and

evaporated under reduced pressure. The orange residue was extracted with 2 ml portions of 2:1 pentane/CS<sub>2</sub> until nothing more dissolved, and then the combined extracts were diluted to 4:1 pentane/CS<sub>2</sub>. This solution was filtered and cooled to -20°, affording orange needles of CpW(CO)(PPh<sub>3</sub>)(CS-Ph) (43%).

IR(CS<sub>2</sub>): 1886 cm<sup>-1</sup>. <sup>1</sup>H NMR(CDCl<sub>3</sub>):  
 δ5.24d (Cp, J<sub>P-Cp</sub> = 0.75 Hz), 7.32m (Ph). <sup>13</sup>C NMR(CDCl<sub>3</sub>):  
 δ-91.48s (Cp), -114 to -139m (Ph),  
 -237.70d (CO, J<sub>P-CO</sub> = 7 Hz), -254.90 (CS, J<sub>P-CS</sub> = 12 Hz).  
Anal. Calc. for C<sub>31</sub>H<sub>25</sub>OPSW: C, 56.37; H, 3.82. Found:  
 C, 56.19; H, 3.76.

When CH<sub>2</sub>Cl<sub>2</sub> was used as the moving phase on the chromatography column mentioned above, all bands eluted from the column. The third, yellow band showed a CO absorbance at 1940 cm<sup>-1</sup> and a CS absorbance at 1230 cm<sup>-1</sup>, suggesting the possible presence of CpW(CO)(CS)(PPh<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) in solution, but the instability of the product in this fraction prevented its isolation.

Methyl lithium reacted instantly with a solution of CpW(CO)(CS)(PPh<sub>3</sub>)I at -78°, causing the solution to turn yellow and the CO band in the IR spectrum to shift from 1967 to 1890 cm<sup>-1</sup>. The product decomposed as the solution was evaporated.

36. Reaction of trans-CpW(CO)<sub>2</sub>(CS)I with other nucleophiles

The thiocarbonyl reacted rapidly with [PPN]N<sub>3</sub> in THF to give a deep orange solution; vigorous gas evolution was observed. The IR spectrum of a sample of the solution showed one predominant product with bands at 2096m, 1948m, and 1849s. However, this compound could not be isolated.

Bubbling MeNH<sub>2</sub> through a hexane solution of trans-CpW(CO)<sub>2</sub>(CS)I caused the precipitation of a salmon-colored solid. The solid was filtered from the solution, dried, redissolved in acetone, and put through an ion-exchange column in the PF<sub>6</sub><sup>-</sup> form. Attempts to crystallize the product were unsuccessful.

IR(CH<sub>2</sub>Cl<sub>2</sub>): 2020w, 1960s.

37. Reaction of trans-CpW(CO)<sub>2</sub>(CS)I with various reducing agents

After trans-CpW(CO)<sub>2</sub>(CS)I (0.17 g, 0.36 mmol) and Ph<sub>3</sub>SnH (0.14 g, 0.36 mmol) had stirred in 15 ml of THF for seven days, the color of the solution had faded from purple to orange. The IR spectrum of a sample of the solution showed that a reaction had occurred. The solution was evaporated to dryness under reduced pressure, and the residue was resolved into its components by elution on a Florisil column with CS<sub>2</sub>. The components were identified by their IR and NMR spectra as

cis-CpW(CO)<sub>2</sub>(CS)SnPh<sub>3</sub> (see Sect. 16) and some remaining trans-CpW(CO)<sub>2</sub>(CS)I.

A mixture of trans-CpW(CO)<sub>2</sub>(CS)I and an equivalent of magnesium or zinc in THF became yellow, and new CO bands were observed between 1900 and 2000 cm<sup>-1</sup> in the IR spectrum of a sample of the solution. The yellow product decomposed upon exposure to air and was never isolated. Addition of Ph<sub>3</sub>SnCl to these yellow solutions gave a mixture of products, one of which was identified by its IR spectrum as cis-CpW(CO)<sub>2</sub>(CS)SnPh<sub>3</sub>.

The thiocarbonyl complex showed no sign of reaction after stirring with Hg(CH<sub>3</sub>)<sub>2</sub> in THF for 7 days.

### 39. Miscellaneous reactions of Bu<sub>4</sub>N[CpW(CO)<sub>2</sub>CS]

Oxidation of Bu<sub>4</sub>N[CpW(CO)<sub>2</sub>CS] with Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> yielded a mixture of products, all of which were air-sensitive, none of which were isolated. Likewise, oxidation with [C<sub>7</sub>H<sub>7</sub>]BF<sub>4</sub> also produced a mixture of products. Chromatographic resolution of these products on a silica gel column with CS<sub>2</sub> gave a purple compound and an orange compound. Both were oils, and neither was crystallized.

IR of purple compound (CS<sub>2</sub>): 1959s, 1888m.

IR of orange compound (CS<sub>2</sub>): 2035s, 1956s.

When AgBF<sub>4</sub> was added to a THF solution of the thiocarbonyl anion, an orange powder precipitated. The

precipitate was not soluble in organic solvents and did not react with  $O_2$ . The product was not identified.

Reaction of  $Bu_4N[CpW(CO)_2CS]$  with  $[p-CH_3C_6H_4N_2]BF_4$  in THF or  $CH_3CN$  produced a red solution with a complex pattern of CO bands and no CS band in its IR spectrum. No complex could be isolated from these mixtures.

Trifluoroacetic anhydride reacts with the thiocarbonyl anion at  $0^\circ$  in the presence of iodide to give a bright copper-colored product. This compound was insoluble in most organic solvents and decomposed during recrystallization from  $CH_2Cl_2$ . Attempts to identify the compound were unsuccessful.

IR( $CH_2Cl_2$ ): 2018m, 2003w, 1952s, 1930m.

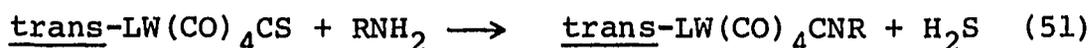
Evidence was seen for the protonation of  $Bu_4N[CpW(CO)_2CS]$  by  $CF_3OSO_2H$  and  $CH_3CO_2H$  in THF, but the product could not be isolated.

No reaction was observed between  $Bu_4N[CpW(CO)_2CS]$  and  $(EtO)_2POCl$  or  $(PhO)_2POCl$ .

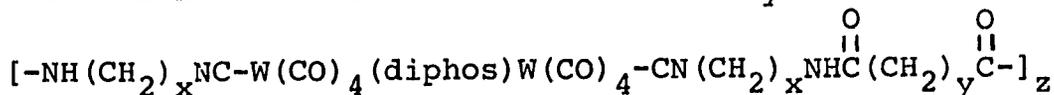
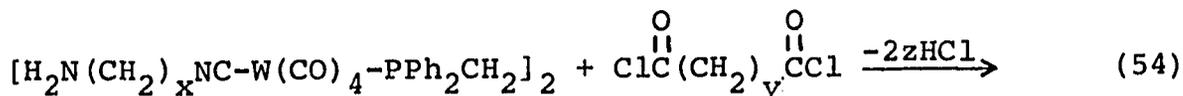
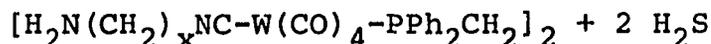
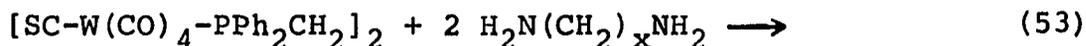
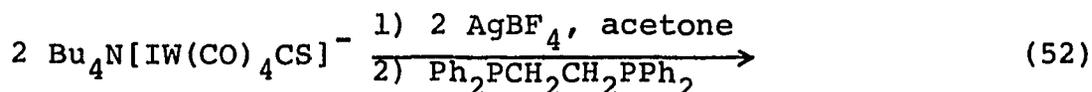
## III. RESULTS AND DISCUSSION

## A. Attempts to Prepare Polymers that Contain Tungsten

Dombek and Angelici<sup>6</sup> found that primary amines react with the tungsten-thiocarbonyl complexes trans-LW(CO)<sub>4</sub>CS (L = CO or PPh<sub>3</sub>) to form isocyanide complexes of the same stereochemistry, eq. 51. This reaction was investigated



further in the hope that it could be adapted to the synthesis of nylon-like polymers containing tungsten atoms in the polymer backbone. If a binuclear complex bridged by diphos were prepared as in eq. 52, then subsequent treatment of



this complex as shown in eqs. 53 and 54 would produce

a polymer. This would be the first polymer containing a tungsten atom in the backbone and would be a transition-metal-complex somewhat similar to nylon. The properties of such a material would, no doubt, be of some interest.

Addition of diphos to a solution containing the stoichiometric amount of  $W(CO)_4(CS)$  (acetone) gave the binuclear complex  $[SC-W(CO)_4-PPh_2CH_2]_2$  in good yield. Interestingly, only this product is obtained, even when equimolar amounts of the reactants are used. The two carbonyl moieties cannot be introduced stepwise as in the synthesis of  $[W(CO)_5PPh_2CH_2]_2$ .<sup>122</sup>

Before attempting a reaction of the binuclear complex with diamine, reaction with butylamine was studied to determine optimum conditions for conversion of the thio-carbonyl to isocyanide. When trans- $[SC-W(CO)_4PCH_2CH_2]_2$  was stirred with excess butylamine in the presence of pyridine and  $CaH_2$  for 5 days, only about 95% conversion to the isocyanide complex trans- $[BuCN-W(CO)_4-PPh_2CH_2]_2$  was observed. This result was not unexpected, since it has been found that the base-catalyzed reaction of trans- $W(CO)_4(CS)(PPh_3)$  with amines is  $2 \times 10^4$  times slower than that of  $W(CO)_5CS$ .<sup>6</sup> The product was identified by the appearance of an absorption band at  $2130\text{ cm}^{-1}$  in the infrared spectrum of a sample of the solution, consistent with the absorption of a coordinated isocyanide. Attempts

to isolate the product resulted in its decomposition. In the analogous reaction with hexanediamine the infrared showed that all of the thiocarbonyl had reacted after four days, but attempts to isolate the supposed product,  $[\text{H}_2\text{N}(\text{CH}_2)_6\text{NC-W}(\text{CO})_4\text{PPh}_2\text{CH}_2]_2$ , by column chromatography or protonation of the amine group were unsuccessful.

Reactions of the binuclear thiocarbonyl complex with primary amines appear to form inseparable mixtures of products, thereby prohibiting a controlled synthesis of the polymeric material.

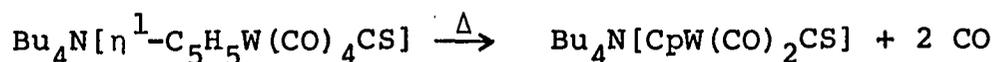
#### B. Preparation of $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$ and $\text{Bu}_4\text{N}[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]$

The reported tungsten thiocarbonyl complexes in which the thiocarbonyl sulfur atom acts as a Lewis base,  $\text{W}(\text{CO})(\text{CS})(\text{diphos})_2$  and trans- $[\text{IW}(\text{CO})_4\text{CS}]^-$ , have thiocarbonyl ligands possessing high electron density, as evidenced by their low CS stretching frequencies.<sup>5</sup> It was expected that the nucleophilic character of the thiocarbonyl ligand might be enhanced in anionic complexes containing ligands which are strong electron donors such as the  $\eta^5$ -cyclopentadienyl and pyrazolyborate ligands.

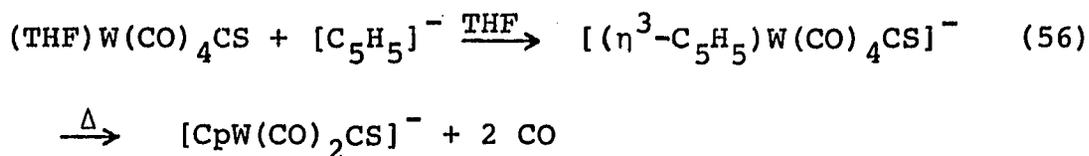
The carbonyl anion  $[\text{CpW}(\text{CO})_3]^-$  has been prepared by the reaction of  $\text{Na}[\text{C}_5\text{H}_5]$  with  $\text{W}(\text{CO})_6$  in refluxing glyme,<sup>40</sup> by the reduction of  $[\text{CpW}(\text{CO})_3]_2$  with  $\text{Na}(\text{Hg})$  or  $\text{C}_8\text{K}$ ,<sup>42</sup> and by the interaction of  $\text{Na}[\text{C}_5\text{H}_5]$  and  $\text{Et}_4\text{N}[\text{IW}(\text{CO})_5]$  in refluxing

THF.<sup>45</sup> Of these three methods, only the last is applicable to the production of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$ . The reaction of  $\text{Na}[\text{C}_5\text{H}_5]$  or  $\text{Tl}[\text{C}_5\text{H}_5]$  with  $\text{W}(\text{CO})_5\text{CS}$  does not yield  $[\text{CpW}(\text{CO})_2\text{CS}]^-$ , possibly because the nucleophilic cyclopentadienide ion attacks the thiocarbonyl carbon or sulfur, although no thioacyl or S-alkyl products have been isolated from this reaction. The reduction of  $[\text{CpW}(\text{CO})_2(\text{CS})]_2$  would presuppose the existence of such a dimer. However, direct addition of  $\text{Na}[\text{C}_5\text{H}_5]$  to a cold, anhydrous THF solution of  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$  (or, if  $\text{I}^-$  will interfere with any subsequent reaction, a solution of  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$  that has been treated with  $\text{AgBF}_4$ ) followed by heating to  $60^\circ$  gives  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  in good yield. After the reaction is complete it is best to protonate any remaining  $\text{Na}[\text{C}_5\text{H}_5]$  with isopropyl alcohol thus precluding any later interference by this species.

Formation of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  from  $\text{Na}[\text{C}_5\text{H}_5]$  and  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$  probably occurs by replacement of the iodide ligand by cyclopentadienide, forming a  $\eta^1\text{-C}_5\text{H}_5$  ligand, and subsequent replacement of two CO ligands, as shown in reaction 55. From  $(\text{THF})\text{W}(\text{CO})_4\text{CS}$  the reaction



most likely proceeds through a  $\eta^3\text{-C}_5\text{H}_5$  complex similar to a  $\eta^3$ -allyl complex, reaction 56. These intermediates



are too unstable to detect by spectroscopic methods, but the above proposals are supported by observed color changes during the reaction. In both cases attack at the thiocarbonyl ligand has been circumvented.

The thiocarbonyl complex  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  dissolves in most polar organic solvents but is insoluble in water. Solutions of the compound may be handled in air for periods of 5-10 min; prolonged contact with air results in decomposition. The isolation of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  is a problem of separating the anion from the  $\text{I}^-$  or  $\text{BF}_4^-$  present in the solution. Attempts to precipitate the anion as the  $\text{Et}_4\text{N}^+$  or  $\text{PPN}^+$  salt gave oils instead of solids. The anion was therefore reacted in situ, and the neutral products were separated from the ionic side-products.

The infrared spectrum of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  in  $\text{CH}_2\text{Cl}_2$  solution shows two absorptions, at 1890s and 1804s, assignable to the  $\nu_{\text{sym}}$  and  $\nu_{\text{as}}$  of the terminal CO ligands (Table 2). These absorptions occur in about the same region as the CO band of  $\text{W}(\text{CO})(\text{CS})(\text{diphos})_2$ ,<sup>4</sup> a

complex which forms S-adducts, and indicate a relatively high electron density at the CS group (Table 2). The CS absorption is obscured by the solvent.

The pyrazolylborate thiocarbonyl anion  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]^-$  can be synthesized in a manner similar to  $[\text{CpW}(\text{CO})_2\text{CS}]^-$ . An equivalent of solid  $\text{K}[\text{HB}(\text{pz})_3]$  is added to an acetone solution of  $\text{Bu}_4\text{N}[\text{IW}(\text{CO})_4\text{CS}]$  that has been treated with  $\text{AgBF}_4$ . After the solution refluxes for about 1.5 hr the infrared spectrum of a sample of the solution shows that  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]^-$  is the only complex present. Again, all attempts to precipitate the anion as a solid salt produced oils; therefore, this anion was also prepared and used in situ. The infrared spectrum of the anion in  $\text{CH}_2\text{Cl}_2$  shows CO absorptions at 1884s and 1787s, slightly lower than those of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  (Table 2); this can be attributed to the better electron donor properties of the pyrazolylborate ligand as compared to the  $\eta^5$ -cyclopentadienyl ligand.<sup>98,99</sup>

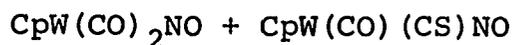
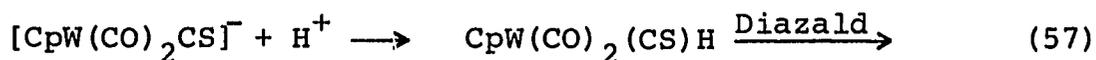
### C. Reactions at the Metal Center

#### 1. Reactions of $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$ and $\text{Bu}_4\text{N}[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]$

Addition of N-methyl-N-nitroso-p-toluenesulfonamide<sup>48</sup> (Diazald) and acetic acid to a solution of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  in THF gives a mixture of  $\text{CpW}(\text{CO})_2\text{NO}$  and  $\text{CpW}(\text{CO})(\text{CS})\text{NO}$  which can be separated by column chromatography. The

olive-green  $\text{CpW(CO)(CS)NO}$  shows strong absorbances in the IR spectrum for each of its diatomic ligands, and its  $^1\text{H}$  NMR spectrum has a single resonance for the cyclopentadienyl ring (Tables 2 and 3). The thiocarbonyl ligand appears to have little effect on this reaction, since the NO ligand adds to the metal center as it does with  $[\text{CpW(CO)}_3]^-$ . Unlike the dicarbonyl analogue,  $\text{CpW(CO)(CS)NO}$  has a chiral metal center, but no attempt to separate the enantiomers was made.

An indication of the reactive intermediates was found in a recent report that  $\text{CpW(CO)}_3\text{H}$  reacts with Diazald to give  $\text{CpW(CO)}_2\text{NO}$  in good yield.<sup>49</sup> Protonation of  $\text{Bu}_4\text{N}[\text{CpW(CO)}_2\text{CS}]$  may yield the hydride derivative  $\text{CpW(CO)}_2(\text{CS})\text{H}$ , which could then react with Diazald to produce  $\text{CpW(CO)(CS)NO}$ , reaction scheme 57. Addition of  $\text{CF}_3\text{SO}_3\text{H}$  or  $\text{CH}_3\text{CO}_2\text{H}$  to a solution of  $\text{Bu}_4\text{N}[\text{CpW(CO)}_2\text{CS}]$



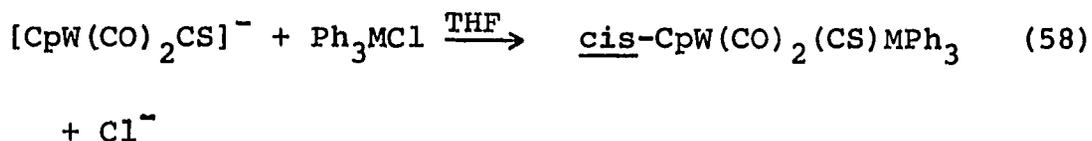
causes a color change and shifts the  $\nu(\text{CO})$  bands to higher frequency, suggesting the possible formation of  $\text{CpW(CO)}_2(\text{CS})\text{H}$ . The product was unstable, however, and could not be positively identified.

Trofimenko<sup>99</sup> first reported the preparation of  $\text{HB(pz)}_3\text{W(CO)}_2\text{NO}$ . Instead of the sulfonamide, he used

isopentyl nitrite or nitrosyl chloride to introduce the NO ligand. Nitrosyl hexafluorophosphate proved to be the best reagent with  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]^-$ , though the yield of  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$  is low. As with the cyclopentadienyl anion, the reaction produces a mixture of the dicarbonyl and thiocarbonyl complexes. In this case  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{NO}$  and  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$  cannot be completely separated by chromatography, but partial separation can be achieved by repeated elution of the crude product. The complex  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$ , an air-stable, emerald solid, exhibits the expected spectral characteristics (Tables 2-4). Enantiomers of this complex undoubtedly exist but have not been separated.

Since the preparation of  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$ , McCleverty and co-workers<sup>101</sup> have used Diazald to synthesize  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{NO}$ . It is possible that this reagent may react more specifically with  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]^-$  to improve the yield of  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$  and thus facilitate its purification. This reaction has not been attempted.

Nucleophilic displacement is a common reaction of  $[\text{CpW}(\text{CO})_3]^-$ ; addition occurs at the metal center. For example,  $[\text{CpW}(\text{CO})_3]^-$  displaces halide from  $\text{R}_3\text{MX}$  ( $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}; \text{R} = \text{Me}, \text{Ph}$ ) to produce metal-metal bonded derivatives,  $\text{CpW}(\text{CO})_3\text{MR}_3$ .<sup>78-80</sup> The similar reaction of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  with  $\text{Ph}_3\text{SnCl}$  and  $\text{Ph}_3\text{PbCl}$  gives the  $\text{CpW}(\text{CO})_2(\text{CS})\text{MPh}_3$



derivatives. These golden, crystalline complexes are air-stable. For the carbonyl complexes the germanium and tin derivatives are reported to be more stable than the lead compound, but for the thiocarbonyl analogues the lead derivative appears more air stable than the tin.

With the thiocarbonyl ligand present in  $[\text{CpW}(\text{CO})_2\text{CS}]^-$ , addition at the metal center produces a cis isomer, a trans isomer, or a mixture of both, see Figure 2. The assignment of configuration in similar cases is usually based on the relative intensities of the two carbonyl infrared stretching bands,  $\nu_{\text{sym}}$  and  $\nu_{\text{as}}$ , because these intensities are directly related to the angle between the carbonyl ligands.<sup>62,123-125</sup> A cis isomer is characterized by a strong band followed by a medium to weak band, whereas a medium band followed by a strong band denotes a trans isomer (Figure 2). Another aid in assignment of configuration is  $^{13}\text{C}$  NMR. In cis-complexes the carbonyls reside in different electronic environments and thus appear as two distinct resonances in the  $^{13}\text{C}$  spectrum, while in trans-complexes the carbonyls are in identical environments and show only a single resonance.

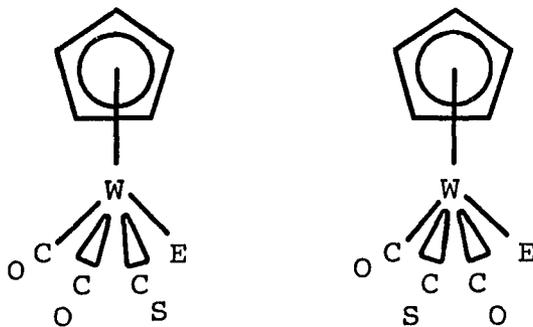
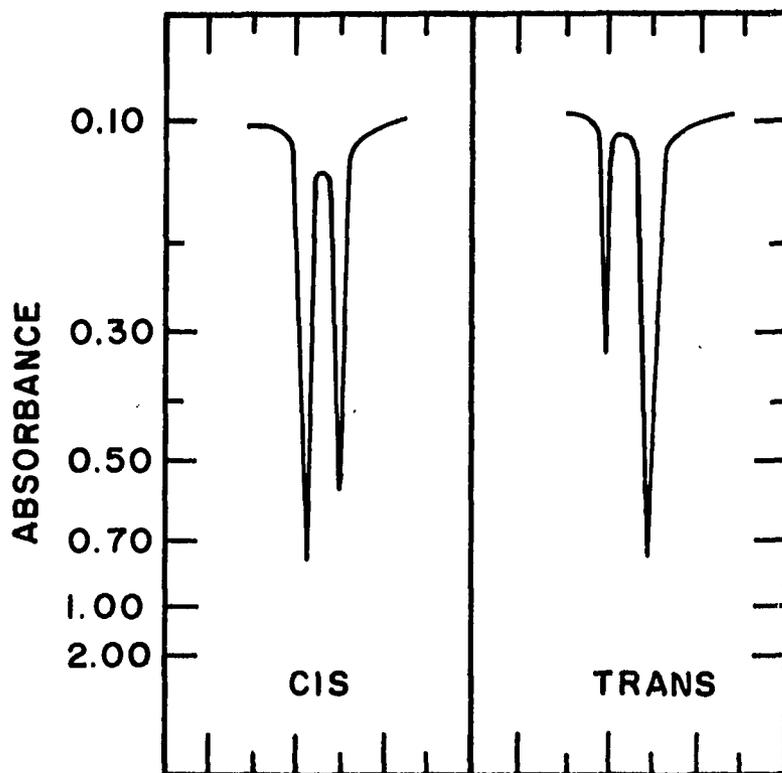


Figure 2. Possible isomers of  $\text{CpW}(\text{CO})_2(\text{CS})\text{E}$  ( $\text{E} = \text{X}, \text{MPh}_3, \text{HgI}, \text{etc.}$ ) and their characteristic IR spectra

The infrared spectra of the bimetallic complexes  $\text{CpW(CO)}_2\text{(CS)MPh}_3$  have strong symmetric absorptions followed by medium asymmetric absorptions (Table 2), and therefore these compounds must have cis configuration. The  $^{13}\text{C}$  NMR spectra, which show two CO resonances, confirm this assignment (Table 4). The thiocarbonyl absorptions in the IR spectra of these compounds occur at  $1237\text{ cm}^{-1}$ ; this value is about  $20\text{ cm}^{-1}$  lower than might be expected for a terminal thiocarbonyl ligand in tungsten complexes of this type.<sup>4</sup> Further results from this investigation suggest that an absorption at this frequency is characteristic of cis-thiocarbonyl complexes, while a thiocarbonyl absorption about  $1265\text{ cm}^{-1}$  indicates a trans-complex (see below). Therefore the  $\nu(\text{CS})$  value of a complex of the type  $\text{CpW(CO)}_2\text{(CS)E}$  ( $\text{E} = \text{X}, \text{SnPh}_3, \text{HgI}, \text{etc.}$ ) is a clue to the structural configuration. The high frequency of the CS absorption in trans-complexes was unexpected; however, as suggested in other cases,<sup>6</sup> tungsten-E  $\pi$ -bonding trans to the CS may decrease the  $\pi$ -donation from the CS ligand to the metal and thus increase the C-S bond strength.

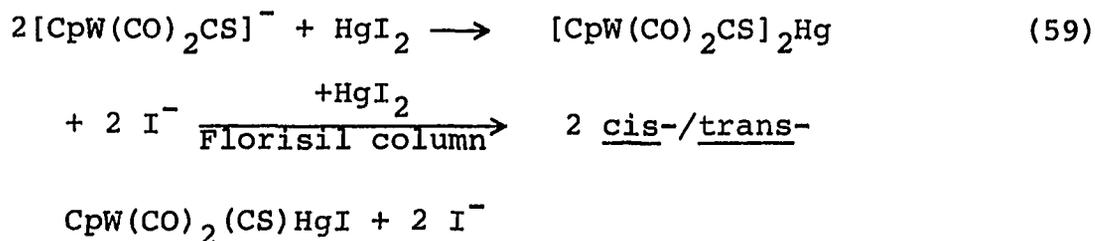
Reaction of  $[\text{CpW(CO)}_2\text{CS}]^-$  with  $\text{Ph}_3\text{GeCl}$ ,  $\text{Me}_3\text{SnCl}$ ,  $\text{PhHgCl}$ , and  $\text{MeHgCl}$  appeared to give the desired bimetallic derivatives; the products, however, were too unstable to isolate. Reaction of  $[\text{CpW(CO)}_2\text{CS}]^-$  with  $\text{CpM(CO)}_3\text{Cl}$

(M = Mo or W) gave only  $[\text{CpM}(\text{CO})_3]_2$ ; with  $\text{Mn}(\text{CO})_5\text{Br}$ , only  $\text{Mn}_2(\text{CO})_{10}$ . Addition of  $\text{CpFe}(\text{CO})_2\text{Cl}$ ,  $\text{CpFe}(\text{CO})(\text{CS})\text{Br}$ , or  $[\text{CpFe}(\text{CO})_2(\text{CS})]\text{PF}_6$  to solutions of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  caused changes in the IR spectra, but no products were isolated. The thiocarbonyl anion did not react with  $\text{CpW}(\text{CO})_2(\text{CS})\text{Br}$  in refluxing THF. In view of these results, synthesis of other metal-metal bonded thiocarbonyl complexes may only be possible by reactions of  $\text{CpW}(\text{CO})_2(\text{CS})\text{X}$  with appropriate carbonyl anions or metal hydrides (see below).

Dombek and Angelici<sup>5</sup> reported that  $\text{W}(\text{CO})(\text{CS})(\text{diphos})_2$  reacts with  $\text{HgCl}_2$  or  $\text{HgI}_2$  to form complexes of the formula  $(\text{diphos})_2\text{W}(\text{CO})(\text{CS}-\text{HgX}_2)$ , and other researchers<sup>20,39</sup> found that bridging thiocarbonyl ligands also form mercuric halide adducts, as in  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})(\text{CS}\cdot\text{HgCl}_2)$ . It was believed, therefore, that  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  would react with  $\text{HgI}_2$  to form an S-adduct, perhaps  $\text{CpW}(\text{CO})_2(\text{CS}-\text{HgI})$ .

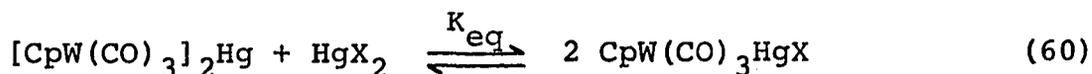
Addition of  $\text{HgI}_2$  to two equivalents of  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$  in THF gives an orange substance which has been tentatively identified as  $[\text{CpW}(\text{CO})_2\text{CS}]_2\text{Hg}$  by its IR and NMR spectra (Tables 2 and 3). Unfortunately this compound was not soluble or stable enough in common organic solvents to obtain a  $^{13}\text{C}$  NMR spectrum or an analytical sample. When excess  $\text{HgI}_2$  is added to  $\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$ , a sample of the solution shows that  $[\text{CpW}(\text{CO})_2\text{CS}]_2\text{Hg}$  is formed as above. However, elution of the reaction mixture on a Florisil

column with  $\text{CH}_2\text{Cl}_2$  gives a different orange product whose IR spectrum shows bands at 1990s and 1918s. This compound has been identified by its spectra (Tables 2 and 3) and chemical analysis as  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$ . From the above observations the reaction scheme shown in eq. 59 is



postulated. Obviously, the elution of the reaction mixture is crucial to the formation of  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$ , but its function remains obscure, inasmuch as addition of Florisil to the reaction mixture causes no change in the mixture.

The behavior of the thiocarbonyl mercury compounds differs from that of the carbonyl analogs. The complex  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  reacts rapidly with excess  $\text{HgX}_2$  in acetone or methanol to give two equivalents of  $\text{CpW}(\text{CO})_3\text{HgX}$ .<sup>73</sup> In solution, reactants and products are in labile equilibrium, eq. 60, although equilibrium constants



strongly favor the product ( $K_{\text{eq}} > 10^3$ ). Despite the large value of  $K_{\text{eq}}$ , the symmetrical mercurials can be recovered. For example, when a solution of  $\text{CpMo}(\text{CO})_3\text{HgX}$  in acetone is

passed through an alumina column, the  $[\text{CpMo}(\text{CO})_3]_2\text{Hg}$  is eluted and  $\text{HgX}_2$  remains on the column.<sup>73</sup> As can be seen, the thiocarbonyl complexes exhibit the reverse behavior. The reason for this is not evident.

In any event, the mercuric halide derivative  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$  is an orange crystalline solid which may be stored indefinitely in air at room temperature. It is sparingly soluble in polar organic solvents and in solution is susceptible to air oxidation and thermal decomposition; consequently, no  $^{13}\text{C}$  data have been obtained. The  $^1\text{H}$  NMR spectrum of  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$  shows a broad singlet for the cyclopentadienyl protons (Table 3). The infrared spectrum displays strong CO absorptions at 1990 and 1935  $\text{cm}^{-1}$ . There are two absorptions in the CS region at 1268m and 1234s (Table 2; Fig. 3). Apparently  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$  exists in solution as a mixture of cis and trans isomers with identical CO absorption frequencies but different  $\nu(\text{CS})$  values. If it is assumed the CS band at 1234  $\text{cm}^{-1}$  arises from the cis isomer (by analogy to the  $\nu(\text{CS})$  of cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$ ; see discussion above and Table 2), then based on the intensities of the CS absorptions the product consists of about 60% cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$ .

Sodium mercaptides,  $\text{NaSR}$  ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ), react smoothly with  $\text{CpW}(\text{CO})_3\text{Cl}$  to give complexes of the type  $\text{CpW}(\text{CO})_3\text{SR}$ .<sup>87</sup> Decomposition of these compounds in

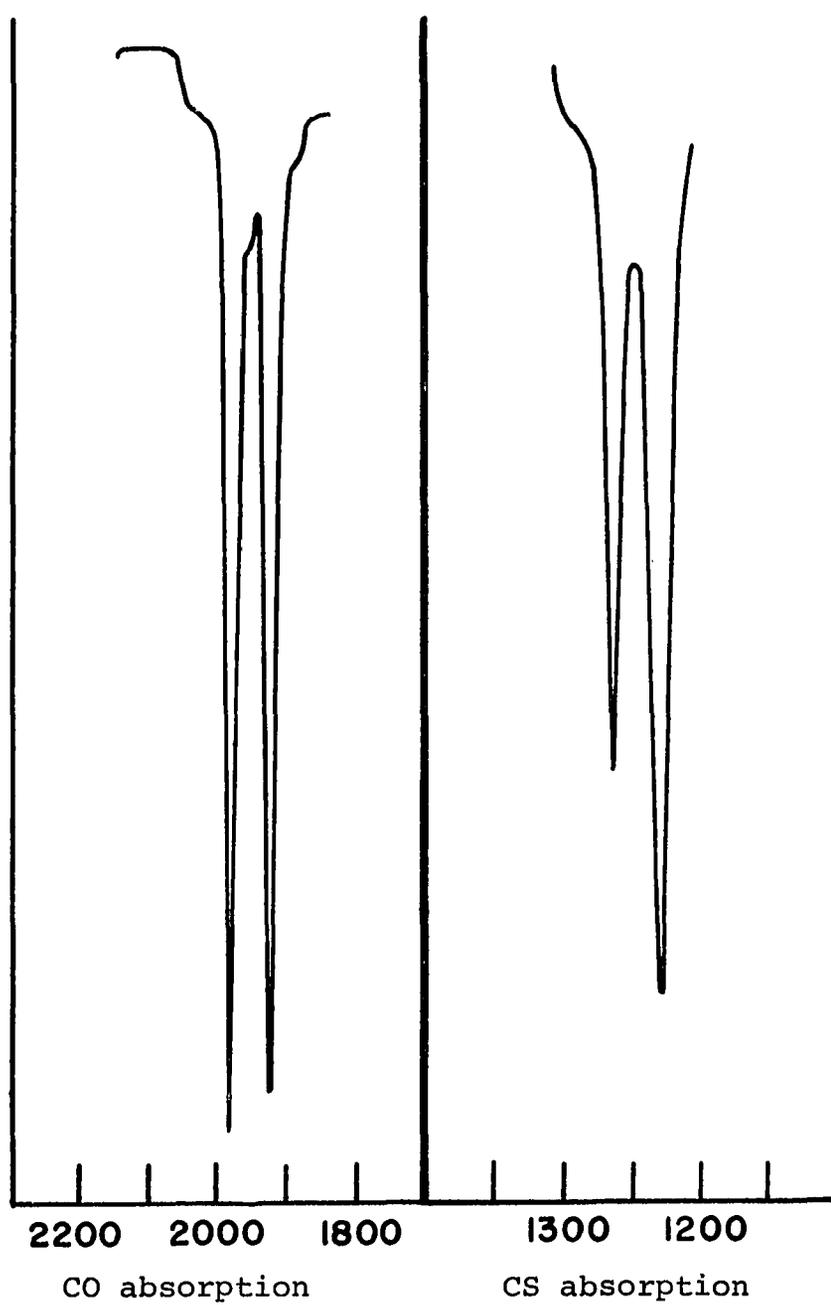


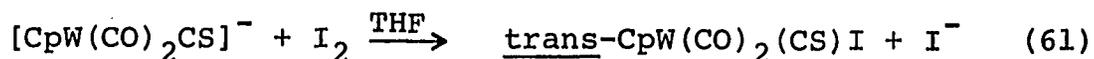
Figure 3. IR spectrum of  $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$  in  $\text{CS}_2$  solution

solution produces binuclear species,  $[\text{CpW}(\text{CO})_2\text{SR}]_2$ , which contain bridging mercaptide ligands. The complexes  $\text{CpW}(\text{CO})_3\text{SR}$  also undergo  $\text{CS}_2$  insertion, producing alkyl- or aryl-trithiocarbonato complexes,  $\text{CpW}(\text{CO})_2(\text{S}_2\text{CSR})$ .

Thiocarbonyl complexes similar to  $\text{CpW}(\text{CO})_3\text{SR}$  are prepared somewhat differently because of difficulty in obtaining solutions of  $\text{NaSR}$  in THF. The thiocarbonyl anion acts upon  $\text{PhSeBr}$  to produce  $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$ . This complex is a magenta, crystalline solid. The product may be stored under nitrogen in its crystalline state, but in solution it decomposes to  $(\text{PhSe})_2$  and unidentified compounds. No dimeric phenylselenide derivative,  $[\text{CpW}(\text{CO})(\text{CS})\text{SePh}]_2$ , has been isolated. No reaction between  $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$  and  $\text{CS}_2$  has been observed. The IR and  $^1\text{H}$  NMR spectra of  $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$  (Tables 2 and 3) are typical of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{E}$  compounds; the shoulder at  $2008\text{ cm}^{-1}$  in the IR spectrum and the weak cyclopentadienyl resonance 0.2 ppm downfield from the major resonance suggest the presence of a small amount of the cis isomer.

The analogous reaction with  $\text{PhSCl}$  gives a purple solution; the infrared spectrum of the product suggests that trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{SPh}$  is formed, but the product decomposes before it can be isolated. On the other hand, the major product from the reaction of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  with 2,4-dinitrophenylsulfenylchloride is  $\text{CpW}(\text{CO})_2(\text{CS})\text{Cl}$ .

The CpW(CO)<sub>3</sub>X compounds are commonly prepared in good yield by reaction of CpW(CO)<sub>3</sub>H with CCl<sub>4</sub>, CBr<sub>4</sub>, MeI, or I<sub>2</sub>.<sup>40,53</sup> In contrast, the thiocarbonyl anion reacts directly with Br<sub>2</sub> or I<sub>2</sub> to produce the respective halide, eq. 61. The chloride has been produced only by indirect

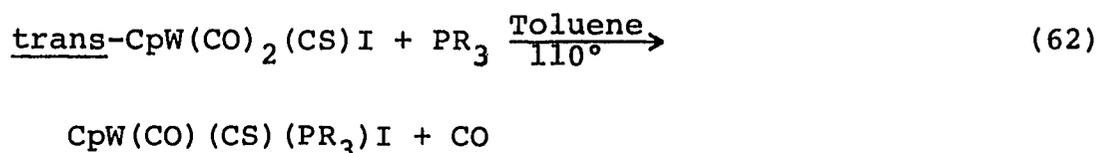


methods, for example, reaction of [CpW(CO)<sub>2</sub>CS]<sup>-</sup> with FeCl<sub>3</sub>·6H<sub>2</sub>O, [Cp<sub>2</sub>Fe]FeCl<sub>4</sub>, or p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl; yields were low and these reactions were not pursued. Both the bromide and iodide complexes could be obtained as solids, but the iodide was easier to crystallize and so was used in further reactions. The thiocarbonyl iodide complex exhibits IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra consistent with a trans configuration, including a CS stretching frequency of 1267 cm<sup>-1</sup> (Tables 2-4).

Addition of iodine to a solution of Bu<sub>4</sub>N[HB(pz)<sub>3</sub>W(CO)<sub>2</sub>CS] gives the deep red, air-stable trans-HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS)I. The spectra of this complex (Tables 2-4) are consistent with the assigned configuration; the low CS stretching of 1243 cm<sup>-1</sup> is attributed to the strong electron donor properties of the pyrazolylborate ligand, as mentioned earlier.<sup>98,99</sup> The product is sparingly soluble in aliphatic hydrocarbons but more soluble in polar organic solvents.

## 2. Reactions of $\text{trans-CpW(CO)}_2(\text{CS})\text{I}$

The thiocarbonyl complex  $\text{trans-CpW(CO)}_2(\text{CS})\text{I}$  undergoes thermal carbonyl substitution by  $\text{PMe}_2\text{Ph}$ ,  $\text{P(NMe}_2)_3$ ,  $\text{P(OPh)}_3$ ,  $\text{PPh}_3$ , and  $\text{CNMe}$  to give the monosubstituted complexes  $\text{CpW(CO)(CS)(L)I}$ . These reactions were tried in several different solvents. The reactions were slow, and the yields, poor, in THF and  $\text{CH}_3\text{CN}$  at reflux; in the cases of  $\text{PMe}_2\text{Ph}$  and  $\text{CNMe}$ , reaction in these solvents led to a mixture of products (see below). In refluxing toluene, substitution proceeds rapidly and with little decomposition. For the ligands mentioned,  $\text{PMe}_2\text{Ph}$  and  $\text{CNMe}$  were observed

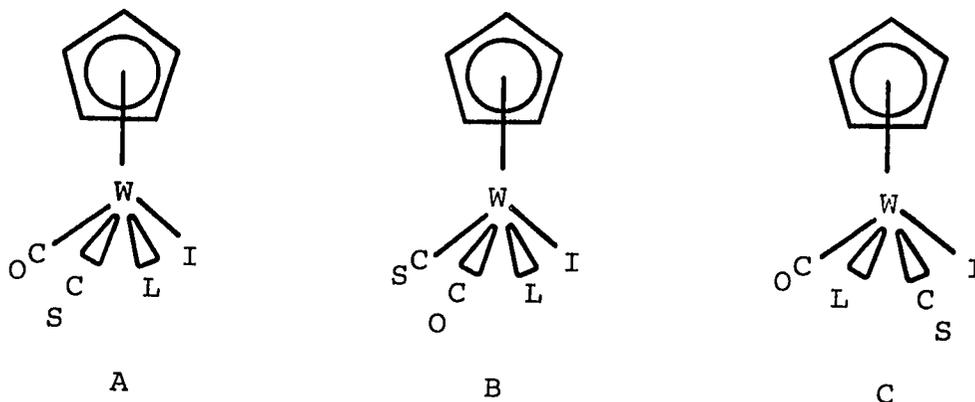


to react faster than  $\text{P(NMe}_2)_3$ ,  $\text{P(OPh)}_3$ , and  $\text{PPh}_3$ .

Carbon monoxide substitution of  $\text{CpW(CO)}_3\text{X}$  has been accomplished with a variety of ligands.<sup>60-64</sup> In most cases these reactions have been performed in refluxing benzene. Treichel reports that the reaction of  $\text{CpW(CO)}_3\text{Cl}$  with  $\text{PPh}_3$  in benzene requires 20 hr to give a 60% yield,<sup>60</sup> while other researchers<sup>85</sup> say the carbonyl iodide takes longer than 12 days to react completely with  $\text{PPh}_3$  in the same solvent. The carbonyl ligands of  $\text{trans-CpW(CO)}_2(\text{CS})\text{I}$  are much more labile. Reaction of the thiocarbonyl complex with 20% excess  $\text{PPh}_3$  in refluxing benzene is virtually

complete in 3-4 hr; reactions with  $\text{PMe}_2\text{Ph}$  or  $\text{CNMe}$  are faster but do not give the same products (see below). This effect of the CS ligand has been observed in other thiocarbonyl complexes.<sup>4,35,36</sup> Minute quantities of thiocarbonyl-substituted product,  $\text{CpW}(\text{CO})_2(\text{L})\text{I}$ , are always isolated from the reaction of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  with ligands.

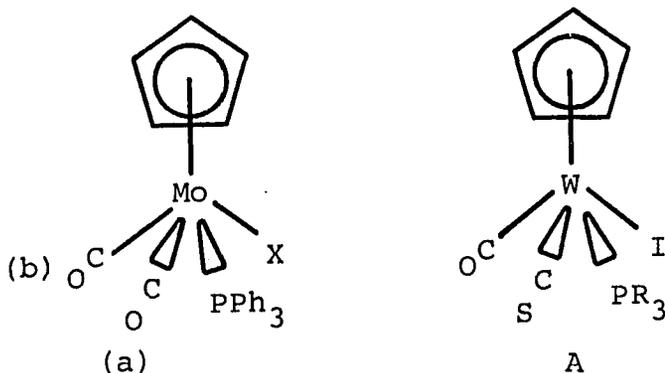
Substitution of a carbonyl ligand in trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  creates a chiral center at the metal. (For  $\text{CpW}(\text{CO})_3\text{X}$ , only cis substitution creates an asymmetric metal center.) Three different structures are possible for  $\text{CpW}(\text{CO})(\text{CS})(\text{L})\text{I}$ , as shown below, structure A being the most probably based



on the structure of the starting material. The IR spectra of all mono-substituted derivatives (Table 2) display one terminal CO stretch and a single strong band for the terminal CS ligand. These bands occur at lower frequencies

than in trans-CpW(CO)<sub>2</sub>(CS)I, as would be expected, because the introduction of a donor ligand increases the electron density on the metal. The <sup>1</sup>H NMR spectra of the CpW(CO)(CS)(L)I complexes (Table 3) contain one singlet resonance for the cyclopentadienyl protons; also, the spectrum of CpW(CO)(CS)(CNMe)I contains only one singlet for the methyl protons. The data indicate the presence of a single isomer of CpW(CO)(CS)(L)I in solution. The <sup>13</sup>C NMR spectra are consistent with this conclusion. The <sup>13</sup>C NMR spectrum of CpW(CO)(CS)(CNMe)I shows singlet CO and CS resonances, and the spectra of the phosphine and phosphite derivatives show doublet CO and CS resonances, the splitting caused by the phosphorus.

Much attention has been given to the spectral characteristics of the cis and trans isomers of CpM(CO)<sub>2</sub>(L)E (E = X,<sup>64,66-69</sup> Me,<sup>86</sup> SnMe<sub>3</sub>,<sup>85</sup> etc.) complexes. Various methods of determining structure from spectra have been devised,<sup>63,64,74,85,124</sup> some of them suspect, but a recent report<sup>69</sup> clearly demonstrates that in the <sup>13</sup>C NMR spectrum of cis-CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)X, the J(P-C) value for CO cis to PPh<sub>3</sub> (a) is larger than for CO trans to PPh<sub>3</sub> (b); see structure below. In the <sup>13</sup>C NMR spectra of the CpW(CO)(CS)(PR<sub>3</sub>)I complexes the J(P-C) values for the CS ligands are larger than for the CO ligands (Table 3); therefore, based on the above report, the structure of the phosphine and phosphite



derivatives is most likely the one labeled A, as expected. The structure of  $\text{CpW}(\text{CO})(\text{CS})(\text{CNMe})\text{I}$  is not so easily determined, but it is probably the same as the structure of the phosphine complexes.

At this point the  $^1\text{H}$  NMR spectrum of  $\text{CpW}(\text{CO})(\text{CS})(\text{PMe}_2\text{Ph})\text{I}$  should be mentioned. The  $^1\text{H}$  NMR signals of the methyl groups in a  $\text{PMe}_2\text{Ph}$  ligand are known to be sensitive to the configuration of the complex. In asymmetric molecules such as  $\text{CpMo}(\text{CO})(\text{PMe}_2\text{Ph})\text{NO}$ <sup>126</sup> and cis- $\text{CpMo}(\text{CO})_2(\text{PMe}_2\text{Ph})\text{X}$ <sup>127</sup> the methyl groups are observed as a doublet of doublets, while in the symmetric trans- $\text{CpMo}(\text{CO})_2(\text{PMe}_2\text{Ph})\text{X}$ <sup>127</sup> the methyls are observed as a doublet. It has already been stated that substitution of a CO ligand in trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  produces an asymmetric metal center, hence the  $^1\text{H}$  NMR signal for the methyl groups in  $\text{CpW}(\text{CO})(\text{CS})(\text{PMe}_2\text{Ph})\text{I}$  was expected to be a doublet of doublets. In fact, the signal is a doublet,  $J_{\text{P}-\text{CH}_3} = 9.5$  Hz. There is no apparent reason for this anomaly. The only explanation which can

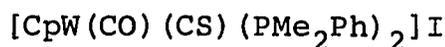
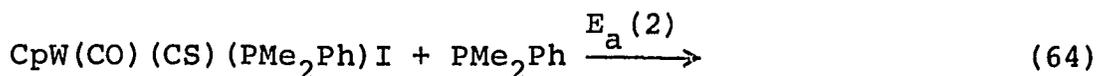
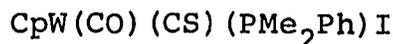
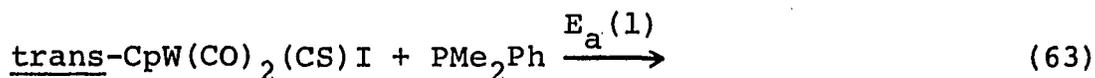
be offered is that electronic effects may render the methyl groups accidentally equivalent so that their  $^1\text{H}$  NMR resonances occur at the same  $\delta$  value.

The mono-substituted derivatives  $\text{CpW}(\text{CO})(\text{CS})(\text{L})\text{I}$  are dark red or wine-colored, air-stable, crystalline solids. They are insoluble in aliphatic hydrocarbons but more soluble in other organic solvents, forming burgundy solutions.

When a solution of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  and  $\text{PMe}_2\text{Ph}$  in toluene is allowed to react below  $100^\circ$ , the yield of  $\text{CpW}(\text{CO})(\text{CS})(\text{PMe}_2\text{Ph})\text{I}$  is low, some trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  remains, and a golden-yellow precipitate is observed. The yellow product is soluble only in polar organic solvents. An infrared spectrum in  $\text{CH}_2\text{Cl}_2$  displays one CO bond, and an  $^1\text{H}$  NMR indicates that the compound contains two  $\text{PMe}_2\text{Ph}$  ligands. The precipitate has been formulated as  $[\text{CpW}(\text{CO})(\text{CS})(\text{PMe}_2\text{Ph})_2]\text{I}$ . Also, it was observed that as the temperature of the reaction mixture was increased the amount of precipitate decreased until, above  $105^\circ$ , no precipitate was formed. Addition of two equivalents of  $\text{PMe}_2\text{Ph}$  to a solution of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  at  $100^\circ$ , however, gives close to a 90% yield of the cationic complex, which can be crystallized as the  $\text{PF}_6^-$  salt.

It appears that two reactions can occur in this solution, eq. 63 and 64; and the activation energy,  $E_a$ ,

of reaction 63 is greater than the  $E_a$  of reaction 64,



$E_a(1) > E_a(2)$ . Fischer and Moser<sup>61</sup> observed similar behavior in the reaction between  $\text{CpW(CO)}_3\text{Cl}$  and  $\text{PEt}_3$ . A singlet phosphine resonance at -8.89 ppm upfield from  $\text{H}_3\text{PO}_4$  in the  $^{31}\text{P}$  NMR plus other spectroscopic data (Tables 2-4) are consistent with a trans configuration for the cationic complex, the same as observed for  $[\text{CpMo(CO)}_2(\text{PEt}_3)_2]\text{I}$ .<sup>63</sup>

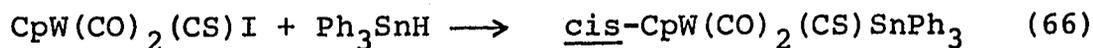
Reaction of CNMe with trans- $\text{CpW(CO)}_2\text{(CS)I}$  follows the same pattern described for the  $\text{PMe}_2\text{Ph}$ . Instead of a yellow precipitate, however, a yellow oil coats the reaction vessel. The oil was identified by its IR and NMR spectra as  $[\text{CpW(CO)(CS)(CNMe)}_2]\text{I}$ . Replacement of the iodide anion with hexafluorophosphate fails to induce crystallization. Adams<sup>121</sup> reported somewhat similar behavior between CNMe and  $\text{CpMo(CO)}_3\text{Cl}$ ; a 2:1 mixture of CNMe and  $\text{CpMo(CO)}_3\text{Cl}$  in refluxing toluene produces some  $[\text{CpMo(CNMe)}_4]\text{Cl}$  along with the expected  $\text{CpMo(CO)(CNMe)}_2\text{Cl}$ . The only product isolated from the reaction between

trans-CpW(CO)<sub>2</sub>(CS)I and two equivalents of PPh<sub>3</sub> in refluxing toluene is CpW(CO)(CS)(PPh<sub>3</sub>)I, even when a halide acceptor such as AlCl<sub>3</sub> or AgPF<sub>6</sub> is added to the reaction mixture, probably because of the lower nucleophilicity of this phosphine.

Reactions of trans-CpW(CO)<sub>2</sub>(CS)I with various reducing agents were attempted in hope of attaining a dimeric tungsten thiocarbonyl complex analogous to [CpW(CO)<sub>3</sub>]<sub>2</sub>. Mixtures of the thiocarbonyl and activated zinc or magnesium in THF become yellow over three to four days, and new CO bands can be observed between 2000 and 1900 cm<sup>-1</sup> in the IR spectrum, but the yellow product is extremely air sensitive and has not been isolated. Triphenyltin hydride is known to be a potent reducing agent;<sup>128</sup> it readily exchanges its hydrogen with an alkyl halide,<sup>128</sup> eq. 65. It was hoped that the analogous reaction with



CpW(CO)<sub>2</sub>(CS)I would yield CpW(CO)<sub>2</sub>(CS)H, which would then decompose to [CpW(CO)<sub>2</sub>CS]<sub>2</sub> and H<sub>2</sub>. However, this reaction proceeds in the opposite manner to give cis-CpW(CO)<sub>2</sub>(CS)SnPh<sub>3</sub> in about 60% yield, reaction (66). This product apparently

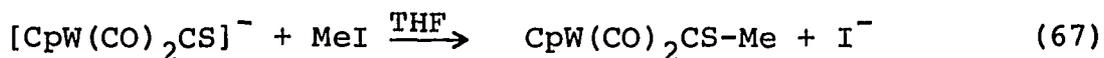


results from the stability of the W-Sn bond in these complexes.

#### D. Reactions at the Thiocarbonyl Sulfur Atom

##### 1. Reaction of thiocarbonyl anions with alkyl and aryl halides

Addition of MeI or MeOSO<sub>2</sub>F to a solution of Bu<sub>4</sub>N<sup>-</sup>[CpW(CO)<sub>2</sub>CS] in THF gives an orange compound whose infrared spectrum in CS<sub>2</sub> displays strong CO absorptions at 1985 and 1911 cm<sup>-1</sup>, but no CS absorption; the <sup>1</sup>H NMR spectrum shows a Cp resonance at δ5.65 and an Me resonance at δ2.58 in a ratio of 5:3. This Me peak occurs near the delta values shown by the Me resonances of trans-IW(CO)<sub>4</sub>CS-Me<sup>5</sup> and [(diphos)<sub>2</sub>W(CO)(CS-Me)]FSO<sub>3</sub>,<sup>5</sup> which contain S-alkylated terminal CS ligands. Therefore, it appears that alkylation of the thiocarbonyl anion gives the S-methyl compound CpW(CO)<sub>2</sub>CS-Me rather than a metal-alkylated product, since the Me resonance of a metal-alkylated product would

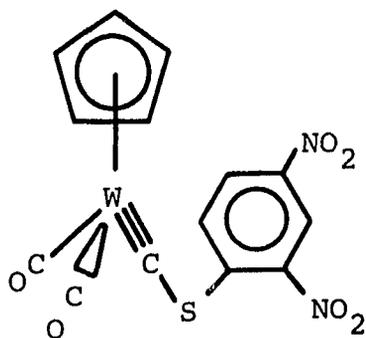


be expected at much higher field (e.g., δMe of CpW(CO)<sub>3</sub>Me in 0.4 ppm<sup>129</sup>). Similar reactions were observed with EtI and BzBr. All of these products were separated from the reaction mixtures, but the complexes were air-sensitive oils. The S-methyl complex did not react with PPh<sub>3</sub>.

Reaction of the thiocarbonyl anion with chloro-2,4-dinitrobenzene gives another deep orange compound. Again, the IR spectrum shows two CO absorptions, at 2001s and 1930s, but no CS band (Table 5). The  $^1\text{H}$  NMR spectrum contains a Cp resonance at  $\delta$ 5.8 plus three resonances for the three phenyl protons, and the  $^{13}\text{C}$  NMR spectrum of this product displays one CO resonance at -219.3s, a W-C-S resonance at -261.7, and four phenyl resonances (Tables 6 and 7). The W-C-S resonance is shifted upfield from the CS resonances of terminal thiocarbonyl ligands (Table 4) to a value close to that of trans-IW(CO)<sub>4</sub>CS-Me,<sup>5</sup> and the phenyl resonance at -138.5 is close to reported values for a phenyl carbon attached to a sulfur atom.<sup>130</sup> This product appears to be the S-aryl compound CpW(CO)<sub>2</sub>CS-DNP (DNP = 2,4-dinitrophenyl). The complex, a copper-colored, crystalline solid, is insoluble in aliphatic hydrocarbons but soluble in more polar organic solvents. It is somewhat air sensitive, though it can be handled briefly in air without significant decomposition.

Fischer and his coworkers<sup>94-96</sup> have prepared a series of carbyne complexes, CpW(CO)<sub>2</sub>CR, which are similar in structure to the S-aryl compound and exhibit similar IR and  $^1\text{H}$  NMR characteristics (Tables 5-6). The CO absorptions of CpW(CO)<sub>2</sub>CS-DNP occur within the range of  $\nu(\text{CO})$  shown by Fischer's compounds<sup>95</sup> (Table 5), illustrating

the similar electronic effect of the CS-R and C-R ligands. X-ray analyses<sup>95,96</sup> of these carbyne complexes have demonstrated that they contain a tungsten-carbon triple bond,  $W \equiv C-R$ . The S-aryl thiocarbonyl ligand may be considered an aryl-mercaptocarbyne ligand, and the structure below is suggested for  $CpW(CO)_2CS-DNP$ .



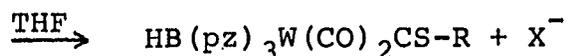
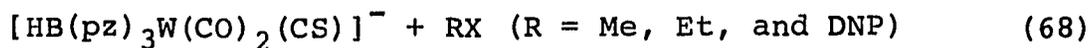
Structural studies are underway to confirm this proposal.<sup>131</sup>

Alkoxy- and phenoxycarbyne analogs of these sulfur bound complexes are unknown, an indication that the sulfur atom of a thiocarbonyl complex is a stronger nucleophile than the oxygen atom of an analogous carbonyl. The apparently high nucleophilicity of the CS sulfur atom in  $[CpW(CO)_2CS]^-$  may be attributed to the stronger electron-withdrawing ability of CS and the inherently greater nucleophilicity of sulfur compared to oxygen.

Spectroscopic evidence for the formation of mercaptocarbyne complexes was also obtained in reactions

of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  with *i*-PrI, MeC(O)Cl, PhC(O)Cl,  $\text{Ph}_2\text{PCl}$ , and  $(\text{Ph}_3\text{P})\text{AuCl}$ , but the products were too unstable to isolate.

Methyl iodide and ethyl iodide react rapidly with  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]^-$ . Although MeI and EtI add to the metal in  $[\text{HB}(\text{pz})_3\text{Mo}(\text{CO})_3]^-$ ,<sup>98</sup> they alkylate the sulfur atom of the thiocarbonyl anion. Chloro-2,4-dinitrobenzene also reacts with  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2(\text{CS})]^-$  at the sulfur atom.



The pyrazolyborate S-alkyl and S-aryl thiocarbonyl complexes form crystalline solids which may be recrystallized many times with little decomposition. These compounds display spectral properties similar to those of Fischer's carbyne complexes<sup>95,96</sup> and the mercaptocarbyne complexes discussed above (Tables 5-7). The chemical shift of the  $\text{W-C-S}$  carbon in  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS-Me}$  is comparable to those of the  $\text{W-C-S}$  resonances in trans- $\text{IW}(\text{CO})_4\text{CS-Me}$  and  $\text{CpW}(\text{CO})_2\text{CS-DNP}$ . These resonances are found significantly upfield from the  $\text{W-C-R}$  values reported by Fischer *et al.*,<sup>95</sup> though no explanation for this behavior has been determined.

Nucleophilic reactions of  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]^-$  with *i*-PrI, BzBr, AllBr, and PhSCl also appear to occur at the

thiocarbonyl sulfur atom, but, owing to their instability, the products have not been isolated.

2. Reaction of thiocarbonyl iodide complexes with alkyl- and aryllithium compounds

When MeLi is added to a solution of trans-CpW(CO)<sub>2</sub>(CS)I in THF at -78°, the solution fades from purple to orange and the CS band disappears. The reaction gives an orange product which displays IR and <sup>1</sup>H NMR spectra identical to those of CpW(CO)<sub>2</sub>CS-Me produced from Bu<sub>4</sub>N[CpW(CO)<sub>2</sub>CS] and MeI (see above). Low temperature reactions of trans-CpW(CO)<sub>2</sub>(CS)I with PhLi, p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Li and C<sub>6</sub>F<sub>5</sub>Li also produce spectroscopic evidence for the formation of mercaptocarbyne complexes (see Fig. 4), and the products

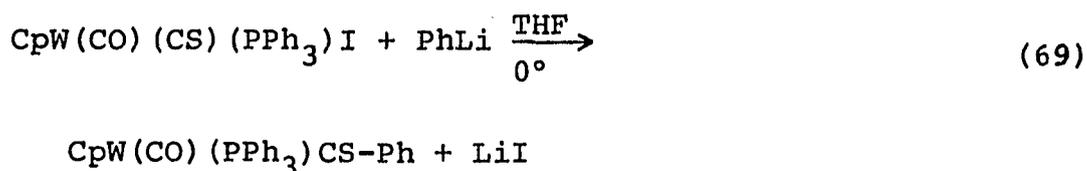
<u>R</u>	<u>ν(CO), cm<sup>-1</sup><sup>a</sup></u>	<u>δCp<sup>b</sup>(ppm)</u>	<u>δR<sup>b</sup>(ppm)</u>
Me	1985, 1911s	5.65(s)	2.58(s,Me)
Ph	1989s, 1917s	5.70(s)	7.42(m,Ph)
p-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	1983s, 1911s	5.63(s)	2.96(s,Me), 7.00(m,Ph)
C <sub>6</sub> F <sub>5</sub>	1999s, 1929s		---

<sup>a</sup>Recorded in CS<sub>2</sub>  
<sup>b</sup>Recorded CDCl<sub>3</sub>

Figure 4. Infrared and <sup>1</sup>H NMR data for CpW(CO)<sub>2</sub>CS-R complexes

can be isolated. Like  $\text{CpW}(\text{CO})_2\text{CS-Me}$ , however, these compounds are intractable oils. The thiocarbonyl iodide complex does not react with malonate anion, which is a weak nucleophile.

Treatment of a solution of  $\text{CpW}(\text{CO})(\text{CS})(\text{PPh}_3)\text{I}$  with  $\text{PhLi}$  at  $0^\circ$  gives the monosubstituted mercaptocarbyne complex  $\text{CpW}(\text{CO})(\text{PPh}_3)\text{CS-Ph}$ , eq. 69. The compound



exhibits a CO absorption at  $1888 \text{ cm}^{-1}$ , lower than  $\nu(\text{CO})$ 's observed for similar unsubstituted mercaptocarbynes, and the CO resonance in the  $^{13}\text{C}$  NMR is shifted downfield from the CO values of  $\text{CpW}(\text{CO})_2\text{CS-DNP}$  and  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS-Me}$ . This is behavior expected for a phosphine substituted complex. The absence of a CS band in the IR, the doublet Cp resonance in the  $^1\text{H}$  NMR, and the  $\text{W-C-S}$  peak at  $-254.9$  in the  $^{13}\text{C}$  NMR are further evidence for a substituted mercaptocarbyne (Tables 5-7). The product can be isolated as air-sensitive, orange needles, and an x-ray analysis is in progress.<sup>131</sup>

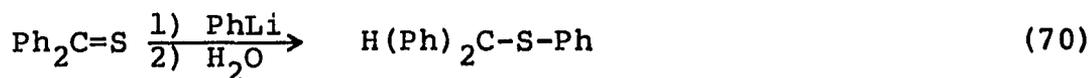
The yield of  $\text{CpW}(\text{CO})(\text{PPh}_3)\text{CS-Ph}$  is only 43%. IR spectra obtained during this reaction (II, Sect. 35)

suggests the possible formation of some  $\text{CpW(CO)(CS)(PPh}_3\text{)Ph}$ ; however, the instability of this product prevented its isolation.

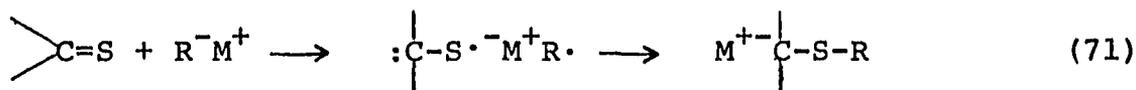
Substitution of  $\text{CpW(CO)}_2\text{CS-Me}$  was not achieved by refluxing a solution of the complex and  $\text{PPh}_3$ , so the reaction of  $\text{CpW(CO)(CS)(PPh}_3\text{)I}$  with  $\text{MeLi}$  was of interest. Addition of  $\text{MeLi}$  to a solution of  $\text{CpW(CO)(CS)(PPh}_3\text{)I}$  at  $-78^\circ$  shifts the  $\nu(\text{CO})$  from 1967 to  $1890\text{ cm}^{-1}$  and causes a color change; but unfortunately, the product decomposes before it can be isolated.

Reaction of trans- $\text{HB(pz)}_3\text{W(CO)}_2\text{(CS)I}$  with  $\text{MeLi}$  is more straightforward, giving  $\text{HB(pz)}_3\text{W(CO)}_2\text{CS-Me}$ . This product, identified by its IR and  $^1\text{H}$  NMR spectra (Tables 5 and 6) and chemical analysis, is identical to the compound produced from  $\text{Bu}_4\text{N}[\text{HB(pz)}_3\text{W(CO)}_2\text{CS}]$  and  $\text{MeI}$ . On the other hand, reaction of trans- $\text{HB(pz)}_3\text{W(CO)}_2\text{(CS)I}$  and  $\text{PhLi}$  does not give  $\text{HB(pz)}_3\text{W(CO)}_2\text{CS-Ph}$  as expected. IR spectra of the reaction mixture display CO bands at 1885s and 1785s, similar to the CO absorptions of  $[\text{HB(pz)}_3\text{W(CO)}_2\text{CS}]^-$ . The product of this reaction has not been isolated.

Nucleophilic attack on organic thiocarbonyl groups has been studied extensively, and the reactions discussed above are reminiscent of a reaction first reported by Beak and Worley,<sup>132,133</sup> eq. 70. Ohno and coworkers<sup>134,135</sup>

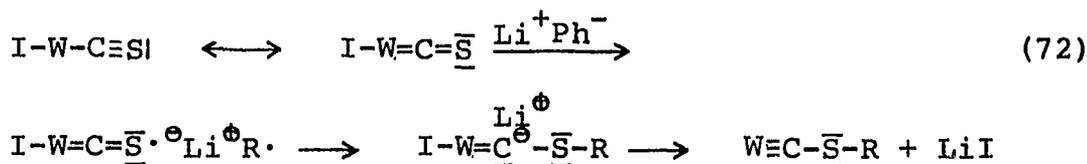


later found evidence supporting the formation of a charge-transfer complex in this reaction, eq. 71, followed by an



in-cage radical combination to give an ionic pair.

Whether or not a similar mechanism, reaction scheme 72, accounts for the thiophilic attack on thiocarbonyl ligands

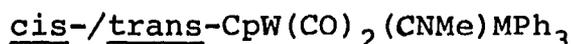
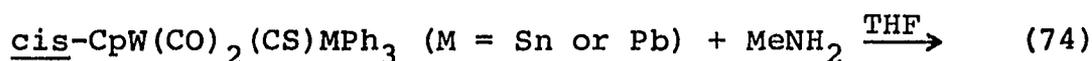
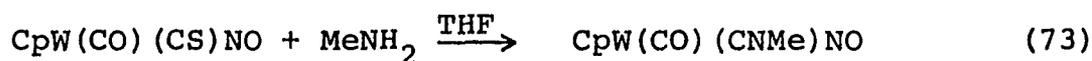


remains unknown.

Although thiophilic addition to thiocarbonyl ligands should be applicable to other thiocarbonyl complexes, products formally resulting from nucleophilic addition to the carbon of thiocarbonyls have also been reported.<sup>20,6,14,21,38</sup> It also appears that nucleophilic attack may occur at the metal. The selectivity between the two reaction paths as well as the possibility of reversible and undetected additions by each pathway needs further investigation.

## E. Reactions at the Thiocarbonyl Carbon Atom

The terminal CS ligands in  $\text{CpW}(\text{CO})(\text{CS})\text{NO}$ , cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$ , and cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{PbPh}_3$ , like those in  $\text{W}(\text{CO})_5\text{CS}^6$  and other thiocarbonyl complexes,<sup>6,21,38</sup> react with methylamine to give methylisocyanide complexes, indicated by the disappearance of the  $\nu(\text{CS})$  band in the IR spectra and the appearance of the isocyanide  $\nu(\text{CN})$  absorption (Table 8). Methyl amine reacts rapidly with



$\text{CpW}(\text{CO})(\text{CS})\text{NO}$  ( $\nu(\text{CS}) = 1260 \text{ cm}^{-1}$ ), but with cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{MPh}_3$  ( $\nu(\text{CS}) = 1238 \text{ cm}^{-1}$ ), the reaction requires 24 hr. Thus increasing the electron density on the terminal thiocarbonyl ligand lowers the tendency of the CS to undergo nucleophilic attack, a behavior pattern also observed by Dombek and Angelici.<sup>6</sup> These reactions probably occur by the same mechanism proposed for the reaction of  $\text{W}(\text{CO})_5\text{CS}^6$  with amines, in which attack of a hydrogen-bonded amine complex occurs at the thiocarbonyl carbon atom. Spectroscopic data for the isocyanide derivatives are shown in Tables 8 and 9.

The  $\text{CpW}(\text{CO})(\text{CNMe})\text{NO}$  complex is the first isocyanide nitrosyl complex reported for tungsten. Enantiomers of this complex probably exist, but no attempt to isolate them has been made.

In the CO region the IR spectra of  $\text{CpW}(\text{CO})_2(\text{CNMe})\text{MPh}_3$  display a marked dependence on solvent polarity; examples are shown in Fig. 5. This variation is also observed in the IR spectra of  $\text{CpMo}(\text{CO})_2(\text{CNMe})\text{SnMe}_3$  and  $\text{CpMo}(\text{CO})_2(\text{CNCH}_3)\text{PbPh}_3$ ; it may be interpreted in the same manner for the tungsten compounds as was done for the molybdenum analogs.<sup>121</sup> In solution these isocyanide complexes exist as a mixture of interconverting cis and trans isomers, the trans isomer being favored in polar media. Thus, in the spectrum of  $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$  in n-hexane solution, the bands at 1947vs and 1888 vs may be assigned to  $\nu_{\text{sym}}$  and  $\nu_{\text{as}}$  of the carbonyls of the cis isomer; the bands at 1932w and 1875s are assigned to the trans isomer (Table 8). The cis/trans ratio in a particular solvent is established immediately upon dissolving the compound and does not change with time.

Ambient-temperature  $^1\text{H}$  NMR spectra of the  $\text{CpW}(\text{CO})_2(\text{CNMe})\text{MPh}_3$  complexes in  $\text{CDCl}_3$  are reported in Table 9. Two sharp resonances are seen for the cyclopentadienyl protons and two, for the methyl protons; the IR spectra (Fig. 5) show that the trans isomer predominates

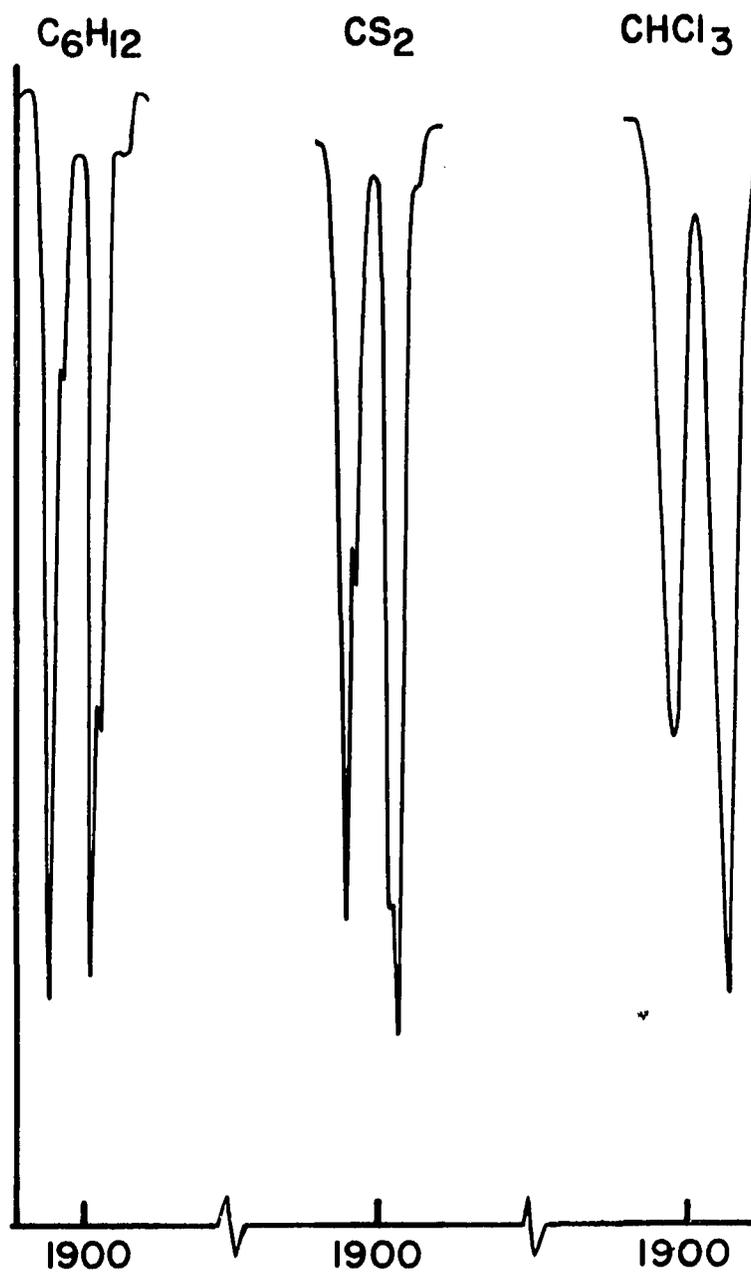
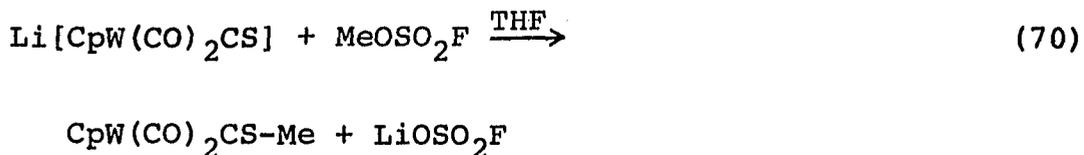
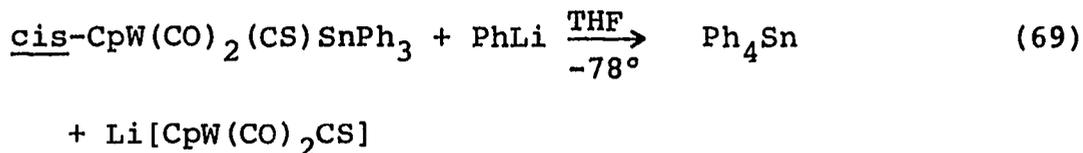


Figure 5. Carbonyl absorptions of  $\text{CpW(CO)}_2\text{(CNMe)SnPh}_3$  in various solvents

in  $\text{CHCl}_3$ , so the larger peaks are assigned to the trans isomer. The Sn or Pb coupling to the methyl and cyclopentadienyl protons is greater for the cis isomer than for the trans isomer.<sup>121</sup> The  $^{13}\text{C}$  NMR spectrum of  $\text{CpW}(\text{CO})_2(\text{CNMe})\text{PbPh}_3$  in  $\text{CD}_2\text{Cl}_2$  displays a singlet CO resonance and therefore supports the conclusion that the trans isomer is predominant in polar media.

The iron thiocarbonyl complex  $\text{CpFe}(\text{CO})(\text{CS})\text{SnPh}_3$  reacts with ethylenediamine to give a cyclic diaminocarbene complex  $\text{CpFe}(\text{CO})(\text{CN}_2\text{C}_2\text{H}_6)\text{SnPh}_3$ .<sup>21</sup> All these complexes,  $\text{CpW}(\text{CO})(\text{CS})\text{NO}$  and cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{MPh}_3$  ( $\text{M} = \text{Sn}$  or  $\text{Pb}$ ), react with ethylene diamine, and infrared spectra suggest that diaminocarbenes are formed, but no products have been isolated because of their instability.

Dean and Graham<sup>84</sup> transformed a carbonyl ligand of  $\text{CpW}(\text{CO})_3\text{MPh}_3$  ( $\text{M} = \text{Ge}$  or  $\text{Sn}$ ) into a carbene ligand,  $\text{CpW}(\text{CO})_2(\text{MPh}_3)\text{C}(\text{OR})\text{Ph}$ , by reaction of the complex with  $\text{PhLi}$  followed by alkylation. Successive treatment of cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{MPh}_3$  ( $\text{M} = \text{Sn}$  or  $\text{Pb}$ ) with  $\text{PhLi}$  and  $\text{MeOSO}_2\text{F}$  gave two products, an orange oil and a white powder. The IR and NMR spectra of the oil were identical to those reported for  $\text{CpW}(\text{CO})_2\text{CS-Me}$  (Fig. 4); the white powder was identified by its NMR spectrum and melting point as  $\text{Ph}_4\text{M}$  ( $\text{M} = \text{Sn}$  or  $\text{Pb}$ ). Apparently  $\text{PhLi}$  attacks at the W-M bond to form  $\text{Ph}_4\text{M}$  and  $[\text{CpW}(\text{CO})_2\text{CS}]^-$ , eq. 69, and the



anion is alkylated by the subsequent addition of  $\text{MeOSO}_2\text{F}$ , eq. 70.

Azide ion is known to react with  $\text{W(CO)}_5\text{CS}$  to form  $[\text{W(CO)}_5\text{NCS}]^-$ .<sup>6</sup> Prolonged reaction of  $[\text{PPN}]\text{N}_3$  and cis- $\text{CpW(CO)}_2\text{(CS)SnPh}_3$  produces an orange substance with infrared absorbances at 2055m, 1920m, and 1805s. This spectrum might be expected for  $[\text{CpW(CO)}_2\text{(NCS)SnPh}_3]^-$ , but all attempts to isolate the anion as a salt, or alkylate the anion and isolate the neutral species, failed. Azide reacts quickly with trans- $\text{CpW(CO)}_2\text{(CS)I}$  to form another orange product. Again, the IR spectrum shows three absorbances in CO region (2096m, 1948m, and 1849s), suggesting the product is  $[\text{CpW(CO)}_2\text{(NCS)I}]^-$ . Because of its instability, however, this substance has not been isolated.

Table 2. IR stretching frequencies of various cyclopentadienyl tungsten carbonyl and thiocarbonyl compounds<sup>a</sup>

Compound	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$
$\text{W}(\text{CO})_6$	1984 <sup>b</sup>	---
$\text{W}(\text{CO})_5\text{CS}^4$	2096w, 2020m, 1995vs <sup>b</sup>	1247vs <sup>c</sup>
$\text{W}(\text{CO})(\text{CS})(\text{diphos})_2^4$	1883s <sup>d</sup>	1161s <sup>d</sup>
$[\text{HW}(\text{CO})(\text{CS})(\text{diphos})_2]\text{CF}_3\text{SO}_3^5$	1958s <sup>d</sup>	1207s <sup>d</sup>
$[\text{C}_{10}\text{H}_{12}\text{N}_2][\text{CpW}(\text{CO})_3]^{136}$	1888s, 1767s, 1745s <sup>e</sup>	---
$\text{Bu}_4\text{N}[\text{CpW}(\text{CO})_2\text{CS}]$	1890s, 1804s <sup>d</sup>	
$\text{Bu}_4\text{N}[\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS}]$	1884s, 1787s <sup>d</sup>	1149 <sup>d</sup>

<sup>a</sup>Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very.

<sup>b</sup>Recorded in hexane solution.

<sup>c</sup>Recorded in  $\text{CS}_2$  solution.

<sup>d</sup>Recorded in  $\text{CH}_2\text{Cl}_2$  solution.

<sup>e</sup>Recorded in nujol mull.

Table 2. (Continued)

Compound	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$
$\text{CpW}(\text{CO})_2\text{NO}^{52}$	2012s, 1933s <sup>b</sup>	---
$\text{CpW}(\text{CO})(\text{CS})\text{NO}$	1990s <sup>c</sup> , 1680s <sup>f,c</sup>	1260s <sup>c</sup>
$\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$	1982s <sup>c</sup> , 1670s <sup>f,c</sup>	1252s <sup>c</sup>
$\text{CpW}(\text{CO})_3\text{SnPh}_3^{79}$	2014, 1927, 1902 <sup>g</sup>	---
<u>cis</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$	1988s, 1924m <sup>c</sup>	1238s <sup>c</sup>
<u>cis</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{PbPh}_3$	1985s, 1926m <sup>c</sup>	1237s <sup>c</sup>
$[\text{CpW}(\text{CO})_3]_2\text{Hg}^{73}$	1997s, 1967vs, 1900sh, 1883s <sup>h</sup>	---
$\text{CpW}(\text{CO})_3\text{HgI}^{73}$	2012s, 1939sh, 1918s <sup>h</sup>	---
$[\text{CpW}(\text{CO})_2\text{CS}]_2\text{Hg}$	1980sh, 1975s, 1920m, 1900sh <sup>c</sup>	1198m(br) <sup>c</sup>
<u>cis</u> -/ <u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$	1990s, 1945s <sup>c</sup>	1268m, 1234s <sup>c</sup>

<sup>f</sup> $\nu(\text{NO})$  absorption.

<sup>g</sup>Recorded in  $\text{CCl}_4$  solution.

<sup>h</sup>Recorded in  $\text{CHCl}_3$  solution.

Table 2. (Continued)

Compound	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$
$\text{CpMo}(\text{CO})_3\text{SePh}^{137}$	2026vs, 1948vs <sup>c</sup>	---
<u>cis-/trans-</u> $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$	2008sh, 2000m, 1958s <sup>c</sup>	1262s
$\text{CpW}(\text{CO})_3\text{Cl}^{57}$	2049, 1969, 1919 <sup>e</sup>	---
<u>cis-/trans-</u> $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{I}^{66}$	1960s, 1876s <sup>h</sup>	---
<u>trans-</u> $[\text{CpW}(\text{CO})_2(\text{PEt}_3)_2]\text{PF}_6^{61}$	1942m, 1852s <sup>e</sup>	---
<u>trans-</u> $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$	2025m, 1972s <sup>c</sup>	1267s <sup>c</sup>
<u>trans-</u> $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2(\text{CS})\text{I}$	2017m, 1961s <sup>c</sup>	1243s <sup>c</sup>
$\text{CpW}(\text{CO})(\text{CS})(\text{PPh}_3)\text{I}$	1964s <sup>c</sup>	1225s <sup>c</sup>
$\text{CpW}(\text{CO})(\text{CS})(\text{P}[\text{OPh}]_3)\text{I}$	1974s <sup>c</sup>	1240s <sup>c</sup>
$\text{CpW}(\text{CO})(\text{CS})(\text{P}[\text{NMe}_2]_3)\text{I}$	1958s <sup>c</sup>	1221s <sup>c</sup>
$\text{CpW}(\text{CO})(\text{CS})(\text{CNMe})\text{I}$	1969s <sup>c</sup>	1241s <sup>c</sup>
$\text{CpW}(\text{CO})(\text{CS})(\text{PMe}_2\text{Ph})\text{I}$	1967s <sup>c</sup>	1220s <sup>c</sup>
<u>trans-</u> $[\text{CpW}(\text{CO})(\text{CS})(\text{PMe}_2\text{Ph})_2]\text{PF}_6$	1932 <sup>i</sup>	1234s <sup>i</sup>

<sup>i</sup>Recorded in  $\text{CH}_3\text{CN}$  solution.

Table 3.  $^1\text{H}$  NMR chemical shifts of various cyclopentadienyl tungsten thiocarbonyl compounds in  $\text{CDCl}_3$  solution<sup>a</sup>

Compound	$\delta\text{Cp}$ (ppm)	$\delta\text{R}$ (ppm)
$\text{CpW}(\text{CO})(\text{CS})\text{NO}$	5.87 (s)	---
<u>cis</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$	5.31 (s)	7.25 (m, Ph)
<u>cis</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{PbPh}_3$	5.47 (s)	7.44 (m, Ph)
$[\text{CpW}(\text{CO})_2\text{CS}]_2\text{Hg}$	5.83 (s, br)	---
<u>cis</u> -/ <u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{HgI}$	5.76 (s)	---
<u>cis</u> -/ <u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{SePh}$	5.67 (s) <sup>b</sup> , 5.73 (s) <sup>c</sup>	7.18 (m, Ph), 7.48 (m, Ph)
<u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$	5.84 (s)	---

<sup>a</sup>Abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = complex multiplet, br = broad.

<sup>b</sup>cis isomer.

<sup>c</sup>trans isomer.

Table 3. (Continued)

Compound	$\delta_{\text{Cp}}$ (ppm)	$\delta_{\text{R}}$ (ppm)
<u>trans</u> -HB(pz) <sub>3</sub> W(CO) <sub>2</sub> (CS)I	---	6.23(t,pz) <sup>d</sup> , 7.61(d,pz) <sup>e</sup> , 8.45(d,pz) <sup>f</sup>
CpW(CO)(CS)(PPh <sub>3</sub> )I	5.62(s)	7.52(m,Ph)
CpW(CO)(CS)(P[OPh] <sub>3</sub> )I	5.30(s)	7.42(m,Ph)
CpW(CO)(CS)(P[NMe <sub>2</sub> ] <sub>3</sub> )I	5.60(s)	2.68(d,Me) <sup>g</sup>
CpW(CO)(CS)(CNMe)I	5.74(s)	3.95(s,Me)
CpW(CO)(CS)(PMe <sub>2</sub> Ph)I	5.52(s)	2.21(d,Me) <sup>h</sup> , 7.55(m,Ph)
<u>trans</u> -[CpW(CO)(CS)(PMe <sub>2</sub> Ph)]PF <sub>6</sub> <sup>i</sup>	5.40(t) <sup>j</sup>	2.18(dd,Me) <sup>k</sup> , 7.52(m,Ph)

$$^{\text{d}}J = 2 \text{ Hz.}$$

$$^{\text{e}}J = 2 \text{ Hz.}$$

$$^{\text{f}}J = 2 \text{ Hz.}$$

$$^{\text{g}}J_{\text{P-CH}_3} = 8 \text{ Hz.}$$

$$^{\text{h}}J_{\text{P-CH}_3} = 9.5 \text{ Hz.}$$

<sup>i</sup>Recorded in CD<sub>3</sub>CN solution.

$$^{\text{j}}J_{\text{P-Cp}} = 3 \text{ Hz.}$$

$$^{\text{k}}J_{\text{P-CH}_3} = 10 \text{ Hz, } J'_{\text{P-CH}_3} = 3 \text{ Hz.}$$

Table 4.  $^{13}\text{C}$  NMR chemical shifts of Cp, CO, and CS ligands for various tungsten carbonyl and thiocarbonyl complexes in  $\text{CDCl}_3$  solution<sup>a</sup>

Compounds	$\delta\text{Cp}$ (ppm)	$\delta\text{CO}$ (ppm)	$\delta\text{CS}$ (ppm)
$\text{W}(\text{CO})_6$	---	-191.1	
$\text{W}(\text{CO})_5\text{CS}^4$	---	-192.4 ( <u>cis</u> ), -189.3 ( <u>trans</u> )	-298.7
$\text{Bu}_4\text{N}[\text{trans-IW}(\text{CO})_4\text{CS}]^4$	---	-196.5	-285.7
$\text{CpW}(\text{CO})(\text{CS})\text{NO}$	-94.4 (s)	-215.1 (s)	-329.7 (s)
$\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS})\text{NO}$	---	-217.89 (s)	-319.2 (s)
<u>cis</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{SnPh}_3$	-89.0 (s)	-201.3 (s), -199.9 (s)	-283.3 (s)
<u>cis</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{PbPh}_3^b$	-88.8 (s)	-215.3 (s), -218.0 (s)	-311.7 (s)
<u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$	-93.5 (s)	-195.0 (s)	-310.5 (s)

<sup>a</sup>Abbreviations: s = singlet, d = doublet.

<sup>b</sup>Recorded in  $\text{CD}_2\text{Cl}_2$  solution.

Table 4. (Continued)

Compound	$\delta\text{Cp}$ (ppm)	$\delta\text{CO}$ (ppm)	$\delta\text{CS}$ (ppm)
<u>trans</u> -HB(pz) <sub>3</sub> W(CO) <sub>2</sub> (CS)I	---	-224.0 (s)	-300.0 (s)
CpW(CO)(CS)(PPh <sub>3</sub> )I	-94.6 (s)	-224.5 (d) <sup>c</sup>	-353.1 (d) <sup>c</sup>
CpW(CO)(CS)(P[OPh] <sub>3</sub> )I	-94.1 (s)	-218.9 (d) <sup>d</sup>	-348.4 (d) <sup>d</sup>
CpW(CO)(CS)(P[NMe <sub>2</sub> ] <sub>3</sub> )I	-94.7 (s)	-227.3 (d) <sup>e</sup>	-355.9 (d) <sup>e</sup>
CpW(CO)(CS)(CNMe)I	-93.9 (s)	-222.9 (s)	-353.6 (s)
CpW(CO)(CS)(PMe <sub>2</sub> Ph)I	-93.8 (s)	-224.1 (d) <sup>f</sup>	-352.8 (d) <sup>f</sup>
<u>trans</u> -[CpW(CO)(CS)(PMe <sub>2</sub> Ph) <sub>2</sub> ]PF <sub>6</sub> <sup>g</sup>	-95.5 (d) <sup>h</sup>	-229.8 (t) <sup>h</sup>	-338.1 (t) <sup>h</sup>

<sup>c</sup>J<sub>P-CO</sub> = 10.0 Hz; J<sub>P-CS</sub> = 23.8 Hz.

<sup>d</sup>J<sub>P-CO</sub> = 10.4 Hz; J<sub>P-CS</sub> = 37.2 Hz.

<sup>e</sup>J<sub>P-CO</sub> = 10.4 Hz; J<sub>P-CS</sub> = 29.8 Hz.

<sup>f</sup>J<sub>P-CO</sub> = 10.0 Hz; J<sub>P-CS</sub> = 24.0 Hz.

<sup>g</sup>Recorded in CD<sub>3</sub>CN solution.

<sup>h</sup>J<sub>P-Cp</sub> = 28.0 Hz; J<sub>P-CO</sub> = 21.0 Hz; J<sub>P-CS</sub> = 21.0 Hz.

Table 5. IR stretching frequencies of various tungsten thiocarbonyl and carbyne complexes in CS<sub>2</sub> solution<sup>a</sup>

Compound	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$
Bu <sub>4</sub> N[ <u>trans</u> -IW(CO) <sub>4</sub> CS] <sup>4</sup>	2062w, 1947vs <sup>b</sup>	1195vs <sup>b</sup>
<u>trans</u> -IW(CO) <sub>4</sub> CS-Me <sup>5</sup>	2115w, 2033s <sup>c</sup>	1118 <sup>c</sup>
W(CO)(CS)(diphos) <sub>2</sub> <sup>4</sup>	1838s <sup>b</sup>	1161s <sup>b</sup>
[(diphos) <sub>2</sub> W(CO)CS-Me]FSO <sub>3</sub> <sup>5</sup>	1898s <sup>b</sup>	1095 <sup>b</sup>
CpW(CO) <sub>3</sub> CH <sub>3</sub> <sup>40</sup>	2020vs, 1930vs <sup>d</sup>	---
CpW(CO) <sub>2</sub> (PPh <sub>3</sub> )CH <sub>3</sub> <sup>86</sup>	1936s, 1860sh, 1850vs <sup>d</sup>	---
CpW(CO) <sub>2</sub> CPh <sup>95</sup>	1991s, 1922s <sup>c</sup>	---
CpW(CO) <sub>2</sub> CNEt <sub>2</sub> <sup>95</sup>	1958s, 1880s <sup>c</sup>	---
CpW(CO) <sub>2</sub> CSiPh <sub>3</sub> <sup>96</sup>	2003s, 1926vs <sup>b</sup>	---
CpW(CO) <sub>2</sub> CS-DNP	2001s, 1930s	---

<sup>a</sup>Abbreviations: s = strong, w = weak, v = very.

<sup>b</sup>Recorded in CH<sub>2</sub>Cl<sub>2</sub> solution.

<sup>c</sup>Recorded in hexane solution.

<sup>d</sup>Recorded in CCl<sub>4</sub> solution.

Table 5. (Continued)

Compound	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{CS}), \text{cm}^{-1}$
$\text{CpW}(\text{CO})(\text{PPh}_3)\text{CS-Ph}$	1888s	
$\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS-Me}$	1979s, 1893s	
$\text{HB}(\text{pz})_2\text{W}(\text{CO})_2\text{CS-Et}$	1979s, 1892s	
$\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS-DNP}$	1999s, 1914s	

Table 6.  $^1\text{H}$  NMR chemical shifts of various tungsten carbyne compounds in  $\text{CDCl}_3$  solution<sup>a</sup>

Compound	$\delta\text{Cp}$ (ppm) <sup>b</sup>	$\delta\text{R}$ (ppm) <sup>b</sup>
<u>trans</u> -IW(CO) <sub>4</sub> CS-Me <sup>5</sup>	---	2.60 (s, Me)
CpW(CO) <sub>3</sub> CH <sub>3</sub> <sup>129</sup>	5.40 (s) <sup>c</sup>	0.40 (s, Me) <sup>c</sup>
CpW(CO) <sub>2</sub> CPh <sup>95</sup>	5.80 (s) <sup>d</sup>	7.51 (m, Ph) <sup>d</sup>
CpW(CO) <sub>2</sub> CNEt <sub>2</sub> <sup>95</sup>	5.66 (s) <sup>d</sup>	1.28 (t, CH <sub>3</sub> ), 3.33 (q, CH <sub>2</sub> ) <sup>d</sup>
CpW(CO) <sub>2</sub> CSiPh <sub>3</sub> <sup>96</sup>	5.89 (s) <sup>e</sup>	7.53 (m, Ph) <sup>e</sup>
CpW(CO) <sub>2</sub> CS-DNP	5.80 (s)	8.50 (dd, Ph), 9.05 (d, Ph), 9.05 (d, Ph) <sup>f</sup>

<sup>a</sup>Pyrazolyl resonances have been omitted for clarity; see Sect. II for data.

<sup>b</sup>Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = complex multiplet.

<sup>c</sup>Recorded in  $\text{CCl}_4$  solution.

<sup>d</sup>Recorded in  $\text{CD}_2\text{Cl}_2$  solution.

<sup>e</sup>Recorded in  $d_6$ -acetone solution.

<sup>f</sup>dd:  $J = 9$  Hz,  $J' = 2$  Hz; d:  $J = 9$  Hz; d:  $J = 2$  Hz, respectively.

Table 6. (Continued)

Compound	$\delta_{\text{Cp}}$ (ppm) <sup>b</sup>	$\delta_{\text{R}}$ (ppm) <sup>b</sup>
CpW(CO) (PPh <sub>3</sub> )CS-Ph	5.24 (d) <sup>g</sup>	7.32 (m, Ph)
HB (pz) <sub>3</sub> W(CO) <sub>2</sub> CS-Me	---	2.59 (s, Me)
HB (pz) <sub>3</sub> W(CO) <sub>2</sub> CS-Et	---	1.45 (t, CH <sub>3</sub> ), 2.97 (q, CH <sub>2</sub> ) <sup>h</sup>
HB (pz) <sub>3</sub> W(CO) <sub>2</sub> (CS-DNP) <sup>i</sup>	---	8.35 (dd, Ph), 9.02 (d, Ph), 9.06 (d, Ph) <sup>j</sup>

<sup>g</sup>J<sub>P-Cp</sub> = 0.8 Hz.

<sup>h</sup>J = 7 Hz.

<sup>i</sup>Recorded at -60°.

<sup>j</sup>dd: J = 9 Hz, J' = 3 Hz; d: J = 3 Hz; d: J = 9 Hz, respectively.

Table 7.  $^{13}\text{C}$  NMR chemical shift of Cp, CO, and W-C-R ligands for various tungsten carbyne complexes in  $\text{CDCl}_3$  solution<sup>a</sup>

Compound	$\delta\text{Cp}$ (ppm)	$\delta\text{CO}$ (ppm)	$\delta\text{W-C-R}$ (ppm)
<u>trans</u> -IW(CO) <sub>4</sub> CS-Me <sup>5</sup>	---	-188.8 (s)	-252.7 (s)
CpW(CO) <sub>2</sub> CPh <sup>95</sup>	-92.1 (s) <sup>b</sup>	-221.3 (s) <sup>b</sup>	-299.0 (s) <sup>b</sup>
CpW(CO) <sub>2</sub> (C-C <sub>6</sub> H <sub>3</sub> -3-Br-4-OMe) <sup>95</sup>	-92.0 (s) <sup>b</sup>	-221.9 (s) <sup>b</sup>	-300.0 (s) <sup>b</sup>
CpW(CO) <sub>2</sub> CSiPh <sub>3</sub> <sup>96</sup>	-92.6 (s) <sup>b,c</sup>	-222.2 (s) <sup>b,c</sup>	-354.3 (s) <sup>b,c</sup>
CpW(CO) <sub>2</sub> CS-DNP	-92.5 (s)	-219.3 (s)	-261.7 (s)
CpW(CO)(PPh <sub>3</sub> )CS-Ph	-91.5 (s)	-237.7 (d) <sup>d</sup>	-254.9 (d) <sup>d</sup>
HB(pz) <sub>3</sub> W(CO) <sub>2</sub> CS-Me	---	-224.7 (s)	-264.4 (s)

<sup>a</sup>Abbreviations: s = singlet, d = doublet.

<sup>b</sup>Recorded in  $\text{CD}_2\text{Cl}_2$  solution.

<sup>c</sup>Recorded at  $-20^\circ$ .

<sup>d</sup> $J_{\text{P-CO}} = 7 \text{ Hz}$ ;  $J_{\text{P-WCS}} = 12 \text{ Hz}$ .

Table 8. IR stretching frequencies of various isocyanide complexes<sup>a</sup>

Compound	Solvent	$\nu(\text{CN}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$
CpW(CO)(CNMe)(NO)	CH <sub>2</sub> Cl <sub>2</sub>	2141m	1911s, 1601s <sup>b</sup>
<u>cis-/trans-</u> CpW(CO) <sub>2</sub> (CNMe)SnPh <sub>3</sub>	C <sub>6</sub> H <sub>12</sub>	2105m	1947vs, 1932w, 1888vs, 1875s
<u>cis-/trans-</u> CpW(CO) <sub>2</sub> (CNMe)PbPh <sub>3</sub>	C <sub>6</sub> H <sub>12</sub>	2112m	1950s, 1936w, 1892s, 1882m

<sup>a</sup>Abbreviations: s = strong, m = medium, w = weak, v = very.

<sup>b</sup> $\nu(\text{NO})$  absorption.

Table 9.  $^1\text{H}$  NMR chemical shifts for various isocyanide complexes in  $\text{CDCl}_3$  solution<sup>a</sup>

Compound	$\delta\text{Cp}$ (ppm)	$\delta\text{R}$ (ppm)
$\text{CpW}(\text{CO})(\text{CNMe})\text{NO}$	5.60 (s)	3.77 (s, Me)
<u>cis</u> -/ <u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CNMe})\text{SnPh}_3$	5.21 (s, <u>trans</u> ), 5.35 (s, <u>cis</u> )	2.94 (s, <u>cis</u> Me) <sup>b</sup> 3.68 (s, <u>trans</u> Me) 7.58 (m, Ph)
<u>cis</u> -/ <u>trans</u> - $\text{CpW}(\text{CO})_2(\text{CNMe})\text{PbPh}_3$	5.16 (s, <u>trans</u> ), 5.34 (s, <u>cis</u> ) <sup>c</sup>	2.96 (s, <u>cis</u> Me) <sup>d</sup> 3.61 (s, <u>trans</u> Me) <sup>d</sup> 7.41 (m, Ph)

<sup>a</sup>Abbreviations: s = singlet, m = multiplet.

<sup>b</sup> $J_{\text{Sn-Me}_{\text{cis}}}$  = 14 Hz.

<sup>c</sup> $J_{\text{Pb-Cp}_{\text{trans}}}$  = 6 Hz;  $J_{\text{Pb-Cp}_{\text{cis}}}$  = 2 Hz.

<sup>d</sup> $J_{\text{Sn-Me}_{\text{cis}}}$  = 29 Hz;  $J_{\text{Sn-Me}_{\text{trans}}}$  = 8 Hz.

## F. Summary of Spectroscopic Data

1. CpW(CO)<sub>2</sub>(CS)E and HB(pz)<sub>3</sub>W(CO)<sub>2</sub>(CS)E (E = X, SnPh<sub>3</sub>, HgI, SePh, etc.)

The infrared spectra of the cyclopentadienyl and hydrotris(1-pyrazolyl)borate derivatives of W(CO)<sub>5</sub>CS shown in Table 2 exhibit carbonyl bands corresponding to the  $\nu_{\text{sym}}$  and  $\nu_{\text{as}}$  of the carbonyl ligands. The frequencies of these carbonyl absorptions are higher than those shown by CpW(CO)<sub>2</sub>(L)R; this increase in frequency is most probably due to the  $\pi$ -acidity of the CS ligand, which decreases the metal electron density. In general, all of the thiocarbonyl derivatives prepared in this study have infrared carbonyl absorptions at higher frequencies than those of the corresponding carbonyl complexes. Among the thiocarbonyl derivatives,  $\nu(\text{CO})$  is lower for the pyrazolylborate derivatives than for the cyclopentadienyl derivatives, owing to the better electron donor properties of the pyrazolylborates.<sup>98,99</sup> The CS absorption occurs in the range of 1267 cm<sup>-1</sup> to 1220 cm<sup>-1</sup>. As expected, substitution of a carbonyl ligand with a stronger donor ligand, such as PR<sub>3</sub> or CNR, shifts the CO and CS absorptions to lower frequencies; small variations of the donor ligand, such as replacing PPh<sub>3</sub> with PMe<sub>2</sub>Ph, cause anomalous shifts in  $\nu(\text{CO})$  and  $\nu(\text{CS})$  (Table 2).<sup>9</sup>

Because of the CS ligand in  $\text{CpW(CO)}_2(\text{CS})\text{E}$  and  $\text{HB(pz)}_3\text{W(CO)}_2(\text{CS})\text{E}$  ( $\text{E} = \text{X, MPh}_3, \text{HgI, etc.}$ ), these complexes exist as either a cis or trans isomer. The relative intensities of the  $\nu_{\text{sym}}$  and  $\nu_{\text{as}}$  can be used as a guide to the structure of these derivatives, as explained in Chapter III, part C.

Those CS complexes whose mass spectra were determined display abundant parent ion peaks and the fragments owing to sequential loss of ligands. Fragments resulting from the loss of CS are of low abundance and the  $\text{CpW(CS)}^+$  and  $\text{C}_3\text{H}_3\text{W(CS)}^+$  or  $\text{HB(pz)}_3\text{W(CS)}^+$  fragments are always observed.

The  $^{13}\text{C}$  NMR spectra of these thiocarbonyl derivatives (Table 4) show low-field CS carbon resonances, consistent with  $^{13}\text{C}$  NMR recorded for other thiocarbonyl complexes.<sup>4,20,32</sup> Increase of the metal electron density by substitution of a carbonyl ligand with  $\text{PR}_3$  or  $\text{CNR}$  causes the CS carbon resonance to shift downfield by 38-45 ppm; but as observed in the IR spectra (Table 2), changes within the ligand cause anomalous shifts.<sup>9</sup>

2.  $\text{CpW(CO)(L)CSR}$  and  $\text{HB(pz)}_3\text{W(CO)}_2\text{CSR}$  ( $\text{L} = \text{CO}$  or  $\text{PPh}_3$ ;  
 $\text{R} = \text{Me, Et, Ph, or DNP}$ )

The infrared spectra exhibited by the mercaptocarbyne complexes (Table 5) are similar to those reported for similar arylcarbynes.<sup>95</sup> Two strong CO absorptions are

observed, corresponding to  $\nu_{\text{sym}}$  and  $\nu_{\text{as}}$  of the CO ligands. No CS stretch is observed for any of these complexes; presumably it is too weak to be easily measured. Substitution of a carbonyl in these complexes causes a significant decrease in the frequency of CO absorption.

The  $^1\text{H}$  NMR of these mercaptocarbyne complexes (Table 6) are what would be expected: protons affected by the sulfur are shifted downfield. The  $^{13}\text{C}$  NMR spectra (Table 7) exhibit distinctive  $\text{W-C-S}$  resonances about 260 ppm downfield from TMS; these resonances are not changed significantly by increase of electron density on the tungsten or by electron-withdrawing groups on the S-alkyl or aryl substituent. The positions of the CO carbon resonances are close to those of the carbonyl analogs; increase of metal electron density results in a downfield shift of the CO peaks.

The mass spectrum of  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2\text{CS-Me}$  displays peaks which correspond to the parent ion and the following fragments:  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CS-Me})^+$ ,  $\text{HB}(\text{pz})_3\text{W}(\text{CO})_2^+$  and  $\text{HB}(\text{pz})_3\text{W}(\text{CS-Me})^+$ ,  $\text{HB}(\text{pz})_3\text{W}(\text{CO})(\text{CH}_3)^+$ , and  $\text{HB}(\text{pz})_3\text{W}^+$ .

#### G. Conclusion

The preceding results represent the first investigation of the  $\eta^5$ -cyclopentadienyl and hydrotris(1-pyrazolyl)borate derivatives of a Group VI thiocarbonyl,  $\text{W}(\text{CO})_5\text{CS}$ . It is

evident that the replacement of a CO ligand with a CS ligand in the "half-sandwich" complexes  $[\text{CpW}(\text{CO})_3]^-$  and  $[\text{HB}(\text{pz})_3\text{W}(\text{CO})_3]^-$  has a pronounced effect on the chemistry of the anion as well as that of the CS ligand.

Nucleophilic displacement at the sulfur of  $[\text{CpW}(\text{CO})_2\text{CS}]^-$  points out the higher nucleophilicity of a thiocarbonyl sulfur as opposed to a carbonyl oxygen. Reagents which have not been observed to interact with the carbonyl oxygen of  $[\text{CpW}(\text{CO})_3]^-$  add to the sulfur of the thiocarbonyl anion. As said before, this reactivity may be attributed to the strong electron-withdrawing ability of CS and the greater polarizability of sulfur as compared to oxygen.

The factors which determine whether nucleophilic displacement occurs at the sulfur or the metal in  $[\text{CpW}(\text{CO})_2\text{CS}]^-$ , and, if at the metal, whether cis or trans isomers are formed, are not evident. Nucleophilic reactions occur at the sulfur with alkyl and aryl halides and at the metal with halogens, organometallic halides, and metallic halides; this behavior may reflect the strength of the S-C bond (167 kcal mole<sup>-1</sup>) as opposed to the S-Sn (111 kcal mole<sup>-1</sup>), S-Pb (82 kcal mole<sup>-1</sup>), S-Se (91 kcal mole<sup>-1</sup>), and S-Hg (51 kcal mole<sup>-1</sup>) bonds.<sup>138</sup>

In reactions of trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  with various donor ligands, much more carbonyl-substituted product is formed than thiocarbonyl-substituted product, which shows

the high stability of the W-CS bond. These substitution reactions also suggest that CS is a stronger  $\pi$ -acceptor ligand than CO. The thiocarbonyl complex behaves as if there is less electron density at the metal than in  $\text{CpW}(\text{CO})_3\text{I}$ , CO substitution occurring much faster for trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  than for  $\text{CpW}(\text{CO})_3\text{I}$ .

In view of the many nucleophilic reactions which occur at the thiocarbonyl carbon, attack by organolithium reagents at the thiocarbonyl sulfur is puzzling. This reactivity is perhaps explained by the mechanism proposed by Beak and Worley<sup>133</sup> for the reaction of organic thiocarbonyls with PhLi. All strong reducing agents may react with trans- $\text{CpW}(\text{CO})_2(\text{CS})\text{I}$  in this manner. An extensive investigation of this reaction is warranted.

The chemistry of the  $[\text{CpW}(\text{CO})_3]_2\text{Hg}$  and  $[\text{CpW}(\text{CO})_3]\text{HgX}$  complexes is well-known. The substitution reactions, cleavage reactions, and reduction of the thiocarbonyl analogues should be studied, especially since a preliminary reaction of  $[\text{CpW}(\text{CO})_2(\text{CS})]_2\text{Hg}$  and anhydrous  $\text{CuCl}_2$  produced a substance which appeared to be cis- $\text{CpW}(\text{CO})_2(\text{CS})\text{Cl}$ .

Finally, Brunner<sup>50</sup> has reported substitution reactions of  $\text{CpW}(\text{CO})_2\text{NO}$ ; the thiocarbonyl counterpart should be even more reactive. A series of  $\text{CpW}(\text{L})(\text{CS})\text{NO}$  and  $\text{HB}(\text{pz})_3\text{W}(\text{L})(\text{CS})\text{NO}$  complexes might be synthesized, and perhaps dithiocarbonyl complexes could be prepared in a

manner similar to the preparation of  $\text{CpMn}(\text{CO})(\text{CS})$ .  
Possibly  $\text{CpW}(\text{CO})_2\text{NO}$  could be used as a precursor to  
 $\text{CpW}(\text{CO})(\text{CS})\text{NO}$ .

## IV. LITERATURE CITED

1. L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, 57, 749 (1890).
2. M. C. Baird and G. Wilkinson, *Chem. Commun.*, 267 (1967).
3. B. D. Dombek and R. J. Angelici, *J. Amer. Chem. Soc.*, 95, 7516 (1973).
4. B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, 15, 1089 (1976).
5. B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, 15, 2397 (1976).
6. B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, 15, 2403 (1976).
7. I. S. Butler and A. E. Fenster, *J. Organometal. Chem.*, 66, 161 (1974).
8. I. S. Butler, *Acc. Chem. Res.*, 10, 359 (1977).
9. P. V. Yaneff, *Coord. Chem. Rev.*, 23, 183 (1977).
10. A. E. Fenster and I. S. Butler, *Inorg. Chem.*, 13, 915 (1974).
11. I. S. Butler, N. J. Coville, and D. Cozak, *J. Organometal. Chem.*, 133, 59 (1977).
12. G. Jaouen and R. Dabard, *J. Organometal. Chem.*, 72, 377 (1974).
13. B. D. Dombek and R. J. Angelici, *Inorg. Synth.*, 17, in press.
14. T. A. Wnuk and R. J. Angelici, *Inorg. Chem.*, 16, 1173 (1977).
15. J. W. Dunker, M. H. Quick, and T. A. Wnuk, Dept. of Chemistry, Iowa State University, unpublished results.
16. R. E. Dessy and P. M. Weissman, *J. Amer. Chem. Soc.*, 88, 5129 (1966).
17. D. F. Shriver, *Acc. Chem. Res.*, 3, 231 (1970).

18. A. M. English, K. R. Plowman, I. S. Butler, G. Jaouen, P. LeMaux, and J-Y. Thepot, *J. Organometal. Chem.*, 132, C1 (1977).
19. L. Busetto, U. Belluco, and R. J. Angelici, *J. Organometal. Chem.*, 18, 213 (1969).
20. M. H. Quick, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1978.
21. M. H. Quick and R. J. Angelici, *J. Organometal. Chem.*, to be published.
22. G. R. Dobson, *Acc. Chem. Res.*, 9, 300 (1976).
23. W. G. Richards, *Trans. Faraday Soc.*, 63, 257 (1967).
24. D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, 15, 2015 (1976).
25. I. S. Butler and D. A. Johnson, *Inorg. Chem.*, 14, 701 (1975).
26. K. Burger, L. Korecz, P. Mag, U. Belluco and L. Busetto, *Inorg. Chim. Acta*, 5, 362 (1971).
27. Y. Souma, J. Iyoda, and H. Sano, *Inorg. Chem.*, 15, 968 (1976).
28. S. S. Woodward, R. A. Jacobson, and R. J. Angelici, *J. Organometal. Chem.*, 117, C75 (1976).
29. J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc. Dalton Trans.*, 2410 (1972).
30. D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972).
31. I. S. Butler and A. E. Fenster, *Inorg. Chim. Acta*, 7, 79 (1973).
32. G. M. Bodner, *Inorg. Chem.*, 13, 2563 (1974).
33. A. Efraty, R. Arneri, and J. Sikora, *J. Organometal. Chem.*, 91, 65 (1975).
34. A. Efraty, R. Arneri, and W. A. Ruda, *Inorg. Chem.*, 16, 3124 (1977).

35. L. Busetto and A. Palazzi, *Inorg. Chim. Acta*, 19, 233 (1976).
36. G. Simmoneaux, A. Meyer, and G. Jaouen, *J. Chem. Soc. Chem. Commun.*, 69 (1975).
37. J. W. Dunker, Dept. of Chemistry, Iowa State University, personal communication, 1978.
38. L. Busetto, M. Graziani, and U. Bellico, *Inorg. Chem.*, 10, 78 (1971).
39. J. W. Dunker, J. S. Finer, J. Clardy, and R. J. Angelici, *J. Organometal. Chem.*, 114, C49 (1976).
40. T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).
41. R. B. King, *Organometallic Synthesis*, Vol. 1, Academic Press, New York, 1965.
42. C. Ungureanu and M. Palie, *J. Chem. Soc. Chem. Commun.*, 388 (1975).
43. R. Weiss and R. N. Grimes, *J. Organometal. Chem.*, 113, 29 (1976).
44. E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).
45. W. W. Greaves, M. H. Quick, and T. Wnuk, Dept. of Chemistry, Iowa State University, unpublished results, 1978.
46. R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 88, 5121 (1966).
47. E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, 10b, 1598 (1955).
48. R. B. King and M. B. Bisnette, *Inorg. Chem.*, 6, 469 (1967).
49. R. P. Stewart, Jr., and G. T. Moore, *Inorg. Chem.*, 14, 2699 (1975).
50. H. Brunner, *J. Organometal. Chem.*, 16, 119 (1969).
51. H. Brunner, *Chem. Ber.*, 102, 305 (1969).
52. E. O. Fischer and H-J. Beck, *Chem. Ber.*, 104, 3101 (1971).

53. T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 7, 1268 (1968).
54. A. R. Manning and D. J. Thornhill, *J. Chem. Soc. (A)*, 637 (1971).
55. A. N. Nesmeyanov, L. G. Makarova, and V. N. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2796 (1972).
56. C. E. Coffey, *J. Inorg. Nucl. Chem.*, 25, 179 (1963).
57. E. O. Fischer and E. Moser, *J. Organometal. Chem.*, 2, 230 (1964).
58. E. O. Fischer, K. Fichtel, and K. Ofele, *Chem. Ber.*, 95, 3172 (1962).
59. E. O. Fischer and K. Fichtel, *Chem. Ber.*, 94, 1200 (1961).
60. P. Treichel, K. W. Barnett, and R. L. Schubkin, *J. Organometal. Chem.*, 7, 449 (1967).
61. E. O. Fischer and E. Moser, *J. Organometal. Chem.*, 5, 63 (1966).
62. R. J. Haines, R. S. Nyholm, and M.H.B. Stiddard, *J. Chem. Soc. (A)*, 94 (1967).
63. A. R. Manning, *J. Chem. Soc. (A)*, 1984 (1967).
64. K. W. Barnett and D. W. Slocum, *J. Organometal. Chem.*, 44, 1 (1972) and references therein.
65. J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 92, 5852 (1970).
66. D. L. Beach and K. W. Barnett, *J. Organometal. Chem.*, 97, C27 (1975).
67. D. G. Alway and K. W. Barnett, *J. Organometal. Chem.*, 99, C52 (1975).
68. D. L. Beach, M. Dattilo, and K. W. Barnett, *J. Organometal. Chem.*, 140, 47 (1977).
69. L. J. Todd, J. R. Wilkin, J. P. Hickey, D. L. Beach, and K. W. Barnett, *J. Organometal. Chem.*, 154, 151 (1978).
70. A. R. Manning, *J. Chem. Soc. (A)*, 651 (1968).

71. J. M. Birmingham, *Adv. Organometal. Chem.*, 2, 365 (1964).
72. A. N. Nesmeyanov, L. G. Makarova, V. N. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 122 (1972).
73. M. J. Mays and J. D. Robb, *J. Chem. Soc. (A)*, 329 (1968).
74. J. J. Mays and S. M. Pearson, *J. Chem. Soc. (A)*, 2291 (1968).
75. J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, 9, 563 (1970).
76. A. N. Nesmeyanov, L. G. Makarova, and V. N. Vinogradova, *Izv. Akad. Nauk SSSR*, 2798 (1972).
77. A. N. Nesmeyanov, L. G. Makarova, and V. N. Vinogradova, *Izv. Akad. Nauk SSSR*, 2605 (1972).
78. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, J. Ya Zakharov, *Dokl. Akad. Nauk SSSR*, 156, 612 (1964).
79. H.R.H. Patil and W.A.G. Graham, *Inorg. Chem.*, 5, 1401 (1966).
80. A. Carrick and F. Glocking, *J. Chem. Soc. (A)*, 913 (1968).
81. D. J. Cardin, S. A. Keppie, B. M. Kingston, and M. F. Lappert, *Chem. Commun.*, 1035 (1967).
82. R.E.J. Bichler, H. C. Clark, B. K. Hunter, and A. T. Rake, *J. Organometal. Chem.*, 69, 367 (1974).
83. R.M.G. Roberts, *J. Organometal. Chem.*, 40, 359 (1972).
84. W. K. Dean and W.A.G. Graham, *Inorg. Chem.*, 16, 1061 (1977).
85. T. A. George and C. D. Turnipseed, *Inorg. Chem.*, 12, 394 (1973).
86. T. A. George and C. D. Sterner, *Inorg. Chem.*, 15, 165 (1976).
87. R. Havlin and G. R. Knox, *Z. Naturforsch.*, 21b, 1108 (1966).

88. E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allg. Chem.*, 282, 47 (1955).
89. A. N. Nesmeyanov, Yu. A. Chapovskii, B. V. Lokshin, A. V. Kisin, and L. G. Makarova, *Dokl. Akad. Nauk SSSR*, 171, 637 (1966).
90. K. W. Barnett, D. L. Beach, S. P. Gaydos, and T. G. Pollmann, *J. Organometal. Chem.*, 69, 121 (1974).
91. K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, 6, 294 (1967).
92. A. N. Nesmeyanov, N. A. Ustynyuk, L. V. Bogatyreva, and L. G. Makarova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 62 (1973).
93. E. O. Fischer, G. Kreis, C. G. Kreiter, J. Muller, G. Huttner, and H. Lorenz, *Angew. Chem.*, 85, 618 (1973).
94. E. O. Fischer, T. L. Lindner, and F. R. Kreissl, *J. Organometal. Chem.*, 112, C27 (1976).
95. E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 110, 3397 (1977).
96. E. O. Fischer, H. Hollfelder, P. Friedrich, F. R. Kreissl, and G. Huttner, *Angew. Chem. Int. Ed. Engl.*, 16, 401 (1977).
97. S. Trofimenko, *J. Amer. Chem. Soc.*, 89, 3170 (1967).
98. S. Trofimenko, *J. Amer. Chem. Soc.*, 91, 588 (1969).
99. S. Trofimenko, *Inorg. Chem.*, 8, 2675 (1969).
100. J. A. McCleverty, D. Seddon, N. A. Bailey, and N. W. Walker, *J. Chem. Soc. Dalton Trans.*, 898 (1976).
101. S. Trofimenko, *Accts. Chem. Res.*, 4, 17 (1971).
102. D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*, McGraw-Hill, New York, 1969, p. 147.
103. R. B. King and F.G.A. Stone, *Inorg. Synth.*, 7, 196 (1963).
104. O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc. Chem. Commun.*, 456 (1972).

105. R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Syn. Coll.*, 5, 772 (1973).
106. J. K. Ruff, *Inorg. Chem.*, 8, 86 (1969).
107. Hyp. J. Daubin, Jr., L. Hornen, and K. M. Harmon, *J. Org. Chem.*, 25, 1442 (1960).
108. M. Fieser and L. F. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, New York, 1975, Vol. V, p. 523.
109. M. Fieser and L. F. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, New York, 1975, Vol. V, p. 518.
110. A. Roess, *Organic Reactions*, 5, 193 (1949).
111. F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, 79, 67 (1959).
112. J. D. Cook and B. J. Wakefield, *J. Chem. Soc. (C)*, 2376 (1969).
113. P. L. Coe and J. C. Tatlow, *J. Chem. Soc.*, 3227 (1962).
114. M. Schmeisser, N. Wessel, and M. Weidenbruch, *Chem. Ber.*, 101, 1897 (1968).
115. M. H. Quick, K. J. Reimer, R. J. Angelici, and A. Shaver, *Inorg. Synth.*, 18, in press.
116. J. E. Ellis and G. P. Hagen, *Inorg. Chem.*, 16, 1357 (1977).
117. B. D. Dombek and R. J. Angelici, *Inorg. Synth.*, 19, in press.
118. S. Trofimenko, *Inorg. Synth.*, 12, 99 (1970).
119. T. Blackmore, M. I. Bruce, and F.G.A. Stone, *J. Chem. Soc. (A)*, 2158 (1968).
120. V. R. Miller, R. Weiss, and R. N. Grimes, *J. Amer. Chem. Soc.*, 99, 5646 (1977).
121. R. D. Adams, *Inorg. Chem.*, 15, 169 (1976).

122. J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc. Dalton Trans.*, 347 (1973).
123. V. A. Pfister, H. Behrens, and M. Moll, *Z. Anorg. Allg. Chem.*, 428, 53 (1977).
124. F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, 93, 2672 (1971).
125. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Interscience Publishers, New York, 1972, p. 696.
126. H. Brunner, H-D. Schindler, E. Schmidt, and M. Vogel, *J. Organometal. Chem.*, 24, 515 (1970).
127. R. J. Mawby and G. Wright, *J. Organometal. Chem.*, 21, 169 (1970).
128. H. G. Kuivila, *Adv. Organometal. Chem.*, 1, 47 (1964).
129. A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).
130. L. F. Johnson and W. C. Jankowski, Carbon-13 NMR Spectra, Wiley-Interscience, New York, 1972, p. 164.
131. R. A. Jacobson and R. Klima, Dept. of Chemistry, Iowa State University, unpublished results, 1978.
132. P. Beak and J. W. Worley, *J. Amer. Chem. Soc.*, 92, 4142 (1970).
133. P. Beak and J. W. Worley, *J. Amer. Chem. Soc.*, 94, 597 (1972).
134. A. Ohno, K. Nakamura, M. Uohama, S. Oka, T. Yamabe, and S. Nagata, *Bull. Chem. Soc. Japan*, 48, 3718 (1975).
135. A. Ohno, K. Nakamura, Y. Schizume, and S. Oka, *Bull. Chem. Soc. Japan*, 50, 1003 (1977).
136. R. B. King, *Inorg. Chem.*, 4, 1518 (1968).
137. E. W. Tillay, E. D. Schermer, and W. H. Baddley, *Inorg. Chem.*, 7, 1925 (1968).
138. R. C. Weast, ed., CRC Handbook of Chemistry and Physics, CRC Press, Inc., West Palm Beach, Florida, 1978, p. F-219.

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